Density Functional Studies of $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$, $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}PMe_2)]^-$ and $[\{Mo(\eta^5\text{-}Cp)(CO)_3\}_2]$: Do the Metal–Metal Bonds Exist?

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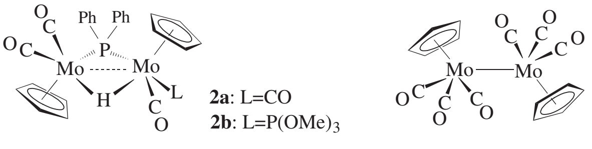
Computational methods employing the Kohn–Sham description of density functional theory with the hybrid B3LYP-DFT means were used to investigate the nature of the metal–metal interactions of $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$ **1** and its deprotonated form, $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}PMe_2)]^-$ **4** as well as a dimeric compound, $[\{Mo(\eta^5\text{-}Cp)(CO)_3\}_2]$ **3**. Both the Boys localization procedures as well as NBO analysis were performed to probe the character of the localized orbitals for all the three compounds. Consequently, a direct molybdenum–molybdenum bond was found in compound **3** and **4**. However, there is neither a direct metal–metal bond found in **1** at its singlet ground state nor any unpaired electron around each metal center.

The past few decades has witnessed the rapid development and extensive applications of transition metal complexes in metal-promoted reactions in the area of known and brand new types of organic reactions.[1] A comprehensive knowledge of the structure and bonding in each particular transition metal complex is indispensable for a successful catalytic reaction. Unfortunately, crystal structure determination of a target compound by means of X-ray or even neutron diffraction method does not always lead to an unambiguous conclusion inside the chemical bonding of its comprised atoms. A theoretic approach such as computational quantum calculations is generally regarded as a promising complementary tool to the previously existing methods.[2] Thanks to the rapid progress in computing power and ready-to-use software packages, ab initio calculations for transition metal complexes are no longer an affectionate dream for organometallic chemists.[3] As a result, many efforts have been devoted to the development of reliable computational methods for transition metal complexes. Lately, the density functional theory method with greater computational efficiency has been applied extensively to transition metal complexes and has gained wider and wider acceptance among the experimental chemists.[4]

The preparation of an unexpected phosphido- and hydrido-bridged dimetallic complex **1**, $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$ was first reported by Hayter[5] (Scheme 1). Subsequently, its crystal structure was determined by Dahl.[6] On account of the structural ambiguity caused by the conventional X-ray diffraction method, the position of the bridged-hydride on **1** was not located beyond doubt until the neutron diffraction studies reported by Williams et al.[7] Moreover, it was found that the distance between two metal centers is 3.267 Å, which is close to the maximum limit of all reported Mo–Mo single bonds.[8] For that reason, the existence of a Mo–Mo bond in **1** is doubtful.[9]

A closely related compound, $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ **2a**, was prepared through the direct reaction of $[\{Mo(\eta^5\text{-}Cp)(CO)_3\}_2]$ **3** with diphenylphosphine.[10] Further, the replacement of its one of the carbonyls by a $P(OMe)_3$ ligand gave $[Mo_2(\eta^5\text{-}Cp)_2(CO)_3\{P(OMe)_3\}(\mu\text{-}H)(\mu\text{-}PPh_2)]$ **2b** (Chart 1). The structural pattern for **2b** was similar to that in **1**. The distance between the two metal centers is 3.254 Å.

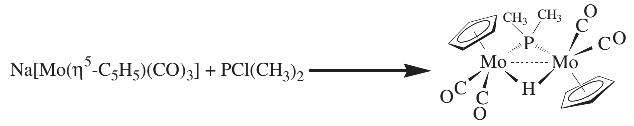
To account for the bonding of the metal centers in transition metal complexes, Sidgwick extended the octet rule of Lewis to an *18-electron rule*, a special case of the more generalized EAN (Effective Atomic Number) rule.[11] It states that when the complex reaches its most favorable stability the valence shell of metal achieves the $ns^2(n-1)d^{10}np^6$ configuration. By this principle, compound **1** does obey the EAN rule, but only when the direct metal–metal bond exists (Scheme 2). Nevertheless,



2a: L=CO
2b: L=P(OMe)$_3$

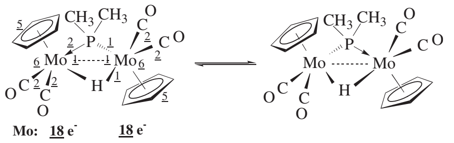
3

Chart 1.



