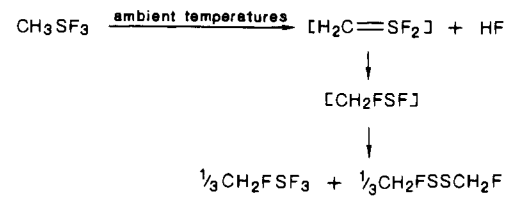
distinction has already been partially eliminated in a C_{2v} molecule like SF_4 or $(CF_3)_2SF_2$ (with $2a_1 + b_1 + b_2$ σ-type 1-electron bonding MO's, where the a_1 orbitals span both axial and equatorial ligands), and relaxed still further in a C_s molecule like CF_3SF_3 (with $3a' + a''$ σ-type bonding MO's, where the a' orbitals span both axial and equatorial ligands).

We are unsure of the significance to be attached to the C-H bond length in CH_3SF_3, which, according to our analysis of the electron-diffraction pattern, is 4-5 pm longer than the corresponding distance in other methyl-sulfur compounds, e.g. CH_3SH,[37a] CH_3SSCH_3,[37c] and $(CH_3)_2SO$.[39] Such an attenuation is anticipated neither by our ab initio calculations nor by the vibrational properties displayed by the CH_3SF_3 molecule[11] that parallel quite closely those of CH_3SH,[40] at least with respect to the vibrations localized mainly within the CH_3 group. Moreover, there is no echo of anything similar in the dimensions of the CF_3 group as it occurs in the molecules CF_3SF_3 and CF_3SX (X = H, F, Cl, or Br).[38] Otherwise, it would be tempting to link a weak C-H bond in CH_3SF_3 to the facility of HF elimination in accordance with the following scheme:[11,41]



$$\begin{array}{l} CH_3SF_3 \xrightarrow{\text{ambient temperatures}} [H_2C{=}SF_2] + HF \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad [CH_2FSF] \\ \qquad\qquad\qquad\qquad \downarrow \\ \tfrac{1}{3}CH_2FSF_3 + \tfrac{1}{3}CH_2FSSCH_2F \end{array}$$

With the dimethyl derivative $(CH_3)_2SF_2$, the susceptibility to HF elimination is such that the compound cannot be vaporized without decomposition.[11,42]

Acknowledgment. We thank the SERC for the award of a research studentship (to G.S.M.), for financial support of the Edinburgh Electron-Diffraction Service, and for provision of the microdensitometer facilities. We are grateful also to Professor Dr. mult. A. Haas for the provision of a sample of CF_3SCl and to P. T. Brain for practical assistance with the gas-phase NMR measurements on CF_3SF_3. The computational portion of the work was supported by a grant from the Robert A. Welch Foundation; computing resources for computation with the GAUSSIAN-82 program were provided by the University of Texas System Center for High Performance Computing.

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Electronic Structure of Asymmetric Metal-Metal Multiple Bonds: The d^2-d^6 Complexes X_4Mo-$Mo(PH_3)_4$ (X = OH, Cl)

Bruce E. Bursten*,[1] and William F. Schneider

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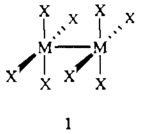
The electronic structure of compounds containing the Mo_2^{4+} dimeric unit with a formally asymmetric Mo(0)-Mo(IV) charge distribution is investigated with the SCF-Xα-SW method. Such systems are known for mixed phosphine-alkoxide ligand systems. Strong π-donor ligands such as the alkoxides inhibit the formation of a polar δ bond between the two metal centers and lead to a sterically induced staggered ligand conformation. These complexes contain a formal Mo-Mo triple bond. Weaker π-donor ligands such as halides permit the δ charge transfer to occur and should lead to a stable, eclipsed ligand conformation with a net Mo-Mo quadruple bond. Comparisons are made to the electronic structure of more conventional Mo(II)-Mo(II) dimers, particularly those with bidentate phosphine ligands and with a twisted ligand conformation about the dimetal unit.

The majority of complexes that contain multiple metal-metal bonds are homodinuclear molecules with symmetry-equivalent metal atoms. With reference to quadruple metal-metal bonds, the best studied systems are the d^4-d^4 dimers of Mo(II) or Re(III).[2] The electronic structure of these d^4-d^4 complexes is fairly well understood in terms of the "usual" quadruple-bond description: one σ metal-metal bond, two π metal-metal bonds, and one δ metal-metal bond, each of which is symmetrically disposed between the two metal atoms.

