

Magnesium, Zinc, Aluminium and Gallium Hydride Complexes of the Transition Metals

Michael J. Butler and Mark R. Crimmin*

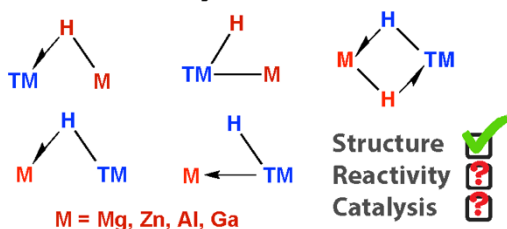
Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, U.K.

Tel: +44(0)2075942846.

E-mail: m.crimmin@imperial.ac.uk

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Heterobimetallic Hydrides



Abstract: The preparation and applications of heterobimetallic complexes continue to occupy researchers in the fields of organometallic, main group, and coordination chemistry. Interest that stems from the promise these complexes hold as precursors to materials, reagents in synthesis and as new catalysis. Here we survey and organise the state-of-the-art understanding of the TM–H–M linkage (M = Mg, Zn, Al, Ga). We discuss the structure and bonding in these complexes, their known reactivity, and their largely unrealised potential in catalysis.

Biographies



Mark R. Crimmin received his PhD in main group chemistry and catalysis from Imperial College London in 2008 supervised by Prof. Mike Hill (now at Bath) and Prof. Tony Barrett. In the same year, he moved to UC Berkeley to study with Prof. Bob Bergman. and Prof. Dean Toste. In 2011, he returned to London as a Royal Society University Research Fellow, initially at UCL and now back at Imperial. Work in the Crimmin group focuses on new methods to break strong carbon–fluorine, carbon–oxygen and carbon–hydrogen bonds in small molecules and the development of heterobimetallic complexes for catalysis.



Michael J. Butler was born in Tottenham, London in 1989 and in 2012 graduated with an MSci from the University of Glasgow. These studies included a year at Bayer Crop Science AG (Frankfurt am Main), working under Dr. Klemens Minn. After some time studying surface chemistry at Sika AG in Zurich, he began an organometallic chemistry PhD in the Crimmin group in 2013.

1. Introduction

The catalytic practices of C–H bond functionalisation, dehydrocoupling (for hydrogen storage), hydroboration and hydrosilylation are all attractive prospects for the future chemical economy. The modern development in these methodologies continues to be enhanced by the perception of borane and silane σ -complexes as intermediates in reaction mechanisms (Figure 1).

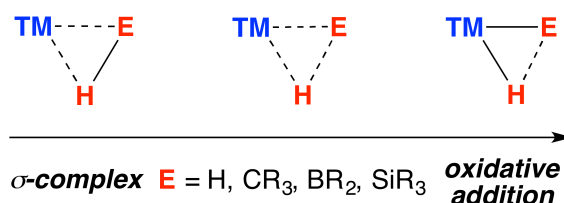


Figure 1. The continuum between σ -complex and oxidative addition for the coordination of E–H bonds to a transition metal.

A σ -complex can be described as an η^2 -binding of the σ -E–H bond to a transition metal centre ($E = C, Si, B, H$).^{1,2} Along with dihydrogen complexes,^{3–6} σ -silanes are the most comprehensively studied type of this bonding mode.^{7–12} While the latter appear as potential intermediates in alkene hydrosilylation via the Chalk–Harrod mechanism,^{13,14} the former bear significance for a range of industrially relevant hydrogenation reactions.^{15,16} In C–H borylation, stabilisation of catalytic intermediates by a TM–H–B (TM = transition metal) interaction has been supported by significant experimental mechanistic studies.^{17–19}

A 3-centre 2-electron interaction, the η^2 -ligation of E–H to TM can be viewed within the Dewar–Chatt–Duncanson model and interpreted as a combination of: i) donation of the σ -electrons in the E–H bond to a vacant orbital on the transition metal and ii) back-donation from the metal into the σ^* -orbital of the same E–H bond. The resulting σ -E–H adduct represents an intermediate along the oxidative addition reaction coordinate (Figure 1) – part of a continuum of bonding descriptions between free E–H and E–TM–H. It is clear that the nature of the bonding in TM–H–E containing complexes is a tuneable property, being a consideration of the symmetry and energy of the frontier orbitals of the transition metal fragment along with the substituents on, and nature of, E.

A fundamental question that arises when considering this model, is: what happens when C, B and Si are replaced by metallic main group elements such as Mg, Zn, Al, or Ga? The increased ionic contribution within the TM–H–M interaction will necessarily give another dimension to the bonding description. As with silicon, the ability of these elements to expand their coordination sphere leads to the possibility of forming additional bonding interactions with existing ligands on the TM fragment. Furthermore, for the heavier group 13 elements the formation of low-valent M^I ligands through manifestation of the inert-pair effect becomes an important consideration.

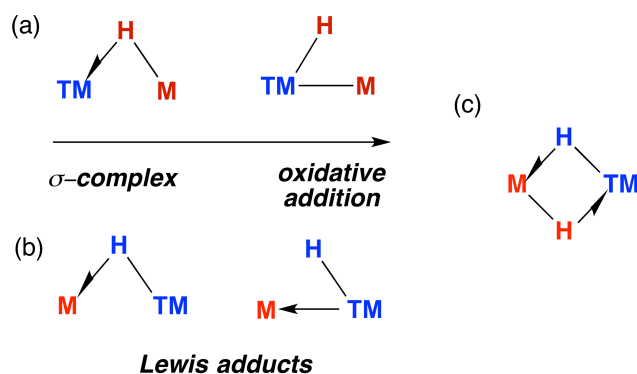


Figure 2. (a) The continuum for addition of M–H to a transition metal. (b) Lewis adducts between a TM hydride and M, (c) combination of interactions.

The TM–H–M motif is one way of adjoining two metal centres bearing at least one reactive hydride ligand (Figure 2a). This motif can also be obtained by coordinating a transition metal hydride to a neutral main group metal fragment (Figure 2b), and multiply bridged species formed by a combination of the two aforementioned donor-acceptor interactions (Figure 2c).

Herein we survey the known heterobimetallic complexes of transition metal and main group hydrides (M = Mg, Zn, Al, Ga). The coordination chemistry of heterobimetallic transition metal hydrides,^{20–22} and of Al, Ga, In and Zn-based ligands at transition metal centre have been summarised previously.^{23–26} To focus the discourse, a loose definition ‘heterobimetallic hydride complexes’ is employed. The complexes mostly fit these criteria: (a) crystallographically characterised; (b) 1:1 ratio of transition:main group metal; (c) the absence of TM---TM interactions; (d) a hydride ligand in a bridging role. The survey is arranged: $\text{TM} \leftarrow \text{H}-\text{M}$, $\text{TM}-\text{H} \rightarrow \text{M}$, $\text{TM}-\text{H}_n-\text{M}$ ($n > 1$).

The half-arrow notation and covalent bond classification advocated by Green, Green and Parkin are used to represent the TM–H–M 3-centre 2-electron interactions.¹¹ This formalism is employed as an organisational principle not as an absolute interpretation of the bonding within TM–H–M units. The line drawings are constructed from the perspective of the transition metal coordination environment in order to represent charge neutral species rather than an accurate representation of the bonding within the TM–H–M group. The literature survey is followed by discussion of the “continuum” of bonding descriptions, reactivity and the potential these complexes hold for catalysis.

2. σ -Complexes ($\text{TM} \leftarrow \text{H}-\text{M}$)

We have reported **1**, a Zn congener of structurally related σ -alane complexes (Figure 3).²⁷ The binding of the zinc hydride to the Cu^{I} centre is weak and reversible. In toluene or benzene solution, an equilibrium exists between the heterobimetallic complex and the η^2 -arene complex of Cu^{I} . The electronic structure of the three-centre linkage has been investigated by DFT calculations. The analysis suggests that the formal L donation of the M–H σ -bond to the 4s orbital on Cu^{I} is accompanied by weak $\text{Cu} \rightarrow \text{M}$ back-donation into the M–H σ^* -orbital (see discussion section). In

combination, the data allow **1** to be described as a weakly bound σ -complex.

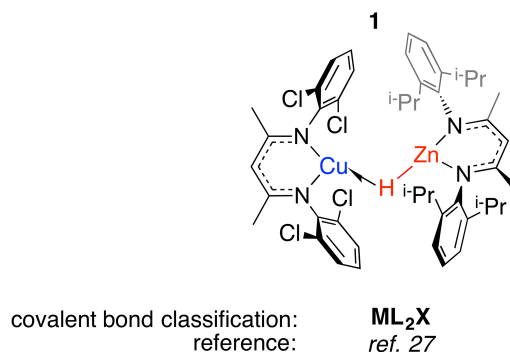


Figure 3. A σ -zincane complex of Cu^I

Coordination of Al–H bonds to Cu^I has also been examined; complexes possessing four-coordinate and five-coordinate aluminium centres have been isolated (Figure 4, **2** and **3**). The binding of Cu–H–Al is again weak and reversible based on solution NMR studies and crossover experiments. In DFT calculations, the coordination of exogenous ligands to the Cu^I fragment was found to be increasingly exergonic across the series C₆F₆ < H–B < H–Si < C₆H₆ < H–Zn < H–Al – a trend that is manifest in the experimental data.²⁷

In **2** the Cu---Al vector lies outside of the H–Al–H wedge – the only example of this structural feature we are aware of in main group metal σ -complexes.²⁷ The ‘lee side’ coordination of the Al–H bond and very long intermetallic distance in **2** are notable. For comparison, σ -complexes of HBpin (pinacolborane) or HBcat (catecholborane) show different coordination geometries to those of four-coordinate boranes BH₃•EMe₃ (E = N, P).^{28,29} The discrepancy has been rationalised by disruption of the TM---B back-donation due to the absence of a vacant orbital of suitable energy in BH₃•EMe₃, be it the boron p-orbital or the σ^* -orbital of the B–H bond.²⁸ While steric factors are undoubtedly important, a similar effect may explain the solid state structures of **2** and **3**. DFT calculations are consistent with reduced back-donation from d¹⁰ Cu^I into the Al–H σ^* -orbital of the five-coordinate species when compared to the four-coordinate analogue.²⁷ Higher nuclearity species containing Cu–H–Al interactions are known and the intermetallic cluster [(Cp*AlCu)₆H₄] has been obtained from reaction of [Cp*Al]₄ with [Ph₃PCuH]₆.³⁰

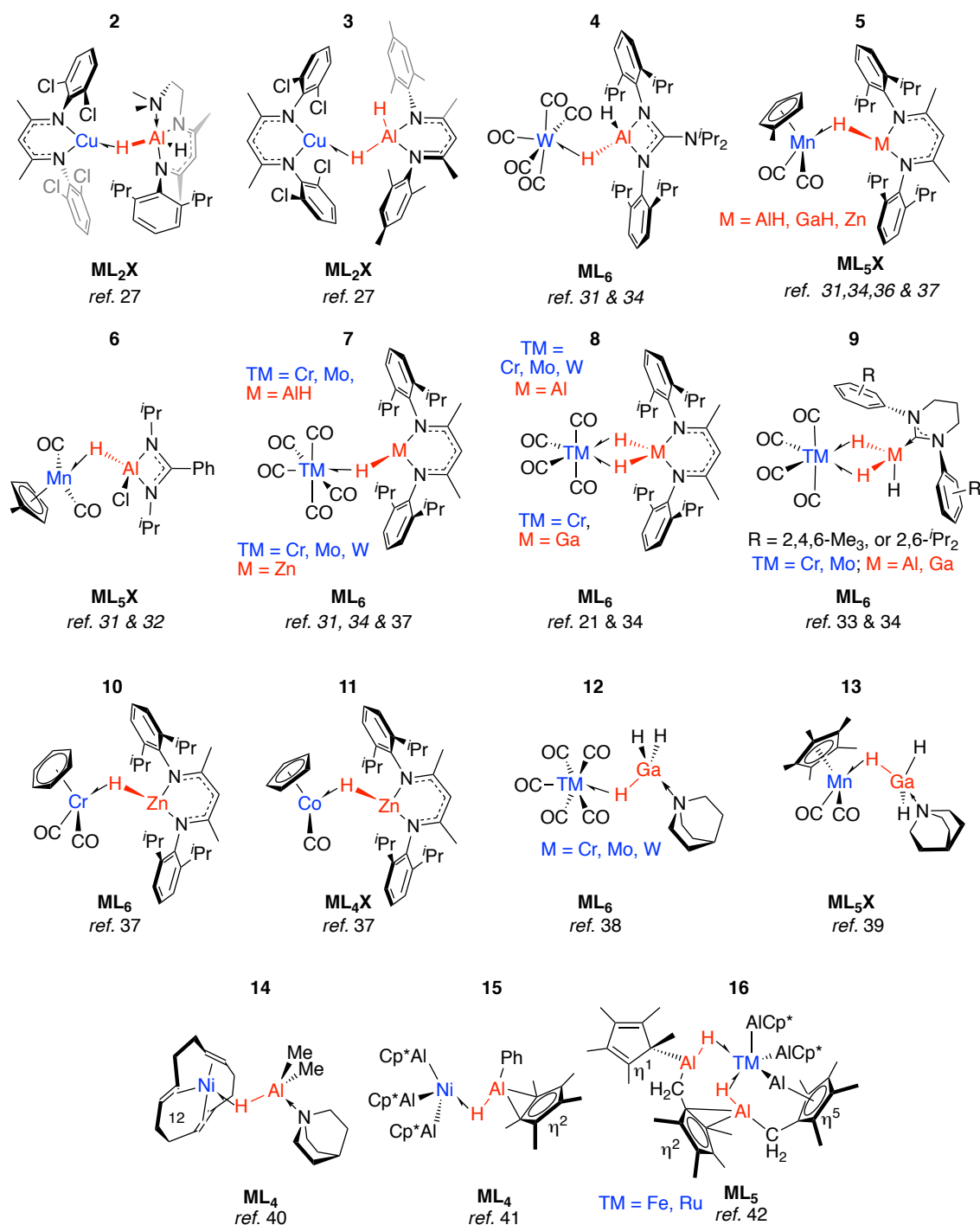


Figure 4 (double column). σ -Alane, σ -gallane and σ -zincane complexes of late TM.

