

Cite this: *Chem. Commun.*, 2012, **48**, 11481–11503

www.rsc.org/chemcomm

FEATURE ARTICLE

The occurrence and representation of three-centre two-electron bonds in covalent inorganic compounds

Jennifer C. Green,^a Malcolm L. H. Green^{*a} and Gerard Parkin^{*b}

Received 23rd July 2012, Accepted 12th September 2012

DOI: 10.1039/c2cc35304k

Although compounds that feature 3-centre 2-electron (3c–2e) bonds are well known, there has been no previous effort to classify the interactions according to the number of electrons that each atom contributes to the bond, in a manner analogous to the classification of 2-centre 2-electron (2c–2e) bonds as either normal covalent or dative covalent. This article provides an extension to the Covalent Bond Classification (CBC) method by categorizing 3c–2e interactions according to whether (i) the two electrons are provided by one or by two atoms and (ii) the central bridging atom provides two, one, or zero electrons. Class I 3c–2e bonds are defined as those in which two atoms each contribute one electron to the 3-centre orbital, while Class II 3c–2e bonds are defined as systems in which the pair of electrons are provided by a single atom. Class I and Class II 3c–2e interactions can be denoted by structure–bonding representations that employ the “half-arrow” notation, which also provides a convenient means to determine the electron count at a metal centre. In contrast to other methods of electron counting, this approach provides a means to predict metal–metal bond orders that are in accord with theory. For example, compounds that feature symmetrically bridging carbonyl ligands do not necessarily have to be described as “ketone derivatives” because carbon monoxide can also serve as an electron pair donor to two metal centres. This bonding description also provides a simple means to rationalize the theoretical predictions of the absence of M–M bonds in molecules such as Fe₂(CO)₉ and [CpFe(CO)₂]₂, which are widely misrepresented in textbooks as possessing M–M bonds.

1. Introduction

Together with simple electron counting procedures (e.g. the octet^{1,2} and 18-electron^{2a,3} rules), the concept of the 2-centre

^a Department of Chemistry, Oxford University, Oxford OX1 3QR, UK

^b Department of Chemistry, Columbia University, New York, New York 10027, USA



Jennifer C. Green

Jennifer C. Green (née Bilham) was born in Tadworth, Surrey on 30th December, 1941. She was educated at St. Hugh's College, Oxford where she obtained her B.A., M.A. and D.Phil., the latter being supervised by Professor Jack Linnett and Dr Peter Atkins. She is currently an Emeritus Professor in the Chemistry Department at Oxford University. Her research interests centre around the electronic structure and bonding of transition metal compounds,

and the relation of their electronic properties to their chemical reactivity. The main investigative tools used in these studies have been photoelectron spectroscopy and density functional theory.



Malcolm L. H. Green

Malcolm Green became an Emeritus Professor of Chemistry in 2003 after spending 40 years in the Inorganic Chemistry Department of Oxford University. He is still interested and working on aspects of heterogeneous catalysis, the chemistry of carbon nanotubes and, his first area of interest, organo-transition metal chemistry. He follows the progress of the company Oxford Catalysts Group, which he co-founded. His 138th and final graduate student is now

writing her thesis. About 60 ex-members of his research group hold, or have held, academic posts around the world.

2-electron (2c–2e) bond,¹ and its representation as a solid black line between two atoms in so-called “Lewis structures”,⁴ have been of immense importance in the development of chemistry. Specifically, such structure-bonding (S-B) representations provide a simple means both to (i) describe the structures and bonding of a wide variety of covalent organic and inorganic molecules and (ii) convey chemical reactions and their mechanisms. However, despite the importance of the concept of the 2c–2e bond and its representation, its limitations as a model are well-known. For example, it is not possible to describe the structures of many molecules (e.g. B₂H₆) in terms of only 2c–2e bonds because the bonding involves multicentre interactions. The bonding within such molecules may, nevertheless, be analyzed by application of either molecular orbital theory or more sophisticated theoretical methods. However, while these theoretical methods provide insight into the nature of a compound, they lack the convenience of simple electron counting procedures in evaluating the chemical reasonableness of a proposed covalent molecule.

Fortunately, regardless of the fact that molecular orbitals are highly delocalized, the bonding in molecules with multi-centred bonding can often be expressed in terms of a combination of 2-centre 2-electron and 3-centre 2-electron (3c–2e) interactions. The purpose of this article is to describe how electron counting procedures can be applied to such molecules. Specifically, we (i) classify 3c–2e bonds according to three different types that are distinguished by whether the bridging atom contributes zero, one or two electrons, and (ii) provide a simple means to represent these interactions in a conveniently employed “Lewis-type” manner with respect to electron counting procedures. Furthermore, we describe a new Lewis-type representation for the bonding in certain transition metal compounds with symmetrically bridging carbonyl

ligands. Significantly, the new representations may be used to predict M–M bond orders that are in accord with the values that are obtained theoretically, in contrast to the bond orders that are predicted by conventional electron counting methods. As an illustration, the article will reconcile why compounds such as Fe₂(CO)₉ and [CpFe(CO)₂]₂ are misrepresented in many text books as possessing Fe–Fe bonds, despite the fact that, for many years, theoretical calculations have indicated the absence of such bonding interactions.

2. Classification of 3-centre 2-electron bonds

It is well recognized that there are two fundamentally different classes of 2c–2e interactions that are distinguished according to the number of electrons that each partner contributes to the interaction. If each partner contributes one electron to the bonding orbital, the interaction is described as a normal covalent single bond, while if both electrons are contributed by a single partner, the interaction is described as a dative (or coordinate) covalent bond (Fig. 1); the atom that provides the electrons is referred to as an electron pair donor. Thus, a bond is classified as dative covalent if minimum energy bond rupture, in either the gas phase or in an inert solvent, proceeds heterolytically (*i.e.* both electrons transfer to a single atom), while a bond is classified as normal covalent if minimum energy bond rupture proceeds homolytically (*i.e.* one electron is transferred to each atom) to yield a pair of radicals.⁵

The important distinction between these two classes of bonds has been highlighted by Haaland,⁵ and this difference is an important feature of the Covalent Bond Classification (CBC) of molecules.⁶ Specifically, the CBC method classifies a molecule in terms of the nature of the ligands around the



Gerard Parkin

Gerard Parkin received his B.A., M.A., and D.Phil. degrees from the Queen's College, Oxford University. Both his graduate and undergraduate research was carried out under the guidance of Professor Malcolm L. H. Green. In 1985, he moved to the California Institute of Technology as a NATO postdoctoral fellow with Professor John E. Bercaw and joined the faculty of Columbia University in 1988. He is a Fellow of both the American Chemical

Society and the Royal Society of Chemistry. Among other awards, he is a recipient of the ACS Award in Pure Chemistry, the ACS Award in Organometallic Chemistry, the RSC Corday Morgan Medal, the RSC Award in Organometallic Chemistry, the RSC Chem Soc Rev Lecture Award, and the Presidential Award for Excellence in Science, Mathematics and Engineering Mentoring. His principal research interests are in the areas of synthetic, structural, and mechanistic inorganic chemistry.

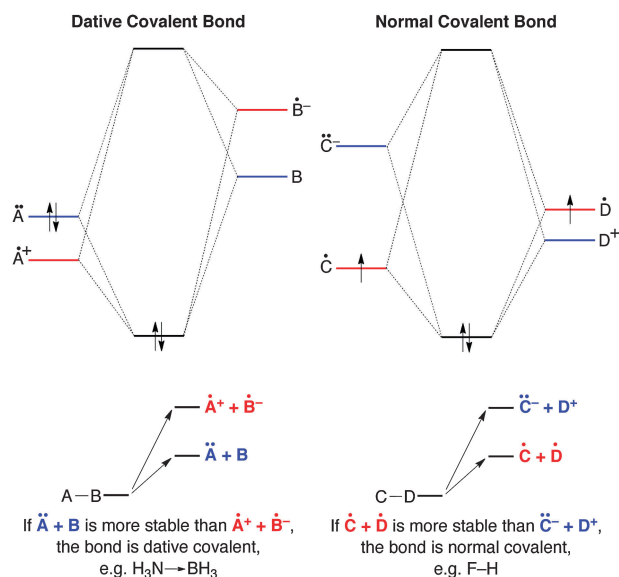


Fig. 1 Schematic illustration of the distinction between a normal covalent bond and a dative covalent bond. A bond is (i) dative covalent (left) if minimum energy rupture proceeds heterolytically, *i.e.* both electrons transfer to one atom to give diamagnetic fragments (coloured blue), and is (ii) normal covalent (right) if minimum energy rupture proceeds homolytically, *i.e.* one electron is transferred to each atom, to yield radicals (coloured red).

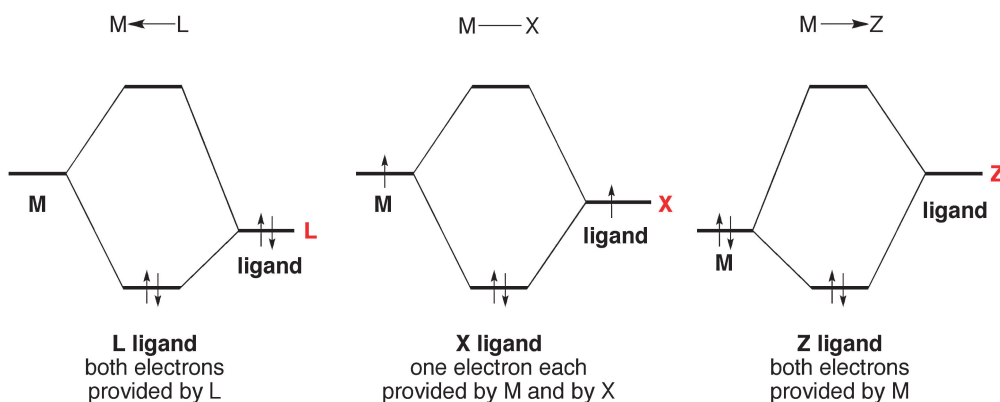


Fig. 2 The Covalent Bond Classification (CBC) of L, X, and Z ligands.

element of interest (M), according to whether the neutral ligands contribute two, one or zero electrons to the bond (Fig. 2). These ligands are respectively represented in the CBC method by the symbols L (for 2-electrons), X (for 1-electron) and Z (for 0-electrons). Simple molecular orbital diagrams that illustrate the different occupancies for L, X and Z ligands are depicted in Fig. 2. A normal 2c–2e covalent bond is described as an [X–X] interaction, while a dative bond is described as an [L → Z] interaction.

According to the CBC method, a molecule is classified as $[ML_iX_xZ_z]^{Q\pm}$ by summing all the L-, X-, and Z- functionalities, as illustrated in Fig. 3 for some tungsten complexes. For example, Cp_2WH_2 is classified as $[ML_4X_4]$ since $Cp \equiv [L_2X]$ and $H \equiv [X]$, while $[Cp_2WH_3]^+$ is classified as $[ML_4X_5]^+$. However, in order to compare molecules that have different charges, the $[ML_iX_xZ_z]^{Q\pm}$ assignment is reduced to its “equivalent neutral class”, which is the classification that results if the $Q\pm$ charge were to be localized on the ligands rather than on the metal centre. Although the procedure for obtaining the equivalent neutral class is presented in detail elsewhere,⁶ the essential transformations are as follows: for cations, $L^+ \rightarrow X$ and, if no L ligand is present, $X^+ \rightarrow Z$; for anions, $X^- \rightarrow L$ and, if no X ligand is present, $L^- \rightarrow LX$. If the derived classification after performing these transformations contains both an L and a Z function, the classification is reduced further by using the transformation $LZ \rightarrow X_2$. As an illustration of this

procedure, $[Cp_2WH_3]^+$, which is classified as $[ML_4X_5]^+$, transforms to $[ML_3X_6]$ by applying the rule $L^+ \rightarrow X$.

As an extension of the notion that 2c–2e bonds can be classified according to the number of electrons that each partner contributes, 3c–2e interactions may likewise be conveniently classified according to whether the bridging atom contributes none (μ -Z), one (μ -X) or two (μ -L) electrons (Fig. 4). Thus, in this article, we use the descriptions μ -Z, μ -X and μ -L to indicate

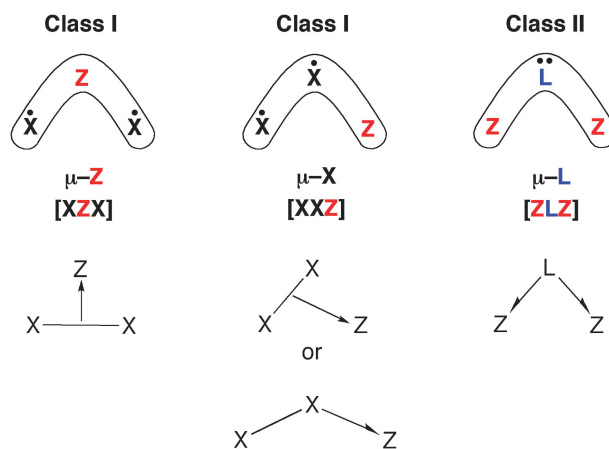


Fig. 4 Classification of 3-centre 2-electron (3c–2e) interactions according to the nature of the specified bridging atom.

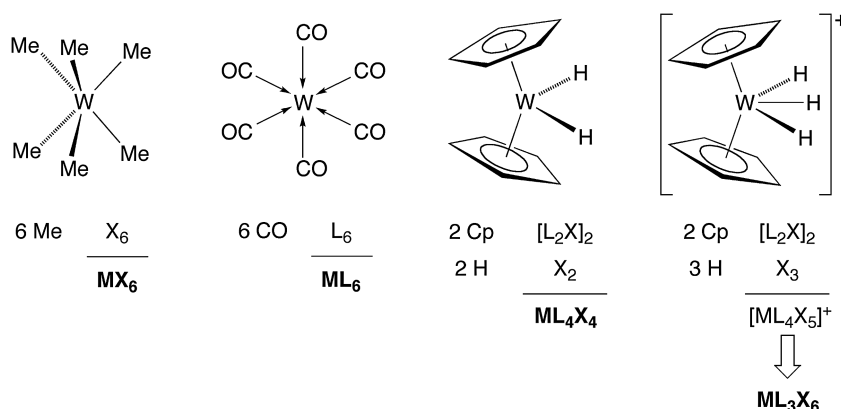


Fig. 3 $[ML_iX_xZ_z]$ classifications of some simple tungsten compounds. The initially derived $[ML_4X_5]^+$ classification of $[Cp_2WH_3]^+$ is transformed to the equivalent neutral class of ML_3X_6 upon applying the rule $L^+ \rightarrow X$.

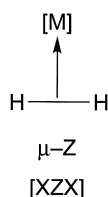


Fig. 5 An example of a 3c–2e interaction with a μ -Z bridge.

the number of electrons that a specified bridging atom⁷ contributes to the 3c–2e bond, and a simple way to represent the interactions is presented in Fig. 4.

Molecules with bridging μ -Z atoms are depicted with the familiar structure-bonding notation in which an arrow is drawn from the midpoint of the X–X bond to Z, thereby indicating that an X–X bonding pair of electrons serves as a “dative bond” to Z and thus contributes two electrons to the electron count of the latter. Representative examples of this type of interaction are provided by dihydrogen complexes, $[M](\eta^2-H_2)$ (Fig. 5),⁸ which belong to a class of molecules referred to as σ -complexes.

Molecules with bridging μ -X atoms can also be depicted by drawing an arrow from the centre of the X–X bond to the outer Z atom (Fig. 4). This structure-bonding representation is most commonly employed if the angle at the central atom is distinctly nonlinear and the outer Z atom is considered to be within a bonding distance to both X atoms (*i.e.* a “closed” system¹⁰), as illustrated by alkane σ -complexes (Fig. 6). However, if the [XXZ] interaction is almost linear (*i.e.* an “open” system¹⁰), the outer Z atom interacts primarily with only the central X atom, and so the interaction is more conveniently represented by using the X–X \rightarrow Z “half-arrow” notation in which the “half-arrow” is drawn from the central X atom to the outer Z atom (Fig. 4),⁹ as illustrated for the bridging hydride complex, $\{[(CO)_5Cr]_2(\mu-H)\}^-$ (Fig. 6).¹⁰ The reason for using a half-arrow from the atom (rather than a full arrow) is to emphasize that the arrow does not correspond to donation of a lone pair, but rather donation of a bond pair. The two representations (*i.e.* a full-arrow from the centre of the bond and a half-arrow from the central atom) are intended to convey the same information with respect to electron counting purposes, and the form that is used is often a matter of convenience (*cf.* representing a dative covalent bond as either $A \rightarrow B$ or $A^+ - B^-$).

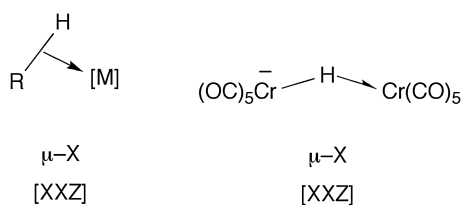


Fig. 6 Two ways of representing 3c–2e interactions with a μ -X bridge. The representation on the left is often used when the angle at the bridging atom is distinctly nonlinear and Z is within bonding distance to both X atoms, while the representation on the right is more commonly used when the angle at the central atom is closer to linear. Both representations are intended to convey the same information with respect to electron counting. Note that the molecule on the right can also be drawn with an equivalent structure-bonding representation in which the half-arrow is drawn to the chromium on the left and the formal charge is located on the chromium on the right.

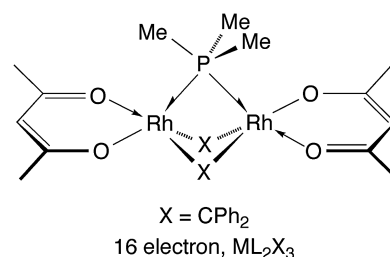


Fig. 7 An example of a compound that features a 3c–2e interaction with a μ -L bridge.

For molecules with [ZLZ] 3c–2e interactions, the bridging L atom contributes a pair of electrons to the three-centre orbital, while the orbitals on the outer atoms are initially empty and provide no electrons. Since all three atoms share the pair of electrons, the donor atom may be regarded as effectively contributing two electrons to the electron count of *both* outer atoms (Fig. 4). This bonding situation may, therefore, be represented by a pair of half-arrows that are drawn from the central atom (L) to each outer atom (Z); the reason for the use of half-arrows is to emphasize that the donor atom is not using two lone pairs, but rather that a single electron pair is being shared with both Z atoms. An example of this type of interaction is provided by complexes that feature bridging PR_3 ligands,¹¹ as illustrated in Fig. 7.