Most complexes with d^4-d^4 quadruple bonds conform to two common coordination geometries, namely M_2X_8 systems with D_{4h} symmetry (**1**) or $M_2X_4Y_4$ complexes that are D_{2d} (**2**). The eclipsed orientation of the ligands on each metal center, even when it would appear to be sterically unfavorable, is, of course, attributed to the presence of the δ bond, which is sensitive to variations in the rotational angle between the two metal fragments. The eclipsed orientation maximizes the δ interaction and the metal-metal bonding.



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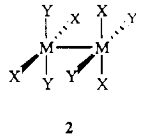

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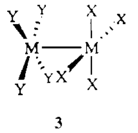

3

The symmetry equivalence of the two metal centers is removed in the heterodinuclear complexes that are based on Cr(II)-Mo(II) or Mo(II)-W(II) dinuclear fragments.[3] These lower symmetry systems do not demonstrate any significant chemical or spectroscopic differences from the homodinuclear ones, however; apparently the differences between the two metal centers are not great enough to induce a sizably different electronic structure, and they are best considered as "slightly polarized" d^4-d^4 systems.[4]

Recent efforts have yielded truly asymmetric homodinuclear complexes, wherein the two metal atoms are in different formal oxidation states. Cotton, Walton, and co-workers have found that certain Re(III)-Re(III) dimers can disproportionate to give formal d^3-d^5 Re(IV)-Re(II) dimers such as the C_{2v} molecules

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(1) Camille and Henry Dreyfus Teacher-Scholar (1984-1989).

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

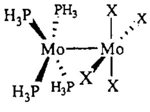
(3) See, for example: (a) Garner, C. D.; Senior, R. G.; King, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3526-3529. (b) Katović, V.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5586-5587. (c) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1978**, *17*, 3237-3240.

(4) See, for example: Bursten, B. E.; Cotton, F. A.; Cowley, A. H.; Hanson, B. E.; Lattman, M.; Stanley, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 6244-6249.

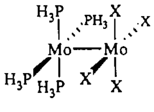
$(RO)_2X_2ReReX_2(PPh_3)_2$ (X = Cl or Br; R = Me, Et, or Pr).[5] More recently, Chisholm and co-workers have reported the synthesis and structure of a unique compound that contains a d^2–d^6 Mo(IV)–Mo(0) metal core.[6] This complex, $(i\text{-PrO})_4MoMo(dmpe)_2$ (**4**; dmpe = 1,2-bis(dimethylphosphino)ethane), can be considered as a structural variant of the $M_2X_4Y_4$ coordination type, now with C_{4v} symmetry (**3**).

4 has the correct number of metal-based d electrons to form the four components of a quadruple bond, but they are distributed unsymmetrically between the two metal atoms. The formation of a δ bond between these centers (and, to a lesser extent, the π bonds) requires a formal donation of electron density from Mo(0) to Mo(IV). If this interaction is strong enough, it will overcome interligand repulsions and impart an eclipsed conformation to the molecule. If it is not, however, the two square-planar metal fragments will most likely twist relative to each other, resulting in a staggered structure and the localization of a pair of electrons in the d_{xy} orbital of the Mo(0) atom. In fact, the crystal structure of **4** reveals a nearly perfectly staggered arrangement of the ligands about the Mo–Mo vector. Apparently the driving force to form the fourth component of the metal–metal bond is not enough to overcome ligand–ligand repulsions in the eclipsed geometry. The metal–metal bond order is thus at most 3. The Mo–Mo bond distance (2.236 Å) is in agreement with that typically observed for triple bonds.[6]

In an effort to understand the differences between the bonding in the symmetric dimers **1** and **2** and that in the unsymmetric dimer **4** we have performed SCF–Xα–SW calculations[7] on the model compound $(HO)_4MoMo(PH_3)_4$ in both the staggered (**5a**) and eclipsed (**5b**) conformations. An analysis and comparison of the molecular orbital schemes for these will aid in describing the metal–metal bond in **4** and also clarify the role of the polar δ bond in determining the preference for the staggered ligand arrangement. In order to gauge the influence of the alkoxide ligands on the structure of **4**, we have also carried out calculations on the chloride analogues $Cl_4MoMo(PH_3)_4$ (**6a,b**). While such compounds are not presently known to exist, it will be of interest to note the differences in the electronic influence of the chloride and alkoxide ligands on the metal framework and to speculate on the structure of the hypothetical molecule **6**.

