

Chemistry of Compounds Containing Metal-to-Metal Triple Bonds between Molybdenum and Tungsten

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The recognition that the anion $\text{Re}_2\text{Cl}_8^{2-}$ contains a rhenium-to-rhenium quadruple bond^{1,2} and the rapidly following discovery of other quadruple M–M bonds constituted a turning point in transition-metal chemistry: it raised questions which were previously inconceivable. Aside from obvious questions as to the electronic structure and the propensity of transition metals to form quadruple bonds,³ there were also broader implications. For example, the existence of a compound containing an M–M bond of order four implied the probable existence of compounds containing M–M multiple bonds of lower order, namely two and three, though few of the former and none of the latter were known at that time. It also suggested that one might speculate on the ability of metals to form M–M multiple bonds of even higher order, such as five and six.⁴

This Account traces the emergence of a new class of compounds of formula M_2X_6 , where X = R(alkyl), NR_2 , and OR, which contain metal-to-metal triple bonds (M = Mo and W) unsupported by bridging ligands.⁵ It also deals with the organometallic compounds $\text{Cp}_2\text{M}_2(\text{CO})_4$ (M = Cr, Mo, W), which on the basis of short metal-metal distances (Mo–Mo = 2.40 Å⁶) relative to those in the precursor compounds $\text{Cp}_2\text{M}_2(\text{CO})_6$ (Mo–Mo = 3.27 Å⁷) and the attainment of the inert gas structure by the metals may be considered to have metal-to-metal triple bonds.

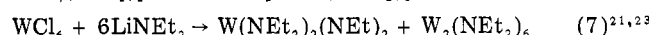
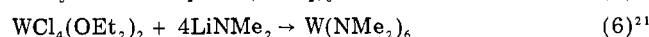
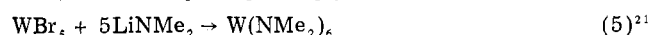
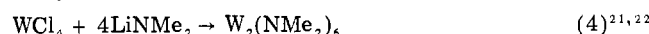
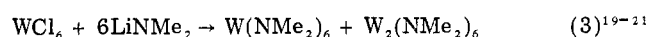
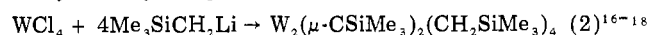
Certain aspects of the structural and dynamical solution behavior of these compounds, in addition to a number of interesting reactions, warrant specific attention. It seems that organometallic reaction schemes evolved for mononuclear transition-metal chemistry may be extended to these dinuclear systems and, furthermore, that these dinuclear compounds may provide building blocks for the systematic syntheses of new polynuclear and cluster compounds. Both of these considerations have important catalytic implications.^{8,9} In an earlier account, the theoretical treatment of these triple bonds was discussed.¹⁰ In this paper we deal entirely with experimental studies of structure, dynamics, and reactions.

Syntheses

M_2X_6 Compounds (X = R, NR_2 , OR). The first member of this series, $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$, was discovered serendipitously by Wilkinson and his co-workers¹¹ as a product formed in the reaction of MoCl_5 with 5 equiv

of $\text{LiCH}_2\text{SiMe}_3$. Analogous reactions involving MoCl_5 and LiNR_2 (5 equiv) lead to mononuclear $\text{Mo}(\text{NR}_2)_4$ ¹² and dinuclear $\text{Mo}_2(\text{NR}_2)_6$ ^{13–15} compounds (R = Me, Et) which may be separated by fractional sublimation. However, a better route to $\text{Mo}_2(\text{NR}_2)_6$ involves the reaction between the polymeric MoCl_3 and LiNR_2 (3 equiv); only a trace of $\text{Mo}(\text{NR}_2)_4$ is formed in these reactions.¹⁵

Some similar reactions involving tungsten halides and organolithium reagents are summarized in eq 1 through 7.