Thus, to summarize with respect to electron counting procedures, a μ -X bridging group behaves as if it were a “ μ -XL” ligand, in the sense that the 3c–2e interaction results in one of the other partners (X) receiving one electron, and the other (Z) receiving two electrons. A μ -L bridging group behaves as if it were a “ μ -L₂” ligand, in the sense that each Z partner receives a pair of electrons. On the other hand, a μ -Z ligand contributes no electrons to either of the X partners, but each X atom contributes a single electron that is shared with both its X partner and the Z atom.

3. The occurrence of 3c–2e bonds

Of the three types of 3c–2e interactions illustrated in Fig. 4, those involving μ -Z and μ -X bridging atoms are similar in that they feature a pair of electrons that is provided by *two* atoms, with the arrangement differing merely by the location of Z, *i.e.* [XZX] *versus* [XXZ]. In contrast, for a 3c–2e interaction with a μ -L bridging atom (*i.e.* [ZLZ]), the pair of electrons are provided by a *single* atom.¹² These two categories may be respectively represented as Class I and Class II (Fig. 4). Of these, compounds belonging to Class I with μ -Z and μ -X bridging atoms are most commonly encountered, as illustrated by bridging hydride complexes, dihydrogen complexes and agostic derivatives.¹³ Specific examples of compounds that are categorized according to the nature of the bridging atom are described below and the CBC designation for coordination of representative ligands to a metal are provided in Table 1.

3.1. Class I μ -Z 3c–2e bonds

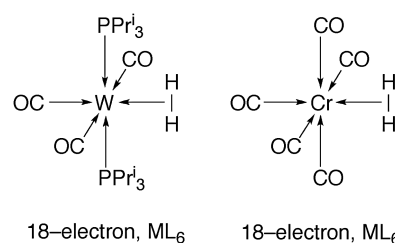
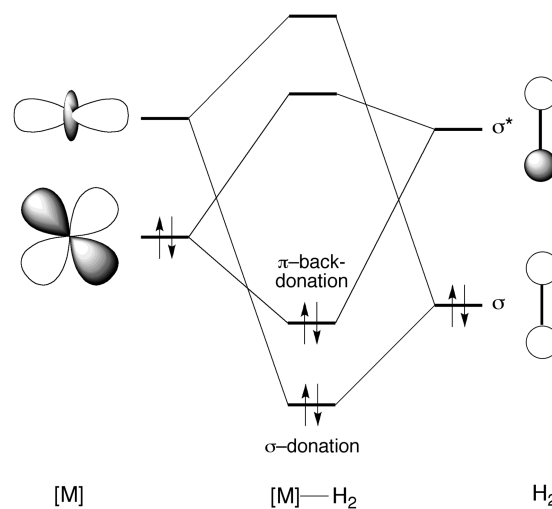
The best examples of compounds with 3c–2e interactions in which the bridging atom utilizes a Z function are provided by dihydrogen complexes, in which the metal is defined as

Table 1 Summary of CBC designations for coordination of various ligands to M

Ligand	CBC classification with respect to M
	L
	L
	L
	LX
	LZ = X ₂
	X
	LX
	L ₂ X
	X
	L

bridging the two hydrogens (Fig. 5). Some early examples of dihydrogen complexes are illustrated in Fig. 8.⁸

However, while the bonding in dihydrogen complexes is normally represented with the metal centre serving as a Lewis acid, it is important to note that supplementary π -backbonding involving the H–H σ^* orbital is crucial for stabilizing the interaction (Fig. 9). This π -backbonding interaction is also responsible for cleaving the H–H bond to form a dihydride tautomer. As such, a continuum of structures exists in which the H–H distance depends on the degree of backbonding (Fig. 10).^{8c} Despite this continuum, dihydrogen complexes are invariably represented without illustrating the backbonding interaction (*cf.* metal carbonyls) because, in the limit that

**Fig. 8** Early examples of transition metal dihydrogen complexes.**Fig. 9** Qualitative molecular orbital diagram for dihydrogen complexes.

backbonding competes with σ -donation, the H–H bond is broken and the compound exists as the dihydride tautomer.

3.2. Class I μ -X 3c–2e bonds

Compounds with Class I interactions that feature a μ -X bridge are very common, as illustrated by (i) hydrocarbon and silane σ -complexes, (ii) bridging hydride, alkyl and silyl complexes, and (iii) agostic complexes, each of which is discussed in this section.

3.2.1. Hydrocarbon and silane σ -complexes. Transition metal hydrocarbon¹⁴ and silane¹⁵ adducts, in which C–H and Si–H bonds interact with a metal centre (Fig. 11), bear a close relationship to dihydrogen complexes, with each belonging to the class of molecules described as σ -complexes.^{8,16} Hydrocarbon and silane σ -complexes are, however, much less commonly encountered than dihydrogen complexes. Indeed, alkane adducts are particularly unstable and have only been spectroscopically identified (i) in matrices at low temperature and (ii) in solutions at either low temperature or by the use of flash photolysis.^{16–19} Such complexes are, nevertheless, commonly invoked as intermediates in reductive-elimination and oxidative-addition reactions on the basis of deuterium labeling and kinetic isotope effects.²⁰

Although there are no crystal structures of stable transition metal alkane σ -complexes,²¹ a variety of silane σ -complexes have been structurally characterized by X-ray diffraction,^{15a–d} as illustrated in Fig. 12.^{22,23} These studies demonstrate that the extent of the M···Si interaction is highly variable and, in one

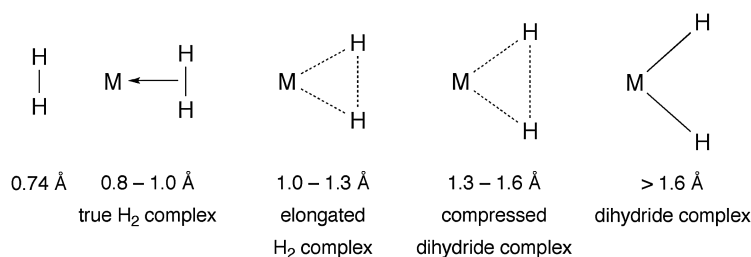


Fig. 10 Classification of $\text{M}[\text{H}_2]$ tautomers as a function of H–H distance. Structure-bonding representations are not given for the intermediate classifications of “elongated H_2 complex” and “compressed dihydride complex” that are shown with dotted lines.

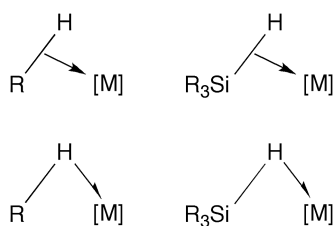


Fig. 11 Two representations of hydrocarbon and silane σ -complexes. Both representations are intended to convey the same information with respect to electron counting.

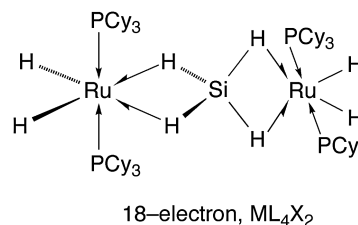


Fig. 14 A bridging silane compound.

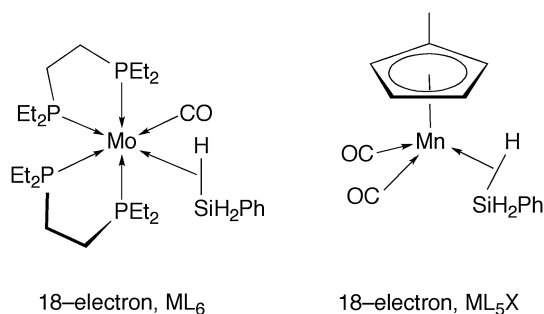


Fig. 12 Examples of structurally characterized silane σ -complexes.

case, the bond angle at hydrogen is close to linear [$157(1)^\circ$] (Fig. 13).²⁴ For this reason, it is evident that hydrogen, rather than the metal, is better identified as the bridging atom ($\mu\text{-X}$) in alkane and silane σ -complexes. The greater preponderance of silane complexes has been attributed to the Si–H bond being more polar and polarizable than a C–H bond, such that it is both a better σ -donor and π -acceptor.^{15,16} As with dihydrogen compounds, the length of the Si–H bond depends critically on the extent of π -backbonding. However, the bonding situation for σ -silanes is more complicated than that for dihydrogen compounds because the multicentre interaction is not restricted to three centres and can involve four or more atoms, situations

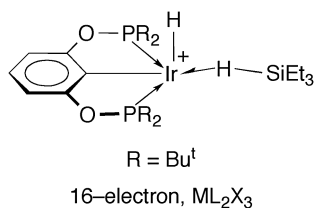


Fig. 13 An example of a silane σ -complex with a large Si–H–M bond angle (157°).

that have been referred to as “interligand hypervalent interactions” (IHI)^{15d} and “secondary interaction between a silicon and a hydrogen atom (SISHA)”.^{15g,25} Furthermore, silanes can also bridge metal centres, as illustrated by $[(\text{PCy}_3)_2\text{-RuH}_2]_2(\mu\text{-SiH}_4)$ ²⁶ and $\{[\text{PhBCH}_2\text{PPh}_2]\text{Ru}\}_2(\mu\text{-SiH}_6)$,^{27,28} which are presented in Fig. 14 and 15, respectively.

3.2.2. Borane, alane and gallane σ -complexes. Lewis base adducts of boranes, alanes and gallanes (LEH_3 ; $\text{E} = \text{B}, \text{Al}, \text{Ga}$) are isoelectronic with methane and silanes. As such, the interaction of the E–H bonds in these molecules can be represented by the use of the half-arrow notation (Fig. 16), akin to that used for alkane and silane σ -complexes.

The first examples of borane compounds that feature such interactions are the chromium, molybdenum and tungsten complexes, $(\text{CO})_5\text{M}(\kappa^1\text{-H}_3\text{BL})$ ($\text{L} = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3$), as illustrated in Fig. 17.²⁹ A variety of other adducts of 4-coordinate neutral boranes have also been synthesized,^{30,31} including compounds in which the borane coordinates *via* two of the hydrogen atoms, *e.g.* $[\text{Rh}(\text{PBU}_3)_2\text{H}_2(\kappa^2\text{-H}_3\text{BNMe}_3)]^+$, *via* two 3c–2e Rh–H–B bonds (Fig. 17).³²

σ -Complexes of Lewis base adducts of alanes^{33,34} and gallanes³⁵ have also been reported, with the first structurally characterized monomeric alane complex being the nickel cyclo-dodeca-1,5,9-triene (cdt) derivative, $(\text{cdt})\text{Ni}(\kappa^1\text{-HAlEt}_2\text{Q})$ ($\text{Q} = \text{quinuclidine}$),³³ illustrated in Fig. 18. Another structurally characterized alane complex is provided by the zirconocene compound $\text{Cp}_2\text{Zr}(\kappa^1\text{-HAlBu}^i\text{L})$ ($\text{L} = 2\text{-vinylpyridine}$), in which the olefin of the 2-vinylpyridine also coordinates to the zirconium centre (Fig. 18).³⁴

In addition to the aforementioned monomeric compounds, dinuclear $[\text{Cp}_2\text{YCl}(\kappa^1\text{-HAlH}_2\text{NET}_3)]_2$ ³⁶ and oligonuclear $\{[\text{Cp}_2\text{YCl}]_2(\mu\text{-}\kappa^2\text{-H}_3\text{AlOEt}_2)\}_x$ ³⁷ have also been reported, although the former complex exhibits an additional weak $\text{Al}\cdots\text{Cl}$ interaction (3.0 \AA) such that the aluminum adopts an approximately trigonal bipyramidal geometry. Furthermore, compounds that feature more complex alane ligands, namely amidate,

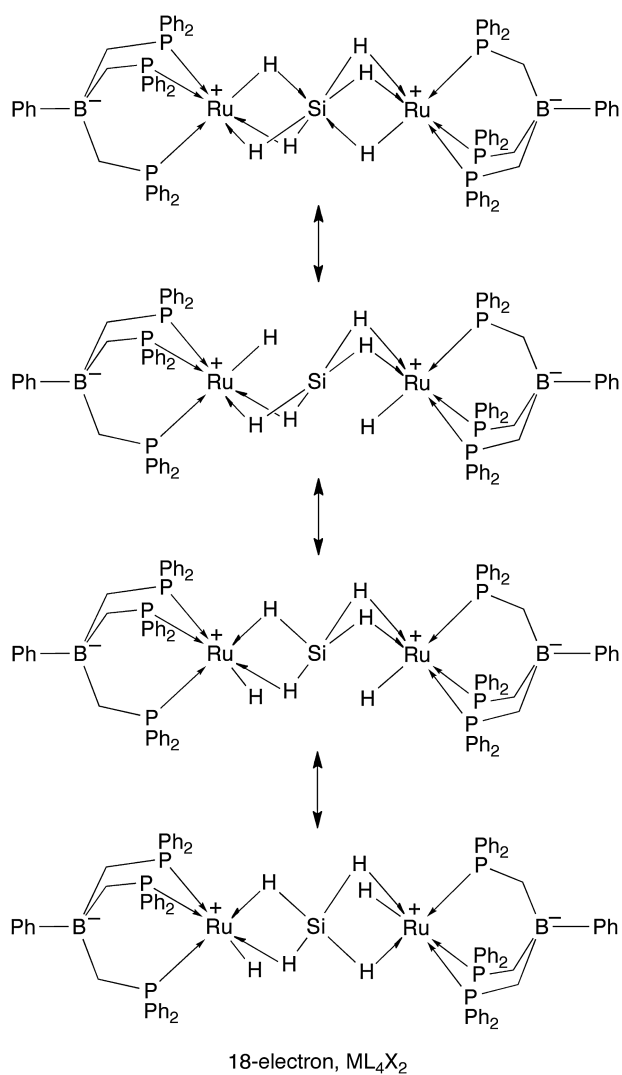


Fig. 15 A bridging silane compound that features a 6-coordinate hypervalent silicon centre. Note that the bridging hydrogens are equivalent and only some of the resonance structures are shown. The upper structure is not considered to be significant because it corresponds to an expanded octet for silicon.

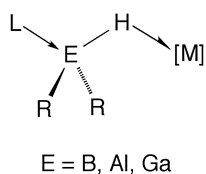


Fig. 16 Structure-bonding representation for coordination of E–H σ -bonds of Lewis base adducts of boranes, alanes and germanes to a metal centre.

guanidate and β -diketiminate derivatives, are also known.³⁸ Gallane σ -complexes have also been synthesized,³⁵ as illustrated by the quinuclidine derivatives, $(CO)_5W(\kappa^1-H_3GaQ)^{39}$ and $Cp^*Mn(CO)_2(\kappa^1-H_3GaQ)$ (Fig. 19).

Further to coordination of the B–H bond of tetrahedral LBH_3 , the B–H bond of electronically unsaturated 3-coordinate boranes, R_2BH , can also interact with a metal centre. However, an important distinction is that the boron of R_2BH has an

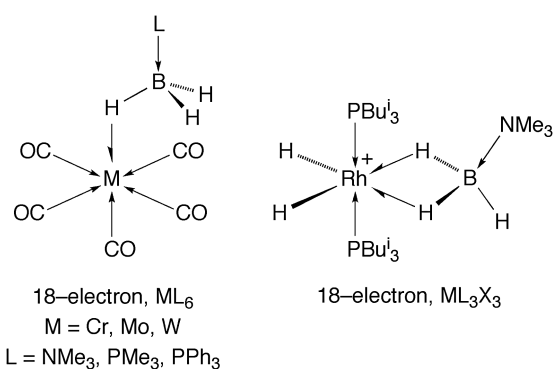


Fig. 17 B–H σ -complexes of Lewis base adducts of boranes.

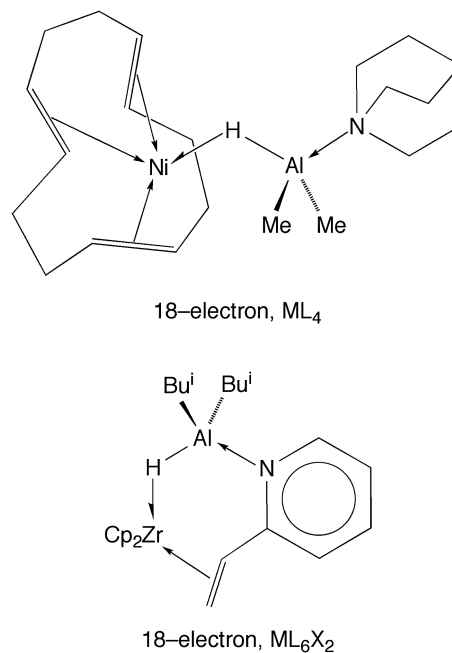


Fig. 18 Al–H σ -complexes of Lewis base adducts of alanes.

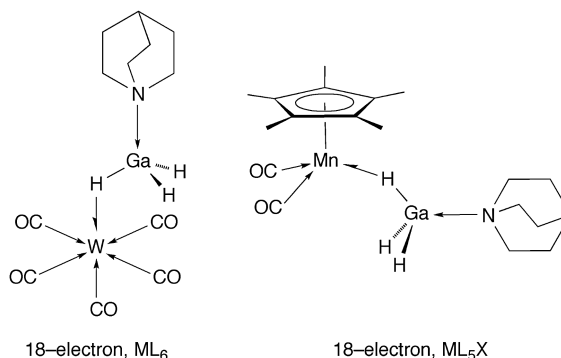


Fig. 19 Ga–H σ -complexes of Lewis base adducts of gallanes.

additional empty orbital that can be used to strengthen the backbonding interaction.^{15e,40} In view of the existence of this orbital, the bonding in a R_2BH σ -borane complex is best represented as including the backbonding interaction, which thereby allows the boron to achieve an octet configuration (Fig. 20, left). Thus, the bonding interaction can be described

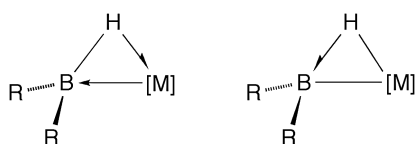


Fig. 20 Two alternative, but equivalent, structure-bonding representations for coordination of R_2BH to a metal centre. From the perspective of the metal, the structure on the left illustrates donation from the B–H bond to the metal (L), coupled with backdonation from the metal to boron (Z), while the structure on the right illustrates a boryl-hydride species in which donation from a M–H bond achieves an octet configuration for boron. Note that these different descriptions do not represent different electronic structures, but are merely different ways of viewing the same molecule.

in terms of (i) donation from the B–H bond to the metal (*i.e.* L) and (ii) backdonation from the metal to boron (*i.e.* Z).

