Tunable Binding of Dinitrogen to a Series of Heterobimetallic Hydride Complexes

Samantha Lau, a Andrew J. P. White, a Ian J. Casely, *a Mark R. Crimmin*, a

a Department of Chemistry, Imperial College London, South Kensington London, SW7 2AZ, UK.
b Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH, UK.

Abstract: The reaction of [Ru(H)(N2)2(PCy3)2] (1) with β-diketiminate stabilised hydrides of Al, Zn and Mg generates a series of new heterobimetallic complexes with either H2 or N2 ligated to the ruthenium centre. Changing the main group fragment of the M•Ru-N2 (M = Al, Zn, Mg) complexes can subtly alter the degree of binding, and therefore activation, of the diatomic ligand as evidenced by the v(N= N) absorptions in the infrared data. Experimental and computational data rationalise this tunable binding; decreasing the electronegativity of the main group from Al > Zn > Mg infers greater ionic character of these M•Ru-N2 complexes, this in turn results in greater destabilisation of the frontier molecular orbitals of ruthenium and therefore greater back-donation from Ru(4d) → π*(N2).

Introduction

Detailed understanding of the coordination of N2 at transition metal centers has paved the way for countless discoveries in dinitrogen fixation.1-3 End-on N2 binding can be considered within the Dewar-Chatt-Duncanson model (Figure 1a). Donation of electron-density from the filled bonding σ-orbital to a vacant orbital of suitable symmetry on the transition metal is accompanied by back-donation from the transition metal to the 1πg* anti-bonding orbitals of the diatomic. The back-donation is synonymous with lowering of the v(N= N) stretching frequency and is often associated with activation of N2 and catalytic methods for its transformation to NH3 (or related nitrogen containing molecules at the amine or hydrazine oxidation level).4,5

The extent of back-donation is a tuneable property. It can be regulated by the judicious control of the ligand environment at the transition metal. Modification of the oxidation state, coordination number, or geometry of the transition metal or the electronic or steric properties of the ligands all affect the symmetry and energy of the frontier orbitals (fMOs) of the transition metal fragment and influence the extent of back-donation. For example, as part of detailed investigations into N2 fixation with carefully designed trigonal bipyrimal group 8 complexes, Peters and coworkers have shown that the extent of back-donation to N2 is a function of both the metal and the σ-donating properties of the ligand trans to the N2 coordination site.6
More recently bimetallic complexes have been explored in dinitrogen fixation. For example, Lu and coworkers have reported a [Co–Co] bimetallic complex as a catalyst for the reductive silylation of \( \text{N}_2 \) with \( \text{Me}_3\text{SiCl} \).\(^7\) As part of these studies, it has been shown that \( \text{N}_2 \) binding to [Co–M] bimetallics can be subtly modulated by the choice of the second metal, with \( \nu_{\text{NeN}} \) decreasing across the first row period \( M = V > Cr > Co \) (\( \Delta \nu = 25 \text{ cm}^{-1} \)).\(^8\) In related studies, Thomas and co-workers have shown that modification of the early transition metal in [Co–M] complexes from \( M = Ti \) to \( Zr \) has an impact on \( \text{N}_2 \) binding to the late transition metal, again reported by the change in the \( \text{N}_2 \) stretch in vibrational spectroscopy (\( \Delta \nu = 39 \text{ cm}^{-1} \)).\(^9,10\)

![Dewar-Chatt-Duncanson Model for N\(_2\) binding and Tuneable N\(_2\) binding to heterobimetallic complexes](image)

**Figure 1.** (a) Dewar-Chatt-Duncanson Model for \( \text{N}_2 \) binding and (b) Tuneable \( \text{N}_2 \) binding to heterobimetallic complexes

Both these systems contain defined and quantifiable metal–metal bonds and \( \text{N}_2 \) coordination occurs at a site in line with the metal–metal bond maximising the prospect for bimetallic cooperation. Herein we demonstrate \( \text{N}_2 \) (and \( \text{H}_2 \)) binding to a series of Ru---M heterobimetallic hydride complexes (\( M = Al, Zn, Mg \)).\(^11\) These complexes possess weak metal---metal interactions at best; the main group metal sits in the secondary coordination sphere of a pseudo-octahedral ruthenium complex. A combination of characterisation techniques (single crystal X-ray diffraction and infrared spectroscopy) and calculations indicate that the variation of main group metal has an effect on \( \text{N}_2 \) activation with the more electropositive ligands resulting in a subtle but measurable increase in back-donation to the diatomic. We rationalise the results through detailed DFT calculations and ultimately show that the electronegativity of the main group metal impacts the energy of fMOs on ruthenium and, hence, dinitrogen binding.
**Results and Discussion**