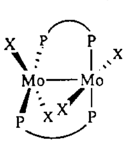


5,6a

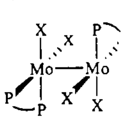


5,6b

All known compounds of the type $Mo_2X_4(PP)_2$ (X = halide; PP = bidentate phosphine ligand) have either two bridging diphosphine ligands (β isomers, **7a**) or one diphosphine ligand chelated to each metal (α isomers, **7b**).[8] The former, thermodynamic, products have a semistaggered geometry in which only some δ bonding is allowed,[9] while the latter kinetic products exhibit an eclipsed geometry in which a complete quadruple bond is possible.[10] Thus, it is curious that the alkoxide complex **4** should choose the structure that it does. Our calculations should be an aid in determining if the structural difference is due to ligand electronic effects and thus characteristic of alkoxides in general, or steric effects in this particular molecule.



7a



7b

Table I. Assumed Geometric Parameters for $(HO)_4MoMo(PH_3)_4$ (**5**, X = OH) and $Cl_4MoMo(PH_3)_4$ (**6**, X = Cl)

	5	**6**
	Bond Lengths (Å)	
Mo–Mo	2.236	2.147
Mo–X	2.000	2.371
Mo–P	2.438	2.444
	Bond Angles (deg)	
Mo–Mo–X	101.4	105.4
Mo–Mo–P	99.4	103.8
Mo–O–H	128.0	

Table II. Assumed Geometric Parameters for $Mo_2(OH)_4(PH_3)_4$ (**8**, X = OH) and $Mo_2Cl_4(PH_3)_4$ (**9**, X = Cl)

	8	**9**
	Bond Lengths (Å)	
Mo–Mo	2.218	2.130
Mo–X	2.036	2.414
Mo–P	2.539	2.545
	Bond Angles (deg)	
Mo–Mo–X	110.5	112.2
Mo–Mo–P	96.6	102.3
Mo–O–H	128.0	

Computational Details

Nonrelativistic calculations were carried out by using existing SCF–Xα–SW codes with minor modification as described below. The coordinate system chosen in all cases has the *z* axis oriented along the Mo–Mo bond and *x* and *y* parallel to the Mo–P bonds in a right-handed manner. The bond lengths and angles for **5a** were taken from the crystal structure of **4**[6] and were idealized to a perfectly staggered C_{4v} symmetry; i.e., the Mo–Mo–O–H dihedral angles are all 0°. **5b** was generated from **5a** by rotating the $Mo(OH)_4$ unit by 45° about the *z* axis. The structural parameters of **6a** and **6b** were taken from the crystal structure of $Mo_2Cl_4(PMe_3)_4$[11] (eclipsed D_{2d}). These parameters are summarized in Table I. In order to address more fully the effect of the alkoxide ligands on the dimolybdenum unit, we have also carried out calculations on the model D_{2d} compounds $Mo_2(OH)_4(PH_3)_4$ (**8**) and $Mo_2Cl_4(PH_3)_4$ (**9**), the latter for comparison to earlier results by Cotton and co-workers.[12] The structural parameters of **8** were taken from the crystal structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(PMe_3)_4$,[13] and those of **9**, from the crystal structure of $Mo_2Cl_4(PMe_3)_4$.[11] These parameters are summarized in Table II.

The initial charge densities for **5a** and **6a** were generated by superposition of the neutral atomic charges as given by Herman and Skillman.[14] The α exchange parameters used were those of Schwarz,[15] and a valence-electron weighted average was used for the intersphere and outer-sphere regions. Overlapping atomic sphere radii were determined by the nonempirical procedure of Norman, using 89% of the atomic number radii.[16] Extended partial wave basis sets, including spherical harmonics through $l = 5$ on the outer sphere, $l = 3$ on molybdenum, $l = 2$ on phosphorus, chlorine, and oxygen, and $l = 0$ on hydrogen, were found to be necessary for satisfactory convergence of the molecular potentials.

Two minor extensions of the SCF–Xα–SW formalism were incorporated here. First, a fragment analysis of converged molecules was carried out for all six model compounds. The potential of the converged molecule was truncated to contain contributions only from those atoms present in the fragment of interest, and then this potential was used as input for the

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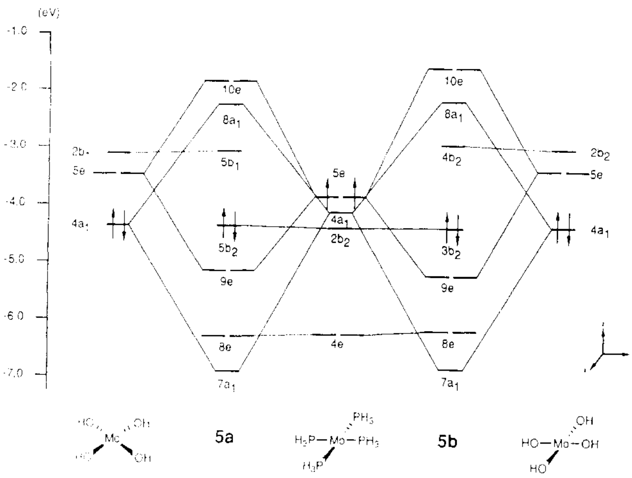