Aldridge and co-workers pioneered this area of research and have isolated a series of σ -alane and σ -gallane complexes of groups 6 and 7 transition metal carbonyls.³¹⁻³⁵ Like **2** and **3**, the structures of **4–7** contain σ -Al–H adducts and derive from ligand exchange reactions, in this case from the parent metal carbonyl under either thermal or photochemical conditions. Four-electron, $\eta^2:\eta^2$ -coordination of H–Al–H (**8–9**) requires a 14-electron transition metal fragment, $\{\text{M}(\text{CO})_4\}$ and necessitates displacement of two ligands from ML_6 starting materials.^{31,33,36} Complexes **7-Cr/Al** and **8-Cr/Al** have not been separated and, like their heavier congeners, **7-Mo/Al** and **8-Mo/Al** were

isolated in an approximate 9:1 mixture with the minor component containing the $\eta^2:\eta^2$ -coordination mode.³⁴ The adduct **8-W/Al** could not be obtained by photoejection of CO from $[\text{W}(\text{CO})_6]$ and was finally obtained under thermal conditions using $[\text{W}(\text{CO})_4(1,5\text{-COD})]$ as a precursor (COD = cyclooctadiene).³⁴ The M---Al distance in **8-W/Al** is shorter than would be expected based on the lighter members of the series, presumably due to a tighter binding of the σ -alane to the more expanded 5d orbitals of W. In contrast to the W analogue, **8-Cr/Al** may be formed directly upon heating **7-Cr/Al**: Eyring analysis and the first order kinetics of this reaction have led Aldridge and co-workers to suggest it proceeds by an associative pathway.³⁴

All TM-H-Al heterobimetallic complexes characterised by Aldridge and co-workers show slow exchange between the bridging and terminal hydride ligands on the NMR timescale at ambient temperature.^{31-34,36} From structural and spectroscopic evaluation of these complexes (**4-9**), it appears that back-donation into the M-H σ^* orbital is negligible. While the close TM---M contacts (especially in **9-Ga**) are short enough to hint at TM-M interaction, the four-membered ring imparted by the $\eta^2:\eta^2$ -coordination mode in **8-9** demands such a short contact.³³ The weaker nature of the Ga-H bonds (*cf.* Al-H) means **8-Ga** is only a minor product of the reaction of the corresponding gallane with $[\text{M}(\text{CO})_4(1,5\text{-COD})]$ as this species is unstable with respect to dihydrogen elimination (*vide infra*).³⁶

Although the coordination chemistry of Zn-H-TM and Mg-H-TM groups remains underdeveloped when compared to the aluminium analogues, we have recently reported a series of σ -zincane complexes of closely related transition metal carbonyl fragments. Ligand exchange reactions readily occur under photochemical conditions and **5-Zn**, **7-Zn**, **10-11** have been isolated and crystallographically characterised.³⁷

Ueno and co-workers provided evidence that the $\eta^2:\eta^2$ -coordination mode is not necessary for the stabilisation of σ -gallanes, and reported **12** and **13**.^{38,39} These complexes were formed from displacement of THF or CO from group 6 transition metal carbonyls by $\text{GaH}_3\cdot\text{quinuclidine}$. While there is little account for TM---Ga interactions in **12**, **12-W** again contains a shorter TM---Ga separation than what would be reasoned from inspection of the solid state structures **12-Cr** and **12-Mo**.^{38,39} Complex **13** is noticeably similar to **6** in terms of the TM-H-M parameters. In both cases, the $\text{Cp}_{\text{centroid}}\text{-Mn-H-M}$ torsion angle is near 90° allowing for overlap of the M-H σ^* -orbital with the HOMO of the Mn fragment. There are also similarities to the first reported example of a σ -alane complex. Formally a Ni^0 species possessing a triene ligand and a coordinated alane, **14** contains an unsupported Ni-Al-H linkage that survives the substitution of the tridentate ligand with three equivalents of CO to form $[(\text{CO})_3\text{Ni}(\mu\text{-H})\text{AlMe}_2\cdot\text{quinuclidine}]$.⁴⁰

An alternative approach to TM–H–Al groups has been discovered by Fischer and co-workers. Addition of $[\text{Cp}^*\text{Al}]_4$ to transition metals with labile ligands is proposed to generate intermediates of the form $[\text{TM}(\text{AlCp}^*)_n]$ which react further, effecting the inter- or intramolecular C–H activation of arenes or alkanes.^{41,42} Complexes **15**–**16** are formed through this route and possess geometries that are consistent with the σ -alanes described above (Figure 4). For example, the Al–H distance in **15** of 1.76(3) Å lies within the range established σ -alanes. While **16** possesses elongated Al–H distances ranging from 1.88(8) to 1.89(7) Å, these are still substantially shorter than the >2.0 Å separation required to suggest oxidative addition (*vide infra*). The latter may be described as a complex containing stretched σ -alane ligands with an Al–H–TM geometry somewhere between coordination and oxidative addition.

3. Oxidative Addition / Hydride Transfer (H–TM–M)

We have reported the thermal reaction of M–H bonds (M = Al, Zn, Mg) with $[\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2]$ to form **17** and **18**,⁴³ a reaction that is believed to proceed through the 16-electron intermediate $\{\text{Cp}^*\text{RhH}(\text{SiEt}_3)\}$. These species are different to the σ -complexes described above and data are consistent with the product of oxidative addition (Figure 5).

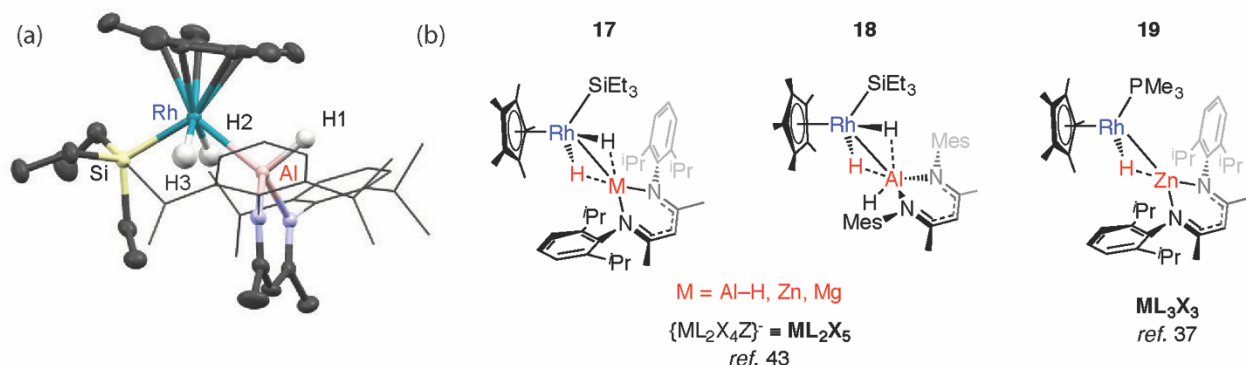


Figure 5 (double column). (a) The crystal structure of **17-Al**. Selected bond lengths (Å): Rh(1)–Si(1) 2.3668(7), Rh(1)–Al(1) 2.4579(7), Al(1)–H(1) 1.51(2), Al(1)–H(2) 2.13(3), Al(1)–H(3) 2.22(3), Rh–H(2), 1.47(3), Rh–H(3) 1.53(3). (b) Oxidative addition (hydride transfer) of M–H bonds to a Rh complex.

In all cases the TM–M distances are within the sum of covalent radii and the M---H distances stretch to well beyond 2.0 Å. Moreover the four-legged piano-stool geometry around the Rh centre, including the *trans*-relation of the hydride ligands, is conserved when compared with silane and borane analogues, $[\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)(\text{X})]$ (X = SiEt₃, Bpin). The description of **18** as an oxidative addition product is supported by the significant $^1J_{\text{Rh-H}}$ value of 40.2 Hz and terminal $\nu(\text{Rh-H})$ frequency of 1966 cm⁻¹. The calculated charges (NBO analysis) on Rh are significant for only the Zn and Mg analogues. As such, while these Zn and Mg complexes could be described as oxidative addition products, hydride transfer to form an is also a fair description.⁴³

The structure of **17-Al**, an analogue of **18** that incorporates more sterically demanding substituents on the β -diketiminate ligand, shows a geometry with familiar *trans*-disposed hydrides, short TM–Al distance and long Al---H distances (Figure 5). Reaction of **17-Zn** with an excess of PMe_3 under photochemical conditions leads to the elimination of an equivalent of silane and formation of **19**. This latter heterobimetallic complex again contains a short TM–M distance and a M---H separation of greater than $> 2.1 \text{ \AA}$.³⁷

Mindiola and co-workers have isolated a related Fe–H–Mg complex, albeit as a minor component of a mixture formed upon reaction of EtMgCl with an iron chloride precursor.⁴⁴ Complex **20** also results from C–H activation of the ligand (Figure 6).⁴⁵ While it could be assigned as an σ -Mg–H complex of Fe the long Mg---H distance and short Fe–H separation make this debatable, it is arguably closer to an ate-complex formed by a tightly bound $\text{Fe-H}^- \rightarrow \text{Mg}^+$ ion-pair. Although both **20** and **17-19** can be described as the products of hydride transfer the key difference is that the latter are formed from addition of the M–H bond to the TM centre and contain a defined and quantifiable TM–M bond.

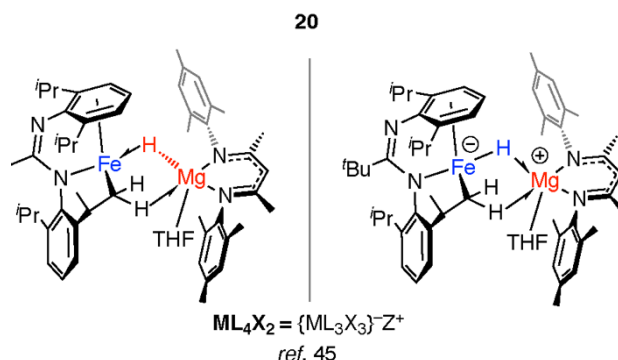


Figure 6. Hydride transfer to form a tightly bound ion-pair in **20**

4. Low-Valent Main Group Ligands from Dehydrogenation ($\text{TM} \leftarrow \text{M}$)

The products of oxidative addition of M–H bonds to transition metals may only be intermediates on a path to coordinated low-valent fragments ($\text{M} = \text{Al}, \text{Ga}$). As the main group is descended, not only does the reduced M–H bond strength result in easier M–H “bond activation”, but the manifestation of the inert pair effect means the lower common oxidation state becomes increasingly stable.

Two examples of the generation of Al^{I} ligands by the dehydrogenation of aluminium dihydride precursors in the coordination sphere of a transition metal have been reported. The products of these reactions retain an undeniable H---Al interaction. The photochemical elimination of HSiEt_3 from **19** leads to the dimer **21** (Figure 7).⁴³ Complex **21** contains a $\text{Rh}_2\text{Al}_2\text{H}_4$ core. Supporting the argument for Al^{I} is the deviation of the alumocycle from planarity, suggestive of decreased π -donation by the N atoms into the 3p orbital of Al. This allows for Al^{I} to act as both a Z- and L-type ligand with respect to Rh.⁴³ Structurally related intermetallic compounds containing $\text{Pt}_2\text{Ga}_2\text{H}_4$,⁴⁶ Ru_2GaH_2 ,⁴⁷ $\text{Ru}_2\text{Ga}_2\text{H}_4$,⁴⁸

$\text{Ru}_2\text{Al}_2\text{H}_4$,⁴⁸ $\text{Co}_2\text{H}_2\text{Al}_2$,⁴⁹ $\text{Rh}_2\text{Zn}_2\text{H}_2$ groups are all known,^{50,51} as are higher nuclearity species in which multiple main group fragments act as ligands for the transition metal (see supporting information, Figure S1).⁵²⁻⁵⁷ The work on cluster complexes supported by organozinc, organoaluminum and organogallium ligands has been reviewed before.²³⁻²⁶

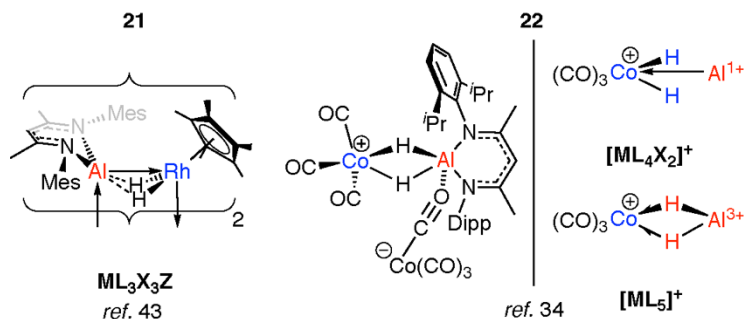


Figure 7. Generation of Al^I ligands from addition of aluminium dihydrides to TM.

Coordination of a related aluminium dihydride to a 14-electron $\{\text{Co}^{\text{I}}(\text{CO})_3\}^+$ synthon gives **22** (Figure 7).³⁴ This latter species appears to be a product of simultaneous addition of both Al–H bonds to Co. The bridging Al---H distances of 1.92(3)-1.98(3) Å in **22** are not as long as those found in the oxidative addition products **17-Al** or **18** of 2.0-2.2 Å but are significantly longer than those found in σ -complexes of the same aluminium species which typically range from 1.6–1.8 Å. As with **21**, the aluminium centre receives additional electron density, here by end-on coordination of an isocarbonyl ligand of the formally anionic $\{\text{Co}(\text{CO})_4\}^-$ moiety. The electronic structure of **22** lies somewhere between the *bis* σ -complex and the dehydrogenated $\text{Co}^{\text{III}}/\text{Al}^{\text{I}}$ species (Figure 7).

Complexation of gallanes to late transition metal carbonyls (TM = Cr, Mo, W, Mn, Fe, Co) has been shown to lead to the formation of Ga^I ligands through spontaneous or photoinduced extrusion of dihydrogen (Figure 8).^{34,36} Complexes **23** and **24** are formed from addition of gallanes to $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3]$ and $[\text{TM}(\text{CO})_n]$ (TM = Cr, Mo, W, n = 6; TM = Fe, n = 5) precursors. A bimetallic reaction intermediate is proposed, from which 1,2-elimination of dihydrogen occurs. Reactions employing 34-electron carbonyls $[\text{Mn}_2(\text{CO})_{10}]$ or $[\text{Co}_2(\text{CO})_8]$ in place of the 18-electron $[\text{M}(\text{CO})_n]$ complexes proceed similarly. For Co, oxidative addition is followed by H₂ elimination across the TM–M bond to give **25**. For Mn, oxidative addition of the Ga–H bond is followed by reductive elimination of H–TM(CO)₄ and α -migration of the remaining hydride from Ga to Mn to form **26** (see discussion, Figure 23).³⁶ The proposed intermediate of the latter reaction contains a Mn–Ga–H group and finds experimental support from the work of the groups of both Driess and Fischer who have reported complexes containing $\text{Fe} \leftarrow \text{Ga}-\text{H}$,⁵⁸ and $\text{TM} \leftarrow \text{M}-\text{H}$ moieties (TM = Cr, Mo, Zn; M = Al, Ga).⁵⁹⁻⁶¹

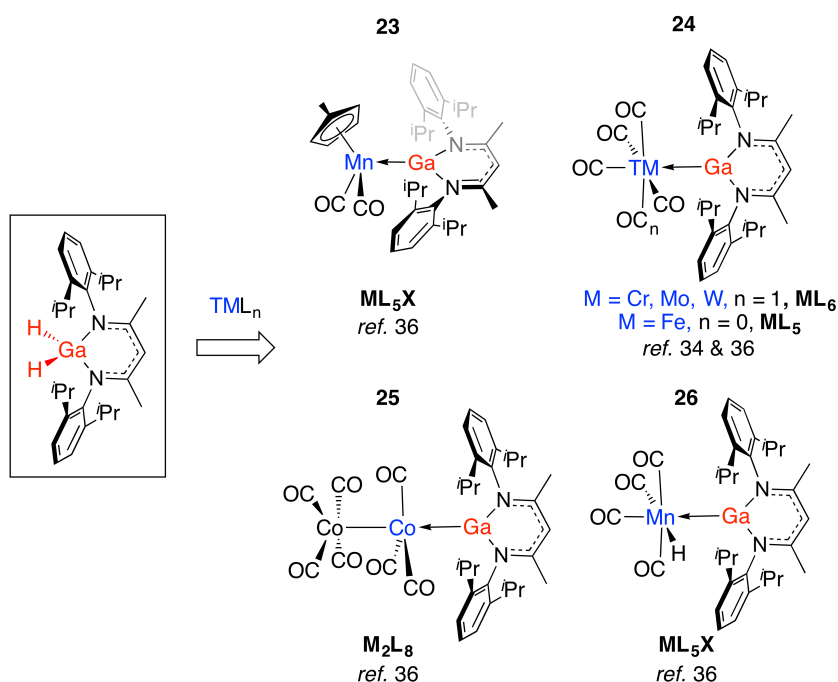


Figure 8. Generation of Ga^I ligands from addition of gallium dihydrides to TM.