**Preparation of N₂ and H₂ Complexes of Ru—M Heterobimetallics:** Reaction of [Ru(H)₂(N₂)₂(PCy₃)₂] (1)¹² with a series of the β-diketiminate stabilised hydrides of aluminium, zinc and magnesium under an atmosphere of H₂ proceeded at 25 °C over the course of 24 h to generate the new heterobimetallic dihydrogen complexes M•Ru-H₂ (M = Al, Zn, Mg, Scheme 1). The new dihydrogen complexes are only stable under an atmosphere of H₂ precluding their full characterisation in the solid state.

![Scheme 1. Preparation of dihydrogen and dinitrogen complexes of a series of heterobimetallic hydrides.](image)

In solution, the heterobimetallic dihydrogen complexes are characterised by a single broad resonance, integrating to five protons, in the hydride region of the ¹H NMR spectrum (Al, δ_H = −10.85 ppm; Zn, δ_H = −10.71 ppm; Mg, δ_H = −10.32 ppm). While low temperature ¹H NMR data acquired at 193 K failed to resolve the fluxional process that interconverts the hydride and dihydrogen ligands of M•Ru-H₂, the formulation of these complexes is supported by T₁-relaxation times, DFT calculations and D₂ exchange reactions. T₁ measurements were taken across a 193 - 293 K temperature range at 400 MHz and all three complexes exhibit short T₁(min) times (Al, 36 ms; Zn, 35 ms; Mg, 52 ms) indicative of non-classical hydrides.¹³ These species, and the related complexes described below, are highly unstable with decomposition beginning at temperatures above 40 °C. While these decomposition reactions have not been fully identified, typically the formation of free ligand and 1 is observed. In addition, for the aluminium analogue, two decomposition products have been identified through single crystal X-ray diffraction experiments. [Ru(H)(N₂)(Cl)(PCy₃)₂] (see supporting information, S1) and a heterobimetallic ruthenium-aluminium hydroxide (see supporting information, S2) are present in decomposition mixtures and are likely formed from a ligand exchange reaction in which the chloride exchanges from Al to Ru and a hydrolysis reaction respectively.
Exposure of $\text{M•Ru-H}_2$ to a $\text{N}_2$ atmosphere results in gradual formation of $\text{M•Ru-N}_2$ (Scheme 1). While ruthenium dinitrogen complexes are well known, and include [Ru(NH$_3$)$_3$(N$_2$)]$^{12}$ the first isolated dinitrogen complex, those incorporating main group metals are rare. Despite conducting reactions at modest pressures of $\text{N}_2$ (4 atm) and also bubbling $\text{N}_2$ through a solution of $\text{M•Ru-H}_2$, in all cases a mixture is formed and the position of the equilibrium could not be forced entirely toward the dinitrogen complexes. The ratio of the $\text{H}_2$: $\text{N}_2$ complexes after addition of $\text{N}_2$ (4 atm) was calculated to be 6 : 1 and 5 : 1 for the Zn and Mg heterobimetallic complexes respectively. The direct reaction of 1 with the $\beta$-diketiminate stabilised hydrides also results in the formation of a mixture of $\text{M•Ru-N}_2$ and $\text{M•Ru-H}_2$ and we ascribe this result to unavoidable decomposition of the hydride species leading to the generation of $\text{H}_2$ in situ. A third species was observed in these reactions at low concentration which has been tentatively assigned as $\text{M•Ru}$. The apical ruthenium site of $\text{M•Ru}$ is not occupied by a diatomic ligand and this is the expected intermediate in a dissociative exchange mechanism between $\text{M•Ru-H}_2$ and $\text{M•Ru-N}_2$. A further reaction of mixtures of $\text{Al•Ru-N}_2$ and $\text{Al•Ru-H}_2$ with CO provide additional evidence for ligand exchange occurring primarily with the apical site on ruthenium (for further details see the supporting information). Attempts to generate $\text{M•Ru}$ cleanly by carrying out reactions under an argon atmosphere or placing $\text{M•Ru-N}_2$/H$_2$ mixtures under vacuum lead to the onset of the previously mentioned decomposition.