Since an LZ combination is equivalent to X_2 ,⁶ an alternative structure-bonding representation is one in which the molecule is viewed as a boryl-hydride derivative in which the M–H bond donates its electron density to an electronically deficient boron centre (Fig. 20, right). This description is akin to that of an agostic alkyl, although in this case it is a M–H bond that relieves the electron deficiency of boron, rather than a C–H bond relieving the electron deficiency of a metal centre. It must be emphasized that the two structure-bonding representations in Fig. 20 are merely intended to facilitate rationalizing the chemical reasonableness of a molecule and are not intended to convey different electronic structures for the molecule. Thus, in both cases, the boron atom is classified as $[BLX_3]$ according to the Covalent Bond Classification, while the metal is classified as $[MX_2]$.⁶

The first well-defined examples of complexes that feature coordination of electronically unsaturated R_2BH molecules to a metal centre are provided by titanocene catecholborane compounds $Cp_2Ti(\eta^2-HBcat^X)(PMe_3)$, of which the 3-fluoro derivative $Cp_2Ti(\eta^2-HBcat^F)(PMe_3)$ was structurally characterized by X-ray diffraction (Fig. 21).⁴¹ A variety of other borane σ -complexes have subsequently been reported, some examples of which are illustrated in Fig. 21.⁴²

3.2.3. Bridging hydride complexes. Class I $\mu-X$ 3c–2e bonds are well represented by a multitude of bridging hydride complexes.^{10,43–45} Compounds that feature single hydride bridges may possess large bond angles at hydrogen such that the half-arrow representation is particularly appropriate, as illustrated by $[(Ph_3P)_2N]\{[(CO)_5Cr]_2(\mu-H)\}$, for which the average Cr–H–Cr angle is 155.8° .⁴⁶ In addition to single

hydride bridges, a variety of dinuclear compounds that feature double, triple and quadruple hydride bridges are also known, as illustrated in Fig. 22 and 23.⁴³

Significantly, use of the half-arrow representation predicts direct metal–metal bond orders that are in accord with calculations, whereas the use of an electron counting formalism that apportions half of the valence electron of hydrogen to each metal centre results in direct metal–metal (M–M) bond orders that are greater than the values predicted theoretically.⁴⁷ For example, a comparison of the M–M bond orders predicted by the two methods is provided in Fig. 22 and, in every case, that obtained by the half-arrow method correlates with theory.

Of particular note, the half-arrow method is also capable of predicting the existence of M–M antibonding interactions, as illustrated for $[Cp^*Re(CO)_2]_2(\mu-H)_2$. Thus, neglecting the Re–Re interaction, application of the “half-arrow” method predicts a 19-electron configuration for $[Cp^*Re(CO)_2]_2(\mu-H)_2$; however, since the compound is diamagnetic, a direct Re–Re interaction is implied, thereby resulting in a 20-electron configuration at each metal. This electron count indicates that a M–M antibonding orbital is occupied, such that the direct interaction may be described as an M– \times –M antibond.⁴⁸ Overall, the bonding situation is best represented as involving two 3c–2e Re–H–Re bonds and a Re– \times –Re antibond. This result is in marked contrast to the half electron method that predicts a Re–Re single bond. Similar situations are observed for a variety of other compounds such as $[(R_2PhP)_2ReH_2]_2(\mu-H)_4$ ($R = Me, Ph$) and $[Cp^*Ru]_2(\mu-H)_4$,^{49,50} as illustrated in Fig. 23. For example, the tetrahydride bridged ruthenium complex $[Cp^*Ru]_2(\mu-H)_4$ was proposed to have a $Ru \equiv Ru$ triple bond (Fig. 23) on the basis of the half electron method,⁴⁹ but it was subsequently noted that “...the Ru atoms do not have enough atomic orbitals to form so many bonds as suggested by the 18-electron rule” and that the direct Ru–Ru interaction is repulsive.⁴⁹ This result is, nevertheless, in accord with the half-arrow electron counting procedure which predicts a Ru– \times –Ru antibond.

3.2.4. Borohydride complexes. Transition metal borohydride complexes constitute an extensively studied class of molecules in which the borohydride ligand exhibits a variety of coordination modes.⁵¹ With respect to mononuclear compounds, the coordination mode can be classified according to whether the borohydride ligand coordinates by either one (κ^1), two (κ^2) or three (κ^3) hydrogen atoms,⁵² as illustrated in Fig. 24. In each case, the M–H–B linkage is a 3c–2e interaction that may be represented with the half-arrow notation, similar

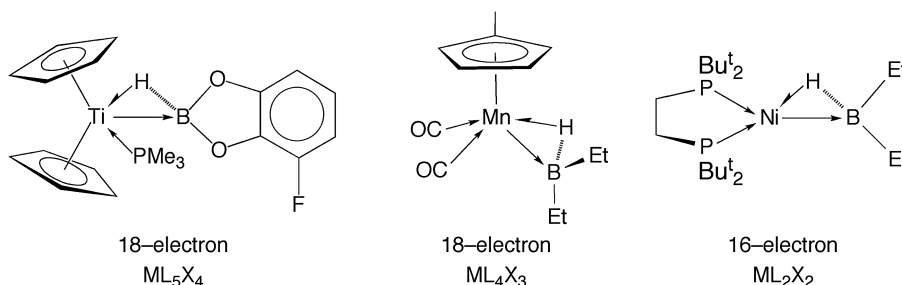


Fig. 21 Examples of B–H σ -complexes that feature coordination of electronically unsaturated boranes.

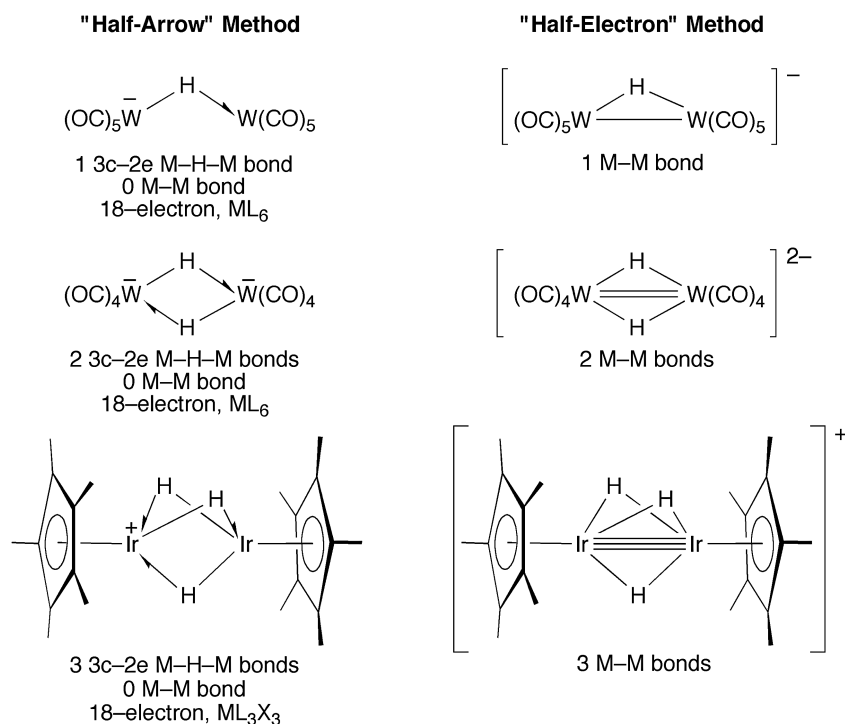


Fig. 22 Different descriptions of the metal-metal bond orders in some dinuclear complexes with bridging hydride ligands according to the electron counting method. Note that the "half-arrow" method predicts M-M bond orders that are in accord with theory, whereas the "half-electron" method predicts bond orders that are greater than predicted theoretically (adapted from ref. 43).

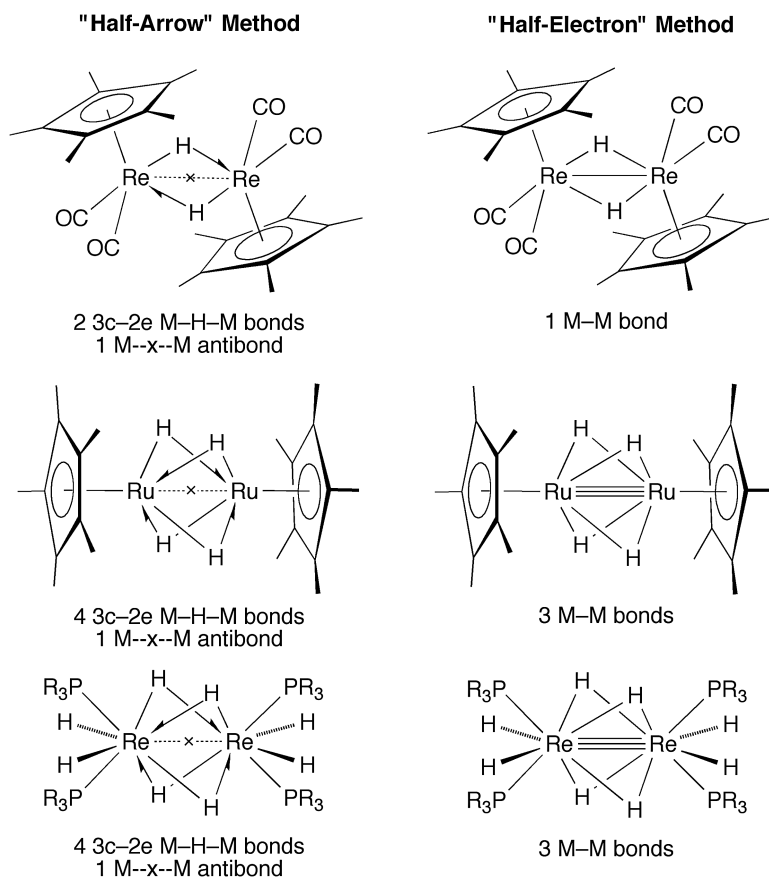


Fig. 23 Bridging hydride compounds that feature M-x-M antibonding interactions.

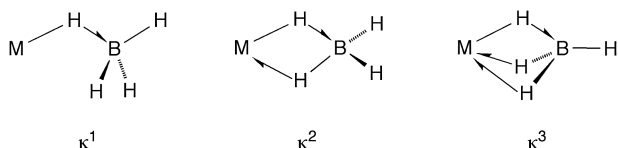


Fig. 24 Structure-bonding representations for $M[BH_4]$ tautomers.

to that used for coordination of Lewis base adducts of boranes, LBH_3 , as discussed in Section 3.2.2. However, an important difference with respect to the structure-bonding representations for $[BH_4]$ and $[LBH_3]$ pertains to the direction of the half-arrows. Specifically, whereas coordination of LBH_3 is depicted with all half-arrows drawn from the hydrogen to the metal (e.g. Fig. 17), coordination of borohydride requires that one of the half-arrows is drawn from hydrogen to boron in order for the latter to achieve an octet configuration (Fig. 24).

For example, while the half-arrow for a κ^1 - HBH_2L compound is from hydrogen to the metal (Fig. 17), that for a κ^1 - HBH_3 borohydride complex is drawn from the hydrogen to boron (Fig. 24). Likewise, for a κ^2 - H_2BHL compound, both half-arrows are drawn from the hydrogen to the metal (Fig. 17), whereas for a κ^2 - H_2BH_2 derivative, one half-arrow is drawn from hydrogen to the metal, while the other is drawn from the hydrogen to boron (Fig. 24).

3.2.5. Agostic alkyl and aryl complexes. The term “agostic” refers specifically to 3c–2e M–H–C interactions (Fig. 25) and was introduced (i) to highlight the novelty of 3c–2e interactions involving C–H bonds (in contrast to the numerous examples that feature, for example, B–H bonds) and (ii) to emphasize the role that such interactions could play in determining structures and reaction mechanisms.⁵³

An important early example that emphasized the significance of these interactions is provided by the titanium ethyl compound, $(dmpe)TiEtCl_3$, which exhibits an unusually acute Ti–C–C bond angle of 85.9° , with the titanium interacting with the β -C–H bond (Fig. 26).^{54,55} Likewise, a similar interaction with an α -C–H bond is observed in the methyl counterpart, $(dmpe)TiMeCl_3$, which possesses a Ti–C–H bond angle of 96.5° (Fig. 26).^{55,56} Agostic interactions are not restricted to alkyl groups and are also observed in aryl compounds, as

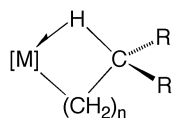


Fig. 25 Structure-bonding representation of an agostic interaction.

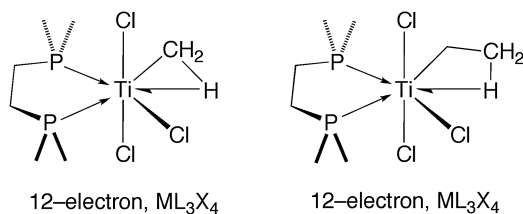


Fig. 26 Early examples of compounds that feature α - and β -agostic interactions.

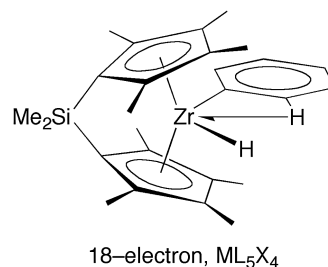


Fig. 27 An example of an agostic phenyl ligand.

illustrated in Fig. 27.⁵⁷ In each case, an agostic alkyl or aryl ligand is considered to be a 3-electron donor according to the neutral electron counting method.⁵⁸

In addition to agostic alkyl and aryl compounds, the term agostic can also be used to refer to situations in which hydrocarbons coordinate to a transition metal solely *via* C–H bonds (Section 3.2.1). However, compounds that feature such interactions are more commonly referred to as σ -complexes.

3.2.6. Bridging alkyl complexes. Although bridging alkyl groups are much less commonly encountered than bridging hydride ligands, a variety of coordination modes have been encountered.^{59–61} For example, the coordination modes of a methyl group can be classified as (i) symmetric pyramidal, (ii) symmetric trigonal planar, (iii) monohapto agostic, (iv) dihapto agostic, and (v) trihapto agostic, as illustrated in Fig. 28.^{60,61}

In the absence of agostic interactions, a methyl group can bridge two metals *via* two distinct coordination modes. For example, the methyl can be planar with a M–C–M angle of 180° , or the methyl group can be pyramidal with a M–C–M angle that is significantly less than 180° . Examples of the former coordination mode are provided by $[Cp_2Zr(\eta^2-OCMe_2)]_2(\mu-AlMe_2)(\mu-Me)$ ⁶² and $(Cp^{Me})_3U(\mu-Me)U(Cp^{Me})_3$,⁶³ while examples of the latter are provided by $Me_2Al(\mu-Me)_2AlMe_2$ ⁶⁴

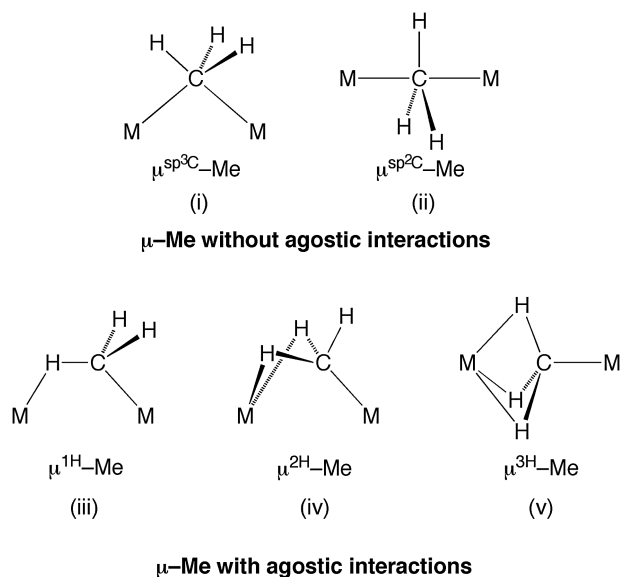


Fig. 28 Coordination modes of bridging methyl ligands (the lines between atoms are only to indicate connectivity and are not intended to be structure-bonding representations; see Fig. 29 for structure-bonding representations).

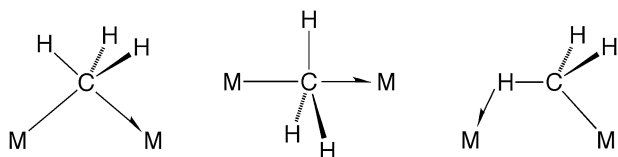


Fig. 29 Half-arrow structure-bonding representations for symmetrically bridging and monoagostic methyl groups.

and $\text{ArMn}(\mu\text{-Me})_2\text{MnAr}$.⁶⁵ The bonding in these complexes can be described by the half-arrow representations in Fig. 29, and are analogous to those for the bridging hydride complexes illustrated in Fig. 22. Thus, despite the distinctly different coordination modes, the bridging methyl ligand behaves like a $\mu\text{-LX}$ donor, regardless of whether it is symmetric pyramidal or symmetric trigonal planar.

As discussed for bridging hydride compounds, the $\mu\text{-LX}$ nature of a symmetric pyramidal bridging methyl ligand has an impact on the direct M–M bond order. For example, adopting this view, the Mo–Mo interaction in $[\text{CpMo}(\text{CO})_2(\mu\text{-PCy}_2)(\mu\text{-Me})]$ is assigned a bond order of two, as illustrated by the structure bonding representation in Fig. 30. Although this description is counter to the previously reported value of three,⁶⁶ it is in accord with the fact that analysis of the molecular orbitals of $[\text{CpMo}(\text{CO})_2(\mu\text{-PCy}_2)(\mu\text{-Me})]$ indicates a $\sigma^2(\pi)^2(\delta)^2(\delta^*)^2$ electronic configuration for the Mo–Mo interaction.^{66a}

In addition to these symmetric coordination modes, the hydrogen atoms can also participate in agostic interactions, although the energetic preference for one particular mode is small.⁶⁷ The structure-bonding representation for a monohapto agostic interaction is illustrated in Fig. 29 (right).

3.2.7. Bridging silyl complexes. Silyl ligands can bridge two metals in symmetric and asymmetric manners (Fig. 31), similar to those observed for alkyl ligands (Section 3.2.6). As with alkyl ligands, the symmetric coordination mode is not very common,⁶¹ but has been observed for tertiary silyl ligands,^{68,69} as illustrated by $[(\text{Pr}^i_3\text{P})\text{RhH}]_2(\mu\text{-Cl})(\mu\text{-SiPh}_2)(\mu\text{-SiPh}_3)$ ⁶⁹ in Fig. 32.

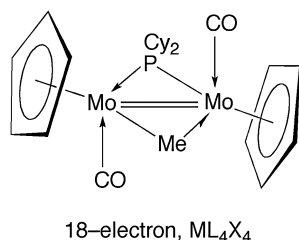


Fig. 30 Structure-bonding representation indicating a Mo=Mo double bond for $[\text{CpMo}(\text{CO})_2(\mu\text{-PCy}_2)(\mu\text{-Me})]$ with an 18-electron configuration (the Cp ligand is a 5 electron L_2X donor ligand).

