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Theoretical investigation of the metal–metal interaction in dimolybdenum complexes with bridging hydride and methyl ligands

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Dedicated to Malcolm L.H. Green for being a tremendous mentor whose enthusiasm and excitement for chemistry, together with his numerous discoveries, have provided inspiration for many

Abstract

DFT calculations on dinuclear molybdenum complexes with bridging hydride and methyl ligands, namely [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H) and [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me), indicate that the bonding is best described in terms of: (i) a 2-center-2-electron Mo–Mo single bond and (ii) a 3-center-2-electron Mo–H–Mo or Mo–Me–Mo bond. The presence of a 2-center-2-electron Mo–Mo single bond is in accord with an electron counting procedure that views the bridging hydride and methyl ligands as μ-LX ligands; in contrast, an electron counting procedure which apportions half of the valence electron of the hydrogen atom or methyl radical to each metal dictates a Mo=Mo double bond, a result that is contrary to the theoretical calculations. Consideration of a variety of other bridging hydride complexes indicates that the μ-LX electron counting method provides the best general description of the bonding by clearly distinguishing between the number of 3-center-2-electron M–H–M interactions and direct 2-center-2-electron M–M interactions.
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1. Introduction

The ability to discern whether or not the proposed structure of a molecule is reasonable is paramount to understanding and predicting its properties, such as stability. While these issues can be addressed by theoretical studies of various levels of sophistication, the first order evaluation is normally performed by the application of simple qualitative and empirical rules, such as the octet rule and those embodied in valence shell electron pair repulsion theory. For example, the chemistry of carbon is dictated by the octet rule and application of this rule successfully predicts the existence of single, double, and triple bonds in ethane, ethylene, and acetylene, respectively. The transition metals, however, with their multi-

ple valence states, are not so readily rationalized by such simple rules. Nevertheless, a notable exception pertains to the organometallic chemistry of the transition elements (and especially for the metals Groups 6–8), for which many structures are governed by the "18-electron rule" [1,2]. By analogy with the octet rule, the successful application of the 18-electron rule merely requires knowledge of how many electrons the ligand array contributes to the valence shell of the metal. For example, the Mn–Mn bond order in (CO)$_5$Mn–Mn(CO)$_5$ is predicted to be one on the basis that each [Mn(CO)$_5$] fragment posseses a 17-electron configuration (cf. the single C–C bond in ethane is a consequence of the fact that each methyl radical possesses a 7-electron configuration). Despite this simplicity, inspection of the literature makes it evident that certain ligands cause confusion with respect to the number of electrons that they contribute to the metal center; bridging hydride and alkyl

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ligands, in particular, are two of the most common ligands for which opinions differ. An important ramification of employing different electron counts for a given bridging ligand is that the inferred bond order between the two metal centers will vary. As an illustration, the molecule $Os_3(CO)_{10}(\mu_2\text{-H})_2$ [3] has been represented in the literature with no less than five bonding descriptions in which the Os···Os bond order varies from zero to two, including variants with less certain bonding depictions (Fig. 1). Thus, although the formal classification of the bridging ligands and the resulting differences of the formal electron-count may be subjective, the consequences for predicting the electronic structure, of which the most salient feature is the nature of the metal–metal interaction, are significant. Therefore, we address this issue here by performing density functional theory (DFT) [4] electronic structure calculations on a series of dimolybdenum compounds with bridging hydride, methyl and chloride ligands. Specifically, evaluation and comparison of the derived Mo–Mo bond orders provides a means to assess which of the literature electron counting methods for treating symmetrically bridging hydride and methyl ligands is the most apt. The conclusion of this study is that symmetrically bridging hydride and methyl ligands are best represented as 3-center-2-electron interactions, and that electron counting schemes that apportion half of the valence electron of the hydrogen atom or methyl radical to each metal are not appropriate.

2. Results and discussion

2.1. Electron counting and bond order ambiguities

The theoretical calculations that are described in this paper are intended to evaluate which is the most appropriate method for counting electrons in complexes that possess $[M(\mu\text{-X})M]$ (X = H, R) 3-center-2-electron interactions [5,6]. To place this work in context, it is pertinent to review the two basic methods for evaluating the number of electrons contributed to each metal center by symmetrically bridging hydride and alkyl ligands.

2.1.1. Method I: the "half-electron" method

This method merely apportions the electrons associated with the isolated hydride and alkyl ligands equally to both metals [7,8]. If one employs a neutral ligand electron counting procedure, this method has the outcome that a bridging hydrogen atom or alkyl radical contributes 0.5 electrons to the electron count at each metal center of a dinuclear complex [9].

2.1.2. Method II: the μ-LX "half-arrow" method

An alternative method to evaluate the number of electrons contributed to the metal center by bridging hydride and alkyl ligands fully recognizes the 3-center-2-electron nature of the $[M(\mu\text{-X})M]$ interaction [10]. A simplified molecular orbital representation of the 3-center-2-electron $[M(\mu\text{-H})M]$ interaction is illustrated in Fig. 2. An important point to note is that, depending upon the geometry of the system, the amount of direct M–M interaction can vary from being significant to insignificant; such extremes are termed "closed" and "open" 3-center-2-electron interactions and are illustrated in Fig. 3 [11]. As a consequence, while the MO description of the 3-center-2-electron interaction is unambiguous, the schematic depiction of this interaction is not definitive; thus, 3-center-2-electron $[M(\mu\text{-H})M]$ bonds have been represented by a variety of means, as illustrated in Fig. 4. Dahl originally formulated $[M(\mu\text{-H})M]$ interactions with two solid lines between M and H (**A**) [14,15], but this representation can give the mistaken impression that the two "bonds" at-
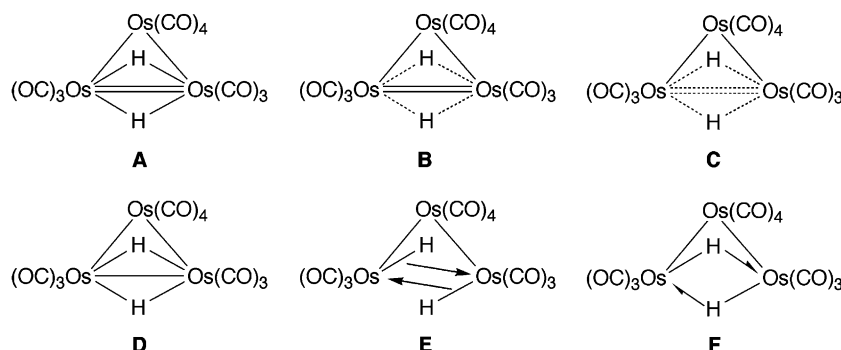

Fig. 1. Structural representations for $Os_3(CO)_{10}(\mu_2\text{-H})_2$. **A**: (a) Ref. [63c]. (b) M.R. Churchill, H.J. Wasserman, Inorg. Chem. 19 (1980) 2391; (c) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley–Interscience, New York, 1988, p. 1057; (d) A.F. Hill, Organotransition Metal Chemistry, Wiley–Interscience, New York, 2002, p. 34. **B**: J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987 p. 37. **C**: Ref. [3b]. **D**: (a) Ref. [60a]. (b) M.G. Karpov, S.P. Tunik, V.R. Denisov G.L. Starova, A.B. Nikolskii, F.M. Dolgushin, A.I. Yanovsky, Y.T. Struchkov, J. Organomet. Chem. 485 (1995) 219; (c) G.O. Spessard, G.L. Miessler, Organometallic Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1996, p. 454. **E**: (a) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 3rd ed., Wiley–Interscience, New York, 2001, p. 373; (b) N.A. Richardson, Y.M. Xie, R.B. King, H.F. Schaefer, J. Phys. Chem. A 105 (2001) 11134. **F**: this work.
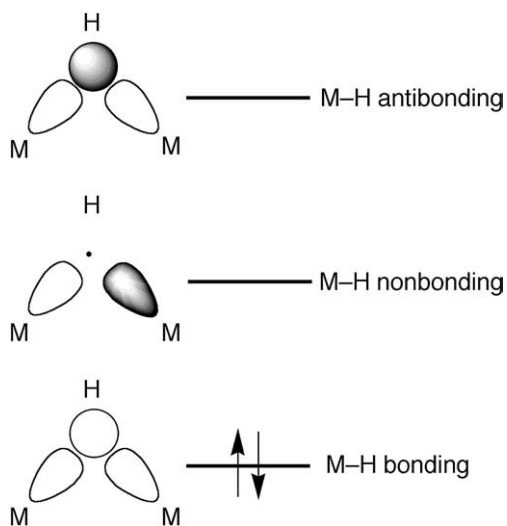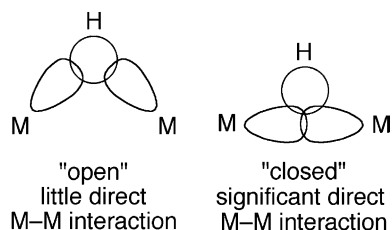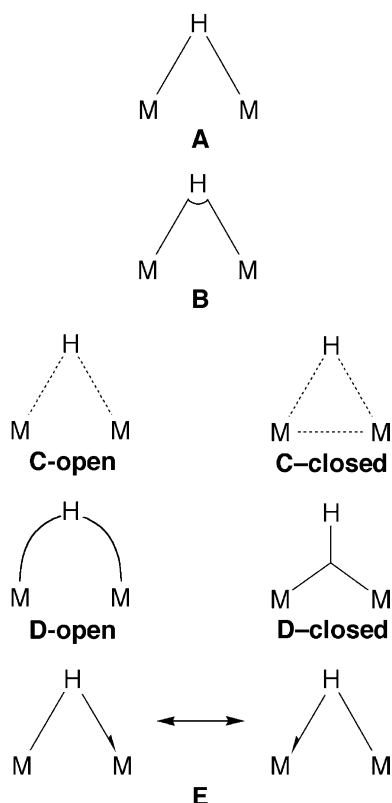
Fig. 2. Simplified MO diagram for a 3-center-2-electron interaction.

Fig. 3. "Open" and "closed" 3-center-2-electron interactions with varying degrees of M···M interaction.

Fig. 4. Representations of 3-center-2-electron M–H–M interactions.

tached to hydrogen are independent 2-center-2-electron bonds. A simple modification of the Dahl representation involves joining the two bonds by a curved line around the hydrogen atom (**B**) to indicate that the two bonds are not independent and thereby emphasize the 3-center-2-electron nature of the interaction [16]. Churchill has employed a "dashed-bond" depiction of the 3-center-2-electron bond that also emphasizes the possible "open" (**C-open**) and "closed" (**C-closed**) nature of the interactions [17,18]. Bau, Koetzle and Kirtley have also proposed representations for "open" and "closed" 3-center-2-electron [M(μ-H)M] interactions by using "bent" (**D-open**) and "Y" (**D-closed**) bonds [12,13], a symbolism that is used in borane chemistry and which is intended to convey the same information portrayed by Churchill's "dashed-bond" depictions. While Churchill's "dashed-bond" depiction of the "closed" 3-center-2-electron [M(μ-H)M] interaction (**B-closed**) is a good representation, Dahl has noted that a problem which has arisen is that others have redrawn the dashed lines as solid lines, thereby implying the incorrect notion that *there is a separate M–M 2-center-2-electron bond in addition to the 3-center-2-electron M–H–M interaction* [15,19]. Another problem associated with each of the representations (**A**) to (**D**) is that they are not particularly useful for electron counting purposes. It is, therefore, significant that Green's μ-LX "half arrow" notation (**E**) (Fig. 4) is of particular benefit in this regard [20,21]. Thus, the representation M–H ⇀ M′ depicts the essence of the valence bond description of the 3-center-2-electron bond in that the pair of electrons associated with the M–H sigma bond (i.e. an "X" type interaction) [21] is donated into a vacant orbital on M′ (i.e. an "L" type interaction) [21], as illustrated in Fig. 5; obviously, by resonance, the bridge (M ↼ H–M′) is symmetric (Fig. 4,**E**). It is important to emphasize that the absence of a "line" between the M atoms bridged by the hydrogen atom in the "half arrow" notation does *not* imply that there is no interaction between
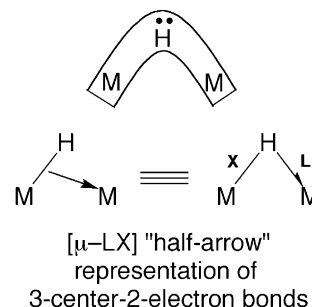

[μ–LX] "half-arrow"
representation of
3-center-2-electron bonds

Fig. 5. The [μ-LX] "half-arrow" representation of a 3-center-2-electron M–H–M interaction; the hydrogen atom may be viewed as a μ-LX ligand, where X refers to the one electron contribution to the normal covalent M–H component and L is associated with donation of the pair of electrons associated of the M–H sigma bond into a vacant orbital on M′.

these atoms. Rather, the "half-arrow" notation indicates that any M···M interaction that does exist is one that is mediated by the bridging atom.

