σ-Complexes of Copper(I)

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Thesis Abstract

Three new bent {CuL_2} fragments of copper(I) supported by □–diketiminate ligands have been synthesised and characterised in the solid state, in solution and *via* DFT calculations. The suitability of these {CuL_2} fragments to be used as precursors for the formation of σ-complexes with an E–H (E = B) or M–H (M = Zn, Al, Mg, Ca, Au, W) bond has been investigated. Their electronic properties and bent confirmation make them ideal fragments for the stabilisation of σ-complexes of copper(I).

A range of σ-complexes of the type Cu–H–E and Cu–H–M (E = B, M = Zn, Al, Mg, Ca, Au) have been isolated and characterised in the solid state, in solution and *via* DFT calculations. In the case of E = B and M = Zn, Mg and Ca, an insight into their decomposition to 4 coordinate $M(L^n)_2$ species' (L^n = □–diketiminate ligand) has been summarised. Increased Cu---M bond character is observed when the heavier transition metal tungsten is employed, and these complexes can be considered as well defined heterobimetallic hydride species of Cu–H–W.

The reactivity of heterobimetallics of the type Cu–H–E and Cu–H–M, whereby E = B and M = Zn, W has been investigated through ligand exchange reactions. σ-Complexes of Cu–H–Au, along with mixtures of isolable group 10 fragments and the gold hydride complex IPrAu–H (IPr = 1,3-di(2,6-diisopropylphenyl)imidazol-2-ylidine), have shown to be selective in the reduction of carbon dioxide to a formate equivalent with HBPin (HBPin = pinacolborane).

In summary, this thesis provides new insights into the synthesis, characterisation, stability and reactivity of σ-complexes of copper(I).

Declaration of Originality

The work contained within this thesis was performed at Imperial College London between October 2014 and March 2018. Unless stated otherwise, through cited reference or other acknowledgement, it is entirely my own work and has not been previously submitted for a degree at this, or any other university.

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List of Abbreviations

δ	Chemical shift
η	Hapticity
μ	Bridging ligand
Å	Angstroms
AIM	Atoms in Molecules
Ar	Aromatic
BDI	β-diketiminate
Bu	Butyl
Calc.	Calculated
Cat	Catechol
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
d	Doublet
Dipp	2,6-Diisopropylphenyl
DFT	Density Functional Theory
DOSY	Diffusion Ordered NMR Spectroscopy
Et	Ethyl
Eq.	Equivalent
{^{1}H}	Proton decoupled
Hz	Hertz
IMes	1,3-Di(mesityl)imidazol-2-ylidine
i	*iso*
IPr	1,3-di(2,6-diisopropylphenyl)imidazol-2-ylidine
IR	Infrared spectroscopy
HMDS	Bis(trimethylsilylamide)
K	Kelvin
Mes	1,3,5-trimethylphenyl
MHz	Megahertz
mol	moles
NBO	Natural Bond Orbital
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance

o	*ortho*
p	*para*
Pin	Pincolato
Ph	Phenyl
ppm	parts per million
Pr	Propyl
q	quartet
QTAIM	Quantum Theory of Atoms in Molecules
s	singlet
sept	septet
t	triplet
t	tertiary
THF	Tetrahydrofuran
TOF	Turnover frequency
Tol	Toluene
TON	Turnover Number
VT	Variable Temperature
W	Watts
WBI	Wiberg Bond Index
w.r.t	with respect to

even monkeys fall from trees

Chapter 1

Heterobimetallic Hydride Complexes Containing 3-Centre,2-Electron Bonds

A selective review of heterobimetallics of the type M–H–E featuring 3-centre,2-electron interactions is presented (M = Ti, Zr, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni; E = Mg, Zn, B, Al, Ga). The bonding in these complexes is described and importance as intermediates in catalysis is noted. A review of coinage metal complexes featuring agostic interactions (M = Cu, Ag, Au; E = C, B, Si, Sn) alongside genuine σ-complexes of the coinage metals (M = Cu, E = B, Zn, Al) is also documented. Three methods to stabilise this type of σ-complex are outlined.

1. 3-Centre,2-Electron Interactions

The term σ-complex can be used to describe a complex containing a 3-centre,2-electron bond, or 3-centre,2-electron interaction and these descriptors will be used interchangeably throughout this thesis. These expressions are used to describe the interaction of a metal centre (M') with a nearby σ-E–H or σ-M–H bond (E = H, C, Si, B; M = Mg, Zn, Al, Ga) bonded in a η^2-fashion. This bonding mode can be rationalised *via* the Dewar-Chatt-Duncanson-type bonding model (Figure 1a). Specifically, the metal centre accepts electron density from an E–H or M–H bond whilst simultaneously back-donating into the σ* orbital of the E–H or M–H bond. The back-donation from a metal centre occurs to varying degrees depending on the availability of the d-orbitals. Thus, the coordinated E–H or M–H bond exists on a continuum from 'free' E–H or M–H bond to 3-centre,2-electron bond to full bond cleavage (Figure 1b). The stabilisation of σ-complexes can be tuned by varying the electronics of the metal centre and nature of substituents on E or M.[1]

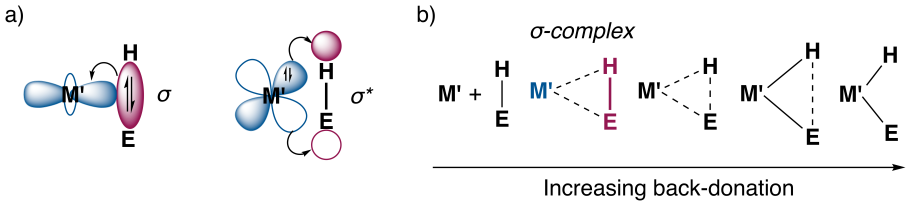


Figure 1 - a) Dewar-Chatt-Duncanson-type representation of a 3-centre,2-electron bond between a metal centre M and E–H bond, b) E–H bond cleavage spectrum

Use of the phrase agostic interactions has also been used interchangeably with σ-complex in the literature, however, for this thesis the term agostic interaction will only be used in the case of describing *intramolecular* 3-centre,2-electron interactions.

1.1 Characterisation of σ-complexes

Evidence for the formation of σ-complexes has been shown both spectroscopically and theoretically, through a range of techniques. Experimentally, geometrical parameters gathered from X-ray crystallography can be used to determine the formation of a σ-complex. In general, a complex containing a long M'---E or M'---M bond and relatively short E–H or M–H bond could be considered as a σ-complex. Due to the inaccuracies associated with locating the position of hydrides through X-ray crystallography, these data should be used in conjunction with DFT

calculations in order to confirm the geometric parameters in the 3-centre core and thus the position of the hydrides. Computationally, the use of AIM (atoms in molecules) theory can aid the characterisation of an E–H or M–H interaction with a metal centre.[2] A rationalisation of the bond critical paths and bond critical points between the three atoms in the core that reveals little M'---E or M'---M interaction and more significant interactions between M', E or M with the hydride would allow for consideration of the complex to be characterised as a σ-complex. Wiberg bond indices (WBI's) of the three interactions in the core can also be used to characterise a 3-centre,2-electron interaction through relatively small M'–H and M'---E or M'---M WBI's and larger E–H or M–H WBI's.[3] Additionally, using second order perturbation theory to quantify the donor and acceptor interactions in the 3-centre,2-electron core should reveal donation occurring from an E–H or M–H bond into M' and back-donation from M' into the E–H or M–H bond. In general, there are difficulties associated with comparing σ-complexes of different E–H or M–H bonds and thus care must be taken to compare and describe the interactions of complexes within a series.

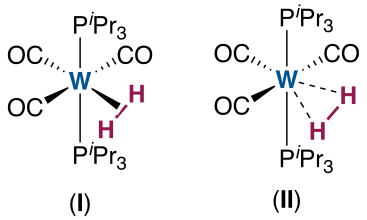
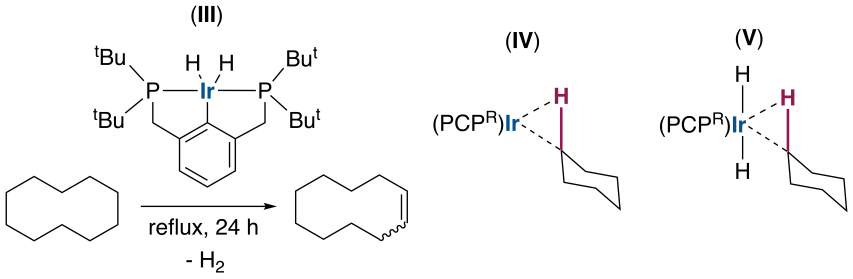


Figure 2 - A tungsten complex containing a 3-centre,2-electron interaction

The first isolated dihydrogen complexes were achieved through activation of dihydrogen by phosphine-stabilised molybdenum and tungsten complexes by Kubas in 1984.[4] Evidence for 'side-on' bonded dihydrogen was gathered through the observation that the H–D coupling constant in the ^{1}H NMR spectra of **I**, in Figure 2, is smaller than that of HD gas (**I** $^1J_{H–D}$ = 34 Hz, H–D gas $^1J_{H–D}$ = 43 Hz). The authors note the significance of this complex as an 'arrested form' of oxidative addition of H_2 to a metal centre and subsequently, 35 years of investigation into σ-complexes has followed. The bonding in σ-complexes has been depicted in multiple different ways throughout the literature. During this thesis, if there is satisfactory spectroscopic evidence provided, the bonding in a 3-centre,2-electron interaction will be depicted as in Figure 2 - **II**. A solid line will be used to represent the strongest interaction in the core (E–H or M–H) and dotted lines used to represent weaker interactions (M'---E or M'---M and M'---H).

1.2 Importance in Catalysis

It is widely accepted that bond-breaking processes are related to the binding of substrates to transition metal centres.[5,6] The reversible coordination of a σ-bond in a substrate to the metal centre is often a key step in a number of catalytic reactions.[7] Bond breaking often occurs through oxidative addition to the transition metal.[8,9] One example of the prevalence of 3-centre,2-electron bonds in mechanisms featuring transition metal catalysts has been outlined through DFT calculations on the thermal dehydrogenation of alkanes by an iridium pincer complex (Scheme 1 - **III**).[10]



Scheme 1 - The model iridium pincer complexes featuring 3-centre,2-electron interactions in the proposed mechanisms for thermal hydrogenation of alkanes

Despite controversies surrounding the proposal of two different mechanisms for this transformation, both the associative and dissociative mechanisms proposed by Hall and co-workers and Goldman and co-workers feature an iridium complex containing a 3-centre,2-electron σ-alkane interaction (Scheme 1 – **IV** and **V**).[11,12]

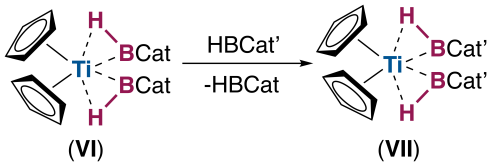
There have been many examples in transition metal chemistry whereby the approach and coordination of an E–H (E = H, C, Si) bond to a metal centre has been postulated as an important step in catalysis and these complexes have undergone extensive characterisation and scrutiny in the literature.[7,13] For the purpose of this thesis, a review of these lighter σ-complexes will not be completed, and the focus will be on neutral σ-boranes and σ-complexes featuring E–H and M–H moieties (E = B, M = Al, Ga, Zn).[14] The complexes featured in this introduction aim to span the periodic table and will either have; a) been reported with sufficient spectroscopic or theoretical evidence for the characterisation of a 3-centre,2-electron interaction or b) contain M'–H–E or M'–H–M interactions and provide discussion points for well-characterised examples of σ-complexes.

2. σ-Complexes of Transition Metals

2.1 σ-Complexes of Early Transition Metals

Titanium and Zirconium

Examples of σ-complexes of the early transition metals are dominated by interactions of boranes and alanes with titanium and zirconium fragments. Reaction of 3-5 equivalents of catechol borane (HBCat) or 4-methylcatechol borane (HBCat') with titanocene dimethyl affords methane, methylcatecholborane and the σ-complexes **VI** and **VII** (Scheme 2).[15] The B–H bond distance in **VI** and B–H stretching frequencies in its IR spectra shows a reduced B–H bond order compared to free catechol borane (**VI** B–H = 1.268 Å; **VI** ν_{B-H} = 1611 cm^{-1}, HBCat ν_{B-H} = 2660 cm^{-1}). In addition, the Ti–B distance in **VI** is significantly longer than that of metallocene boryl complexes and the authors comment that the Ti–H distance is typical for that of a bridging hydride (**VI** Ti–B = 2.335(5) Å, Ti–H = 1.779 Å). This spectroscopic evidence is consistent with **VI** being described as a d^2 σ-borane complex of titanium, complexed to two neutral borane fragments.



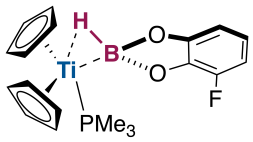
(**VI**) (**VII**)

Scheme 2 - A crossover reaction to form the complex VII from VI reported by Hartwig and co-workers

A crossover experiment was performed on a pure sample of **VI** with the addition of HBCat' to generate **VII**, confirming the kinetically labile interaction between the titanium and B–H fragments. Using the model complex $[Cp_2Ti(HB(OH)_2)_2]$, DFT calculations were performed to probe the bonding between the transition metal fragments and the boranes.[16] Stabilisation occurs *via* donation of electron density from the σ-B–H bond to the titanium centre and concurrent back-donation occurs into the p-orbital on the boron. Additional *intramolecular* stabilisation is also occurring, whereby a 3-centre,2-electron bond involving the B–Ti–B triangle in **VI** was noted due to the observation of a short B---B distance in the crystal structure and analysis of the Laplacian plot.

Reaction of **VII** with one equivalent of PMe_3 generated $[Cp_2Ti(HBCat')(PMe_3)]$. Hartwig and co-workers subsequently expanded the series of σ-complexes of this type through the synthesis of the fluorinated analogue, **VIII** (Figure 3). This complex was independently synthesised from the

3-fluoro borane [HBCat-3-F] and [$Cp_2Ti(PMe_3)_2$] in order to gain further understanding of the interactions in the Ti–H–B core.[17]

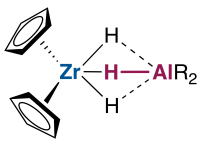


(**VIII**)

Figure 3 - A σ-borane complex of titanium reported by Hartwig and co-workers

An acute H–Ti–B angle of 36(2) °, relatively long Ti–B bond (2.267(6) Å) and typical Ti–H bond (1.61(5) Å) are indicative of the presence of a 3-centre,2-electron interaction in **VIII**. The basicity of the phosphine ligand on **VIII** alters the electronics of the titanium centre such that **VIII** contains a 3-centre,2-electron interaction with shorter B–H, B–Ti and longer Ti–H bonds than **VI**. Therefore, **VIII** represents an intermediary structure in the oxidative addition of a B–H bond at titanium.

With regards to the heavier group 4 metals, the first examples of coordination of Al–H to a zirconium centre was reported by Schwartz and co-workers.[18] Reaction of the zirconocene dihydride [Cp_2ZrH_2] with diisobutylaluminium hydride (DIBAL) generates [$Cp_2Zr(H)_3AlR_2$], **IX** (Figure 4). This structure was proposed due to the presence of a peak at -0.28 ppm and a broad peak at -2.03 ppm in the ^{1}H NMR spectra integrating to two semi-bridging hydrides and one bridging hydride respectively. Whilst not enough evidence is provided to specifically characterise complex **IX** as a σ-alane complex of zirconium, it is noted that the alane fragment acts both as an acceptor and a donor towards the zirconium hydride fragment.



(**IX**)

Figure 4 - Complex IX reported by Schwartz and co-workers featuring an example of a Zr–H–Al interaction

With enhanced appreciation of zirconium-aluminium hydride complexes as intermediates in catalytic reactions, reaction of the zirconium dichloride complex [Cp_2ZrCl_2] with an excess of $LiAlH_4$ in THF followed by subsequent ligand transfer from gallium to aluminium with [H_3GaL]

(L = quinuclidine, NMe_3), was reported by Raston and co-workers.[19] This generated the aluminium hydride complexes of zirconium $[Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(quinuclidine)]$ **X** and $[Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NMe_3)]$ **XI** respectively (Figure 5).

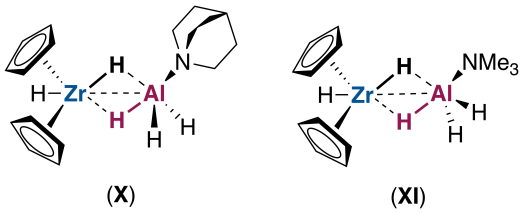


Figure 5 - Aluminium hydride complexes of zirconium reported by Raston and co-workers

These complexes can be considered as adducts of the two metal fragments and can indeed also be synthesised by reaction of one equivalent of $[Cp_2Zr(H)_2]$ and H_3AlL (L = quinuclidine, NMe_3). The Zr–$H^{bridiging}$ distances in **X** and **XI** are comparable to those within the zirconocene dimer $[\{(\eta^5\text{-}C_5H_2Me)_2ZrH\}_2(\mu\text{-}H_2)]$, suggestive of a weak interaction with the aluminium centre. Furthermore, the Al---Zr distances in **X** and **XI** are long (**X** = 3.0005(7) Å, **XI** = 2.994(3) Å) and suggest that little M'–M interaction is occurring in the Zr–$(H)_2$–Al core. The use of approximate density functional theory confirmed a similar bonding picture to that outlined for **VI** and **VII**, whereby a vacant d orbital on the zirconium centre accepts electron density from the Al-H σ-bond, whilst simultaneous donation from the σ-Zr–H bond into a p-orbital on aluminium occurs.

The Crimmin group have also reported the isolation of complexes of zirconium featuring multiply-bridged M–H interactions of the type $[LM(H)_n(\mu\text{–}H)_2Zr(H)Cp_2]$ (M = Al, n = 1; M = Zn, n = 0; M = Mg, n = 0; L = β-diketimate).[20,21] Whilst investigations into the zinc and magnesium analogues reveal that the metal fragments are not in equilibrium in solution, the aluminium analogue forms reversibly and establishes an equilibrium with its parent metal fragments.

2.2 σ-Complexes of Mid Transition Metals

Niobium and Tantalum

Smith and co-workers reported the isolation of a complex containing a Nb–H–B interaction in 1997, through the isolation of $[Cp^*_2Nb(H_2BO_2C_6H_3\text{-}3\text{-}^tBu)]$, Figure 6 - **XII**.[22] Initially, a comprehensive investigation into the bonding of a Cp analogue of **XII**, $(Cp_2Nb[BH_2(O_2C_6H_4)])$,

was carried out by Hartwig and co-workers, whereby they suggest that this complex is more accurately described as a d^0-niobium(V) boryl.[23] In comparison, complex **XII** crystallises with an acute H–Nb–H angle and longer B–H distances than found for the free borane, as well as a relatively long Nb–B bond (**XII** H–Nb–H = 73(2)°, Nb–B = (2.348(4) Å), however, the authors conclude that **XII** can be considered as a HBL (L = $O_2C_6H_3$-3-^{t}Bu) adduct of [Cp*$_2$NbH].

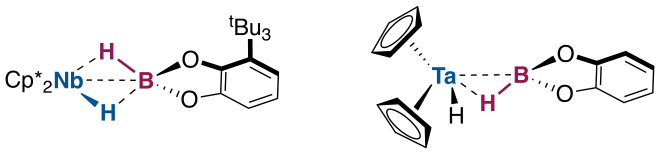


Figure 6 - Complexes of niobium and tantalum reported by Smith and co-workers

This series of σ-complexes with B–H bonds was expanded to include the heavier group 5 metal, tantalum.[24] The *exo*-isomer of [$Cp_2Ta(H)(\eta^2$-$HB(OC_2H_2O)$] **XIII**, was synthesised *via* the reaction of catecholborane with [Cp_2TaH_2Li] and identified as its *endo*-form by characteristic doublet and broad singlet in the ^{1}H NMR spectrum at δ = -4.2 ppm and δ = -5.2 ppm respectively. Subsequent DFT calculations on this complex confirm its characterisation as a σ-complex of tantalum, whilst the Laplican plots of the *endo*-isomer do not show a B–H interaction, the corresponding *exo*-isomer shows significant charge along the B–H bond.

Chromium, Molybdenum, Tungsten and Manganese

σ-Complexes of the group 6 and 7 metals focussed on the coordination chemistry of alanes and boranes. In 2012, Aldridge and co-workers reported examples of σ-complexes of these metals with various N-supported aluminium fragments Figure 7 - **XIV** – **XV**.[25]

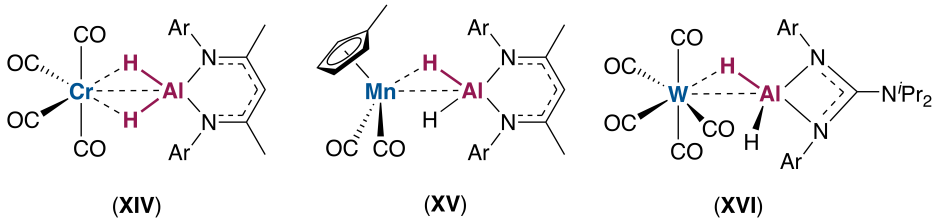
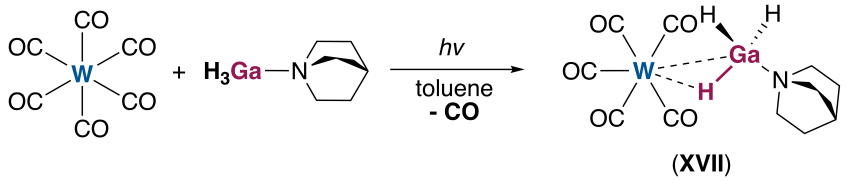


Figure 7 - σ-Complexes of group 6 and 7 metals reported by Aldridge and co-workers, Ar = Dipp

Photolysis of a 1:1 mixture of [{HC(CMeNDipp)$_2$}AlH_2] and [Cp′$Mn(CO)_3$] generated **XV**, confirmed by a high-field shifted Mn–H–Al signal at δ = -15.4 ppm in the ^{1}H NMR spectrum.

Slow exchange of the 'bound and unbound' hydrides are reported on the NMR time scale at temperatures up to 75 °C. The relative geometry of the two fragments is indicative of σ-donation from the alane, with a Cp–Mn–Al–H torsion angle of 67°, suggesting minimal overlap of the σ*-Al–H bond with the HOMO on manganese and back-donation from the transition metal into the σ*-Al–H orbital. Additionally, photolytic treatment of either [{HC(CMeNDipp)$_2$}AlH$_2$] or [{PhC(^{i}PrN)$_2$}AlClH] with [M(CO)$_6$] (M = Cr, W) generated **XIV** and **XVI** respectively *via* substitution of the carbonyl ligands on the transition metal fragment. In the case of the chromium analogue, a shorter Cr---Al distance (**XIV** Cr---Al = 2.420(1) Å) than the tungsten analogue is observed, even when considering the different ionic radii (**XVI** W---Al = 2.841(1) Å). Additionally, the orientation of the alane ligands around the chromium centre in an equatorial position allows the probing of the σ-donating nature of the ligands through analysis of the Cr–C distances in the carbonyl ligands (Cr–C$_{trans\ to\ Al–H}$ = 1.834(3) Å, 1.846(3) Å; Cr–C$_{trans\ to\ CO}$ = 1.892(2) Å). The shorter Cr–C bond lengths in the case of the Cr–C distances *trans* to Al–H suggest that the alane ligands are weaker σ-donors than the carbonyl ligands. The relatively long M---Al interaction in complex **XVI** suggests that the dominant bonding interaction is through the Al–H fragment. DFT calculations on **XV** and **XVI** confirm the minor role of π-back-donation in alane coordination.

Ogino and co-workers reported an example of a σ-complex of tungsten in 2002 through the reaction outlined in Scheme 3.[26] Photolysis of a 1:1 mixture of [W(CO)$_6$] with [H$_3$GaL] (L = quinuclidine) generated the σ-complex [(OC)$_5$W(GaH$_3$L)] **XVII**, confirmed by the presence of Ga–H^{terminal} and Ga–H^{bridging} at δ = 5.51 and δ = -7.32 ppm in the ^{1}H NMR spectra. Whilst the Ga–H^{terminal} signal appeared broad due to the quadrapolar gallium nuclei, the Ga–H^{bridiging} signal featured tungsten satellites ($^1J_{W–H}$ = 48 Hz). Complex **XVII** crystallises with a Ga---W bond (3.0194(5) Å) that is much longer than previously reported for a Ga–W single bond, suggesting that a weak Ga---W interaction is present in the Ga–H–W core. In addition, **XVII** shows thermal instability and decomposes gradually at room temperature.



(**XVII**)

Scheme 3 - The synthesis of a σ-complex of tungsten with a W–H–Ga 3-centre,2-electron interaction reported by Ogino and co-workers

The Crimmin group have investigated the trajectory of an approach of a Zn–H bond to group 6 and 7 metals fragments, with 'snapshots' of the approach ranging from bridging hydride to σ-complex.[3] Photolysis of a 1:1 mixture of the zinc hydride fragment [{HC(CMeNDipp)$_2$}ZnH] and [M(CO)$_6$] (M = Cr, Mo), [(η^6-C$_6$H$_6$)Cr(CO)$_3$] or [(η^5-C$_5$H$_4$Me)Mn(CO)$_3$] in hydrocarbon solutions, and the pre-photolysis of [W(CO)$_6$] followed by subsequent addition of the zinc hydride fragment, generated the corresponding heterobimetallic complexes (Figure 8 - **XVIII** – **XXII**).

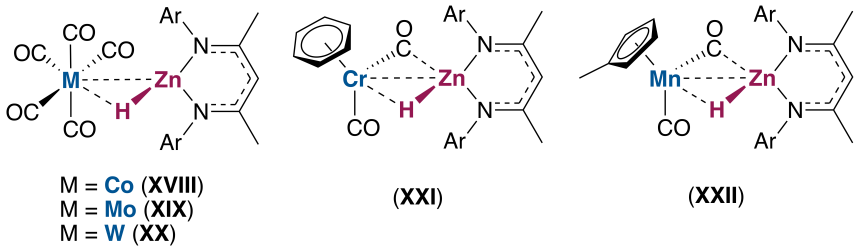


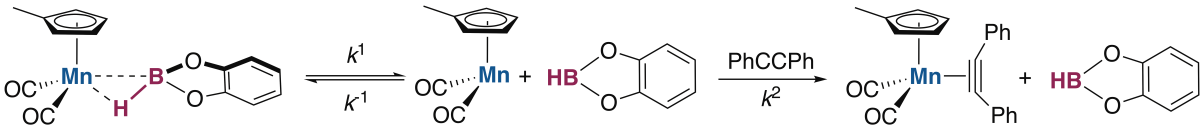
Figure 8 - σ-Zincane and hydride transfer complexes of chromium, molybdenum and tungsten reported by the Crimmin group, Ar = Dipp

Calculation of the formal shortness ratio (*fsr*) of each of these complexes normalises the M–Zn bond distances, allowing evaluation of the 3-centre,2-electron interaction. For **XVIII** – **XX**, the *fsr* are 1.08 – 1.09 and thus can be considered as σ-zincane complexes of the transition metal fragment. Alteration of the ligands around the metal centre to include a π-donating ligand in **XXI** and **XXII** decreases the fsr to 1.02 – 1.04, and is suggestive of the complexes being further down the continuum towards a hydride transfer complex. DFT calculations reveal that as the *fsr* decreases, the Wiberg Bond Indices (WBI) of the M–Zn and M–H bonds increases and the extent of the M–H→Zn donor-acceptor interaction increases. This progression is said to resemble a scale from a σ-zincane to hydride transfer complex, with increasing M–Zn and M–H contributions in the M–H–Zn core.

σ-Complexes of Manganese

In a report by Hartwig and co-worker, a number of ligand substitution reactions of the σ-borane complex **XXIII** were performed in order to investigate the reversibility of borane coordination to a manganese centre.[27] The σ-borane complex **XXIII** reacts with excess HSiPh$_2$Me or HSnPh$_3$ to form the corresponding σ-silane and σ-stannane complexes, whereby it was noted that the stannane derivative is much more stable than the borane and silane analogues. Additionally, for the reaction outlined in Scheme 4, kinetic studies reveal that the rate of ligand

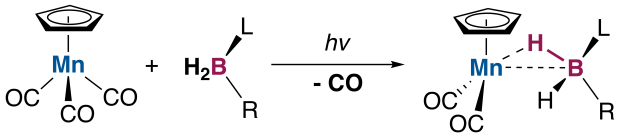
substitution of **XXIII** is reduced with added catecholborane. A disassociation enthalpy of ΔH = 24 kcal mol^{-1} is suggested to represent an upper limit for the manganese-borane bond disassociation energy, which is similar to that reported for the dissociation of catecholborane from a titanocene fragment in **VII**.[17]



(**XXIII**)

Scheme 4 - A ligand substitution reaction for a σ-borane complex of manganese reported by Hartwig and co-workers

Additionally, investigations into the stability of σ-borane complexes of manganese have been conducted by Shimoi and co-workers through a variation of the ligand on the borane.[28] Amongst the range of complexes identified by NMR spectroscopy, only **XXIV** was isolated and crystallographically characterised (Scheme 5). The borane fragment possesses a σ*-B–H which is high in energy and is arranged as such that the orientation of the σ*-B–H bond is not adequate for significant overlap with the HOMO of the manganese fragment.



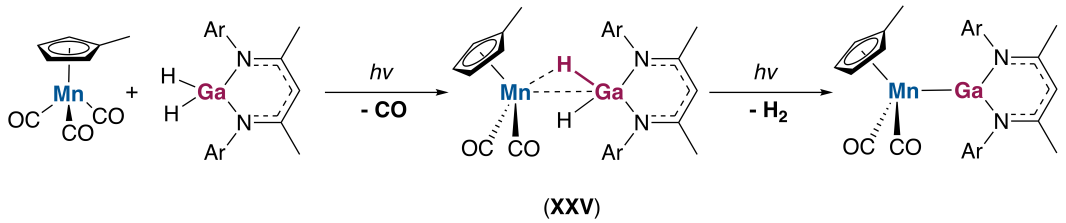
L = PMe_3, NMe_3
R = *m*-C_6H_4F, Ph, H, Me, Et

(**XXIV**)
L = NMe_3, R = Me

Scheme 5 - The synthesis of a series of σ-borane complexes of manganese reported by Shimoi and co-workers

The relative thermodynamic stability of the series of σ-borane complexes of manganese outlined in Scheme 5 was investigated through photolysis of [$MnCp(CO)_3$] with a 1:1 solution of [H_3BL] and [H_2BRL] to give an equilibrium mixture containing [$CpMn(CO)_2(\mu^1$-$H_3BL)$] and [$CpMn(CO)_2(\mu^1$-$H_2BRL)$] and the free borane fragments. The stability of the borane complexes was found to increase with the electron donating ability of the substituent on boron resulting in an increase in energy of the B–H σ-orbital.

Whilst the chemistry of the gallium dihydride [$H_2Ga\{(NDippCMe)_2CH\}$] mimics its lighter aluminium analogue somewhat, the heavier dihydride showed interesting reactivity with a [$Cp'Mn(CO)_3$] fragment, as outlined in Scheme 6.



(**XXV**)

Scheme 6 - Synthesis of a σ-gallane complex of Mn and subsequent dehydrogenation, Ar = Dipp

Photolysis of a 1:1 solution of the two metal fragments generated the σ-complex [Cp'Mn(CO)–H–Ga{(NDippCMe)CH}] **XXV**, which under forcing photolytic conditions subsequently expels H_2 to generate [$Cp'Mn(CO)_2$[$Ga\{(NDippCMe)_2CH\}$].[29] The dehydrogenation of **XXV** can be observed by ^{1}H NMR spectroscopy. Whereas the ^{1}H NMR spectrum of **XXV** features a doublet at δ = -13.5 ppm ($^2J_{H–H}$ = 19.2 Hz), the spectrum of the gallalyne complex features no signals in this region. Additionally, the geometric change on loss of H_2 from **XXV** is confirmed by a significant shortening of the Mn–Ga distance from 2.643(2) Å to 2.311(2) Å.

Rhenium

Hartwig and co-workers reported the synthesis of a σ-borane complex of rhenium *via* reaction of [*cis*-$Cp^*Re(CO)_2(BPin)_2$] with either methanol or neopentyl alcohol in benzene. After 2 hours at room temperature, a σ-borane complex [$Cp^*Re(CO)_2HBPin$] was confirmed due to the observation of a B–H–Re peak at δ = -11.1 ppm in the ^{1}H NMR spectra and a peak at δ = 46 ppm in the ^{11}B NMR spectrum corresponding to the borane. Despite multiple efforts, crystals suitable for X-ray diffraction were not generated.[27]

In a purely theoretical study by Pandey, a study of σ-borane complexes of rhenium of the type [$Cp'Re(CO)_2HBL$] (L = catechol, pinocolato, dimethyl) featuring three different borane ligands was conducted Figure 9 - **XXVI** – **XXVIII**.[30] The optimised Re–B bond distances in **XXVI** – **XXVIII** (**XXVI** = 2.212 Å, **XXVII** = 2.234 Å, **XXVIII** = 2.284 Å) are longer than expected for a Re–B single bond (2.10 Å) and the B–H bonds are significantly longer than calculated for the corresponding free boranes (**XXVI** = 1.445 Å, HBCat = 1.186 Å; **XXVII** = 1.479 Å,

HBPin = 1.194 Å, **XXVIII** = 1.422 Å, $HBMe_2$ = 1.208 Å). These complexes were described as being formally Re(I), in which both the boron and hydride have bonding interactions with the rhenium centre.

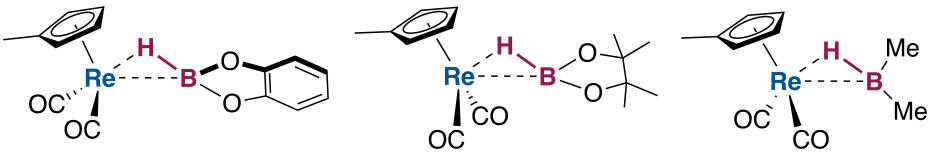


Figure 9 - The theoretical σ-complexes of rhenium investigated by Pandey

2.3 σ-Complexes of Late Transition Metals

Iron, Ruthenium and Osmium

A complex which perhaps outlines the complexities surrounding the characterisation of complexes that lie on a spectrum of a bonding model was discovered serendipitously from the reaction of [(PNP)FeCl•(C_7H_8)] with excess EtMgCl.[31] In this instance **XXIX** was generated and features a Fe–H–Mg moiety, with a Fe---Mg bond length of 2.6026(15) Å, which is slightly longer than the single bond radii reported by Pauling (2.529 Å)[32] and Pyykkö (2.55 Å).[33] The authors of this paper report the complex as featuring an intermetallic Fe–Mg bond and state that **XXIX** could not be unambiguously characterised in solution.

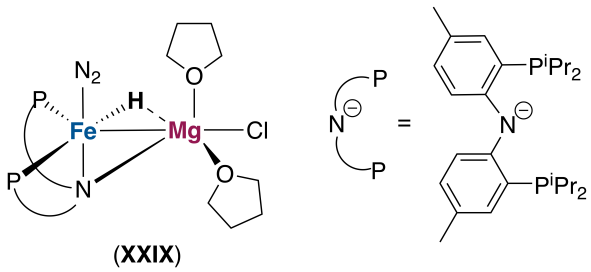
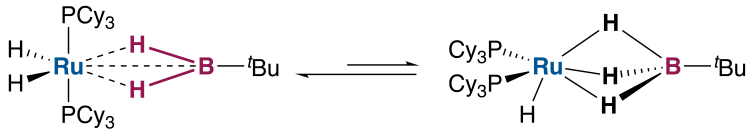


Figure 10 - A heterobimetallic featuring a Fe–H–Mg moiety reported by Mindiola and co-workers

Reports by Sabo-Etienne and co-workers have outlined different coordination modes of boranes to ruthenium centres, notably through the formation of mono and *bis*-σ-boranes.[34-36] Borane coordination to the ruthenium centre proceeds predominantly through σ-donation from a σ-B–H bond into a σ*-Ru−H orbital with simultaneous back-donation from the equatorial d_{xy} lone pair into the σ*-B−H orbital. The borane ligand is forced to lie in the equatorial plane for better orbital overlap. The σ-complex **XXX** was prepared *via* [$RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$] and lies in

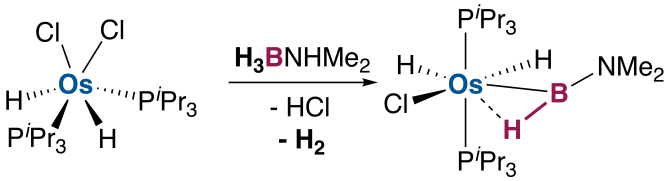
equilibrium in solution with the *tris*-borohydride ruthenium hydroborate analogue **XXX'**. At 273 K, both species can be observed by NMR spectroscopy and cross peaks observed in the ^{1}H EXSY spectra suggests that at this temperature, the hydrides are interconverting. A van't Hoff analysis of the equilibrium outlined in Scheme 7 was conducted through evaluation of the ^{1}H and ^{31}P NMR spectra to generate thermodynamic properties consistent with its reversibility ($\Delta G° = -0.65$ to -0.88 kcal mol^{-1}). The geometries of **XXX** and **XXX'** were optimised to clearly show the position of the three hydride ligands in **XXX'**.



(**XXX**) (**XXX'**)

Scheme 7 - The equilibrium between complexes XXX and XXX' reported by Sabo-Etienne and co-workers

Reaction of the octahedral osmium trihydride complex [$OsH_3Cl(P\textit{i}Pr_3)_2$] with a series of boranes was reported by Esteruelas and co-workers to generate three complexes featuring an Os–H–B interaction.[37] Complex **XXXI** was also prepared in this study *via* the reaction outlined in Scheme 8 and then subsequently investigated through a DFT study by Sabo-Etienne and co-workers.[38]



(**XXXI**)

Scheme 8 - The synthesis of XXXI, a complex of osmium featuring a B–H agostic interaction

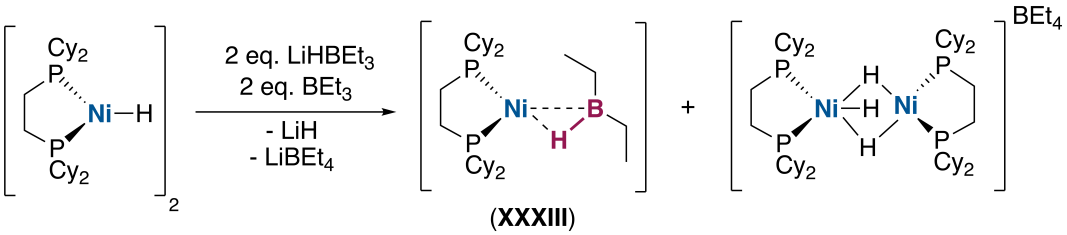
Whereas the initial study by Esteruelas and co-workers reported this complex as a σ-complex of osmium, DFT calculations suggest that it can better be described as an osmium(IV) hydrido-boryl complex with an α-agostic interaction of the B–H bond.

Rhodium, Iridium, Cobalt and Nickel

A number of cationic σ-borane complexes of rhodium have been synthesised as intermediates in the catalytic dehydrogenation of amine-boranes by Weller and co-workers.[39] The formation of a

cationic σ-gallane complex of rhodium was also reported by Aldridge and co-workers in a report on structural snapshots of E–H bond activation at a metal centre, as well as the synthesis of cationic σ-complexes of iridium.[40,41] The rhodium and cobalt analogues of the σ-zincane complexes of group 6 metals reported by the Crimmin group are more accurately characterised as transition metal zinc hydride transfer complexes. Additionally, reports by Aldridge and co-workers of the addition of two alane fragments to a cobalt centre concludes that far more Al–H activation has occurred in comparison to other isolated alane complexes of early transition metals.[42]

The observation and subsequent isolation of a series of σ-borane complexes of Ni(0) was achieved by García and co-workers.[43] The addition of two equivalents of the Ni–H to a mixture of $LiHBEt_3$ and BEt_3 resulted in the concomitant formation of the Ni(0) σ-borane and Ni(II) trihydride complexes as outlined in Scheme 9.



(**XXXIII**)

Scheme 9 - Synthesis of a σ-borane complex of nickel reported by García and co-workers

The Ni–B bond distance in **XXXII** (2.172(6) Å) is comparable to the Mn–B bond of a σ-borane complex reported by Hartwig and co-workers (2.187(3) Å). Furthermore, the $^{31}P\{^{1}H\}$ NMR signals are characteristic of a Ni(0) compound and thus suggest that a 3-centre,2-electron Ni–H–B moiety is present.

σ-Complexes of Main Group Elements

The synthesis of σ-complexes of main group elements still remain elusive, with the propensity to promote full oxidative addition of a bond the most common outcome in stoichiometric reactions with E–H (E = H, Si, B, Sn).[44,45]

In the oxidative addition of E–H bonds to a tin centre, reported by Aldridge and co-workers, the authors ponder over the characterisation of a σ-borane complex of tin, however, suggest that due to the short Sn–B separation and large Sn–H coupling constant ($^{1}J_{Sn–H}$ = 900 Hz), the

complex is better represented as an oxidative addition product.[46] Similarly, Aldridge and co-workers also report a series of E–H bond activations to a germanium centre, whereby the oxidative addition products are suggested.[47]

3. Coinage Metal Complexes Containing 3-Centre,2-Electron Interactions

Despite catalytic proficiencies of the coinage metals being a flourishing area of research, there are very few examples of interactions of an E–H or M–H bond with a coinage metal compared to transition metals.[48] Dihydrogen complexes of the coinage metals are essentially unknown in the condensed phase. Those of copper(I) have been considered as intermediates in the catalytic hydrogenation of CO_2, and semi-hydrogenation of alkynes with heterobimetallic catalysts, while those of gold(I) have been proposed as a high energy intermediates in alkene hydrogenation based on DFT calculations.[49-51] The occurrence of the +1 oxidation state in group 11 complexes and the associated d^{10}-configuration of the metal may explain the lack of observable and isolable σ-complexes. The electron configuration of group 11 M(I) (M = Cu, Ag, Au) complexes ensures that no unoccupied metal-based d-orbitals are available to accept electron density from a nearby σ-E–H bond.

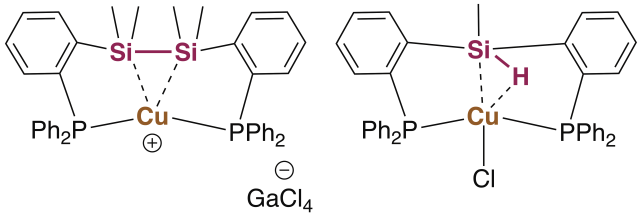
3.1 Methods of Stabilisation

A number of approaches to stabilise 3-centre,2-electron interactions of coinage metal compounds have emerged including *intramolecular* chelation of an E–H bond, increasing the number of E–H interactions to a metal centre and increasing the ionic component of the σ-bond from E–H to M–H (E = H, C, Si, M = Al, Zn). Thus, a small number of σ-complexes of the coinage metals have been reported in the past few years.

Chelation

Bourissou and co-workers have adopted a chelation strategy to prepare and isolate σ-complexes of Cu(I) and Au(I). *Intramolecular* coordination and activation of Si–Si, Si–H and Sn–Sn bonds, within *trans*-coordinating phosphine frameworks have been reported.[52-54] In the case of copper(I), activation of Si–Si occurred through reaction of the diphosphine-disilane ligand $[Ph_2P(C_6H_4)Me_2Si\text{-}SiMe_2(C_6H_4)PPh_2]$ with CuCl and $GaCl_3$ at reduced temperatures (-80 °C to 20

°C) generating **XXXIII** (Figure 11). This agostic complex of copper(I) was unstable at room temperature, however, crystals suitable for X-ray diffraction were obtained at -60 °C. The structure of **XXXIII** reveals Cu---Si distances of 2.7196(14) Å and 2.7212(14) Å. The copper centre is pointing towards the Si–Si σ-bond, which has lengthened significantly on coordination (ligand = 2.3581(11) Å, **XXXIII** = 2.4505(19) Å). The coordination of silver(I) to the same diphosphine-disilane ligand was also attempted, however, it was concluded through the same geometric parameters that the silane ligand does not bond to the silver centre through a σ-Si–Si bond.



(**XXXIII**) (**XXXIV**)

Figure 11 - Complexes of copper(I) featuring agostic interactions reported by Bourissou and co-workers

A similar method was also used for the coordination of a σ-Si–H bond to copper(I), through reaction with the diphosphine hydrosilane ligand [$Ph_2P(C_6H_4)SiH(Me)(C_6H_4)PPh_2$] and CuCl at -40 °C to generate **XXXIV**. Coordination of the Si–H bond is confirmed through the observation of reduced Si–H coupling in **XXXIV** compared to the free ligand in the ^1H NMR spectra (ligand $^1J_{Si-H}$ = 204 Hz, **XXXIV** $^1J_{Si-H}$ = 180 Hz) and reduced stretching frequency of the Si–H bond (ligand ν_{Si-H} = 2142 cm^{-1}, **XXXIV** ν_{Si-H} = 1996 cm^{-1}). Reaction of **XXXIV** with $GaCl_3$ forms the Lewis-adduct **XXXIV•GaCl$_3$**, whereby the Lewis acid interacts with the Cl atom but does not completely abstract it. This perturbation of the electronics of the copper centre results in a slightly stronger interaction between the Si–H σ-bond and the copper(I) centre.

In the case of an Sn–Sn analogue, oxidative addition of the Sn–Sn bond was observed owing to the isolation and characterisation of the corresponding Cu(III) distannyl complex.[55] Additionally, the oxidative addition of σ-Si–Si bonds is known to occur in both an *intra-* and *intermolecular* sense at gold(I) as outlined in Figure 12.[52,56]

Using chelation as a means to force coordination, claims have been made for agostic interactions in complexes of copper(II) bearing chelating organic ligands. While the intramolecular interaction between a carbon–hydrogen bond of a chiral ephedrine ligand and a copper(II)

centre was initially classified as agostic,[57] careful reanalysis shows that its characterisation as a multicentre intramolecular hydrogen bond is more accurate.[58] Similarly, weak and primarily electrostatic interactions in copper(I) and copper(II) complexes have been classified as anagostic.[59,60]

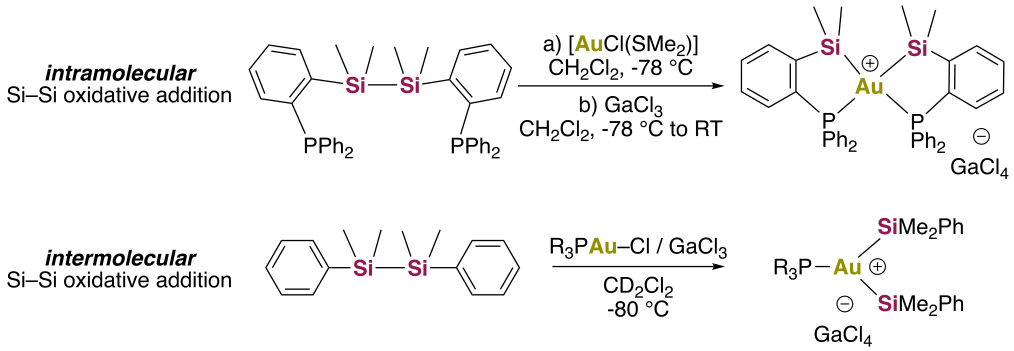


Figure 12 - Examples of oxidative addition of a σ-Si–Si bond at Au(I) to generate the corresponding Au(III) complexes; R = Ph or Ph(2-SiMe$_3$Ph)

Only in 2010 was convincing experimental (EPR) and computational (DFT) support for a C–H agostic interaction within a copper(II) azamacrocycle (Figure 13 - **XXXV**) provided by Stack, Ribas and co-workers.[61] The C–H interaction in **XXXV** was suggested to proceed *via* nonconventional σ-donation from the C–H bond to the half-filled $d_{x^2-y^2}$ orbital on copper.

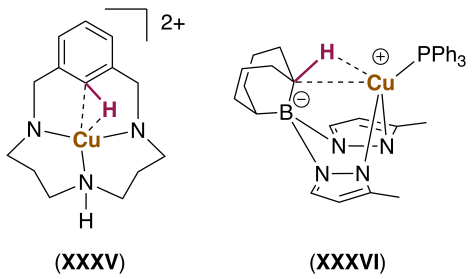
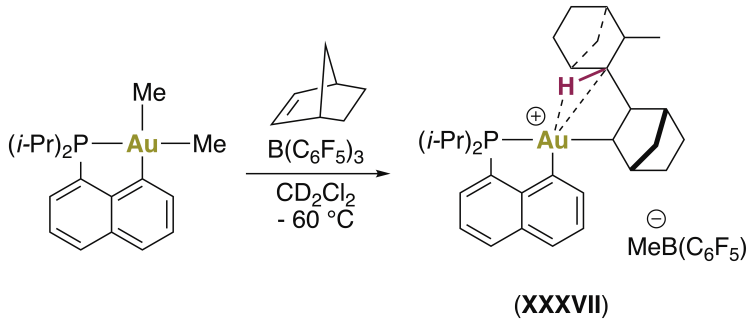


Figure 13 - Agostic C–H complexes of copper(II) and copper(I) reported by Stack and co-workers and Chen and co-workers

In addition, an agostic bond was reported in **XXXVI** prepared by Chen and co-workers. A relatively short Cu–H bond (2.22 Å) and more obtuse C–H–Cu angle (135.47°) compared to a complex featuring a similar B^- Cu^+ interaction was observed.[59] The copper(I) complexes reported were subsequently investigated in a range of N–H functionalisation reactions, whereby the formation of an agostic C–H interaction with copper(I) was proposed as an intermediate on the catalytic cycle.

Similarly to the chemistry of its lighter coinage metal counterpart, a comparable trend of speculation followed by unambiguous characterisation can be found for gold(I) and gold(III) agostic complexes. Bourissou and co-workers recently carried out low temperature spectroscopic characterisation and computational modelling of a square-planar d^8-gold complex possessing an agostic C–H interaction.[62,63] **XXXVII** was prepared *via* addition of $B(C_6F_5)_3$ to a solution of the gold precursor and norbornene at low temperatures (-90 °C), with its formation occurring at -60 °C as outlined in Scheme 10.



(**XXXVII**)

Scheme 10 - The synthesis of a complex of Au(III) featuring a C–H agostic interaction by Bourissou and co-workers

Spectroscopically, an agostic C–H interaction in **XXXVII** was observed *via* the presence of a relatively small C–H coupling constant ($C–H^{agostic}$ $^1J_{C–H}$ = 97 Hz, $C–H^{classical}$ $^1J_{C–H}$ = around 130 Hz). These findings were corroborated with DFT calculations, which through a combination of quantum theory of atoms in molecules (QTAIM) and second order perturbation theory analysis showed a bond critical path between the $C–H^{agostic}$ and Au atoms and a stabilisation energy of 18.6 kcal mol^{-1}. In addition, a series of gold-alkyl species were synthesised and their reactivity with norbornene investigated.[64]

The synthesis of complexes with agostic-like interactions of C–H and B–H with a silver centre has been reported, however, the lack of evidence to support these complexes suggests that no silver(I) agostic interactions are known to date.[65,66]

Increasing Interactions

An alternative strategy adopted to prepare σ-complexes of the coinage metals is to maximise the number of binding events. This approach has been argued as a means to stabilise notoriously weak *intermolecular* σ-alkane complexes of transition metals.[67] By deviating from a 1:1 ratio of transition metal:σ-bond the number of potential interactions, and the binding enthalpy, can be

maximised. Two cationic copper(I) diborane complexes have been isolated in which the diborane coordinates to the metal through two σ-B–H bonds.[68,69]

An IR spectra of **XXXVIII** reveals a difference in B–H stretching frequencies for the bridging B–H bonds and terminal B–H bonds, with reduced vibrational frequency observed in the former ($B–H^{bridging}$ $\nu_{B–H}$ = 1938 cm^{-1}; $B–H^{terminal}$ $\nu_{B–H}$ = 2340 cm^{-1}). For the series of complexes reported by Himmel and co-workers (Figure 14 - **XXXIX**), ^{11}B NMR spectra showed broad resonances that are significantly downfield shifted compared to the free borane (X = I δ = -10.31 ppm; X = Br δ = -10.02 ppm; X = Cl δ = -10.01 ppm; borane δ = -2.41 ppm).

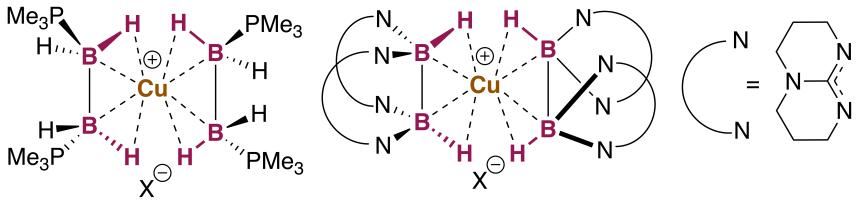
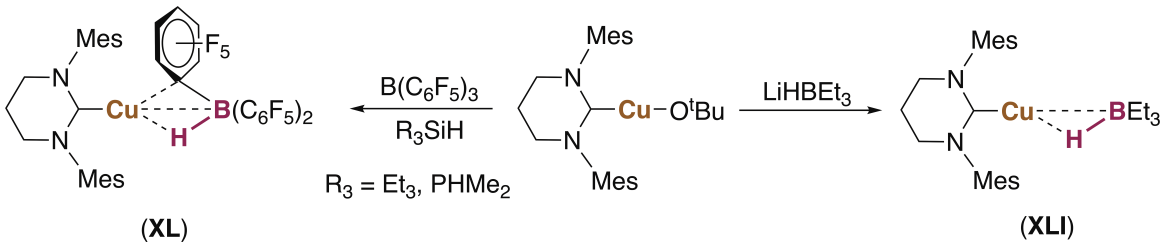


Figure 14 - Diborane B–H complexes of copper synthesised by Onigo and co-workers and Himmel and co-workers, X = Br, Cl, I

Increasing Ionic Component

Borane-capped copper(I) hydrides have been prepared by addition of boranes to a terminal copper hydride.[70,71] Initially, Bertrand and co-workers reported a borane-stabilised CAAC-copper complex [CAAC = cyclic(alkyl)(amino)carbene], which was shown to be active in the hydrolytic dehydrogenation of BH_3NH_3.[69] More recently, an extensive study into the stabilisation of σ-boranes of copper(I) has been performed by Whittlesey and co-workers, as outlined in Scheme 11.



Scheme 11 - The formation of complexes containing Cu–H–B moieties by Whittlesey and co-workers

Complexes **XL** and **XLI** were prepared *via* reaction of the copper complex [(6Mes)Cu(OtBu)] with the corresponding boron fragment, and in the case of $B(C_6F_5)_3$ the addition of silane as a

hydride source. The Cu–H interaction in **XLI** was confirmed *via* ^{13}C NMR spectroscopy, whereby coupling to the carbenic carbon at δ = 202 ppm ($^{2}J_{C–H}$ = 12 Hz) was observed. In addition, a relatively small B–H coupling constant in the ^{11}B NMR spectrum of complex **XL** ($^{1}J_{B–H}$ = 60 Hz) is suggestive of a significant Cu–H–B interaction. DFT calculations on **XL** and **XLI** reveal that the charge distribution is most similar to that in the free ions, rather than the neutral fragments. NBO analysis highlights a significant σ-B–H to Cu donation, quantified by second order perturbation theory (**XL** = 43 kcal mol^{-1}, **XLI** = 67 kcal mol^{-1}).

Through serendipitous discovery, the Crimmin group reported that copper(I) β-diketiminate (*BDI*) fragments are well suited for E–H binding (E = B, Al, Zn).[72,73] In the case of E = B, this represents stabilisation *via* multiple interactions and for E = Al, Zn, represents stabilisation *via* increasing ionic component of E–H. Reaction of one equivalent of the toluene stabilised inverse sandwich *BDI* copper(I) complex [{HC(ArNCMe$_3$)$_2$}Cu$_2$•toluene] (Ar = 2,6-Cl$_2$C$_6$H$_3$) with a series of main group hydride fragments allowed for isolation and full characterisation of **XLII** – **XLVI**.

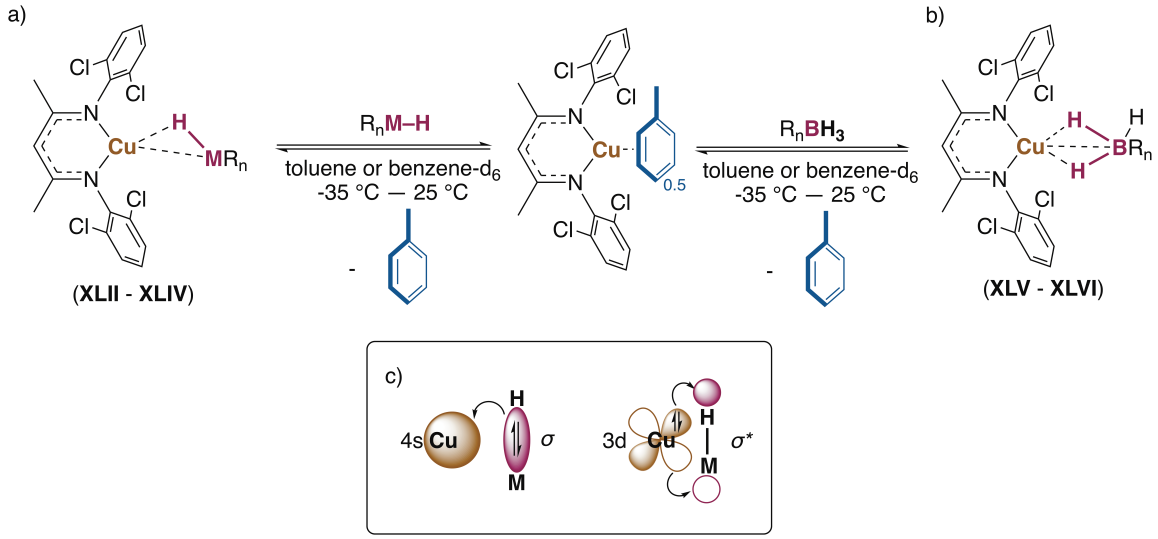


Figure 15 - a) XLII $R_nM–H$ = [{HC(CMeNDipp)$_2$}ZnH], XLIII $R_nE–H$ = [{HC(CMeNMes)$_2$}AlH$_2$], XLIV $R_nM–H$ = [{HC(CMe)$_2$NMes(NMe$_3$)}AlH$_2$], b) XLV R_n = NMe$_3$, XLVI R_n = 2-methylpyridine, c) Dewar-Chatt-Duncanson-type representation of bonding within σ-complexes of copper(I)

In all examples, either loss of or significant broadening of the E–H peak was observed in the ^{1}H NMR spectra at room temperature on complexation to the copper(I) fragment. Dissolving pure samples of **XLII**, **XLV** and **XLVI** in toluene-d$_8$ allowed for the investigation into the solution dynamics of these complexes. Variable temperature NMR show that at reduced temperatures (**XLII** 243 K, **XLV** = 333 K, **XLVI** = 193 K), the equilibrium outlined in Figure 15a enters the

slow-exchange regime and both sides of the equilibrium can be observed. A van't Hoff analysis of these equilibria generated thermodynamic properties consistent with weak and reversible binding of the main group metal hydrides to copper(I) (**XLII** ΔG_{298K} = +0.65(8) kcal mol^{-1}, **XLV** ΔG_{298K} = -0.23(4) kcal mol^{-1}, **XLVI** ΔG_{298K} = +0.17(3) kcal mol^{-1}). DFT calculations reveal that the bent {CuL_2} fragment possesses an accessible LUMO (or LUMO+1) that is largely 4s in character and orientated in between the flanking arms of the ligand. The symmetry and energy of the 4s-based orbital circumvents the problem of available d-orbitals as it is capable of accepting electron density from a σ-E–H bond, similarly the HOMO (or HOMO-1) is of suitable symmetry to back-donate into the σ*-E–H orbital, as outlined in Figure 15c. Thus, reversible *intermolecular* binding of σ-boranes, σ-alanes and σ-zincanes to these copper(I) fragments is possible. By increasing the ionicity of the E–H bond from E = B to E = Al, Zn the binding energy is maximised. The utilisation of bent complexes of copper(I) for the synthesis of σ-complexes promotes increased back-donation from the metal centre and subsequently increased stability. This, in combination with increasing ionicity, resulted in the isolation and characterisation of previously inaccessible types of σ-complexes of copper(I).

3.2 Bent d^{10}-{ML_2} Complexes

Previous investigations into the effect of bending the L–M–L angle in d^{10}-{ML_2} complexes on oxidative addition reactions have been reported.[43,74-77]

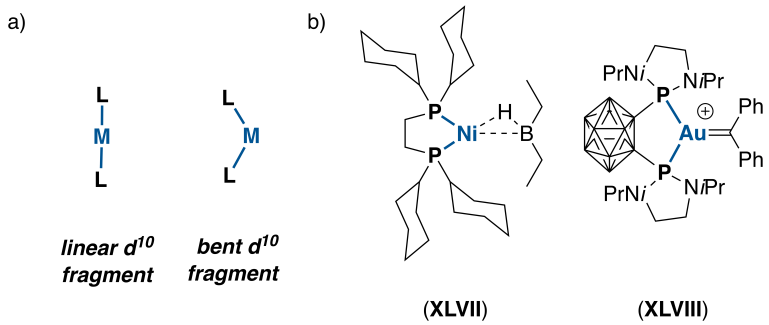


Figure 16 - a) linear to bent formation of ligands around a metal centre, b) two examples of bent complexes of d^{10} complexes of nickel and gold

For diphosphine complexes of gold(I), bending caused by increased steric bulk on the ligand enhances π-back-donation to the coordinated substrate (Figure 16 - **XLVIII** redrawn from Figure 7). This structural feature has been reported as an important stereoelectronic requirement for efficient back-donation upon binding of small molecules and can ultimately result in

oxidative addition reactions.[77] The formation and characterisation of Ni(0)-alkylboranes possessing a bent phosphine ligand has also been reported (Figure 16 - **XLVII**).[43]

A number of groups have considered the Walsh diagram for a linear to bent deformation of d^{10}-{ML_2} complexes.[75,76] DFT calculations performed using the ωB97X-D functional and a hybrid 6-311G*/SDD basis set (6-311G* (C, H, N, Cl) SDD (Cu)) on the naked copper fragment [{$HC(ArNCMe_3)_2$}Cu] (Ar = 2,6-$Cl_2C_6H_3$) are in good agreement with the MO diagram of a C_{2v}-symmetric d^{10} ML_2 complex containing a π-donating ligand, as shown in Figure 17.[74]

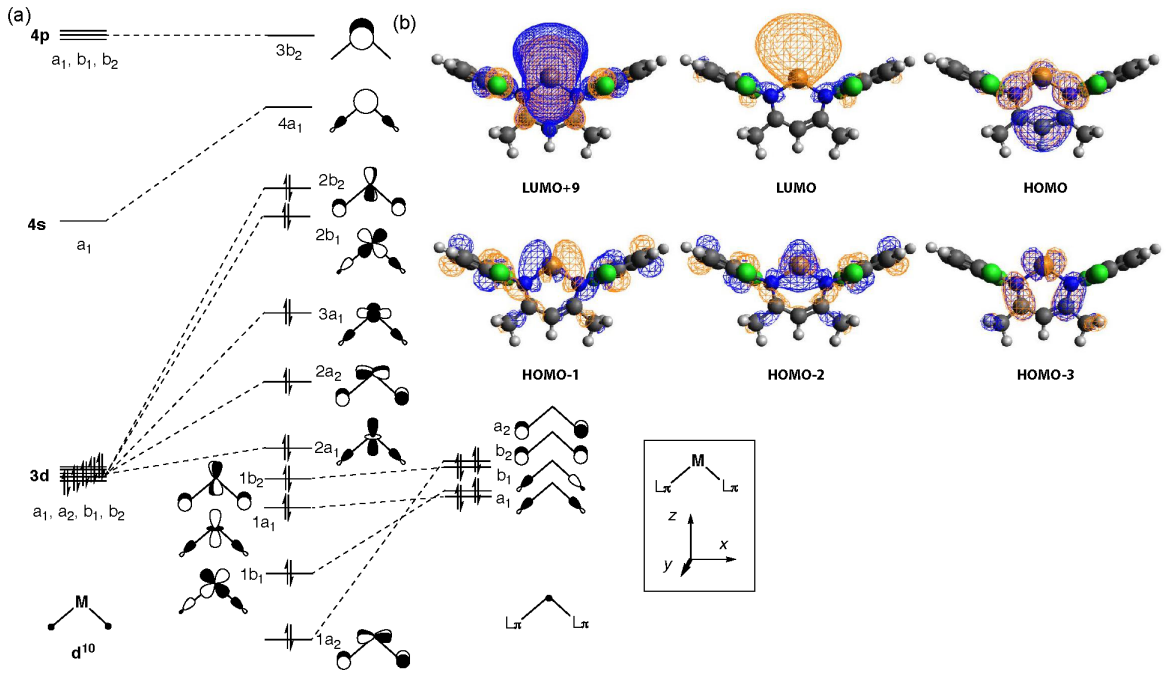


Figure 17 - a) Qualitative MO diagram for a C_{2v} {CuL_2} fragment with a π-donor ligand, b) selected calculated molecular orbitals for a copper(I) fragment

4. Thesis Outline

4.1 Aims

The aim of the work presented in this thesis is to expand the series of already known σ-complexes of copper(I), as outlined in Figure 15. Initially, a novel series of electron-deficient β-diketiminate copper(I) complexes will be synthesised and their electronic properties probed. Subsequently, investigations into the suitability of different M–H moieties (M = Mg, Ca, Au, W) as binding substrates to the copper(I) centre will be carried out. The new heterobimetallic complexes will be characterised by X-ray crystallography, in solution by NMR spectroscopy and *via* DFT calculations to provide an enhanced description of the bonding in the Cu–H–M 3-centre,2-electron core.

4.2 Contributions

The author of this thesis performed all of the experimental work as detailed in the experimental sections at the end of each chapter. The author performed the variable temperature NMR experiments featured in chapter 3 and all additional NMR experiments were either performed by one of the NMR technicians at Imperial College London or *via* automated NMR programmes. The author performed all DFT calculations and Dr Mark Crimmin produced the qualitative MO diagrams. Dr Andrew White at Imperial College London carried out X-ray data generation and analysis.

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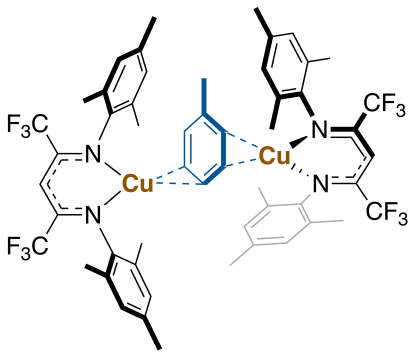
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a frog in a well does not know the great sea

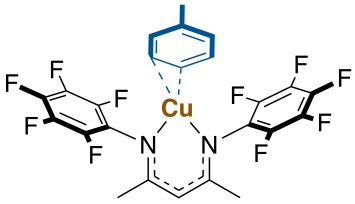
Chapter 2

Synthesis & Characterisation of β-Diketiminate Complexes of Copper(I)

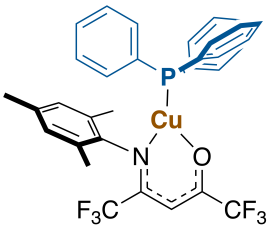
A series of copper(I) complexes bearing electron-deficient β–diketiminate ligands have been prepared. The study includes the symmetric complexes [{{ArNC(CR$_3$)}$_2$CH}Cu(η^2-toluene)$_n$] (Ar = Mes, R = F, n = 0.5, [1$_2$•tol]; Ar = C$_6$F$_5$, R = Me, n = 1, [2•tol]) and asymmetric complex [{{ArNO(CCF$_3$)$_2$}CH}CuPPh$_3$], 4•PPh$_3$ (Ar = Mes). Their electronic properties have been probed by IR spectroscopy and DFT analysis in preparation for use as fragments for the synthesis of σ-complexes of copper(I).



dimeric inverse sandwich



monomeric arene adduct



asymmetric phosphine adduct

Sections of this chapter have been published – *Inorg. Chem.*, 2017, **56**, 8669–8682

1. Introduction

1.1 β–Diketiminate ligands in coordination chemistry

β–Diketiminate ligands, *BDI* ligands or *nac-nacs* as they are more anecdotally known, are a class of ligand utilised extensively for the stabilisation of main group, transition metal and alkaline earth metal compounds.[1,2] Whilst the initial synthesis of these ligands occurred some 50 years ago, it was not until a cascade of publications throughout the 1990's by, amongst others, Lappert and co-workers, that they became a prominent fixture in an organometallic chemists toolkit.[1,3] Characterised as a ligand anion, this ligand traditionally stabilises metal ions through the formation of a delocalised 6-membered imine-amine ring motif. Compared to the traditional di-chelating acetylacetone ligand (*acac*), *BDI* ligands offer more steric protection at the metal centre, making them less labile and more suited as spectator ligands.[4]

As a ligand class, *BDI* ligands possess structural versatility, with examples containing a wide-range of functional groups known. This adaptability allows the tuning of steric and electronic effects in order to influence the properties of the metal centre.[4] They are formally referred to as L_2X-type ligands as, for metal ions that possess formally low-lying, vacant d-orbitals, *BDI* ligands are able to provide extra stabilisation through additional π-bonding.[2]

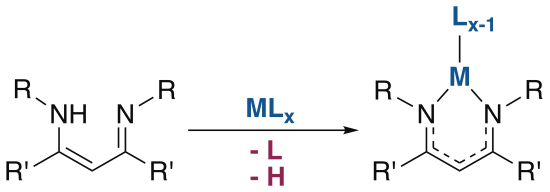


Figure 1 - A typical *BDI* ligand and its reaction with a metal salt to form a metal *BDI* complex

Generally, metal ions adopting a tetrahedral or pseudo-tetrahedral bonding mode assume an arrangement within the plane of the ligand.

Nomenclature

Throughout this thesis, *BDI* ligands will be referred to as **L^{n}H** whereby the ligands will possess different aromatic groups or backbone moieties. On complexation of a copper centre to arene solvent (solv), or other ligand (L) the copper complexes will be given the labels **1-11•solv** or **1-11•L** respectively (for examples see Figure 3). In future chapters, when the ligands are used as

supports for metal hydride complexes, they will be referred to as **L^{n}M–H**. In prose, the groups directly bonded to the nitrogen will be referred to as the aromatic group, and the functional groups on the backbone of the ligand will be referred to as such.

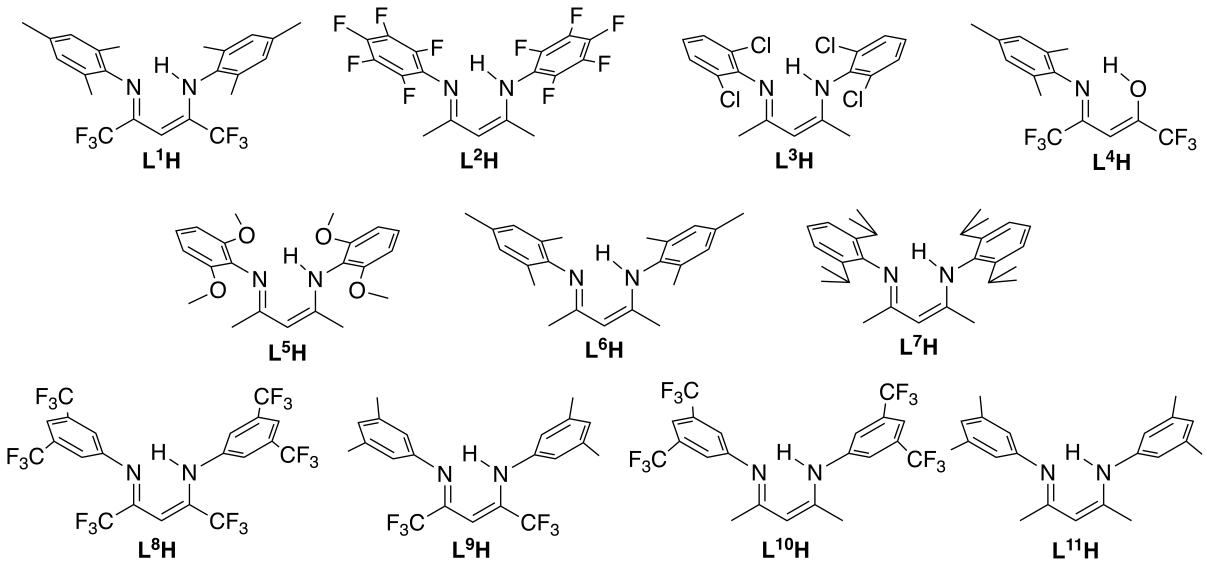


Figure 2 - Line drawings of the *nac-nac* and *ac-nac* ligands to be used throughout this thesis

1.2 BDI complexes of copper(I)

The first structurally characterised *BDI* complex of copper(I) featured a nitro group in the backbone position of the ligand.[5] Since then, extensive work detailing the synthesis and characterisation of *BDI* complexes of copper(I) for the activation of small molecules has been described (Figure 3).[6-16]

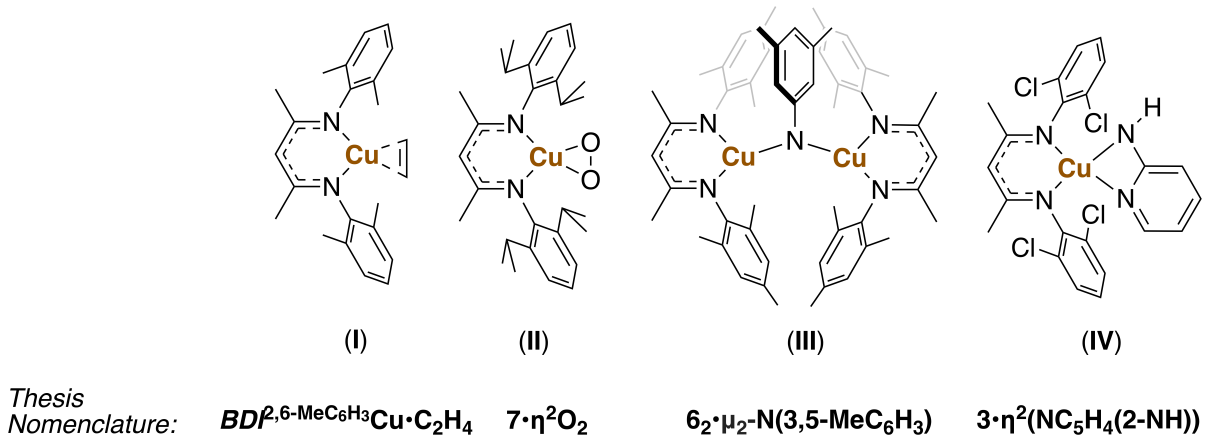


Figure 3 - Examples of copper complexes with *BDI* ligands used for small molecule activation and catalysis

Furthermore, *BDI* complexes of copper have been used as catalysts for C–H amination (Figure 3 - **III - IV**).[17] Work by Warren and co-workers showed that the use of the *BDI* ligand **L^{6}H** was able to provide sufficient stabilisation for the isolation of a dicopper nitrene species as intermediates in C–H amination.[6] In many cases, *BDI* complexes of copper(I) stabilised with arene solvents and have been used as catalytic precursors and shown great versatility.[18]

1.3 Altering the Electronics at Copper

In addition to the use of bent {CuL_2} fragments, it was postulated by the Crimmin Group that changing the electronics of the *BDI* ligand thus the {CuL_2} fragment would invoke further stabilisation of σ-complexes of copper(I). Through removing electron density from the metal centre, the metal centre itself would be encouraged to receive more electron density from nearby E–H or M–H bonds.[19] As part of the studies on *BDI* complexes of copper(I) for small molecule activation and catalysis, several groups have prepared and studied fluorinated derivatives of these ligands.[16,18] Studies by Sadighi and co-workers previously revealed that adding fluorines to either the aromatic ring or backbone of the *BDI* ligand would alter the electronic properties of the copper(I) centre.[18] The preparation of new fluorinated, bent complexes of copper(I) for the binding of E–H and M–H bonds (E = B, M = Zn, Mg, Ca, B, Au, W) will form the basis of the work in this thesis.

2. Synthesis and Characterisation

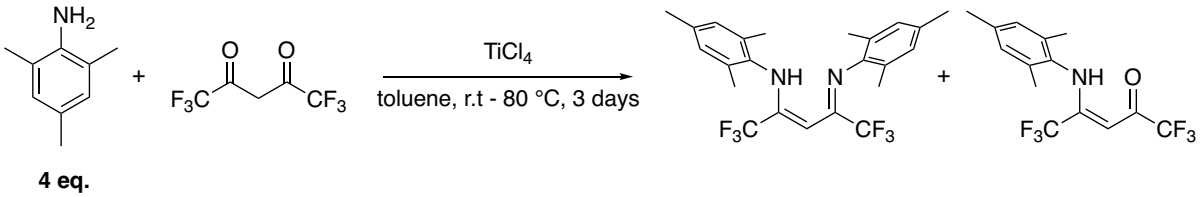
2.1 Fluorinated BDI Ligands

Preparation

BDI ligands can be prepared on a multi-gram scale, *via* a condensation reaction between a 1,3-dicarbonyl and a primary amine in the presence of an acid. As outlined in Scheme 1, condensation of the fluorinated diketone, 1,1,1,5,5,5-hexafluoroacetylacetone with the primary amine mesitylaniline was conducted in the presence of titanium tetrachloride ($TiCl_4$) as a stoichiometric source of acid and dehydrating agent.

After initial addition of $TiCl_4$ to a solution of the aniline and heating to 80 °C, the fluorinated dicarbonyl was added to the reaction mixture and left to stir at room temperature for 3 days. Following aqueous workup, analysis of the crude mixture by NMR spectroscopy revealed a

mixture of the mono and dicondensation products, **L^{4}H** and **L^{1}H** (*ac-nac* and *nac-nac*). These products were separated by column chromatography with *n*-hexane as the eluent and subsequently isolated in 23% and 27% yield respectively. These new ligands were isolated on 2-3 gram scales and characterised by NMR spectroscopy and elemental analysis.



Scheme 1 - Synthesis of the fluorinated nac-nac and ac-nac ligands L^{1}H and L^{4}H

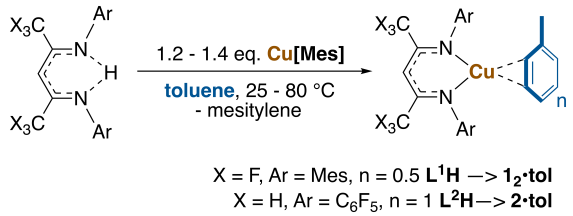
NMR Characterisation

Analysis of the ^{1}H NMR spectra of **L^{1}H** and **L^{4}H** shows singlet's at δ = 11.7 and δ = 11.4 ppm (benzene-d_6, 298 K) respectively, diagnostic of the deshielded *BDI* ligand N–H proton. The ^{19}F NMR spectra show one singlet and two singlet's for **L^{1}H** and **L^{4}H** respectively (**L^{1}H** δ = -67.2 ppm; **L^{4}H** δ = -67.6, -76.9 ppm). This difference in symmetry allowed for unambiguous distinction between the two ligands.

2.2 Fluorinated BDI complexes of copper(I)

Preparation

Initial reactions of each of the *BDI* ligand precursors **L^{1}H** and **L^{2}H**, prepared according to a literature procedure,[20] with an excess of the copper(I) source **Cu[Mes]** (1.2 – 1.4 equivalents) in benzene-d_6 (see Scheme 2) were monitored by ^{1}H and ^{19}F NMR spectroscopy.



Scheme 2 - Synthesis of the copper(I) arene complexes 1$_2$-2•tol

In the case of **L^{1}H**, temperatures of 80 °C were required in order to observe deprotonation of the ligand and complexation to the metal, whereby the reaction was completed after 3 days. This was confirmed by a small, downfield shift *via* ^{19}F NMR spectroscopy (δΔ = +2.3 ppm),

corresponding to the CF_3 groups on the backbone of the ligand. Observation of two singlets in the ^{1}H NMR spectra corresponding to free mesitylene (δ = 2.2 ppm, 3H & δ = 6.7 ppm, 9H) also inferred complexation of copper(I) to the *BDI* ligand. Performing the same reaction with **L^{2}H** did not require heating. A similar shift in ligand peaks in the ^{19}F NMR spectra and observation of mesitylene in the ^{1}H NMR spectra was observed after 24 hours at room temperature. Scale up of these reactions in toluene affords the coordinated complexes **1$_2$-2•tol** in 71% and 56% yield, respectively.

X-Ray Characterisation

Crystal structures (see Figure 4) were obtained from single crystals of **1$_2$-2•tol** grown from hydrocarbon solutions at -30 °C whereby **1$_2$•tol** crystallised in the form of orange blocky needles and **2•tol** crystallised as light green needles. Complex **1$_2$•tol** crystallises with each copper(I) centre in a trigonal planar geometry, with the toluene coordinating in an η^2-fashion. Complex **2•tol** crystallises with the copper centre distorted over two sites whereby the coordinated toluene molecule remains planar and lies perpendicular to the copper(I) centre.

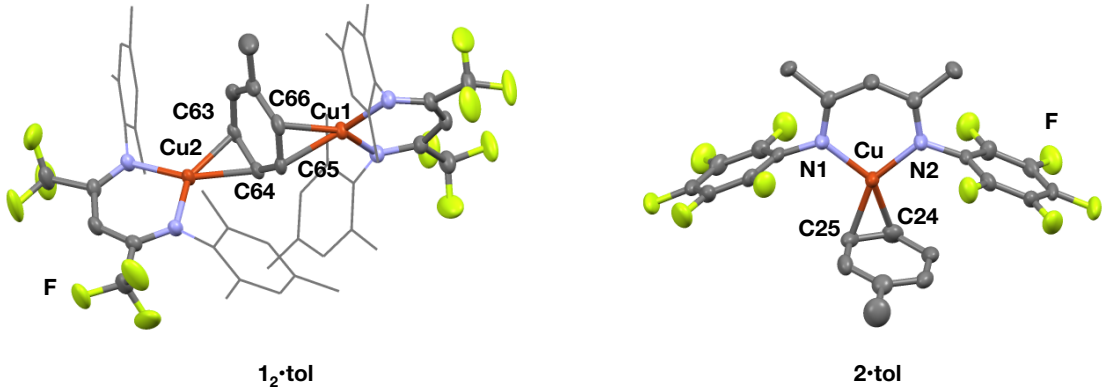


Figure 4 - Crystal structures of 1$_2$•tol and 2•tol

Complex **1$_2$•tol** crystallises as an inverse sandwich compound, adopting a η^2-coordination mode. On complexation to copper(I), the C–C bond lengths of the η^2-coordinated toluene is within error of that of free toluene (toluene = 1.39 Å, **1$_2$•tol** = 1.400(3) Å & 1.430(3) Å), suggesting minimal π-back-bonding from copper(I) to the arene. The arene co-ordinated complex **2•tol** is mononuclear in copper and crystallises with the copper(I) centre disordered over two sites. Similarly to what is observed for **1$_2$•tol**, there is little back-bonding observed from the copper(I) centre to the arene solvent in **2•tol** (C–C^{toluene} = 1.384(6) Å).

The angle created by the N–Cu–N moiety in the isolated complexes of **1_2-2•tol** are more obtuse than the bite angle created by the phosphine ligands in the bent gold(I) and nickel(0) complexes discussed in chapter 1, section 3.2 (Au = 90.26(4)°, Ni = 89.52(5)°).

Table 1 - Selected geometrical parameters for 1_2•tol and 2•tol

	1_2•tol	**2•tol**
Bond Lengths (Å)		
Cu–N	1.9376(19)	1.932(3)
	1.9465(19)	1.952(4)
	1.9310(19)	
	1.9367(19)	
Cu–C	2.085(2)	2.073(5)
	2.097(2)	2.192(5)
	2.069(2)	
	2.073(2)	
C–C	1.400(3)	1.384(6)
	1.430(3)	
Bond Angles (°)		
N–Cu–N	99.89(8)	97.85(12)
	100.02(8)	

The synthesis of mononuclear and dinuclear arene-adducts of copper(I) of this type have previously been reported.[21] Comparison of these new structures with those in the literature does not reveal a correlation between the sterics and electronics of the ligand with the nuclearity of the complex. On the basis of repeated CHN analysis of **2•tol** and the repeated preparation of the complexes described herein, it appears that desolvation occurs upon extended drying of these samples in the solid state. In all cases, the inverse sandwich complexes form, with the two copper centres bound to adjacent positions of the aromatic system. The most likely effect of the variation in X-ray data is due to the precise crystallisation conditions and crystal packing for each sample.

NMR Characterisation

Diffusion-ordered spectroscopy (DOSY) NMR experiments were performed in order to determine the nuclearity of the copper(I) complexes in arene solvents. During investigations into

the synthesis of σ-complexes of copper(I) with the copper fragment **3•tol**, reports by the Crimmin group have shown that in a toluene or benzene solution the monomeric species **3•tol** and not dinuclear **3_2•tol**, is present, as evidenced by a comparison of the diffusion coefficient (0.989×10^{-9} m^2 s^{-1}) against that for the control sample **3•cyclohexane** (0.967×10^{-9} m^2 s^{-1}).[22] The data correspond with solution hydrodynamic radii of 4.1 - 4.2 Å. In benzene solution (Figure 5), DOSY experiments on **1_2•tol** and **2•tol** return similar hydrodynamic radii (4.4 - 4.5 Å) and leave little doubt that in arene solvents monomers **1•tol** and **2•tol** persist.

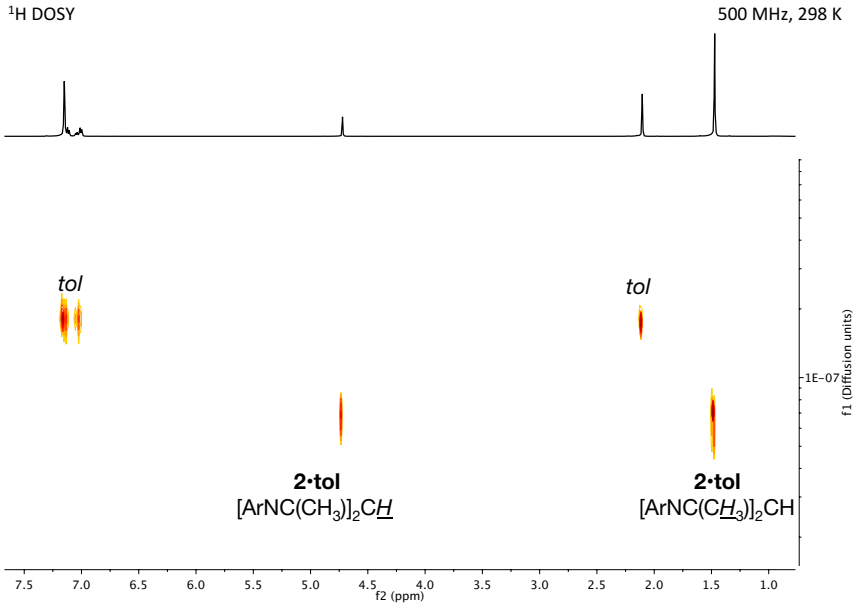


Figure 5 - DOSY NMR Spectra of 2•tol

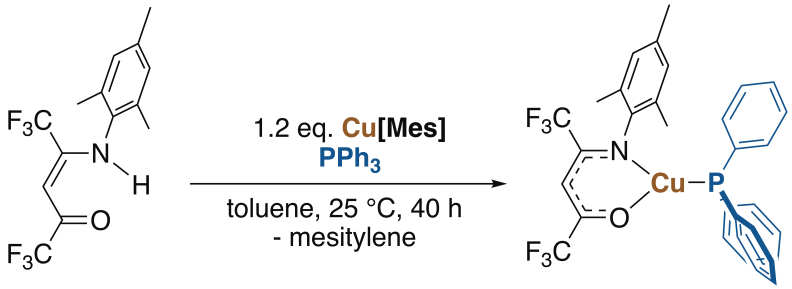
Whilst only the monomeric form has been observed in solution for the complexes **1-3•tol**, Warren and co-workers have previously suggested that the complex **6•tol** forms both monomeric and dimeric species in a benzene solution.[23]

2.3 Asymmetric Fluorinated Complexes of Copper(I)

Preparation

With regards to the asymmetric pro-ligand **L^4H**, *in-situ* formation of the arene complex **4•benzene-d_6** was achieved through reaction of the ligand with **[CuMes]** in benzene-d_6 for 40 h at room temperature. Performing synthesis of the copper(I) complex **4_n•tol** on a preparative scale in toluene was unsuccessful. The formation of a copper mirror and regeneration of the free ligand was observed. Stabilisation of the asymmetric complex was accomplished with the addition of 1 equivalent of triphenylphosphine, a ligand previously utilised in the literature for

the stabilisation of *BDI* complexes of copper(I).[15,23-26] When the reaction was performed in toluene at room temperature, after 40 hours the isolation of **4•PPh$_3$** was achieved in 74% yield.

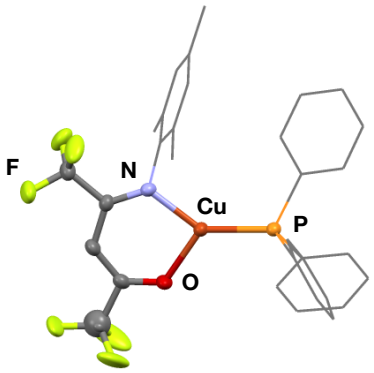


Scheme 3 - Preparation of 4•PPh$_3$

X-Ray Characterisation

A crystal structure of **4•PPh$_3$** was obtained from a single crystal grown from *n*-hexane at -30 °C (Figure 6). The asymmetric unit consisted of two independent molecules, each co-crystallising with a molecule of hexane. The copper is in a distorted trigonal planar geometry, with the backbone carbon of the ligand, copper and phosphorus all residing in the same plane.

a)



4•PPh$_3$

b)

	4•PPh$_3$(A)	**4•PPh$_3$(B)**
	Bond Lengths (Å)	
Cu–N	1.973(3)	1.961(3)
Cu–O	1.997(2)	1.995(2)
Cu–P	2.1639(10)	2.1593(10)
	Bond Angles (°)	
N–Cu–O	94.69(11)	94.80(11)

Figure 6 - a) The crystal structure of 4•PPh$_3$(B), b) Selected geometrical parameters for the two independent molecules 4•PPh$_3$(A) and 4•PPh$_3$(B)

A comparison of the bond lengths found within **4•PPh$_3$** and complex **6•PPh$_3$**, synthesised by Warren and co-workers, shows a significantly shorter Cu–N bond length in **4•PPh$_3$**, indicative of a less electron rich metal centre.[27] The Cu–P bond lengths are comparable with those found in the literature (**6•PPh$_3$** = 2.161(1) Å).[15,27] In addition, the bite angle created by the bent *ac-nac* ligand in complex **4•PPh$_3$** is more acute than for the *nac-nac* complexes **1$_2$-2•tol**, which will in turn affect the frontier molecular orbitals of copper fragment **4**. It has been reported that an increasing bite angle in palladium bis-phosphine complexes results in decreased back-donation

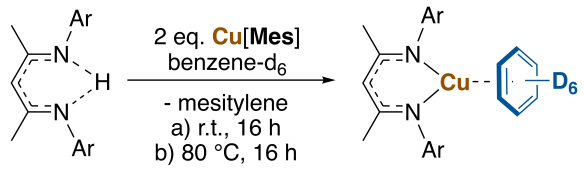
from the metal centre to bound allyl groups.[28] The results from this study allows us to hypothesise that the copper fragment **4** will provide extra stabilisation for σ-complexes of copper(I) through increased back-donation into the E–H bond.

NMR Characterisation

On dissolving a sample of **4•PPh$_3$** in benzene-d$_6$, the ^{31}P NMR spectrum shows a sharp singlet at δ = 5.3 ppm. This peak is significantly shifted downfield from free PPh$_3$ (δ = -5.3 ppm) and is in good comparison with known *BDI* complexes of copper(I) coordinated to phosphine ligands (**6•PPh$_3$**, δ = 5.2 ppm; **11•PPh$_3$**, δ = 5.4 ppm; **7•PPh$_3$**, δ = 3.6 ppm). Warren and co-workers reported a broad signal in the ^{31}P NMR spectra for the complex **6•PPh$_3$**, indicating reversible coordination of the phosphine is occurring in solution, however, this is not observed for **4•PPh$_3$**.[23]

2.4 Non-Fluorinated Complexes of Copper(I)

The synthesis of non-fluorinated *BDI* complexes of copper(I) was also attempted to provide σ-complex precursors with differing electronic properties. Reaction of the pro-ligands **L^{6}H** and **L^{7}H** with 2 equivalents of **Cu[Mes]** in benzene-d$_6$ either at room temperature or at elevated temperatures (80 °C) generated the copper(I) complexes **6•benzene-d$_6$** and **7•benzene-d$_6$** *in-situ*. This was inferred from the loss of signals corresponding to the pro-ligands **L^{6}H** and **L^{7}H** in the ^{1}H NMR spectra and the observation of free mesitylene.



a) Ar = Mes, **L^{6}H —> 6•benzene-d$_6$**
b) Ar = Dipp, **L^{7}H —> 7•benzene-d$_6$**

Scheme 4 – *In-situ* generation of 6•benzene-d$_6$ and 7•benzene-d$_6$

Synthesis of these complexes *via* the method outlined in Scheme 4 was not successful on a large scale in toluene. In the case of **L^{7}H**, formation of **7•tol** was competitive with decomposition at 80 °C and thus observation of a copper mirror and regeneration of the pro-ligand **L^{7}H** occurred. Similarly, isolation of the complex **6•tol** was unsuccessful due to a difficult synthetic step to separate the complex from mesitylene. The use of the copper(I) precursor CuO*t*Bu for the

synthesis of **6•tol** has previously been reported and use of CuO*t*Bu as a catalyst for the reaction between a *BDI* ligand and **Cu[Mes]** has also proven successful.[24] In this instance, the choice not to pursue these different synthetic routes were taken and the focus was placed on investigating the ability of the electron deficient copper complexes $\mathbf{1_2}$**-2•tol** and **4•PPh$_3$** to stabilise σ-complexes of copper(I).

3. Discussion of Electronic and Steric Properties

3.1 Experimental Studies

Carbonyl ligands can be used in order to probe the extent of π-back-bonding from a metal centre due to their IR activity and ability to accept back-donation of electron density from a metal centre. A sample of each of the copper(I) arene complexes **1-3•tol** in benzene-d_6 was exposed to an atmosphere of CO to generate the carbonyl complexes **1-3•CO**. The reactions were followed by ^{1}H NMR spectroscopy and where necessary, ^{19}F NMR spectroscopy whereby a diagnostic shift in the peaks corresponding to the ligand was observed on coordination of the copper complex to CO (**1•CO**; Δ = +0.4 ppm). This technique has previously been utilised for fluorinated *BDI* complexes of copper(I) by Sadighi and co-workers and the results of their studies (**8-11•CO**), combined with those conducted as outlined in section 5.3 can be seen in Figure 7.[18]

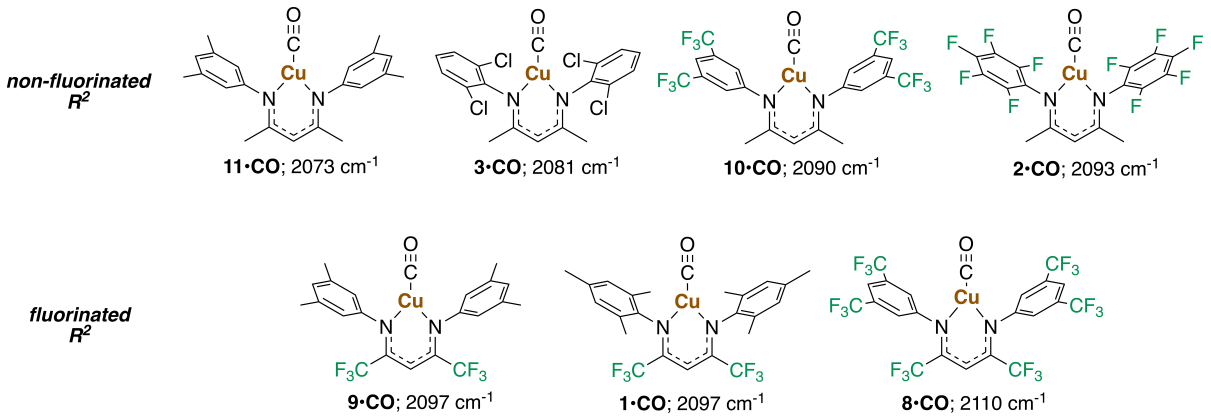


Figure 7 - Carbonyl stretching frequencies complexes of copper(I) bearing *BDI* ligands with varying levels of fluorination, data for complexes 8-11•CO gathered either by Sadighi and co-workers

It is worth noting that the synthesis of **4•CO** was attempted however when performing the reaction of both **4•benzene-d_6** and **4•PPh_3** with CO in an NMR tube, no changes was observed in the ^{1}H and ^{19}F NMR spectra compared to the starting complexes.

The increase in stretching frequency across the series on the addition of fluorine to the ligand (from left to right in Figure 7) signifies that less back donation is occurring into the empty π-orbitals on CO and thus it is inferred that the copper(I) centre is more electron deficient.[29] A more significant shift is observed when the fluorine atoms are located on the backbone of the ligand rather than the aromatic ring. This suggests that the increase in stretching frequency is not solely linked to the number of fluorine atoms present but also where they are located on the ligand, which is consistent with previous reports for fluorinated complexes of copper(I).[18]

3.2 DFT Studies

Method

In order to further investigate the effect of different ligands on the electronic properties of the copper(I) complex, a series of DFT experiments were performed. The naked copper(I) fragments (no arene complexation) **1-11** and carbonyl complexes **1-11•CO** were optimised using the functional ωB97x-D and hybrid basis set (6-31G+(d,p) (others), SDD (Cu)). An analysis of the frontier molecular orbitals on the fragments is presented. In addition, the calculated vibrational spectra of the complexes **1-11•CO** was analysed and NBO calculations performed using NBO 6.0 allow quantification of the interaction with the carbonyl ligand. These investigations will provide an insight into these orbitals involved in bonding with an E–H bond.

Molecular Orbital Analysis

It has previously been concluded that *BDI* copper(I) fragments possess a 4s orbital as their lowest unoccupied molecular orbital (LUMO), which is accessible for coordination to an E–H bond (E = Zn, Al, B). In addition, the highest occupied molecular orbital (HOMO - HOMO-1) of *BDI* complexes of copper(I) is of suitable symmetry to back-donate into the σ*-E–H orbital.[22,30] Further investigations show that the 4s orbital is spherical, and is orientated in between the arms of the *BDI* ligand. The energy of the 4s orbital can vary from LUMO to LUMO+4, as shown in Figure 9b. Either the HOMO or HOMO-1 consists of an out-of-phase combination of the d_{yz} orbital and antisymmetric ligand SALC as seen for complex **3** in Figure 8.

In general, the difference in energy between the 4s and $3d_{yz}$ orbitals of the copper(I) fragments does not vary across the series of complexes. The energy of the 4s and $3d_{yz}$ orbitals decreases when fluorine is added either onto the aromatic ring or the backbone of the ligand, as outlined in Figure 9a.

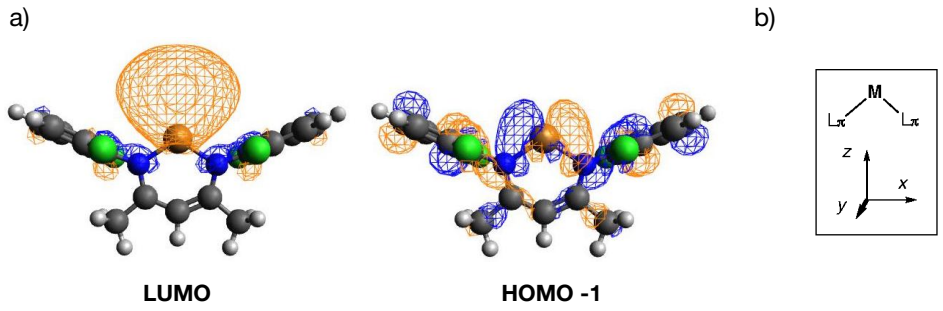
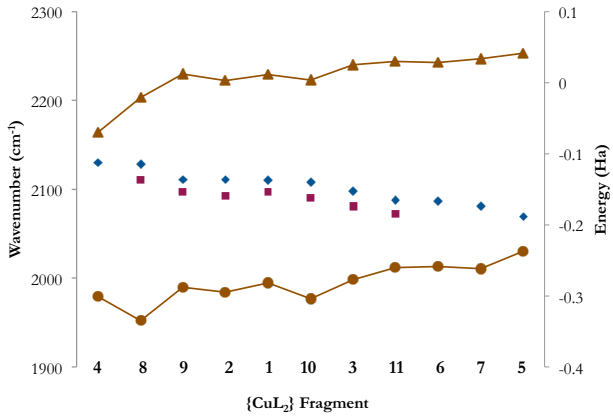


Figure 8 - a) A representation of the LUMO and HOMO-1 of copper fragment 3, b) axis system for {CuL_2} fragments

a)



b)

Complex	4s	$3d_{yz}$
4	LUMO +2	HOMO
8	LUMO	HOMO
9	LUMO+1	HOMO
2	LUMO+1	HOMO-1
1	LUMO+1	HOMO
10	LUMO+4	HOMO
3	LUMO	HOMO-1
11	LUMO	HOMO-1
6	LUMO	HOMO-1
7	LUMO	HOMO-1
5	LUMO	HOMO-1

Figure 9 - a) A chart outlining νCO (exp.) and νCO (DFT) of the carbonyl copper complexes 1-11•CO and the energy of the orbitals possessing the correct symmetry for overlap with an E–H or M–H bond in complexes 1-11 b) Assignment of the 4s and $3d_{yz}$ orbitals for the naked copper fragments 1-11

Although the absolute values of the experimentally determined and calculated νCO's are not in agreement, the trend is. In general, complexes possessing orbitals that lie higher in energy show a lower νCO stretch, which is consistent with a more electron rich copper(I) centre. To further investigate the effect of the alteration of the electronics of the copper(I) fragments on **1-11•CO**, second order perturbation theory analysis was performed in order to quantify the donor-acceptor interactions with a carbonyl ligand.

Table 2 – A comparison of calculated νCO, Cu to CO back-donation, C to Cu donation and N–Cu–X ° (X = N, O) angle for the copper carbonyl complexes 1-11•CO

	νCO (DFT) cm^{-1}	Cu --> π-CO kcal mol^{-1}	Cu•CO (DFT) N–Cu–X °
4	2130	26.7	95.8
8	2128	17.7	98.6
9	2111	28.4	99.3
2	2111	29.9	98.4
1	2110	28.4	99.3
10	2108	29.6	98.4
3	2098	30.7	98.4
11	2088	31.6	99.0
6	2087	27.1	99.1
7	2081	29.0	98.7
5	2069	33.9	99.3

In general, the copper carbonyl complexes possessing a lower νCO show increased back-donation into the π-C–O orbital. However, this increase in back-donation is more pronounced for complexes **2•CO**, **11•CO** and **5•CO**. Analysis of the N–Cu–X ° (X = N, O) angle of the bent carbonyl complexes reveals that aside from the predicted differences observed with the *ac-nac* complex **4•CO**, the subtleties in decreasing stretching frequency and increasing back-donation is not reflected in the bite angle of the ligand. Analysis of these bonding parameters perhaps does not show the full extent of the electronic differences of the ligand and thus care should be taken in subsequent chapters to analyse a range of different spectroscopic and computational data.

3.3 Summary

The synthesis and characterisation of two new *BDI* ligands containing fluorine has been reported. Three new complexes of copper(I) possessing fluorinated *BDI* ligands have been synthesised and fully characterised. In addition, two non-fluorinated analogues have been prepared *in-situ*. It has been shown by experimental methods and DFT calculations that increasing levels of fluorination on the *BDI* ligand, with particular regards to fluorine on the backbone, causes a decrease in electron density at the metal centre. Specifically, this increase in

fluorination decreases the energy of the HOMO of the naked copper fragment, and increases the IR stretching frequency of the bound carbonyl ligand in carbonyl complexes of copper(I). The electronic properties of these complexes of copper(I), along with their bent confirmation make them an ideal starting point for continuing investigations into the stabilisation of σ-complexes of copper(I).

4. Future Work

In order to enhance understanding of the effect of the crystallisation conditions on the geometries of copper(I) complexes possessing *BDI* ligands, investigations into isolating these complexes with different arene solvents should be carried out. Attempts to synthesise and isolate the naked copper fragments with halogenated arenes such as hexafluorobenzene or 1,2-difluorobenzene could provide an insight into the propensity of these complexes to form either monomeric or dimeric structures and thus in turn lead to more reactive $\{CuL_2\}$ fragments.

In addition, more work should be performed to analyse the effect of the coordinating ligand on the N–Cu–N° bite angle, and its subsequent effect on the frontier molecular orbitals of the copper(I) complex. Synthesising a range of copper(I) complexes with differing sterics on the aromatic group and groups on the backbone of the ligand may alter the electronics enough in order to observe the effect of the N–Cu–N° bite angle on the frontier molecular orbitals. [20,31]

5. Experimental

5.1 General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 and toluene-d_8 were stored over molecular sieves and distilled prior to use. NMR-scale reactions were conducted in J. Youngs tap tubes and prepared in a glovebox. All heating mentioned was conducted through the use of silicone oil baths. ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated; all peak intensities are derived from an internal standard peak with values quoted in ppm. Data was processed using the MestReNova or Topspin software. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University. CO was purchased from CK Gasses and passed through an Agilent oxygen and moisture trap before use. $TiCl_4$ and 1,1,1,5,5,5-hexafluoroacetylacetone were purchased from Sigma Aldrich and mesitylaniline was purchased from Fischer Scientific.

5.2 Preparative-scale Synthesis

[CuMes],[32] **L^2H**,[20] **L^3H** and **3•tol**,[33] **L^5H**,[31] **L^6H** and **L^7H**[34] and **5•tol**[21] were prepared according to, or through slight modification of, literature procedures.

L^1H and L^4H

The following method was modified from an existing literature procedure.[13] $TiCl_4$ (2.2 mL, 20 mmol) in toluene (20 mL) was added *via* syringe, dropwise, to a solution of mesitylamine (11.2 mL, 80 mmol, 4 eq.) in toluene (50 mL) in an ampoule fitted with Young's tap. The resulting dark brown mixture was stirred at 90 °C for 30 min upon which point 1,1,1,5,5,5-hexafluoroacetylacetone (2.83 mL, 20 mmol) was added. The reaction mixture was stirred for 72 h at 25 °C, then poured on to a dilute Na_2CO_3 solution (1.7 g in 200 mL) whereby a colourless precipitate and orange supernatant were observed. The organic layer was extracted with dichloromethane (30 mL) and dried over anhydrous $MgSO_4$ before the solvent removed *in vacuo* to give an orange oil. The crude was purified by column chromatography on silica gel with *n*-hexane as the eluent affording the β-diketiminate ligand L^1H (r_f = 0.64) as dark yellow crystals

(2.0 g, 4.53 mmol, 22.7%) on removal of the solvent *in vacuo* and the mono-condensation product, L^3H (r_f = 0.13) as light orange crystals on removal of the solvent *in vacuo* (1.8 g, 5.46 mmol, 27.3%). Characterisation data for **L^1H**: ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 2.05 (s, 12 H), 2.09 (s, 6H), 6.03 (s, 1H), 6.71 (s, 4H), 11.74 (s, 1H); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) δ 18.2, 20.9, 87.1, 119.5 (q, $^2J_{C-F}$ = 283.8 Hz), 128.9, 131.1, 135.6, 138.7; ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -67.2 (s). Elemental analysis calc. for $C_{23}H_{24}F_6N_2$: C, 62.44; H, 5.47; N, 6.33. Found: C, 62.38; H, 5.56; N, 6.38. Characterisation data for **L^4H**: ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 11.35 (s, 1H), 6.49 (s, 2H), 6.00 (s, 1H), 1.96 (s, 3H), 1.79 (s, 6H); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 138.6, 136.0, 131.6, 129.1, 128.2, 127.7, 119.2 (q, $^1J_{C-F}$ = 278.9 Hz), 117.3 (q, $^1J_{C-F}$ = 287.9 Hz) 87.4, 20.7, 17.6; ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -67.6 (s, 3F), -76.9 (s, 3F). Elemental analysis calc. for $C_{14}H_{13}F_6NO$: C, 51.70; H, 4.03; N, 4.31. Found: C, 51.91; H, 3.85; N, 4.44.

1_2•tol

In a glovebox, **[CuMes]$_n$** (n = 4, 5) (262 mg, 1.4 mmol, 1.2 eq.) was dissolved in toluene (13 mL). The pro-ligand **L^1H** was added to the reaction mixture as a solid (534 mg, 1.2 mmol) and the mixture turned bright red. The solution was stirred for 3 days at 80 °C, then allowed to cool to room temperature and any precipitate allow to settle. The solution was filtered through glass fibre and slow evaporation of the solvent yielded **1_2•tol** as an orange crystalline solid (468 mg, 0.85 mmol, 71%). The crystalline solid was used for NMR analysis: ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.97 (s, 12H), 2.11 (s, 1.3H, *tol*), 2.19 (s, 6H), 6.07 (s, 1H), 6.82 (s, 4H), 7.01-7.16 (m, 2H); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 18.7, 21.0, 21.4 (*tol*), 83.4, 122.0 (q, $^1J_{C-F}$ = 288.0 Hz), 125.7 (*tol*), 128.6 (*tol*) 128.8, 129.3 (*tol*), 129.9, 133.4, 137.9 (*tol*), 145.3, 152.6 (q, $^2J_{C-F}$ = 24.9 Hz); ^{19}F NMR (C_6D_6, 470.4 MHz, 298 K) δ -64.9 (s, 6F). Elemental analysis calc. for $C_{53}H_{50}Cu_2F_{12}N_4$: C, 57.97; H, 4.59; N, 5.10. Found from a heavily dried solid of *1_2•tol*: C, 57.89; H, 4.68; N, 5.03.

2•tol

In a glovebox, **[CuMes]$_n$** (n = 4, 5) (508 mg, 2.8 mmol, 1.2 eq.) was dissolved in toluene (30 mL). The pro-ligand **L^2H** was added to the reaction mixture as a solid (998 mg, 2.3 mmol) at which point the mixture turned bright red. The solution was stirred overnight at 25 °C and the now green solution was diluted with toluene (20 mL) and filtered through glass fibre. The solvent volume was reduced to *ca.* 10 mL upon which point crystallisation of a light-green solid was observed. The product was isolated by filtration and dried *in vacuo* to give **2•tol** as a light-

green crystalline solid (764 mg, 1.3 mmol, 56%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.49 (s, 6H), 2.12 (s, 2.5 H, *tol*), 4.73 (s, 1H), 7.01-7.13 (m, 3.7H); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 21.4 (*tol*), 23.7, 97.4, 125.7 (*tol*), 127.2 (tm, $^{2}J_{C\text{-}F}$ = 15.8 Hz), 128.5 (*tol*), 129.4 (*tol*), 137.5 (dm, $^{1}J_{C–F}$ = 248.2 Hz), 137.9 (*tol*), 137.9 (dm, $^{1}J_{C–F}$ = 248.2 Hz), 141.3 (dm, $^{1}J_{C–F}$ = 242.4 Hz), 166.9; ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -164.0 (td, 4F, $^{3}J_{F–F}$ = 23.1 Hz, $^{4}J_{F–F}$ = 5.3 Hz), 162.9 (t, 2F, $^{3}J_{F–F}$ = 21.9 Hz), -150.5 (dd, 4F, $^{3}J_{F–F}$ = 25.6 Hz, $^{4}J_{F–F}$ = 5.3 Hz). Elemental analysis calc. for **2•tol** $C_{41}H_{22}Cu_2F_{20}N_4$: C, 45.89; H, 2.06; N, 5.20. Found: C, 45.90; H 1.95; N, 5.11.

4•PPh$_3$

In a glovebox, **[CuMes]$_n$** (n = 4, 5) (1.09 g, 6.0 mmol, 1.4 eq.) was dissolved in toluene (100 mL). The pro-ligand **L^{4}H** (1.63 g, 5.0 mmol, 1.2 eq.) and triphenylphosphine (1.57 g, 4.2 mmol) were added to the reaction mixture, each as a solid, upon which point the solution turned orange. The solution was stirred for 40 h at 25 °C. The red mixture was filtered through a sinter funnel and the solvent removed *in vacuo* to give the crude as a red oil. Trituration with *n*-hexane (10 mL) yielded **4•PPh$_3$** as an orange crystalline solid (0.55 g, 0.89 mmol, 21%). Storage of the mother liquor at -18 °C overnight yielded a second batch of orange crystals (1.37 g, 2.22 mmol, 53%), combined yield 74%. ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.90 (s, 6H, Ar*Me*), 2.03 (s, 3H, Ar*Me*), 6.37 (s, 1H, C*H*), 6.54 (s, 2H, Ar*H*), 6.93-7.19 (m, 15H, P*Ph$_3$*); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 18.7 (Ar*Me*), 20.8 (Ar*Me*), 86.5 (C*H*), 120.0 (q, $^{1}J_{C–F}$ = 288.1 Hz, *C*F$_3$), 120.4 (q, $^{1}J_{C–F}$ = 285.4 Hz, *C*F$_3$), 128.0 (Ar), 128.4 (Ar), 128.9 (Ar), 129.0 (d, $^{1}J_{C–P}$ = 10 Hz, PPh$_3$), 130.3 (PPh$_3$), 132.5 (d, $^{1}J_{C–P}$ = 36.3 Hz, PPh$_3$), 133.9 (d, $^{1}J_{C–P}$ = 15.5 Hz, PPh$_3$), 145.8 (Ar-*ipso*), 157.4 (q, $^{2}J_{C–F}$ = 26.4 Hz, N*C*–CF$_3$), 170.7 (q, $^{2}J_{C–F}$ = 31.9 Hz, OC–CF$_3$); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -65.7(s, 3F), -74.3 (s, 3F); ^{31}P NMR (C_6D_6, 298 K, 202.4 MHz,) δ 5.26, Elemental analysis calc. for $C_{32}H_{27}CuF_6NOP$: C, 59.12; H, 4.19; N, 2.15. Found: C, 58.87; H, 4.13; N, 2.09. Attempts to isolate the complex **4•tol** proved unsuccessful, performing the reaction in the absence of triphenylphosphine yielded a copper mirror.

5.3 NMR-scale Reactions

4•benzene-d$_6$

In a glovebox, to a solution of **[CuMes]$_n$** (n = 4, 5) (3 mg, 0.018 mmol, 1.2 eq.) in benzene-d$_6$ (300 μL) in an NMR tube fitted with Young's adapter was added the pro-ligand **L^{4}H** (5 mg, 0.015 mmol) in benzene-d$_6$ (300 μL). The reaction was followed by ^{1}H spectroscopy and left to

react at room temperature for 54 hours whereby the copper(I) complex, **4•benzene-d_6** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.69 (s, 6H), 2.11 (s, 3H), 6.07 (s, 1H), 6.64 (s, 2H); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -66.2 (s, 3F), -74.4 (s, 3F).

6•benzene-d_6

In a glovebox, to a solution of **[CuMes]**$_n$ (n = 4, 5) (8 mg, 0.044 mmol, 2.5 eq.) in benzene-d_6 (300 μL) in an NMR tube fitted with Young's adapter was added the pro-ligand **L^{6}H** (6 mg, 0.018 mmol) in benzene-d_6 (300 μL). The reaction was followed by ^{1}H spectroscopy and left to stand at room temperature overnight whereby the copper(I) complex, **6•benzene-d_6** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.69 (s, 6H), 2.04 (s, 12H), 2.29 (s, 6H), 4.82 (s, 1H), 6.93 (s, 4H).