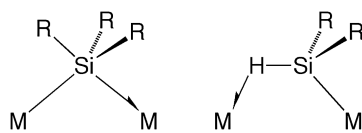


Fig. 31 Structure-bonding representations of a symmetrically bridging silyl ligand (left) and an asymmetric interaction in which a Si–H group also interacts with one of the metals (right).

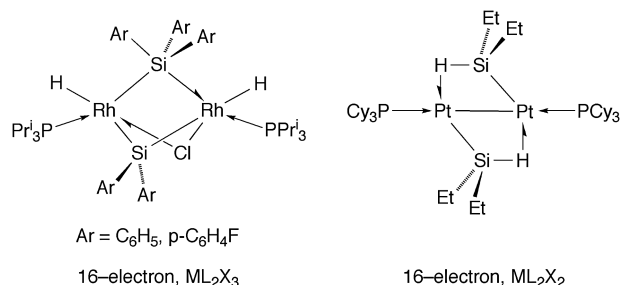


Fig. 32 Examples of silyl ligands bridging in symmetric and asymmetric manners, in which the latter also involves interaction with Si–H bonds.

Interestingly, although $[(\text{Pr}^i_3\text{P})\text{RhH}]_2(\mu\text{-Cl})(\mu\text{-SiPh}_2)(\mu\text{-SiPh}_3)$ has been represented with a Rh–Rh single bond,⁶⁹ consideration of the structure-bonding representation (Fig. 32, left) indicates that the diamagnetic molecule either belongs to the 16-electron class ML_2X_3 without a Rh–Rh bond, or the 18-electron class ML_2X_5 with a Rh=Rh double bond. Of these, the former is the most reasonable description for the molecule because the interaction of two d^6 metal centres will necessarily result in the occupation of M–M antibonding orbitals, thereby thwarting the formation of M–M bonds. Furthermore, rhodium compounds with a valence number of 3 are much more common than those with a valence number of 5.^{6b}

More commonly encountered than symmetric bridging silyl ligands are asymmetric variants in which Si–H groups also interact with the metal centre, an example of which is provided by $[(\text{R}_3\text{P})\text{Pt}(\mu\text{-SiR}_2\text{H})]_2$ (Fig. 32, right).⁷⁰

3.3. Class II $\mu\text{-L}$ 3c–2e bonds

By comparison to compounds that feature Class I bonds, those that possess Class II interactions with $\mu\text{-L}$ bridges are much less common and the impact of the bonding is less appreciated. Here, we first discuss the existence of Class II interactions in compounds for which the bridging atom has little acceptor character (for example, compounds with bridging PR_3 ligands) and then describe situations in which the bridging atom also has an available acceptor orbital (for example, compounds with bridging CO ligands). Finally, we conclude by providing alternative descriptions of compounds in the literature that may be viewed as possessing Class II $\mu\text{-L}$ 3c–2e bonds.

3.3.1. Bridging PR_3 , AsR_3 and SbR_3 complexes. PR_3 ligands are ubiquitous and almost exclusively coordinate in a terminal manner. Recently, however, it has been demonstrated that PR_3 ligands, and their AsR_3 and SbR_3 counterparts, may also coordinate in a bridging manner. For example, Werner synthesized a series of dirhodium compounds that feature these ligands, a selection of which is presented in Fig. 33.^{11,71–75} $\mu\text{-PR}_3$ complexes have also been postulated as intermediates in the migration of PR_3 ligands between two metal centres,⁷⁶ and closely related $\mu\text{-phosphole}$ derivatives of Pd,^{77,78} Pt,^{77,79} Cu,^{77,80} and Ag⁸¹ have also been synthesized (Fig. 34).

3.3.2. Bridging MeCN ligands. In addition to the ability of P, As, and Sb of ER_3 ligands to bridge two metal centres, the nitrogen atom of acetonitrile has also recently been shown to bind in a similar manner in a variety of compounds.^{82–89}

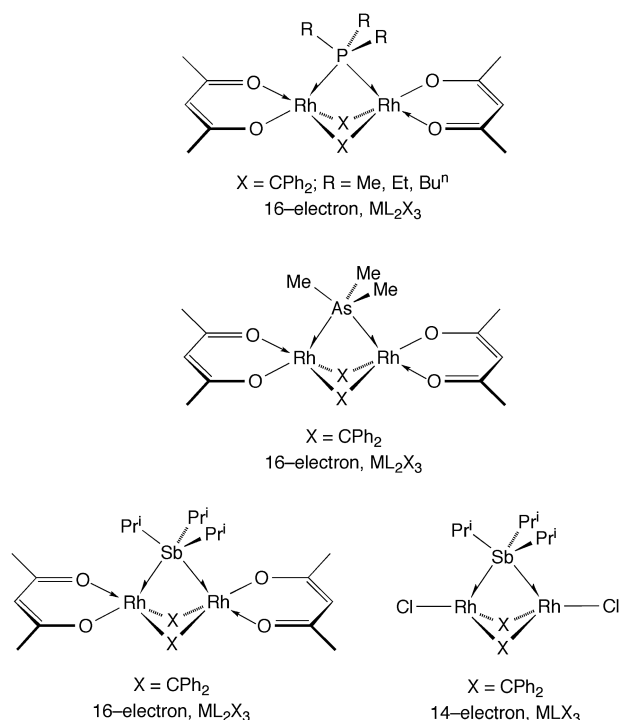
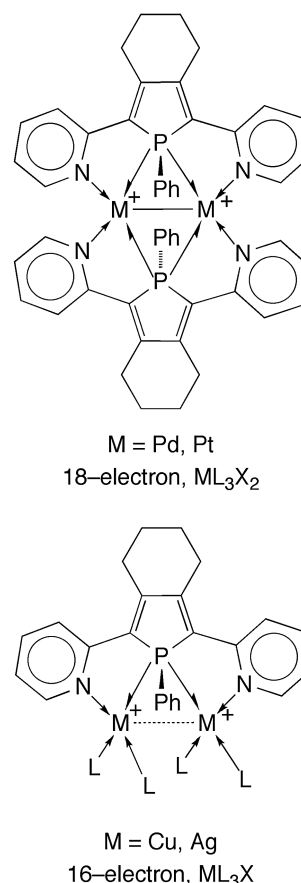


Fig. 33 Examples of compounds that feature bridging PR_3 , SbR_3 , and AsR_3 ligands.

For example, Tilley has reported a dinuclear copper compound, $[(dpen)Cu_2(\mu-NcMe)]^{2+}$, in which the MeCN ligand binds to both copper atoms *via* only the nitrogen atom (Fig. 35).⁸³ The bonding in this complex was described in terms of overlap of the nitrogen lone pair with an empty in-phase combination of sp^7 hybrids on each copper (Fig. 36). The structure bonding representation of this molecule (Fig. 35) indicates that each copper belongs to the 18-electron class ML_3X , such that a direct Cu–Cu bond would not be expected. Consistent with this description, density functional theory calculations indicate that there is no formal bond between the two copper centres of $[(dpen)Cu_2(\mu-NcMe)]^{2+}$ because all pairs of Cu–Cu bonding and antibonding orbitals are filled.⁸³ Furthermore, the quantum theory of atoms in molecules predicts the existence of a bond critical point between the two copper atoms that has characteristics which are consistent with a cuprophilic closed-shell interaction, rather than that of a formal single bond.

3.3.3. Symmetrically bridging carbonyl complexes. Transition metal compounds that feature symmetrically bridging carbonyl ligands⁹⁰ are ubiquitous and have received much attention, especially with respect to the nature of the associated M–M interactions. In particular, the first polynuclear metal carbonyl, $Fe_2(CO)_9$,⁹¹ has been the subject of many investigations. For example, $Fe_2(CO)_9$ was the first polynuclear metal carbonyl to be characterized by X-ray diffraction,^{92,93} thereby demonstrating the presence of the now common symmetric bent carbonyl ligand, $Fe(\mu-CO)Fe$, rather than the alternative asymmetric linear bridging carbonyl, $Fe \leftarrow CO \rightarrow Fe$, that had been previously proposed.⁹⁴ Interestingly, while there was originally caution in attributing the Fe–Fe distance of 2.46 \AA ^{93,95} to that of a chemical bond,⁹³ in 1940 Sidgwick and Powell⁹⁶ represented



(neglecting the possibility of a metallophilic interaction that is indicated by a dotted bond)

Fig. 34 Examples of compounds that feature bridging phosphole ligands.

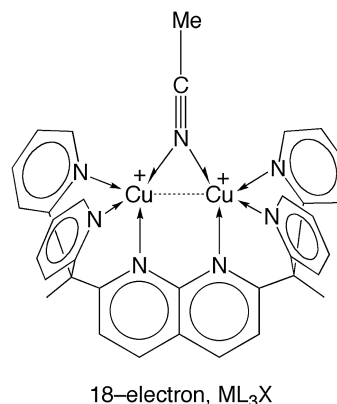


Fig. 35 An example of a compound that features a bridging MeCN ligand, $[(dpen)Cu_2(\mu-NcMe)]^{2+}$ (the dotted line indicates a cuprophilic interaction).

the compound with the familiar Fe–Fe bond that has subsequently appeared in many articles and textbooks.⁹⁷ Undoubtedly, the widespread acceptance of this representation is a consequence of the notion that the “ketonic”⁹⁸ description of the three bridging carbonyl ligands requires $Fe_2(CO)_9$ to possess an Fe–Fe bond in order for each iron centre to achieve an 18-electron configuration. Indeed, the perceived significance of this Fe–Fe

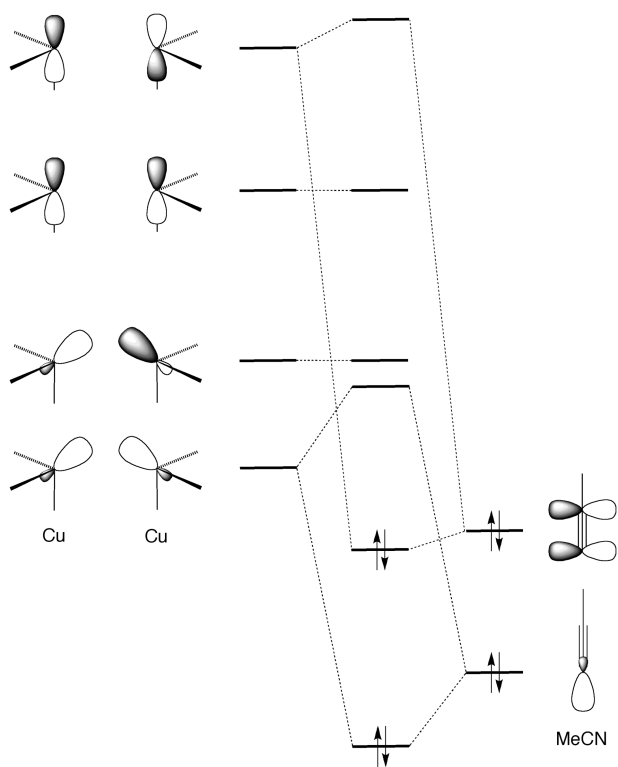


Fig. 36 Qualitative molecular orbital diagram for a bridging acetonitrile compound adapted from ref. 83; the primary interaction involves donation of the nitrogen lone pair into the empty in-phase combination of sp^n hybrid orbitals on copper.

interaction is highlighted by Braterman's statement that "This bond is real, not formal".⁹⁹

However, with respect to the notion that $\text{Fe}_2(\text{CO})_9$ possesses an Fe–Fe bond, it is of considerable interest that, in the late 1970s, Hoffmann *et al.* pointed out that the $\text{Fe} \cdots \text{Fe}$ interaction in $\text{Fe}_2(\text{CO})_9$ is actually *antibonding* and *repulsive*.^{100,101} Hoffmann's view has subsequently been supported by a large variety of calculations.¹⁰² For example, Heijser *et al.* comment that "...along the Fe–Fe bond axis there is a negative density difference."¹⁰³ Bauschlicher concludes "No evidence is found for a direct Fe–Fe bond. The Fe's are held together by three center Fe–CO–Fe bonds."¹⁰⁴ Rosa and Baerends state "...the two $\text{Fe}(\text{CO})_3$ fragments are not kept together by direct Fe–Fe bonding but by the presence of the bridging carbonyls."¹⁰⁵ Ponec *et al.* state "...the bonding interactions between the metal atoms do not have the character of a direct Fe–Fe bond anticipated on the basis of 18-electron rule."¹⁰⁶ Poblet *et al.* note that "...the topology of the charge density does not detect this [an Fe–Fe] interaction."¹⁰⁷ Although some theoretical articles have suggested the possibility of a weak direct Fe–Fe attractive interaction in $\text{Fe}_2(\text{CO})_9$,¹⁰⁸ other studies have questioned this conclusion, *viz.*: "The orbital localization shows, however, that there is no orbital (electron pair) corresponding to direct Fe \cdots Fe bond and so the vague interpretation of residual Fe \cdots Fe interactions as 'some, albeit weak' bond is questionable."¹⁰⁶ and "In our opinion, for any interaction to be classified as [a] 'chemical bond', it must be possible to associate it with an electron pair, but as it is clearly evident from the DAFH analysis, there is no electron pair that could be associated with the Fe \cdots Fe bond."¹⁰⁹

In view of the above preponderance of evidence, it is surprising that, decades after Hoffmann's original comment, the molecular structure of $\text{Fe}_2(\text{CO})_9$ continues to appear in textbooks^{97,110} with a Fe–Fe bond. In addition to $\text{Fe}_2(\text{CO})_9$, other dinuclear bridging carbonyl compounds have also been represented with M–M bonds, for which calculations and experiments indicate the absence of such interactions. Common examples of such complexes include the bridged form¹¹¹ of $\text{Co}_2(\text{CO})_8$,^{106,112,113} and $[\text{CpFe}(\text{CO})(\mu\text{-CO})]_2$.^{114,115} The widespread misrepresentation of such molecules is undoubtedly a consequence of the deep-rooted notion that symmetrically bridging carbonyl ligands are $\mu\text{-X}_2$ "ketonic" in character. As will be discussed in more detail below, such misrepresentations with respect to metal–metal bond order can be averted by recognizing that a symmetrically bridging carbonyl ligand can also be described as a $\mu\text{-L}$ donor.

(i) *3c–2e bonds in symmetrically bridging carbonyl systems $M(\mu\text{-CO})M$ and their representations.* An indisputable feature of many calculations is that the bonding of a symmetrically bridging carbonyl ligand can be expressed in terms of two 3-centre molecular orbitals derived from the interactions of the 5σ HOMO and a $2\pi^*$ orbital of CO with appropriate metal d orbitals.^{99,101–109,116} Specifically, if each metal is considered to use a single suitably oriented d orbital, the in-phase combination of metal orbitals is of appropriate symmetry to interact with the 5σ HOMO¹¹⁷ of CO (*i.e.* σ -donation), while the out-of-phase metal combination is of appropriate symmetry to interact with one of the $2\pi^*$ C–O antibonding orbitals (*i.e.* π -backbonding), as illustrated in Fig. 37. The bonding orbital derived from interaction with the 5σ HOMO ($\lambda+$) is lower in energy than that derived from interaction with the $2\pi^*$ orbital ($\lambda-$).

If there is both σ -bonding and π -backbonding, such that both the $\lambda+$ and $\lambda-$ bonding orbitals are occupied, the overall interaction can be represented in terms of two $2c\text{-}2e$ bonds, as in ketones (Fig. 38a). However, if there is no backbonding and only the $\lambda+$ orbital is occupied, the bonding must be represented as a $3c\text{-}2e$ interaction (Fig. 38b).

In terms of electron counting, a bridging carbonyl ligand that participates in backbonding is classified as a $\mu\text{-X}_2$ donor, such that each metal receives one electron according to a neutral electron counting procedure (Fig. 38a). In the absence of backbonding, however, there is only a single $3c\text{-}2e$ interaction and the carbonyl ligand is a $\mu\text{-L}$ donor, such that the

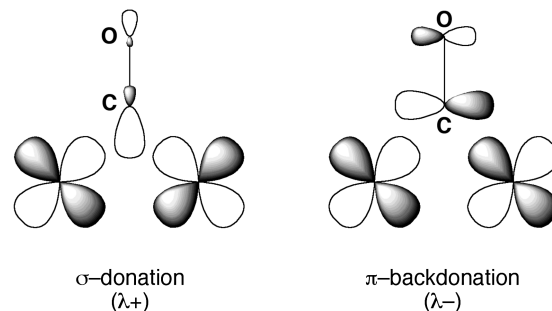


Fig. 37 The two bonding molecular orbitals derived from interaction of the 5σ HOMO ($\lambda+$) and one of the $2\pi^*$ C–O antibonding orbitals ($\lambda-$) with the in-phase and out-of-phase combination of metal d orbitals.

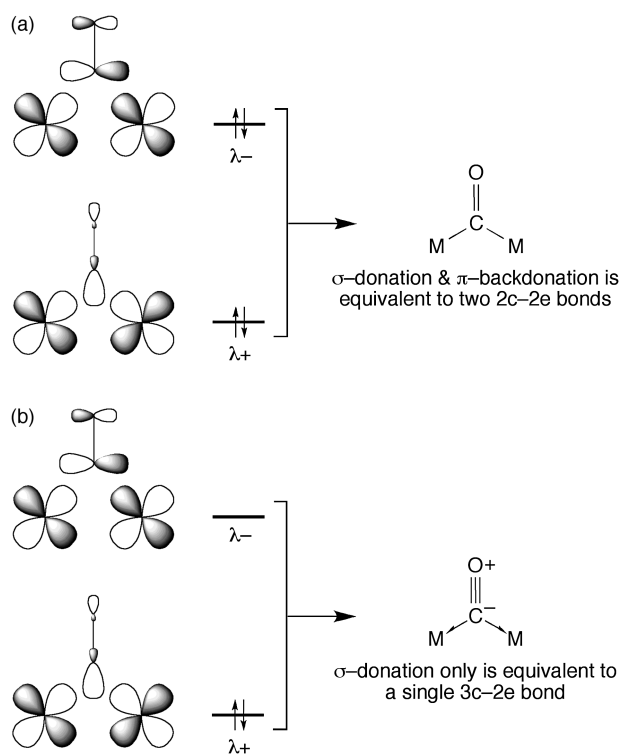


Fig. 38 MOs for a $M(\mu\text{-CO})M$ interaction (a) occupied by 4 electrons, giving two 2c-2e bonds and (b) occupied by 2 electrons, giving a 3c-2e bond. For (a), the CO is classified as a $\mu\text{-X}_2$ donor and contributes one electron to each metal, whereas for (b), the CO is classified as a $\mu\text{-L}$ donor and contributes a pair of electrons to both metals.

pair of electrons contributes to the electron count of *both* metals (Fig. 38b). The former situation is readily represented by a conventional Lewis structure with a “ketonic” CO, and two 2c-2e bonds, whereas the latter situation is conveniently represented by a half-arrow symbolism in which a single pair of electrons is donated to both metal centres (Fig. 38). It is evident that these two bonding situations result in different electron counts for the metal centres and, as described below, provide a simple means to reconcile the theoretically computed M-M bond orders with those predicted on the basis of electron counting.