The "half arrow" notation is not restricted to M–H–M interactions, but applies equally well to other complexes that exhibit 3-center-2-electron bonds, such as those involving coordination of: (i) C–H bonds, e.g. agostic alkyl complexes [22] and hydrocarbon σ-complexes [M](σ-HR) [23,24], (ii) B–H bonds, e.g. diborane [5], borane adducts [25], and borohydride derivatives [26], and (iii) M–C bonds, e.g. symmetrically bridging methyl ligands.

The existence of two different electron counting procedures causes confusion with respect to the full bonding description of molecules that possess 3-center-2-electron [M(μ-X)M] (X = H, R) interactions, as exemplified by the various bonding descriptions of Os$_3$(CO)$_{10}$(μ$_2$-H)$_2$ described above. Furthermore, even though Dahl reported in 1965 the first structure of a transition metal complex with a bridging hydride ligand, namely [CpMo(CO)$_2$]$_2$(μ-PMe$_2$)(μ-H), and stated that "the bent, three-center Mo–H–Mo bond involving one electron from the two molybdenum atoms and one from the hydrogen accounts for the compound's diamagnetism without the invoking of a separate Mo–Mo bond" [14,15], more than thirty five years later closely related [CpMo(CO)$_2$]$_2$(μ-PRR′)(μ-H) derivatives are represented by some chemists with direct Mo–Mo bonds [27]. A further illustration of the confusion that may ensue is illustrated by the description of the bonding in [(η^6-C$_6$H$_6$)Re]$_2$(μ-H)(μ-CHR). Thus, taking into account the 3-center-2-electron nature of the bonding, [(η^6-C$_6$H$_6$)Re]$_2$(μ-H)(μ-CHR) was originally assigned a Re–Re single bond, a result that was also confirmed by calculations [28]; a subsequent report, however, does not properly recognize the nature of the bonding and states that the previous assignment is incorrect and that the bond order is three [29]!

To address these issues in more detail, and thereby provide evidence for which of the electron counting methods provides a better description of the bonding in molecules with bridging hydride and methyl ligands, we have used computational methods to investigate the bonding in a series of derivatives with bridging ligands, namely [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) [30] and [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$) (μ-X) (X = H, Me, Cl).

2.2. The Mo–Mo bond length and bond order in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me)

In contrast to bridging hydride derivatives, complexes with bridging methyl groups are uncommon [31,32]. Bridging methyl ligands also differ from bridging hydride ligands by virtue of the fact that a variety of coordination modes are possible, which may be classified as: (i) symmetric pyramidal, (ii) symmetric trigonal

planar, (iii) monohapto agostic [33], (iv) dihapto agostic, and (v) trihapto agostic (Fig. 6) [30,31]. We are aware of only one dimolybdenum complex with a bridging methyl ligand that has been structurally characterized by X-ray diffraction, namely [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) 1 [30,34], as illustrated in Fig. 7. With chemically equivalent Mo–C bond lengths [2.300(7) and 2.301(7) Å] and an acute Mo–C–Mo bond angle [76.4(2)°], the bridging methyl group in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) may be appropriately described as symmetric pyramidal. There is also a short Mo···H separation of 2.02 Å which suggests that some monohapto agostic character to the interaction could be considered, but the equivalence of the Mo–C bond lengths and the acute Mo–C–Mo bond angle is considered to be a more important indicator of the symmetric pyramidal coordination mode [35].

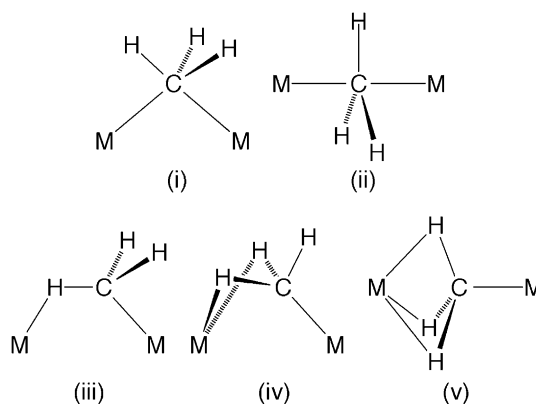The Mo–Mo interaction in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is predicted to be a single bond using the
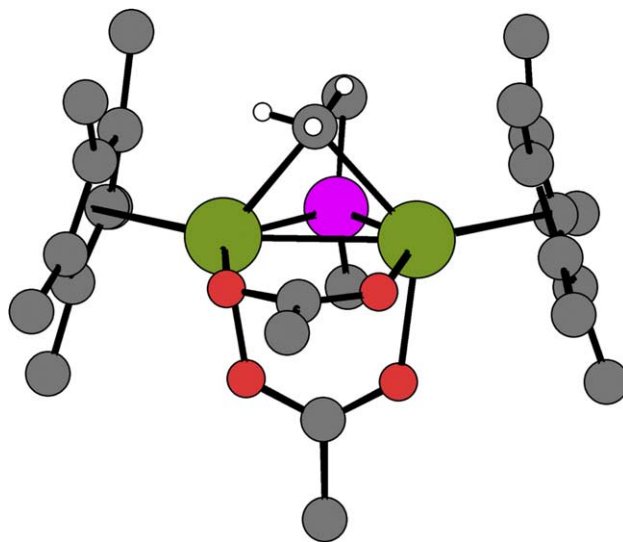

Fig. 6. Coordination modes of bridging methyl complexes.

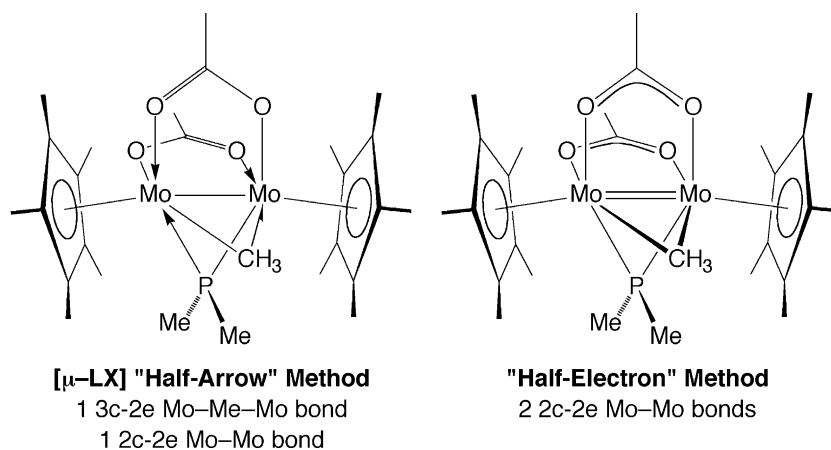Fig. 7. Experimental molecular structure of [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me).

Fig. 8. Predicted Mo–Mo bond orders for [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) using two different electron counting procedures.

μ-LX ''half-arrow'' electron counting procedure that recognizes the 3-center-2-electron nature of the interaction, but a double bond using the ''half-electron'' procedure that does not consider the 3-center-2-electron nature of the interaction, as illustrated in Fig. 8. Specifically, application of the formula [7b]

$$m = (18n - N)/2,$$

where m is the number of 2-center-2-electron M–M bonds, n is the number of M atoms, and N is the total electron count, predicts a Mo=Mo double bond using the ''half-electron'' method. It is evident from this formula that the higher Mo–Mo bond order for the μ-LX ''half-electron'' method is merely a consequence of a reduced electron count (N) due to the 3-center-2-electron nature of the interaction not being recognized [7].

Experimental evidence for the Mo–Mo bond order in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) could be expected to be procured from the Mo–Mo bond length, in a manner similar to that in which C–C bond distances may be used to distinguish between single (1.53 Å), double (1.32 Å) and triple (1.18 Å) bonds in organic compounds [36]. Indeed, it is evident from the summary of Mo–Mo bond lengths for dinuclear molybdenum complexes provided in Table 1 that Mo–Mo bond lengths span a substantial range; for example, the Mo–Mo single bond in [CpMo(CO)$_3$]$_2$ [3.235(1) Å] [37] is approximately 1 Å longer than in compounds with Mo≡≡Mo quadruple bonds, which are typically in the range 2.06–2.17 Å [38]. However, despite this large range of Mo–Mo bond lengths, the presence of bridging ligands creates a significant problem in attempting to correlate metal–metal distances with bond order because the steric and electronic requirements of the bridging group exert an additional influence that causes the metal–metal distance to be either shorter or longer than that in the absence of the bridge [39–42]. For example, complexes with bridging ligands may have Mo–Mo single bonds that are more than 0.5 Å shorter than the Mo–Mo single bond in un-

bridged [CpMo(CO)$_3$]$_2$ [3.235(1) Å] [37], as illustrated by [CpMo(SMe)$_2$]$_2$ [2.603(2) Å] [43], [Cp$^{Pr^i}$Mo(μ-Cl)$_2$]$_2$ [2.607(1)Å] [44,45], and [Cp*Mo(μ-I)$_2$]$_2$ [2.708(3) Å] [46,47]. Furthermore, Mo–Mo single bond lengths in complexes with bridging ligands may be comparable to the formal Mo=Mo double bonds in complexes such as [Cp*Mo(μ-S)(μ-SH)]$_2$ [2.573(1) Å] [46], [CpMo(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$) [2.623(2) Å] [27c,48], and [(Bu^{t}O)$_2$Mo$_2$(μ-OBu^t)]$_2$(μ-CO) [2.498(1) Å] [49]. Likewise, the Mo=Mo double bond lengths in these complexes are comparable to the formal Mo≡Mo triple bond lengths in [CpMo(CO)$_2$]$_2$ [2.448(1) Å] [50] and [IndMo(CO)$_2$]$_2$ [2.500(1) Å] [51,52]. It is, therefore, apparent that assigning a Mo–Mo bond order on the basis of the bond length may be fraught with difficulty. Nevertheless, it is apparent that the Mo–Mo bond length of 2.8447(5) Å for [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is much more in accord with that of a Mo–Mo single bond than that of a Mo=Mo double bond. Moreover, the Mo–Mo bond in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is substantially shorter than that in [CpMo(CO)$_2$]$_2$(μ-PMe$_2$)(μ-H) [3.267(7) Å], a compound that was reported by Dahl as having no direct Mo–Mo bond [14]. As such, these limited bond length comparisons support the notion that electron counting using the μ-LX ''half-arrow'' method, which recognizes the 3-center-2-electron nature of the interaction, is more appropriate than that of the ''half-electron'' method. However, in view of the aforementioned caveat, we deemed it essential to establish the Mo–Mo bond order using theoretical methods.