Figure 1. Molecular orbital diagram showing the metal–metal interactions of the $Mo(OH)_4$ and $Mo(PH_3)_4$ fragments in both the staggered (left, **5a**) and eclipsed (right, **5b**) conformations. The 4e MO of $Mo(PH_3)_4$, and the 8e MO's of **5a** and **5b**, which are ligand-based orbitals, are included for comparison with Figures 4 and 5.

noniterative solution of the Hartree–Fock–Slater equation. In this manner the energies of the one-electron orbitals in the molecular fragment are determined in the potential of the converged molecule. This procedure has been described previously.[17] Second, the charge density contributions from the various atomic centers to the one-electron energy levels were partitioned into those from each symmetry-adapted basis function rather than by spherical harmonic angular quantum numbers.[18] The result is essentially a Mulliken population analysis with nonoverlapping basis functions.[19] The intersphere charge is not partitioned in this scheme. This more extensive breakdown of the charge density more readily facilitates an interpretation of the orbitals as pseudo-LCAO's and greatly simplifies the fragment-orbital analysis.

Results and Discussion

$(HO)_4MoMo(PH_3)_4$. Figure 1 summarizes the molecular orbital diagrams of **5a** and **5b**, along with their fragment decompositions into two monometallic units. For clarity, only the valence levels important in Mo–Mo bonding have been included. The $Mo(PH_3)_4$ fragment shows the d-orbital splitting pattern expected for a square-planar molecule with four σ-only donor ligands. The energetic ordering of the frontier orbitals is $2b_2(\delta) < 4a_1(\sigma) < 5e(\pi)$, where the C_{4v} symmetry labels and the symmetry with respect to the Mo–Mo axis are given. The energetic separation of these levels is small (about 0.5 eV), and they have negligible contributions from, and hence negligible perturbation by, the phosphine ligands. As expected, the Mo 5s, $5p_x$, $5p_y$, and $4d_{x^2-y^2}$ orbitals interact strongly with the ligands and are energetically removed from the frontier orbital region. For this d^6 square-planar fragment, the 5e HOMO is doubly occupied. **5a** and **5b** yield energetically identical $Mo(PH_3)_4$ fragment orbital diagrams.

The $Mo(OH)_4$ fragment orbital diagrams for **5a** and **5b** are shown on the left- and right-hand sides of Figure 1, respectively, and are nearly identical. Inasmuch as the molybdenum atom is formally in the +4 oxidation state, the d orbitals might be expected to be at a lower energy than those associated with Mo(0) in $Mo(PH_3)_4$. Clearly, this is not the case. The hydroxide ligands are strong σ *and* π donors, and thus tend to destabilize all the metal-based d orbitals. The σ interaction is the strongest and raises the $d_{x^2-y^2}$ orbital high in energy. The π-donating ability of the hydroxides has a marked effect on the energies of the remaining d orbitals. The splitting of these four d orbitals is increased to almost 1.5 eV, and the resultant ordering of them, $4a_1(\sigma) < 5e(\pi) < 2b_2$ or $2b_1(\delta)$, is significantly modified from that seen in $Mo(PH_3)_4$. The δ orbital in $Mo(PH_3)_4$ is nearly 1.5 eV lower than that in $Mo(OH)_4$, and the π orbitals of the former are about 0.5 eV lower in energy than those of the latter. The doubly occupied σ level of $Mo(OH)_4$, which is the HOMO, is slightly lower in energy than that of the Mo(0) fragment because of the higher formal metal oxidation state and the poor overlap of the Mo $4d_{z^2}$ orbital with the OH σ-donor orbitals. Clearly, phosphine and hydroxide ligands lead to markedly different d-orbital splitting patterns.

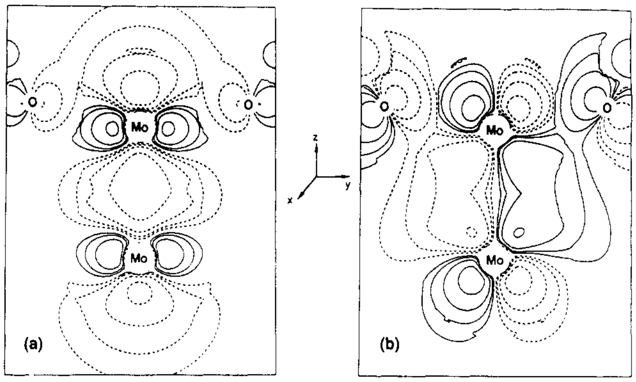

Figure 2. Contour plots of the $7a_1$ (a) and 9e (b) molecular orbitals of **5a** in a plane containing the metal–metal bond and two of the hydroxide ligands. Contour values are ±0.16, ±0.08, ±0.04, and ±0.02.