It is also important to emphasize that while the presence/absence of π -backbonding influences the electron count of the metals in bridging carbonyl compounds (Fig. 38), it does not influence the electron count for terminal carbonyl compounds. Specifically, even though the degree of backbonding for a terminal carbonyl ligand is highly variable, such that it may be classified as either L (no backbonding) or X_2 (significant backbonding), the ligand contributes two electrons to the metal centre in both cases (Fig. 39).

(ii) *Molecular orbital analysis of the bridging interactions in $\text{Fe}_2(\text{CO})_9$.* As discussed above, the bonding within $\text{Fe}_2(\text{CO})_9$ has received considerable attention and a simple molecular orbital description that focuses on the aforementioned 3-centre interactions (Fig. 38) is provided in Fig. 40. Thus, adopting the fragment approach of Hoffmann *et al.*,^{100,101} each $[\text{Fe}(\text{CO})_3]$ fragment, which is isolobal with $[\text{BH}]$,¹¹⁸ has three orbitals and

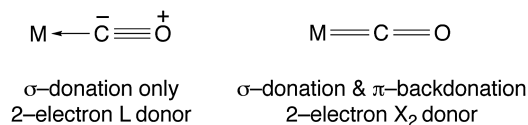


Fig. 39 Regardless of the degree of backbonding, a terminal carbonyl ligand is a two electron donor.

two electrons available for interacting with the three bridging carbonyl ligands, each of which contribute a 5σ orbital and the $2\pi_z^*$ orbital that lies parallel to Fe-Fe axis (z). The other $2\pi^*$ orbitals of CO, which are perpendicular to the Fe-Fe axis, are neglected from the analysis on the basis that there is little overlap with the metal d orbitals. The qualitative molecular orbital diagram (employing D_{3h} symmetry) that describes the $\text{Fe}(\mu\text{-CO})_3\text{Fe}$ bridging interaction contains ten electrons, with six being contributed by the three CO ligands, and four being contributed by the two $[\text{Fe}(\text{CO})_3]$ moieties (Fig. 40).

The essential feature of this molecular orbital diagram is that while there are three occupied bonding orbitals (a_1' and e') that correspond to donation by the three 5σ orbitals (*i.e.* the $\lambda+$ type; Fig. 37), there are only two occupied bonding orbitals that correspond to backbonding into the $2\pi_z^*$ orbitals (*i.e.* the $\lambda-$ type; Fig. 37). Since each $\mu\text{-X}_2$ “ketonic” description of the bonding

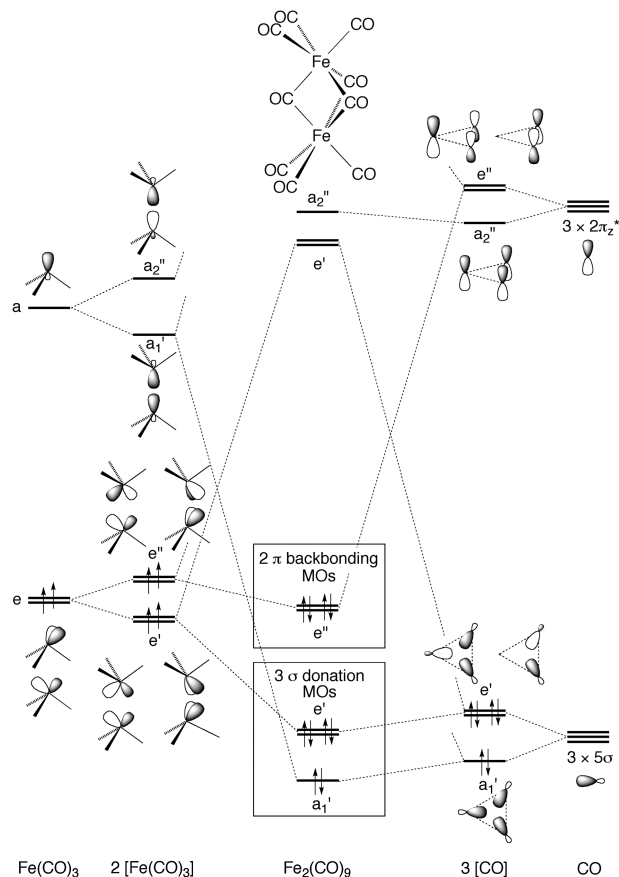


Fig. 40 Qualitative molecular orbital diagram showing the interaction of fragment orbitals involved in bridge bonding in $\text{Fe}_2(\text{CO})_9$ with D_{3h} symmetry (the z axis is coincident with the Fe-Fe vector). For clarity, orbitals associated with bonding to the terminal carbonyl ligands are not illustrated, while only the carbon $2p_z$ orbital is used to represent the $2\pi^*$ orbital of CO.

requires a pair of $\lambda+$ and $\lambda-$ type interactions, it is evident that it is not possible to describe the bonding within $\text{Fe}_2(\text{CO})_9$ as possessing three “ketonic” bridging carbonyl ligands. Rather, the bonding is more appropriately described as a resonance hybrid in which each structure possesses two $\mu\text{-X}_2$ “ketonic” carbonyl ligands and one $\mu\text{-L}$ carbonyl ligand (Fig. 41). This resonance description of the bridge bonding is in accord with that by Ponc and Gatti, who state “. . . 4 out of the 5 bonding electron pairs are involved in localized $2c\text{-}2e$ bonding of two bridging ligands, while the remaining ligand is bonded *via* a delocalized electron pair with the character of [a] $3c\text{-}2e$ bond”.¹⁰⁹

Adopting the view that the three bridging carbonyl ligands are described by one $\mu\text{-L}$ and two $\mu\text{-X}_2$ interactions, the electron count of each iron centre is 18, as illustrated by the structure-bonding representation in Fig. 42. As such, the 18-electron configuration obtained using this approach predicts the absence of an Fe–Fe bond. While this result is in marked contrast to that predicted using previous electron counting procedures, it is in accord with theory. Specifically, the d_{z^2} based a_1' orbital (Fig. 40) that could form a Fe–Fe σ -bond is heavily involved in backbonding to the terminal carbonyl ligands and therefore cannot be assigned to a formal single bond. Likewise, there is no formal Fe–Fe π -bond because the e'' orbitals, which have substantial Fe–Fe π -antibonding character, are occupied. Furthermore, since the e'' orbitals have more metal character than do the e' Fe–Fe π -bonding counterparts (because the former are involved in interactions with the empty CO π^* orbitals, whereas the latter are a result of interactions with the filled CO 5σ orbitals), the occupation of the e' and e'' orbitals actually results in a repulsive interaction between the two iron centres.¹⁰¹

The fact that the $\mu\text{-L}$ description for a bridging carbonyl ligand provides a means to predict the absence of an Fe–Fe bond in $\text{Fe}_2(\text{CO})_9$ is of considerable significance, especially

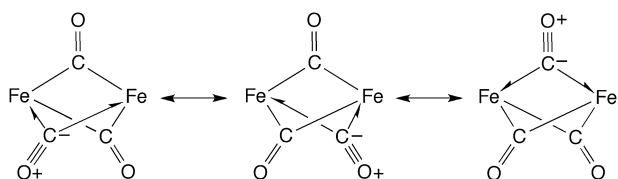


Fig. 41 Three resonance structures that correspond to the bonding illustrated in the molecular orbital diagram of Fig. 40. Each structure corresponds to three donor ($\lambda+$) and two backbonding ($\lambda-$) interactions.

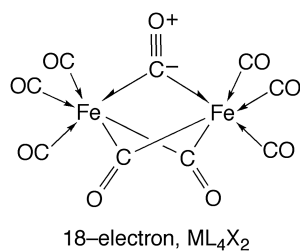


Fig. 42 Structure-bonding representation of $\text{Fe}_2(\text{CO})_9$ illustrating that each iron can achieve an 18-electron configuration without an Fe–Fe bond.

given the number of times that electron counting has been invoked in the literature to indicate the presence of an Fe–Fe bond. This approach is by no means restricted to $\text{Fe}_2(\text{CO})_9$, and structure-bonding representations of the bridged form of $\text{Co}_2(\text{CO})_8$ ¹¹¹ and $[\text{CpFe}(\text{CO})(\mu\text{-CO})_2]$ that depict the absence of M–M bonds (in accord with theory^{106,112,114}) are illustrated in Fig. 43.

Considering the ability of CO to serve as a $\mu\text{-L}$ donor, it is pertinent to discuss the possibility that electronically related ligands, with potential σ -donor and π -acceptor functions, can also be described as $\mu\text{-L}$ donors. In this regard, calculations on a series of ligands, namely CO, CS, CH_2 , CF_2 , SiMe_2 , GeMe_2 and InMe , indicate that CO is the weakest π -acceptor, while CH_2 is the strongest.^{108d} The origin of this difference is that the acceptor orbital of CH_2 is a pure nonbonding carbon p orbital, whereas that for CO is a higher energy C–O π -antibonding orbital.^{108d,114f,119} As such, for compounds that feature both CO and CH_2 bridging ligands, CO is more likely to serve the role of a $\mu\text{-L}$ donor, while CH_2 is more likely to be an X donor to each metal. Thus, $[\text{CpFe}(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)]$ ^{114f,120,121} is best represented with the methylene group serving as an X donor to each iron, while the bridging carbonyl ligand serves as an L ligand to each iron (Fig. 44). This structure-bonding representation allows each iron centre to achieve an 18-electron configuration without the formation of an Fe–Fe bond, a description that is in accord with calculations.^{114f}

In concluding this section, it is important to emphasize that, contrary to the descriptions in the majority of textbooks, a symmetrically bridging carbonyl ligand should not always be represented as $\mu\text{-X}_2$ “ketonic” in character because it can also serve as a $\mu\text{-L}$ donor. As a consequence of this dual functionality, simple application of the 18-electron rule does not result in an unambiguous M–M bond order, but rather gives possibilities that are dependent on the $\mu\text{-L}$ versus $\mu\text{-X}_2$ description of the

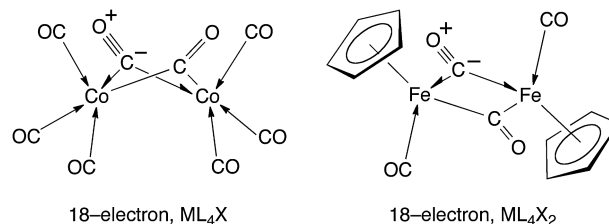


Fig. 43 Structure-bonding representations of $\text{Co}_2(\text{CO})_8$ and $[\text{CpFe}(\text{CO})(\mu\text{-CO})_2]$ which depict that each metal can achieve an 18-electron configuration without the presence of a M–M bond (Cp is an L_2X donor).

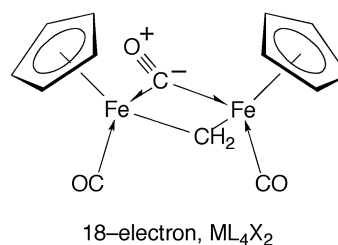


Fig. 44 Structure-bonding representation for $[\text{CpFe}(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)]$ which illustrates that CH_2 serves as the X_2 ligand in preference to CO due to the former being a better π -acceptor.

carbonyl ligands. Thus, in the absence of a theoretical evaluation of the bonding, it is not prudent for one to be dogmatic in the assignment of the M–M bond order in a symmetrically bridging carbonyl compound. Correspondingly, the μ -L *versus* μ -X₂ description of symmetrically bridging carbonyl ligands provides a means to reconcile theoretically derived M–M bond orders with the values obtained by electron counting methods. Recognition of the dual functionality of a symmetrically bridging carbonyl ligand, therefore, provides a means to understand the bonding in polynuclear metal carbonyl compounds with more clarity.

3.3.4. Dinuclear pentalene complexes. Pentalene, C₈H₆, is an 8 π -electron bicyclic antiaromatic molecule (Fig. 45) that is unstable with respect to dimerisation. Nevertheless, it has long been known that this moiety may be stabilized by either formation of the dianion or by coordination to a metal centre.¹²² A wide variety of metal complexes that contain pentalene or its derivatives are known.¹²³ Indeed, pentalenes exhibit a variety of coordination modes and a particularly interesting class of molecules are those in which the pentalene ligand coordinates to two metal centres. In such compounds, the two metals may reside on either the same face of the pentalene ligand (*syn*) or on opposite faces (*anti*), as illustrated in Fig. 46.

If the two metals have a *syn* disposition, the possibility exists for the formation of metal–metal bonds. Since metal–metal bond orders are typically inferred by electron counting procedures, evaluation of the degree of metal–metal bonding requires an understanding of the nature of the metal–pentalene interaction. In this regard, although pentalene can be represented by a variety of resonance structures (Fig. 45), conventional electron counting procedures simply apportion four electrons of a neutral bridging pentalene ligand to each metal centre,^{124,125} *i.e.* the pentalene behaves as an L₂ donor to each metal (Fig. 47, left).

On this basis, the metal–metal bond orders required to achieve an 18-electron configuration in dinuclear bis(pentalene) derivatives, $(\mu\text{-}\eta^5, \eta^5\text{-Pn}^R)_2\text{M}_2$, would be predicted to be, for example, 5 for V, 4 for Cr and 3 for Mn (Fig. 48). These values are, however, greater

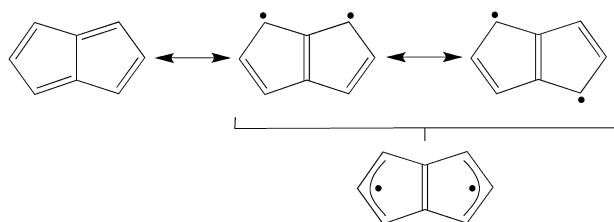


Fig. 45 Some of the many resonance structures of pentalene.

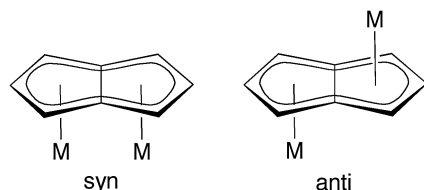


Fig. 46 *Syn* and *anti* dispositions for coordination of two metals to a pentalene ligand.

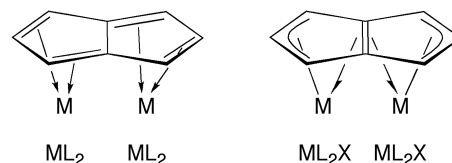


Fig. 47 Conventional electron counting assigns a pentalene ligand as a 4-electron donor to each metal (left). However, a pentalene ligand behaves as a 5-electron L₂X donor (right) to each metal if the double bond of the ring junction is considered to serve as a μ -L donor (the allyl portion is an LX donor). The covalent bond classification is listed below each structure.

than the values computed by density functional theory calculations.^{124–126} For example, $(\mu\text{-}\eta^5, \eta^5\text{-Pn}^{1,4\text{-}(\text{SiPr}_3)_2})_2\text{Cr}_2$ is calculated to have a formal Cr=Cr double bond, rather than a quadruple bond.¹²⁵ Similarly, the molybdenum counterpart $(\mu\text{-}\eta^5, \eta^5\text{-Pn}^{1,4\text{-}(\text{SiPr}_3)_2})_2\text{Mo}_2$ is also predicted to have a Mo=Mo double bond.¹²⁴

The disagreement between the results of the theoretical calculations and the bond orders predicted by employing electron counting procedures can, however, be reconciled if it is recognized that the double bond associated with the ring junction of the bis(allyl) class of resonance structures (Fig. 45) can serve as an L donor to *both* metals, such that the pentalene ligand acts as a five-electron L₂X donor to each metal centre (Fig. 47). The increase (from four to five) in the effective electron count of the pentalene ligand for each metal causes a reduction in the metal–metal bond order to a value that is in accord with theory (*i.e.* 3 for V, 2 for Cr and 1 for Mn), as illustrated by the structure–bonding representations illustrated in Fig. 48 (bottom).

Similar conclusions pertaining to metal–metal bond orders apply to dinuclear mono(pentalene) compounds. For example, $(\mu\text{-}\eta^5, \eta^5\text{-Pn}^*)[\text{Co}(\text{CO})_2]_2$ (Pn* = C₈Me₆) would be predicted to possess a Co–Co single bond if the Pn* ligand served as a 4-electron donor to each metal (Fig. 49), but the Co...Co distance [2.675(3) Å] is greater than that associated with

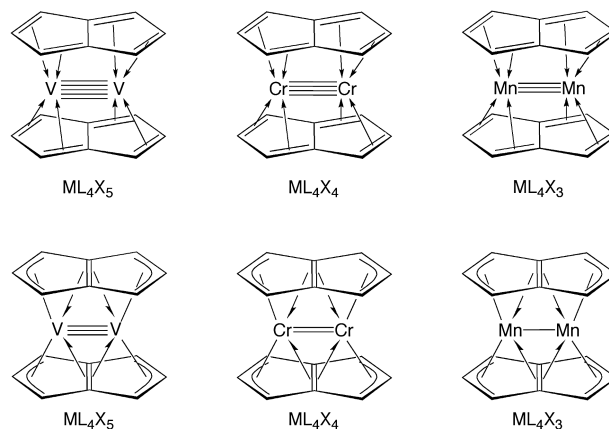


Fig. 48 M–M bond orders predicted by assuming that the bridging pentalene is (i) a 4-electron L₂ donor to each metal (top) and (ii) a 5-electron L₂X donor to each metal (bottom); the allyl portion is an LX donor. The M–M bond orders predicted by the latter method are in accord with theory, whereas those predicted by the former approach are in disagreement. Pentalene substituents are not shown for clarity.

Co–Co single bonds.¹²⁷ Furthermore, calculations indicate that there is no formal Co–Co single bond and that there is only a very weak closed-shell type interaction between the two cobalt centres.¹²⁷ However, recognizing that the μ -Pn* ligand can serve as a 5-electron donor to each metal centre, it is evident that both cobalt centres belong to the well known 18-electron ML_4X class *without* a Co–Co bond (Fig. 49).