5. Hydride-Bridged Lewis Adducts (TM–H→M)

Late Transition Metal Adducts: Lewis acidic main group metal centres *without* hydride substituents may be coordinated by transition metal hydrides in two different ways: i) through a direct metal–metal interaction from donation of d-electrons of the TM to the main group metal (Z-type ligand) or ii) through 3-centre 2-electron hydride bridges of the form TM–H→M (Figure 2). Elimination reactions may result from these adducts provided the pK_a of the hydride is low enough and the metal alkyl (or aryl) basic enough to effect alkane (or arene) elimination.

For example, Andersen and Bergman have reported the reaction of $[\text{Cp}^*\text{Ir}(\text{H})_2(\text{PMe}_3)]$ with a series of organo-aluminium and -magnesium compounds (Figure 9).⁶² Coordination of Ph_3Al to form **27** results in the widening of the H–Ir–H angle by 20° and signifies dominant TM–M bonding. In contrast, the reaction of $[\text{Cp}^*\text{Ir}(\text{H})_2(\text{PMe}_3)]$ with $\text{Ph}_2\text{Mg}(\text{THF})_2$ eliminates benzene and forms **28**, while that with AlEt_3 eliminates two equiv. of ethane and yields the dimeric species $[\text{Cp}^*\text{IrPMe}_3(\mu\text{-AlEt})]_2$, **29**. Both **28** and **29** activate CO_2 , giving $[\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{CO}]$ as the TM-containing product.⁶²

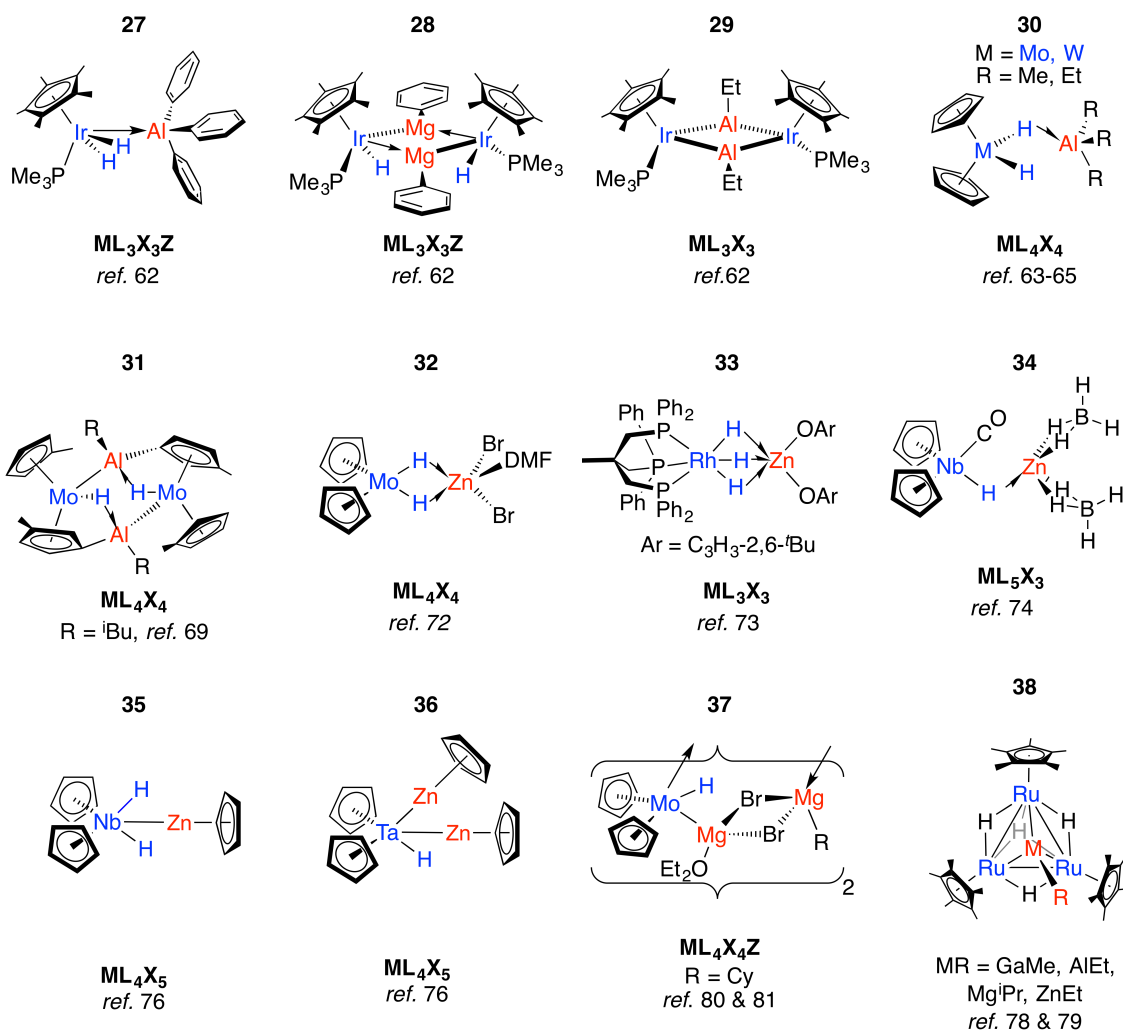


Figure 9 (double column). Late Transition Metal Adducts.

The TM---M distances in **27–29** are in range of the sum of the covalent radii, and the coordination at iridium in **27** is such that the Ir–Al bond is distorted away from the IrH₂ plane by 37°. ⁶² The geometries contrast with those of **30-W** and **30-Mo**. First reported by Wailes *et al.* ⁶³ and Storr *et al.*, ⁶⁴ **30-W** has been characterised by X-ray diffraction and analysed by DFT methods. ^{65,66} While the current understanding is that the two metals interact through a single hydride bridge to Al, there is limited data to support a non-negligible TM→M donation. Firstly, the HOMO on the TM fragment is calculated to be a metal-localised d-orbital-type suitable for electron donation. Secondly, the BX₃ (X = F, Cl) adducts of the same TM fragments were calculated with the boron atom lying outside of the H–TM–H wedge. ⁶⁶

Although the gallium and boron analogues of **30** are yet to be isolated, ¹H NMR data for a GaMe₃/[Cp₂WH₂] admixture shows likely equilibrium between free compounds and a weakly bound adduct. ⁶⁷ These data are consistent with the known acceptor strength of the Lewis acids AlMe₃ > GaMe₃ > BMe₃. Rhenium analogues of **30** were discovered by Wailes *et al.* using the metallocene [Cp₂ReH]. ⁶³ The potential for reversible H/D exchange between the hydrides and protons of the

cyclopentadienyl ring of **30-W** has been highlighted and proposed to occur by a mechanism involving anchimeric assistance.⁶⁵ Non-reversible intramolecular deprotonation of the cyclopentadienyl ligands is also well established, and often leads to high nuclearity species such as complex **31**.⁶⁸⁻⁷¹ When [Cp₂MoH₂] was treated with ethylzinc bromide, **32** was isolated and presumed to derive from ZnBr₂ formed from a Schlenk-type equilibrium.⁷² An $\eta^2:\eta^2$ -bonding mode of the Mo hydrides is implied by the narrowing of the MoH₂ wedge upon adduct formation, data that contrast those of **27**. A similar adduct, **33**, is formed from addition of a *bis*-aryloxy zinc solvate to a Rh trihydride complex.⁷³

Reaction of a mixture of NbCl₅, sodium cyclopentadienyl and zinc powder in THF under an atmosphere of CO, and subsequent treatment with NaBH₄ gives **34**.⁷⁴ The metal---metal distance in **34** is just within the sum of the covalent radii and there is a shift of the $\nu(\text{CO})$ absorption upon coordination of the Lewis acid to [Cp₂Nb(CO)H] (1960 to 1910 cm⁻¹). Both findings mark a significant Nb→Zn interaction. In contrast, only a small shift in the $\nu(\text{CO})$ absorption is seen upon reaction of [Cp₂NbH(CO)] with AlEt₃.⁷⁵ Based on significant changes to the hydride resonance observed by ¹H NMR data, the coordination of AlEt₃ in [Cp₂Nb(L)H•AlEt₃] (L = CO, C₂H₂, PMe₃) is proposed to occur through a μ -hydride ligand rather than a direct metal---metal interaction. Related reactions between a 1:1 mixture of [Cp₂NbH₃] or [Cp₂TaH₃] and [Cp₂Zn] do not lead to adduct formation but cyclopentadiene elimination and formation of new species **35** and **36** both of which contain TM–Zn bonds.^{76,77} Tebbe and co-workers reported the d¹ complex [(Cp₂NbH₂)₂Zn] from the 1:2 reaction of Et₂Zn with [Cp₂NbH₃].⁷⁵ Higher nuclearity species **36–38** have been isolated from reactions of ruthenium polyhydride complexes or [Cp₂MoH₂] with main group alkyls (Figure 9).⁷⁸⁻⁸¹

In more recent work, Bourissou, Uhl and co-workers have shown that hydrogenation of an intramolecularly coordinated Pt→Al adduct leads to the heterobimetallic hydride **39** (Figure 10).⁸² Calculations suggest that H₂ addition occurs across the Pt→Al bond. There is precedent for this intramolecular coordination mode: Fischer and co-workers have reported the gallium adduct **40**.⁸³ Related hydrogenation reactions of platinum diene complexes either bearing a Z-type Al ligand or in the presence of Ga^I co-ligands lead to the formation of heterobimetallic complexes bearing terminal hydride ligands on the transition metal (Figure S1).^{46,84} For example, **41** is formed upon hydrogenation of a Pt---norbornadiene precursor; it is currently unclear if the Pt→Al moiety plays a role in dihydrogen activation (Figure 10).⁸⁴

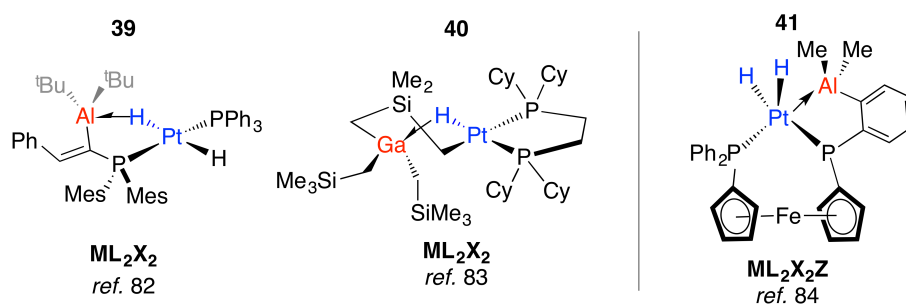


Figure 10. Adducts from H₂ or C-H addition across a Pt→Al Bond.

Early Transition Metal Adducts: Relevant to Ziegler-Natta polymerisation, Zr-H→Al Lewis acid-base interactions have been known for some time.⁸⁵ Coordinatively saturated, d⁰ heterobimetallic complexes may be formed by coordination of the parent hydride to a Lewis acid. For example, **42** was suggested by Wailes and co-workers based on ¹H NMR experiments as early as 1972.⁶⁷ Crystallographic characterisation of related adducts **43** and **44** containing inter- and intramolecular Zr-H-Al moieties was later reported.^{86,87} While there is less data for hafnium, the adduct **45** has been reported and is notable for the location of the Al centre outside of the H-Hf-H wedge. The position of the hydrides are unusual when compared to related group 4 metallocenes as is the 16-electron configuration of Hf.⁸⁸ For group five analogues, [Cp₂TaH₃•MEt_n] forms irreversibly for M = Al, Ga (n = 3) but reversibly for Zn (n = 2).⁷⁵ Solid state infrared spectroscopy and X-ray diffraction data for a related complex, **46**, are consistent with formation of an adduct containing two Ta-H-Zn linkages forming an η²:η²-coordination mode, although NMR data suggest that only one bridging hydride is retained in solution (Figure 11).⁸⁹

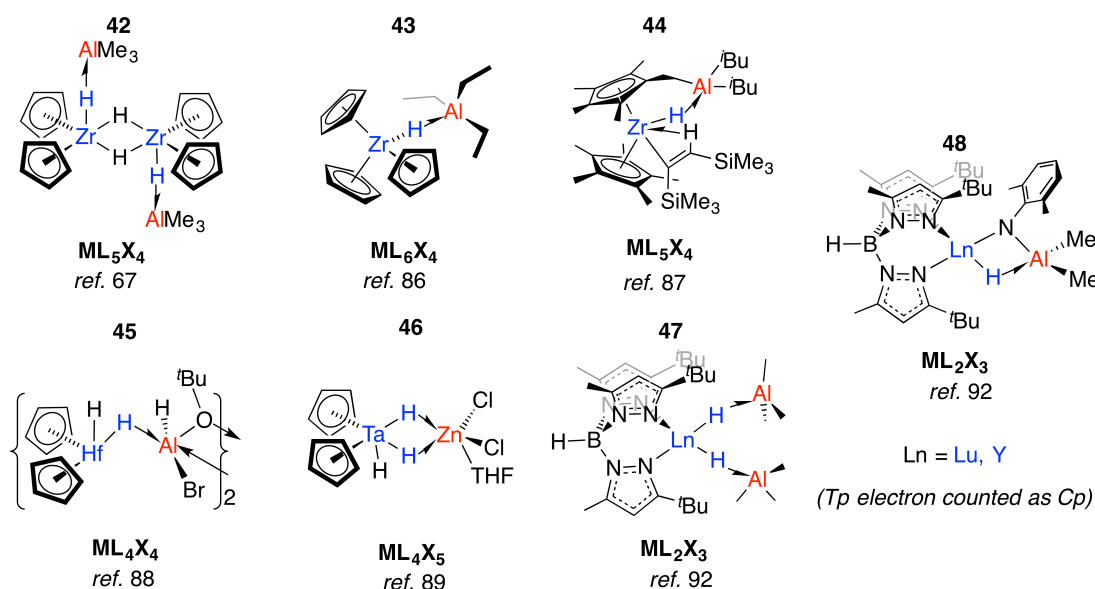


Figure 11. Early TM / main group adducts.