2.3. Geometry optimization of [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) and related complexes

The geometry optimized structure of [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) (**1**) is illustrated in Fig. 9 and the derived Mo–Mo bond length (2.88 Å) compares favorably with the experimental value (2.85 Å); likewise,

Table 1
Mo–Mo bond lengths and formal bond orders in dinuclear cyclopentadienyl molybdenum complexes and related derivatives

	$d_{\text{Mo}\cdots\text{Mo}}$ (Å)	Mo–Mo bond order: [μ-LX] "half-arrow" method	Mo–Mo bond order: "half-electron" method	Ref.
[CpMo(CO)$_2$]$_2$(μ-PMe$_2$)(μ-H)	3.267(2)	0	1	1
[CpMo(CO)$_2$]^2(μ-PBu$_2^t$)(μ-H)	3.247(1)	0	1	2
[CpMo(CO)$_2$]$_2$(μ-PPh$_2$)(μ-H)	3.244(1)	0	1	3
[CpMo(CO)$_2$]$_2$(μ-PPhEt)(μ-H)	3.278(1)	0	1	4
[CpMo(CO)$_2$]$_2$](μ-P{C$_6$H$_2$Bu$_2^t$CMe$_2$CH$_2$})(μ-H)	3.250(1)	0	1	5
[CpMo(CO)$_3$]$_2$	3.235(1)	1	1	6
{[CpMo(CO)$_2$]$_2$(μ-PMe$_2$)}$^-$	3.157(2)	1	1	7
{[CpMo(CO)$_2$]$_2$(μ-PPh$_2$)}$^-$	3.185(2)	1	1	3
[Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me)	2.8447(5)	1	2	8
[Cp$^{Pr^i}$Mo(μ-Cl)$_2$]$_2$	2.607(1)	1	1	9
[Cp*Mo(μ-Br)$_2$]$_2$	2.643(2)	1	1	10
[Cp*Mo(μ-I)$_2$]$_2$	2.708(3)	1	1	11
[(C$_5$Me$_4$Et)Mo]$_2$(μ-Cl)$_3$(μ-PPh$_2$)	2.6388(8)	1	1	12
[CpMo(μ-SMe)$_2$]$_2$	2.603(2)	1	1	13
[(Cp^{Me_4Et})Mo(μ-SMe)$_2$]$_2$	2.616(1)	1	1	11
[(Cp^{Me})Mo(μ-S)(μ-SMe)]$_2$	2.582(1)	2	2	14
[Cp*Mo(μ-S)(μ-SH)]$_2$	2.573(1)	2	2	11
[Cp*Mo(μ-S)(μ-SMe)]$_2$	2.573(1)	2	2	15
[CpMo(μ-S)]$_2$(μ-SPr^i)(μ-PPh$_2$)	2.623(2)	2	2	16
[CpMo(CO)$_2$]$_2$	2.448(1)	3	3	17
[IndMo(CO)$_2$]$_2$	2.500(1)	3	3	18

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(16) Ref. [27c].
(17) Ref. [50].
(18) Ref. [51].

there is good agreement between the calculated (75.3°) and experimental (76.4°) Mo–C–Mo bond angles [30,53]. However, whereas the experimental Mo–CH$_3$ bond lengths are identical (2.30 Å), the calculation predicts a slight asymmetry of the Mo–CH$_3$–Mo interaction, with Mo–CH$_3$ bond lengths of 2.23 and 2.45 Å, indicative of the presence of a weak agostic interaction [22]. We were unable to find a symmetric local minimum where the methyl group is oriented such that there is no agostic interaction. However, although the asymmetric orientation of the methyl group perturbs the shapes of the molecular orbitals, the agostic interaction is quite weak and does not change the overall bonding significantly (vide infra).

To facilitate the interpretation of the theoretical analysis, we have performed additional calculations on simpler derivatives with bridging hydride and chloride ligands, namely [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-X) (X = H, **2**; Cl, **3**) (Fig. 9). In particular, comparison of the bridging hydride and methyl complexes serves to highlight the electronic similarity of the two systems, while the chloride complex CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-Cl) provides an example of an unambiguous Mo–Mo single bond (in the sense that both electron counting methods predict the same bond order due to the presence of lone pair electrons on chlorine). Comparisons with {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$ (**4**$^-$) are also pertinent since the absence of a bridging X ligand results in the molecule possessing a formal Mo=Mo double bond according to both electron counting procedures. Thus, using the electronic structures of [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-Cl) (**3**) and {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$ (**4**$^-$) as reference points, it is possible to assess critically whether the characteristics of the Mo–Mo interaction in
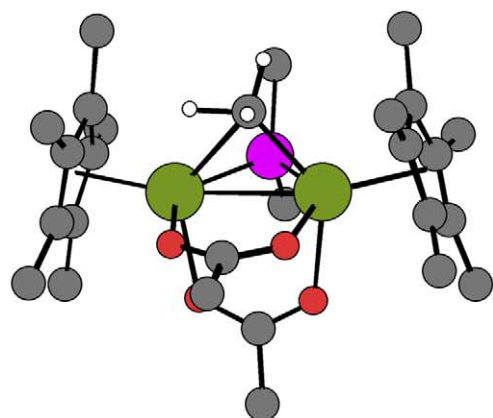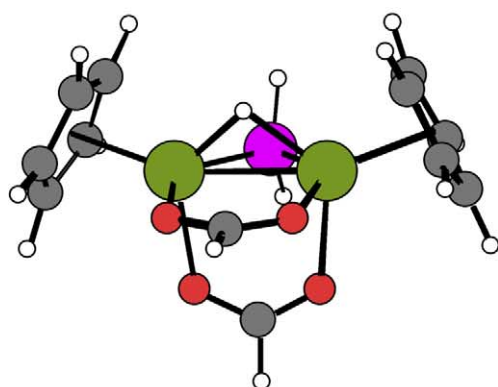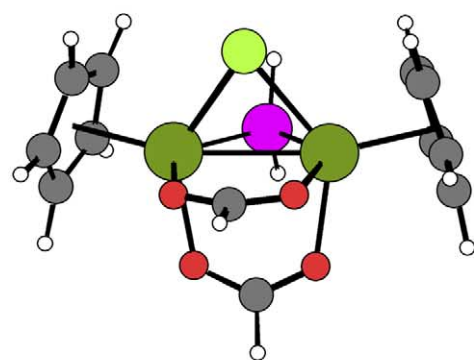
[Cp*Mo(μ-O₂CMe)]₂(μ–PMe₂)(μ–Me), **1**

[CpMo(μ-O₂CH)]₂(μ–PH₂)(μ–H), **2**

[CpMo(μ-O₂CH)]₂(μ–PH₂)(μ–Cl), **3**

Fig. 9. Geometry optimized structures of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me), [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H), and [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl).

[Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) and [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) resemble those of a typical single or double bond.

2.4. Bond orders and bond lengths

Quantum mechanical calculations of the electronic structure of a molecule provide a means for determining bond order. In this regard, although bond orders are not

observables in a quantum mechanical sense, such that their derivation is not uniquely defined, a number of protocols have been suggested in the literature [54], of which Wiberg's bond index W is particularly relevant to the goal of the present study [55]. Specifically, Wiberg has shown that the sum of squares of the off-diagonal elements of the density matrix P involving the atomic orbitals of the nuclei that are directly connected to each other gives a good estimate for the bond order

$$W = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2. \tag{1}$$

A slightly more robust and more generally applicable modification of the Wiberg bond index is the Mayer bond order (M) [56], where the orbital overlap matrix S is also included in the computation of the bond order

$$M = \sum_{\mu \in A} \sum_{\nu \in B} (PS)_{\mu\nu} (PS)_{\nu\mu}. \tag{2}$$

Mayer's protocol has been shown to give bond order values that are in fairly good agreement with intuitive expectations for both organic [57] and inorganic systems [58]. In the following discussion we utilize only the Mayer bond orders and list the Wiberg bond index only for comparison purposes (Table 2).

Examination of the array of complexes shown in Fig. 10 indicates how the computed Mayer bond orders vary as a function of the bridging ligand. Notably, the computed bond order of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) is 0.72, while that of the bridging hydride derivative [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) is 0.97. These values are clearly too low to be assigned to a Mo=Mo double bond and more closely correspond to that of a Mo–Mo single bond. A particularly important comparison is with the chloride derivative, [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl), which serves as a reference point for an undisputed formal Mo–Mo single bond since both electron counting methods predict the same bond order. In this regard, the Mayer Mo–Mo bond order of 0.78 for [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl) is comparable to those of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) (0.72) and [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) (0.97), thereby indicating that the Mo–Mo interactions are similar and thus support the assignment of a single Mo–Mo bond to each of these complexes.

Further evidence that the Mayer bond orders for the above derivatives correspond to formal Mo–Mo single bonds is provided by comparison with the hypothetical species {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ which is derived by proton abstraction from [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H). {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ provides a convenient reference point for an undisputed formal Mo=Mo double bond according to both electron counting methods and this is reflected by the Mayer bond order for {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ (1.53) being

Table 2
Comparison of calculated bond orders for a series of dinuclear molybdenum compounds with those predicted by two alternative electron counting methods. In each case, the bond order predicted by the [μ-LX] "half-arrow" method corresponds exactly to that obtained from the calculations, whereas the "half-electron" method fails for the compounds with bridging hydride and methyl ligands

	$d_{Mo\cdots Mo}$ (Å)	Wiberg bond index W	Mayer bond index M	Mo–Mo configuration and calculated bond order	Electron count bond order: [μ-LX] "half-arrow" method	Electron count bond order: "half-electron" method
$\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)\}^{2-}$ (2^{2-})	3.07	0.39	0.45	$\sigma^2\delta^2\delta*^2\pi*^2$, BO = 0	0	1
$[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$ (1)	2.88	0.61	0.72	$\sigma^2\delta^2\delta*^2$, BO = 1	1	2
$[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$ (2)	2.77	0.87	0.97	$\sigma^2\delta^2\delta*^2$, BO = 1	1	2
$[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}Cl)$ (3)	2.91	0.60	0.78	$\sigma^2\delta^2\delta*^2$, BO = 1	1	1
$\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^{-}$ (4^{-})	2.64	1.41	1.53	$\sigma^2\delta^2\pi^2\delta*^2$, BO = 2	2	2
$\{[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)\}^{2+}$ (1^{2+})	2.81	1.02	1.17	$\sigma^2\delta^2$, BO = 2	2	3
$\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)\}^{2+}$ (2^{2+})	2.67	1.40	1.52	$\sigma^2\delta^2$, BO = 2	2	3
$\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}Cl)\}^{2+}$ (3^{2+})	2.83	1.10	1.23	$\sigma^2\delta^2$, BO = 2	2	2
$\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^{+}$ (4^{+})	2.35	2.17	2.38	$\sigma^2\delta^2\pi^2$, BO = 3	3	3

notably greater than the values for [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) (0.72), [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) (0.97), and [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl) (0.78).

An additional comparison is provided by the cation {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ (4⁺) which is derived by hydride abstraction from [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) and provides a reference point for an undisputed formal Mo≡Mo triple bond according to both electron counting methods. As expected, the Mayer bond order for {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ (2.38) is substantially greater than that for {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ (1.53). Thus, consideration of the Mayer bond orders of [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl) (0.78), {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ (1.53), and {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ (2.38), which, respectively, have Mo–Mo single, double and triple bonds according to both electron counting methods, demonstrates that the Mayer bond orders are sensitive to the changes in Mo–Mo interaction in this system. In accord with the increase in Mayer bond order, a corresponding reduction in Mo–Mo bond length is observed for this series of complexes with formal single, double and triple Mo–Mo bonds: [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl) (2.91 Å), {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ (2.64 Å), and {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ (2.35 Å).

While [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl), {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻, and {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ provide examples of the changes expected in the Mayer bond order and bond length as a function of the formal Mo–Mo bond order, the comparison is not perfect because the presence of the bridging ligand exerts an intrinsic effect on bond length [39–42]. This problem can be circumvented by consideration of dicationic and dianionic counterparts of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me), [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H), and [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl). Thus, removal of two electrons from each of the aforementioned complexes is expected to increase the formal bond order by one,

while addition of two electrons is expected to reduce the bond order by one (Table 2). As an illustration, the Mayer bond orders for the anionic, neutral, and cationic hydride bridged complexes increase progressively, concomitant with a reduction of Mo–Mo bond length: {[CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H)}²⁻ (2²⁻) (0.45, 3.07 Å), [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) (2) (0.97, 2.77 Å), and {[CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H)}²⁺ (2²⁺) (1.52, 2.67 Å).

2.5. Molecular orbital diagrams

While the Mayer bond orders provide a convenient and quantitative evaluation of the metal–metal interaction, a more detailed picture is required to understand fully the nature of the Mo–Mo interaction. Therefore, we have used the results of DFT calculations to deduce partial molecular orbital (MO) diagrams for the above systems and thereby identify the frontier orbitals that are involved in the Mo–Mo bonding.

Considering initially the hydride bridged complex, [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H), it is evident that there are two possible fragmentation patterns for constructing the MO diagram, both of which are useful for understanding the electronic structure of the series of bridged complexes. Thus, the MO diagram can be constructed by using either: (i) an anionic dinuclear fragment, {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻, and the cationic form of the bridging ligand, H⁺ or (ii) a cationic dinuclear fragment, {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺, and the anionic form of the ligand, H⁻. The MO diagram constructed for the first possibility is illustrated in Fig. 11, where all 10 metal-d dominated MOs are shown as simplified iconic representations. Isosurface plots of the most important MOs are shown in Fig. 12.