7•benzene-d_6

In a glovebox, to a solution of **[CuMes]**$_n$ (n = 4, 5) (9 mg, 0.049 mmol, 1.2 eq.) in benzene-d_6 (300 μL) in an NMR tube fitted with Young's adapter was added **L^{7}H** (17 mg, 0.040 mmol) in benzene-d_6 (300 μL). The reaction was followed by ^{1}H spectroscopy and heated to 80 °C for 18 hours whereby the copper(I) complex, **7•benzene-d_6** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.11 (d, 12H, $^3J_{H–H}$ = 6.7 Hz), 1.13 (d, 12H, $^3J_{H–H}$ = 6.7 Hz), 1.77 (s, 6H), 2.11 (sept, 4H, $^3J_{H–H}$ = 6.7 Hz), 4.85 (s, 1H), 7.11 - 7.18 (m, 6H).

1•CO

In a glovebox, **1_2•tol** (12 mg, 0.021 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (600 μL) before being transferred to an NMR tube fitted with Young's adapter. The NMR tube was removed from the glove box, freeze-pumped-thaw degassed three times and exposed to an atmosphere of CO. The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy whereby the carbonyl compound **1•CO** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 2.10 (s, 6H), 2.16 (s, 12H), 6.10 (s, 1H), 6.76 (s, 4H), 7.01-7.16 (m, 4H); ^{19}F NMR (C_6D_6, 376.5 MHz, 298 K) δ -64.5 (s, 6F). The NMR tube was freeze-pumped-thaw degassed again to remove any excess CO and transferred to the glovebox whereby the solvent was removed *in vacuo* to give a brownish powder. This was then removed from the glovebox and analysed *via* FTIR spectroscopy; ν_{CO} = 2097 cm^{-1}.

2•CO

In a glove box, **2•tol** (12 mg, 0.021 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (600 μL) before being transferred to an NMR tube fitted with Young's adapter. The NMR tube was removed from the glovebox, freeze-pumped-thaw degassed three times and exposed to an atmosphere of CO. The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy whereby the carbonyl compound **2•CO** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.52 (s, 6H), 2.11 (s, *tol*) 4.83 (s, 1H), 7.0 - 7.13 (m, *tol*); ^{19}F NMR (C_6D_6, 376.5 MHz, 298 K) δ -163.2 (td, $^{3}J_{F–F}$ = 23.4 Hz, $^{4}J_{F–F}$ = 5.6 Hz), -161.9 (t, $^{3}J_{F–F}$ = 22.2 Hz), -150.5 (dd, $^{3}J_{F–F}$ = 24.1 Hz, $^{4}J_{F–F}$ = 5.6 Hz). The NMR tube was freeze-pumped-thaw degassed again to remove any excess CO and transferred to the glovebox whereby the solvent was removed *in vacuo* to give a brownish powder. This was then removed from the glovebox and analysed *via* FTIR spectroscopy; ν_{CO} = 2093 cm^{-1}.

3•CO

In a glovebox, **3_2•tol** (20 mg, 0.04 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (600 μL) before being transferred to an NMR tube fitted with Young's adapter. The NMR tube was removed from the glovebox, freeze-pumped-thaw degassed three times and exposed to an atmosphere of CO. The reaction was followed by ^{1}H spectroscopy whereby the carbonyl compound **3•CO** was observed *in-situ*. ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.71 (s, 6H), 2.11 (s, *tol*), 4.83 (s, 1H), 6.93 (t, 2H, $^{3}J_{H–H}$ = 8.0 Hz), 7.00 - 7.13 (m, tol). The NMR tube was freeze-pumped-thaw degassed again to remove any excess CO and transferred to the glovebox whereby the solvent was removed *in vacuo* to give a brownish powder. This was then removed from the glovebox and analysed *via* FTIR spectroscopy; ν_{CO} = 2081 cm^{-1}.

Multinuclear NMR spectra for preparative scale (section 2.1) and NMR scale (section 3.1) reactions along with X-ray acquisition parameters (section 4.1) and Z-matrices for DFT-optimised structures (section 5.1) can be found in the appendix.

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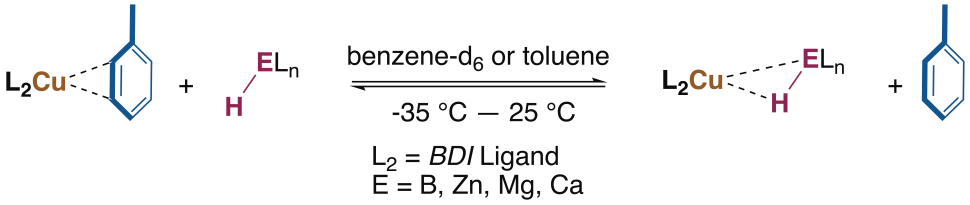
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unless an idiot dies, he won't be cured

Chapter 3

σ-Complexes of Copper(I) with Main Group Hydrides (E = B; M = Mg, Zn, Ca)

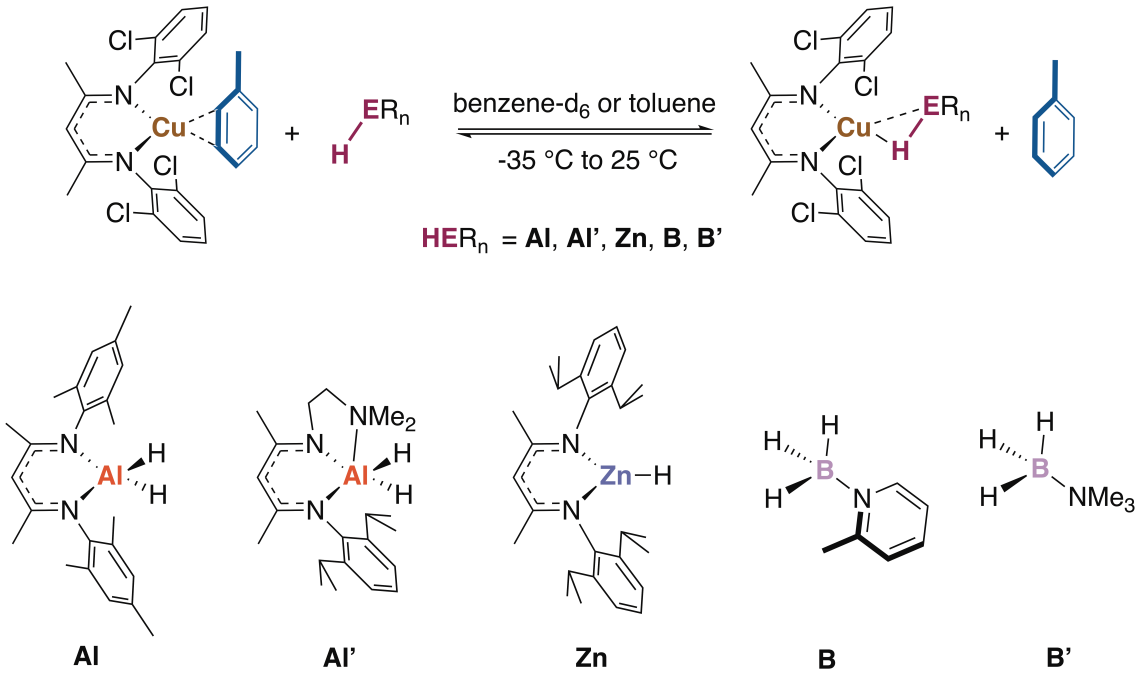
Reactions of the copper(I) arene adducts ***1-5•solv (solv = toluene or benzene-d_6)*** *with boranes, a zinc hydride, a magnesium hydride and a calcium hydride generate the isolable σ-complexes* ***1-2•B***, ***1-2•Zn*** *and* ***1•Mg***. *The related σ-complexes* ***4•B***, ***3-4•Zn***, ***3-5•Mg*** *and* ***3-5•Ca*** *have also been observed in-situ. The nature of the interaction between the copper(I) centre and corresponding main group hydrides has been investigated via solid-state and solution based experiments and density functional theory calculations. In all cases, the data suggest a weak and reversible formation of σ-complexes of copper(I).*



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1. Introduction

Previously, the Crimmin Group reported that reversible *intermolecular* binding of σ-boranes, σ-alanes and σ-zincanes to copper(I) fragments can be achieved through the utilisation of *BDI* complexes of copper(I).[1,2] In this instance, an approach to preparing complexes containing M–H–M' linkages is through addition of monomeric metal hydride complex to a suitable electrophilic metal fragment.[3-6] Reaction of the copper(I) complex **3_2•tol** with a range of main group hydride fragments generated the σ-complexes **3•Zn**, **3•Al**, **3•Al'**, **3•B** and **3•B'** as outlined in Scheme 1.[1,2]



Scheme 1 - The synthesis of σ-complexes 3•Al, 3•Al', 3•Zn, 3•B and 3•B' previously reported by the Crimmin group

These heterobimetallics were characterised as σ-complexes following a series of experimental and computational investigations. Dissolving pure, crystalline samples of these complexes in toluene-d_8 allowed for variable temperature NMR experiments that confirmed the reversibility of the formation of the σ-complexes *via* dynamic equilibria. In the case of **3•Al'**, **3•Zn** and **3•B'**, the rate of exchange at reduced temperatures (193 K) is slow enough for both sides of the equilibrium to be observed. Additionally, calculations revealed that the LUMO on the copper(I) fragment is largely 4s in character, whereby stabilisation of the σ-complexes occurs *via* donation of electron density from the E–H or M–H bond on the main group fragment into the 4s orbital

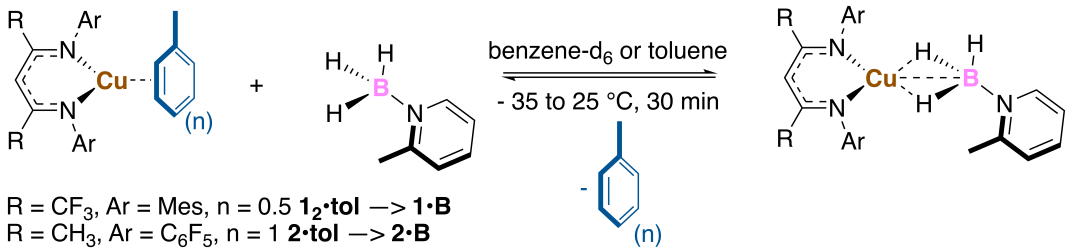
on the copper fragment and concurrent back-donation from the HOMO or HOMO-1 on the copper fragment into the σ*-E–H or σ*-M–H orbital. This chapter aims to enhance the understanding of the 3-centre,2-electron Cu–H–B or Cu–H–M interactions within σ-complexes of copper(I) with main group hydrides (E = B, M = Zn), and expand the series to contain group 2 hydrides (M = Mg, Ca).

2. Synthesis and Characterisation

2.1 σ-Borane Complexes of Copper(I)

Preparation

Initial reactions between the copper(I) complexes **1_2•tol** and **2•tol** and the 4 coordinate borane, **H_3BL** (L = 2-methylpyridine) was performed on an NMR scale in benzene-d_6. The reaction progressions were followed by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy. In both cases, complexation of the copper(I) centre to **H_3BL** was confirmed through the loss of multiplicity in the signals corresponding to the B–H peaks in the ^{1}H and ^{11}B spectra along with a shift in the ^{19}F NMR corresponding to the ligand on the copper(I) fragment (^{19}F NMR: **1•B** Δδ = +0.28 ppm (s); **2•B** Δδ = -2.1 ppm (t), **2•B** Δδ = -0.7 ppm (d)).



Scheme 2 - The synthesis of 1•B and 2•B

In the case of **1•B** and **2•B**, on complexation of **H_3BL** to the copper fragments **1-2**, the sharp quartet observed in the ^{11}B NMR spectrum at δ = -12.3 ppm for the parent borane **H_3BL** becomes a broad singlet, as seen in Figure 1 (**1•B**, δ = -18.0 ppm; **2•B**, δ = -19.7 ppm). Similarly, the quartet observed at δ = 3.3 ppm in the ^{1}H NMR spectra corresponding to the borane broadens (**1•B**, δ = 3.0 ppm; **2•B**, δ = 3.1 ppm).

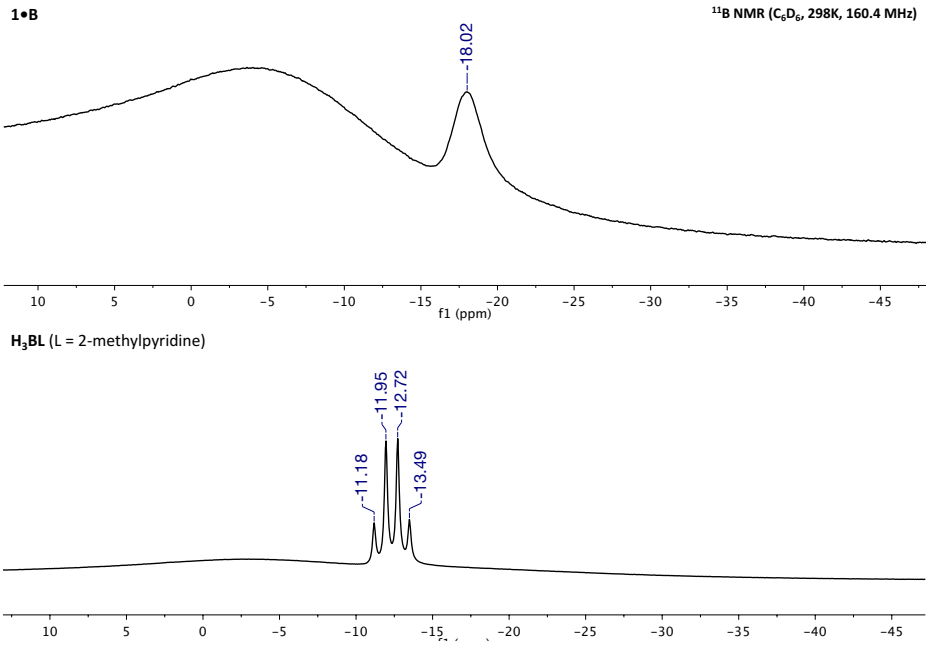


Figure 1 - The ^{11}B NMR spectra of the borane fragment H_3BL (L= 2-methylpyridine) and following complexation to the copper centre to form 1•B

Preparation of the complexes **1•B** and **2•B** was achieved on a larger scale. In order to prevent decomposition, solutions of the copper(I) complexes **1_2•tol** and **2•tol** were dissolved in toluene and stored in the glovebox freezer at -35 °C for 5 minutes before being added to the prepared samples of **H_3BL**. This method has previously been reported for the preparation of bis σ-complexes of copper(I) by the Crimmin group.[1] Following a toluene and *n*-hexane work up, **1•B** and **2•B** were isolated in 80% and 62% yield respectively.

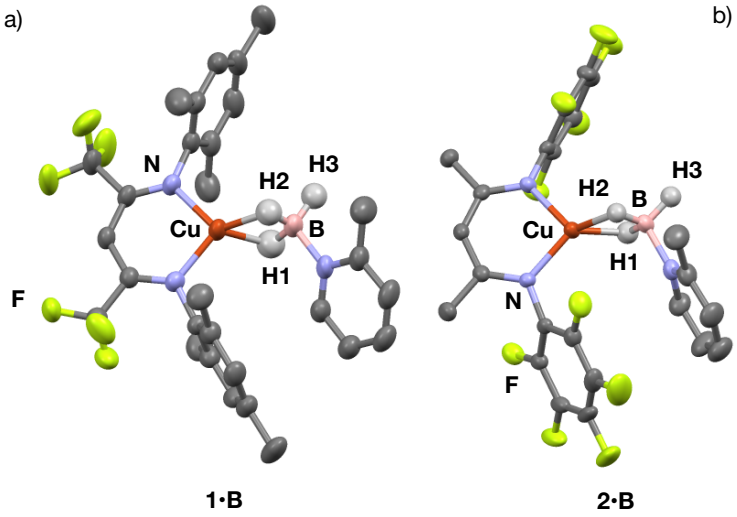
Structural Characterisation

Single crystals of **1•B** and **2•B** could be grown from toluene/*n*-hexane mixtures at -35 °C, with **1•B** taking the form of dark orange plates and **2•B** yellow blocky needles. In both cases, the quality of the data was such that the hydride positions were determined from a difference electron density map. Isolation of these species show that they contained a borane fragment with an η^2:η^2 binding mode, with the σ-complexes containing a 4-centre,4-electron (4c,4e) interaction. This type of interaction has previously been observed in the coordination of boranes to transition metal centres, notably ruthenium.[7-10]

Comparison of the geometric parameters of **1•B** and **2•B** shows Cu–H and B–H distances within experimental error of one another, with the alteration in ligand having little effect on the geometric parameters of the 4-centre,4-electron core. One significant difference in the structures

of the two complexes lies within the interaction of 2-methylpyridine and the corresponding aromatic group on the *BDI* ligand. Despite the aromatic rings being a similar distance apart in both complexes (**1•B** = 4.2 Å; **2•B** = 4.1 Å), the angle between the planes created by each aromatic ring differs (**1•B** = 40 °; **2•B** = 15 °). The previously reported complex **3•B** shows a small torsion angle, similar to that of **2•B**, at 14 °.[1] This data suggests that π-π stacking is present between the electron rich 2-methylpyridine and electron-poor *BDI* ligands found on complexes **2•B** and **3•B**. This type of π-π stacking has previously been noted to occur in phosphine complexes of iridium with increasing fluorination on the aromatic rings.[11]

a)



b)

	1•B	2•B
	Bond Lengths (Å)	
Cu---B	2.162(3)	2.127(3)
B–H1	1.16(3)	1.19(3)
B–H2	1.25(3)	1.12(2)
B–H3	1.07(3)	1.09(3)
Cu–H1	1.78(3)	1.71(2)
Cu–H2	1.80(3)	1.74(2)
Cu–N	1.952(2)	1.949(2)
	1.966(2)	1.950(2)

Figure 2 - a) Crystal Structures of 1-2•B, b) Selected geometric parameters for 1-2•B

For both complexes **1•B** and **2•B**, the terminal B–H bond is shorter than that of the bridging B–H bonds, however, it was not possible to detect this subtle B–H bond activation through IR spectroscopy. The experimental limitation of being unable to detect this subtlety in B–H stretching frequencies for B–H bonds in 3-centre,2-electron interactions has previously been reported in a review of various methods used for the characterisation of B–H bonds.[12] IR spectra obtained from DFT frequency calculations on the free borane (**BH_3L**, L = 2-methylpyridine) show one symmetric B–H stretch (ν_{B-H} = 2437 cm^{-1}) and two asymmetric B–H stretches (ν_{B-H} = 2506 cm^{-1}, 2475 cm^{-1}). In the calculated spectra of complex **1•B**, three asymmetric B–H stretches are present (ν_{B-H} = 2293 cm^{-1}, 2346 cm^{-1}, 2547 cm^{-1}).

NMR Characterisation

Upon dissolving isolated samples of **1•B** and **2•B** in deuterated solvents (benzene-d_6 or toluene-d_8), the equilibrium outlined in Scheme 2 is established between the copper(I) arene complex and borane species. At 298 K, fast exchange is observed with the chemical shifts reported being time-averaged contributions of both sides of the equilibrium. On cooling a sample of **2•B** in toluene-d_8 to 193K, the fast exchange regime is still observed, with both sides of the equilibrium still in exchange. A similar fast-exchange equilibrium at low temperatures was previously observed for σ-complexes of copper(I) by the Crimmin group.[1]

In-situ Preparation of 4•B

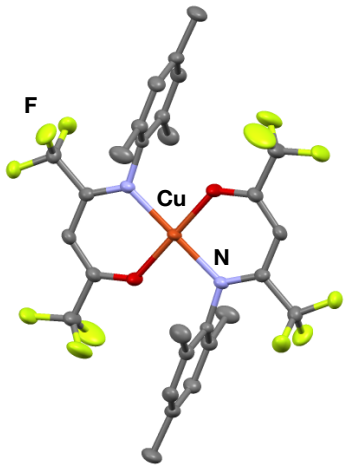
Following generation of the copper(I) complex **4•benzene-d_6** *in situ*, addition of one equivalent of the 4 coordinate borane, **H_3BL** (L = 2-methylpyridine) was performed on an NMR scale in benzene-d_6 to generate the σ-complex **4•B**. Within 30 minutes, complexation was confirmed *via* a broad singlet in the ^{11}B NMR spectrum at δ = -20.2 ppm.

Decomposition of the σ-complex was observed after 3 hours in solution through the formation of a copper mirror on the wall of the NMR tube and signals in the ^{1}H NMR spectra corresponding to the N–H peak of the ligand L^4H (δ = 11.4 ppm) and the formation of H_2 (δ = 4.47 ppm). Attempts at scaling up the reaction to form **4•B** in toluene resulted in isolation of the 4 coordinate, paramagnetic copper(II) complex **Cu(L^4)$_2$**, as shown in Figure 3**.** Single crystals of **Cu(L^4)$_2$** were grown from toluene/*n*-hexane at -35 °C and submitted for X-ray analysis. Complex **Cu(L^4)$_2$** crystallised with C_{2V} symmetry passing through the plane created by both of the *BDI* ligands and copper centre. The bond lengths between the copper centre and X (X= N, O) in the *ac-nac* ligand are slightly shorter than the 4 coordinate copper complex featuring a saturated *ac-nac* ligand reported by Willis and co-workers (Cu–N = 2.045(9) Å and 2.075(11) Å; Cu–O = 1.934(8) Å and 1.906(8) Å). Additionally, the N–Cu–O angle in **Cu(L^4)$_2$** is more obtuse (O–Cu–N = 93.1(4)° and 87.7(4)°).[13]

a)

Bond Lengths (Å)	
Cu–N	2.029(3)
Cu–O	1.881(2)
Bond Angles (°)	
N–Cu–O^{L4}	91.33(11)

b)



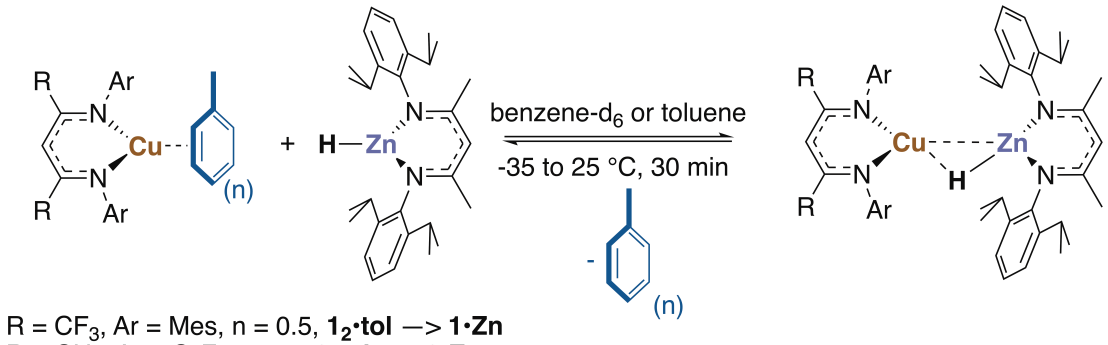
$Cu(L^4)_2$

Figure 3 - a) Crystal structure of $Cu(L^4)_2$, b) Selected geometrical parameters for $Cu(L^4)_2$

2.2 σ-Zincane Complexes of Copper(I)

Preparation

Initial reaction of either one or two equivalents of the zinc hydride species **L^7Zn–H** with the copper(I) complexes **1_2•tol** and **2•tol** was monitored by ^{1}H and ^{19}F NMR spectroscopy.



R = CF_3, Ar = Mes, n = 0.5, **1_2•tol** —> **1•Zn**
R = CH_3, Ar = C_6F_5, n = 1, **2•tol** —> **2•Zn**

Scheme 3 - Synthesis of 1•Zn and 2•Zn

After 30 minutes at room temperature, complexation of **L^7Zn–H** to the copper fragment was observed due to the loss of the singlet in the ^{1}H NMR spectra corresponding to the Zn–H peak, and a shift in the peaks corresponding to the ligand on the copper(I) fragment. Using the same method as outlined in section 2.1, **1•Zn** and **2•Zn** were isolated in 58% and 25% yield respectively.[2] In the case of **2•Zn**, the yield was lower than for **1•Zn** due to the reduced solubility of **2•tol** in toluene compared to **1_2•tol**, promoting its co-crystallisation with **2•Zn**.

X-Ray Characterisation

Single crystals of **1-2•Zn** were grown from toluene/*n*-hexane mixtures at –35 °C, and afforded high quality data such that the position of the hydrides could be determined from a difference electron density map (see Figure 4).

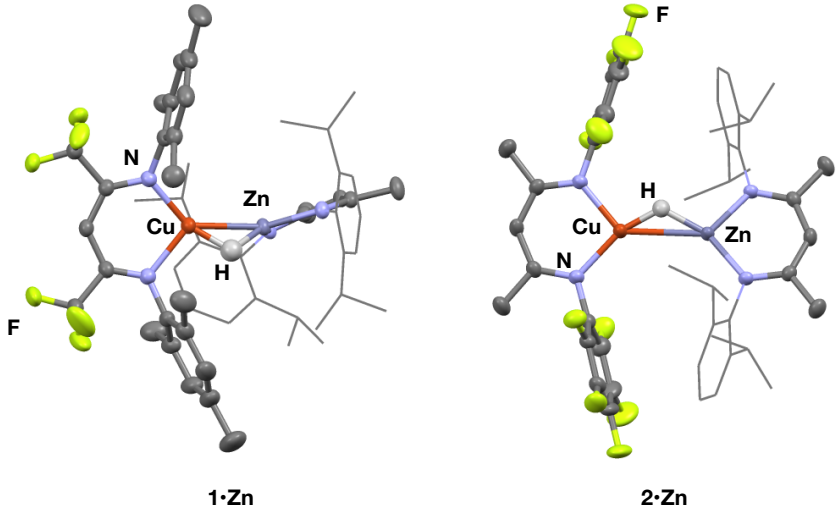


Figure 4 - Crystal structures of 1•Zn and 2•Zn

Table 1 - Selected geometric parameters for 1•Zn and 2•Zn

	1•Zn	**2•Zn**
Bond Lengths (Å)		
Cu---Zn	2.5747(4)	2.6884(4)
Zn–H	1.63(3)	1.63(3)
Cu–H	1.53(3)	1.47(4)
Cu–N	1.9297(18)	1.9599(16)
	2.0118(18)	1.9599(16)
Bond Angles (°)		
Cu–H–Zn	109.0(2)	120.6(3)
N–Cu–Zn	132.31(5)	131.45(5)
	125.80(5)	131.45(5)

Complex **1•Zn** crystallises with *BDI* ligand corresponding to the zinc hydride sitting perpendicular to the plane created by the copper(I) *BDI* ligand. In contrast, **2•Zn** crystallises with the two *nacnac* moieties possessing C_{2v} symmetry; whereby the ligands are orientated in the same plane.

On comparison of the Cu---Zn distances within these complexes, and the previously isolated complex **3•Zn,** a slight geometric difference between the complexes is revealed (**1•Zn** = 2.5747(4) Å, **2•Zn** = 2.6884(4) Å, **3•Zn** = 2.4684(5) Å). Calculation of the formal shortness ratio (fsr) of a M---M bond has previously been used to gain insight into the electronic properties of 3-centre,2-electron interactions containing a Zn–H moiety.[14] This crude structural parameter normalises the M'---M bond length with respect to the sum of the single-bond radii of the metals.[15] With regards to the approach of a Zn–H bond to transition metals, it has been shown that as the distance between the metals decreases the TM–H–Zn angle becomes increasingly more acute and the 3-centre,2-electron interaction can be described more accurately as a transition-metal zinc hydride complex than a σ-complex.

In the case of the complexes **1-3•Zn**, the calculated *fsr* is consistent with the formation of σ-complexes of copper(I) (**1•Zn** = 1.06, **2•Zn** = 1.11, **3•Zn** = 1.02). The trend observed in the *fsr* of **2•Zn** > **1•Zn** > **3•Zn** is not in agreement across all structural parameters, with the Cu–H–Zn angle being most acute in the case of **1•Zn** and the Zn–H bond distances all being within experimental error. It has previously been shown that only when very short TM---M separations are observed there is a significant elongation of the Zn–H bond.[16]

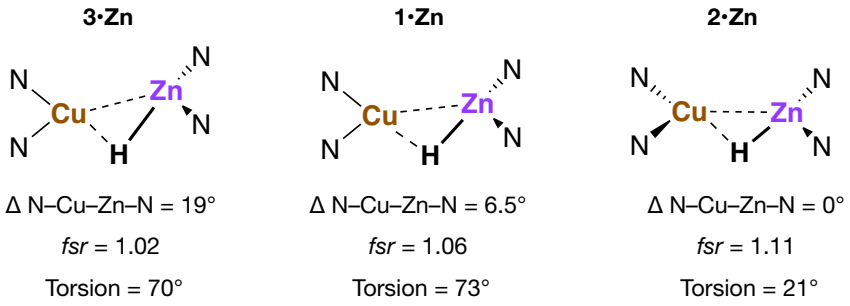


Figure 5 – Values of ΔN–Cu–Zn–N °, *fsr* and torsion angle of complexes 1-3•Zn

The flexibility of the coordination geometry at copper can be observed across the complexes **1-3•Zn**. In the case of **1•Zn** and **2•Zn**, the N–Cu–Zn° angles are consistent with a distorted trigonal-planar confirmation with respect to the heavy atoms. In the case of **3•Zn**, the N–Cu–Zn bond angles are slightly perturbed towards T-shaped geometry (**3•Zn** = 136.89(6)°, 119.54(7 °). Across this series of σ-complexes, the N–Cu–N bite angle remains consistent (97 - 99°) and thus the changes in the geometry can be analysed *via* the difference of the two angles created by the

N–Cu–Zn bonds for each complex (**1•Zn**, Δ = 6.5°; **2•Zn**, Δ = 0°; **3•Zn**, Δ = 19°). In this case, the larger values of Δ represent distortion from trigonal planar towards T-shaped (Δ = 90°).

This trend across the series **2•Zn** to **1•Zn** to **3•Zn** from trigonal planar towards T-shaped is also in good agreement with decreasing *fsr* and a shorter Cu---Zn bond, which occurs with rotation of the *BDI* ligands out of the plane with one another. This rotation of the ligands widens the dihedral angle N–Cu–Zn–N, in order to accommodate the approach of the two metals.

NMR Characterisation

On dissolving an isolated sample of **1•Zn** in hydrocarbon solvent (benzene-d_6 or toluene-d_8), the equilibrium between **1•tol** & **L^{7}Zn–H** and **1•Zn** & toluene as outlined in Scheme 3 is established. In a solution of toluene-d_8, fast exchange is observed between all species at 298 K, with the ^{1}H NMR chemical shift of the broad singlet at δ = 3.88 ppm assigned to the time-averaged resonance of coordinated and uncoordinated hydrides. Similarly in the case of **2•Zn**, fast exchange is also observed at 298 K with the time-averaged resonance of coordinated and uncoordinated hydrides being observed at δ = -0.22 ppm. The Zn–H peak in **L^{7}Zn–H** resonates at δ = 4.49 ppm in benzene-d_6 at 298 K and thus a more significant upfield shift is observed in the case of **2•Zn** than **1•Zn**.[17]

Upon cooling a sample of **1•Zn** in toluene-d_8 to 233 K, decoalescence occurs and both sides of the equilibrium can be observed (see Figure 6). In this instance, the equilibrium enters the slow exchange regime and a sharp singlet at δ = -0.44 ppm can be observed at 196 K corresponding to the σ-H. With regards to **2•Zn**, on cooling a sample in toluene-d_8, the equilibrium still remains in fast exchange, however, the hydride resonance sharpens and shifts increasingly upfield as the temperature is lowered. At 193 K a sharp singlet at δ = -0.64 ppm is observed. These values are in good agreement with the previously reported complex **3•Zn**, which shows a hydride resonance at δ = -0.55 ppm in toluene-d_8 at 193 K.[2]

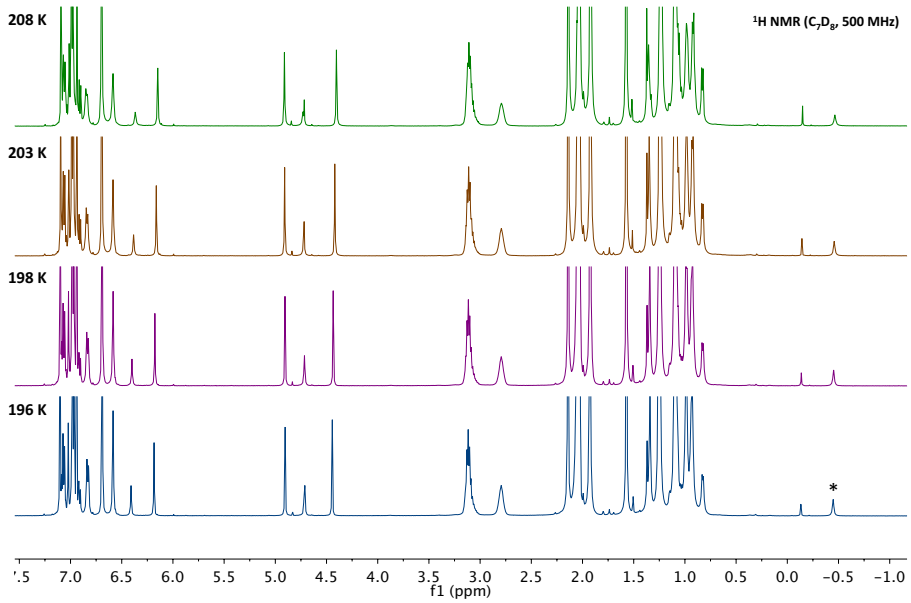


Figure 6 - ^{1}H NMR spectra of 1•Zn from 196 K to 208 K

In-situ Preparation of 4•Zn

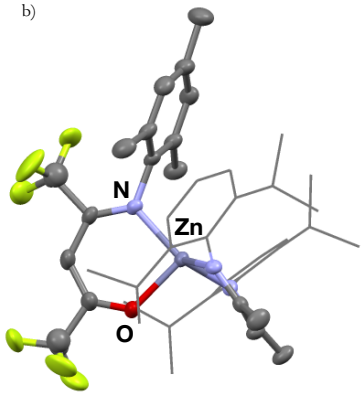
Aside from the synthesis of σ-complexes of Zn–H with the symmetric copper fragments **1•tol** & **2•tol**, reactions with the asymmetric copper(I) complex **4•benzene-d$_6$**, generated *in situ* from the pro-ligand **L^{4}H** and **Cu[Mes]** were also attempted. Reaction of one equivalent of **4•benzene-d$_6$** and one equivalent of the zinc hydride **L^{7}Zn–H** was followed by ^{1}H and ^{19}F NMR spectroscopy. After 30 minutes, complexation of the copper(I) centre to **L^{7}Zn–H** was confirmed by the disappearance of the signal corresponding to the Zn–H at around 4.5 ppm and a shift in peaks corresponding to the *BDI* ligand on copper(I) by ^{1}H and ^{19}F NMR spectroscopy. Complex **4•Zn** was characterised *in-situ* whereby the σ-Zn–H peak could be observed at δ -1.19 ppm in the ^{1}H NMR spectra. After 2 hours, formation of the 4-coordinate decomposition product **L^{4}ZnL^7** was observed, with simultaneous observation of a copper(0) mirror on the wall of the NMR tube and small amounts of H_2 by ^{1}H NMR. This decomposition was most likely facilitated by the ligand exchange reaction between copper and zinc generating a Cu–H moiety and **L^{4}ZnL^7**, with the former readily decomposing.

Attempts to isolate and crystallise the σ-complex **4•Zn** through performing the reaction on a preparative scale in toluene resulted in the observation of a copper(0) mirror on the wall of the scintillation vial and concurrently, the isolation of the aforementioned decomposition product **L^{4}ZnL^7** was achieved. Single crystals suitable for X-ray diffraction were grown from toluene/*n*-hexane mixtures at -35 °C (see Figure 7).

a)

Bond Lengths (Å)	
Zn–N^{L4}	2.036(3)
Zn–O^{L4}	2.009(2)
Zn–N^{L7}	1.972(3)
	1.976(3)
Bond Angles (°)	
N–Zn–O^{L4}	93.97(12)
N–Zn–N^{L7}	97.98(13)

b)



L^4ZnL^7

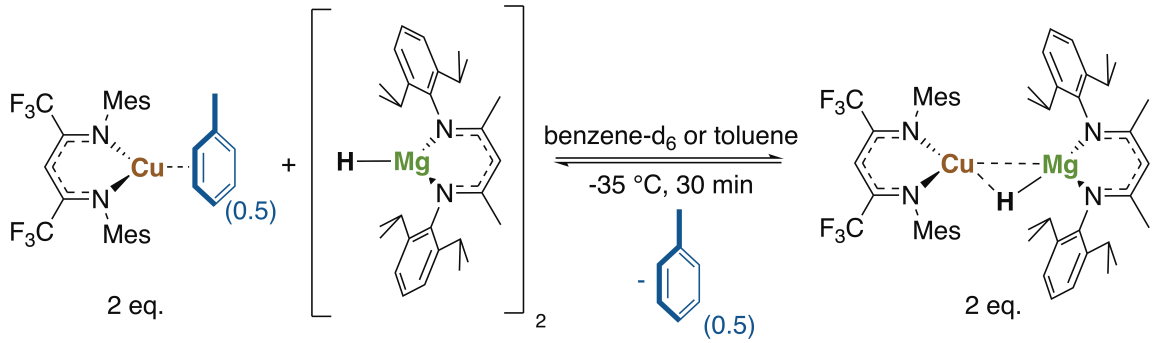
Figure 7 - a) Selected geometrical parameters for L^4ZnL^7, b) Crystal structure of L^4ZnL^7

Complex **L^4ZnL^7** crystallises with the *BDI* ligand L^7 in a puckered formation with regards to the plane created by the ligand L^4. The Zn–O^{L4} and Zn–N^{L4} bond lengths are longer than those found in the homoleptic compound Zn(*ac-nac*^{Dipp})$_2$ (Zn–O = 1.9617(9) Å, 1.9570(8) Å; Zn–N = 1.9818(9) Å, 1.9792(9) Å) reported by Mehn and co-workers.[18] The angle created by the N–Zn–O moiety is also slightly more acute, (N–Zn–O = 1.9617(9)°, 1.9570(8)°).

2.3 σ-Complexes of Copper(I) with Magnanes and Calcanes

Preparation

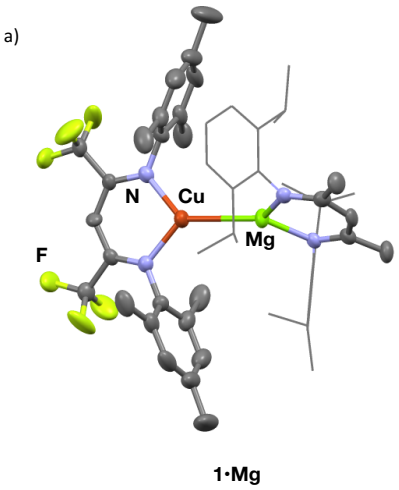
Reaction of the dimeric main group hydride complex **{L^7Mg–H}$_2$** with one equivalent of **1_2•tol** results in the *in-situ* formation of **1•Mg** (Scheme 4). Initial reactions performed in benzene-d_6 confirm the formation of the σ-complex after 30 minutes. Loss of the Mg–H peak of the starting material observed by ^{1}H NMR spectroscopy at δ = 4.00 ppm is accompanied by a shift in the peaks corresponding to the *BDI* ligand on the copper(I) fragment by ^{19}F NMR spectroscopy (Δδ = +1.48 ppm). Complex **1•Mg** decomposes in hydrocarbon solutions within a few hours at room temperature. A modest scale preparation of **1•Mg** was successful, provided it was performed in the glovebox freezer, with stirring at -35 °C. Performing the reaction at reduced temperatures, followed by a low temperature workup, stunted the decomposition of the σ-complex enough in order to allow the isolation of **1•Mg** in 29% yield and obtain single crystal X-ray diffraction data.



Scheme 4 - Synthesis of 1•Mg

X-Ray Characterisation

Single crystals of **1•Mg** could be grown from toluene/*n-hexane* mixtures at -35 °C, however, the quality of data was not good enough to allow the location of the hydride position on a difference electron density map.



b)

Bond Lengths (Å)	
Cu---Mg	2.905(2)
Mg–N	2.008(4)
Cu–N	1.975(4)
Bond Angles (°)	
N–Cu–N	98.4(2)
N–Mg–N	96.8(2)
N–Mg–Cu	131.61(12)

Figure 8 - a) The crystal structure of 1•Mg, b) Selected geometrical parameters for 1•Mg

Complex **1•Mg** crystallises with a plane of symmetry passing through the backbone carbon atoms on each *BDI* ligand and the metal centres (see Figure 8a). The two *BDI* ligands are sitting within planes that have an inter-plane angle of 61°. The distance between the two metals (Cu---Mg) is 2.905(2) Å, which is significantly longer than the equatorial Cu–Mg bonds found within the cluster [Cu_4MgPh_6] but significantly shorter than the nonbonding Cu---Mg axial interactions within the same cluster (Cu---Mg equatorial = 2.754(4) Å, axial = 3.828(4) Å), suggesting a weak Cu---Mg interaction. The *fsr* for the Cu---Mg bond is 1.10, consistent with a formation of a weakly bound σ-complex (see section 2.2). The Mg–N bond lengths are slightly longer than those found within the parent magnesium hydride complex **{L^{7}Mg–H}$_2$**

(Mg–N; 1.990(2) - 1.991(2) Å).[19] This is consistent with a small amount of perturbation of the electronic properties at the magnesium centre on complexation to copper.

NMR Characterisation

On dissolving an isolated sample of **1•Mg** in toluene-d_8, decomposition was observed within a few hours. On cooling a sample of **1•Mg** in toluene-d_8 to 193 K the σ-complex was observed along with **1•tol**. A sharp singlet at δ = -1.94 ppm corresponds to the σ-H as seen in Figure 9. Due to its propensity to decompose at elevated temperatures, a range of variable temperature NMR spectra were not gathered on **1•Mg** and thus a van't Hoff analysis was not conducted.

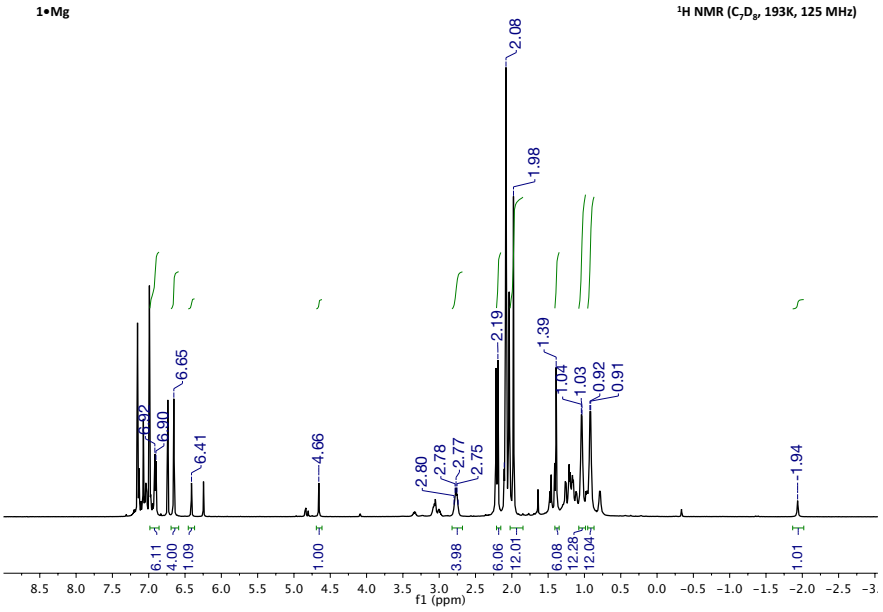
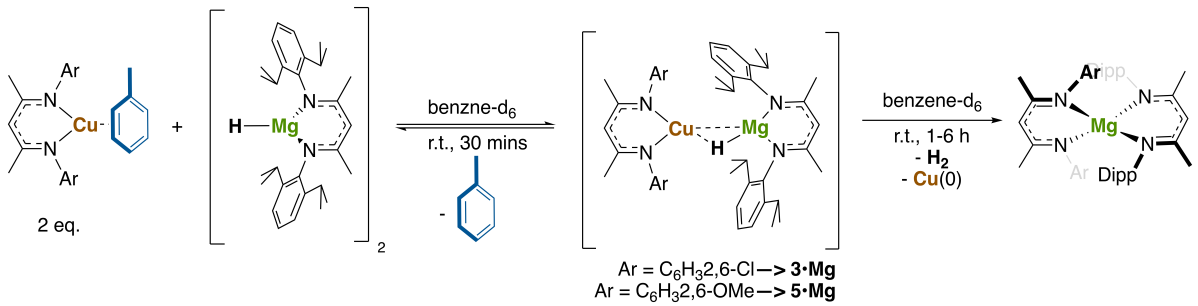


Figure 9 - The ^{1}H NMR spectrum of 1•Mg at 193K

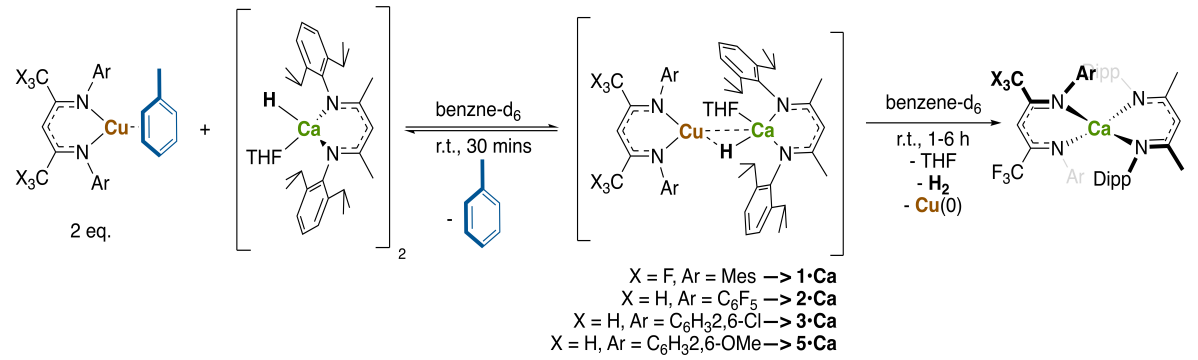
In-situ preparation of 3•Mg, 5•Mg, 1•Ca, 2•Ca, 3•Ca and 5•Ca

In order to probe the effect of the ligand on copper for the stabilisation of σ-complexes of copper(I) with main group hydrides, a series of experiments were performed with different ligands and main group fragments. On an NMR scale, reaction of the symmetrical copper(I) complexes **2•tol**, **3•tol** and **5•tol** with the dimeric main group hydride **{L^{7}Mg–H}$_2$** was performed.



Scheme 5 - *On-situ* preparation of σ-complexes 3•Mg and 5•Mg

In the case of reactions with **3•tol** and **5•tol**, the corresponding σ-complexes **3-5•Mg** were observed *in-situ* through loss of the Mg–H peak by ^{1}H NMR spectroscopy at δ = 4.00 ppm and a shift in the peaks corresponding to the *BDI* ligand on the copper(I) fragment, confirmed by ^{19}F NMR spectroscopy. The σ-complex **2•Mg** could not be observed as it is believed its decomposition in benzene-d_6 is too fast. In all cases, decomposition to the corresponding 4 coordinate heteroleptic complex **L^{n}MgL^{7}** (n = 1-3 and 5) was observed, along with the formation of H_2 and copper(0) mirror on the sides of the NMR tube, as outlined in Scheme 5.



Scheme 6 - *In-situ* preparation of σ-complexes of and Ca–H with the copper(I) complexes 1, 2, 3 and 5

Additionally, NMR scale reactions between the calcium complex **{L^{7}Ca(THF)–H}$_2$** and the copper(I) complexes **1•tol**, **2•tol**, **3$_2$•tol** and **5•tol** resulted in the *in-situ* formation of **1•Ca**, **2•Ca**, **3•Ca** and **5•Ca** respectively (see Scheme 6). This was confirmed through the loss of the Ca–H peak by ^{1}H NMR spectroscopy δ = 4.40 ppm and a shift in the peaks corresponding to the *BDI* ligand on the copper(I) fragment, confirmed by ^{19}F NMR spectroscopy. In addition, the σ-Ca–H proton can be observed in all cases, confirming the σ-complex in solution after 30 minutes. Analogous to what was observed with σ-complexes of Mg–H, decomposition to the corresponding 4 coordinate heteroleptic product **L^{n}CaL^{7}** (n = 1, 2, 3 or 5) and the formation of H_2 and copper(0) was observed.

Table 2 - NMR ppm values of σ-H peak of 3•Mg and 5•Mg and 1-3•Ca and 5•Ca measured in benzene-d_6 or toluene-d_8 at room temperature

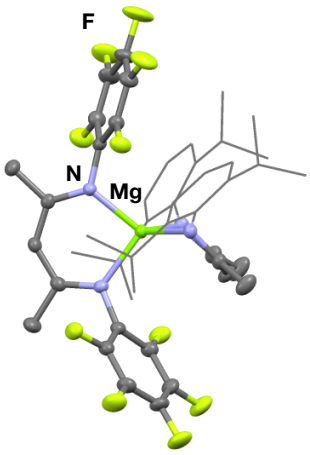
	δ σ-M–H (ppm)
3•Mg	-0.97
5•Mg	-0.16
1•Ca	-0.36
2•Ca	-0.79
3•Ca	-0.97
5•Ca	-0.76

Scale-up of the reaction between **2•tol** and **{L^{7}Mg–H}$_2$** resulted in the crystallisation of the 4 coordinate species **L^{2}MgL^7** from toluene/hexane at -35 °C. The product was confirmed by independent synthesis *via* reaction of **L^{7}MgI(OEt$_2$)** and **L^{2}K** (see section 5.2). Complex **L^{2}MgL^7** crystallises with the L^7 ligand in a puckered formation, in a similar geometry to that of the homoleptic *BDI* complexes of main group metals previously reported by Harder and co-workers.[20]

a)

Bond Lengths (Å)	
Mg–N^{L2}	2.0359(16)
	2.0844(15)
Mg–N^{BDI}	2.0330(16)
	2.0459(16)
Bond Angles (°)	
N–Mg–N^{L2}	93.11(6)
N–Mg–N^{BDI}	95.61(7)

b)



L^{2}MgL^7

Figure 10 - a) Selected geometrical parameters of L^{2}MgL^7, b) The crystal structure of L^{2}MgL^7

The Mg–N bond lengths and N–Mg–N angles in **L^{2}MgL^7** are slightly shorter and more obtuse than those given for the corresponding homoleptic compound, **Mg(L^7)$_2$** (Mg–N average = 2.111(2) Å; N–Mg–N average = 92.97°).[20] The slightly shorter bond is possibly due to less steric

crowding created by one *BDI* ligand and one ligand with a relatively smaller C_6F_5 aromatic group in **L²MgL⁷**. Due to the relative instability of the σ-complexes of magnesium and calcium in benzene-d_6 solution at 25 °C compared to their zinc and boron analogues, no further scale-up reactions were attempted.

3. Discussion

Reports from the Crimmin Group previously provided evidence for reversibility of the coordination of E–H and M–H bonds to copper(I) (E = B, M = Zn, Al).[1,2] This was either evidenced due to line broadening of the E–H or M–H peak by ^{1}H NMR spectroscopy, crossover experiments or evidence of both sides of the equilibrium being observed by NMR. Regarding the σ-complexes synthesised on a preparative scale reported in this chapter, investigations into their solution behaviour have been performed. In order to gain a deeper understanding into the bonding interaction between E–H or M–H and Cu in the σ-complexes, a series of DFT calculations were performed. The following calculations were performed using the ωB97X-D functional and a hybrid basis set (6-31G+(d,p)/ SDD) unless stated otherwise.

3.1 Energy of Formation

Due to the decoalescence observed for the ^{1}H NMR resonances of **1•Zn** at low temperatures, the thermodynamic properties of the equilibrium between the monometallic and heterobimetallic species as outlined in Scheme 3 was investigated. A van't Hoff analysis of the equilibrium was performed through dissolving a sample of **1•Zn** in toluene-d_8 and gathering multiple variable temperature ^{1}H NMR spectra. Measuring the integration of each constituent of the equilibrium at a range of low temperatures allowed the thermodynamic parameters $\Delta H°$ and ΔS° to be determined, and subsequently ΔG°_{298K}.

The values generated for **1•Zn** are in agreement with those previously reported for the σ-complexes **3•Zn** and **3•B'**, as shown in Table 3. The small values of ΔG°_{298K} are consistent with a weak and reversible interaction between the copper fragments and metal hydride fragment whereby the formation of the σ-complex in solution is in competition with coordination of the copper fragments to the arene solvent.

Table 3 - Thermodynamic data for copper(I) σ-complexes, errors measured using least-squares regression

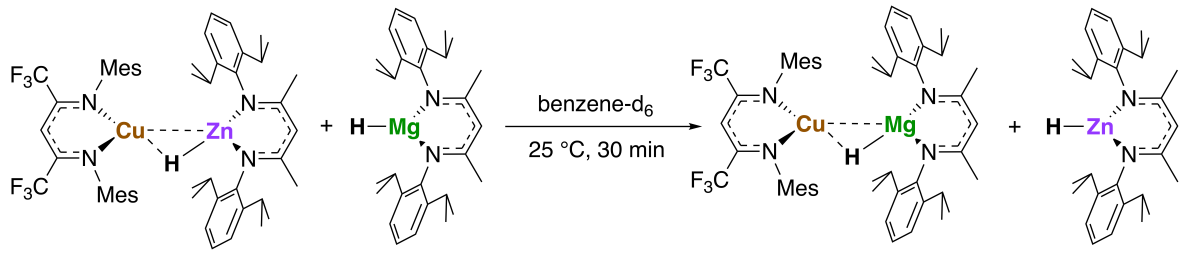
Complex	ΔH° kcal mol^{-1}	ΔS° kcal K^{-1} mol^{-}	$\Delta G°_{298K}$ kcal mol^{-1}
1•Zn	-4.92(11)	-27.6(6)	+3.31(5)
3•B'	-1.40(4)	-5.9(2)	+0.17(3)
3•Zn	-2.47(9)	-10.8(4)	+0.65(8)
3•Al	-1.75(9)	-5.0(2)	-0.23(4)

Previous reports from the Crimmin group found that the binding energies of ligands to {CuL_2} fragments modelled with the B3PW91 functional and a hybrid basis set (6,31G+d,p/ LanL2DZ) are increasingly exergonic across the series C_6F_6 < H–B < H–Si < C_6H_6 < H–Zn < H–Al. Comparison of the calculated Gibbs free energy of binding of Zn to **1** or **3** to form either **1•Zn** or **3•Zn** suggests that the former should be more favourable. This prediction is in contrast with the experimental equilibrium data for the reaction of **1•tol** and **3•tol** with **L^{7}Zn–H** which take values of $\Delta G°_{298K}$ = 3.31(5) kcal mol^{-1} and $\Delta G°_{298K}$ = +0.65(8) kcal mol^{-1} respectively. The reaction of **3•tol** with Al'–H has an experimentally generated value of $\Delta G°_{298K}$ = -0.23(4) kcal mol^{-1}, this finding is consistent with the DFT studies and the five coordinate alane **3•Al'** binds more tightly than the zincane **3•Al** to this ligand fragment. In combination, the data show that while DFT calculations predict some trends, they do not yet accurately or quantitative model the thermodynamics of the binding events. The reason for this is not clear and it is postulated that it could be due to inaccuracies in the modelling of dispersion or issues surrounding the entropy contribution for this dissociative reaction. The underestimation of C–C bond dissociation energies of a range of alkanes has been previously reported with first-generation functionals such as B3LYP, which are known not to correctly describe dispersion forces. This underestimation is more pronounced with larger molecules containing many C–C bonds.[21] Despite B3LYP not being employed in this instance, a similar issue may be occurring.

3.2 Crossover and Ligand Exchange Experiments

A crossover experiment was performed in order to confirm the reversibility of formation of **1•Zn** from its two metal fragments. To an isolated sample of **1•Zn** was added one equivalent of **L^{7}Mg–H**. The formation of **1•Mg** was observed and DFT experiments help to estimate thermodynamics of this reaction. The formation of **1•Mg** and **L^{7}Zn–H** from the reaction of **1•Zn** and **L^{7}Mg–H** has been calculated to be favourable by -3.9 kcal mol^{-1}. A similar trend has been reported previously by the Crimmin Group in the case of heterobimetallics containing Zr–

H–M (M = Al, Zn, Mg) moieties, whereby the formation of the magnesium analogue was calculated to be the most favoured.[22] This trend is anticipated and consistent with a larger ionic contribution to the M–H–Cu bond when M = Mg.



Scheme 7 - Crossover reaction between 1•Zn and L[7]Mg–H

Additional experiments to confirm the lability of the main group hydride fragment in the σ-borane and σ-zincane complexes were conducted. Solutions of **2•B** and **1•Zn** react readily under 1 atmosphere of CO at 25 °C in order to generate the respective copper(I) carbonyl species **2•CO** and **1•CO** and the corresponding borane or zincane after 24 hours at room temperature (see Figure 11).

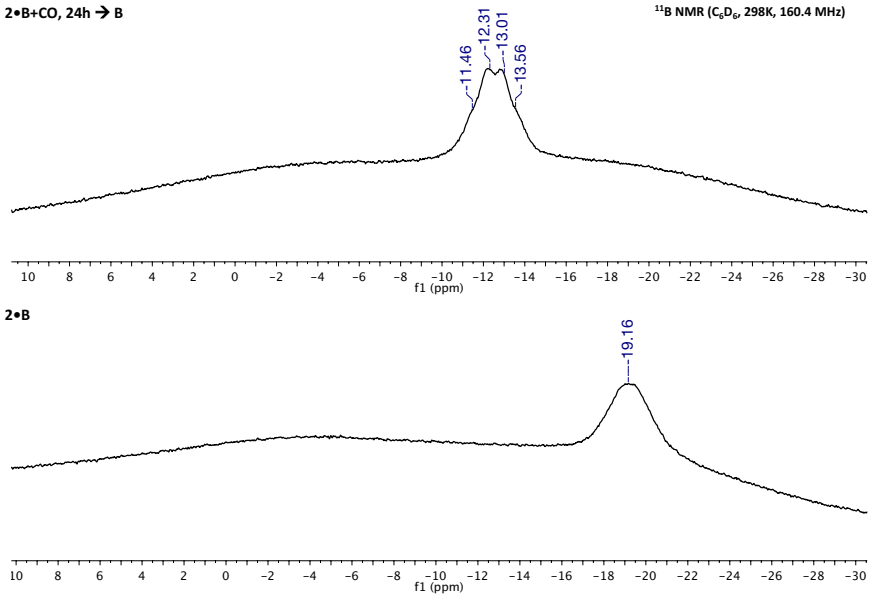


Figure 11 - ^{11}B NMR spectra of the ligand exchange reaction between 2•B and CO

3.3 Half-Life Experiments

In order to determine the relative instability of the σ-complexes in solution, experiments to monitor the decomposition of the complexes were performed in benzene-d_6 or toluene-d_8 at

room temperature. For **1-2•Zn**, **1-2•B** and **1•Mg**, isolated samples of these complexes were dissolved in deuterated solvents and a series of NMR spectra at various time points were measured. In all cases, the singlet corresponding to the backbone of the *BDI* ligand on the copper fragment was measured against ferrocene as an internal standard.

Calculating the natural log of the relative concentration of σ-complex in solution and plotting it against time confirmed the first order nature of decomposition of the σ-complexes. In general, the $t_{1/2}$ decreases across the series **n•B** > **n•Zn** > **n•M** (n = 1-2, M = Mg, Ca). The decomposition of σ-complexes of copper(I) with metal hydrides is likely to occur *via* the formation of a Cu–H species, which subsequently decomposes to generate a copper(0) mirror and H_2. This trend in decreasing half life is consistent with increasing covalency of the Cu–H bond in the Cu–H–M core, as confirmed by Wiberg bond indices (WBI's, see section 3.4) (**1•B**; 0.04 < **1•Zn**; 0.29 < **1•Mg**; 0.36 < **1•Ca**; 0.45). The increasing covalency in the Cu–H bond suggests a greater degree of hydride transfer to copper and may be a factor in determining the shorter half-lives of **1•Mg** and **1•Ca** compared to **1•Zn** and **1•B**.

a)

Complex	$t_{1/2}$
1•B	> 1 year
2•B	> 140 days
1•Zn	60 days
2•Zn	24 days
1•Mg	3.5 h
1•Ca	10.5 h

b)

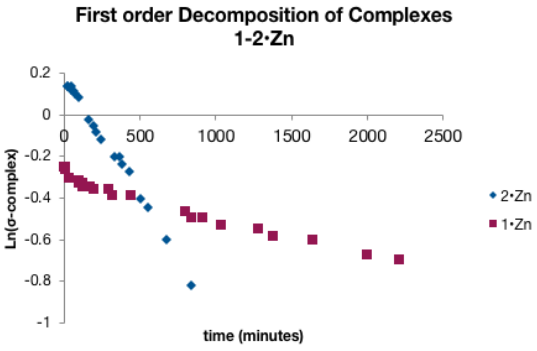


Figure 12 - a) Half-lives of complexes 1-2•B, 2•Mg and 1•Ca, b) a graphical representation of the first order decomposition of complexes 1-2•Zn

3.4 Density Functional Theory Calculations

σ-Complexes of the late transition metals are often discussed in the context of the Dewar-Chatt-Duncanson model, as outlined in chapters 1 and 2. Donation from the E–H bond into a vacant d-orbital is accompanied by back-donation from a filled d-orbital to the σ*-E–H orbital. The electron configurations of the Cu(I) fragments, however, exclude the involvement of vacant d-orbitals. The qualitative MO diagram for a C_{2v}-symmetric d^{10}-{ML_2} complex

containing a π-donating ligand matches well with DFT calculations performed on naked two-coordinate copper complexes **1-3** (see chapter 1, section 3.2).[23]

Considering a dihydrogen complex as a model for E–H or M–H bonding, in the case of the copper fragment **3**, the LUMO is 4s-based and suitable for overlap with the σ-H–H orbital. In addition, the HOMO-1, consisting of an out-of-phase combination of the d_{yz} orbital and anti-symmetric ligand SALC, is suitable for back-donation into the σ*-H–H orbital. Filled and empty b_2-symmetric orbitals remain essentially non-bonding with respect to the H_2 fragment (Figure 13).

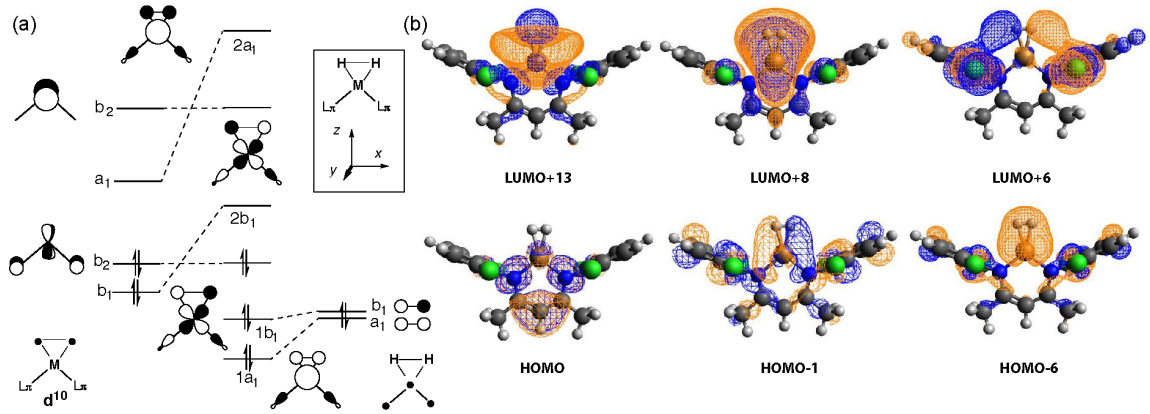


Figure 13 - a) Qualitative MO diagram for combination of the C_{2v} {CuL_2} fragment with a σ-H–H bond, b) selected calculated molecular orbitals for theoretical 3•H_2

Geometry of σ-Borane Complexes

Molecular orbital analysis of the $\eta^2;\eta^2$-coordination mode found in σ-borane complexes of copper(I) provides an explanation for the experimental tetrahedral geometry. In the DFT model, BH_4^- was used as an approximation of the σ-borane ligand in order to preserve the symmetry of the Cu–H_2 model.[24] Simplified qualitative analysis outlined in Figure 14 combines filled a_1, b_1 and b_2 symmetric orbitals of the BH_4-SALCs with the frontier orbitals of the copper(I) fragment. The totally symmetric a_1 ligand SALC remains essentially non-bonding. The preference for tetrahedral geometry can be rationalised by considering the b_1 and b_2-symmetric orbitals as the newly formed MO's. While d-/ p- mixing can occur in both the b_2- and b_1-symmetric orbitals the former are stabilized to a greater extent than the latter due to the relative low energy of the 4_{py} orbital (+0.127 Ha in **3**) with respect to the 4_{px} orbital (+0.184 Ha in **3**). In the resulting MO diagram, and in quantitative calculations on theoretical **3•BH_4**, the b_2-symmetric MOs (HOMO-1, HOMO-12) are stabilised relative to the b_1-symmetric (HOMO, HOMO-6) MO's. Hence,

there is a preference for the coordinated BH_4 unit to sit orthogonal to the plane created by the copper fragment. The twist from tetrahedral to planar was investigated by single point calculations in which the N–Cu–H–B torsion angle was varied incrementally from +90° to 0°. These calculations reveal that the planar geometry is 4.7 kcal mol^{-1} higher in energy than the observed tetrahedral ground state and is a maximum on the potential energy surface (Figure 14c).

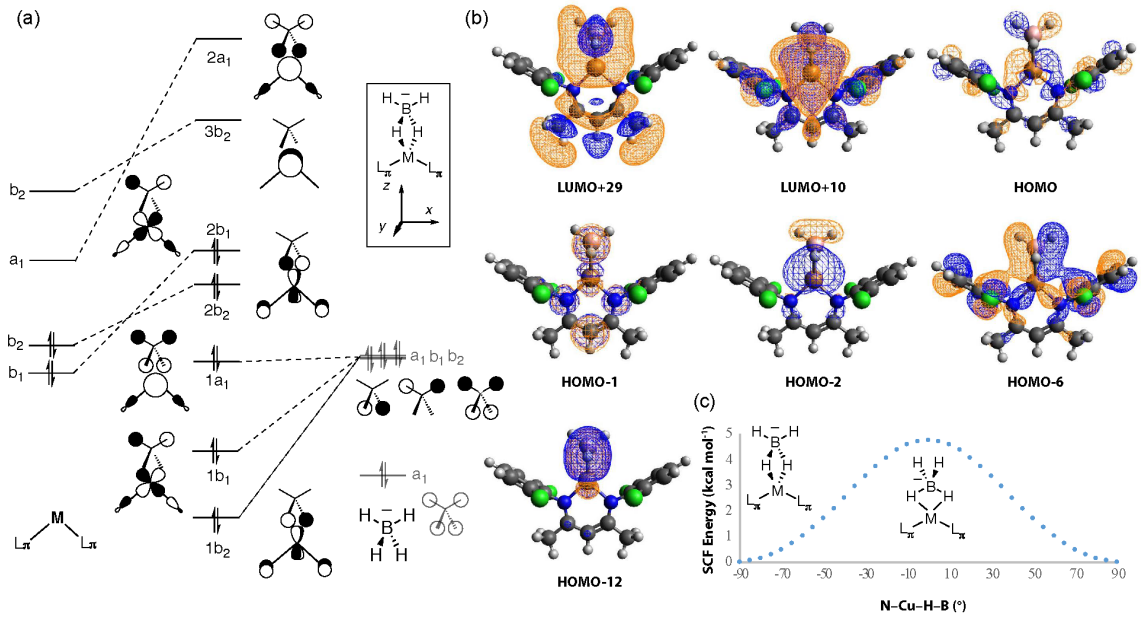


Figure 14 - a) Qualitative MO diagram for the combination of the C_{2V} {CuL_2} fragment with a BH_4 unit (d-/p- mixing not drawn), b) Selected calculated molecular orbitals for theoretical 3•BH_4, c) energy as a function of dihedral angle

Quantification of Donor-Acceptor Interactions

As previously reported for σ-complexes of copper(I), quantifications of the donor-acceptor interactions can be achieved using second-order perturbation theory.[1,2] In all cases, the donor contribution from the σ-M–H to the Cu 4s orbital is more significant than back-donation from Cu 3d to σ*-M–H (see Table 4). In comparison across a series for complexes of Zn–H, as the filled $2b_1$ orbital on the copper fragment is destabilised; the back-bonding contribution from M–H becomes slightly more significant. For the same series of complexes, this subtle theoretical effect is mirrored experimentally, with the Cu---Zn distance also decreasing with increasing back-bonding contribution. Across the series **3** < **1** < **2**, the coordination geometry at copper deviates from trigonal towards T–shaped as outlined in Figure 15.

When considering the hydride as a discrete ligand, the T-shaped geometry could be described as slight perturbation towards square planar with supplementary increased back-donation and a small perturbation toward a d^8-copper(III) species.

Table 4 - Calculated donor-acceptor contirbutions from second order perturbation theory

M–H	{CuL_2}	σ(M–H) donation	σ*(M–H) back-donation
		kcal mol^{-1}	
B–H	**3**	47	3
	2	49	2
	1	49	2
Al–H	**3**	85	17
Al'–H	**3**	54	5
Zn–H	**3**	144	22
	2	124	19
	1	142	19
Mg–H	**1**	136	10

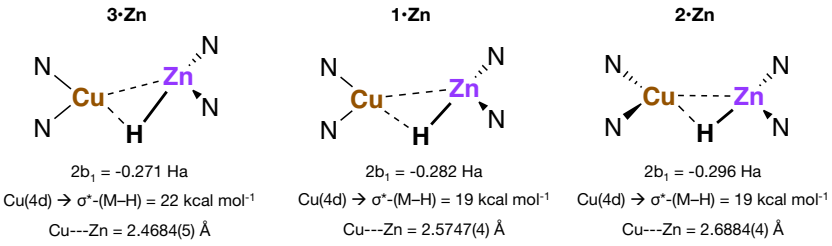


Figure 15 - Energy of copper $2b_1$ orbital, quantification of back-donation and distance between the metals across a series of complexes of Zn–H

The geometries of *BDI* copper(I) complexes with ethylene ligands reported by Warren and co-workers have also been rationalised using similar methods. In these complexes, the back-bonding appears to be weak from analysis of the ethylene coupling constant ($^1J_{CH}$ = 158 Hz) and facile rotation achievable about the Cu–ethylene bond ($\Delta G^{\ddagger}$ = 10.7(3) kcal mol^{-1} at 215 K). The *BDI* and alkene ligands are believed to be co-planar, however, because of increased stabilisation of the π* orbital of the alkene due to back-donation from copper(I).[25] A more in-depth analysis by Warren and co-workers into the back-donation of *BDI* copper(I) complexes of nirtosobenzene, diazine and dioxygen has been performed using X-ray adsorption spectroscopy

and theoretical methods in order to model multiconfigurational ground-states. In this instance, as the electronegativity of the combined coordinating atoms to copper increased, a trend to higher oxidation states of copper was observed, which can be considered as a complimentary depiction of increased back-donation.[26]

Ligand sensitivity

Investigations into the effect of the ligand on the copper fragment for the synthesis of σ-complexes of copper(I) were conducted through an analysis of the Wiberg bond indices (WBI) of the 3-centre,2-electron or 4-centre,4-electron core, from natural bond orbital calculations (NBO). WBI's excludes the ionic component of the bonding and thus in all cases, the electronic differences of the ligands on complexes of Zn–H and B–H were not reflected in a perturbation of the Wiberg bond indices. These are, however, reflected in the charge analysis (*vide infra*).

Table 5 - Selected Wiberg bond indices for complexes 1-3•B, 1-3•Zn, 1•Mg and 1•Ca

		WBI		
M–H	**{CuL$_2$}**	M–H	Cu–H	Cu–M
B–H	**3**	0.93[a]	0.04	0.12
		0.95[a]	0.04	
		0.96[b]		
	2	0.92[a]	0.04	0.12
		0.95[a]	0.05	
		0.96[b]		
	1	0.93[a]	0.04	0.11
		0.94[a]	0.05	
		0.96[b]		
Zn–H	**3**	0.39	0.28	0.15
	2	0.39	0.29	0.15
	1	0.39	0.29	0.15
Mg–H	**1**	0.25	0.36	0.11
Ca–H	**1**	0.14	0.45	0.12

a - bridging B–H, b - terminal B–H

Ionicity

The ionic contribution to bonding in the core of these complexes can be inferred by analysis of the natural population analysis (NPA) charge on the bridging hydride ligand. Whilst it is in fact the increasing number of binding events for E = B which has been the reason behind being able to isolate these σ-complexes of copper(I), the increased ionic contribution in the bonding from B–H to M–H (M = Zn, Al) is the cause behind the increased stability and ease of isolation of the heavier σ-complexes of copper(I) compared to those of lighter elements (E = Si, H, C).

Table 6 - NPA charges on complexes 1•M (M = Zn, Al, Al', Mg, Ca)

	NPA Charges	
	H	**M**
Zn–H	-0.46	+1.38
Al–H	-0.26	+1.42
Al'–H	-0.45	+1.39
Mg–H	-0.57	+1.09
Ca–H	-0.61	+1.79

Furthermore, an increase in ionic contribution from zinc and aluminium to analogues of magnesium and calcium could be the reason behind their comparatively fast decomposition, and thus heterobimetallics of the type Cu–H–M (M = Zn, Al) may represent the 'sweet spot' for σ-complexes copper(I) possessing fluorinated *BDI* ligands.

Additional stabilisation

The investigation into additional, intermolecular and non-covalent interactions between the ligands on copper(I) and the subsequent element or metal fragment (E = B, M = Zn, Mg) was realised using quantum theory of atoms in molecules (QTAIM) calculations. Similarly to the WBI analysis, the differing ligand on the complexes of Zn–H did not show any difference in the QTAIM data. The expected bond critical paths between Zn–H and Cu–H were observed with no perturbation across the series **1•Zn**, **2•Zn** and **3•Zn**.

Intramolecular non-covalent interactions between the substituents on Cu and either B or M (M = Al, Zn, Mg) likely play an important role in stabilizing the weakly bound σ-complexes described herein. The structure of **2•B** shows a clear π–π stacking interaction while those of **1-2•Zn** contain multiple C–F---H–C and C–H---H–C interactions. This is evidenced from the

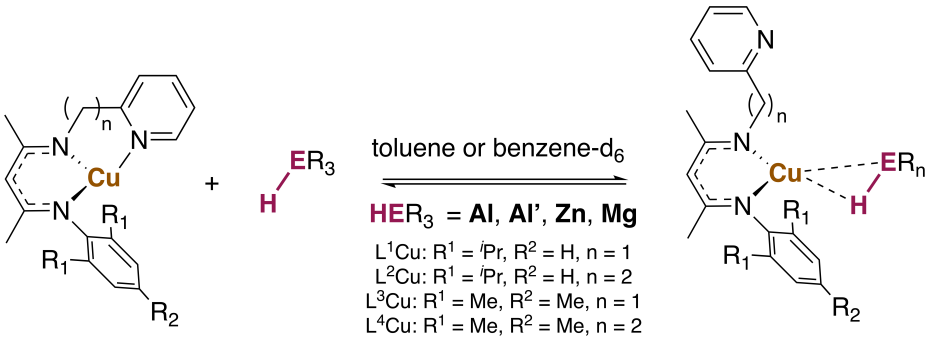
close contacts in solid-state data and further emphasised due to clear but weak bond critical paths in the QTAIM contour plots. The non-covalent interactions in **1-3•Zn** may be estimated by single point calculations using the ωB97x and ωB97x-D functionals. The latter method includes a long-range dispersion correction and may more accurately capture weak intramolecular forces than the former. Power and others have begun to consistently argue the importance of dispersion forces in stabilising both transition metal and main group complexes stabilized by bulky hydrocarbon ligands.[27] These experiments reveal that inclusion of the dispersion correction results in stabilization of the heterobimetallic complexes by 12-15 kcal mol^{-1} and it can be concluded that non-covalent interactions are likely to play an important part in their formation.

3.5 Summary

The preparation, characterisation and solution dynamics of a series of new σ-complexes of copper(I) which contain either 3-centre,2-electron (Cu–H–Zn, Cu–H–Mg) or 4-centre,4-electron (Cu–H_2B) bonds has been reported. The bonding within these complexes can be viewed within a Dewar-Chatt-Duncanson-type model. Formation of a bent d^{10}-{CuL_2} fragment is essential to produce frontier molecular orbitals of suitable symmetry and energy to overlap with B–H or M–H (M= Zn, Mg) bonds. Substrate binding is weak and in solution the σ-complexes readily undergo ligand exchange with toluene or benzene solvent. Consideration of simplified qualitative MO diagrams allows rationalisation of the observed solid-state structures, including the diverse geometries found at copper. In all cases, donation of electron-density from the ligand to a largely 4s-based orbital of the {CuL_2} fragment greatly outweighs back-donation from a $3d_{xy}$-based orbital to the ligand. Calculations suggest that π-π stacking and C–F---H–C bonds play an important part in stabilising the new molecular species reported herein.

4. Future Work

Modification of the σ-donating ability of the ligand and the L–Cu–L angle within bent {CuL_2} fragments, along with fine tuning of ligand---ligand interactions may all be important design features for the preparation of new σ-complexes of copper(I). Asymmetric *BDI* copper(I) complexes reported by Hsu and co-workers, which feature N-aryl-N′-alkylpyridyl moieties, reversibly bind CO with loss of the pyridyl arm coordination.[28] Expanding the coordination of these fluxional two/three coordinate copper(I) complexes to main group metal hydrides may result in the isolation of new, increasingly stable σ-complexes of copper(I).



Scheme 8 - The proposed synthesis of σ-complexes of main group hydrides with a fluxional 2- or 3-coordinate copper complex

Whilst it has been postulated that reduced stability of the σ-complexes of copper(I) outlined in this chapter with magnesium and calcium hydrides are as a result of their being heavier hydrides, preparing σ-complexes of copper(I) with heavier main group metal hydrides may increase the ionic contribution of the bonding even further from the heavier hydrides outlined in this chapter (M = Zn, Mg, Ca). The utilisation of a calcium hydride dimer bearing amidinate ligands as main group hydride source could allow for the structural characterisation of the first examples of a σ-complex of copper(I) with a calcium hydride.[29] The preparation of σ-complexes with the tin hydride complex supported by electron rich, amino functionalised 'N-*nacnac*' ligands reported by Aldridge and co-workers could also lead to increased ionicity and subsequent stabilisation.[30]

5. Experimental

5.1 General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 and toluene-d_8 were stored over molecular sieves and distilled prior to use. NMR-scale reactions were conducted in J. Young's tap tubes and prepared in a glovebox. All heating mentioned was done using silicone oil baths. ^{1}H, ^{19}F, ^{11}B, ^{31}P and ^{13}C NMR spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated. All peak intensities are derived internal standard peak with values quoted in ppm and data was processed using the MestReNova or Topspin software. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University. CO was purchased from CK Gases and used as received. Boranes were purchased from Sigma Aldrich and used without further treatment.

5.2 Preparative-Scale Synthesis

L^{7}Zn–H,[17] **{L^{7}Mg–H}$_2$**,[19] **{L^{7}Ca–H(THF)}$_2$**,[31] **L^{7}MgI(OEt)$_2$**[32] and KHMDS[33] were prepared according to literature procedures.

1•B

In a glovebox, **1$_2$•tol** (61 mg, 0.055 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **H$_3$BL** (L = 2-methylpyridine) (12 mg, 0.11 mmol, 2 eq.) was weighed and dissolved in toluene (1.5 mL). The solution containing **H$_3$BL** was added dropwise over 5 minutes to the stirred solution of **1$_2$•tol**. The reaction mixture was stirred for 1 hour at 25 °C. The green solution was filtered using a glass fibre and the concentrated *in vacuo* to ¼ of its original volume before *n*-heptane (1.5 mL) was added. The reaction mixture was left at –35 °C overnight to give yellow crystals of **1•B** (53 mg, 0.088 mmol, 80%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.99 (br s, 3H, Ar–Me_B), 2.08 (br s, 6H, Me_{Cu}), 2.22 (br s, 12H, Ar–Me_{Cu}), 2.98 (br m, 3H, B–(H)$_3$–Cu), 5.94 (t, 1H, $^{3}J_{H–H}$ = 7.3 Hz, Ar–H_B), 5.98 (d, 1H, $^{3}J_{H-H}$ = 7.3 Hz, $_B$Ar–H), 6.17 (s, 1H, CH_{Cu}), 6.47 (td, 1H, $^{3}J_{H–H}$ = 5.0 Hz, $^{4}J_{H–H}$ = 1.5 Hz, Ar–H_B), 6.66 (s, 4H, Ar–H_{Cu}), 7.01 - 7.13 (m), 7.55 (br s, 1H Ar–H_B); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 18.8, 20.9, 22.2, 83.4

(sept, $^{3}J_{C–F}$ = 5.2 Hz), 121.3 (q, $^{1}J_{C–F}$ = 288.7 Hz), 126.3, 128.7, 129.3, 129.5, 132.2, 138.5, 146.6, 148.0, 151.9 (q, $^{2}J_{C–F}$ 25.7), 156.9; ^{11}B NMR (C_6D_6, 298 K, 160.4 MHz) δ -18.0 (br); ^{19}F NMR (C_6D_6, 470.4 MHz, 298 K) δ -64.6 (s). Elemental analysis calc. for $C_{29}H_{23}BCuF_6N_3$: C, 56.92; H, 5.44; N, 6.87. Found: C, 56.84; H 5.45; N, 6.90.

2•B

In a glovebox, **2•tol** (64 mg, 0.11 mmol, 1 eq.) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **H_3BL** (L = 2-methylpyridine) (12 mg, 0.11 mmol, 1 eq.) was weighed and dissolved in toluene (1.5 mL). The solution containing **H_3BL** was added dropwise over 5 minutes to the stirred solution of **2•tol**. The reaction mixture was stirred for 1 hour at 25 °C. The green solution was filtered using a glass fibre and the concentrated *in vacuo* to ¼ of its original volume before *n*-heptane (1.5 mL) was added. The reaction mixture was left at –35 °C overnight to give yellow crystals of **2•B** (0.042 g, 0.069 mmol, 62%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.65 (s, 6H, Me_{Cu}), 1.97 (s, 3H, Me_B), 3.07 (br m, 3H, B–(H)$_3$–Cu), 4.92 (s, 1H, CH_{Cu}), 5.96 (t, 1H, $^{3}J_{H–H}$ = 7.6 Hz, Ar–H_B), 6.00 (d, 1H, $^{3}J_{H–H}$ = 7.6 Hz, Ar–H_B), 6.51 (br t, 1H, $^{3}J_{H–H}$ = 7.6 Hz, Ar–H_B), 7.62 (br d, 1H, $^{3}J_{H–H}$ = 5.8 Hz, Ar–H_B); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 21.9, 23.2, 97.7, 122.1, 126.6, 136.8 (dm, $^{1}J_{C–F}$ = 250.7 Hz), 138.0 (dm, $^{1}J_{C–F}$ = 250.7 Hz), 139.4, 140.2 (dm, $^{1}J_{C–F}$ = 239.0 Hz); ^{11}B NMR (C_6D_6, 298 K, 160.4 MHz) δ -19.7 (br); ^{19}F NMR (C_6D_6, 376.5 MHz, 298 K) δ -166.1 (t, 2F, $^{3}J_{F–F}$ = 21.5 Hz), -164.8 (t, 4F, $^{3}J_{F–F}$ = 23.5 Hz), -151.2 (d, 2F, $^{3}J_{F-F}$ = 23.1 Hz), Elemental analysis calc. for $C_{23}H_{16}BCuF_{10}N_3$: C, 46.06; H, 2.86; N, 7.01. Found: C, 46.17; H 2.79; N, 7.07.

1•Zn

In a glovebox, **1_2•tol** (61 g, 0.055 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **L^{7}Zn–H** (53 mg, 0.11 mmol, 2 eq.) was weighed and dissolved in toluene (1.5 mL). The solution containing **L^{7}Zn–H** was added dropwise over 5 minutes to the stirred solution of **1_2•tol**. The reaction mixture was allowed to warm to 25 °C and stirred for 30 minutes. The orange solution was filtered using a glass fibre and the concentrated *in vacuo* to ¼ of its original volume before *n*-heptane (3 mL) was added. The reaction mixture was left at -35 °C overnight to give orange crystals of **1•Zn** (63 mg, 0.07 mmol, 58%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.16 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$CHMe_2), 1.25 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$CHMe_2), 1.68 (s, 6H, Me_{Zn}), 1.97 (s, 12H, Ar–Me_{Cu}), 2.19 (s, 6H, Ar–Me_{Cu}), 3.16 (sept, 4H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$CHMe$_2$), 5.01 (s, 1H, CH_{Zn}), 6.08 (s, 1H, CH_{Cu}), 6.81 (s, 4H, ArH_{Cu}) 6.99 - 7.15 (m, 6H, ArH_{Zn}); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 18.7, 21.0, 23.2, 23.5, 24.8, 28.5, 83.6, 96.1,

120.9 (q, $^{1}J_{C–F}$ = 287.9 Hz), 124.0, 126.3, 128.8, 130.0, 133.4, 141.8, 144.6, 145.4, 152.6 (q, $^{2}J_{C–F}$ = 25.4 Hz), 168.2; ^{19}F NMR (C_6D_6, 298 K, 470.7 MHz,) δ -64.8 (s). At low temperature, the equilibrium enters the slow exchange regime. ^{1}H NMR (C_7D_8, 195 K, 500 MHz) δ -0.40 (s, 1H), 0.98 (br d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$CH*Me*$_2$), 1.04 (br d, $^{3}J_{H–H}$ = 6.8 Hz, 12H, $_{Zn}$CH*Me*$_2$), 1.39 (br s, 6H, *Me*$_{Zn}$), 2.10 (s, 6H, Ar–*Me*$_{Cu}$), 2.19 (s, 12H, Ar–*Me*$_{Cu}$), 2.84 (br m, 4H, $_{Zn}$C*H*Me$_2$), 4.76 (s, 1H, C*H*$_{Zn}$), 6.46 (s, 1H, C*H*$_{Cu}$), 6.64 (s, 4H, Ar*H*$_{Cu}$), 6.87 – 6.98 (m, 6H, Ar*H*$_{Zn}$); ^{13}C NMR (C_7D_8, 193 K, 125 MHz) δ 18.6, 21.0, 23.6, 24.1, 25.3, 32.6, 83.1, 97.4, 121.0 (q, $^{1}J_{C–F}$ = 287.9 Hz), 126.2, 126.5, 130.1, 133.3, 141.6, 142.6, 145.8, 146.3, 152.4 (m), 168.3; ^{19}F NMR (C_7D_8, 193 K, 407.4 MHz) δ -63.3 (s). Elemental analysis calc. for $C_{52}H_{65}CuF_6ZnN_4$: C, 63.15; H, 6.62; N, 5.66. Found: C, 63.14; H, 6.58; N, 5.75.

2•Zn

In a glovebox, **2•tol** (64 mg, 0.11 mmol, 1 eq.) was weighed into a vial and dissolved in toluene (0.75 mL). Similarly, **L^{7}Zn–H** (53 mg, 0.11 mmol, 1 eq.) was weighed and dissolved in toluene (0.75 mL). The solution containing the copper complex was cooled to -35 °C, with stirring. After 10 minutes the solution containing **L^{7}Zn–H** was added dropwise to the stirred reaction mixture. The reaction mixture was allowed to warm to 25 °C and stirred for 30 minutes. The light green solution was filtered using a glass filter and the solvent removed under vacuum to ¼ of its original volume. *n*-Heptane (1.5 mL) was added and the reaction mixture stored at –35 °C for 3 days to give light green crystals of **2•Zn** (27 mg, 0.028 mmol, 25%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.07 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$CH*Me*$_2$), 1.12 (d, 12H, $^{3}J_{H–H}$= 6.8 Hz, $_{Zn}$CH*Me*$_2$), 1.45 (s, 6H, *Me*$_{Zn}$), 1.50 (s, 6H, *Me*$_{Cu}$), 2.97 (hept, 4H, $^{3}J_{H–H}$ = 6.8 Hz, $_{Zn}$C*H*Me$_2$), 4.82 (s, 1H, C*H*$_{Cu}$), 4.92 (s, 1H, C*H*$_{Zn}$), 7.04 - 7.15 (m, 6H, Ar*H*); ^{13}C NMR (C_6D_6, 298 K, 125 MHz); δ 23.4, 23.5, 24.4, 28.6, 97.4, 98.8, 124.0, 125.6 (m), 126.7, 129.3 (br s), 137.6 (dm, $^{1}J_{C–F}$ = 249.6 Hz), 138.1 (dm, $^{1}J_{C–F}$ = 246.5 Hz), 141.3 (dm, $^{1}J_{C–F}$ = 242.2 Hz), 141.6, 143.6, 166.7, 169.1; ^{19}F NMR (C_6D_6, 298 K, 470.7 MHz) δ -150.0 (d, 4F, $^{3}J_{F–F}$ = 23.0 Hz), -163.3 (t, 4F, $^{3}J_{F–F}$ = 23.0 Hz), -164.5 (br m, 2F). Elemental analysis calc. for $C_{46}H_{49}CuF_{10}N_4Zn$: C, 56.56; H, 5.06; N, 5.74. Found: C, 56.42; H, 5.04; N, 5.66.

1•Mg

In a glovebox, **1_2•tol** (61 mg, 0.055 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **L^7Mg–H** (49 mg, 0.11 mmol, 2 eq.) was weighed and dissolved in toluene (1.5 mL). Vials containing both complexes were placed in the glovebox freezer and cooled to -35 °C. After 20 minutes, the solution containing **L^7Mg–H** was added drop-wise over 5 minutes to the stirred reaction mixture at –35 °C and was left to stir at this temperature for 30 minutes. The solvent volume was reduced *in vacuo*, with stirring, to ¼ of its original volume, before the addition of cold *n*-heptane (3 mL). The orange crude reaction mixture was stored at -35 °C overnight to give red crystals of **1•Mg** (30 mg, 0.032 mmol, 29%). At room temperature, the complex is unstable and thus NMR data is given at 193 K. ^{1}H NMR (C_7D_8, 193 K, 500 MHz) δ -1.94 (s, 1H), 0.92 (br d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.04 (br d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.39 (s, 6H, *Me*$_{Mg}$), 1.98 (s, 12H, Ar–*Me*$_{Cu}$), 2.19 (s, 6H, Ar–*Me*$_{Cu}$), 2.77 (br sept, 4H, C*H*Me$_2$), 4.66 (s, 1H, C*H*$_{Mg}$), 6.41 (s, 1H, C*H*$_{Cu}$), 6.65 (s, 4H, Ar*H*$_{Cu}$) 6.90 - 6.99 (m, 6H, Ar*H*$_{Zn}$); ^{13}C NMR (C_7D_8, 193 K, 125 MHz); δ 18.9, 20.9, 23.0, 23.9, 24.8, 83.1, 95.9, 121.0 (m), 129.8, 131.9, 133.1, 136.0, 141.2, 143.0, 144.6, 146.9, 151.6 (m), 169.8; ^{19}F NMR (C_7D_8, 193 K, 470.4 MHz) δ -63.4. Elemental analysis calc. for $C_{52}H_{65}CuF_6MgN_4$: C, 65.89; H, 6.91; N, 5.91. Found: C, 65.75; H, 6.95; N, 6.00.

L^2K

In a glovebox, KHMDS (88 mg, 0.44 mmol) was weighed into a vial, and toluene (6 mL) was added. Similarly, L^2H (189 mg, 0.44 mmol) was weighed and dissolved in toluene (6 mL). The solution containing KHMDS was added to the solution containing the ligand, and a yellow precipitate was formed. The reaction was left to stir for 15 minutes and the precipitate left to settle overnight before the solvent was removed *in vacuo* to give **L^2K** as a yellow powder (171 mg, 0.37 mmol, 83%), and used without further purification. The insolubility of **L^2K** in hydrocarbon and coordinating solvents inhibited its full characterisation.

L^2MgL^7

Method A: In a glovebox, **L^7Mg–H** (0.024 g, 0.055 mmol) was weighed into a vial and dissolved in toluene (0.75 mL). Similarly, **2•tol** (0.032 g, 0.055 mmol) was weighed and dissolved in toluene (0.75 mL). The solution containing the copper complex was cooled to -35°C and after 10 minutes, was added dropwise to the solution containing **L^7Mg–H**. The reaction mixture was allowed to warm to 25°C and stirred for 30 minutes. The dark brown solution was filtered using a glass fibre and the solvent reduced under vacuum to ¼ of its original volume. *n*-Hexane

(1.5 mL) was added and the reaction mixture was then stored at -35 °C overnight to give colourless crystals of **L²MgL⁷** which was submitted for single crystal X-ray diffraction without further analysis. **Method B:** In a glovebox, to a suspension of **L²K** (102 mg, 0.22 mmol) in toluene (3 mL) was added ***L⁷*MgI(OEt₂)** (135 mg, 0.22 mmol) to give a colorless, cloudy solution. The solution was left to stir for 30 minutes before the precipitate was left to settle overnight, filtered through glass fibre and solvent removed *in vacuo* to give the crude as an off-white powder. The crude was recrystallized form *n*-hexane (3 mL) at -35 °C to give colourless crystals of **L²MgL⁷** (67 mg, 0.077 mmol, 35%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.06 (d, 6H, $^{3}J_{H–H}$= 6.8 Hz), 1.09 (d, 6H, $^{3}J_{H–H}$ = 6.8 Hz), 1.22 (s, 3H), 1.28 (d, 6H, $^{3}J_{H–H}$ = 6.8 Hz), 1.36 (d, 6H, $^{3}J_{H–H}$ = 6.8 Hz), 1.52 (s, 6H), 1.63 (s, 3H), 2.90 (sept, 2H, $^{3}J_{H–H}$ = 6.8 Hz), 3.19 (sept, 2H, $^{3}J_{H–H}$ = 6.8 Hz), 4.48 (s, 1H), 4.81 (s, 1H), 7.00 – 7.16 (m, 6H); ^{13}C NMR (C_6D_6, 298 K, 125 MHz); δ 24.4, 24.6, 25.1, 25.4, 25.4, 28.4, 29.0, 29.0, 94.0, 100.0, 123.6 (br t), 123.9, 124.3, 125.4, 125.6 (br t), 137.1 (br t), 139.1 (br t), 140.7 (br d), 141.7 (br d), 141.9, 142.6 (br d), 142.8, 143.7 (br d), 144.8, 171.2, 172.2, 172.4. ^{19}F NMR (C_6D_6, 298 K, 470.7 MHz) δ -143.6 (d, 2F, $^{3}J_{F–F}$ = 23.5 Hz), -147.4 (dd, 2F, $^{3}J_{F–F}$ = 23.5 Hz, $^{4}J_{F–F}$ = 4.7 Hz), -161.4 (t, 1F, $^{3}J_{F–F}$ = 23.5 Hz), -161.7 (t, 1F, $^{3}J_{F–F}$ = 18.8 Hz), -162.8 (td, 2F, $^{3}J_{F–F}$ = 23.5 Hz, $^{4}J_{F–F}$ = 4.7 Hz), -164.3 (td, 2F, $^{3}J_{F–F}$ = 23.5 Hz, $^{4}J_{F–F}$ = 4.7 Hz); Elemental analysis calc. for $C_{46}H_{48}F_{10}MgN_4$: C, 63.42; H, 5.55; N, 6.43. Found: C, 63.37; H, 5.67; N, 6.34.

5.3 NMR-scale Reactions

Synthesis of 4•B

In a glovebox, **H_3BL** (L = 2-methylpyridine) (6 mg, 0.057 mmol) in benzene-d_6 (300 μL) was transferred to an NMR tube fitted with Young's adapter. adapter containing **4•benzene-d_6** (generated *in-situ*) (22 mg, 0.057 mmol) in benzene-d_6 (300 μL). The reaction was followed by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy. After 30 minutes, formation of the σ-complex **4•B** was observed *in-situ*. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.94 (s, 3H, Ar–Me_B), 2.00 (s, 3H, Me_{Cu}), 2.14 (s, 6H, Ar–Me_{Cu}), 2.96 (br m, 3H, B–(H)$_3$–Cu), 6.04 (d, 1H, $^{3}J_{H–H}$ = 7.7 Hz, Ar–H_B), 6.13 (t, 1H, $^{3}J_{H-H}$ = 6.6 Hz, $_B$Ar–H), 6.21 (s, 1H, CH_{Cu}), 6.54 (s, 4H, Ar–H_{Cu}), 6.56 (m, 1H, Ar–H_B), 7.85 (d, 1H, $^{3}J_{H–H}$ = 5.8 Hz Ar–H_B); ^{11}B NMR (C_6D_6, 298 K, 160.4 MHz) δ -20.2 (br); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -74.6 (s, 3F), -65.8 (s, 3F).

Synthesis of 4•Zn

In a glovebox, **4•benzene-d_6** (8 mg, 0.021 mmol) in benzene-d_6 (300 μL) was added to an NMR tube fitted with Young's adapter containing **L⁷Zn–H** (10 mg, 0.021 mmol) in benzene-d_6 (300

μL). The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy. The σ-complex **4•Zn** was observed *in-situ*. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ -1.19 (s, 1H, Cu–*H*–Zn), 1.09 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz), 1.15 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz), 1.60 (s, 6H), 1.60 (s, 3H), 2.09 (s, 3H), 3.03 (sept, 4H, $^{3}J_{H–H}$ = 6.3 Hz), 4.97 (s, 1H), 6.08 (s, 1H), 6.55 (s, 2H), 7.01 – 7.14 (m, 4H); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -73.9 (s, 3F), -66.6 (s, 3F).

Synthesis of 3•Mg and 5•Mg

In a glovebox, either **3_2•tol** (10 mg, 0.01 mmol) or **5•tol** (10 mg, 0.02 mmol, 2 eq.) was weighed in a scintillation vial and dissolved in benzene-d_6 (300 μL). Similarly, **{L^{7}Mg–H}$_2$** (9 mg, 0.01 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (300 μL). The solution containing the copper complex was added to the solution containing the main group hydride and transferred to an NMR tube fitted with Young's adapter. In both cases, the solutions changed colour and then quickly decomposed as evidenced by the formation of a Cu(0) mirror on the sides of the reaction vessel. The σ–H could be observed in all cases (**3•Mg**, δ = -0.97 ppm, **5•Mg**, δ = -0.16 ppm) along with the formation of the 4 coordinate decomposition products **L^{n}MgL^7** (n = 3, 5) and H_2.

Synthesis of 1•Ca and 2•Ca

In a glovebox, either **1_2•tol** (23 mg, 0.21 mmol) or **2•tol** (24 mg, 0.42 mmol) was weighed into a scintillation vial and dissolved in benzene-d_6 (300 μL). Similarly, **{L^{7}Ca–H(THF)}$_2$** (11.7 mg, 0.021 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (300 μL). The solution containing the copper complex was added to the solution containing the main group hydride and transferred to an NMR tube fitted with Young's adapter. The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy. **1•Ca**; ^{1}H NMR (C_7D_8, 298 K, 400 MHz) δ -0.36 (s, 1H, Cu–*H*–Ca), 1.13 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, CH*Me*$_2$), 1.18 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz, CH*Me*$_2$), 1.55 (s, 6H, *Me*$_{Ca}$), 2.09 (s, 6H, Ar–*Me*$_{Cu}$), 2.23 (s, 12H, Ar–*Me*$_{Cu}$), 2.85 (m, 8H, $_{Ca}$C*H*Me$_2$ & THF), 4.48 (s, 1H, C*H*$_{Ca}$), 6.17 (s, 1H, C*H*$_{Cu}$), 6.63 (s, 4H, Ar*H*$_{Cu}$), 6.95 – 7.13 (m, 6H, Ar*H*$_{Ca}$); ^{19}F NMR (C_7D_8, 193 K, 376.5 MHz) δ -64.5 (s). In the case of reaction with **2•tol**, after 30 minutes at room temperature the σ-complex **2•Ca** was not the major product solution however a σ-proton could be observed at δ = -0.79 ppm.

Synthesis of 3•Ca and 5•Ca

In a glovebox, either **3_2•tol** (10 mg, 0.01 mmol) or **5•tol** (10 mg, 0.02 mmol, 2 eq.) was weighed into a scintillation vial and dissolved in benzene-d_6 (300 μL). Similarly, **{L^{7}Ca–H(THF)}$_2$** (6 mg,

0.01 mmol) was weighed in a scintillation vial and dissolved in benzene-d_6 (300 μL). The solution containing the copper complex was added to the solution containing the main group hydride and transferred to an NMR tube fitted with Young's adapter. In both cases, the solutions changed colour and then quickly decomposed as evidenced by the formation of a Cu(0) mirror on the sides of the reaction vessel. The σ–H could be observed in all cases (**3•Ca**; δ = -0.97 ppm, **5•Ca**; δ = -0.76 ppm) along with the formation of the 4 coordinate decomposition products $\mathbf{L^nCaL^7}$ (n = 3, 5) and H_2.

Crossover Reaction

In a glovebox, **1•Zn** (22 mg, 0.022 mmol, 1 eq.) was dissolved in benzene-d_6 (600 μL) in an NMR tube fitted with a Young's adapter. $\mathbf{L^7Mg–H}$ (10 mg, 0.022 mmol, 1 eq.) was added and the reaction was followed by ^{1}H and ^{19}F NMR spectroscopy. The formation of **1•Mg** and $\mathbf{L^7Zn–H}$ was observed.

Reactions with CO

In a glovebox, either **1•Zn** (22 mg, 0.22 mmol) or **2•B** (13 mg, 0.22 mmol) was dissolved in benzene-d_6 (600 μL) and added to NMR tubes fitted with a Young's adapter. The tubes were freeze-pump-thaw degassed three times on a schlenk line before being exposed to an atmosphere of CO. The reactions were kept at room temperature for 24 h and followed by ^{1}H and ^{19}F NMR spectroscopy. The formation of **1•CO** or **2•CO** and $\mathbf{L^7Zn–H}$ or $\mathbf{H_3BL}$ (L = 2-methylpyridine) was observed.

Half-life measurements

In a glovebox, a σ-complex (x mg, 0.022 mmol) was dissolved in benzene-d_6 or toluene-d_8 (600 μL) and transferred to an NMR tube fitted with a Young's adapter and the sample kept at 25 °C in between spectroscopic measurements. Ferrocene was added as an internal standard and the decomposition of the σ-complex was monitored by integration of the backbone methyne proton on the copper fragment observed by ^{1}H NMR spectroscopy relative to that of ferrocene.

VT NMR Experiments

In a glovebox, **n•Zn** (n = 1, 2) (x mg, 0.022 mmol) was dissolved in toluene-d_8 (600 μL) and transferred to independent NMR tubes fitted with a Young's adapter. The tubes were transferred to the NMR suite in a dewer of liquid nitrogen and inserted into the NMR machine at low

temperature whereby ^{1}H and ^{19}F NMR spectra were recorded at a range of temperatures (193 K - 353 K).

Multinuclear NMR spectra for preparative scale (section 2.2) and NMR scale (section 3.2) reactions along with X-ray acquisition parameters (section 4.2) and Z-matrices for DFT-optimised structures (section 5.2) can be found in the appendix.

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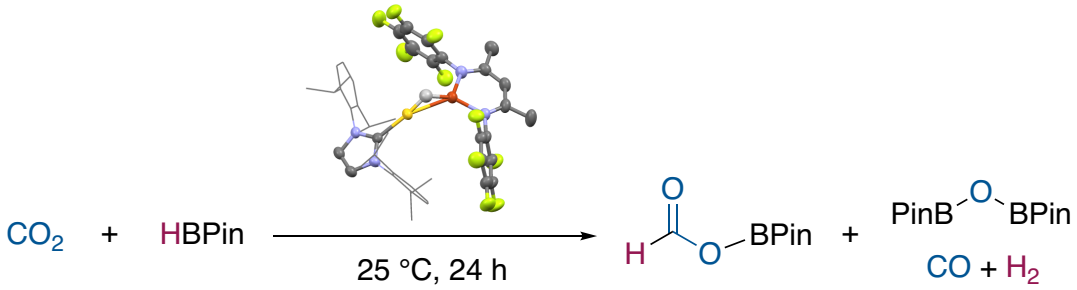
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fall down seven times stand up eight

Chapter 4

σ-Complexes of the Coinage Metals and the Selective Reduction of CO_2 to a Formate Equivalent

The first examples of heterobimetallic complexes of the coinage metals containing 3-centre,2-electron Cu–H–Au interactions are reported. These species are prepared by the addition of a monomeric gold(I) hydride to a bent d^{10} $\{CuL_2\}$ fragment and are selective catalysts for reduction of CO_2 with HBPin (HBPin = pinacolborane) to a formate equivalent.



Sections of this chapter have been published – *Angew. Chem. Int. Ed.*, **2017**, 56, 15127-15130

1. Introduction

1.1 Monomeric Coinage Metal Hydrides

In recent years, there has been increasing interest in the synthesis and catalytic applications of coinage metal hydrides (M = Cu, Ag, Au).[1-9] The electronic configuration of monomeric coinage metal hydrides has been described as representing the middle ground between transition metal and main group hydrides.[6] Their occupied yet energetically accessible d-subshells allow for interesting and unique reactivity. Despite monomeric copper hydrides being postulated as intermediates in catalytic reactions, the isolation of a monomeric copper(I) hydride in the solid state still remains elusive. Phosphines, N-heterocyclic carbenes (NHCs), cyclic (alkyl)(amino)carbenes (CAACs) and ring-expanded NHCs have been used as ligands in attempts to stabilise a monomeric copper(I) hydride.

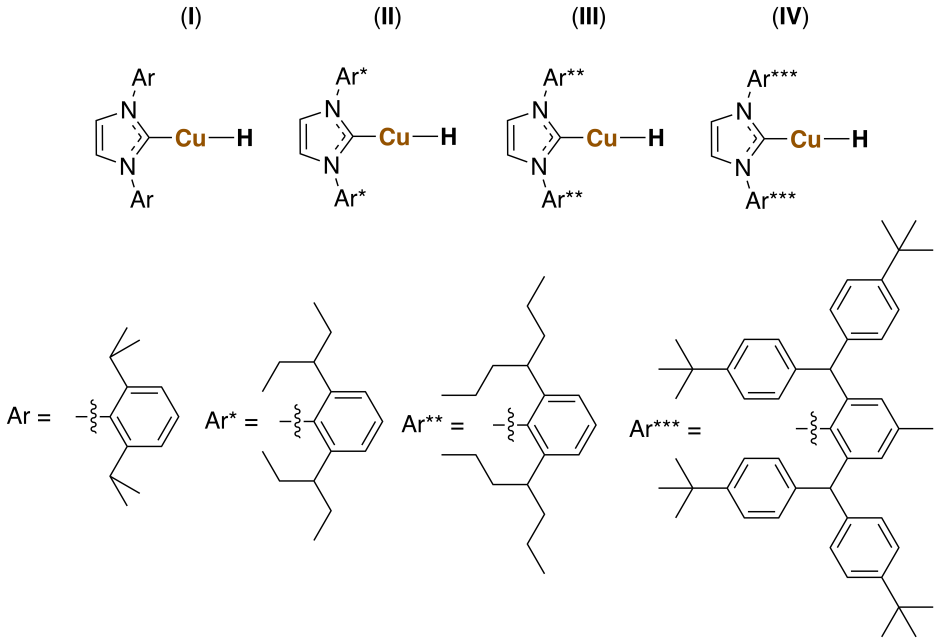


Figure 1 - Monomeric copper hydrides observed by Schmidt and co-workers and Bertrand and co-workers

In reports by Schmidt and co-workers, an increase in stability of a series of copper hydrides was observed with increasingly bulky NHC ligands. Whereas **I** decomposes with a half-life of 72 minutes at 30 °C in THF-d_8, the 3-pentyl analogue **II** exhibits a half-life of 98 minutes at 50 °C and the 4-heptyl analogue **III** 80 minutes at 45 °C (see Figure 1). Despite this increased stability, in solution the monomer-dimer equilibrium still lies far over to the side of the dimer.[10] Spectroscopic evidence for the formation of a monomeric copper(I) hydride with the extremely

bulky NHC ligand Ar*** (Ar*** = (1,3-bis[2,6-bis[di(4-tert-butylphenyl)methyl]-4-methylphenyl] imidazol-2-ylidene) has also been reported by Bertrand and co-workers, however, this is also found in equilibrium with its dimeric form in solution and the dimeric form was crystalised.[4]

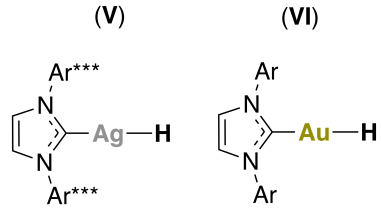
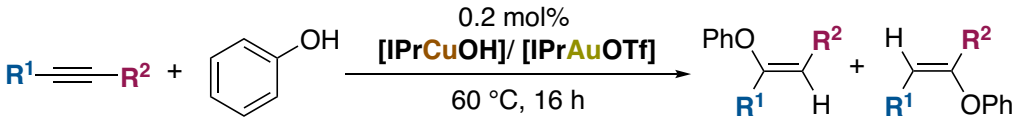


Figure 2 - Examples of monomeric coinage hydrides

With regards to the heavier coinage metals, the first monomeric silver hydride **V** was prepared using the bulky NHC ligand Ar*** as outlined by Bertrand and co-workers *vide supra*, whereby single crystals were isolated after leaving the reaction mixture at -40 °C overnight.[11] A monomeric gold hydride **VI** was successfully prepared and isolated by Tsui with the less bulky NHC ligand Ar.[12]

1.2 Coinage Metal Hydrides in Catalysis

The majority of catalytic studies have focused on the *in situ* generation of terminal metal hydride complexes stabilized by NHC ligands.[10,13] There is, however, a growing appreciation that species possessing 3-centre,2-electron M–H–M bonds may play a role in catalysis. In addition, combinations of copper and gold NHC complexes catalyse the addition of phenols to internal alkynes with activities in excess of the individual components of the mixture (scheme 1).[14]

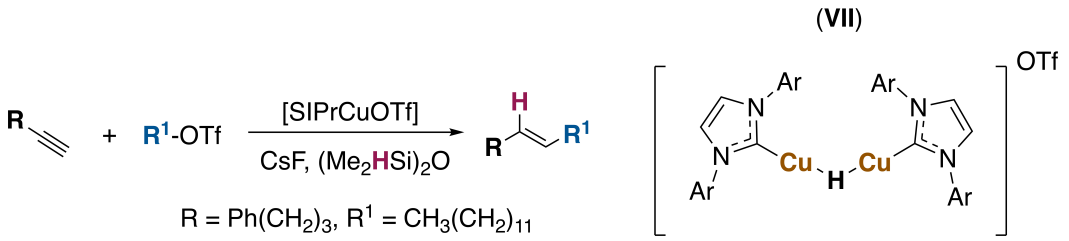


Scheme 1 - Example of heterobimetallic catalysis by mixtures of the coinage metals

In this instance, a mechanism operating *via* a dual activation process involving both metals is postulated based on independent stoichiometric reactions and previously reported catalysis involving two gold metal centres.

Lalic and co-workers have shown that cationic dinuclear copper(I) hydride complexes such as **VII** are key catalytic intermediates in the hydroalkoxylation of alkynes (Scheme 2).[2,15] The

original structural characterisation of dicopper hydride complexes supported by the expanded ring NHC, 6Dipp, **VIII**, along with related silver analogues, **IX**, has been established by Sadighi and co-workers.[16,17]



Scheme 2 - A general reaction scheme for the hydroxylation of alkynes and the dinuclear copper(I) hydride active species, see Figure 1 for description of Ar

The structural features and reactivity of these complexes have been investigated. In the case of the copper analogue **VIII**, the bridging hydride is said to be very reactive with rapid insertion of CO_2 observed to give the corresponding formate complex.[17] Reaction of the silver analogue **IX** with CO_2 also generated a bridging formate species, however, in this case the reaction was reported to be incomplete with only 5% conversion after 4 days.[16]

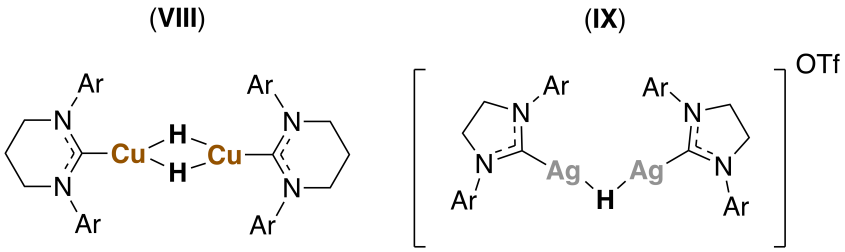


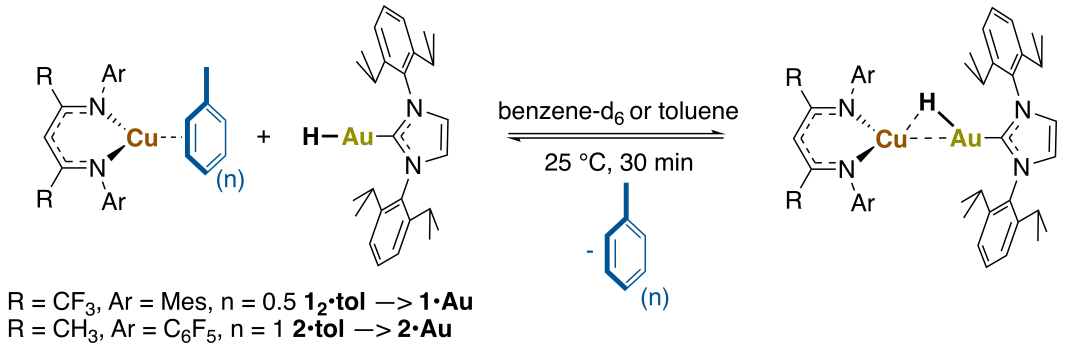
Figure 3 - Dihydride complexes of the coinage metals reported by Sadighi and co-workers

Despite detailed studies on the preparation and reactivity of *symmetric* dinuclear coinage metal hydrides, little is known about heterobimetallic compounds metals containing *asymmetric* M–H–M' interactions. This chapter aims to investigate the synthesis and bonding motif of asymmetric M–H–M' interactions of the coinage metals and probe the ability of these complexes to catalyse the hydroboration of CO_2 with HBPin (HBPin = pinacolborane).

2. Synthesis and Characterisation

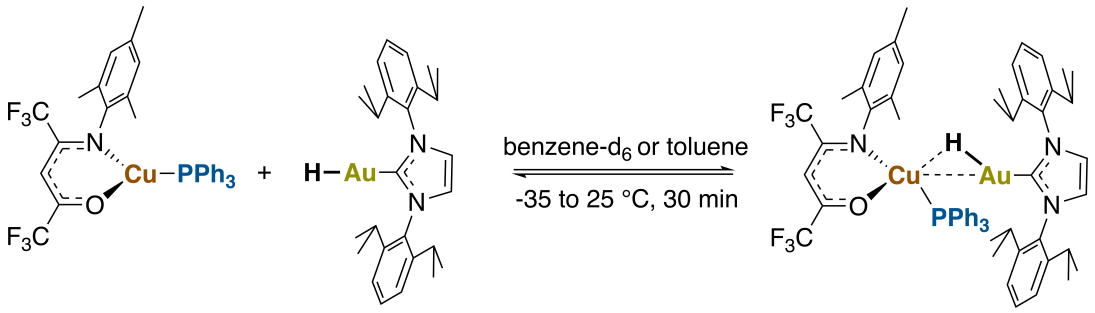
2.1 Synthesis of Heterobimetallics of Cu–H–Au

Initial reactions of the fluorinated copper(I) *BDI* complexes **1_2-2•tol** and **4•PPh_3** with the monomeric gold hydride complex **IPrAu–H** (Figure 2 - **VI**) were performed in benzene-d_6 at 25 °C to generate the corresponding heterobimetallics **1-2•Au** and **4•Au**. In all cases after 30 minutes, coordination of **IPrAu–H** to the copper(I) complex was confirmed by a loss of signal in the ^{1}H NMR spectra at δ = 5.11 ppm corresponding to the terminal gold hydride.