Anwander *et al.* have investigated the reactions of yttrium and lutetium alkyl and amide complexes with aluminium hydrides.⁹⁰⁻⁹³ For example, lanthanide hydride bonds in **47** are capped and stabilised by Lewis acidic aluminium sites.⁹² This motif is not unique to **48**, and X-ray data has been collected on monomeric $[\text{Cp}_2\text{Lu}(\mu\text{-H})\cdot\text{AlH}_3\cdot\text{NEt}_3]$,⁹⁴ and dimeric $[\text{Cp}^*\text{Y}(\text{Me})(\mu\text{-H})\text{AlMe}_2(\mu\text{-H})]_2$.⁹⁵ Despite the coordinated Lewis acid, **47** displays reactivity consistent with a terminal hydride; deprotonation of 2,6-dimethylaniline gave complex **48**. Here, the imide linker supports an intramolecular $\text{Ln-H}\rightarrow\text{Al}$ interaction (Figure 11).⁹²

6. Multiply-Bridged Complexes ($\text{TM-H}_n\text{-M}$, $n > 1$)

Rare Earth Metal Adducts: $[(\text{C}_5\text{Me}_5)_2\text{YMe}(\text{THF})]$ reacts with $\text{HAl}\{\text{N}(\text{SiMe}_3)_2\}_2$ allowing trapping of $\mu\text{-H}_2$ -bridged **49**.⁹⁶ The alane in this complex is strongly bound and addition of donor, including chelating, ligands could not effect separation of the heterobimetallic complex. The coordination mode in **49** is predated by those found in **50–55** reported by Bulychev and co-workers in the 1980s.^{94,97-105} In these latter complexes, the Al fragment and hydride source derive from either LiAlH_4 or $\text{AlH}_3\cdot\text{L}$ ($\text{L} = \text{NEt}_3$, THF, OEt_2), and either the chloride or hydride ligands take up μ^3 -coordination modes. Amongst the complexes $[\text{Cp}_2\text{YH}\cdot\text{AlH}_3\text{L}]_2$ (**50**), the Y---Al distances decrease, and Al-H stretching frequencies increase, across the series $\text{L} = \text{Et}_2\text{O} < \text{THF} < \text{NEt}_3$. The five-coordinate Al centres found in these complexes are notably different to the borate analogues, where the boron atom does not engage in coordination numbers higher than 4 and solvation occurs at the rare earth metal centre (Figure 12).¹⁰⁶

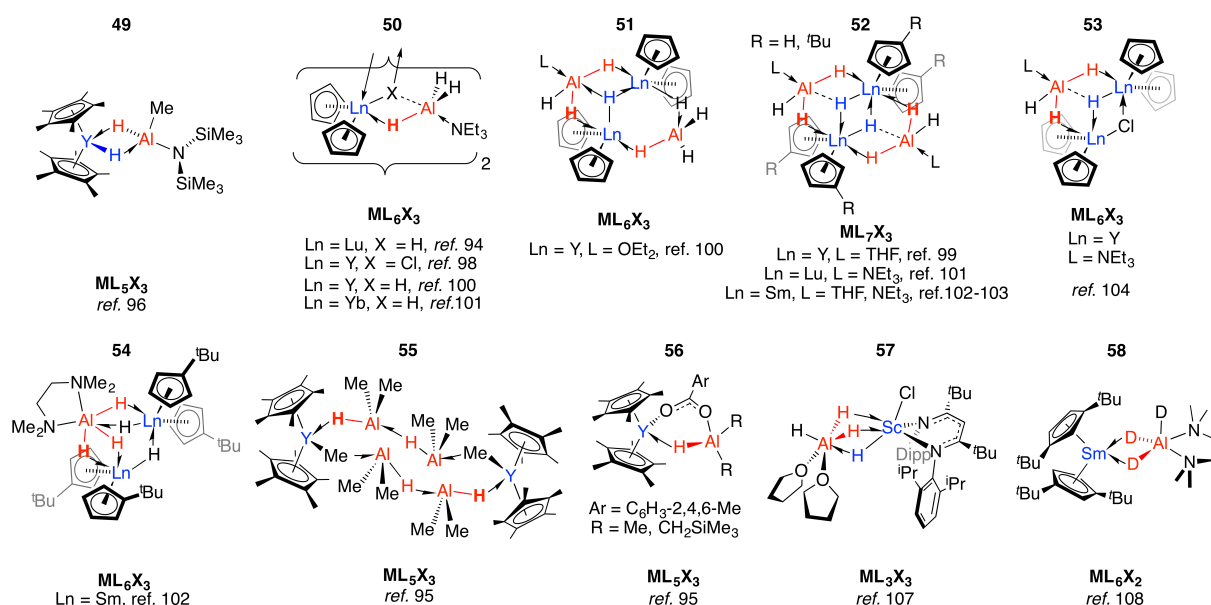


Figure 12. (double column) Coordination of aluminium hydrides to rare earth metal centres.

Alanes react with yttrocene hydride or carboxylate complexes to form $\text{Y}\leftarrow\text{H-Al}$ adducts (**55–56**).⁹⁵

While investigating the salt metathesis of a β -diketiminato-supported Sc dichloride complex with LiAlH_4 , Piers and co-workers isolated the alane adduct, **57**.¹⁰⁷ In **57**, both metals are six coordinate, and this is the only time a $(\mu\text{-H})_3$ bridging motif seen in the absence of a late TM. Heterobimetallic hydrides of rare earth metals are not limited to those in which the heavy metal is in the +3 oxidation. Bulychev *et al.* found that $[(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)_2\text{Sm}]$ partially decomposes into an octanuclear aggregate of Sm^{III} and alane, when treated with AlH_3 in the presence of TMEDA. Upon substitution of the alane for AlD_3 , however, **58** may be isolated: an apparent effect of isotopic substitution.¹⁰⁸

Group 4 Metal Adducts: As part of understanding the role of methylaluminoxane in polymerization catalysis,¹⁰⁹ Bercaw, Britzinger and others have reported NMR studies on hydride-bridged Zr/Al oligomers, trimers and dimers in solution (**59–60**).^{85,110–112} They concluded that binuclear structures of type **60** are only produced for *ansa*-metallocenes and inclusion of a terminal Me ligand on Zr causes decomposition. Cationic Zr- and Hf-analogues are known.^{113–115} It has been shown that $\{\text{Zr}(\mu\text{-H})_3\text{Al}_2\}^+$ reacts reversibly with AlMe_3 or ClAl^iBu_2 to give dimethyl- or dichloro-bridged Zr/Al species (Figure 13).¹¹⁴

An early example of a Zr–H–Al complex was published in 1997 by Raston and co-workers.¹¹⁶ Structurally and synthetically, **61** is logical extension of the work of Bulychev *et al.* (*vide supra*). These species are poorly soluble in all common organic solvents but THF, and require stabilisation by a base. Power and Wehmschulte added a super bulky aryl group (**62**) improving solubility and eradicating the need for base stabilisation.¹¹⁷ Base-free complexes have also been reported by Stephan and colleagues.¹¹⁸ NMR data and calculations for the monomers **62** suggest both fast intramolecular hydride exchange and an intermolecular exchange between the heterobimetallic complex and its homometallic parts in solution. Our group has also published an example of this type: soluble in toluene and hexane **63-Al** exists in equilibrium with the alane and $[\text{Cp}_2\text{ZrH}(\mu\text{-H})_2]$.¹¹⁹ In contrast, the homologues, **63-Mg** and **63-Zn** show no sign of dissociation into monometallic parts. This may be a result of tighter binding due to an increased ionic contribution to the donor-acceptor linkage (Figure 13).¹²⁰

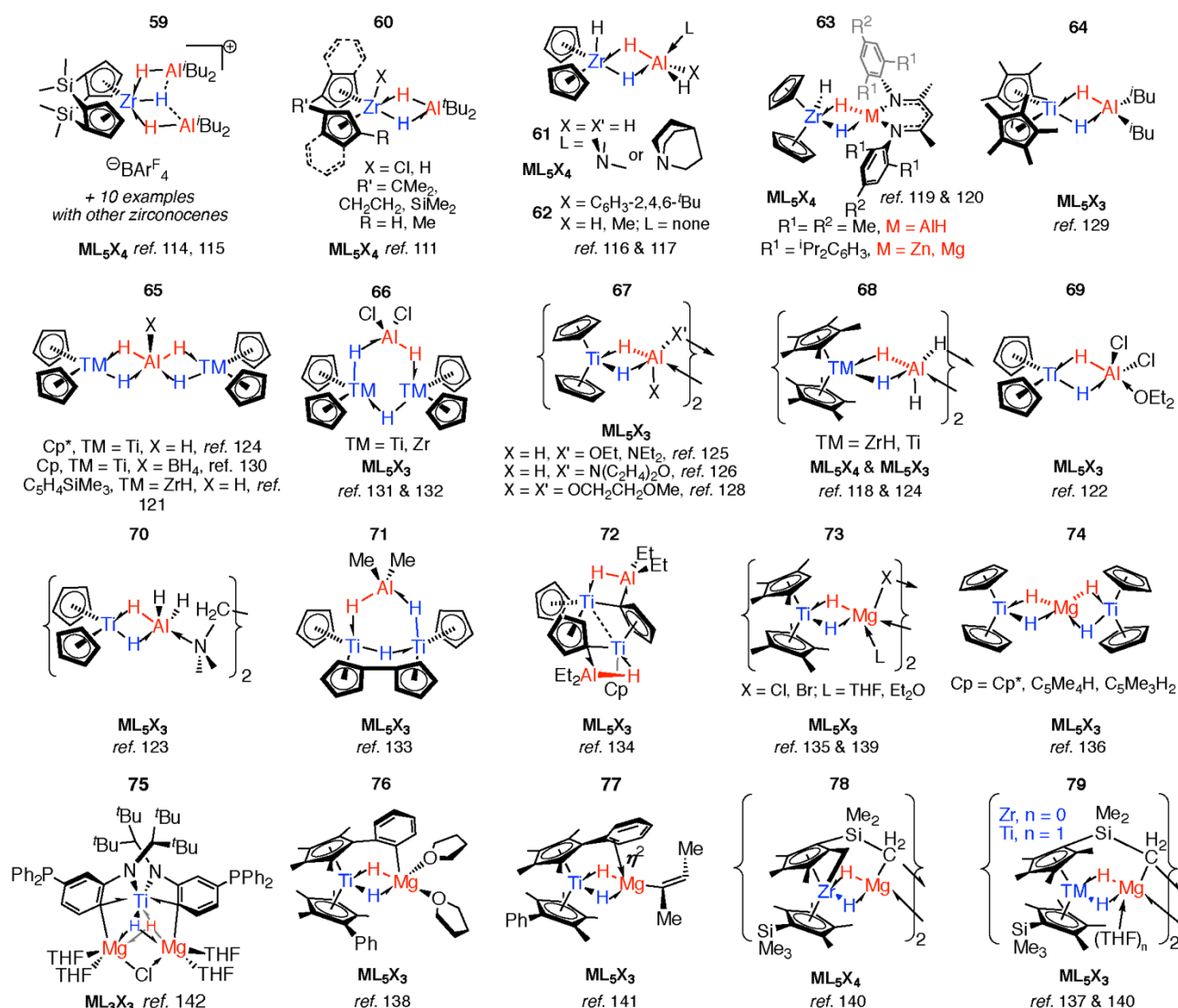


Figure 13. (double column) Group 4 complexes with multiple hydride bridges.

Many of the $\text{Zr}^{\text{IV}}/\text{Al}$ heterobimetallic hydride complexes are synthetically accessible by salt-metathesis reactions of the parent zirconocene dihalide with aluminium hydride reagents.¹²¹ Similar reactions with titanium(IV) precursors commonly lead to isolation of products with Ti in the +3 oxidation state.¹²²⁻¹²⁸ This is displayed most nakedly in the recent report of **64** by Beweries.¹²⁹ Six-, five- and four- coordinate aluminium centres have been reported in $\{\text{Ti}_2\text{Al}_2\text{H}_8\}$, $\{\text{Ti}_2\text{AlH}_5\}$, and $\{\text{TiAlH}_2\}$ cores respectively (**65–72**).^{118,121-134} There is only limited precedent for similar reduction chemistry occurring with Zr.^{131,132} The observed coordination modes of Al_xH_y units in these and related group 4 complexes are common to heterobimetallics and are found in related Ta, Nb, Mn and Ru complexes (*vide infra*).

Substitution of the terminal hydride ligands on aluminium for halide, alkyl, alkoxide or amide has little influence on structure.^{133,134} Magnesium-based heterobimetallic complexes of group 4 metallocenes (**73–77**) can be prepared by reaction of the parent metallocene dichloride with either Grignard reagents or Mg^0 powder in etheric solvents.¹³⁵⁻¹⁴² For preparations in which a main group

hydride is not used as a reagent the hydride ligands result from either: i) C–H atom abstraction from the solvent (THF), ii) β -hydride elimination group derived from a main group alkyl, or iii) C–H bond activation of the cyclopentadienyl ligand (or its substituents). Ligand activation is common in these complexes and intramolecular deprotonation to form dianionic Cp ligands, including “tuck-in” complexes has been observed to lead to both diamagnetic TM^{IV} and paramagnetic Ti^{III} complexes (72 & 78–79).^{126,133,134,143,144}

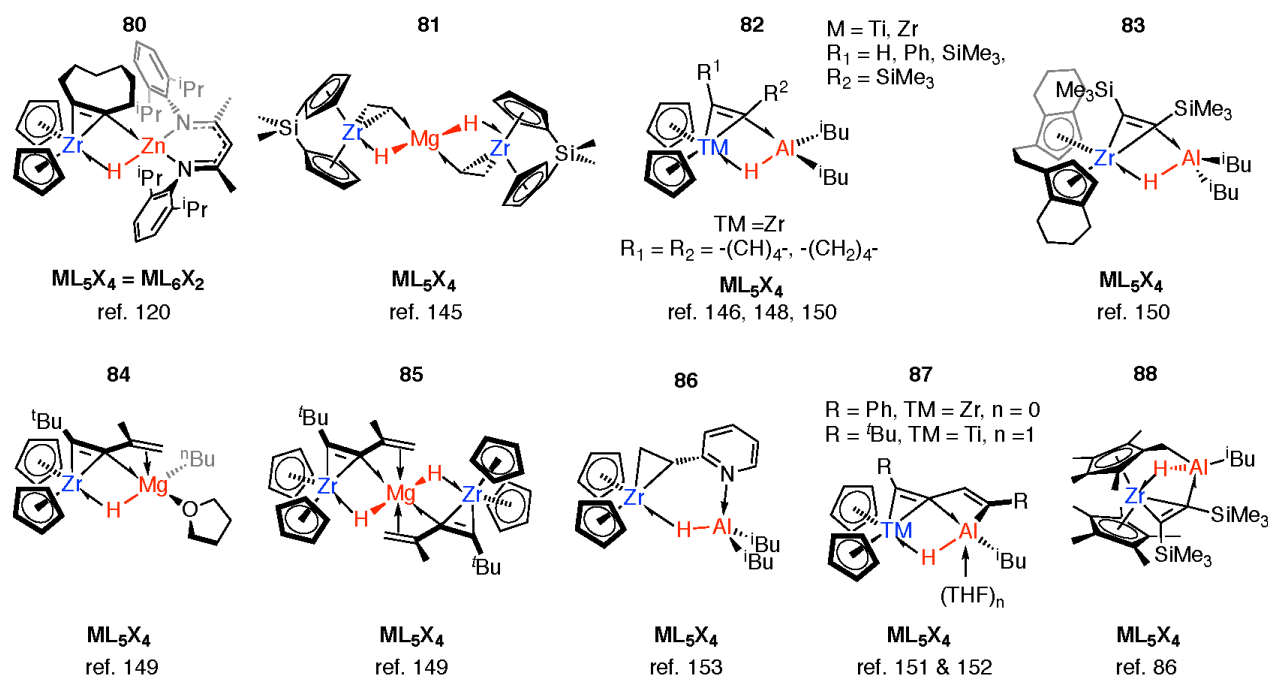


Figure 14. (double column) Coordination of M–H to Zr and Ti metallocyclopropene and metallocyclopropane complexes