It is important to note that the local coordinate system that is used for each molybdenum center is one in which the z-axis is defined as the Mo–Cp_cent vector and that these are *not* in alignment with the Mo–Mo
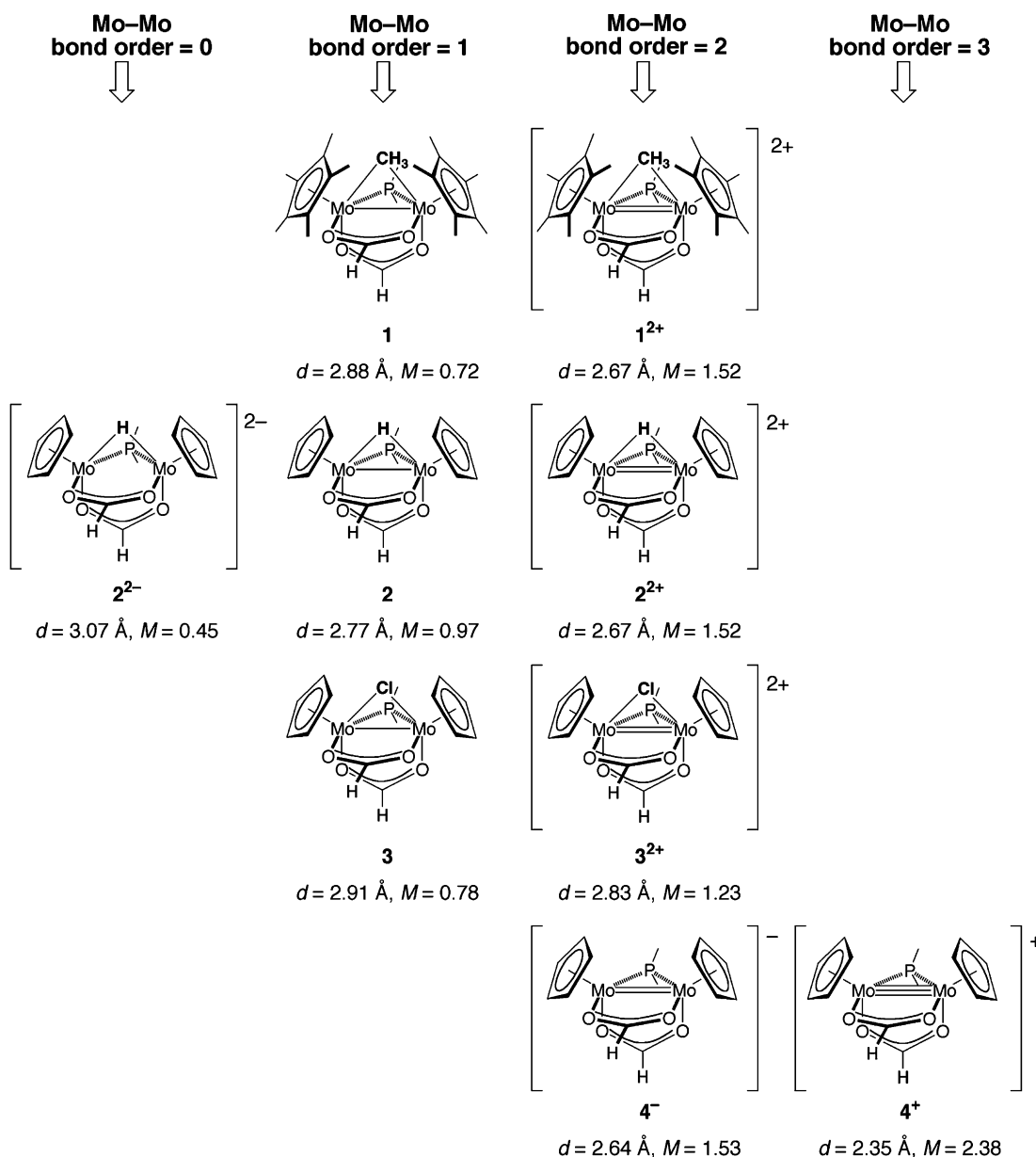
Fig. 10. Metal–metal distances (Å) and Mayer bond orders for a variety of dinuclear complexes. Note that for simplicity the lines between the bridging ligands and the molybdenum centers are only intended to convey connectivity and are not intended to be used for electron counting purposes; in this regard, the resonance structure on the left hand side of Fig. 8 illustrates the appropriate method for counting the bridging ligands.

vector. Thus, whereas the overlap of two d_{xy} orbitals would be expected to give rise to δ and δ* molecular orbitals, the lack of alignment of the Mo–Cp$_{cent}$ and Mo–Mo vectors causes the derived orbitals to have some π-character such that they are best described as "slipped" δ and δ* orbitals. Correspondingly, the overlap of the two d_{xy} orbitals is normally expected to give rise to π and π* molecular orbitals, but the lack of alignment of the Mo–Cp$_{cent}$ vector with the Mo–Mo vector causes these interactions to have some σ-character such that the MOs are best described as "slipped" π and π* orbitals. For brevity, however, we will simply refer to these orbitals as δ/δ* and π/π*, respectively.

The lowest metal-d dominated MO of the {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ fragment, [σ, MO-⟨57⟩], is an in-phase combination of the Mo-d_{z^2} orbitals and forms the basis of the Mo–Mo σ-bond (left hand side of Fig. 11). The second lowest metal-d dominated MO of the {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ fragment [δ, MO-⟨58⟩] is derived from overlap of the two Mo-d_{xy} orbitals, while the third lowest MO [π, MO-⟨59⟩] is derived from overlap of the two Mo-d_{xz} orbitals. This orbital is of particular importance with respect to the interaction with the bridging ligands and is therefore marked in red in Fig. 11. The highest occupied molecular orbital (HOMO) of {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ is the
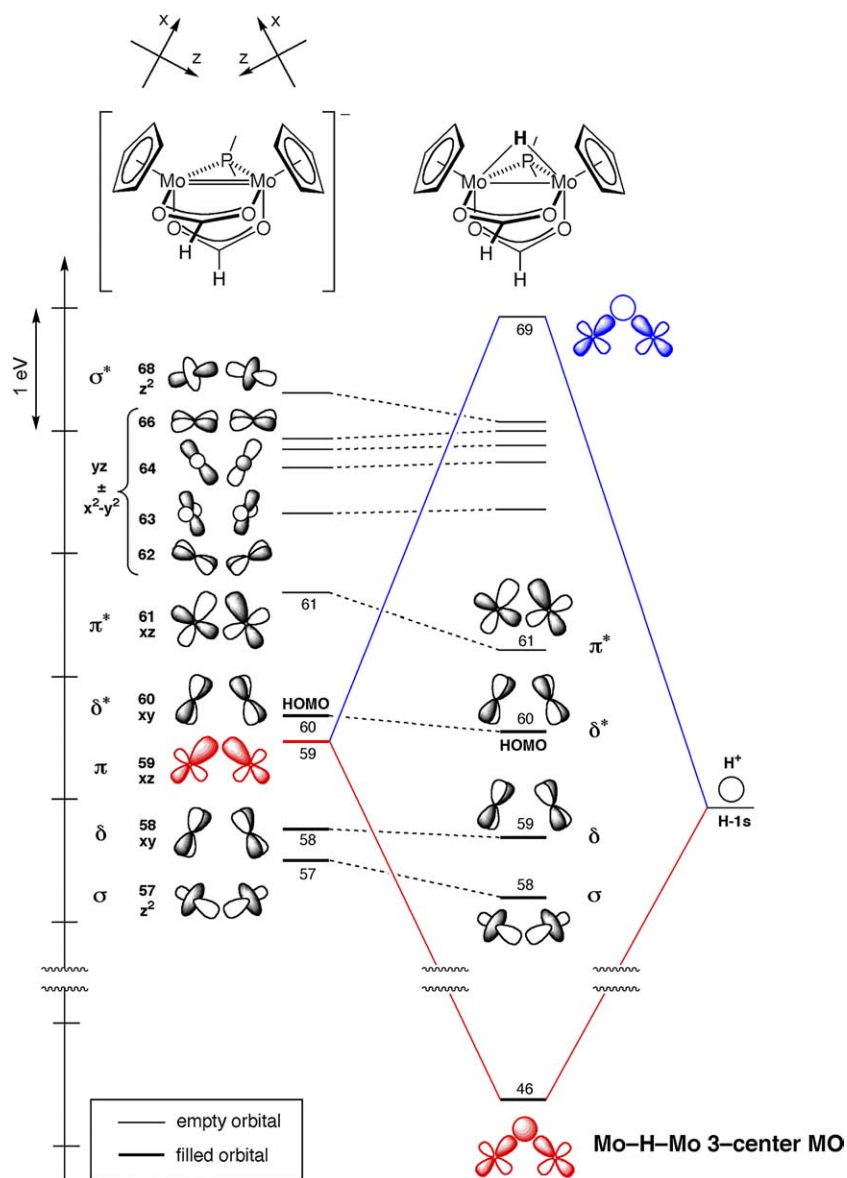
Fig. 11. MO diagram for [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H) derived from {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$ and H$^+$ fragments. The d orbitals listed correspond to the significant component of the molecular orbital.

out-of-phase combination of the metal d$_{xy}$ orbitals [δ*, MO-⟨60⟩], while the lowest unoccupied molecular orbital (LUMO) is the out-of-phase combination of the metal d$_{xz}$ orbitals [π*, MO-⟨61⟩] [59]. With two Mo(II)-d^4 centers in the dinuclear fragment, it is evident that the σ^2(δ)^2(π)^2-(δ*)^2 configuration corresponds to a formal Mo≡Mo double bond in {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$, consisting of one σ and one π bond, which is in accord with the bond order predicted by both electron counting methods.

With respect to construction of the MO diagram for the bridging hydride complex [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H) from the {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$ and H$^+$ fragments, it is only the π orbital [MO-⟨59⟩] of {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$ that has the appropriate

symmetry and sufficient overlap with the empty 1s orbital of the proton fragment to give a significant electronic interaction. Thus, the in-phase combination gives rise to a three-center Mo–H–Mo bonding orbital [MO-⟨46⟩, E = −9.76 eV] which, as expected for a metal-ligand bonding orbital, is highly dominated by the ligand, i.e. the 1s orbital of hydrogen (Fig. 13). The out-of-phase combination of this interaction [MO-⟨69⟩, E = −1.76 eV] has metal based character and is of significantly higher energy (Fig. 14).

As a result of the transfer of electron density from the metal based π orbital to the bridging ligand, only three metal-dominated MOs remain occupied in [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H), as shown in Figs. 11 and 14. Of these three MOs, the lowest in energy is the metal–metal
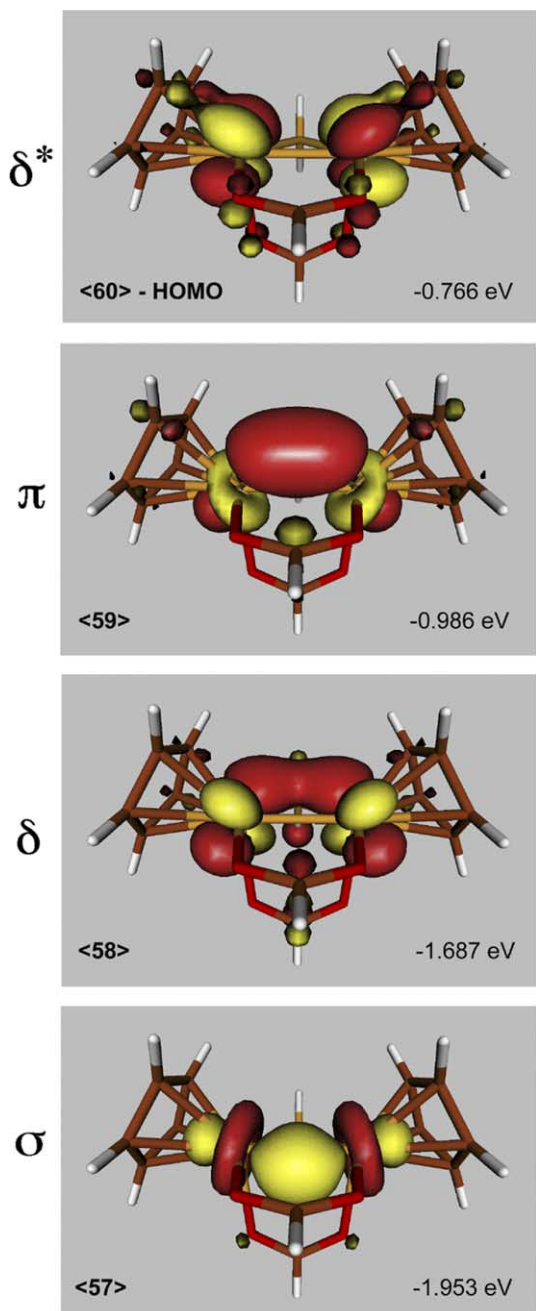
Fig. 12. Isosurface plots of the occupied σ, δ, π and δ^* orbitals corresponding to the direct Mo–Mo interaction in $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^-$. The $\sigma^2(\delta)^2(\pi)^2(\delta^*)^2$ configuration corresponds to a formal Mo=Mo double bond.