$\text{M•Ru-N}_2$ display diagnostic hydride resonances for both bridging (Al, $\delta_{\text{H}} = -11.95$ ppm, fwhm = 113 Hz; Zn, $\delta_{\text{H}} = -11.40$ ppm; Mg, $\delta_{\text{H}} = -11.36$ ppm) and terminal (Al, $\delta_{\text{H}} = -15.81$ ppm, fwhm = 37 Hz; Zn, $\delta_{\text{H}} = -15.20$ ppm; Mg, $\delta_{\text{H}} = -15.69$ ppm) hydrides. Assignment of these hydrides was confirmed by calculation of the NMR spectra by DFT methods. The larger fwhm value for the resonance assigned to the bridging hydride, relative to the terminal hydride, in $\text{Al•Ru-N}_2$ is consistent with the bridging hydride coupling to the quadrupolar I = 5/2 $^{27}$Al nucleus. The T$_1$(min) relaxation times are all long (0.2 – 0.5 s) as would be expected in the absence of the dihydrogen ligand. The terminal hydride resonance of $\text{Mg•Ru-N}_2$ is sharp enough to resolve the cis couplings from the $^1$H NMR data at 298 K ($^2J_{\text{H,H}} = 9.4$ Hz; $^2J_{\text{H,H}} = 17.9$ Hz). $^3$P\{$^1$H\} NMR data collected on $\text{M•Ru-N}_2$ provide support for the cis-relation between the large PCy$_3$ ligands. At room temperature in toluene-$d_8$ two $^3$P resonances are observed in $\text{Al•Ru-N}_2$ ($\delta_{\text{P}} = 51.8$ and 38.5 ppm at 298 K) due to the chlorine atom on the aluminium centre leading to magnetic and chemical inequivalence of the phosphine ligands. At the same temperature, $\text{M•Ru-N}_2$ (M = Zn, Mg) display a single $^3$P NMR resonance (Zn, $\delta_{\text{P}} = 46.6$ ppm; Mg, $\delta_{\text{P}} = 45.6$ ppm). The three-coordinate Zn- and Mg- imparts a higher symmetry on the complexes and the cis-phosphine ligands are now chemically equivalent due to the higher symmetry. At lower temperature
the $^{31}$P resonance of $\text{M•Ru-N}_2$ decoalesces to two resonances ($\text{Zn}$, $\delta_P = 47.5$ and $43.8$ ppm at $253$ K; $\text{Mg}$, $\delta_P = 45.5$ and $42.8$ ppm at $233$ K) consistent with a further fluxional process that renders the phosphine ligands chemically inequivalent. Over the same temperature range the methyl and methine $^1$H resonances of the iso-propyl groups of the main group fragment decoalesce to a complex series of resonances. While we cannot unambiguously rule out the formation of isomers that differ in the coordination environment about ruthenium, the data are consistent with $\text{M•Ru-N}_2$ retaining cis-phosphine ligands but adopting a low symmetry due to a locked conformation of the $\beta$-diketiminate ligand. Hindered rotation about the N–CAr bond of these ligand systems is common. The main group fragments in these complexes appear tightly bound across $193 – 353$ K and no data have been collected that support bimetallic dissociation into the monometallic components.\textsuperscript{19,20}

The dinitrogen ligand was found to display a strong $\nu_{\text{N=NN}}$ stretching frequency ($\text{Al}$, $2160$ cm$^{-1}$; $\text{Zn}$, $2135$ cm$^{-1}$, $\text{Mg}$, $2130$ cm$^{-1}$) acquired on solid samples of $\text{M•Ru-N}_2$. These vibrational frequencies are consistent with that reported for $1$ and their assignment as N$_2$ and not H$_2$ stretches was confirmed by preparation of $\text{M•Ru-D}_2$ an isotopomer of $\text{M•Ru-H}_2$.