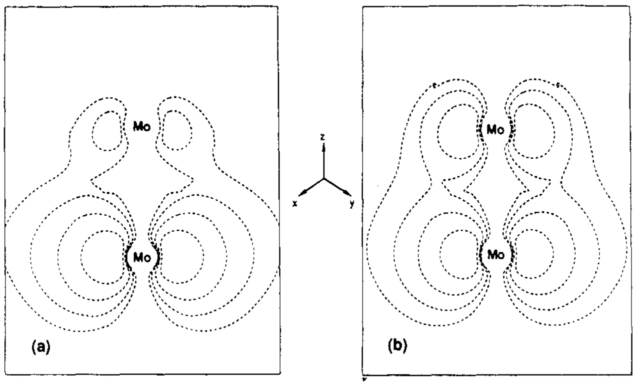

Figure 3. Contour plots of the $3b_2$ molecular orbital of **5b** (a) and **6b** (b) in a plane containing the metal–metal bond and bisecting the metal–ligand axes. The $Mo(OH)_4$ fragment is located above the $Mo(PH_3)_4$ fragment. Contour values are ±0.16, ±0.08, ±0.04, and ±0.02.

When the two fragments are combined to form either **5a** or **5b**, almost identical molecular orbital pictures emerge. Interaction between the energetically similar $4a_1$ orbitals of the two fragments leads to the formation of a strong σ bond (the $7a_1$ MO) between the two. As is to be expected from the energies of the interacting orbitals, the σ bond is slightly polarized toward the Mo(IV) center (Figure 2a). The 5e fragment orbitals are somewhat further separated in energy but still can interact reasonably well to form a π bond. In contrast to the σ bond, the π bond is more localized on the Mo(0) center (Figure 2b) and may be thought to result from partial electron donation from Mo(0) to Mo(IV). As noted above, the δ orbital on $Mo(OH)_4$ ($2b_2$ in the eclipsed case, $2b_1$ in the staggered one) is much higher in energy than the corresponding orbital on $Mo(PH_3)_4$; this, in concert with the generally poor overlap associated with a δ-type interaction, should lead to minimal δ bonding. The interaction of the two fragment δ orbitals is, of course, symmetry forbidden in the staggered conformation **5a**, but it is also negligible in the eclipsed one, as evidenced by the charge density analysis (there is only a 2.11% contribution of Mo(IV) d_{xy} in the $3b_2$ orbital of **5b**) and by a contour plot of the molecular orbital (Figure 3a). The total charge on each metal is virtually unchanged on going from **5a** to **5b**; no additional electronic charge transfer occurs, even when allowed by symmetry. We conclude that no δ-bonding interaction is present in **5b**, and as was originally postulated, the metal–metal bond is best considered as a polarized triple bond with a localized pair of δ electrons on the Mo(0) fragment.[6] The δ interaction does not contribute to the barrier to rotation about the Mo–Mo vector. Ligand steric

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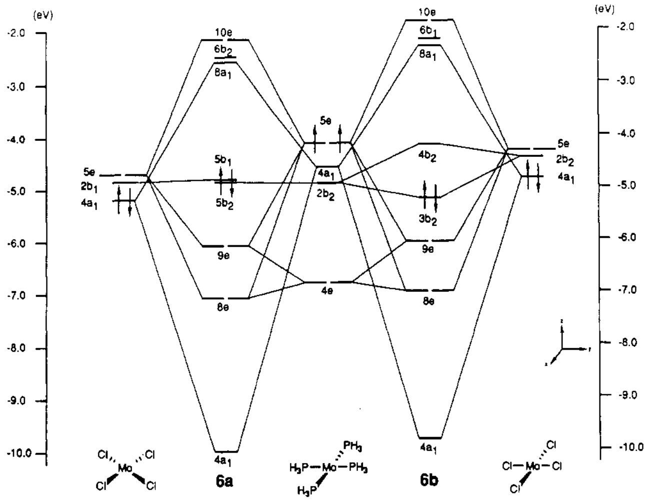

Figure 4. Molecular orbital diagram showing the metal–metal interactions of the $MoCl_4$ and $Mo(PH_3)_4$ fragments in both the staggered (left, **6a**) and eclipsed (right, **6b**) conformations. The HOMO of **6a** is the $5b_2$ orbital.

effects should determine the relative orientation of the two fragments, and since the staggered conformation is the least sterically hindered, that conformation would be expected. Thus, the observation of a staggered geometry for **4**, in which no effective δ bond can be formed for energetic reasons, is parallel to the observation of a staggered geometry in the d^3–d^3 dimers Mo_2X_6 (X = R, OR, NR_2),[2] wherein there are not enough electrons to form a δ bond.