σ-bonding orbital [MO-$\langle 58 \rangle$]. The remaining two orbitals are δ-bonding and δ^*-antibonding [MO-$\langle 59 \rangle$ and MO-$\langle 60 \rangle$], and since these are both occupied, there is a net zero δ-bonding interaction. Thus, the $\sigma^2(\delta)^2(\delta^*)^2$ configuration for $[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$ is most consistent with a Mo–Mo single bond. In essence, the π-bond component of the double bond in $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^-$ is destroyed as a consequence of removal of the π-bond electron density upon protonation.

As indicated above, an alternative approach for constructing the MO diagram for $[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$ is to employ the cationic dinuclear species $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ and anionic hydride ligand as the fragments. This approach is chemically more meaningful since the bridging H is usually viewed as a hydride rather than a proton, and it allows for a more intuitive comparison with the bridging chloride derivative since Cl is normally treated as Cl$^-$ rather than Cl$^+$. While the final MO diagram is, of course, unchanged, it is instructive to consider how the addition of H$^-$ to $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ causes the formal Mo≡Mo triple bond to be reduced to a single Mo–Mo bond. In essence, there are two factors responsible for the two fold reduction of the Mo–Mo bond order: (i) the Mo–Mo π-bond is eradicated by virtue of the fact that it becomes a component of the three-center Mo–H–Mo interaction, (ii) the additional pair of electrons is elevated to an orbital that is Mo–Mo δ^* antibonding (i.e. the LUMO of $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$, [MO-$\langle 60 \rangle$]), as illustrated in Fig. 15.

To understand in more detail the reason for why addition of H$^-$ causes the formal Mo≡Mo triple bond in $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ to be reduced to a single Mo–Mo bond, the hypothetical transformation is traced in Fig. 15. Iconic representations of the frontier molecular orbitals of $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ derived from interactions of the d orbitals are illustrated on the left hand side of Fig. 15, from which it is evident that the $\sigma^2(\delta)^2(\pi)^2$ configuration resulting from the two Mo(III)-d^3 centers predicts a formal Mo≡Mo triple bond in $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$. There are two factors that deserve attention upon the hypothetical coordination of H$^-$ to $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$. Firstly, a significant structural distortion of the $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ fragment is required to form the hydrogen bridged dimer, $[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$, with the Mo–Mo bond being required to expand from 2.35 to 2.77 Å upon hydride addition. Secondly, the negative charge density centered on the bridging hydride ligand introduces a purely Coulombic response from the dimetallic fragment. The results of these two changes are illustrated in the MO-correlation diagram shown in Fig. 15: the first step illustrates the consequence of distorting the geometry of the dinuclear $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ fragment from its equilibrium structure to that of the hydrogen-bridged species $[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$, while the second step illustrates the result of incorporating a single negative point charge at the position of the hydride bridge. The elongation of the Mo–Mo distance in the first step has the effect of raising the energy of the MOs that are Mo–Mo bonding in character, while stabilizing the MOs that are Mo–Mo antibonding in character. At the distance of 2.77 Å, the HOMO (π) of $\{[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)\}^+$ in its equilibrium geometry becomes
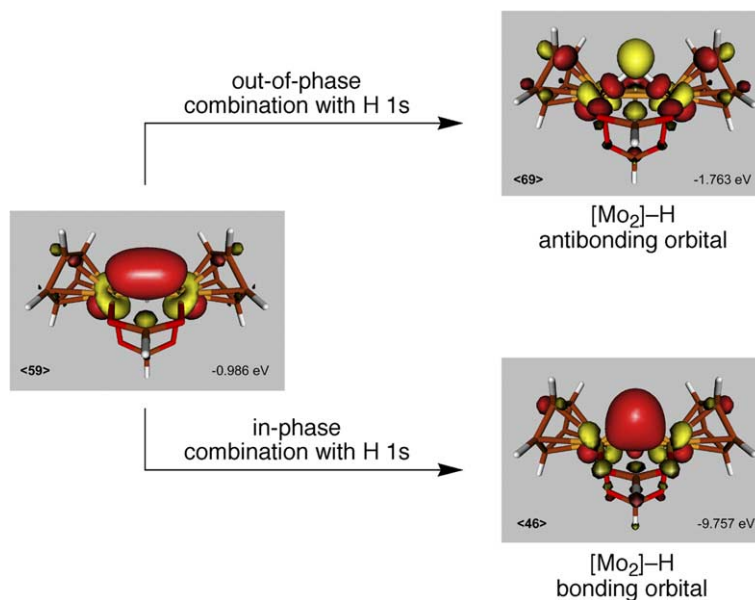
Fig. 13. Mo–H bonding and antibonding orbitals derived by interaction of the H$^+$ 1s orbital with the Mo–Mo π-bonding orbital of {[CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)}$^-$.
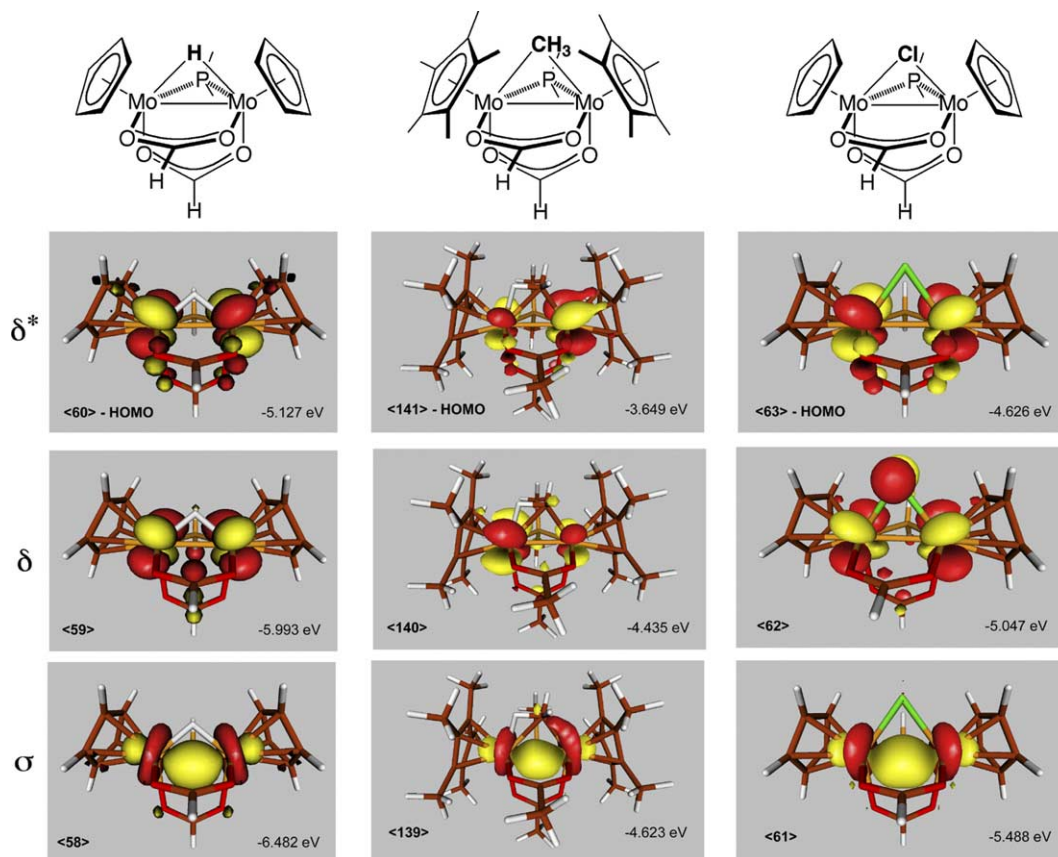
Fig. 14. Comparison of the occupied σ, δ, and δ^* orbitals corresponding to the direct Mo–Mo interaction in [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H), [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me), and [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-Cl). The $\sigma^2(\delta)^2(\delta^*)^2$ configuration corresponds to a formal Mo–Mo single bond for each complex.
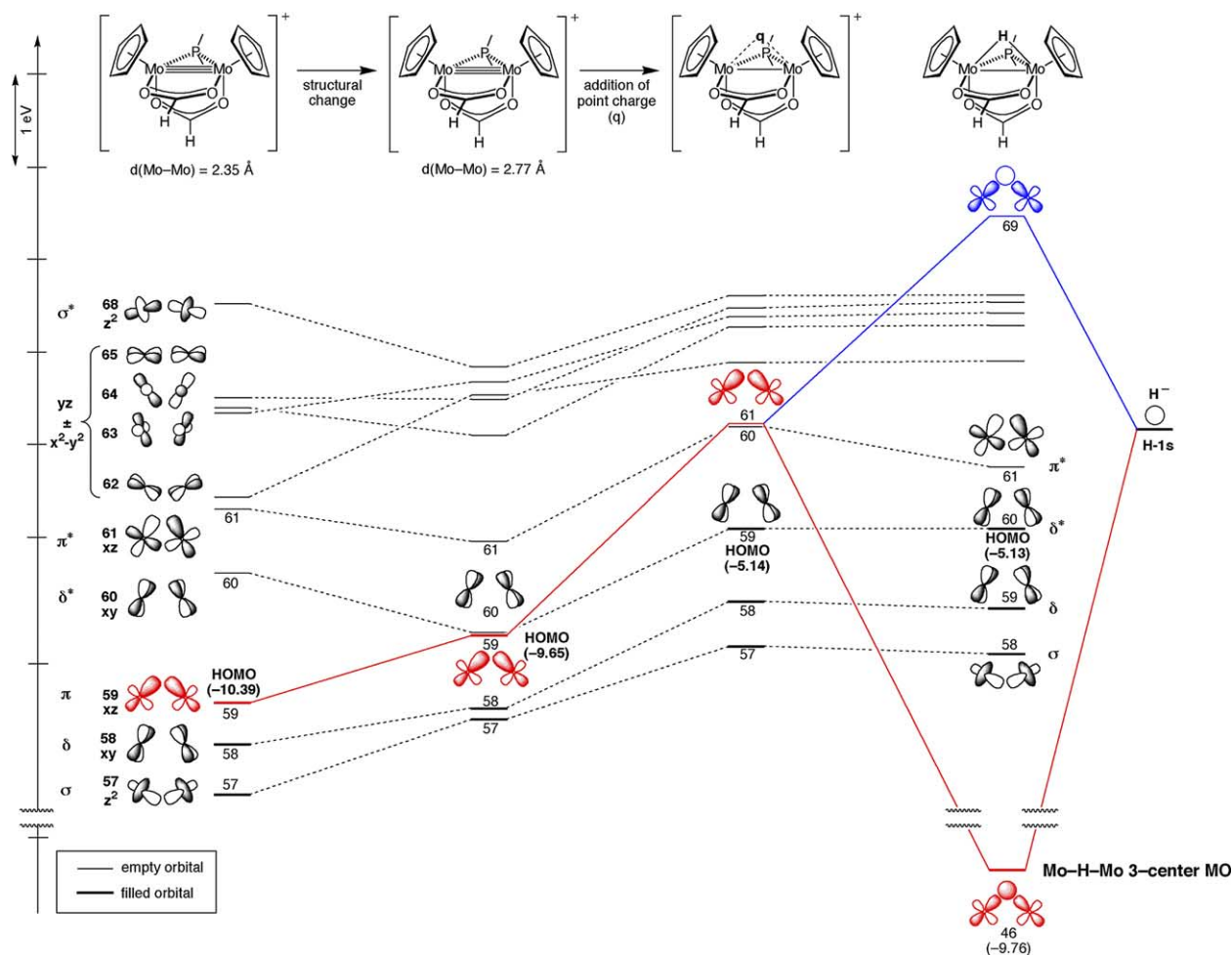
Fig. 15. MO diagram for [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) derived from {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ and H⁻ fragments, highlighting the variation in orbital energies of the {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ fragment resulting from: (i) the change in structure to that of [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H) and (ii) the Coulombic response to the negative charge of the hydride ligand.

almost degenerate with its LUMO (δ*). Upon addition of the negative point charge at the hydride site, all the MOs of the {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ fragment are raised in energy, but especially so for the π HOMO because the shape of this orbital causes it to be fully exposed to the negative charge. As a consequence, the π orbital becomes higher in energy than δ* orbital, such that the latter becomes the HOMO of the hypothetical {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ fragment. The σ²(δ)²-(δ*)² configuration thus predicts a formal Mo–Mo single bond for the {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ fragment with a point charge at the vacant hydride site. The subsequent interaction of this fragment with the 1s orbital of the hydride ligand is primarily with the Mo–Mo π orbital, which is empty as the result of the structural distortion and the presence of the Coulombic potential; this interaction corresponds to the Mo–H–Mo 3-center-2-electron bond, thereby resulting in a σ²(δ)²(δ*)² configuration for [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-H), i.e. a single bond between the two molybdenum centers. As would be expected, the empty π orbital of the

{[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁺ fragment with a negative point charge (q) at the site to be occupied by the hydride ligand corresponds closely to the filled π* orbital of the anionic {[CpMo(μ-O₂CH)]₂(μ-PH₂)}⁻ fragment that interacts with H⁺ (Figs. 11 and 13).