1

Scheme 1.



Scheme 2. Two resonance forms of **1**: Neutral atom electron count numbers are underlined.

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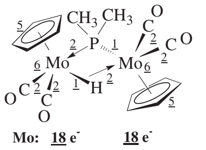


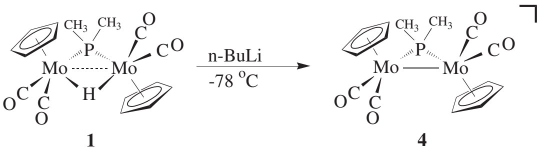
Chart 2.

the existence of a direct metal–metal bond is controversial because of the phenomenally long distance between the two metal ions.

According to the EAN rule, for the removal of the possibility of a direct metal–metal bond in **1** or **2**, both the two metal centers are assumed as having 17 valence electrons with one unpaired electron on each metal center. Alternatively, two metal centers can be regarded as one having 16 and the other 18 electrons, respectively, without unpaired electron in each metal center. The latter view is favored in terms of eliminating active unpaired electrons. On the other hand, inclusion of a direct metal–metal bond is necessary for both the metal centers either in **1** or **2** to obey the EAN rule, which is considered to be the best arrangement. Nevertheless, as stated above, the assertion of a direct metal–metal bond in **1** (or **2**) remains to be validated because of the unusually long distance between two metal centers.[7,12] Alternatively, Crabtree cleverly described the bonding of the complex by importing the concept of σ-bond 2e$^-$ donation, which is donated from the Mo–H bond to the other Mo center[13] (Chart 2). In this way, it is no need for the existence of a metal–metal bond, while at the same time it avoids the violation of the EAN rule. The noble gas configurations for both Mo centers are achieved by adding up all the valence electrons contributed from all the relevant units. In a recent theoretical study of $[Cr_2(\mu\text{-}CO)(\mu\text{-}H)_2(CO)_8]$ complex,[14] Richardson et al. employed the same methodology in which no direct Cr–Cr bond was assumed and the noble gas configurations for both Cr centers are achieved through the donation of electrons from each σ-bond of the Cr–H.

It was reported that the deprotonation of **1** gave an anionic compound $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}PMe_2)]^-$ **4**[15] (Scheme 3). Apparently, a direct metal–metal bond is formed and each metal center obeys the EAN rule. A careful investigation found that the large structural changes in **4** versus **1** were caused by only a small difference in chemical formulas, these results provide us with valuable information about the bondings inside the molecules.

To our best knowledge, a thorough study by computational quantum methods of the nature of the metal–metal bonding in **1** has not been presented elsewhere. Therefore, it is of interest to explore the character of the metal–metal interaction in **1** by theoretical means. Molecular quantum calculations employing the density functional theory method at the RB3LYP level of theory have been proved to reproduce the best experimental results for transition metals. Hence this method is performed in the present study to provide the requisite information.[2c,4b]



Scheme 3.

Computational Methods

All the calculations were carried out using the GAUSSIAN 98 package.[16] The structural data of **1** and **3**, which were taken from the neutron diffraction and the X-ray diffraction studies, respectively, were previously deposited in the Cambridge Structure Database.[8i] The data from Cambridge Structure Database are retrieved as starting models in the present study.[7] All the geometry optimizations were performed within the Kohn–Sham description of density functional theory[17] with the hybrid B3LYP-DFT method and without symmetric restrictions. In this method, the Becke's three-parameter exchange functional[18] and the Lee–Yang–Parr's correlation functional[19] were used. The LANL2DZ, including the double-ζ basis set for the valence and outermost core orbitals combined with pseudopotential were used for Co.[20] The 6-311+G(d,p) basis set for the other atoms were denoted as 6311LAN. All of the stationary points found were characterized via harmonic vibrational analysis. The total energies for both singlet and triplet states of **1** employing UB3LYP/6311LAN//RB3LYP/6311LAN means are also calculated. Stability analysis[21] has been performed to determine the stability of Kohn–Sham solutions with respect to variations of break spin- and spatial symmetry of the restricted and unrestricted wavefunctions, respectively.