$Cl_4MoMo(PH_3)_4$. The localization of the δ electrons on the Mo(0) center in **5b** was a direct consequence of the destabilization of the Mo(IV) d_{xy} orbital by the strongly π-donating OH ligands. In order to investigate further the influence of ligand π donation, we have also performed calculations on the analogues of **5** in which the OH ligands are replaced with more weakly π-donating Cl ligands. The complexes **6** are model structural isomers of the well-known d^4–d^4 complexes $Mo_2X_4(PR_3)_4$, which generally adopt an eclipsed D_{2d} conformation as in **2**.[11,20] The MO diagrams for the hypothetical molecules **6a** and **6b** are presented in Figure 4. Again, only the interactions important for metal–metal bonding are included for clarity. The fragment orbitals of $Mo(PH_3)_4$ exhibit the same d-orbital ordering as those in compounds **5**. Unlike compounds **5**, however, the orbital energies of the $Mo(PH_3)_4$ fragment in **6** are conformer dependent: the orbital energies in the fragment derived from **6b** are uniformly 0.15 eV lower than those from **6a**. For clarity, the energy levels of the two fragments are drawn coincident in Figure 4, and the energy scales for the two conformers are displaced by 0.15 eV. The source of this shift is an electronic charge transfer from $Mo(PH_3)_4$ to $MoCl_4$ in the eclipsed geometry, which increases the apparent oxidation state of the former (thus lowering the average d-orbital energies) and lowers that of the latter. This transfer is indicative of the formation of a fourth bonding component between the two metals.

The ordering of the fragment orbitals for $MoCl_4$ derived from **6a** and **6b** differs from those presented for $Mo(PH_3)_4$ or $Mo(OH)_4$. Analysis of the fragment orbital energies clearly reveals that in these model compounds chloride is intermediate in π-donor ability between alkoxide and phosphine ligands and is a weaker σ donor than the latter. The d orbitals are split by only about 0.5 eV, similar to that seen in the phosphine fragment. The frontier orbital ordering is now $4a_1(\sigma) < 2b_2$ or $2b_1(\delta) < 5e(\pi)$, with the major difference from $Mo(OH)_4$ being a much smaller destabilization of the δ orbital as a result of the poorer metal–ligand π interaction. The absolute energies of the orbitals derived from **6a** and **6b** are significantly different and shift in a direction opposite to that noted for the $Mo(PH_3)_4$ fragments. This difference is again the result of increased electron density transfer between the formally Mo(0) and Mo(IV) centers in the eclipsed geometry.

The two fragments interact as in the alkoxide case to form σ and π bonds that are independent of the rotational orientation of the ligands. Note that the π bonding is divided between both the 8e and 9e molecular orbitals. A three-orbital interaction between the $d\pi$ levels of each fragment and the highest energy ligand-bonding level of the $Mo(PH_3)_4$ fragment generates two orbitals that have significant metal–metal and metal–ligand bonding characteristics, along with a third, high-energy, metal–metal antibonding orbital. While this is a more complex interaction than that observed in the alkoxide-supported compounds, it has no conformational consequence since the energy levels are invariant with rotation about the metal–metal axis. A similar effect, albeit to a lesser extent, is observed in Xα–SW calculations on the $Mo_2Cl_4(PH_3)_4$ D_{2d} dimer.[12]