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The products depend on the choice of tungsten halide in a manner not yet understood. The reaction pathway leading to the dinuclear compounds W_2X_6 ($X = R, NR_2$) is evidently complex. Neither $Mo(NMe_2)_4$ nor $W(NMe_2)_6$ appears to be a precursor for $M_2(NMe_2)_6$, and there is evidence that the $M_2(NMe_2)_6$ compounds are not formed by the coupling of two reactive $M(NMe_2)_3$ units.²⁴

Despite the enigmas associated with these metathetic reactions, the crystalline compounds M_2X_6 ($Mo = Mo, W$ and $X = R, NR_2$) may be prepared on a large scale and are thus themselves useful starting materials. The dimethylamides react with alcohols and trialkylsilanols to give compounds of empirical formula $Mo(OR)_3$. For molybdenum a fairly extensive series of dinuclear alkoxides $Mo_2(OR)_6$ ($R = Bu-t, PhMe_2C, Me_2CH,$ and Me_3CCH_2) and trialkylsiloxides $Mo_2(OSiR_3)_6$ ($R = Me, Et$) have been isolated.^{13,25} Less bulky alkoxy ligands give polynuclear compounds, such as the ethoxide which is tetrameric in benzene. A similar situation holds for tungsten, although polynuclear complexes are more common.^{22,25-27}

$M_2X_{6-n}Y_n$ Compounds In an attempt to establish a much more general class of dinuclear compounds of general formula $M_2X_{6-n}Y_n$, where X and Y are uninegative ligands, we sought ways in which to replace M-NR₂ groups by M-Cl groups and discovered a very smooth and efficient route²⁸ (eq 8). The chloro-for-

$M_2(NMe_2)_6 + 2Me_3SiCl \rightarrow M_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2$ (8)

dimethylamido group exchange proceeds via an

amine-catalyzed sequence (eq 9). Although other

$Me_2NH + Me_3SiCl \rightleftharpoons Me_3SiNMe_2 + HCl$ (9i)

$M_2(NMe_2)_6 + HCl \rightleftharpoons M_2(NMe_2)_5Cl + HNMe_2$ (9ii)

$M_2(NMe_2)_6 + M_2Cl_2(NMe_2)_4 \rightleftharpoons 2M_2Cl(NMe_2)_5; K \sim 1, 30^\circ C.$ (9iii)

$M_2Cl_x(NMe_2)_{6-x}$ compounds are formed in the reactions

between $M_2(NMe_2)_6$ and Me_3SiCl , none has been isolated in a pure state. It appears that continued Cl-for-NMe₂ group exchange leads to polymeric rather than dinuclear compounds.

The M-Cl bonds in $M_2Cl_2(NR_2)_4$ compounds ($R = Me$ or Et) are labile to a large number of metathetic reactions. With alkylaluminum reagents $M_2R_2(NEt_2)_4$,

compounds have been isolated with $R = Me, Et, n-Bu,$ and CH_2SiMe_3 .²⁹⁻³² Attempts to prepare $M_2R(Cl)-$

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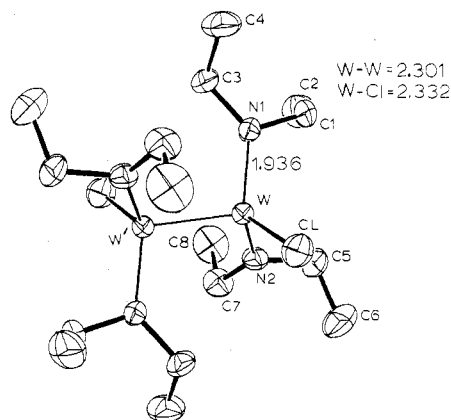


Figure 1. An ORTEP view of the $W_2Cl_2(NEt_2)_4$ molecule in which each atom is represented by its ellipsoid of thermal vibration drawn to enclose 50% of the electron density.