The Boys localization procedure[22] was performed to obtain the localized Kohn–Sham orbitals (LOs) from the occupied B3LYP/6311LAN Kohn–Sham molecular orbitals (MO) for the B3LYP/6311LAN geometries. The wavefunctions were analyzed with MOLDEN[23] to plot the electronic density contours. Natural charges, Wiberg bond indices[24] and natural bond orbitals for **1**, **3** and **4** were carried with NBO 5.0[25] at the RHF/3-21G**//RB3LYP/6-311LAN level.

Results and Discussion

Equilibrium Geometries of $[\{Mo(\eta^5\text{-}Cp)(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$ 1 and $[\{Mo(\eta^5\text{-}Cp)(CO)_3\}_2]$ 3. With the purpose of being more precise in interpreting the bonding in **1** and for the purpose of comparison, the optimized geometries of **1** and its related compound **3** were obtained through the calculations with the level of restricted B3LYP/6311LAN. The resulting geometric parameters of **1** are in rather good agreement with the neutron diffraction experiment except the bearable deviation of the metal-metal bond length (Table 1). There are several observations from the calculations which are noteworthy. (1) The largest deviation of the Mo1–Mo2 distance in the optimized structure (Fig. 1) is found to be slightly longer (ca. 0.091 Å). Similarly, the largest discrepancy also found at the Mo1–Mo2 bond in **3** is ca. 0.122 Å which is longer for the optimized structure (Fig. 2). These features show that the same tendency of slightly overestimated metal–metal bond lengths (or distances) is followed for both cases using the same level of theory. (2) The bond lengths between the unique hydride, H4 and molybdenum atoms are almost the same; they are 1.870 Å and 1.871 Å (optimized) respectively. In contrast, they are slightly different from experimental results, i.e. 1.851 Å and 1.869 Å respectively. Meanwhile, the bond lengths of Mo1–P3 and Mo2–P3 are 2.478 Å and 2.477 Å (optimized), respectively; they are

Table 1. Selected Bond Lengths (Å), Angles (°) and Dihedral Angle (°) for **1**

	expt[a)]	R-B3LYP
	Bond lengths (Å)	
Mo1–Mo2	3.267(2)	3.358
Mo1–H4	1.851(4)	1.870
Mo2–H4	1.869(4)	1.871
Mo1–P3	2.432(3)	2.478
Mo2–P3	2.411(3)	2.477
Mo1–CO[b)]	1.960	1.975
Mo2–CO[b)]	1.962	1.975
P3–C[c)]	1.831	1.853
Mo1–C21	2.299(3)	2.335
Mo2–C26	2.288(3)	2.334
CO[d)] of Mo1	1.155	1.157
CO[e)] of Mo2	1.151	1.157
	Bond angles (°)	
Mo1–H4–Mo2	122.9(2)	127.7
Mo1–P3–Mo2	84.8(1)	85.3
P3–Mo–H4[f)]	76.2	73.5
	Dihedral angle (°)	
Mo1–P3–Mo2–H4	−0.7	−0.3

a) Ref. 7; Average values of b) two Mo-COs; c) P3–C5 and P3–C6; d) C13–O14 and C15–O16; e) C17–O18 and C19–O20; f) P3–Mo1–H4 and P3–Mo2–H4.

2.432 Å and 2.411 Å from experimental results.

In the neutron diffraction studies of **1**, the authors drew attention to the fact that the thermal ellipsoid of H4 only provides a single minimum potential well; this is also true for the P3 atom. Consequently the four-atoms cores, $Mo_2(\mu\text{-H})(\mu\text{-P})$ are in a relatively rigid frame. This is also supported by the fact that almost equal distances from the bridging atoms to metals are obtained from the calculated optimized structure of **1**. The calculated dihedral angle of the butterfly-like four atoms core, $Mo_2(\mu\text{-H})(\mu\text{-P})$ is 0.3°. It indicates that these four atoms are almost coplanar. In the case of **3**, a C_2 symmetry can be found through the center of the two metals after reaching its equilibrium geometry. It is beyond doubt that there is a direct metal–metal bond between two metal centers and that each center contains an identical 17-electronic fragment, $(\eta^5\text{-Cp})Mo(CO)_3$ for obeying the EAN rule. It is worthy of noting that although the Mo1–Mo2 distances are alike in both compound **1** and **3**, the question that whether there is a direct metal–metal bond in **1** remains to be validated.