The weak π-donating ability of the chloride ligand balances the higher oxidation state of the Mo(IV) fragment almost perfectly, and as a result the δ-orbital energy in $MoCl_4$ matches that in the Mo(0) fragment rather well. Thus, in the staggered conformation **6a**, they become nearly degenerate, in sharp contrast to the case of **5a**. As in **5a**, the Mo–Mo bond order is 3, although the small HOMO–LUMO gap suggests that it would be unstable toward a second-order Jahn–Teller distortion to the eclipsed geometry. Unlike the case of the hydroxide complexes, the rotation of **6a** to the eclipsed conformation **6b** leads to a strong δ interaction. The MO diagram of **6b** shows a δ–δ^* orbital splitting of approximately 1.0 eV, which is as large as that given by the SCF–Xα–SW method for compounds of the type **1** with chloride[12] or alkoxide (vide infra) ligands. The charge density analysis reveals a 15% contribution of the Mo(IV) d_{xy} orbital to the polar $3b_2$ δ bond, which is further reflected in the contour diagram of the orbital (Figure 3b). This bonding interaction amounts to an added charge transfer from Mo(0) to Mo(IV) of 0.05 e and accounts for the increase in energy of the fragment d orbitals of the latter (and decrease of the former) in the eclipsed geometry. The formal bond order between the metals is increased to 4, although it is a polarized quadruple bond. On the basis of these calculations, it is clear that a δ bond of reasonable magnitude is possible between tetrachloro- and tetrakis(phosphine)molybdenum fragments and that the preferred geometry of such a species would be eclipsed rather than staggered.

Bisbridging vs Bischelating Phosphines. The SCF–Xα–SW calculations clearly demonstrate that **4** cannot have a δ bond in any rotational conformation, and thus the choice of a staggered geometry for steric reasons is clear. However, one wonders why this compound—the first dimolybdenum compound containing both alkoxide and bidentate phosphine ligands—exists with a highly unusual asymmetric distribution of ligands, when all the analogous halide compounds adopt the twisted, bridging structure **7a** with symmetrically disposed ligands in their thermodynamically most stable form.[8] Presumably, the latter compounds exist in the semistaggered form in order to retain some component of their δ bonding while accommodating the steric requirements of the bidentate phosphines,[8,9] but this argument is weakened somewhat by our conclusion that δ bonding is also possible in eclipsed $Cl_4MoMo(PH_3)_4$. Why then do the geometries of the halide and alkoxide complexes differ? Is this a manifestation of the electronic effect of the isopropoxide ligands or of the influence of the greater steric bulk of alkoxides compared to halides?

Chisholm and co-workers have speculated that the electronic influence of alkoxide ligands in the coordination sphere of the dimetal unit greatly reduces the capacity for δ-bond formation in the D_{2d} compounds of type **2**.[13] The result is a lengthening and weakening of the metal–metal bond. They further suggest that the δ contribution to bonding is so diminished by the presence of the alkoxides that when bidentate phosphines are added to the molecule, there is little energetic cost in terms of metal–metal interaction in assuming the staggered Mo(0)–Mo(IV) structure **5a**, in which no δ bonding is possible.[6] In order to test this hypothesis we have performed calculations on model D_{2d} compounds to compare with our results on the asymmetric complexes.

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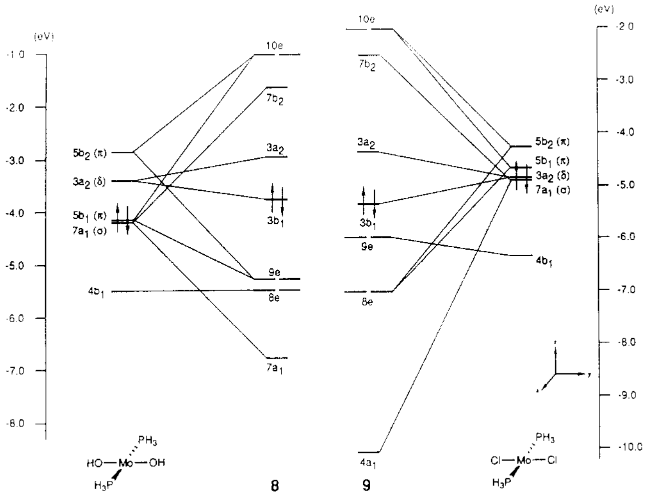


Figure 5. Molecular orbital diagram showing the metal–metal interactions to generate $Mo_2(OH)_4(PH_3)_4$ (left, **8**) and $Mo_2Cl_4(PH_3)_4$ (right, **9**) in the eclipsed conformation. The energy scale has been shifted downward 1.46 eV for **8** to make the midpoints of the HOMO–LUMO gap coincident. The HOMO of the $Mo(OH)_2(PH_3)_4$ fragment is the $5b_1$ orbital, and that of the $MoCl_2(PH_3)_4$ fragment is the $3a_2$.