Scheme 3 - Synthesis of the Cu–H–Au heterobimetallics, 1-2•Au

For the asymmetric complex **4•Au**, PPh_3 remained ligated to the copper(I) centre as evidenced by a broad signal in the $^{31}P\{^1H\}$ NMR spectra at δ = -3.3 ppm. These initial NMR experiments revealed that complexes **1-2•Au** were stable in benzene-d_6 solution for days at room temperature. In contrast, complex **4•Au** was relatively unstable, with a copper mirror observed on the wall of the NMR tube within 10 hours.



Scheme 4 - Synthesis of 4•Au

Preparative scale reactions performed in a glovebox afforded complexes **1•Au** and **2•Au** in 89% and 92% yield respectively. Similarly, **4•Au** was prepared from a sample of **4•PPh$_3$** in toluene that had been placed in the glovebox freezer and allowed to cool to -35 °C before addition of the gold hydride in order to slow down the decomposition of the σ-complex, which was subsequently isolated in 32% yield.

2.2 Characterisation of Heterobimetallics of Cu–H–Au

X-Ray Characterisation

Single crystals of **1-2•Au** and **4•Au** were grown from 1:3 mixtures of benzene-d$_6$/*n*-heptane at -35 °C and, in the case of **1-2•Au**, afforded data of a quality that allowed the position of the hydrides to be determined from the difference electron density map.

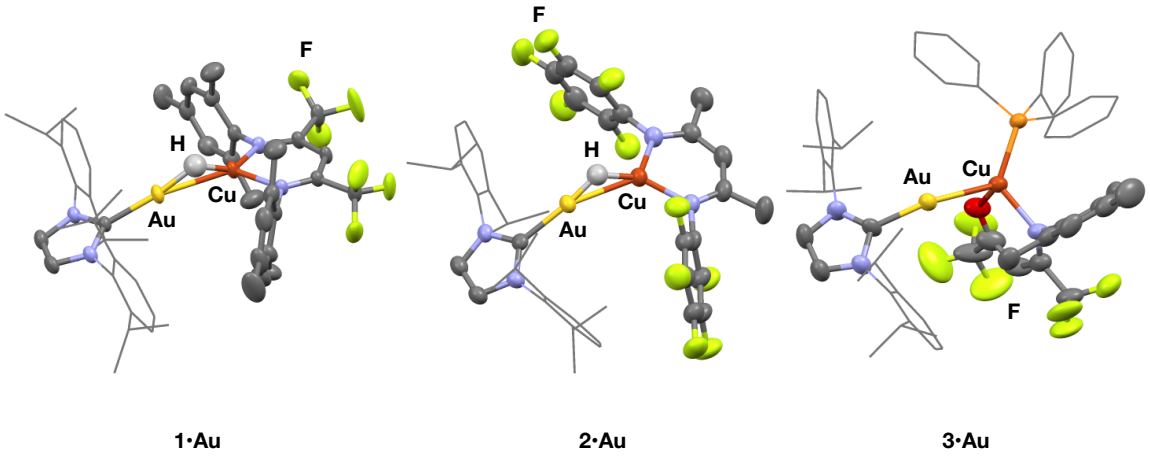


Figure 4 - X-ray crystal structures of 1-2•Au and 4•Au

Complex **1•Au** was found to crystallise with two independent complexes in the unit cell and despite the hydrides being located from a difference Fourier map, the hydride positions are uncertain due to the high residual electron density around the gold centre. Data for the crystal structure of **2•Au** was gathered twice and again despite the hydride position being located each time, the hydride position was distinctly different in each case. In the case of complex **4•Au**, the **IPrAu–H** fragment was found to be disordered over two sites with 64% and 36% occupancy.

A notable difference in the structures of **1-2•Au** and **4•Au** lies within the Cu---Au separation. The distance between the two metal centres varies across the series taking values of 2.5910(6) Å, 2.6376(5) Å, and 2.7525(7) Å for **2•Au** < **1•Au** < **4•Au** respectively, however, these values are still significantly longer than the single bond radii as outlined by Pauling (2.512 Å)[17] and Pyykkö

(2.36 Å).[18] The Au–C distances observed in **1•Au** and **2•Au** are within experimental error of one another (2.026(3) – 2.025(4) Å) and are marginally shorter than that reported for **IPrAu–H** (2.045(3) Å).[3] This can be explained by a diminished *trans*-influence of the hydride ligand in **1-2•Au** compared to the monomeric complex due to its involvement in a 3-centre,2-electron bond.

Table 1 - Selected geometric parameters for 1-2•Au and 4•Au

	1•Au	**2•Au**	**4•Au**
		Bond Lengths (Å)	
Cu---Au	2.6376(5)	2.5910(6)	2.7525(7)
Au–C	2.026(3)	2.025(4)	2.043(8)
Cu–X	1.944(3)	1.943(3)	2.068(4)[a]
	1.979(3)	1.969(3)	2.060(4)[b]
		Bond Angles (°)	
Au–C–Cu	161.86(10)	153.00(11)	153.4(4)

In **4•Au**, significant lengthening of the Cu–P bond is observed with respect to the parent copper complex **4•PPh$_3$** due to the increased coordination number at copper (**4•Au**, 2.2401(11) Å; **4•PPh$_3$**, 2.1639(10) Å). This increased competition for election density causes decreased back-donation from the copper centre to the σ*-P–C orbitals on the phosphine ligand, and thus a lengthening of the Cu–P bond. This effect is, however, too subtle to be observed in the C–P bond distances of the phosphine ligand on complexes **4•Au** and **4•PPh$_3$**, which fall within error of one another.

NMR Characterisation

Dissolving a sample of **1-2•Au** in toluene-d$_8$ at 298 K, the equilibrium outlined in Scheme 3 is re-established and the components are in fast exchange. A single set of resonances are observed in the $^{19}F\{^1H\}$ and ^1H NMR spectra due to a time averaged contribution of both sides of the equilibrium. In the case of **2•Au**, the bridging hydride was observed at room temperature at δ = 0.70 ppm. This value is in good agreement with a characteristic coinage metal hydride reported for the symmetric expanded NHC dicopper hydride complex **VIII** by Sadighi and co-workers (δ = 0.77 ppm, benzene-d$_6$, 298 K).[17] The bridging hydride of **4•Au**, was observed at δ = 4.33 ppm, indicating a smaller upfield shift from the parent hydride complex compared to that of **2•Au**. $^{13}C\{^1H\}$ data for **2•Au** revealed that the peak corresponding to the quaternary

NHC carbon lies at δ = 195.6 ppm, compared to δ = 204.9 ppm in the parent gold hydride complex **IPrAu–H**. Despite solution NMR data for **4•Au** being obtained at 193 K, its decomposition in solution hindered the ability to collect clean $^{13}C\{^{1}H\}$ data. Variable temperature (VT) NMR of **1-2•Au** across a temperature range of 193 K – 303 K resulted in observation of both sides of the equilibrium at low temperature (**1•Au** = 213 K, **2•Au** = 253 K). At 193 K, the σ-Au–H of **1•Au** and **2•Au** was observed at δ = 0.32 ppm and δ = 0.73 ppm respectively.

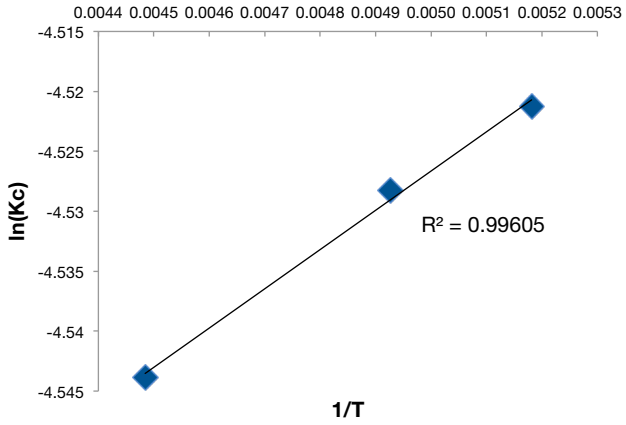


Figure 5 - van't Hoff Plot of 2•Au between 193 and 223 K

In the case of **2•Au**, VT NMR spectra allowed van't Hoff analysis to give the thermodynamic parameters: $\Delta H° = -0.1$ kcal mol^{-1}, $\Delta S° = -9.3$ cal K^{-1} mol^{-1}, $\Delta G°_{298K} = +2.7$ kcal mol^{-1}. Whilst the author appreciates the lack of data points gathered for this analysis, these values are consistent with weak and reversible binding previously reported for σ-complexes of copper(I) as outlined in chapter 3.[19-21]

DFT Calculations

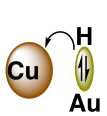
In order to gain a deeper understanding into the nature of the bonding in the 3-centre,2-electron Cu–H–Au core, DFT calculations were performed with the ωB97x functional and a hybrid basis set (6-311G* (C, H, N, F, O)/ SDDAll (Cu, Au)). NBO analysis confirms a common electronic structure in the 3-centered core of complexes **1-2•Au and 4•Au**. Wiberg bond indices indicate that the strongest covalent interaction occurs between the gold and hydride atoms with weaker interactions between Cu and H and Cu and Au. In all cases, second-order perturbation analysis reveals that donation of σ-Au–H → Cu (4s) is far more significant than back-donation from Cu (3d) → σ*-Au–H. In order to gain further insight into the extent of the back-donation in

these complexes, comparison between the complexes **1-2•Au** and **4•Au** and theoretical complexes **1-2•C_2H_4** and **4•C_2H_4** was performed. As expected, these calculations confirm that the back-bonding in **1-2•Au** and **4•Au** is negligible with the back-donation in the ethylene complexes being an order of magnitude greater than that observed in **1-2•Au** and **4•Au**.

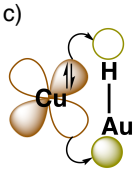
a)

	σ(M–H) donation	σ*(M–H) back-donation
	kcal mol^{-1}	
1•Au	82 (77)	8 (58)
2•Au	84 (88)	8 (63)
4•Au	54 (87)	3 (60)

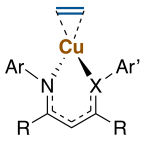
b)



c)



d)



R = CF_3, Ar = Ar' = Mes, X = N, **1·C_2H_4**
R = CH_3, Ar = Ar' = C_6F_5, X = N, **2·C_2H_4**
R = CF_3, Ar = Mes, X = O, **4·C_2H_4**

Figure 6 - a) Quantification of the donation and back-donation for complexes 1-2•Au and 4•Au, value in parentheses represents the value calculated for the corresponding theoretical ethylene complexes 1-2•C_2H_4 and 4•C_2H_4, b) donation from the σ-Au–H bond to the 4s orbital on copper, c) back-donation from the filled 3d orbital on copper into the σ*-Au–H bond, d) theoretical complexes 1-2•C_2H_4 and 4•C_2H_4

QTAIM calculations describe the same bonding picture with bond critical paths present between both the Au and H and Cu and H atoms but not the metals themselves. A Bader analysis of these bond critical paths within **2•Au** gives values of ρ_{bco} (e bohr^{-3}) and $\nabla^2\rho_{bco}$ (e bohr^{-5}) (Au–H; ρ_{bco} = 0.11, $\nabla^2\rho_{bco}$ = 0.13 Cu–H; ρ_{bco} = 0.08, $\nabla^2\rho_{bco}$ = 0.25). In the case of the Cu–H bond critical path, the interaction is significantly weaker than for Au–H as outlined by a smaller value of ρ_{bco}.

a)

	Au–H	Cu---H	Cu---Au
1•Au	0.38	0.28	0.15
2•Au	0.40	0.29	0.15
4•Au	0.52	0.15	0.10

b)

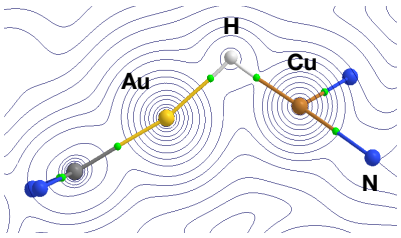


Figure 7 - a) Wiberg bond indices of 1-2•Au and 4•Au, b) QTAIM image for the 3-centre,2-electron core of 1•Au

Estimating $\Delta G°_{298K}$ for the Formation of 2•Au

In the case of σ-complexes of copper(I) with main group hydrides, the DFT estimation of $\Delta G°_{rxn}$ is not in good agreement with experimental data (see chapter 3 section 3.1). The calculated value for complex **2•Au** for the reaction outlined in Scheme 3 is also poorly estimated (DFT = -20.6 kcal mol^{-1}, exp. = +2.7 kcal mol^{-1}). Investigations into the effect of the ωB97x

functional on the overestimation of the favourability of the formation of **2•Au** were carried out. In a new model, the isopropyl groups were removed from the **IPrAu–H** fragment, and $\Delta G°_{rxn}$ re-calculated to give a value slightly closer to that gathered experimentally (-15.8 kcal mol^{-1}). The issues surrounding the estimation of $\Delta G°_{rxn}$ with the ωB97x functional could therefore arise from an overestimation of the stabilisation caused by the large, bulky ligands. Despite the reason for this significant overestimation still not being clear, it is consistent with the data presented in chapter 3.

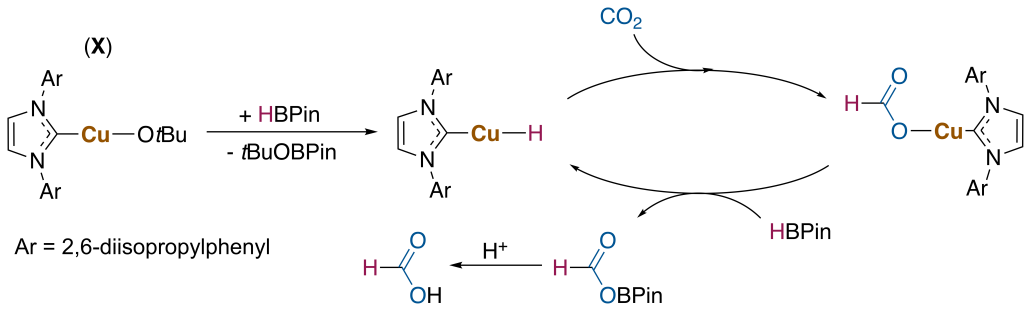
2.3 Summary

The presented data confirm the formation of complexes **1-2•Au** as weak and reversible σ-complexes of copper(I), whereby the equilibrium enters the slow exchange regime at low temperatures. In combination, the solid state and computational data show that the 3-centre,2-electron interaction is dominated by metal–hydride bonding and not metal–metal bonding. The conclusions are consistent with the analysis of cationic dinuclear coinage metal hydride complexes but with the key difference that the Cu–H–Au moiety possess an asymmetric distribution of electron density.[16,22]

3. Catalytic Investigations

3.1 Hydroboration of CO_2 with HBPin

The ever-rising levels of carbon dioxide in the earth's atmosphere, along with its low cost, have led to an interest in the use of carbon dioxide as a C_1 carbon source for many chemical transformations.[23]



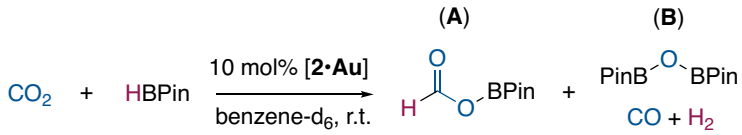
Scheme 5 - Proposed catalytic cycle for the copper-catalysed hydroboration of CO_2

The reduction of CO_2 using a borane source such as HBPin has been studied as an example of such transformation from CO_2 to many different C_1 compounds such as CO, formaldehyde, methane, formic acid and methanol-equivalents.[24] Monomeric transition metal and coinage metal complexes and main group heterobimetallic complexes have been employed as catalysts for this transformation.[25-28] Shintani and co-workers have reported that copper-NHC complexes have been reported for the selective hydroboration of CO_2 with TON<10.[26] In this instance, the copper complex **X** was employed as a catalyst for the reaction of HBPin with CO_2, and protonolysis of the resulting reaction mixture with HCl gave formic acid as the final product.

More recently, a heterobimetallic complex consisting of a nickel hydride moiety and Lewis-acidic gallium has been utilised by Lu and co-workers for the hydrogenation of CO_2 to formic acid. This stabilization of Ni–H through the σ-accepting gallium centre allowed for facile transfer of a hydride from Ni–H to CO_2 and reduced the tendency of re-insertion of formate in the subsequent step, promoting catalytic turnover. [25,29,30]

3.2 Initial Catalytic Investigations

Initial investigations were performed with 10 mol% of complex **2•Au** in benzene-d_6 at room temperature for the hydroboration of HBPin with CO_2 (1 atm.) as outlined in Scheme 6. An NMR tube with Young's adapter was charged with a solution of **2•Au** in benzene-d_6 in a glovebox, whereby HBPin and an internal standard was added. The NMR tube containing the reaction mixture was removed from the glovebox and freeze-pump-thaw degassed three times, before being exposed to an atmosphere of CO_2.



Scheme 6 - General reaction scheme for the hydroboration of CO_2 with HBPin

Initial reactions showed that performing catalysis with 10 mol% of **2•Au** produced predominantly the formoxyborane product (**A**), HCO_2Bpin, through insertion of CO_2 into the B–H bond, driven by formation of a strong B–O bond (Scheme 6).[23] Reactions with a catalytic amount of **IPrAu–H** and **2•tol** were also performed using the same method, whereby significantly lower conversions of HBPin were observed in both cases. Due to the relatively poor yields and TON's observed when performing this reaction with **2•Au** compared to that reported

in the literature, efforts to optimise the catalytic conditions were undertaken. Reactions were attempted in THF-d_8 and at slightly elevated temperatures, with the results outlined in Table 2.

Table 2 - Catalytic results from the hydroboration of CO_2 with HBPin with complexes IPrAu–H, 2•tol and 2•Au at 25 °C and 40 °C in benzene-d_6 and 25 °C in THF-d_8

Catalyst	Temp (°C)	Solvent	time (h)	conversion[a]	TON[b]		Selectivity[c]
					A	**B**	
IPrAu–H	25	benzene-d_6	24	13%	0.1	0.4	23%
	40	benzene-d_6	23	5%	0.3	0.5	38%
	25	THF-d_8	24	10%	0.1	1.1	7%
2•tol	25	benzene-d_6	24	38%	0.1	1.1	6%
	40	benzene-d_6	23	56%	0.3	1.6	15%
	25	THF-d_8	24	34%	0	1.1	0%
2•Au	25	benzene-d_6	24	64%	4.1	0.8	85%
	40	benzene-d_6	23	88%	4.1	0.7	85%
	25	THF-d_8	24	76%	0.2	1.1	16%
No Catalyst	25	benzene-d_6	22	< 1%	0	0.5	0%

a) based on HBPin, b) TON = mmol product / mmol catalyst, c) selectivity = mmol HCO_2BPin / mmol all products. $CH_2(SiMe_3)_2$ was employed as an internal standard.

In general, higher conversions were observed when the reactions were performed at 40 °C in benzene-d_6, compared to 25 °C. In the case of **2•Au**, despite higher conversions being observed at elevated temperatures (25 °C = 64%, 40 °C = 88%), selectivity for formoxyborane remained the same (85%). When catalysis with **2•Au** was performed in THF-d_8, selectivity for formoxyborane was significantly reduced (benzene-d_6 = 85%, THF-d_8 = 16%). This is most probably due to the presence of small amounts of water in the THF-d_8, which caused a general increase in the formation of (**B**). A control reaction was also performed in order to determine the background reactivity of benzene-d_6 in the absence of catalyst. Due to small amounts of water present, reduction of HBPin to the ester product (**B**) is observed. The decision to proceed with reactions in benzene-d_6 at 25 °C was undertaken due to the relatively lower cost of the solvent compared to THF-d_8 and increased energy efficiency associated with performing the reactions at ambient temperature.[31]

3.3 Heterobimetallic Effect in Catalysis

The absolute activity and selectivity of the heterobimetallic catalysts **1-2•Au** are greatly inferior to a number of transition metal systems.[26,32-35] Significantly, the monomeric complexes **1-2•tol** and **IPrAu–H** show negligible activity for CO_2 reduction and neither complex produces significant amounts of HCO_2Bpin (**A**) in the absence of its coinage metal counterpart. On comparison of the data in Table 3, it seems clear that both metal fragments are required for the selective conversion of CO_2 and HBPin to HCO_2Bpin.[25,36-38]

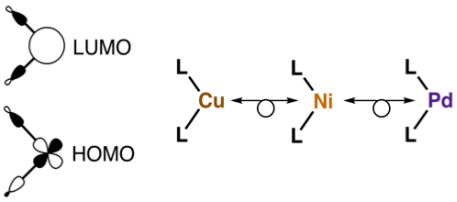
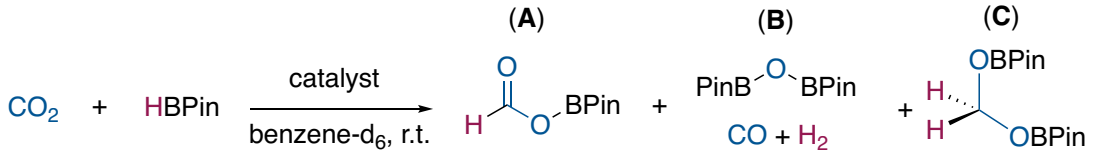


Figure 8 - Representation of the frontier molecular orbitals of $\{ML_2\}$ d^{10} fragments (M = Cu, Ni, Pd)

Additional reactions were run to explore the generality of the heterobimetallic effect. The frontier molecular orbitals of **1-2** are isolobal with bent $\{ML_2\}$ d^{10} fragments (M = Ni, Pd) as outlined in Figure 8. Both **$[\{Ni(PCy_3)_2\}_2(\mu\text{-}N_2)]$** and **$[Pd(PCy_3)_2]$** were investigated in catalysis, with and without the formation of mixtures containing **IPrAu–H**.[19,39]

Comparing the product distribution from the group 10 analogues revealed that the heterobimetallic effect was also observed for the Pd/Au ad-mixtures (Table 3). In the case of catalysis with Pd, the formation of a third boron-containing product (**C**) is observed through reaction of formoxyborane (**A**) with a second equivalent of HBPin. Ni/Au ad-mixtures, while catalytically competent, resulted in CO_2 reduction with a similar selectivity to the parent nickel complex (Table 4).

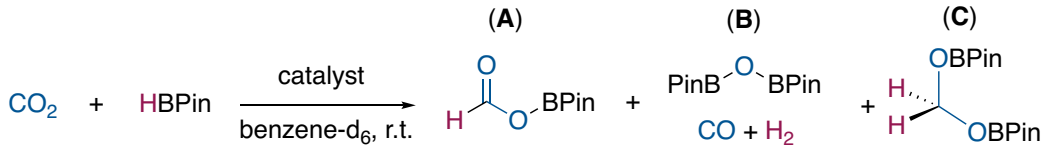
Table 3 - Full catalytic data for complexes IPrAuH, 1-2•tol, $Pd(PCy_3)_2$, 1-2•Au and mixtures of Au/Pd



Catalyst	mol%	time (h)	conversion[a]	TON[b] A	TON[b] B	TON[b] C	selectivity[c]
IPrAu–H	10	24	10	0.1	0.6	-	**21%**
			13	0.1	0.3	-	**29%**
1•tol	10	24	10	-	0.8	-	**5%**
			56	-	3.8	-	**0%**
2•tol	10	24	38	0.1	0.9	-	**8%**
			56	0.1	1.3	0.1	**6%**
$Pd(PCy_3)_2$	10	< 1	100	4.9	2.4	2.5	**51%**
			100	3.8	1.8	1.9	**50%**
	5	< 1	100	5.5	6.5	6.9	**29%**
			100	4.5	6.0	6.0	**27%**
1•Au	10	24	50	2.9	1.0	-	**75%**
			56	2.3	1.0	-	**70%**
2•Au	10	24	64	3.6	0.7	-	**84%**
			56	4.6	0.8	-	**85%**
Au / Pd[d]	10	< 1	100	8.6	1.6	0.1	**84%**
			100	7.9	2.0	0.3	**78%**
	5	< 1	100	14.2	1.7	0.5	**86%**
			100	10.6	2.8	0.8	**75%**

a) based on HBPin, b) TON = mmol product / mmol catalyst, c) selectivity = mmol HCO_2BPin / mmol all products, d) 1:1 mixture of IPrAu–H and $[Pd(PCy_3)_2]$

Table 4 - Full catalytic data for complexes $[Ni(PCy_3)_2N]_2$, mixtures of IPrAu–H/ $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)]$, $[(PCy_3)_2Ni{\bullet}CO_2]$ and mixtures of IPrAu–H/ $[(PCy_3)_2Ni{\bullet}CO_2]$



Catalyst	mol%	time (h)	conversion[a]	TON[b] A	TON[b] B	TON[b] C	selectivity[c]
$[Ni(PCy_3)_2]_2(\mu\text{-}N_2)]$	10[d]	24	63	2.0	1.4	1.0	**45%**
			45	0.3	3.5	-	**8%**
			85	4.9	1.7	0.1	**73%**
IPrAu–H/ $[Ni(PCy_3)_2]_2(\mu\text{-}N_2)]$	10[d]	24	74	2.3	1.9	1.0	**47%**
			64	3.3	2.7	0.2	**53%**
$[(PCy_3)_2Ni{\bullet}CO_2]$	10[d]	24	26	0.5	2.8	-	**16%**
			70	1.1	1.7	-	**39%**
IPrAu–H/ $[(PCy_3)_2Ni{\bullet}CO_2]$[e]	10[d]	24	59	2.1	2.3	-	**48%**
			48	4.1	2.6	0.2	**60%**

a) based on HBPin, b) TON = mmol product / mmol catalyst, c) selectivity = mmol HCO_2BPin / mmol all products, d) mmol Ni, e) 1:1 mixture of IPrAu–H and $[(PCy_3)_2\ M{\bullet}CO]$

3.4 Product identification

Boron Containing Products

In order to confirm the presence of the boron containing products, HCO_2Bpin and $(BPin)_2O$ were independently synthesised and *in-situ* NMR data was gathered. HCO_2BPin was synthesised *via* two methods, both catalytically through the reduction of CO_2 with HBPin using the previously reported **IPrCu•OtBu** and from the addition of formic acid to HBPin. In the case of $(BPinO)_2CH_2$ the multinuclear NMR values match those outlined in the literature.[27,40]

Fluorine containing products

One set of peaks is observed in the ^{19}F NMR spectra of catalytic reaction with **2•Au** after 24 hours. Monitoring catalysis with **2•Au** by ^{19}F NMR spectroscopy using a fluorinated internal standard revealed that 90% of the fluorine containing starting material converts to one product. A number of stoichiometric reactions were performed in order to ascertain the nature of this product, referred to as '**Y**' however, the addition of one equivalent of HBPin to **2•Au**, **2•tol** and **L^2K** and independent synthesis of **2•CO** did not identify **Y**.

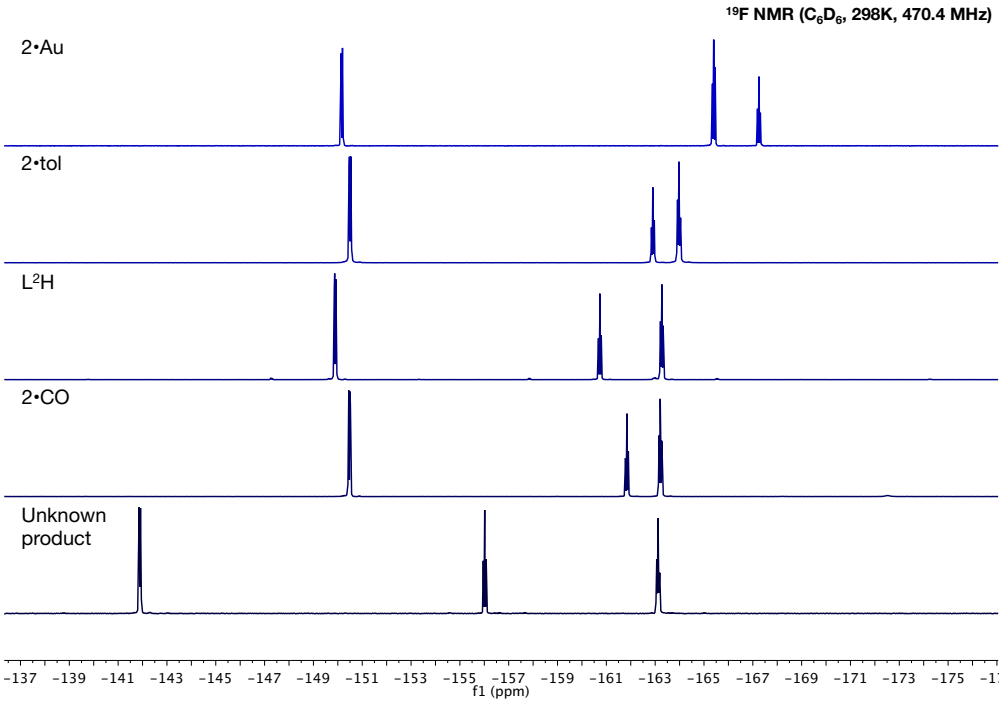
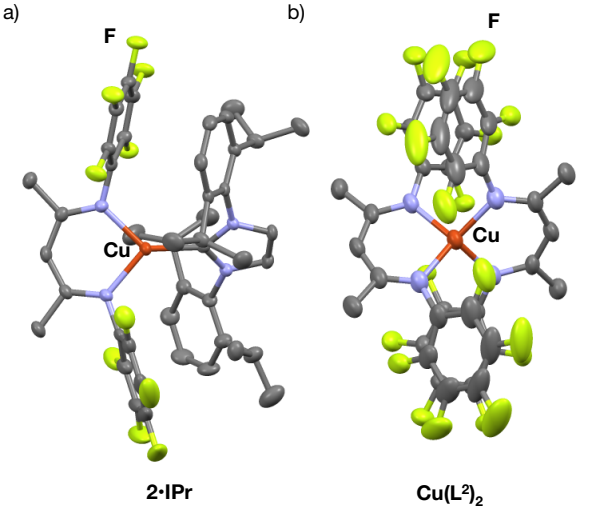


Figure 9 - ^{19}F NMR stack plot of potential candidates for product Y

Further attempts were made to try and independently synthesise potential candidates for the unknown product. These included the NHC-bound copper complex **2•IPr**, the oxo-complex **2•O$_2$** and 4 coordinate homoleptic *BDI* product **Cu(L^2)$_2$**. In the case of **2•IPr**, the complex was characterised *in-situ* and a crystal structure was obtained, however, the ^{19}F NMR spectra did not match that of **Y**. The oxo-complex **2•O$_2$** was also synthesised through bubbling O_2 through a solution of **2•tol**, the solution turned dark green indicating the formation of a copper(II) paramagnetic species, and this appeared silent by ^{19}F and ^{1}H NMR. Attempts to isolate the unknown product directly from a scale up of the catalysis with **2•Au** were not successful. Despite the product being visible following vacuum distillation and workup, direct crystallisation from the mixture yielded the 4 coordinate product **Cu(L^2)$_2$**, which appeared silent by NMR and thus is not **Y**.

Complex **2•IPr** crystallises with the plane created by the NHC ligand at 49° to the plane created by the *BDI* ligand. The Cu–C bond is shorter than that calculated for the Au–C bonds in complexes **1-2•Au** and **4•Au** and the Cu–C bond in the expanded NHC copper coordinated isonitrile complex prepared by Sadighi and co-workers (1.933(2) Å) (expanded NHC = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene).[17]

a) b) c)



	2•IPr	$Cu(L^2)_2$
	Bond Lengths (Å)	
Cu–N	1.9958(19)	1.967(4)
	2.001(2)	1.972(4)
Cu–C	1.910(2)	-
	Bond Angles (°)	
N–Cu–N	93.68(8)	96.88(17)

Figure 10 - a) X-ray structure of 2•IPr, b) X-ray structure of $Cu(L^2)_2$, c) selected bond lengths and angles for 2•IPr and $Cu(L^2)_2$

Complex **$Cu(L^2)_2$** crystallises with two independent molecules in the asymmetric unit, both with C_2 symmetry. In one molecule, the C_2 axis passes in-between the two ligands such that one complete ligand is unique. In the case of the other, the C_2 axis passes through both ligands such that two half ligands are unique. The Cu–N bond distances in **$Cu(L^2)_2$** are within experimental error of the arene complex **2•tol**, however, the N–Cu–N angle is slightly more acute (see chapter 2, section 2.2).

Carbon-containing products

Repeating catalytic runs with $^{13}CO_2$ provided evidence for the generation of ^{13}CO expected from the production of PinBOBPin.[27,40-42] In the case of catalysis with complex **2•Au**, the carbonyl complex **2•CO** was not observed. **$[(PCy_3)_2Ni•CO]$** was observed by $^{13}C\{^1H\}$ NMR spectroscopy following completion of the catalytic reaction with 10 mol% **$[Ni(PCy_3)_2]_2(\mu\text{-}N_2)$** (d = 203.1 ppm, t, $^2J_{C-P}$ = 3.3 Hz) and confirmed through independent synthesis of **$[(PCy_3)_2Ni•CO]$**.[43-45] The formation of H_2 was also confirmed by its observation in ^1H NMR spectroscopy (d = 4.8 ppm).

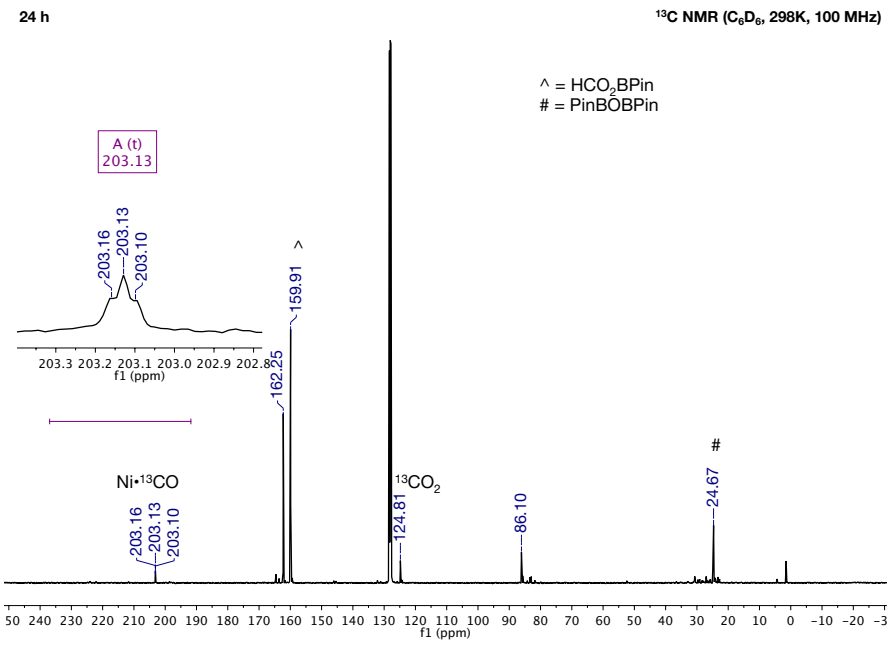
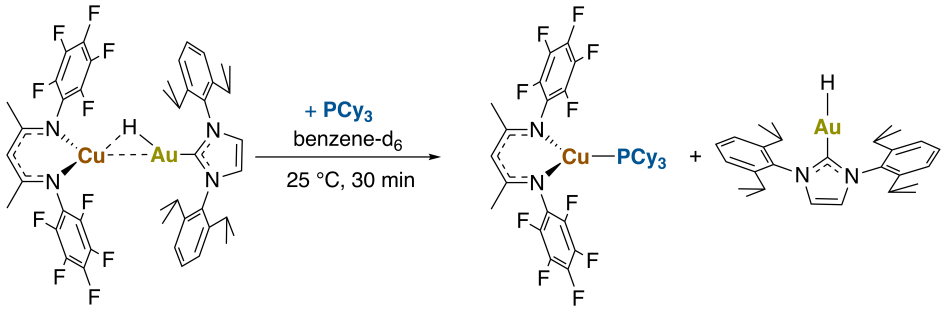


Figure 11 - ^{13}C NMR spectra of catalysis with Ni using $^{13}CO_2$ after 24h

3.5 Mechanistic Studies

Initial Steps

Interrogation of the solution dynamics of **1-2•Au** provides insight relevant to the plausible mechanisms of CO_2 reduction. On dissolution of the heterobimetallic complexes in benzene-d_6, an equilibrium is established between the heterobimetallic complex and the parent copper and gold fragments as outlined in Scheme 3. To further investigate the solution dynamics of **2•Au**, a phosphine trapping experiment was performed.



Scheme 7 - The addition of 1 equivalent of PCy_3 to 2•Au to generate 2•PCy_3 and IPrAu–H

Reaction of one equivalent of **2•Au** with **PCy_3** resulted in the formation of **2•PCy_3** and the parent gold hydride complex **IPrAu–H**. Thus, equilibrium inhibition is a possible first step in the catalytic cycle.

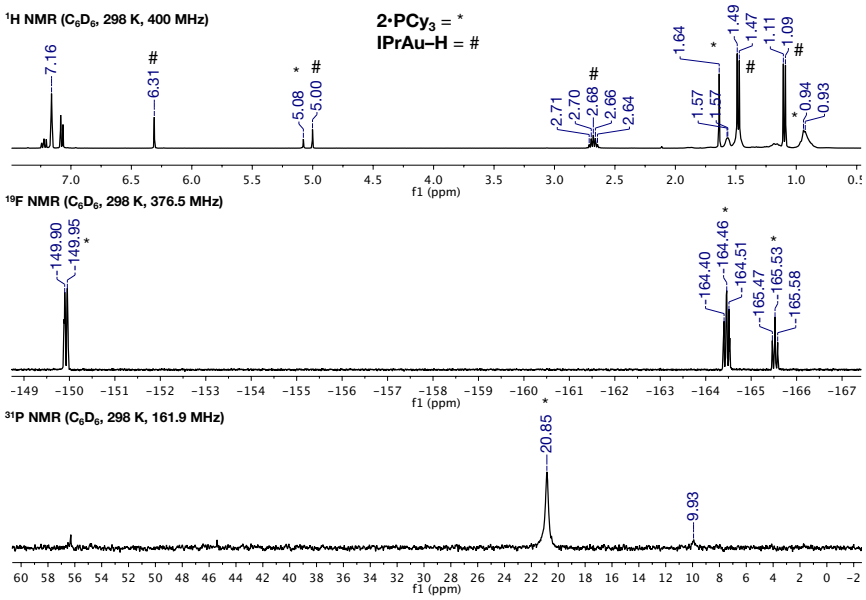


Figure 12 - ^{1}H, ^{19}F and ^{31}P NMR spectra of reaction between 2•Au and PCy_3

Figure 13 outlines a speculative mechanistic cycle for the hydroboration of CO_2 with HBPin with **2•Au** as catalyst. Dissociation of **1-2•Au** creates a pair of nucleophilic and electrophilic coinage metal complexes reminiscent of a frustrated Lewis pair. One plausible mechanism for CO_2 reduction involves coordination of the C_1 reagent to the d^{10} metal fragment following by nucleophilic attack by either the gold- or boron-hydride species.

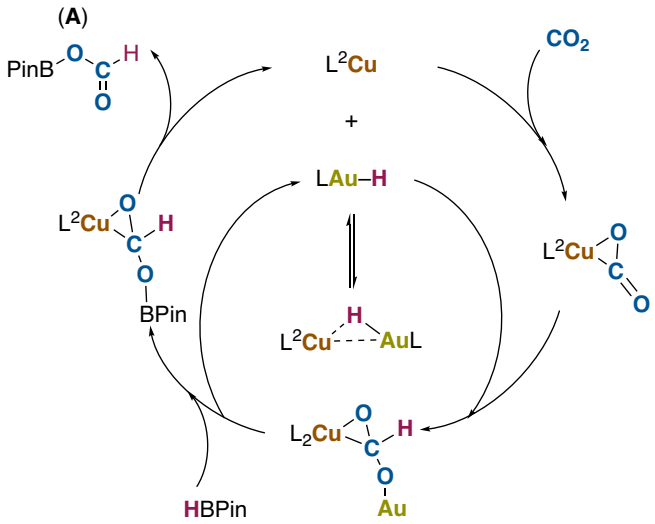


Figure 13 - Speculative mechanistic cycle for the hydroboration of CO_2 with HBPin with 2•Au

Feasibility of proposed mechanism

The frustrated Lewis pair mode of activation of CO_2 and CO with transition metal complexes has been suggested previously.[46-50] **2•CO_2**, the metal bound CO_2 adduct of **2** is isoelectronic with Aresta's complex **[$(PCy_3)_2$Ni•CO_2]**.[51] **[$(PCy_3)_2$Ni•CO_2]** is stable in solution, and was independently synthesised and used as a mechanistic probe. Reaction of **[$(PCy_3)_2$Ni•CO_2]** with 10 equivalents of HBPin leads to mixtures containing HCO_2BPin, **[$(PCy_3)_2$Ni•CO]** and $O(Bpin)_2$.

Despite the heterobimetallic effect not being observed as prominently when M = Ni, catalytic data was collected in order to compare the results of that with **Ni$(PCy_3)_2$•CO_2**. Aresta's complex appears to be catalytically competent for CO_2 reduction with HBPin, with the general trend of higher selectivity for formoxyborane arising when both Ni and Au are employed. These experiments demonstrate that metal bound CO_2 is a plausible C_1 source during catalytic turnover. In addition, catalytic reactions were also performed in the absence CO_2 and in all cases, the formation of formoxyborane was not observed.

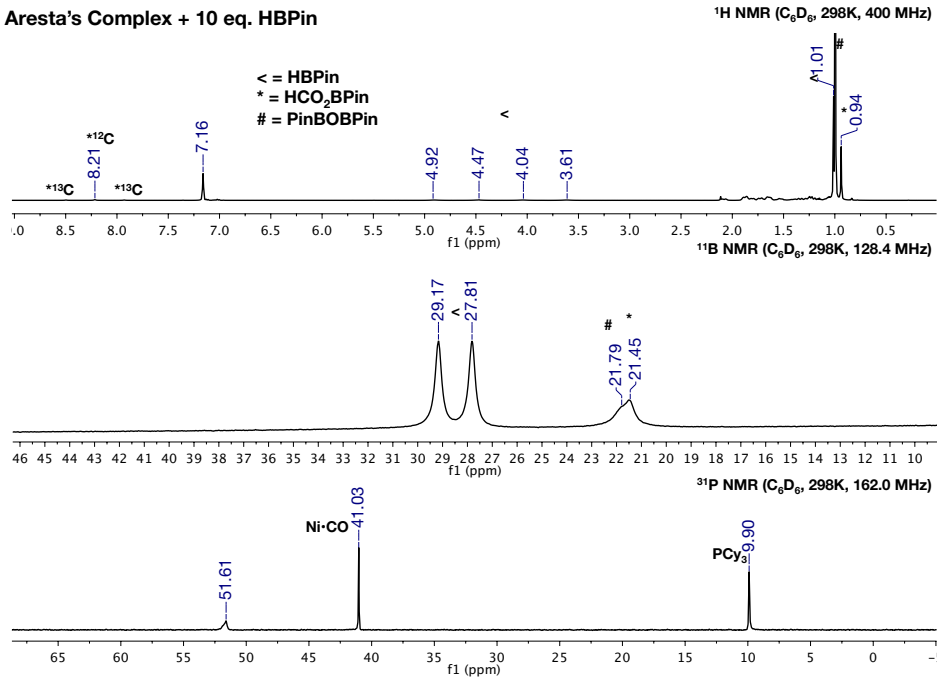


Figure 14 - ^{1}H, ^{11}B and ^{31}P NMR spectra following the reaction of Aresta's complex with HBPin at room temperature

Trapping of further metal bound CO_2 adducts was attempted by the addition of CO_2 to a sample of **2•Au**, as well as to an ad-mixture of **IPrAu–H** and **[Pd$(PCy_3)_2$]**. In the case of **2•Au**, no reactivity was observed. With mixtures of Au and Pd, at room temperature the solution turned

red on addition of the gas, however, obvious decomposition was observed before an NMR spectra could be measured. On measuring an ^{1}H NMR spectra of the decomposed mixture, two peaks in the formate region could be observed at δ = 8.6 and 9.6 ppm, which are in good agreement with a previously reported formate of a Ni---Ga heterobimetallic by Lu and co-workers (δ = 8.6 ppm, THF-d_8, 298 K). Repeating the reaction at lower temperatures in an attempt to slow down decomposition proved synthetically challenging as the solubility of the metal complexes was drastically reduced in toluene-d_8 at low temperatures.

Table 5 - The energy of formation of various substrate and product bound adducts of 2

Complex	Energy of formation ($\Delta G°$, kcal mol^{-1})
2•CO_2	+0.1
2•HCO_2BPin	-8.0
2•tol	-9.6
2•CO	-18.8

Coordination of CO_2, HCO_2Bpin and CO to the copper fragment **2** was investigated by DFT calculations and compared to solvation to form **2•tol**, as summarised in Table 5. Gibbs free energies of substrate or product (CO_2 or HCO_2BPin) coordination to **2** are both within 10 kcal mol^{-1} of solvation with toluene. The binding events are within reasonable energy range for catalytic turnover at 25 °C. The putative complex **2•CO_2** is thermodynamically uphill based on DFT calculations and could not be prepared by addition of CO_2 to **2•tol**. Additionally, the coordination of CO to **2** is highly favoured compared to that of substrate or product.

Ligand Scrambling

Ligand scrambling of **2•Au** could lead to catalytically active IPrCu–H which would be expected to selectively produce HCO_2Bpin.[26] Whilst we cannot unambiguously rule it out, the possibility of ligand exchange appears prohibitive based on DFT. **L^{2}Au–H–CuIPr** was found to be significantly higher in energy than **2•Au** ($\Delta G°_{rxn}$ = +20 kcal mol^{-1}). In addition, there are no known β-diketiminate ligand stabilised gold(I) species in the literature. Monitoring the first three hours of reaction of **2•Au** with CO_2 and HBpin supports a subtle induction period for catalysis and suggests that **2•Au** is off-cycle. This finding is consistent with breaking apart of the equilibrium and formation of an alternative active species.

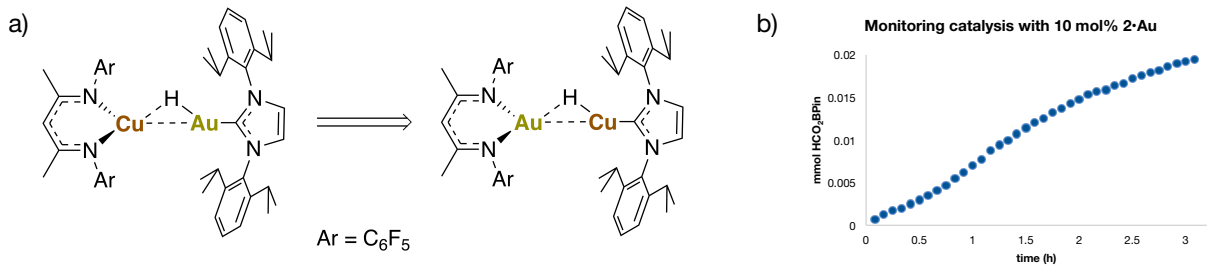


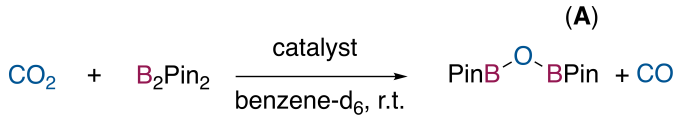
Figure 15 - a) ligand scrambling to form L²Au–H–CuIPr from 2•Au, b) point kinetics for the first 3 hours of catalysis with 10 mol% 2•Au

To further investigate the possibility for ligand exchange and thus the active species in catalysis with **2•Au**, the catalytic activity of **2•IPr** was assessed. Investigations by Mankad and co-workers previously revealed that heterobimetallics of copper NHC complexes are active for the reduction of CO_2 with HBPin.[52] The utilisation of **2•IPr** as a catalyst provided similar results to that of **2•Au** (see Table 6). The copper hydride complex **IPrCu–H** has been shown to be an active species in the reduction of CO_2 to CO with the use of B_2Pin_2.[53] A solution of **2•Au** also catalyses the reduction of CO_2 to CO with the use of B_2Pin_2

Table 6 & Table 7 - Catalytic data for the hydroboration of CO_2 with HBPin and reduction of CO_2 with B_2Pin_2

Catalyst	mol%	time (h)	conversion[a]	TON[b] (**A**)	TON[b] (**B**)	Selectivity[c] (**A**)
2•Au	10	24	64	3.6	0.7	**84%**
			56	4.6	0.8	**85%**
2•IPr	10	26	79	3.0	1.3	**70%**
2•tol	10	24	38	0.1	0.9	**8%**
			56	0.1	1.3	**6%**

a) based on HBPin, b) TON = mmol product / mmol catalyst, c) selectivity = mmol HCO_2BPin / mmol all products.



Catalyst	mol%	time (h)	conversion[a]	TON[b] (**A**)	Selectivity[c] (**A**)
2•Au	10	21	51	4.8	**100%**
IPrCu•O^{t}Bu[53]	1	20	100	< 10	**100%**

a) based on HBPin, b) TON = mmol product / mmol catalyst, c) selectivity = mmol HCO_2BPin / mmol all products

Catalysis with M•CO (M = Cu, Ni, Pd)

Due to the relatively low conversions observed when performing the reactions with the copper complex **2** and **[{Ni(PCy$_3$)$_2$}$_2$(μ-N$_2$)]** compared to **[Pd(PCy$_3$)$_2$]**, investigations into whether the formation of the carbonyl species **2•CO**, **[(PCy$_3$)$_2$Ni•CO]** and **[(PCy$_3$)$_2$Pd•CO]** during catalysis would inhibit reactivity, with the results outlined in Figure 17.

In the case of the palladium analogue, performing the hydroboration of CO_2 with the carbonyl adduct **Pd•CO** does not decrease the conversion of HBPin, however, the selectivity for formoxyborane is increased. In the case of **Ni•CO**, the conversion is decreased and selectivity is only marginally increased. For **2•CO**, the conversion is decreased slightly but there is no overall change in selectivity for formoxyborane. This suggests that a similar mechanism may be occurring in the case of M = Cu and Ni but not for M = Pd. It has been reported by Turcuret and co-workers that nickel and palladium complexes of pincer ligands have different selectivity for the hydroboration of CO_2.[54] The increased selectivity for formoxyborane when M = Pd could be arising due to the inability of the carbonyl bound palladium species to promote a second transformation to product (**C**).

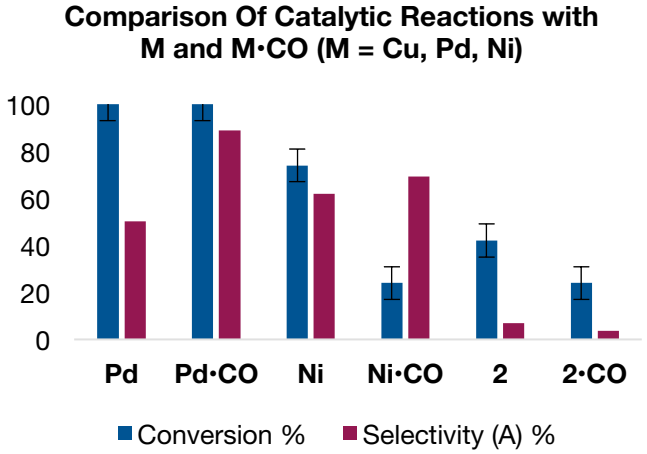


Figure 16 - A graph to show the difference in conversion and selectivity between complexes 2, Pd and Ni and their carbonyl adducts 2•CO, [(PCy$_3$)$_2$Pd•CO] and [(PCy$_3$)$_2$Ni•CO] for the hydroboration of CO_2 with HBPin NB: Catalysis with the carbonyl complexes was only performed once, error shown for conversion is associated with a 10% integration error from measuring integrals in the NMR software

3.6 Summary

In summary, the data have shown that **1-2•Au** and mixtures of the group 10 fragments **[{Ni(PCy$_3$)$_2$}$_2$(μ-N$_2$)]** and **[Pd(PCy$_3$)$_2$]** with **IPrAu–H** are selective in the formation of HCO$_2$Bpin, a formate equivalent, from CO_2 and HBPin. A consistent heterobimetallic effect was observed, and both metal centres are required for the selective formation of formoxyborane. Mechanistic experiments and DFT calculations suggest that activation of CO_2 by coordination to the d^{10} metal fragment is feasible under the catalytic conditions. The use of complex **[{Ni(PCy$_3$)$_2$}$_2$(μ-N$_2$)]** as a mechanistic probe is valid due to its isolobal electronic structure with the copper(I) fragment **2** and similar behaviour in the case of inhibition by CO, compared to the palladium fragment. We cannot rule out the possibility that the active species for this transformation is either **2•IPr** or **IPrCu–H**, as shown by a comparison of the activity of these complexes for the reduction of CO_2 with either HBPin or B_2Pin_2. However, the propensity for ligand transfer to form the *BDI* gold(I) complex **L^{2}Au–H–CuIPr** from **2•Au** has been shown to be unfavourable by DFT. If correct, ligand exchange would not explain the enhanced selectivity of mixtures of **[Pd(PCy$_3$)$_2$]** and **IPrAu–H**. An FLP-like mechanism still remains viable but future studies are required to allow definite conclusion.

4. Future Work

Synthesis and Characterisation

Expanding the series of σ-complexes of the coinage metals from **1-2•Au** and **4•Au** could be achieved through the use of copper(I) fragment **5**, which possesses a HOMO-1 that's significantly higher in energy than **1-2** and **4** (see chapter 2, section 3.2). This increase in stability of the HOMO-1 may induce the formation of a σ-complex of copper(I) with increased Cu---Au bond character. Initial NBO calculations on the putative complex **5•Au** reveal increased Cu---Au bond character through analysis of the wiberg bond indices (Cu---Au; **1•Au** = 0.148, **2•Au** = 0.148, **4•Au** = 0.101, **5•Au** = 0.210) and an increase in donation from the σ-Au–H orbital into the 4s orbital of the copper fragment (σ-Au–H → Cu; **1•Au** = 82 kcal mol^{-1}, **2•Au** = 84 kcal mol^{-1}, **4•Au** = 54 kcal mol^{-1}, **5•Au** = 99 kcal mol^{-1}). In turn, the investigation into the catalytic ability of this putative complex would provide a good comparison with the heterobimetallics of copper(I) reported by Mankad and co-workers.[55] Alternatively, expanding the series of σ-complexes of the coinage metals using the recently published silver hydride supported by an extremely bulky NHC ligand by Bertrand and co-workers.[11] This smaller coinage metal would reduce the ionicity in the 3-centre,2-electron core (see chapter 3, section 3.4) and the bulky NHC ligand may cause increased ligand-stabilisation effects and allow for the characterisation of the first σ-complex containing a Cu–H–Ag core.

Catalysis

Continuing from this work, efforts should be made to investigate the possibility of achieving the hydrogenation of CO_2 directly from mixtures of CO_2 and H_2. When utilising the correct base, it has been shown that a nickel hydride, amongst other complexes, is successful in the full conversion of CO_2 to formate under H_2.[25,56] The expansion of this research to investigate the ability of other heterobimetallics containing 3-centre,2-electon interactions to reduce CO_2 using HBPin should also be attempted to improve on the TON's outlined by the complexes in this chapter. In addition, preparing complexes of the type **IPrPd•L**[2] and investigating their suitability as catalysts for the reduction of boranes with CO_2 would also provide further indication as to whether ligand exchange is indeed the first step in the mechanism for the heterobimetallics reported herein.

5. Experimental

5.1 General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 and toluene-d_8 were stored over molecular sieves and distilled prior to use. NMR-scale reactions were conducted in J. Young's tap tubes and prepared in a glovebox. All heating mentioned was done using silicone oil baths. ^{1}H, ^{19}F, ^{11}B, ^{31}P and ^{13}C NMR spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated; all peak intensities are derived internal standard peak with values quoted in ppm. Data was processed using the MestReNova or Topspin software. CO_2 and CO were purchased from CK Gases and $^{13}CO_2$ from Sigma Aldrich. Both $^{13}CO_2$ and CO_2 gases were passed through an Agilent oxygen/moisture trap before use., HBPin was purchased from Sigma Aldrich and distilled under vacuum prior to use. $OPPh_3$, PCy_3 and 1-trifluoro(methyl)naphthalene were purchased from Sigma Aldrich and $(Me_3Si)_2CH_2$ was purchased from fluorochem. Catalytic yields were quantified against an internal standard peak of $(Me_3Si)_2CH_2$, and standardised to represent 1 proton in order to make quantification of different catalytic pathways comparable (see appendix section 1.1). In the case that the reaction was heated at 40 °C, this was achieved by placing the NMR tube in a silicon oil isothermal bath in-between spectroscopic measurements.

5.2 Preparative-Scale Synthesis

Complexes **1_2•tol**, **2•tol** and **4•PPh_3** were prepared according to the procedures outlined in chapter 2. **IPrAu–H**,[3] **[$Ni(PCy_3)_2]_2(\mu\text{-}N_2)$]** and **$Ni(PCy_3)_2$•$CO_2$**[57] and **[$Pd(PCy_3)_2$]**[58] were synthesised *via* or through slight modification of known literature procedures.

1•Au

In a glovebox, **1_2•tol** (61 mg, 0.055 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **IPrAu–H** (65 mg, 0.11 mmol, 2 eq.) was weighed and dissolved in toluene (1.5 mL). The solution containing **IPrAu–H** was added dropwise over 5 minutes to the stirred solution of **1_2•tol** before being left to stir for 30 minutes at 25 °C. The red solution was filtered

through glass fibre and solvent removed *in vacuo* to give a red oil which was being triturated with *n*-heptane (2 mL) to give a red crystalline solid of **1•Au** (107 mg, 0.10 mmol, 89%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 1.01 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 1.13 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 2.12 (s, 12H, Ar*Me*$_{Cu}$), 2.30 (s, 6H, Ar*Me*$_{Cu}$), 2.36 (sept, 4H, $^{3}J_{H–H}$ = 6.8 Hz, iPrC*H*$_{Au}$), 6.15 (s, 2H, iPrC$_2$*H*$_{2Au}$), 6.16 (s, 1H, C*H*$_{Cu}$), 6.70 (s, 4H, *Ar*$_{Cu}$), 6.97 – 6.99 (m, 4H, iPr*Ar*$_{Au}$), 7.18 – 7.19 (m, 2H, iPr*Ar*$_{Au}$); ^{13}C NMR (C_6D_6, 298 K, 125 MHz) δ 19.3 (Ar*Me*$_{Cu}$), 21.3 (Ar*Me*$_{Cu}$), 23.9 (iPr*Me*$_{Au}$), 24.8 (iPr*Me*$_{Au}$), 29.0 (iPr*C*H$_{Au}$), 83.8 (m, *C*H$_{Cu}$), 121.6 (q, ^{1}J$_{C–F}$ 288.1 Hz, *C*F$_{3Cu}$), 122.7 (iPr*C*$_2$H$_{2Au}$), 123.4 (Ar$_{Cu}$) 124.2 (iPrA$_{Au}$), 128.4 (*Ar*$_{Cu}$), 129.5 (*Ar*$_{Cu}$), 130.9 (iPr*Ar*$_{Au}$), 134.3 (iPr*Ar*$_{Au}$), 145.6 (iPr-*ipso*$_{Au}$), 147.3 (Ar-*ipso*$_{Cu}$), 151.0 (q, $^{2}J_{C–F}$ 24.2, N*C*–CF$_{3Cu}$), quaternary NHC carbon is not observed; ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -64.0. ^{1}H NMR (C_7D_8, 195 K, 500 MHz) δ 0.32 ppm (s, 1H, Au–*H*–Cu). Elemental analysis calc. for $C_{50}H_{60}AuCuF_6N_4$: C, 55.02; H, 5.54; N, 5.13. Found: C, 54.93; H, 5.65; N, 5.14.

2•Au

In a glovebox, **2•tol** (64 mg, 0.11 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Separately, **IPrAu–H** (64 mg, 0.11 mmol) was weighed and dissolved in toluene (1.5 mL). The solution containing **IPrAu–H** was added dropwise over 5 minutes to the stirred solution of **2•tol** before being left to stir for 30 minutes at room temperature. The green solution was filtered through glass fibre and solvent removed *in vacuo* to give a yellow crystalline solid which was washed with cold *n*-heptane (2 mL) to give **2•Au** (109 mg, 0.10 mmol, 92%). ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 0.70 (s, 1H, Au–*H*–Cu), 0.97 (d, 12H, $^{3}J_{H–H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 1.21 (d, 12H, $^{3}J_{H–H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 1.62 (s, 6H, Me$_{Cu}$), 2.31 (sept, 4H, $^{3}J_{H–H}$ = 6.8 Hz, iPrC*H*$_{Au}$), 4.83 (s, 1H, C*H*$_{Cu}$), 6.08 (s, 2H, iPrC$_2$*H*$_{2Au}$), 7.01 (s, 2H, iPr*Ar*$_{Au}$), 7.03 (s, 2H, iPr*Ar*$_{Au}$), 7.35 (t, 2H, $^{3}J_{H–H}$ = 7.7 Hz, iPr*Ar*$_{Au}$); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) δ 23.0 (*Me*$_{Cu}$), 23.6 (iPr*Me*$_{Au}$), 24.5 (iPr*Me*$_{Au}$), 28.8 (iPr*C*H$_{Au}$), 98.1 (*C*H$_{Cu}$), 122.7 (iPr*C*$_2$H$_{2Au}$), 124.0 (iPr*Ar*$_{Au}$), 129.5 (m, *Ar*$_{Cu}$), 130.8 (iPr*Ar*$_{Au}$), 133.8 (iPr*Ar*$_{Au}$), 136.7 (m, *Ar*$_{Cu}$), 139.2 (m, *Ar*$_{Cu}$), 140.9 (m, *Ar*$_{Cu}$), 145.5 (iPrAr-*ipso*$_{Au}$), 165.2 (N–C$_{Cu}$), 195.6 (iPrC$^{q}_{Au}$); ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -167.3 (m, 2F), -165.4 (m, 4F), -150.2 (m, 4F). ^{1}H NMR (C_7D_8, 195 K, 500 MHz) δ 0.73 ppm (s, 1H, Au–H–Cu). Elemental analysis calc. for $C_{44}H_{44}AuCuF_{10}N_4$: C, 48.96; H, 4.11; N, 5.19. Found: C, 49.09; H, 4.11; N, 5.26.

4•Au

In a glovebox, **4•PPh$_3$** (68 mg, 0.11 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **IPrAu–H** (65 mg, 0.11 mmol) was weighed and dissolved in toluene (1.5 mL). The solution containing **IPrAu–H** was added dropwise over 5 minutes to the stirred solution of **4•PPh$_3$** before being left to stir for 30 minutes at room temperature. The brown solution was filtered through glass fibre and solvent removed *in vacuo* to ¼ of its original volume before *n*-heptane (2 mL) was added. The solution was left at -35 °C overnight to give orange crystals of **4•Au** (42 mg, 0.04 mmol, 32%).^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.09 (d, 12H, $^3J_{H–H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 1.46 (d, 12H, $^3J_{H–H}$ = 6.7 Hz, iPr*Me*$_{Au}$), 1.89 (s, 6H, Ar*Me*$_{Cu}$), 2.04 (s, 3H, Ar*Me*$_{Cu}$), 2.64 (sept, 4H, $^3J_{H–H}$ = 6.8 Hz, iPrC*H*$_{Au}$), 4.33 (s, 1H, Au–*H*–Cu), 6.27 (s, 2H, iPrC$_2$*H*$_{2Au}$), 6.32 (s, 1H, C*H*$_{Cu}$), 6.55 (s, 2H, *Ar*$_{Cu}$), 6.89 – 6.99 (m, 10H, PPh_3), 7.05 (s, 2H, iPr*Ar*$_{Au}$), 7.07 (s, 2H, iPr*Ar*$_{Au}$), 7.16 – 7.24 (m, 7H, PPh_3/ iPr*Ar*$_{Au}$); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -65.7 (s, 3F), - 74.2 (s, 3F). ^{31}P NMR (C_6D_6, 298 K, 161.9 MHz) δ -3.29. Elemental analysis calc. for $C_{59}H_{64}AuCuF_6N_4OP$: C, 57.30; H, 5.22; N, 3.40. Found: C, 57.41; H, 5.27; N, 3.38. Note: This complex readily decomposes in solution and thus this has prevented the acquisition of satisfactory ^{13}C NMR data.

5.3 NMR-scale Reactions

Equilibrium Inhibition

In a glovebox, **2•Au** (7.5 mg, 0.007 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. **PCy$_3$** (2 mg, 0.007 mmol) was also added to the tube and the reaction followed by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy. Subsequent control reactions between **2•tol** and **PCy$_3$** confirmed the formation of **2•PCy$_3$** and **IPrAu–H**. **2•PCy$_3$**; ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.16 - 1.21 (m, 33H) 1.64 (s, 6H), 5.00 (s, 1H); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -149.9 (m, 4F), -164.4 (m, 4F), -165.5 (m, 2F); ^{31}P NMR (C_6D_6, 298 K, 161.9 MHz) δ 20.9 (s).

General Method for Catalytic Hydroboration of CO_2

In a glovebox, [catalyst] (x mg, 0.007 mmol) was dissolved in C_6D_6 (600 μL) and transferred to an NMR tube with Young's adapter. $(Me_3Si)_2CH_2$ (3 μL) was added as an internal standard and HBPin (10.2 μL, 0.07 mmol) was added before the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs). The yields of products were calculated from ^{1}H NMR spectroscopy *in-situ* and

the reaction progression monitored by ^{1}H and ^{11}B NMR at room temperature. The chemical shifts of the products match those already reported in the literature and independent *in-situ* NMR-scale synthesis. Each catalytic run was repeated to give at least two sets of values per complex.

5.3.1 Product Identification

Synthesis of HCO_2BPin, (A)

Formic acid (113 μL, 3.3 mmol) was dried *via* reflux over phthallic anhydride for 16 hours and added *via* syringe to HBPin (515 μL, 3.3 mmol) in benzene-d_6 (5 ml) in an ampoule. The solution was left to stir for 48 h whereby an aliquot was taken (600 μL) in order to confirm the formation of formoxyborane by ^{1}H and ^{11}B NMR. The formation of formoxyborane was confirmed. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 0.94 (s, 12H), 8.16 (s, 1H); ^{11}B NMR (C_6D_6, 298 K, 128.4 MHz) δ 21.7 (s).

Catalytic formation of HCO_2BPin, (A)

In a glovebox, **IPrCu•OtBu** (0.018 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. $(Me_3Si)_2CH_2$ (3 μL) was added as an internal standard and HBPin (26.2 μL, 0.18 mmol, 10 eq.) was added before the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, 9.5 eq.). The reaction was heated to 40 °C and after 20 h, formation of formoxyborane was observed by ^{1}H and ^{11}B NMR spectroscopy. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.00 (s, 12H), 8.22 (s, 1H); ^{11}B NMR (C_6D_6, 298 K, 128.4 MHz) δ 20.3 (s).

Synthesis of $O(BPin)_2$, (B)

In a glovebox, triphenylphosphine oxide (9 mg, 0.03 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter containing HBPin (9 μL, 0.06 mmol. 2 eq.). The reaction was monitored by ^{1}H, ^{11}B and ^{31}P NMR. The reaction was heated to 100 °C for 5 days to afford the product $O(BPin)_2$ (77% conversion w.r.t. HBPin). ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.01 (s, 24H); ^{11}B NMR (C_6D_6, 298 K, 128.4 MHz) δ 21.9 (s).

5.3.2 Identifying Y

Following ^{19}F NMR

In a glovebox, **2•Au** (7.5 mg, 0.007 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. A capillary containing 1-Trifluoro(methyl)napthalene (3 μL) in benzene-d_6 was added as an internal standard and HBPin (10.2 μL, 0.07 mmol) was added before the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs). The yields of products were calculated from ^{1}H NMR spectroscopy *in-situ* and the reaction progression monitored by ^{19}F NMR at room temperature in order to quantify the fluorine-containing products left at the end of the reaction. ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -141.9 (d, $^3J_{F–F}$ = 21Hz, 2F), -156.0 (t, $^3J_{F–F}$ = 22Hz, 1F), -163.1 (m, 2F).

Reaction between 2•tol + HBPin

In a glovebox, **2•tol** (4 mg, 0.007 mmol) was dissolved in benzene-d_6 (600 μl) and transferred to an NMR tube with Young's adapter. **HBPin** (1 μl, 0.007 mmol) was added and reaction followed for 5 days at room temperature by ^{1}H and ^{11}B NMR spectroscopy. Small amounts of decomposition to the free ligand **L^{2}H** was observed.

The purpose of the synthesis outlined in the rest of this section was to determine the nature of Y. Thus, once initial ^{19}F NMR spectra had been gathered and it was ascertained that they did not match that of Y, no further characterisation data was gathered.

Synthesis of L^{2}BPin

In a glovebox, **L^{2}K** (5.5 mg, 0.01 mmol) was suspended in benzene-d_6 (600 μl) and transferred to an NMR tube with Young's adapter. **HBPin** (1.5 μl, 0.01 mmol) was added and tube heated for 1 hour at 100 °C and analysed by ^{1}H and ^{11}B NMR spectroscopy. After 10 days, a small amount of **L^{2}BPin** was observed along with H_2, however considerable quantities of HBPin was still remaining.

Synthesis of Cu(L^2)$_2$

In a glovebox, to a suspension of **L^{2}K** (87 mg, 0.09 mmol) in toluene (8 mL) was added a suspension of **$CuCl_2$** (13 mg, 0.09 mmol) and left to stir for 2 hours whereby a green solution and grey precipitate was observed. The suspension was left to settle overnight and the solution

isolated *via* filtration through glass fibre before the solvent was removed *in vacuo* to give a green solid (23 mg, 0.02 mmol, 28%). This complex is paramagnetic and thus only small quantities of free ligand **L^2H** was observed in the ^{19}F NMR spectra.

Synthesis of 2•O_2

In a glovebox, **2•tol** (63 mg, 0.11 mmol) was dissolved in toluene (10 mL) and transferred to a schlenk. The solution was removed from the glovebox and oxygen was bubbled through. The solution transformed from green to dark brown and was left to stir for 30 minutes. The solvent was removed *in vacuo* to give a dark green solid (10 mg, 0.01 mmol, 20%). Similarly to what was observed with the synthesis of **Cu(L^2)$_2$** the NMR of **2•O_2** was also paramagnetic and only small amounts of **L^2H** was observed in the ^{19}F NMR spectra.

5.3.3 Mechanistic Studies

Catalysis with L_2M•CO (L_2M = 2, [Ni(PCy_3)$_2$], [Pd(PCy_3)$_2$])

In a glovebox, **L_2M** (x mg, 0.007 mmol) was weighed in a scintillation vial, dissolved in benzene-d_6 (600 μl) and transferred to an NMR tube with Young's adapter. The tube was freeze-pump-thaw de-gassed three times before being exposed to an atmosphere of **CO**. Formation of the **L_2M–CO** adducts was observed by multinuclear NMR spectroscopy before the tube was freeze-pump-thaw degassed to remove any excess CO. The tube was then transferred to a glovebox whereby an internal standard and HBPin were added. It was finally freeze-pump-thaw de-gassed again before being exposed to an atmosphere of CO_2. The reaction was followed by ^1H, ^{11}B and ^{19}F NMR spectroscopy.

Synthesis of [{Ni(PCy_3)$_2$}•CO]

In a glovebox, **[{Ni(PCy_3)$_2$}$_2$μ-N_2]** (22 mg, 0.017 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO (0.14 mmol, xs). Initial NMR's were taken to reveal 60% conversion of **[{Ni(PCy_3)$_2$}$_2$μ-N_2]** to **[{Ni(PCy_3)$_2$}•CO]**. ^1H NMR (C_6D_6, 298 K, 400 MHz) δ 1.07 - 2.11 (m, 33H); ^{31}P NMR (C_6D_6, 298 K, 160.4 MHz) δ 41.0 (s). ^{13}C NMR data was generated from catalytic reactions with labelled $^{13}CO_2$ (C_6D_6, 298 K, 100 MHz) δ 203.1 (t, $^2J_{C–P}$ = 3.3 Hz, Ni–<u>C</u>O).

Reaction of 2•Au + CO

In a glovebox, **2•Au** (18 mg, 0.018 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO (0.14 mmol, xs.). The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy however no changes from the initial spectra of **2•Au** were observed.

Catalysis of 2•Au for the reduction of CO_2 with B_2Pin_2

In a glovebox, **2•Au** (7.6 mg, 0.007 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to an NMR tube with Young's adapter. Similarly, B_2Pin_2 (17.8 mg, 0.07 mmol, 10 eq.) was dissolved in benzene-d_6 (300 μL) and transferred to the same NMR tube. $(Me_3Si)_2CH_2$ (3 μL) was added as an internal standard before the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs.). The reaction was followed by ^{1}H and ^{11}B NMR spectroscopy.

Synthesis of 2•IPr

In a glovebox, **•IPr** (21 mg, 0.036 mmol) in toluene (0.5 mL) was added to **2•tol** (14 mg, 0.036 mmol) in toluene (1 mL) and left to stir for 2 hours whereby the yellow solution became orange. The solution was filtered *via* glass fibre and the solvent removed *in vacuo* to give an orange oil. Crystallisation from *n*-hexane yielded yellow crystals (4 mg, 0.005 mmol, 13%). ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 0.88 (d, 12H, $^{3}J_{H–H}$ = 6.7 Hz), 1.14 (d, 12H, $^{3}J_{H–H}$ = 6.7 Hz), 3.15 (sept, 4H, $^{3}J_{H–H}$ = 6.8 Hz), 4.79 (s, 1H), 6.20 (s, 2H, 6.32 (s, 1H, CH_{Cu}), 6.55 (s, 2H, Ar_{Cu}), 7.02 (s, 2H), 7.04 (s, 2H); ^{19}F NMR (C_6D_6, 298 K, 376.5 MHz) δ -149.1 (d, 4F, $^{3}J_{F–F}$ = 24 Hz), -163.5 (t, 4F, $^{3}J_{F–F}$ = 22 Hz), -167.0 (t, 2F, $^{3}J_{F–F}$ = 22 Hz).

Catalysis with 2•IPr for the Reduction of CO_2 with HBPin

In a glovebox, **2•IPr** (0.005 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. $(Me_3Si)_2CH_2$ (3 μL) was added as an internal standard and HBPin (5.8 μL, 0.045 mmol) was added before the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs). The yields of products were calculated from ^{1}H NMR spectroscopy *in-situ* and the reaction progression monitored by ^{1}H and ^{11}B NMR spectroscopy at room temperature.

Catalysis with Aresta's Complex for the reduction of CO_2 with HBPin

In a glovebox, **[{Ni(PCy$_3$)$_2$}$_2$μ-N$_2$]** (4.4 mg, 0.007 mmol) was dissolved in benzene-d$_6$ (600 μL) and transferred to an NMR tube with Young's adapter. $(Me_3Si)_2CH_2$ (3 μL) was added as an internal standard and the NMR tube was removed from the glovebox and placed directly in liquid nitrogen. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs). Initial NMR spectra were taken to reveal 90% conversion of **[{Ni(PCy$_3$)$_2$}$_2$μ-N$_2$]** to **[{Ni(PCy$_3$)$_2$}•CO$_2$]**. The solution was freeze-pump thawed and transferred back into the glovebox, whereby HBPin (10.2 μL, 0.07 mmol) was added before being re-exposed to the reaction conditions. The yields of products were calculated from ^{1}H NMR spectroscopy *in situ* and the reaction progression monitored by ^{1}H, ^{11}B and ^{31}P NMR at room temperature.

Reaction of Aresta's Complex and HBPin

In a glovebox, **[{Ni(PCy$_3$)$_2$}$_2$μ-N$_2$]** (4.4 mg, 0.007 mmol) was dissolved in benzene-d$_6$ (600 μL) and transferred to an NMR tube with Young's adapter. The tube was freeze-pump-thaw degassed on a Schlenk-line with Young's adapter three times before being exposed to an atmosphere of $^{13}CO_2$ (0.14 mmol, xs). Initial NMR's were taken to reveal 70% conversion of **[{Ni(PCy$_3$)$_2$}$_2$μ-N$_2$]** to **[{Ni(PCy$_3$)$_2$}•CO$_2$]**. The solution was freeze-pump-thaw degassed and transferred back into the glovebox, whereby HBPin (10.2 μL, 0.07 mmol) was added. The reaction progression was monitored by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy at room temperature and the formation of formoxyborane, HCO_2BPin and $O(BPin)_2$ was observed.

Attempted synthesis of Pd•Au

In a glovebox, **[Pd(PCy$_3$)$_2$]** (5 mg, 0.007 mmol) was dissolved in benzene-d$_6$ (300 μL) and transferred to an NMR tube with Young's adapter Similarly, **IPrAu–H** (4 mg, 0.007 mmol) was dissolved in benzene-d$_6$ (300 μL) and added to the NMR tube containing the nickel complex. The tube was removed from the glovebox and reaction followed *via* ^{1}H and ^{31}P NMR spectroscopy. No reaction was observed by NMR.

Addtion of CO_2 to mixtures of Au•Pd

In a glovebox, **IPrAu–H** (29 mg, 0.049 mmol) was suspended in benzene-d$_6$ (300 μL) and transferred to an NMR tube with Young's adapter Similarly, **[Pd(PCy$_3$)$_2$]** (33 mg, 0.049 mmol) was suspended in benzene-d$_6$ (300 μL) and added to the tube containing the gold complex. The tube was removed from the glovebox, freeze-pump-thaw degassed on a Schlenk-line with

Young's adapter three times before being exposed to an atmosphere of CO_2 (0.14 mmol, xs). The sample immediately became red before becoming brown just prior to a ^1H NMR spectra being measured, however two peaks in the formate region were be observed by ^1H NMR spectroscopy. The reaction was also monitored *via* VT NMR in toluene-d_8 however no formate peak was observed.

2•Au + HBPin

In a glovebox, **2•Au** (8 mg, 0.007 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with Young's adapter. HBPin (1 μl, 0.007 mmol) was added and reaction followed by ^1H, ^{11}B and ^{19}F NMR spectroscopy whereby no reaction was observed by NMR.

Ni•Au + HBPin

In a glovebox, **[{Ni(PCy$_3$)$_2$}$_2$μ-N$_2$]** (4 mg, 0.0035 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to an NMR tube with Young's adapter. Similarly, **IPrAu–H** (4 mg, 0.007 mmol, 2 eq) was dissolved in benzene-d_6 (300 μL) and transferred to the tube containing the nickel complex. HBPin (1 μl, 0.007 mmol) was added and reaction followed by ^1H, ^{11}B and ^{31}P NMR spectroscopy whereby no reaction was observed by NMR.

Pd•Au + HBPin

In a glovebox, **[Pd(PCy$_3$)$_2$]** (5 mg, 0.007 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to an NMR tube with Young's adapter. Similarly, **IPrAu–H** (4 mg, 0.007 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to the tube containing the nickel complex. HBPin (1 μl, 0.007 mmol) was added and reaction followed by ^1H, ^{11}B and ^{31}P NMR spectroscopy whereby no reaction was observed by NMR.

Multinuclear NMR spectra for preparative scale (section 2.3) and NMR scale (section 3.3) reactions along with X-ray acquisition parameters (section 4.3) and Z-matrices for DFT-optimised structures (section 5.3) can be found in the appendix.

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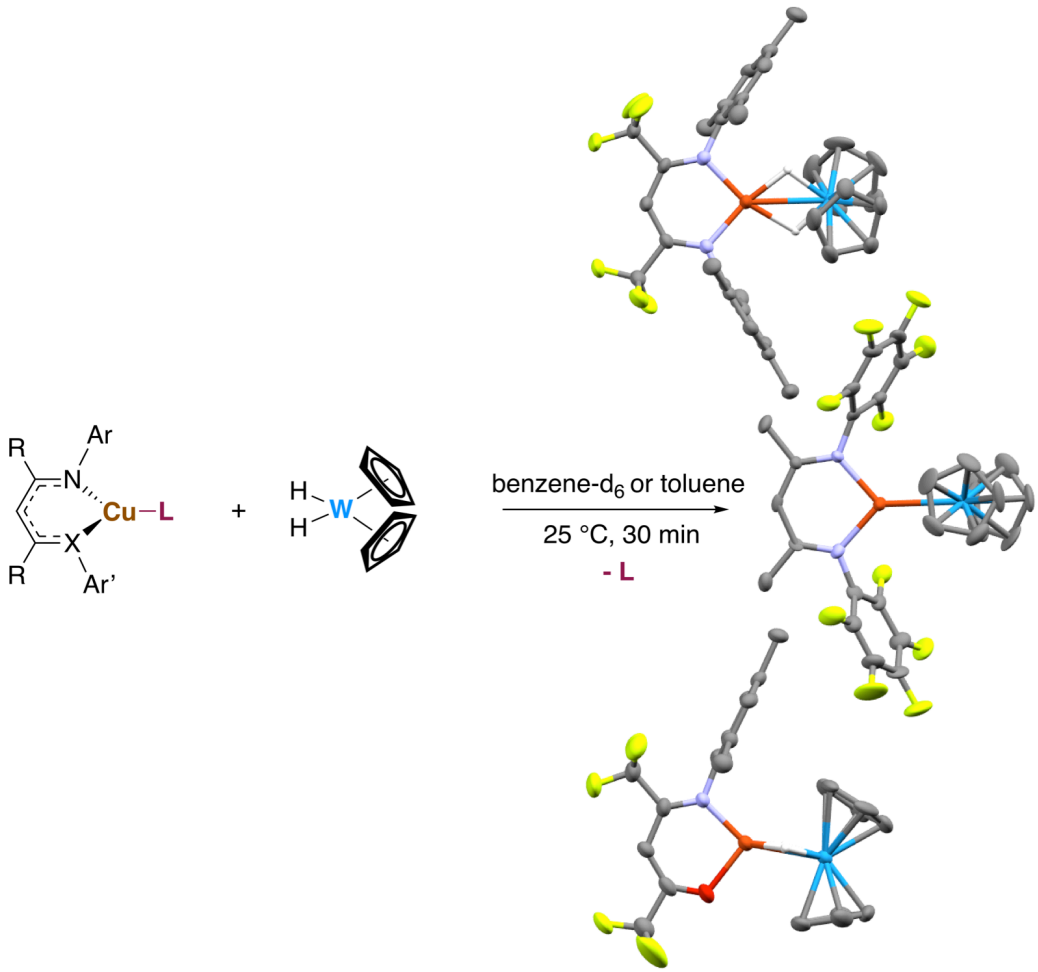
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Chapter 5

Heterobimetallics of Copper(I) with Tungsten Hydrides

The preparation and structural characterisation of three new heterobimetallic hydride complexes containing 3-centre,2-electron W–H–Cu bonds is reported. These complexes have been characterised by single crystal X-Ray crystallography and multinuclear NMR spectroscopy. The bonding in these complexes has been analysed by DFT calculations.



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1. Introduction

1.1 M---M' Cooperativity in Catalysis

In the past few years, metal---metal cooperativity has gained increasing attention as a new strategy in catalysis.[1-4] Not least because of the investigations into the active sites of enzymes that contain two metal centres, for example, the nitrosase enzyme has been shown to contain an Fe---Mo cofactor. The reversible addition of dihydrogen across metal–metal bonds is potentially a key step in a number of reactions that either consume or produce H_2 (Figure 1 - **I**). Mankad and co-workers have invoked this step in both the semi-hydrogenation of alkynes catalysed by Ag–Ru bimetallics and the borylation of arenes catalysed by Cu–Fe bimetallics.[5-8]

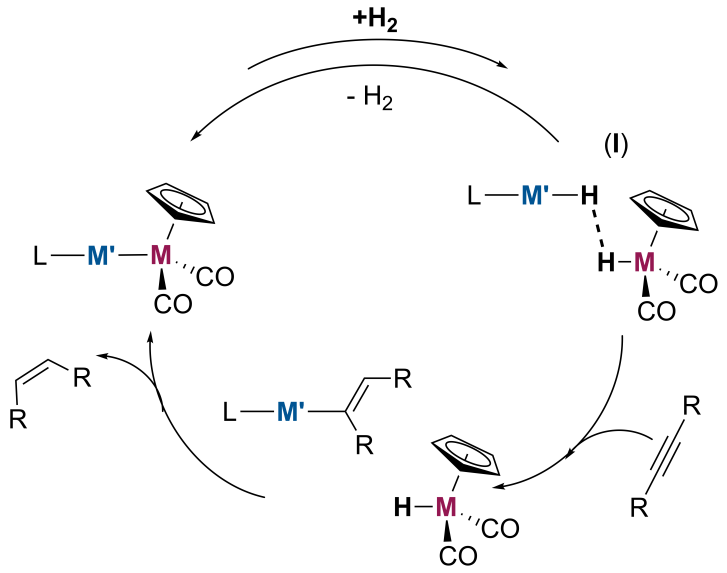
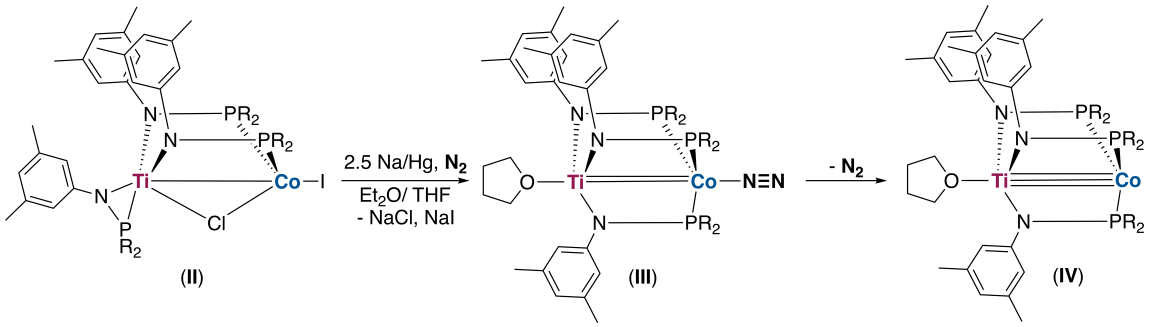


Figure 1 - Proposed mechanism for the semi-hydrogenation of alkynes by Mankad and co-workers, M = Fe or Ru, M' = Cu or Ag, L = IPr or IMes.

Heterobimetallic complexes of Zr–Co featuring M–M' double and triple bonds prepared by Thomas and co-workers have been shown to activate alkyl halides, CO_2, diaryl ketones and organic azides.[9-14] In addition, heterobimetallic complexes of Ti–Co featuring an M–M' triple bond that promote N_2 bond cleavage have also been reported by Thomas and co-workers.[15] The reduction of the Ti–Co heterobimetallic **II** with a Na/Hg amalgam under an atmosphere of dinitrogen gives the end-on N_2 bound heterobimetallic Ti=Co–N_2, **III**. Despite the IR spectra of Ti=Co–N_2 exhibiting an activated N_2 stretch (ν_{N2}= 2084 cm^{-1}), the N_2 molecule is so weakly bound that on exposure to vacuum or an atmosphere of argon, the formation of an unsaturated heterobimetallic Ti≡Co is observed, **IV**. Natural population analysis reveals that, on

coordination, the natural charge on the cobalt centre decreases and thus complex **III** can best be described as a Ti^{IV}–Co^{-1} heterobimetallic.



Scheme 1 - Activation of N_2 by a Ti–Co heterobimetallic reported by Thomas and co-workers, R = ^{i}Pr

Lu and co-workers recently reported the synthesis and characterisation of a heterobimetallic of Ni–Ga which is an extremely active catalyst in the hydrogenation of CO_2 to formate at room temperature (TOF = 9700 h^{-1}).[16,17] In the initial study, the isolation of an anionic gallium-supported nickel(0) hydride **V** and anionic gallium supported nickel-formate **VI** was achieved. In the case of the nickel(0) hydride, the gallium fragment acts as a σ-acceptor toward nickel and strengthens the Ni−H bond directly *trans* to it.

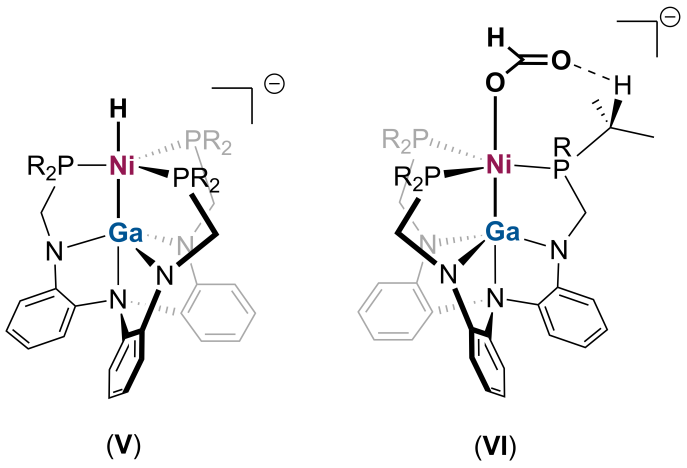


Figure 2 - A gallium-supported nickel hydride and formate reported by Lu and co-workers

Experiments to confirm the significance of the stabilisation by the Lewis acidic gallium fragment were performed. Use of the monometallic complex $NiLH_3$ (L = $\{N(o\text{-}(NCH_2PiPr_2)C_6H_4)_3\}^{3-}$) for CO_2 hydrogenation proved unsuccessful and the authors suggest that this is due to its inability to bind and activate H_2 and stabilise an anionic hydride, analogous to **V**. In a DFT study, a series of heterobimetallics were investigated for this transformation (M–M', where M = Fe, Co, Pd or Pt

and M' = Al or Ga, and Ni−M, where M = Fe, Co, Al, Ga or In). It was predicted that NiGaL and CoGaL would be the optimum complexes for use as catalysts due to their relative binding energies of H_2 and formate being neither too weak or too strong and thus acceptable for catalytic turnover.

1.2 Heterobimetallics of the Crimmin Group

In a complementary approach, the Crimmin Group is investigating heterobimetallic hydride complexes in catalysis. The selective reduction of CO_2 with HBPin (HBPin = pinacolborane) can be achieved with Au---Cu hydride complexes (see chapter 4) and the reaction of Zr---Zn hydride complexes (Figure 3 - **VII**) with cycloocta-1,3-diene leading to a highly unusual on-metal diene-to-alkyne isomerisation.[18]

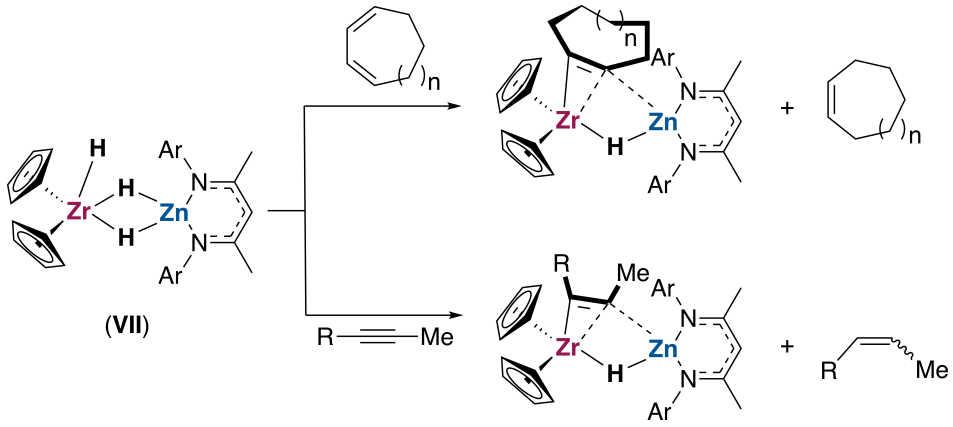


Figure 3 - Isomerisation of alkenes with heterobimetallics of Zr---Zn reported by the Crimmin group, Ar = Dipp, n = 1 or 2, R = ^{t}Bu or Me_3Si

Mechanistic analysis indicates that the heterobimetallic complexes do not remain intact throughout the reaction sequence but rather separate into monometallic components that act in concert as M---M' pairs to achieve new modes of selectivity.[19]

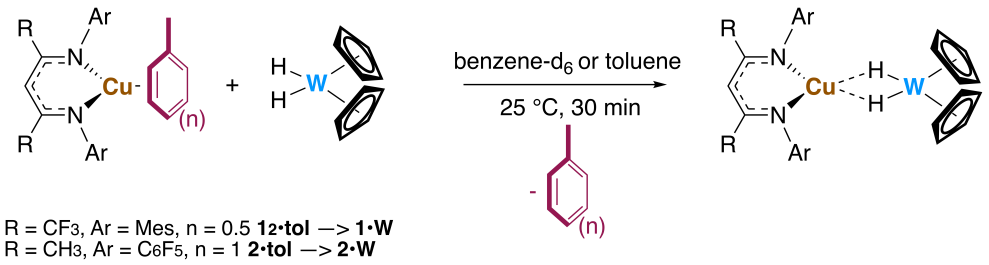
Herein, the preparation and properties of a series of heterobimetallics formed from the addition of tungsten dihydrides to bent d^{10} copper(I) fragments is reported. These new species find rich precedent in the work of Caulton, Chaudret and others who have prepared related complexes of the coinage metals containing TM–H–Cu, TM–H–Ag, and TM–H–Au linkages.[20-26]

2. Synthesis and Characterisation

2.1 Synthesis of Heterobimetallics of Cu–H–W

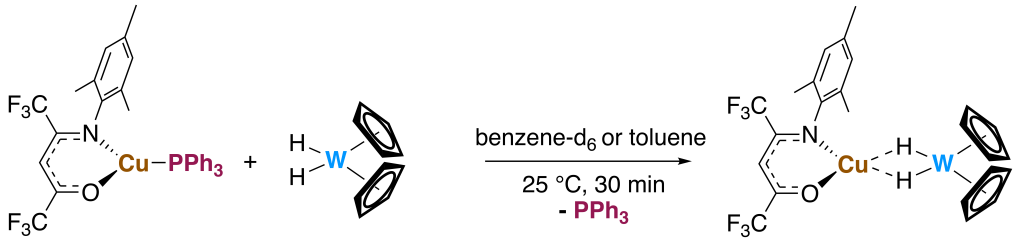
Preparation

Initial reactions between one equivalent of the copper(I) fragments **1-2•tol** and the tungsten dihydride $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (**W**) were performed on an NMR scale in benzene-d_6. After 30 minutes, the signal corresponding to the tungsten dihydride at δ = -12.0 ppm is shifted upfield on complexation to the copper(I) fragment (**1•W**, δ = -12.4 ppm; **2•W**, δ = -12.2 ppm).



Scheme 2 - The synthesis of 1-2•W

Similarly, reaction between one equivalent of **4•PPh$_3$** and one equivalent of **W** also showed complexation to the copper(I) fragment through an upfield shift of the signal corresponding to the tungsten hydride moiety (δ = -13.5 ppm) and observation of free PPh_3 in the ^{31}P NMR spectrum. Scale up of these reactions in toluene gave the corresponding heterobimetallics **1•W**, **2•W** and **4•W** in 49%, 69% and 46% yield respectively.



Scheme 3 - The synthesis of 4•W

2.2 Characterisation of Heterobimetallics of Cu–H–W

X-Ray Data

Single crystals of **1-2•W and 4•W** could be grown from toluene/*n*-heptane mixtures at -35 °C, and in the case of **1•W** and **4•W**, afforded data of high enough quality to locate the positions of

the hydrides from the difference electron density map (Figure 4). The metal---metal distances in these complexes (**1•W**, 2.7369(6) Å; **2•W**, 2.7220(12) Å; **4•W**, 2.6263(10) Å) are beyond the sum of single bond radii defined by Pauling (2.47 Å)[27] and Pyykkö (2.49 Å).[28] For comparison, the Cu–W bond in $[(\eta^5\text{-}C_5H_5)W(CO)_2\{Cu(PPh_3)_2\}]$ is 2.721(1) Å and is supported by semi-bridging carbonyl ligands.[29] The most striking structural distinction between complexes **1-2•W** and **4•W** lies in the angle created by the planar $\{CuL_2\}$ fragments and the Cu–W bond. In the solid state, this varies from 0-79° depending on the ligand on the $\{CuL_2\}$ fragment (**1•W**, 44°; **2•W**, 79°; **4•W**, 0°). This is in contrast to what was previously reported for σ-borane complexes of copper(I) adopting η^2:η^2 coordination.

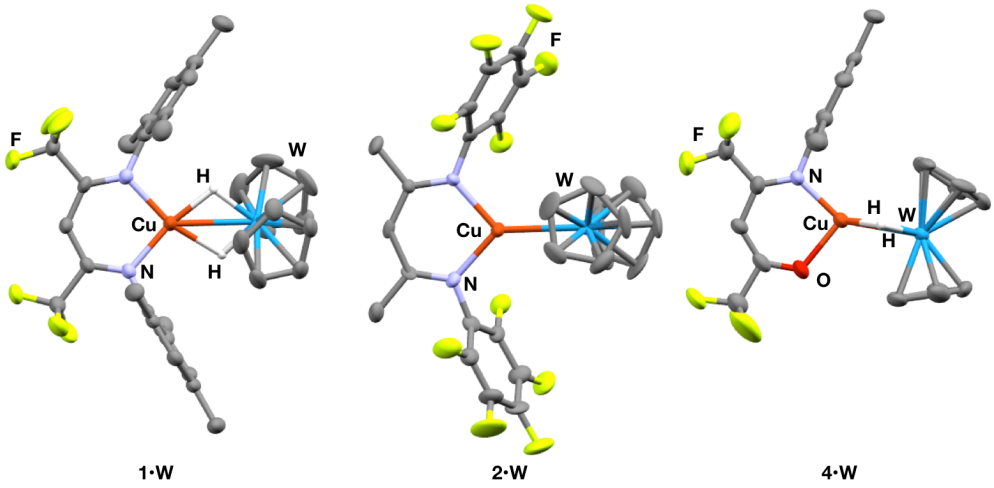


Figure 4 - X-Ray structures of 1-2•W and 4•W

Table 1 – Selected geometric parameters for the complexes 1-2•W and 4•W

	Bond Lengths (Å)			*Bond Angles (°)*
	Cu---W	W–H	Cu–H	Cu–H–W
1•W	2.7369(6)	1.55 (3) 1.62 (4)	1.77 (3) 1.85 (5)	111 (2) 104 (2)
2•W	2.7220(12)	-	-	-
3•W	2.6263(10)	-	-	-

NMR Spectroscopy

On dissolving crystals of **1-2•W** and **4•W** in benzene-d_6, a sharp singlet was observed upfield in the ^{1}H NMR spectra, indicative of W–H bond (**1•W**; -12.4 ppm, **2•W**; -12.2 ppm, **4•W**; -13.5

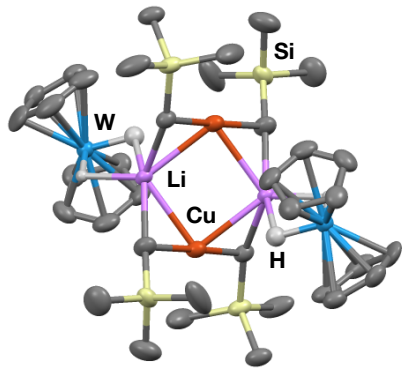
ppm). An increase in the $^{1}J_{W-H}$ coupling constants across the series **W** < **1•W** < **2•W** < **4•W** reflects an increasing amount of σ-character from tungsten being donated into the W–H bonds on coordination to the copper fragments **1**, **2** and **4** (**W**; 72.0 Hz, **1•W**; 72.3 Hz, **2•W**; 75.7 Hz, **4•W**; 76.4 Hz). The sharp, well defined nature of the peak corresponding to the W–H bonds in these complexes indicated that they should be described as heterobimetallics of Cu–H–W, and not σ-complexes. This NMR data suggests that the two metal fragments are not in equilibrium and the heterobimetallic is well defined.

3. Reactivity Studies of Heterobimetallics of Cu–H–W

3.1 Elimination of H_2 and H/D Exchange

Attempts to eliminate H_2 from the heterobimetallics of Cu–H–W have proven unsuccessful. Isolated samples of **1-2•W** and **4•W** were dissolved in benzene-d_6 and subjected to photolysis (400 W Hg lamp) and elevated temperatures (100 °C), however, decomposition of the heterobimetallic was observed in all cases. DFT calculations suggest that H_2 elimination from these heterobimetallic complexes to form **{L_2Cu–WCp_2}** is significantly endergonic with ΔG°_{rxn} +39 to +45 kcal mol^{-1}. Further experiments suggest that the hydrides of **2•W** do not undergo chemical exchange with external dihydrogen. The reaction of **2•W** with an atmosphere of D_2 was followed by ^{1}H NMR spectroscopy. While at room temperature no exchange was observed, the use of elevated temperatures (80 °C) led to the decomposition of the complex **2•W** with no evidence for H/D exchange.

a)



W•Li Organocuprate

b)

Bond Lengths (Å)					*Bond Angles (°)*
Li---W	Cu---Li[a]	Cu---Li[b]	W–H	Li–H	W–H–Li
2.996(6)	2.604(7)	2.640(6)	1.5754 (0.0345)	2.0619 (0.0363)	110.19 (1.88)
			1.5997 (0.0456)	2.1311 (0.0442)	105.96 (2.23)

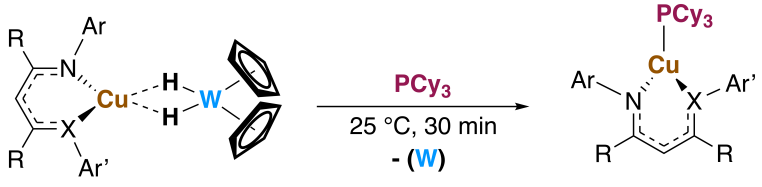
Figure 5 - a) Crystal structure of a W•Li organocuprate, b) selected geometrical parameters

Attempts to deprotonate the complexes **1-2•W** with an excess of $LiCH_2SiMe_3$ resulted in a rearrangement of the metal fragments. In the case of **1•W**, direct crystallisation from the reaction mixture with *n*-hexane allowed the formation of a tungsten-bound-lithium organocuprate.[30]

On comparison of the structural parameters of **W•Li** with a previously reported anionic organocuprate reported by Power and co-workers $[\{Li_2Cu_3Ph_6\}^{2-}\{Li_4Cl_2(Et_2O)_{10}\}]$, the Cu–C and Li–C distances are in good agreement (**W•Li**, Cu–C = 1.960(4) Å, 1.961(4) Å; Li–C = 2.281(7) Å, 2.314(7)Å; $[\{Li_2Cu_3Ph_6\}^{2-}\{Li_4Cl_2(Et_2O)_{10}\}]$, Cu–C = 1.929(6) Å; Li–C = 2.240(14) Å).[31] Additionally, the W---Li bonds found in **W•Li** are longer than the average W---Li bond found in $[\{W(PMe_3)_3H_5Li)_4]$ reported by Green and co-workers ($[\{W(PMe_3)_3H_5Li)_4]$; W–Li = 2.85(1) Å)[32] and longer than the sum of the single bond radii reported by Pauling (2.524 Å)[27] and Pyykkö (2.70 Å).[28]

3.2 Ligand Exchange Experiments

A series of ligand exchange experiments were carried out in order to investigate the availability of both metal fragments for subsequent reactivity. Exposure of a sample of the heterobimetallics **1-2•W** in solution to the coordinating ligand PCy_3 results in ligand exchange between **W** and PCy_3, confirmed by independent *in-situ* synthesis of **2•PCy$_3$** and **4•PCy$_3$**. In contrast to what was observed with the main group complexes outlined in chapter 3, when **2•W** was exposed to 1 atmosphere of CO, decomposition of the heterobimetallic was favoured over ligand exchange at room temperature.



R = CF_3, X = N, Ar = Ar' Mes, **1•W —> 1•PCy$_3$**
R = CH_3, X = N, Ar = Ar' = C_6F_5, **2•W —> 2•PCy$_3$**
R = CF_3, X = O, Ar = Mes, **4•W —> 4•PCy$_3$**

Figure 6 - Reactivity of the heterobimetallics 1-2•W and 4•W with PCy_3

DFT Calculations to predict the feasibility of ligand exchange reactions with **2•W** have been performed, with $\Delta G°_{rxn}$ for the formation of **2•PCy$_3$** and **2•CO** giving values of -7.54 kcal mol^{-1} and +12.4 kcal mol^{-1} respectively. Whilst the value for **2•PCy$_3$** suggests thermodynamic

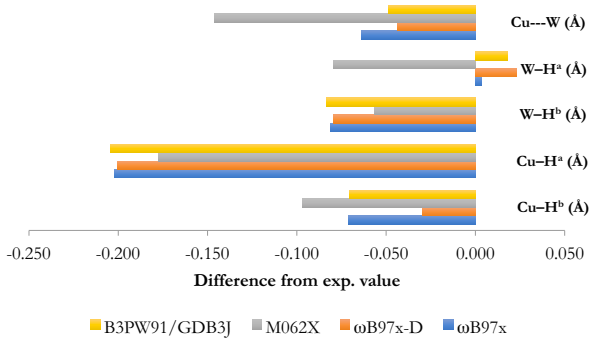
favourability, calculations confirm the thermodynamically uphill formation of **2•CO** and **W** from **2•W** and CO.

4. Analysis of Bonding in Heterobimetallics of Cu–H–W

4.1 DFT Benchmarking Studies

DFT optimisation of the solid-state structures were performed using the B3PW91 functional with GD3BJ dispersion and hybrid basis set SDDAll (Cu, W), 6-311G* (others), NBO calculations were performed using NBO 6.0. The parameters W–H–Cu (°), and W---Cu (Å) gathered from X-Ray data for **1•W** were compared against calculated values for the functionals M062X, B3PW91, ωB97x and ωB97xD (see Figure 7a). Despite the functionals ωB97x-D and B3PW91-GD3BJ giving similar geometric parameters, the use of B3PW91-GD3BJ has allowed calculation of reaction parameters that are in closer agreement with experimental work. Notably, these experimental parameters include reaction thermodynamics for the formation of previously reported σ-complexes of copper(I) with a series of main group and coinage metal hydrides (M = B, Zn, Al, Au - see Figure 7b) and relative energies of key transition states in C–F bond activation.[33]

a)



b)

	exp.	ωb97xD	B3PW91-GDB3J
1•Zn	+3.31	-25.5	-7.36
3•Zn	+0.65	-21.2	-6.18
3•Al'	-0.23	-23.8	-12.3
2•Au	+2.70	-38.7	-21.9

Figure 7 - a) Comparison of the structural parameters derived from optimising complex 1•W with four different functionals, b) comparison of the experimentally derived $\Delta G°_{rxn}$ of complexes 1•Zn, 3•Zn, 3•Al' and 2•Au with two different functionals

4.2 NBO Calculations

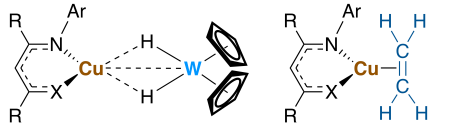
WBI

Inspection of the Wiberg bond indices (WBI) generated from NBO calculations on complexes **1-2•W** and **4•W** confirm the strongest interaction in the W–H–Cu core can be found between

the W–H bonds and weaker interaction between the Cu–H and Cu–W bonds, similar to what has previously been reported for σ-complexes of B–H in the $\eta^2;\eta^2$-coordination mode (see Chapter 3).[34,35]

Second-Order Perturbation Theory

Second order perturbation analysis on **1-2•W and 4•W** reveals in all cases there is significantly more donation from the W–H bonds to the copper 4s orbital than back-donation from the copper d-orbitals into the σ*-W–H orbital. Calculations have been performed in order to benchmark the amount of back-donation observed in **1-2•W** and **4•W** with that of corresponding copper-ethylene adducts **1-2•C_2H_4** and **4•C_2H_4**, whereby back-donation occurs from the copper d-orbitals to the anti-bonding orbital on the C=C bond. Significantly more back-donation is observed in the case of **1-2•C_2H_4** and **4•C_2H_4**, thus showing that the back-donation observed in **1-2•W** and **4•W** is negligible, as observed in the case of complexes **1-2•Au** and **4•Au** in chapter 4.



a)

	Cu---W	W–H	Cu---H
1•W	0.11	0.65	0.10
2•W	0.11	0.64	0.10
4•W	0.13	0.67	0.10

b)

	σ-(W–H) to Cu/ π(C=C) to Cu	Cu to W–H/ Cu to π(C=C)	Cu to W
1•W	80	3	5
1•C_2H_4	84	35	-
2•W	60	4	8
2•C_2H_4	93	37	-
4•W	106/107	5/6	16
4•C_2H_4	89	35	-

Figure 8 - a) WBI for the Cu---W, W–H and Cu---H interactions within complexes 1-2•W and 4•W, b) quantification of the donor and acceptor properties of 1-2•W, 4•W, 1-3•C_2H_4 and 4•C_2H_4 (kcal mol^{-1})

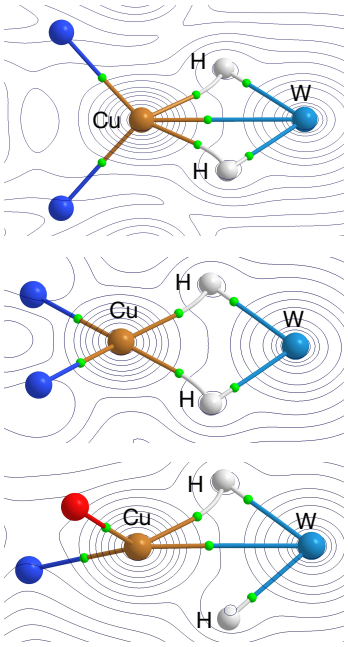
QTAIM

QTAIM calculations reveal that even though the M–M' interaction across **1-2•W** and **4•W** is indeed weak, bond critical paths between Cu and W can be seen in the case of **1•W** and **4•W**. The acuteness of H–M–H angle of metallocene complexes has been used as a crude metric to assess the possibility of metal–metal interactions in donor-acceptor complexes. A more obtuse H–M–H angle may indicate increased metal-metal interaction. For example, Bergman and co-workers have shown that upon coordination of Ph_3Al to [Cp*Ir(PMe_3)($H)_2$] the H–Ir–H angle widens by 20°.[36] This result has been interpreted as evidence for metal–metal bonding in the

adduct [Cp*Ir(PMe_3)($H)_2$($AlPh_3$)]. Consistent with the NBO and QTAIM analysis, the calculated structures reveal a small increase in the H–W–H bond angle across the series (**1•W** ≈ **2•W** < **4•W**), suggesting a more significant Cu–W interaction in the latter (**1•W**; 81.7°, **2•W**; 81.2°, **4•W**; 84.3°).

The presence of weak M–M′ bond character in **1•W** and **4•W** is in contrast to similar complexes containing 3-centre,2-electron M–H–M′ interactions (see chapter 3 and chapter 4). Sadighi and co-workers concluded that a symmetrical, cationic complex containing a $\{Cu–H–Cu\}^+$ moiety is characterised by an open three-centre interaction. In this instance, the only metal–metal interaction occurs through the bridging hydride.[37] Our own investigations into neutral complexes containing asymmetric {Au–H–Cu} groups have led to similar conclusions (see chapter 4), with the main difference to the $\{Cu–H–Cu\}^+$ analogue being the asymmetry of the electron density in the three-centre core. Furthermore, QTAIM analysis on related main group adducts in which **W** is coordinated to either BF_3 or $AlMe_3$ indicates that no bond critical point is observed between the two electropositive atoms.[38]

a)



b)

	ρbcp	$\nabla^2\rho$ bcp
1•W	W–H = 0.15 Cu–H = 0.06 Cu---W = 0.06	W–H = +0.03 Cu–H = +0.19 Cu---W = +0.15
2•W	W–H = 0.15 Cu–H = 0.07	W–H = +0.03 Cu–H = +0.19
4•W	W–H = 0.15 Cu–H = 0.07 Cu---W = 0.07	W–H = +0.03 Cu–H = +0.21 Cu---W = +0.17

Figure 9 – a) QTAIM contour plots detailing bond critical points and bond critical paths for complexes 1-2•W and 4•W, b) selected data from QTAIM calculations

Geometry of the Tungsten Fragment

Single-point calculations in which the torsion angle N–Cu–W–C° was varied incrementally from +90° to -90° were performed on complexes **1•W** and **4•W** in order to investigate the geometry

of the tungsten dihydride fragment. These calculations show that for **1•W**, +45° is the optimal dihedral angle, with an energy difference of +19 kcal mol^{-1} calculated for maximum on the potential energy surface at -61°. In the case of **4•W**, a pseudo-planar geometry is preferred (+7.5°) with a pseudo-tetrahedral geometry being the maximum (-73 °, ΔSCF +9 kcal mol^{-1}).

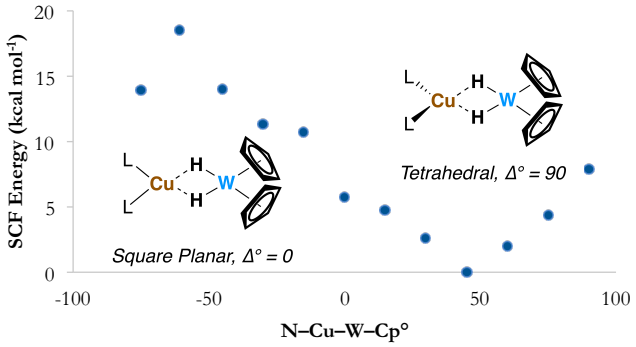


Figure 10 - Graphical representation of the energy of different geometries of 1•W

This enhanced bonding analysis provides an explanation for the structural variation in the single crystal diffraction studies of **1-2•W** and **4•W**. While borane adducts of these copper fragments demonstrated solid-state structures that are strictly tetrahedral at copper (see chapter 3), the tungsten analogues appear to adopt a variety of geometries between the extremes of tetrahedral and square planar in the solid state. This lack of a geometric preference can be comprehended by a combination of analysis of the frontier molecular orbitals (fMOs) of the $\{CuL_2\}$ fragment and considering them in combination with the NBO calculations. The dominant bonding interaction involves donation into an orbital that is largely 4s-based and approximately spherically symmetric. It is this large spherical orbital that ensures the W–H to Cu donation is retained regardless of the torsion angle between the two metal fragments. Moreover, back-donation from copper to the tungsten fragment, while weak, is possible from two orthogonal filled orbitals on the $\{CuL_2\}$ fragment (outlined in chapter 2) and as such is possible in both square planar and tetrahedral geometries.

4.3 Summary

In summary, the preparation and characterisation of three new heterobimetallic hydride complexes containing Cu–H–W bonds has been reported. In all cases an η^2:η^2-coordination mode is observed with the tungsten dihydride acting as a chelating ligand for copper(I). Multinuclear NMR spectroscopy data are consistent with these complexes being robust under ambient conditions in solution, although ligand exchange, likely by a dissociative mechanism, can be observed upon addition of an external phosphine ligand. Computational analysis of the bonding shows that the dominant interaction in the W–H–Cu 3-centre,2-electron core can be found between the tungsten and hydride atoms with weaker bonds between the copper and hydride atoms and the two metals. The calculations, in combination with solid state structures suggest that the inter-conversion between tetrahedral and square planar geometries at copper(I) is facile.

5. Future Work

As mentioned in chapter 4 for the series of Cu–H–Au heterobimetallics, expanding the series of Cu–H–W heterobimetallics to include the putative complex **5•W** with the use of copper(I) fragment **5**, which possesses a HOMO-1 that's significantly higher in energy than **1-2** and **4** may provide interesting comparison to the heterobimetallics reported in this chapter. Additionally, the synthesis and characterisation of heterobimetallics of the lighter group 6 metal molybdenum dihydride with copper(I) would provide an insight into the significance of the ionicity of the transition metal fragment in the formation of an M–M' interaction.

Continuation of the reactivity studies outlined in this chapter to include reactions of alkenes and alkynes should also be considered. Despite the heterobimetallics outlined in this chapter not favourably exchanging H_2 with external dihydrogen, activation of an alkene or alkyne by these heterobimetallics and subsequent reactivity in an atmosphere of H_2 may promote its reactivity. DFT calculations into the reaction between **2•W** and 4-octyne have been performed and suggest that the formation of **2•C_8H_{14}** could possibly be accessed to explore future reactivity ($\Delta G_{rxn}° = +8.26$ kcal mol^{-1}).

6. Thesis Conclusion

The synthesis and characterisation of a range of novel fluorinated *BDI* ligands, copper(I) complexes, σ-complexes and heterobimetallics has been achieved. In conjunction with DFT calculations, solution and solid state data has been used to provide a more in-depth analysis into the bonding confirmation within these types of complexes. In addition, mixtures of group 10 fragments with a gold hydride are selective in the formation of HCO_2Bpin, a formate equivalent, from CO_2 and HBPin.