Equilibrium Geometry of $[\{Mo(\eta^5\text{-Cp})(CO)_2\}_2(\mu\text{-PMe}_2)]^-$ 4. For comparison, the processes of obtaining the optimized geometry of the anionic compound $[\{Mo(\eta^5\text{-Cp})(CO)_2\}_2(\mu\text{-PMe}_2)]^-$ **4** and the deprotonation form of **1** were pursued. Since the crystal data are not available for **4**, the initial guess for the input structure was simply taken as the bridging proton out of **1**.[27] The optimized structure of **4** shows shortening in metal–metal bond length, 3.278 Å (Fig. 3, Table 2). Moreover, both the bond lengths of Mo1–P3 and Mo2–P3 are 2.425 Å. A C_2 symmetry with a point bisecting the metal–metal bond center can be assigned for this compound. That a direct metal–metal bond exists between the two metal centers is without doubt and the EAN rule is obeyed for both metal centers.

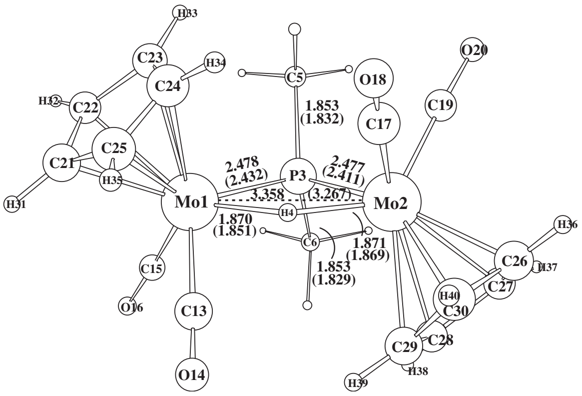


Fig. 1. Fully optimized structure of **1**: Geometric parameters were calculated at RB3LYP/6311LAN level of theory. Some selected bond lengths (in Å) are depicted. The values in parentheses are from neutron diffraction studies by Williams et al.[7]

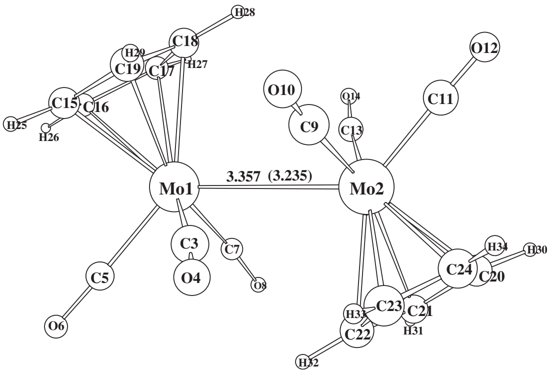


Fig. 2. Fully optimized structure of **3**: Geometric parameters were calculated at RB3LYP/6311LAN level of theory. Mo1–Mo2 bond length (in Å) is depicted. The value in the parenthesis is from X-ray studies by Cotton et al.[26]

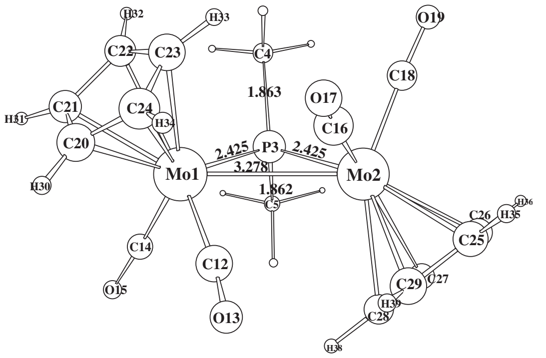


Fig. 3. Fully optimized structure of **4**: Geometric parameters were calculated at RB3LYP/6311LAN level of theory. Some selected bond lengths (in Å) are depicted.