The MO diagram for the chloride derivative [CpMo(μ-O₂CH)]₂(μ-PH₂)(μ-Cl) is illustrated in Fig. 16. Significantly, the σ²(δ)²(δ*)² configuration indicates the presence of a Mo–Mo single bond that is formally identical to that of the hydride derivative. Indeed, comparison of the isosurface plots of the most important MOs of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me), [CpMo-(μ-O₂CH)]₂(μ-PH₂)(μ-H) and [CpMo(μ-O₂CH)]₂(μ-PH₂)-(μ-Cl) (Fig. 14) indicates that the frontier orbital signatures of these complexes are essentially identical. Thus, even though the slight asymmetry of the bridging mode of the methyl ligand and the presence of high-energy p-orbitals on the chloride ligand give rise to small changes in the shapes of these frontier orbitals, these effects do not have a significant consequence for the qualitative classification of the Mo–Mo interactions.
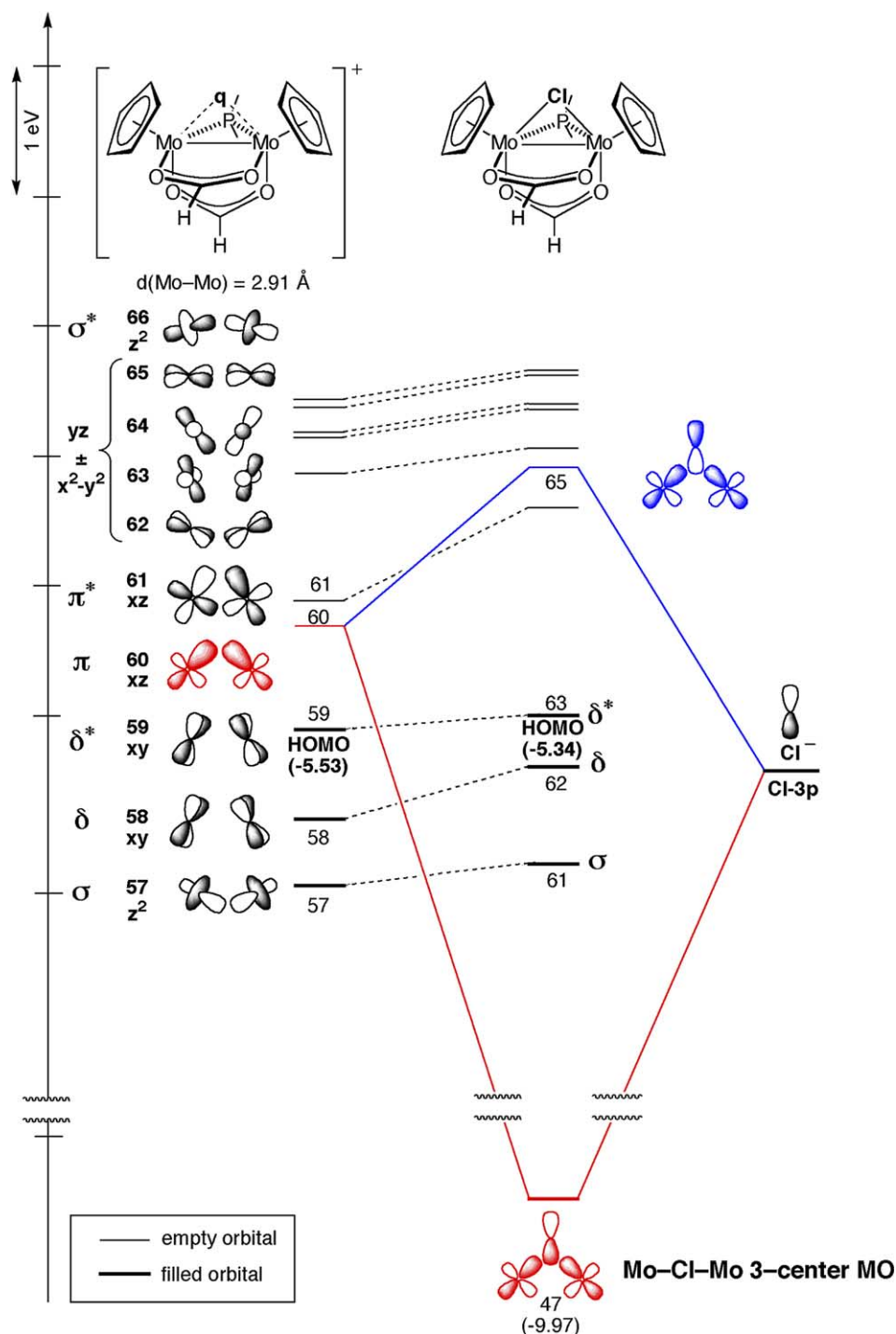
Fig. 16. MO diagram for $[CpMo(\mu-O_2CH)]_2(\mu-PH_2)(\mu-Cl)$ derived from $\{[CpMo(\mu-O_2CH)]_2(\mu-PH_2)\}^+$ and Cl^- fragments; the orbital energies for $\{[CpMo(\mu-O_2CH)]_2(\mu-PH_2)\}^+$ correspond to the geometry in $[CpMo(\mu-O_2CH)]_2(\mu-PH_2)(\mu-Cl)$ and incorporate the Coulombic response to the negative charge of the chloride ligand.

2.6. Comparison of computed bond orders with those predicted by electron counting methods

Examination of the data in Table 2 indicates that there is qualitative agreement between the computed Wiberg and Mayer bond orders and the bond orders derived by consideration of the molecular orbital electronic configurations. It is also evident that, of the two methods for electron counting, there is a much better correspondence between calculated bond order and the μ-LX "half-arrow" method, i.e. the method that explicitly takes into account the 3-center-2-electron nature of

the interaction involving bridging hydrogen and alkyl groups. For example, while the $\sigma^2(\delta)^2(\delta^*)^2$ configuration of both [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-H) and [CpMo(μ-O$_2$CH)]$_2$(μ-PH$_2$)(μ-Cl) indicates a Mo–Mo single bond, in accord with the formal single bonds predicted using the μ-LX "half-arrow" method, the formal bond orders derived by using the "half-electron" method differ, with the latter being predicted to have a Mo=Mo double bond rather than a Mo–Mo single bond. Thus, in cases where ambiguities arise in the prediction of the Mo–Mo bond orders by the two electron counting methods, the μ-LX "half-arrow" method provides results that are closer to the theoretically predicted values since it clearly differentiates between the 3-center-2-electron M–H–M interactions and direct 2-center-2-electron M–M interactions.

In addition to the results described here, other studies are also in accord with the μ-LX "half-arrow" representations of bridging hydride ligands. For example, whereas the "half-electron" method predicts an Os=Os double bond in Os$_3$(CO)$_{10}$(μ-H)$_2$ (Fig. 1A), the μ-LX "half-arrow" method predicts that there is no 2-center-2-electron Os–Os interaction (Fig. 1E and F). Both experimental and theoretical studies are more in accord with the latter description. For example, UV PES studies on Os$_3$(CO)$_{10}$(μ-H)$_2$ and related bridging hydride complexes have been interpreted with the M(μ-H)M bonding orbital as being localized principally on the hydrogen atom, rather than the metal atoms; [60,61] as such, it would seem inappropriate to describe the Os–Os interaction as that of a Os=Os double bond. Furthermore, MO calculations also indicate that the major interaction between the two osmium centers is via the two 3-center-2-electron Os–H–Os bonds [62,63]. The cyclopentadienyl compound [Cp*(CO)Os]$_2$(μ-H)$_2$ contains a similar [Os$_2$H$_2$] unit that has also been reported to have a Os=Os double bond; [64] by analogy to Os$_3$-(CO)$_{10}$(μ-H)$_2$, however, the direct 2-center-2-electron Os–Os bond order is reduced to zero upon consideration of the 3-center-2-electron nature of the Os–H–Os interactions.

{[(CO)$_5$M]$_2$(μ-H)}$^-$ (M=Cr, Mo, W) [13] provide a classic series of complexes with single 3-center-2-electron M–H–M interactions for which the "half-electron" method predicts a M–M single bond, whereas the μ-LX "half-arrow" method indicates that there is no 2-center-2-electron M–M interaction (Fig. 17); calculations on these complexes also indicate that there is no direct M–M bond and that the interactions are exclusively through the hydride bridge [65]. The closely related complex {[(CO)$_4$W(μ-H)]$_2$}$^{2-}$ [66], with two 3-center-2-electron W–H–W bridges, has also been investigated theoretically, and likewise demonstrates that there is effectively no direct W–W interaction, with the interactions being exclusively through the hydride bridge [67,68]. The results of the calculation are once again
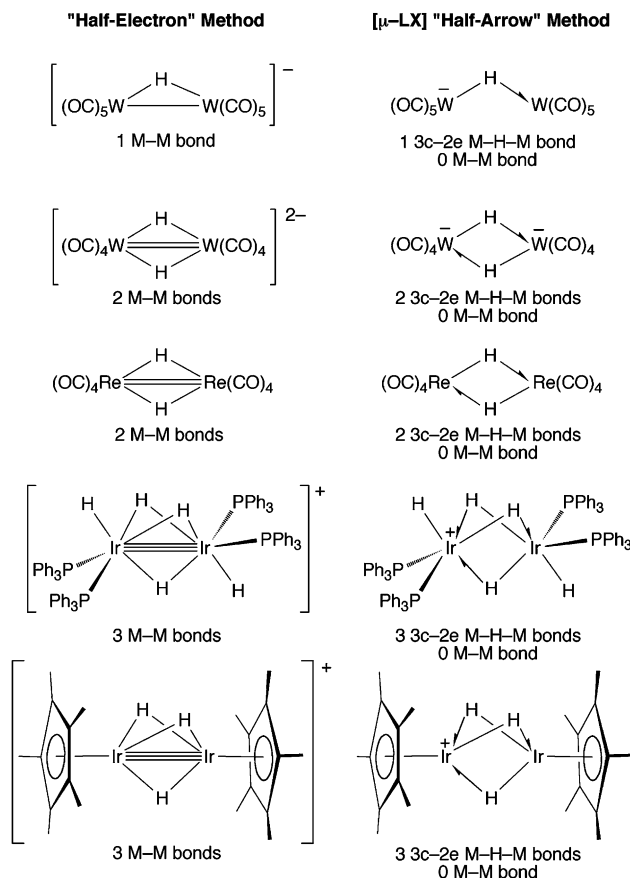

Fig. 17. Different descriptions of the metal–metal bond orders in some dinuclear complexes with bridging hydride ligands according to the electron counting method. The "half-electron" method does not explicitly take into account the 3-center-2-electron nature of the M–H–M interaction and thus results in a greater M–M bond order than would be predicted theoretically. In contrast, the [μ-LX] "half-arrow" method treats the 3-center-2-electron nature of the M–H–M interactions explicitly and thereby predicts a M–M bond order which is in accord with theory.

more in accord with the μ-LX "half-arrow" electron counting method that predicts no 2-center-2-electron W–W interaction, compared to the double bond predicted by the "half-electron" method (Fig. 17). Calculations also indicate that the isostructural neutral rhenium analogue [(CO)$_4$Re(μ-H)]$_2$ [8] is predicted to have effectively no direct Re–Re interaction [67].