The work in this thesis has resulted in the publication of three peer-reviewed journal articles. The author believes this is a valid contribution to the field of σ-complexes and heterobimetallics of the coinage metals. She hopes it will provide inspiration for future research.

7. Experimental

7.1 General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 and toluene-d_8 were stored over molecular sieves and distilled prior to use. NMR-scale reactions were conducted in J. Young's tap tubes and prepared in a glovebox. All heating mentioned was done using silicone oil baths. ^{1}H, ^{19}F, ^{11}B, ^{31}P and ^{13}C NMR spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated; all peak intensities are derived internal standard peak with values quoted in ppm. Data was processed using the MestReNova or Topspin software. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University. PCy_3 and **[(η^5-C_5H_5)$_2$$WH_2$]** were purchased from sigma Aldrich, $LiCH_2SiMe_3$ was purchased from Fischer Scientific and CO was purchased from CK gasses and used without further purification.

7.2 Preparative-Scale Synthesis

The copper(I) complexes **1_2•tol**, **2•tol** and **4•PPh$_3$** were synthesised according to procedures outlined in chapter 2.

1•W

In a glovebox, **1_2•tol** (61 mg, 0.055 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **[(η^5-C_5H_5)$_2$$WH_2$]** (38 mg, 0.11 mmol, 2 eq.) was weighed and dissolved in toluene (1.5 mL). The solution containing **[(η^5-C_5H_5)$_2$$WH_2$]** was added dropwise over 5 minutes to the stirred solution of **1_2•tol**. The reaction mixture was stirred for 30 minutes at room temperature before the red solution was filtered using glass fibre and the concentrated *in vacuo* to ½ of its original volume. *n*-Heptane (1.5 mL) was added and the reaction mixture was left at -35 °C overnight to give dark red crystals of **1•W** (46 mg, 0.05 mmol, 49%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ -12.4 (s, 2H, $^{1}J_{W-H}$ = 73.6 Hz, W–(*H*)$_2$–Cu), 2.17 (s, 6H, Ar–*Me*$_{Cu}$), 2.32 (s, 12H, Ar–*Me*$_{Cu}$), 3.65 (s, 10H, *Cp*$_W$), 6.26 (s, 1H, C*H*$_{Cu}$), 6.81 (s, 4H, Ar–*H*$_{Cu}$); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125 MHz) δ 19.2, 21.0, 22.2, 74.3, 83.6 (m), 122.7 (q, $^{1}J_{C-F}$ = 288.3 Hz), 129.0, 130.4, 132.6, 147.2, 151.7 (q, $^{2}J_{C-F}$ = 24.2 Hz); ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -64.0 (s).

Elemental analysis calc. for $C_{33}H_{35}CuF_6N_2W$: C, 48.28; H, 4.30; N, 3.41. Found: C, 48.39; H, 4.20; N, 3.54.

2•W

In a glovebox, **2•tol** (62 mg, 0.11 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **[(η^5-C_5H_5)$_2$WH$_2$]** (38 mg, 0.11 mmol) was weighed and dissolved in toluene (1.5 mL). The solution containing **[(η^5-C_5H_5)$_2$WH$_2$]** was added dropwise over 5 minutes to the stirred solution of **2•tol**. The reaction mixture was stirred for 30 minutes at room temperature before the orange solution was filtered using glass fibre and concentrated *in vacuo* to ½ of its original volume. *n*-Heptane (1.5 mL) was added and the reaction mixture was left at -35 °C overnight to give yellow crystals of **2•W** (64 mg, 0.08 mmol, 69%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ -12.2 (s, 2H, $^1J_{W–H}$ = 72.2 Hz, W–(*H*)$_2$–Cu), 1.73 (s, 6H, Ar–*Me*$_{Cu}$), 3.76 (s, 10H, *Cp*$_W$), 4.98 (s, 1H, C*H*$_{Cu}$); ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 125 MHz) δ 23.8, 73.6, 97.6, 129.5 (m), 135.7 (m), 138.3 (m), 141.5 (m), 165.4; ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -166.2 (m, 2F), -165.2 (m, 4F), -150.8 (m, 4F). Elemental analysis calc. for $C_{27}H_{19}CuF_{10}N_2W$: C, 40.09; H, 2.37; N, 3.46. Found: C, 40.20; H, 2.35; N, 3.56.

4•W

In a glovebox, **4•PPh$_3$** (67.7 mg, 0.11 mmol) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, **[(η^5-C_5H_5)$_2$WH$_2$]** (38 mg, 0.11 mmol) was weighed and dissolved in toluene (1.5 mL). The solution containing **[(η^5-C_5H_5)$_2$WH$_2$]** was added dropwise over 5 minutes to the stirred solution of **4•PPh$_3$**. The reaction mixture was stirred for 30 minutes at room temperature before the red solution was filtered using glass fibre and the solvent removed *in vacuo* to give the crude as an orange solid. The crude was triturated with *n*-hexane (3 mL) giving **4•W** as a red crystalline solid (39 mg, 0.05 mmol, 48%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ -13.5 (s, 2H, $^1J_{W–H}$ = 76.4 Hz, W–(H)$_2$–Cu), 2.07 (s, 3H, Ar–Me$_{Cu}$), 2.19 (s, 6H, Ar–Me$_{Cu}$), 3.99 (s, 10H, Cp$_W$), 6.20 (s, 1H, CH$_{Cu}$), 6.69 (s, 2H, Ar–H$_{Cu}$); ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 125 MHz) δ 18.8, 20.9, 75.6, 85.4, 120.5 (q, $^1J_{C–F}$ = 286.6 Hz), 120.5 (q, $^1J_{C–F}$ = 288.4 Hz), 128.8, 133.4, 145.6, 155.1 (q, $^2J_{C–F}$ = 26.2 Hz), 170.3 (q, $^2J_{C–F}$ = 30.9 Hz); ^{19}F NMR (C_6D_6, 298 K, 470.4 MHz) δ -74.7 (3F), -65.9 (3F). Elemental analysis calc. for $C_{26}H_{30}CuF_6NOW$: C, 40.96; H, 3.44; N, 1.99. Found: C, 40.77; H, 3.52; N, 2.05.

7.3 NMR-Scale Reactions

H/D Exchange

In a glovebox, **2•W** (19 mg, 0.023 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube with J Young's adapter. The tube was freeze-pump-thaw degassed on a Schlenk-line three times before being exposed to an atmosphere of D_2. The reaction was followed *via* ^{1}H NMR spectroscopy. No H/D exchange was observed before the onset of complex decomposition at 80 °C.

{CpWH$_2$•LiCH$_2$SiMe$_3$•Cu}$_2$

In a glovebox, **1•W** (6 mg, 0.008 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube fitted with Young's adapter, whereby a 1M solution of $LiCH_2SiMe_3$ (14.2 μL, 0.016 mmol, 2 eq.) was added *via* graduated pipette. The tube was removed from the glovebox and the reaction followed *via* ^{1}H, ^{19}F and ^{7}Li NMR spectroscopy.

1•W + PCy$_3$

In a glovebox, **1•W** (6 mg, 0.007 mmol) was dissolved in benzene-d_6 (500 μL) and transferred to an NMR tube fitted with Young's adapter. Similarly, PCy_3 (2 mg, 0.007 mmol) was dissolved in benzene-d_6 (100 μL) and added to the tube containing the copper complex. The tube was removed from the glovebox and the reaction followed *via* ^{1}H, ^{19}F ^{31}P NMR spectroscopy.

2•W + PCy$_3$

In a glovebox, **2•W** (6 mg, 0.007 mmol) was dissolved in benzene-d_6 (500 μL) and transferred to an NMR tube fitted with Young's adapter. Similarly, PCy_3 (2 mg, 0.007 mmol) was dissolved in benzene-d_6 (100 μL) and added to the tube containing the copper complex. The tube was removed from the glovebox and the reaction followed *via* ^{1}H, ^{19}F ^{31}P NMR spectroscopy.

4•W + PCy$_3$

In a glovebox, **4•W** (10 mg, 0.01 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to an NMR tube fitted with Young's adapter. Similarly, PCy_3 (4 mg, 0.01 mmol) was dissolved in benzene-d_6 (300 μL) and added to the tube containing the copper complex. The tube was removed from the glovebox and the reaction followed *via* ^{1}H, ^{19}F ^{31}P NMR spectroscopy.

1•W + CO

In a glovebox, **1•W** (18 mg, 0.021 mmol) was dissolved in benzene-d_6 (600 μL) and transferred to an NMR tube fitted with Young's adapter. The tube was freeze-pump thawed on a Schlenk-line fitted with Young's adapter three times before being exposed to an atmosphere of CO (0.14 mmol, xs.). The reaction was followed by ^{1}H and ^{19}F NMR spectroscopy whereby decomposition of **1•W** was observed at room temperature.

4•PCy₃

In a glovebox, **4•PPh₃** (8 mg, 0.01 mmol) was dissolved in benzene-d_6 (300 μL) and transferred to an NMR tube fitted with Young's adapter. Similarly, **PCy₃** (4 mg, 0.01 mmol) was dissolved in benzene-d_6 (300 μL) and added to the tube containing the copper complex. The tube was removed from the glovebox and the reaction followed *via* ^{1}H, ^{19}F ^{31}P NMR spectroscopy whereby the formation of **4•PCy₃** was observed.

Multinuclear NMR spectra for preparative scale (section 2.4) and NMR scale (section 3.4) reactions along with X-ray acquisition parameters (section 4.4) and Z-matrices for DFT-optimised structures (section 5.4) can be found in the appendix.

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dumplings rather than flowers

Appendix

1. Key Equations

1.1 Stokes Einstein Equation

DOSY NMR is a pulse-field spin-gradient experiment, in which complexes diffuse through solution. The signal corresponding to each complex decays at different diffusion rates and thus a diffusion coefficient for each set of signals can be calculated.[1] For radius R, let k_B be the Boltzmann constant (1.38064852×10^{-23} JK^{-1}), T the temperature by which the NMR experiment conducted at (K), η represent solvent viscosity and D the diffusion coefficient gathered from NMR experiments.

$$R = \frac{k_B T}{6\pi\eta D}$$

1.2 Calculation of yields for reduction of CO_2 with HBPin

In order to compare the yields and TON's for the products of reactions occurring with differing reaction stoichiometry, each product was normalised to 1 proton *via* the equations outlined below. The integration of HBPin was measured from the methyl peak, (A) was measured from the peak corresponding to the formate proton and the value of (C) was taken from the peak corresponding to the methylene protons.

$$mmol\ HCO_2BPin\ (\boldsymbol{A}) = \frac{mmol\ HBPin \times 12}{\int HBPin} \times \int HCO_2BPin$$

$$mmol\ O(BPin)_2\ (\boldsymbol{B}) = \frac{mmol\ HBPin \times 12}{\int HBPin} \times \frac{\int O(BPin)_2}{24}$$

$$mmol\ CH_2(OBPin)_2\ (\boldsymbol{C}) = \frac{mmol\ HBPin \times 12}{\int HBPin} \times \frac{\int CH_2(OBPin)_2}{2}$$

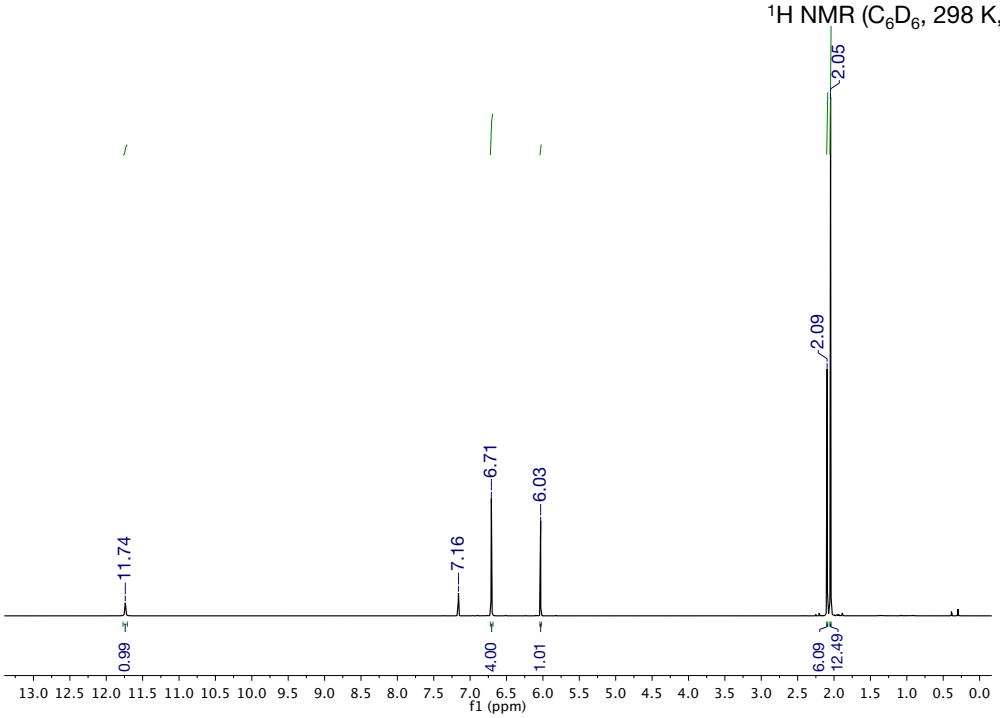
[1] R. Huo, R. Wehrens, J. van Duynhoven, L. M. C. Buydens, *Anal. Chim. Acta,* **2003**, *490*, 231–251.

2. Preparative Scale NMR Data

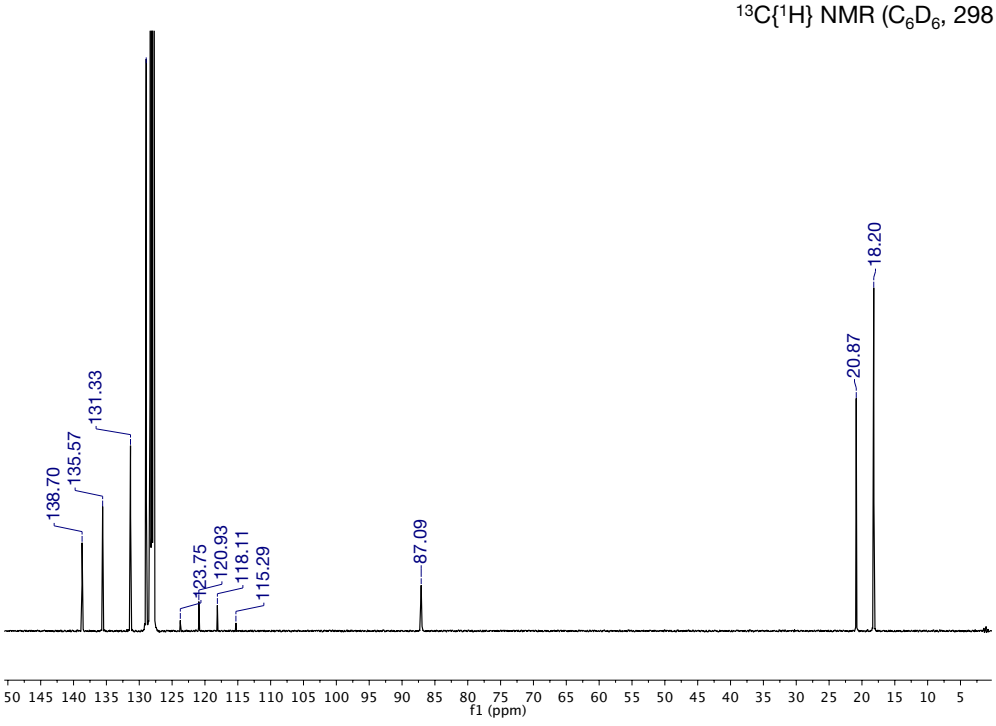
2.1 Chapter 2

L^1H - ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra

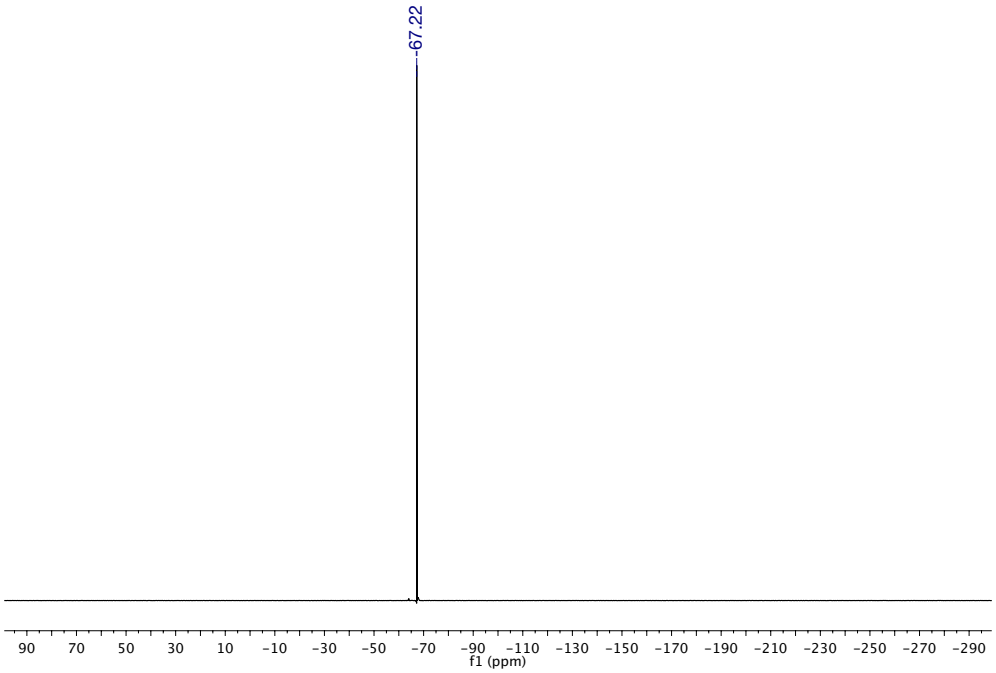
L^1H ^1H NMR (C_6D_6, 298 K, 400.0 MHz)



L^1H $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 100 MHz)

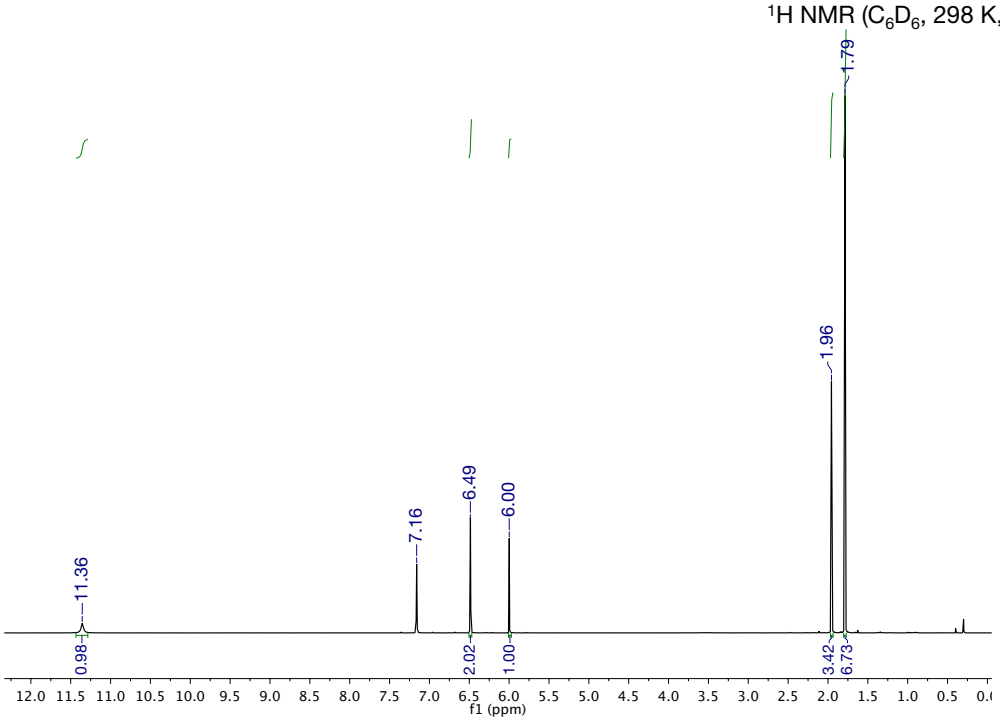


L[1]H $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

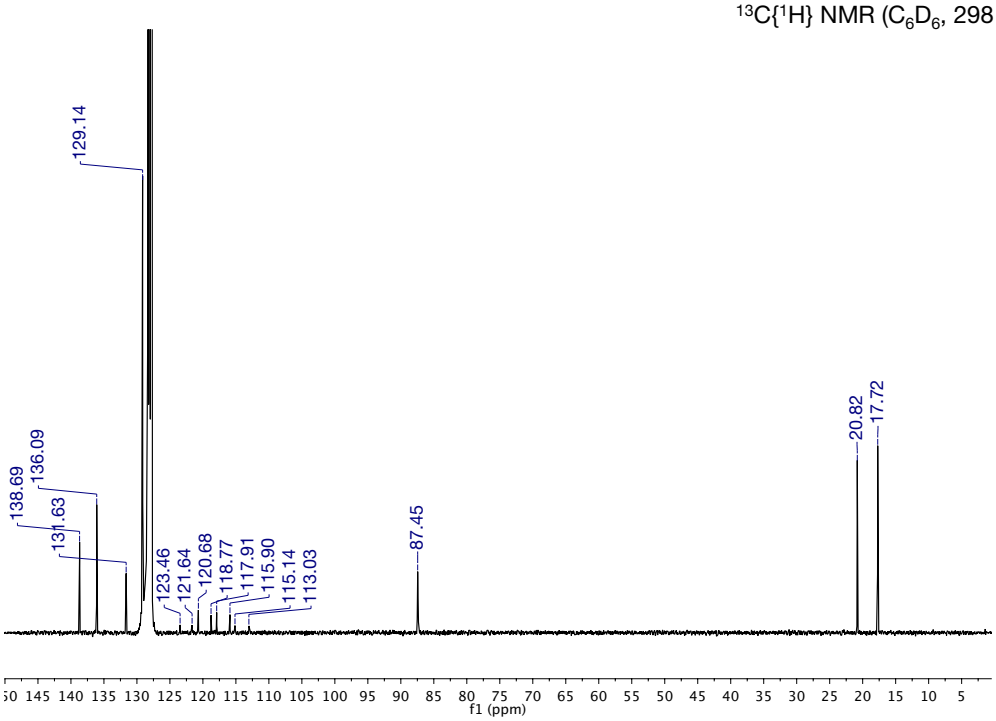


L^4H - ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra

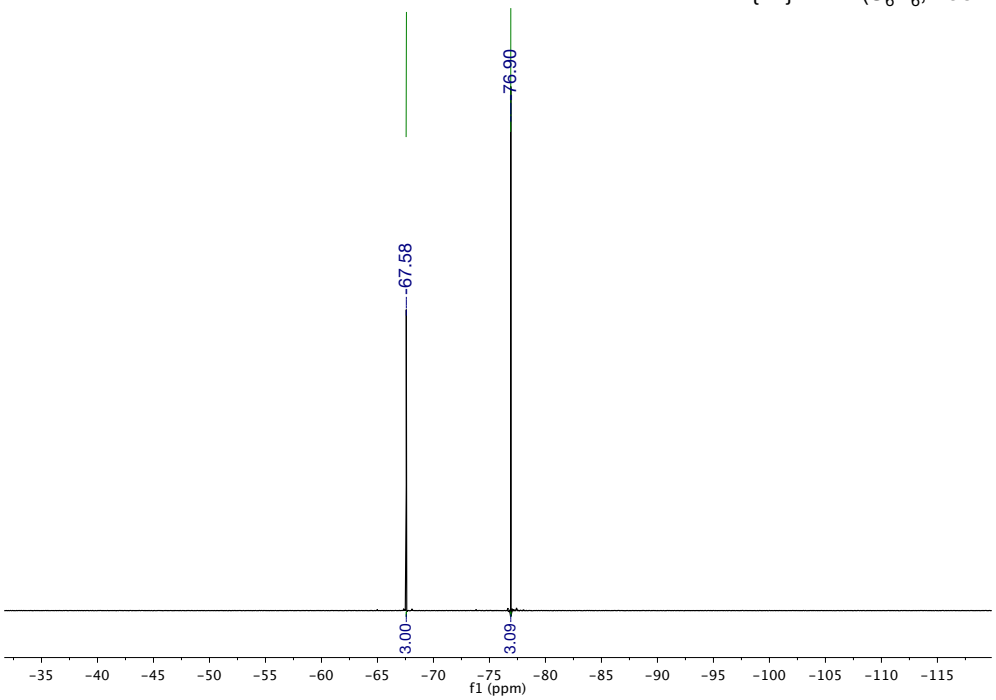
L[4]H ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



L^{4}H $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 100 MHz)

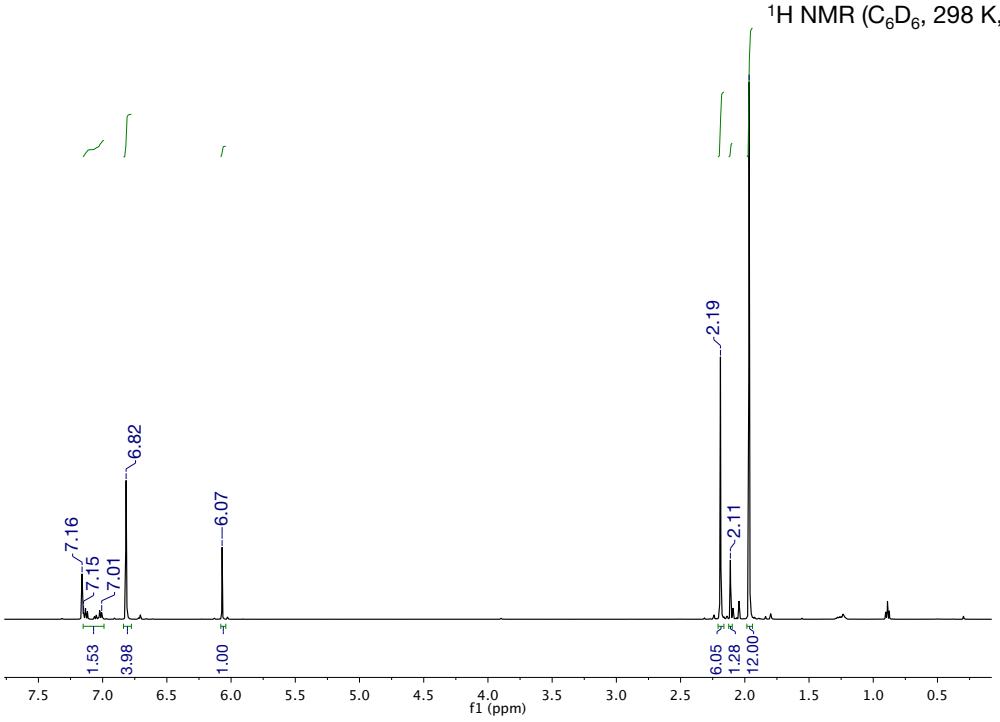


L^{4}H $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

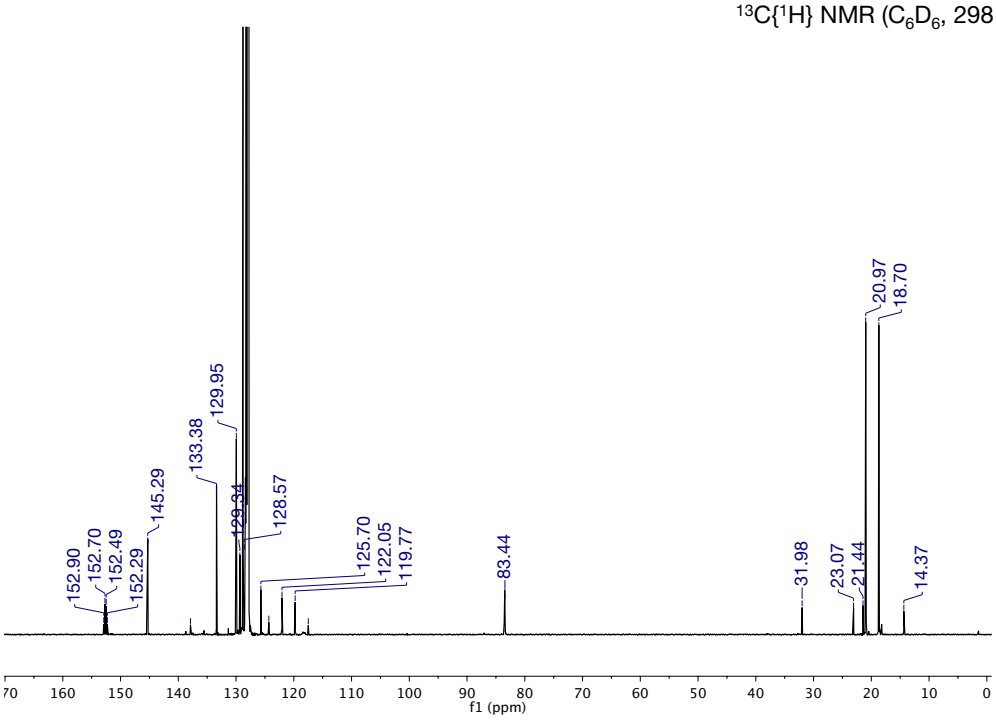


1_2•tol - ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra

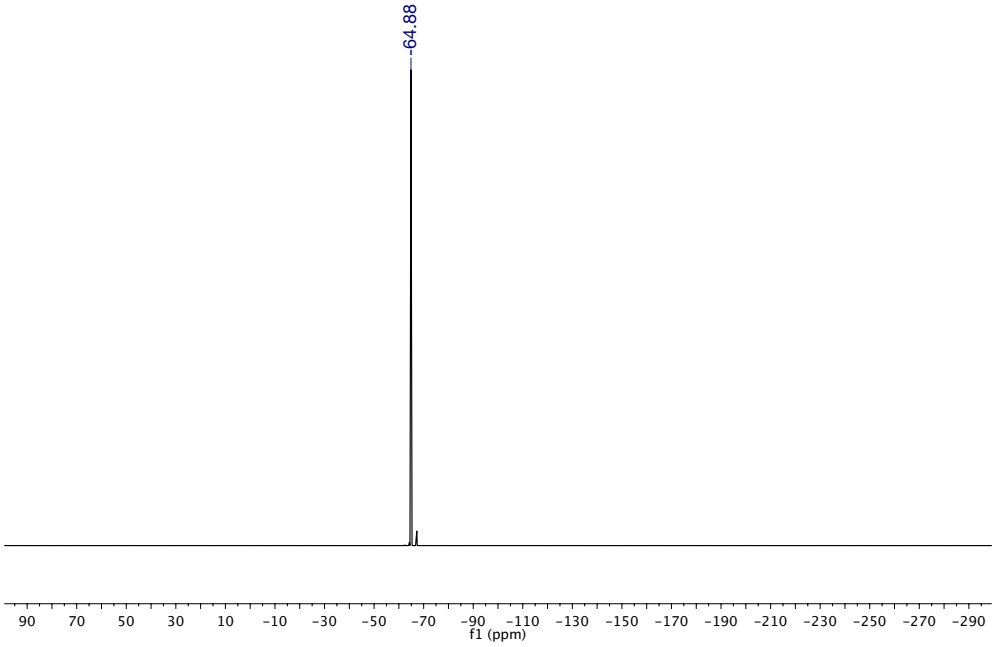
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1_2•tol $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125 MHz)

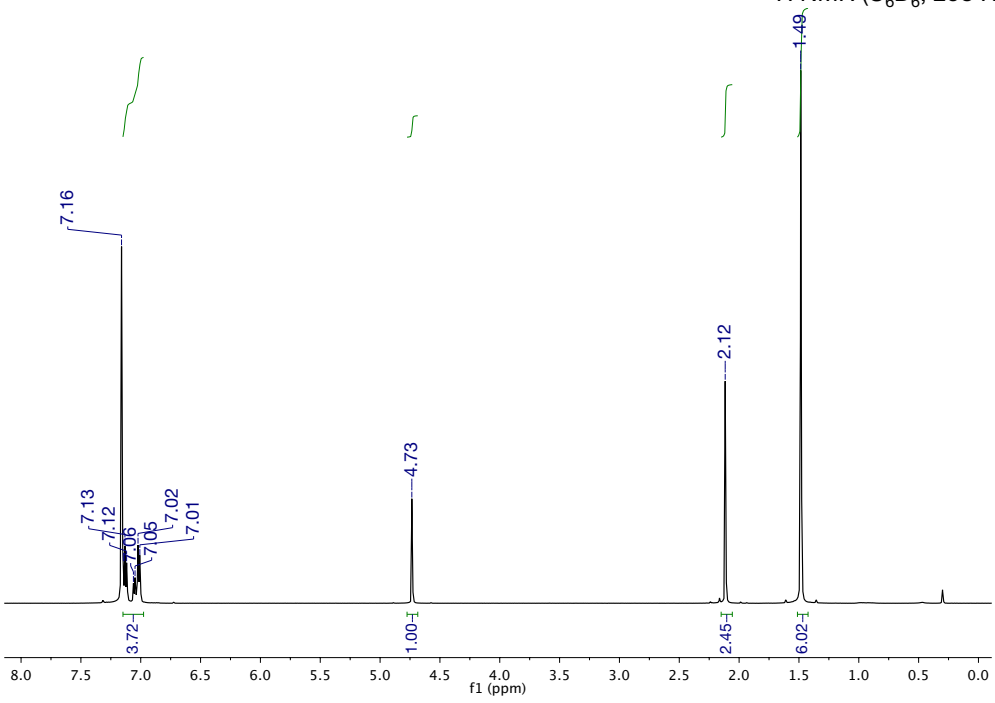


1_2•tol $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)

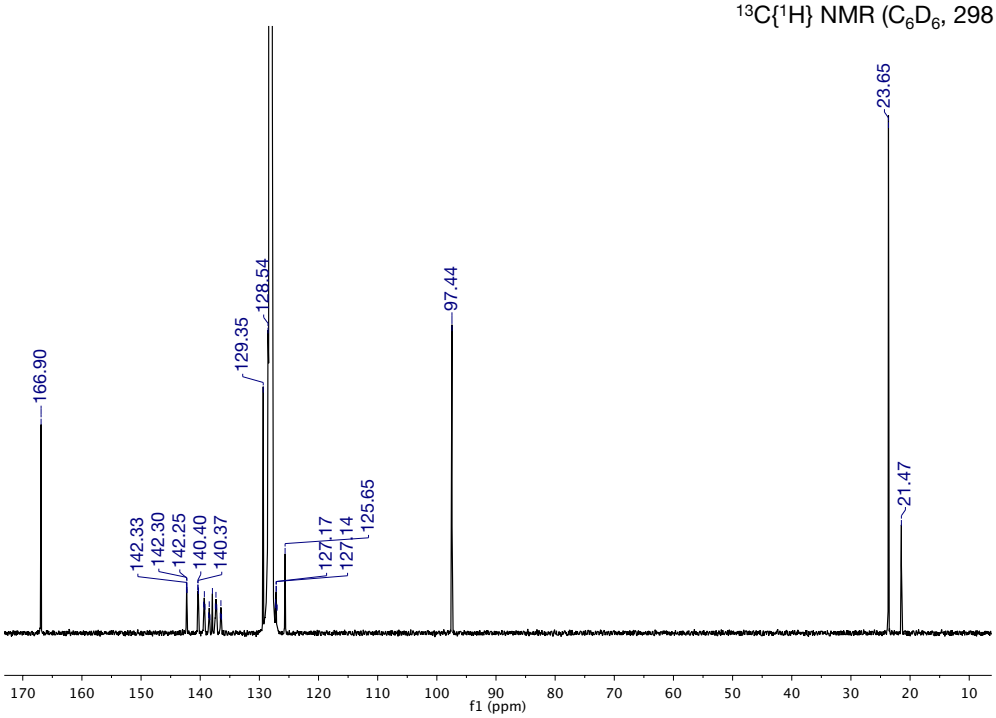


2•tol - ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra

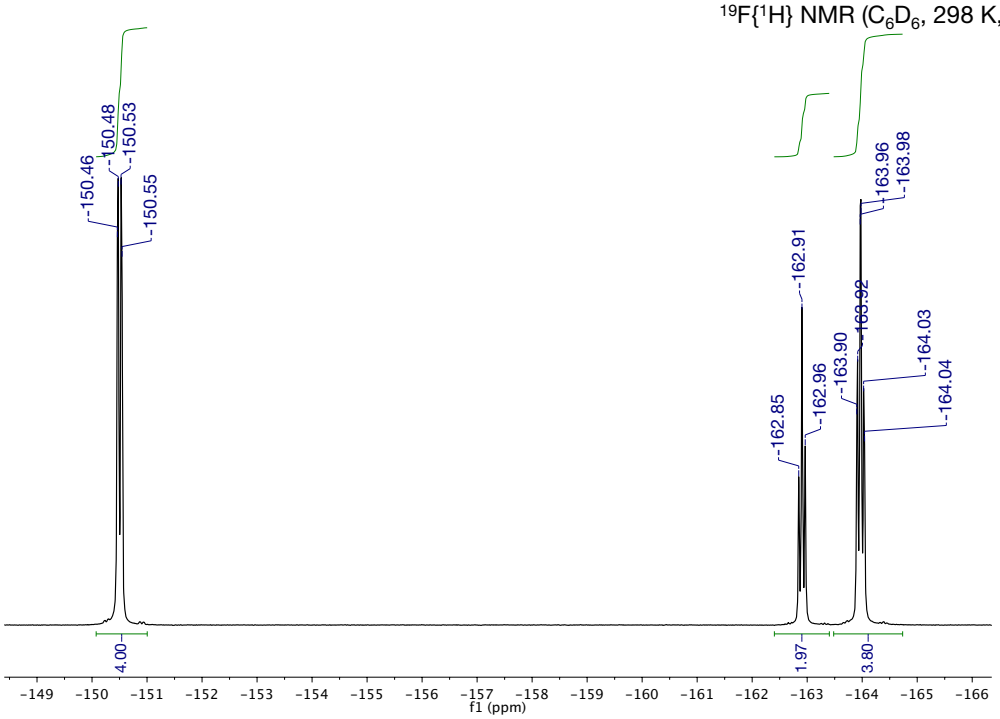
2•tol ^1H NMR (C_6D_6, 298 K, 500.0 MHz)



2·tol $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125 MHz)

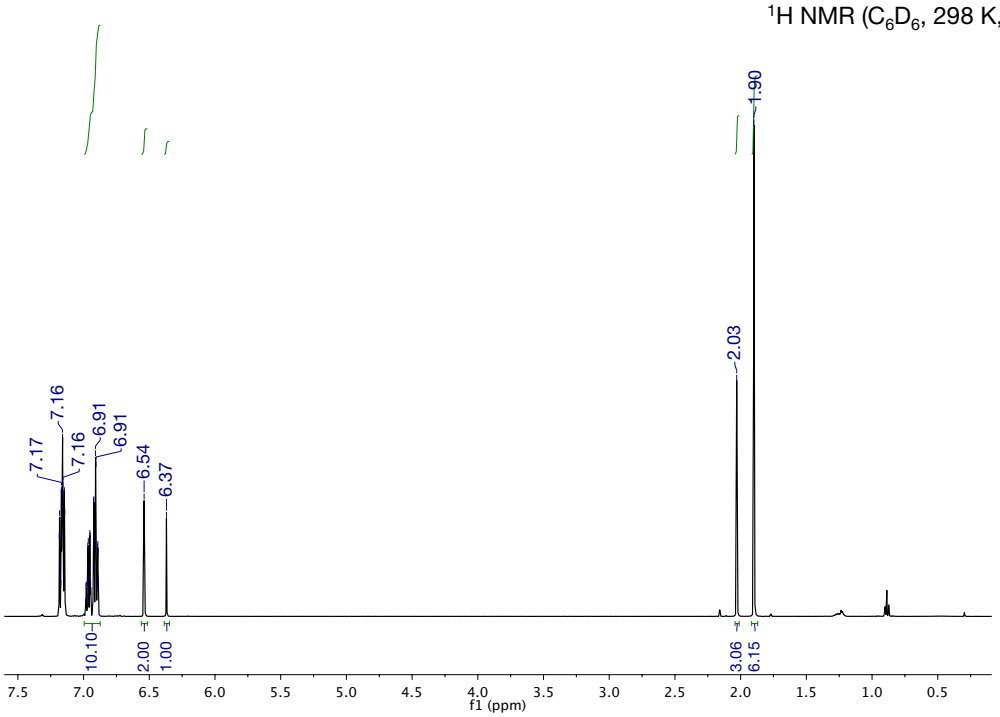


2·tol $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)

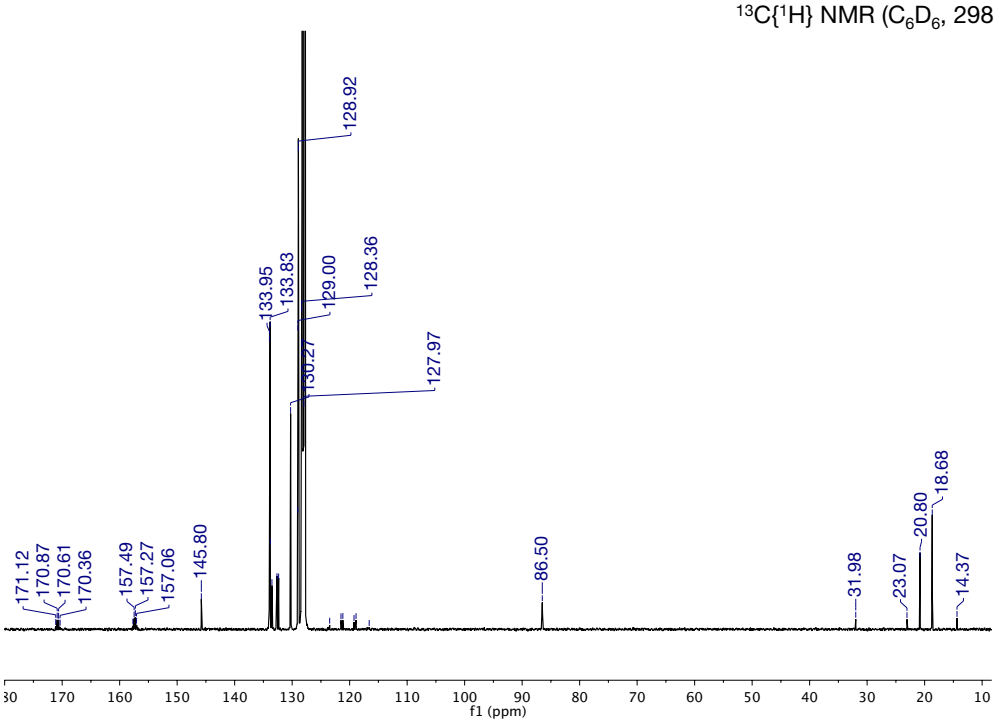


4•PPh₃ - ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra

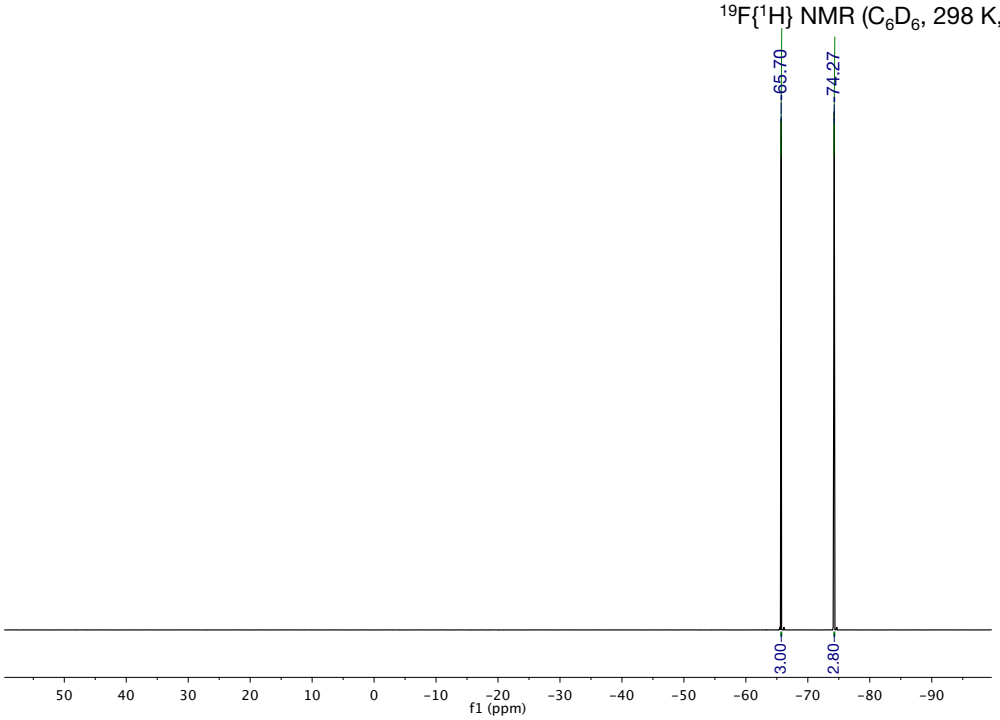
4•PPh$_3$ ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



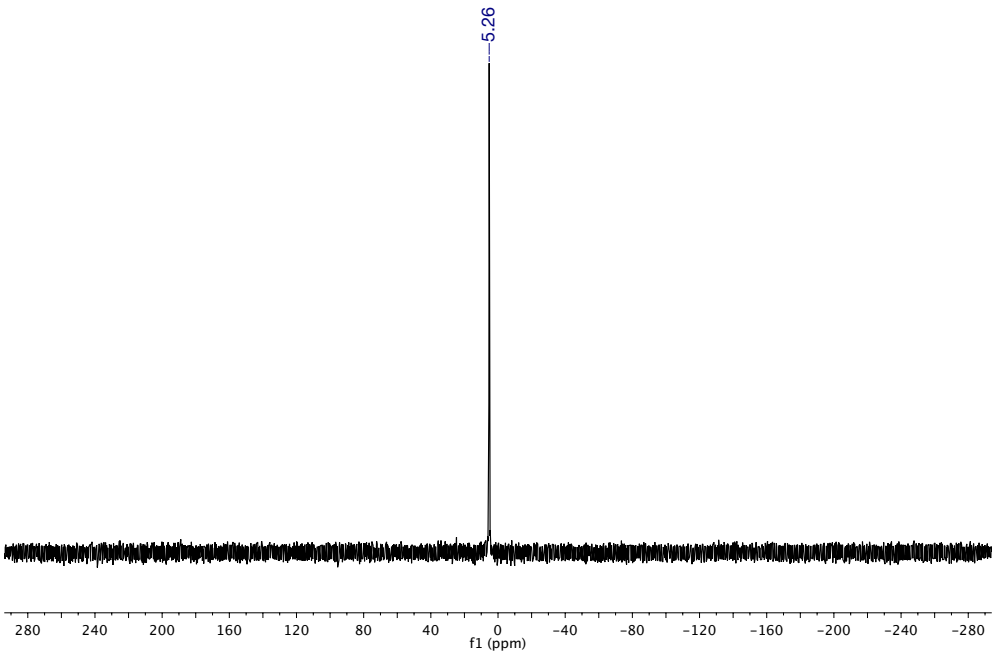
4•PPh$_3$ ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 125 MHz)



4·PPh$_3$ $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



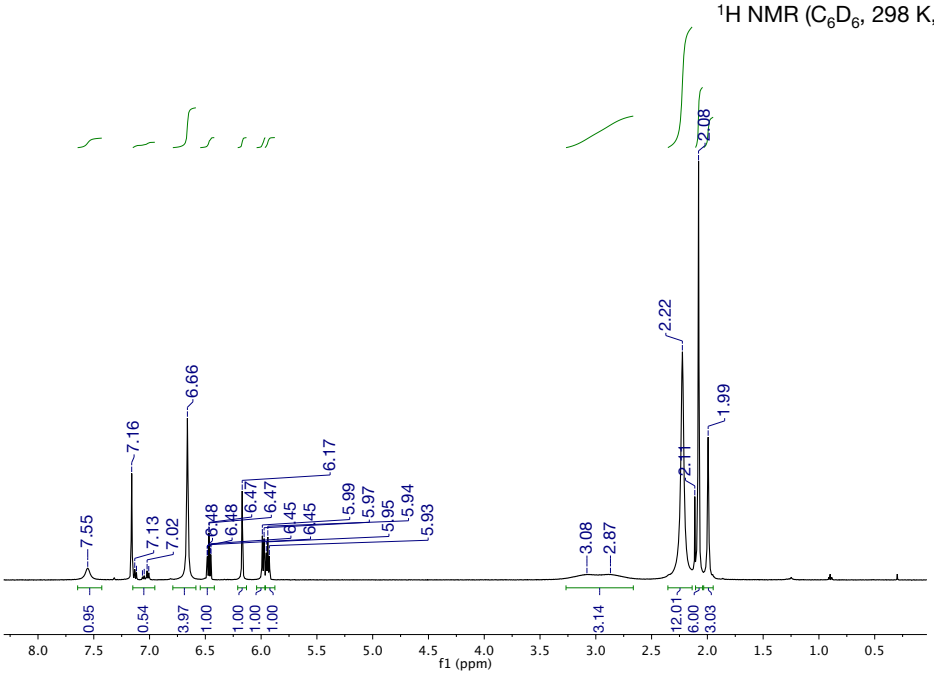
4·PPh$_3$ $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 202.4 MHz)



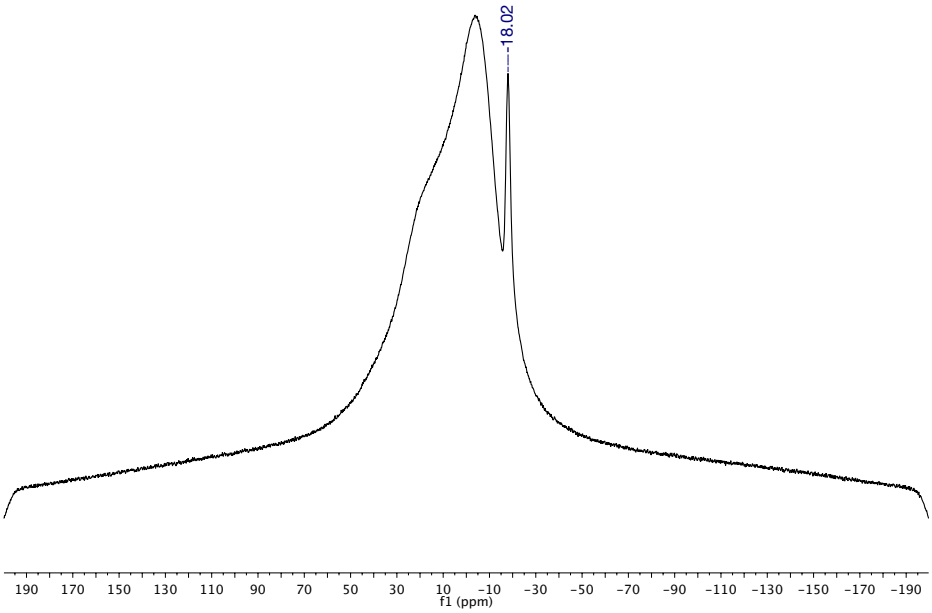
2.2 Chapter 3

1•B - ^{1}H, $^{11}B\{^{1}H\}$ $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

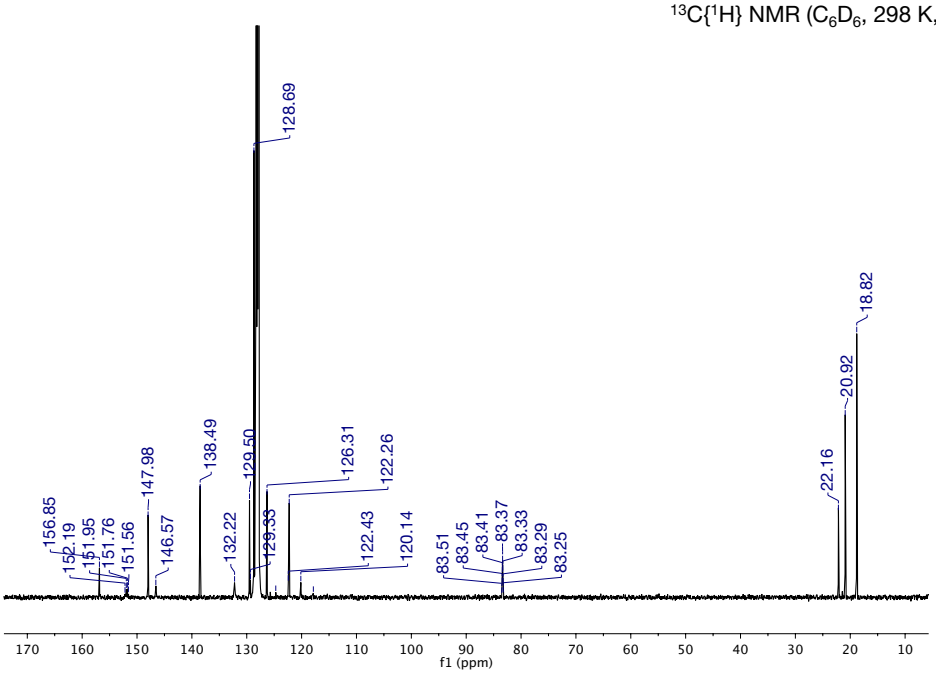
1•B ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



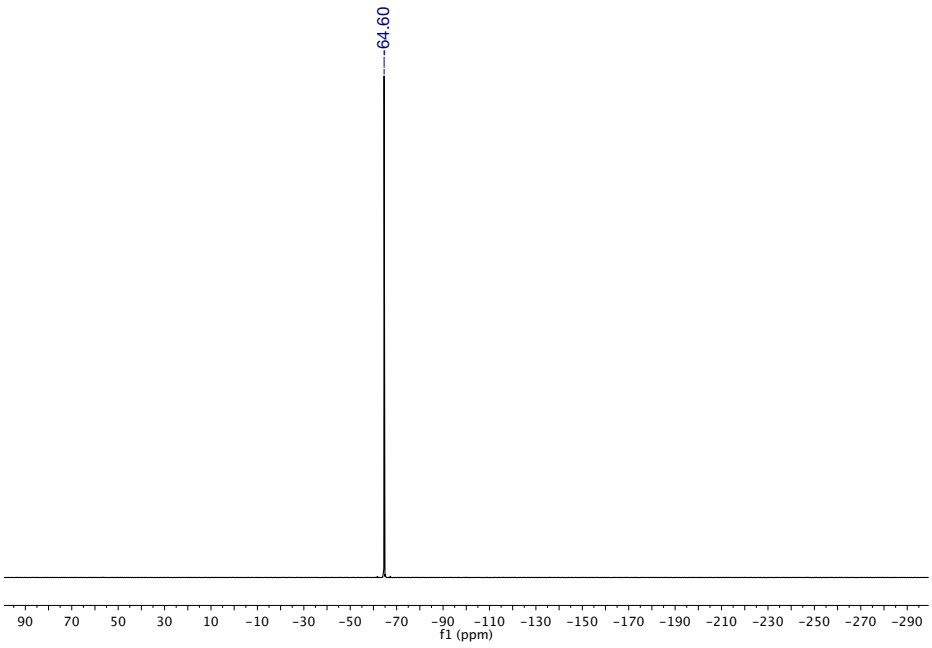
1•B $^{11}B\{^{1}H\}$ NMR (C_6D_6, 298 K, 160.4 MHz)



1·B $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



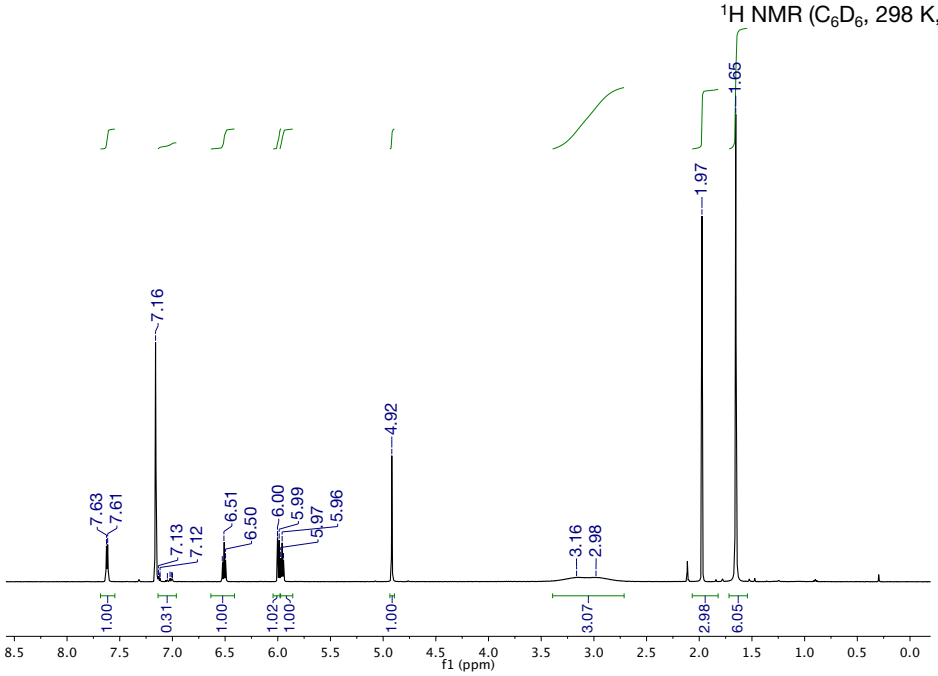
1·B $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



2•B - ^{1}H, $^{11}B\{^{1}H\}$ $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

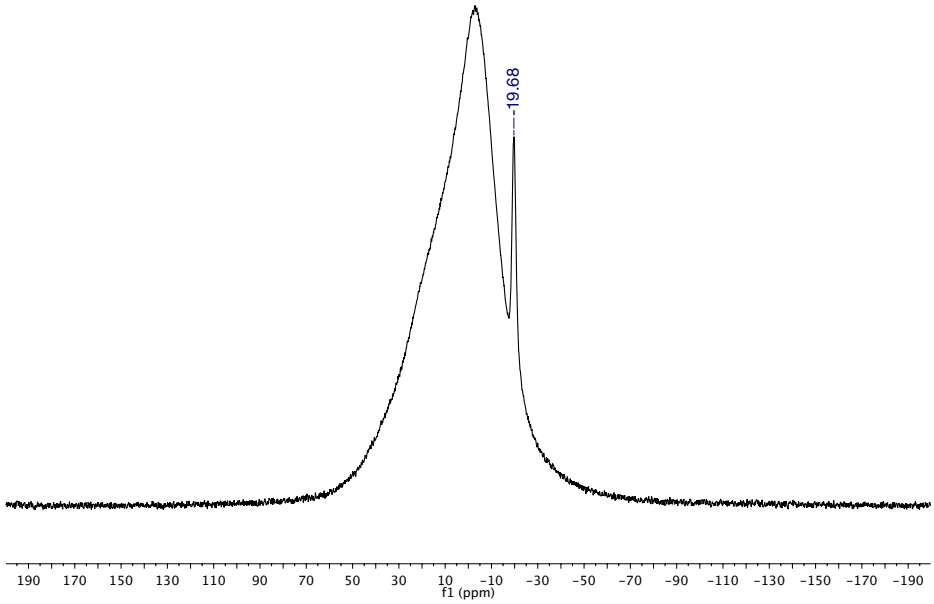
2•B

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)

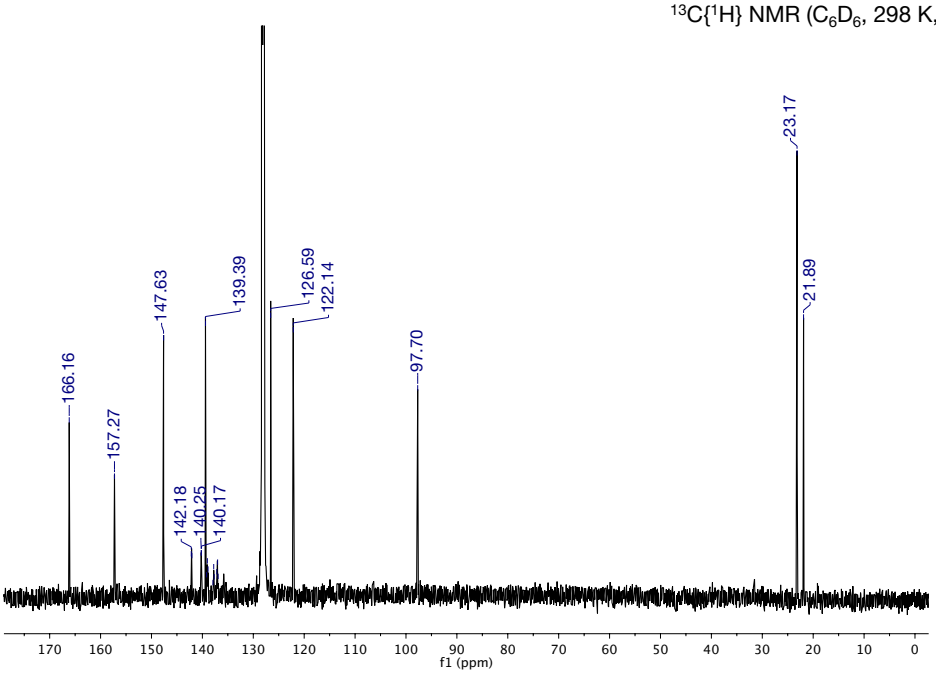


2•B

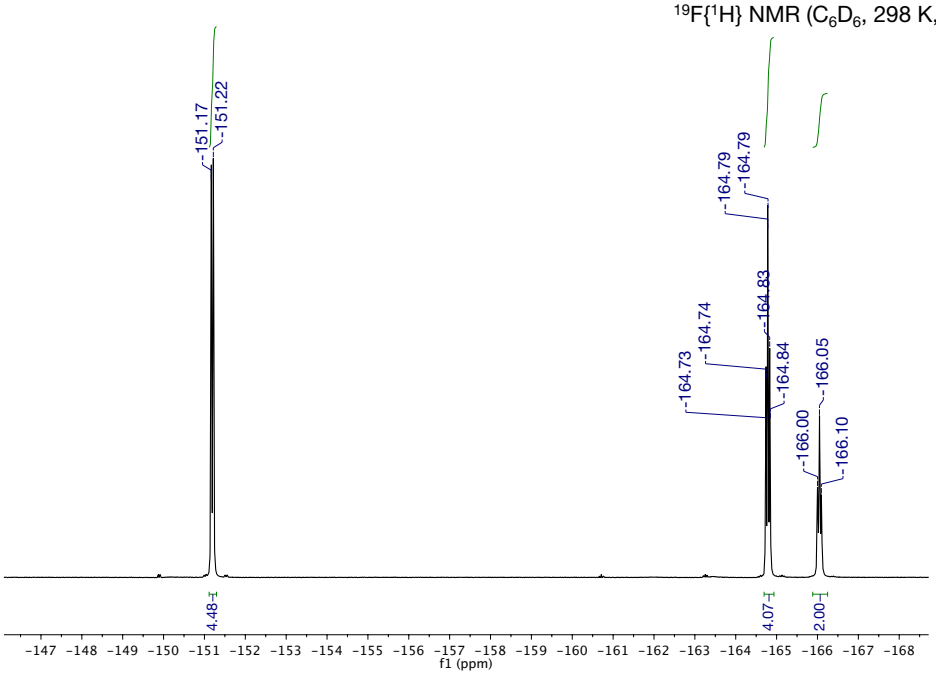
$^{11}B\{^{1}H\}$ NMR (C_6D_6, 298 K, 160.4 MHz)



2•B $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)

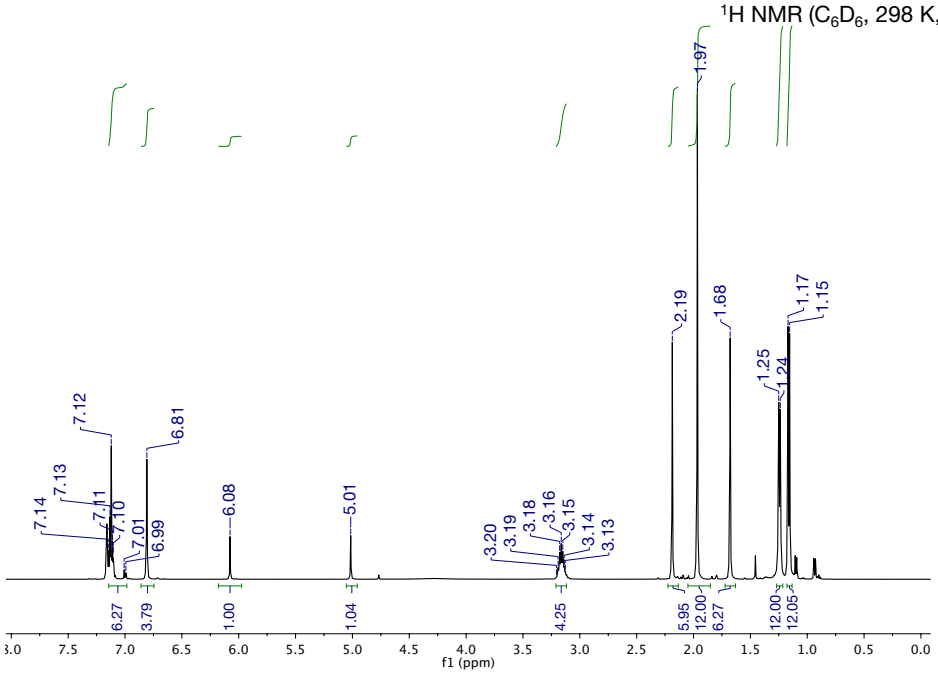


2•B $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)

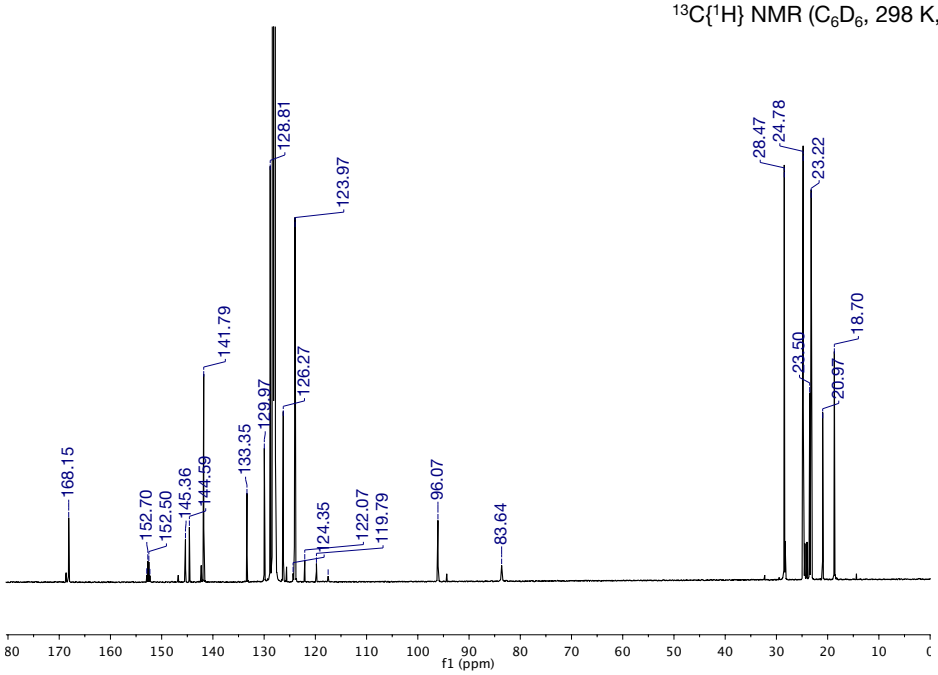


1•Zn - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

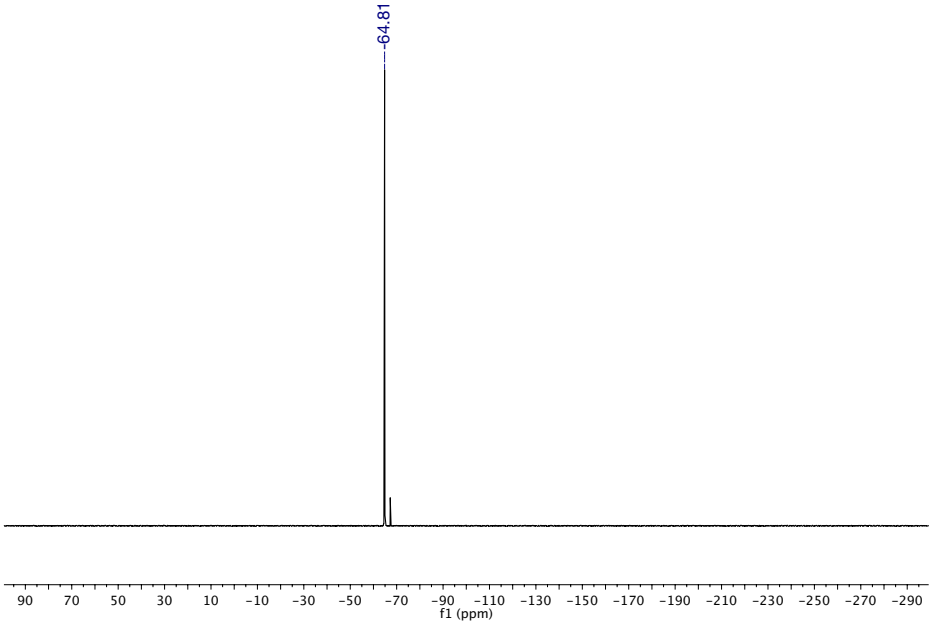
1·Zn ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



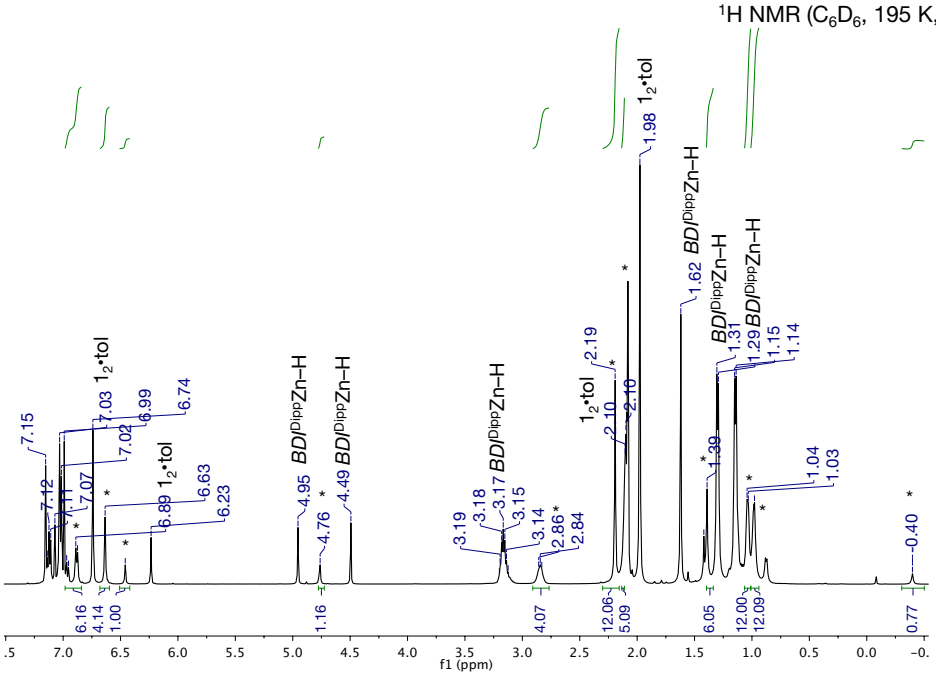
1·Zn $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



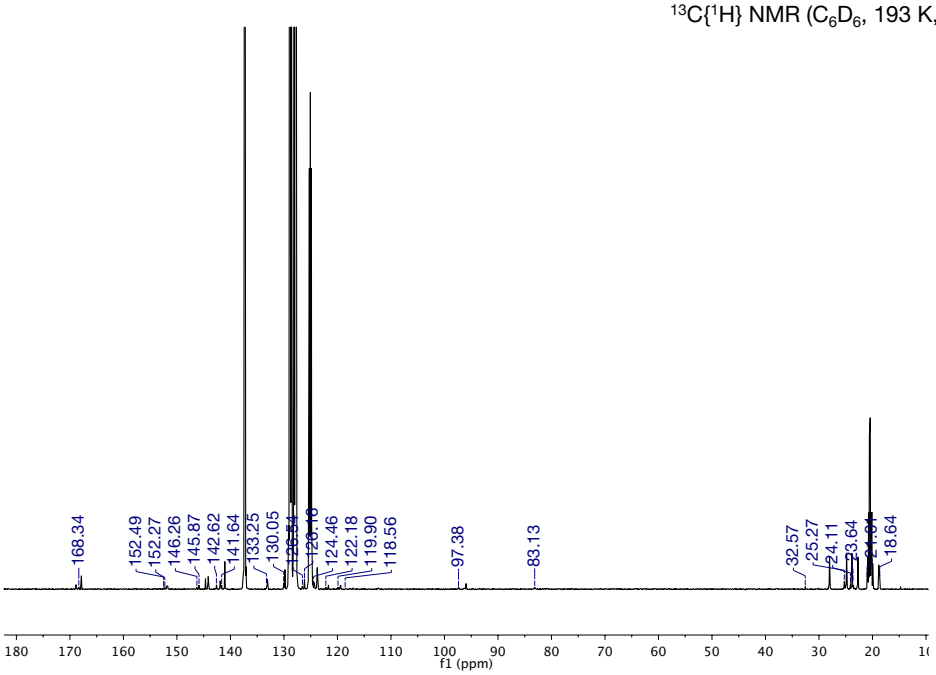
1·Zn $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



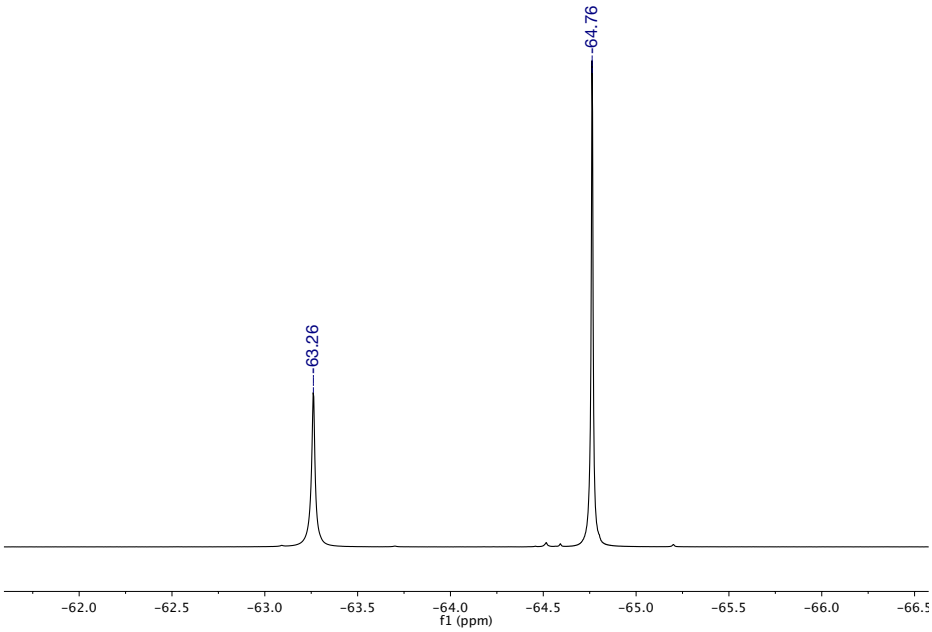
1·Zn ^{1}H NMR (C_6D_6, 195 K, 500.0 MHz)



1·Zn $^{13}C\{^{1}H\}$ NMR (C_6D_6, 193 K, 125.0 MHz)

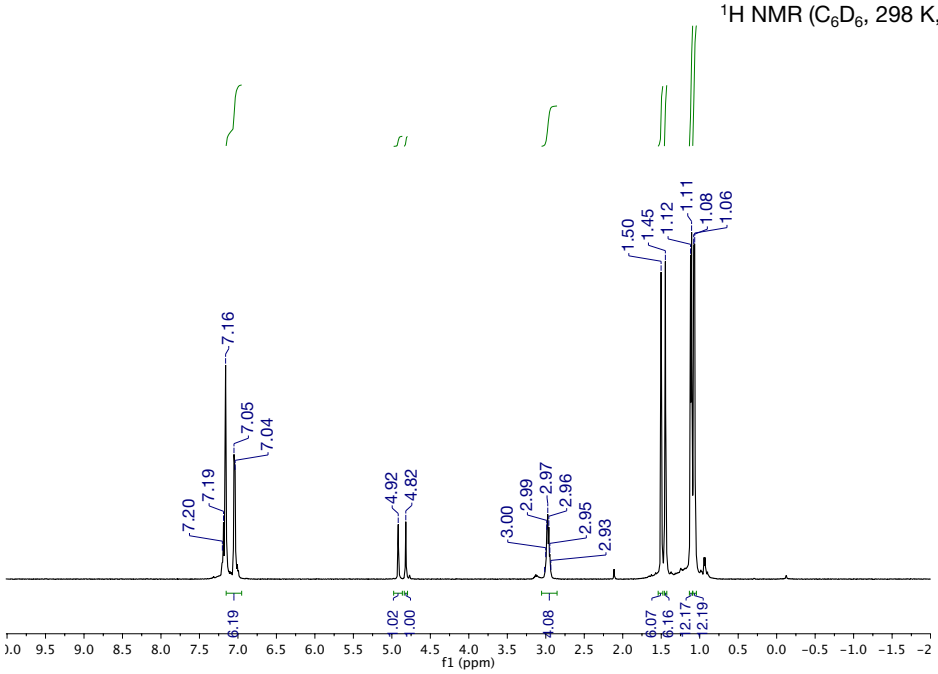


1·Zn $^{19}F\{^{1}H\}$ NMR (C_6D_6, 193 K, 470.4 MHz)

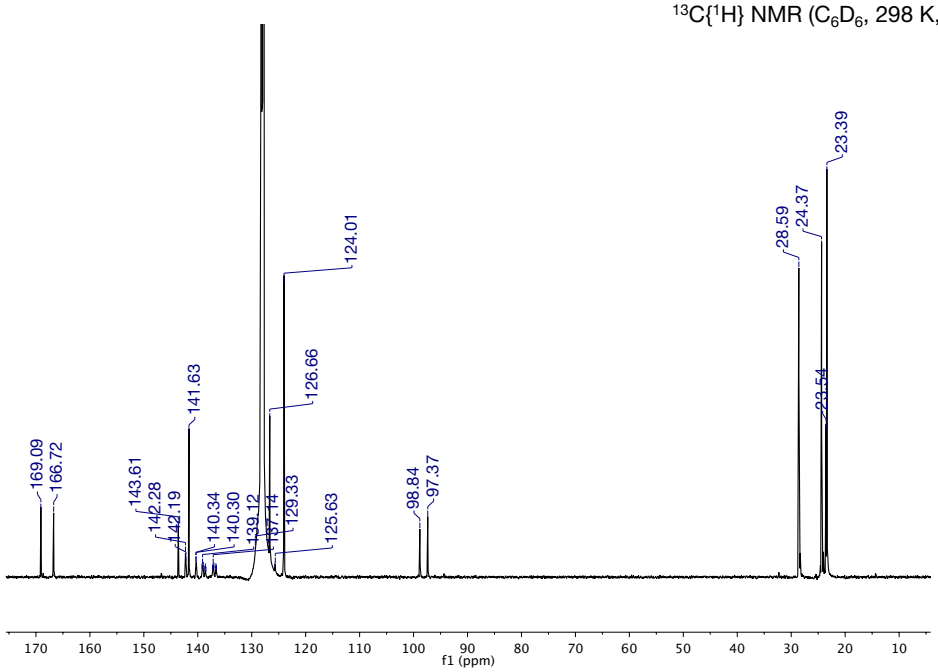


2•Zn - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

2·Zn ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)

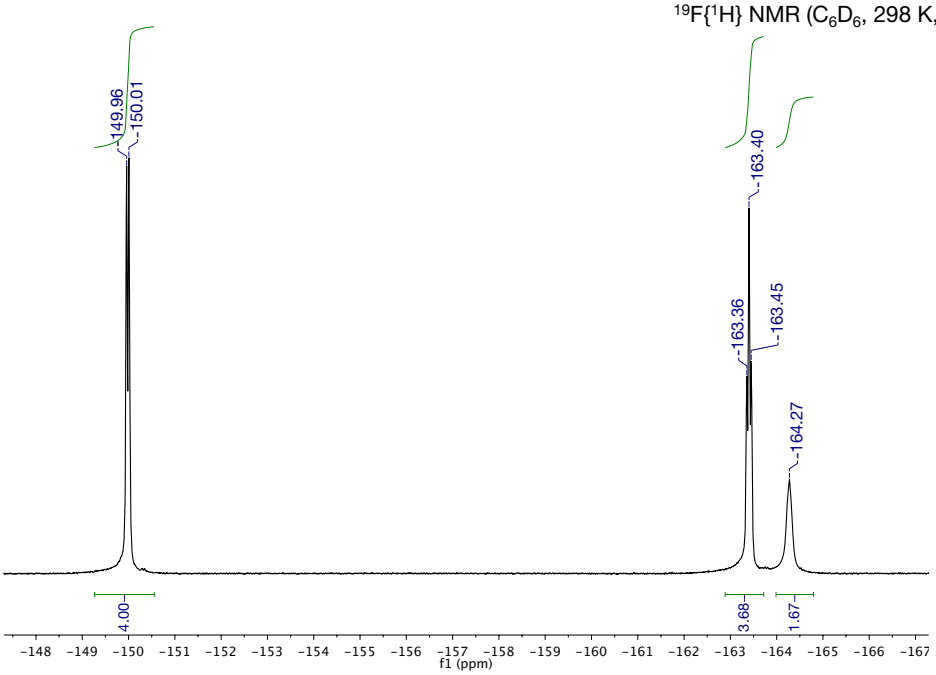


2·Zn $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



2·Zn

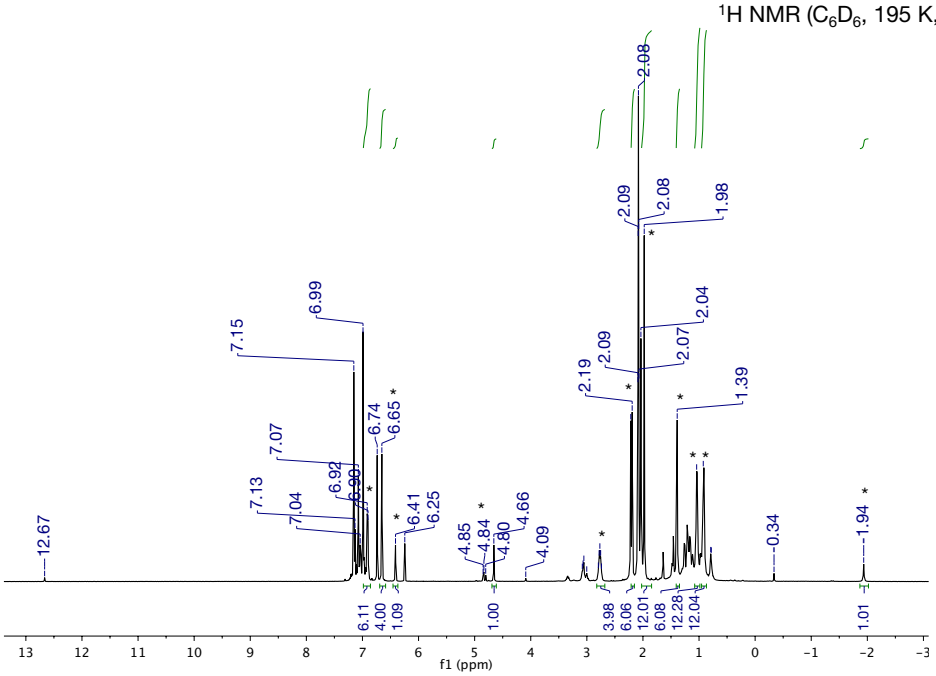
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



1•Mg - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

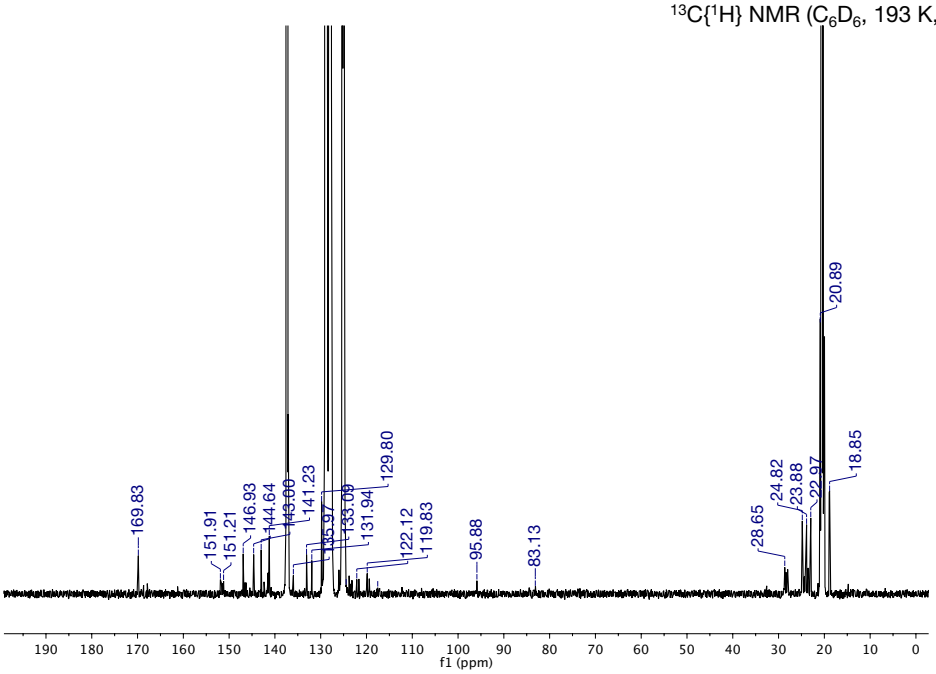
1·Mg

^{1}H NMR (C_6D_6, 195 K, 500.0 MHz)



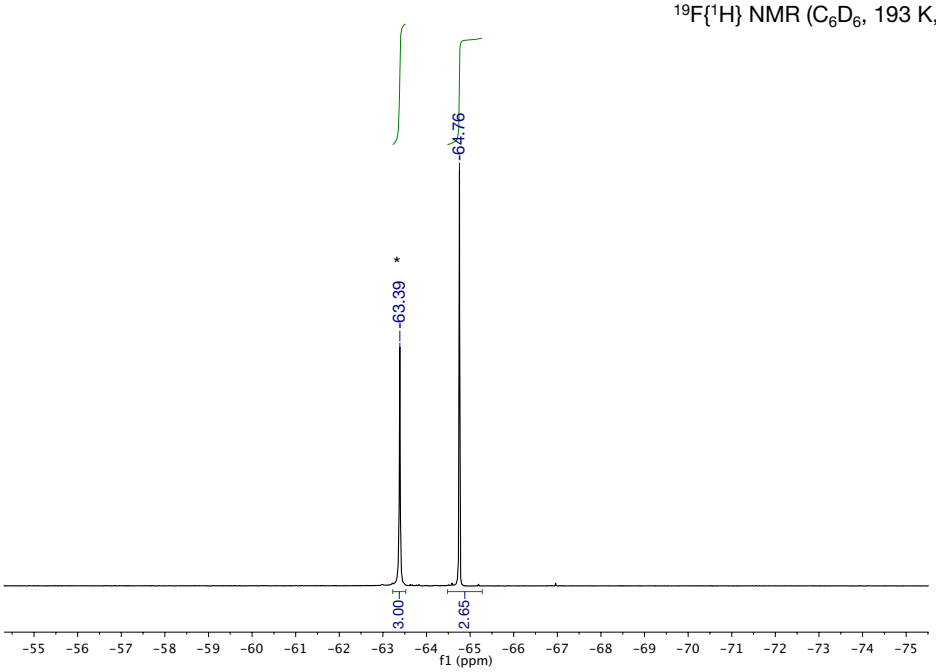
1·Mg

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 193 K, 125.0 MHz)



1·Mg

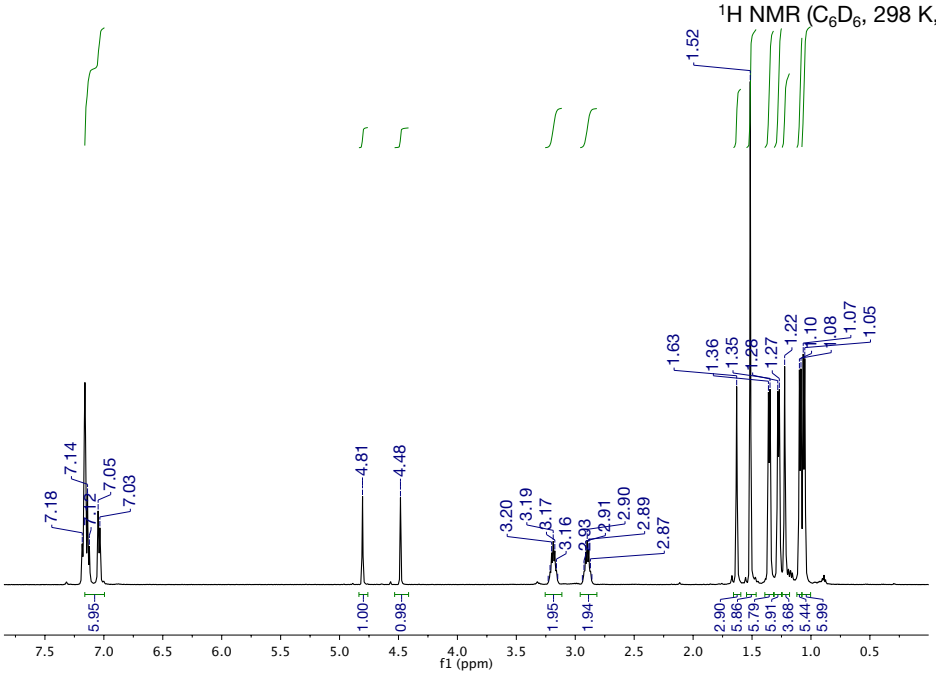
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 193 K, 470.4 MHz)



L^2MgL^7 - ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra

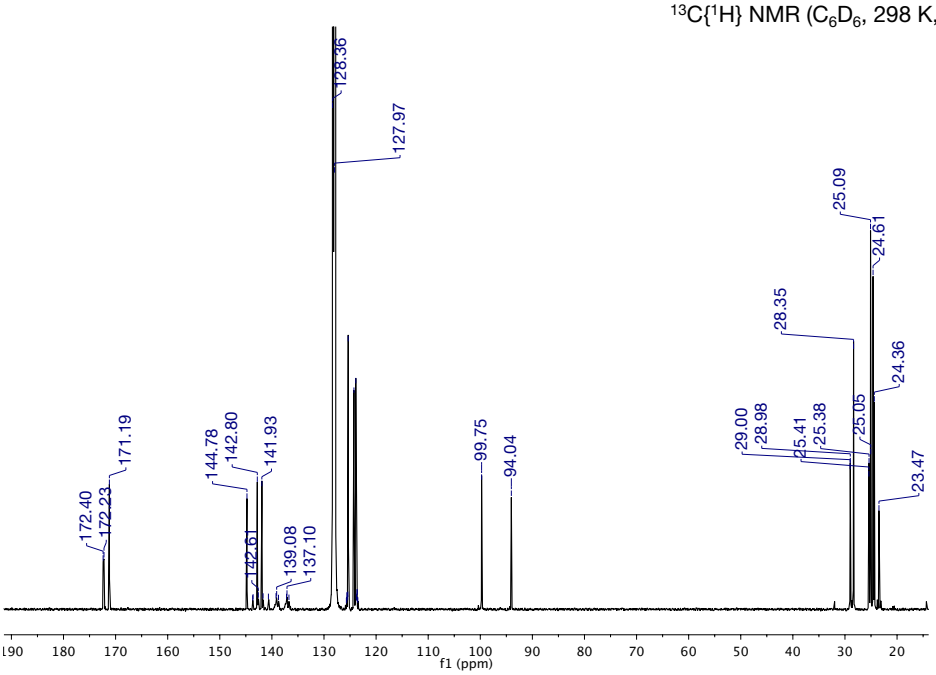
L²Mg*BDI*

^1H NMR (C_6D_6, 298 K, 500.0 MHz)



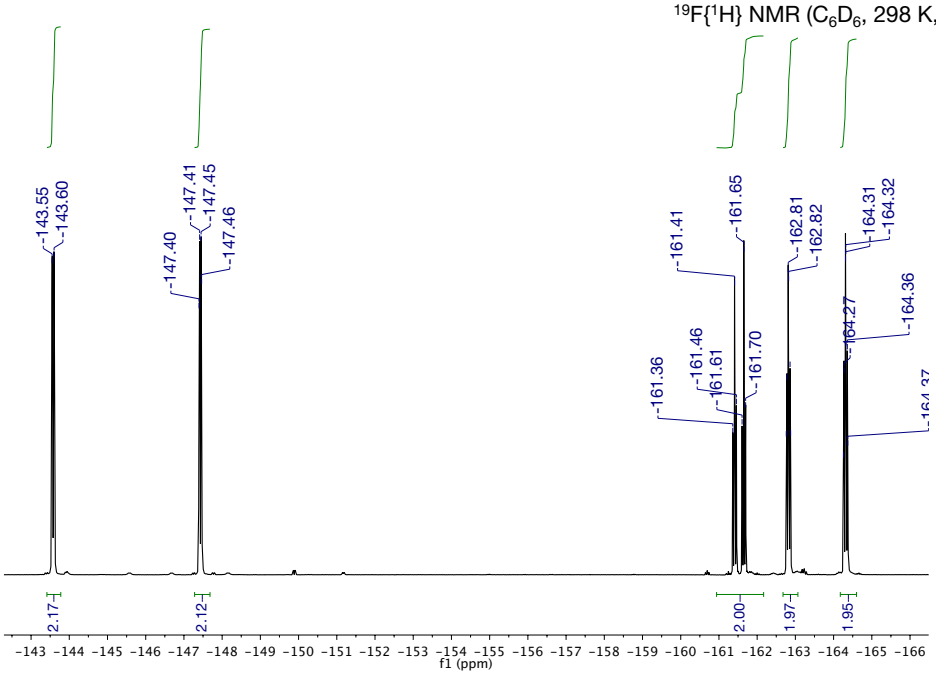
L²Mg*BDI*

$^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



L²Mg*BDI*

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)

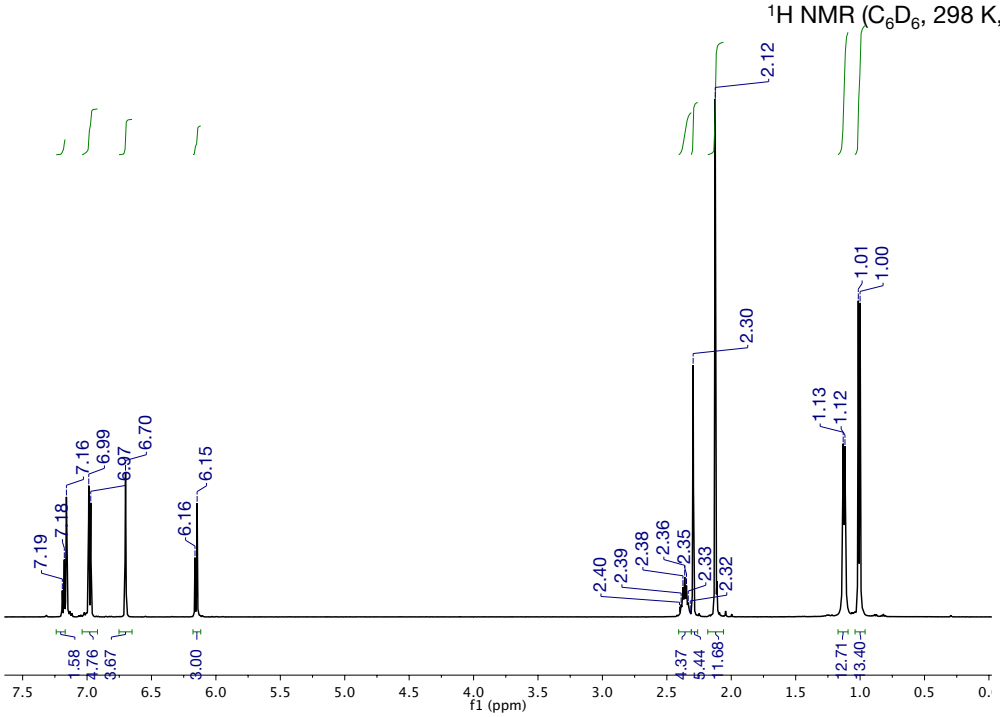


2.3 Chapter 4

1•Au - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

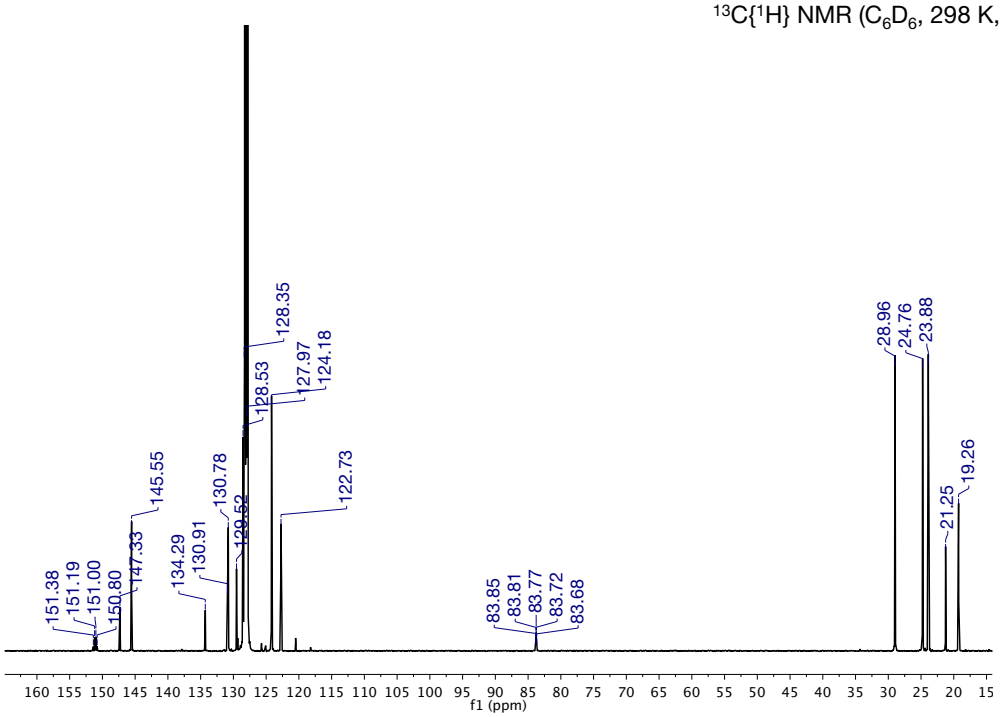
1•Au

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



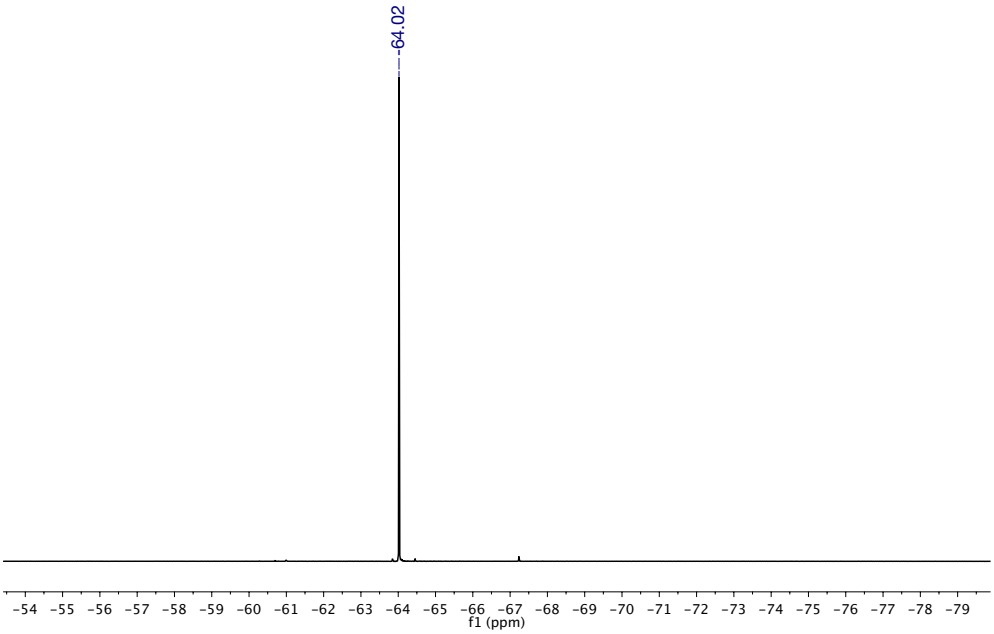
1·Au

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



1·Au

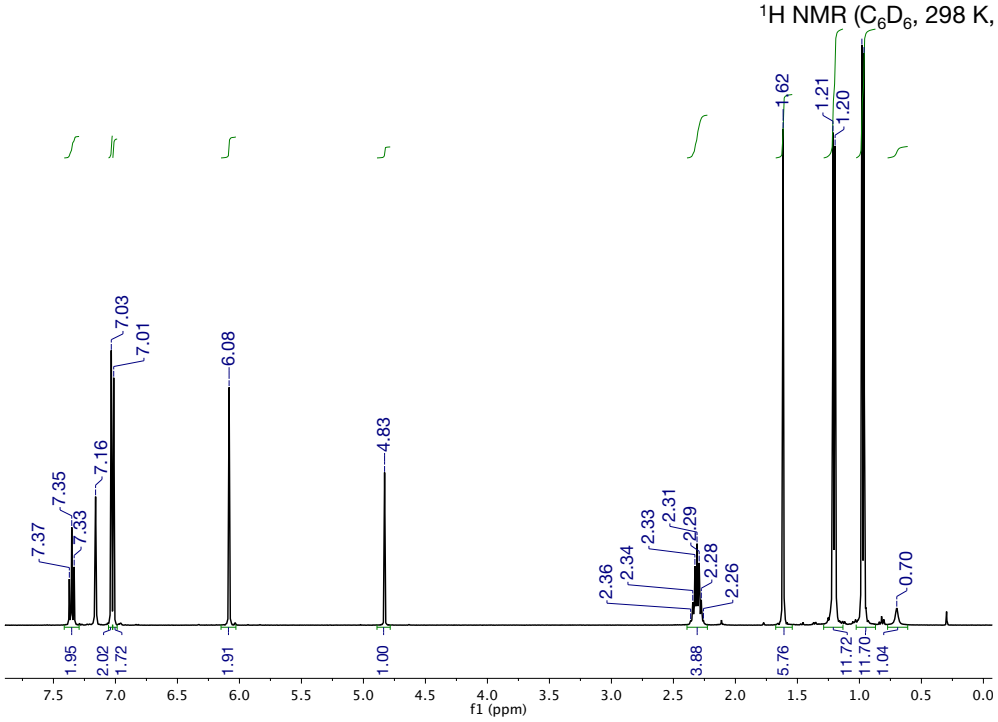
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



2•Au - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

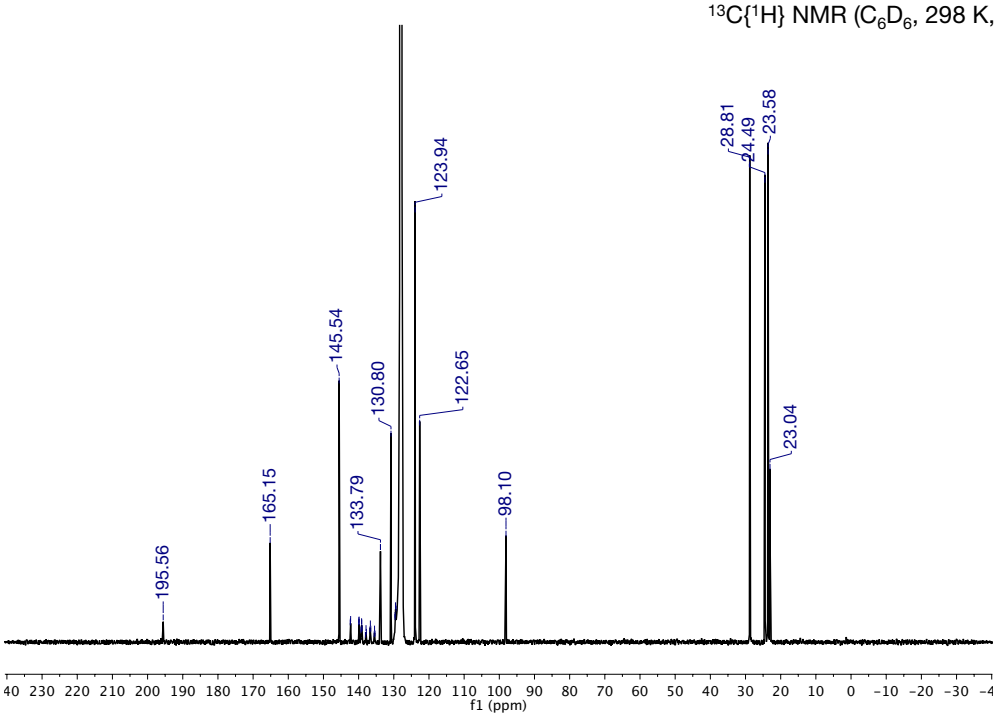
2•Au

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



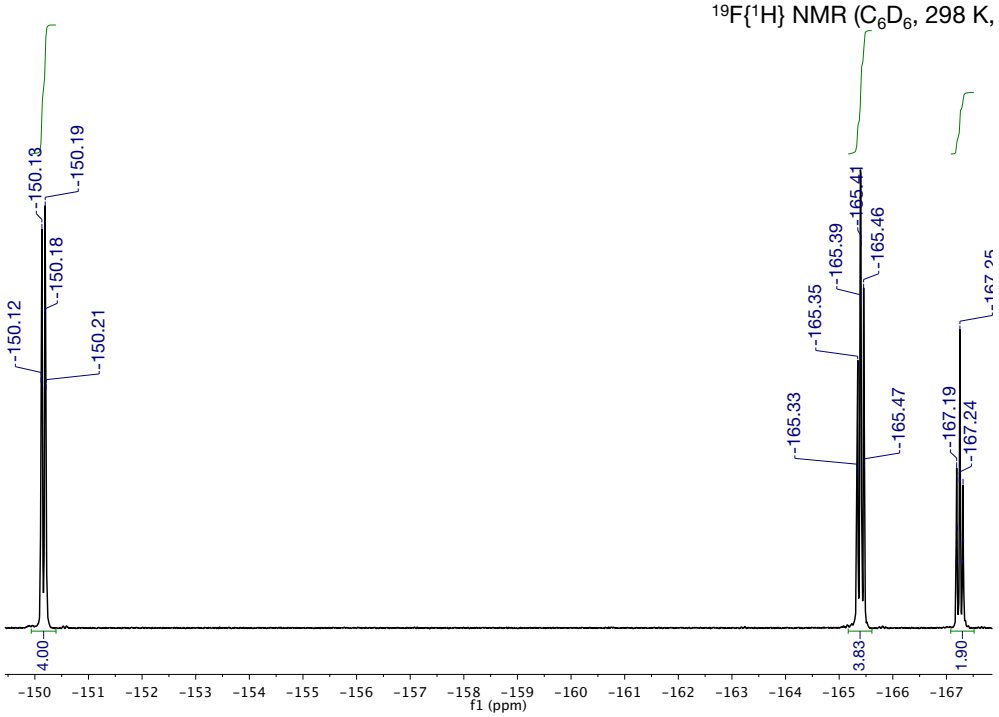
2•Au

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



2·Au

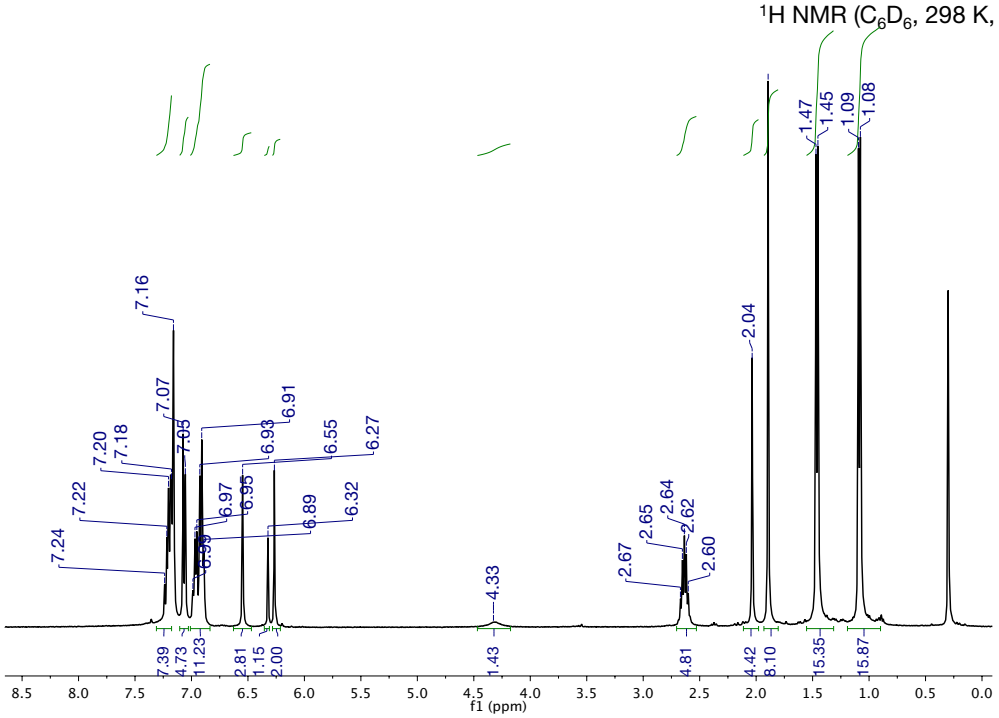
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



4·Au - ^{1}H, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra

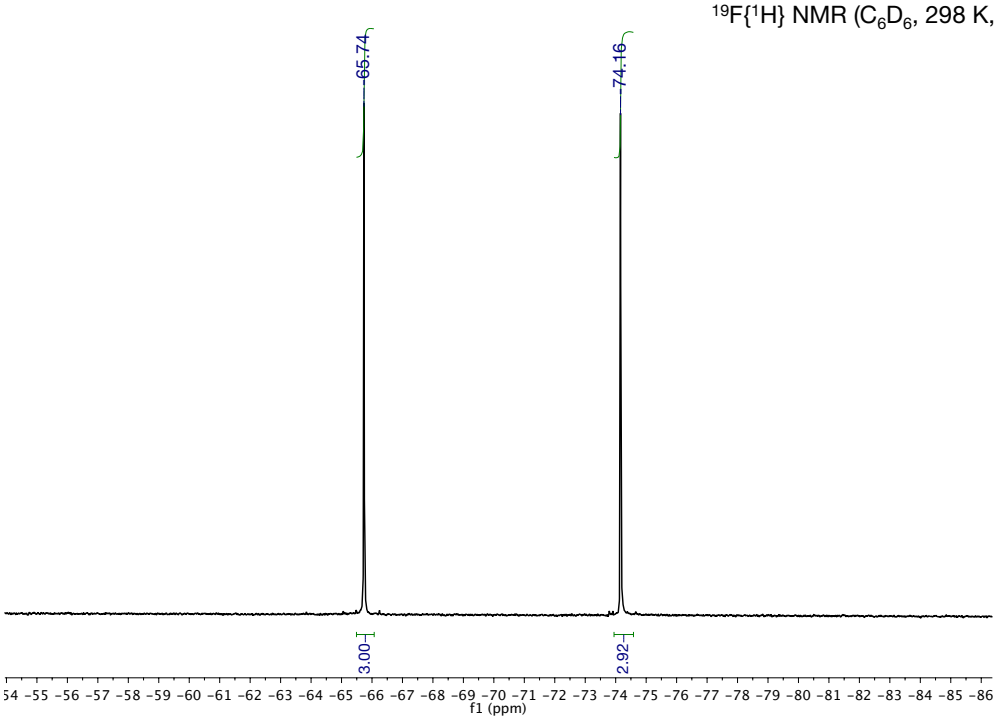
4·Au

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



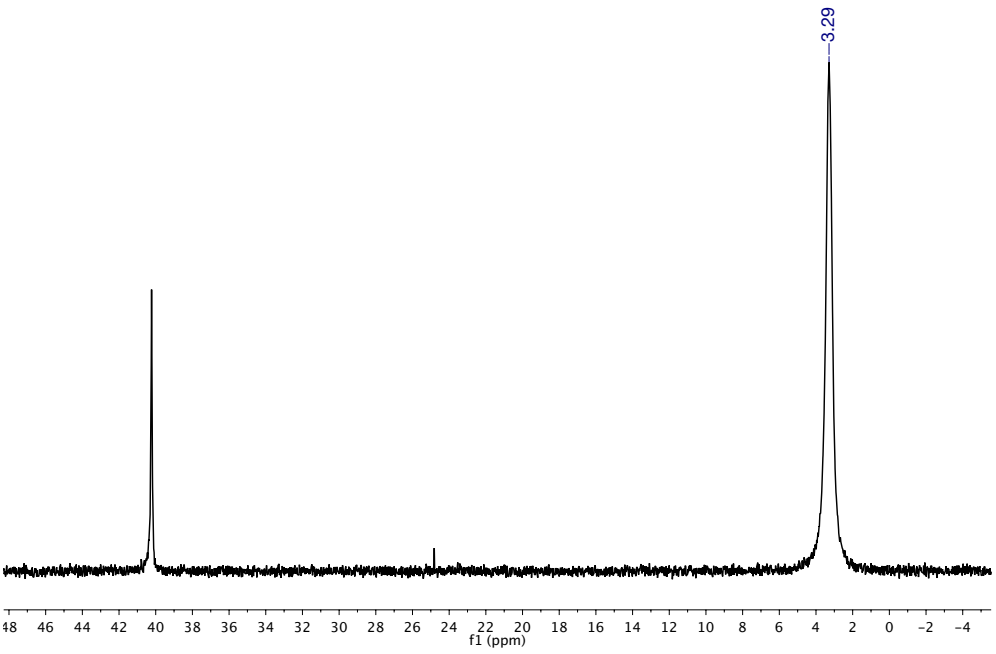
4·Au

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



4·Au

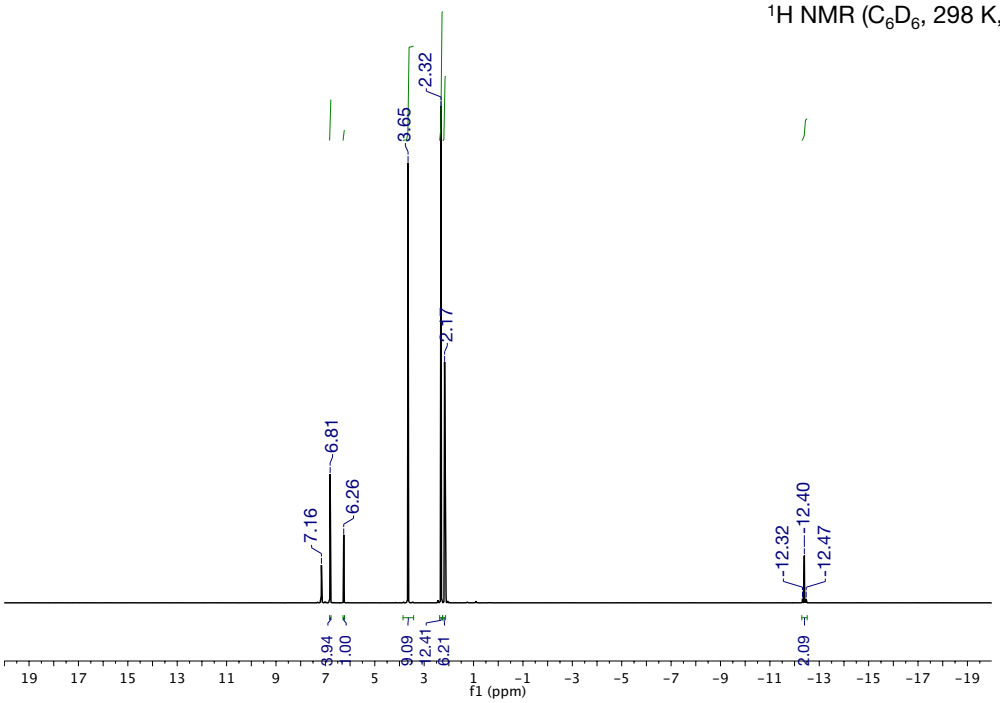
$^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 161.9 MHz)