The calculated total energies are the same for the singlet state of **1**; both RB3LYP/6311LAN//RB3LYP/6311LAN and UB3LYP/6311LAN//RB3LYP/6311LAN methods give the same result. The results indicate that there is no unpaired elec-

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **4**

	R-B3LYP
	Bond lengths (Å)
Mo1–Mo2	3.278
Mo1–P3	2.425
Mo2–P3	2.425
Mo1–CO[a]	1.951
Mo2–CO[a]	1.951
P3–C[b]	1.862
CO[c] of Mo1	1.171
CO[d] of Mo2	1.171
	Bond angles (°)
Mo1–P3–Mo2	85.0

Average values of a) two Mo–COs; b) P3–C5 and P3–C6; c) C12–O13 and C14–O15; d) C16–O17 and C18–O19.

tron around both the metal centers. Furthermore, the energy gap between singlet and triplet states (at UB3LYP/6311LAN//RB3LYP/6311LAN level) in **1** is found to be as high as 51.3 kcal/mol (the triplet state is higher in energy). The result is also ruling out the possibility of **1** being at the triplet ground state. Alternatively, the impossibility of **1** being with unpaired electrons can be derived from the symmetry viewpoint. The optimized geometries show that the idealized symmetry for **1**, **3**, and **4** are C_2 and these shall have no degenerate molecular orbital for all cases. Therefore, the even number of electrons in **1**, **3**, and **4** shall be paired in their ground states.

Analysis of Metal–Metal Interaction of Compound 1, 3 and 4 at the B3LYP/6311LAN Level. The MOs plots were providing us useful information concerning the bonding within the molecules. As shown in Fig. 4, the left column depicts the orbitals that are in the sequence of [LUMO], [HOMO], [HOMO-1], [HOMO-2], [HOMO-3] of **4** from top to bottom and the right column presents the corresponding orbitals for **1**.[28] It is clearly seen that there is a strong interaction between two metals in [HOMO-2] or [HOMO-3] of **4**. Nevertheless, there is no matching orbital with such character observed in **1**. Rather, a strong interaction of Mo1–H4–Mo2 and Mo1–P3–Mo2 is clearly seen in [HOMO-9] in **1**, as shown in Fig. 5. A similar conclusion was obtained by Koga and Morokuma in an ab initio study of CpRu(μ-H)$_4$RuCp complex.[29] They deduced that there is no direct Ru–Ru bond existed even though a metal–metal triple bond is required for both metal centers to follow the EAN rule.

Although viewing the orbitals in the delocalized means is regarded as more accurate way, representations of certain particular interested molecular orbitals by the localized methods are still receive great interest in many conventional aspects of chemistry.[20,30] Here, Boys localized Kohn–Sham orbitals (LMOs) procedures were employed to examine the characteristics of the bonding in **1**, **3** and **4**, particularly surrounding the four atoms core, Mo$_2$(μ-H)(μ-P) (Table 3).

As depicted in Fig. 6, there exists a direct bond between two metals in **3**; this is in accord with the generally believed assertion from the crystal data. Orbital interactions between two metal centers are essentially from their dσ orbitals. The Wiberg bond index shows that its bond order is 0.328. On the contrary,