Table I
M-M Triple Bond Distances in M_2X_6 and $M_2X_2Y_4$ Compounds

Compounds	M-M, Å	Compounds	M-M, Å
$Mo_2(CH_2SiMe_3)_6$	2.167 (?)	$W_2Br_2(NEt_2)_4$	2.301 (2)
$W_2(CH_2SiMe_3)_6$	2.255 (2)	$W_2I_2(NEt_2)_4$	2.300 (4)
$Mo_2(NMe_2)_6$	2.214 (3)	$W_2Me_2(NEt_2)_4$	2.291 (1)
$W_2(NMe_2)_6$	2.294 (2)	$Mo_2Me_2(NMe_2)_4$	2.201 (1)
$Mo_2(OCH_2-CMe_3)_6$	2.222 (2)	$Mo_2(OBu^t)_2(O_2COBu^t)_2$	2.241 (1)
$Mo_2Cl_2(NMe_2)_4$	2.201 (2)	$Mo_2(OSiMe_3)_6(HNMe_2)_2$	2.242 (1)
$W_2Cl_2(NMe_2)_4$	2.285 (2)	$W_2Me_2(O_2CNEt_2)_4$	2.272 (1)
$W_2Cl_2(NEt_2)_4$	2.301 (1)	$W_2(O_2CNMe_2)_6$	2.279 (1)

(NEt_2)₄ compounds failed, presumably because the second R for Cl substitution proceeds faster than the first.³⁰

$M_2(NR_2)_6$ and $M_2X_2(NR_2)_4$ compounds are susceptible to a number of the M-N insertion reactions typical of mononuclear dialkylamides.³³ With CO_2 , $W_2(NMe_2)_6$ gives $W_2(O_2CNMe_2)_6$ ³⁴⁻³⁶ while $Mo_2(NMe_2)_6$ yields only $Mo_2(NMe_2)_2(O_2CNMe_2)_4$.³⁷ The latter is believed to adopt a structure akin to that of $W_2Me_2(O_2CNEt_2)_4$ which is formed in the reaction between CO_2 and $W_2Me_2(NEt_2)_4$.³⁴⁻³⁶ $M_2(OR)_6$ compounds react reversibly with CO_2 to give $M_2(OR)_4(O_2COR)_2$ compounds.^{22,26,27,38} Reactions involving CS_2 and COS also give products of M-N or M-O bond insertion, but these have not yet been properly characterized. Insertions into M-C bonds have not been observed.

All of the aforementioned compounds are diamagnetic crystalline solids with appreciable solubilities in hydrocarbon solvents. They are all sensitive to oxygen

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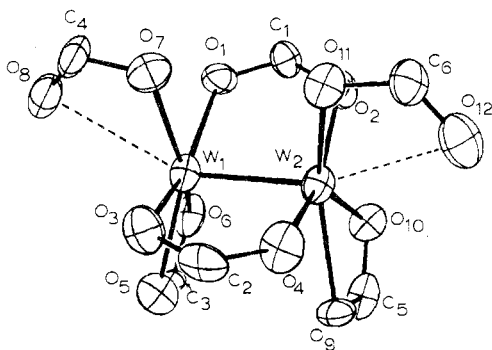


Figure 2. The central $W_2(O_2C)_6$ skeleton of the $W_2(O_2CNMe_2)_6$ molecule. The dotted lines indicate the long, quasi-axial W-O bonds. The W(1)-W(2) distance is 2.279 (1) Å.

and moisture but quite thermally stable. Many may be sublimed, and all (with the exception of $M_2(OR)_4(O_2COR)_2$ compounds which readily lose CO_2) give molecular ions in the mass spectrometer. They range in color from pale yellow to dark red but show no absorption maxima in the visible region of the spectrum. The color is derived from a tailing of intense UV absorptions into the visible region of the electronic spectra.