The rhenium counterpart $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{Re}(\text{CO})_3]_2$ has also been structurally characterized by X-ray diffraction, and the $\text{Re}\cdots\text{Re}$ distance (3.23 Å) indicates that it does not possess a Re–Re bond.¹²⁸ This situation can be accurately represented by the structure-bonding representation illustrated in Fig. 50, in which an 18-electron configuration can be achieved in the absence of a Re–Re bond. Furthermore, this description is also in agreement with calculations on $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{M}(\text{CO})_3]_2$ (M = Mn, Tc, Re), which indicate that there is no M–M bond in such complexes.¹²⁹

The iron compound $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{Fe}(\text{CO})_2]_2(\mu\text{-CO})$ has been described as possessing a formal Fe–Fe single bond on the basis that the pentalene ligand donates four π -electrons to each iron (Fig. 51).¹³⁰ However, DFT calculations on the permethylated counterpart, $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn}^*)[\text{Fe}(\text{CO})_2]_2(\mu\text{-CO})$, indicate that there is no Fe–Fe bond.¹²⁷ A structure-bonding representation that achieves an 18-electron configuration for each iron centre without requiring the presence of an Fe–Fe bond, can, nevertheless, be constructed if the pentalene ligand is considered to be an L_2X donor to each metal centre (Fig. 51).

Another example of a molecule that has been represented with a metal–metal bond¹³¹ that, according to calculations, does not have such a bond¹³² is provided by $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{Ru}(\text{CO})_2(\text{GeMe}_3)]_2$

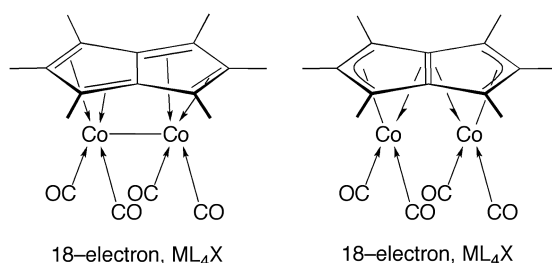


Fig. 49 $(\mu-\eta^5, \eta^5\text{-Pn}^*)[\text{Co}(\text{CO})_2]_2$ is predicted to have a Co–Co single bond if the bridging pentalene is a 4-electron L_2 donor to each metal (left) and no Co–Co bond if it is a 5-electron L_2X donor to each metal (the allyl portion is an LX donor). The latter description is in accord with both experiment and theory.

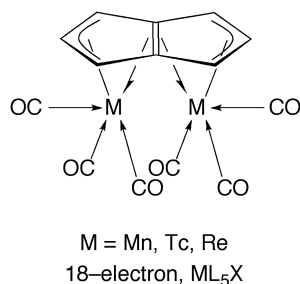


Fig. 50 Structure-bonding representation of $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{M}(\text{CO})_3]_2$ (M = Mn, Tc, Re) indicating that a M–M bond is not required to achieve an 18-electron configuration.

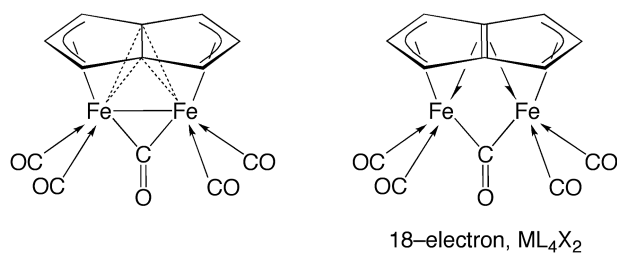


Fig. 51 Literature representation of $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn})[\text{Fe}(\text{CO})_2]_2(\mu\text{-CO})$ that includes a Fe–Fe bond (left) and a structure-bonding representation that requires no Fe–Fe bond to achieve an 18-electron configuration (left). The latter description is in accord with theoretical calculations on $\text{syn}-(\mu-\eta^5, \eta^5\text{-Pn}^*)[\text{Fe}(\text{CO})_2]_2(\mu\text{-CO})$.

(Fig. 52, top). The results of the theoretical calculations are, nevertheless, consistent with a structure-bonding representation that invokes the pentalene ligand as an L_2X donor to each ruthenium (Fig. 52, bottom).

As noted above, a single pentalene ligand can also coordinate two metal centres in an *anti* manner. The bonding in such complexes can likewise be described in terms of the double bond of the ring junction acting as a μ -L donor, such that each ring serves as a 5-electron L_2X donor to each metal. For example, the manganese and iron complexes, *anti*-($\mu-\eta^5, \eta^5\text{-Pn}$)[$\text{Mn}(\text{CO})_3]_2$ ¹²⁸ and *anti*-($\mu-\eta^5, \eta^5\text{-Pn}$)[FeCp^*_2],¹³³ are predicted to have 18-electron configurations if the pentalene ligand serves as a 5-electron L_2X donor to each metal, as illustrated in Fig. 53. In contrast, the metals would have 17-electron configurations if the pentalene ligands were simply considered to be 4-electron donors to each metal. The manganese and iron centres in these compounds are formally analogous to those in the well-known cyclopentadienyl compounds, $\text{CpMn}(\text{CO})_3$ and Cp_2Fe , thereby underscoring the fact that each pentalene ring of the $[(\mu-\eta^5, \eta^5\text{-Pn})\text{M}_2]$ moiety serves as an L_2X ligand to a metal centre.

3.3.5. Inverse sandwiches and multidecker compounds.

Closely related to the above pentalene compounds in which two metals coordinate to opposite faces of an unsaturated hydrocarbon ligand are so-called “inverse sandwiches”, in which two metals coordinate to opposite faces of the *same* ring, as illustrated by the bridging arene compounds in Fig. 54.^{134–136} Furthermore, this motif may be elaborated into a multidecker structure,^{137,138} an early example of which is provided by the mesitylene complex $(\eta^6\text{-MesH})\text{Cr}(\mu-\eta^6, \eta^6\text{-MesH})\text{Cr}(\eta^6\text{-MesH})$ ¹³⁹ (Fig. 54).

As with the ability of the double bond of the ring junction of pentalene to serve as an L donor to each metal (Fig. 53), bridging arene ligands are also capable of serving as L_3 donors to each metal centre,¹³⁷ and a structure-bonding representation for the interaction is illustrated in Fig. 55. Thus, both chromium centres of $(\eta^6\text{-MesH})\text{Cr}(\mu-\eta^6, \eta^6\text{-MesH})\text{Cr}(\eta^6\text{-MesH})$ possess 18-electron configurations. It is also pertinent to note that bridging arenes are capable of participating effectively in backbonding interactions,¹⁴⁰ such that novel compounds, as illustrated by $(\text{THF})_3\text{Ca}(\mu-\eta^6, \eta^6\text{-C}_6\text{H}_3\text{Ph}_3)\text{Ca}(\text{THF})_3$, have been isolated.^{140a}

3.3.6. Coordination of a d^2 metal centre to a pair of Lewis acid centres. An interesting example of a compound that features a Class II 3c–2e bond is provided by the

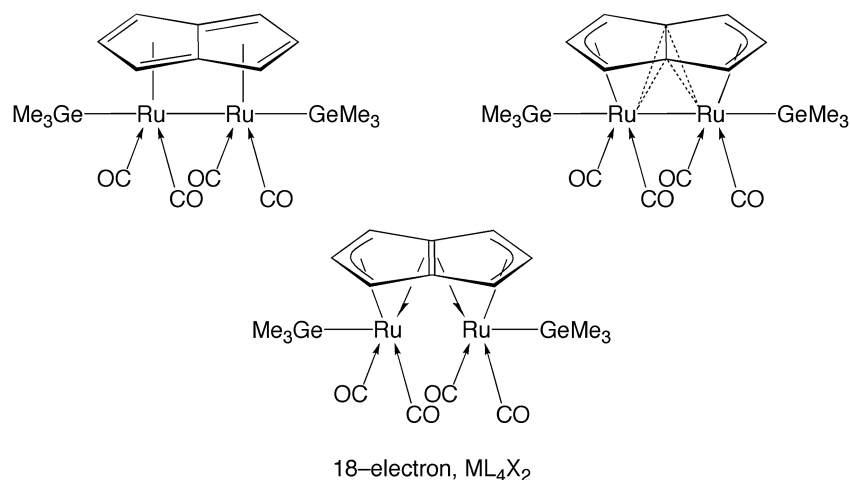


Fig. 52 Literature representations of *syn*-(μ - η^5, η^5 -Pn)[Ru(CO)₂(GeMe₃)₂] which include a Ru–Ru bond (top) and a structure-bonding representation that requires no Ru–Ru bond to achieve an 18-electron configuration (bottom). The latter description is in accord with theoretical calculations.

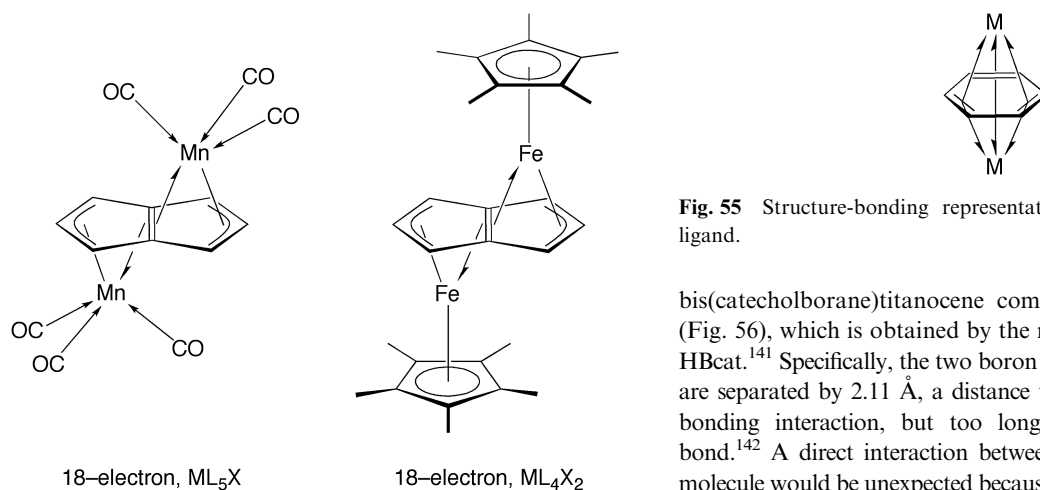


Fig. 53 Structure-bonding representations of *anti*-(μ - η^5, η^5 -Pn)[Mn(CO)₃]₂ and *anti*-(μ - η^5, η^5 -Pn)[FeCp*]₂ which illustrate how each metal achieves an 18-electron configuration if the pentalene serves as an L₂X ligand to each metal.

Fig. 55 Structure-bonding representation for a bridging benzene ligand.

bis(catecholborane)titanocene compound, Cp₂Ti(η^2 -HBcat)₂ (Fig. 56), which is obtained by the reaction of Cp₂TiMe₂ with HBcat.¹⁴¹ Specifically, the two boron atoms of Cp₂Ti(η^2 -HBcat)₂ are separated by 2.11 Å, a distance that is too short for a non-bonding interaction, but too long for a conventional B–B bond.¹⁴² A direct interaction between the boron atoms in this molecule would be unexpected because the boron atoms in HBcat are trivalent with a sextet configuration and, therefore, do not have any electrons to form a B···B interaction of any type. The bonding in Cp₂Ti(η^2 -HBcat)₂ may, nevertheless, be rationalized by recognizing that the titanium centre would possess a d²

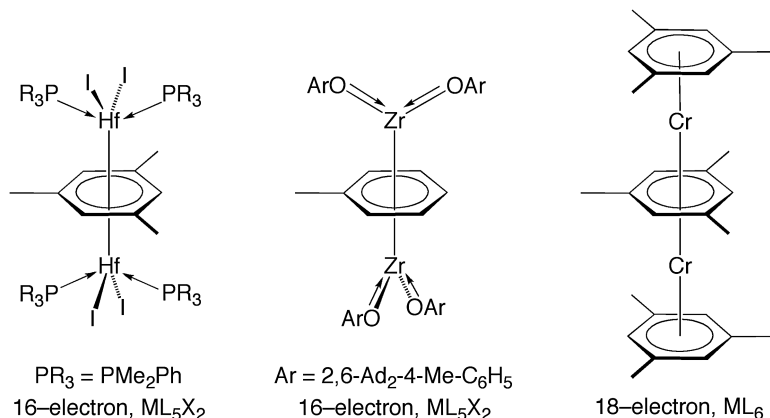


Fig. 54 Examples of compounds that feature bridging arene ligands.

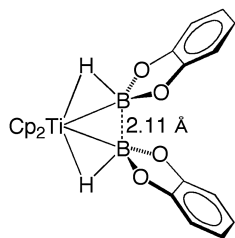


Fig. 56 Structural representation of $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ in which lines are used merely to indicate connectivity.

configuration if the interactions with the HBcat molecules were to occur only *via* coordination of the B–H bond. The pair of electrons on titanium thereby provides a means to allow the boron atoms to come into close proximity *via* formation of a Class II $\mu\text{-L}$ 3c–2e bond, as described by the structure-bonding representation in Fig. 57 (left).

Calculations support the 3c–2e description of the bonding, with the key orbital being highlighted in the molecular orbital diagram of Fig. 58.^{40a,143} As a consequence of the titanium providing a pair of electrons to enable a $\text{B}\cdots\text{B}$ interaction, the titanium adopts a d^0 , rather than a d^2 , configuration (Fig. 58). In this regard, the impact on the metal centre of using a single lone pair to coordinate to a pair of Lewis acid centres is the same as coordination to a single Lewis acid centre, *i.e.* a d^n metal centre becomes d^{n-2} .^{144,145} The titanium centre of $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ is, therefore, classified as tetravalent d^0 18-electron ML_5X_4 (Fig. 57), rather than as a $\text{Ti}(\text{II})$ derivative.¹⁴¹ It should also be noted that this description of the bonding results in the boron being classified as MLX_3 with an octet configuration.

While the structure-bonding representation of $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ that portrays the compound as an adduct between $[\text{Cp}_2\text{Ti}]$ and two

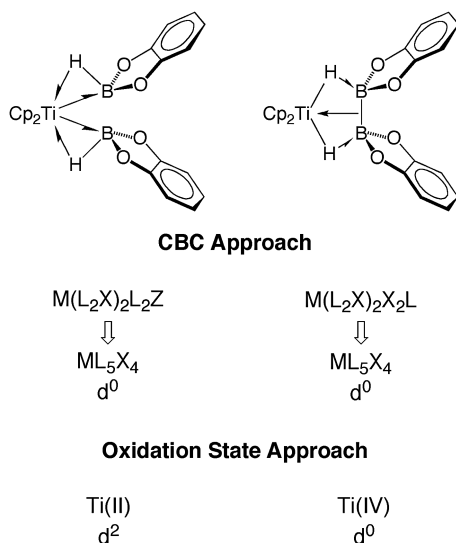


Fig. 57 Structure-bonding representations for $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$. The structure on the left views the compound as an adduct between $[\text{Cp}_2\text{Ti}]$ and two HBcat moieties, whereas the structure on the right views the compound as an adduct between Cp_2TiH_2 and catBBcat. The CBC method predicts the same classification and d^n configuration for these two descriptions, whereas the oxidation state approach predicts different d^n configurations.

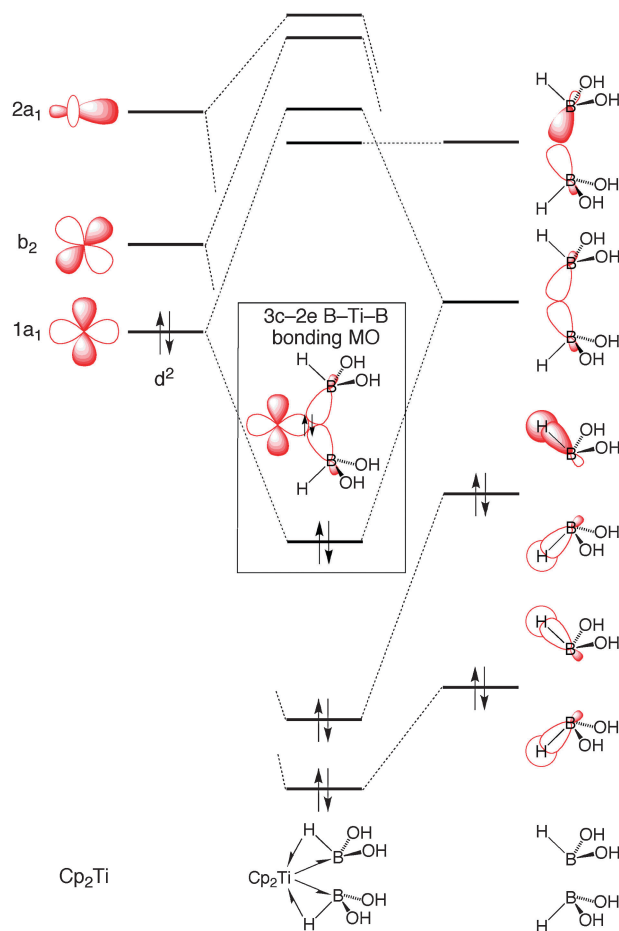


Fig. 58 Qualitative molecular orbital diagram for $\text{Cp}_2\text{Ti}[\eta^2\text{-HB(OH)}_2]_2$ (adapted from ref. 143 and, for clarity, not to scale). Note that while the configuration of the titanium in the $[\text{Cp}_2\text{Ti}]$ moiety is d^2 , it becomes d^0 upon coordination of the two borane ligands and formation of the 3c–2e bond.

HBcat molecules (Fig. 57, left) is appealing because the compound is obtained *via* a reaction with HBcat, it is worth noting that other descriptions are possible. For example, $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ can also be regarded as an adduct between Cp_2TiH_2 and the diborane, catBBcat, in which the electronic unsaturation of each boron is satisfied by interaction with the hydride ligands, while the electronic unsaturation of the titanium is satisfied by interacting with the electrons of the B–B bond (Fig. 57, right). The latter description is helpful because it emphasizes the B–B bonding interaction and indicates how it would be lengthened as a result of forming a σ -complex.

Significantly, the structure-bonding representation of $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ as an adduct between Cp_2TiH_2 and catBBcat (Fig. 57, right) results in the same ML_5X_4 classification of the titanium centre as that for the coordination of two HBcat ligands to Cp_2Ti (Fig. 57, left). This observation is of relevance because approaches based on oxidation state assignments predict either d^0 or d^2 metal centres for these different representations.¹⁴¹ The latter is not a satisfactory situation because, regardless of which fragments one chooses to describe the construction of a molecule, the molecule itself is invariant, such that the molecular orbitals of

$\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$ are the same whether one decides to construct the molecule from (i) Cp_2Ti and two HBcat molecules, (ii) Cp_2TiH_2 and catBBcat, or even (iii) $[\text{Cp}_2\text{Ti}]^{2+}$ and $[\text{HcatBBcatH}]^{2-}$. Unlike formalisms based on oxidation states, however, the CBC method seeks to classify the nature of an atom *in the molecule*. Consequently, the two CBC approaches give the same classification (Fig. 57), whereas different classifications result from application of the oxidation state approach. The fact that the CBC method predicts the same classification for the titanium centre of $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})_2$, regardless of whether it is described as a either an adduct of (i) Cp_2Ti and two HBcat molecules or (ii) Cp_2TiH_2 and catBBcat, provides a good indication that it captures an accurate description of the molecule.