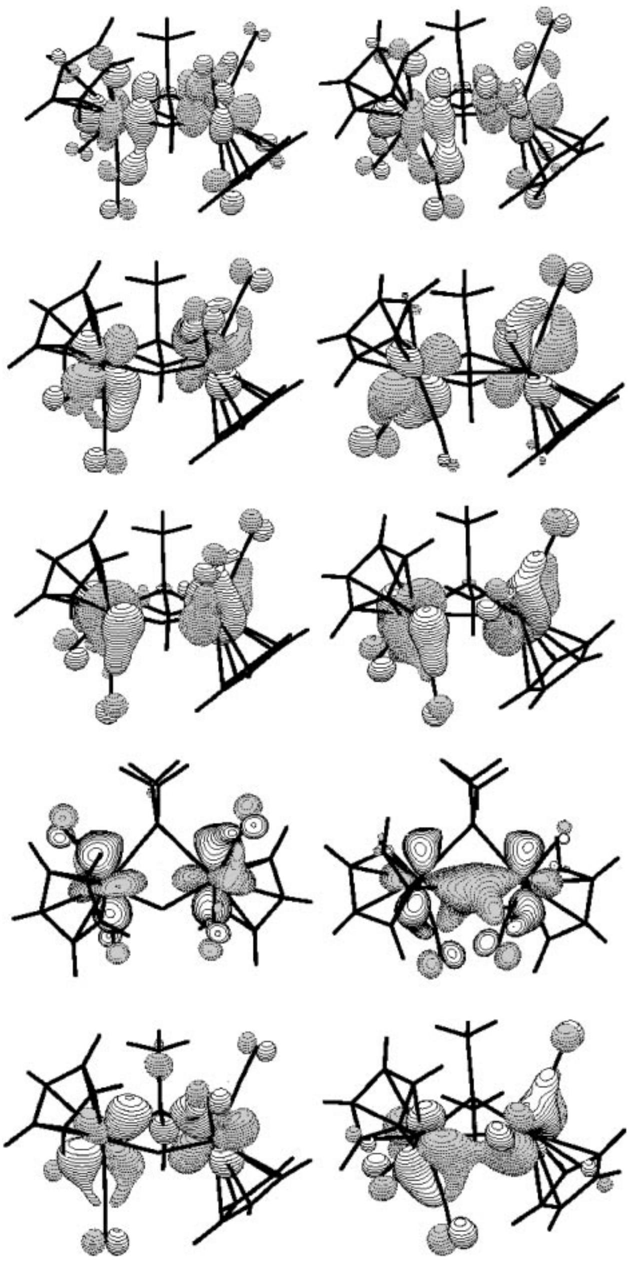


Fig. 4. Molecular orbital representations for the five selected frontier orbitals (Left: **1**; Right: **4**). From top to bottom: LUMO, HOMO, HOMO-1, HOMO-2, and HOMO-3.

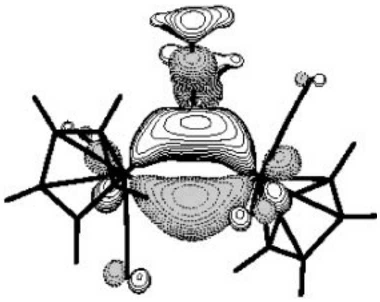


Fig. 5. [HOMO-9] MOs plotting of **1**: The orbital energy is −204.595 kcal/mol.

Table 3. NBO Analysis of Compound **1**, **3**, and **4** at the RB3LYP/3-21G**//B3LYP/6311LAN Level of Theory

Bond orbital	Cpd	Atom	Occup	% Mo	% s	% p	% d	Charge	P(Mo–X)[a)]
	1	*Mo1*	—	—	—	—	—	0.21	0.127
		Mo2	—	—	—	—	—	0.21	
Mo1–Mo2	**3**	*Mo1*	1.54	50.0	0.0	0.0	100.0	0.14	0.328
		Mo2		50.0	0.0	0.0	100.0	0.14	
	4	*Mo1*	1.44	49.9	11.7	0.9	87.4	0.11	0.333
		Mo2		50.1	11.7	0.9	87.4	0.11	
Mo1–P3	**1**	*Mo1*	1.85	28.7	23.8	0.1	76.1	—	0.649
Mo2–P3		*Mo2*	1.85	28.5	24.1	0.1	75.8	—	0.649
Mo1–P3	**4**	*Mo1*	1.84	28.1	29.7	0.2	70.1	—	0.714
Mo2–P3		*Mo2*	1.84	28.1	29.7	0.2	70.1	—	0.714
Mo1–Mo2–H4	**1**	*Mo1*	1.83	19.2	25.1	0.1	74.8	—	0.353
		H4		61.6	100.0	0.0	0.0	−0.21	
		Mo2	—	19.2	24.8	0.1	75.1	—	0.353

a) Wiberg bond index.