Reaction of **63-Zn** with an excess of 1,5-cyclooctadiene resulted in the on-metal transformation of the organic diene to an alkyne adduct, **80** (Figure 14).¹²⁰ This is an example of a heterobimetallic complex containing a planar, four-coordinate carbon and is related to the first confirmed zirconium-ethylene complex **81**, reported by Parkin and co-workers.¹⁴⁵ Structurally related zirconium(IV) and titanium(IV) species are known in which the TM–H–M connection is supported by bridging metallocyclopropane or metallocyclopropene ligands (**80–88**, Figure 14).^{86,120,146–153} A ketene analogue is also known which incorporates an oxycyclopropane ring.¹⁵⁴ The structures of **84–87** are distorted to accommodate additional intramolecular binding interactions. Calculations have shown that electron donation from the bridging Zr–C bond to the Lewis acidic main group centre plays a key role in the stabilisation of these species (**82**) and explains the unusual geometry at the bridging carbon.¹⁴⁷ A combination of computational methods (NBO and QTAIM) have led our group to describe the bridging ligand of **80** as a slipped metallocyclopropene.¹²⁰

Late Transition Metal Adducts: Multiply-bridged main group complexes (M = Mg, Zn, Al and Ga) of late transition metals have been known for more than 50 years. Much of the early work is limited by the accuracy of the spectroscopic methods of the period.²⁰ Nevertheless, it has been clear for

some time that the electronegativity difference between late TM and main group metals creates a significant ionic contribution to the bonding.²⁰ Complexes **89–97** are mostly products of salt metathesis between lithium aluminohydrides and TM chlorides (Figure 15).^{155–171}

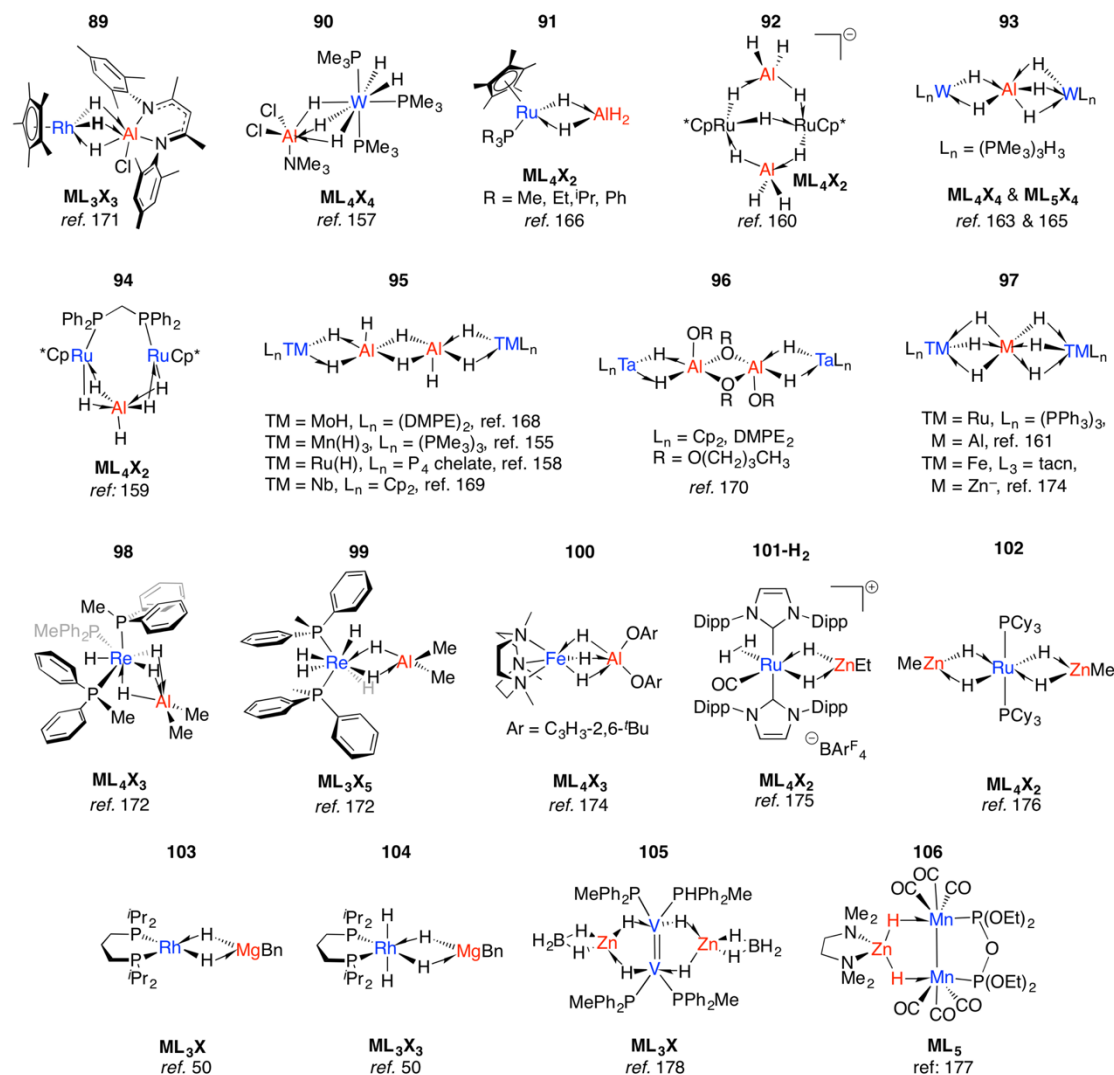


Figure 15. (double column) Late TM Heterobimetallics containing multiple bridging hydrides (tacn = 1,4,7-triazacyclononane).

Common themes emerge in the coordination geometries of these complexes.¹⁷⁰ Unlike the group 4 analogues described above, the $(\mu-H)_3$ bridge is a reoccurring feature. Geometries at aluminium are typically trigonal pyramidal (5-coordinate)¹⁵⁹ or *distorted*-octahedral (6-coordinate). The high coordination number and the geometry of ligands around the TM centres provides coordinative saturation, and in most cases makes the existence of a metal–metal bond very unlikely. For **89**, this finding is in direct contrast to the data reported for the related Rh/Al species **17-AI** and **18** (Figure 5).¹⁷¹

In solution many of these complexes are fluxional and provide time-averaged 1H NMR chemical shifts for bridging and terminal hydrides. In relation to this phenomenon, the complexes **98** and **99** reillustrate the ionic component of the bonding. The main group fragment of **98** and **99** is $\{AlMe_2\}^+$,

which may exchange between different positions on the face of the $\{P_3ReH_4\}^-$ and $\{P_2ReH_6\}^-$ polyhedra.¹⁷² For comparison, $[ReH_9]^{2-}$ is well-known as the dipotassium salt.¹⁷³

The low-spin ground state structure of **100** has been thoroughly investigated by computational methods.¹⁷⁴ The frontier molecular orbitals of **100** do not support bonding between Fe and Al, and the authors present the complex as being dominated by a strong donation of electron density from a $\{Fe-H\}^-$ fragment to $\{AlX_2\}^+$ ($X = O-C_6H_3-2,6-tBu$). This conclusion is a good general insight into the electronic structure of the late-TM(H)_nAl bonding, the dimeric examples of which are summarised in **95–96**.

An alternative synthetic approach to multiply-bridged main group complexes of the late transition metals is through the addition of H₂ across an unsupported Ru–Zn bond. The Ru(H)₂Zn moiety in **101-H₂** discovered by Whittlesey and co-workers demonstrated good thermodynamic stability and survives extrusion of dihydrogen by heating *in vacuo* to form **101**.¹⁷⁵ The hydride ligand *trans* to H₂ in **101-H₂** is protic and significantly closer to Ru, while the hydride *trans* to CO is hydridic and equidistant between the metals. NBO calculations show no sign of Ru–Zn interaction in either complex. However, a QTAIM calculation on **101** shows a Ru–Zn bond path and only one Zn–H bond. It can tentatively be concluded that the μ -H atoms in **101-H₂** and **101** are intermediate and “flexible” between terminal and bridging character. Fischer and co-workers have reported the related complex **102**, which results from addition of 4.5 equivalents of ZnMe₂ to a Ru/Al heterometallic complex prepared *in situ* by mixing $[Ru(PCy_3)_2(\eta^2-H_2)(H)_2]$ and $[Cp^*Al]_4$.¹⁷⁶ Two decades before, Rh/Mg complexes **103** and **104** were prepared by Fryzuk, however their thermal instability precluded characterisation by anything other than ¹H and ³¹P NMR spectroscopy (Figure 15). A number of dinuclear (with respect to TM) complexes supported by chelating ligands or involving TM–TM bonding including **105–106** are also known.^{177,178}

7. Discussion

An exhaustive account of the preparation and structures of heterobimetallic hydride complexes reported over the last half a century is presented above. During our own research in this area and through analysis of the material above, we have alighted upon recurring issues in the understanding this family of complexes. For the benefit of potential future studies, these issues are discussed below.

i) Structure and Bonding

Sigma-Complexes and Oxidative Addition: The current understanding of the TM←H–M linkage (M = Mg, Zn, Al, Ga) in σ -complexes is that it is comprised primarily of a donor interaction from main group metal hydride to a vacant orbital of suitable symmetry on the transition metal fragment. There is limited data to support significant back-donation from the metal to the M–H σ^* -orbital. For example, calculations on complexes **1–3** elucidate a donor-acceptor interaction with the 4s-orbital of the Cu d¹⁰ fragment acting as the acceptor: second-order perturbation calculations reveal only a small

contribution from back-donation (Figure 16).²⁷

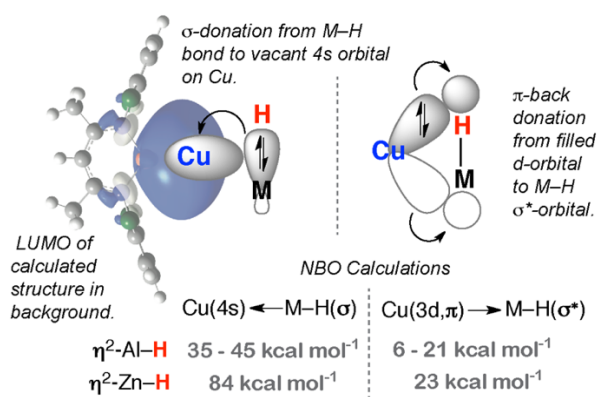


Figure 16. Bonding description of 1–3.

The model is supported by comparison of the carbonyl stretching frequencies of complexes of the form $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{L}]$ where L is an E–H or M–H bond. Listed in Table 1 these data show that σ -alane, σ -gallane and σ -zincane complexes are similar to those formed from four coordinate boranes such as $\text{H}_3\text{B}\cdot\text{NMe}_3$. The data are consistent with limited back bonding into the M–H bond and contrast those of three coordinate σ -boranes and σ -silanes where increased back-donation to the E–H bond results in higher frequency carbonyl stretching frequencies.³⁷ The domination of the σ -donation component of the bonding, and the importance of the ionic component to bonding, is readily understood by considering the difference in the Pauling electronegativity of the elements involved for coordination of E–H ($\Delta\chi_p$: B = 0.18, Si = 0.32) and M–H bonds ($\Delta\chi_p$: Mg = 0.92, Zn = 0.57, Al = 0.61, Ga = 0.41).

Table 1. Comparison of CO stretching frequencies in $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{L}]$. BDI = (2,6-*i*-Pr₂C₆H₃CNMe)₂CH. Adapted from reference 37.

L	ν_1 / cm^{-1}	ν_2 / cm^{-1}
H ₂	1982	1922
HBCat	1995	1937
HSiPh ₃	1983	1926
HGePh ₃	1965	1910
HSnPh ₃	1934	1925
H ₃ B·NMe ₃	1918	1839
H–Al(H)BDI	1947	1879
H–Ga(H)BDI	1951	1886
H–ZnBDI	1937	1852

Considering the structures of the isolated complexes in sections 2 and 3, it becomes clear that the well understood continuum between σ -complexes and oxidative addition products detailed for addition of E–H bonds to transition metals also applies to M–H bonds.

The triangular TM–H–M unit is subject to structural changes as the electron density changes at the TM (Figure 17). The formal shortness ratio (*f_{sr}*) normalises the metal---metal distance and has been used to evaluate the intermetallic interaction in complexes containing two metals in close proximity.

For data collected to date, this metric appears to conveniently describe the extremes of the reaction coordinate: σ -complexes (*fsr* approx. > 1) and products of oxidative addition / hydride transfer (*fsr* approx. ≤ 1).¹⁷⁹ One caveat of this approach is that short metal---metal distances can arise due to the geometric constraints imposed by multiple bridging ligands, to date the analysis has only been applied to molecules containing a single TM–H–M unit.

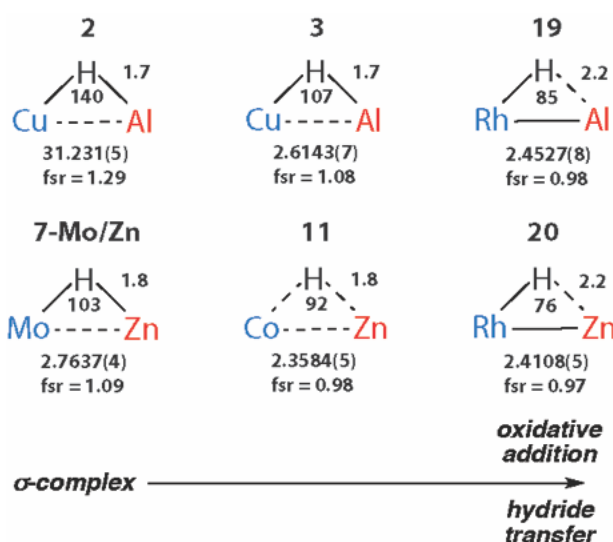


Figure 17. Comparison of key distances (Å) and angles (°) from X-ray (TM---M) structures of coordinated (a) Al–H and (b) Zn–H bonds. Trends confirmed by DFT studies.