Solid-State Structures

The M_2X_6 compounds all have an ethane-like (D_{3d} symmetry) M_2L_6 core ($L = C, N, O$). The M-M-L angles are ca. 104° and the M-M distances fall in the range 2.167 to 2.30 Å. For a given ligand X the W-W distance is longer than the Mo-Mo distance by about 0.08 Å. $M_2X_2(NR_2)_4$ compounds, where X = halide or alkyl, adopt closely related structures. In the solid state they have anti conformations; the central $M_2L_2N_4$ core ($L = C$ or halide) belongs to the symmetry group C_{2h} . An ORTEP view of the molecular structure of $W_2Cl_2(NEt_2)_4$ ³⁹ is shown in Figure 1 and is representative of this class of compounds.

All dialkylamido structures have planar nitrogen atoms with the alkyl groups oriented to comprise two sets. Those directed over the M-M bond are termed proximal, those directed away distal. M-M triple bond distances for M_2X_6 and $M_2X_4Y_2$ type compounds are given in Table I.

In $Mo_2(OSiMe_3)_6(HNMe_2)_2$ ⁴⁰ and $Mo_2(O_2COBu-t)_2(OBu-t)_4$ ³⁸ there are triple bonds between molybdenum atoms which form four σ bonds to the ligand atoms. The $M-L_4$ geometry approximates to a square plane.

$W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ adopt closely related structures having approximate C_{2v} symmetry and provide examples of compounds containing M-M triple bonds ($W-W_{av} = 2.275$ Å) between metal atoms that are coordinated to five and six ligand atoms, respectively.³⁶ The central $W_2(O_2C)_6$ skeleton of the $W_2(O_2CNMe_2)_6$ molecule is shown in Figure 2. There are two bridging dialkylcarbamato (O_2CNR_2) ligands, and each tungsten atom is at the apex of an irregular pentagonal pyramid. The basal vertices of each pyramid are defined by the two oxygen atoms of the bidentate nonbridging carbamato ligand ($W-O_{av} = 2.16$

Å), one oxygen atom from each of the two bridging carbamato groups ($W-O_{av} = 2.09$ Å), and either an oxygen atom from the carbamato ligand ($W-O_{av} = 2.07$ Å) in $W_2(O_2CNMe_2)_6$ or a methyl group ($W-C_{av} = 2.20$ Å) in $W_2Me_2(O_2CNEt_2)_4$. In $W_2(O_2CNMe_2)_6$ the second oxygen atoms from the nonbridging carbamato ligands, which are axially aligned, coordinate weakly ($W-O_{av} = 2.67$ Å) along an extension of the W-W triple bond.

Remarks on Bonding

M-M triple bonds have now been found between metal atoms that are coordinated to either three, four, five, or six ligand atoms. Since the formation of a M-M triple bond requires the use of three metal valence orbitals, the total number of metal valence orbitals used in bonding may vary from six in M_2X_6 compounds to nine in $W_2(O_2CNMe_2)_6$. In all the compounds a simple analysis of the symmetry types of orbitals required to form M-M and M-L bonds and a consideration of the symmetry properties of the metal valence shell orbitals lead to a satisfactory qualitative formulation of electronic structure.

Consider, for example, the bonding in the molecules $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$. We may assume that the $W \equiv W$ bond is formed primarily by overlap of metal d_{z^2} orbitals to give the σ component and metal d_{xz} and d_{yz} orbitals to give the π components. This is in accord with the assumption originally made² and subsequently supported by SCF $X\alpha$ calculations⁴¹ for the quadruple bonds in $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$. For the five quasi-coplanar bonds to the ligands, we may then use the metal s , p_x , p_y , d_{xy} , and $d_{x^2-y^2}$ orbitals. In the case of $W_2(O_2CNMe_2)_6$, tungsten p_z orbitals may be employed to help form the weak axial W-O bonds.