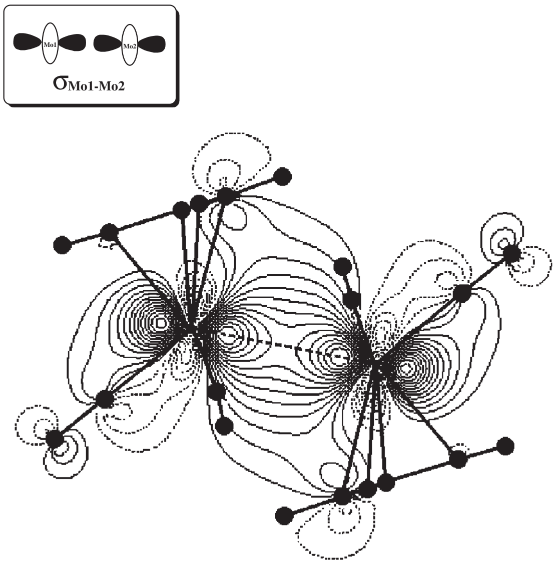


Fig. 6. Localized Kohn–Sham orbitals (R-B3LYP/6311LAN) of complex **3** in the Mo1–Mo2–C5 plane at the contours intervals of 0.0125 in e•au^{-3} and schematic orbital interactions.

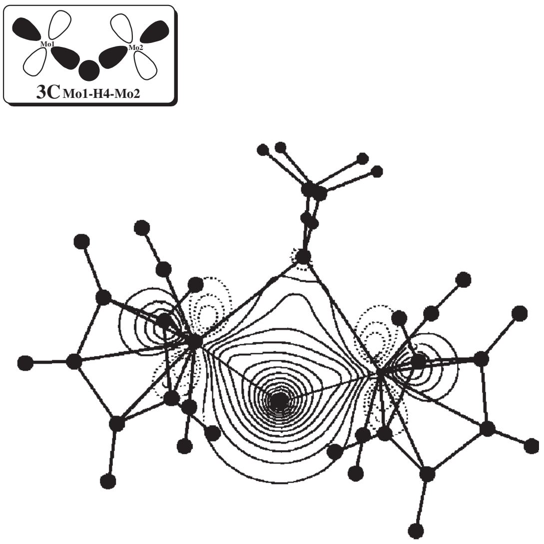


Fig. 7. Localized Kohn–Sham orbitals (R-B3LYP/6311LAN) of complex **1** in the Mo1–Mo2–H4 plane at the contours intervals of 0.025 in e•au^{-3} and schematic orbital interactions.

as shown in Fig. 7 there is no direct Mo1–Mo2 bond observed for **1**; a three-center two-electron bond is obvious for Mo1–H4–Mo2. The corresponding bond orders of Mo1–H4 and Mo2–H4 are equivalent, i.e. 0.353 and 0.353 respectively. Meanwhile, two equivalent bond interactions between P3–Mo1 and P3–Mo2 with bond orders of 0.649 and 0.649, respectively, as shown in Fig. 8, are evident in **1**. As anticipated, a direct metal–metal interaction is existing in **4**, as depicted in Fig. 9. The two most critical atomic orbitals that contribute to this metal–metal bond are dσ + sp. It is interesting to compare the calculated bond order values for **1** (0.127), **3** (0.328), and **4** (0.333). Since the existence of a metal–metal bond within **3** is beyond doubt, the metal–metal bond must exist for **4** as well. However, the bond order value of **1** is much smaller than in **3** and **4**. This small value is regarded as showing a lack of significant bonding between two metal centers in **1**. The significant feature found here is that the bond distance is not the reliable criterion for judging the existence of a metal–metal bonding even though the Mo1–Mo2 bond distances between **1** and **3** are almost the same.