Very recently we have described the reaction coordinate for the addition of zinc–hydrides to transition metal centres.³⁷ Through isolation of a series of different transition metal complexes and DFT studies we outlined a continuum which is characterised by the transfer of electron density from the breaking largely ionic Zn–H bond to forming, increasingly covalent, TM–H and TM–Zn bonds (Figure 18). Only at very short TM---Zn separations does the Zn–H bond begin to lengthen significantly. The Zn–H bond varies between approx. 1.7–1.8 Å for σ -zincane complexes but increase dramatically to 2.2 Å for the product of oxidative addition. Similarly for σ -alane complexes the Al–H separation of 1.6–1.8 Å increases to > 2.0 Å for products defined as oxidative addition. The breaking point of this bond appears to occur quite late along the reaction coordinate. While high quality and low temperature X-ray data is becoming increasingly well established for the location of hydride ligands in solid state structures, there is clearly significant error in the TM–H and M–H distances an associated TM–H–M. In the case of the analysis presented below, this concern is circumvented by performing DFT calculations to confirm the location of the hydride.

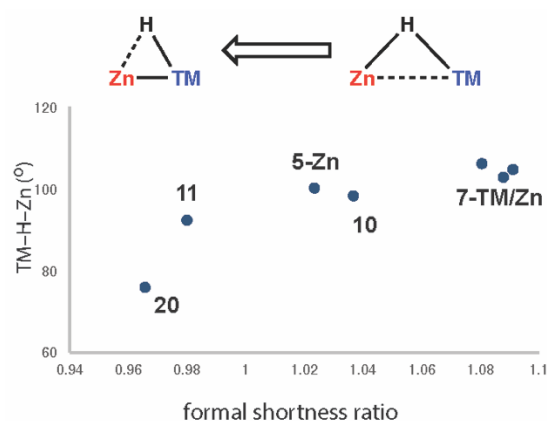


Figure 18. Reaction coordinate for the approach of a Zn-H bond to a transition metal. Adapted from reference 37.

Comparison of a series of E-H and M-H complexes of a single transition metal fragment, {Cp*Rh(H)(SiEt₃)} has allowed us to conclude that the ionic component to bonding remains important for the products of oxidative addition and is such that for M = Zn and Mg these complexes can accurately be described as a result of hydride transfer. The two extreme valence bond description of **17** and the related H-SiEt₃ and H-Bpin complexes are represented in Figure 19. DFT calculations show that the covalent contribution to the TM-M bond (Wiberg Bond Index) decreases along the series Mg ~ Zn < Al < Si ~ B while the charge on rhodium becomes significant for the Zn and Mg members of the series (NPA charge on Rh: Bpin = -0.03, SiEt₃ = -0.06, Al(H)BDI = -0.11, ZnBDI = -1.01, MgBDI = -0.99).⁴³ In combination the data suggest that the ionic contribution becomes more significant for the more electropositive elements.

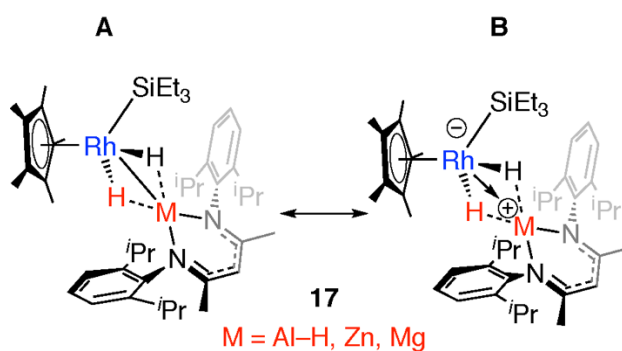


Figure 19. Extreme bonding description of **17** and related complexes. Adapted from reference 43.

Hydride transfer can also occur to generate complexes that do not possess a TM-M bond such as the tight ion-pair **20**.⁴⁵ In the extreme case, charge separation could occur to form a completely ionic species, such as the salt [Zn(NH₃)₄][Cr₂(μ-H)(CO)₁₀]₂.¹⁸⁰

There are clear parallels between the zwitterionic valence bond description **B** and the neutral donor-acceptor complexes, TM→M-H. These species are connected parts of a continuum of bonding descriptions as are σ-complexes of the form TM←H-M and TM-H→M adducts. It appears that as the *fsr* provides some insight when comparing coordination complexes of the M-H bond to TM, it

may also be of some use in considering coordination of the TM–H fragment to M. The bond distances and angles around the Nb–H–Zn moiety of **34** and **35** are compared in Figure 20. The *fsr* ratio decreases and TM–H–M angle becomes increasingly acute when comparing a complex with a genuine TM–M bond (**34**) against that in which the primary interaction between the two metals occurs through a 3-centre 2-electron TM–H–M bond.

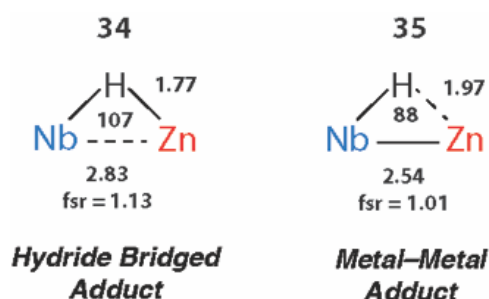


Figure 20. Comparison of the bond lengths (Å) and angles (°) in **34** and **35**. Figure adapted from reference 76.

While, in general, the higher electronegativity of the main group element in silanes (and to an extent boranes) means that TM–H→ER_n bonding descriptions are less common, there is growing appreciation that these descriptions may be relevant in σ -silane and σ -borane chemistry. For example, an Ir–H[−]→SiR₃⁺ interaction has recently been invoked to explain the electronic structure of an intermediate isolated during catalytic studies in the dehydrocoupling of silanes and alcohols.¹⁸¹ Related borane-capped transition metal hydrides, especially those generated by reversible addition across TM→B bonds are gaining increasing attention in catalytic hydrogenation processes.¹⁸²

Multiply-bridged hydride complexes: As the number of bridging hydride ligands increases so does the complexity of the structure and of the bonding descriptions. Wilkinson has commented: “The similarity of...transition metal aluminohydrides to alanes suggest that, whereas it is correct to consider transition metal borohydrides as consisting of L_nM⁺ and BH₄[−] moieties, similar models for aluminium analogues are not as accurate. It may be wiser to consider the complexes as being derived from donor-acceptor interactions.”²⁰ Although generally true for rare earth and group 4 complexes described in section 6, many late transition metal adducts are described as ate-complexes formed of {TM–H_n}[−] and M⁺ fragments (Figure 21).

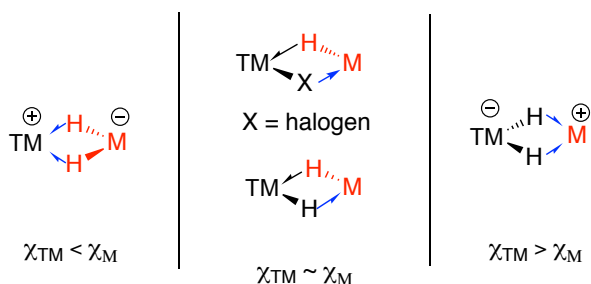


Figure 21. Limiting bonding descriptions in multiply bridged heterobimetallic complexes

A number of species have been isolated that can be considered coordinate complexes of the trapped parent hydrides, these include MgH_4^{2-} , AlH_4^- , AlH_5^{2-} , AlH_6^{2-} , ZnH_6^{4-} , and $\text{Al}_2\text{H}_8^{2-}$ the structural cores of which can be compared to similar complexes containing SiH_4 , SiH_6^{2-} trapped between two transition metals. These species elucidate the general coordination modes found in multiply hydride bridged species (Figure 22). More recently, we have found that the aggregation state of the complexes may be reduced by incorporating kinetically stabilising ligands on M.^{27,37,43,119,120,171}

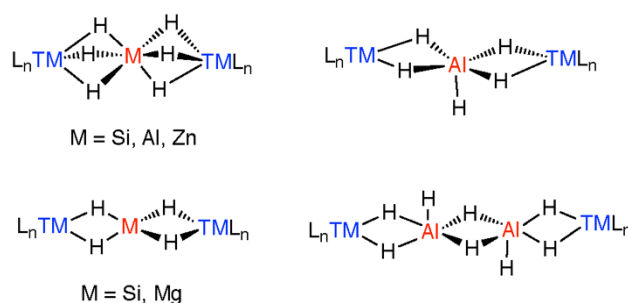


Figure 22. Coordination geometries of trapped MH_x^{n-} units and comparison to silane chemistry.

ii) Reactivity

The 3-centre 2-electron TM-H-M moiety is surprisingly stable. The novel ground state structures found in heterobimetallic TM-H-M complexes are often assumed to herald unusual reactivity. This correlation is far from proven. Indeed, when it comes to reactivity, the understanding of the ground state structure is not enough. For example, a common feature of the data for the multiply-bridged hydrides is exchange between hydride positions in the solution phase.¹⁷⁵

By far the most well understood reaction of TM-H-M groups are those which involve elimination of dihydrogen. Experimentally, while this reactivity has been observed for both Al and Ga complexes, examples of the latter dominate. Through the isolation of intermediates and kinetic analysis, a number of mechanisms for H_2 elimination have been identified and are presented in Figure 23. Both α -migration and 1,2-elimination of H_2 across a TM-M bond have been used to rationalise the formation of Ga^{I} ligands in the coordination sphere of transition metals.

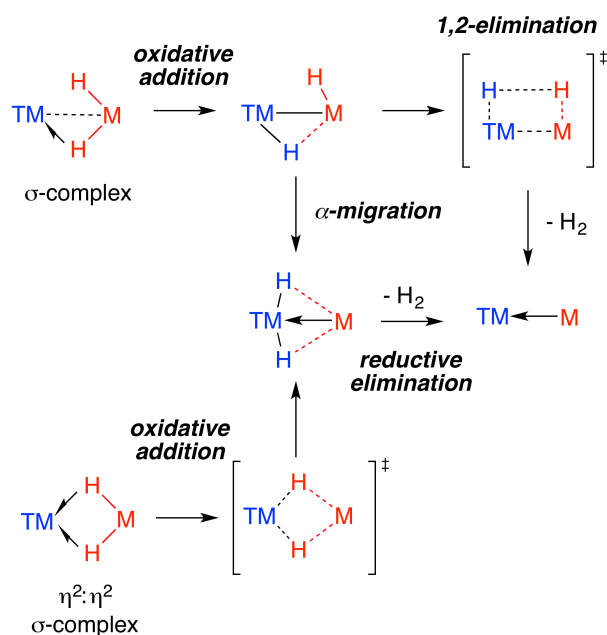


Figure 23. Proposed mechanisms for H₂ elimination from heterobimetallic hydrides

The microscopic reverse of the 1,2-elimination of dihydrogen from a TM(H)–M(H) unit is H₂ addition across a dative TM←M bond. A handful of examples of this type of reactivity are known, albeit from adducts in which the roles of the metals in the Lewis acid-base adduct are reversed. For example, the addition of dihydrogen across Pt→Al and Ru→Zn bonds to form heterobimetallic complexes is known.^{82,175} It remains likely that similar reactivity will be discovered for TM←M adducts. This may well be foreshadowed by the existing observations of both inter- and intramolecular addition of carbon–hydrogen bonds across *in situ* generated TM←M (**16**) and TM–M (**20**, **31**, **44**) complexes.

By considering the properties of the TM–H–Zn complexes on the reaction trajectory presented in Figure 18, DFT studies have shown that as the hydride is transferred from zinc it becomes less hydridic and more acidic.³⁷ While the data would suggest that a rich acid/base chemistry may be possible with heterobimetallic hydride complexes, the reactivity of these species remains understudied. The same with insertion of unsaturated substrates (e.g. alkenes, alkynes, CO, CO₂, carbonyls, etc.) into 3-centre 2-electron TM–H–M bonds: it remains unclear how this chemistry will compare to the well-studied reactions of transition metal hydrides.

iii) Potential in Catalysis

Transition metal hydride complexes are known intermediates in the hydrogenation of unsaturated hydrocarbons, CO (Fischer-Tropsch), and CO₂ along with numerous other small molecules.^{185–187} They also play a key role in hydrogenase enzymes and related catalysts for H⁺ reduction to H₂ and have been invoked as (off-cycle) intermediates during a number of important polymerisation reactions including Ziegler-Natta catalysis.^{85,109}

To date however, defined catalytic reactions believed to involve heterobimetallic hydride complexes are limited. Systems that are catalytic in both the transition and main group metal are the most attractive. Lu and co-workers have reported the heterobimetallic complexes **107** as catalysts for alkene hydrogenation and isomerisation and demonstrated that the nature of the main group metal, M, effects the activity (Figure 24).¹⁸⁸ Dihydrogen activation by addition across a Ni→M bond has been proposed as a key step in hydrogenation catalysis.

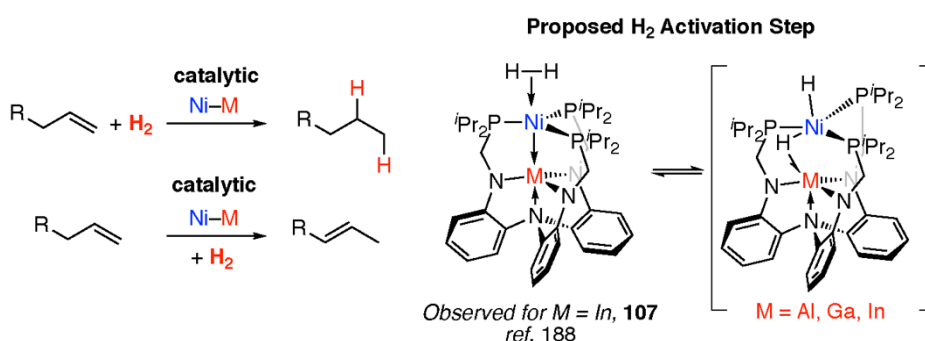


Figure 24. Catalytic alkene hydrogenation and isomerisation by heterobimetallic complexes

The importance of transition metal hydrides to numerous aspects of catalysis is not up for debate. Whether or not heterobimetallic complexes will be able to offer advantages over existing monometallic systems remains an open question for the community. It is clear that substantial developments in the stoichiometric and catalytic reactivity of heterobimetallic hydrides need to be made. Nevertheless, the co-location of two metals by direct metal–metal bonds and/or bridging ligands offers two opportunities in catalysis: new fundamental reactivity, and fine tuning of selection events in known reactions.