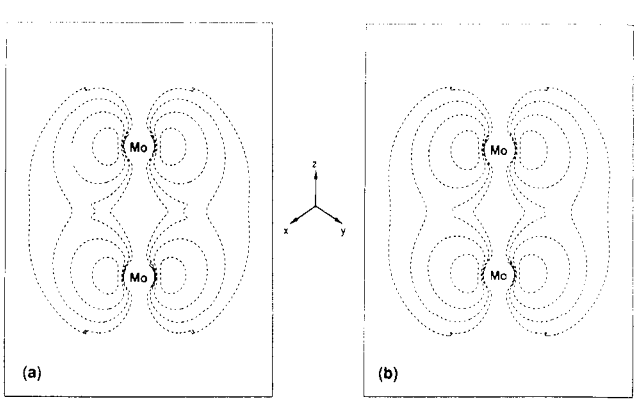
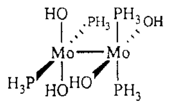
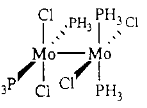


Figure 6. Contour plots of the $3b_1$ molecular orbital of **8** (a) and **9** (b) in a plane containing the metal–metal bond and bisecting the metal–ligand axes. Contour values are ±0.16, ±0.08, ±0.04, and ±0.02.

Figure 5 shows the molecular orbital diagram for the model D_{2d} compound $Mo_2(OH)_4(PH_3)_4$ (**8**) along with its chloride analogue **9**. Our results for **9** are in excellent agreement with



8



9

those first presented by Cotton and co-workers.[12] For clarity only the interactions most important for metal–metal bond formation are included. It is apparent that the presence of the alkoxide ligands diminishes the strength of all of the metal–metal interactions; the alkoxides interact more strongly with the metal orbitals and reduce their ability to participate in metal–metal bond formation. The important point to note, however, is that the δ interaction in **8** is nearly as great as that in **9**, as measured by the separation of the δ and δ* molecular orbitals. While a molecular orbital correlation diagram cannot be directly related to bond strengths, it seems apparent that there is a reasonably strong δ bond in **8**, consistent with the observation of an eclipsed geometry.[13] This point is reinforced in parts a and b of Figure 6, which are contour plots of the $3b_1$ (δ) orbitals for **8** and **9**, respectively. These reveal nearly identical δ interaction in the two model compounds. Combined with our results above, it is apparent that there *is* a loss in δ-bond energy in going from the symmetric D_{2d} complex **8** to the asymmetric Mo(0)–Mo(IV) structure **5a**.

Why then does $(i\text{-PrO})_4MoMo(dmpe)_2$ (**4**) not exist in the β geometry **7a** in which it could retain some δ bonding? Our results above indicate that there is no inherent electronic favorability for the asymmetric structure. However, a careful analysis of the crystal structure of **4** reveals some interesting information about the orientation of the isopropoxide ligands.[6] The two sets of trans ligands adopt different orientations with respect to the metal–metal bond, so that one set has a small Mo–Mo–O–C dihedral angle and places the isopropyl group perpendicular to the bond, while the other set has a larger dihedral angle and isopropyl groups parallel to the bond. We find that variation of the Mo–Mo–O–H dihedral angle in **5a** has little electronic consequence;[21] however, when the hydroxides are replaced by isopropoxide ligands, their orientation greatly affects the *steric* interactions about the metals. We have generated a computer graphical model of the hypothetical molecule β-$Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$ by starting with the crystal structure of β-$Mo_2Cl_4(dmpe)_2$,[22] replacing the chloride ligands with isopropoxide ligands, and constraining the phosphine bridges to remain invariant. Under these constraints we were not able to find an orientation in which interligand steric interactions were not considerably greater than in **4**. While we were not able to carry out a quantitative search of the conformation space, our results are strongly suggestive that this geometry is sterically unfavorable compared to the asymmetric one. Combined with our molecular orbital calculations, we thus conclude that the unusual structure of **4** is due to the steric demands of the pendant ligands and not to the electronic influences of alkoxide ligands. We would not be surprised to see complexes like **4** adopt the β structure when smaller alkoxide ligands are used.

Conclusions

The SCF–Xα–SW calculations demonstrate that the staggered conformation of **4** most likely results from ligand steric repulsions, since strong interaction between the Mo(IV)-based d_{xy} orbital and the alkoxide ligands raises the energy of the former and prevents formation of a δ bond.[6] The bond order is 3 in any ligand conformation. The hypothetical chloride analogue does not exhibit the same degree of d_{xy} splitting and could conceivably contain a δ bond with the concomitant eclipsed arrangement of ligands. The preference of $(i\text{-PrO})_4MoMo(dmpe)_2$ for the Mo(0)–Mo(IV) structure **4** with chelating diphosphines over the β structure **7a** preferred by the halides is not a result of electronic factors but rather reflects the greater steric demands of the isopropoxide ligands as compared to halide ligands.

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(21) We thank one of the reviewers for suggesting an investigation of the electronic effects of different alkoxide ligand orientations.

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