Such a qualitative picture may be viewed as satisfactory to the extent that it readily accounts for the observed diamagnetic nature of the compounds and the short M-M distances which are well below the range for M-M distances in compounds containing Mo-Mo single bonds.^{10b} It may also be noted that a triple bond consisting of a σ component and two equivalent π components has cylindrical symmetry and imposes no restriction on geometry [cf. in $Re_2Cl_8^{2-}$ where the eclipsed geometry of the two $ReCl_4$ groups is imposed by the M-M δ bond]. The observed geometries are thus determined by the steric requirements of the ligands. M_2X_6 , $M_2X_4Y_2$ ($X = R, NR_2, OR$, and $Y =$ halide or alkyl), and $Mo_2(OR)_6(HNR_2)_2$ compounds adopt staggered geometries because steric repulsive interactions dominate. On the other hand, the eclipsed geometries found in $Mo_2(OBu-t)_4(O_2COBu-t)_2$, $W_2Me_2(O_2CNEt_2)_4$, and $W_2(O_2CNMe_2)_6$ are imposed by the bridging $O_2COBu-t$ and O_2CNR_2 ligands.

The detailed electronic structure of Mo_2X_6 compounds was the subject of recent SCF $X\alpha$ SW calculations.⁴² Here the calculated and observed PE spectra were in good agreement.

Dynamical Solution Behavior

Since all the compounds are diamagnetic, their dynamical solution behavior is readily investigated by

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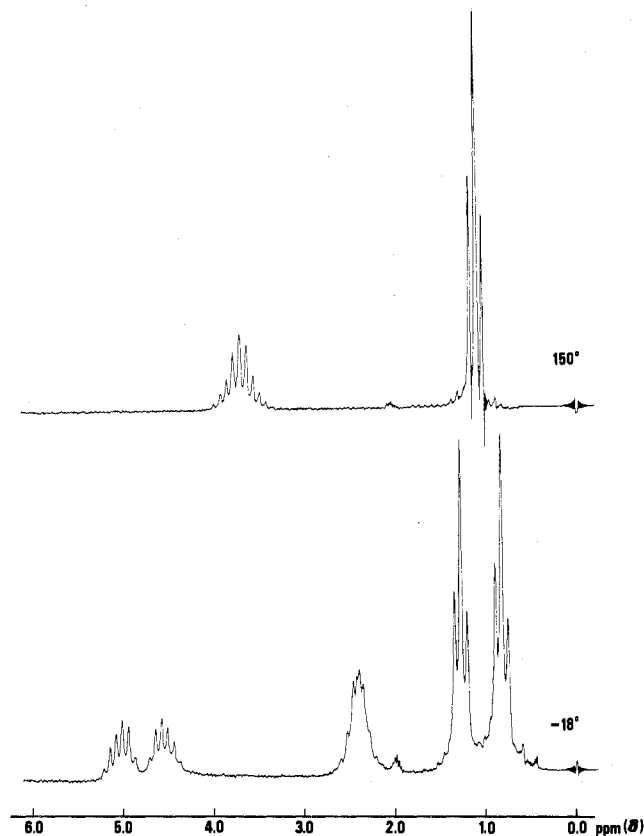


Figure 3. ^1H NMR spectra of $\text{W}_2\text{Cl}_2(\text{NEt}_2)_4$ in toluene- d_6 recorded at 100 MHz. Top at $+150^\circ\text{C}$, bottom at -18°C corresponding to fast and slow proximal \rightleftharpoons distal exchange spectra on the NMR time scale, respectively.

variable-temperature NMR spectroscopy. The dialkylamido compounds afford a natural opportunity to examine the diamagnetic anisotropy expected for triple bonds. In acetylenes and cyanides the construction of a molecule that places probe nuclei over, as well as along, the axis of the triple bond is a difficult task. For $\text{M}_2(\text{NR}_2)_6$ and $\text{M}_2\text{X}_2(\text{NR}_2)_4$ molecules the two alkyl groups of each R_2N unit naturally adopt the desired placement. Variable-temperature NMR studies show that proximal \rightleftharpoons distal alkyl exchange occurs on the NMR time scale.