The task for the current generation of chemists is to transcribe the known methods for preparation, and the structural understanding of, heterobimetallic hydride complexes into new reactivity. While progress in this area seems to have been made in stops and starts, given the renewed interest in heterobimetallics and main group complexes for catalysis, the challenge appears timely.¹⁸⁹⁻¹⁹⁰

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Notes and references

- 1 R. H. Crabtree, *Angew. Chem. Int. Ed.*, 1993, **32**, 789–805.
- 2 M. Brookhart, M. L. H. Green and G. Parkin, *PNAS*, 2007, **104**, 6908–6914.
- 3 G. J. Kubas, *PNAS*, 2007, **104**, 6901–6907.
- 4 G. J. Kubas, *J. Organomet. Chem.*, 2001, **635**, 37–68.
- 5 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120–128.
- 6 S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, **178-180**, 381–407.
- 7 G. Alcaraz, M. Grellier and S. Sabo-Etienne, *Acc. Chem. Res.*, 2009, **42**, 1640–1649.
- 8 J. Y. Corey, *Chem. Rev.*, 2016, **116**, 11291–11435.
- 9 S. Lachaize and S. Sabo-Etienne, *Eur. J. Inorg. Chem.*, 2006, 2115–2127.
- 10 G. I. Nikonov, *J. Organomet. Chem.*, 2001, **635**, 24–36.
- 11 J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481–11503.
- 12 J. Y. Corey, *Chem. Rev.*, 2011, **111**, 863–1071.
- 13 S. B. Duckett and R. N. Perutz, *Organometallics*, 1992, **11**, 90–98.
- 14 S. Sakaki, N. Mizoe and M. Sugimoto, *Organometallics*, 1998, **17**, 2510–2523.
- 15 G. J. Kubas, *Catal Lett*, 2005, **104**, 79–101.
- 16 G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152–4205.
- 17 C. E. Webster, Y. Fan, M. B. Hall, D. Kunz and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 858–859.
- 18 J. F. Hartwig, K. S. Cook, M. Hapke, C. D. Incarvito, Y. Fan, C. E. Webster and M. B. Hall, *J. Am. Chem. Soc.*, 2005, **127**, 2538–2552.
- 19 I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890–931.
- 20 A. R. Barron and G. Wilkinson, *Polyhedron*, 1986, **5**, 1897–1915.
- 21 G. L. Soloveichik and B. M. Bulychev, *Russ. Chem. Rev.*, 1983, **51**, 43–60.
- 22 G. Parkin, in *Metal-Metal Bonding*, ed. G. Parkin, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, vol. 136, pp. 113–145.
- 23 R. A. Fischer and J. Weiß, *Angew. Chem. Int. Ed.*, 1999, **38**, 2830–2850.
- 24 C. Gemel, T. Steinke, M. Cokoja, A. Kempter and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2004, 4161–4176.
- 25 T. Bollermann, C. Gemel and R. A. Fischer, *Coord. Chem. Rev.*, 2012, **256**, 537–555.
- 26 S. Gonzalez-Gallardo, G. Prabusankar, T. Cadenbach, C. Gemel, M. von Hopffgarten, G. Frenking and R. A. Fischer, in *Metal-Metal Bonding*, 2010, pp. 147–188.
- 27 A. E. Nako, Q. W. Tan, A. J. P. White and M. R. Crimmin, *Organometallics*, 2014, **33**, 2685–2688.
- 28 S. Schlecht and J. F. Hartwig, *J. Am. Chem. Soc.*, 2000, **122**, 9435–9443.
- 29 T. Kakizawa, Y. Kawano and M. Shimoi, *Organometallics*, 2001, **20**, 3211–3213.
- 30 C. Ganesamoorthy, J. Weißing, C. Kroll, R. W. Seidel, C. Gemel and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2014, **53**, 7943–7947.
- 31 I. M. Riddlestone, S. Edmonds, P. A. Kaufman, J. Urbano, J. I. Bates, M. J. Kelly, A. L. Thompson, R. Taylor and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 2551–2554.
- 32 I. M. Riddlestone, J. Urbano, N. Phillips, M. J. Kelly, D. Vidovic, J. I. Bates, R. Taylor and S. Aldridge, *Dalton Trans.*, 2013, **42**, 249–258.
- 33 J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin, N. Phillips, J. I. Bates and S. Aldridge, *Chem. Commun.*, 2013, **49**, 5547–3.
- 34 J. A. B. Abdalla, I. M. Riddlestone, J. Turner, P. A. Kaufman, R. Tirfoin, N. Phillips and S. Aldridge, *Chem. Eur. J.*, 2014, **20**, 17624–17634.
- 35 I. M. Riddlestone, J. A. B. Abdalla and S. Aldridge, in *Advances in Organometallic Chemistry*, 2015, vol. 63, pp. 1–38.
- 36 J. Turner, J. A. B. Abdalla, J. I. Bates, R. Tirfoin, M. J. Kelly, N. Phillips and S. Aldridge, *Chem. Sci.*, 2013, **4**, 4245–4250.
- 37 O. Ekkert, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2016, DOI:10.1002/anie.201608599.
- 38 K. Ueno, T. Yamaguchi, K. Uchiyama and H. Ogino, *Organometallics*, 2002, **21**, 2347–2349.
- 39 T. Muraoka and K. Ueno, *Coord. Chem. Rev.*, 2010, **254**, 1348–1355.
- 40 K.-R. Porschke, W. Kleimann, Y.-H. Tsay, C. Kruger and G. Wilke, *Chem. Ber.*, 1990, **123**, 1267–1273.
- 41 T. Steinke, C. Gemel, M. Cokoja, M. Winter and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2004, **43**, 2299–2302.
- 42 T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2005, **44**, 2943–2946.
- 43 O. Ekkert, A. J. P. White, H. Toms and M. R. Crimmin, *Chem. Sci.*, 2015, **6**, 5617–5622.
- 44 L. J. Hounjet, D. Adhikari, M. Pink, P. J. Carroll and D. J. Mindiola, *Z. Anorg. Allg. Chem.*, 2015, **641**,

45–48.

- 45 L. Fohlmeister, S. Liu, C. Schulten, B. Moubarak, A. Stasch, J. D. Cashion, L. Gagliardi and C. Jones, *Angew. Chem. Int. Ed.*, 2012, **51**, 8294–8298.
- 46 A. Kempter, C. Gemel and R. A. Fischer, *Chem. Eur. J.*, 2007, **13**, 2990–3000.
- 47 A. Doddi, G. Prabusankar, C. Gemel, M. Winter and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2013, 3609–3615.
- 48 T. Cadenbach, T. Bollermann, C. Gemel and R. A. Fischer, *Dalton Trans.*, 2009, 322–329.
- 49 J. J. Schneider, C. Kruger, M. Nolte, I. Abraham, T. S. Ertel and H. Bertagnoli, *Angew. Chem. Int. Ed.*, 1994, **33**, 2435–2437.
- 50 M. D. Fryzuk, D. H. McConville and S. J. Rettig, *Organometallics*, 1990, **9**, 1359–1360.
- 51 M. D. Fryzuk, D. H. McConville and S. J. Rettig, *Organometallics*, 1993, **12**, 2152–2161.
- 52 T. Cadenbach, C. Gemel, R. Schmid, M. Halbherr, K. Yusenko, M. Cokoja and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2009, **48**, 3872–3876.
- 53 T. Cadenbach, T. Bollermann, C. Gemel, M. Tombul, I. Fernandez, M. V. Hopffgarten, G. Frenking and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 16063–16077.
- 54 T. Cadenbach, C. Gemel, T. Bollermann, I. Fernandez, G. Frenking and R. A. Fischer, *Chem. Eur. J.*, 2008, **14**, 10789–10796.
- 55 A. Kempter, C. Gemel, T. Cadenbach and R. A. Fischer, *Organometallics*, 2007, **26**, 4257–4264.
- 56 M. Molon, C. Gemel and R. A. Fischer, *J. Organomet. Chem.*, 2014, **751**, 573–578.
- 57 B. Buchin, C. Gemel, A. Kempter, T. Cadenbach and R. A. Fischer, *Inorg. Chim. Acta*, 2006, **359**, 4833–4839.
- 58 G. Tan, T. Szilvási, S. Inoue, B. Blom and M. Driess, *J. Am. Chem. Soc.*, 2014, **136**, 9732–9742.
- 59 R. A. Fischer, T. Priermeier and W. Scherer, *J. Organomet. Chem.*, 1993, **459**, 65–71.
- 60 R. A. Fischer, M. M. Schulte, J. Weiß, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme and S. F. Vyboishchikov, *J. Am. Chem. Soc.*, 1998, **120**, 1237–1248.
- 61 R. A. Fischer and T. Priermeier, *Organometallics*, 1994, **13**, 4306–4314.
- 62 J. T. Golden, T. H. Peterson, P. L. Holland, R. G. Bergman and R. A. Andersen, *J. Am. Chem. Soc.*, 1998, **120**, 223–224.
- 63 H. Brunner, P. C. Wailes and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 125–129.
- 64 A. Storr and B. S. Thomas, *Can. J. Chem.*, 1971, **49**, 2504–2507.
- 65 J. W. Bruno, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 444–445.
- 66 M. Amati and F. Leij, *Can. J. Chem.*, 2009, **87**, 1406–1414.
- 67 P. C. Wailes, H. Weigold and A. P. Bell, *J. Organomet. Chem.*, 1972, **43**, C29–C31.
- 68 M. L. H. Green, R. E. MacKenzie and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1976, 1993–1994.
- 69 M. Stender, H. Oesen, S. Blaurock and E. Hey Hawkins, *Z. Anorg. Allg. Chem.*, 2001, 980–984.
- 70 R. A. Forder and K. Prout, *Acta Cryst.*, 1974, **B30**, 2312–2317.
- 71 S. J. Rettig, A. Storr, B. S. Thomas and J. Trotter, *Acta Cryst.*, 1974, **B30**, 666–672.
- 72 D. E. Crotty, T. J. Anderson, M. D. Glick and J. P. Oliver, *Inorg. Chem.*, 1977, **16**, 2346–2350.
- 73 R. L. Geerts, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1986, **25**, 590–591.
- 74 M. A. Porai-Koshits, A. S. Antsyshkina, A. A. Pasynskii, G. G. Sadikov, Y. V. Skripkin and V. N. Ostrikova, *Inorg. Chim. Acta*, 1979, **34**, L285–L287.
- 75 F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 5412–5414.
- 76 P. H. M. Budzelaar, A. A. H. Van Der Zeijden, J. Boersma, G. J. M. Van Der Kerk, A. L. Spek and A. J. M. Duisenberg, *Organometallics*, 1984, **3**, 159–163.
- 77 P. H. M. Budzelaar, K. H. Den Haan, J. Boersma, G. J. M. Van Der Kerk and A. L. Spek, *Organometallics*, 1984, **3**, 156–159.
- 78 M. Ohashi, K. Matsubara, T. Iizuka and H. Suzuki, *Angew. Chem. Int. Ed.*, 2003, **49**, 937–940.
- 79 M. Ohashi, K. Matsubara and H. Suzuki, *Organometallics*, 2007, **26**, 2330–2339.
- 80 K. Prout and R. A. Forder, *Acta Cryst.*, 1975, **B31**, 852–856.
- 81 M. L. H. Green, G. A. Moser, I. Packer, F. Petit, R. A. Forder and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1974, 839–840.
- 82 M. Devillard, R. Declercq, E. Nicolas, A. W. Ehlers, J. Backs, N. Saffon-Merceron, G. Bouhadir, J. C. Sootweg, W. Uhl and D. Bourissou, *J. Am. Chem. Soc.*, 2016, **138**, 4917–4926.
- 83 R. A. Fischer, D. Weiß, M. Winter, I. Müller, H. D. Kaesz, N. Fröhlich and G. Frenking, *J. Organomet. Chem.*, 2004, **689**, 4611–4623.
- 84 B. E. Cowie, F. A. Tsao and D. J. H. Emslie, *Angew. Chem. Int. Ed.*, 2014, **54**, 2165–2169.
- 85 L. V. Parfenova, P. V. Kovyazin, I. E. Nifant'ev, L. M. Khalilov and U. M. Dzhemilev, *Organometallics*, 2015, **34**, 3559–3570.
- 86 V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics*, 2006, **25**, 519–522.
- 87 J. Kopf, H. J. Vollmer and W. Kaminsky, *Cryst. Struct. Commun.*, 1980, **9**, 985.
- 88 A. I. Sizov, T. M. Zvukova, A. A. Gorkovskii, Z. A. Starikova and B. M. Bulychev, *Russ. Chem. Bull.*, 2004, **53**, 2175–2178.

- 89 T. M. Arkhireeva, V. K. Bel'skii, B. M. Bulychev and G. L. Soloveichik, *Russ. Chem. Bull.*, 1986, **35**, 2585–2587.
- 90 D. Schädle, C. Schädle, D. Schneider, C. Maichle-Mössmer and R. Anwander, *Organometallics*, 2015, **34**, 4994–5008.
- 91 C. Schädle, C. Maichle-Mössmer, K. W. Törnroos and R. Anwander, *Organometallics*, 2015, **34**, 2667–2675.
- 92 C. Schädle, D. Schädle, K. Eichele and R. Anwander, *Angew. Chem. Int. Ed.*, 2013, **52**, 13238–13242.
- 93 M. G. Klimpel, P. Sirsch, W. Scherer and R. Anwander, *Angew. Chem. Int. Ed.*, 2003, **42**, 574–577.
- 94 S. Y. Knjazhanski, B. M. Bulychev, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1987, **327**, 173–179.
- 95 C. Schädle, A. Fischbach, E. Herdtweck, K. W. Törnroos and R. Anwander, *Chem. Eur. J.*, 2013, **19**, 16334–16341.
- 96 C. Schädle and R. Anwander, *Eur. J. Inorg. Chem.*, 2013, 3302–3306.
- 97 E. B. Lobkovskii, G. L. Soloveichik, A. B. Erofeev, B. M. Bulychev and V. K. Bel'skii, *J. Organomet. Chem*, 1982, **235**, 151–159.
- 98 E. Lobkovsky, G. L. Soloveychik, B. M. Bulychev, A. B. Erofeev, A. I. Gusev and N. I. Kirillova, *J. Organomet. Chem*, 1983, **254**, 167–172.
- 99 V. K. Bel'skii, B. M. Bulychev, A. B. Erofeev and G. L. Soloveichik, *J. Organomet. Chem*, 1984, **268**, 107–111.
- 100 V. K. Belsky, A. B. Erofeev, B. M. Bulychev and G. L. Soloveichik, *J. Organomet. Chem*, 1984, **265**, 123–133.
- 101 S. Y. Knjazhanski, B. M. Bulychev, O. K. Kireeva, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1991, **414**, 11–22.
- 102 V. K. Belsky, Y. K. Gun'ko, B. M. Bulychev and G. L. Soloveichik, *J. Organomet. Chem*, 1991, **419**, 299–310.
- 103 Y. K. Gun'ko, B. M. Bulychev, A. I. Sizov, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1990, **390**, 153–158.
- 104 A. B. Erofeev, B. M. Bulychev, V. K. Bel'skii and G. L. Soloveichik, *J. Organomet. Chem*, 1987, **335**, 189–199.
- 105 S. Y. Knjazhanski, E. B. Lobkovsky, B. M. Bulychev, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1991, **419**, 311–324.
- 106 M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1983, 206–207.
- 107 K. D. Conroy, W. E. Piers and M. Parvez, *Organometallics*, 2009, **28**, 6228–6233.
- 108 Y. K. Gun'ko, B. M. Bulychev, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1992, **440**, 47–52.
- 109 H. G. Alt and A. Köppl, *Chem. Rev.*, 2000, **100**, 1205–1222.
- 110 L. I. Shoer, K. I. Gell and J. Schwartz, *J. Organomet. Chem*, 1977, **136**, C19–C22.
- 111 S. M. Baldwin, J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, 2008, **130**, 17423–17433.
- 112 U. M. Dzhemilev and A. G. Ibragimov, *Russ. Chem. Rev.*, 2012, **81**, 524–548.
- 113 K. P. Bryliakov, E. P. Talsi, A. Z. Voskoboynikov, S. J. Lancaster and M. Bochmann, *Organometallics*, 2008, **27**, 6333–6342.
- 114 S. M. Baldwin, J. E. Bercaw, L. M. Henling, M. W. Day and H. H. Brintzinger, *J. Am. Chem. Soc.*, 2011, **133**, 1805–1813.
- 115 S. M. Baldwin, J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, 2010, **132**, 13969–13971.
- 116 K. Khan, C. L. Raston, J. E. McGrady, B. W. Skelton and A. H. White, *Organometallics*, 1997, **16**, 3253–3254.
- 117 R. J. Wehmschulte and P. P. Power, *Polyhedron*, 1999, **18**, 1885–1888.
- 118 N. Etkin, A. J. Hoskin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 11420–11424.
- 119 S. Yow, S. J. Gates, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2012, **51**, 12559–12563.
- 120 M. J. Butler, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.*, 2016, **55**, 6951–6953.
- 121 N. Etkin and D. W. Stephan, *Organometallics*, 1998, **17**, 763–765.
- 122 E. B. Lobkovskii, G. L. Soloveichik, B. M. Bulychev, R. G. Gerr and Y. T. Struchkov, *J. Organomet. Chem*, 1984, **270**, 45–51.
- 123 E. B. Lobkovskii, G. L. Soloveichik, A. J. Sisov, B. M. Bulychev, A. I. Gusev and N. I. Kirillova, *J. Organomet. Chem*, 1984, **265**, 167–173.
- 124 V. K. Bel'sky, A. I. Sizov, B. M. Bulychev and G. L. Soloveichik, *J. Organomet. Chem*, 1985, **280**, 67–80.
- 125 T. Y. Sokolova, A. I. Sizov, B. M. Bulychev, E. A. Rozova, V. K. Belsky and G. L. Soloveichik, *J. Organomet. Chem*, 1990, **288**, 11–19.
- 126 A. I. Sizov, T. M. Zvukova, V. K. Belsky and B. M. Bulychev, *Russ. Chem. Bull.*, 1998, **47**, 1186–