4. Conclusions

In summary, although compounds that feature 3c–2e bonds are well known, there has been no previous attempt to classify the interactions according to the number of electrons that the component atoms contribute to form the bond. This article provides such a classification by categorizing 3c–2e interactions according to whether the pair of electrons is provided by one or by two atoms. Specifically, Class I 3c–2e bonds are defined as those in which two atoms each contribute one electron to the 3-centre orbital, *i.e.* [XZX] or [XXZ], while Class II 3c–2e bonds are defined as systems in which the pair of electrons are provided by a single atom, *i.e.* [ZLZ]. The relationship between these two classes of 3c–2e bonds is akin to that between normal covalent and dative covalent 2c–2e bonds.

3c–2e interactions can be represented by the use of “half-arrows” (Fig. 4) that are generally applicable to a wide range of compounds, which include bridging hydride complexes, bridging alkyl complexes, σ -complexes and agostic complexes. Significantly, the use of the half-arrow method provides a convenient means to determine the electron count at a metal centre and thereby provide insight into the nature of the compound. For example, application of the half-arrow method to compounds with bridging hydride ligands predicts M–M bond orders that are in accord with theory, whereas electron counting procedures that simply apportion half of an electron to each metal centre predict incorrect values.

Also of relevance to the determination of M–M bond orders is the recognition that a symmetrically bridging carbonyl ligand does not have to be described as ketonic, but can alternatively serve as a μ -L donor and contribute a pair of electrons to two metal centres. Invoking this μ -L bonding mode provides a simple means to rationalize the absence of a M–M bond in a variety of compounds, such as $\text{Fe}_2(\text{CO})_9$ and $[\text{CpFe}(\text{CO})_2]_2$, which are widely misrepresented in many text books as possessing Fe–Fe bonds. It is also very likely that the μ -L carbonyl ligand bonding description is applicable to many other polynuclear carbonyl compounds with bridging CO ligands.

Hoffman has previously noted that “...in bridged complexes neither a short metal–metal distance by itself nor electron counting conventions are a good guide to the presence or absence of substantial direct metal–metal interaction.”¹⁰¹ However, while this statement is true with respect to the

electron counting procedures that were in use at the time, the examples discussed in this article make it evident that electron counting conventions can be used as a good guide to the nature of a M–M interaction if the electron counting procedure employed accurately reflects 3c–2e bonding situations. In this regard, the use of half-arrows to represent 3c–2e interactions in structure–bonding representations provides a simple and convenient means to predict M–M bond orders that are in accord with theory.

Acknowledgements

G. P. thanks the US Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) for support.

Notes and References

- (a) G. N. Lewis, *Valence and The Structure of Atoms and Molecules*, The Chemical Catalog Company, 1923; (b) G. N. Lewis, *J. Chem. Phys.*, 1933, **1**, 17–28.
- (a) I. Langmuir, *Science*, 1921, **54**, 59–67; (b) I. Langmuir, *Proc. Natl. Acad. Sci. U. S. A.*, 1919, **5**, 252–259.
- (a) D. M. P. Mingos, *J. Organomet. Chem.*, 2004, **689**, 4420–4436; (b) W. B. Jensen, *J. Chem. Educ.*, 2005, **82**, 28–28.
- R. J. Gillespie and E. A. Robinson, *J. Comput. Chem.*, 2007, **28**, 87–97.
- A. Haaland, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 992–1007.
- (a) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148; (b) G. Parkin, *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2006, vol. 1, ch. 1; (c) <http://www.covalentbondclass.org/>.
- Unless one is dealing with symmetric $[\text{AB}_2]$ 3c–2e interactions where the identity of the bridge (A) is self-evident, more than one reasonable interpretation is possible for an asymmetric $[\text{ABC}]$ arrangement. Therefore, for clarity, the identity of the bridging atom should always be specified when using the μ -Z, μ -X and μ -L classification to describe the bonding within an asymmetric $[\text{ABC}]$ arrangement.
- (a) G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes: Structure, Theory, and Reactivity*, Kluwer Academic/Plenum Publishers, New York, 2001; (b) G. J. Kubas, *J. Organomet. Chem.*, 2001, **635**, 37–68; (c) G. J. Kubas, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6901–6907; (d) G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152–4205; (e) G. J. Kubas, *J. Organomet. Chem.*, 2009, **694**, 2648–2653; (f) J. C. Gordon and G. J. Kubas, *Organometallics*, 2010, **29**, 4682–4701.
- M. Berry, N. J. Cooper, M. L. H. Green and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1980, 29–41.
- R. Bau, R. G. Teller, S. W. Kirtley and T. F. Koetzle, *Acc. Chem. Res.*, 1979, **12**, 176–183.
- (a) H. Werner, *Angew. Chem., Int. Ed.*, 2004, **43**, 938–954; (b) T. Pechmann, C. D. Brandt and H. Werner, *Dalton Trans.*, 2004, 959–966.
- In principle, it is also possible to have a [ZZL] class of 3c–2e interaction in which an outer atom donates the pair of electrons. However, we are not aware of any examples of this class and so we do not include this category here.
- It must be emphasized that not all M–H–Y interactions must be described as 3c–2e bonds because some are better represented as 3c–4e “hydrogen bond” interactions. See, for example: L. Brammer, *Dalton Trans.*, 2003, 3145–3157.
- (a) C. Hall and R. N. Perutz, *Chem. Rev.*, 1996, **96**, 3125–3146; (b) R. H. Crabtree, *Chem. Rev.*, 1995, **95**, 987–1007; (c) R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299–338.
- (a) J. Y. Corey, *Chem. Rev.*, 2011, **111**, 863–1071; (b) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175–292; (c) Z. Lin, *Chem. Soc. Rev.*, 2002, **31**, 239–245; (d) G. I. Nikonov, *Adv. Organomet. Chem.*, 2005, **53**, 217–309; (e) G. Alcaraz and S. Sabo-Etienne, *Coord. Chem. Rev.*, 2008, **252**, 2395–2409; (f) U. Schubert, *Adv. Organomet. Chem.*, 1990,

- 30, 151–187; (g) S. Lachaize and S. Sabo-Etienne, *Eur. J. Inorg. Chem.*, 2006, 2115–2127.
- 16 (a) R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789–805; (b) R. N. Perutz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2007, **46**, 2578–2592; (c) G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383–392; (d) R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299–338.
- 17 R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4791–4800.
- 18 (a) S. Geftakis and G. E. Ball, *J. Am. Chem. Soc.*, 1998, **120**, 9953–9954; (b) D. J. Lawes, T. A. Darwish, T. Clark, J. B. Harper and G. E. Ball, *Angew. Chem., Int. Ed.*, 2006, **45**, 4486–4490; (c) D. J. Lawes, S. Geftakis and G. E. Ball, *J. Am. Chem. Soc.*, 2005, **127**, 4134–4135; (d) G. E. Ball, C. M. Brookes, A. J. Cowan, T. A. Darwish, M. W. George, H. K. Kawanami, P. Portius and J. P. Rourke, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6927–6932; (e) W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg and M. Brookhart, *Science*, 2009, **326**, 553–556; (f) R. D. Young, A. F. Hill, W. Hillier and G. E. Ball, *J. Am. Chem. Soc.*, 2011, **133**, 13806–13809; (g) R. D. Young, D. J. Lawes, A. F. Hill and G. E. Ball, *J. Am. Chem. Soc.*, 2012, **134**, 8294–8297.
- 19 (a) A. J. Cowan and M. W. George, *Coord. Chem. Rev.*, 2008, **252**, 2504–2511; (b) J. A. Calladine, S. B. Duckett, M. W. George, S. L. Matthews, R. N. Perutz, O. Torres and Q. V. Khuong, *J. Am. Chem. Soc.*, 2011, **133**, 2303–2310; (c) J. A. Calladine, K. Q. Vuong, X. Z. Sun and M. W. George, *Pure Appl. Chem.*, 2009, **81**, 1667–1675; (d) B. K. McNamara, J. S. Yeston, R. G. Bergman and C. B. Moore, *J. Am. Chem. Soc.*, 1999, **121**, 6437–6443.
- 20 (a) W. D. Jones, *Acc. Chem. Res.*, 2003, **36**, 140–146; (b) R. M. Bullock and B. R. Bender, Isotope Methods in Homogeneous Catalysis, in *Encyclopedia of Catalysis*, ed. I. T. Horváth, 2003; (c) G. Parkin, *Acc. Chem. Res.*, 2009, **42**, 315–325; (d) G. Parkin, *J. Labelled Compd. Radiopharm.*, 2007, **50**, 1088–1114; (e) K. E. Janak, *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2006, vol. 1, ch. 20; (f) M. Gómez-Gallego and M. A. Sierra, *Chem. Rev.*, 2011, **111**, 4857–4963.
- 21 Interactions between alkanes and a metal centre have been observed in the solid state by X-ray diffraction. However, there is no evidence that these persist in solution. See: (a) D. R. Evans, T. Drovetskaya, R. Bau, C. A. Reed and P. D. W. Boyd, *J. Am. Chem. Soc.*, 1997, **119**, 3633–3634; (b) I. Castro-Rodriguez, H. Nakai, P. Gantzel, L. N. Zakharov, A. L. Rheingold and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 15734–15735; (c) S. D. Pike, A. L. Thompson, A. G. Algarra, D. C. Apperley, S. A. Macgregor and A. S. Weller, *Science*, 2012, **337**, 1648–1651.
- 22 X.-L. Luo, G. J. Kubas, J. C. Bryan, C. J. Burns and C. J. Unkefer, *J. Am. Chem. Soc.*, 1994, **116**, 10312–10313.
- 23 (a) W. Scherer, G. Eickerling, M. Tafipolsky, G. S. McGrady, P. Sirsch and N. P. Chatterton, *Chem. Commun.*, 2006, 2986–2988; (b) G. S. McGrady, P. Sirsch, N. P. Chatterton, A. Ostermann, C. Gatti, S. Altmannshofer, V. Herz, G. Eickerling and W. Scherer, *Inorg. Chem.*, 2009, **48**, 1588–1598.
- 24 J. Yang, P. S. White, C. K. Schauer and M. Brookhart, *Angew. Chem., Int. Ed.*, 2008, **47**, 4141–4143.
- 25 I. Atheaux, F. Delpach, B. Donnadieu, S. Sabo-Etienne, B. Chaudret, K. Hussein, J. C. Barthelat, T. Braun, S. B. Duckett and R. N. Perutz, *Organometallics*, 2002, **21**, 5347–5357.
- 26 (a) I. Atheaux, B. Donnadieu, V. Rodriguez, S. Sabo-Etienne, B. Chaudret, K. Hussein and J. C. Barthelat, *J. Am. Chem. Soc.*, 2000, **122**, 5664–5665; (b) R. Ben Said, K. Hussein, J. C. Barthelat, I. Atheaux, S. Sabo-Etienne, M. Grellier, B. Donnadieu and B. Chaudret, *Dalton Trans.*, 2003, 4139–4146.
- 27 M. C. Lipke and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2012, DOI: 10.1002/anie.201202328.
- 28 Note that the silicon of $\{[\text{PhBCH}_2\text{PPh}_2]\text{Ru}\}_2(\mu\text{-SiH}_6)$ is hypervalent.
- 29 (a) M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi and H. Ogino, *J. Am. Chem. Soc.*, 1999, **121**, 11704–11712; (b) M. Shimoi, K. Katoh, M. Uruichi, S. Nagai and H. Ogino, in *Current Topics in the Chemistry of Boron*, ed. G. W. Kabalka, The Royal Society of Chemistry, London, 1994, pp. 293–296; (c) A. Ariafard, M. M. Amini and A. Azadmehr, *J. Organomet. Chem.*, 2005, **690**, 1147–1156.
- 30 (a) G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2010, **49**, 7170–7179; (b) W. E. Piers, *Angew. Chem., Int. Ed.*, 2000, **39**, 1923–1925.
- 31 B. Bera and B. R. Jagirdar, *Inorg. Chim. Acta*, 2011, **372**, 200–205.
- 32 T. M. Douglas, A. B. Chaplin and A. S. Weller, *J. Am. Chem. Soc.*, 2008, **130**, 14432–14433.
- 33 K.-R. Pörschke, W. Kleimann, Y. H. Tsay, C. Krüger and G. Wilke, *Chem. Ber.*, 1990, **123**, 1267–1273.
- 34 P. Arndt, A. Spannenberg, W. Baumann, V. V. Burlakov, U. Rosenthal, S. Becke and T. Weiss, *Organometallics*, 2004, **23**, 4792–4795.
- 35 T. Muraoka and K. Ueno, *Coord. Chem. Rev.*, 2010, **254**, 1348–1355.
- 36 E. B. Lobkovsky, G. L. Soloveychik, B. M. Bulychev, A. B. Erofeev, A. I. Gusev and N. I. Kirillova, *J. Organomet. Chem.*, 1983, **254**, 167–172.
- 37 E. B. Lobkovskii, G. L. Soloveichik, A. B. Erofeev, B. M. Bulychev and V. K. Belskii, *J. Organomet. Chem.*, 1982, **235**, 151–159.
- 38 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.
- 39 K. Ueno, T. Yamaguchi, K. Uchiyama and H. Ogino, *Organometallics*, 2002, **21**, 2347–2349.
- 40 (a) Z. Lin, *Struct. Bonding*, 2008, **130**, 123–148; (b) K. K. Pandey, *Coord. Chem. Rev.*, 2009, **253**, 37–55.
- 41 J. F. Hartwig, C. N. Muhoro, X. He, O. Eisenstein, R. Bosque and F. Maseras, *J. Am. Chem. Soc.*, 1996, **118**, 10936–10937.
- 42 (a) S. Schlecht and J. F. Hartwig, *J. Am. Chem. Soc.*, 2000, **122**, 9435–9443; (b) M. G. Crestani, M. Muñoz-Hernández, A. Arévalo, A. Acosta-Ramírez and J. J. García, *J. Am. Chem. Soc.*, 2005, **127**, 18066–18073.
- 43 G. Parkin, *Struct. Bonding*, 2010, **136**, 113–146.
- 44 M. Bortz, R. Bau, J. J. Schneider and S. A. Mason, *J. Cluster Sci.*, 2001, **12**, 285–291.
- 45 A. Albinati and L. M. Venanzi, *Coord. Chem. Rev.*, 2000, **200**, 687–715.
- 46 J. L. Petersen, R. K. Brown, J. M. Williams and R. K. McMullan, *Inorg. Chem.*, 1979, **18**, 3493–3498.
- 47 Some authors focus on the use the total valence electron count (TVEC) to predict metal–metal bond orders in dinuclear compounds by using the relationship: number of M–M bonds = $(36 - \text{TVEC})/2$. However, although this expression often gives results in accord with theory, it fails in situations in which there are bridging hydride ligands because the hydrogen atom is considered to contribute only one electron to the TVEC. It is, of course, possible to use the above expression to predict M–M bond orders if the TVEC is modified to recognize that the bridging hydride ligand serves the role of a 3-electron donor.
- 48 C. P. Casey, H. Sakaba, P. N. Hazin and D. R. Powell, *J. Am. Chem. Soc.*, 1991, **113**, 8165–8166.
- 49 H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida and Y. Moro-oka, *Organometallics*, 1988, **7**, 2243–2245.
- 50 N. Koga and K. Morokuma, *J. Mol. Struct.*, 1993, **300**, 181–189.
- 51 (a) T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263–293; (b) Z. Xu and Z. Lin, *Coord. Chem. Rev.*, 1996, **156**, 139–162; (c) M. Besora and A. Lledós, *Struct. Bonding*, 2008, **130**, 149–202.
- 52 Although the haptic “ η^x ” notation^a is often used to describe the coordination mode of borohydride ligands,^b such notation is strictly inappropriate because η^x refers to the number of contiguous atoms that are attached to a specific element.^c If the atoms are not contiguous, the kappa “ κ^x ” notation^d should be used instead, e.g. $\kappa^2\text{-O}_2\text{CMe}$ versus $\eta^2\text{-O}_2\text{CMe}$. Therefore, because the hydrogen atoms in borohydride are not contiguous, it is preferable to use the κ^x notation to indicate the number of hydrogen atoms attached to the metal in borohydride compounds. (a) F. A. Cotton, *J. Am. Chem. Soc.*, 1968, **90**, 6230–6232; (b) Ref. 51; (c) N. G. Connelly, T. Damhus, R. M. Hartshorn and A. T. Hutton, *International Union of Pure and Applied Chemistry, Nomenclature for Inorganic Chemistry (2005)*, RSC Publishing, 2005, IR-10.2.5.1, p. 216; (d) T. E. Sloan and D. H. Busch, *Inorg. Chem.*, 1978, **17**, 2043–2047.
- 53 (a) M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6908–6914; (b) M. Brookhart,