The dinuclear iridium complex {[(Ph$_3$P)$_2$HIr]$_2$(μ-H)$_3$}$^+$ with three bridging hydride ligands was originally described as possessing a direct Ir≡Ir triple bond to satisfy the 18-electron rule [69]. However, upon recognizing the 3-center-2-electron nature of the interaction it was later realized that there is no direct Ir···Ir interaction and the shortness of the Ir···Ir separation is a geometric consequence of having three bridging hydrogen atoms [70,71] The cyclopentadienyl analogue {[Cp*Ir]$_2$(μ-H)$_3$}$^+$ was likewise originally reported to possess an Ir≡Ir triple bond [72], but by analogy to {[(Ph$_3$P)$_2$HIr]$_2$-(μ-H)$_3$}$^+$ can be viewed as possessing no direct Ir–Ir

bond. Structurally related isoelectronic complexes with three bridging hydride ligands that face the same bonding ambiguity description include $\{[(CO)_3Re]_2(\mu\text{-}H)_3\}^-$ [73] and $\{[\{MeC(CH_2PPh_2)_3\}Fe]_2(\mu\text{-}H)_3\}^+$ [74]. Interestingly, while the iron complex was reported to have a Fe≡Fe triple bond, the rhenium complex $\{[(CO)_3Re]_2(\mu\text{-}H)_3\}^-$ was *not* described as possessing a Re≡Re triple bond, but rather described as having 3-center-2-electron Re–H–Re bonds. Hoffmann [75] has analyzed the general class of $[LM]_2(\mu\text{-}H)_3$ molecules theoretically in terms of 3-center-2-electron interactions.

It is important to note that situations arise where the μ-LX "half–arrow" method does *not* predict an 18-electron configuration for both metals in a dinuclear complex with bridging hydrogen atoms. For example, the "half–arrow" method predicts that each of the metal centers in $[Cp^*Re(CO)_2]_2(\mu\text{-}H)_2$, $\{[\{MeC(CH_2AsPh_2)_3\}Co]_2(\mu\text{-}H)_3\}^+$, $[Cp^*Ru]_2(\mu\text{-}H)_4$, and $[(Et_2PhP)_2Re(H)_2]_2(\mu\text{-}H)_4$ would possess a 20-electron configuration (Fig. 18) [76]. However, rather than being a failure of the method, the

prediction of a 20-electron configuration is actually a strength of the method since it indicates that the HOMO is an *antibonding* orbital. Occupation of this antibonding orbital thus weakens the bonding interaction that derives from the M–H–M 3-center-2-electron interactions, a notion that has been discussed by Hoffmann and co-workers [77], Dahl [15], and Bursten [78]. As an illustration, consider the hypothetical protonation of a dinuclear system in which there is no formal 2-center-2-electron M–M bond because both bonding and antibonding components are occupied (Fig. 19). The hydrogen 1s orbital interacts specifically with the bonding component, thereby forming the 3-center-2-electron bond. Since the M–M bonding orbital is effectively converted to the M–H–M 3-center-2-electron bond, the pair of electrons that remains in the M–M antibonding orbital constitutes an "antibond". Whereas a bond is conventionally represented by a line between two atoms, an antibond may be depicted by using a crossed-dashed M–×–M representation in which the cross is intended to emphasize that the direct interaction is *antibonding*. Despite the presence of an "antibond", the overall interaction between the two metal centers is favorable because of the stabilization resulting from the formation of the 3-center-2-electron bond. For example, Casey has described the bonding of the $[Re_2H_2]$ unit of $[Cp^*Re(CO)_2]_2(\mu\text{-}H)_2$ as being composed of two 3-center-2-electron Re–H–Re bonds and a Re–×–Re "antibond", such that there is a *net* bond order of one between the two rhenium centers [79].

Another illustration is provided by the tetrahydride bridged ruthenium complex $[Cp^*Ru]_2(\mu\text{-}H)_4$ which, on the basis of electron counting according to the "half-electron" method, was proposed to have a Ru≡Ru triple bond [80,81]. However, calculations by Morokuma indicate that the direct Ru–Ru interaction is *repulsive*, and that the two ruthenium centers are only held together by the 3-center-2-electron Ru–H–Ru bonds [82,83]. Again, the μ-LX "half-arrow" method predicts a 20-electron configuration for each ruthenium, thereby correctly suggesting that the direct Ru–Ru interaction is antibonding. An Fe≡Fe triple bond has also been considered as a possibility for the iron counterpart $[Cp^*Fe]_2(\mu\text{-}H)_4$, but has been recognized to be erroneous on the basis of the theoretical study on the ruthenium analogue [84].

$[(Et_2PhP)_2Re(H)_2]_2(\mu\text{-}H)_4$ belongs to the same category of complex that was described as possessing a formal Re≡Re triple bond [85], but the μ-LX "half-arrow" notation would indicate a Re–×–Re antibonding interaction (Fig. 18), which is also in accord with the $\sigma^2(\delta^*)^2(\sigma^*)^2$ electronic configuration that has been calculated for $[(H_3P)_2Re(H)_2]_2(\mu\text{-}H)_4$ [77]. Likewise, the cobalt complex $\{[\{MeC(CH_2AsPh_2)_3\}Co]_2(\mu\text{-}H)_3\}^+$ was proposed to have a double Co=Co bond [74], but is now recognized to have Co–×–Co antibonding interaction (Fig. 18) [77].

"Half-Electron" Method

1 M–M bond

2 M–M bonds
$L_3 = MeC(CH_2PAsPh_2)_3$

3 M–M bonds

3 M–M bonds

[μ–LX] "Half-Arrow" Method

2 3c–2e M–H–M bonds
1 M---M antibond

3 3c–2e M–H–M bonds
1 M---M antibond

4 3c–2e M–H–M bonds
1 M---M antibond

4 3c–2e M–H–M bonds
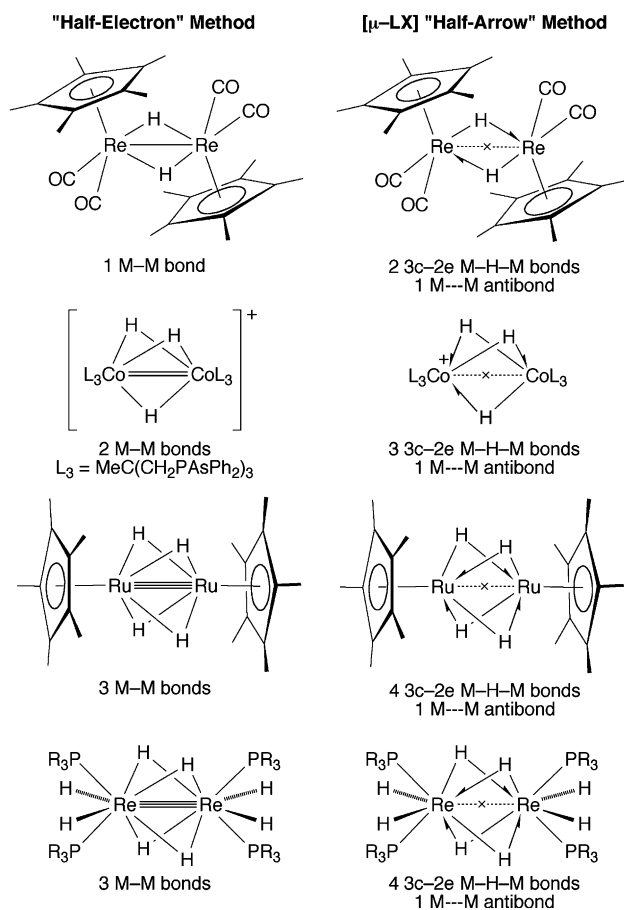1 M---M antibond

Fig. 18. Examples of compounds that exhibit M–×–M antibonding interactions resulting from a 20-electron configuration that places a pair of electrons in a M–M antibonding orbital. In contrast, the formula employing the "half-electron" method defines each metal center as possessing an 18-electron configuration and so the true nature of the M–M interaction is not evident.
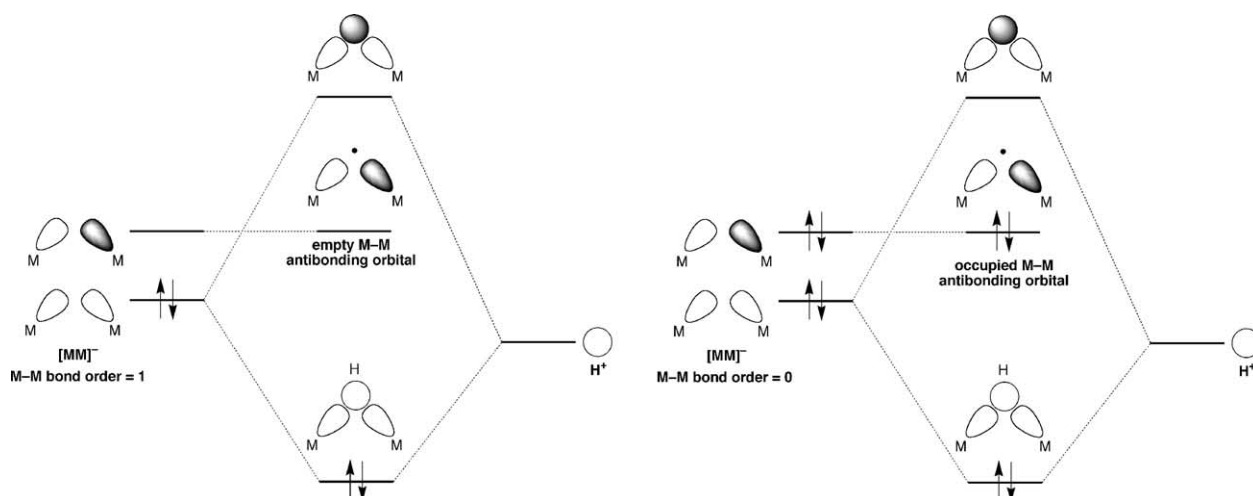
Fig. 19. Molecular orbital description of a M–×–M antibonding interaction in a [MHM] species derived by interaction of $[M_2]^-$ and H^+ fragments in which each atom uses a single orbital. Protonation of the $[M_2]^-$ fragment results in the interaction of the H 1s orbital with the M–M bonding orbital, thereby forming the 3-center-2-electron M–H–M bonding and antibonding orbitals. The M–M antibonding orbital does not have the appropriate symmetry to interact with the H 1s orbital and thus remains M–H nonbonding. If the $[M_2]^-$ fragment possesses two electrons only the M–M bonding orbital is occupied and there is a M–M bond order of one; upon protonation these electrons occupy the 3-center-2-electron M–H–M bonding orbital and the direct M–M bond is eradicated. A similar situation arises for a $[M_2]^-$ fragment that possesses four electrons such that both the M–M bonding and antibonding orbitals are occupied and the M–M bond order is zero; however, in this case, a pair of electrons remains in the M–M antibonding orbital after protonation so that the direct M–M interaction becomes repulsive, i.e. an *antibond*.

Consideration of the above complexes with bridging hydrogen ligands demonstrates that for every 3-center-2-electron M–H–M interaction, the "half-electron" method over counts the M–M bond order by one from the value predicted by the µ-LX "half-arrow" method. At one level, this is not really an issue once it is recognized that the M–M bond orders derived by the two different electron counting methods are merely *formalisms* and, as such, do not necessarily reflect reality. Problems of this type are commonplace in chemistry. For example, the formal charge [86] on an atom does not necessarily bear any relationship to the actual charge, viz. the formal charge on nitrogen in NH_4^+ is +1, whereas the actual charge is *negative* [87,88]. At another level, the derivation of different M–M bond orders for the same compound is an issue because, from a pedagogical point of view, it causes confusion (as aptly demonstrated by the various descriptions of $Os_3(CO)_{10}(\mu\text{-}H_2)$ shown in Fig. 1). Recognizing that both methods are formalisms, it is more appropriate to adopt the formalism that approximates more closely to the bond orders that are derived theoretically. For all of the examples discussed above, the µ-LX "half-arrow" electron counting method provides the best description of the bonding by clearly distinguishing between the number of 3-center-2-electron M–H–M interactions and direct 2-center-2-electron M–M interactions.