This is exemplified by the ^1H NMR spectra obtained for $\text{W}_2\text{Cl}_2(\text{NEt}_2)_4$ shown in Figure 3. At high temperatures, $>130^\circ\text{C}$, proximal \rightleftharpoons distal ethyl exchange is rapid on the NMR time scale, while at low temperatures, $<-16^\circ\text{C}$, proximal and distal resonances are frozen out. Three further points are noteworthy. (1) The high-temperature limiting spectrum corresponds to an ABX_3 spectrum and the low-temperature limiting spectrum to two ABX_3 spectra. Evidently the mechanism of proximal \rightleftharpoons distal exchange does not remove the diastereotopic nature of the methylene protons. (2) The spectra correspond to the presence of only the anti rotamer in solution. This is the rotamer found in the solid state; see Figure 1. (3) There is a large chemical shift separation between proximal and distal methylene proton resonances, ca. 2.5 ppm.⁴³ The separation between proximal and distal methylene carbon resonances is much larger, ca. 30 ppm.

(43) Since the proximal CH_2 group is not fully over the center of the triple bond and the distal one is closer to the core of zero anisotropy than to the bond axis, this observed shift difference is presumably much smaller than that which would result from the full range of the anisotropy.

The variable-temperature NMR spectra of $\text{M}_2\text{R}'_2(\text{NR}_2)_4$ compounds, where $\text{R}' = \text{Me}$ or CH_2SiMe_3 and $\text{R} = \text{Me}$ or Et , are more complex because both anti and gauche rotamers exist in equilibria in solution. A gauche $\text{M}_2\text{R}'_2(\text{NR}_2)_4$ molecule (C_2 symmetry) has two types of NR_2 ligands. Detailed variable-temperature ^{13}C NMR studies have been reported for $\text{W}_2\text{X}_2(\text{NEt}_2)_4$ compounds where $\text{X} = \text{Me}$,³¹ CH_2SiMe_3 ,³⁰ Br ,³⁰ and I .³⁰ From these and related studies we have shown that proximal \rightleftharpoons distal alkyl exchange occurs by M–N bond rotations. The compounds $\text{M}_2(\text{NR}_2)_6$ and $\text{M}_2\text{X}_2(\text{NR}_2)_4$ behave in solution as molecular propellers and are stereochemically correspondent to 1,1,2,2-tetraaryl-substituted ethanes.⁴⁴

For $\text{M}_2\text{R}'_2(\text{NR}_2)_4$ compounds ($\text{R}' = \text{Me}$ or CH_2SiMe_3 and $\text{R} = \text{Me}$ or Et) anti-to-gauche isomerization has been monitored and found to occur with an energy of activation of 20 to 24 kcal mol⁻¹ depending upon the specific R'/R combination. The detailed mechanism of anti \rightleftharpoons gauche isomerization is not yet known; however, it is known to be intramolecular. Future studies of compounds of the type $\text{M}_2\text{X}(\text{NR}_2)_5$ are planned. Here each metal atom is effectively labeled, and a distinction between a process involving a simple M–M bond rotation and processes involving intramolecular ligand exchange mechanisms are distinguishable.

One final point worthy of mention concerns the absolute assignment of proximal and distal resonances in $\text{M}_2(\text{NR}_2)_6$ compounds. In view of the closed-shell electronic structure of these molecules we expect the dominant induced magnetic field to be in opposition to the applied field and symmetric about the molecular threefold axis. This will lower the effective magnetic field in the region of the distal alkyl groups and increase it in the region of the proximal alkyl groups, with the result that the signals for distal and proximal resonances (both ^1H and ^{13}C) will lie, respectively, upfield and downfield from the nearly identical positions they would otherwise have had. Experimental support for this line of reasoning is seen in the spectra obtained for $\text{M}_2(\text{NMeEt})_6$ compounds. Steric considerations suggest that $\text{M}_2(\text{NMeEt})_6$ compounds would prefer structures with proximal rather than distal methyl groups since this relieves the internal crowding of the molecule, and ^1H NMR studies show that they also in fact have low-field NMe resonances. Even at high temperatures when proximal \rightleftharpoons distal exchange is rapid $\text{M}_2(\text{NMeEt})_6$ compounds show NMe resonances which are deshielded relative to those found in mononuclear compounds such as $\text{Zr}(\text{NMeEt})_4$.