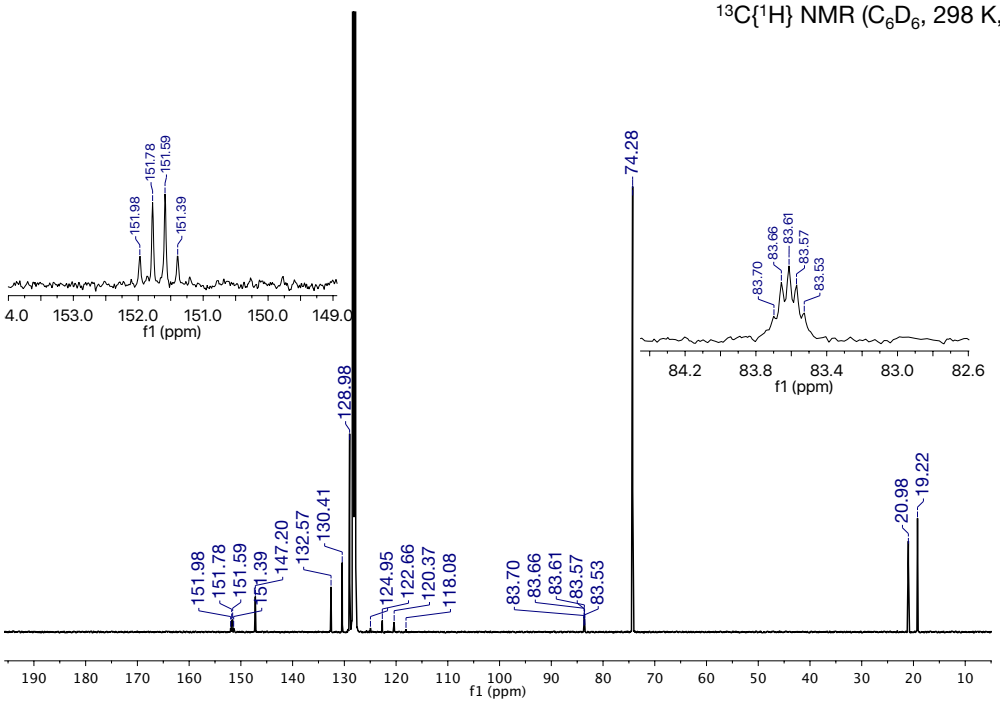
2.4 Chapter 5

1•W - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

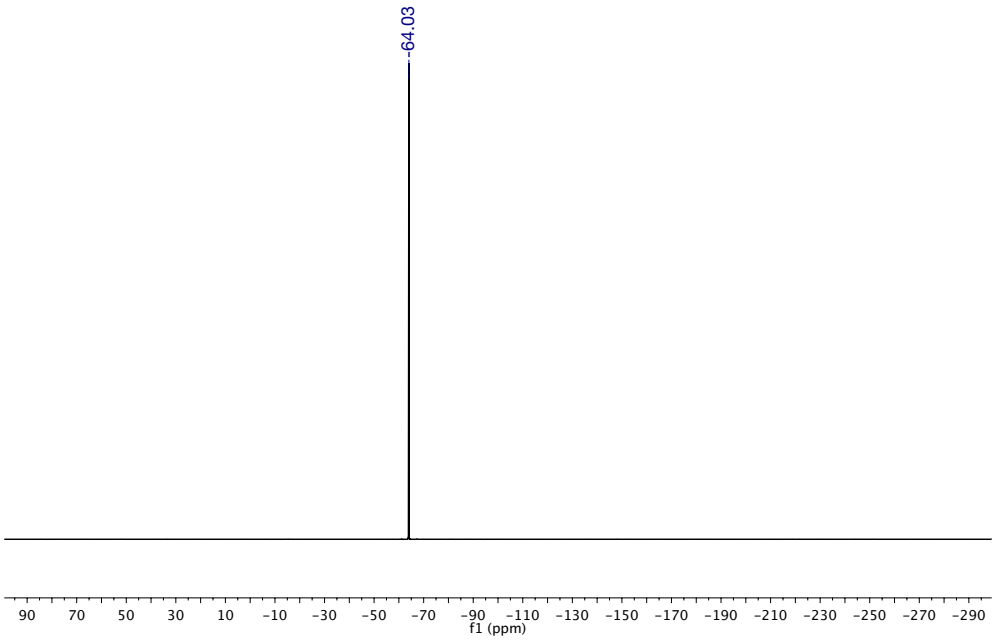
1•W ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



1•W $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)

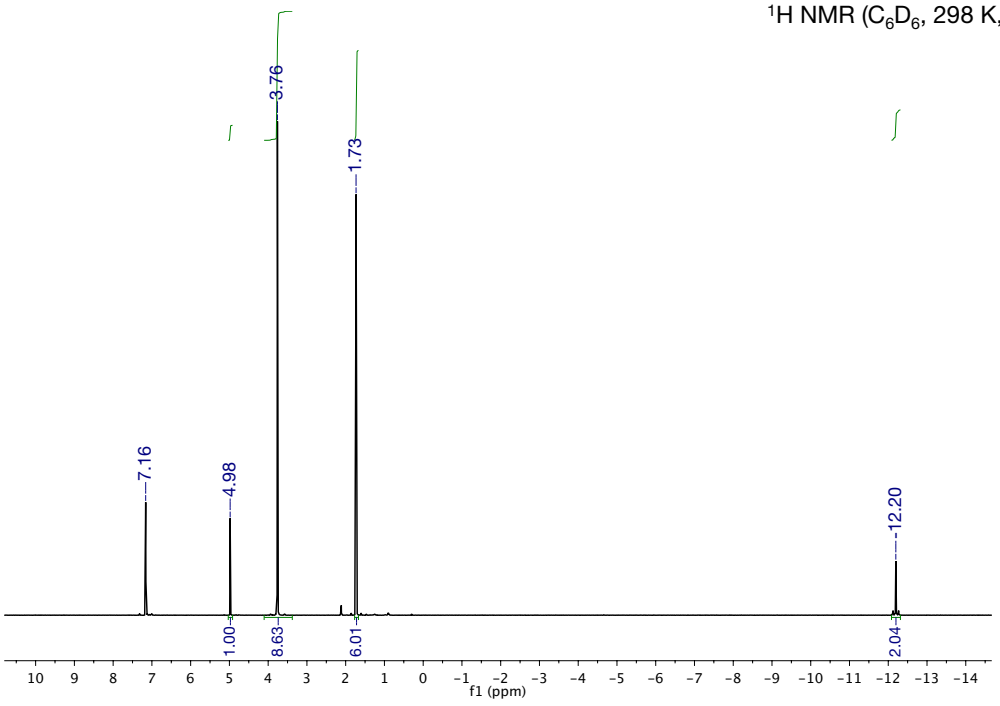


1•W $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



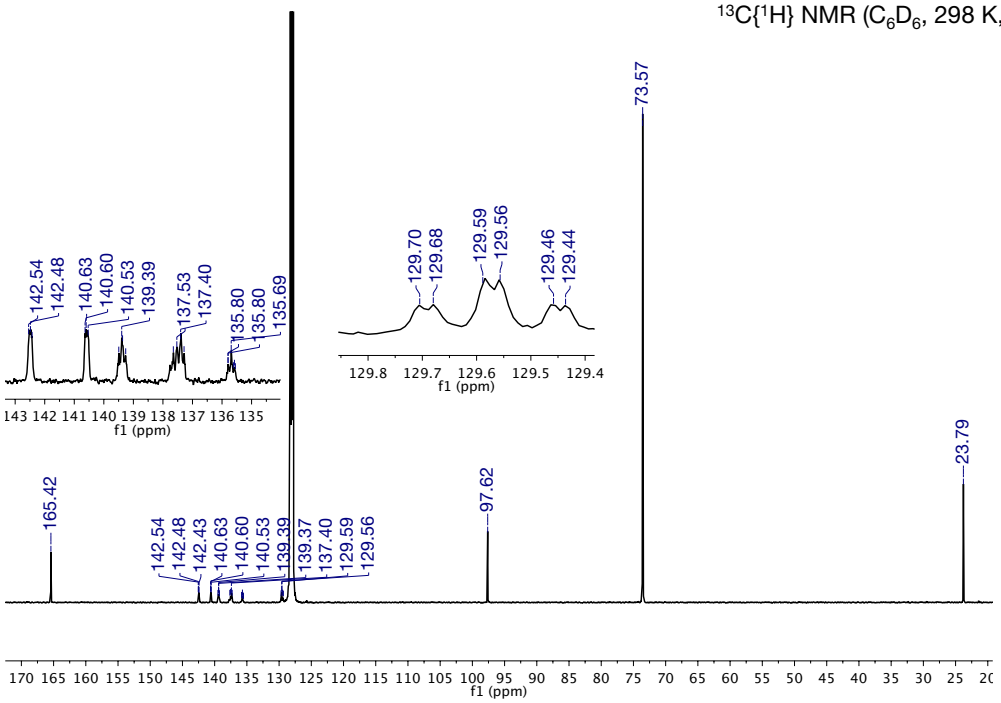
2•W - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

2•W ^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



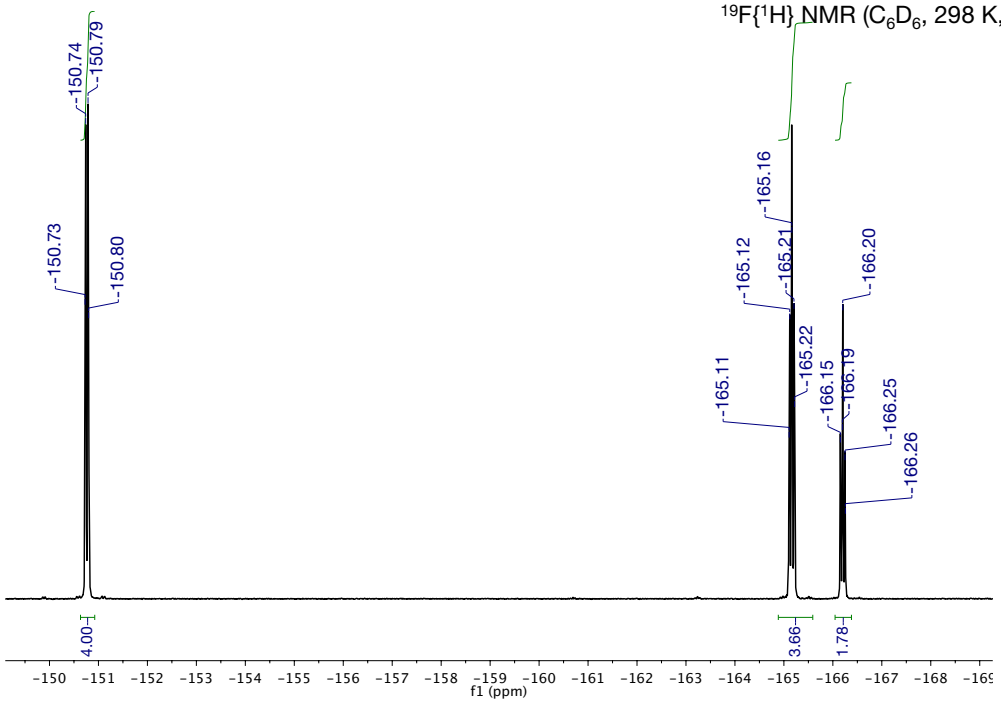
2·W

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



2·W

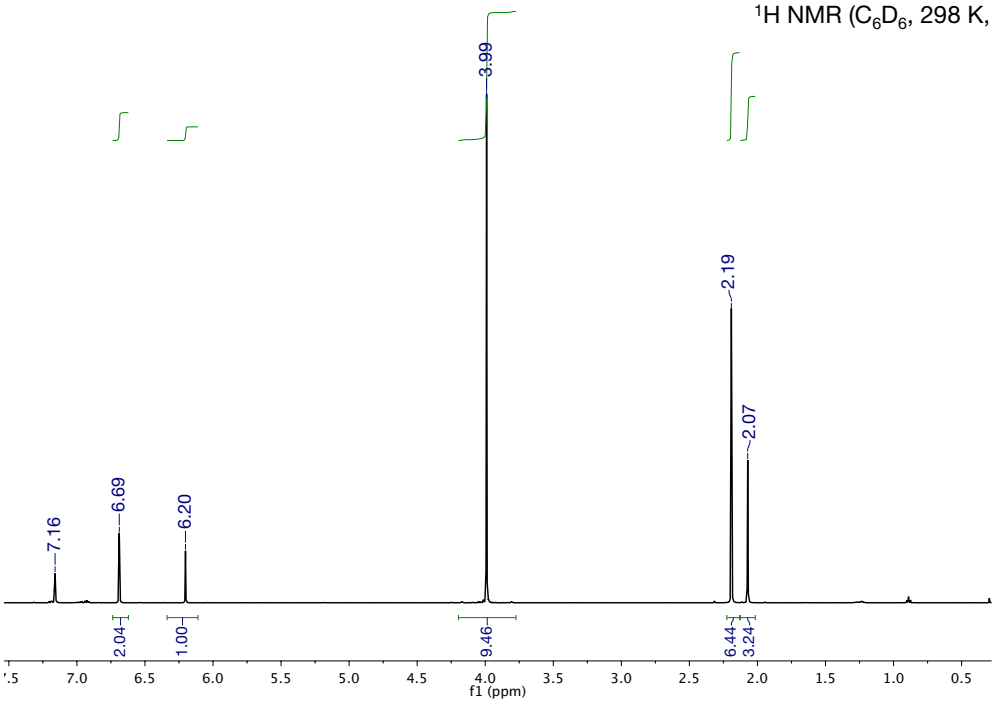
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 470.4 MHz)



4•W - ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra

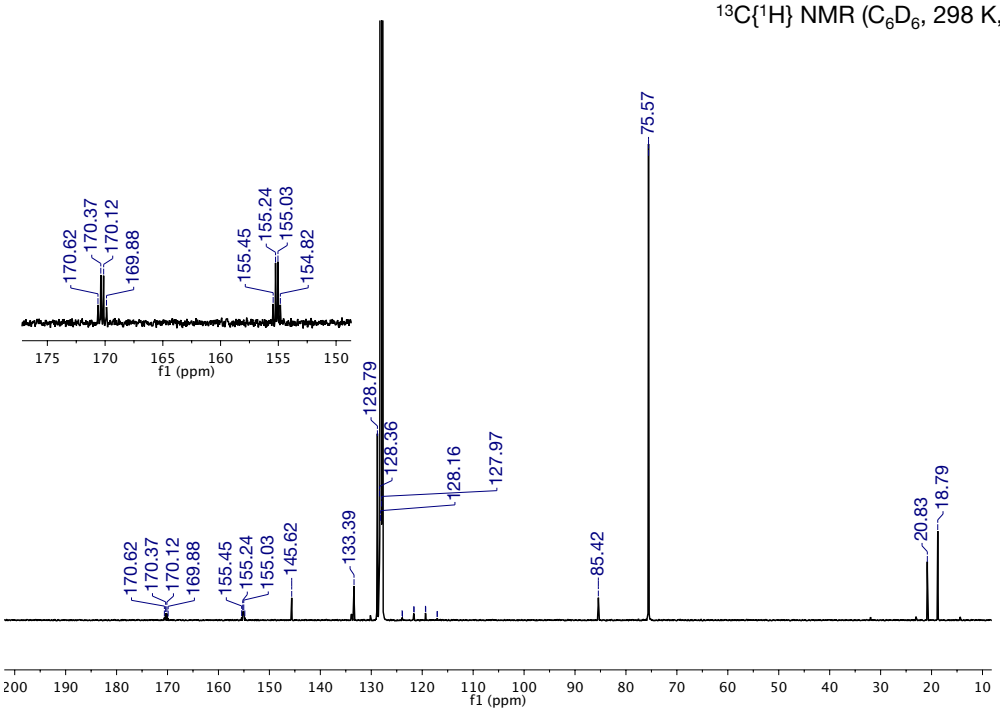
4•W

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



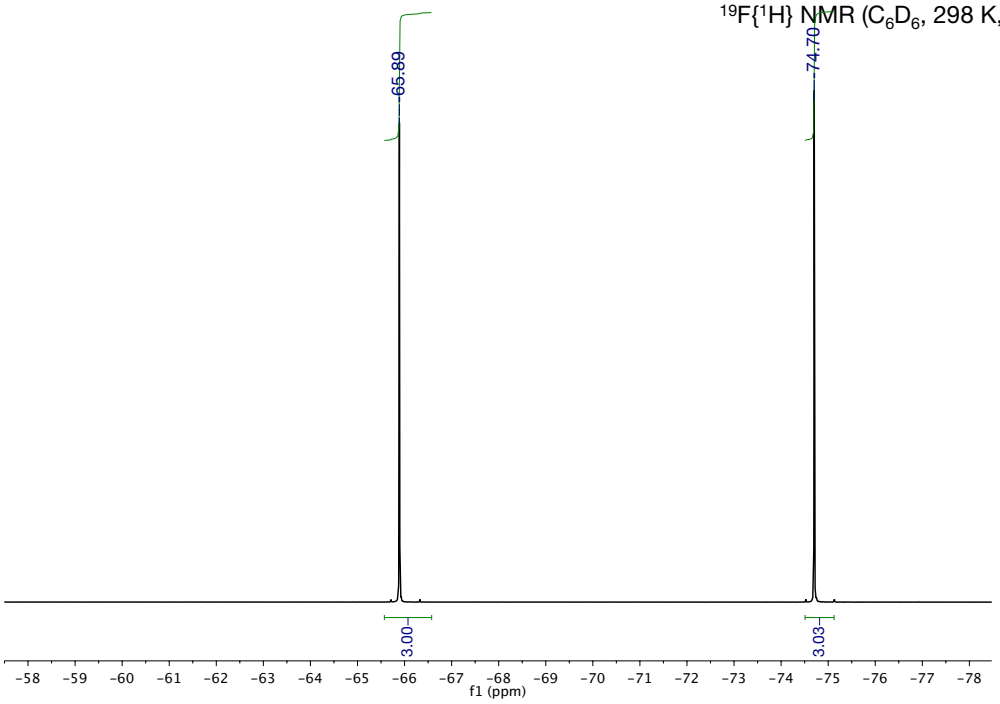
4•W

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.0 MHz)



4·W

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

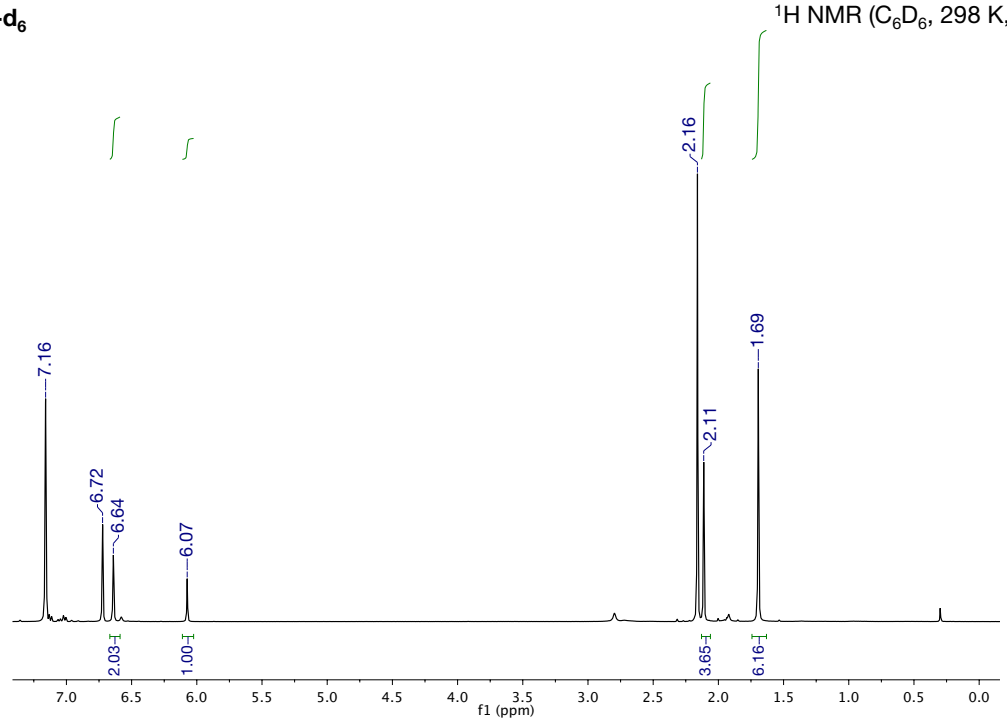


3. *In-situ NMR Data*

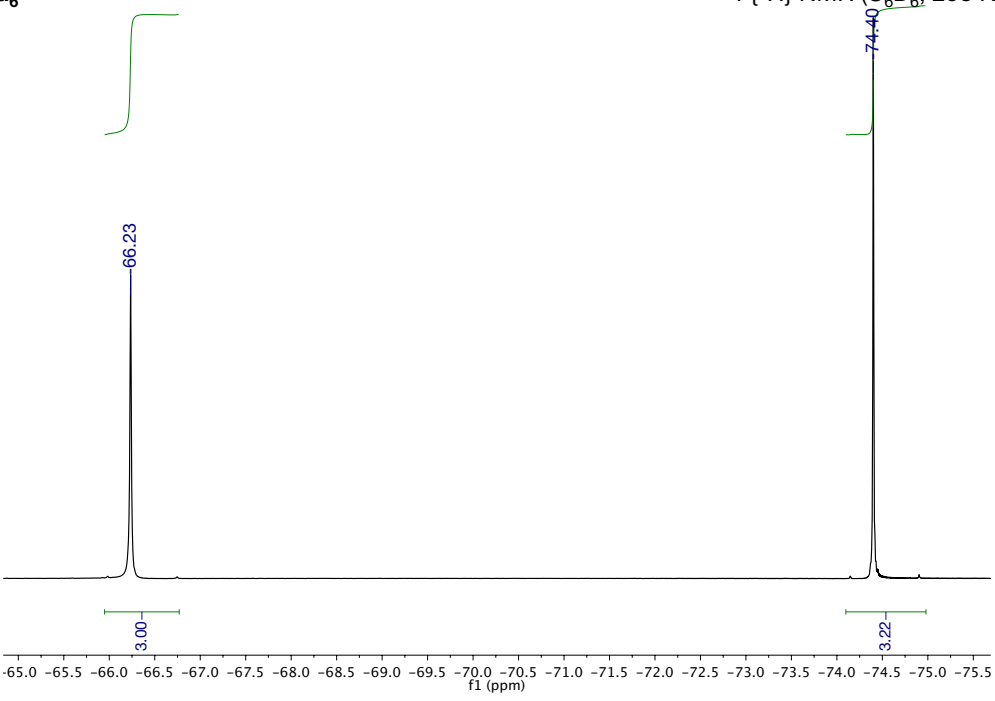
3.1 Chapter 2

4•benzene-d_6 - ^1H and $^{19}F\{^1H\}$ NMR spectra

4•benzene-d_6 ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



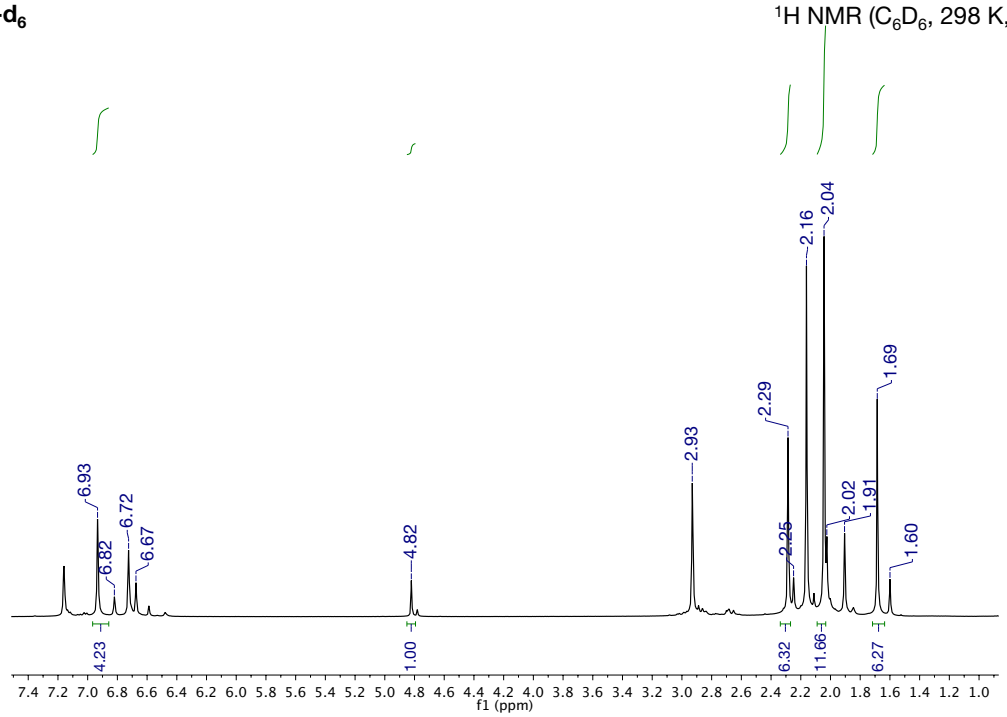
4•benzene-d_6 $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



6•benzene-d_6 – ^{1}H NMR Spectra

6•benzene-d_6

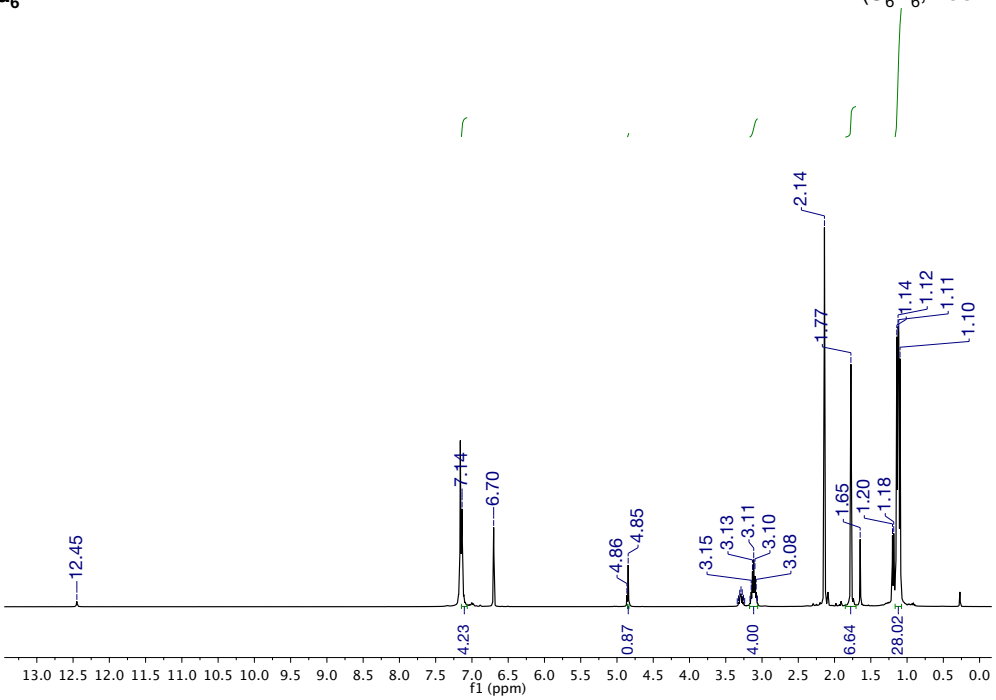
^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



7•benzene-d_6 – ^{1}H NMR spectra

7•benzene-d_6

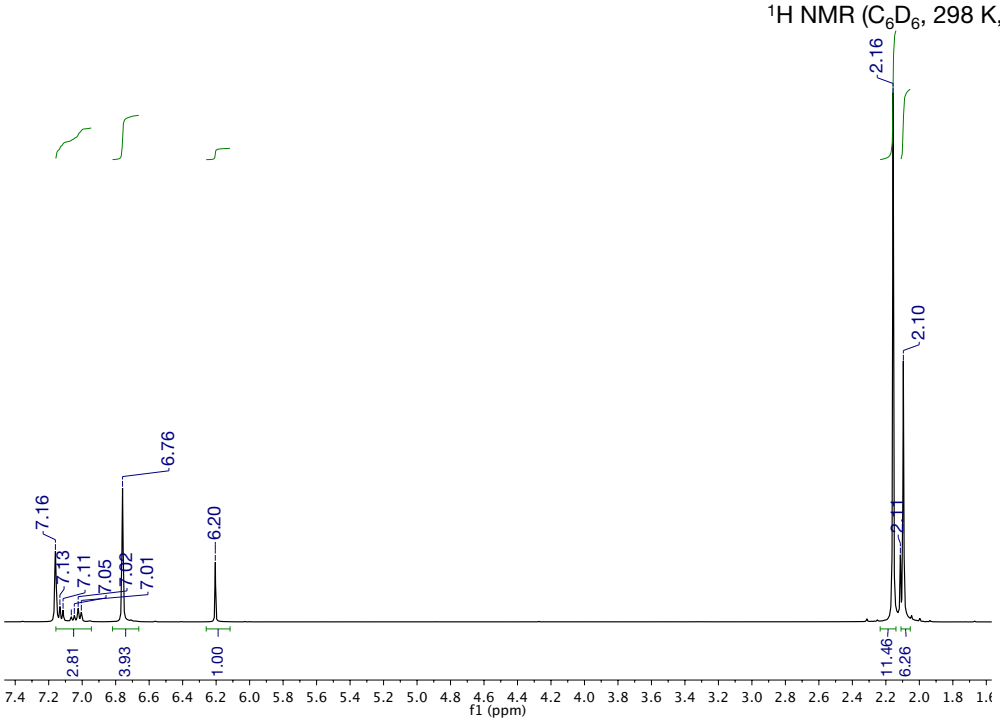
^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



1•CO - ^{1}H and $^{19}F\{^{1}H\}$ NMR spectra

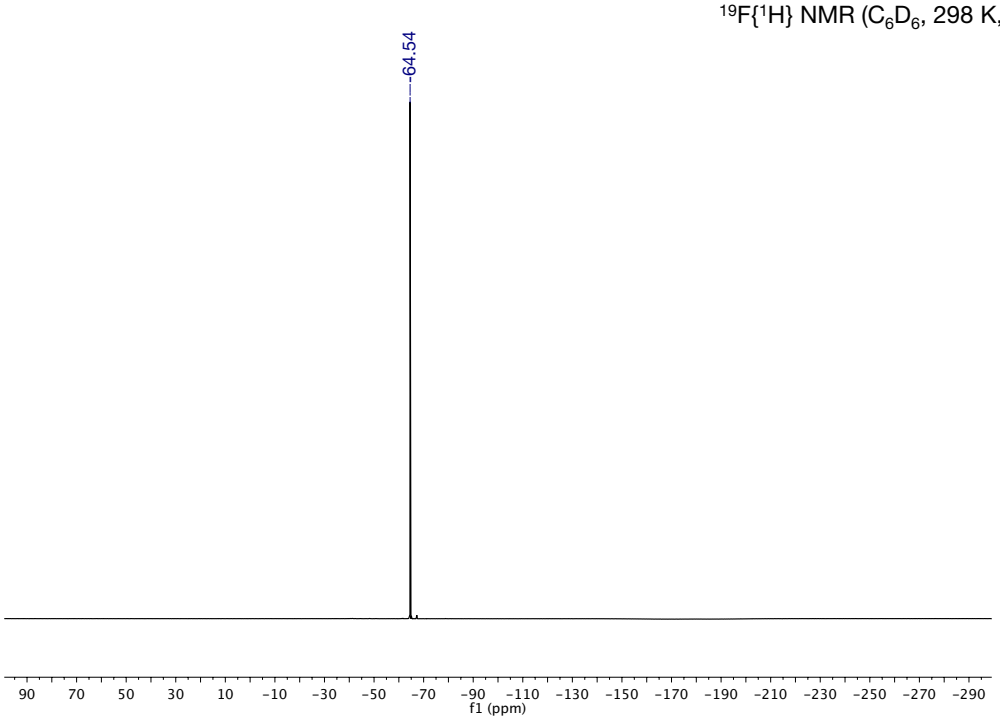
1•CO

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



1•CO

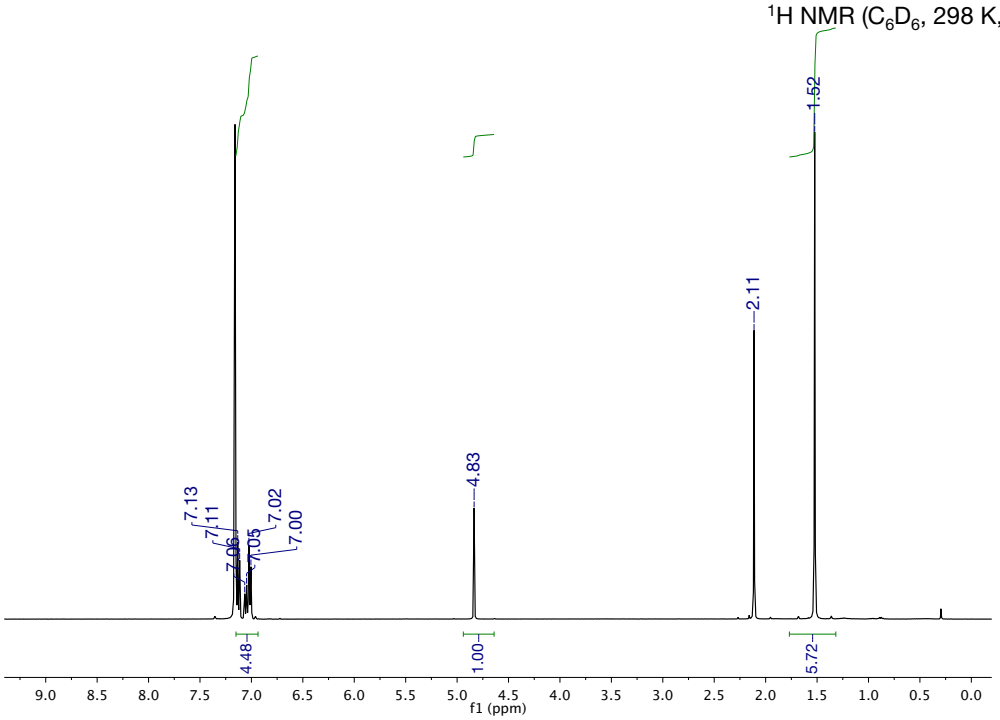
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



2•CO - ^{1}H and $^{19}F\{^{1}H\}$ NMR spectra

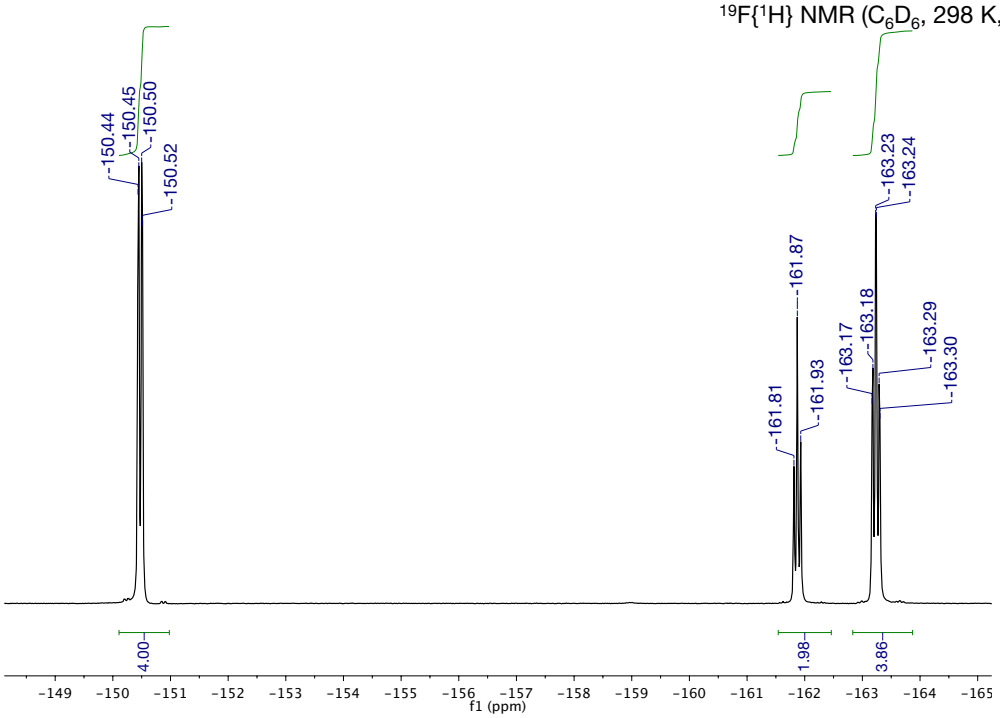
2•CO

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



2•CO

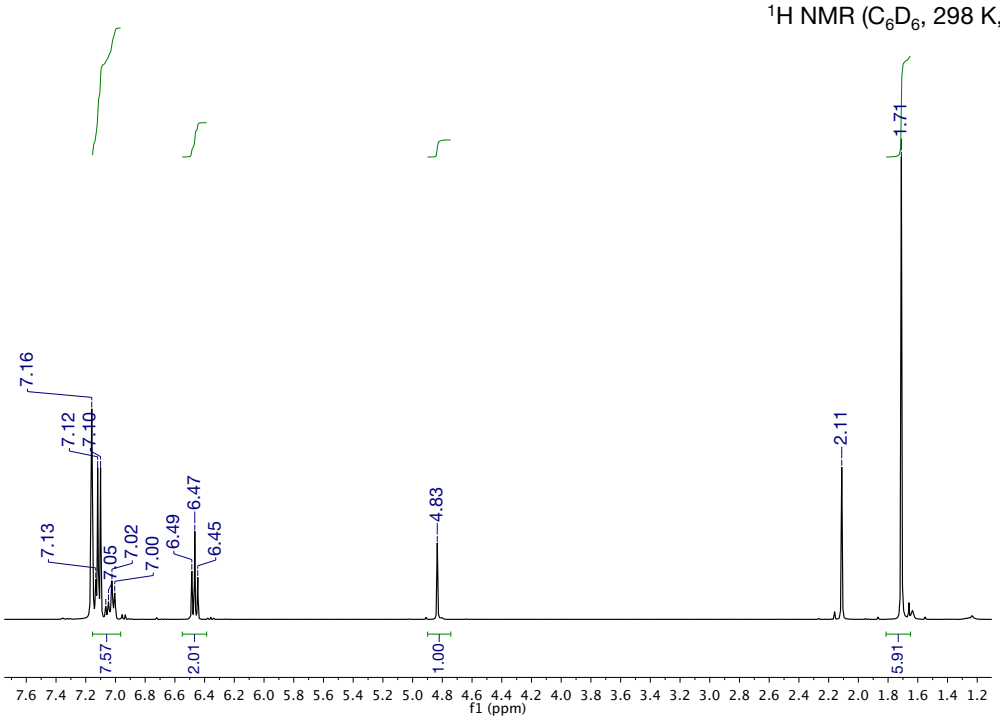
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



3•CO - ^{1}H NMR Spectra

3•CO

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)

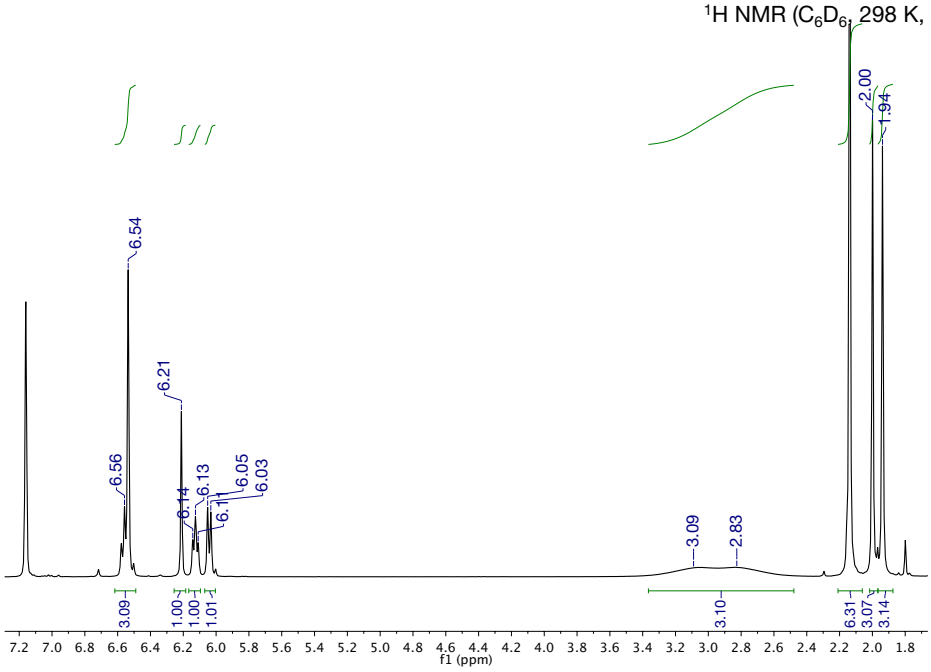


3.2 Chapter 3

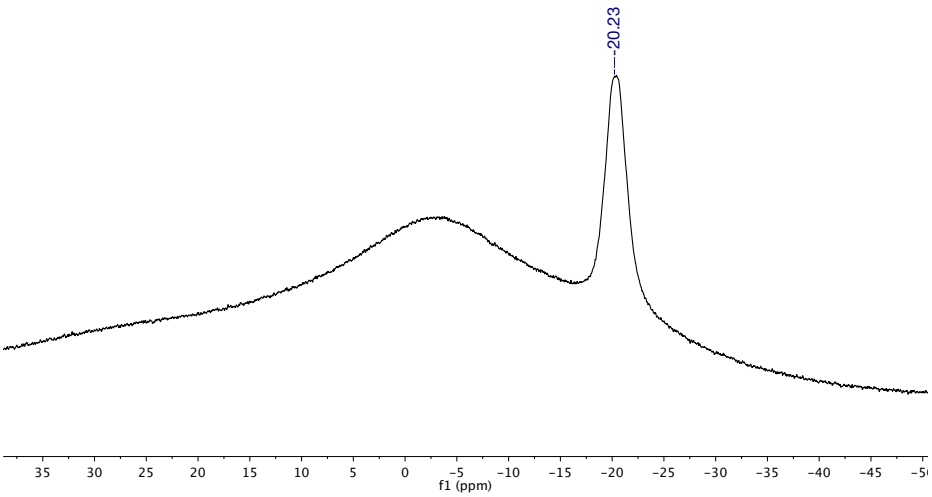
4•B - ^{1}H, $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR Spectra

4•B

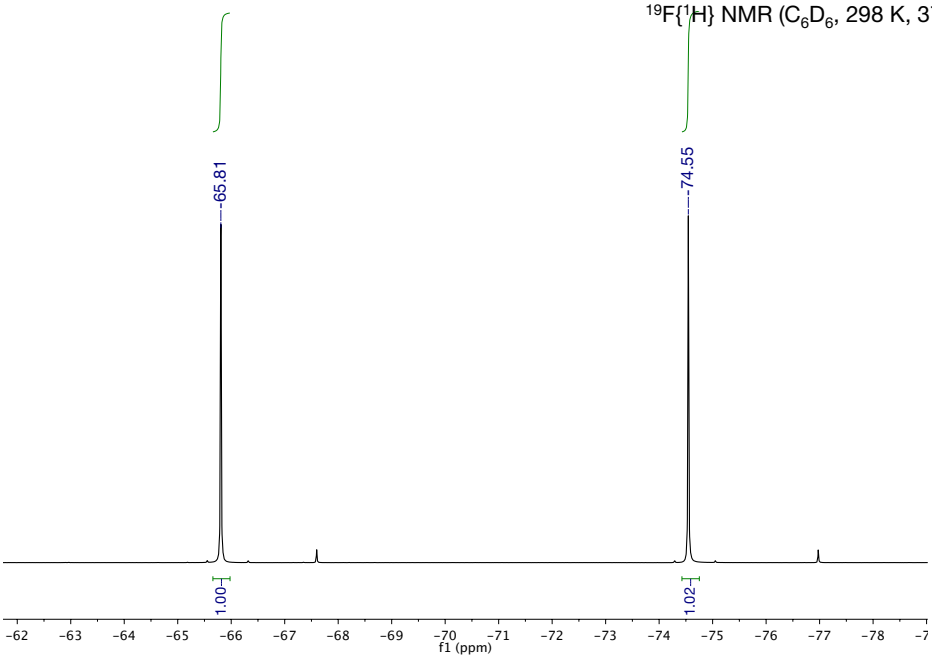
^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



4·B ^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)

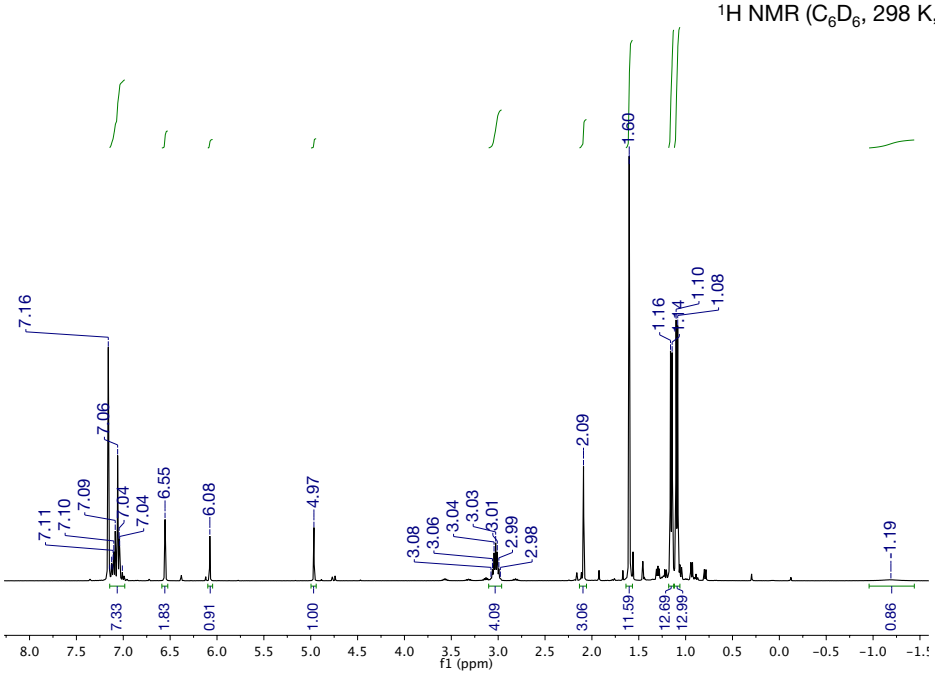


4·B $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

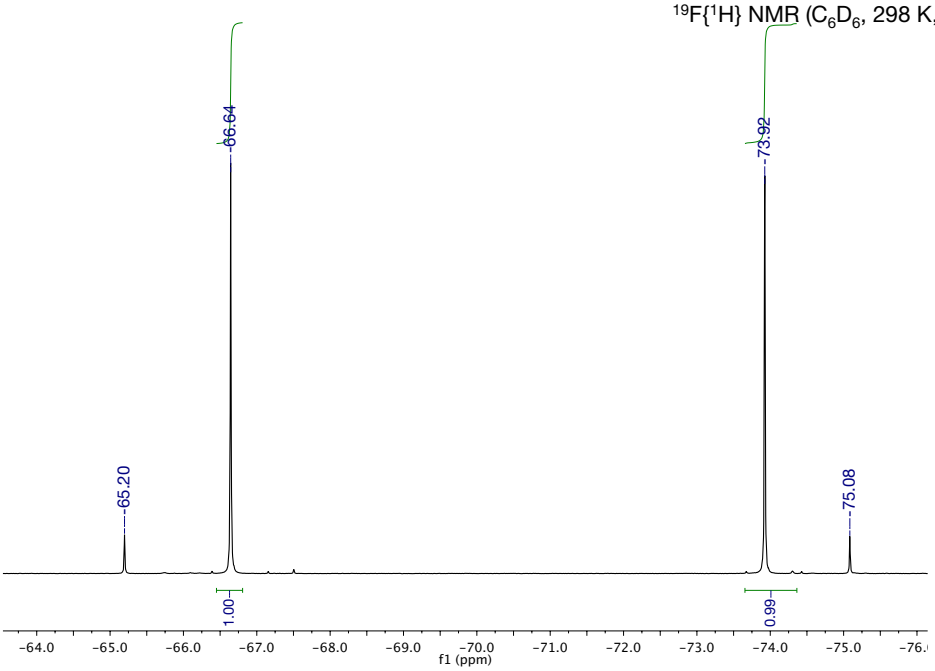


4•Zn - ^{1}H, and $^{19}F\{^{1}H\}$ NMR Spectra

4·Zn ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)

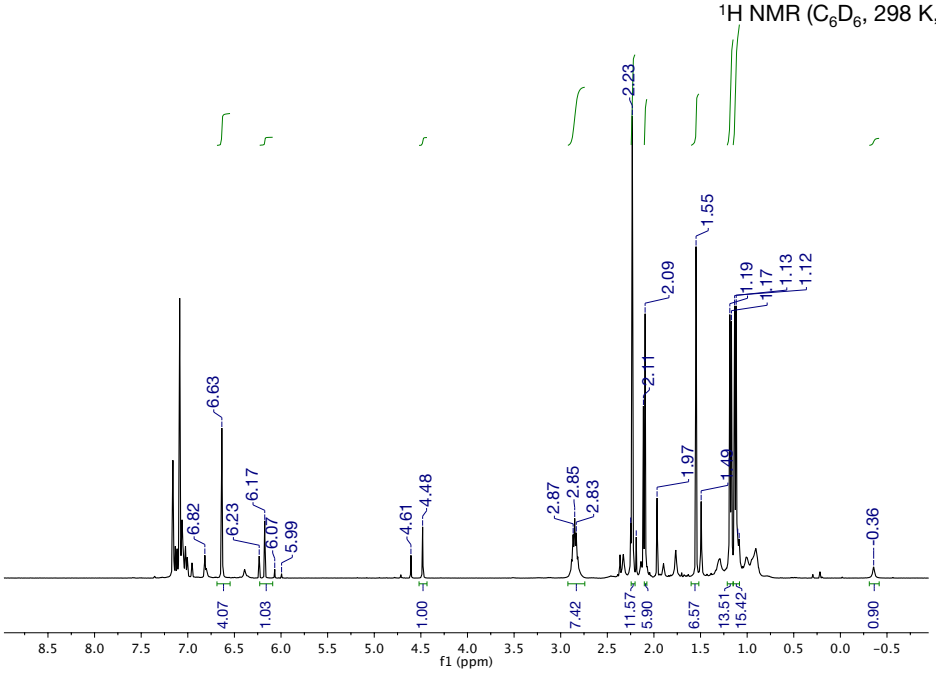


4·Zn $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

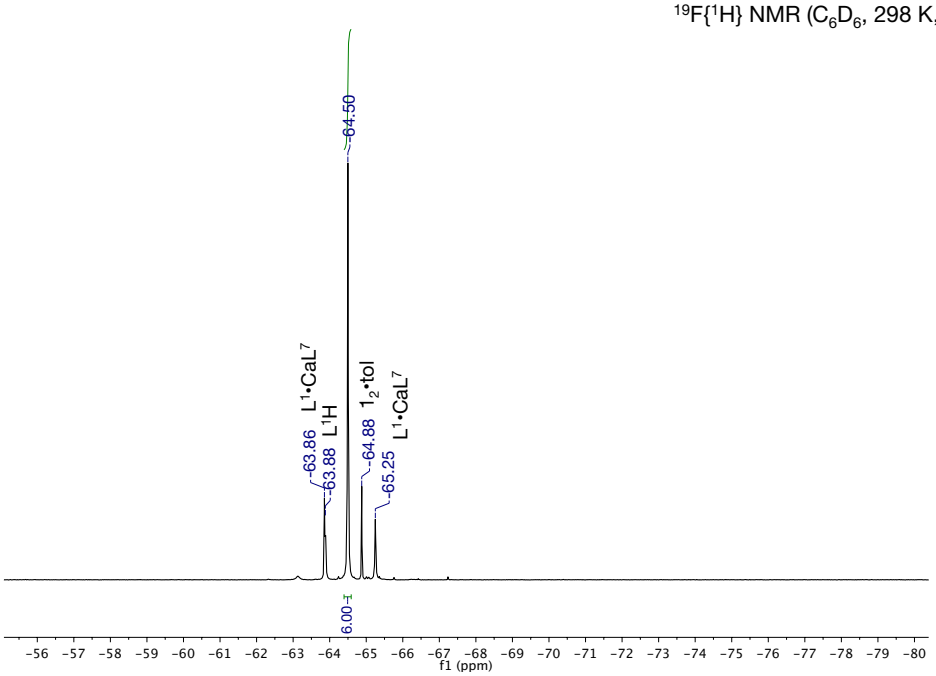


1•Ca - ^{1}H, and $^{19}F\{^{1}H\}$ NMR Spectra

1·Ca ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)

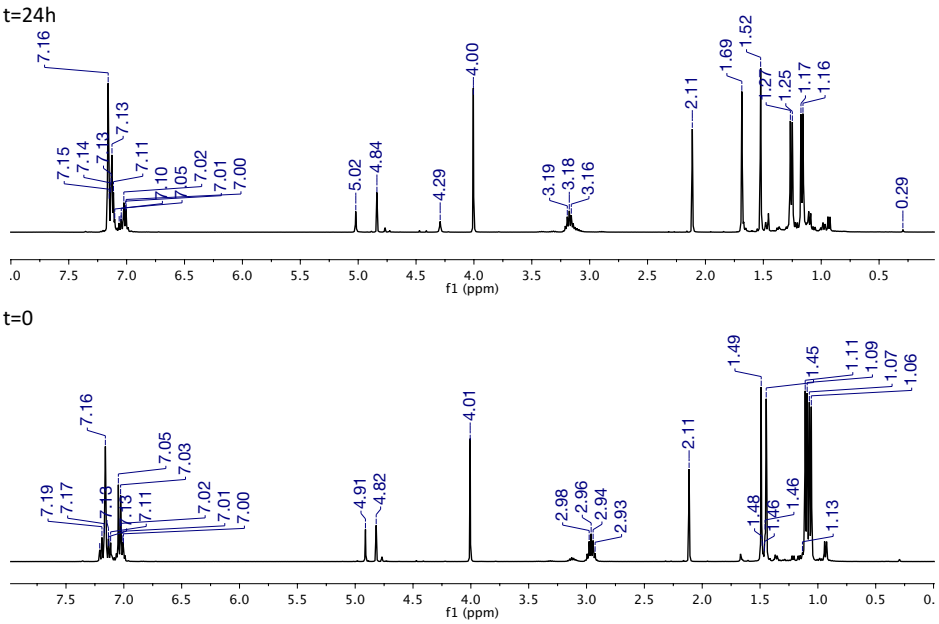


1·Ca $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

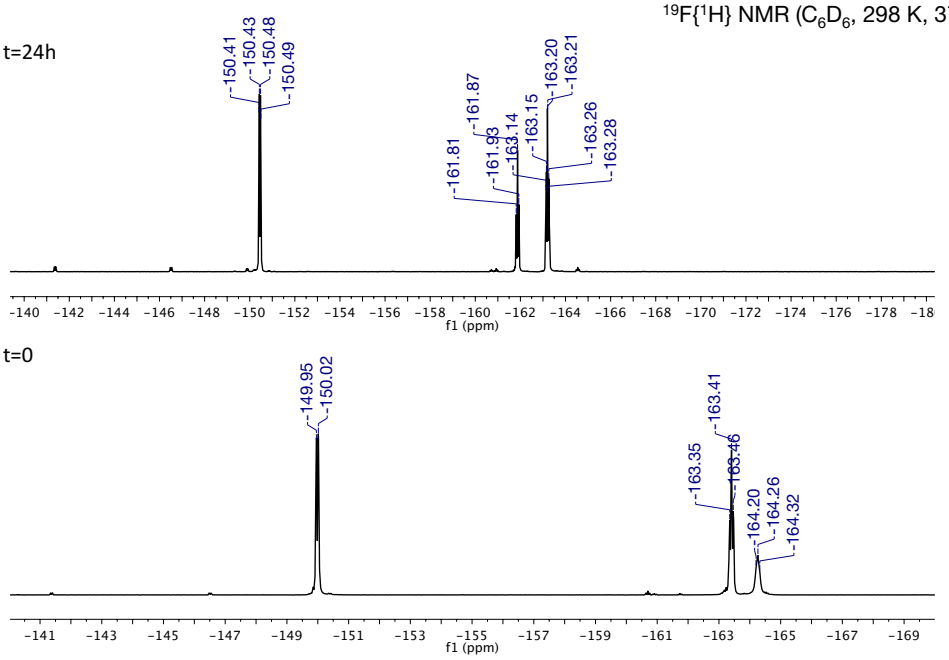


1•Zn + CO - ^{1}H, and $^{19}F\{^{1}H\}$ NMR Spectra

1•Zn + CO ^{1}H NMR (C_6D_6, 298 K, 400 MHz)

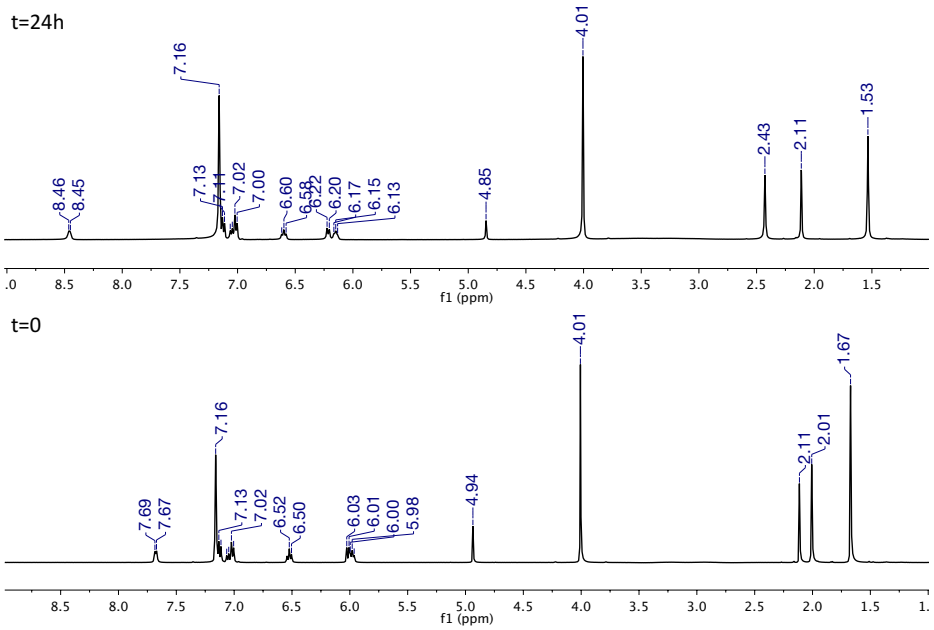


1•Zn + CO $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

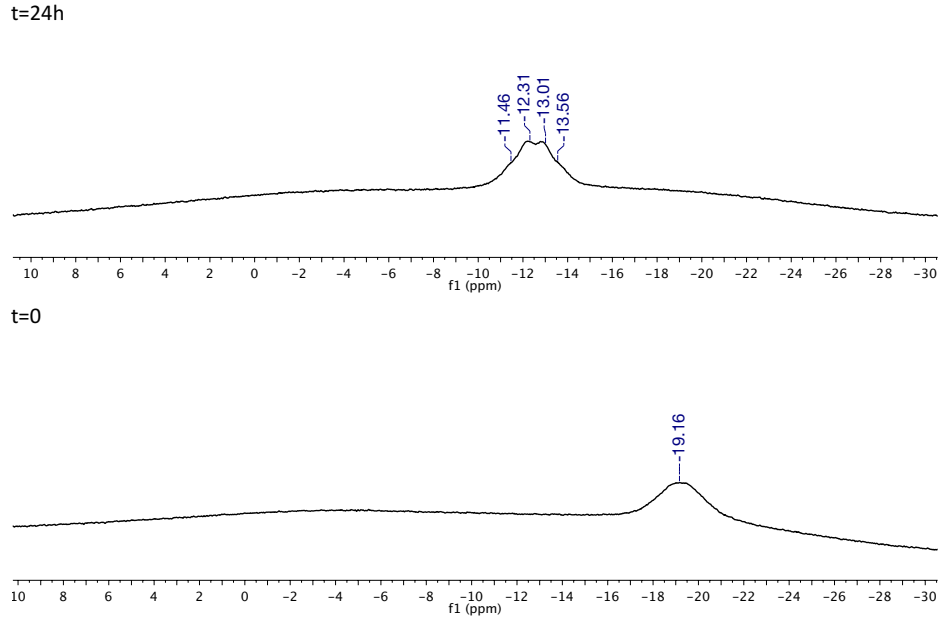


2•B + CO - ^{1}H, ^{11}B and $^{19}F\{^{1}H\}$ NMR Spectra

2•B + CO ^{1}H NMR (C_6D_6, 298 K, 400 MHz)

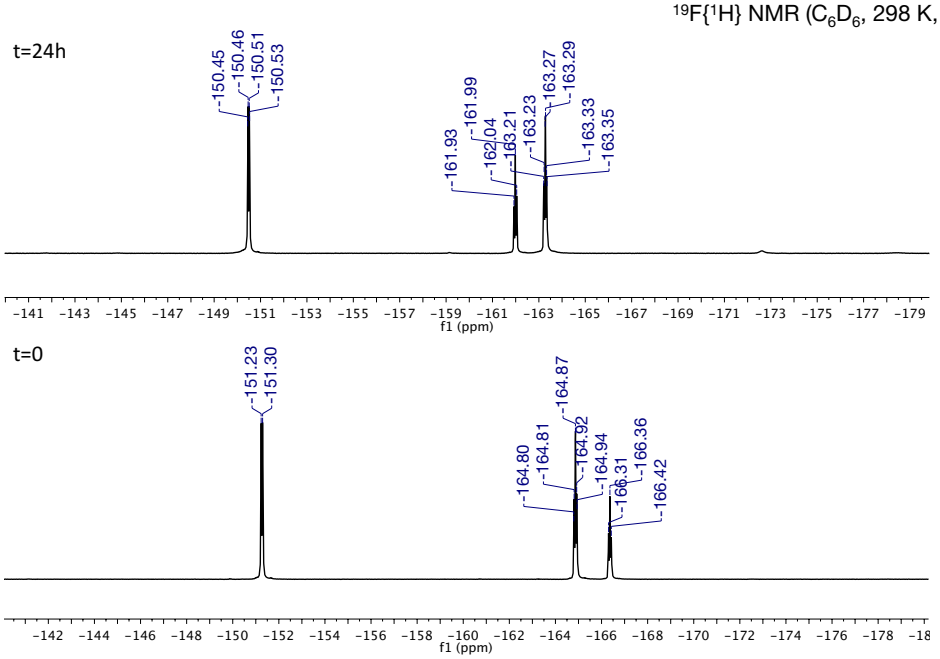


2•B + CO ^{11}B NMR (C_6D_6, 298K, 160.4 MHz)



2·B + CO

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

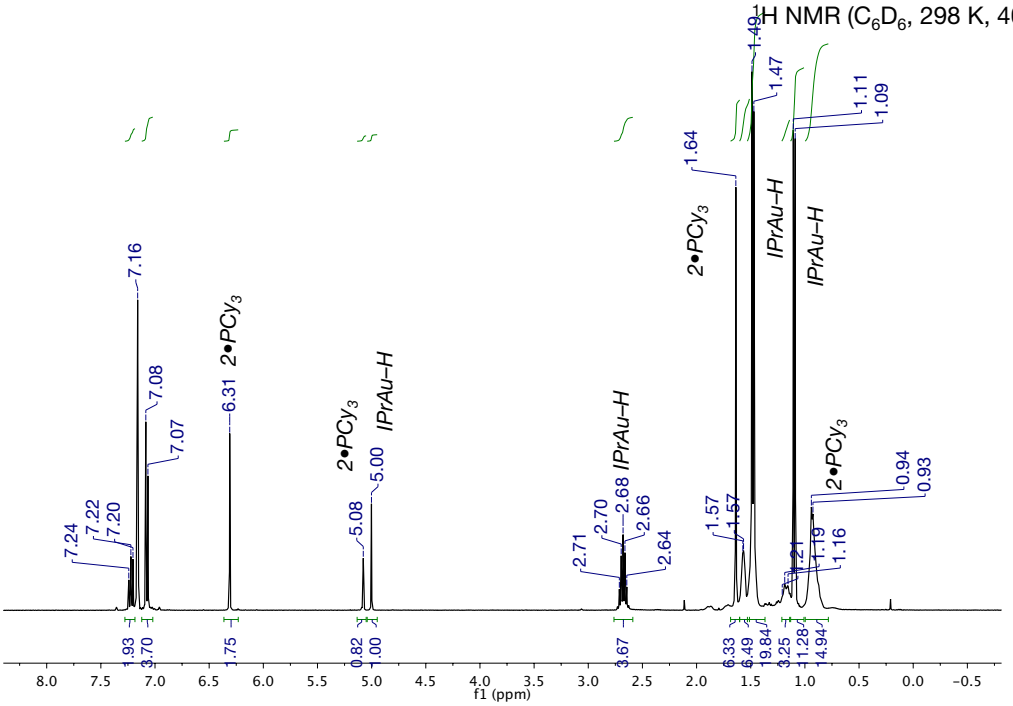


3.3 Chapter 4

2•Au + PCy_3 - ^{1}H, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra

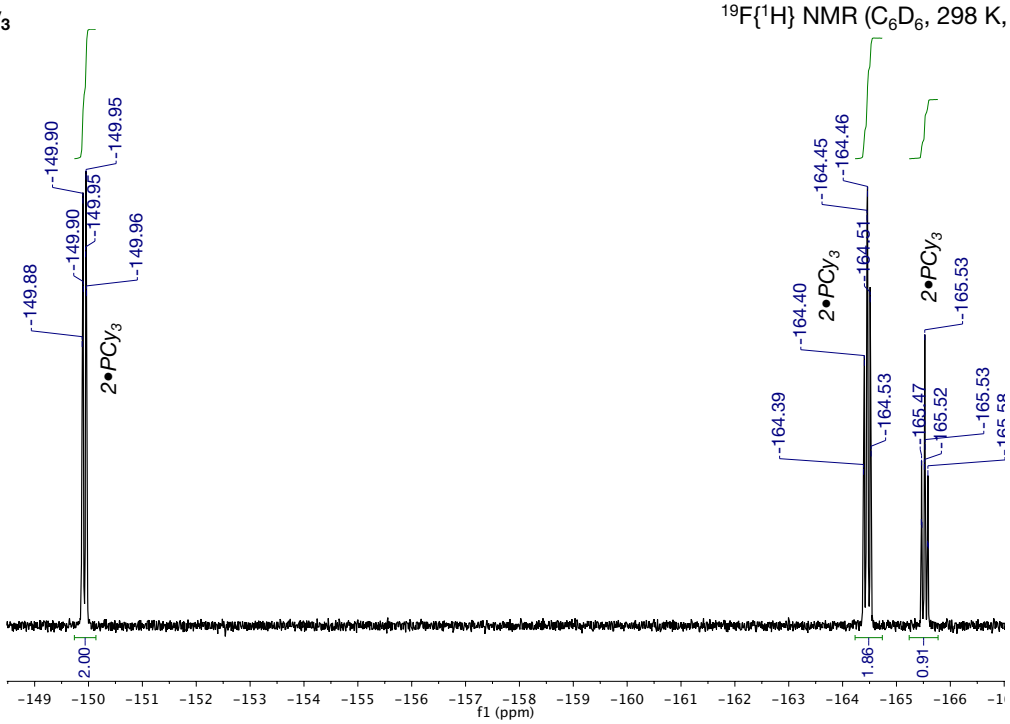
2·Au + PCy_3

^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



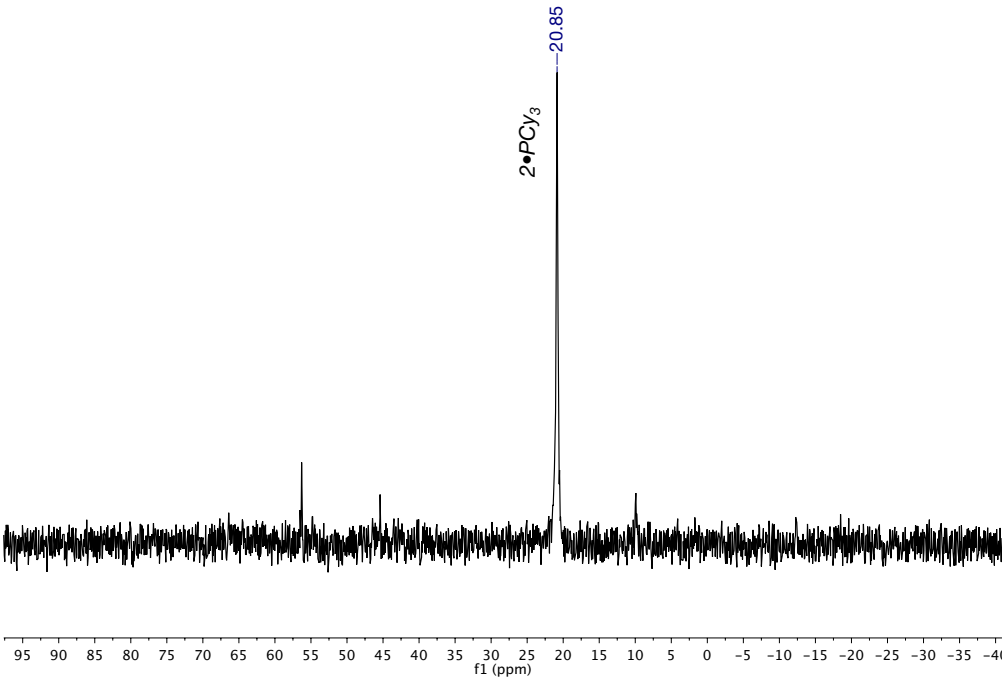
2·Au + PCy_3

$^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



2·Au + PCy_3

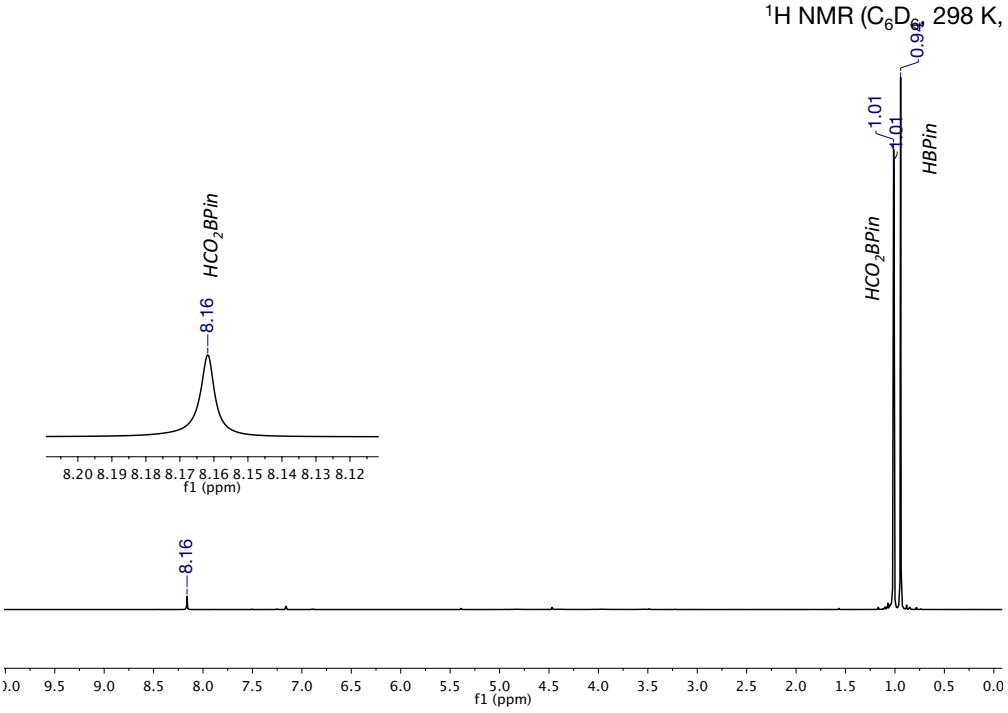
$^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



Synthesis of HCO_2BPin (A) - ^1H and $^{11}B\{^1H\}$ NMR spectra

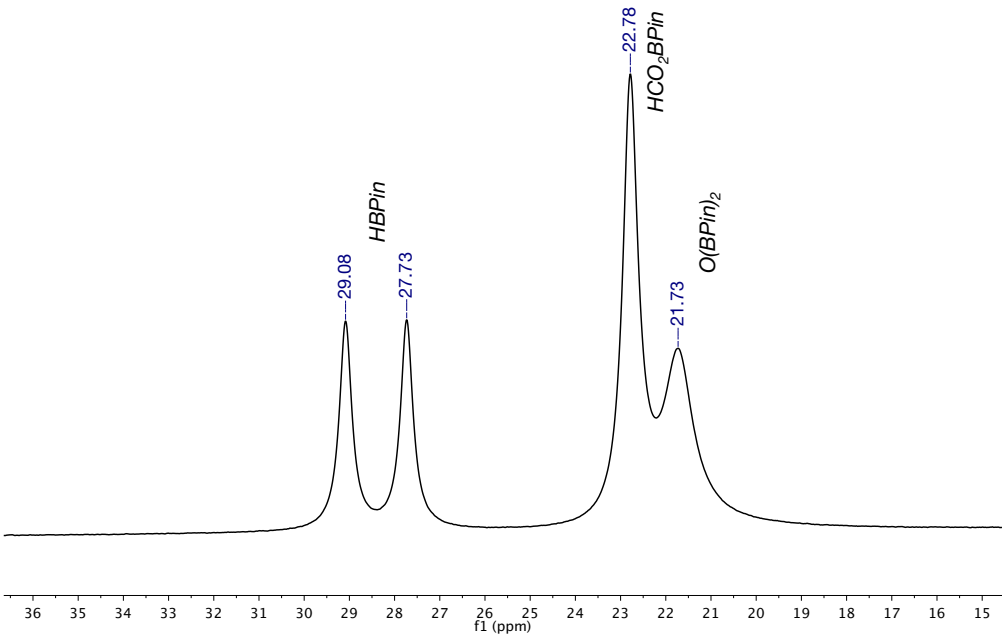
HCO_2BPin

^1H NMR (C_6D_6, 298 K, 400.0 MHz)



HCO_2BPin

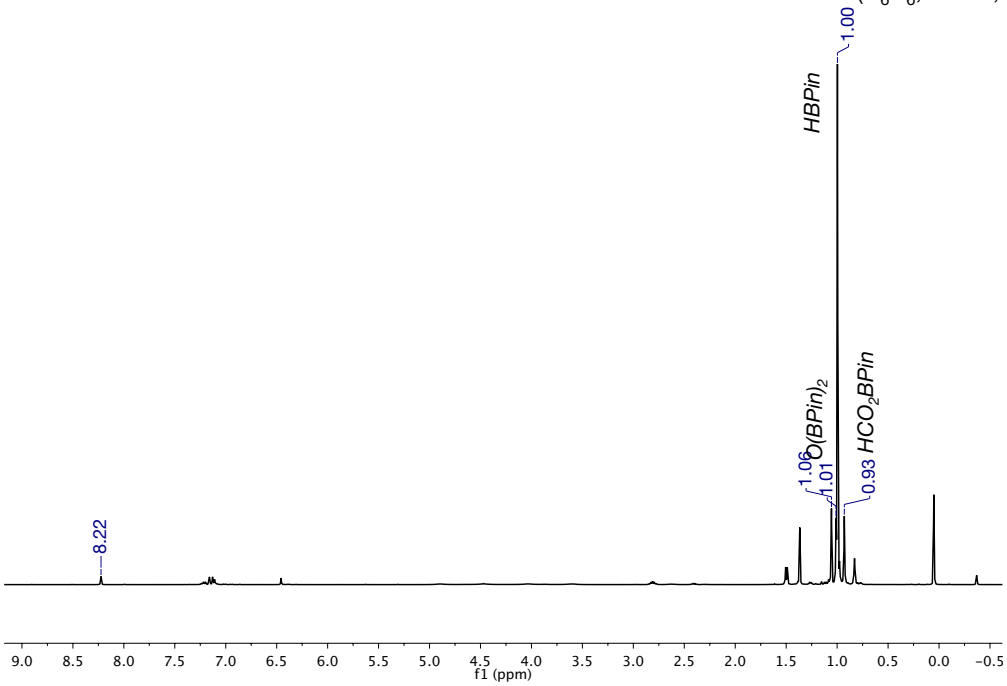
^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



Catalytic formation of HCO_2BPin (A) - ^1H and $^{11}B\{^1H\}$ NMR spectra

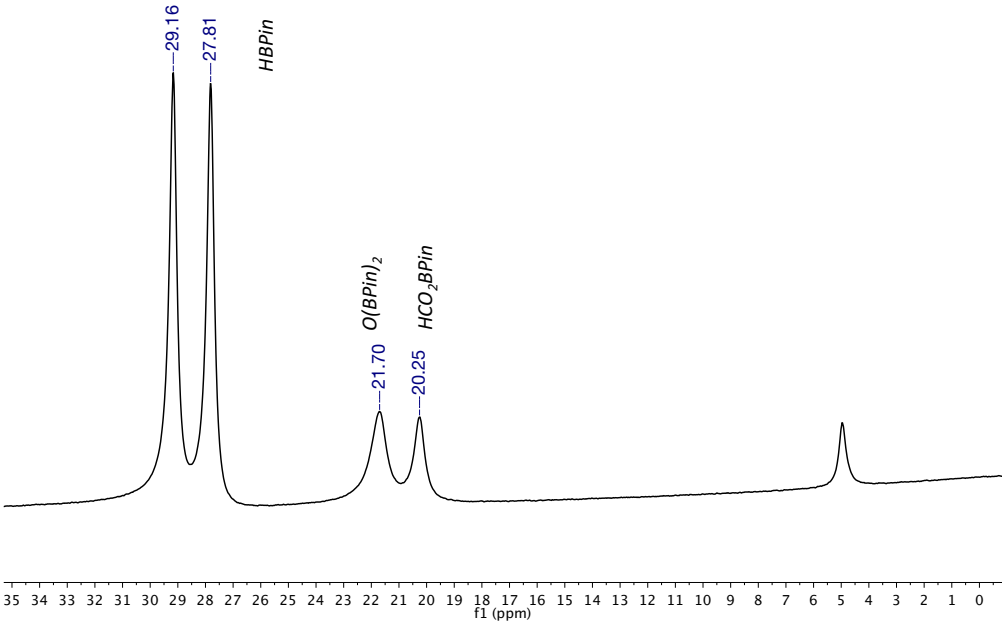
10 mol% Cu·O*t*Bu

^1H NMR (C_6D_6, 298 K, 400.0 MHz)



10 mol% Cu·O*t*Bu

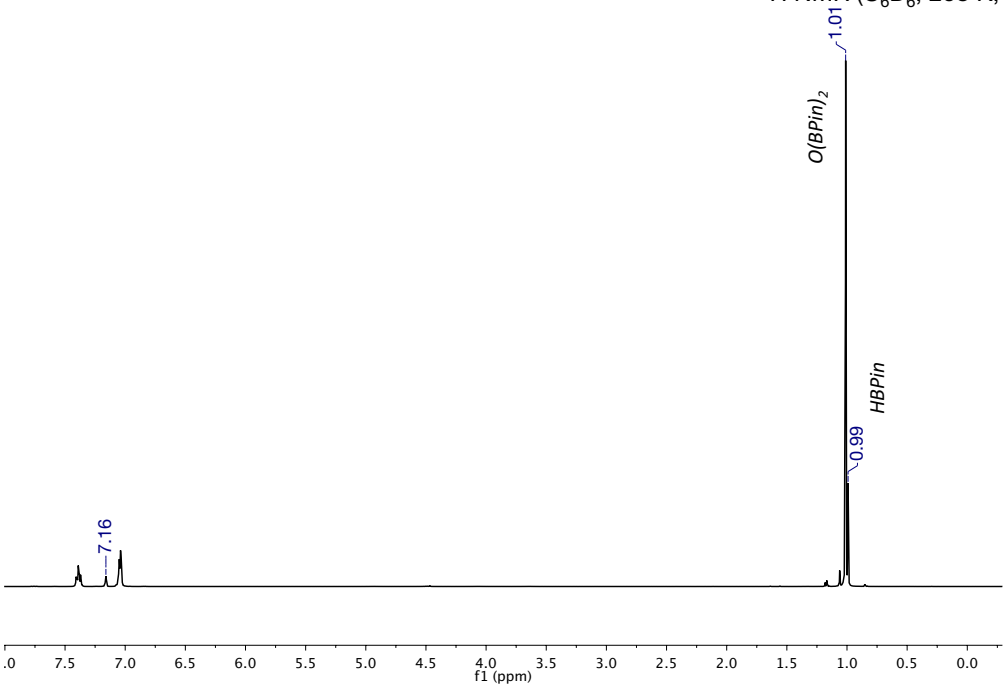
^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



Synthesis of $O(BPin)_2$ (B) - ^1H and $^{11}B\{^1H\}$ NMR spectra

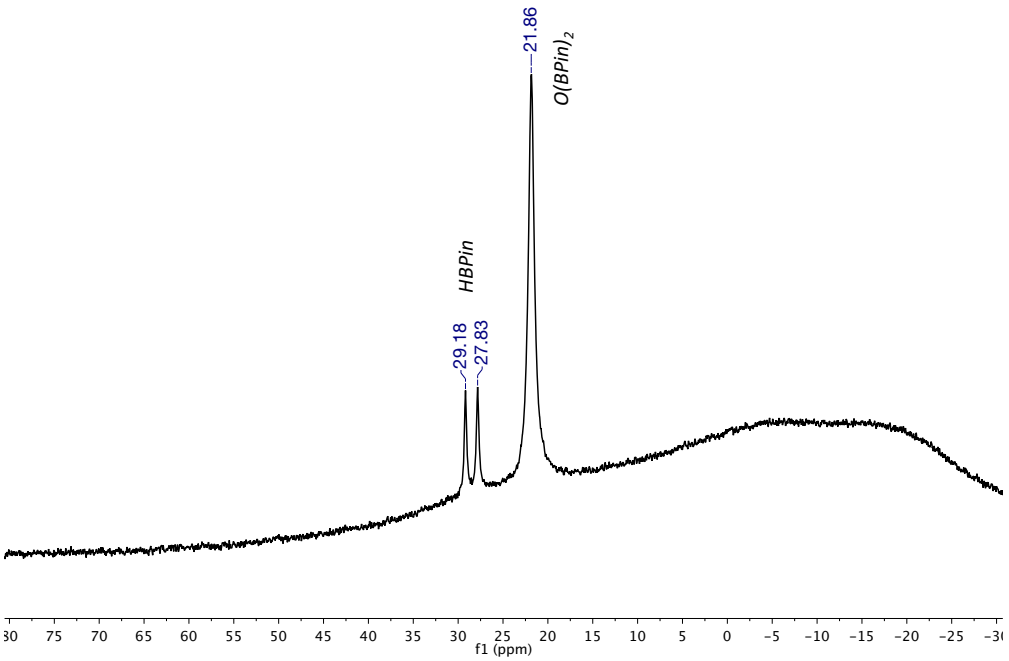
$O(Bpin)_2$

^1H NMR (C_6D_6, 298 K, 400.0 MHz)



$O(Bpin)_2$

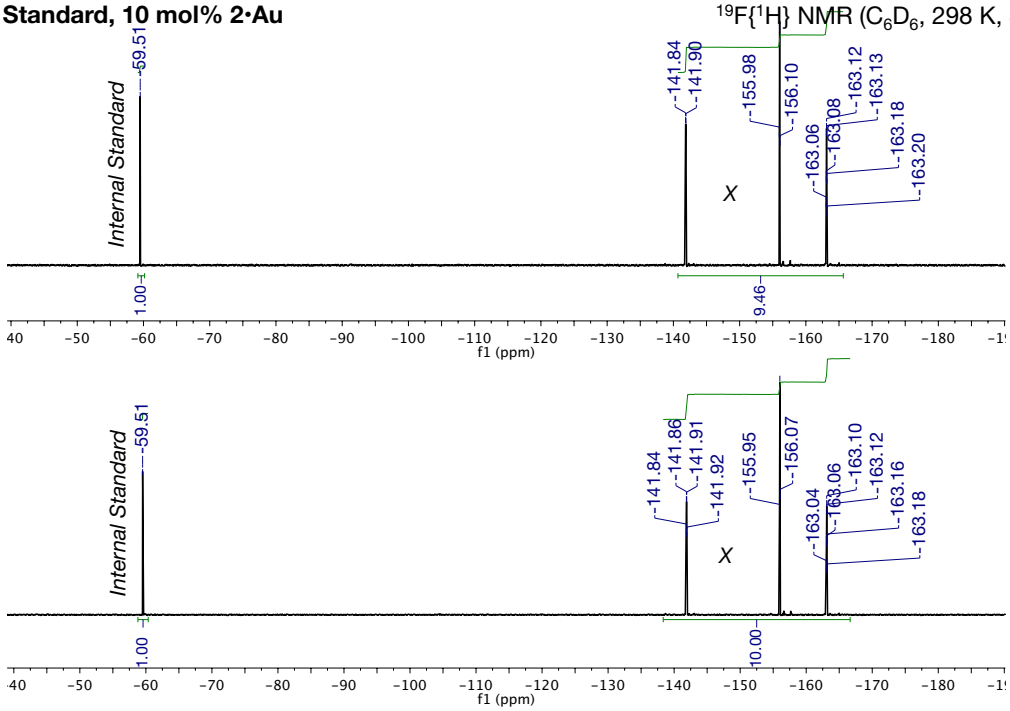
^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



Following catalysis with 2•Au via $^{19}F\{^1H\}$ NMR

^{19}F Internal Standard, 10 mol% 2·Au

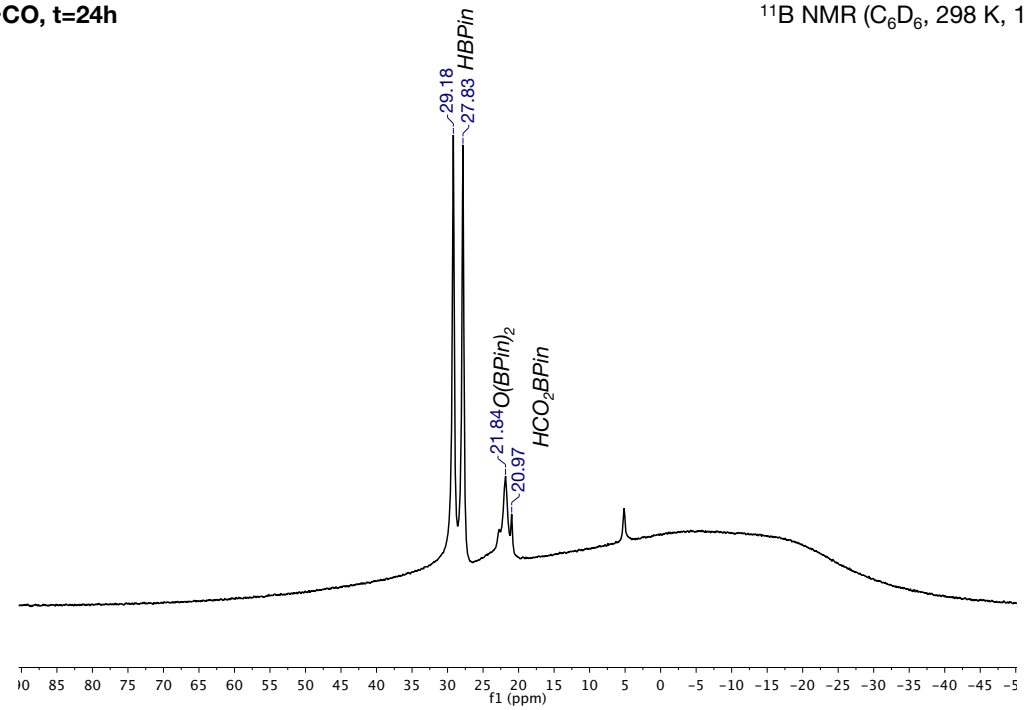
^{19}F{^{1}H} NMR (C_6D_6, 298 K, 376.5 MHz)



Reduction of CO_2 with HBPin using L_2M•CO (L_2M = 2, [Ni(PCy$_3$)$_2$], [Pd(PCy$_3$)$_2$]) - ^{1}H, ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra

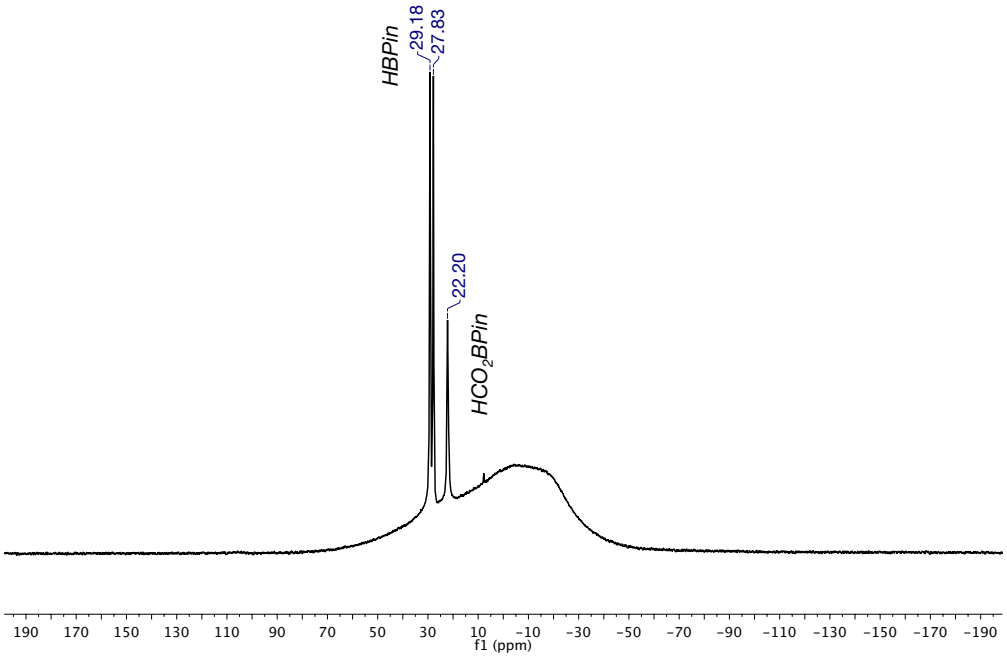
10 mol% 2·CO, t=24h

^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



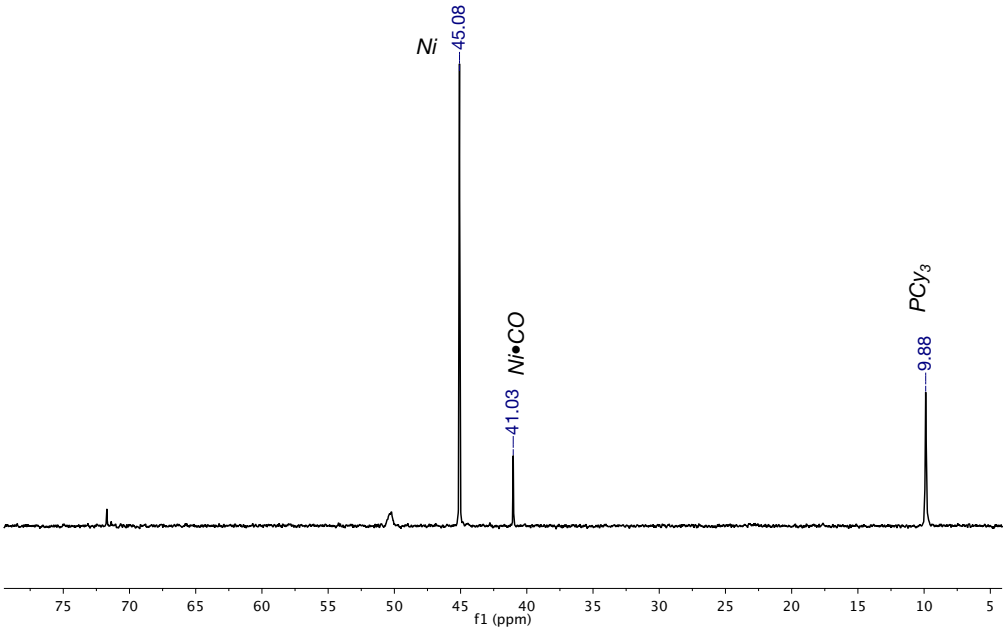
10 mol% Ni•CO, t=24h

^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



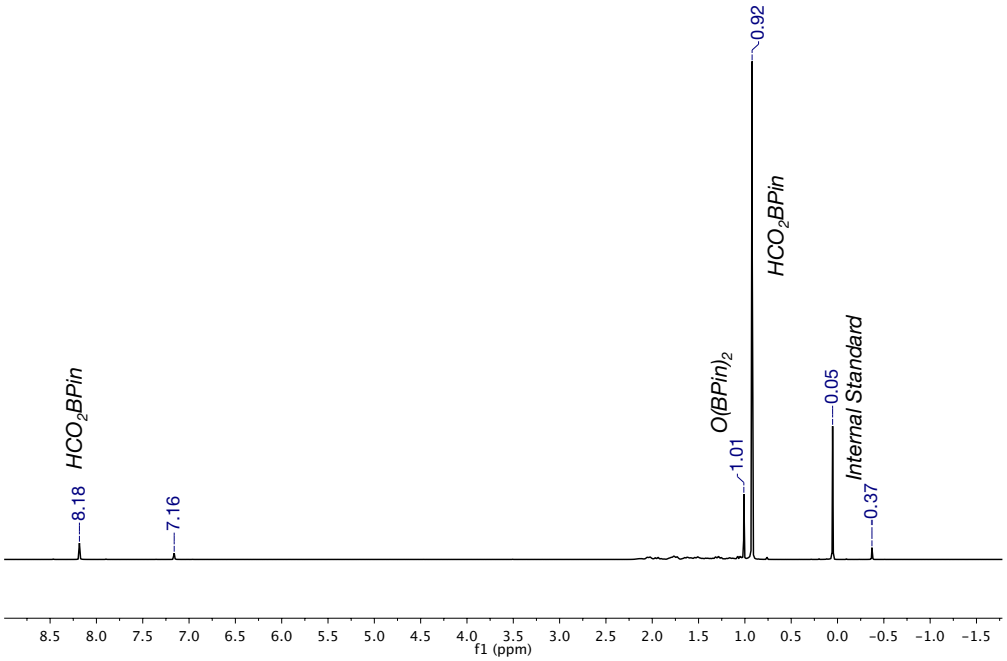
10 mol% Ni•CO, t=24h

$^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



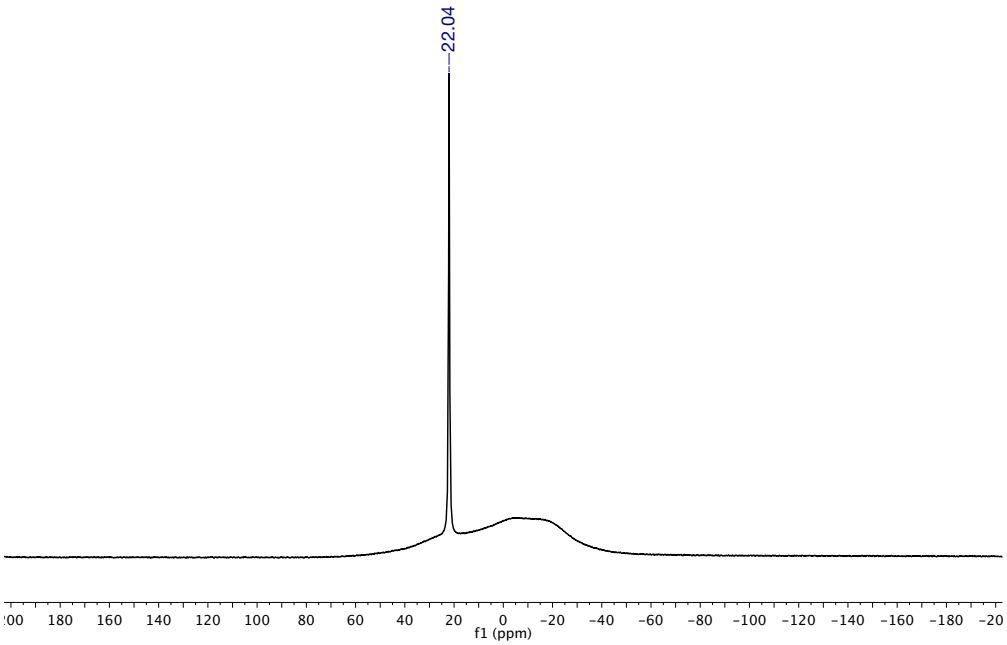
10 mol% Pd·CO, t=0.5h

^{1}H NMR (C_6D_6, 298 K, 400 MHz)



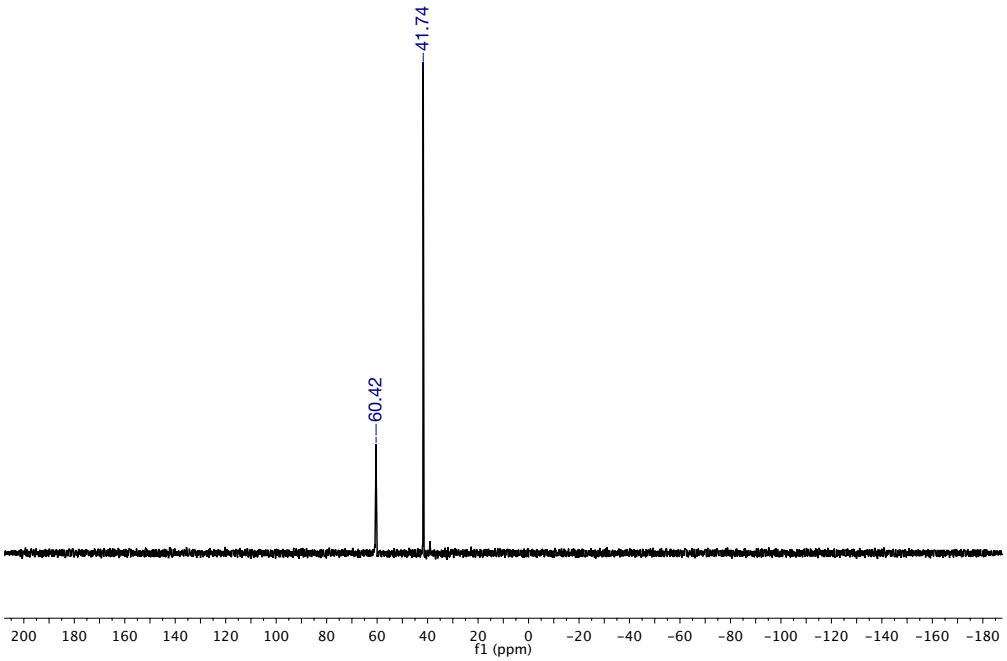
10 mol% Pd·CO, t=0.5h

^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



10 mol% Pd·CO, t=0.5h

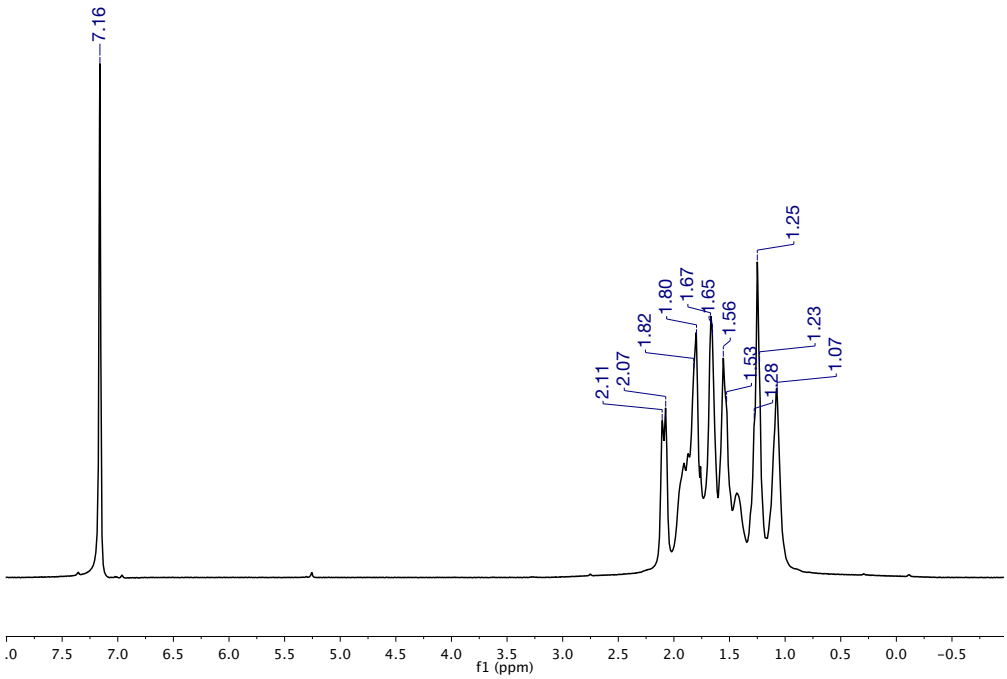
$^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



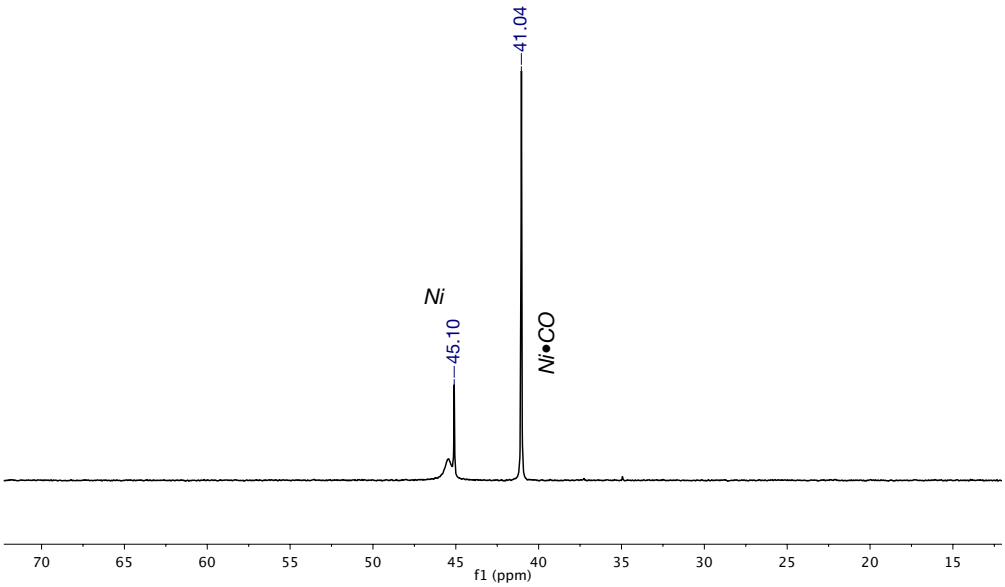
Ni•CO -^{1}H and $^{31}P\{^{1}H\}$ NMR spectra

Ni·CO

^{1}H NMR (C_6D_6, 298 K, 400 MHz)

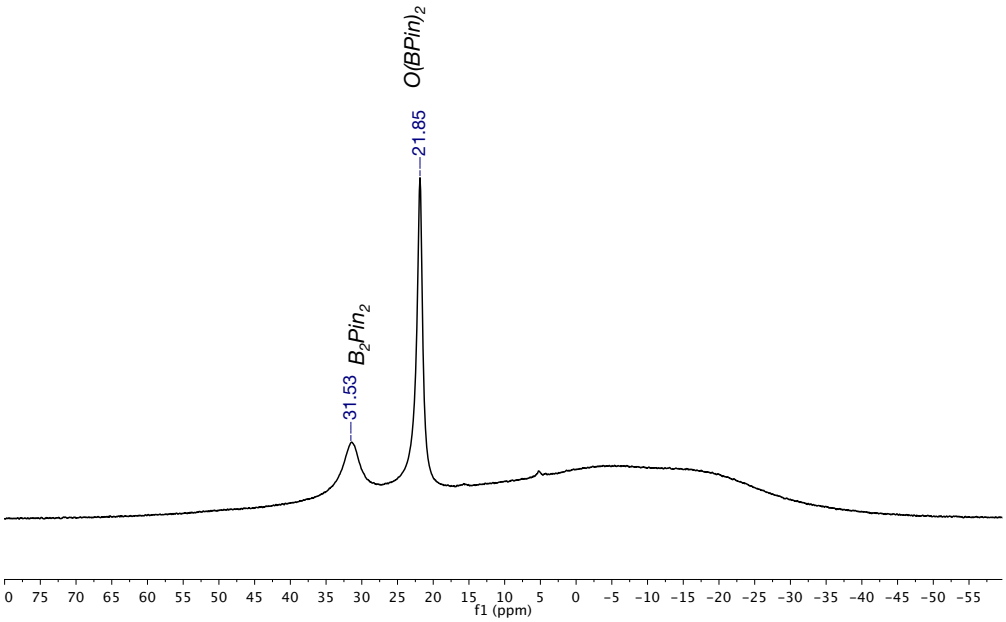


Ni·CO $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



Catalysis of 2•Au for the reduction of B_2Pin_2 with CO_2 - $^{11}B\{^{1}H\}$ NMR spectra

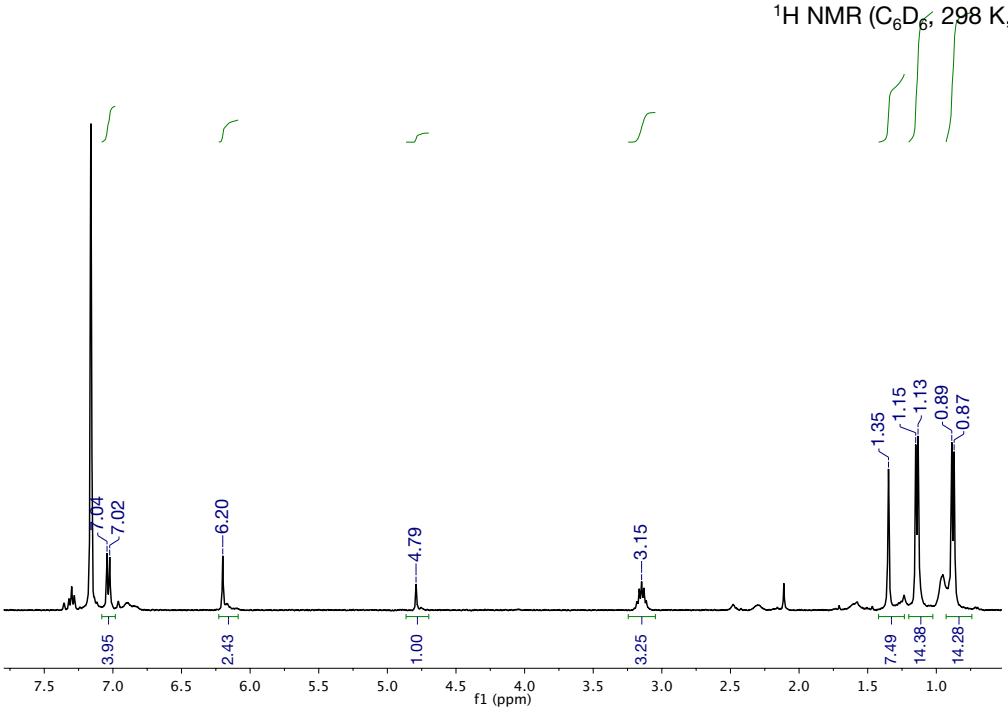
10 mol% 2·Au, CO_2+B_2Pin_2, t=24h ^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



In-situ Synthesis of 2•IPr - ^{1}H and $^{19}F\{^{1}H\}$ NMR spectra

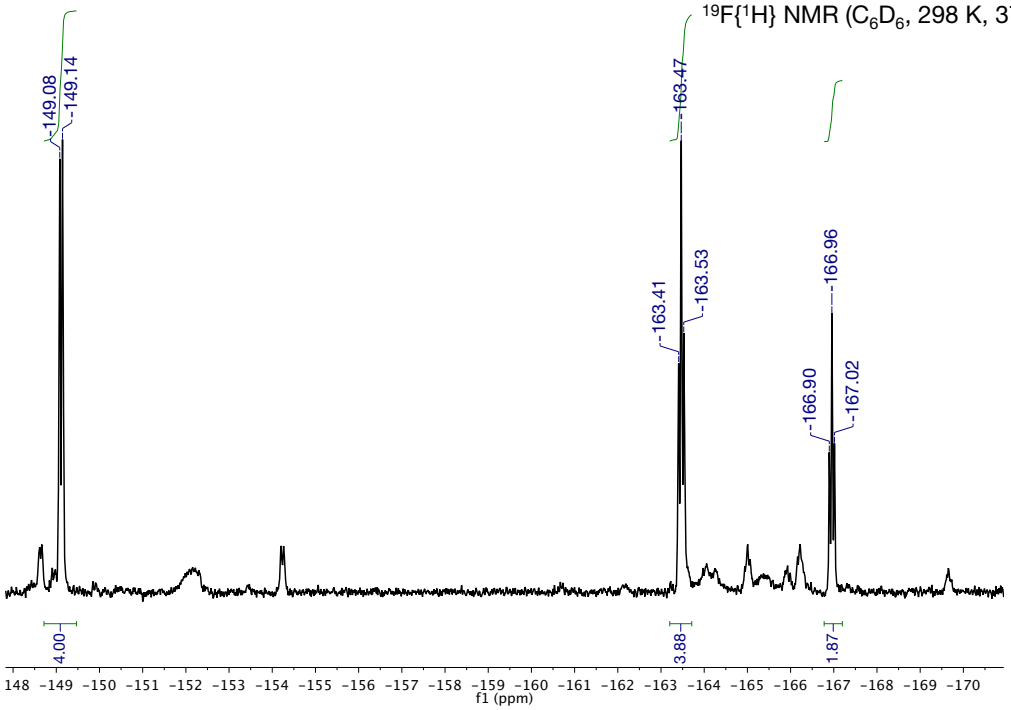
2•IPr

^{1}H NMR (C_6D_6, 298 K, 400 MHz)



2•IPr

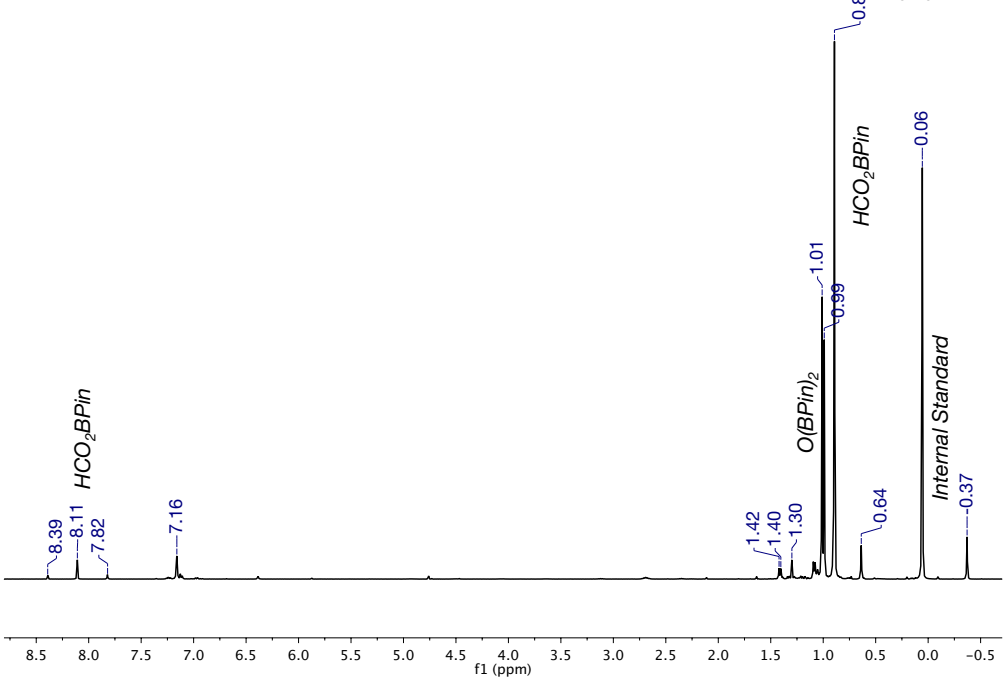
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



Catalysis with 2•IPr for the reduction of HBPin with CO_2 - ^1H and $^{11}B\{^1H\}$ NMR spectra

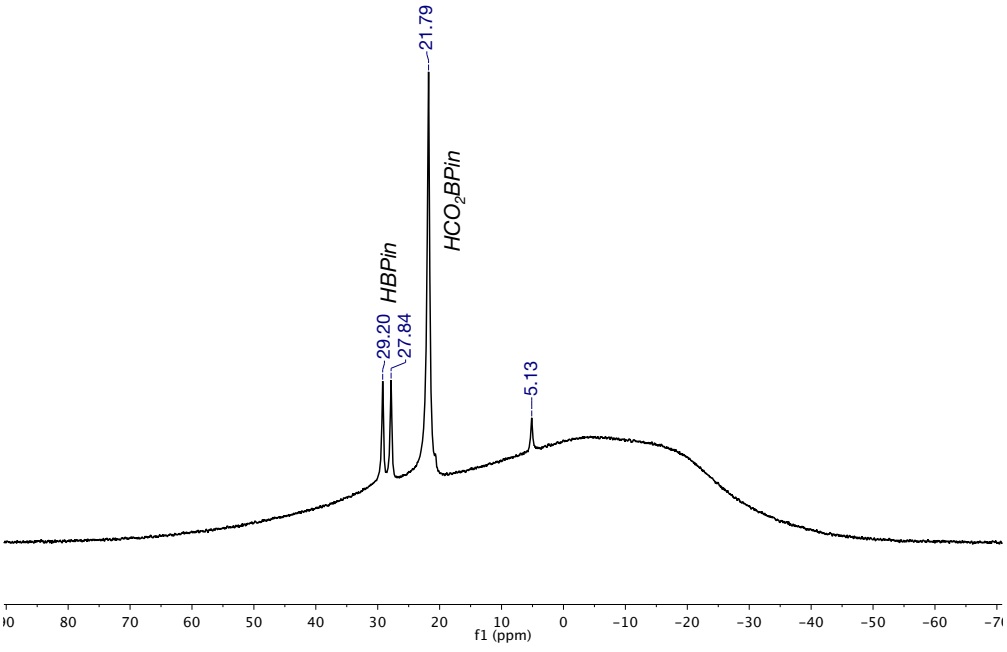
10 mol% 2·IPr, CO_2+HBPin, t=24h

^1H NMR (C_6D_6, 298 K, 400 MHz)