$\text{M•Ru-N}_2$ crystallise upon slow evaporation of concentrated hydrocarbon solutions under an N$_2$ atmosphere (Figure 2). The solid-state structures reflect the solution characterisation data and in the case of $\text{Zn•Ru-N}_2$ the data were of sufficient quality to locate the terminal and bridging hydride ligands from the electron density difference map. The geometry at ruthenium is a heavily distorted octahedron with the main group metal sitting in the secondary coordination sphere attached by bridging hydride ligands and 3-center,2-electron interactions. In the equatorial plane, the P–Ru–P angles are obtuse (X-ray = $104 – 107$ $^\circ$; DFT = $104 – 106$ $^\circ$) and the $\text{H}_\text{eq}$–Ru–$\text{H}_\text{eq}$ angles are close to $90$ $^\circ$ (DFT = $92 – 94$ $^\circ$). The length of the terminal Ru–H$_\text{ax}$ bond of $\text{Zn•Ru-N}_2$ (1.45(3) Å) is shorter than both the bridging Ru–$\text{H}_\text{eq}$ (1.62(3) and 1.70(2) Å) and bridging Zn–H bonds (1.82(3) and 1.88(3) Å). The Ru–M distances are short ($\text{Al}$, 2.443(2) Å; $\text{Zn}$, 2.4957(3) Å; $\text{Mg}$, 2.5974(19) Å) and could be interpreted as an indication of a metal--metal interaction.
Bonding Analysis of M•Ru-N₂: The metal---metal distances in M•Ru-N₂ are all within the sum of the single bond radii as defined by Pauling and only the Ru---Zn distance is longer than the sum of the covalent radii defined by Pyykkö. We, and others, have considered normalised metal---metal bond distances and the formal shortness ratio as a crude metric to interrogate the nature of metal---metal bonds. The fsr of M•Ru-N₂ determined using the Pauling radii are all ~1 and could be an indicator of a metal--metal bond (Al, 0.99; Zn, 1.00; Mg, 0.99). The presence of multiple bridging ligands is well known to contract metal---metal separations, however, to a point that the true nature of the bonding can become opaque. We have previously used the fsr as an indicator of metal--metal bonding, but only in combination with detailed spectroscopic (NMR, Infrared) and computational analysis (DFT, QTAIM) to support the conclusion.

To interrogate the position of the hydride ligands and gain insight into the electronic structure of M•Ru-N₂, a series of calculations were conducted using Gaussian 09. The oB97x-D functional was employed. Ru, Al, Mg and Zn centres were described with Stuttgart RECPs and associated basis sets, the 6-31++G(d,3pd) basis set was used for all hydrides, 6-31G* basis set was used to describe C and H atoms and 6-311+G* basis set was used to describe N, P and Cl atoms.

The calculations reproduce the position of the heavy atoms in M•Ru-N₂ and confirm the location and bond lengths of the hydride ligands in Zn•Ru-N₂. The bridging hydride ligands of M•Ru-N₂ are located in the equatorial plane of ruthenium and coordinate to the main group metal in a k²-binding mode through short Ru–Hₑq (DFT = 1.6 –1.7 Å) and long M–Hₑq distances (DFT = 1.8 – 1.95 Å). The location of the main group metal is not perfectly within the equatorial plane and slippage toward the axial hydride on ruthenium and the resulting k¹-binding mode is observed for the whole series. The effect can be
quantified by considering both the M---H\text{ax} distance from the DFT calculations (Al, 2.1 Å; Zn, 2.55 Å; Mg, 2.4 Å) and the N–Ru–M angle from the X-ray data (Al, 112.15(18)°; Zn, 95.64(8)°; Mg, 107.32(16)°) and is most pronounced for the aluminium analogue. For comparison, the Al---H\text{ax} distance is on the upper limit of the range suggested for a significant bonding interaction in analysis of σ-complexes of aluminium,\(^{11}\) and is slightly longer than Al–H distances (1.9 – 2.0 Å) in a related rhodium---aluminium heterobimetallic hydride that has been formulated with a κ\(^3\)-binding mode (Figure 3).\(^{32}\)

![Figure 3. Calculated bond lengths and angles in M•Ru-N\(_2\) along with selected NPA charges and WBI.](image)