Two additional examples serve to point out the inadequacies of electron counting using the "half-electron" method. Firstly, the "half-electron" method would predict a Zr=Zr double bond in dinuclear $[Cp_2Zr(H)]_2(\mu\text{-}$

$H)_2$ [89] whereas the µ-LX "half-arrow" method indicates that each Zr center can attain an 18-electron configuration without forming two 2-center-2-electron Zr–Zr bonds. The latter description is clearly preferable because the Zr center of mononuclear Cp_2ZrH_2 is d^0 and, as such, is incapable of forming a 2-center-2-electron Zr–Zr bond with the Zr center of another molecule. Secondly, the metal–metal bond order predicted by the "half-electron" method is *independent* of whether or not the hydrogen atoms bridge the two metals. As an illustration, the three isomers of $[CpReH_3]_2$ with: (i) no bridging hydrogens, $[CpReH_3]_2$, (ii) two bridging hydrogens, $[CpReH_2]_2(\mu\text{-}H)_2$ and (iii) four bridging hydrogens, $[CpReH]_2(\mu\text{-}H)_4$ are each predicted by the "half-electron" method to have Re≡Re triple bonds (Fig. 20) [78]. The notion that the Re–Re bond order is not influenced by whether or not the hydrogen atoms bridge is far from intuitive. In contrast, the µ-LX "half-arrow" method for counting electrons predicts that the Re–Re bond order decreases from a triple bond in $[CpReH_3]_2$ to a single bond in $[CpReH_2]_2(\mu\text{-}H)_2$, and to an "antibond" in $[CpReH_2]_2(\mu\text{-}H)_2$ (Fig. 20). Indeed, calculations by Bursten [78] are in accord with the changes predicted by the µ-LX "half-arrow" method. Thus, focusing on the metal-based orbitals: (i) the $\sigma^2(\pi)^4$ electronic configuration for $[CpReH_3]_2$ indicates a direct Re≡Re triple bond, (ii) the $(\sigma/\delta)^2(\pi)^2(\delta^*)^2$ configuration of $[CpReH_2]_2(\mu\text{-}H)_2$ indicates a direct Re–Re single bond, and (iii) the $(\sigma/\delta)^2(\delta^*)^2(\delta^*)^2$ configuration of $[CpReH]_2(\mu\text{-}H)_4$ indicates a direct Re–×–Re antibonding interaction [78].
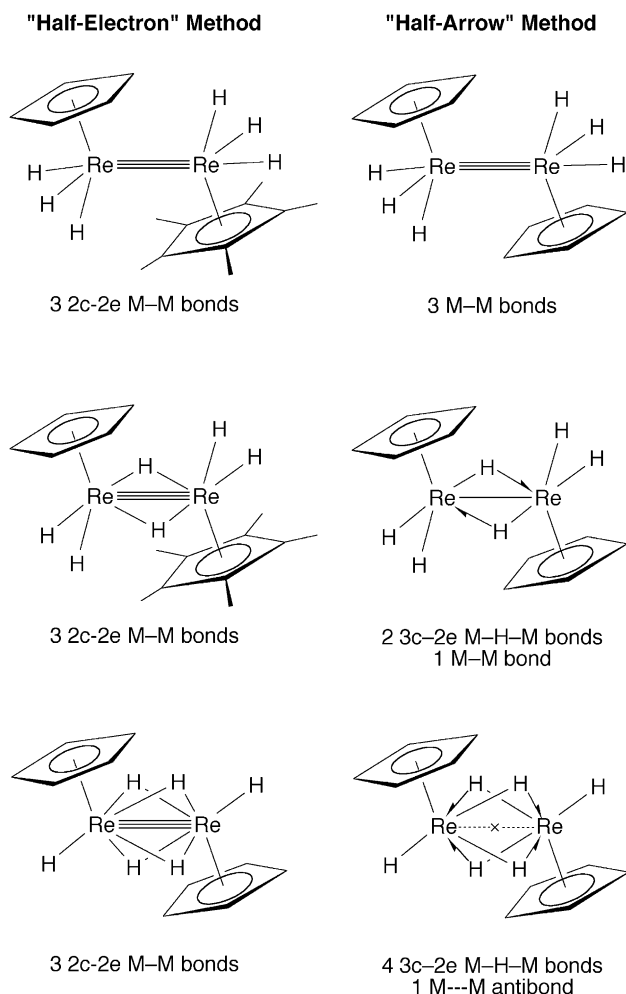
"Half-Electron" Method   **"Half-Arrow" Method**

3 2c-2e M–M bonds   3 M–M bonds

3 2c-2e M–M bonds   2 3c–2e M–H–M bonds
                            1 M–M bond

3 2c-2e M–M bonds   4 3c–2e M–H–M bonds
                            1 M---M antibond

Fig. 20. Three postulated isomeric rhenium hydride complexes for which formal Re≡Re triple bonds were invoked to satisfy the 18-electron rule (left hand side); the corresponding description of their bonding in terms of 3-center-2-electron bonds and direct Re–Re bonds (right hand side).

Why does the "half-electron" method predict the same bond order for the above rhenium complexes regardless of whether or not the hydrogen atoms bridge? This counter-intuitive result is, in essence, a consequence of the "half-electron" method assigning the same number of electrons to bridging and terminal hydride ligands [7]. As such the "half-electron" method fails to address properly the 3-center-2-electron nature of the [M–H–M] bridge.

Hoffmann has aptly concluded that for complexes with 3-center-2-electron bonds "it is best not to argue over whether there is or is not metal–metal bonding in these molecules. The orbitals in question are delocalized and are used to bond a metal atom *both* to its metal partner and to the bridging group" [75]. It is, however, important to emphasize that: (i) the "direct" M···M component for a 3-center-2-electron interaction cannot be viewed as equivalent to that of a normal 2-center-2-

electron M–M bond [90], and (ii) there may be additional direct M···M interactions that do not have a significant component from the bridging ligands. These issues are not addressed by the "half-electron" method for counting electrons which merely applies a formula to predict the M–M bond order [7], a formula that does not even require knowledge of the structure of the molecules since the same result is obtained regardless of whether or not the hydrogen atoms bridge. In contrast, the μ-LX "half-arrow" method of counting electrons requires one to draw the structure of the molecule prior to determining the electron count at a metal center from which the M–M bond order is inferred. The μ-LX "half-arrow" method thus provides a more complete picture of the bonding by clearly distinguishing between: (i) the number of 3-center-2-electron M–H–M interactions and (ii) the number of direct 2-center-2-electron M–M interactions. Furthermore, by not forcing an 18-electron count on a metal center (which is *explicitly* forced by the formula employed by the "half-electron" method [7]), the μ-LX "half-arrow" method has the advantage of providing an indication of whether or not a M–M antibonding interaction exists.

One of the significant features of separating the bonding into 3-center-2-electron M–H–M interactions and 2-center-2-electron M–M interactions is that it provides a greater understanding of the bonding. In fact, these two interactions may be viewed as the "*s*" and "*y*" counterparts in Lipscomb's *styx* nomenclature, [91] that has found much use in evaluating the topological structures of boranes [92], and which has also been extended to the structures of metal-hydride clusters [60b].

3. Computational details

All calculations were carried out using density functional theory as implemented in the Jaguar 4.1 suite [93] of quantum chemistry programs, Amsterdam Density Functional 2000.02 package (ADF) [94] and DMOL3 version 2.1 [95,96]. Geometries were optimized using Jaguar and the B3LYP [97] functional with the 6-31G** basis set. Molybdenum was represented using the Los Alamos LACVP** basis [98] that includes relativistic effective core potentials. Vibrational frequency calculation results based on analytical second derivatives at the B3LYP/6-31G** level of theory were used to confirm proper convergence to local minima. Owing to computational cost vibrational frequencies for $[Cp*Mo(\mu-O_2CMe)]_2(\mu-PMe_2)(\mu-Me)$ and $\{[Cp*Mo(\mu-O_2CMe)]_2(\mu-PMe_2)(\mu-Me)\}^{2+}$ were not computed. Additional single point calculations on the Jaguar-optimized structures were carried out using ADF to obtain fragment wavefunctions that were helpful for constructing the MO-diagrams. In these calculations, a double-ζ STO basis set was utilized, with one set of polarization

functions as provided in the ADF package (Basis Set III – frozen core), together with the BLYP functional. Relativistic effects on Mo are included using the "zeroth-order regular approximation" (ZORA) [99]. Mayer bond order [56,57] calculations were carried out using DMOL3 [95,97] and the Jaguar-optimized geometries. The BLYP functional was used in combination with the DNP basis set, which corresponds to the 6-31G** basis. Note that the B3LYP functional is not available in "pure DFT" packages, such as ADF and DMOL. Some of the calculations presented above incorporate a point charge placed at appropriate coordinates in space to mimic the electrostatic effect of bridging ligand moieties on the orbitals of the dinuclear metal fragment. In these calculations, the Coulombic potential generated by the point charge in space is included natively in the self-consistent field procedure as implemented in ADF [100].

4. Conclusions

DFT calculations on dinuclear molybdenum complexes with bridging hydride and methyl ligands, namely $[CpMo(\mu\text{-}O_2CH)]_2(\mu\text{-}PH_2)(\mu\text{-}H)$ and $[Cp^*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$, indicate that the bonding is best described in terms of: (i) a 2-center-2-electron Mo–Mo single bond and (ii) a 3-center-2-electron Mo–H–Mo or Mo–Me–Mo bond. The presence of a 2-center-2-electron Mo–Mo single bond is in accord with the prediction of the "half-arrow" electron counting method that views the bridging hydride and methyl ligands as μ-LX ligands. In contrast, the "half-electron" counting procedure, which apportions half of the valence electron of the hydrogen atom or methyl radical to each metal, predicts a Mo=Mo double bond, a result that is contrary to the theoretical calculations. Consideration of the structures of a variety of other bridging hydride complexes indicates that the "half-arrow" electron counting method provides the best general description of the bonding by clearly distinguishing between the number of 3-center-2-electron M–H–M interactions and direct 2-center-2-electron M–M interactions. Several simple examples serve to highlight the failings of the "half-electron" method, namely:

1. The "half-electron" counting procedure predicts a Zr=Zr double bond for $[Cp_2Zr(H)]_2(\mu\text{-}H)_2$. A Zr=Zr double bond is clearly implausible because the Zr center of each Cp_2ZrH_2 fragment is d^0 and is thereby *incapable* of forming a 2-center-2-electron Zr–Zr bond with a second fragment. In contrast, the μ-LX "half-arrow" method predicts that there is no direct Zr–Zr bond in $[Cp_2Zr(H)]_2(\mu\text{-}H)_2$.
2. The M–M bond order predicted by the "half-electron" method is *independent* of whether or not the hydrogen atoms bridge the two metals. As an illustra-

tion of this counter-intuitive prediction, the three isomers of $[CpReH_3]_2$ with: (i) no bridging hydrogens, $[CpReH_3]_2$, (ii) two bridging hydrogens, $[CpReH_2]_2(\mu\text{-}H)_2$ and (iii) four bridging hydrogens, $[CpReH]_2(\mu\text{-}H)_4$ are each predicted to have Re≡Re triple bonds by the "half-electron" method. Calculations by Bursten, however, demonstrate that the Re–Re bond orders do indeed vary with the number of bridging hydrogens, in a manner as predicted exactly by the "half-arrow" method.
3. The M–M bond order that is determined by the "half-electron" method is derived by forcing the metal centers to have an 18-electron configuration. In contrast, the M–M bond order derived by the μ-LX "half-arrow" electron counting method does not enforce such a restriction. For example, the μ-LX "half-arrow" electron counting method predicts $[Cp^*Ru]_2(\mu\text{-}H)_4$ to have a 20-electron configuration for each ruthenium. The 20-electron configuration indicates that the HOMO is a Ru–×–Ru *antibonding* orbital which reduces the overall bonding associated with the four Ru–H–Ru 3-center-2-electron interactions. This prediction is in full accord with a theoretical study by Morokuma which indicates that the direct Ru–Ru interaction is *repulsive*, a result that is in marked contrast to the Ru≡Ru triple bond predicted by the "half-electron" method.

In conclusion, the "half-arrow" method is the procedure of choice for counting electrons for complexes that possess 3-center-2-electron M–×–M interactions. In all cases evaluated, the "half-arrow" method provides results that are much more in accord with theoretical calculations than those obtained by the "half-electron" method.

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