10 mol% 2·IPr, CO_2+HBPin, t=24h

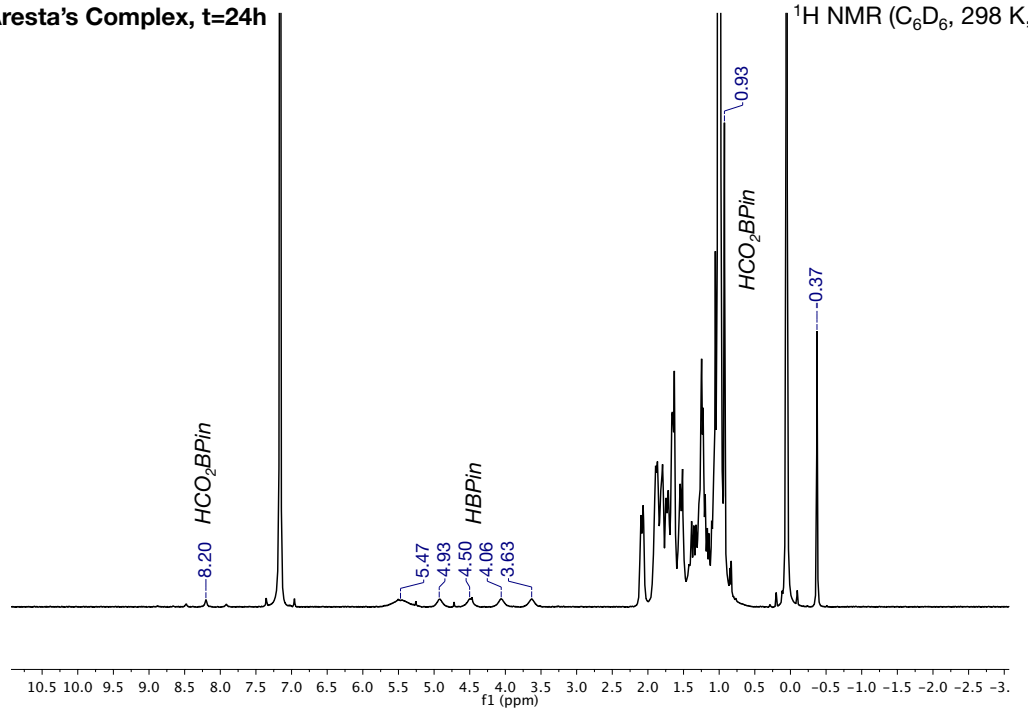
^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



Using Aresta's Complex for the reduction of CO_2 with HBPin - ^{1}H, $^{11}B\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra

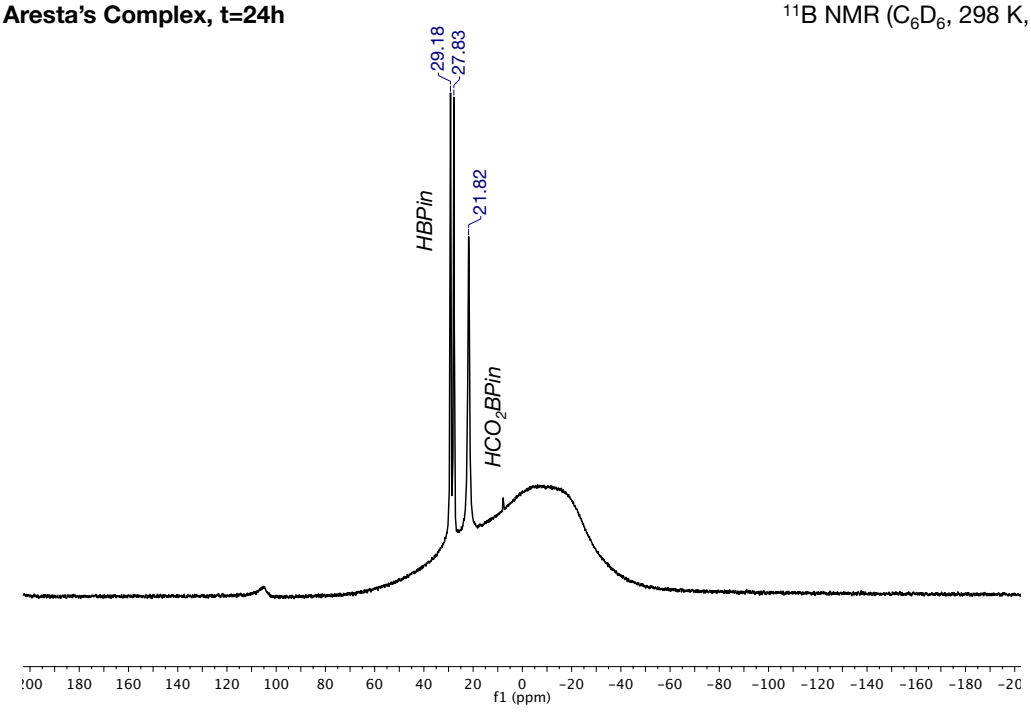
10 mol% Aresta's Complex, t=24h

^{1}H NMR (C_6D_6, 298 K, 400 MHz)



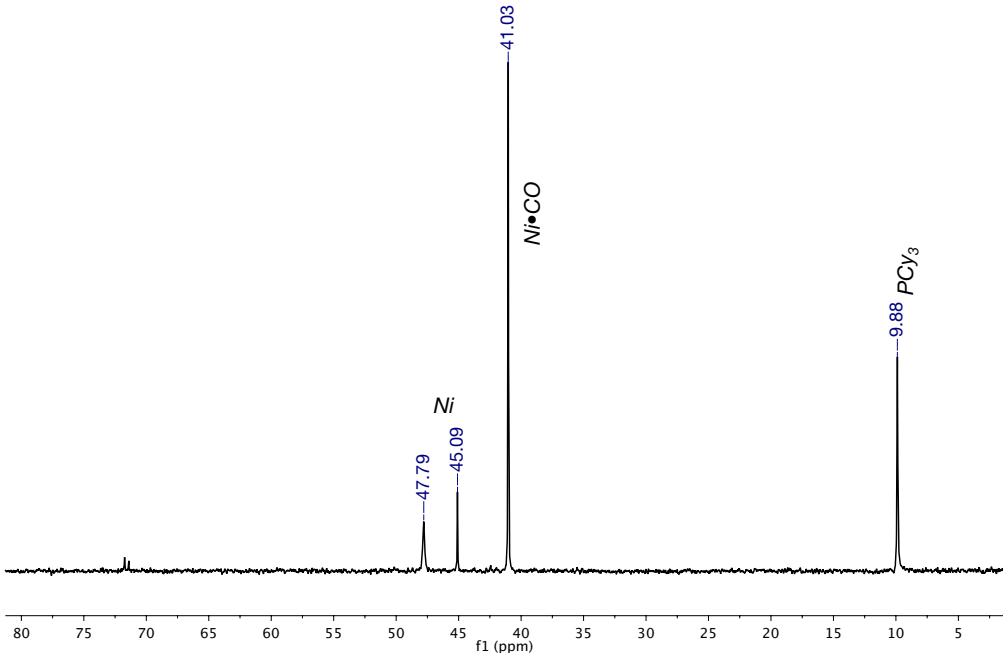
10 mol% Aresta's Complex, t=24h

^{11}B NMR (C_6D_6, 298 K, 128.4 MHz)



10 mol% Aresta's Complex, t=24h

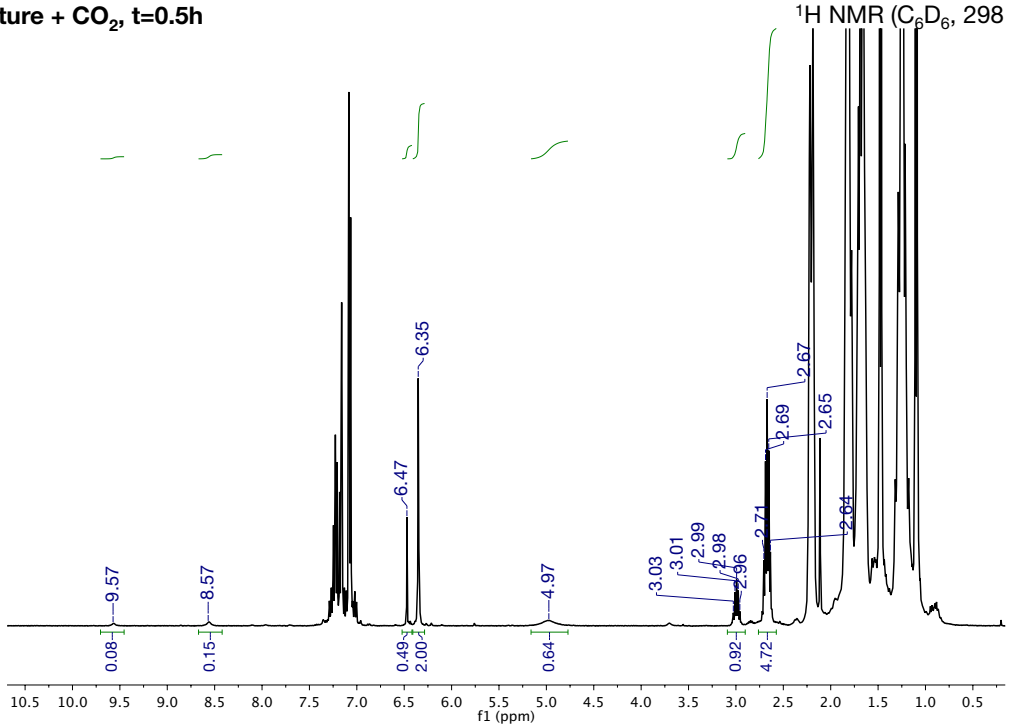
$^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



Addition of CO_2 to mixtures of Au•Pd - ^{1}H NMR spectra

Pd·Au mixture + CO_2, t=0.5h

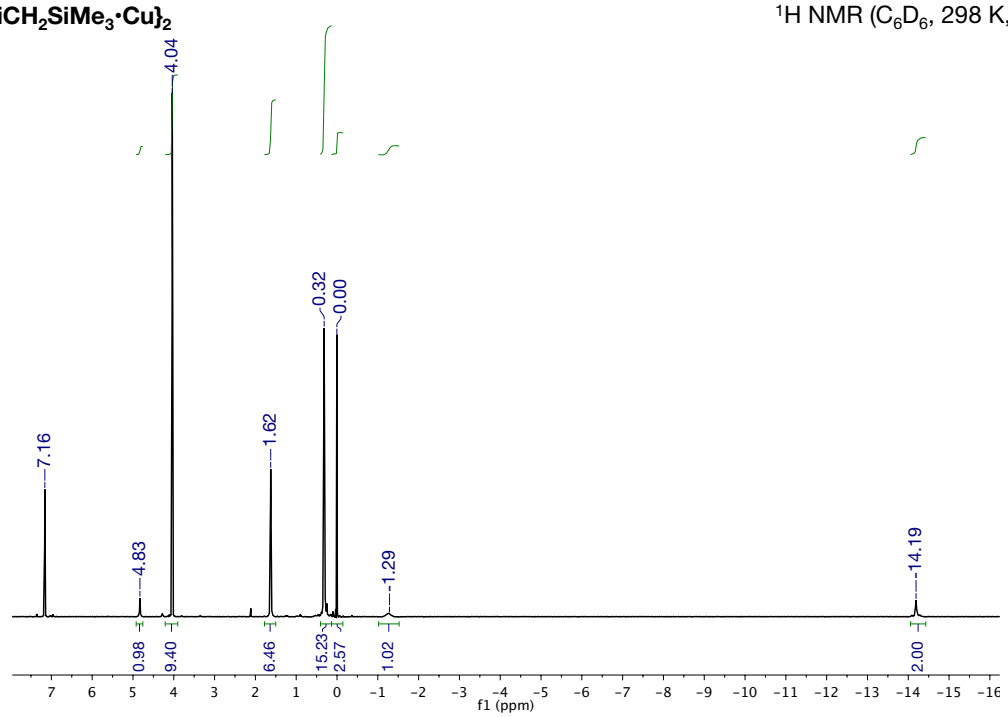
^{1}H NMR (C_6D_6, 298 K, 400 MHz)



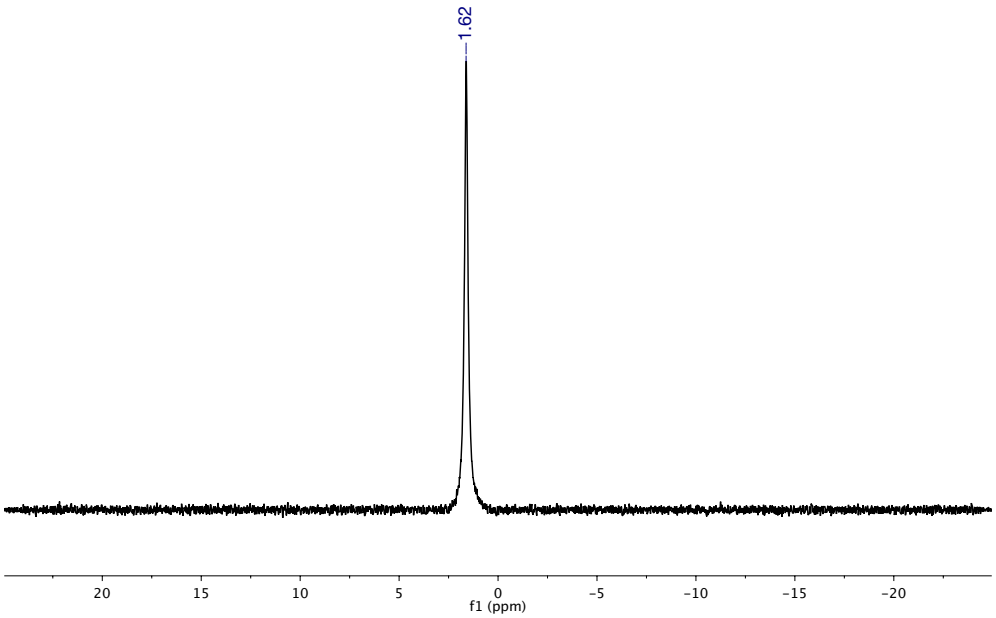
3.4 Chapter 5

In-situ synthesis of $\{Cp_2WH_2{\bullet}LiCH_2SiMe_3{\bullet}Cu\}_2$ *-* ^1H *and* ^7Li *NMR spectra*

$\{Cp_2WH_2{\cdot}LiCH_2SiMe_3{\cdot}Cu\}_2$ ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)



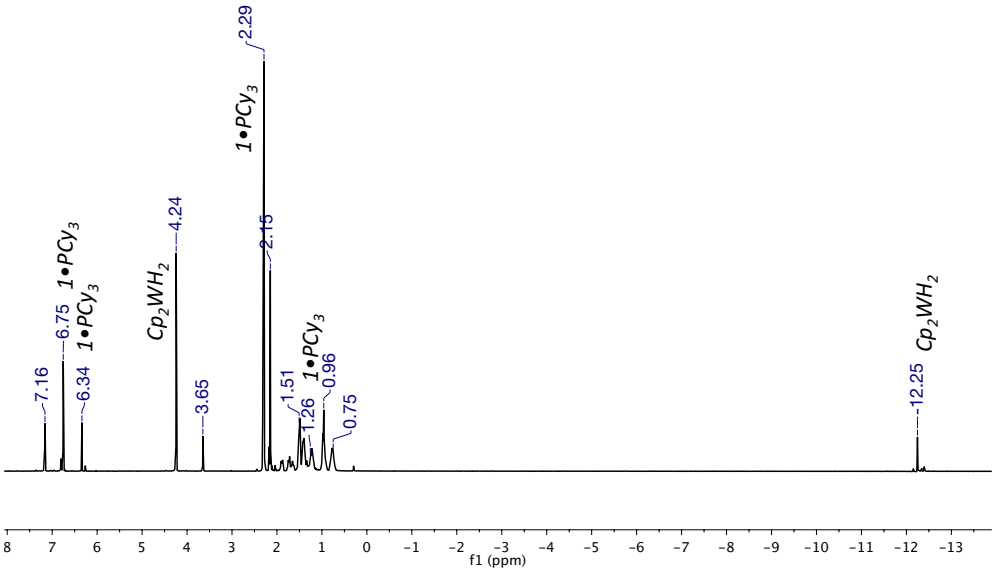
$\{Cp_2WH_2{\cdot}LiCH_2SiMe_3{\cdot}Cu\}_2$ ^{7}Li NMR (C_6D_6, 298 K, 155.5 MHz)



1•W + PCy_3 - ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra

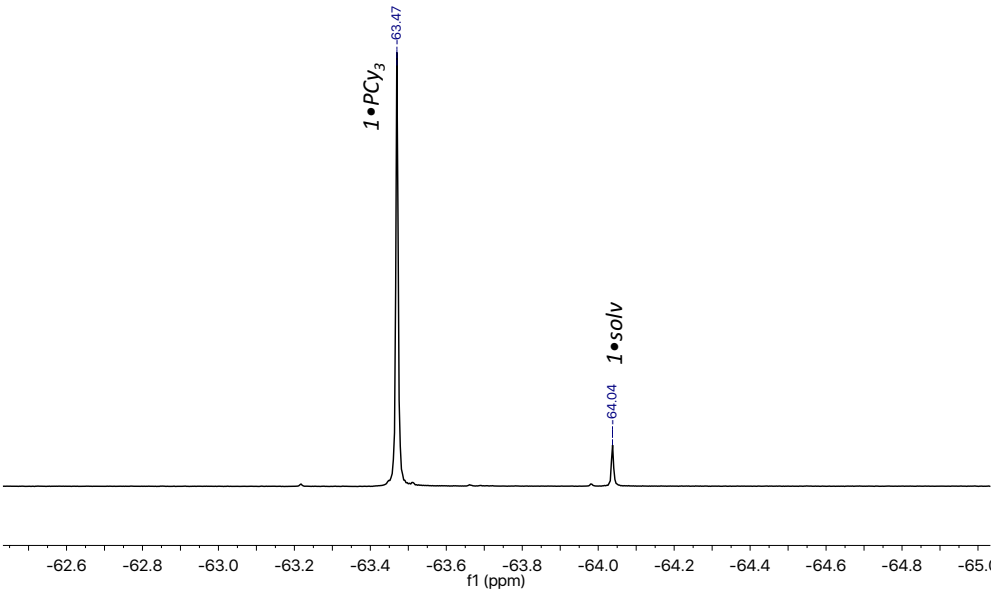
1•W + PCy_3

^1H NMR (C_6D_6, 298 K, 400.0 MHz)

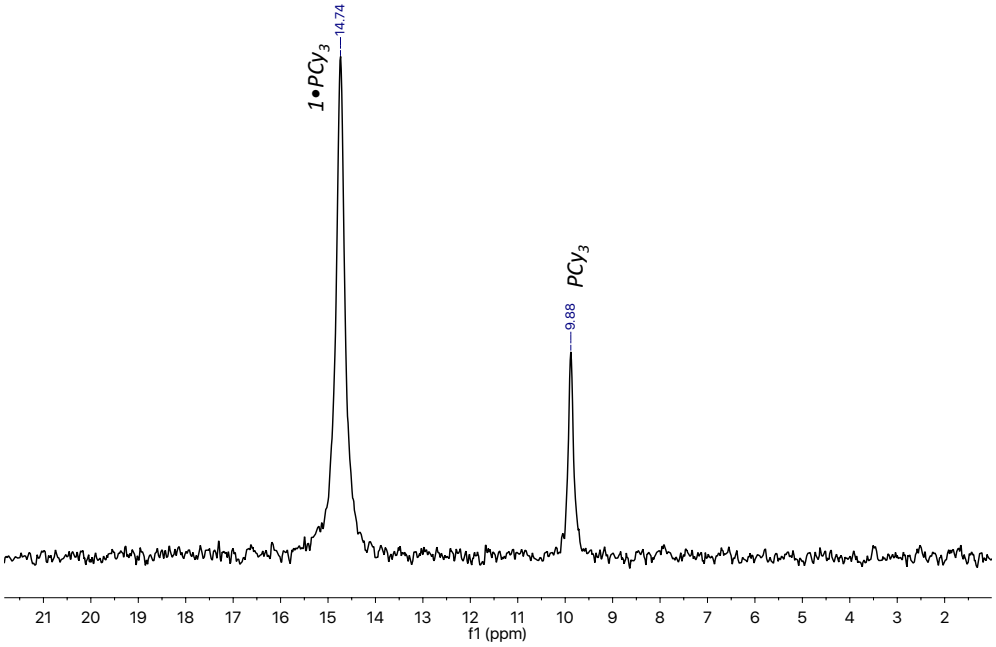


1•W + PCy_3

$^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)

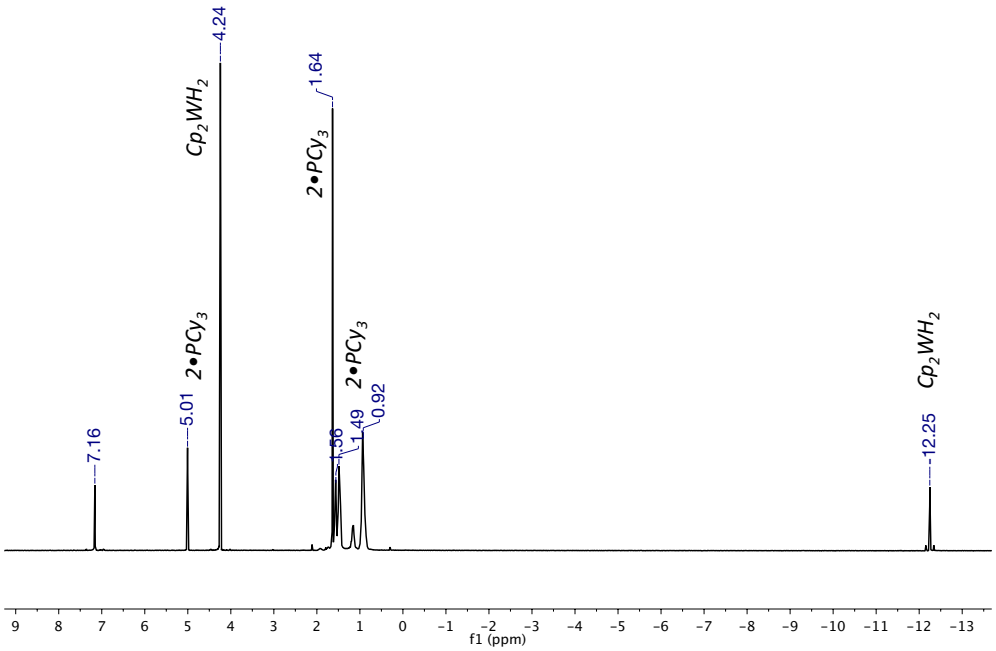


1·W + PCy_3 $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



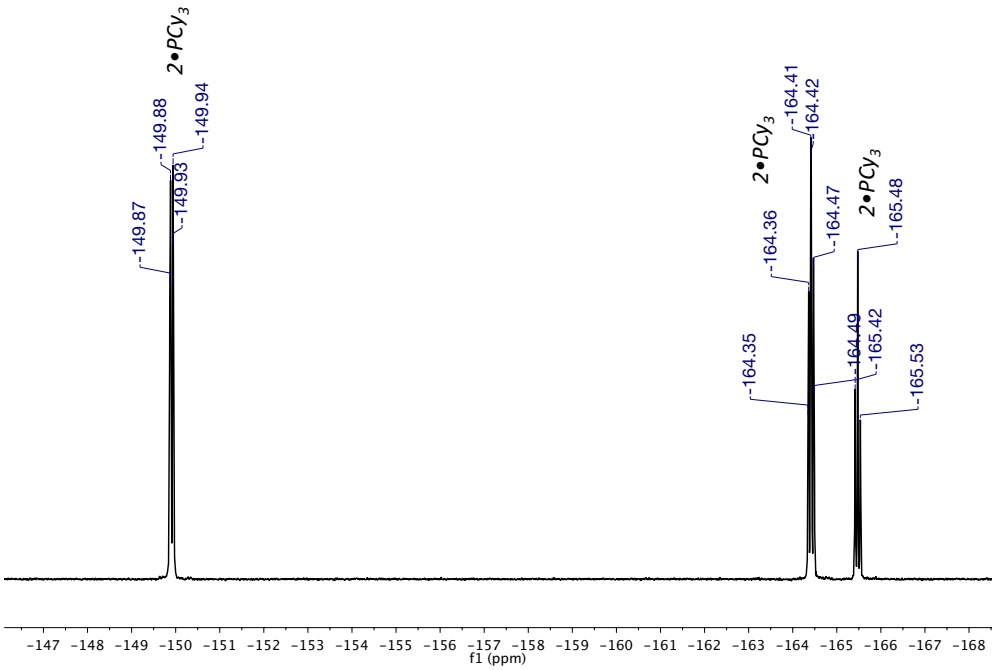
2•W + PCy_3 - ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra

2·W + PCy_3 ^1H NMR (C_6D_6, 298 K, 400.0 MHz)



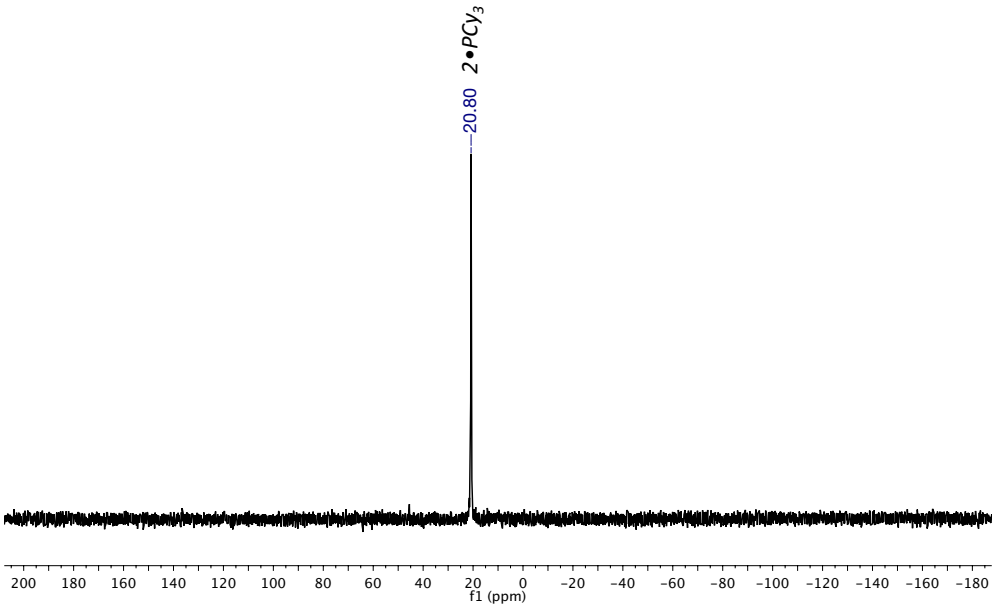
2•W + PCy_3

$^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



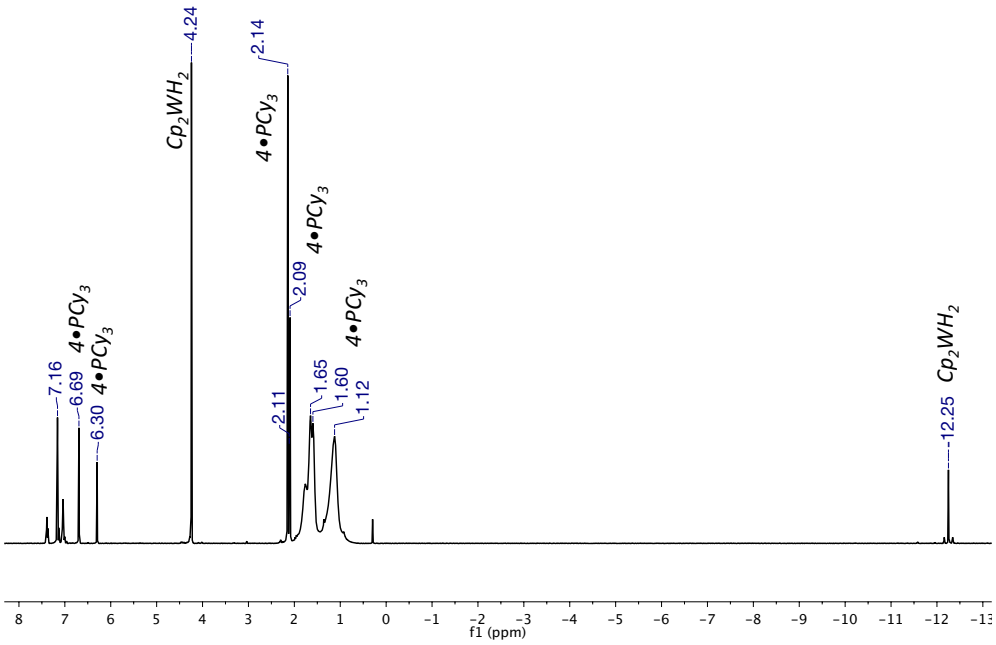
2•W + PCy_3

$^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)

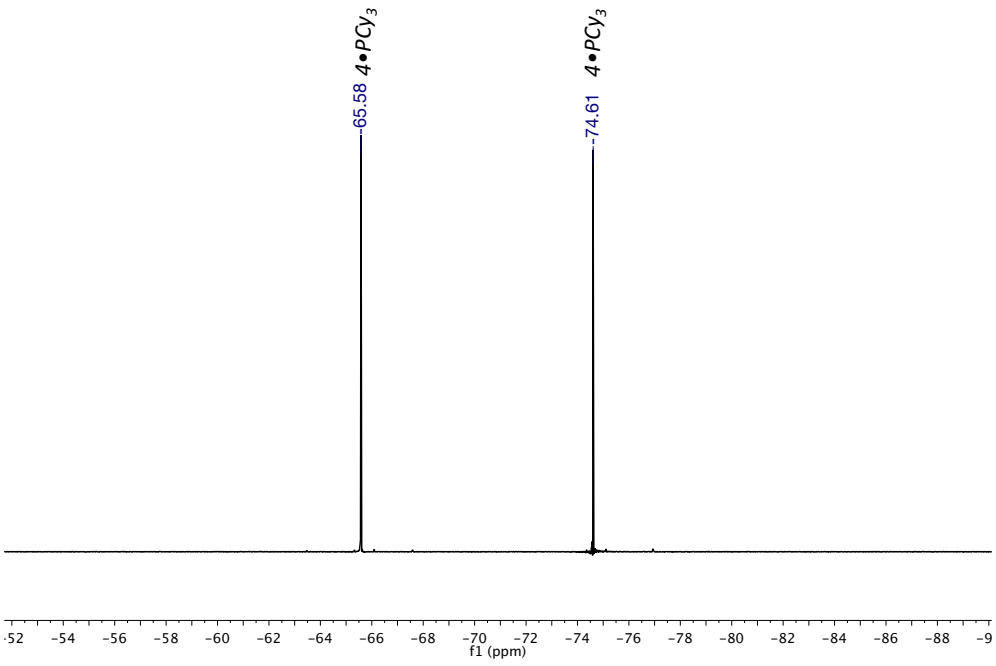


4•W + PCy₃ - ^{1}H, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra

4·W + PCy_3 ^{1}H NMR (C_6D_6, 298 K, 400.0 MHz)

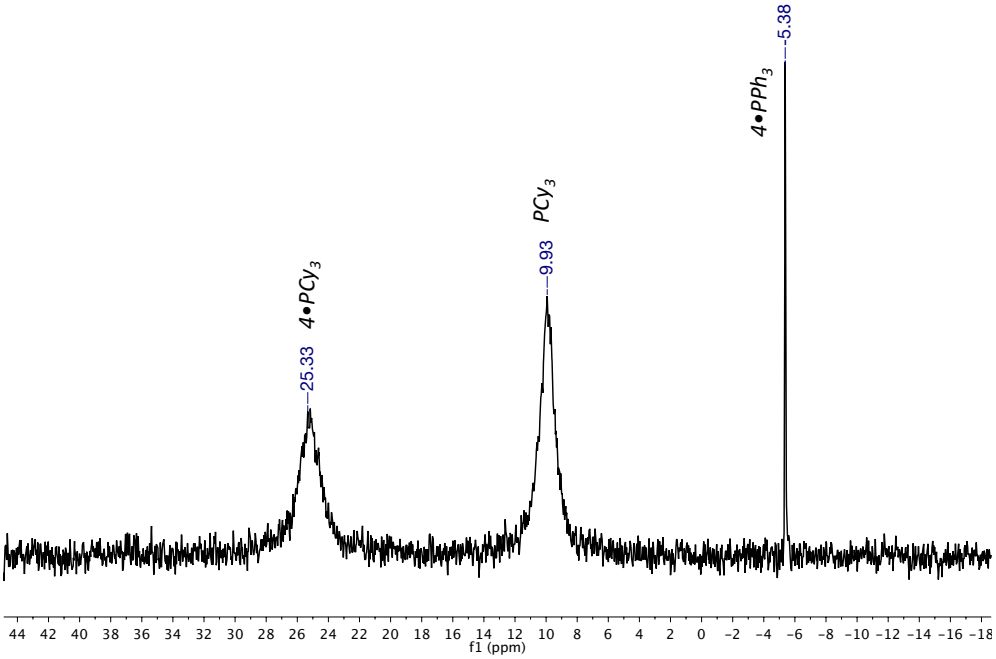


4·W + PCy_3 $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 376.5 MHz)



4·W + PCy_3

$^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz)



4. X-Ray Data

4.1 Chapter 2

1_2-2•tol and 4•PPh_3 - X-ray experiment acquisition parameters and selected data

data	1_2•tol	4•PPh_3	2•tol
Molecular formula	$C_{53}H_{54}Cu_2F_{12}N_4$• ($C_6H_{14}$)	$C_{32}H_{27}CuF_6NOP$• 0.5(C_6H_{14})	$C_{24}H_{15}CuF_{10}N_2$
Formula weight (g mol^{-1})	1188.25	693.14	584.92
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P $2_1/c$	$P2_1/n$ (no. 14)	P $2_12_12_1$
Temperature (K)	173(2)	173(2)	173(2)
a (Å)	14.0542(2)	17.4429(7)	6.1845(3)
b (Å)	22.2862(4)	16.3467(4)	18.1622(8)
c (Å)	18.7418(3)	23.0174(7)	20.0419(7)
α (deg)	–	-	–
β (deg)	91.8186(15)°	93.735(3)	–
γ (deg)	–	-	–
V (Å^3)	5867.24(16)	6549.1(4)	2251.17(17)
Z	4	8[b]	4
μ (mm^{-1})	0.803	0.779	1.070
ρ (g cm^{-3})	1.345	1.406	1.726
R_1 (obs)	0.0401	0.524	0.0370
wR_2[a] (all data)	0.1096	0.1492	0.0704

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two crystallographically independent molecules in the unit cell.

4.2 Chapter 3

1-2•B and 1-2•Zn - X-ray experiment acquisition parameters and selected data

data	1·B	2·B	1·Zn	2·Zn
Molecular formula	$C_{29}H_{33}BCuF_6N_3$	$C_{23}H_{17}BCuF_{10}N_3$	$C_{52}H_{65}CuF_6N_4Zn$	$C_{46}H_{49}CuF_{10}N_4Zn$
Formula weight (g mol^{-1})	611.93	599.74	988.99	976.80
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	C2/c
Temperature (K)	173(2)	173(2)	173(2)	173(2)
a (Å)	8.53577(17)	15.3260(4)	11.2064(4)	14.6898(7)
b (Å)	18.8782(4)	13.3574(5)	12.6573(5)	13.7067(5)
c (Å)	19.0194(4)	11.8161(4)	19.4151(7)	22.9433(10)
α (deg)	–	–	87.006(3)°	–
β (deg)	101.409(2)	93.483(3)	88.111(3)°	102.708(5)°
γ (deg)	–	–	67.584(4)°	–
V (Å^3)	3004.23(11)	2414.47(14)	2542.08(18)	4506.4(4)
Z	4	4	2	4
μ (mm^{-1})	1.551	1.000	1.586	1.082
ρ (g cm^{-3})	1.353	1.650	1.292	1.440
R_1 (obs)	0.0387	0.0377	0.0356	0.0305
wR_2[a] (all data)	0.1058	0.0823	0.0935	0.0756
Unique / observed reflections	5834 / 4712	4784 / 3660	9741 / 7990	4502 / 3702
R_{int}	0.0267	0.0239	0.0248	0.0144

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two crystallographically independent molecules in the unit cell.

1•Mg, L^2MgL^7, $Cu(L^4)_2$ and L^4ZnL^7 - X-ray experiment acquisition parameters and selected data

data	1•Mg	L^2MgL^7	$Cu(L^4)_2$	L^4ZnL^7
Molecular formula	$C_{52}H_{65}CuF_6MgN_4$	$C_{46}H_{48}F_{10}MgN_4$	$C_{43}H_{53}CuF_6N_3O$	$C_{43}H_{53}F_6N_3OZn$
Formula weight (g mol^{-1})	947.93	871.19	805.42	807.25
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic
Space group	Pbcn	P-1	$P2_12_12_1$	$P2_12_12$
Temperature (K)	173(2)	173(2)	173(2)	173(2)
a (Å)	15.5618(8)	10.4434(7)	11.1238(3)	11.1238(3)
b (Å)	14.1127(7)	11.0570(6)	17.0012(4)	17.0012(4)
c (Å)	23.1335(19)	20.7656(11)	21.8049(6)	21.8049(6)
α (deg)	–	86.963(4)	-	-
β (deg)	–	79.146(5)	-	-
γ (deg)	–	67.432(6)	-	-
V (Å^3)	5080.6(6)	2174.1(2)	4123.71(18)	4123.71(18)
Z	4	2	4	4
μ (mm^{-1})	0.502	0.121	0.592	0.658
ρ (g cm^{-3})	1.239	1.331	1.297	1.300
R_1 (obs)	0.0839	0.0450	0.0386	0.0397
wR_2[a] (all data)	0.1863	0.1099	0.0883	0.0934

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two crystallographically independent molecules in the unit cell.

4.3 Chapter 4

1-2•Au and 4•Au - X-ray experiment acquisition parameters and selected data

data	1•Au	2•Au-I	2•Au-II	4•Au
Molecular formula	$C_{50}H_{60}AuCuF_6N_4$	$C_{44}H_{44}AuCuF_{10}N_4$	$C_{44}H_{44}AuCuF_{10}N_4$	$C_{59}H_{64}AuCuF_6N_3OP$• 0.75(C_7H_{16})
Formula weight (g mol^{-1})	1091.52	1079.34	1079.34	1131.75
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	P-1 (no. 2)
Temperature (K)	173(2)	173(2)	173(2)	173(2)
a (Å)	15.47601(15)	12.8188(2)	12.81672(18)	12.6727(5)
b (Å)	28.4914(2)	23.1429(3)	23.1476(3)	12.6879(5)
c (Å)	23.7046(2)	16.2770(3)	16.2665(3)	22.0070(9)
α (deg)	90	90	90	89.669(3)
β (deg)	106.3386(10)	111.430(2)	111.4219(17)	83.790(3)
γ (deg)	90	90	90	62.215(4)
V ($Å^3$)	10030.03(16)	4494.99(15)	4492.51(12)	3108.1(2)
Z	8[b]	4	4	2
μ (mm^{-1})	6.427	7.299	7.303	5.527
ρ (g cm^{-3})	1.446	1.595	1.596	1.402
R_1 (obs)	0.0335	0.0304	0.0314	0.0406
wR_2[a] (all data)	0.0882	0.0741	0.0762	0.1047

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two crystallographically independent molecules in the unit cell.

$Cu(L^2)_2$ and 2•IPr - X-ray experiment acquisition parameters and selected data

data	$Cu(L^2)_2$	2•IPr
Molecular formula	$C_{34}H_{14}CuF_{20}N_4$	$C_{44}H_{43}CuF_{10}N_4$
Formula weight (g mol^{-1})	922.03	881.36
Crystal system	orthorhombic	Triclinic
Space group	*Pnna* (no. 52)	P-1
Temperature (K)	173(2)	173(2)
a (Å)	15.6754(14)	9.3029(4) Å
b (Å)	47.036(2)	11.0644(4)
c (Å)	9.0462(5)	21.1959(9)
α (deg)	90	99.389(3)°
β (deg)	90	100.472(4)°
γ (deg)	90	105.729(3)
V ($Å^3$)	6669.9(7)	2012.39(15)
Z	8[b]	2
μ (mm^{-1})	2.301	0.627
ρ (g cm^{-3})	1.836	1.455
R_1 (obs)	0.0770	0.0434
wR_2[a] (all data)	0.2142	0.0983

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two independent C_2-symmetric molecules.

4.4 Chapter 5

1-2•W, 4•W and W•Li - X-ray experiment acquisition parameters and selected data

data	1·W	2·W	4·W	W·Li
Molecular formula	$C_{33}H_{35}CuF_6N_2W$	$C_{27}H_{19}CuF_{10}N_2W$	$C_{24}H_{24}CuF_6NOW{\cdot}C_6H_6$	$C_{36}H_{68}Cu_2Li_2Si_4W_2$
Formula weight (g mol^{-1})	821.02	808.83	781.94	1121.92
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/m$ (no. 11)	P-1 (no. 2)
Temperature (K)	173(2)	173(2)	173(2)	173(2)
a (Å)	20.6872(2)	7.5947(3)	11.3041(5)	10.2525(5)
b (Å)	21.27381(17)	17.2024(7)	9.7028(5)	10.8355(7)
c (Å)	15.15393(18)	20.5126(10)	13.4827(7)	12.4680(7)
α (deg)	90	90	90	67.095(6)
β (deg)	110.5350(13)	98.831(5)°,	101.228(4)	72.887(5)
γ (deg)	90	90	90	63.990(6)
V (Å^3)	6245.42(12)	2648.2(2)	1450.49(13)	1133.80(13)
Z	8[b]	4	2	1
μ (mm^{-1})	8.082	5.235	4.758	11.352
ρ (g cm^{-3})	1.746	2.029	1.790	1.643
R_1 (obs)	0.0292	0.0445	0.0393	0.0265
wR_2[a] (all data)	0.0726	0.1053	0.0803	0.0669

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(Fo^2) + (aP)^2 + bP$.

[b] There are two independent molecules in the asymmetric unit.

5. DFT Z Matrices

5.1 Chapter 2

1
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2067.180512
Sum of electronic and thermal Energies= -2067.140911
Sum of electronic and thermal Enthalpies= -2067.139966
Sum of electronic and thermal Free Energies= -2067.254085

0 1

Cu	-0.04132100	-0.60617300	0.46495000
N	-1.53363300	0.65402700	0.14824200
C	-1.28967000	1.92529100	-0.05698200
C	-0.02713200	2.53431200	-0.07903900
H	-0.01949600	3.60111300	-0.21183300
C	1.22715900	1.91526900	0.00005800
N	1.45879400	0.63324000	0.17161400
C	-2.46875500	2.88198200	-0.32477400
F	-3.10289300	2.56685100	-1.46365000
F	-2.08656800	4.15974900	-0.44152900
F	-3.37559900	2.84702700	0.66155400
C	2.42006400	2.88233800	-0.15435600
F	3.10362700	2.64989500	-1.28432500
F	2.04467900	4.16727500	-0.19538500
F	3.28154800	2.77445300	0.86673200
C	-2.82921000	0.07057600	0.08300800
C	-3.26516600	-0.47990200	-1.12805300
C	-4.47718200	-1.16259600	-1.15026800
H	-4.82329100	-1.58357400	-2.09130600
C	-5.24568300	-1.33696800	-0.00356500
C	-4.75982900	-0.82014200	1.19445900
H	-5.33258600	-0.96628700	2.10727900
C	-3.55849200	-0.12174200	1.26227500
C	-2.40224700	-0.39601800	-2.35550900
H	-2.88773600	-0.87179700	-3.20976800
H	-1.44515000	-0.90233400	-2.18566100
H	-2.17436800	0.63608500	-2.62595400
C	-6.57178200	-2.04895600	-0.05819700
H	-6.59972100	-2.78479500	-0.86543400
H	-7.38749700	-1.34023800	-0.23361900
H	-6.78740800	-2.56896400	0.87837600
C	-3.03845900	0.39480600	2.57494200
H	-3.61572700	-0.00332200	3.41164600
H	-3.08606200	1.48472400	2.61951900
H	-1.98793700	0.12454300	2.71986000
C	2.76447000	0.06756300	0.11061400
C	3.46343800	-0.19194500	1.29481300
C	4.71564800	-0.79348600	1.20972600
H	5.26708200	-0.98604100	2.12697900
C	5.28313200	-1.14317400	-0.01212800
C	4.53902900	-0.91959000	-1.16604300
H	4.94506300	-1.22485500	-2.12759700
C	3.27428700	-0.34288800	-1.12684800
C	2.87050100	0.17908500	2.62556300
H	2.79353500	1.26276400	2.73606800
H	3.47744000	-0.20358700	3.44828500
H	1.85533000	-0.21675700	2.73475500
C	6.66335600	-1.74132900	-0.08358300
H	6.76149100	-2.42406500	-0.93111000
H	6.90781400	-2.29658900	0.82512900
H	7.42111900	-0.96040700	-0.20365000
C	2.43908500	-0.22170000	-2.37147100
H	1.50426800	-0.78295200	-2.26070500
H	2.97081400	-0.61572500	-3.23975000
H	2.16445600	0.81248600	-2.58508100
C	-1.34346600	-3.53071900	-0.85135800
C	-1.76852700	-2.94655400	0.32007100
H	-2.82458600	-2.85795000	0.54559000
C	-0.81509200	-2.44504800	1.23022500
H	-1.14417200	-2.10340900	2.20751800
C	0.56315200	-2.59292800	0.95987300
H	1.29992100	-2.38252000	1.73084200
C	0.98834500	-3.23832200	-0.22764700
C	0.02588300	-3.66855900	-1.12347800
H	0.33967300	-4.15705200	-2.04170800
H	-2.07331700	-3.89681200	-1.56559600
C	2.44634100	-3.52354200	-0.45540600
H	3.08388500	-2.92076200	0.19136400
H	2.65912800	-4.57787400	-0.25072100
H	2.73789300	-3.32281700	-1.48834100

2
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1956.045160
Sum of electronic and thermal Energies= -1956.017799
Sum of electronic and thermal Enthalpies= -1956.016855
Sum of electronic and thermal Free Energies= -1956.105044

0 1

Cu	0.00000000	0.40520800	-0.08780500
N	1.57867600	-0.43014700	0.50118600
C	1.29998400	-1.45445700	1.33429000
C	0.00000000	-1.87292800	1.69468500
H	0.00000000	-2.69852700	2.39489500
C	-1.29998400	-1.45445700	1.33429000
N	-1.57867600	-0.43014700	0.50118600
C	2.45065800	-2.21599800	1.95908600
H	2.89495900	-2.89963000	1.22883600
H	2.11239400	-2.80414200	2.81230600
H	3.23326900	-1.53274600	2.30327100
C	-2.45065800	-2.21599800	1.95908600
H	-3.23326900	-1.53274600	2.30327100
H	-2.11239400	-2.80414200	2.81230600
H	-2.89495800	-2.89963000	1.22883700
C	2.88895900	-0.09535700	0.12860000
C	3.69614900	-0.92673700	-0.65382900
F	3.23120100	-2.16760900	-1.01873500
C	4.95480200	-0.53600900	-1.08681400
F	5.71599500	-1.38276100	-1.84522400
C	5.43835900	0.72284000	-0.75962700
F	6.67642400	1.11691300	-1.18498100
C	4.65473100	1.58027200	0.00099100
F	5.12279900	2.82408500	0.32438000
C	3.40327600	1.16907000	0.43409900
F	2.63877400	2.04029800	1.16880400
C	-2.88895900	-0.09535700	0.12860000
C	-3.40327600	1.16907000	0.43409900
F	-2.63877400	2.04029800	1.16880400
C	-4.65473100	1.58027200	0.00099100
F	-5.12279900	2.82408500	0.32438100
C	-5.43835900	0.72284000	-0.75962700
F	-6.67642400	1.11691300	-1.18498100
C	-4.95480200	-0.53600900	-1.08681400
F	-5.71599500	-1.38276100	-1.84522500

C	-3.69614900	-0.92673700	-0.65382900
F	-3.23120100	-2.16760900	-1.01873600

3
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2802.455593
Sum of electronic and thermal Energies= -2802.432412
Sum of electronic and thermal Enthalpies= -2802.431467
Sum of electronic and thermal Free Energies= -2802.511963

0 1

Cu	0.00000000	0.00000100	-0.69820600
N	-1.57725900	-0.00000400	0.31927800
C	-1.29713000	-0.00000900	1.63576800
C	0.00000000	-0.00001300	2.19503000
H	0.00000000	-0.00001800	3.27754600
C	1.29713000	-0.00000900	1.63576800
N	1.57725800	-0.00000400	0.31927800
C	-2.46176800	-0.00000500	2.60502400
C	2.46176800	-0.00000800	2.60502400
C	-2.90066000	0.00000000	-0.16290800
C	-3.58240800	1.19017600	-0.45733000
C	-4.85492200	1.20730300	-1.01219200
H	-5.33615300	2.15362400	-1.22345100
C	-5.49411900	0.00000900	-1.29066600
C	-4.85492900	-1.20728900	-1.01219400
H	-5.33616500	-2.15360700	-1.22345500
C	-3.58241500	-1.19017100	-0.45733200
C	2.90065900	0.00000000	-0.16290800
C	3.58241400	-1.19017100	-0.45733400
C	4.85492800	-1.20729000	-1.01219600
H	5.33616300	-2.15360800	-1.22345800
C	5.49411900	0.00000800	-1.29066600
C	4.85492300	1.20730200	-1.01218900
H	5.33615400	2.15362300	-1.22344700
C	3.58240900	1.19017500	-0.45732900
H	3.08952400	-0.88451700	2.45163000
H	3.08949300	0.88452900	2.45165800
H	2.11627000	-0.00003000	3.63896100
H	-2.11627000	-0.00002500	3.63896200
H	-3.08949400	0.88453100	2.45165700
H	-3.08952400	-0.88451600	2.45163300
H	-6.48609500	0.00001200	-1.72540500
Cl	-2.77081900	2.76356900	-0.11157800
Cl	-2.77083400	-2.76356900	-0.11158400
Cl	2.77083200	-2.76357000	-0.11158900
Cl	2.77082100	2.76356900	-0.11157400
H	6.48609700	0.00001100	-1.72540500

4
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1466.200015
Sum of electronic and thermal Energies= -1466.177197
Sum of electronic and thermal Enthalpies= -1466.176253
Sum of electronic and thermal Free Energies= -1466.255250

0 1

O	2.50180300	-1.59979100	-0.00000200
C	2.73916500	-0.32382300	-0.00000300
C	1.86374000	0.75351000	-0.00000200
H	2.32778400	1.72672000	-0.00000200
C	0.44267100	0.75297800	0.00000000
N	-0.34880500	-0.30597800	-0.00000100
C	4.23236600	-0.02477800	0.00000200
F	4.84035700	-0.56848300	-1.11245800
F	4.84034200	-0.56845500	1.11248600
F	4.51876500	1.32856200	-0.00001300
C	-0.19614300	2.14649100	0.00000100
F	0.73837000	3.16095500	0.00001600
F	-0.99025000	2.35055700	-1.11282800
F	-0.99027800	2.35054900	1.11281000
C	-1.78983100	-0.26863700	0.00000100
C	-2.47195700	-0.32444300	-1.22621000
C	-3.86789600	-0.36917500	-1.20052800
H	-4.40701300	-0.40438300	-2.14299300
C	-4.58370600	-0.37722600	0.00000200
C	-3.86789400	-0.36918100	1.20053200
H	-4.40700900	-0.40439300	2.14299800
C	-2.47195500	-0.32444900	1.22621200
C	-1.71878000	-0.36724300	-2.53144900
H	-1.14227700	0.54773400	-2.69351300
H	-2.40701600	-0.48662300	-3.37173800
H	-1.00993200	-1.20490300	-2.55245400
C	-6.09333800	-0.38552500	0.00000400
H	-6.48910500	-0.89159100	-0.88569600
H	-6.48840600	0.63752900	0.00003600
H	-6.48910200	-0.89164400	0.88567600
C	-1.71877600	-0.36725200	2.53145000
H	-1.00992300	-1.20490700	2.55244900
H	-2.40701000	-0.48664000	3.37173900
H	-1.14227900	0.54772900	2.69351800
Cu	0.61712900	-1.92879600	-0.00000600

5
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1421.828015
Sum of electronic and thermal Energies= -1421.799429
Sum of electronic and thermal Enthalpies= -1421.798485
Sum of electronic and thermal Free Energies= -1421.890012

0 1

Cu	-0.00000100	-0.36388600	-0.46625900
N	1.58953600	0.14615500	0.38642700
C	1.30260300	0.74440600	1.55446400
C	0.00000100	0.99091700	2.05287300
H	0.00000200	1.47060300	3.02448600
C	-1.30260200	0.74441100	1.55446500
N	-1.58953600	0.14615500	0.38643000
C	2.45399100	1.18636800	2.43646000
C	-2.45398800	1.18638200	2.43645800
C	2.91049700	-0.04287500	-0.07200100
C	3.42774300	-1.34530300	-0.18618300
C	4.69482400	-1.57782800	-0.72819300
C	5.45626000	-0.49798900	-1.17023500
C	4.96807800	0.80339600	-1.08087300
C	3.69842100	1.02304200	-0.53892400
C	-2.91049600	-0.04287200	-0.07200000
C	-3.69841600	1.02304500	-0.53892900
C	-4.96807200	0.80340100	-1.08088000
C	-5.45626000	-0.49798200	-1.17023600
C	-4.69482800	-1.57782100	-0.72818700
C	-3.42774800	-1.34529900	-0.18617600
H	-5.09128600	-2.58177000	-0.80774900
H	-5.57260800	1.62871000	-1.43441200

H	5.57261700	1.62870300	-1.43440000
H	5.09127800	-2.58177700	-0.80775900
H	-2.10977500	1.42740900	3.44343800
H	-2.92946600	2.07314700	2.00506400
H	-3.21244700	0.39998600	2.50559000
H	2.10977900	1.42739400	3.44344100
H	2.92947500	2.07313300	2.00507000
H	3.21244500	0.39996800	2.50559000
H	-6.44101900	-0.67291600	-1.58877500
H	6.44101900	-0.67292500	-1.58877300
O	3.12872200	2.27791400	-0.42011400
O	2.59428400	-2.35098300	0.26469600
O	-3.12871300	2.27791700	-0.42012400
O	-2.59429400	-2.35098000	0.26471000
C	-3.82237500	3.41079400	-0.97414100
H	-3.15948200	4.25798500	-0.81072100
H	-3.99935500	3.28059600	-2.04746400
H	-4.77617500	3.58391600	-0.46278100
C	-3.03751400	-3.71616200	0.15934500
H	-3.22607900	-3.99495100	-0.88368200
H	-2.21828300	-4.31161200	0.55693200
H	-3.94155500	-3.88793600	0.75445900
C	3.03749700	-3.71616700	0.15932500
H	2.21826500	-4.31161400	0.55691200
H	3.22606000	-3.99495300	-0.88370300
H	3.94154000	-3.88794700	0.75443700
C	3.82238800	3.41079300	-0.97412300
H	3.99936400	3.28060400	-2.04744800
H	3.15950100	4.25798500	-0.81069300
H	4.77619100	3.58390500	-0.46276500

6

wB97XD / 6-31G+(d,p) / SDD (Cu)

Sum of electronic and zero-point Energies= -1199.803745

Sum of electronic and thermal Energies= -1199.775258

Sum of electronic and thermal Enthalpies= -1199.774314

Sum of electronic and thermal Free Energies= -1199.865617

0 1

Cu	0.00000100	0.01195300	-0.57513800
N	1.58946800	-0.01557900	0.40798000
C	1.30079400	-0.05407800	1.72127100
C	0.00000000	-0.07127400	2.28260100
H	0.00000000	-0.10334000	3.36526400
C	-1.30079400	-0.05407700	1.72127000
N	-1.58946800	-0.01558200	0.40797900
C	2.46207900	-0.08135100	2.69905200
C	-2.46207900	-0.08134500	2.69905200
C	2.93880300	0.00097700	-0.05903000
C	3.58545200	-1.21131100	-0.35671100
C	4.88799100	-1.17180500	-0.86159100
C	5.55611000	0.03699800	-1.07907700
C	4.88238500	1.22785200	-0.79137300
C	3.57974600	1.23160600	-0.28519400
C	-2.93880300	0.00097600	-0.05903100
C	-3.57974500	1.23160500	-0.28519600
C	-4.88238300	1.22785200	-0.79137300
C	-5.55611000	0.03700000	-1.07907700
C	-4.88799300	-1.17180500	-0.86159000
C	-3.58545400	-1.21131200	-0.35670900
H	-5.39038700	-2.10737700	-1.09440900
H	-5.38031600	2.17779500	-0.96904400
H	5.38031900	2.17779400	-0.96904300
H	5.39038400	-2.10737800	-1.09441000

7

wB97XD / 6-31G+(d,p) / SDD (Cu)

Sum of electronic and zero-point Energies= -1435.385180

Sum of electronic and thermal Energies= -1435.350168

Sum of electronic and thermal Enthalpies= -1435.349223

Sum of electronic and thermal Free Energies= -1435.453217

0 1

Cu	-0.04354100	-0.09966900	-0.56495100
N	-1.63433300	-0.17211100	0.42082400
C	-1.36784400	-0.07518000	1.73406800
C	-0.07453900	0.02645300	2.30485700
H	-0.08440500	0.07365000	3.38689200
C	1.22759400	0.09193600	1.75105600
N	1.52310200	0.05736400	0.44018800
C	-2.53522800	-0.07367600	2.70352100
C	2.38091200	0.21182500	2.72934700
C	-2.97537800	-0.22612100	-0.07054200
C	-3.69056600	0.98389200	-0.22514700
C	-4.99197400	0.93639600	-0.73246200
C	-5.57862700	-0.27580100	-1.08555700
C	-4.85227000	-1.45485700	-0.95416700
C	-3.54202100	-1.45974800	-0.45702800
C	2.87108300	0.13395200	-0.03008800
C	3.60080100	-1.05520800	-0.23243700
C	4.89049500	-0.96216000	-0.76522400
C	5.44611500	0.27421700	-1.08509300
C	4.71319000	1.44065900	-0.87801000
C	3.42005500	1.39342900	-0.34805000
H	5.15438100	2.39805900	-1.13335000
H	5.46768600	-1.86496000	-0.93436500
H	-5.30290700	-2.39800600	-1.24942000
H	-5.55355300	1.85578700	-0.85666100

H	2.02719900	0.23492600	3.76063100
H	3.07233600	-0.63033700	2.61472600
H	2.95762600	1.12299800	2.53563600
H	-2.19180400	-0.16072100	3.73505900
H	-3.22030600	-0.89856000	2.48829700
H	-3.11376400	0.85259000	2.60970700
H	6.44802200	0.32890500	-1.49733000
H	-6.59188900	-0.29978800	-1.47176900
C	-3.01878700	2.32102200	0.07239800
H	-2.24172800	2.15354600	0.82499500
C	-2.79557700	-2.79465300	-0.44799600
H	-3.55469800	-3.55231300	-0.68960900
C	2.96373400	-2.40742600	0.06289300
H	2.16586200	-2.24617300	0.79618600
C	2.58866400	2.65855200	-0.17244100
H	1.84913800	2.46404000	0.61251600
C	3.94556800	-3.42609800	0.66292100
H	3.40576500	-4.32744500	0.97313700
H	4.70619800	-3.73454400	-0.06338800
H	4.45905600	-3.01379300	1.53807000
C	2.30315500	-2.96716400	-1.21296600
H	1.77798700	-3.90526700	-1.00009100
H	1.57772800	-2.25342500	-1.61974900
H	3.05945200	-3.15827000	-1.98345500
C	-2.31024500	2.84138000	-1.19504600
H	-1.78129300	3.77844500	-0.98674500
H	-1.57917600	2.11000200	-1.55843000
H	-3.03857000	3.02281400	-1.99409300
C	-3.98049300	3.37999600	0.63377300
H	-4.70165300	3.71624500	-0.11987900
H	-4.54082600	2.99353500	1.49202500
H	-3.41593100	4.26040100	0.95933500
C	-1.74427300	-2.85741000	-1.57404700
H	-0.92878400	-2.14856500	-1.38022400
H	-1.30375700	-3.85924600	-1.63299100
H	-2.19093300	-2.61334700	-2.54318600
C	-2.18078000	-3.21474400	0.89924400
H	-1.30610700	-2.61015600	1.15071000
H	-2.91018100	-3.12865900	1.71162200
H	-1.86225600	-4.26235400	0.84408800
C	3.41607500	3.87806500	0.26298100
H	4.08938500	4.21767500	-0.53239300
H	2.75034900	4.71356100	0.50531200
H	4.02109100	3.65190600	1.14745700
C	1.80868200	2.96203700	-1.46769700
H	1.17760300	2.11108600	-1.75037600
H	1.16230200	3.83733500	-1.33695500
H	2.50154200	3.16067300	-2.29381300

8

wB97XD / 6-31G+(d,p) / SDD (Cu)

Sum of electronic and zero-point Energies= -2906.818368

Sum of electronic and thermal Energies= -2906.780897

Sum of electronic and thermal Enthalpies= -2906.779953

Sum of electronic and thermal Free Energies= -2906.901968

0 1

Cu	0.00000000	0.41597400	0.30422400
N	-1.57845000	-0.31098600	-0.40486700
C	-1.28096800	-1.22991500	-1.32697500
C	0.00000000	-1.63666600	-1.74178000
H	0.00000000	-2.38379800	-2.51856800
C	1.28096900	-1.22991500	-1.32697500
N	1.57845000	-0.31098600	-0.40486700
C	-2.43826200	-1.95083800	-2.01502100
C	2.43826200	-1.95083800	-2.01502200
C	-2.90141000	0.04559600	0.00599900
C	-3.60268600	-0.74381700	0.91755900
C	-4.85217500	-0.32310700	1.37020100
C	-5.41225400	0.87195700	0.92806400
C	-4.69755900	1.65215600	0.02167800
C	-3.44619000	1.25115200	-0.43741300
C	2.90141000	0.04559600	0.00599900
C	3.44618900	1.25115300	-0.43741200
C	4.69755800	1.65215700	0.02167800
C	5.41225400	0.87195800	0.92806300
C	4.85217500	-0.32310700	1.37020100
C	3.60268600	-0.74381800	0.91755800
F	3.36316900	-1.05662400	-2.51884500
F	3.10458300	-2.77841700	-1.12534000
F	2.03719500	-2.74189000	-3.06727500
F	-2.03719400	-2.74189100	-3.06727400
F	-3.10458300	-2.77841600	-1.12534000
F	-3.36316900	-1.05662400	-2.51884600
H	3.17163400	-1.67037900	1.27361800
H	2.89580400	1.85713300	-1.14683500
H	6.38263900	1.19134800	1.28495000
H	-2.89580500	1.85713200	-1.14683600
H	-3.17163300	-1.67037800	1.27361900
H	-6.38263900	1.19134700	1.28495000
C	5.62497700	-1.20749300	2.29359500
C	5.23625000	2.97885900	-0.40272500
C	-5.23625100	2.97885800	-0.40272600
C	-5.62497600	-1.20749300	2.29359700
F	4.79357400	-1.90497500	3.15358100
F	6.51894000	-0.49409600	3.07025100
F	6.36401700	-2.15576500	1.60514100
F	4.76214000	4.00524200	0.40308900
F	6.61498400	3.02893900	-0.33810600
F	4.86697800	3.29778400	-1.69739100
F	-4.86698000	3.29778200	-1.69739200
F	-4.76214100	4.00524100	0.40308700
F	-6.61498500	3.02893700	-0.33810700
F	-6.51894000	-0.49409600	3.07025200
F	-4.79357300	-1.90497300	3.15358300
F	-6.36401600	-2.15576500	1.60514300

9

wB97XD / 6-31G+(d,p) / SDD (Cu)

Sum of electronic and zero-point Energies= -1716.435137

Sum of electronic and thermal Energies= -1716.405192

Sum of electronic and thermal Enthalpies= -1716.404248

Sum of electronic and thermal Free Energies= -1716.503892

0 1

Cu	0.00000000	-1.06494000	0.00815700
N	1.58491300	-0.07328400	-0.08708800
C	1.28480000	1.21539000	-0.25599900
C	0.00000000	1.78884800	-0.34313500
H	0.00000000	2.85208400	-0.51643800
C	-1.28480000	1.21539000	-0.25599800
N	-1.58491400	-0.07328300	-0.08708900
C	2.43012400	2.22182100	-0.34729300
C	-2.43012400	2.22182200	-0.34729000
C	2.90715000	-0.61116500	0.06538800
C	3.60925200	-0.45116600	1.25842400
C	4.86525800	-1.05070200	1.41927200
C	5.38887200	-1.81287500	0.37311700

C	4.68724400	-1.98890800	-0.82822500
C	3.43664400	-1.38780000	-0.96963100
C	-2.90715000	-0.61116500	0.06538700
C	-3.43664000	-1.38780600	-0.96963000
C	-4.68724000	-1.98891500	-0.82822600
C	-5.38887100	-1.81287700	0.37311300
C	-4.86526200	-1.05069800	1.41926600
C	-3.60925600	-0.45116100	1.25842000
F	-3.42838500	1.80138100	-1.20269700
F	-3.01234100	2.44372500	0.89206900
F	-2.02557100	3.46061400	-0.80806400
F	2.02557000	3.46061400	-0.80806300
F	3.01234600	2.44372100	0.89206400
F	3.42838100	1.80138100	-1.20270500
H	-3.17758100	0.13519400	2.06152800
H	-2.86708200	-1.50455100	-1.88621400
H	-6.36083400	-2.28379400	0.49301800
H	2.86709000	-1.50454100	-1.88621700
H	3.17757300	0.13518400	2.06153400
H	6.36083400	-2.28379200	0.49302300
C	-5.63027900	-0.86059000	2.70729100
C	-5.28876600	-2.79353500	-1.95567600
C	5.28877500	-2.79352100	-1.95567800
C	5.63027000	-0.86060100	2.70730100
H	-5.83022000	-3.66570300	-1.57600000
H	-6.00012000	-2.18761300	-2.52943300
H	-4.51958100	-3.14611800	-2.64893500
H	-5.92716200	0.18680200	2.83350400
H	-6.53731000	-1.47103900	2.72504900
H	-5.02041600	-1.13542600	3.57471000
H	4.51959200	-3.14611000	-2.64893500
H	5.83023800	-3.66568500	-1.57600500
H	6.00012300	-2.18759300	-2.52943500
H	5.92714600	0.18679200	2.83352300
H	6.53730500	-1.47104300	2.72505600
H	5.02040600	-1.13544800	3.57471500

10
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2311.648573
Sum of electronic and thermal Energies= -2311.615237
Sum of electronic and thermal Enthalpies= -2311.614292
Sum of electronic and thermal Free Energies= -2311.724482

0 1

Cu	0.00000000	0.15687500	-0.10667200
N	1.58033500	-0.18051800	0.84429300
C	1.29912700	-0.60144800	2.09378400
C	0.00000000	-0.77002400	2.62596700
H	0.00000000	-1.10066500	3.65681500
C	-1.29912700	-0.60144900	2.09378400
N	-1.58033500	-0.18051800	0.84429200
C	2.45890600	-0.91184600	3.02165300
C	-2.45890600	-0.91184700	3.02165300
C	2.91559200	-0.07484600	0.37390200
C	3.62019300	-1.20993400	-0.03873200
C	4.91168900	-1.08238700	-0.54651000
C	5.52135600	0.16531100	-0.65468900
C	4.81069900	1.29193900	-0.24687100
C	3.51798400	1.18149100	0.26182900
C	-2.91559200	-0.07484600	0.37390200
C	-3.51798400	1.18149000	0.26183100
C	-4.81070000	1.29193800	-0.24686900
C	-5.52135600	0.16531000	-0.65468800
C	-4.91168900	-1.08238800	-0.54651200
C	-3.62019200	-1.20993400	-0.03873400
H	-3.14438600	-2.18176000	0.02282900
H	-2.96832900	2.06019600	0.57800100
H	-6.52369600	0.25799000	-1.05120000
H	2.96832800	2.06019600	0.57799800
H	3.14438700	-2.18176000	0.02283200
H	6.52369600	0.25799100	-1.05120000
C	-5.66883800	-2.31598600	-0.91181800
C	-5.40584300	2.64979100	-0.42244000
C	5.40584200	2.64979200	-0.42244400
C	5.66884000	-2.31598600	-0.91181400
H	-3.16564400	-0.07631700	3.05393400
H	-3.01391500	-1.79119400	2.67766400
H	-2.10975300	-1.10752400	4.03546400
H	2.10975300	-1.10752200	4.03546400
H	3.01391500	-1.79119400	2.67766400
H	3.16564400	-0.07631700	3.05393300
F	5.03985900	3.51133100	0.59847000
F	4.99102700	3.24839400	-1.60372200
F	6.78745000	2.61758900	-0.45899900
F	6.69609300	-2.06112900	-1.80016700
F	6.24466200	-2.91570500	0.20045800
F	4.85171400	-3.27431700	-1.48792300
F	-6.78745200	2.61758700	-0.45899500
F	-4.99103000	3.24839500	-1.60371700
F	-5.03986100	3.51132900	0.59847500
F	-6.69609200	-2.06112800	-1.80017100
F	-4.85171100	-3.27431600	-1.48792800
F	-6.24466000	-2.91570700	0.20045300

11
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1121.257428
Sum of electronic and thermal Energies= -1121.231542
Sum of electronic and thermal Enthalpies= -1121.230598
Sum of electronic and thermal Free Energies= -1121.321602

0 1

Cu	0.00000000	0.15267000	0.52500600
N	-1.58661900	-0.09847400	-0.43377600
C	-1.30072600	-0.42735200	-1.70700900
C	0.00000000	-0.56528700	-2.25028100
H	0.00000000	-0.83440800	-3.29947700
C	1.30072600	-0.42735500	-1.70700800
N	1.58661900	-0.09847900	-0.43377500
C	-2.46153600	-0.67474200	-2.65387900
C	2.46153600	-0.67475000	-2.65387700
C	-2.93509000	0.01015800	0.02431000
C	-3.58862300	-1.10812500	0.55145100
C	-4.89632900	-1.00493300	1.03521300
C	-5.53741200	0.23880200	0.98888100
C	-4.89657600	1.37043600	0.47195900
C	-3.59045400	1.24431800	-0.01228100
C	2.93509000	0.01015400	0.02431100
C	3.59046300	1.24430800	-0.01230500
C	4.89658500	1.37042600	0.47193500
C	5.53741300	0.23879800	0.98888200
C	4.89632000	-1.00493100	1.03523800
C	3.58861400	-1.10812300	0.55147600
H	3.06068400	-2.05652800	0.58456400
H	3.06485800	2.10538400	-0.41423400
H	6.55245100	0.32850800	1.36743400
H	-3.06484100	2.10539800	-0.41419300

H	-3.06070100	-2.05653400	0.58452100
H	-6.55245100	0.32851200	1.36743300
C	5.61332600	-2.22121000	1.57298300
C	5.58884700	2.71326700	0.46488000
C	-5.58882700	2.71328200	0.46492900
C	-5.61334600	-2.22121700	1.57293200
H	5.34163900	3.28491700	1.36774400
H	6.67670600	2.60008800	0.43297900
H	5.28395800	3.31355100	-0.39798300
H	6.14848800	-2.74638100	0.77228200
H	6.34886800	-1.94470900	2.33452200
H	4.91098000	-2.93089200	2.02071300
H	-5.28395800	3.31356700	-0.39794000
H	-5.34158800	3.28492700	1.36778800
H	-6.67668800	2.60011200	0.43305900
H	-6.14854400	-2.74634500	0.77222700
H	-6.34885900	-1.94472900	2.33450400
H	-4.91100300	-2.93093300	2.02061300
H	3.10767100	0.20735400	-2.71134100
H	3.08403900	-1.50060400	-2.29394800
H	2.10919600	-0.91567200	-3.65736400
H	-2.10919600	-0.91564800	-3.65737000
H	-3.08403100	-1.50060700	-2.29396000
H	-3.10767800	0.20735800	-2.71132900

1•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1908.251092
Sum of electronic and thermal Energies= -1908.215611
Sum of electronic and thermal Enthalpies= -1908.214666
Sum of electronic and thermal Free Energies= -1908.323815

0 1

N	-1.47188300	-0.23646600	0.00001700
C	-1.25370000	-1.54420100	0.00002300
C	0.00000100	-2.16949500	0.00002700
H	0.00000200	-3.24574500	0.00003600
C	1.25370100	-1.54419900	0.00002200
N	1.47188300	-0.23646400	0.00001700
C	-2.44851600	-2.49710700	0.00002500
F	-3.25372400	-2.32554100	1.11230100
F	-2.07363700	-3.82670700	0.00007600
F	-3.25366600	-2.32561000	-1.11230500
C	2.44851600	-2.49710500	-0.00001100
F	3.25373100	-2.32557600	1.11226400
F	2.07363200	-3.82670300	0.00000100
F	3.25365500	-2.32556900	-1.11234500
C	-2.77843100	0.37052600	-0.00000300
C	-3.36537900	0.73101600	1.22447100
C	-4.58948000	1.40378100	1.20005500
H	-5.05409100	1.67946900	2.14282300
C	-5.22412900	1.73619900	-0.00004700
C	-4.58945700	1.40374500	-1.20012700
H	-5.05404900	1.67940400	-2.14291300
C	-3.36535300	0.73098300	-1.22449900
C	-2.67221500	0.43172700	2.52947800
H	-3.24265100	0.83034100	3.37227600
H	-1.66984600	0.87849700	2.55511100
H	-2.54840200	-0.64412700	2.68065500
C	-6.56593800	2.42855400	-0.00007100
H	-6.68878400	3.05945300	0.88560100
H	-7.38300100	1.69685800	-0.00008700
H	-6.68878400	3.05945300	0.88560100
H	-7.38300100	1.69685800	-0.00008700
H	-6.68875200	3.05945500	-0.88574700
C	-2.67216500	0.43165200	-2.52948500
H	-3.24258300	0.83024400	-3.37230500
H	-2.54835100	-0.64420600	-2.68062800
H	-1.66979500	0.87842000	-2.55511000
C	2.77843200	0.37052700	-0.00000100
C	3.36534800	0.73100600	-1.22449300
C	4.58945200	1.40376900	-1.20011400
H	5.05403800	1.67944900	-2.14289800
C	5.22413000	1.73619800	-0.00003200
C	4.58948900	1.40375500	1.20006800
H	5.05410700	1.67942000	2.14283900
C	3.36538700	0.73099300	1.22447700
C	2.67214900	0.43170800	-2.52948100
H	2.54833100	-0.64414600	-2.68064700
H	3.24256400	0.83031700	-3.37229600
H	1.66978100	0.87848100	-2.55508900
C	6.56594000	2.42855100	-0.00004900
H	6.68879600	3.05942600	0.88564000
H	7.38300300	1.69685400	-0.00009300
C	2.67223500	0.43166400	2.52948200
H	1.66986400	0.87842700	2.55513400
H	3.24267500	0.83026000	3.37228500
H	2.54842900	-0.64419400	2.68063200
C	-0.00000200	2.81536800	0.00006900
Cu	-0.00000100	1.01313100	0.00002600
O	-0.00000300	3.97144400	0.00011100

2•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2069.314340
Sum of electronic and thermal Energies= -2069.284177
Sum of electronic and thermal Enthalpies= -2069.283232
Sum of electronic and thermal Free Energies= -2069.378314

0 1

N	-1.46444200	0.74017800	0.52899100
C	-1.26921300	1.90084000	1.17883900
C	0.00000100	2.41207700	1.48551200
H	0.00000200	3.34658700	2.03093200
C	1.26921500	1.90083900	1.17883900
N	1.46444400	0.74017800	0.52899100
C	-2.46742300	2.71101500	1.62295100
H	-2.94152900	3.19145500	0.76085800
H	-2.17148600	3.49133200	2.32449300
H	-3.21407400	2.07595300	2.11003700
C	2.46742600	2.71101300	1.62295200
H	3.21407700	2.07595100	2.11003700
H	2.17148800	3.49133000	2.32449600
H	2.94153100	3.19145500	0.76086000
C	-2.76299800	0.30548800	0.20120600
C	-3.53756300	0.92176600	-0.78511800
F	-3.05915400	2.05132200	-1.40459300
C	-4.77653100	0.42696500	-1.16528300
F	-5.50626300	1.06212000	-2.13251100
C	-5.27333500	-0.72303000	-0.56781200
F	-6.49142100	-1.22041300	-0.93895900
C	-4.52380300	-1.36638600	0.40785200
F	-5.00515600	-2.50210600	0.99879200
C	-3.29225200	-0.85039300	0.78255200
F	-2.55965400	-1.51428500	1.73492500
C	2.76300000	0.30548700	0.20120600
C	3.29225400	-0.85039400	0.78255100
F	2.55965500	-1.51428600	1.73492400

C	4.52380400	-1.36638800	0.40785100
F	5.00515700	-2.50210800	0.99879100
C	5.27333700	-0.72303200	-0.56781300
F	6.49142200	-1.22041600	-0.93896000
C	4.77653300	0.42696300	-1.16528400
F	5.50626500	1.06211700	-2.13251200
C	3.53756500	0.92176500	-0.78511900
F	3.05915600	2.05131900	-1.40459600
C	-0.00001000	-1.98538400	-0.87393600
O	-0.00002300	-3.01376500	-1.40275100
Cu	0.00000200	-0.39210600	-0.03499900

3•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2915.725154
Sum of electronic and thermal Energies= -2915.699274
Sum of electronic and thermal Enthalpies= -2915.698330
Sum of electronic and thermal Free Energies= -2915.785797

0 1

N	-1.46037200	0.00000100	-0.60773400
C	-1.26657500	0.00000700	-1.93464800
C	0.00000000	0.00001000	-2.53719400
H	0.00000000	0.00001500	-3.61933100
C	1.26657500	0.00000700	-1.93464800
N	1.46037200	0.00000100	-0.60773400
C	-2.47584800	0.00001400	-2.84476400
C	2.47584800	0.00001300	-2.84476400
C	-2.76473800	0.00000000	-0.06619200
C	-3.43156700	-1.18966300	0.26147000
C	-4.67666800	-1.20725800	0.87542900
H	-5.14666300	-2.15362000	1.11048200
C	-5.30240800	-0.00000200	1.18315900
C	-4.67666800	1.20725400	0.87543500
H	-5.14666200	2.15361600	1.11049300
C	-3.43156600	1.18966200	0.26147600
C	2.76473800	0.00000000	-0.06619200
C	3.43156600	1.18966200	0.26147600
C	4.67666800	1.20725400	0.87543500
H	5.14666200	2.15361600	1.11049300
C	5.30240800	-0.00000200	1.18315900
C	4.67666800	-1.20725700	0.87542900
H	5.14666300	-2.15362000	1.11048200
C	3.43156700	-1.18966300	0.26147000
H	3.09592600	0.88438700	-2.66236100
H	3.09593900	-0.88435100	-2.66235700
H	2.17772700	0.00000800	-3.89363500
H	-2.17772700	0.00001300	-3.89363500
H	-3.09593800	-0.88435100	-2.66235900
H	-3.09592800	0.88438800	-2.66235900
H	-6.27271600	-0.00000300	1.66430300
Cl	-2.63267200	-2.76313900	-0.11487100
Cl	-2.63267100	2.76313900	-0.11485700
Cl	2.63267000	2.76313900	-0.11485700
Cl	2.63267200	-2.76313900	-0.11487200
H	6.27271600	-0.00000300	1.66430300
C	0.00000000	-0.00001300	2.44970500
Cu	0.00000000	-0.00000500	0.65275500
O	0.00000000	-0.00001700	3.60789700

4•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1579.471592
Sum of electronic and thermal Energies= -1579.445955
Sum of electronic and thermal Enthalpies= -1579.445011
Sum of electronic and thermal Free Energies= -1579.531257

0 1

O	2.33208900	1.29176200	0.00001900
C	2.73314900	0.06685100	0.00000300
C	1.97357600	-1.08772100	-0.00001200
H	2.49612400	-2.02998800	-0.00002300
C	0.56041500	-1.11941300	-0.00001200
N	-0.22722400	-0.06303800	-0.00000500
C	4.24892600	-0.05983800	0.00000700
F	4.79299100	0.54809300	1.11250500
F	4.79300200	0.54814700	-1.11245400
F	4.68018800	-1.37400200	-0.00002200
C	-0.05857300	-2.52024600	-0.00002000
F	0.89516500	-3.51680900	-0.00003500
F	-0.84887300	-2.73828100	1.11284600
F	-0.84888700	-2.73826200	-1.11287900
C	-1.67038400	-0.12530800	0.00000200
C	-2.35420700	-0.07588300	1.22579500
C	-3.75056600	-0.04221300	1.20038900
H	-4.28992900	-0.01174800	2.14292300
C	-4.46667200	-0.03895400	0.00001600
C	-3.75057700	-0.04219300	-1.20036400
H	-4.28994900	-0.01171400	-2.14289300
C	-2.35421800	-0.07586300	-1.22578300
C	-1.60207900	-0.02608900	2.53168000
H	-1.00825100	-0.93073900	2.68879800
H	-2.29261300	0.07573400	3.37241400
H	-0.90863500	0.82436800	2.55862600
C	-5.97632500	-0.04119100	0.00002400
H	-6.37559600	0.46219200	0.88568900
H	-6.36436900	-1.06692400	0.00002100
H	-6.37560600	0.46220000	-0.88563300
C	-1.60210200	-0.02604700	-2.53167500
H	-0.90868600	0.82443300	-2.55862600
H	-2.29264500	0.07575300	-3.37240400
H	-1.00824600	-0.93067700	-2.68879700
Cu	0.44484100	1.77353200	0.00000500
C	-0.33710200	3.39516300	-0.00001200
O	-0.88499800	4.41069300	-0.00002900

5•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1535.098025
Sum of electronic and thermal Energies= -1535.066728
Sum of electronic and thermal Enthalpies= -1535.065783
Sum of electronic and thermal Free Energies= -1535.164490

0 1

N	1.46806400	0.38376300	0.58119800
C	1.27003300	1.14286600	1.66494300
C	0.00000000	1.47686300	2.16501400
H	0.00000100	2.08348100	3.06224700
C	-1.27003300	1.14286500	1.66494500
N	-1.46806500	0.38376100	0.58120100

C	2.46977000	1.67188000	2.42261500
C	-2.46976900	1.67187900	2.42261900
C	2.77046800	0.10917500	0.09855600
C	3.27609500	-1.20122500	0.15963200
C	4.51376700	-1.52912800	-0.39985100
C	5.25842000	-0.53776200	-1.03557600
C	4.78145100	0.76794300	-1.12156400
C	3.54011300	1.08219000	-0.56070300
C	-2.77046800	0.10917500	0.09855700
C	-3.54011300	1.08219000	-0.56070100
C	-4.78145100	0.76794300	-1.12156400
C	-5.25841900	-0.53776200	-1.03558000
C	-4.51376600	-1.52912900	-0.39985500
C	-3.27609500	-1.20122600	0.15963000
H	-4.90009800	-2.53868800	-0.34573100
H	-5.37210000	1.52270900	-1.62461000
H	5.37210100	1.52270800	-1.62461000
H	4.90009900	-2.53868700	-0.34572500
H	-2.17332000	2.07715800	3.39164300
H	-2.95248100	2.46519800	1.84288800
H	-3.20709000	0.87917500	2.58507900
H	2.17332200	2.07716300	3.39163700
H	2.95248300	2.46519600	1.84288000
H	3.20708900	0.87917600	2.58507700
H	-6.22066200	-0.78611000	-1.46901900
H	6.22066400	-0.78611000	-1.46901400
O	2.98203700	2.34707200	-0.60737600
O	2.45712300	-2.11858800	0.79159900
O	-2.98203900	2.34707300	-0.60737100
O	-2.45712400	-2.11859000	0.79159600
C	-3.65240100	3.37453000	-1.36018200
H	-3.00157600	4.24416100	-1.29669900
H	-3.77640300	3.08042300	-2.40822400
H	-4.63056200	3.61281300	-0.92708700
C	-2.86327600	-3.49915600	0.82901400
H	-2.98703300	-3.90450000	-0.18166900
H	-2.05409900	-4.01883700	1.33800400
H	-3.79431500	-3.62510600	1.39278400
C	2.86327600	-3.49915400	0.82902100
H	2.05409700	-4.01883400	1.33800900
H	2.98703600	-3.90449900	-0.18166100
H	3.79431300	-3.62510300	1.39279500
C	3.65240000	3.37452800	-1.36018800
H	3.77640400	3.08041900	-2.40822900
H	3.00157400	4.24415900	-1.29670800
H	4.63056000	3.61281400	-0.92709200
C	0.00000100	-1.65302100	-1.66756800
Cu	-0.00000100	-0.42996300	-0.36452400
O	0.00000300	-2.52231600	-2.43967700

6•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1313.072395
Sum of electronic and thermal Energies= -1313.041268
Sum of electronic and thermal Enthalpies= -1313.040324
Sum of electronic and thermal Free Energies= -1313.141052

0 1

N	1.46367800	0.73100900	0.00000600
C	1.26744900	2.05581800	-0.00000500
C	-0.00000100	2.66349300	-0.00000800
H	-0.00000200	3.74629400	-0.00001400
C	-1.26745100	2.05581700	-0.00000500
N	-1.46368000	0.73100800	0.00000600
C	2.47705400	2.97067000	-0.00001400
C	-2.47705700	2.97066800	-0.00001400
C	2.79277400	0.19736000	0.00000100
C	3.42223100	-0.09926900	1.22160900
C	4.69605800	-0.67382700	1.20012200
C	5.35268600	-0.96237700	-0.00000700
C	4.69604700	-0.67383500	-1.20013100
C	3.42222000	-0.09927700	-1.22161000
C	-2.79277500	0.19735900	0.00000100
C	-3.42222100	-0.09927900	-1.22161000
C	-4.69604800	-0.67383700	-1.20013100
C	-5.35268700	-0.96237900	-0.00000700
C	-4.69605900	-0.67382900	1.20012200
C	-3.42223200	-0.09927100	1.22160900
H	-5.18436200	-0.90586600	2.14332600
H	-5.18434300	-0.90588000	-2.14333800
H	5.18434200	-0.90587800	-2.14333800
H	5.18436100	-0.90586400	2.14332600
C	2.71576400	0.17910300	-2.52474600
H	1.76556400	-0.36629400	-2.57830900
H	2.46942200	1.24124100	-2.63641300
H	3.33316200	-0.11926100	-3.37646000
C	6.74266500	-1.55404600	-0.00001100
H	6.91059400	-2.17523900	-0.88536600
H	7.50670800	-0.76671900	-0.00002400
H	6.91060700	-2.17522300	0.88535200
C	2.71578800	0.17912200	2.52474900
H	2.46944100	1.24126000	2.63640600
H	1.76559100	-0.36627900	2.57832900
H	3.33319600	-0.11922900	3.37646000
C	-2.71578900	0.17912000	2.52474900
H	-3.33319800	-0.11923000	3.37646000
H	-1.76559200	-0.36628000	2.57832900
H	-2.46944200	1.24125800	2.63640600
C	-6.74266600	-1.55404800	-0.00001100
H	-6.91060800	-2.17522600	0.88535200
H	-7.50670900	-0.76672100	-0.00002400
H	-6.91059500	-2.17524200	-0.88536600
C	-2.71576500	0.17910100	-2.52474600
H	-1.76556500	-0.36629500	-2.57831000
H	-3.33316300	-0.11926300	-3.37646000
H	-2.46942300	1.24123900	-2.63641300
H	-2.17640600	4.01933300	-0.00000800
H	-3.10460700	2.78708200	-0.87859900
H	-3.10462500	2.78707700	0.87855700
H	2.17640200	4.01933500	-0.00000800
H	3.10460400	2.78708400	-0.87859900
H	3.10462200	2.78707900	0.87855700
C	0.00000600	-2.30862700	0.00001600
Cu	-0.00000100	-0.51543000	0.00001700
O	0.00001400	-3.46841600	0.00000900

7•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1548.654581
Sum of electronic and thermal Energies= -1548.617044
Sum of electronic and thermal Enthalpies= -1548.616100
Sum of electronic and thermal Free Energies= -1548.724717

0 1

N	-1.51409500	-0.14064100	0.63637800
C	-1.34001000	-0.05135700	1.95888800
C	-0.07826200	-0.00925900	2.58087200
H	-0.09080200	0.02210700	3.66316500

C	1.19432800	0.01654200	1.98610100
N	1.40170600	0.03119300	0.66317500
C	-2.55548700	0.03964500	2.85986800
C	2.39652300	0.04476500	2.90777000
C	-2.82823700	-0.19798300	0.06644900
C	-3.50386100	1.01074400	-0.21186500
C	-4.75072900	0.95845100	-0.84288800
C	-5.32748300	-0.25937400	-1.18742200
C	-4.64944300	-1.44262700	-0.90808500
C	-3.39407100	-1.44446300	-0.28607900
C	2.73214800	0.09222200	0.13119300
C	3.39341300	-1.10206600	-0.21894200
C	4.64975300	-1.01685800	-0.82831000
C	5.24265100	0.21709100	-1.08090700
C	4.58091400	1.38929300	-0.72173600
C	3.32440300	1.34998200	-0.10965000
H	5.04761100	2.34769700	-0.92490800
H	5.16776700	-1.92737500	-1.11343900
H	-5.09810800	-2.39286600	-1.18263700
H	-5.27352500	1.88181200	-1.07119100
H	2.09247400	0.00137400	3.95444700
H	3.06116700	-0.80046500	2.69934900
H	2.98486000	0.95562400	2.75092400
H	-2.28561800	-0.13869000	3.90205900
H	-3.32824900	-0.67424700	2.56618700
H	6.21593200	0.26627700	-1.55722700
H	-6.29589600	-0.28810700	-1.67488500
C	-2.87030000	2.36015300	0.11005300
H	-2.02044100	2.18466100	0.77707500
C	-2.73067500	-2.80366200	-0.04754900
H	-3.43560100	-3.53740800	-0.46317400
C	2.74155500	-2.45897400	0.01578900
H	1.85216700	-2.29815900	0.63437300
C	2.58784100	2.63819600	0.23896400
H	1.79287600	2.38674900	0.94892600
C	3.66469400	-3.43022200	0.77211500
H	3.13180700	-4.36079300	0.99705700
H	4.54932500	-3.68892300	0.17903700
H	4.00832600	-2.99407900	1.71614200
C	2.27179900	-3.07194200	-1.31750600
H	1.75490500	-4.02293300	-1.14566000
H	1.58184500	-2.39681700	-1.83537900
H	3.12396800	-3.25754300	-1.98188700
C	-2.31416300	3.01376600	-1.17026300
H	-1.82204500	3.96487700	-0.93716100
H	-1.58142600	2.35970000	-1.65504900
H	-3.11975700	3.20816900	-1.88800200
C	-3.83927600	3.31244100	0.83240800
H	-4.66488500	3.61982700	0.18061300
H	-4.27152000	2.83996600	1.72095600
H	-3.31174700	4.21994100	1.14624500
C	-1.40465700	-3.00477800	-0.80652800
H	-0.59032100	-2.45017000	-0.32942200
H	-1.12888000	-4.06588600	-0.79997400
H	-1.48914200	-2.68082600	-1.84923400
C	-2.55321100	-3.16899100	1.43854900
H	-1.76989700	-2.56579800	1.90650300
H	-3.48611700	-3.03002000	1.99490800
H	-2.25962200	-4.22150400	1.52734400
C	3.49541400	3.68255200	0.91038800
H	4.25372200	4.06611100	0.21841000
H	2.89855900	4.53639000	1.24948900
H	4.01305900	3.25808800	1.77729100
C	1.90865200	3.22540200	-1.01397200
H	1.21153200	2.50312300	-1.45253400
H	1.34758500	4.13261200	-0.76201400
H	2.65598400	3.48011900	-1.77464000
C	-0.04705800	0.02346100	-2.39738100
Cu	-0.04035700	-0.01853700	-0.60345600
O	-0.05621000	0.04348000	-3.55720900

8•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -3020.087084
Sum of electronic and thermal Energies= -3020.046787
Sum of electronic and thermal Enthalpies= -3020.045843
Sum of electronic and thermal Free Energies= -3020.172557

0 1

N	-1.46971400	-0.61173000	-0.44543400
C	-1.25157500	-1.72009000	-1.14563100
C	0.00000000	-2.24442100	-1.48195000
H	0.00000000	-3.14750000	-2.06914800
C	1.25157500	-1.72009000	-1.14563100
N	1.46971400	-0.61173000	-0.44543400
C	-2.45179100	-2.52802300	-1.63073000
C	2.45179100	-2.52802300	-1.63072900
C	-2.77520500	-0.12629200	-0.10572700
C	-3.44967200	-0.62473400	1.00880500
C	-4.66881700	-0.06174500	1.38286100
C	-5.22620000	0.99049100	0.66183600
C	-4.54038400	1.47875400	-0.44818200
C	-3.32005000	0.93149200	-0.83430400
C	2.77520500	-0.12629200	-0.10572600
C	3.32005000	0.93149100	-0.83430400
C	4.54038400	1.47875400	-0.44818200
C	5.22620000	0.99049100	0.66183600
C	4.66881700	-0.06174500	1.38286100
C	3.44967200	-0.62473300	1.00880600
F	3.33998700	-1.74121500	-2.33901000
F	3.14392400	-3.07795800	-0.56427000
F	2.09916200	-3.57143900	-2.45576400
F	-2.09916200	-3.57143800	-2.45576400
F	-3.14392400	-3.07795900	-0.56427000
F	-3.33998700	-1.74121500	-2.33901000
H	3.01906100	-1.43710400	1.57999900
H	2.79232700	1.31050200	-1.70117800
H	6.17164700	1.42397700	0.96038400
H	-2.79232700	1.31050300	-1.70117700
H	-3.01906200	-1.43710500	1.57999800
H	-6.17164600	1.42397700	0.96038400
C	5.41133600	-0.64540600	2.54035800
C	5.06818500	2.66358700	-1.18810700
C	-5.06818400	2.66358800	-1.18810700
C	-5.41133700	-0.64540700	2.54035700
F	4.55082500	-1.09310500	3.52904400
F	6.26990100	0.26823000	3.12246600
F	6.18132900	-1.73466800	2.16670600
F	4.50591200	3.84597900	-0.72449700
F	6.43636200	2.79687000	-1.05829600
F	4.78061400	2.60056500	-2.53993900
F	-4.78061300	2.60056700	-2.53993800
F	-4.50591100	3.84598000	-0.72449600
F	-6.43636100	2.79687200	-1.05829600
F	-6.26990200	0.26822900	3.12246500
F	-4.55082600	-1.09310700	3.52904300
F	-6.18133000	-1.73466900	2.16670400
C	-0.00000100	1.98946400	1.19411500
Cu	0.00000000	0.46156900	0.22333800
O	-0.00000100	2.96077100	1.81586800

9•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1829.702763
Sum of electronic and thermal Energies= -1829.670177
Sum of electronic and thermal Enthalpies= -1829.669232
Sum of electronic and thermal Free Energies= -1829.774224

0 1

N	1.47300500	0.23253300	-0.09332800
C	1.25389700	1.53742800	-0.19532300
C	-0.00000100	2.15799300	-0.25456700
H	-0.00000200	3.22922600	-0.36239900
C	-1.25390000	1.53742600	-0.19533200
N	-1.47300700	0.23253100	-0.09333900
C	2.44559100	2.49045300	-0.23101700
C	-2.44559200	2.49045300	-0.23103200
C	2.78071600	-0.35999300	0.01738900
C	3.45493400	-0.36223100	1.23659300
C	4.68501500	-1.02209300	1.35848900
C	5.21104300	-1.68036800	0.24510900
C	4.53881300	-1.69046200	-0.98562600
C	3.31445900	-1.02994400	-1.08767900
C	-2.78071600	-0.35999700	0.01738100
C	-3.31444000	-1.02998500	-1.08767200
C	-4.53879400	-1.69050500	-0.98561500
C	-5.21104000	-1.68037700	0.24511000
C	-4.68502900	-1.02206400	1.35847700
C	-3.45495000	-0.36220200	1.23657800
F	-3.39774300	2.10439800	-1.15314700
F	-3.07088400	2.56931700	1.00367200
F	-2.08741600	3.78302600	-0.56421000
F	2.08741400	3.78303500	-0.56415800
F	3.07090300	2.56928500	1.00367800
F	3.39772500	2.10441600	-1.15315700
H	-3.02116100	0.14823400	2.08928700
H	-2.76811900	-1.01974400	-2.02559100
H	-6.16181700	-2.19898300	0.33393100
H	2.76815100	-1.01967400	-2.02560500
H	3.02113300	0.14818200	2.08931000
H	6.16182300	-2.19897000	0.33392500
C	-5.42243300	-1.00379900	2.67611300
C	-5.14424300	-2.38350000	-2.18291900
C	5.14428200	-2.38342600	-2.18293800
C	5.42239400	-1.00387200	2.67614000
H	-5.62925400	-3.32161800	-1.89524000
H	-5.90462000	-1.75025100	-2.65526200
H	-4.38636400	-2.61030900	-2.93835300
H	-5.79271500	0.00303600	2.90104300
H	-6.28091400	-1.68090800	2.66103000
H	-4.76819600	-1.30456900	3.50137600
H	4.38645400	-2.61000900	-2.93848900
H	5.62908600	-3.32166800	-1.89530800
H	5.90483500	-1.75026200	-2.65511200
H	5.79253300	0.00298900	2.90118900
H	6.28096900	-1.68086200	2.66099600
H	4.76818500	-1.30482500	3.50135700
C	-0.00000200	-2.81461100	0.12038600
Cu	0.00000100	-1.01728400	-0.01659600
O	-0.00000500	-3.96755700	0.20544100

10•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2424.916972
Sum of electronic and thermal Energies= -2424.881829
Sum of electronic and thermal Enthalpies= -2424.880885
Sum of electronic and thermal Free Energies= -2424.994341

0 1

N	1.46095700	-0.05479900	1.13132600
C	1.26742000	-0.11401000	2.45886800
C	0.00000000	-0.14153500	3.06125000
H	0.00000000	-0.19005500	4.14234500
C	-1.26741900	-0.11401000	2.45886800
N	-1.46095600	-0.05479900	1.13132600
C	2.47544500	-0.15334300	3.37266500
C	-2.47544500	-0.15334300	3.37266500
C	2.77965900	-0.02853600	0.59499300
C	3.42116900	-1.21848700	0.23947600
C	4.68511300	-1.18130900	-0.34676600
C	5.33168500	0.02941200	-0.58462900
C	4.68619000	1.21081500	-0.22705100
C	3.42033200	1.19056400	0.35581700
C	-2.77965900	-0.02853500	0.59499300
C	-3.42033100	1.19056400	0.35581600
C	-4.68618900	1.21081600	-0.22705200
C	-5.33168500	0.02941300	-0.58462800
C	-4.68511400	-1.18130800	-0.34676500
C	-3.42116900	-1.21848700	0.23947700
H	-2.91600200	-2.16225100	0.40927400
H	-2.91912300	2.11278800	0.62605900
H	-6.31182300	0.05200000	-1.04199400
H	2.91912400	2.11278700	0.62606100
H	2.91600200	-2.16225100	0.40927300
H	6.31182400	0.05200000	-1.04199400
C	-5.37413200	-2.46863100	-0.65783300
C	-5.31529400	2.52827800	-0.53859100
C	5.31529500	2.52827800	-0.53859000
C	5.37413200	-2.46863100	-0.65783500
H	-3.09691700	0.73830500	3.23746500
H	-3.10564800	-1.02119700	3.15103400
H	-2.17413200	-0.20608200	4.41901600
H	2.17413200	-0.20608200	4.41901600
H	3.10564900	-1.02119700	3.15103300
H	3.09691700	0.73830400	3.23746500
F	5.07047600	3.46490900	0.45262400
F	4.82150000	3.07169200	-1.71617800
F	6.68605400	2.43562800	-0.68817000
F	6.36642800	-2.31961600	-1.60783000
F	5.97808600	-3.01586300	0.46611500
F	4.49169000	-3.42721100	-1.12811600
F	-6.68605200	2.43562900	-0.68817200
F	-4.82149900	3.07169200	-1.71618000
F	-5.07047400	3.46491000	0.45262100
F	-6.36642800	-2.31961600	-1.60782800
F	-4.49169100	-3.42721200	-1.12811300
F	-5.97808700	-3.01586200	0.46611800
C	-0.00000200	0.07752400	-1.92760900
Cu	0.00000000	0.00003700	-0.12876300
O	-0.00000500	0.12554100	-3.08321700

11•CO
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1234.525708
Sum of electronic and thermal Energies= -1234.497191
Sum of electronic and thermal Enthalpies= -1234.496247

Sum of electronic and thermal Free Energies= -1234.593303

0 1

N	1.46400300	0.78668500	-0.03545700
C	1.26812900	2.11142600	-0.08700400
C	-0.00000400	2.71641300	-0.11172100
H	-0.00000500	3.79838100	-0.15463900
C	-1.26813500	2.11142300	-0.08700400
N	-1.46400700	0.78668300	-0.03545700
C	2.47588400	3.02806300	-0.12117400
C	-2.47589200	3.02805800	-0.12117400
C	2.79299300	0.25350200	-0.01052000
C	3.43299500	0.02235000	1.21092200
C	4.71303900	-0.53963800	1.24852200
C	5.34025000	-0.87234700	0.04216800
C	4.71264000	-0.65465700	-1.18977400
C	3.43495000	-0.08601400	-1.20515600
C	-2.79299700	0.25349800	-0.01052000
C	-3.43495200	-0.08602100	-1.20515600
C	-4.71264300	-0.65466400	-1.18977400
C	-5.34025300	-0.87235200	0.04216700
C	-4.71304300	-0.53964100	1.24852100
C	-3.43299900	0.02234700	1.21092200
H	-2.91599600	0.28011700	2.13059500
H	-2.91996400	0.08913700	-2.14519300
H	-6.33300500	-1.31456600	0.06283700
H	2.91996200	0.08914500	-2.14519300
H	2.91599000	0.28011800	2.13059500
H	6.33300200	-1.31456000	0.06283700
C	-5.41556200	-0.75824300	2.56804600
C	-5.38747000	-1.05694100	-2.48016800
C	5.38746900	-1.05693100	-2.48016800
C	5.41555700	-0.75824200	2.56804600
H	-5.10859300	-2.07895400	-2.76435700
H	-6.47718900	-1.02629500	-2.38578800
H	-5.09857800	-0.39610000	-3.30327500
H	-5.98534700	0.13226400	2.86071100
H	-6.11830000	-1.59497200	2.51039400
H	-4.70030100	-0.96978000	3.36876400
H	5.09857200	-0.39609300	-3.30327500
H	5.10859900	-2.07894600	-2.76435500
H	6.47718900	-1.02627800	-2.38578900
H	5.98534100	0.13226400	2.86071400
H	6.11829500	-1.59497100	2.51039400
H	4.70029500	-0.96978100	3.36876300
H	-3.10691900	2.80546400	-0.98782000
H	-3.09745800	2.88301700	0.76852900
H	-2.17283900	4.07483800	-0.16875200
H	2.17283000	4.07484200	-0.16874900
H	3.09745100	2.88302100	0.76852900
H	3.10691200	2.80547100	-0.98782000
C	0.00001700	-2.25441800	0.07682800
Cu	-0.00000200	-0.46257200	0.01058900
O	0.00003700	-3.41344800	0.11871000

5.2 Chapter 3

1
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1794.980378
Sum of electronic and thermal Energies= -1794.948467
Sum of electronic and thermal Enthalpies= -1794.947523

Sum of electronic and thermal Free Energies= -1795.045897

0 1

Cu	0.00000700	-1.04197500	-0.01226400
N	-1.58601100	-0.05301100	-0.00682800
N	1.58601600	-0.05300700	-0.00717200
C	-1.28479900	1.24552000	-0.00276100
C	0.00000500	1.82772900	-0.00289500
H	0.00001400	2.90453400	-0.00057800
C	1.28480500	1.24551800	-0.00356800
C	-2.43716700	2.25107900	0.00505200
C	2.43716800	2.25108300	0.00222200
C	-2.91252200	-0.60554900	-0.00227900
C	-3.51005500	-0.93922800	1.22391300
C	-4.76580800	-1.55218500	1.20299000
H	-5.23987800	-1.80559600	2.14718600
C	-5.42021600	-1.85063500	0.00538400
C	-4.77521200	-1.54676400	-1.19738100
H	-5.25724500	-1.79659700	-2.13867300
C	-3.52093400	-0.93364800	-1.22592200
C	2.91252400	-0.60555100	-0.00221900
C	3.52064700	-0.93540400	-1.22550500
C	4.77494600	-1.54849700	-1.19636500
H	5.25676800	-1.79967100	-2.13740700
C	5.42020100	-1.85065900	0.00667400
C	4.76604900	-1.55049800	1.20401300
H	5.24032400	-1.80258900	2.14846100
C	3.51033900	-0.93748500	1.22433900
C	-2.82169100	-0.65893700	-2.53282400
H	-2.66559200	0.41256900	-2.68595400
H	-1.83422000	-1.13691200	-2.55917200
H	-3.40640300	-1.04086300	-3.37357800
C	-2.80010300	-0.67253300	2.52669500
H	-1.81304600	-1.15192300	2.54246100
H	-2.64138400	0.39781900	2.68469100
H	-3.37840800	-1.05860100	3.36997400
C	-6.79331900	-2.47883100	0.00603900
H	-6.99714400	-2.98815300	0.95258100
H	-7.57097100	-1.71845300	-0.13518500
H	-6.89749500	-3.21011200	-0.80188600
C	2.80069700	-0.66881600	2.52689200
H	2.64254100	0.40182200	2.68359700
H	1.81341400	-1.14770200	2.54341100
H	3.37895800	-1.05409300	3.37056200
C	2.82112100	-0.66259800	-2.53264900
H	1.83381300	-1.14096200	-2.55825500
H	2.66460400	0.40865400	-2.68706400
H	3.40583400	-1.04537900	-3.37301200
C	6.79333300	-2.47878800	0.00802100
H	7.57105200	-1.71826900	-0.13209500
H	6.99644400	-2.98866500	0.95442300
H	6.89820400	-3.20956200	-0.80026200
F	-3.25677400	2.11180100	-1.10165100
F	-3.24155100	2.11032500	1.12280400
F	-2.01350500	3.56575800	0.00281800
F	2.01344900	3.56574300	-0.00053400
F	3.25525400	2.11082700	-1.10550600
F	3.24307200	2.11134300	1.11898300

2
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -1956.044819
Sum of electronic and thermal Energies= -1956.017573
Sum of electronic and thermal Enthalpies= -1956.016629

Sum of electronic and thermal Free Energies= -1956.104087

0 1

Cu	0.00000300	-0.38557200	-0.11586600
N	-1.57854700	0.44079600	0.48537200
N	1.57854900	0.44080300	0.48537400
C	-1.29994000	1.45778600	1.32738300
C	-0.00000300	1.87577000	1.68881500
H	-0.00000500	2.69536100	2.39607400
C	1.29993600	1.45779300	1.32738400
C	-2.45168200	2.20857600	1.96291900
C	2.45167100	2.20858100	1.96293500
C	-2.89013600	0.09990800	0.12227900
C	-3.39579600	-1.16658300	0.43335100
C	-4.64826400	-1.58471400	0.01028900
C	-5.44161800	-0.73245100	-0.74589400
C	-4.96707500	0.52854700	-1.07804100
C	-3.70743200	0.92670500	-0.65441300
C	2.89013800	0.09991700	0.12228000
C	3.70742700	0.92670400	-0.65443100
C	4.96707100	0.52854300	-1.07805700
C	5.44161900	-0.73244800	-0.74589200
C	4.64827000	-1.58470200	0.01030600
C	3.39580300	-1.16656900	0.43336700
H	-2.11167800	2.79997200	2.81314400
H	-2.90942300	2.88759300	1.23662900
H	-3.22407500	1.51716900	2.31393700
H	2.11166000	2.79996100	2.81316800
H	2.90941100	2.88761300	1.23665900
H	3.22406700	1.51717300	2.31394600
F	-3.25272300	2.17076200	-1.02166600
F	-5.73852200	1.37050400	-1.83152900
F	-6.68061600	-1.13363700	-1.16173800
F	-5.10764100	-2.83038100	0.33903700
F	-2.62137300	-2.03295800	1.16333900
F	3.25271000	2.17075000	-1.02170800
F	5.73851000	1.37049000	-1.83156400
F	6.68061700	-1.13363600	-1.16173500
F	5.10765300	-2.83036300	0.33906900
F	2.62138500	-2.03293600	1.16337000

3
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2802.455449
Sum of electronic and thermal Energies= -2802.432162
Sum of electronic and thermal Enthalpies= -2802.431217
Sum of electronic and thermal Free Energies= -2802.512554

0 1

Cu	0.00004300	0.00031500	-0.69900700
Cl	-2.77129800	-2.76335200	-0.10860400
Cl	-2.77165300	2.76324300	-0.10803800
Cl	2.77133400	2.76330900	-0.10849400
Cl	2.77159400	-2.76329000	-0.10819000
N	-1.57646800	-0.00004400	0.31798500
N	1.57649600	-0.00005000	0.31806400
C	-1.29686700	-0.00004600	1.63459000
C	-0.00002100	-0.00005100	2.19472000
H	-0.00004700	-0.00006600	3.27735600
C	1.29685100	-0.00002100	1.63465900
C	-2.46316300	-0.00025700	2.60173600
H	-3.09030500	0.88427200	2.44624600
H	-2.11993000	-0.00026100	3.63647300
H	-3.09000100	-0.88498400	2.44612100
C	2.46309100	-0.00011500	2.60187100
H	3.08963500	-0.88512900	2.44670100
H	2.11979900	0.00047600	3.63658900
H	3.09053800	0.88412900	2.44601100
C	-2.90002400	-0.00005200	-0.16383700
C	-3.58183000	-1.19020500	-0.45772400
C	-4.85372500	-1.20742800	-1.01392800
H	-5.33500100	-2.15380600	-1.22465000
C	-5.49246400	-0.00012200	-1.29325800
H	-6.48350000	-0.00015600	-1.73018900
C	-4.85391100	1.20721000	-1.01364500
H	-5.33529900	2.15358100	-1.22412900
C	-3.58201000	1.19002000	-0.45744300
C	2.90004500	0.00001600	-0.16376700
C	3.58188800	1.19012400	-0.45759200
C	4.85376300	1.20736800	-1.01384900
H	5.33503100	2.15375800	-1.22452200
C	5.49244800	0.00006400	-1.29328200
H	6.48346000	0.00007400	-1.73026700
C	4.85385200	-1.20726900	-1.01374600
H	5.33521100	-2.15362800	-1.22436300
C	3.58197200	-1.19010300	-0.45750400

1•benzene
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2027.040853
Sum of electronic and thermal Energies= -2027.003436
Sum of electronic and thermal Enthalpies= -2027.002492
Sum of electronic and thermal Free Energies= -2027.1115770 1

0 1

Cu	0.00910500	-0.61583400	0.45328300
N	-1.46244000	0.61767500	0.16164200
N	1.52219200	0.56961600	0.15200900
C	-1.20770200	1.90313100	-0.02881800
C	0.06019200	2.50168200	-0.07988700
H	0.07677500	3.57017600	-0.20944200
C	1.30903100	1.86418900	-0.02710200
C	-2.37885000	2.85993500	-0.24214700
C	2.51041200	2.78754600	-0.22015200
C	-2.76160800	0.01575300	0.09765300
C	-3.46827500	-0.22536400	1.28770100
C	-4.66226000	-0.94820400	1.21887100
H	-5.21547400	-1.13351400	2.13583000
C	-5.16058800	-1.43557900	0.00647400
C	-4.41506300	-1.20900100	-1.15447700
H	-4.77164800	-1.60445100	-2.10195000
C	-3.21073100	-0.50126800	-1.13035700
C	2.80301600	-0.07149500	0.09406200
C	3.25452100	-0.58273900	-1.13571100
C	4.43987000	-1.32243500	-1.15417600
H	4.79911400	-1.71284400	-2.10283700
C	5.16442500	-1.58448900	0.01286400
C	4.66473400	-1.09946300	1.22487400
H	5.20120600	-1.31157100	2.14592400
C	3.48889000	-0.34698200	1.28904300
C	-0.70111400	-2.53547600	1.12878500
H	-1.10275400	-2.26357200	2.10085500
C	0.70188200	-2.58283500	0.91761000
H	1.39499200	-2.36141900	1.72395600
C	1.20336800	-3.13506000	-0.28966400
H	2.27555800	-3.17824300	-0.44338500
C	-1.57735700	-3.05753900	0.14327200

H	-2.64683200	-3.03527800	0.31974000
C	-1.06593400	-3.57281500	-1.03440700
C	0.32836700	-3.60762700	-1.25313500
H	0.71663300	-4.02408200	-2.17617300
H	-1.74010600	-3.95789200	-1.79135800
C	-2.37353400	-0.35468700	-2.37446200
H	-2.20081900	0.69536900	-2.62440900
H	-1.39087800	-0.82375100	-2.23264700
H	-2.85932000	-0.83330700	-3.22898500
C	-2.93547000	0.26556600	2.60895000
H	-1.88767300	-0.02845200	2.74721400
H	-2.96646900	1.35761100	2.66494700
H	-3.52098900	-0.13594800	3.44035100
C	-6.47619300	-2.17483600	-0.04994300
H	-6.69129400	-2.67858000	0.89745900
H	-7.30349200	-1.48363300	-0.25159500
H	-6.47701600	-2.92853200	-0.84355300
C	2.95105300	0.13824200	2.61072100
H	2.97418400	1.23018200	2.66972700
H	1.90488800	-0.16404900	2.74869200
H	3.53799600	-0.26156100	3.44187600
C	2.43988800	-0.39341400	-2.38950900
H	1.43965700	-0.82855100	-2.26632500
H	2.30718300	0.66447900	-2.63000700
H	2.92104700	-0.87880200	-3.24285900
C	6.45900500	-2.36025400	-0.03762000
H	7.30615100	-1.69364700	-0.23978200
H	6.65708800	-2.86643700	0.91211200
H	6.44053800	-3.11682200	-0.82834800
F	-3.07415500	2.57803900	-1.40708000
F	-3.29685800	2.80592000	0.79327100
F	-1.99075700	4.18223100	-0.33745200
F	2.16253000	4.12142700	-0.31042800
F	3.21303900	2.49465000	-1.37776500
F	3.41237700	2.69866300	0.82704300

2•benzene
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2188.101407
Sum of electronic and thermal Energies= -2188.068432
Sum of electronic and thermal Enthalpies= -2188.067488
Sum of electronic and thermal Free Energies= -2188.166937

0 1

Cu	0.00017000	-0.03816200	0.47744100
N	-1.47739900	1.22297600	0.35346800
N	1.47771400	1.22307000	0.35347900
C	-1.27153800	2.54754300	0.29719200
C	0.00008800	3.14189000	0.31769600
H	0.00003400	4.22422300	0.30107300
C	1.27170800	2.54765000	0.29699800
C	-2.46809400	3.47006700	0.20350000
C	2.46822600	3.47023500	0.20324800
C	-2.75397700	0.66745400	0.19693400
C	-3.37448500	-0.01352500	1.24846500
C	-4.55353200	-0.72312600	1.07647400
C	-5.16377700	-0.75765700	-0.17048500
C	-4.57909800	-0.08506200	-1.23501400
C	-3.39463100	0.61044500	-1.04468600
C	2.75421200	0.66749600	0.19695300
C	3.39521500	0.61064300	-1.04449700
C	4.57961900	-0.08500700	-1.23470600
C	5.16392400	-0.75801200	-0.17023600
C	4.55332600	-0.72374500	1.07656000
C	3.37439300	-0.01394200	1.24842700
C	-0.71043700	-2.04464800	0.63665000
H	-1.25361500	-1.99507800	1.57597600
C	0.71026000	-2.04456000	0.63610000
H	1.25417400	-1.99503900	1.57499900
C	1.40440400	-2.35163000	-0.56443800
H	2.48864400	-2.39315200	-0.55518200
C	-1.40551300	-2.35211100	-0.56322800
H	-2.48973000	-2.39407100	-0.55300700
C	-0.70736700	-2.61291100	-1.72776200
C	0.70533200	-2.61261400	-1.72837500
H	1.24024600	-2.83807200	-2.64392300
H	-1.24297400	-2.83864300	-2.64283400
H	-2.18123200	4.50614000	0.38604300
H	-2.91221000	3.41274800	-0.79610400
H	-3.23611900	3.19103700	0.93178300
H	2.18122500	4.50636600	0.38524500
H	2.91265900	3.41251700	-0.79617700
H	3.23601400	3.19156300	0.93193100
F	-2.82012000	1.24204200	-2.12081900
F	-5.16941400	-0.12098200	-2.46948200
F	-6.33123200	-1.44850900	-0.34840000
F	-5.11986800	-1.38703000	2.13120500
F	-2.77449000	-0.02555500	2.48463700
F	2.82106900	1.24248900	-2.12072200
F	5.17019900	-0.12071100	-2.46905600
F	6.33128000	-1.44904700	-0.34807200
F	5.11919300	-1.38810000	2.13125400
F	2.77407200	-0.02631100	2.48446900