NBO analysis in combination with QTAIM calculations reveal that, despite the short distances, metal–metal bonding in M•Ru-N\(_2\) is nominal at best. The Wiberg bond indices of the Ru---M interactions are small and decrease across the series Al (0.15) > Zn (0.07) > Mg (0.02). The WBIs of the Ru–H\text{ax} bonds are similar to the Ru–H\text{eq} bonds suggestive of a similar covalent character despite the bridging interaction. The M–H\text{eq} WBIs are much smaller and decrease across the series Al > Zn > Mg suggestive of decreasing covalent character as the main group metal becomes more electropositive. NPA charges on both these hydrides and ruthenium are negative while the main group metal is, expectedly, highly positive. The combined NPA charge on the ruthenium, hydride and dinitrogen moieties becomes more negative across the series Mg ~ Zn > Al. In combination the analysis is consistent with a large ionic component to the bonding and in the extreme these complexes could be formulated as [M][Ru-N\(_2\)] adducts in which the key interaction between the two fragments is via the bridging hydride ligands.
For comparison, in 2015 we reported a series of rhodium hydride complexes which possess similar \( \text{fsr} \) to those reported herein but with defined Rh–M bonds.\(^{23}\) The metal–metal bonding was supported by both calculations and spectroscopic data and crucially these complexes possess a four-legged piano-stool geometry at rhodium and long M–H distances (> 2.0 Å) that are conserved across a series (M = B, Si, Al, Zn, Mg). More recently Whittlesey, Macgregor and co-workers isolated a heterobimetallic complex in which Ru and Zn sites are bridged by two hydride ligands in a \( \kappa^2 \)-fashion.\(^{33}\) The bonding mode and computational analysis are near identical to that found for Zn•Ru–N\(_2\) and the authors of this study also concluded that no significant direct Ru–Zn interaction is found in this species.

**Tuneable N\(_2\) activation:** Experimentally determined \( \nu_{\text{NeN}} \) stretches for M•Ru–N\(_2\) decrease across the series Al > Zn > Mg. The calculated vibrational modes also follow this trend, and while the absolute values are systematically over-estimated compared to experiment, the differences relative to \( \nu_{\text{NeN}} \) of Al, \( \Delta \nu \), match closely (Table 1). The differences in the experimental N≡N and Ru–N bond lengths are very small and are well within the measurement error of the X-ray diffraction data. For comparison, the Raman stretch of free N\(_2\) is 2331 cm\(^{-1}\) and 1 shows two vibrational modes at 2163 and 2121 cm\(^{-1}\). Comparison of the latter vibrations with the heterobimetallic is complicated by the presence of IR active asymmetric and symmetric vibrations of the two coupled N\(_2\) ligands in 1, however broadly it can be seen that inclusion of the main group fragment only results in a slight perturbation of the N\(_2\) stretches consistent with the conclusion that the heterobimetallic influence is only subtle.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru–N (Xray)</td>
<td>2.004(6) Å</td>
<td>2.022(2) Å</td>
<td>2.011(6) Å</td>
</tr>
<tr>
<td>N–N (Xray)</td>
<td>1.086(7) Å</td>
<td>1.107(3) Å</td>
<td>1.088 (8) Å</td>
</tr>
<tr>
<td>N–N (DFT)</td>
<td>1.104 Å</td>
<td>1.106 Å</td>
<td>1.107 Å</td>
</tr>
<tr>
<td>WBI (DFT)</td>
<td>2.76</td>
<td>2.75</td>
<td>2.74</td>
</tr>
<tr>
<td>( \nu_{\text{NeN}} ) (IR)</td>
<td>2160 cm(^{-1})</td>
<td>2135 cm(^{-1})</td>
<td>2130 cm(^{-1})</td>
</tr>
<tr>
<td>( \nu_{\text{NeN}} ) (DFT)(^{[a]})</td>
<td>2342 cm(^{-1})</td>
<td>2320 cm(^{-1})</td>
<td>2311 cm(^{-1})</td>
</tr>
<tr>
<td>( \Delta \nu ) (IR)</td>
<td>0 cm(^{-1})</td>
<td>25 cm(^{-1})</td>
<td>30 cm(^{-1})</td>
</tr>
<tr>
<td>( \Delta \nu ) (DFT)</td>
<td>0 cm(^{-1})</td>
<td>21 cm(^{-1})</td>
<td>30 cm(^{-1})</td>
</tr>
</tbody>
</table>

\([a]\) Uncorrected values.

The molecular orbital analysis of some simplified models delivers an explanation for the tuneable N\(_2\) activation and the trend disclosed above. The frontier molecular orbitals of the square-based pyramidal transition metal fragment, \( \text{cis} \)-[Ru(H)\(_3\)(PMe\(_3\))\(_2\)]\(^{-}\) are represented in Figure 4a. The LUMO is
preferentially orientated to accept electron density from the $3\sigma_g$ orbital of $N_2$ while the HOMO and HOMO-2 are orientated in a fashion to back-donate to the degenerate and orthogonal $1\pi_g$ orbitals. The model was expanded to include the main group fragment and similar symmetry fMOs are calculated for model heterobimetallic complexes in which peripheral groups on the ligands have been truncated (see supporting information).