- 1192.
- 127 A. I. Sizov, T. M. Zvukova, B. M. Bulychev and V. K. Belsky, *J. Organomet. Chem*, 2000, **603**, 167–173.
- 128 R. Sun, J. Liu, S. Yang, M. Chen, N. Sun, H. Chen, X. Xie, X. You, S. Li and Y. Liu, *Chem. Commun.*, 2015, **51**, 6426–6429.
- 129 J. Thomas, M. Klahn, A. Spannenberg and T. Beweries, *Dalton Trans.*, 2013, **42**, 14668–14672.
- 130 A. I. Sizov, I. V. Molodnitskaya, B. M. Bulychev, V. K. Bel'skii and G. L. Soloveichik, *J. Organomet. Chem*, 1988, **344**, 185–193.
- 131 A. I. Sizov, T. M. Zvukova, V. K. Belsky and B. M. Bulychev, *J. Organomet. Chem*, 2001, **619**, 36–42.
- 132 A. I. Sizov, T. M. Zvukova, V. K. Belsky and B. M. Bulychev, *Russ. Chem. Bull.*, 2001, **50**, 2200–2202.
- 133 L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 7870–7872.
- 134 F. N. Tebbe and L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 1973, 227–228.
- 135 S. I. Troyanov, V. Varga and K. Mach, *J. Organomet. Chem*, 1993, **461**, 85–90.
- 136 R. Gyepes, K. Mach, I. Cisarova, J. Loub, J. Hiller and P. Sindelar, *J. Organomet. Chem*, 1995, **497**, 33–41.
- 137 M. Horacek, J. Hiller, U. Thewalt, M. Polášek and K. Mach, *Organometallics*, 1997, **16**, 4185–4191.
- 138 V. Kupfer, U. Thewalt, M. Horacek, L. Petrusova and K. Mach, *Inorg. Chem. Commun.*, 1999, **2**, 540–544.
- 139 M. Horáček, I. Cisarova, J. Cejka, J. Karban, L. Petrusova and K. Mach, *J. Organomet. Chem*, 1999, **577**, 103–112.
- 140 M. Horáček, P. Štěpnička, J. Kubišta, K. Fejfarová, R. Gyepes and K. Mach, *Organometallics*, 2003, **22**, 861–869.
- 141 K. Mach, R. Gyepes, M. Horáček, L. Petrusová and J. Kubišta, *Collect. Czech. Chem. Commun.* 2003, **68**, 1877–1896.
- 142 Q. F. Mokuolu, P. A. Duckmanton, A. J. Blake, C. Wilson and J. B. Love, *Organometallics*, 2003, **22**, 4387–4389.
- 143 E. B. Lobkovskii, G. L. Soloveichik, A. I. Sizov and B. M. Bulychev, *J. Organomet. Chem*, 1985, **280**, 53–66.
- 144 E. B. Lobkovskii, A. I. Sizov, B. M. Bulychev and I. V. Sokolova, *J. Organomet. Chem*, 1987, **319**, 69–75.
- 145 H. Lee, T. Hascall, P. J. Desrosiers and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 5830–5831.
- 146 G. Erker, M. Albrecht, C. Kruger, S. Werner, P. Binger and F. Langhauser, *Organometallics*, 1992, **11**, 3517–3525.
- 147 R. Gleiter, I. Hyla-Kryspin, S. Niu and G. Erker, *Angew. Chem. Int. Ed.*, 1993, **32**, 754–756.
- 148 M. Albrecht, G. Erker and C. Kruger, *Synlett*, 1993, 441–448.
- 149 G. Bender, T. Wiegand, H. Eckert, R. Fröhlich, C. G. Daniliuc, C. Mück-Lichtenfeld, S. Ndambuki, T. Ziegler, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.*, 2012, **51**, 8846–8849.
- 150 P. Arndt, A. Spannenberg, W. Baumann, S. Becke and U. Rosenthal, *Eur. J. Inorg. Chem.*, 2001, 2885–2890.
- 151 V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics*, 2004, **23**, 4160–4165.
- 152 V. V. Burlakov, K. Kaleta, T. Beweries, P. Arndt, W. Baumann, A. Spannenberg, V. B. Shur and U. Rosenthal, *Organometallics*, 2011, **30**, 1157–1161.
- 153 P. Arndt, A. Spannenberg, W. Baumann, V. V. Burlakov, U. Rosenthal, S. Becke and T. Weiss, *Organometallics*, 2004, **23**, 4792–4795.
- 154 R. M. Waymouth, B. D. Santarsiero, R. J. Coots, M. J. Bronikowski and R. H. Grubbs, *J. Am. Chem. Soc.*, 1986, **108**, 1427–1441.
- 155 G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 6752–6753.
- 156 G. S. Girolami, C. G. Howard, G. Wilkinson, H. M. Dawes, M. Thornton-Pett, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 921–929.
- 157 A. R. Barron, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 837–846.
- 158 R. Gilbert-Wilson, L. D. Field and M. Bhadbhade, *Inorg. Chem.*, 2014, **53**, 12469–12479.
- 159 G. S. Girolami, *Organometallics*, 1997, 2987–2994.
- 160 M. Plois, T. Wiegand and R. Wolf, *Organometallics*, 2012, **31**, 8469–8477.
- 161 M. Plois, R. Wolf, W. Hujo and S. Grimme, *Eur. J. Inorg. Chem.*, 2013, 3039–3048.
- 162 T. N. Gieshoff, M. Villa, A. Welther, M. Plois, U. Chakraborty, R. Wolf and A. Jacobi von Wangelin, *Green Chem.*, 2015, **17**, 1408–1413.
- 163 A. R. Barron, M. B. Hursthouse, M. Motevalli and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1985, 664–665.
- 164 A. R. Barron and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1986, 287–3.

- 165 A. R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A. J. Howes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 279–285.
- 166 D. H. Lee, H. Suzuki and Y. Moro-oka, *J. Organomet. Chem.*, 1987, **330**, C20–C22.
- 167 M. D. Fryzuk, G. K. B. Clentsmith and S. J. Rettig, *Inorg. Chim. Acta*, 1997, **259**, 51–59.
- 168 V. Saboonchian, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1991, **10**, 595–603.
- 169 G. I. Nikonov, L. G. Kuzmina and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 2002, 3037–3046.
- 170 T. J. McNeese, S. S. Wreford and B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 1978, 500–502.
- 171 O. Ekkert, S. D. A. Strudley, A. Rozenfeld, A. J. P. White and M. R. Crimmin, *Organometallics*, 2014, **33**, 7027–7030.
- 172 W. A. Skupinski, J. C. Huffman, J. W. Bruno and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8128–8136.
- 173 K. Knox and A. P. Ginsberg, *Inorg. Chem.*, 1964, **3**, 555–558.
- 174 M. Oishi, T. Endo, M. Oshima and H. Suzuki, *Inorg. Chem.*, 2014, **53**, 5100–5108.
- 175 I. M. Riddlestone, N. A. Rajabi, J. P. Lowe, M. F. Mahon, S. A. Macgregor and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2016, **138**, 11081–11084.
- 176 M. Molon, C. Gemel and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2013, 3616–3622.
- 177 V. Riera, M. A. Ruiz, A. Tiripicchio and M. Tiripicchio-Camellini, *Organometallics*, 1993, **12**, 2962–2972.
- 178 R. L. Bansemer, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 6163–6164.
- 179 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.
- 180 P. Klufers, U. Wilhem, *J. Organomet. Chem.* 1991, 421, 39–54.
- 181 M. Hamdaoui, M. Ney, V. Sarda, L. Karmazin, C. Bailly, N. Sieffert, S. Dohm, A. Hansen, S. Grimme and J.-P. Djukic, *Organometallics*, 2016, **35**, 2207–2223.
- 182 W. H. Harman and J. C. Peters, *J. Am. Chem. Soc.*, 2012, **134**, 5080–5082.
- 183 I. Atheaux, B. Donnadiou, V. Rodriguez, S. Sabo-Etienne, B. Chaudret, K. Hussein and J.-C. Barthelat, *J. Am. Chem. Soc.*, 2000, **122**, 5664–5665.
- 184 M. C. Lipke and T. D. Tilley, *Angew. Chem. Int. Ed.*, 2012, **51**, 11115–11121.
- 185 R. N. Perutz and B. Procacci, *Chem. Rev.*, 2016, **116**, 8506–8544.
- 186 E. S. Wiedner, M. B. Chambers, C. L. Pitman, R. M. Bullock, A. J. M. Miller and A. M. Appel, *Chem. Rev.*, 2016, **116**, 8655–8692.
- 187 A. Maity and T. S. Teets, *Chem. Rev.*, 2016, **16**, 8873–8911.
- 188 R. C. Cammarota and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 12486–12489.
- 189 N. P. Mankad, *Chem. Eur. J.*, 2016, **22**, 5822–5829.
- 190 R. J. Eisenhart, L. J. Clouston and C. C. Lu, *Acc. Chem. Res.*, 2015, **48**, 2885–2894.

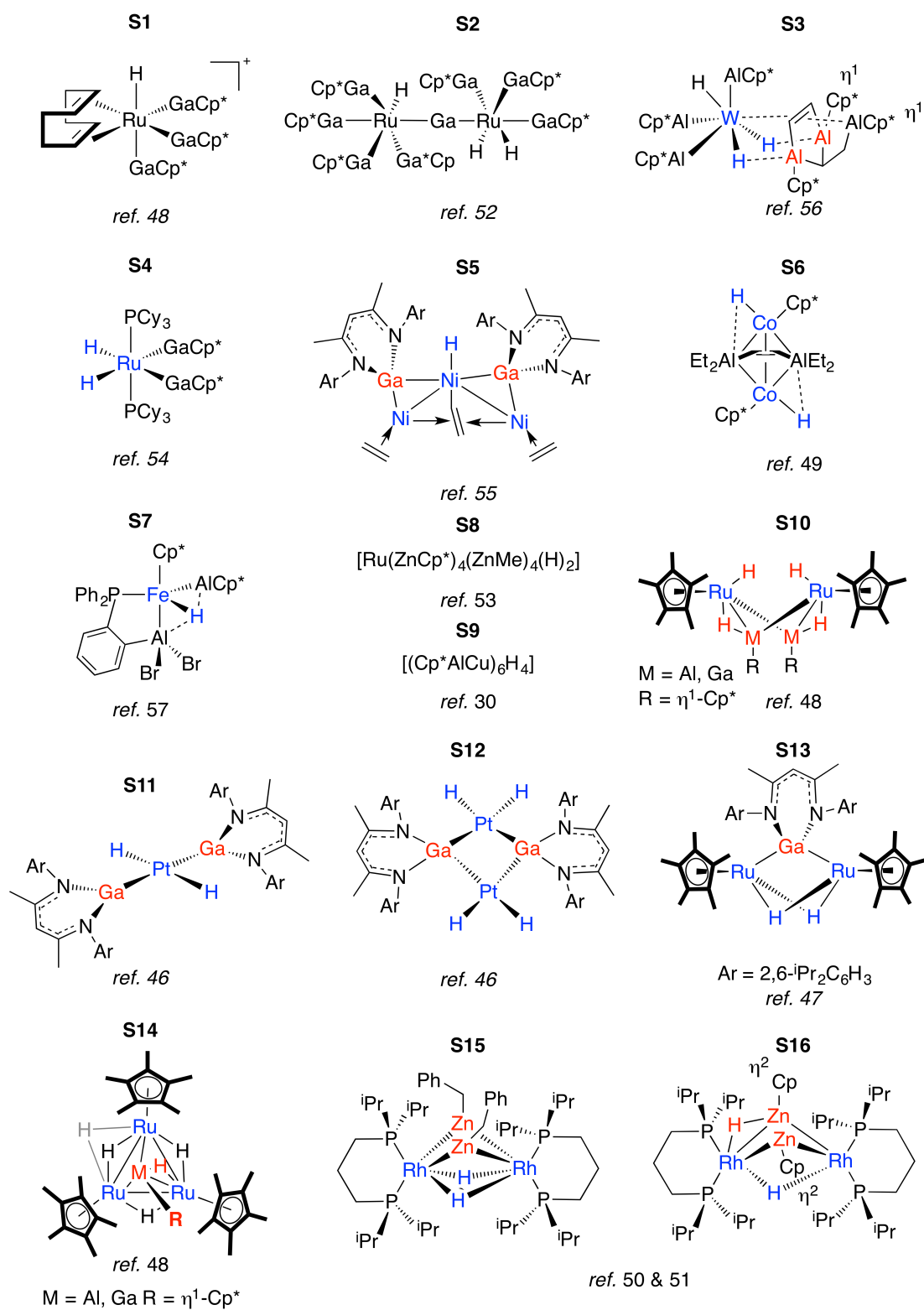


Figure S1. Additional heterobimetallic hydrides (many containing non-bridging hydrides) not included in main text.