3•benzene
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -3034.510654
Sum of electronic and thermal Energies= -3034.481658
Sum of electronic and thermal Enthalpies= -3034.480713
Sum of electronic and thermal Free Energies= -3034.573648

0 1

Cu	0.00658000	-0.02097900	-0.49903900
Cl	-2.91847200	-2.00597800	-2.01670500
Cl	-2.30496800	1.18621600	2.45171100
Cl	2.35814500	1.18663300	2.45049600
Cl	2.91915000	-1.95304500	-2.06263400
N	-1.46121300	-0.90361700	0.41441100
N	1.49340600	-0.88608100	0.40192200
C	-1.24507000	-1.91502500	1.26360700
C	0.02981600	-2.39925200	1.60119900
H	0.03752600	-3.24248500	2.28007100
C	1.29616900	-1.90253000	1.25003100
C	-2.44072300	-2.57428900	1.91857900
H	-2.95029000	-1.86617100	2.58195600
H	-2.13967200	-3.43970800	2.51025500
H	-3.16311900	-2.90295400	1.16400800
C	2.50506000	-2.55381200	1.88857800
H	3.22250400	-2.87142400	1.12459200
H	2.21849200	-3.42546800	2.47830900
H	3.01492500	-1.84471800	2.55064500
C	-2.73948000	-0.36372700	0.20151900
C	-3.51582500	-0.70491100	-0.91649600
C	-4.71402500	-0.07490700	-1.22426900
H	-5.26950800	-0.37635700	-2.10328700
C	-5.18505100	0.93971100	-0.39079900
H	-6.11929200	1.43849700	-0.61802200
C	-4.45219500	1.30795200	0.73710700

H	-4.80080900	2.09390100	1.39504500
C	-3.25507800	0.66132500	1.01181100
C	2.76487300	-0.33561000	0.17591000
C	3.28931500	0.68111000	0.99118900
C	4.48150700	1.33337400	0.70810600
H	4.83801500	2.11142800	1.37119400
C	5.19954400	0.98053100	-0.43423800
H	6.12956000	1.48406600	-0.66816400
C	4.71900100	-0.02443400	-1.27358800
H	5.26285000	-0.31388800	-2.16384900
C	3.52666600	-0.66112300	-0.95687900
C	-0.71074600	1.28897800	-2.02364600
H	-1.19990600	0.57578700	-2.68124600
C	0.70775500	1.35344900	-1.96585700
H	1.31289100	0.69525300	-2.58297600
C	1.32643600	2.42988200	-1.27634400
H	2.40925800	2.48883800	-1.25062600
C	-1.48048900	2.30650700	-1.40043300
H	-2.56248100	2.26771700	-1.46950900
C	-0.85505300	3.32788700	-0.70992500
C	0.55469400	3.38841500	-0.64556300
H	1.03198200	4.19939100	-0.10708300
H	-1.44722000	4.09252200	-0.21989400

Al
wB97XD / 6-31G+(d,p) / SDD (Al, Cu)
Sum of electronic and zero-point Energies= -1246.089358
Sum of electronic and thermal Energies= -1246.063751
Sum of electronic and thermal Enthalpies= -1246.062807
Sum of electronic and thermal Free Energies= -1246.142546

0 1

Al	-0.00000100	-0.79040400	0.01391700
H	-0.00000200	-1.66547100	-1.33197300
H	-0.00000200	-1.62186800	1.38712100
N	-1.42200100	0.51508600	-0.00672900
C	-1.25705900	1.82561700	-0.02642700
C	0.00000400	2.44870000	-0.03562700
H	0.00000700	3.53010400	-0.05186800
C	1.25706300	1.82561100	-0.02643000
N	1.42199900	0.51508400	-0.00673000
C	-2.48897300	2.69886900	-0.03959200
H	-3.10940300	2.47993500	-0.91499700
H	-2.21963700	3.75526400	-0.05566300
H	-3.10920000	2.50656900	0.84217000
C	2.48898100	2.69885500	-0.03958300
H	3.10913100	2.50663600	0.84225300
H	2.21965200	3.75524900	-0.05577500
H	3.10948700	2.47983500	-0.91491100
C	-2.75170000	-0.03924000	0.00071000
C	-3.37984100	-0.30993500	1.22931000
C	-4.65193300	-0.88853700	1.21301200
H	-5.14490700	-1.09911600	2.15835200
C	-5.30010800	-1.20660200	0.01583600
C	-4.64942200	-0.92558300	-1.18858000
H	-5.14012900	-1.16492500	-2.12815600
C	-3.37714900	-0.34690900	-1.21978800
C	-2.69425400	0.01609100	2.53314600
H	-3.33103500	-0.24814100	3.38175200
H	-2.45257300	1.08255200	2.61008000
H	-1.75098700	-0.53317900	2.62590300
C	-6.65787400	-1.86771300	0.02616400
H	-7.21122700	-1.65524100	-0.89362000
H	-7.26139300	-1.52578100	0.87286100
H	-6.56031400	-2.95692900	0.10961700
C	-2.68962400	-0.05952900	-2.53165100
H	-3.32571500	-0.34730300	-3.37307400
H	-1.74686500	-0.61229400	-2.60742300
H	-2.44661500	1.00404900	-2.63881600
C	2.75169900	-0.03924100	0.00071100
C	3.37714900	-0.34690800	-1.21978700
C	4.64942200	-0.92558000	-1.18857900
H	5.14013100	-1.16491900	-2.12815400
C	5.30010800	-1.20660100	0.01583900
C	4.65193100	-0.88853900	1.21301300
H	5.14490300	-1.09911900	2.15835300
C	3.37983700	-0.30993700	1.22931000
C	2.68962500	-0.05952400	-2.53164900
H	2.44661700	1.00405500	-2.63881100
H	1.74686600	-0.61228800	-2.60742300
H	3.32571500	-0.34729600	-3.37307300
C	6.65787300	-1.86771300	0.02616000
H	6.56030200	-2.95695300	0.10929900
H	7.26128200	-1.52601200	0.87302700
H	7.21134300	-1.65499000	-0.89349600
C	2.69425000	0.01608500	2.53314800
H	2.45255900	1.08254300	2.61008100
H	3.33103500	-0.24814000	3.38175300
H	1.75098900	-0.53319400	2.62590700

Al'
wB97XD / 6-31G+(d,p) / SDD (Al, Cu)
Sum of electronic and zero-point Energies= -1227.570545
Sum of electronic and thermal Energies= -1227.542874
Sum of electronic and thermal Enthalpies= -1227.541930
Sum of electronic and thermal Free Energies= -1227.626473

0 1

Al	1.14413400	0.58216300	-0.44377000
H	0.73724100	-0.07396100	-1.86759000
H	0.93944900	2.16346400	-0.14265100
N	-0.40173200	-0.12627400	0.61728700
C	-0.33665300	-0.56270900	1.87056000
C	0.88900700	-0.80157300	2.52751000
H	0.82982100	-1.10462100	3.56465700
C	2.15388400	-0.82627900	1.93639400
N	2.40077700	-0.44480000	0.66866700
C	3.73496400	-0.69932400	0.10560400
H	3.97036900	-1.77185300	0.09905000
H	4.51938600	-0.20711600	0.69778000
C	3.77255300	-0.18262100	-1.33030400
H	4.80989500	-0.11730100	-1.69388300
H	3.21806600	-0.86276400	-1.98510300
N	3.08938300	1.12485000	-1.39476500
C	-1.66565400	-0.08429800	-0.07131300
C	-2.03165000	-1.19641000	-0.86003600
C	-3.24892800	-1.15746300	-1.54569700
H	-3.54941900	-2.01054600	-2.14614600
C	-4.07787700	-0.04091700	-1.47514600
H	-5.01865100	-0.02547700	-2.01532800
C	-3.69075700	1.05788900	-0.71546700
H	-4.33296400	1.93235100	-0.67409100
C	-2.48525400	1.05993500	-0.00272800
C	-1.60799700	-0.84788000	2.63861800
H	-2.13026000	0.08852400	2.86039500
H	-1.39350500	-1.35617100	3.57984600
H	-2.29429600	-1.46269000	2.05007100
C	3.29714200	-1.34830300	2.78231500

H	3.72305700	-2.26184600	2.35194900
H	2.95742100	-1.57870100	3.79255900
H	4.10581500	-0.61198900	2.85303500
C	2.86878000	1.56999300	-2.78343500
H	3.82124600	1.78996800	-3.28817200
H	2.24973800	2.47038300	-2.77012500
H	2.32892700	0.79361000	-3.32813700
C	3.77143300	2.17378600	-0.61037000
H	4.79640900	2.34018800	-0.97497000
H	3.79820300	1.89854900	0.44543200
H	3.19660800	3.09719600	-0.69333800
C	-1.14049500	-2.42848800	-0.96540600
H	-0.19139900	-2.19417000	-0.47407700
C	-1.76824800	-3.63346700	-0.23818800
H	-1.93624300	-3.41647300	0.82211300
H	-2.73296500	-3.89952600	-0.68650500
H	-1.10959100	-4.50702200	-0.30606300
C	-0.82246600	-2.77511100	-2.43049900
H	-0.37510500	-1.91195400	-2.93149700
H	-0.11395900	-3.61076700	-2.47399600
H	-1.72363100	-3.07329300	-2.97961100
C	-2.09351300	2.29339300	0.80258900
H	-1.15222000	2.07517200	1.31783100
C	-1.83646100	3.49518000	-0.12607700
H	-1.50845800	4.36276600	0.45804400
H	-1.05389300	3.25671500	-0.85077200
H	-2.74869900	3.77281700	-0.66834900
C	-3.15619300	2.65374400	1.85901300
H	-2.80032500	3.47764000	2.48771500
H	-4.09074600	2.97624800	1.38510700
H	-3.39176600	1.80364300	2.50789800

Zn
wB97XD / 6-31G+(d,p) / SDD (Zn)
Sum of electronic and zero-point Energies= -1465.785073
Sum of electronic and thermal Energies= -1465.749797
Sum of electronic and thermal Enthalpies= -1465.748853
Sum of electronic and thermal Free Energies= -1465.851358

0 1

Zn	-0.00447700	-0.28851500	-0.80071000
N	1.45601500	-0.17345000	0.50254400
C	1.27797000	-0.27283200	1.82671500
C	0.01727300	-0.38660200	2.43857500
H	0.02458200	-0.47848200	3.51713200
C	-1.25059800	-0.32328400	1.83931700
N	-1.44923600	-0.24118100	0.51560600
C	2.49180200	-0.27249700	2.73396900
H	3.04316200	-1.21407800	2.62936300
H	2.19960600	-0.15995600	3.77898500
H	3.18435700	0.53142500	2.47031200
C	-2.45835900	-0.31527200	2.75119500
H	-2.99887300	0.63341800	2.65962500
H	-2.16715500	-0.45109500	3.79349100
H	-3.16061400	-1.10800600	2.47339100
C	2.76340700	0.06298800	-0.04413900
C	3.10641600	1.38043600	-0.41916300
C	4.37802200	1.60317900	-0.95756700
H	4.67056700	2.60617600	-1.24653100
C	5.27290600	0.55274500	-1.14528700
H	6.25362600	0.74501500	-1.56686700
C	4.89907800	-0.74685700	-0.81585400
H	5.59174000	-1.56196800	-0.99614100
C	3.64174700	-1.01585300	-0.26545600
C	-2.77124500	-0.03396600	-0.01188200
C	-3.55537700	-1.13962900	-0.39384100
C	-4.80001300	-0.89911800	-0.98509000
H	-5.41532700	-1.73710500	-1.29593400
C	-5.25917800	0.39947700	-1.18820000
H	-6.22521600	0.56739700	-1.65193400
C	-4.47380300	1.48231400	-0.80077100
H	-4.83574200	2.49143900	-0.96887900
C	-3.22276000	1.28769200	-0.20724600
C	2.11013600	2.52499100	-0.24927500
H	1.10461600	2.10217300	-0.37134200
C	3.20216500	-2.44992200	0.00459400
H	2.36058000	-2.42104400	0.70465000
C	-3.04216600	-2.56267100	-0.21640000
H	-2.19820800	-2.52750000	0.48101200
C	-2.34810000	2.47907300	0.16820200
H	-1.55288500	2.11752600	0.82915300
H	0.00870500	-0.33917700	-2.34383300
C	-2.51188500	-3.11071000	-1.55653000
H	-1.73381100	-2.45882400	-1.96827400
H	-2.09147300	-4.11420200	-1.42399000
H	-3.32186800	-3.17091500	-2.29302500
C	-4.09828300	-3.50621900	0.38413900
H	-4.50960700	-3.10207100	1.31556500
H	-4.93072000	-3.67282200	-0.30877400
H	-3.64979600	-4.48217500	0.59952200
C	-3.12061900	3.56736900	0.93299100
H	-3.87694700	4.04593200	0.30087900
H	-3.62697000	3.15113700	1.81041300
H	-2.43136500	4.34865300	1.27188000
C	-1.67202200	3.06629600	-1.08691000
H	-1.09712600	2.30341300	-1.62450500
H	-2.42403100	3.46267900	-1.77927400
H	-0.99255900	3.88157800	-0.81169800
C	2.17021200	3.13381900	1.16552700
H	1.91043400	2.39652600	1.93048000
H	3.17633600	3.51488500	1.37646000
H	1.46260600	3.96692300	1.24956000
C	2.26813200	3.62175900	-1.31362400
H	3.18876200	4.19870500	-1.16845000
H	2.28240700	3.19509400	-2.32134900
H	1.43016900	4.32418900	-1.24966500
C	4.30350600	-3.31323900	0.64134700
H	5.12639700	-3.49860800	-0.05810100
H	4.72005000	-2.83482000	1.53453300
H	3.89480700	-4.28755700	0.93030600
C	2.68474200	-3.08981400	-1.30016700
H	1.86951600	-2.49852300	-1.73145600
H	3.48818600	-3.14404100	-2.04393600
H	2.31730700	-4.10537300	-1.11352600

Mg
wB97XD / 6-31G+(d,p) / SDD (Mg)
Sum of electronic and zero-point Energies= -1438.720386
Sum of electronic and thermal Energies= -1438.684742
Sum of electronic and thermal Enthalpies= -1438.683798
Sum of electronic and thermal Free Energies= -1438.788604

0 1

H	-0.00003700	-0.00140000	-2.62802600
N	-1.46284700	0.00046500	0.49185800
C	-1.26794900	0.00076600	1.81799200
C	0.00002800	0.00086800	2.42683900
H	0.00005900	0.00110900	3.50950500

C	1.26797700	0.00059000	1.81792800
N	1.46286700	0.00031400	0.49178200
C	-2.47852700	0.00094700	2.72800300
H	-3.10310100	0.87996700	2.53524200
H	-2.18679300	0.00103400	3.77888400
H	-3.10325000	-0.87800200	2.53541700
C	2.47857100	0.00068200	2.72792600
H	3.10358900	-0.87796000	2.53492900
H	2.18685000	0.00020100	3.77881200
H	3.10285100	0.88000800	2.53557000
C	-2.79701000	0.00015000	-0.04555300
C	-3.42049900	-1.22815200	-0.34791200
C	-4.67607600	-1.20536600	-0.96357700
H	-5.16725800	-2.14020600	-1.21307800
C	-5.30276300	-0.00050900	-1.26986900
C	-4.67646800	1.20468200	-0.96406600
H	-5.16795900	2.13925300	-1.21395600
C	-3.42089100	1.22812000	-0.34843800
C	-2.72033700	-2.55149700	-0.06213700
H	-1.90421500	-2.35147600	0.64084300
C	-2.72102100	2.55176100	-0.06333300
H	-1.90506000	2.35230900	0.64000100
C	2.79704500	-0.00009700	-0.04558500
C	3.42120200	1.22785000	-0.34802200
C	4.67679500	1.20434200	-0.96361500
H	5.16851100	2.13888600	-1.21314800
C	5.30284700	-0.00088100	-1.26979300
C	4.67589600	-1.20570300	-0.96391900
H	5.16689900	-2.14056600	-1.21367700
C	3.42028600	-1.22843300	-0.34831100
C	2.72155900	2.55151100	-0.06246600
H	1.90584000	2.35203300	0.64114200
C	2.71981100	-2.55170500	-0.06300400
H	1.90358800	-2.35170300	0.63986500
C	-3.64819100	-3.58702300	0.59563300
H	-4.12168800	-3.17918500	1.49505100
H	-4.44143800	-3.91081400	-0.08739300
H	-3.07653900	-4.47711300	0.88065200
C	-2.09466100	-3.11770500	-1.35305800
H	-2.87547400	-3.35690000	-2.08434300
H	-1.41885000	-2.39479900	-1.82558100
H	-1.52997500	-4.03286600	-1.14117500
C	-3.64917700	3.58764200	0.59344500
H	-4.44218200	3.91097600	-0.09007400
H	-4.12298000	3.18033200	1.49294000
H	-3.07767800	4.47794000	0.87812200
C	-2.09506800	3.11715000	-1.35448000
H	-1.41909100	2.39397400	-1.82635800
H	-2.87572500	3.35575700	-2.08612300
H	-1.53049400	4.03249400	-1.14310200
C	3.64731900	-3.58759800	0.59470700
H	4.44056200	-3.91149100	-0.08827800
H	4.12081200	-3.18002200	1.49424600
H	3.07540500	-4.47758700	0.87951200
C	3.65001400	3.58727500	0.59409200
H	4.12431400	3.17973300	1.49322100
H	4.44263400	3.91085600	-0.08975900
H	3.07862300	4.47746400	0.87931600
H	6.27453700	-0.00118300	-1.75164100
H	-6.27442500	-0.00076400	-1.75177300
Mg	-0.00004100	-0.00001700	-0.89220900
C	2.09430000	-3.11748200	-1.35418500
H	1.41879600	-2.39431500	-1.82674900
H	2.87522700	-3.35672400	-2.08533600
H	1.52933300	-4.03253800	-1.14261400
C	2.09514500	3.11711200	-1.35328600
H	2.87553200	3.35577900	-2.08519600
H	1.41897000	2.39403400	-1.82503000
H	1.53068600	4.03244300	-1.14155900

3•H_2
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2803.630243
Sum of electronic and thermal Energies= -2803.605458
Sum of electronic and thermal Enthalpies= -2803.604514
Sum of electronic and thermal Free Energies= -2803.688522

0 1

Cu	0.00001400	0.00024800	-0.79667100
H	-0.40363300	0.00109000	-2.41967200
H	0.40566700	0.00106100	-2.41870100
N	1.49133800	-0.00030200	0.40610100
C	1.27387700	-0.00077200	1.72985200
C	-0.00002700	-0.00111500	2.32185000
H	-0.00006200	-0.00152700	3.40428700
N	-1.49133400	-0.00030200	0.40601900
C	-1.27390600	-0.00083400	1.72977300
C	2.47251600	-0.00075500	2.65531700
H	3.09475900	-0.88479600	2.47881900
H	2.16336500	-0.00155900	3.70094000
H	3.09375800	0.88421100	2.47986800
C	-2.47258400	-0.00090000	2.65518700
H	-3.09374700	0.88414900	2.47987100
H	-2.16347400	-0.00191700	3.70082100
H	-3.09489600	-0.88485600	2.47851100
C	2.80216200	0.00002300	-0.11493400
C	3.47586000	1.18963300	-0.43021700
C	4.73094500	1.20763500	-1.02343100
C	5.36210600	0.00074800	-1.32132600
C	4.73144800	-1.20650000	-1.02379600
C	3.47635900	-1.18922600	-0.43058200
C	-2.80215700	-0.00001100	-0.11501600
C	-3.47630100	-1.18927700	-0.43071000
C	-4.73143200	-1.20658100	-1.02382800
C	-5.36218200	0.00065200	-1.32122700
C	-4.73107300	1.20755400	-1.02329000
C	-3.47595100	1.18958400	-0.43015200
H	6.34049600	0.00101100	-1.78586800
H	5.20537800	2.15433700	-1.24803300
H	5.20629200	-2.15292400	-1.24870600
H	-5.20557700	2.15424500	-1.24779100
H	-6.34060600	0.00089100	-1.78569800
H	-5.20624100	-2.15301700	-1.24876700
Cl	2.67447700	-2.76354600	-0.06399000
Cl	2.67332300	2.76349800	-0.06305600
Cl	-2.67430600	-2.76357200	-0.06426000
Cl	-2.67348500	2.76347200	-0.06293400

[3•BH_4]$^-$
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2829.725024
Sum of electronic and thermal Energies= -2829.698937
Sum of electronic and thermal Enthalpies= -2829.697993
Sum of electronic and thermal Free Energies= -2829.784519

-1 1

Cu	0.00189800	-0.00086000	-0.79160000
H	-0.02450400	-1.05212800	-2.25559400

H	-0.02496900	1.05081800	-2.25573000
N	-1.46303800	-0.00067400	0.58212100
C	-1.26458500	-0.00012000	1.89774600
C	0.00473900	0.00017200	2.50259800
H	0.00705400	0.00054700	3.58649000
N	1.46604800	-0.00032000	0.57558000
C	1.27097500	0.00039200	1.89262200
C	-2.47458800	0.00006100	2.81538800
H	-3.09384100	0.88505400	2.62968300
H	-2.17614600	-0.00017100	3.86568900
H	-3.09424000	-0.88459300	2.62936100
C	2.48439000	0.00179300	2.80587900
H	3.10523700	-0.88144700	2.61720700
H	2.18951200	0.00000300	3.85715900
H	3.10135900	0.88818400	2.61913700
C	-2.73640500	-0.00021000	0.01005000
C	-3.40158000	-1.18688000	-0.34752300
Cl	-2.65880500	-2.76789600	0.11558800
C	-4.59989900	-1.20457700	-1.04521600
H	-5.05044100	-2.15292500	-1.31030800
C	-5.20286200	0.00065200	-1.40260700
H	-6.13260100	0.00097800	-1.95936800
C	-4.59947800	1.20543300	-1.04449000
H	-5.04966600	2.15411100	-1.30899700
C	-3.40113900	1.18689600	-0.34681400
Cl	-2.65774000	2.76742300	0.11700700
C	2.73925900	0.00005700	0.00268600
C	3.40454900	1.18716300	-0.35392600
Cl	2.66023700	2.76783400	0.10735100
C	4.60398000	1.20542600	-1.04985600
H	5.05456700	2.15403100	-1.31399200
C	5.20826700	0.00052900	-1.40625200
H	6.13906800	0.00070000	-1.96123400
C	4.60510000	-1.20460100	-1.04872000
H	5.05658100	-2.15304000	-1.31192900
C	3.40565200	-1.18677400	-0.35282700
Cl	2.66279100	-2.76770200	0.10998800
B	-0.05896500	-0.00071100	-2.96525000
H	0.92950000	-0.00046400	-3.67936100
H	-1.10620700	-0.00087500	-3.59076700

1•B
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2108.970246
Sum of electronic and thermal Energies= -2108.929558
Sum of electronic and thermal Enthalpies= -2108.928614
Sum of electronic and thermal Free Energies= -2109.045501

0 1

Cu	-0.28952400	-0.49965200	0.12844400
H	-0.02515700	-2.01607900	-0.88702700
H	0.07787200	-1.95931200	1.18774100
H	-0.19721800	-3.66407300	0.19413100
N	0.84499700	1.08057500	-0.00935800
C	0.26946000	2.25274500	-0.25476000
C	-1.10432300	2.51024000	-0.34373000
H	-1.38073500	3.53110700	-0.54400000
N	-2.06082300	0.30192600	0.01043000
C	-2.16881800	1.60094600	-0.19455700
C	1.15828100	3.47543000	-0.47461700
C	-3.56129100	2.22232200	-0.29354800
C	2.25197000	0.89032900	0.16004200
C	3.02905900	0.44286700	-0.92529300
C	4.39493700	0.23321400	-0.72849100
H	5.00116100	-0.09301800	-1.57007000
C	5.00098100	0.43511700	0.51551700
C	4.19399500	0.81722500	1.58955900
H	4.64085900	0.95513500	2.57118300
C	2.82046700	1.03308300	1.43900200
C	-3.15746700	-0.61128600	0.15346300
C	-3.62720400	-0.92206000	1.44083900
C	-4.62744700	-1.88841000	1.56897500
H	-4.99967100	-2.12788800	2.56171700
C	-5.15131600	-2.55830300	0.46002600
C	-4.62894800	-2.25975000	-0.80141100
H	-5.00287300	-2.79107900	-1.67281100
C	-3.62935000	-1.30010700	-0.97705100
B	0.34060900	-2.58704200	0.14987700
N	1.92131700	-2.77913600	0.09339900
C	2.51556500	-3.35006600	-0.99214200
C	3.89785400	-3.54523900	-0.99365000
H	4.35753500	-3.99677800	-1.86339300
C	4.66576000	-3.16902400	0.10199300
H	5.73826600	-3.32262600	0.09793100
C	4.03683100	-2.58218700	1.19828000
H	4.59475500	-2.24824100	2.06147800
C	2.66851500	-2.39283900	1.15677400
H	2.12782500	-1.92234900	1.96398500
C	1.66350200	-3.75803000	-2.15258100
H	0.86034100	-4.42717100	-1.83066900
H	2.26818000	-4.26198900	-2.90845800
H	1.18469300	-2.88547100	-2.60821500
C	6.47889500	0.18658200	0.70101300
H	6.69127900	-0.88451700	0.82419700
H	7.05241300	0.53375900	-0.16424700
H	6.86183100	0.70122700	1.58722200
C	2.38963500	0.19221900	-2.26533100
H	1.52680800	-0.47770000	-2.16303800
H	2.01726400	1.12113600	-2.70724200
H	3.10379700	-0.25688700	-2.96173500
C	1.95527700	1.38579800	2.62170200
H	1.55592500	2.40010600	2.53697700
H	1.09309500	0.70995100	2.68655000
H	2.52186000	1.32078900	3.55481400
C	-3.02935800	-0.25707400	2.65392400
H	-1.94502400	-0.42294200	2.69051900
H	-3.19096200	0.82458000	2.63946800
H	-3.46893700	-0.65624300	3.57203400
C	-3.03820900	-1.03560700	-2.33790200
H	-3.22116300	-0.00712400	-2.66200000
H	-1.95102800	-1.18297200	-2.32171000
H	-3.46609400	-1.71011900	-3.08472000
C	-6.25814900	-3.57349800	0.61988100
H	-6.21020000	-4.06357900	1.59737600
H	-7.24297700	-3.09735500	0.53697800
H	-6.20160200	-4.34853300	-0.15098400
F	2.06430200	3.27877300	-1.50642500
F	0.45254300	4.61674600	-0.80399100
F	1.90397500	3.80294600	0.64833900
F	-3.53539500	3.58762100	-0.51328600
F	-4.29874700	2.03754000	0.86468600
F	-4.30579100	1.68526100	-1.33100100

2•B
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -2270.034829
Sum of electronic and thermal Energies= -2269.998931
Sum of electronic and thermal Enthalpies= -2269.997986

Sum of electronic and thermal Free Energies= -2270.104367

0 1

Cu	0.47620000	-0.10441600	-0.19648400
H	0.12809800	1.57257300	-0.73535300
H	0.39012800	1.10961800	1.27600600
H	0.58862300	2.96871300	0.58316400
N	-0.79254500	-1.56893000	-0.53098800
C	-0.36577100	-2.80770000	-0.83016100
C	0.98543800	-3.16458000	-0.93229200
H	1.16437000	-4.19713300	-1.20438600
N	2.13992400	-1.09870000	-0.41495100
C	2.15017900	-2.39798500	-0.72939500
C	-1.39079500	-3.89153200	-1.09734100
H	-1.88565700	-4.18626300	-0.16606100
H	-0.92204600	-4.77771200	-1.52656700
H	-2.15975400	-3.53980400	-1.79339700
C	3.47831900	-3.10808800	-0.89499000
H	4.16508600	-2.51509000	-1.50758300
H	3.34717300	-4.08088900	-1.37013000
H	3.94727300	-3.26592800	0.08200800
C	-2.14271600	-1.25828200	-0.38169600
C	-2.76051000	-0.34053700	-1.24383400
C	-4.05037200	0.11881700	-1.03776700
C	-4.78834800	-0.34495700	0.04113200
C	-4.21790200	-1.26256700	0.90952000
C	-2.92046200	-1.70277000	0.69646300
C	3.31771700	-0.38877800	-0.14731900
C	4.06829800	-0.58777200	1.01603000
C	5.15879200	0.20591600	1.33756500
C	5.53056500	1.24265800	0.49393700
C	4.80515800	1.47111400	-0.66749500
C	3.72384900	0.66143800	-0.97870300
B	-0.00882500	1.93067100	0.44673500
N	-1.56088700	2.17884800	0.73258100
C	-2.31212900	2.96334400	-0.09124700
C	-3.65308500	3.20307400	0.22415100
H	-4.24127900	3.81623100	-0.44521300
C	-4.22513700	2.64178500	1.35908600
H	-5.26900500	2.81367700	1.58948500
C	-3.43897700	1.83158800	2.18096800
H	-3.84618500	1.35803700	3.06424100
C	-2.11600500	1.62119700	1.83919400
H	-1.45756600	1.00023100	2.42908800
C	-1.68496400	3.52103100	-1.32799300
H	-0.75674200	4.04994800	-1.09592100
H	-2.37398200	4.20317600	-1.82804100
H	-1.43064700	2.71048400	-2.01884400
F	-2.05383400	0.16573700	-2.30766600
F	-4.59263300	1.05706100	-1.87922500
F	-6.04610600	0.14828500	0.27942900
F	-4.92281300	-1.68822100	2.00594600
F	-2.36828300	-2.57459100	1.60575800
F	3.70855100	-1.59508800	1.88145300
F	5.86654500	-0.02374000	2.48803000
F	6.60479600	2.03389300	0.80339000
F	5.16731400	2.49214500	-1.50579100
F	3.01803200	0.91761100	-2.12704600

3•B
wB97XD / 6-31G+(d,p) / SDD (Cu)
Sum of electronic and zero-point Energies= -3116.436796
Sum of electronic and thermal Energies= -3116.404941
Sum of electronic and thermal Enthalpies= -3116.403997

Sum of electronic and thermal Free Energies= -3116.503348

0 1

Cu	-0.43838800	0.12304900	-0.12914800
H	-0.14876500	1.89527400	0.18162700
H	-0.11516300	1.07195600	-1.72525300
H	-0.28152400	3.03588300	-1.42692400
N	0.67232000	-1.32100900	0.57660600
C	0.10449200	-2.35832400	1.21519200
C	-1.27646700	-2.53453300	1.37834600
H	-1.56262500	-3.42770400	1.91953800
N	-2.20473300	-0.58387600	0.28794100
C	-2.35223300	-1.73294900	0.94658900
C	1.00908500	-3.41702100	1.81740800
H	1.55923200	-3.95091700	1.03460500
H	0.43250200	-4.14763600	2.38602900
H	1.74444600	-2.96061900	2.48917400
C	-3.75324600	-2.21444700	1.26551400
H	-4.28722400	-1.47215400	1.86900000
H	-3.73316700	-3.15612300	1.81562300
H	-4.32422200	-2.36610000	0.34274500
C	2.06020700	-1.24788100	0.40987000
C	2.87361100	-0.44959100	1.23514800
Cl	2.10117800	0.46499400	2.58618000
C	4.24733600	-0.34057700	1.07092700
H	4.82009000	0.28169700	1.74700200
C	4.87282300	-1.04455400	0.04250200
H	5.94619800	-0.97750400	-0.08843500
C	4.10871900	-1.82819500	-0.82064000
H	4.57158600	-2.37570100	-1.63244600
C	2.73510100	-1.90729600	-0.63473100
Cl	1.77277700	-2.89555800	-1.79924600
C	-3.30259300	0.19369800	-0.11484900
C	-3.90414700	0.04230800	-1.37436800
Cl	-3.32463700	-1.28221400	-2.45580800
C	-4.91588300	0.87526700	-1.83123300
H	-5.33960200	0.71618400	-2.81470300
C	-5.37013800	1.90982200	-1.01429400
H	-6.15594400	2.57002900	-1.36066900
C	-4.80795900	2.09527900	0.24812000
H	-5.14714700	2.89276900	0.89699900
C	-3.79856200	1.24391800	0.67421300
Cl	-3.08150300	1.50908100	2.31037400
B	0.20466800	2.01798600	-0.99866500
N	1.79604900	2.13768900	-1.04243100
C	2.45173300	3.02948300	-0.24877500
C	3.84219600	3.13496000	-0.34007600
H	4.35092200	3.84638600	0.29777100
C	4.55437500	2.34174400	-1.23090300
H	5.63213500	2.42748400	-1.30077900
C	3.86130900	1.42988900	-2.02684700
H	4.37394900	0.77791100	-2.72012100
C	2.48747700	1.34764300	-1.90152000
H	1.89408900	0.65010700	-2.47475500
C	1.65889400	3.86784000	0.70171500
H	0.86745200	4.41084600	0.17720200
H	2.30830300	4.58032400	1.21322300
H	1.16931000	3.23358900	1.44801200

1•Zn
wB97XD / 6-31G+(d,p) / SDD (Cu, Zn)
Sum of electronic and zero-point Energies= -3260.835624
Sum of electronic and thermal Energies= -3260.768015
Sum of electronic and thermal Enthalpies= -3260.767071

Sum of electronic and thermal Free Energies= -3260.937829

0 1

Zn	-1.19474000	0.70159400	0.50174800
Cu	0.95244100	-0.24414600	-0.37256600
H	-0.56982000	-0.07014200	-0.78084500
N	-1.87704700	0.22629300	2.25467400
C	-2.48447000	1.16920700	3.00203800
C	-2.80218200	2.46082200	2.55182100
H	-3.26710200	3.10361500	3.28836000
C	-2.75657900	2.98042600	1.24423300
N	-2.15705800	2.36137200	0.21767100
C	-2.95572700	0.81081900	4.39635100
H	-3.92902100	0.30958900	4.34835000
H	-3.07015300	1.71100300	5.00302600
H	-2.26705800	0.12653300	4.89523700
C	-3.45664000	4.29840200	0.99770700
H	-4.21698000	4.18842700	0.21746800
H	-2.74898400	5.05467700	0.64451500
H	-3.93553900	4.66496100	1.90617200
C	-1.93554900	-1.14782900	2.69611800
C	-3.14722000	-1.85560100	2.53578500
C	-3.21824500	-3.17456200	2.99311700
H	-4.14182300	-3.73135400	2.87327400
C	-2.12036600	-3.78891000	3.58722600
H	-2.19420800	-4.81006700	3.94491700
C	-0.92108600	-3.09436600	3.69930100
H	-0.06079700	-3.58635000	4.13828200
C	-0.80095200	-1.77489900	3.24713100
C	-4.33700400	-1.25996600	1.79204500
H	-4.18096400	-0.18223300	1.68172600
C	-4.39483900	-1.86478300	0.37620400
H	-4.56259600	-2.94724500	0.42788100
H	-3.45547300	-1.70105100	-0.16314400
H	-5.21112800	-1.41789600	-0.20227300
C	-5.67393200	-1.45659400	2.52649900
H	-5.95443500	-2.51437800	2.57902300
H	-6.47391300	-0.92949400	1.99522000
H	-5.62977900	-1.06980300	3.55011600
C	0.53163700	-1.05162700	3.35529200
H	0.51755900	-0.23840600	2.62408600
C	0.71496600	-0.42389600	4.75007000
H	0.64843200	-1.19346900	5.52817300
H	-0.04951100	0.33416300	4.94871400
H	1.69560800	0.05709400	4.83018500
C	1.72059700	-1.95706900	2.99791400
H	1.57483100	-2.43232700	2.02237500
H	1.87774600	-2.74223100	3.74590000
H	2.64037200	-1.36689200	2.95135100
C	-2.27269800	2.89654300	-1.11680500
C	-1.41322600	3.93248000	-1.53523900
C	-1.57478800	4.45912100	-2.82008700
H	-0.91807400	5.25520300	-3.15503400
C	-2.54949700	3.96578100	-3.68218400
H	-2.66743300	4.39131800	-4.67279200
C	-3.35133300	2.90469100	-3.27650400
H	-4.08404200	2.49592700	-3.96507200
C	-3.22265100	2.34451400	-1.99992100
C	-0.24949600	4.39689700	-0.67315900
H	-0.39260200	4.00892800	0.34119100
C	-0.12818500	5.92689400	-0.57631400
H	0.12178700	6.37317100	-1.54532900
H	0.67129000	6.19201900	0.12393400
H	-1.05875100	6.38657400	-0.22535700
C	1.04872300	3.78078300	-1.22666800
H	0.99616500	2.68599400	-1.21971100
H	1.90719100	4.08311100	-0.62375000
H	1.21832400	4.10456500	-2.26035900
C	-4.06270100	1.12497400	-1.64032200
H	-3.84344600	0.85058400	-0.60211200
C	-3.66424700	-0.06302100	-2.53888300
H	-2.60807900	-0.32203800	-2.40670200
H	-3.81826900	0.17735900	-3.59714900
H	-4.25978400	-0.95099500	-2.30572300
C	-5.57204000	1.41282300	-1.72215700
H	-6.14421600	0.53272100	-1.40698400
H	-5.87591200	1.65852700	-2.74597900
H	-5.84915400	2.25233600	-1.07547400
N	2.76348400	0.08054900	0.16140800
C	3.58467000	-0.97417400	0.25934700
C	3.37164800	-2.27022600	-0.20887900
H	4.15625900	-2.98393400	-0.02259500
C	2.28149000	-2.73283900	-0.97544500
N	1.15900400	-2.07808600	-1.16334000
C	4.93836800	-0.77985500	0.94616700
F	4.80735800	-0.09076900	2.14305900
F	5.54456900	-1.98031900	1.27463400
F	5.86343100	-0.08835000	0.18301800
C	2.47696300	-4.09512900	-1.63465000
F	1.50764000	-5.01166200	-1.26548300
F	3.69096500	-4.67841700	-1.32425900
F	2.43300900	-3.99904200	-3.01618300
C	3.30166800	1.41947800	0.18831100
C	3.98230800	1.87745100	-0.95845600
C	4.52638400	3.16288800	-0.94896600
H	5.06063600	3.51164500	-1.82873700
C	4.39626100	4.01003900	0.15512000
C	3.66572900	3.55117200	1.25301100
H	3.52859500	4.20237600	2.11227200
C	3.09792600	2.27338600	1.28242700
C	4.10226200	1.00616800	-2.18425800
H	4.81438700	0.18836500	-2.03329800
H	4.44232200	1.59239600	-3.04205900
H	3.13805200	0.55063700	-2.43536000
C	4.97340600	5.40493700	0.12978400
H	5.95603800	5.41977400	-0.35225500
H	5.08642300	5.80816500	1.14056000
H	4.32233700	6.08823300	-0.43001800
C	2.27086400	1.84111700	2.45926300
H	2.60441800	0.87472300	2.84134400
H	1.21542400	1.73382600	2.17410500
H	2.32549100	2.57268900	3.26996300
C	0.05099800	-2.51732700	-1.95991100
C	-0.99980300	-3.21281900	-1.34082500
C	-2.13175400	-3.52245400	-2.10149800
H	-2.94641200	-4.06249800	-1.62647100
C	-2.24730100	-3.14257500	-3.43962600
C	-1.19926900	-2.41632800	-4.01501600
H	-1.28386400	-2.08535900	-5.04688600
C	-0.05258300	-2.08137400	-3.29298100
C	-0.92321300	-3.57103500	0.11782500
H	-0.12662700	-4.29399500	0.31598400
H	-1.86536400	-3.99597600	0.47217200
H	-0.70903100	-2.68336700	0.72333500
C	-3.48239100	-3.47295900	-4.24314800
H	-3.24152200	-4.12262400	-5.09241700
H	-3.94584100	-2.56442100	-4.64500400
H	-4.22830600	-3.98730600	-3.62996600
C	1.02267900	-1.21887000	-3.90223400
H	2.00957300	-1.68305000	-3.82371700
H	1.07356400	-0.25007000	-3.38755500
H	0.81768600	-1.02804800	-4.95892700

2•Zn

wB97XD / 6-31G+(d,p) / SDD (Cu, Zn)

Sum of electronic and zero-point Energies= -3421.908186
Sum of electronic and thermal Energies= -3421.844970
Sum of electronic and thermal Enthalpies= -3421.844026
Sum of electronic and thermal Free Energies= -3422.006271

0 1

Zn	-0.03798700	-1.22882700	-0.22032500
Cu	-0.01963100	1.40797300	-0.24933700
N	-1.37714500	-2.52913300	0.39085500
C	-1.11287600	-3.83539400	0.49413000
C	0.08070000	-4.41855300	0.03005800
H	0.11990100	-5.49956100	0.07069600
C	-2.13522700	-4.75359300	1.12922200
H	-2.42491300	-4.37012500	2.11290900
H	-1.73234200	-5.76001900	1.24862500
H	-3.05079900	-4.81275500	0.53236800
C	-2.67401100	-2.03413600	0.76273900
C	-2.83400200	-1.36517200	1.98891200
C	-4.11332500	-0.91001100	2.33421700
H	-4.26035900	-0.38732600	3.27394400
C	-5.19572100	-1.11427100	1.48685600
H	-6.17887300	-0.75097200	1.76396300
C	-5.01060000	-1.74255900	0.25460800
H	-5.85959700	-1.85711500	-0.40898000
C	-3.75243000	-2.20478100	-0.13700300
C	-1.65870300	-1.12000500	2.92625900
H	-0.77370200	-1.59453200	2.48770900
C	-1.87859000	-1.76813800	4.30529500
H	-2.73762200	-1.32265300	4.81946700
H	-0.99582300	-1.62135600	4.93730700
H	-2.06081600	-2.84413900	4.21165600
C	-1.36513200	0.38581900	3.06284600
H	-1.21204900	0.85243700	2.08304100
H	-0.46070300	0.54852200	3.65873200
H	-2.19694800	0.90866300	3.54737900
C	-3.52869500	-2.85094400	-1.50336900
H	-2.78333200	-3.64561900	-1.38505800
C	-2.94373100	-1.83789100	-2.50838000
H	-2.65947500	-2.34545900	-3.43697300
H	-2.05762400	-1.33508600	-2.10975000
H	-3.68188900	-1.07161300	-2.75632600
C	-4.79306200	-3.49996400	-2.08683900
H	-5.25763300	-4.19023100	-1.37434800
H	-4.53639700	-4.06102700	-2.99153800
H	-5.53602100	-2.74673300	-2.37175700
N	-1.51818100	2.75619400	-0.36696600
C	-1.28791400	4.07330800	-0.33024400
C	-0.00807800	4.62970200	-0.18196600
H	0.02408200	5.71146200	-0.18718400
C	-2.44426200	5.04712200	-0.44114400
H	-3.13063200	4.75941700	-1.24340500
H	-2.08341000	6.05621400	-0.64381200
H	-3.01009100	5.07258000	0.49660100
C	-2.84271000	2.29470700	-0.41058500
C	-3.37252800	1.70105800	-1.55933900
F	-2.59059400	1.58545500	-2.68170400
C	-4.68214900	1.24781800	-1.60882300
F	-5.18052300	0.68134100	-2.75603900
C	-5.49782500	1.35469700	-0.49413100
F	-6.77764000	0.86678200	-0.52676400
C	-4.99574100	1.91838000	0.66705900
F	-5.78483300	1.99473100	1.78469200
C	-3.68874600	2.37215800	0.69976300
F	-3.22063500	2.94265000	1.86083700
N	1.42288600	-2.45082300	-0.47988900
C	1.23931100	-3.78908700	-0.43524000
C	2.37483700	-4.68901500	-0.88031100
H	2.76437600	-4.36263500	-1.84929600
H	2.03446600	-5.72168100	-0.96654600
H	3.21220300	-4.65818700	-0.17566300
C	2.76172900	-1.96502300	-0.68752300
C	3.14692200	-1.47468400	-1.94614200
C	4.48148000	-1.08543300	-2.12527700
H	4.80173600	-0.69621700	-3.08613400
C	5.40201200	-1.19797600	-1.09080000
H	6.43217900	-0.89747700	-1.24452200
C	4.99334200	-1.65237400	0.16452800
H	5.72051500	-1.70223300	0.96613800
C	3.66930300	-2.02731800	0.39797700
C	2.15514600	-1.36452800	-3.09587500
H	1.22573000	-1.85286500	-2.78215900
C	2.64594800	-2.09468900	-4.35884800
H	3.55061300	-1.62867900	-4.76503200
H	1.87574400	-2.05930600	-5.13678100
H	2.87233300	-3.14527500	-4.14704200
C	1.83575900	0.11175200	-3.39848800
H	1.45420600	0.62515500	-2.50874000
H	1.07815900	0.18759200	-4.18621200
H	2.73249700	0.64645100	-3.72922200
C	3.19583100	-2.50828000	1.77060500
H	2.53642200	-3.36999200	1.61480900
C	2.36078100	-1.43353500	2.49906300
H	1.80652200	-1.88145700	3.33163700
H	1.63806600	-0.94764300	1.83459500
H	3.00875500	-0.65698000	2.91116600
C	4.33840100	-2.97659600	2.68385700
H	4.96121500	-3.73403700	2.19599600
H	3.92341600	-3.41258400	3.59856000
H	4.97937300	-2.13950100	2.98263400
N	1.41871600	2.66519200	0.03626700
C	1.22556400	4.00225300	0.00835100
C	2.41845500	4.92133700	0.19702400
H	2.98488800	4.65942000	1.09655800
H	2.09491700	5.95795700	0.29220600
H	3.09625800	4.85669300	-0.66076200
C	2.73287100	2.20792800	0.25511600
C	3.14368500	1.76639000	1.51416500
F	2.24157300	1.75782200	2.54955500
C	4.44736000	1.36352100	1.75882800
F	4.81418700	0.90721200	3.00104600
C	5.38590200	1.40337400	0.74096200
F	6.66497600	0.96832000	0.96578400
C	5.00945400	1.83566800	-0.52024900
F	5.92854400	1.85693100	-1.53525600
C	3.70045900	2.22117600	-0.75175800
F	3.36239600	2.68262500	-2.00145600
H	-0.85477900	0.12392300	-0.56967000

3•Zn
wB97XD / 6-31G+(d,p) / SDD (Cu, Zn)
Sum of electronic and zero-point Energies= -4268.302844
Sum of electronic and thermal Energies= -4268.243372
Sum of electronic and thermal Enthalpies= -4268.242427
Sum of electronic and thermal Free Energies= -4268.397672

0 1

Zn	0.88838400	0.51581700	-0.23714200
Cu	-1.28814400	-0.51033600	0.36533100

H	0.10970800	-0.14875000	1.04740100
N	-2.84642800	-0.35341300	-0.77492600
C	-3.55511000	-1.46205100	-1.09684500
C	-3.42721800	-2.70695900	-0.47941000
H	-4.06873900	-3.48609700	-0.87223800
C	-2.66624100	-3.06996100	0.65413200
N	-1.73720500	-2.28136500	1.17952400
C	-4.57271100	-1.36756700	-2.21984600
H	-5.50514500	-0.90869600	-1.87477400
H	-4.81058100	-2.36235900	-2.60071700
H	-4.18503300	-0.76382900	-3.04622300
C	-2.94143800	-4.41827700	1.28470700
H	-2.04877800	-5.05196300	1.24935700
H	-3.75500700	-4.93568400	0.77461200
H	-3.21867100	-4.29220100	2.33716300
C	-3.33079900	0.90174300	-1.18448000
C	-4.52432500	1.44572700	-0.66525900
Cl	-5.43242700	0.53353900	0.60072900
C	-5.02351700	2.68366700	-1.04391000
H	-5.94845400	3.04252000	-0.61086400
C	-4.31155600	3.46153600	-1.95576700
H	-4.68661000	4.43279700	-2.25421500
C	-3.10574600	2.98767800	-2.46698900
H	-2.52520000	3.57899600	-3.16374900
C	-2.64569800	1.73542000	-2.08217200
Cl	-1.08324900	1.18056900	-2.79260800
C	-1.00151000	-2.63275100	2.32323500
C	0.17932500	-3.38692700	2.25472200
Cl	0.69324300	-4.04931700	0.65904700
C	0.98346400	-3.62510400	3.36108000
H	1.88950100	-4.20710200	3.24923600
C	0.61347700	-3.10473100	4.60027700
H	1.23405300	-3.28075500	5.47043300
C	-0.55636900	-2.35480600	4.71696500
H	-0.85943900	-1.94017900	5.66993900
C	-1.33708600	-2.13339500	3.59123400
Cl	-2.83733300	-1.14522000	3.75840100
N	1.55606700	2.34872600	-0.21578300
C	2.07904900	2.85222400	-1.34565100
C	2.48512700	2.06708900	-2.43719000
H	2.88475100	2.61486600	-3.28061900
C	2.59935400	0.66603700	-2.51993100
N	2.05554000	-0.19362000	-1.64236000
C	2.28019400	4.34875700	-1.45263200
H	1.31060700	4.85637700	-1.41684100
H	2.77881900	4.61334100	-2.38593800
H	2.87059200	4.73178800	-0.61524300
C	3.43011600	0.11799500	-3.66053500
H	4.28710400	-0.44230700	-3.27166300
H	3.79955800	0.92339600	-4.29613500
H	2.84948000	-0.57657200	-4.27412700
C	1.49177000	3.16869700	0.96777000
C	0.35456800	3.94833000	1.24433800
C	0.35768700	4.75720600	2.38784900
H	-0.51495800	5.36188200	2.61332900
C	1.45279000	4.79155900	3.24085400
H	1.44281400	5.43072900	4.11719500
C	2.55512800	3.98040700	2.98109100
H	3.38895700	3.98820800	3.67318700
C	2.59265600	3.14765000	1.85918100
C	-0.89435400	3.89487800	0.37780000
H	-0.66909400	3.29677600	-0.51242500
C	-2.02983600	3.19212800	1.14600300
H	-1.77124200	2.15078600	1.36827000
H	-2.95163600	3.20157300	0.55981800
H	-2.22729900	3.70062700	2.09687700
C	-1.34424800	5.29064200	-0.09135400
H	-1.67583000	5.90655000	0.75245800
H	-2.18673300	5.19702100	-0.78459300
H	-0.53498900	5.82724200	-0.59863100
C	3.77996800	2.21807500	1.62139900
H	3.37599200	1.31134100	1.15792100
C	4.81971100	2.80641200	0.64647100
H	5.19346000	3.76749300	1.01947400
H	4.40430300	2.95569500	-0.35260700
H	5.67101200	2.12182000	0.55092900
C	4.48015900	1.79416700	2.92269700
H	3.76539200	1.40351900	3.65415900
H	5.02324900	2.62863400	3.38110100
C	2.40423900	-1.59522500	-1.72940000
C	3.45344600	-2.08019100	-0.91986400
C	3.81969800	-3.42476000	-1.02680500
H	4.62100600	-3.81098400	-0.40585100
C	3.16075400	-4.27987400	-1.90440200
H	3.45486700	-5.32147900	-1.97558900
C	2.10799800	-3.79689400	-2.67437200
H	1.57743300	-4.47120800	-3.33842400
C	1.71301900	-2.45644800	-2.60384200
C	4.11978300	-1.19104400	0.11953400
H	3.92346600	-0.15018300	-0.15682800
C	5.64596400	-1.35760400	0.18909100
H	5.93137200	-2.34451100	0.57030100
H	6.07069600	-0.60919600	0.86817700
H	6.10465400	-1.22675600	-0.79659900
C	3.47400900	-1.45728000	1.49548200
H	2.39365700	-1.27369300	1.47389300
H	3.91660400	-0.82378700	2.27057300
H	3.61862100	-2.50600600	1.78020100
C	0.51590400	-1.98172500	-3.41070900
H	0.50118900	-0.88954400	-3.37528600
C	0.57270400	-2.39923900	-4.88999200
H	0.48116000	-3.48513300	-5.00606600
H	1.51044400	-2.08890000	-5.36419500
H	-0.25714800	-1.93833100	-5.43677900
C	-0.78025600	-2.48217500	-2.74894800
H	-1.65889800	-2.05448400	-3.24350400
H	-0.81543700	-2.19860600	-1.69311000
H	-0.84599700	-3.57551600	-2.80219500
H	5.21698800	1.01283000	2.70618700

1•Mg
wB97XD / 6-31G+(d,p) / SDD (Cu, Mg)
Sum of electronic and zero-point Energies= -3233.782473
Sum of electronic and thermal Energies= -3233.716008
Sum of electronic and thermal Enthalpies= -3233.715064
Sum of electronic and thermal Free Energies= -3233.881298

0 1

Mg	0.36514900	-1.69237000	-0.03633200
Cu	-0.22700300	1.10522300	-0.01476700
N	-0.38202800	-3.23990600	-1.07031800
C	0.00071900	-4.51432300	-0.93212800
C	0.93754100	-4.94803500	0.02480700
H	1.13244600	-6.01274800	0.04196500
C	-0.59301000	-5.55903400	-1.85410100
H	-1.68003300	-5.61794600	-1.73892000
H	-0.16817500	-6.54480100	-1.66101100
H	-0.40050700	-5.29174600	-2.89911600
C	-1.45119100	-2.88468000	-1.95960600
C	-2.78459500	-2.95806200	-1.49475500
C	-3.79688600	-2.51586900	-2.35199600
H	-4.83016100	-2.55907300	-2.03167600

C	-3.50557900	-2.01149600	-3.61864000
H	-4.30945800	-1.66729000	-4.26043700
C	-2.18818500	-1.94390800	-4.05646900
H	-1.97057400	-1.54656800	-5.04230900
C	-1.14180800	-2.38476600	-3.23853100
C	-3.10151100	-3.52516400	-0.10670400
H	-2.55355700	-4.47254500	-0.00660300
C	-2.62638100	-2.60537100	1.04416900
H	-1.55933400	-2.74446800	1.24836300
H	-3.15792600	-2.85088800	1.97020000
H	-2.81521200	-1.55271200	0.82006600
C	-4.59213400	-3.85135300	0.07593100
H	-5.19392200	-2.93672200	0.09785600
H	-4.74037400	-4.36591800	1.03087500
H	-4.96839800	-4.50057400	-0.72176000
C	0.30578500	-2.29297700	-3.70491200
H	0.90535700	-2.93591900	-3.05017800
C	0.50402100	-2.79626300	-5.14454400
H	0.09632500	-3.80477200	-5.26975600
H	1.57129400	-2.82216500	-5.38993300
H	0.01424100	-2.14035100	-5.87280200
C	0.82528700	-0.85129100	-3.55566600
H	0.26784200	-0.17518200	-4.21370300
H	1.88966100	-0.78046600	-3.80659400
H	0.69862000	-0.47132200	-2.53299000
N	-1.90640900	2.16523500	0.36280900
C	-1.89700200	3.47824100	0.25556000
C	-0.76368800	4.26942800	-0.00097100
H	-0.91892100	5.33402100	-0.00021100
F	-3.04446700	5.62267300	0.23000500
F	-4.14364600	3.86341800	-0.53482300
F	-3.79013000	4.10295800	1.64764700
C	-3.06416700	1.39399200	0.70531400
C	-3.83161100	0.80994100	-0.31455600
C	-4.93604300	0.03141200	0.04734400
H	-5.54983700	-0.39926600	-0.73923600
C	-5.26356500	-0.20733200	1.38406200
C	-4.43895400	0.33495400	2.37512300
H	-4.66124500	0.13902800	3.42120400
C	-3.33746500	1.13300400	2.06055700
C	-3.44718600	0.99389000	-1.75873000
H	-3.30510400	2.04871200	-2.00740200
H	-4.21080600	0.58179900	-2.42216500
H	-2.50519700	0.47088600	-1.97179000
C	-6.46018200	-1.04828000	1.76137400
H	-7.13014400	-0.50227800	2.43463300
H	-6.15410100	-1.96744400	2.27565000
H	-7.03740300	-1.33735400	0.87760100
C	-2.46465400	1.71258700	3.14400900
H	-1.40514800	1.62949500	2.88029600
H	-2.62753100	1.19587600	4.09396000
H	-2.67698700	2.77559600	3.29491700
N	1.55638600	-2.84921700	1.07555100
C	1.64099500	-4.18401800	0.97217400
C	2.53944500	-4.92961500	1.93745400
H	3.56712600	-4.55559500	1.89499700
H	2.54571600	-5.99966800	1.72709400
H	2.19107500	-4.77721100	2.96541400
C	2.41623300	-2.13981400	1.97923300
C	3.69517000	-1.75249100	1.51829900
C	4.50910000	-1.01765400	2.38369700
H	5.49843300	-0.71177300	2.06630600
C	4.06472600	-0.66010100	3.65698700
H	4.70876000	-0.08027000	4.30932200
C	2.79599700	-1.03328100	4.08565500
H	2.45715800	-0.74202000	5.07440500
C	1.95244900	-1.78629900	3.25924000
C	4.15041100	-2.15851700	0.11452000
H	3.98334500	-3.24021100	0.01994000
C	3.31374300	-1.47460300	-1.00342400
H	2.51762200	-2.13821200	-1.36347600
H	3.93733700	-1.23795500	-1.87118700
H	2.89457800	-0.51852900	-0.66621900
C	5.64966500	-1.92424400	-0.12012800
H	5.88858000	-0.85651400	-0.11556500
H	5.93573200	-2.32412800	-1.09838100
H	6.25947200	-2.42300900	0.64064500
C	0.55986700	-2.19355500	3.72473200
H	0.19884000	-2.97236800	3.04339400
C	0.56098100	-2.78855000	5.14330300
H	1.28047700	-3.60992300	5.22796600
H	-0.43416900	-3.17471300	5.38870300
H	0.81772100	-2.03546400	5.89663500
C	-0.41515300	-1.00438400	3.62994200
H	-0.09882800	-0.19299200	4.29614200
H	-1.43024900	-1.30638000	3.91213200
H	-0.46325100	-0.59719100	2.61347300
N	0.96127400	2.57297100	-0.35508800
C	0.53893400	3.83433500	-0.25437500
C	1.55253000	4.97198800	-0.40727200
F	0.98809800	6.22573000	-0.25570700
F	2.55799500	4.89584200	0.54381800
F	2.17415200	4.99456200	-1.64502800
C	2.31196800	2.24382400	-0.72043000
C	3.25623900	1.98294200	0.28559500
C	4.56635700	1.67467000	-0.09598200
H	5.30833700	1.50489300	0.67955400
C	4.94117700	1.58500800	-1.43852600
C	3.96094600	1.78652300	-2.41577500
H	4.22874400	1.70248300	-3.46627000
C	2.64693400	2.11947200	-2.08204500
C	2.85408900	2.00931900	1.73621700
H	2.32278300	2.92926200	1.99083700
H	3.72816400	1.92274700	2.38480000
H	2.18617000	1.16788800	1.96815800
C	6.36136300	1.26138300	-1.83825000
H	6.74942900	2.00135500	-2.54664100
H	6.42597400	0.27882600	-2.32176700
H	7.02687800	1.24884100	-0.96967300
C	1.61943300	2.37655500	-3.15442400
H	0.64593800	1.95967100	-2.87779600
H	1.93073500	1.93657100	-4.10592500
H	1.47702600	3.45064800	-3.30791800
C	-3.20346000	4.25956500	0.40269800
H	-0.77883900	-0.32344100	0.15190600

3•Mg

wB97XD / 6-31G+(d,p) / SDD (Cu, Mg)

Sum of electronic and zero-point Energies= -4241.245263

Sum of electronic and thermal Energies= -4241.186036

Sum of electronic and thermal Enthalpies= -4241.185092

Sum of electronic and thermal Free Energies= -4241.340520

0 1

Mg	0.27629300	-1.30895100	-0.01968400
Cu	-0.29131100	1.42629400	0.09196100
N	-0.75337600	-2.85791800	-0.79604100
C	-0.35326800	-4.13425500	-0.77754200
C	0.81032300	-4.57858000	-0.12250400
H	0.98648800	-5.64627500	-0.15282700
C	-1.18159300	-5.17380200	-1.50467800
H	-2.20243900	-5.21599200	-1.11239500

H	-0.73343100	-6.16462200	-1.42050200
H	-1.26298300	-4.91350900	-2.56596800
C	-2.01543900	-2.50339400	-1.38380700
C	-3.19096000	-2.59280800	-0.60496100
C	-4.39091100	-2.16795000	-1.18355600
H	-5.31218600	-2.23137700	-0.61764600
C	-4.42935200	-1.65780400	-2.47978700
H	-5.36962500	-1.31862800	-2.90071000
C	-3.26214100	-1.57423800	-3.22931700
H	-3.29906400	-1.16533400	-4.23339000
C	-2.04084700	-2.00160900	-2.69900800
C	-3.14780000	-3.14060800	0.82418200
H	-2.53556300	-4.05279500	0.81384000
C	-2.47932500	-2.15529900	1.81003800
H	-1.38876100	-2.18600600	1.72987000
H	-2.72940600	-2.41932700	2.84386200
H	-2.80871300	-1.12986100	1.62653600
C	-4.53451500	-3.53542600	1.35779200
H	-5.15518700	-2.64913400	1.53474100
H	-4.42432300	-4.05559000	2.31485500
H	-5.06408000	-4.19970300	0.66690500
C	-0.75809500	-1.89139400	-3.51310000
H	-0.00542300	-2.52506300	-3.02939300
C	-0.92064200	-2.40163900	-4.95493700
H	-1.32767500	-3.41823700	-4.97102800
H	0.05042500	-2.40946500	-5.46190600
H	-1.59028400	-1.75900200	-5.53718500
C	-0.23685500	-0.44201100	-3.50400200
H	-0.94844200	0.22867700	-3.99744800
H	0.72577000	-0.36446700	-4.02176900
H	-0.10622700	-0.05287200	-2.48532000
N	-1.85449400	2.56018700	0.67886700
C	-1.82955800	3.89006600	0.62154500
C	-0.71495800	4.62260300	0.17428200
H	-0.82387100	5.69880300	0.21542100
C	-3.00175600	1.87735700	1.11185500
C	-3.96415000	1.40624200	0.20454500
C	-5.07393100	0.67140100	0.59751400
H	-5.78347100	0.33577200	-0.14717100
C	-5.25839500	0.38138800	1.94904800
C	-4.32716900	0.82551000	2.88725500
H	-4.45156200	0.60850400	3.94056100
C	-3.22557100	1.55402900	2.45929600
N	1.74797200	-2.48422900	0.67539800
C	1.76855000	-3.82280100	0.57341200
C	2.88686900	-4.58737100	1.25393900
H	3.86920500	-4.26723900	0.89310500
H	2.78543100	-5.66082700	1.09031700
H	2.86980700	-4.39394100	2.33228400
C	2.85570500	-1.81086900	1.29463800
C	3.98664600	-1.50820100	0.50315300
C	5.05762100	-0.85131500	1.11450000
H	5.94960300	-0.62205100	0.54378700
C	5.00183300	-0.48126400	2.45849200
H	5.84112800	0.03549500	2.91120400
C	3.86804300	-0.75955800	3.21185600
H	3.82437400	-0.44852000	4.25045400
C	2.77802200	-1.43108300	2.64645500
C	4.01265700	-1.91177400	-0.97361900
H	3.77710400	-2.98383200	-1.02496200
C	2.92717600	-1.17147200	-1.80405300
H	2.01960400	-1.77860600	-1.89798500
H	3.27869700	-0.97367500	-2.82175000
H	2.67845100	-0.20083800	-1.35980300
C	5.39257000	-1.73538100	-1.62507700
H	5.66787400	-0.67740100	-1.69119800
H	5.37139600	-2.13725400	-2.64325900
H	6.17326200	-2.26524500	-1.06921400
C	1.52915400	-1.71414900	3.47091300
H	0.90123500	-2.40214900	2.89285400
C	1.85098500	-2.40358600	4.80818800
H	2.42379200	-3.32428700	4.65281500
H	0.92326300	-2.65905600	5.33164900
H	2.43371100	-1.74973000	5.46670500
C	0.72334200	-0.41962800	3.69774600
H	1.30371700	0.29976100	4.28704600
H	-0.20787800	-0.63165400	4.23463000
H	0.46225500	0.06939500	2.75273200
N	0.84356200	2.86749400	-0.48490400
C	0.50552300	4.16437800	-0.32930200
C	1.51418300	5.22581800	-0.72784000
C	2.10348700	2.56010000	-1.03626000
C	3.21990100	2.29999600	-0.22515000
C	4.47067900	1.99153400	-0.74232000
H	5.29495800	1.80356800	-0.06721700
C	4.64211500	1.93092000	-2.12469000
C	3.56110400	2.17415900	-2.97076900
H	3.67688000	2.13509200	-4.04656900
C	2.32417700	2.48309300	-2.42108100
C	-3.05044900	4.67538600	1.05659900
H	-0.82735300	0.03037900	0.47257000
H	-3.27502500	4.48411000	2.11175900
H	-3.92713500	4.37844700	0.47046800
H	-2.89691000	5.74737900	0.92608300
H	1.13939400	6.22275600	-0.49368900
H	2.46170100	5.08244200	-0.19757500
H	1.72361300	5.18471000	-1.80211600
Cl	-2.03461100	2.11770400	3.69405700
Cl	-3.75985700	1.79730100	-1.54301200
Cl	3.02393500	2.40670500	1.56117800
Cl	0.95767300	2.84852900	-3.54210400
H	-6.12316800	-0.18695800	2.26999700
H	5.61456700	1.69907300	-2.54229500

1•Al
wB97XD / 6-31G+(d,p) / SDD (Cu, Al)
Sum of electronic and zero-point Energies= -3041.145409
Sum of electronic and thermal Energies= -3041.084627
Sum of electronic and thermal Enthalpies= -3041.083683
Sum of electronic and thermal Free Energies= -3041.241084

0 1

Cu	-0.12417200	0.60874000	0.19253100
Al	-0.07225800	-1.97833000	0.60386600
H	0.69672900	-0.66256100	-0.19045200
H	-1.09149300	-1.92269100	1.82004400
N	-1.63012400	1.54885600	0.93397900
C	-1.63196800	2.87705100	0.99250900
C	-0.66463100	3.74261200	0.46852100
H	-0.84412300	4.79527100	0.60173600
C	0.48734800	3.39271900	-0.25260300
N	0.92270200	2.16348600	-0.45963400
C	-2.81243800	3.58831200	1.65686300
C	1.26210200	4.57245200	-0.83816800
C	-2.77165300	0.75029200	1.28982200
C	-2.83739000	0.13458000	2.54920300
C	-3.93430900	-0.68456800	2.82951900
H	-3.99455300	-1.16226600	3.80375400
C	-4.94795500	-0.90574500	1.89359800
C	-4.83507400	-0.30366200	0.63753500
H	-5.60278600	-0.47997300	-0.11158100
C	-3.74978400	0.51038900	0.30841700

C	2.10886000	1.82913200	-1.18754500
C	3.32723600	1.71272600	-0.49614900
C	4.45812400	1.31257900	-1.21039900
H	5.40815900	1.23984200	-0.68705900
C	4.39735000	0.98718900	-2.56886700
C	3.15988000	1.06117100	-3.21311700
H	3.08760500	0.79379400	-4.26423100
C	2.00608400	1.48193700	-2.54493300
N	1.50429000	-2.97399600	1.02408700
C	1.65127700	-4.27084000	0.70978300
C	0.77850400	-4.95740900	-0.15013800
H	0.98195400	-6.00806000	-0.30660500
C	-0.22923600	-4.38877900	-0.94673600
N	-0.63678400	-3.11710900	-0.81775700
C	2.84680200	-5.01822100	1.25101400
H	3.76858600	-4.66017000	0.77963600
H	2.75447100	-6.08821700	1.06068100
H	2.95644800	-4.85389100	2.32689900
C	-0.84609400	-5.24137100	-2.02985400
H	-1.93533300	-5.27464600	-1.93158200
H	-0.45609000	-6.25905700	-1.99463500
H	-0.63090900	-4.81840200	-3.01698900
C	2.58053300	-2.26346700	1.66832200
C	2.54992300	-2.04498900	3.05491700
C	3.60362800	-1.33256400	3.63757800
H	3.58928900	-1.15829100	4.70999900
C	4.67227100	-0.84922000	2.87844100
C	4.67258200	-1.08606200	1.50067200
H	5.49062700	-0.70822500	0.89412900
C	3.63137700	-1.77172500	0.87248300
C	1.41755800	-2.57764500	3.89961800
H	1.62229900	-2.42261800	4.96212700
H	1.26125500	-3.64932400	3.73368800
H	0.46937200	-2.08239300	3.66189200
C	5.78052400	-0.05097700	3.52070200
H	6.73828500	-0.22326200	3.01991100
H	5.89851000	-0.30679300	4.57780100
H	5.56764400	1.02395700	3.46361500
C	3.61473000	-1.94265400	-0.62623500
H	4.58653300	-1.69098000	-1.05693400
H	2.87872200	-1.26450600	-1.07564900
H	3.35197500	-2.96082300	-0.93044200
C	-1.56115100	-2.54468600	-1.76371900
C	-1.05188100	-1.90939200	-2.91011200
C	-1.95624000	-1.31834300	-3.79677500
H	-1.57343000	-0.81966900	-4.68312400
C	-3.33583900	-1.35591500	-3.57021300
C	-3.80772900	-2.00569300	-2.42678600
H	-4.87675000	-2.04161100	-2.23650800
C	-2.93986200	-2.59584400	-1.50389600
C	0.43319100	-1.87162100	-3.17343500
H	0.88102800	-2.87080400	-3.13550400
H	0.95257300	-1.26070000	-2.42639400
H	0.64235400	-1.44046700	-4.15570900
C	-4.29026800	-0.66923300	-4.51617600
H	-4.41410800	0.38611500	-4.24240900
H	-5.27985900	-1.13511500	-4.49226500
H	-3.92364200	-0.70034600	-5.54676700
C	-3.46561400	-3.26611000	-0.25917300
H	-3.11456400	-4.30072200	-0.17292100
H	-4.55853100	-3.27327400	-0.25840900
H	-3.13851600	-2.73508800	0.64178000
C	-1.74764500	0.34638800	3.56599200
H	-0.76066100	0.20461600	3.11014000
H	-1.77471200	1.36198600	3.97221800
H	-1.84738000	-0.36065800	4.39419600
C	-3.60568400	1.09230500	-1.07418600
H	-3.54380200	2.18346300	-1.05234500
H	-2.69360200	0.71829000	-1.55699500
H	-4.45556000	0.81030300	-1.70107000
C	-6.10694100	-1.81956200	2.21271000
H	-5.85108700	-2.86721900	2.00696200
H	-6.38716000	-1.75254000	3.26863300
H	-6.98777800	-1.56984400	1.61294700
C	0.67757800	1.55527700	-3.25320300
H	-0.08414000	0.96106200	-2.73293100
H	0.30851600	2.58419400	-3.29596700
H	0.76167200	1.17995800	-4.27714500
C	3.38904200	1.96741500	0.98740500
H	3.04783400	2.97416500	1.23987400
H	2.75060600	1.25515200	1.52530400
H	4.41018300	1.84786600	1.35828200
C	5.64109800	0.56862600	-3.31637200
H	6.23598900	1.44160400	-3.61134800
H	6.28201500	-0.06983000	-2.69830200
H	5.39148300	0.01623700	-4.22745000
F	-2.61492100	4.95173100	1.78765200
F	-3.99377100	3.44507500	0.94656800
F	-3.05540600	3.12213900	2.93690600
F	0.66970300	5.79419100	-0.57844700
F	2.55298500	4.66422200	-0.34374100
F	1.37011100	4.48622300	-2.21737300

1•Al'

wB97XD / 6-31G+(d,p) / SDD (Cu, Al)

Sum of electronic and zero-point Energies= -3022.624627

Sum of electronic and thermal Energies= -3022.563632

Sum of electronic and thermal Enthalpies= -3022.562688

Sum of electronic and thermal Free Energies= -3022.720489

0 1

Cu	-0.93884200	0.06941500	0.15075600
Al	1.72933400	-1.49984100	-0.64287000
H	0.28666000	-0.95017200	0.04180700
H	2.24861800	-2.91512700	-0.08511200
N	-1.28431200	2.00064800	0.13003700
C	-2.47005200	2.44849000	0.52482100
C	-3.54527500	1.67900600	0.99368900
H	-4.38506600	2.22878700	1.38144900
C	-3.70417000	0.28930000	0.91598700
N	-2.81024700	-0.58366000	0.47259300
C	-2.76764700	3.94872600	0.45516500
C	-5.08111800	-0.21034600	1.35824500
C	-0.26987700	2.87049400	-0.40215800
C	-0.19177400	3.05584400	-1.79462500
C	0.78139500	3.91688900	-2.30299300
H	0.82537100	4.08369100	-3.37658800
C	1.69358300	4.57139200	-1.46906600
C	1.63010900	4.31991900	-0.09782900
H	2.34228000	4.80161600	0.56800000
C	0.66738600	3.46877400	0.45433500
C	-3.16444900	-1.91606300	0.07386700
C	-2.85779100	-3.01241500	0.89977700
C	-3.12708700	-4.30022100	0.43198900
H	-2.89730900	-5.14705100	1.07347200
C	-3.67298300	-4.52764100	-0.83589600
C	-3.93987400	-3.42296600	-1.64632100
H	-4.34932300	-3.57720800	-2.64140200
C	-3.69748300	-2.11470000	-1.21425600
N	3.01025500	-0.35001300	0.32815500
C	3.31577800	0.89110800	-0.06179300
C	2.99599800	1.37391200	-1.34305100

H	3.17935100	2.42057000	-1.53031000
C	2.60781100	0.59496200	-2.43279600
N	2.26801700	-0.70394000	-2.32288300
C	4.10639400	1.79672800	0.85205600
H	5.09955100	1.37763600	1.04562200
H	3.60934400	1.89909000	1.82120200
H	4.21934300	2.78706400	0.40910900
C	2.60595200	1.24727600	-3.79599400
H	2.88082900	2.29908200	-3.71612500
H	1.60958200	1.19273900	-4.25099100
H	3.30994600	0.75435600	-4.47585100
C	2.12290700	-1.52671800	-3.53038800
H	3.09225400	-1.68913300	-4.01889800
H	1.46739300	-1.04721600	-4.26880000
C	1.53247300	-2.87326300	-3.10887400
H	1.12052900	-3.41213000	-3.97410200
H	2.30279600	-3.50070500	-2.64685000
N	0.49203500	-2.62581300	-2.08370800
C	-0.62888700	-1.82816500	-2.62354600
H	-1.37272400	-1.70838300	-1.83870400
H	-1.09959700	-2.33340200	-3.47925600
H	-0.28086600	-0.83912400	-2.92567000
C	-0.01605400	-3.87932300	-1.48500800
H	0.82100600	-4.45204800	-1.08215700
H	-0.56171900	-4.47789000	-2.22725300
H	-0.69664600	-3.62982100	-0.66841700
C	3.70006700	-0.92145600	1.45927300
C	4.87639000	-1.65845700	1.20828800
C	5.54643800	-2.23501600	2.29166800
H	6.45653700	-2.80029800	2.11560000
C	5.06222600	-2.09971000	3.58956900
H	5.59022900	-2.55797600	4.41892900
C	3.89363000	-1.38049600	3.81874900
H	3.51309000	-1.28741500	4.83063800
C	3.19732300	-0.77779100	2.76503200
C	5.42582100	-1.83995400	-0.20220800
H	4.72315600	-1.37357700	-0.89985300
C	6.78465500	-1.13436000	-0.36929500
H	7.53267300	-1.55197900	0.31481800
H	6.69953700	-0.06204300	-0.16279300
H	7.15677800	-1.25650500	-1.39291000
C	5.52182900	-3.32982400	-0.57850000
H	6.24818200	-3.85623400	0.05163900
H	5.84379500	-3.43839100	-1.62111700
H	4.54840800	-3.81545300	-0.45802200
C	1.89837000	-0.03440500	3.03573700
H	1.63381600	0.51898200	2.12735000
C	0.76470100	-1.03968000	3.29900200
H	0.92887000	-1.57633900	4.24127200
H	0.71922400	-1.77665700	2.49232400
H	-0.20230400	-0.52574500	3.35617400
C	2.01669000	0.96936000	4.19429600
H	1.08069500	1.52612300	4.30891000
H	2.82555300	1.68849700	4.02398800
H	2.21438100	0.46201000	5.14499300
C	0.63000500	3.22539400	1.93960700
H	0.03177900	3.98612300	2.45052900
H	0.18150000	2.25337000	2.16238100
H	1.63800200	3.24966600	2.36369200
C	-1.14373500	2.33565500	-2.71357300
H	-1.08646000	1.25163500	-2.55405200
H	-2.18152400	2.63057900	-2.52995400
H	-0.91115100	2.54605500	-3.76163700
C	2.75734500	5.47575100	-2.04565800
H	3.65650400	4.90795700	-2.32166800
H	2.40119500	5.98389500	-2.94715100
H	3.06246200	6.24036300	-1.32497500
C	-2.22388700	-2.79439200	2.24479400
H	-2.02289100	-3.74556800	2.74486900
H	-1.27926700	-2.25659000	2.12970200
H	-2.86330900	-2.18962200	2.89336500
C	-3.97029700	-0.94578100	-2.12941600
H	-4.89859300	-0.43622000	-1.85438100
H	-3.16902700	-0.19981000	-2.07185800
H	-4.06384000	-1.27968900	-3.16692600
C	-3.97127400	-5.93178100	-1.30481800
H	-3.17033900	-6.62447700	-1.02518400
H	-4.89879000	-6.30661300	-0.85559500
H	-4.09167000	-5.97257300	-2.39170800
F	-1.89673500	4.71350500	1.21250400
F	-2.69522600	4.42604100	-0.84491000
F	-4.03370400	4.27522100	0.90586500
F	-4.98913400	-1.27101300	2.24314700
F	-5.86782200	-0.64234800	0.30080700
F	-5.82330200	0.75851900	2.00960400

5.3 Chapter 4

1•Au
wB97X / 6-311G* / SDDAll (Cu, Au)
Sum of electronic and zero-point Energies= -3091.708846
Sum of electronic and thermal Energies= -3091.642720
Sum of electronic and thermal Enthalpies= -3091.641775
Sum of electronic and thermal Free Energies= -3091.817204

0 1

Au	-1.07081800	-0.15250800	-0.56291800
H	0.27346600	-0.16935300	-1.58745400
Cu	1.59101300	0.27963200	-0.72214200
N	3.06127500	-1.11438400	-0.67057800
C	4.31128500	-0.73718900	-0.63020500
C	4.77965700	0.58866200	-0.56297000
H	5.84621800	0.71853900	-0.62531900
C	4.02623200	1.75088400	-0.35034600
N	2.71767100	1.84005300	-0.25902200
C	5.42401700	-1.80347200	-0.64187300
C	4.87531500	3.03243100	-0.22266200
F	5.39299100	-2.55550600	0.47364000
F	5.30940400	-2.63673100	-1.68993300
F	6.65799200	-1.27891700	-0.71181300
F	6.17542900	2.83072600	-0.49128900
F	4.45856900	3.98231800	-1.07799700
F	4.82406000	3.55905800	1.01397900
C	2.64624100	-2.47735400	-0.62914600
C	2.40255500	-3.08200000	0.60996000
C	1.94696100	-4.39800900	0.63243500
H	1.77993300	-4.87573100	1.59689400
C	1.69828900	-5.11166400	-0.53407800
C	1.88877200	-4.46197500	-1.75050700
H	1.67155400	-4.99112000	-2.67732500
C	2.35317100	-3.15266700	-1.82188000
C	2.58929500	-2.31050900	1.88905500
H	1.89497300	-1.46234800	1.93236600
H	3.59949600	-1.90631500	1.98055800
H	2.39670400	-2.94377900	2.75823400
C	1.23796700	-6.54644500	-0.48778400
H	0.51807700	-6.76399200	-1.28237900
H	0.76438600	-6.78624000	0.46922600
H	2.07850100	-7.23657700	-0.61402500
C	2.52395200	-2.46337700	-3.14753300
H	3.56703000	-2.19190800	-3.32581700

H	1.94144900	-1.53688300	-3.18121700
H	2.19517500	-3.10504600	-3.96835200
C	2.05308500	3.02865600	0.17057300
C	1.46705900	3.88434400	-0.77412000
C	0.79001000	5.01082600	-0.32259900
H	0.35391700	5.68785800	-1.05645900
C	0.65150100	5.29729600	1.03381600
C	1.19813400	4.40482500	1.94714700
H	1.09053700	4.59853400	3.01370900
C	1.89621200	3.26801400	1.54116500
C	1.56065200	3.57614100	-2.24287300
H	1.09499700	2.60970700	-2.46571000
H	2.59915800	3.51478500	-2.57494900
H	1.05667100	4.34226600	-2.83684300
C	-0.10440900	6.51984400	1.48656300
H	-1.18205000	6.40620800	1.31977200
H	0.21499900	7.41226900	0.94092800
H	0.04473700	6.71127500	2.55216700
C	2.47545600	2.32224700	2.55977700
H	3.56020200	2.43055400	2.63214700
H	2.27845200	1.28019100	2.29045800
H	2.05407300	2.50958000	3.55050800
C	-2.88808600	-0.31251500	0.40580600
N	-4.05644800	0.26858000	0.05553900
C	-5.08347600	-0.13106900	0.89119900
H	-6.09131900	0.23200700	0.76606200
C	-4.54050900	-0.98400000	1.78563900
H	-4.97126400	-1.52866800	2.61087300
N	-3.19709000	-1.08148300	1.47163900
C	-4.21446200	1.17627600	-1.05179300
C	-4.06106000	2.54632600	-0.81262700
C	-4.20335400	3.40281200	-1.90219700
H	-4.08000100	4.47273500	-1.76240600
C	-4.48700800	2.90806400	-3.16633100
H	-4.58874300	3.59241200	-4.00350100
C	-4.63530900	1.54429100	-3.36896900
H	-4.85004900	1.17251400	-4.36686100
C	-4.50219100	0.64427000	-2.31379900
C	-3.70249900	3.09774300	0.55778300
H	-3.79810000	2.28965300	1.29028300
C	-2.24670900	3.57129200	0.58006900
H	-2.08976000	4.39921500	-0.11868800
H	-1.54904800	2.77579900	0.29973100
H	-1.96549100	3.92323900	1.57752700
C	-4.65243900	4.21586800	0.99440200
H	-5.69734700	3.89257700	0.97198500
H	-4.56342800	5.09829500	0.35352700
H	-4.41842800	4.53313400	2.01475100
C	-4.64079400	-0.84961400	-2.56202500
H	-4.58616100	-1.36568100	-1.59820600
C	-5.99661900	-1.19487400	-3.18389500
H	-6.10795100	-0.75758800	-4.18071000
H	-6.82561700	-0.83284600	-2.56880800
H	-6.10248500	-2.27851000	-3.28966600
C	-3.48623300	-1.37087700	-3.42339500
H	-2.51603900	-1.15820600	-2.96400200
H	-3.49242000	-0.91110100	-4.41687600
H	-3.56629300	-2.45420900	-3.55765100
C	-2.26017300	-1.92026000	2.17458900
C	-2.07045600	-3.22959300	1.71935000
C	-1.16293500	-4.02103000	2.41984800
H	-0.97538200	-5.03896100	2.08988100
C	-0.48272200	-3.52249200	3.51991300
H	0.22301300	-4.15538500	4.05080900
C	-0.68827400	-2.21692900	3.94104300
H	-0.13378500	-1.83770700	4.79457100
C	-1.58390000	-1.38293800	3.27569900
C	-2.78295000	-3.78507200	0.49642900
H	-3.49283100	-3.03235100	0.13875300
C	-3.58949200	-5.04130900	0.83646900
H	-4.31063200	-4.85404300	1.63770200
H	-2.94089400	-5.86168900	1.15860600
H	-4.14226600	-5.38853500	-0.04146600
C	-1.78908100	-4.05462500	-0.63760100
H	-1.07591000	-4.83793200	-0.36499500
H	-1.20553700	-3.16300000	-0.88703600
H	-2.31755400	-4.38131900	-1.53930600
C	-1.75913800	0.06350700	3.71086500
H	-2.61680800	0.48356900	3.17549200
C	-0.52655500	0.88581700	3.32290000
H	-0.32674100	0.83381900	2.24760200
H	0.36500100	0.52207200	3.84380800
H	-0.66022100	1.94069300	3.58431900
C	-2.05704300	0.18604500	5.20705000
H	-1.21162100	-0.14238100	5.81888600
H	-2.92786300	-0.40968600	5.49575400
H	-2.25896000	1.22879900	5.46847300

2•Au
wB97X / 6-311G* / SDDAll (Cu, Au)
Sum of electronic and zero-point Energies=
-3252.917921
Sum of electronic and thermal Energies=
-3252.856412
Sum of electronic and thermal Enthalpies=
-3252.855468
Sum of electronic and thermal Free Energies=
-3253.019930

0 1

Au	0.00026000	-0.65995600	-0.65912900
Cu	-0.00029500	1.98568300	-0.90180200
H	0.00043600	0.59720800	-1.79106900
N	1.48500600	3.25719200	-0.49167100
C	1.27236600	4.54705200	-0.27271700
C	-0.00057800	5.13957300	-0.22759100
H	-0.00069700	6.21298300	-0.07980100
C	-1.27338000	4.54676300	-0.27265100
N	-1.48576400	3.25683500	-0.49153400
C	2.44660500	5.47833600	-0.06020900
H	2.83074200	5.37797000	0.95855800
H	2.15213000	6.51735100	-0.20545500
H	3.26479300	5.25242300	-0.74854500
C	-2.44781700	5.47780300	-0.06015100
H	-3.26596800	5.25169400	-0.74846800
H	-2.15356300	6.51687400	-0.20544200
H	-2.83191800	5.37739700	0.95862400
C	2.77280900	2.72556500	-0.38560500
C	3.45077500	2.64189300	0.83108500
F	2.89371700	3.15172600	1.93870900
C	4.67766100	2.01379100	0.95004200
F	5.27220100	1.91242300	2.14619100
C	5.27258700	1.44518500	-0.16084900
F	6.45470100	0.82835300	-0.04613200
C	4.62085800	1.49248000	-1.38134400
F	5.17951800	0.92067900	-2.45034500
C	3.39634400	2.13111900	-1.48576100
F	2.79689200	2.15706900	-2.67752500
C	-2.77347200	2.72498100	-0.38539600
C	-3.39694600	2.13037100	-1.48549900
F	-2.79752500	2.15632300	-2.67727800
C	-4.62136500	1.49156100	-1.38101000
F	-5.17995500	0.91957100	-2.44994800
C	-5.27306300	1.44426500	-0.16049900
F	-6.45506300	0.82722900	-0.04569800
C	-4.67819400	2.01303000	0.95033900

F	-5.27268200	1.91163500	2.14651000
C	-3.45139200	2.64128300	0.83131600
F	-2.89437100	3.15123600	1.93890200
C	0.00026600	-2.38081200	0.47909800
N	-1.06852800	-3.08369400	0.91066400
C	-0.67509800	-4.21263300	1.60545700
H	-1.39221000	-4.89799700	2.02891600
C	0.67569600	-4.21250300	1.60562900
H	1.39283200	-4.89773100	2.02926700
N	1.06908600	-3.08349000	0.91093400
C	-2.43613500	-2.69864500	0.67090400
C	-3.05226600	-3.13433000	-0.50739000
C	-4.36648400	-2.72744900	-0.72635500
H	-4.87919800	-3.03350100	-1.63374300
C	-5.02655000	-1.92166300	0.18856900
H	-6.04434200	-1.60192100	-0.00846000
C	-4.38515400	-1.50245100	1.34570400
H	-4.91226800	-0.85692600	2.04373500
C	-3.07259500	-1.88494200	1.61558700
C	-2.33442700	-3.98459600	-1.54360700
H	-1.35421000	-4.26289900	-1.14331500
C	-2.09313500	-3.18675600	-2.82910100
H	-3.03768200	-2.89905400	-3.30149000
H	-1.52757100	-3.78360500	-3.55171400
H	-1.52969200	-2.26963700	-2.63136500
C	-3.09110700	-5.28409900	-1.83115100
H	-3.25914500	-5.86250200	-0.91800700
H	-2.52452400	-5.90900100	-2.52776300
H	-4.06744300	-5.09159300	-2.28589500
C	-2.37388100	-1.39819900	2.87556400
H	-1.38610500	-1.86718900	2.92484600
C	-3.13726200	-1.81247100	4.13640300
H	-4.12478300	-1.34351300	4.18057900
H	-2.58944200	-1.50532700	5.03207800
H	-3.28171200	-2.89598600	4.18289600
C	-2.15719900	0.11722800	2.83519800
H	-1.62156500	0.42501100	1.93095300
H	-1.57129000	0.44519800	3.69927100
H	-3.10912900	0.65502500	2.86585700
C	2.43668100	-2.69819900	0.67149100
C	3.07271100	-1.88419600	1.61620200
C	4.38527000	-1.50148700	1.34661900
H	4.91205000	-0.85571900	2.04467600
C	5.02708000	-1.92079100	0.18975000
H	6.04486300	-1.60088200	-0.00704900
C	4.36743100	-2.72687200	-0.72521800
H	4.88046300	-3.03298600	-1.63240600
C	3.05323100	-3.13397100	-0.50655300
C	2.37356800	-1.39738700	2.87591400
H	1.38580100	-1.86642600	2.92492400
C	3.13658600	-1.81151900	4.13701900
H	3.28106200	-2.89502500	4.18365000
H	2.58848800	-1.50431800	5.03250500
H	4.12407800	-1.34252200	4.18144200
C	2.15682000	0.11802400	2.83535500
H	3.10871100	0.65588000	2.86619600
H	1.57067600	0.44604600	3.69924900
H	1.62139300	0.42568900	1.93094900
C	2.33582900	-3.98452100	-1.54284000
H	1.35562000	-4.26308100	-1.14270600
C	2.09454000	-3.18682200	-2.82842300
H	1.53077600	-2.26986600	-2.63084500
H	1.52930400	-3.78388200	-3.55112000
H	3.03909400	-2.89885100	-3.30063600
C	3.09292200	-5.28382800	-1.83017600
H	4.06926500	-5.09108600	-2.28480600
H	2.52661200	-5.90894600	-2.52681500
H	3.26100000	-5.86211200	-0.91696400

4•Au
wB97X / 6-311G* / SDDAll (Cu, Au)
Sum of electronic and zero-point Energies= -3798.796066
Sum of electronic and thermal Energies= -3798.721942
Sum of electronic and thermal Enthalpies= -3798.720998
Sum of electronic and thermal Free Energies= -3798.914584

0 1

Cu	-1.32942300	0.05059200	-0.08307100
P	-2.60774000	1.87170900	-0.60700100
O	-0.84598700	0.27753200	1.97040700
C	-1.32616200	-0.47115000	2.85362600
C	-2.06988300	-1.63369200	2.75103200
H	-2.35454600	-2.12006800	3.66988800
C	-2.44705000	-2.26382500	1.53233400
N	-2.22464700	-1.80825300	0.34089100
C	-1.00615400	0.01664800	4.27755600
F	-1.55946700	1.22896800	4.49822600
F	0.32573900	0.16202200	4.44261400
F	-1.43296400	-0.79100700	5.25994500
C	-3.17954600	-3.61001800	1.71435900
F	-4.43100200	-3.56787500	1.23129200
F	-3.28078700	-3.97830900	3.00201600
F	-2.53639200	-4.60996300	1.08592700
C	-2.65183200	-2.47745800	-0.84912300
C	-3.91632900	-2.21561900	-1.38485100
C	-4.25084600	-2.78348700	-2.61649700
H	-5.23642400	-2.57511600	-3.03114500
C	-3.37011900	-3.58902300	-3.32193100
C	-2.11308600	-3.82496700	-2.76483900
H	-1.40260200	-4.45134500	-3.30239500
C	-1.73291800	-3.28475900	-1.54406200
C	-4.92226400	-1.33724800	-0.68568800
H	-4.46814500	-0.72253000	0.09328700
H	-5.69953000	-1.94088100	-0.20945300
H	-5.41258300	-0.66873200	-1.39955200
C	-3.75132800	-4.20567900	-4.64332100
H	-3.87554200	-5.28950800	-4.55254400
H	-2.98395200	-4.02988500	-5.40305900
H	-4.69325400	-3.79762300	-5.01843200
C	-0.36937200	-3.56764800	-0.97539200
H	0.16906200	-2.64163600	-0.75118300
H	0.23562200	-4.14732600	-1.67672200
H	-0.43669400	-4.13366400	-0.04224700
C	-3.99277000	2.14261400	0.56294400
C	-3.67459400	2.09599000	1.92518200
H	-2.64499000	1.93453700	2.23445200
C	-4.66584400	2.24087000	2.88502300
H	-4.40008200	2.19860800	3.93717100
C	-5.99047100	2.42004500	2.49732100
H	-6.76890000	2.52291900	3.24789400
C	-6.31528100	2.45615200	1.14775800
H	-7.34855100	2.58756600	0.83937500
C	-5.32164100	2.32047500	0.18219500
H	-5.59103500	2.34267700	-0.86956900
C	-3.35892000	1.93925000	-2.27718700
C	-3.36311600	0.77879900	-3.04996200
H	-2.91299800	-0.13144500	-2.66359600
C	-3.93452600	0.77848200	-4.31897200
H	-3.93281900	-0.13628100	-4.90498900
C	-4.49299500	1.94249100	-4.82900800
H	-4.93519100	1.94562500	-5.82133700
C	-4.47565800	3.11147300	-4.07199900

H	-4.90069500	4.02683300	-4.47369300
C	-3.91021000	3.11099900	-2.80477400
H	-3.88799700	4.02973400	-2.22366700
C	-1.68036500	3.45714100	-0.55028300
C	-2.10286400	4.58162700	0.15641100
H	-3.02527500	4.55162700	0.72873400
C	-1.34117900	5.74735800	0.14136700
H	-1.67908100	6.61616700	0.69918600
C	-0.15942400	5.80085500	-0.58517600
H	0.43227100	6.71248800	-0.59749500
C	0.26771300	4.68195300	-1.29421300
H	1.19902100	4.71016300	-1.85233400
C	-0.48265200	3.51605500	-1.27050900
H	-0.13235800	2.63836000	-1.80793300
C	3.23977900	-0.10620200	0.13897300
N	3.99679600	0.91911200	0.59178600
C	5.16059800	0.45282000	1.18197300
H	5.89212600	1.12694700	1.59878300
C	5.13342400	-0.89137000	1.08573800
H	5.82845300	-1.64871500	1.41219100
N	3.95045600	-1.21567900	0.44449100
C	3.76804200	2.32441700	0.34545100
C	2.91793000	3.04865400	1.19193000
C	2.83455500	4.42270900	0.97284700
H	2.18389100	5.02387600	1.59769300
C	3.54660800	5.03508700	-0.04679700
H	3.46509000	6.10917500	-0.19119200
C	4.33897400	4.28288600	-0.89901700
H	4.86633000	4.77314800	-1.71154800
C	4.46512600	2.90621700	-0.72308100
C	2.11840000	2.38492500	2.30452500
H	1.81104400	1.39237400	1.95832300
C	0.83134100	3.14047400	2.63597900
H	0.24023100	3.34351700	1.73796300
H	0.21663100	2.53775700	3.30475100
H	1.03133200	4.09184100	3.14128900
C	2.97445700	2.20653500	3.56379000
H	3.86294800	1.59498200	3.37730800
H	3.30957400	3.17675000	3.94682700
H	2.39101000	1.71568700	4.34702100
C	5.27127000	2.07651000	-1.71289100
H	5.55040700	1.13441100	-1.23115900
C	6.57366700	2.75227900	-2.14582600
H	7.17698100	3.05786500	-1.28630700
H	7.17105200	2.06271100	-2.74914600
H	6.39299500	3.63892800	-2.76063900
C	4.40482400	1.73126000	-2.93038300
H	3.49159900	1.20264800	-2.64008000
H	4.10755100	2.63937300	-3.46517900
H	4.95770300	1.09598400	-3.63092800
C	3.57431000	-2.56435200	0.10150000
C	3.82011100	-3.01596100	-1.20178600
C	3.47256600	-4.33219700	-1.49818100
H	3.64431700	-4.71764800	-2.49940900
C	2.90700900	-5.15688700	-0.53764500
H	2.63940000	-6.17869600	-0.79079600
C	2.67155300	-4.67862600	0.74150400
H	2.21227700	-5.32956400	1.47984300
C	3.00056400	-3.37026700	1.09090300
C	4.42784900	-2.13688500	-2.28366700
H	4.64336800	-1.15471800	-1.85267500
C	5.75387100	-2.71038100	-2.79112100
H	6.20447900	-2.03717400	-3.52700800
H	6.47023400	-2.84774700	-1.97579800
C	3.43879700	-1.92066500	-3.43274700
H	3.86171000	-1.24369700	-4.18166400
H	3.19898300	-2.86274600	-3.93614000
H	2.50103600	-1.48555300	-3.07366200
C	1.17172900	-2.72906500	2.66960400
H	0.73516900	-2.06303200	1.92008300
H	0.67301200	-3.70077800	2.58494900
H	0.93991200	-2.32101500	3.65708900
C	3.31281100	-3.72732700	3.57454000
H	4.39575000	-3.81972500	3.44640300
H	3.12479900	-3.29297500	4.56046300
H	2.89205400	-4.73745700	3.57882300
C	2.68526500	-2.85514500	2.48463800
H	3.10564600	-1.85028300	2.58902900
Au	1.34659000	-0.05579500	-0.68955900
H	5.61460400	-3.68111900	-3.27693000
H	-0.16663600	-0.05749600	-1.42206100

2
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -1957.031678
Sum of electronic and thermal Energies= -1957.004278
Sum of electronic and thermal Enthalpies= -1957.003334
Sum of electronic and thermal Free Energies= -1957.091930

0 1

Cu	0.00000000	0.43937200	-0.19574100
N	1.58477300	-0.35880800	0.46979700
C	1.29994300	-1.30830500	1.36185800
C	0.00000000	-1.70077000	1.75037900
H	0.00000000	-2.47740300	2.50510900
C	-1.29994300	-1.30830500	1.36185800
N	-1.58477300	-0.35880800	0.46979700
C	2.43691200	-2.03730400	2.04190400
H	2.87848000	-2.76827800	1.35972500
H	2.09031300	-2.56867500	2.92673300
H	3.22634900	-1.34494700	2.34404900
C	-2.43691200	-2.03730400	2.04190300
H	-3.22634800	-1.34494700	2.34404900
H	-2.09031300	-2.56867600	2.92673200
H	-2.87848000	-2.76827700	1.35972400
C	2.91085400	-0.07177900	0.11033900
C	3.70305900	-0.95699900	-0.61813600
F	3.22607400	-2.16590700	-0.93577000
C	4.98176500	-0.62401100	-1.03322400
F	5.71420200	-1.49878300	-1.72096900
C	5.49667700	0.62825700	-0.74016300
F	6.72308400	0.95777300	-1.13852600
C	4.72629700	1.53673000	-0.03201400
F	5.21464800	2.74359300	0.24925400
C	3.45374400	1.18270700	0.38434100
F	2.72724000	2.08197900	1.05334800
C	-2.91085400	-0.07177900	0.11033900
C	-3.45374400	1.18270600	0.38434100
F	-2.72724100	2.08197800	1.05334900
C	-4.72629700	1.53672900	-0.03201300
F	-5.21464900	2.74359200	0.24925600
C	-5.49667700	0.62825700	-0.74016300
F	-6.72308400	0.95777300	-1.13852600
C	-4.98176500	-0.62401100	-1.03322500
F	-5.71420100	-1.49878300	-1.72097000
C	-3.70305900	-0.95699900	-0.61813700
F	-3.22607400	-2.16590600	-0.93577100

2•tol
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2228.478243

Sum of electronic and thermal Energies= -2228.443158
Sum of electronic and thermal Enthalpies= -2228.442214
Sum of electronic and thermal Free Energies= -2228.547894

0 1

Cu	0.08038500	-0.08594500	-0.24741100
N	1.62239000	-1.06633500	0.53218700
C	1.45278300	-2.16340800	1.25709300
C	0.19969300	-2.70473900	1.58825900
H	0.23511900	-3.59788500	2.19956400
C	-1.09213800	-2.25555300	1.27091800
N	-1.35102100	-1.18316600	0.53409900
C	2.66525600	-2.89690400	1.78455300
H	2.38148100	-3.67814300	2.48832700
H	3.35053100	-2.21093700	2.28971100
H	3.21223900	-3.36492000	0.96129800
C	-2.24287400	-3.06357800	1.82647100
H	-2.77823000	-3.56729300	1.01692700
H	-2.95830400	-2.42075300	2.34636500
H	-1.89378400	-3.82278900	2.52491000
C	2.91378200	-0.60646200	0.24125800
C	3.72310500	-1.20611700	-0.72288100
F	3.30956900	-2.32777100	-1.32439700
C	4.94697600	-0.67283200	-1.09313400
F	5.69117900	-1.27557000	-2.02002500
C	5.39612700	0.49740300	-0.50243600
F	6.56839200	1.02142100	-0.85671100
C	4.61412900	1.11991000	0.45705900
F	5.03339000	2.25089300	1.02616100
C	3.39975400	0.56370000	0.82415200
F	2.66971200	1.19282800	1.75214200
C	-2.67656900	-0.80302600	0.28063300
C	-3.20541500	0.34498800	0.86770200
F	-2.47886500	1.02557200	1.75964900
C	-4.45222500	0.83875300	0.52294000
F	-4.90423800	1.96639700	1.07728900
C	-5.22499100	0.17080900	-0.41234600
F	-6.42909000	0.63496600	-0.74471900
C	-4.73406500	-0.98345100	-1.00285900
F	-5.47184200	-1.63219300	-1.90428700
C	-3.47748600	-1.45234200	-0.65740700
F	-3.02151400	-2.55580000	-1.26208900
C	-0.69916000	4.29267200	1.09393600
H	-1.33180400	3.93582400	1.91194700
H	-1.15361200	5.20811100	0.70439700
H	0.27671800	4.54890800	1.51071100
C	-0.58773400	3.24302000	0.02245200
C	-1.74247400	2.84103000	-0.68177000
H	-2.69320100	3.31656500	-0.45094600
C	-1.68646800	1.84883600	-1.63083400
H	-2.58429500	1.54797700	-2.16391700
C	-0.45991500	1.21355800	-1.92442200
H	-0.40091000	0.51317600	-2.75307300
C	0.71287200	1.64735300	-1.28040700
H	1.68954300	1.32381200	-1.63227000
C	0.62233200	2.65691400	-0.29358300
H	1.52573700	2.97739500	0.21776400

2•CO_2
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2145.624310
Sum of electronic and thermal Energies= -2145.592750
Sum of electronic and thermal Enthalpies= -2145.591806
Sum of electronic and thermal Free Energies= -2145.691551

0 1

Cu	-0.05880100	-0.25734700	0.05633200
N	1.47063900	0.80069400	-0.51843900
C	1.19308600	1.86432100	-1.26763000
C	-0.10784300	2.29447700	-1.59195700
H	-0.13227700	3.16831200	-2.23177100
C	-1.38331700	1.81576000	-1.23399200
N	-1.60835900	0.73675800	-0.48921000
C	2.31991500	2.68654200	-1.85300100
H	2.69768100	3.39501400	-1.11200700
H	1.97810800	3.25457400	-2.71729700
H	3.15498400	2.05562800	-2.16640900
C	-2.55709000	2.60226400	-1.77396400
H	-3.34373000	1.93961500	-2.14296400
H	-2.24928100	3.25521200	-2.58936200
H	-2.98945500	3.22567700	-0.98736400
C	2.78481600	0.47521100	-0.16875200
C	3.59756200	1.29146400	0.61953100
F	3.15161800	2.48867900	1.01642800
C	4.86244200	0.89931500	1.02718300
F	5.60840600	1.71433000	1.77105200
C	5.34782500	-0.34937400	0.67632900
F	6.56004400	-0.73510700	1.06954300
C	4.55655600	-1.19707700	-0.08221800
F	5.00635500	-2.40597800	-0.41737900
C	3.30199900	-0.78088700	-0.49107200
F	2.55387500	-1.63937800	-1.20650200
C	-2.91329100	0.36036800	-0.14093500
C	-3.41961900	-0.87213700	-0.55474100
F	-2.67627500	-1.65813700	-1.34302500
C	-4.66461700	-1.32804700	-0.15704300
F	-5.11261000	-2.51201200	-0.57469300
C	-5.44995800	-0.54751100	0.67620900
F	-6.65213600	-0.97457000	1.05833700
C	-4.97299500	0.67755100	1.11190000
F	-5.71727900	1.42889900	1.92259400
C	-3.71930900	1.11176900	0.71330300
F	-3.27952500	2.28733300	1.17756500
O	0.34720200	-2.27602400	0.77335600
C	0.72901100	-3.25209800	0.26301700
O	1.09528900	-4.23036400	-0.21475600

2•HCO_2BPin
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2557.334154
Sum of electronic and thermal Energies= -2557.293049
Sum of electronic and thermal Enthalpies= -2557.292105
Sum of electronic and thermal Free Energies= -2557.408909

0 1

Cu	-0.24454100	-1.00565600	-0.43976500
N	1.16178200	-1.66738800	0.70348000
C	0.88167300	-2.24391800	1.87049700
C	-0.41219800	-2.43077500	2.37281100
H	-0.46457600	-2.95502100	3.31917700
C	-1.65143500	-1.98146900	1.87230400
N	-1.79461900	-1.36043200	0.71556500
C	2.01828600	-2.74203700	2.73370300
H	2.77530500	-3.25618900	2.13638200

H	1.65670400	-3.42961800	3.49729400
H	2.50497100	-1.90420600	3.24047100
C	-2.86388100	-2.23439500	2.73764000
H	-3.19399600	-1.30109700	3.20285600
H	-2.64196100	-2.94627200	3.53174600
H	-3.69721100	-2.62214100	2.14647300
C	2.48325800	-1.35187200	0.36127500
C	3.09031100	-1.92262200	-0.75741200
F	2.43531400	-2.85922900	-1.45538400
C	4.33758900	-1.52357400	-1.20723900
F	4.87300400	-2.08811200	-2.28833000
C	5.03049800	-0.53227600	-0.53114600
F	6.23146100	-0.14371300	-0.95327000
C	4.45987000	0.05105000	0.58781600
F	5.10747700	1.01879700	1.23873500
C	3.20807100	-0.35710400	1.01691400
F	2.68255900	0.25069300	2.09133100
C	-3.03827500	-0.85313400	0.31394400
C	-3.59364500	0.29000600	0.88255000
F	-2.98195300	0.87536500	1.92582900
C	-4.75135100	0.86908400	0.39311900
F	-5.23792600	1.97748700	0.95387300
C	-5.39566100	0.30038800	-0.69326900
F	-6.51128700	0.84842300	-1.17266400
C	-4.86972300	-0.83931200	-1.28046400
F	-5.48594000	-1.38859100	-2.32612200
C	-3.70858600	-1.40263600	-0.77754100
F	-3.21645000	-2.49159700	-1.37034400
O	-0.68939200	-0.25029200	-2.22321700
C	0.53943500	-0.31219500	-2.32913300
H	1.05691100	-1.16808800	-2.77321100
O	1.35908700	0.75303000	-2.20303000
B	1.09089700	1.75674600	-1.28053900
O	1.57377900	3.01454500	-1.40810600
O	0.37678500	1.52481700	-0.14216200
C	1.32327700	3.67672800	-0.13443900
C	0.15019400	2.82553000	0.47262900
C	0.18609500	2.65562300	1.97966600
H	0.08744900	3.62429500	2.47925600
H	-0.65042200	2.02610600	2.29118200
H	1.10878600	2.17993800	2.31074000
C	-1.23018800	3.28778700	0.02010200
H	-1.97412200	2.56150000	0.35321300
H	-1.48822700	4.25699100	0.45416400
H	-1.29450400	3.36746900	-1.06822300
C	2.61391400	3.58104000	0.67039600
H	3.42926800	4.01655100	0.08892100
H	2.53706200	4.12386300	1.61588100
H	2.87826400	2.54563100	0.89738800
C	0.97729900	5.12762800	-0.41335400
H	0.70595000	5.64554300	0.51147200
H	1.84374100	5.63499500	-0.84323200
H	0.15027500	5.21698700	-1.11835100

2•HCO_2AuIPr
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -3441.494784
Sum of electronic and thermal Energies= -3441.430245
Sum of electronic and thermal Enthalpies= -3441.429301
Sum of electronic and thermal Free Energies= -3441.598726

0 1

Cu	-1.84139000	-1.50799200	-0.83702600
N	-3.29656500	-1.53425500	0.45404700
C	-3.45190000	-2.51812700	1.33724500
C	-2.57092600	-3.59365000	1.50652600
H	-2.86245200	-4.30655700	2.26835400
C	-1.35664800	-3.88929700	0.85173900
N	-0.85336100	-3.15837100	-0.12201200
C	-4.66332200	-2.50168400	2.24544400
H	-4.60175200	-1.67066400	2.95453000
H	-4.74030500	-3.42586500	2.81658200
H	-5.58551800	-2.37620500	1.67156400
C	-0.61489400	-5.11715000	1.33254400
H	-0.27879300	-5.72947600	0.49185000
H	-1.23959800	-5.73224800	1.97969000
H	0.27260100	-4.81911800	1.89911600
C	-4.25232700	-0.51043900	0.39339100
C	-4.30994500	0.52666100	1.32308900
F	-3.46958800	0.53330300	2.37008500
C	-5.19965500	1.58073500	1.20068700
C	-6.06054800	1.63664100	0.11833100
C	-6.02976000	0.62230100	-0.82586400
F	-6.86130400	0.66388300	-1.86699900
C	-5.14537600	-0.43359500	-0.67760500
F	-5.14149200	-1.39095900	-1.60560500
C	0.38774500	-3.47144300	-0.68502900
C	0.48439800	-3.92637400	-1.99986200
F	-0.62861000	-4.19135500	-2.69105100
C	1.70470500	-4.07609200	-2.63806600
F	1.75193700	-4.48197800	-3.90863900
C	2.87894800	-3.79306600	-1.96207200
F	4.05822400	-3.93075500	-2.57031400
C	2.81835400	-3.36371100	-0.64713100
F	3.94838900	-3.09702000	0.01789100
C	1.59006800	-3.20703700	-0.03040700
F	1.56548100	-2.76767600	1.23641300
O	-1.10091300	-0.93159900	-2.57956600
C	0.02336200	-1.01396900	-3.09402500
H	0.09147500	-1.39112500	-4.12647600
O	1.14085900	-0.70651000	-2.57674300
Au	1.27319800	0.44382100	-0.83745400
C	1.46007700	1.72991700	0.68342700
N	1.15391600	3.04593400	0.60927100
N	1.85669000	1.53358000	1.95819700
C	1.34281600	3.66320300	1.83243500
C	0.86178200	3.76492400	-0.60870800
C	1.78917400	2.71330200	2.67922400
C	2.38845100	0.31032700	2.50931200
H	1.15137600	4.71544500	1.97082600
C	1.93358200	4.38961600	-1.26337200
C	-0.45473400	3.82121600	-1.07593900
H	2.06505600	2.75308100	3.72094200
C	1.58253500	-0.43366700	3.37679100
C	3.70926300	-0.04167300	2.19892400
C	1.64535300	5.11145500	-2.41823100
C	3.37438700	4.25238000	-0.79322500
C	-0.68867700	4.56698800	-2.23095500
C	-1.60836600	3.11764900	-0.38200600
C	2.15089100	-1.56050400	3.96663400
C	0.13451600	-0.07656200	3.66858000
C	4.21609600	-1.19422300	2.79384800
C	4.59913300	0.77923400	1.27725300
H	2.44898300	5.60215100	-2.95922400
C	0.34584700	5.20697400	-2.89334100
H	3.37290300	3.83794800	0.21945700
C	4.13517900	3.26946600	-1.68997500
C	4.09522700	5.60032200	-0.71694300
H	-1.69852500	4.64121000	-2.62234800
H	-1.19697000	2.43213000	0.36562700
C	-2.49388400	4.12959000	0.35251100
C	-2.42102300	2.27442200	-1.36832900

H	1.55631700	-2.16323500	4.64708300
C	3.45106300	-1.93983500	3.67702400
H	-0.14084500	0.79284400	3.06309200
C	-0.06112000	0.30341300	5.13895100
C	-0.79888000	-1.21723700	3.25802900
H	5.22949000	-1.51126000	2.56541500
H	4.03211800	1.64557100	0.92471400
C	5.01803800	-0.02031600	0.04097600
C	5.82127600	1.31798200	2.02726600
H	0.13980400	5.77783800	-3.79396100
H	3.64642800	2.29080400	-1.72053800
H	5.15803300	3.12755500	-1.32517200
H	4.19565100	3.64099200	-2.71784400
H	3.54877200	6.31500500	-0.09496900
H	4.22648700	6.05122200	-1.70488900
H	5.09241000	5.47138500	-0.28627000
H	-1.92056100	4.71339000	1.07951600
H	-3.29806000	3.62376900	0.89383000
H	-1.79624200	1.55033700	-1.89853000
H	-2.93072300	2.89421200	-2.11242500
H	-3.19085400	1.71264300	-0.83498100
H	3.86992100	-2.83120600	4.13469600
H	0.58279400	1.13823500	5.43419600
H	0.16706300	-0.53744500	5.80169600
H	-1.09864000	0.59713800	5.32231400
H	-0.60252400	-2.12875400	3.83169800
H	-0.68784100	-1.46085300	2.19893300
H	-1.84098700	-0.93579700	3.42634600
H	4.14829300	-0.36758500	-0.52449300
H	5.60585900	-0.90234700	0.31017200
H	5.62871800	0.59795500	-0.62428900
H	6.47029600	0.50802000	2.37383900
H	5.52878100	1.90587600	2.90235700
H	6.41873500	1.96017400	1.37251600
H	-2.95456800	4.83368600	-0.34815600
F	-6.91119100	2.65492700	-0.01286300
F	-5.20861800	2.56221800	2.10948200

toluene
wB97X / 6-311G*
Sum of electronic and zero-point Energies= -271.410075
Sum of electronic and thermal Energies= -271.403917
Sum of electronic and thermal Enthalpies= -271.402972
Sum of electronic and thermal Free Energies= -271.440724

0 1

C	2.41579500	0.00000100	0.00935700
H	2.79303300	-0.00011000	1.03718200
H	2.82336900	0.88352200	-0.48817900
H	2.82336900	-0.88341500	-0.48836800
C	0.90884500	0.00000300	-0.01125800
C	0.19371500	1.19702700	-0.00833400
H	0.73360100	2.14140400	-0.01593800
C	-1.19589700	1.20018200	0.00181600
H	-1.73342400	2.14434500	0.00182300
C	-1.89653800	-0.00000200	0.00744200
H	-2.98261000	-0.00000400	0.01257500
C	-1.19589300	-1.20018400	0.00181500
H	-1.73341700	-2.14434900	0.00182300
C	0.19371800	-1.19702500	-0.00833500
H	0.73360800	-2.14140000	-0.01593900

CO_2
wB97X / 6-311G*
Sum of electronic and zero-point Energies= -188.579160
Sum of electronic and thermal Energies= -188.576552
Sum of electronic and thermal Enthalpies= -188.575607
Sum of electronic and thermal Free Energies= -188.599842

0 1

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.15691000
O	0.00000000	0.00000000	-1.15691000

HCO_2BPin
wB97X / 6-311G* / SDDAll
Sum of electronic and zero-point Energies= -600.265360
Sum of electronic and thermal Energies= -600.252860
Sum of electronic and thermal Enthalpies= -600.251916
Sum of electronic and thermal Free Energies= -600.304252