- M. L. H. Green and L. L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1–124; (c) M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395–408.
- 54 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802–803.
- 55 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, K. Prout, A. J. Schultz, J. M. Williams and T. F. Koetzle, *J. Chem. Soc., Dalton Trans.*, 1986, 1629–1637.
- 56 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 1410–1411.
- 57 H. Lee, P. J. Desrosiers, I. Guzei, A. L. Rheingold and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 3255–3256.
- 58 This view of the bonding in agostic compounds is necessarily simplistic. For a more detailed discussions, see: (a) W. Scherer and G. S. McGrady, *Angew. Chem., Int. Ed.*, 2004, **43**, 1782–1806; (b) E. Clot and O. Eisenstein, *Struct. Bonding*, 2004, **113**, 1–36; (c) J. Saßmannshausen, *Dalton Trans.*, 2012, **41**, 1919–1923; (d) W. Scherer, V. Herz and C. Hauf, *Struct. Bonding*, 2012, **146**, 159–208.
- 59 J. Holton, M. F. Lappert, R. Pearce and P. I. W. Yarrow, *Chem. Rev.*, 1983, **83**, 135–201.
- 60 (a) M. H. Baik, R. A. Friesner and G. Parkin, *Polyhedron*, 2004, **23**, 2879–2900; (b) J. H. Shin and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1998, 1273–1274.
- 61 P. Braunstein and N. M. Boag, *Angew. Chem., Int. Ed.*, 2001, **40**, 2427–2433.
- 62 R. W. Waymouth, K. S. Potter, W. P. Schaefer and R. H. Grubbs, *Organometallics*, 1990, **9**, 2843–2846.
- 63 S. D. Stults, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1989, **111**, 4507–4508.
- 64 J. C. Huffman and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 1971, 911–912.
- 65 C. Ni and P. P. Power, *Organometallics*, 2009, **28**, 6541–6545.
- 66 (a) M. E. García, A. Ramos, M. A. Ruiz, M. Lanfranchi and L. Marchio, *Organometallics*, 2007, **26**, 6197–6212; (b) M. A. Alvarez, M. E. García, M. E. Martínez, A. Ramos and M. A. Ruiz, *Organometallics*, 2009, **28**, 6293–6307; (c) M. A. Alvarez, M. E. García, M. E. Martínez and M. A. Ruiz, *Organometallics*, 2010, **29**, 904–916.
- 67 B. E. Bursten and R. H. Cayton, *Organometallics*, 1986, **5**, 1051–1053.
- 68 (a) A. Heine and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 121–122; (b) A. Heine, R. Herbst-Irmer and D. Stalke, *J. Chem. Soc., Chem. Commun.*, 1993, 1729–1731.
- 69 (a) K. Osakada, T. Koizumi and T. Yamamoto, *Angew. Chem., Int. Ed.*, 1998, **37**, 349–351; (b) K. Osakada, *J. Organomet. Chem.*, 2000, **611**, 323–331.
- 70 (a) M. Tanabe, D. Ito and K. Osakada, *Organometallics*, 2008, **27**, 2258–2267; (b) M. Tanabe, D. Ito and K. Osakada, *Organometallics*, 2007, **26**, 459–462; (c) S. Nakajima, M. Sumimoto, Y. Nakao, H. Sato, S. Sakaki and K. Osakada, *Organometallics*, 2005, **24**, 4029–4038.
- 71 Compounds with triply bridging PF₃ ligands are also known. See, for example: (a) A. L. Balch, B. J. Davis and M. M. Olmstead, *Inorg. Chem.*, 1993, **32**, 3937–3942; (b) A. L. Balch, B. J. Davis and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 8592–8593.
- 72 S. Schinzel, R. Müller, S. Riedel, H. Werner and M. Kaupp, *Chem.–Eur. J.*, 2011, **17**, 7228–7235.
- 73 For an early speculation of a complex with a bridging PR₃ ligand, see: R. Bender, P. Braunstein, A. Dedieu and Y. Dusausoy, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 923–925.
- 74 For compounds with asymmetrically bridging PR₃ ligands, see: (a) T. Murahashi, T. Otani, T. Okuno and H. Kurosawa, *Angew. Chem. Int. Ed.*, 2000, **39**, 537–540; (b) P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albinati, F. Lianza, P. S. Pregosin and H. Rieger, *Organometallics*, 1993, **12**, 1702–1713; (c) P. H. M. Budzelaar, P. Vanleeuwen, C. F. Roobeek and A. G. Orpen, *Organometallics*, 1992, **11**, 23–25; (d) A. Albinati, F. Lianza, M. Pasquali, M. Sommovigo, P. Leoni, P. S. Pregosin and H. Rieger, *Inorg. Chem.*, 1991, **30**, 4690–4692.
- 75 For calculations on hypothetical bridging PF₃ complexes, see: H.-Q. Yang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, *J. Phys. Chem. A*, 2010, **114**, 8896–8901.
- 76 H. Sun, J. Gu, Z. Zhang, H. Lin, F. Ding and Q. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 7498–7500.
- 77 C. Lescop, *Actual. Chim.*, 2006, 30–33.
- 78 (a) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J. F. Halet and R. Réau, *Angew. Chem., Int. Ed.*, 2001, **40**, 228–231; (b) F. Leca, M. Sauthier, V. Deborde, L. Toupet and R. Réau, *Chem.–Eur. J.*, 2003, **9**, 3785–3795.
- 79 F. Leca, C. Lescop, E. Rodriguez-Sanz, K. Costuas, J. F. Halet and R. Réau, *Angew. Chem., Int. Ed.*, 2005, **44**, 4362–4365.
- 80 (a) B. Nohra, E. Rodriguez-Sanz, C. Lescop and R. Réau, *Chem.–Eur. J.*, 2008, **14**, 3391–3403; (b) E. Rodriguez-Sanz, C. Lescop and R. Réau, *C. R. Chim.*, 2010, **13**, 980–984.
- 81 S. Welsch, B. Nohra, E. V. Peresykina, C. Lescop, M. Scheer and R. Réau, *Chem.–Eur. J.*, 2009, **15**, 4685–4703.
- 82 W. J. Evans, M. A. Greci and J. W. Ziller, *Chem. Commun.*, 1998, 2367–2368.
- 83 T. C. Davenport and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2011, **50**, 12205–12208.
- 84 C. Lorber, R. Choukroun and L. Vendier, *Organometallics*, 2008, **27**, 5017–5024.
- 85 J. D. Beckwith, M. Tschinkl, A. Picot, M. Tsunoda, R. Bachman and F. P. Gabbai, *Organometallics*, 2001, **20**, 3169–3174.
- 86 P. Lin, W. Clegg, R. W. Harrington and R. A. Henderson, *Dalton Trans.*, 2005, 2349–2351.
- 87 M. R. A. Al-Mandhary, C. M. Fitchett and P. J. Steel, *Aust. J. Chem.*, 2006, **59**, 307–314.
- 88 Z. Hu and S. M. Gorun, *Inorg. Chem.*, 2001, **40**, 667–671.
- 89 X.-L. Li, X.-G. Meng and S.-P. Xu, *Chin. J. Struct. Chem.*, 2009, **28**, 1619–1624.
- 90 In addition to bridging in a symmetric manner, carbonyl ligands are also known to adopt bent semibringing and linear semibringing coordination modes. The bonding in these complexes are highly varied and are not part of the scope of the present article. For key references, see: (a) R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1986, **25**, 805–812; (b) R. Colton and J. J. McCormick, *Coord. Chem. Rev.*, 1980, **31**, 1–52; (c) C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219–305; (d) F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1–28; (e) B. J. Morris-Sherwood, C. B. Powell and M. B. Hall, *J. Am. Chem. Soc.*, 1984, **106**, 5079–5083; (f) A. L. Sargent and M. B. Hall, *J. Am. Chem. Soc.*, 1989, **111**, 1563–1569; (g) A. L. Sargent and M. B. Hall, *Polyhedron*, 1990, **9**, 1799–1808; (h) C. Q. Simpson and M. B. Hall, *J. Am. Chem. Soc.*, 1992, **114**, 1641–1645; (i) T. F. Miller, D. L. Strout and M. B. Hall, *Organometallics*, 1998, **17**, 4164–4168; (j) A. Sironi, *Inorg. Chem.*, 1995, **34**, 1342–1349.
- 91 J. Dewar and H. O. Jones, *Proc. R. Soc. London*, 1905, **76**, 558–577.
- 92 R. Brill, *Z. Kristallogr.*, 1927, **65**, 89–93.
- 93 H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286–292.
- 94 N. V. Sidgwick and R. W. Bailey, *Proc. R. Soc. A*, 1934, **144**, 521–537.
- 95 A subsequent higher quality structure revealed a Fe–Fe distance of 2.523(1) Å. See: F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 1974, 800–802.
- 96 N. V. Sidgwick and H. M. Powell, *Proc. R. Soc. London*, 1940, **176**, 153–180.
- 97 (a) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, New York, 2007, p. 157; (b) G. Wulfsburg, *Inorganic Chemistry*, University Science Books, California, 2000, p. 557; (c) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley Inter-Science, New York, 6th edn, 1999, p. 809; (d) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Inter-Science, New York, 5th edn, 1988, p. 1025; (e) G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, Prentice-Hall, New Jersey, 2nd edn, 1998, p. 440; (f) G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, Prentice-Hall, New Jersey, 1st edn, 1990, p. 430; (g) G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice-Hall, New Jersey, 1996, p. 68; (h) Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1st edn, 1989, p. 224; (i) Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 2nd edn, 1992, p. 224; (j) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York, 1986, p. 1283; (k) R. B. King, *Transition-Metal Organometallic Chemistry: An Introduction*, Academic Press, New York, 1969, p. 118; (l) J. E. Huheey, W. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper Collins College Publishers, New York, 4th edn, 1993, p. 636;

- (m) C. E. Housecroft, *Metal–Metal Bonded Carbonyl Dimers and Clusters*, Oxford University Press, Oxford, 1996, p. 9.
- 98 W. Wardlaw, *Endeavour*, 1948, **26**, 66–69.
- 99 P. S. Braterman, *Struct. Bonding*, 1972, **10**, 57–86.
- 100 J. W. Lauher, M. Elian, R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 3219–3224.
- 101 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3821–3831.
- 102 (a) P. Macchi and A. Sironi, *Coord. Chem. Rev.*, 2003, **238**, 383–412; (b) L. J. Farrugia and P. Macchi, *Struct. Bonding*, 2012, **146**, 127–158.
- 103 W. Heijser, E. J. Baerends and P. Ros, *Faraday Symp. Chem. Soc.*, 1980, **14**, 211–234.
- 104 C. W. Bauschlicher, *J. Chem. Phys.*, 1986, **84**, 872–875.
- 105 A. Rosa and E. J. Baerends, *New J. Chem.*, 1991, **15**, 815–829.
- 106 R. Ponec, G. Lendvay and J. Chaves, *J. Comput. Chem.*, 2008, **29**, 1387–1398.
- 107 C. Bo, J. P. Sarasa and J. M. Poblet, *J. Phys. Chem.*, 1993, **97**, 6362–6366.
- 108 (a) C. Mealli and D. M. Proserpio, *J. Organomet. Chem.*, 1990, **386**, 203–208; (b) J. Reinhold, E. Hunstock and C. Mealli, *New J. Chem.*, 1994, **18**, 465–471; (c) J. Reinhold, O. Kluge and C. Mealli, *Inorg. Chem.*, 2007, **46**, 7142–7147; (d) J. Reinhold, A. Barthel and C. Mealli, *Coord. Chem. Rev.*, 2003, **238**, 333–346.
- 109 R. Ponec and C. Gatti, *Inorg. Chem.*, 2009, **48**, 11024–11031.
- 110 We are aware of only one textbook that discusses the nonexistence of the Fe–Fe bond in $\text{Fe}_2(\text{CO})_9$; however, the molecule is drawn with a dashed Fe–Fe line, and there is no discussion as to how this description should be employed with respect to electron counting purposes. See: Ch. Elschenbroich, *Organometallics*, Wiley-VCH, Weinheim, 3rd edn, 2006, p. 359.
- 111 $\text{Co}_2(\text{CO})_8$ exists as an equilibrium between bridged $(\text{CO})_3\text{Co}(\mu\text{-CO})_2\text{Co}(\text{CO})_3$ and non-bridged isomers, $(\text{CO})_4\text{Co}-\text{Co}(\text{CO})_4$, of which the former is the major isomer.
- 112 A. A. Low, K. L. Kunze, P. J. Macdougall and M. B. Hall, *Inorg. Chem.*, 1991, **30**, 1079–1086.
- 113 Experimental charge-density studies are also in accord with the absence of a direct Co–Co bond in the bridged form of $\text{Co}_2(\text{CO})_8$. See: P. C. Leung and P. Coppens, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1983, **39**, 535–542.
- 114 (a) M. Bénard, *J. Am. Chem. Soc.*, 1978, **100**, 7740–7742; (b) M. Bénard, *Inorg. Chem.*, 1979, **18**, 2782–2785; (c) A. Mitschler, B. Rees and M. S. Lehmann, *J. Am. Chem. Soc.*, 1978, **100**, 3390–3397; (d) E. D. Jemmis, A. R. Pinhas and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576–2585; (e) G. Granozzi, *J. Mol. Struct.*, 1988, **173**, 313–28; (f) B. E. Bursten and R. H. Cayton, *J. Am. Chem. Soc.*, 1986, **108**, 8241–8249; (g) B. E. Bursten, R. H. Cayton and M. G. Gatter, *Organometallics*, 1988, **7**, 1342–1348; (h) M. V. Andreocci, M. Bossa, C. Cauletti, R. Paolesse, G. Ortaggi, T. Vondrak, M. N. Piancastelli, M. Casarin, C. M. Dal and G. Granozzi, *J. Organomet. Chem.*, 1989, **366**, 343–355; (i) M. C. Böhm, *Z. Naturforsch.*, 1982, **37A**, 241–247.
- 115 For another article that describes the absence of M–M bonds in other carbonyl bridged compounds, for a similar reason, see: N. M. Kostic and R. F. Fenske, *Inorg. Chem.*, 1983, **22**, 666–671.
- 116 P. Macchi, L. Garlaschelli, S. Martinengo and A. Sironi, *J. Am. Chem. Soc.*, 1999, **121**, 10428–10429.
- 117 (a) U. Radius, F. M. Bickelhaupt, A. W. Ehlers, N. Goldberg and R. Hoffmann, *Inorg. Chem.*, 1998, **37**, 1080–1090; (b) F. M. Bickelhaupt, J. K. Nagle and W. L. Klemm, *J. Phys. Chem. A*, 2008, **112**, 2437–2446; (c) G. Frenking, C. Loschen, A. Krapp, S. Fau and S. H. Strauss, *J. Comput. Chem.*, 2007, **28**, 117–126.
- 118 M. Elian, M. M. L. Chen, D. M. P. Mingos and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148–1155.
- 119 P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 554–556.
- 120 A. F. Dyke, S. A. R. Knox, P. J. Naish and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1980, 441–442.
- 121 M. I. Altbach, F. R. Fronczek and L. G. Butler, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 644–650.
- 122 (a) T. J. Katz and M. Rosenberg, *J. Am. Chem. Soc.*, 1962, **84**, 865–866; (b) T. J. Katz and M. Rosenberg, *J. Am. Chem. Soc.*, 1963, **85**, 2030–2031; (c) T. J. Katz, R. K. O'Hara and M. Rosenberg, *J. Am. Chem. Soc.*, 1964, **86**, 249–252.
- 123 (a) O. T. Summerscales and F. G. N. Cloke, *Coord. Chem. Rev.*, 2006, **250**, 1122–1140; (b) F. G. N. Cloke, *Pure Appl. Chem.*, 2001, **73**, 233–238.
- 124 F. G. N. Cloke, J. C. Green, C. N. Jardine and M. C. Kuchta, *Organometallics*, 1999, **18**, 1087–1090.
- 125 G. Balazs, F. G. N. Cloke, L. Gagliardi, J. C. Green, A. Harrison, P. B. Hitchcock, A. R. M. Shahi and O. T. Summerscales, *Organometallics*, 2008, **27**, 2013–2020.
- 126 A. E. Ashley, R. T. Cooper, G. G. Wildgoose, J. C. Green and D. O'Hare, *J. Am. Chem. Soc.*, 2008, **130**, 15662–15677.
- 127 A. E. Ashley, G. Balazs, A. R. Cowley, J. C. Green and D. O'Hare, *Organometallics*, 2007, **26**, 5517–5521.
- 128 S. C. Jones, T. Hascall, S. Barlow and D. O'Hare, *J. Am. Chem. Soc.*, 2002, **124**, 11610–11611.
- 129 A. Muñoz-Castro, D. M. L. Carey and R. Arratia-Pérez, *Polyhedron*, 2009, **28**, 1561–1567.
- 130 (a) H. Li, H. Feng, W. Sun, Y. Xie, R. B. King and H. F. Schaefer III, *Eur. J. Inorg. Chem.*, 2011, 2746–2755; (b) H. Li, H. Feng, W. Sun, Q. Fan, Y. Xie and R. B. King, *J. Organomet. Chem.*, 2012, **700**, 4–12.
- 131 (a) J. A. K. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 412–416; (b) A. Brookes, F. Gordon, J. Howard, S. A. R. Knox and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1973, 587–589.
- 132 S. Bendjaballah, S. Kahlal, K. Costuas, E. Bevilion and J. Y. Saillard, *Chem.–Eur. J.*, 2006, **12**, 2048–2065.
- 133 (a) E. E. Bunel, L. Valle, N. L. Jones, P. J. Carroll, C. Barra, M. Gonzalez, N. Munoz, G. Visconti, A. Aizman and J. M. Manriquez, *J. Am. Chem. Soc.*, 1988, **110**, 6596–6598; (b) J. M. Manriquez, M. D. Ward, W. M. Reiff, J. C. Calabrese, N. L. Jones, P. J. Carroll, E. E. Bunel and J. S. Miller, *J. Am. Chem. Soc.*, 1995, **117**, 6182–6193.
- 134 T. Watanabe, Y. Ishida, T. Matsuo and H. Kawaguchi, *Dalton Trans.*, 2010, **39**, 484–491.
- 135 F. A. Cotton, P. A. Kibala and W. A. Wojtczak, *J. Am. Chem. Soc.*, 1991, **113**, 1462–1463.
- 136 The structure-bonding representation for the zirconium compound is one in which only one of the oxygen lone pairs of each aryloxy ligand participates in π -donation; additional π -donation would result in an 18-electron ML_6X_2 classification.
- 137 V. Beck and D. O'Hare, *J. Organomet. Chem.*, 2004, **689**, 3920–3938.
- 138 H. Wadepohl, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 247–262.
- 139 (a) W. M. Lamanna, *J. Am. Chem. Soc.*, 1986, **108**, 2096–2097; (b) W. M. Lamanna, W. B. Gleason and D. Britton, *Organometallics*, 1987, **6**, 1583–1584.
- 140 (a) S. Krieck, H. Gørls, L. Yu, M. Reiher and M. Westerhausen, *J. Am. Chem. Soc.*, 2009, **131**, 2977–2985; (b) W. J. Evans, S. A. Kozimor, J. W. Ziller and N. Kaltsoyannis, *J. Am. Chem. Soc.*, 2004, **126**, 14533–14547.
- 141 (a) C. N. Muhoro, X. He and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 5033–5046; (b) ref. 41.
- 142 For example, the B–B distance of 2.11 Å is ca. 0.4 Å longer than the value in catBBCat derivatives. See: (a) P. Nguyen, C. Y. Dai, N. J. Taylor, W. P. Power, T. B. Marder, N. L. Pickett and N. C. Norman, *Inorg. Chem.*, 1995, **34**, 4290–4291; (b) P. Nguyen, G. Lesley, N. J. Taylor, T. B. Marder, N. L. Pickett, W. Clegg, M. R. J. Elsegood and N. C. Norman, *Inorg. Chem.*, 1994, **33**, 4623–4624.
- 143 W. H. Lam and Z. Lin, *Organometallics*, 2000, **19**, 2625–2628.
- 144 G. Parkin, *Organometallics*, 2006, **25**, 4744–4747.
- 145 (a) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny and G. Parkin, *Inorg. Chem.*, 2006, **45**, 2588–2597; (b) J. S. Figueroa, J. G. Melnick and G. Parkin, *Inorg. Chem.*, 2006, **45**, 7056–7058; (c) K. Pang and G. Parkin, *Chem. Commun.*, 2006, 5015–5017.