Reactions

The M_2X_6 , $\text{M}_2\text{X}_{6-n}\text{Y}_n$, and $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds undergo a wide variety of reactions, many of which retain the M–M triple bond.

Ligand Substitution: $\text{M}_2\text{X}_6 \rightarrow \text{M}_2\text{Y}_6$. Two types of reactions have been observed in this category. The first involves reaction of an M–X bond with an organic substrate containing an active hydrogen atom and is exemplified by the reaction of $\text{M}_2(\text{NMe}_2)_6$ compounds with alcohols which yield $\text{M}_2(\text{OR})_6$ compounds with the liberation of amine. The second is a metathetic reaction of the type $\text{M}_2\text{X}_6 + \text{M}'\text{Y} \rightarrow \text{M}_2\text{X}_5\text{Y} + \text{M}'\text{X}$. An example of this type of reaction is seen in the formation

of $M_2R'_2(NR_2)_4$ compounds from the reaction of $M_2Cl_2(NR_2)_4$ and LiR' compounds.^{30,31} The high reactivity of M-Cl, M-C(alkyl), M-N(dialkylamido), and M-O(alkoxy) bonds suggests that other $M_2X_{6-n}Y_n$ compounds should be synthetically accessible by these reactions.

We noted that *anti*- $W_2Cl_2(NEt_2)_4$ reacts stereospecifically with $LiCH_2SiMe_3$ to give *anti*- $W_2(CH_2SiMe_3)_2(NEt_2)_4$, which then slowly isomerizes to the *gauche* rotamer: *a*- $W_2R_2(NEt_2)_4 \rightleftharpoons$ *g*- $W_2R_2(NEt_2)_4$; $K = 4$, 30 °C, for $R = CH_2SiMe_3$.^{29,30} This observation strongly supports the view that (i) the W-W bond is not cleaved during the R-for-Cl substitution reaction and (ii) alkyl-for-chloro group exchange proceeds with retention of configuration at tungsten. Rather interestingly, *anti*- $W_2Cl(CH_2SiMe_3)(NEt_2)_4$ was not detected during the course of this reaction. Apparently the introduction of one alkyl group labilizes the second R-for-Cl exchange in the *anti* position. This is reminiscent of the high *trans* influence and *trans* effect exerted by alkyl ligands in square-planar platinum(II) chemistry,⁴⁵ though more work needs to be done before any general conclusions can be reached concerning the substitutional behavior of $M_2X_{6-n}Y_n$ compounds.

Lewis Base Association. Several $M_2(OR)_6$ compounds react reversibly with donor ligands L to give adducts $M_2(OR)_6L_2$ where L = an amine or phosphine. Similarly $Cp_2M_2(CO)_4$ react with phosphines and carbon monoxide to give $Cp_2M_2(CO)_4L_2$ compounds. In the latter case the M-M bond order changes from three to one: the Mo-Mo distances in $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ are 2.40⁶ and 3.27 Å,⁷ respectively. No such change accompanies adduct formation with $M_2(OR)_6$ compounds; the Mo-Mo distances in $Mo_2(OCH_2CMe_3)_6$ and $Mo_2(OSiMe_3)_6(HNMe_2)_2$ are 2.222 (1) Å and 2.242 (1) Å, respectively.