0 1

O	-3.08523900	0.69555300	0.72216800
C	-3.21684600	-0.17872800	-0.08209200
H	-4.18236100	-0.52249800	-0.47603900
O	-2.21437800	-0.89308400	-0.61158900
B	-0.89810200	-0.49371800	-0.35402300
O	-0.05242200	-1.24259500	0.40032800
O	-0.35001000	0.63183400	-0.88405900
C	1.26257500	-0.64488200	0.25689400
C	0.91858800	0.81521900	-0.20461000
C	1.90915900	1.42724000	-1.17805100
C	0.65224600	1.76650000	0.95753100
C	1.98280300	-0.73869300	1.58972500
C	1.99813700	-1.45424900	-0.80543400
H	-0.07670800	1.34953200	1.65675300
H	1.56870900	2.00451300	1.50410000
H	0.23299400	2.69466400	0.56371900
H	2.90029900	1.51196300	-0.72175400
H	1.99559200	0.83804700	-2.09164600
H	1.57827400	2.43076600	-1.45466100
H	2.16724500	-1.78707100	1.83519300
H	2.94860000	-0.22579100	1.54647500
H	1.39250600	-0.30287200	2.39619100
H	2.01947700	-2.50286200	-0.50083600
H	1.49390900	-1.39638400	-1.77352800
H	3.02838900	-1.11152200	-0.93240900

HCO_2AuIPr
wB97X / 6-311G* / SDDAll (Au)
Sum of electronic and zero-point Energies= -1484.405007
Sum of electronic and thermal Energies= -1484.369183
Sum of electronic and thermal Enthalpies= -1484.368238
Sum of electronic and thermal Free Energies= -1484.476435

0 1

O	-0.00003800	-3.22011800	-2.33124400
C	-0.00002700	-2.45086700	-3.27893600
H	-0.00003100	-2.83852800	-4.31508200
O	-0.00001100	-1.16070700	-3.23747500

Au	-0.00000500	-0.37650300	-1.31691000
C	0.00000400	0.35832400	0.54046100
N	-1.07039500	0.61052000	1.32478900
N	1.07041000	0.61051600	1.32478000
C	-0.67495500	1.01160400	2.58873600
C	-2.43750800	0.43178700	0.90700800
C	0.67498300	1.01160200	2.58872900
C	2.43752000	0.43177700	0.90698600
H	-1.39193300	1.25498500	3.35673700
C	-3.11568500	1.52842800	0.36229500
C	-3.01313000	-0.83636200	1.04433900
H	1.39196800	1.25498200	3.35672500
C	3.01313300	-0.83637700	1.04430100
C	3.11569800	1.52841800	0.36227600
C	-4.43050900	1.32500500	-0.04933300
C	-2.44749700	2.87959400	0.16196000
C	-4.33125600	-0.98517400	0.61683200
C	-2.26280900	-2.02614000	1.62265800
C	4.33125500	-0.98519400	0.61678100
C	2.26281200	-2.02615400	1.62261900
C	4.43051700	1.32499000	-0.04936600
C	2.44751600	2.87959000	0.16195900
H	-4.98961700	2.14702600	-0.48682500
C	-5.03253000	0.08170600	0.07720700
H	-1.49765500	2.87733100	0.70644500
C	-2.12509200	3.10127800	-1.31977100
C	-3.28637900	4.02983800	0.72369800
H	-4.81266800	-1.95545500	0.69877600
H	-1.25918000	-1.69584400	1.90858000
C	-2.94894100	-2.53920300	2.89283000
C	-2.09562000	-3.14600400	0.59043400
H	4.81266100	-1.95547800	0.69871300
C	5.03253000	0.08168600	0.07715800
H	1.25918600	-1.69585700	1.90854700
C	2.94895000	-2.53922400	2.89278600
C	2.09561300	-3.14601400	0.59039200
H	4.98962600	2.14701200	-0.48685500
H	1.49768600	2.87733400	0.70646600
C	2.12507900	3.10128100	-1.31976400
C	3.28641900	4.02982700	0.72368000
H	-6.05686000	-0.05835700	-0.25560300
H	-1.49615500	2.29894400	-1.71644600
H	-1.59799900	4.05014800	-1.46222500
H	-3.03985700	3.13311500	-1.92042300
H	-3.53222400	3.87273000	1.77789100
H	-4.22650100	4.15302200	0.17782000
H	-2.73920500	4.97348300	0.64118100
H	-3.05595500	-1.74925900	3.64271600
H	-2.36781800	-3.35199900	3.33816500
H	-1.54192800	-2.82430900	-0.29646700
H	-3.06625300	-3.53056500	0.26018700
H	6.05685600	-0.05838000	-0.25566400
H	3.05596900	-1.74928300	3.64267400
H	3.94852900	-2.93045600	2.67905000
H	2.36782800	-3.35202000	3.33812100
H	1.54191800	-2.82431300	-0.29650400
H	1.54539100	-3.98370800	1.03059700
H	1.49612600	2.29895400	-1.71642700
H	3.03983200	3.13311000	-1.92043600
H	1.59799200	4.05015600	-1.46220400
H	4.22652700	4.15301000	0.17777900
H	3.53229100	3.87271500	1.77786700
H	2.73924700	4.97347600	0.64118200
H	3.06624300	-3.53057800	0.26013800
H	-1.54539800	-3.98369800	1.03063800
H	-3.94852200	-2.93043400	2.67910300

[(BDI)Au(H)Cu(IPr)]

wB97X / 6-311G* / SDDAll (Cu, Au)
Sum of electronic and zero-point Energies= -3252.865852
Sum of electronic and thermal Energies= -3252.804099
Sum of electronic and thermal Enthalpies= -3252.803155
Sum of electronic and thermal Free Energies= -3252.969708

0 1

H	-0.83535600	-0.19287000	-1.12317100
N	-2.87209000	-3.08713900	1.04404300
C	-1.95901900	-3.69860000	0.37944200
C	-0.90411400	-4.40771100	1.11748700
H	-1.25220400	-5.10097000	1.87562800
C	0.43067000	-4.20577600	0.99352900
N	0.97719600	-3.19428900	0.23272900
C	-1.96619100	-3.85661600	-1.12610800
H	-2.57062700	-4.73889500	-1.36285800
H	-0.96082200	-4.03657700	-1.50670800
H	-2.40666100	-3.00171100	-1.64509400
C	1.37016100	-5.13571200	1.72353300
H	2.10543600	-5.56025100	1.03252500
H	0.81469200	-5.96110800	2.16813700
H	1.91727700	-4.62473400	2.51845100
C	-3.94357900	-2.47962000	0.38972000
C	-4.96527200	-3.19586100	-0.23261700
F	-4.87991500	-4.53015300	-0.31642400
C	-6.07577200	-2.57349400	-0.77952100
F	-7.02876800	-3.29579700	-1.37159900
C	-6.19484800	-1.19574900	-0.71659300
F	-7.25596700	-0.58372500	-1.24815200
C	-5.19706600	-0.45599200	-0.10298500
F	-5.30086700	0.87677900	-0.04960200
C	-4.10073300	-1.09334000	0.45071300
F	-3.16365100	-0.34233800	1.04238100
C	2.36185400	-3.01888900	0.15860300
C	3.02750200	-3.11658700	-1.06738000
F	2.35285600	-3.50060300	-2.15430900
C	4.36004200	-2.76830800	-1.21832800
F	4.94637900	-2.82696400	-2.41708800
C	5.08623900	-2.33549300	-0.12337200
F	6.36109800	-1.95241900	-0.26496000
C	4.46751600	-2.24306100	1.11028200
F	5.14961100	-1.76042700	2.15843600
C	3.13178200	-2.57799700	1.23920600
F	2.55612000	-2.39720200	2.43572400
C	0.59223900	2.81307000	0.12880600
N	1.86066900	3.27480700	0.06597300
C	1.93538300	4.58550100	0.50337900
H	2.86752200	5.12804700	0.52292900
C	0.68213300	4.94476200	0.85880300
H	0.28692800	5.86701700	1.25467000
N	-0.12409900	3.84662300	0.61801600
C	2.96880200	2.47775100	-0.40079900
C	3.14477300	2.32290000	-1.77936300
C	4.18328800	1.49231300	-2.20171000
H	4.34605900	1.33615300	-3.26431900
C	5.00486100	0.85568400	-1.28679300
H	5.79945100	0.20112900	-1.63317500
C	4.81630000	1.04475000	0.07677100
H	5.47364100	0.53882700	0.77703300
C	3.79339200	1.86025100	0.55248500
C	2.25843400	3.00726300	-2.80860800
H	1.52195400	3.62078400	-2.27994300
C	1.48490100	1.98316400	-3.64436800
H	2.15926000	1.36195800	-4.24184000

H	0.80095800	2.48767600	-4.33388200
H	0.89393100	1.31068800	-3.01436000
C	3.07361600	3.94613600	-3.70285500
H	3.61152400	4.69449200	-3.11379300
H	2.41809200	4.47340800	-4.40233500
H	3.81226100	3.39729600	-4.29489800
C	3.54893500	2.02501900	2.04605400
H	3.06099600	2.99267800	2.20465100
C	4.84070200	2.03374300	2.86552200
H	5.31576800	1.04880600	2.88435200
H	4.62140900	2.30089800	3.90303600
H	5.56633100	2.75405900	2.47721800
C	2.60020000	0.93719800	2.56274900
H	1.67210200	0.88599400	1.98558400
H	2.33552500	1.12250700	3.60898300
H	3.07293000	-0.04635900	2.51511200
C	-1.54368200	3.77359100	0.85897200
C	-1.98837300	3.18617400	2.04827400
C	-3.36666700	3.07982300	2.22918300
H	-3.75297000	2.61248500	3.13019800
C	-4.25077300	3.54005800	1.26797100
H	-5.31984100	3.43077300	1.42081600
C	-3.77783200	4.12010800	0.09939100
H	-4.48669800	4.46104200	-0.64877100
C	-2.41164800	4.24726400	-0.13424700
C	-1.04039200	2.64389300	3.10668200
H	-0.01352100	2.87528800	2.80487200
C	-1.27374100	3.31477800	4.46339000
H	-1.18301000	4.40291100	4.39595300
H	-0.54194600	2.95869000	5.19442400
H	-2.26791300	3.08822800	4.86017700
C	-1.15603600	1.12022700	3.21742500
H	-2.15504000	0.81679600	3.54393600
H	-0.43496500	0.73165800	3.94287100
H	-0.97015900	0.62264800	2.26044500
C	-1.89781100	4.80712000	-1.45251800
H	-0.85386400	5.10781900	-1.31500400
C	-1.92606200	3.72223800	-2.53578800
H	-1.33470300	2.84718400	-2.24739500
H	-1.52403900	4.10515400	-3.47951900
H	-2.94971600	3.38105600	-2.71943000
C	-2.66482500	6.05014900	-1.90789000
H	-3.69616800	5.81580300	-2.18684400
H	-2.18612300	6.48604000	-2.78942500
H	-2.69526900	6.81498900	-1.12696000
Cu	-0.05682700	1.08185100	-0.38389400
Au	-0.00397400	-1.47737000	-0.44093100

IPrAu–H
wB97X / 6-311G* / SDDAll (Au)
Sum of electronic and zero-point Energies= -1295.813892
Sum of electronic and thermal Energies= -1295.781525
Sum of electronic and thermal Enthalpies= -1295.780580
Sum of electronic and thermal Free Energies= -1295.879943

0 1

Au	0.00000200	-0.00000800	-1.71768600
H	0.00000400	-0.00001300	-3.34703200
C	0.00000000	0.00000000	0.37184800
N	-1.06700000	0.00000100	1.20445100
C	-0.67460100	0.00000300	2.53220100
H	-1.39194000	0.00000400	3.33772500
C	0.67459800	0.00000400	2.53220200
H	1.39193600	0.00000600	3.33772700
N	1.06699900	0.00000200	1.20445200
C	-2.43842600	0.00000100	0.76709700
C	-3.07245700	1.23025800	0.56040800
C	-4.39862900	1.20277100	0.13440600
H	-4.92275200	2.13670000	-0.04757600
C	-5.05586700	0.00000300	-0.07524400
H	-6.08813300	0.00000400	-0.41312700
C	-4.39863100	-1.20276500	0.13440600
H	-4.92275600	-2.13669400	-0.04757600
C	-3.07245900	-1.23025500	0.56040700
C	-2.35296000	2.55792000	0.73706500
H	-1.37917800	2.36198900	1.19689400
C	-2.09151200	3.21211600	-0.62357600
H	-1.52306400	2.54876100	-1.28237900
H	-1.52408800	4.14043200	-0.50091500
C	-3.11293900	3.50219500	1.67182800
H	-3.30293500	3.03986900	2.64496200
H	-4.07828900	3.80045900	1.25169600
H	-2.53602200	4.41656800	1.83910600
C	-2.35296500	-2.55791900	0.73706300
H	-1.37918000	-2.36199100	1.19688700
C	-3.11294300	-3.50218900	1.67183100
H	-4.07829700	-3.80044800	1.25170600
H	-3.30293000	-3.03986100	2.64496700
H	-2.53603000	-4.41656400	1.83910700
C	-2.09152700	-3.21211800	-0.62357800
H	-1.52307900	-2.54876600	-1.28238500
H	-3.03066400	-3.45962600	-1.12935000
H	-1.52410500	-4.14043600	-0.50091800
C	2.43842500	0.00000400	0.76710000
C	3.07246000	-1.23025100	0.56041500
C	4.39863300	-1.20276100	0.13441400
H	4.92275900	-2.13668900	-0.04756500
C	5.05586600	0.00000900	-0.07524100
H	6.08813100	0.00001000	-0.41312400
C	4.39862500	1.20277500	0.13440400
H	4.92274600	2.13670500	-0.04758200
C	3.07245300	1.23026100	0.56040500
C	2.35296900	-2.55791700	0.73707400
H	1.37918600	-2.36198900	1.19690300
C	3.11295200	-3.50218700	1.67183800
H	3.30294400	-3.03985900	2.64497200
H	4.07830400	-3.80044600	1.25170700
H	2.53603900	-4.41656200	1.83911700
C	2.09152400	-3.21211400	-0.62356600
H	3.03065900	-3.45962000	-1.12934400
H	1.52307200	-2.54876200	-1.28237000
H	1.52410400	-4.14043300	-0.50090500
C	2.35295300	2.55792300	0.73705700
H	1.37916900	2.36199100	1.19688200
C	2.09151000	3.21211500	-0.62358700
H	1.52306500	2.54875700	-1.28239100
H	3.03064500	3.45962500	-1.12936100
H	1.52408300	4.14043100	-0.50093000
C	3.11292600	3.50220000	1.67182100
H	4.07827900	3.80046300	1.25169300
H	3.30291700	3.03987700	2.64495800
H	2.53600800	4.41657300	1.83909400
H	-3.03064600	3.45962500	-1.12935300

2•CO
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2070.387569
Sum of electronic and thermal Energies= -2070.357493
Sum of electronic and thermal Enthalpies= -2070.356549

Sum of electronic and thermal Free Energies= -2070.451525

0 1

N	-1.47476500	0.67935600	0.51215400
C	-1.27000600	1.80717400	1.18474800
C	-0.00000400	2.30790200	1.50642900
H	-0.00000500	3.22844700	2.07647100
C	1.27000000	1.80717600	1.18474900
N	1.47476000	0.67936000	0.51215500
C	-2.45270900	2.62177000	1.65464500
H	-2.91972700	3.13367100	0.80914200
H	-2.14594600	3.37680200	2.37702800
H	-3.21143600	1.98758000	2.11984400
C	2.45270100	2.62177400	1.65464600
H	3.21142700	1.98758600	2.11985000
H	2.14593600	3.37680900	2.37702500
H	2.91972200	3.13367100	0.80914300
C	-2.78721400	0.28707500	0.19205900
C	-3.55406300	0.94678700	-0.76604300
F	-3.07026700	2.04422600	-1.35926200
C	-4.81452400	0.50260000	-1.13001500
F	-5.52225900	1.16349300	-2.04506900
C	-5.33740300	-0.63944700	-0.54565700
F	-6.54585500	-1.07653500	-0.89306500
C	-4.59350100	-1.32560700	0.40091300
F	-5.08885000	-2.42703700	0.96336700
C	-3.33977200	-0.85958300	0.76041300
F	-2.63779300	-1.54899500	1.66531100
C	2.78720900	0.28707900	0.19206000
C	3.33976800	-0.85957800	0.76041600
F	2.63779000	-1.54899000	1.66531500
C	4.59349700	-1.32560100	0.40091600
F	5.08884800	-2.42703000	0.96337100
C	5.33739900	-0.63944100	-0.54565400
F	6.54585200	-1.07652800	-0.89306300
C	4.81451900	0.50260400	-1.13001300
F	5.52225400	1.16349700	-2.04506800
C	3.55405800	0.94679100	-0.76604200
F	3.07026100	2.04422900	-1.35926200
C	0.00002700	-2.06922500	-0.94879600
Cu	-0.00000300	-0.46668000	-0.07994900
O	0.00005400	-3.06454000	-1.48274600

CO
wB97X / 6-311G*
Sum of electronic and zero-point Energies= -113.310480
Sum of electronic and thermal Energies= -113.308120
Sum of electronic and thermal Enthalpies= -113.307175
Sum of electronic and thermal Free Energies= -113.329598

0 1

C	0.00000000	0.00000000	-0.64325800
O	0.00000000	0.00000000	0.48244300

1•C_2H_4
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -1874.407170
Sum of electronic and thermal Energies= -1874.373023
Sum of electronic and thermal Enthalpies= -1874.372079
Sum of electronic and thermal Free Energies= -1874.474123

0 1

Cu	0.00000000	-1.05175300	0.00000300
N	1.48587600	0.22300800	0.00000300
C	1.25734900	1.51468600	0.00000100
C	0.00000000	2.13713900	0.00000100
H	0.00000000	3.21347300	-0.00000100
C	-1.25734900	1.51468700	0.00000200
N	-1.48587600	0.22300800	0.00000500
C	2.45392200	2.48491900	-0.00000100
C	-2.45392200	2.48491900	0.00000000
C	2.79450500	-0.35838800	0.00000100
C	3.38675700	-0.71646000	1.21711000
C	4.61046000	-1.37951700	1.19257100
C	5.24670700	-1.70912100	-0.00000300
C	4.61045500	-1.37951900	-1.19257500
C	3.38675300	-0.71646200	-1.21711000
C	-2.79450500	-0.35838800	0.00000100
C	-3.38675300	-0.71645900	-1.21711000
C	-4.61045600	-1.37951600	-1.19257600
C	-5.24670700	-1.70912100	-0.00000500
C	-4.61046000	-1.37951900	1.19257000
C	-3.38675800	-0.71646200	1.21711000
C	0.68758700	-2.95182700	0.00000200
C	-0.68758700	-2.95182700	0.00000300
H	-1.25593400	-3.07366400	0.91897300
H	1.25593500	-3.07366300	0.91897200
H	1.25593400	-3.07366200	-0.91896800
H	-1.25593500	-3.07366200	-0.91896700
F	3.22902100	2.31044400	-1.08305200
F	3.22902000	2.31044800	1.08305100
F	2.08225200	3.77293500	-0.00000400
F	-2.08225200	3.77293500	0.00000500
F	-3.22901600	2.31044900	-1.08305500
F	-3.22902400	2.31044300	1.08304800
H	5.07743200	-1.65089800	-2.13781400
H	5.07744100	-1.65089500	2.13780800
H	-5.07743300	-1.65089300	-2.13781600
H	-5.07744100	-1.65089900	2.13780700
C	-6.59045700	-2.39062300	-0.00000600
H	-6.72086100	-3.02054100	0.88359200
H	-7.40171900	-1.65544800	0.00005800
H	-6.72091000	-3.02044200	-0.88366700
C	-2.69904900	-0.42098400	-2.52288200
H	-1.69101200	-0.85084700	-2.54586200
H	-3.26129200	-0.83312100	-3.36343600
H	-2.58659700	0.65297200	-2.68563300
C	-2.69906000	-0.42098700	2.52288600
H	-2.58661800	0.65297000	2.68563900
H	-3.26130200	-0.83313100	3.36343600
H	-1.69102000	-0.85084100	2.54586600
C	2.69905900	-0.42098500	2.52288500
H	1.69102200	-0.85084400	2.54586800
H	3.26130400	-0.83312500	3.36343600
H	2.58661200	0.65297200	2.68563700
C	2.69904900	-0.42098700	-2.52288200
H	2.58660300	0.65297000	-2.68563500
H	3.26128900	-0.83312900	-3.36343600
H	1.69101000	-0.85084400	-2.54586000
C	6.59045700	-2.39062300	-0.00000500
H	6.72089100	-3.02047800	-0.88364300
H	7.40171900	-1.65544800	0.00001100
H	6.72088100	-3.02050400	0.88361500

2•C_2H_4
wB97X / 6-311G* / SDDAll (Cu)

Sum of electronic and zero-point Energies= -2035.605963
Sum of electronic and thermal Energies= -2035.575337
Sum of electronic and thermal Enthalpies= -2035.574393
Sum of electronic and thermal Free Energies= -2035.669054

0 1

Cu	-0.00000400	0.46848900	0.09635700
N	-1.47264100	-0.63965700	-0.56309600
C	-1.26924100	-1.73206100	-1.28999600
C	0.00000000	-2.21592400	-1.64003100
H	0.00000100	-3.10645900	-2.25592200
C	1.26924000	-1.73205700	-1.29000000
N	1.47264400	-0.63966500	-0.56308300
C	-2.45378900	-2.52425300	-1.79293500
H	-2.92015700	-3.07155300	-0.96933500
H	-2.14955400	-3.24805400	-2.54770900
H	-3.21247900	-1.86944200	-2.22886800
C	2.45379000	-2.52423500	-1.79295900
H	3.21246800	-1.86941200	-2.22889400
H	2.14955400	-3.24803000	-2.54773900
H	2.92017300	-3.07153900	-0.96937100
C	-2.78163300	-0.26832000	-0.21240900
C	-3.53041600	-0.96901500	0.73129400
F	-3.03176200	-2.08670300	1.27232000
C	-4.78479000	-0.54435400	1.13764500
F	-5.47239400	-1.24399800	2.03938000
C	-5.32264900	0.61813100	0.60999900
F	-6.52533500	1.03712900	0.99840000
C	-4.59837100	1.34412400	-0.32180400
F	-5.10626200	2.46670400	-0.82951800
C	-3.35104700	0.89652000	-0.72458900
F	-2.67149800	1.62662000	-1.61613500
C	2.78163400	-0.26832300	-0.21240400
C	3.35103300	0.89653300	-0.72457000
F	2.67146800	1.62664200	-1.61609800
C	4.59835500	1.34414400	-0.32178900
F	5.10622700	2.46673900	-0.82949000
C	5.32265100	0.61814200	0.60999300
F	6.52533600	1.03714500	0.99839100
C	4.78480800	-0.54435800	1.13762400
F	5.47242900	-1.24401100	2.03933900
C	3.53043500	-0.96902600	0.73127700
F	3.03180000	-2.08672800	1.27228900
C	0.68814200	2.09069300	1.07556500
C	-0.68815000	2.09069700	1.07556800
H	-1.24974200	1.73508800	1.93592100
H	1.24973900	1.73508700	1.93591600
H	1.24535800	2.67257900	0.34606400
H	-1.24536800	2.67259000	0.34607400

4•C_2H_4
wB97X / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -1545.488935
Sum of electronic and thermal Energies= -1545.462873
Sum of electronic and thermal Enthalpies= -1545.461929
Sum of electronic and thermal Free Energies= -1545.547584

0 1

Cu	0.50240600	1.76971000	-0.00000100
C	2.71228200	0.01424400	-0.00000200
C	1.91874400	-1.12150000	0.00000600
H	2.42033900	-2.07558500	0.00001000
C	0.50397700	-1.12126500	0.00000700
N	-0.25406000	-0.06062200	-0.00000200
C	4.23615400	-0.17524900	-0.00000700
C	-0.14708400	-2.51940000	0.00001700
C	-1.68781400	-0.10114400	-0.00000500
C	-2.37344700	-0.03326800	1.21815100
C	-3.76338700	0.03744100	1.19293500
C	-4.47915300	0.06062300	-0.00001200
C	-3.76338200	0.03741800	-1.19295500
C	-2.37344100	-0.03329100	-1.21816400
C	0.31981400	3.78020700	0.00001700
C	-0.92165000	3.19044300	-0.00000400
H	-1.48636000	3.05642200	-0.91955200
H	0.77847800	4.12865600	-0.92125500
H	0.77845400	4.12863700	0.92130800
H	-1.48638600	3.05640500	0.91952500
F	4.77532400	0.40169800	1.08252700
F	4.77531500	0.40169300	-1.08254900
F	4.61400700	-1.46387900	-0.00000600
F	0.75811200	-3.50587000	0.00002900
F	-0.91783900	-2.70076100	1.08331300
F	-0.91783100	-2.70078100	-1.08328000
H	-4.30180000	0.08081200	2.13795500
H	-4.30179100	0.08077100	-2.13797700
C	-5.98525400	0.09661800	-0.00001000
H	-6.37440300	0.60831900	-0.88377400
H	-6.39964800	-0.91664100	0.00018100
H	-6.37439300	0.60864500	0.88357100
C	-1.62505500	-0.00567100	2.52377000
H	-0.89393900	0.81047400	2.54649100
H	-2.30914600	0.13173400	3.36351600
H	-1.06934100	-0.93097900	2.69014100
C	-1.62504400	-0.00571500	-2.52378000
H	-1.06933400	-0.93102800	-2.69013700
H	-2.30913200	0.13168100	-3.36353000
H	-0.89392500	0.81042600	-2.54650900
O	2.37995300	1.22902100	-0.00000400

5•Au
wB97X / 6-311G* / SDDAll (Au, Cu)
Sum of electronic and zero-point Energies= -2718.366232
Sum of electronic and thermal Energies= -2718.302743
Sum of electronic and thermal Enthalpies= -2718.301799
Sum of electronic and thermal Free Energies= -2718.473085

0 1

Au	-0.75674900	0.06634500	-0.56607700
Cu	1.91722700	-0.23789200	-0.73771400
H	0.52596600	-0.18881200	-1.62017900
N	2.98678900	-1.92035000	-0.39460600
C	4.30522200	-1.89519100	-0.33359600
C	5.07704000	-0.71269000	-0.35433200
H	6.14994600	-0.86751000	-0.34617200
C	4.67184700	0.63761100	-0.32777500
N	3.41219400	1.04278700	-0.36019300
C	5.08161000	-3.19198600	-0.23293400
H	4.98223600	-3.61412500	0.77127000
H	6.14068500	-3.03559500	-0.43928200
H	4.69371600	-3.93839100	-0.93176100
C	5.78829300	1.65955700	-0.25423900
H	5.61556800	2.48106400	-0.95518300
H	6.75311500	1.20493900	-0.47982100

H	5.83764800	2.10031700	0.74560000
C	2.28398000	-3.13717200	-0.25725700
C	2.23311500	-3.86403400	0.94605400
C	1.47249300	-5.02632100	1.05156400
C	0.72594600	-5.47882400	-0.02384800
C	0.73546400	-4.76474200	-1.21451200
C	1.50425100	-3.61462300	-1.32832700
C	3.10016800	2.41347500	-0.21775100
C	2.45958000	3.08957900	-1.27465700
C	2.07440300	4.41820500	-1.16605000
C	2.32116700	5.11786500	0.00769800
C	2.93316100	4.47552700	1.07093800
C	3.30851200	3.13707200	0.97077900
C	-2.52614400	0.34788400	0.46392800
N	-3.09005000	1.51651800	0.84028500
C	-4.31175200	1.30688100	1.45427700
H	-4.91010300	2.12490700	1.82319800
C	-4.51506100	-0.02815800	1.46010600
H	-5.32931100	-0.62777400	1.83528900
N	-3.41112100	-0.59737400	0.85098800
C	-2.50648700	2.81037300	0.59010000
C	-2.80346500	3.44953900	-0.61841600
C	-2.20357000	4.68555200	-0.85044300
H	-2.39933200	5.20953500	-1.78175300
C	-1.34040100	5.24450600	0.07854800
H	-0.86609200	6.19915100	-0.12981600
C	-1.06403100	4.58437000	1.26599100
H	-0.36273100	5.02336000	1.96927300
C	-1.64608700	3.35230700	1.55165500
C	-3.70030600	2.82728500	-1.67691700
H	-4.13714700	1.91199000	-1.26481100
C	-2.88438800	2.42838400	-2.91089600
H	-2.44550400	3.30588600	-3.39634400
H	-3.52037900	1.92383100	-3.64560200
H	-2.06442400	1.75337700	-2.64776800
C	-4.86132500	3.75143300	-2.05315500
H	-5.45288400	4.03207500	-1.17674100
H	-5.52725700	3.25624100	-2.76612600
H	-4.50831900	4.67398000	-2.52393500
C	-1.29486200	2.61729000	2.83494600
H	-1.96842600	1.75986000	2.93611800
C	-1.48918100	3.49415500	4.07413500
H	-0.79652600	4.34087700	4.08473800
H	-1.30450500	2.91320800	4.98258600
H	-2.50563300	3.89466800	4.12966900
C	0.13475600	2.07348200	2.75895600
H	0.26494200	1.42855400	1.88359300
H	0.37569300	1.49062900	3.65474700
H	0.86440800	2.88601200	2.67714900
C	-3.24030400	-2.00865100	0.61191200
C	-2.61423400	-2.78204500	1.59667000
C	-2.42626900	-4.13398900	1.32312200
H	-1.91523400	-4.76264700	2.04599700
C	-2.85524900	-4.68508900	0.12514300
H	-2.68959300	-5.74017600	-0.07260600
C	-3.47982700	-3.89496500	-0.82632500
H	-3.79986100	-4.33940100	-1.76459100
C	-3.68217300	-2.53371800	-0.60710800
C	-2.09025200	-2.17863200	2.88998300
H	-2.52180200	-1.17838900	3.00223700
C	-2.50333100	-2.98847600	4.12091900
H	-3.58702500	-3.13003900	4.16674900
H	-2.19059400	-2.47375000	5.03412600
H	-2.03660700	-3.97776600	4.13281200
C	-0.56853100	-2.01945300	2.81784600
H	-0.07390100	-2.99081500	2.71167800
H	-0.18467500	-1.54013700	3.72511100
H	-0.27634500	-1.40918200	1.95717400
C	-4.32539300	-1.67791200	-1.68682200
H	-4.43902700	-0.66034200	-1.29968600
C	-3.42668100	-1.59633100	-2.92479800
H	-2.42936400	-1.22446800	-2.67151300
H	-3.86217400	-0.92432800	-3.67138800
H	-3.30383300	-2.57835100	-3.39256100
C	-5.72477900	-2.18363400	-2.04750800
H	-5.69141900	-3.18623900	-2.48474900
H	-6.19245200	-1.52193200	-2.78271700
H	-6.37578800	-2.22696400	-1.16930800
H	0.15373100	-5.07829300	-2.07569400
H	0.13591400	-6.38678400	0.06568900
H	1.49040200	-5.55589000	1.99928100
H	1.58249700	4.87977000	-2.01658000
H	2.03480900	6.16249600	0.09407800
H	3.14072200	4.98719900	2.00576400
C	2.62388000	-2.98373300	-3.30717600
H	2.37859800	-2.49905900	-4.25258700
H	2.91499900	-4.02404500	-3.50009500
H	3.45419200	-2.45060000	-2.83618600
C	2.93440000	-2.18523600	2.52770600
H	3.84743400	-1.66017600	2.23552600
H	2.87522300	-2.23347800	3.61786100
H	2.07355000	-1.63842600	2.13823100
C	3.26710900	2.14997600	-3.28104100
H	2.85656900	1.71804400	-4.19406900
H	3.94990500	1.43076700	-2.82021500
H	3.81213300	3.06954200	-3.52907600
C	3.57372500	1.33615000	2.55789200
H	4.31375200	0.58941800	2.25805900
H	2.59354500	1.02882300	2.18970600
H	3.55107400	1.40706000	3.64807100
O	2.16118300	2.43569700	-2.44272900
O	2.95718600	-3.52938500	2.06205400
O	1.44953100	-2.93179100	-2.51641600
O	3.93809500	2.62369600	2.07535100

5.4 Chapter 5

1•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)
Sum of electronic and zero-point Energies= -2251.120766
Sum of electronic and thermal Energies= -2251.077710
Sum of electronic and thermal Enthalpies= -2251.076766
Sum of electronic and thermal Free Energies= -2251.199670

0 1

Cu	-0.00000024	-0.24298713	-0.00000014
W	0.00000079	2.46744724	-0.00000018
H	-0.66669049	1.15292308	-0.93741270
H	0.66669168	1.15292240	0.93741160
N	-1.48034805	-1.57510592	-0.06966646
C	-1.25190444	-2.86853146	-0.09488602
C	-0.00000090	-3.48719582	-0.00000058
H	-0.00000111	-4.56301226	-0.00000078
C	1.25190288	-2.86853201	0.09488525
N	1.48034705	-1.57510662	0.06966604
C	-2.43551951	-3.83544496	-0.24534393
C	2.43551754	-3.83544592	0.24534316
F	-3.28509115	-3.76240513	0.79472211
F	-3.14542073	-3.57262584	-1.35688454
F	-2.05491280	-5.12076426	-0.33334825
F	2.05491030	-5.12076513	0.33334672

F	3.28508959	-3.76240584	-0.79472255
F	3.14541831	-3.57262742	1.35688421
C	-2.77671651	-1.01174377	-0.08649582
C	-3.45109989	-0.78424751	1.12265526
C	-4.68040696	-0.12958628	1.09029501
H	-5.20026291	0.04978302	2.02867120
C	-5.25281637	0.30944995	-0.10060039
C	-4.54330310	0.09851189	-1.28335715
H	-4.95816513	0.45469815	-2.22358696
C	-3.30853827	-0.54362152	-1.29943720
C	-2.85216560	-1.22060494	2.42754464
H	-3.10755417	-2.25853741	2.65386371
H	-3.21514022	-0.60367207	3.25319731
H	-1.76008820	-1.17067802	2.39932326
C	-6.59709232	0.97971638	-0.11393446
H	-7.40185523	0.24532176	-0.23079329
H	-6.68455870	1.68971391	-0.94038652
H	-6.78507073	1.52186876	0.81623855
C	-2.53379960	-0.70521946	-2.57104475
H	-1.55849514	-0.21452521	-2.48907963
H	-3.06889319	-0.26754518	-3.41623202
H	-2.34267967	-1.75672538	-2.79391783
C	2.77671576	-1.01174512	0.08649604
C	3.45109929	-0.78424851	-1.12265486
C	4.68040666	-0.12958787	-1.09029421
H	5.20026277	0.04978162	-2.02867027
C	5.25281627	0.30944735	0.10060147
C	4.54330290	0.09850882	1.28335811
H	4.95816515	0.45469420	2.22358815
C	3.30853777	-0.54362402	1.29943776
C	2.85216478	-1.22060531	-2.42754433
H	3.10755134	-2.25853841	-2.65386284
H	3.21514094	-0.60367348	-3.25319708
H	1.76008746	-1.17067628	-2.39932339
C	6.59709258	0.97971297	0.11393608
H	7.40185497	0.24531806	0.23079709
H	6.68455844	1.68971180	0.94038709
H	6.78507248	1.52186372	-0.81623758
C	2.53379920	-0.70522272	2.57104527
H	1.55849475	-0.21452839	2.48908055
H	3.06889288	-0.26754900	3.41623277
H	2.34267925	-1.75672878	2.79391771
C	1.59508465	2.03126507	-1.62101332
H	1.63152770	1.09624709	-2.15414910
C	2.32939429	2.32991155	-0.44411545
H	2.98130832	1.65244863	0.08207369
C	2.00863319	3.64291078	-0.04354148
H	2.39951833	4.15100953	0.82558491
C	1.09005844	4.17811039	-1.00360941
H	0.68841291	5.18022877	-1.00257097
C	0.81801467	3.17676595	-1.99002739
H	0.22883305	3.29044307	-2.88628755
C	-1.59508312	2.03126435	1.62101274
H	-1.63152648	1.09624602	2.15414789
C	-2.32939274	2.32991195	0.44411513
H	-2.98130702	1.65244964	-0.08207449
C	-2.00863128	3.64291139	0.04354217
H	-2.39951636	4.15101091	-0.82558380
C	-1.09005626	4.17810996	1.00361040
H	-0.68841041	5.18022822	1.00257268
C	-0.81801272	3.17676468	1.99002760
H	-0.22883098	3.29044093	2.88628779

2•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)
Sum of electronic and zero-point Energies= -2412.236443
Sum of electronic and thermal Energies= -2412.198128
Sum of electronic and thermal Enthalpies= -2412.197184
Sum of electronic and thermal Free Energies= -2412.310255

0 1

W	0.00000182	1.89716515	-0.00000080
Cu	0.00000008	-0.81579788	-0.00000286
N	1.45246477	-2.13818331	-0.19739667
C	1.26003454	-3.45039565	-0.15760174
C	-0.00000251	-4.04493821	-0.00000485
H	-0.00000350	-5.12786189	-0.00000511
C	-1.26003834	-3.45039345	0.15759298
N	-1.45246645	-2.13818071	0.19739004
C	2.44250064	-4.37368954	-0.29595937
H	3.12496865	-4.02089446	-1.07353722
H	2.12752700	-5.38673779	-0.54486721
H	3.00582072	-4.41683599	0.64031659
C	-2.44250574	-4.37368550	0.29595191
H	-3.12497055	-4.02089128	1.07353300
H	-2.12753330	-5.38673509	0.54485596
H	-3.00582895	-4.41682826	-0.64032230
C	2.72418056	-1.58417838	-0.24482958
C	3.10923299	-0.79681966	-1.33672273
F	2.32005986	-0.73131877	-2.41091163
C	4.27264559	-0.04635512	-1.32611366
F	4.58468718	0.72674377	-2.36726008
C	5.12087922	-0.09441807	-0.22733066
F	6.24450929	0.62224031	-0.21482369
C	4.78690955	-0.89345246	0.85801346
F	5.59147515	-0.93841786	1.91981582
C	3.60449495	-1.61770349	0.84242088
F	3.27719900	-2.32369923	1.93080494
C	-2.72418171	-1.58417469	0.24482716
C	-3.10923216	-0.79682071	1.33672435
F	-2.32005597	-0.73132276	2.41091118
C	-4.27264570	-0.04635746	1.32612133
F	-4.58468542	0.72673693	2.36727162
C	-5.12088206	-0.09441694	0.22734027
F	-6.24451300	0.62224021	0.21483899
C	-4.78691391	-0.89344611	-0.85800822
F	-5.59148176	-0.93840747	-1.91980902
C	-3.60449837	-1.61769568	-0.84242160
F	-3.27720400	-2.32368602	-1.93080962
C	1.94944827	1.60252015	1.30152710
H	2.67180985	0.83296725	1.08363179
C	0.81797962	1.45621775	2.14312918
H	0.54986876	0.56213422	2.68508593
C	0.07686946	2.67576650	2.13297186
H	-0.79320993	2.89552932	2.73143126
C	0.78654907	3.57724007	1.27010520
H	0.52181266	4.60713408	1.08667865
C	1.93695150	2.90194155	0.74138072
H	2.68244537	3.31201713	0.07728902
C	-0.81799314	1.45620630	-2.14311906
H	-0.54989859	0.56211291	-2.68506763
C	-0.07686462	2.67574493	-2.13297987
H	0.79321431	2.89548860	-2.73144688
C	-0.78652789	3.57723866	-1.27012122
H	-0.52177537	4.60713071	-1.08670684
C	-1.93693835	2.90196338	-0.74138505
H	-2.68242177	3.31205724	-0.07729280
C	-1.94945731	1.60253602	-1.30151529
H	-2.67182933	0.83299661	-1.08360749
H	-0.92341354	0.57454985	0.64904525
H	0.92341459	0.57454570	-0.64904306

4•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)
Sum of electronic and zero-point Energies= -1922.182510
Sum of electronic and thermal Energies= -1922.149022
Sum of electronic and thermal Enthalpies= -1922.148077
Sum of electronic and thermal Free Energies= -1922.251720

0 1

W	2.45814290	-0.42972708	-0.01617137
Cu	-0.16541908	-0.51296619	-0.04122148
H	1.14411057	-0.18611361	1.11272357
O	-1.13059535	-2.31836602	-0.01003682
C	-2.38614999	-2.35444555	-0.04237736
C	-3.31006190	-1.31384343	-0.07738602
H	-4.35257928	-1.58550109	-0.10758070
C	-2.99961523	0.06110442	-0.05798733
N	-1.79360509	0.56105266	-0.03345748
C	-2.93791423	-3.78703159	-0.03097069
F	-4.27848385	-3.85891393	-0.10011169
F	-2.56245041	-4.42163963	1.09345961
C	-4.20145600	1.01559206	-0.06360725
F	-5.37510420	0.37111474	-0.13936405
F	-4.24220541	1.76554037	1.05109382
C	-1.46714642	1.93696328	0.03826930
C	-1.25861748	2.52650025	1.29446780
C	-0.79560312	3.83953963	1.34305249
H	-0.63734526	4.29992849	2.31560558
C	-0.51132208	4.56753139	0.18915661
C	-1.45591927	1.72566286	2.54563702
H	-1.18936721	2.30718621	3.43024492
H	-0.83338377	0.82410114	2.52513728
H	-2.48896218	1.39169583	2.65708046
C	-0.04021486	5.99164031	0.26702352
H	-0.88202100	6.68939152	0.19603158
H	0.64933505	6.23207844	-0.54636654
H	0.47077503	6.19479076	1.21138530
C	1.97486351	-2.50518480	1.00485327
H	1.09746444	-2.65672024	1.61460087
C	3.23499704	-2.00897232	1.44114833
H	3.51697442	-1.79716039	2.46084873
C	4.08057954	-1.94989390	0.28180012
H	5.12646914	-1.68552509	0.27849571
C	2.12591968	1.89228561	0.24783852
H	1.25399672	2.30392293	0.73306706
C	3.33184168	1.47815886	0.88537627
H	3.56917917	1.59491915	1.93134707
C	4.20078450	0.99028466	-0.14622898
H	5.21898504	0.66136620	-0.00823622
C	3.51116453	1.07057572	-1.40143724
H	3.90141945	0.80796738	-2.37277143
C	2.23986094	1.64587231	-1.13846103
H	1.46472977	1.83222707	-1.86411509
F	-2.44743409	-4.48609823	-1.06861628
F	-4.15469882	1.85844788	-1.10951132
C	-1.15604057	2.63016246	-1.14105091
C	-0.68733431	3.93688950	-1.04120384
H	-0.44701441	4.47611851	-1.95475660
C	-1.28473328	1.94732307	-2.46898520
H	-0.87861167	2.56527273	-3.27274707
H	-0.76011754	0.98506659	-2.46653366
H	-2.32766121	1.72801934	-2.70714429
C	2.02872899	-2.72985050	-0.39037517
H	1.19332356	-3.06567544	-0.98558751
C	3.32242472	-2.37767308	-0.86004079
H	3.68077231	-2.48180655	-1.87257288
H	1.19327880	-0.57137490	-1.21517427

1•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -1874.372934
Sum of electronic and thermal Energies= -1874.337597
Sum of electronic and thermal Enthalpies= -1874.336653
Sum of electronic and thermal Free Energies= -1874.441857

0 1

Cu	0.00000000	-0.99187000	-0.00002700
N	1.46777300	0.26100000	-0.00003400
C	1.25375200	1.55796100	-0.00001300
C	0.00000000	2.18106000	-0.00000800
H	-0.00000100	3.25705500	-0.00000600
C	-1.25375300	1.55796000	-0.00000200
N	-1.46777300	0.26100000	0.00000700
C	2.45852800	2.50803800	0.00000800
C	-2.45853000	2.50803600	0.00000400
C	2.75090700	-0.35101900	-0.00001100
C	3.32519800	-0.73373800	1.21905800
C	4.52416700	-1.44079600	1.19444500
C	5.14955300	-1.79150800	0.00002800
C	4.52421200	-1.44078900	-1.19440800
C	3.32524100	-0.73373100	-1.21905900
C	-2.75090600	-0.35102100	0.00000700
C	-3.32522200	-0.73373300	-1.21905200
C	-4.52419200	-1.44079000	-1.19441800
C	-5.14955400	-1.79150800	0.00001000
C	-4.52418600	-1.44079700	1.19443500
C	-3.32521500	-0.73374000	1.21906500
C	0.69062300	-2.87552800	-0.00004700
C	-0.69061500	-2.87553100	-0.00003000
H	-1.26010300	-3.00008900	0.91692300
H	1.26013500	-3.00008500	0.91689000
H	1.26011100	-3.00007600	-0.91700000
H	-1.26012700	-3.00008500	-0.91696800
F	3.23244800	2.32418500	-1.08234800
F	3.23239400	2.32419700	1.08240800
F	2.09895100	3.80104100	-0.00001000
F	-2.09895300	3.80103900	0.00000500
F	-3.23242200	2.32419300	-1.08237600
F	-3.23242300	2.32418400	1.08238000
H	4.97810000	-1.73191500	-2.13885000
H	4.97802200	-1.73193100	2.13890000
H	-4.97806800	-1.73191800	-2.13886500
H	-4.97805400	-1.73193000	2.13888500
C	-6.46505500	-2.51696300	0.00001000
H	-6.57511100	-3.15064900	0.88363000
H	-7.30314000	-1.81111800	0.00006200
H	-6.57515300	-3.15057200	-0.88365800
C	-2.63031700	-0.42587900	-2.51129700
H	-1.60298600	-0.80787400	-2.50433100
H	-3.15471500	-0.87437400	-3.35704700
H	-2.55914000	0.64932100	-2.68715900
C	-2.63030300	-0.42589300	2.51130900
H	-2.55915500	0.64930700	2.68718900
H	-3.15468200	-0.87441600	3.35705600
H	-1.60296300	-0.80785900	2.50432500
C	2.63026300	-0.42589600	2.51129100
H	1.60293300	-0.80789400	2.50429900
H	3.15464400	-0.87439700	3.35704800

H	2.55908000	0.64930200	2.68715900
C	2.63035600	-0.42587600	-2.51131600
H	2.55918800	0.64932500	-2.68717700
H	3.15476700	-0.87437200	-3.35705700
H	1.60302500	-0.80786700	-2.50436500
C	6.46505400	-2.51696400	0.00005300
H	6.57516300	-3.15058500	-0.88360600
H	7.30314000	-1.81112000	0.00010500
H	6.57509900	-3.15063700	0.88368200

2•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2035.491352
Sum of electronic and thermal Energies= -2035.460395
Sum of electronic and thermal Enthalpies= -2035.459451
Sum of electronic and thermal Free Energies= -2035.556910

0 1

Cu	0.00000100	0.40654000	-0.08759100
N	1.45539000	-0.67230400	0.58102700
C	1.26502100	-1.77876600	1.29301600
C	0.00000000	-2.27135900	1.63491200
H	0.00000000	-3.16958900	2.23850600
C	-1.26502000	-1.77877100	1.29300800
N	-1.45538900	-0.67230800	0.58102100
C	2.46073100	-2.55680900	1.77256500
H	2.92975800	-3.08670400	0.93879500
H	2.17713100	-3.29438400	2.52208400
H	3.21432400	-1.89366400	2.20494300
C	-2.46073000	-2.55682300	1.77254400
H	-3.21433400	-1.89368400	2.20491200
H	-2.17713200	-3.29439300	2.52206900
H	-2.92974000	-3.08672300	0.93876900
C	2.74866700	-0.27611700	0.22632500
C	3.47613500	-0.92327600	-0.77315000
F	2.96624600	-2.01112800	-1.35749000
C	4.71441300	-0.46159400	-1.19244500
F	5.38388900	-1.10152500	-2.14919000
C	5.25533700	0.67963600	-0.61650500
F	6.44087300	1.13253700	-1.01577600
C	4.55108400	1.34865900	0.37546900
F	5.06491900	2.44634600	0.92707700
C	3.31971000	0.86587300	0.79013500
F	2.65605800	1.53164100	1.73805900
C	-2.74866700	-0.27612000	0.22632100
C	-3.31971200	0.86586300	0.79014300
F	-2.65606200	1.53162200	1.73807400
C	-4.55108600	1.34865000	0.37548000
F	-5.06492500	2.44633000	0.92709800
C	-5.25533700	0.67963600	-0.61650200
F	-6.44087300	1.13254000	-1.01576900
C	-4.71441100	-0.46158700	-1.19245400
F	-5.38388300	-1.10150900	-2.14920700
C	-3.47613200	-0.92327000	-0.77316100
F	-2.96624000	-2.01111600	-1.35751100
C	-0.69134400	1.98562400	-1.10968400
C	0.69133600	1.98563700	-1.10967200
H	1.25431200	1.60396900	-1.95737000
H	-1.25429800	1.60395200	-1.95739400
H	-1.24733900	2.60082300	-0.40793800
H	1.24730700	2.60084100	-0.40791400

4•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -1545.433648
Sum of electronic and thermal Energies= -1545.407330
Sum of electronic and thermal Enthalpies= -1545.406386
Sum of electronic and thermal Free Energies= -1545.493413

0 1

Cu	0.45722300	1.73292600	0.00002200
C	2.70695600	0.05535900	0.00000100
C	1.93941300	-1.10012200	0.00001800
H	2.46353800	-2.04148600	0.00002300
C	0.53063000	-1.13585300	0.00002300
N	-0.24684000	-0.08503400	0.00002100
C	4.23292900	-0.09591700	-0.00002000
C	-0.09902800	-2.53793000	0.00002300
C	-1.67014100	-0.12740600	0.00000200
C	-2.35338700	-0.04834300	1.21996400
C	-3.74272600	0.03709400	1.19450900
C	-4.45884300	0.06643300	-0.00003900
C	-3.74269100	0.03708500	-1.19456600
C	-2.35335300	-0.04835200	-1.21998100
C	0.18484500	3.72679400	-0.00000100
C	-1.02781300	3.06741300	0.00004200
H	-1.58731900	2.90542400	-0.91726000
H	0.62027200	4.10513700	-0.92080700
H	0.62032200	4.10517400	0.92076600
H	-1.58726900	2.90545600	0.91738000
F	4.75885500	0.49398600	1.08307300
F	4.75882000	0.49394700	-1.08315200
F	4.64087100	-1.37615600	-0.00000300
F	0.82334200	-3.51033800	0.00005100
F	-0.86779800	-2.73083700	1.08262500
F	-0.86775200	-2.73085600	-1.08260900
H	-4.27931300	0.08938500	2.13882500
H	-4.27925200	0.08937000	-2.13889800
C	-5.96011800	0.11653800	-0.00006100
H	-6.34556500	0.63100800	-0.88377900
H	-6.38608300	-0.89288000	-0.00002300
H	-6.34558800	0.63108200	0.88360400
C	-1.59623600	-0.01144400	2.51350800
H	-0.84789000	0.78937300	2.51050700
H	-2.26791500	0.15554300	3.35729200
H	-1.05341300	-0.94174400	2.69227400
C	-1.59616300	-0.01145600	-2.51350200
H	-1.05330900	-0.94174400	-2.69223700
H	-2.26782000	0.15550000	-3.35731000
H	-0.84783800	0.78938200	-2.51049200
O	2.34127100	1.26366700	-0.00000300

1•W_-61
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)

0 1

Cu	0.00000000	0.22902900	-0.00000100
W	0.00000200	-2.52395300	-0.00000100
H	-1.08863900	-1.20092300	-0.35249900
H	1.08864100	-1.20092100	0.35249500
N	1.49245600	1.58850000	0.01799100
C	1.25776400	2.87741700	-0.01595500
C	-0.00000200	3.49483100	-0.00000100
H	-0.00000300	4.56967500	-0.00000100
C	-1.25776800	2.87741400	0.01595400
N	-1.49245900	1.58849800	-0.01799100
C	2.44434300	3.86136700	-0.08450400
C	-2.44434800	3.86136200	0.08450200

F	3.23822800	3.76945000	0.99343900
F	3.20922700	3.63306400	-1.16311400
F	2.06042200	5.14255100	-0.15976800
F	-2.06042900	5.14254900	0.15976500
F	-3.23823200	3.76944600	-0.99344000
F	-3.20923200	3.63306200	1.16311400
C	2.80117000	1.03998700	0.05622600
C	3.41331500	0.79196000	1.29139500
C	4.65481600	0.16184300	1.30882100
H	5.12893900	-0.03096500	2.26842900
C	5.29844600	-0.23176000	0.14099600
C	4.64970500	-0.00286600	-1.07064200
H	5.12291100	-0.32449900	-1.99551600
C	3.40471000	0.61387300	-1.13620500
C	2.74077700	1.18650500	2.57851400
H	2.93925500	2.23242700	2.82211700
H	3.09982500	0.57748700	3.41166900
H	1.65416900	1.08509600	2.50887100
C	6.66027500	-0.87346000	0.18226800
H	7.44995800	-0.11787700	0.11858900
H	6.80350600	-1.56550300	-0.65128100
H	6.81368100	-1.42916200	1.11047500
C	2.69448400	0.78479900	-2.44935400
H	1.75088800	0.22969400	-2.44913800
H	3.30598400	0.41906200	-3.27670300
H	2.45068700	1.83073500	-2.64225500
C	-2.80117200	1.03998400	-0.05622400
C	-3.41331800	0.79195700	-1.29139200
C	-4.65481700	0.16183700	-1.30881800
H	-5.12894100	-0.03097200	-2.26842500
C	-5.29844600	-0.23176800	-0.14099200
C	-4.64970300	-0.00287100	1.07064500
H	-5.12290900	-0.32450600	1.99552000
C	-3.40471000	0.61387000	1.13620700
C	-2.74078300	1.18650300	-2.57851300
H	-2.93926500	2.23242300	-2.82211800
H	-3.09982800	0.57748200	-3.41166600
H	-1.65417400	1.08509900	-2.50887000
C	-6.66027400	-0.87347000	-0.18226100
H	-7.44995800	-0.11788800	-0.11857000
H	-6.80349900	-1.56552100	0.65128100
H	-6.81368400	-1.42916300	-1.11047400
C	-2.69448300	0.78479700	2.44935600
H	-1.75088700	0.22969300	2.44914000
H	-3.30598100	0.41906000	3.27670500
H	-2.45068800	1.83073200	2.64225500
C	-1.13551000	-2.11723400	1.99152000
H	-1.67578500	-1.20294500	2.17197500
C	0.20913200	-2.35910200	2.36290900
H	0.86869700	-1.65299100	2.83980200
C	0.55844500	-3.66067000	1.94983200
H	1.51728200	-4.13405400	2.09658900
C	-0.59999200	-4.24484800	1.34453200
H	-0.67822000	-5.25722300	0.97939300
C	-1.66065000	-3.28550600	1.35729700
H	-2.68163500	-3.44104800	1.04761400
C	1.13551500	-2.11723400	-1.99152300
H	1.67579200	-1.20294500	-2.17197700
C	-0.20912600	-2.35910100	-2.36291100
H	-0.86869100	-1.65299300	-2.83980600
C	-0.55844100	-3.66066800	-1.94983300
H	-1.51727700	-4.13405200	-2.09659100
C	0.59999600	-4.24484900	-1.34453200
H	0.67822400	-5.25722400	-0.97939400
C	1.66065500	-3.28550600	-1.35729700
H	2.68164000	-3.44104800	-1.04761300

1•tol

B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2067.255781
Sum of electronic and thermal Energies= -2067.216517
Sum of electronic and thermal Enthalpies= -2067.215573
Sum of electronic and thermal Free Energies= -2067.329044

0 1

Cu	-0.04579800	-0.57930900	0.49948600
N	-1.52461700	0.66296500	0.17309300
C	-1.28590100	1.93735500	-0.03765900
C	-0.02562200	2.54661800	-0.05455700
H	-0.01691400	3.61442700	-0.18545500
C	1.22503000	1.92318300	0.01908100
N	1.44643200	0.63671900	0.19328500
C	-2.46628900	2.87815400	-0.31676100
F	-3.08545200	2.55848700	-1.46638700
F	-2.09312000	4.16319500	-0.42567400
F	-3.38723800	2.83052400	0.65991300
C	2.42335000	2.87194800	-0.14140100
F	3.09646600	2.63745900	-1.28085700
F	2.06084200	4.16481800	-0.17142800
F	3.29493200	2.74647000	0.87296000
C	-2.80569400	0.06580500	0.08031600
C	-3.20187300	-0.49423600	-1.14248900
C	-4.40043500	-1.20019100	-1.19370100
H	-4.71316400	-1.62999300	-2.14248200
C	-5.19312800	-1.39042200	-0.06379600
C	-4.74532600	-0.86378700	1.14689400
H	-5.33444400	-1.02359300	2.04706800
C	-3.55950700	-0.14045500	1.24342600
C	-2.30804500	-0.39326200	-2.34021600
H	-2.74795500	-0.89727000	-3.20285600
H	-1.33840300	-0.86031100	-2.13319700
H	-2.10848100	0.64362600	-2.61601600
C	-6.49813600	-2.12968100	-0.14923500
H	-6.48808600	-2.87279400	-0.95055700
H	-7.32608400	-1.44203800	-0.35447400
H	-6.73034500	-2.64620100	0.78556400
C	-3.07794600	0.38390100	2.56249200
H	-3.60514300	-0.09060700	3.39261500
H	-3.22853900	1.46325800	2.64016500
H	-2.00426300	0.21340500	2.68652400
C	2.73795400	0.05620400	0.10533500
C	3.45589300	-0.22191200	1.27544000
C	4.69912600	-0.83993900	1.16117100
H	5.26353000	-1.04930800	2.06692400
C	5.23972300	-1.18619100	-0.07567900
C	4.47535700	-0.94406600	-1.21504700
H	4.85707300	-1.24856200	-2.18681800
C	3.21812800	-0.35200500	-1.14696900
C	2.89309600	0.14962000	2.61400500
H	2.91894700	1.23125900	2.76750500
H	3.45472400	-0.32061500	3.42364300
H	1.84294100	-0.14769200	2.70045800
C	6.60577400	-1.80242900	-0.17787800
H	6.67639000	-2.48579200	-1.02799000
H	6.86334800	-2.36158900	0.72505700
H	7.37443600	-1.03371700	-0.31471600
C	2.35818100	-0.20893000	-2.36676600
H	1.40590600	-0.73225000	-2.22628600
H	2.85149600	-0.62895200	-3.24540700
H	2.11602400	0.83356100	-2.58110900
C	-1.34141800	-3.43806400	-0.83869800
C	-1.77932900	-2.86868000	0.33746900

H	-2.83730800	-2.78249800	0.55289900
C	-0.83378200	-2.37986200	1.26361000
H	-1.17081300	-2.05047300	2.24241200
C	0.55189100	-2.53587700	1.00842100
H	1.27914400	-2.34581300	1.79318200
C	0.98676300	-3.17658100	-0.17881500
C	0.03037400	-3.58233900	-1.09592700
H	0.35253200	-4.06034600	-2.01710000
H	-2.06554300	-3.78721800	-1.56766600
C	2.43834900	-3.48983700	-0.37357600
H	3.07938900	-2.82925300	0.20888700
H	2.64447700	-4.51900400	-0.05727100
H	2.73335100	-3.40428700	-1.42091700

2•tol
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2228.370942
Sum of electronic and thermal Energies= -2228.336322
Sum of electronic and thermal Enthalpies= -2228.335378
Sum of electronic and thermal Free Energies= -2228.439612

0 1

Cu	-0.06406500	-0.21632900	0.31031400
N	-1.56279200	-1.15783500	-0.50735700
C	-1.40201300	-2.24819200	-1.24627700
C	-0.15017500	-2.78912700	-1.57013300
H	-0.17620200	-3.68013500	-2.18391200
C	1.13077800	-2.31563200	-1.25642500
N	1.35761000	-1.24579300	-0.50363700
C	-2.62328700	-2.94589100	-1.78264700
H	-2.35723400	-3.76738000	-2.44639100
H	-3.25761900	-2.24659000	-2.33469600
H	-3.22293800	-3.35016000	-0.96195200
C	2.30842100	-3.06526100	-1.81916600
H	2.90507300	-3.50042600	-1.01236200
H	2.96288900	-2.39208700	-2.38019100
H	1.99235700	-3.86962900	-2.48189900
C	-2.83336200	-0.64857300	-0.24242100
C	-3.61868300	-1.13108400	0.80573400
F	-3.20415700	-2.19682400	1.49649500
C	-4.80834900	-0.51936700	1.17085300
F	-5.53168500	-0.99889600	2.18132000
C	-5.24544800	0.60425200	0.48198900
F	-6.38159500	1.20352900	0.83110000
C	-4.48780700	1.10221100	-0.56944700
F	-4.89592100	2.18878300	-1.22503500
C	-3.30830500	0.46988900	-0.92999500
F	-2.59668200	0.96892500	-1.94314200
C	2.65489100	-0.78575600	-0.27814500
C	3.13357100	0.33270000	-0.96181400
F	2.39162100	0.87886200	-1.92642400
C	4.34247900	0.92581100	-0.63556800
F	4.75116800	2.02002500	-1.27980100
C	5.12009200	0.39328900	0.38262000
F	6.28360900	0.95660700	0.70211700
C	4.67662600	-0.72993300	1.06974400
F	5.42241900	-1.24437400	2.04682900
C	3.46070400	-1.30518400	0.73549300
F	3.03998500	-2.36847300	1.42615900
C	0.29539000	4.10620700	-1.10136800
H	0.84418100	3.76578600	-1.98500300
H	0.75304600	5.04604400	-0.77824200
H	-0.73153900	4.31499300	-1.40602800
C	0.35252300	3.07043900	-0.01882900
C	1.59216100	2.73565000	0.56642200
H	2.48655900	3.26137200	0.24547900
C	1.68569700	1.74491300	1.51670000
H	2.64550300	1.50012700	1.95946400
C	0.53430800	1.03602300	1.92410700
H	0.59667700	0.34197100	2.75697200
C	-0.72919700	1.40948200	1.40448300
H	-1.64564400	1.04415500	1.85887300
C	-0.79017700	2.42777100	0.42493300
H	-1.75482900	2.70959300	0.01613100

3•tol
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -3074.413957
Sum of electronic and thermal Energies= -3074.383967
Sum of electronic and thermal Enthalpies= -3074.383023
Sum of electronic and thermal Free Energies= -3074.476365

0 1

Cu	0.03354800	-0.05542300	-0.43492100
N	1.47743600	0.96146600	0.37006700
C	1.26964600	2.06774300	1.06885100
C	0.00200500	2.61801300	1.29862700
H	-0.00665000	3.55039900	1.84831900
C	-1.25717500	2.11243000	0.95442900
N	-1.44802700	0.98195000	0.28306800
C	2.45987900	2.77796100	1.65530000
C	-2.46216800	2.91173000	1.37624900
C	2.75590400	0.43347300	0.22263600
C	3.24905800	-0.54308200	1.10153900
C	4.46556400	-1.17804100	0.89582500
H	4.80284400	-1.92672700	1.60289400
C	5.22730600	-0.85019900	-0.21845900
C	4.77260600	0.10598800	-1.11911600
H	5.35273300	0.36913100	-1.99572100
C	3.55466400	0.72977100	-0.89172900
C	-2.73607700	0.50125000	0.07003400
C	-3.36648800	0.62454300	-1.17829000
C	-4.61881400	0.08570100	-1.43662300
H	-5.06278500	0.21207600	-2.41699200
C	-5.28828700	-0.59705200	-0.42852700
C	-4.69917200	-0.74942900	0.81997200
H	-5.20118100	-1.29334600	1.61138400
C	-3.43925500	-0.21730000	1.05062900
C	1.47833900	-3.13635400	-0.32757500
C	1.81652000	-2.17872700	-1.25912000
H	2.85381100	-2.00044500	-1.51798600
C	0.80133000	-1.41259200	-1.86922600
H	1.05456800	-0.73715600	-2.68140500
C	-0.56026600	-1.68644300	-1.58128500
H	-1.34490200	-1.25644800	-2.19756700
C	-0.89343000	-2.69289500	-0.64043800
C	0.13385500	-3.37752700	-0.01088000
H	-0.11157400	-4.13623900	0.72705100
H	2.25703100	-3.70667700	0.16811400
C	-2.32933700	-3.03405600	-0.37398500
H	-3.00727800	-2.33650600	-0.86610200
H	-2.56184100	-4.04034600	-0.73773400
H	-2.54962100	-3.01476800	0.69591000
H	-3.12864300	3.08150400	0.52601500
H	-3.03797600	2.37548100	2.13590600
H	-2.17291400	3.87748800	1.78899200
H	2.16706800	3.68805800	2.17750900
H	2.97954200	2.12584000	2.36370400

H	3.17778500	3.04067900	0.87311700
H	6.17817500	-1.34344300	-0.38823100
Cl	2.27415200	-0.98795200	2.46872000
Cl	2.96586800	1.89637200	-2.04099900
Cl	-2.53843600	1.49681800	-2.43734000
Cl	-2.67596900	-0.48743100	2.59019400
H	-6.26962400	-1.01734100	-0.61920500

1•Zn
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, Zn)
Sum of electronic and zero-point Energies= -3262.303859
Sum of electronic and thermal Energies= -3262.234184
Sum of electronic and thermal Enthalpies= -3262.233240
Sum of electronic and thermal Free Energies= -3262.412091

0 1

Zn	-1.13129200	0.85249900	0.48270900
Cu	0.88923900	-0.33503100	-0.27411600
H	-0.58905200	-0.09653300	-0.72678800
N	-1.98106600	0.49129300	2.19347500
C	-2.67710800	1.45033100	2.81061200
C	-2.99152100	2.69457300	2.25056400
H	-3.57641600	3.34794200	2.88590100
C	-2.81809200	3.13804500	0.92819700
N	-2.04449000	2.52139800	0.04640300
C	-3.25211200	1.17148300	4.17570200
H	-4.23996200	0.71049000	4.08929600
H	-3.36776300	2.10042800	4.73558100
H	-2.62840600	0.48208700	4.74486600
C	-3.61107800	4.34123800	0.49325900
H	-4.36039900	4.03388800	-0.24240500
H	-2.98821600	5.08991500	0.00139800
H	-4.12457700	4.80362900	1.33530800
C	-2.10371500	-0.84447600	2.68001500
C	-3.33030900	-1.51479100	2.50392400
C	-3.46662700	-2.80050600	3.02087400
H	-4.40636200	-3.32901200	2.89702700
C	-2.41297700	-3.42588100	3.67090400
H	-2.53580800	-4.42735700	4.07144200
C	-1.19035700	-2.78109300	3.77322300
H	-0.35791200	-3.29229800	4.24294200
C	-1.00769000	-1.49261600	3.27153300
C	-4.44134300	-0.92143900	1.66069000
H	-4.28089400	0.15539600	1.57378800
C	-4.34891900	-1.51225600	0.25142100
H	-4.53650300	-2.58971900	0.27193300
H	-3.35693500	-1.37025600	-0.18295900
H	-5.08375700	-1.05418200	-0.41671600
C	-5.83608200	-1.12666600	2.24828000
H	-6.13298900	-2.17929100	2.24363200
H	-6.57831800	-0.58121100	1.65862800
H	-5.89801500	-0.77053400	3.28018000
C	0.33830400	-0.81260100	3.37411800
H	0.41430500	-0.11808400	2.53021600
C	0.43015100	0.01180200	4.65939200
H	0.26662200	-0.62358200	5.53546000
H	-0.31844100	0.80739200	4.67498900
H	1.41395700	0.47665300	4.75980200
C	1.50244900	-1.79071300	3.24771300
H	1.40110400	-2.41825200	2.35933000
H	1.59115700	-2.44362400	4.12077700
H	2.44613800	-1.25036500	3.15912800
C	-1.93479700	3.00051100	-1.29224300
C	-1.06159700	4.07089300	-1.56785200
C	-0.91434800	4.48052300	-2.88938400
H	-0.24852800	5.30352700	-3.12404500
C	-1.60329200	3.84753200	-3.91733500
H	-1.47454400	4.17999600	-4.94285300
C	-2.44972100	2.79044600	-3.62976300
H	-2.98295800	2.29630000	-4.43617300
C	-2.63074800	2.34632800	-2.31835300
C	-0.26247100	4.70508700	-0.45025900
H	-0.88567400	4.71518100	0.44902100
C	0.15176800	6.14739800	-0.72625900
H	0.89904100	6.21198400	-1.52262900
H	0.60311900	6.58333900	0.16918800
H	-0.70101000	6.76996800	-1.01230300
C	0.95995200	3.85060500	-0.12858800
H	0.68687000	2.81479600	0.09163300
H	1.48833600	4.24495000	0.74010900
H	1.66383400	3.82352100	-0.96401600
C	-3.56298500	1.18493900	-2.04552700
H	-3.53825500	0.98093400	-0.97082500
C	-3.10356800	-0.07731800	-2.77360800
H	-2.10066400	-0.37790800	-2.46616500
H	-3.08184200	0.06955000	-3.85708500
H	-3.77214700	-0.91590400	-2.56978700
C	-5.00821800	1.53740500	-2.40266200
H	-5.68084400	0.71247900	-2.14906800
H	-5.11702900	1.73461900	-3.47326700
H	-5.34777800	2.42822700	-1.86723300
N	2.71451900	-0.07644300	0.26482400
C	3.49111500	-1.14796700	0.38597500
C	3.19053900	-2.46007300	0.02714000
H	3.94543400	-3.19555200	0.24433000
C	2.08068500	-2.91454200	-0.70908300
N	1.00339000	-2.21798300	-0.95233700
C	4.90477800	-0.96923500	0.96531200
F	4.88679600	-0.22560400	2.08583500
F	5.47015500	-2.14093500	1.30632600
F	5.74625800	-0.37809400	0.10171700
C	2.21992900	-4.32809800	-1.29203800
F	1.19736300	-5.12590400	-0.94720700
F	3.34022300	-4.94995300	-0.88717200
F	2.26337000	-4.28649500	-2.63510900
C	3.30904600	1.22019600	0.17894500
C	3.87879200	1.60085400	-1.04692000
C	4.47293800	2.85503500	-1.15088600
H	4.91820800	3.14418900	-2.10000800
C	4.52287500	3.73756300	-0.07528300
C	3.91921100	3.34557300	1.11501600
H	3.92115300	4.02718300	1.96287200
C	3.28389400	2.11472900	1.25409200
C	3.83608800	0.67407700	-2.22456600
H	4.46525300	-0.20701200	-2.07357600
H	4.17612300	1.17727400	-3.13155900
H	2.82174900	0.30540400	-2.39589500
C	5.15194200	5.09459700	-0.21152400
H	5.92512000	5.10400300	-0.98352200
H	5.61021400	5.42031700	0.72581200
H	4.40590500	5.84890800	-0.48754000
C	2.54663300	1.78281900	2.50983600
H	2.78987500	0.78547600	2.86958700
H	1.46421100	1.80581000	2.33584300
H	2.76797300	2.50021600	3.30241400
C	-0.07966800	-2.66590900	-1.75269300
C	-1.17408300	-3.28055300	-1.13111200
C	-2.26988400	-3.63586200	-1.91355600
H	-3.11553000	-4.12094100	-1.43232100
C	-2.31399900	-3.38386200	-3.28126000
C	-1.22947100	-2.72884400	-3.85976700
H	-1.25639200	-2.48635900	-4.91968900

C	-0.11605200	-2.34749600	-3.11743500
C	-1.16623300	-3.51308400	0.34569000
H	-0.37237900	-4.19979200	0.64629500
H	-2.11531100	-3.92183000	0.69126300
H	-0.99076300	-2.57993200	0.88650200
C	-3.49914100	-3.78959600	-4.11008500
H	-3.28210700	-4.68417400	-4.70396200
H	-3.78811400	-2.99990500	-4.80966800
H	-4.36596500	-4.01557000	-3.48443000
C	0.98523200	-1.54598600	-3.74220700
H	1.97341100	-1.94198800	-3.50470100
H	0.95569800	-0.51246100	-3.37783900
H	0.88190100	-1.51508400	-4.82851900

Zn
B3PW91 / GB3BJ / 6-311G* / SDDAll (Zn)
Sum of electronic and zero-point Energies= -1466.442646
Sum of electronic and thermal Energies= -1466.406823
Sum of electronic and thermal Enthalpies= -1466.405879
Sum of electronic and thermal Free Energies= -1466.510753

0 1

Zn	0.00000100	-0.00000600	-0.80012800
H	-0.00000300	-0.00001200	-2.34011100
N	1.45608300	-0.00000800	0.52174400
C	1.26303200	-0.00001000	1.83617300
C	0.00000000	-0.00001200	2.44290600
H	0.00000000	-0.00001300	3.52519500
C	-1.26303200	-0.00000800	1.83617200
N	-1.45608200	-0.00001000	0.52174300
C	2.46665100	-0.00000700	2.73973400
H	3.09386000	-0.87452900	2.54675900
H	2.17697500	-0.00001300	3.78984800
H	3.09385000	0.87452300	2.54676600
C	-2.46665100	-0.00000200	2.73973300
H	-3.09386600	-0.87451900	2.54675400
H	-3.09384400	0.87453400	2.54676700
H	-2.17697600	-0.00001300	3.78984700
C	2.78534500	0.00000100	0.00805600
C	3.41464000	-1.22429600	-0.27097700
C	4.68617100	-1.20106000	-0.84122400
H	5.18740100	-2.13618300	-1.07004100
C	5.32059900	0.00001700	-1.12531000
H	6.31095900	0.00002400	-1.57039300
C	4.68615400	1.20108600	-0.84122600
H	5.18737100	2.13621500	-1.07004500
C	3.41462300	1.22430500	-0.27097800
C	2.70356800	-2.53634200	-0.01077200
H	1.89213200	-2.33886000	0.69521100
C	2.06870000	-3.05285600	-1.30522000
H	2.83836600	-3.28044000	-2.04927800
H	1.40060600	-2.30904200	-1.74755600
H	1.49122300	-3.96453700	-1.12360000
C	3.60932400	-3.59402900	0.61747600
H	4.39037300	-3.92770500	-0.07180300
H	3.02615500	-4.47719000	0.89422500
H	4.10076700	-3.21739900	1.51890200
C	2.70353500	2.53634300	-0.01077500
H	1.89209100	2.33884800	0.69519600
C	3.60927300	3.59403400	0.61749100
H	4.39033300	3.92771500	-0.07177200
H	4.10070100	3.21740500	1.51892600
H	3.02609400	4.47719100	0.89423200
C	2.06867800	3.05285800	-1.30522700
H	2.83835100	3.28045500	-2.04927500
H	1.49118900	3.96453200	-1.12360900
C	-2.78534400	-0.00000200	0.00805500
C	-3.41462500	1.22430200	-0.27097600
C	-4.68615500	1.20108100	-0.84122500
H	-5.18737400	2.13621000	-1.07004300
C	-5.32059800	0.00001200	-1.12531200
H	-6.31095700	0.00001700	-1.57039600
C	-4.68616700	-1.20106400	-0.84122800
H	-5.18739500	-2.13618800	-1.07004800
C	-3.41463700	-1.22429900	-0.27098000
C	-2.70354000	2.53634100	-0.01077100
H	-1.89209500	2.33884600	0.69519900
C	-3.60928000	3.59402800	0.61749900
H	-4.39034200	3.92770700	-0.07176200
H	-3.02610300	4.47718600	0.89424000
H	-4.10070500	3.21739600	1.51893400
C	-2.06868500	3.05286000	-1.30522300
H	-1.40060600	2.30904300	-1.74757500
H	-1.49119700	3.96453300	-1.12360400
H	-2.83836000	3.28045800	-2.04926800
C	-2.70356300	-2.53634500	-0.01077600
H	-1.89212300	-2.33886000	0.69520200
C	-2.06870200	-3.05286100	-1.30522600
H	-1.40061100	-2.30904800	-1.74756700
H	-2.83837200	-3.28044600	-2.04928000
H	-1.49122400	-3.96454200	-1.12360800
C	-3.60931600	-3.59402900	0.61748000
H	-3.02614700	-4.47719200	0.89422300
H	-4.39037400	-3.92770100	-0.07179000
H	-4.10074800	-3.21739800	1.51891200
H	1.40059800	2.30904000	-1.74757700

3•Zn
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, Zn)
Sum of electronic and zero-point Energies= -4269.461984
Sum of electronic and thermal Energies= -4269.401776
Sum of electronic and thermal Enthalpies= -4269.400831
Sum of electronic and thermal Free Energies= -4269.557533

0 1

Zn	0.53654800	1.00928600	-0.26688600
Cu	-0.73532000	-1.04360500	0.10010500
H	0.29270000	-0.15104900	0.85862200
N	1.93260600	1.31683200	-1.57415900
C	2.16303500	2.54722900	-2.04373600
C	1.58099500	3.71449800	-1.54081600
H	1.89713900	4.63322700	-2.02061700
C	0.77327500	3.88394200	-0.40065800
N	0.20894900	2.87783400	0.24394900
C	3.17413100	2.71985200	-3.14775700
H	4.19177400	2.71177600	-2.74738700
H	3.02229400	3.66803700	-3.66399700
H	3.11496000	1.90255600	-3.86824100
C	0.62764900	5.29622600	0.10584500
H	1.55780600	5.59538800	0.59926100
H	-0.18045200	5.40252900	0.82731600
H	0.46328200	5.98922000	-0.72162800

C	2.87396400	0.29266700	-1.89120400
C	4.14320900	0.34007700	-1.27824000
C	5.08767800	-0.61998700	-1.62521000
H	6.06939100	-0.59785700	-1.16381000
C	4.78527900	-1.62367500	-2.53635400
H	5.53438100	-2.36330400	-2.80177600
C	3.51144600	-1.69806400	-3.07479900
H	3.26551800	-2.50710300	-3.75508700
C	2.53121700	-0.75671600	-2.75310900
C	4.43264200	1.32862000	-0.16588200
H	3.76028900	2.18312300	-0.27167300
C	4.11205700	0.65792800	1.17333700
H	4.77924200	-0.19166000	1.34407200
H	3.09152900	0.26856200	1.19392900
H	4.22907500	1.35889900	2.00514400
C	5.85908400	1.87242200	-0.17593500
H	6.59635200	1.10085400	0.06403900
H	5.96718600	2.66254800	0.57267000
H	6.12351200	2.29297100	-1.15015500
C	1.13851700	-0.90731900	-3.32056500
H	0.49549000	-0.17341900	-2.82700200
C	1.11448400	-0.60309400	-4.81889500
H	1.76776900	-1.28705300	-5.36978100
H	1.45132700	0.41673200	-5.02457100
H	0.10452100	-0.71251600	-5.22463000
C	0.57363900	-2.29475400	-3.01580600
H	0.59721800	-2.50504600	-1.94525800
H	1.13950200	-3.08299700	-3.52119900
H	-0.46406900	-2.36986400	-3.34240000
C	-0.63182400	3.06714200	1.37524400
C	-1.95103000	3.52397400	1.18461900
C	-2.78672800	3.60549100	2.29442800
H	-3.80620900	3.95398800	2.17328800
C	-2.33997200	3.23882900	3.55849600
H	-3.00940400	3.30389400	4.41068700
C	-1.04225600	2.78570800	3.72636700
H	-0.69832400	2.49937700	4.71532700
C	-0.16760800	2.68906800	2.64344400
C	-2.44659600	3.85257600	-0.20877100
H	-1.64370600	4.36811100	-0.74423900
C	-3.66089600	4.77552000	-0.23127700
H	-4.55568300	4.28005500	0.15726800
H	-3.88250200	5.07391500	-1.25961400
H	-3.49432900	5.68368200	0.35504600
C	-2.74708900	2.56359200	-0.96925800
H	-1.87482800	1.90753800	-1.02029200
H	-3.05943800	2.77641000	-1.99439400
H	-3.54614900	2.00864900	-0.47517900
C	1.25501700	2.21976400	2.85891400
H	1.70820500	2.07241900	1.87425000
C	1.32415400	0.88908900	3.60404400
H	0.74098100	0.11858500	3.09737000
H	0.94429200	0.97339600	4.62619900
H	2.35549300	0.53435200	3.66724000
C	2.07610000	3.30195500	3.56346200
H	3.11862600	2.98860700	3.67644300
H	1.67885000	3.50910200	4.56192400
H	2.06040400	4.23913700	3.00050800
N	-2.23194600	-1.70199500	-0.90207200
C	-2.37799600	-3.01371200	-1.12854300
C	-1.53169400	-4.01603200	-0.65028400
H	-1.76716600	-5.01777900	-0.98599300
C	-0.53372100	-3.93378000	0.33620900
N	-0.09777900	-2.78888400	0.82229800
C	-3.56809600	-3.46803700	-1.93535900
C	0.02974700	-5.22069600	0.87579200
C	-3.34243000	-0.88606700	-1.16187600
C	-4.34985400	-0.72845400	-0.19357500
C	-5.49513500	0.01995200	-0.42479200
H	-6.24299700	0.10328700	0.35482900
C	-5.66763900	0.64163700	-1.65494600
C	-4.68453200	0.53814500	-2.62777000
H	-4.78967200	1.03456900	-3.58508800
C	-3.53786300	-0.19948500	-2.36642800
C	0.78896600	-2.75154700	1.89571600
C	2.17472900	-2.63755400	1.70846500
C	3.05607900	-2.50086600	2.77189400
H	4.11823700	-2.42198400	2.57380900
C	2.56461700	-2.47115000	4.07019800
C	1.19929000	-2.57492000	4.30007700
H	0.79689800	-2.54529500	5.30565100
C	0.33483200	-2.70900500	3.22315900
H	1.12188700	-5.21562100	0.82369900
H	-0.34305500	-6.08489100	0.32674000
H	-0.24300300	-5.33864900	1.92899800
H	-3.50159800	-4.53036800	-2.16643800
H	-4.49569400	-3.30038600	-1.37951500
H	-3.65035000	-2.91109100	-2.87214500
H	-6.56318100	1.22183600	-1.84876100
H	3.24739800	-2.36145900	4.90575600
Cl	-1.37627300	-2.81485900	3.51752700
Cl	2.79654600	-2.67132900	0.08877800
Cl	-2.30159200	-0.26694900	-3.58496600
Cl	-4.15302900	-1.51829800	1.34083800

3•Al'

B3PW91 / GB3BJ / 6-311G* / SDDAll (Al)

Sum of electronic and zero-point Energies= -3809.216484

Sum of electronic and thermal Energies= -3809.163023

Sum of electronic and thermal Enthalpies= -3809.162079

Sum of electronic and thermal Free Energies= -3809.308120

0 1

Cu	-0.11894700	0.70176600	-0.59113500
Al	0.01460500	-1.52720700	0.54813400
H	-0.41023400	0.15488600	0.81338700
H	0.46155700	-2.38043700	-0.72038300
N	0.51422600	0.57795100	-2.39362700
C	0.42920200	1.57289700	-3.26987300
C	-0.11678600	2.82944300	-2.98585000
H	-0.13228600	3.52972600	-3.81110800
C	-0.55338300	3.33369700	-1.75360900
N	-0.62478200	2.60323600	-0.65256000
C	0.98003900	1.34938700	-4.65301000
H	2.06011500	1.17951100	-4.60956500
H	0.79378500	2.20650900	-5.29920900
H	0.53307100	0.46250100	-5.11042400
C	-0.93193500	4.78885000	-1.68209300
H	-1.95236600	4.90629100	-1.30683500
H	-0.86345000	5.26979900	-2.65734700
H	-0.27022000	5.31828000	-0.98970100
C	1.21884300	-0.58249700	-2.71853300
C	0.58362400	-1.72785300	-3.21160900
Cl	-1.13443400	-1.66788400	-3.47177700
C	1.26904100	-2.91281900	-3.43935800
H	0.73262700	-3.77495300	-3.81754500
C	2.62673500	-2.98013600	-3.15711900
H	3.16816600	-3.90506100	-3.32428600
C	3.29096500	-1.87252800	-2.64375000
H	4.34617200	-1.91319500	-2.40187900
C	2.58807000	-0.69621800	-2.43374700
Cl	3.40471500	0.68786200	-1.77190000

C	-0.96321800	3.17238600	0.56959600
C	-2.28578700	3.21219100	1.03528500
Cl	-3.54706200	2.65554400	-0.02449000
C	-2.61110400	3.66613100	2.30549500
H	-3.64833800	3.67577900	2.61930400
C	-1.60208600	4.10235200	3.15460000
H	-1.84786000	4.45600800	4.15001500
C	-0.27905700	4.09117300	2.72998400
H	0.51863600	4.43513700	3.37787300
C	0.02359100	3.63434500	1.45585800
Cl	1.67980300	3.60725000	0.92325200
N	-1.50653800	-2.28840400	1.43111000
C	-1.46830700	-2.95325500	2.58082500
C	-0.30512100	-3.09127400	3.35041000
H	-0.39432300	-3.67348400	4.25802300
C	0.94376500	-2.50368300	3.10631600
N	1.21127200	-1.78911600	2.01909100
C	-2.73660800	-3.57758000	3.08748000
H	-3.48063900	-2.81119000	3.31998100
H	-2.55586800	-4.16962100	3.98381000
H	-3.18444600	-4.21602400	2.32185100
C	2.02813300	-2.67953200	4.12991200
H	2.92744100	-3.10184700	3.67477200
H	1.70443200	-3.32741700	4.94348000
H	2.32260800	-1.71315700	4.54789800
C	-2.74592000	-2.05913200	0.75400200
C	-3.11076500	-2.88690700	-0.31463300
C	-4.27673200	-2.58520800	-1.01466200
H	-4.56401100	-3.21959000	-1.84954000
C	-5.07478600	-1.49479600	-0.67830400
C	-4.68654000	-0.69735800	0.39582300
H	-5.29397900	0.16049700	0.67057000
C	-3.52450400	-0.95231100	1.11837700
C	-2.26415800	-4.06677800	-0.69369100
H	-2.73100700	-4.63763000	-1.49820900
H	-2.10393300	-4.74048100	0.15368300
H	-1.27514900	-3.74994000	-1.03477500
C	-6.30082700	-1.15841100	-1.47842600
H	-7.08394800	-0.72461400	-0.85142500
H	-6.71426400	-2.04075200	-1.97268800
H	-6.06650300	-0.42604700	-2.25877700
C	-3.09917400	-0.04871600	2.23833500
H	-3.86468600	0.69931100	2.44694500
H	-2.17955900	0.48301000	1.98090900
H	-2.89558700	-0.59553500	3.16303000
C	2.48061800	-1.15256500	1.84539600
C	2.65899300	0.15236800	2.31888800
C	3.87143500	0.78802100	2.05852100
H	4.01263500	1.80624100	2.41071100
C	4.89139000	0.16096600	1.34969000
C	4.68426200	-1.14317400	0.90412400
H	5.47136400	-1.64651900	0.34771200
C	3.48830500	-1.81588800	1.13154500
C	1.56826800	0.84568200	3.08095200
H	1.21947600	0.25273300	3.93119000
H	0.69644400	1.02573800	2.44751600
H	1.90815200	1.81142000	3.45588600
C	6.16429000	0.88540900	1.02060900
H	6.14128800	1.25432500	-0.01078600
H	7.03606700	0.23168100	1.11103800
H	6.31899800	1.74673100	1.67421300
C	3.27256600	-3.21172600	0.62434300
H	2.99246500	-3.89986000	1.42767700
H	4.17727900	-3.59717800	0.15057000
H	2.46683500	-3.24159300	-0.11352200

Al'
B3PW91 / GB3BJ / 6-311G* / SDDAll (Al)

Sum of electronic and zero-point Energies= -1006.191522
Sum of electronic and thermal Energies= -1006.162912
Sum of electronic and thermal Enthalpies= -1006.161968
Sum of electronic and thermal Free Energies= -1006.251612

0 1

Al	0.00000000	-0.83590200	-0.00006100
H	-0.00000400	-1.68890600	-1.36934400
H	0.00000200	-1.68910800	1.36909600
N	-1.42297800	0.48415600	0.00003300
C	-1.25485700	1.80251100	0.00012000
C	0.00000000	2.42351700	0.00016300
H	0.00000000	3.50532000	0.00023500
C	1.25485700	1.80251100	0.00012100
N	1.42297800	0.48415600	0.00003500
C	-2.47304300	2.68322400	0.00017400
H	-3.09820200	2.48301500	-0.87367700
H	-2.19772300	3.73705600	0.00025100
H	-3.09821600	2.48289100	0.87398800
C	2.47304400	2.68322400	0.00017800
H	3.09821700	2.48288700	0.87398900
H	2.19772400	3.73705500	0.00025800
H	3.09820100	2.48301700	-0.87367600
C	-2.74819900	-0.05387700	-0.00000500
C	-3.37721500	-0.33064900	1.22016500
C	-4.65741200	-0.87898300	1.19575200
H	-5.15300200	-1.09461700	2.13935600
C	-5.31385200	-1.16126500	-0.00007700
C	-4.65741500	-0.87882300	-1.19586700
H	-5.15300500	-1.09433000	-2.13949900
C	-3.37721600	-0.33048400	-1.22020800
C	-2.68017000	-0.04204400	2.51771300
H	-3.31294500	-0.30377200	3.36779200
H	-2.41005100	1.01438700	2.61121800
H	-1.74921700	-0.61023000	2.59514900
C	-6.67921200	-1.78843500	-0.00011300
H	-7.25385400	-1.50047400	-0.88388300
H	-7.25391000	-1.50045300	0.88361400
H	-6.60826500	-2.88177300	-0.00009700
C	-2.68017700	-0.04170400	-2.51772000
H	-3.31294300	-0.30334600	-3.36783200
H	-1.74920700	-0.60985300	-2.59522300
H	-2.41008800	1.01474700	-2.61109700
C	2.74819900	-0.05387700	-0.00000300
C	3.37721500	-0.33048400	-1.22020800
C	4.65741300	-0.87882300	-1.19586700
H	5.15300300	-1.09433100	-2.13950000
C	5.31385200	-1.16126500	-0.00007700
C	4.65741300	-0.87898400	1.19575100
H	5.15300300	-1.09462000	2.13935500
C	3.37721500	-0.33064900	1.22016600
C	2.68017300	-0.04170800	-2.51771900
H	2.41003800	1.01473300	-2.61107700
H	1.74922700	-0.60989500	-2.59523800
H	3.31295500	-0.30330700	-3.36783200
C	6.67921300	-1.78843200	-0.00011900
H	6.60827000	-2.88177100	-0.00014700
H	7.25389800	-1.50048300	0.88362800
H	7.25386800	-1.50043500	-0.88386900
C	2.68017400	-0.04204300	2.51771400
H	2.41007900	1.01439400	2.61123000
H	3.31294000	-0.30379400	3.36779300
H	1.74920700	-0.61020800	2.59514100

2•Au
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, Au)
Sum of electronic and zero-point Energies= -3252.905995
Sum of electronic and thermal Energies= -3252.843988
Sum of electronic and thermal Enthalpies= -3252.843044
Sum of electronic and thermal Free Energies= -3253.008197

0 1

Au	-0.06491600	-0.63289000	-0.64595100
Cu	0.09419000	1.91667600	-0.84217000
H	-0.03850900	0.58621900	-1.80492900
N	1.66736000	3.03712100	-0.50860500
C	1.54536400	4.33242100	-0.23700000
C	0.31056000	4.97649500	-0.06054400
H	0.37993600	6.04133300	0.12667500
C	-0.99765700	4.46776800	-0.07528200
N	-1.29103100	3.20353400	-0.35611400
C	2.77306000	5.20285800	-0.14011100
H	3.17632500	5.19275900	0.87553700
H	2.53554000	6.23591700	-0.39484900
H	3.56081600	4.85415100	-0.81177500
C	-2.10853900	5.44462000	0.21472400
H	-2.97460900	5.25886300	-0.42533100
H	-1.77850100	6.47180800	0.06074900
H	-2.44050400	5.35122100	1.25223300
C	2.89759700	2.39876600	-0.55077800
C	3.77270500	2.32870300	0.53902800
F	3.47096500	2.96314100	1.68052200
C	4.94570100	1.59367100	0.49987200
F	5.74650300	1.55206800	1.57049000
C	5.27130200	0.86652800	-0.63229000
F	6.38720100	0.13278000	-0.66912500
C	4.41484600	0.89023100	-1.72303200
F	4.71577000	0.17781100	-2.81125700
C	3.26530300	1.65927600	-1.68552500
F	2.48787300	1.68319900	-2.76756400
C	-2.58667800	2.71261300	-0.27893600
C	-3.19865900	2.15127900	-1.40863900
F	-2.57051100	2.18993300	-2.58319900
C	-4.43869300	1.53889000	-1.34526900
F	-4.98394300	1.00050800	-2.43732300
C	-5.12650400	1.49110700	-0.14170000
F	-6.33055700	0.91419700	-0.07197200
C	-4.54623300	2.02735100	0.99530700
F	-5.17805500	1.92542000	2.17024200
C	-3.29718200	2.62157300	0.92184400
F	-2.74518300	3.07497400	2.05446400
C	-0.12423300	-2.29691500	0.50888900
N	-1.20200100	-3.08229700	0.73241300
C	-0.86946800	-4.17878200	1.50723700
H	-1.59996900	-4.91859100	1.78857600
C	0.45365300	-4.06700300	1.78133000
H	1.12360100	-4.68765500	2.35217900
N	0.88850700	-2.91011300	1.15727800
C	-2.51410100	-2.72347700	0.27761800
C	-2.85490100	-2.97456200	-1.05360700
C	-4.10978500	-2.53958900	-1.48047700
H	-4.41037400	-2.70376500	-2.50986500
C	-4.97057700	-1.88510000	-0.61347400
H	-5.93452800	-1.53887500	-0.96843900
C	-4.59888000	-1.64911300	0.70450800
H	-5.27924300	-1.12178100	1.36287500
C	-3.35704100	-2.06155700	1.17974700
C	-1.91938500	-3.67922200	-2.01224900
H	-0.98123800	-3.87969900	-1.48758000
C	-1.58582200	-2.79424400	-3.21391100
H	-2.47283500	-2.58209800	-3.81749800
H	-0.85306000	-3.28631400	-3.85968800
H	-1.16567200	-1.83790000	-2.89080000
C	-2.50041000	-5.02594100	-2.44835000
H	-2.71171900	-5.66671700	-1.58772600
H	-1.79896700	-5.55348900	-3.10131500
H	-3.43500900	-4.89609200	-3.00169900
C	-2.89906500	-1.73162200	2.58529100
H	-2.09637700	-2.42551400	2.85201100
C	-4.00339800	-1.89853500	3.62693800
H	-4.79730100	-1.15798000	3.49900900
H	-3.59541000	-1.75881500	4.63179500
H	-4.45714300	-2.89216300	3.57920900
C	-2.31688300	-0.31640400	2.62930300
H	-1.57984300	-0.15312700	1.83920900
H	-1.83631500	-0.12584400	3.59296200
H	-3.10720000	0.42405900	2.50542500
C	2.22042400	-2.38507900	1.24266000
C	2.48448100	-1.40606700	2.20570200
C	3.80202600	-0.96412500	2.31724400
H	4.05152300	-0.20221200	3.04771700
C	4.79539600	-1.47116200	1.49354900
H	5.81376100	-1.11550600	1.59784600
C	4.48688800	-2.39592900	0.50525000
H	5.26683900	-2.73705300	-0.16596000
C	3.18629900	-2.87173400	0.35480800
C	1.39805100	-0.79126500	3.06067400
H	0.45868500	-1.30751500	2.84747700
C	1.68241400	-0.95586900	4.55352000
H	1.80730600	-2.00819700	4.82374000
H	0.85716900	-0.54862800	5.14474000
H	2.59110000	-0.42513000	4.85115400
C	1.20985600	0.67935400	2.68197200
H	2.10419700	1.26609100	2.90061500
H	0.37717800	1.12109800	3.23489600
H	0.99747200	0.78956800	1.61426000
C	2.81395500	-3.78967600	-0.78950500
H	1.86355900	-4.27374000	-0.54327800
C	2.59155800	-2.94994200	-2.05261200
H	1.81978800	-2.19090000	-1.89305400
H	2.28058500	-3.58168200	-2.89004700
H	3.50849700	-2.42843600	-2.34077700
C	3.83975100	-4.89500800	-1.03067800
H	4.79097800	-4.49621900	-1.39338600
H	3.47300900	-5.58963700	-1.79134300
H	4.04034300	-5.46458000	-0.11910300

IPrAu–H
B3PW91 / GB3BJ / 6-311G* / SDDAll (Au)
Sum of electronic and zero-point Energies= -1295.908056
Sum of electronic and thermal Energies= -1295.876125
Sum of electronic and thermal Enthalpies= -1295.875181
Sum of electronic and thermal Free Energies= -1295.973170

0 1

Au	0.00000900	-0.00000600	-1.66095700
H	0.00002300	-0.00001400	-3.28481100
C	-0.00000300	0.00000400	0.39789900
N	1.06674600	0.00002000	1.23354300
C	0.67711400	0.00002000	2.56191300
H	1.39552000	0.00003200	3.36443700
C	-0.67713300	0.00000000	2.56190900

H	-1.39554300	-0.00000900	3.36442900
N	-1.06675700	-0.00000700	1.23353700
C	2.42431700	0.00002800	0.77843700
C	3.04868600	-1.23042500	0.55363300
C	4.36690000	-1.20444100	0.10141600
H	4.88339600	-2.13825800	-0.09483000
C	5.02038900	0.00003600	-0.11832700
H	6.04557900	0.00003900	-0.47576600
C	4.36685300	1.20450800	0.10130300
H	4.88331400	2.13832700	-0.09502900
C	3.04863800	1.23048400	0.55351600
C	2.31215500	-2.54187500	0.72144800
H	1.35806900	-2.33390600	1.21402100
C	1.99458300	-3.14093100	-0.65092400
H	1.42269100	-2.43630700	-1.26102300
H	1.40903000	-4.05897000	-0.54508400
C	3.07710100	-3.52627700	1.60568300
H	3.30680700	-3.09235400	2.58287700
H	4.02156900	-3.83429200	1.14817400
H	2.48446800	-4.43138800	1.76695600
C	2.31207000	2.54192700	0.72122500
H	1.35793400	2.33395700	1.21369900
C	3.07692000	3.52634600	1.60552800
H	4.02144600	3.83433500	1.14812400
H	3.30650400	3.09244500	2.58276000
H	2.48427700	4.43146800	1.76670600
C	1.99463700	3.14096100	-0.65118800
H	1.42281500	2.43632000	-1.26133300
H	2.91224700	3.38639300	-1.19446200
H	1.40906100	4.05899400	-0.54542100
C	-2.42432700	-0.00002200	0.77842400
C	-3.04870100	1.23042800	0.55361800
C	-4.36691300	1.20443600	0.10139400
H	-4.88341400	2.13825000	-0.09485300
C	-5.02039400	-0.00004500	-0.11835300
H	-6.04558200	-0.00005400	-0.47579800
C	-4.36685200	-1.20451300	0.10128000
H	-4.88330600	-2.13833500	-0.09505400
C	-3.04863800	-1.23048100	0.55350100
C	-2.31217800	2.54188100	0.72143700
H	-1.35810000	2.33392000	1.21402800
C	-3.07714200	3.52628900	1.60565000
H	-3.30687000	3.09237200	2.58284200
H	-4.02159900	3.83430400	1.14811900
H	-2.48451200	4.43140000	1.76693000
C	-1.99458400	3.14092800	-0.65093500
H	-2.91213400	3.38634600	-1.19431600
H	-1.42268000	2.43630100	-1.26101900
H	-1.40903600	4.05897000	-0.54509200
C	-2.31206500	-2.54192000	0.72121600
H	-1.35793600	-2.33394500	1.21370200
C	-1.99461200	-3.14095000	-0.65119300
H	-1.42278600	-2.43630700	-1.26133100
H	-2.91221400	-3.38638700	-1.19448000
H	-1.40903300	-4.05898100	-0.54542100
C	-3.07691900	-3.52634500	1.60550800
H	-4.02143700	-3.83434200	1.14809200
H	-3.30651900	-3.09244600	2.58273800
H	-2.48427200	-4.43146300	1.76669400
H	2.91214100	-3.38635800	-1.19428900

toluene
B3PW91 / GB3BJ / 6-311G*
Sum of electronic and zero-point Energies= -271.410471
Sum of electronic and thermal Energies= -271.405097
Sum of electronic and thermal Enthalpies= -271.404153
Sum of electronic and thermal Free Energies= -271.439428

0 1

C	-2.41343500	0.00000000	0.00935200
H	-2.79154400	-0.00002600	1.03775800
H	-2.82248000	-0.88353000	-0.48680300
H	-2.82248000	0.88355500	-0.48675800
C	-0.91092400	0.00000000	-0.01217700
C	-0.19434900	-1.19792300	-0.00889400
H	-0.73369300	-2.14163800	-0.01670600
C	1.19586200	-1.20093300	0.00212100
H	1.73304400	-2.14472600	0.00191200
C	1.89717500	0.00000000	0.00830900
H	2.98274000	-0.00000100	0.01376300
C	1.19586300	1.20093200	0.00212100
H	1.73304500	2.14472600	0.00191200
C	-0.19434900	1.19792300	-0.00889400
H	-0.73369200	2.14163900	-0.01670600

2•PCy_3
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2668.849810
Sum of electronic and thermal Energies= -2668.801190
Sum of electronic and thermal Enthalpies= -2668.800246
Sum of electronic and thermal Free Energies= -2668.933023

0 1

Cu	-0.17156700	1.00877700	-0.21830100
N	1.23007700	2.39177800	-0.01256800
C	0.99390300	3.69587700	-0.04010400
C	-0.29221200	4.23811900	-0.16664800
H	-0.34372700	5.31942200	-0.16548900
C	-1.52708500	3.57711200	-0.22623500
N	-1.65636400	2.25727800	-0.26683100
C	2.14750600	4.65446300	0.09367500
H	2.77314100	4.39001700	0.95102000
H	1.80422600	5.68052900	0.22084300
H	2.78166700	4.61574300	-0.79655200
C	-2.77166000	4.42507100	-0.22671200
H	-3.41115900	4.17762900	-1.07867000
H	-2.53332100	5.48702700	-0.27133100
H	-3.35676100	4.24517100	0.68034400
C	2.50842500	1.87630500	0.14632600
C	2.85663300	1.21954300	1.33257100
F	2.00937200	1.23973500	2.36598500
C	4.03263200	0.49993000	1.46049300
F	4.29575300	-0.16495500	2.58704200
C	4.93946900	0.46832400	0.40960200
F	6.07216500	-0.22582900	0.51861900
C	4.64747400	1.15080300	-0.76323300
F	5.50918700	1.11303600	-1.77974200
C	3.44729000	1.83330400	-0.88832000
F	3.16847000	2.42326000	-2.05497500
C	-2.91600300	1.66184100	-0.21976900
C	-3.57567300	1.25280400	-1.38051000
F	-3.04254500	1.53318100	-2.57198200
C	-4.75359200	0.52449600	-1.33172900
F	-5.34628400	0.12585800	-2.45864200
C	-5.30340700	0.17682900	-0.10621600
F	-6.41396600	-0.55813000	-0.05527800
C	-4.67879900	0.58311400	1.06513700

F	-5.20049200	0.24889100	2.24565900
C	-3.51518000	1.33271800	0.99899800
F	-2.93172400	1.71349300	2.13886300
P	0.27857300	-1.17240000	-0.12717100
C	0.42156800	-1.61051100	1.71036900
C	-0.64392800	-0.80666300	2.47898700
C	0.39739300	-3.07073200	2.14488400
H	1.40861400	-1.20258700	1.95533900
C	-0.84114200	-1.33987900	3.90575000
H	-1.59748800	-0.83335000	1.94558800
H	-0.34069200	0.24273900	2.50076100
C	0.85362400	-3.17277200	3.61316200
H	-0.61960400	-3.46233700	2.03441600
H	1.04153500	-3.69366200	1.52413200
C	0.45777900	-1.93578200	4.43597700
H	-1.61959100	-2.11254900	3.91452400
H	-1.20403700	-0.53657300	4.55285700
H	1.94037900	-3.30395300	3.64754500
H	0.42070500	-4.07462300	4.05914100
H	1.24619400	-1.17641800	4.37705200
H	0.36815100	-2.19869000	5.49404800
C	1.95317700	-1.55317000	-0.92001200
C	2.61490200	-2.89618200	-0.57869000
C	1.85919700	-1.33508900	-2.42796500
H	2.57491600	-0.75051800	-0.51659300
C	3.62065100	-3.31852000	-1.66241800
H	1.87241600	-3.68520100	-0.46254900
H	3.12234400	-2.80156600	0.38712000
C	3.26278500	-1.24598900	-3.04941400
H	1.29919800	-2.16366600	-2.87577100
H	1.29218500	-0.42486400	-2.64865700
C	4.28979700	-2.10288400	-2.29161900
H	3.10245700	-3.88649500	-2.44483100
H	4.36312200	-3.99844100	-1.23412500
H	3.59334900	-0.20438900	-3.06917900
H	3.20988100	-1.56566900	-4.09532500
H	4.76563100	-1.51487300	-1.50047000
H	5.09828000	-2.40464000	-2.96334900
C	-0.99406100	-2.29115900	-0.97920300
C	-0.67618100	-3.79170800	-1.07428500
C	-2.38541800	-2.07021300	-0.39248500
H	-1.00204400	-1.86529500	-1.98944000
C	-1.95028100	-4.62492100	-1.29645500
H	-0.18177100	-4.14331300	-0.16900300
H	0.02598700	-3.95804700	-1.89716000
C	-3.45222000	-2.60295500	-1.35980200
H	-2.45661300	-2.58054500	0.57401300
H	-2.55231600	-1.00971400	-0.19443700
C	-2.97325100	-3.85215200	-2.11985800
H	-2.39468700	-4.88543900	-0.32843300
H	-1.69252800	-5.57372700	-1.77665900
H	-3.71598400	-1.82349100	-2.07917400
H	-4.36704200	-2.82387500	-0.80040800
H	-2.51359600	-3.55789900	-3.07120900
H	-3.82465400	-4.48688300	-2.38124500

PCy_3
B3PW91 / GB3BJ / 6-311G* / SDDAll (P)
Sum of electronic and zero-point Energies= -711.845213
Sum of electronic and thermal Energies= -711.825054
Sum of electronic and thermal Enthalpies= -711.824110
Sum of electronic and thermal Free Energies= -711.894219

0 1

P	-0.08805100	-0.12919000	-1.23553700
C	1.19464700	-1.31228900	-0.43644500
C	2.46214600	-1.29328800	-1.31557500
C	1.57970700	-1.17551400	1.03332500
H	0.70130200	-2.28515700	-0.56160600
C	3.68428600	-1.88378400	-0.59477800
H	2.68664900	-0.27003500	-1.63076400
H	2.25776800	-1.84925400	-2.23598000
C	2.38706000	-2.40501900	1.49175400
H	2.17378100	-0.26483400	1.16610500
H	0.70364100	-1.06765000	1.67165400
C	3.25875000	-2.98648200	0.36707500
H	4.20158500	-1.09898400	-0.02905300
H	4.40821400	-2.25531600	-1.32675200
H	1.70061900	-3.17511300	1.86078000
H	3.01548700	-2.12314100	2.34403300
H	2.69713500	-3.74550400	-0.19110600
H	4.12791400	-3.50205300	0.78702400
C	-1.76079700	-0.78778800	-0.58188000
C	-1.88797800	-1.19950300	0.89228000
C	-2.87923300	0.17972500	-0.96431700
H	-1.88475000	-1.68526000	-1.20120300
C	-3.36018500	-1.25943100	1.34325900
H	-1.35380600	-0.50182200	1.53671400
H	-1.41383300	-2.17653500	1.03229900
C	-4.24943200	-0.51746800	-0.89099800
H	-2.85546900	1.03674600	-0.28133300
H	-2.71455500	0.58464300	-1.96762800
C	-4.27843700	-1.61968000	0.18085300
H	-3.66355500	-0.28357700	1.74224200
H	-3.47177000	-1.97075100	2.16769700
H	-4.49730100	-0.94833500	-1.86689200
H	-5.02455000	0.22754100	-0.67978400
H	-3.94976800	-2.57293500	-0.25070500
H	-5.30316700	-1.78380800	0.52817200
C	0.11574100	1.59193400	-0.41207700
C	-0.15629900	1.77906100	1.08902400
C	1.47743300	2.17954900	-0.78455900
H	-0.63763900	2.16288000	-0.96920300
C	0.50174500	3.05958600	1.63526000
H	0.20872000	0.92807100	1.66212600
H	-1.23778500	1.82187800	1.25292900
C	1.48621400	3.70523600	-0.58523600
H	2.24958800	1.71260000	-0.16266200
H	1.73164000	1.93633800	-1.82017000
C	0.56412700	4.14243400	0.56483200
H	1.52141800	2.83676800	1.97306900
H	-0.04018200	3.40937100	2.51968400
H	1.17733500	4.19959600	-1.51245100
H	2.51127500	4.03805200	-0.38784600
H	-0.44875000	4.32728300	0.18651200
H	0.90658800	5.09246700	0.98637400

2•CO
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, P)
Sum of electronic and zero-point Energies= -2070.250023
Sum of electronic and thermal Energies= -2070.219533
Sum of electronic and thermal Enthalpies= -2070.218589
Sum of electronic and thermal Free Energies= -2070.316198

0 1

N	1.45716600	0.70532500	-0.52325100
C	1.26590100	1.84414500	-1.18483600
C	-0.00000100	2.35159000	-1.49998000

H	-0.00000100	3.27701600	-2.06102200
C	-1.26590200	1.84414500	-1.18483600
N	-1.45716600	0.70532400	-0.52325100
C	2.45915900	2.64222700	-1.63621000
H	2.92544100	3.14554800	-0.78480600
H	2.17287900	3.40349600	-2.36051900
H	3.21552800	1.99717000	-2.09031300
C	-2.45916100	2.64222600	-1.63620800
H	-3.21553000	1.99716900	-2.09031200
H	-2.17288200	3.40349600	-2.36051700
H	-2.92544200	3.14554500	-0.78480300
C	2.75580500	0.29156800	-0.20079300
C	3.50599100	0.90734100	0.80140400
F	3.01186000	1.97743200	1.42997600
C	4.75555700	0.43522000	1.17246400
F	5.44968100	1.04638500	2.12998300
C	5.28157600	-0.68686100	0.54716500
F	6.47766400	-1.14907900	0.90011300
C	4.55302900	-1.32588600	-0.44722400
F	5.05517900	-2.40244400	-1.04764200
C	3.30992700	-0.83365100	-0.81332400
F	2.62176400	-1.46728900	-1.76468600
C	-2.75580500	0.29156700	-0.20079300
C	-3.30992700	-0.83365200	-0.81332300
F	-2.62176400	-1.46729100	-1.76468400
C	-4.55302900	-1.32588800	-0.44722200
F	-5.05517800	-2.40244600	-1.04764000
C	-5.28157600	-0.68686200	0.54716500
F	-6.47766400	-1.14907900	0.90011300
C	-4.75555800	0.43522000	1.17246300
F	-5.44968300	1.04638600	2.12998000
C	-3.50599200	0.90734100	0.80140300
F	-3.01186200	1.97743400	1.42997300
C	0.00000200	-1.98177500	0.96691000
Cu	0.00000000	-0.41628200	0.08122200
O	0.00000500	-2.97124900	1.52220900

CO
B3PW91 / GB3BJ / 6-311G*
Sum of electronic and zero-point Energies= -113.289972
Sum of electronic and thermal Energies= -113.287611
Sum of electronic and thermal Enthalpies= -113.286667
Sum of electronic and thermal Free Energies= -113.309092

0 1

C	0.00000000	0.00000000	-0.64393100
O	0.00000000	0.00000000	0.48294800

2•Octyne
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)
Sum of electronic and zero-point Energies= -2271.212399
Sum of electronic and thermal Energies= -2271.173097
Sum of electronic and thermal Enthalpies= -2271.172153
Sum of electronic and thermal Free Energies= -2271.286930

0 1

Cu	-0.00000300	-0.24559900	0.00001500
N	-1.43184400	-1.54340400	0.26461400
C	-1.24604700	-2.85857800	0.22370600
C	-0.00000200	-3.45653700	-0.00000500
H	-0.00000100	-4.53915700	-0.00000700
C	1.24604000	-2.85857400	-0.22371900
N	1.43183600	-1.54339900	-0.26462700
C	-2.42112000	-3.77619900	0.43112000
C	2.42111200	-3.77619600	-0.43114300
C	-2.71125500	-0.99715700	0.35809700
C	-3.04844500	-0.18159600	1.44156400
C	-4.20322700	0.58298300	1.45245900
C	-5.08646700	0.51533100	0.38344800
C	-4.80063300	-0.31620000	-0.68931100
C	-3.62847400	-1.05714400	-0.69442200
C	2.71124900	-0.99715500	-0.35810800
C	3.04843600	-0.18158000	-1.44156500
C	4.20321900	0.58299800	-1.45245700
C	5.08646400	0.51532900	-0.38345200
C	4.80063400	-0.31621500	0.68929800
C	3.62847400	-1.05715700	0.69440500
F	3.34057100	-1.78456700	1.77770400
F	6.19046700	1.25846300	-0.37857200
F	2.20578500	-0.07852800	-2.47248000
F	-2.20579900	-0.07856100	2.47248300
F	-4.46756000	1.38917400	2.47936200
F	-6.19046800	1.25846800	0.37857200
F	-5.62984500	-0.35935300	-1.73058800
F	-3.34056600	-1.78454000	-1.77772800
F	5.62985200	-0.35938500	1.73056900
F	4.46754700	1.38920100	-2.47935100
H	-2.09338200	-4.78164500	0.69314500
H	-3.01883100	-3.84460900	-0.48182700
H	-3.07367300	-3.40481200	1.22506500
H	3.07367400	-3.40479400	-1.22507400
H	3.01881400	-3.84463200	0.48180800
H	2.09337100	-4.78163300	-0.69319600
C	-0.68626500	1.66523500	0.08622600
C	-1.68262400	1.91762500	-1.01310400
H	-1.06465700	1.78610300	1.10236800
H	-1.17023500	1.93848600	-1.98142900
H	-2.40944100	1.10301100	-1.07190100
C	0.68627200	1.66522700	-0.08619900
C	1.68263600	1.91761600	1.01312700
H	1.06466200	1.78608400	-1.10234300
H	1.17024900	1.93848800	1.98145400
H	2.40944600	1.10299600	1.07192800
C	-2.45700000	3.21915300	-0.79599200
C	-3.56249400	3.40943000	-1.82565800
H	-1.76200300	4.06647800	-0.81839700
H	-2.89283200	3.20929900	0.21089500
H	-4.10608600	4.34376500	-1.66317600
H	-3.16076400	3.43155500	-2.84342600
H	-4.28980800	2.59277200	-1.77787400
C	2.45702200	3.21913600	0.79600400
C	3.56252300	3.40941100	1.82566300
H	1.76203200	4.06646700	0.81840600
H	2.89284900	3.20927200	-0.21088500
H	4.10612000	4.34374100	1.66317400
H	3.16079900	3.43154400	2.84343300
H	4.28983100	2.59274800	1.77787900

4-Octyne
B3PW91 / GB3BJ / 6-311G*
Sum of electronic and zero-point Energies= -314.236319
Sum of electronic and thermal Energies= -314.225606

Sum of electronic and thermal Enthalpies= -314.224662
Sum of electronic and thermal Free Energies= -314.273304

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C	-0.54276400	0.69065700	-0.38485400
C	-1.95423200	0.66927900	0.10925900
H	-0.41464200	0.68643800	-1.46944200
H	-1.96642500	0.75969100	1.20202300
H	-2.49435900	1.54484900	-0.27819000
C	0.54276400	0.69066000	0.38485300
C	1.95423300	0.66927800	-0.10925800
H	0.41464100	0.68644500	1.46944000
H	1.96642600	0.75968800	-1.20202300
H	2.49435800	1.54484900	0.27818800
C	-2.70892600	-0.59587100	-0.30893800
C	-4.15710800	-0.60168400	0.16215800
H	-2.17992000	-1.46987400	0.08819100
H	-2.67441100	-0.69299500	-1.40123300
H	-4.67644700	-1.51428900	-0.14364300
H	-4.21972400	-0.53615200	1.25323100
H	-4.71188700	0.24803500	-0.24892400
C	2.70892600	-0.59587100	0.30893900
C	4.15710800	-0.60168300	-0.16215800
H	2.17992100	-1.46987600	-0.08818900
H	2.67441200	-0.69299600	1.40123400
H	4.67644700	-1.51428900	0.14364100
H	4.21972200	-0.53615000	-1.25323100
H	4.71188700	0.24803500	0.24892500

Job cpu time: 1351 days 21 hours 8 minutes 42 seconds
File lengths (MBytes): NMR=   8790 Pub.=   2140 Pres.=   768.2
Normal termination of PhD at Thurs Jun 21 06:38:42 2018.