**Figure 4.** (a) Selected fMOs of cis-[Ru(H)$_3$(PMe$_3$)$_2$]$^-$ of relevance for $N_2$ binding, (b) energies of selected fMOs of model heterobimetallic complex.

Inspection of the energies of the fMOs of suitable symmetry for $N_2$ binding reveals that on decreasing the electronegativity of the main group metal ($\chi_m$ Al = 1.61 > Zn = 1.59 > Mg = 1.29) all the molecular orbitals of the model heterobimetallic complex are destabilised to a small extent (Figure 4b). The orbital destabilisation is a direct effect of the second metal on the ruthenium centre. This effect is not exerted through a metal–metal bond nor does it require a trans relationship between the second metal and the binding site, it occurs due to modulation of the degree of ionicity of the metal–hydride bonding and charge localisation on transition metal centre (Figure 3).

The heterobimetallic complex with the least electronegative main group metal, Mg, has the lowest covalent character to the bonding, the largest charge localisation on the transition metal fragment and hence the most destabilised fMOs. Destabilisation of the occupied molecular orbitals on ruthenium raises their energy and increases back-donation to $N_2$, populating the anti-bonding orbital of the diatomic and lower the $N_2$ stretching frequency. The degree of back-donation from ruthenium into $N_2$ can be examined by looking at the values obtained from second-order perturbation calculations on the complexes themselves $M\bullet Ru-N_2$. The most significant donor-acceptor contribution from Ru(4d) →
\[ \pi^*(N-N) \text{ increases from } \text{Al} = 20.0 \text{ kcal mol}^{-1} < \text{Zn} = 23.5 \text{ kcal mol}^{-1} < \text{Mg} = 24.6 \text{ kcal mol}^{-1} \text{ which mirrors the observed trend in the degree activation of } N_2 \text{ in these heterobimetallic complexes.} \]

**Conclusions**

In summary, we report the synthesis and characterisation of a series of ruthenium main group heterobimetallic complexes with X-ray structures obtained for the M•Ru-N\(_2\) complexes (M = Al, Zn and Mg). A small decrease in the \(\nu_{N=N}\) stretch, corresponding to weakening of the N–N bond, was observed from changing the main group metal of the heterobimetallic from Al < Zn < Mg. This trend can be rationalised due to the greater ionic character of the metal–hydride bonding within the M•Ru-N\(_2\) complex which becomes more pronounced with the less electronegative metal. The increased ionic character results in greater destabilisation of the fMOs of ruthenium which in turn allows for increased back donation from Ru(4d) \(\rightarrow\) \(\pi^*(N-N)\) and consequently longer N–N bond lengths. While the net effect on the \(N_2\) stretching frequency for the series of complexes reported herein is subtle, it clearly represents an example of a growing number of phenomenon in which the binding and reactivity of small molecules at a transitional metal centre can be modified by the proximity of a second metal.\(^\text{34-37}\)

**Conflicts of interest**

The authors declare that there are no conflicts of interest.

**Supporting Information.**

The Supporting Information is available free of charge on the ACS Publications website. The following files are available free of charge. Experimental procedures, details of the DFT studies, single crystal X-ray data and multinuclear NMR spectra (.pdf). X-ray crystallographic data for the series M•Ru-N\(_2\) M = Al, Zn, Mg (.cif). Full coordinates for calculated structures (.xyz)

**Corresponding Author**

m.crimmin@imperial.ac.uk
Acknowledgements

We are grateful to the EPSRC and Johnson Matthey for provision of a CASE Award and the Royal Society for a University Research Fellowship (UF090149). Johnson Matthey are also thanked for generous loans of precious metals. Stephen Bennett and Damian Grainger are thanked for productive discussions.

References

(13) Due to the Fluxional Process in Operation These Data Represent a Time-Average of Dihydrogen, Bridging Hydride and Terminal Hydride Ligands and as Such Are Likely to Be Longer Than the True T₁(Min) of the Dihydrogen Ligand.


(20) Hicken, A.; White, A. J. P.; Crimmin, M. R. Reversible Coordination of Boron-, Aluminum-, Zinc-, Magnesium-, and Calcium-Hydrogen Bonds to Bent [Cu₂]