The calculated natural charges for the molybdenum atoms in **1**, **3** and **4** are +0.21, +0.14 and +0.11 respectively. The molybdenum atoms in **1** have the most positive charges among all the three compounds. This implies that some electron densities were withdrawn by the bridging hydride in **1**. Although **4** is an anionic molecule, the natural charges for metals are almost the same as for **3**. In a theoretical study of $[(CO)_5M–H–M(CO)_5]^-$ employing the parameter-free Fenske–Hall method,[31] Jezowska-Trzebiatowska and Nissen-Sobocińska observed that the M–M overlap population is negligible, which implies that there is no direct metal–metal bond in the cases of Cr, Mo, Fe, or Ni carbonyl dimers.[32] A similar conclusion was drawn later in the theoretical studies of $[(CO)_5M–(\mu\text{-}H)_2–M(CO)_5]^n$ (M = Cr,

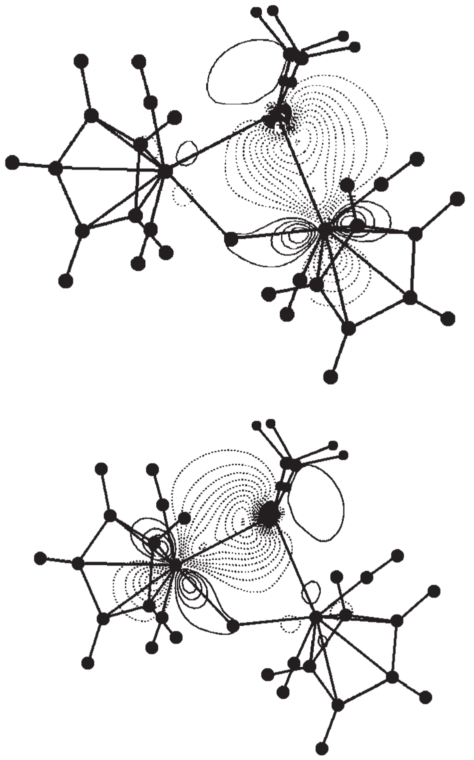


Fig. 8. Localized Kohn–Sham orbitals (R-B3LYP/6311LAN) of complex **1** in the Mo1–Mo2–P3 plane at the contours intervals of 0.025 e•au^{-3}.

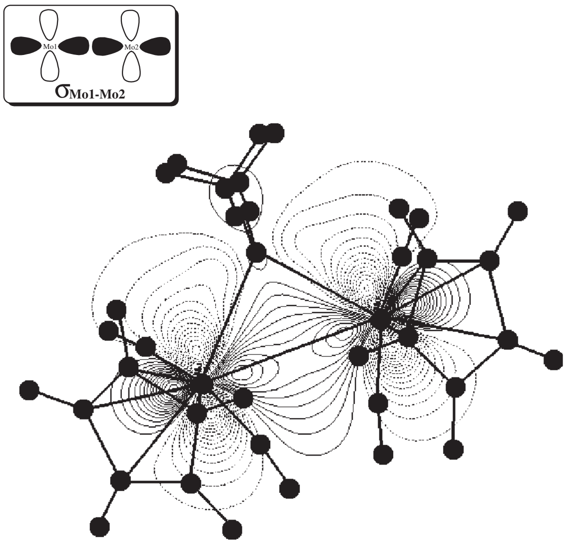


Fig. 9. Localized Kohn–Sham orbitals (R-B3LYP/6311LAN) of complex **4** in the Mo1–Mo2–P3 plane at the contours intervals of 0.0125 e•au^{-3}.

Mo, Mn, Re, W; $n = -2, -2, +0, +0, -2$, respectively).[33] Similarly, we may state here that the two metal atoms in **1** are not bonded via the metal–metal bond but rather through the bridging hydrogen atom. Besides, the bridging hydrogen is believed to oscillate periodically between the two metal centers.[34]

Conclusion

From the present study, we conclude that during the process of protonation of **4** to forming **1**, the electron densities flow from between the two molybdenum atoms toward the upcoming proton. The redirection of electron flow causes the breaking of the metal–metal bond of **4** and forms the Mo–H–Mo three-centers, two electrons bond in **1**.[35] Furthermore, based on the assessment of the calculated results at RB3LYP/6311LAN//RB3LYP/6311LAN and UB3LYP/6311LAN//RB3LYP/6311LAN levels, it is reasonable to state that there is neither an unpaired electron around each metal center nor a direct metal–metal bond inside **1** at its singlet ground state. Through the EAN rule regarded as a convenient method, it is sometimes a misleading concept in interpreting the bonding of multinuclear organometallic compounds.

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Supporting information available: Tables containing coordinates and energies of the optimized structures of **1**, **3**, and **4** are available (deposited as Document No. 03183).

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