This striking difference may be accounted for by a consideration of the electronic structure of the M-M triple bonds in these two classes of compounds. In $Cp_2M_2(CO)_4$ compounds the metal atoms attain 18-valence-shell electron configurations by the formation of the M-M triple bond. In $M_2(OR)_6$ compounds, where each metal forms three σ bonds to OR groups and a triple bond to the other metal atom, only a 12-valence-shell electron configuration is achieved. Thus the metal atoms in the dinuclear alkoxides $M_2(OR)_6$ may increase their coordination number without introducing a significant change in M-M bonding. This point is further illustrated by the reactions which lead to alkylcarbonato and dialkylcarbamato compounds described below.

Insertion Reactions. M-C(alkyl),⁴⁶ M-N(dialkylamide),³³ and M-O(alkoxide)⁴⁷ bonds are known to be labile to a large number of insertion reactions which may be represented by the general eq 10, where X =

$$M-X + un \rightleftharpoons M-un-X \quad (10)$$

R, NR_2 , and OR and un = an unsaturated organic molecule. Thus far, we have examined in detail only the reactivity of M_2X_6 compounds toward CO_2 . We find that insertion into M-NR₂ and M-OR groups occurs

readily, but no reaction is observed for M-R groups. This is clearly seen in the reaction between $W_2Me_2(NEt_2)_4$ and CO_2 which gives $W_2Me_2(O_2CNEt_2)_4$.³⁶

Insertion into M-NR₂ bonds is irreversible and proceeds via an amine-catalyzed sequence: $HNR_2 + CO_2 \rightleftharpoons HO_2CNR_2$; $M-NR_2 + HO_2CNR_2 \rightarrow MO_2CNR_2 + HNR_2$.³⁴ Insertion into M-OR bonds to give $M_2(OR)_4(O_2COR)_2$ compounds is readily reversible and is believed to proceed by a direct insertion mechanism.³⁸

Reductive Elimination. A simple intramolecular reductive elimination of an X-Y group across a M-M triple bond to yield a compound containing a M-M quadruple bond has not yet been established. Several of the compounds described here should serve as excellent models for this type of reaction. For example, we have found that, when $W_2Me_2(O_2CNEt_2)_4$ is heated to above 150 °C, ethane is liberated.³² However, the origin of the ethane and the nature of the residual tungsten containing species have still to be determined. An investigation of the chemistry of molybdenum analogues should be more instructive, since $Mo_2(O_2CR)_4$ compounds (but not $W_2(O_2CR)_4$ compounds) are well-known to contain M-M quadruple bonds.³ In this regard we note that both $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(OPr-i)_6$ react with acetic acid to yield, upon vacuum sublimation, $Mo_2(OAc)_4$.⁴⁸ Here M-M triple to quadruple bond transformation is achieved, but the detailed reaction pathway and the nature of the eliminated organic compound(s) are not yet known.

Oxidative Addition. The addition of an X-Y substrate across a M-M triple bond might be expected to yield a compound containing a M-M double bond: $L_nM \equiv ML_n + X-Y \rightarrow L_nXM = MYL_n$. This transformation has yet to be established structurally, although there are a number of reactions, such as $Cp_2M_2(CO)_4 + I_2 \rightarrow Cp_2M_2(CO)_4I_2$,⁶ in which this might occur. However, an anticipated oxidative addition to a M-M multiple bond may change the M-M bond order by more than one unit. For example, addition of X_2 (X = I or Br) to $Mo_2(S_2COEt)_4$, which contains an M-M quadruple bond, yields $Mo_2X_2(S_2COR)_4$ compounds having Mo-Mo single bonds (Mo-Mo = 2.72 Å) as a result of a surprising rearrangement in the bonding mode of the xanthate ligand.⁴⁹ It is also possible that addition may cause complete rupture of the M-M bond: $Mo_2(NMe_2)_6 + 2Me_2N \cdot \rightarrow 2Mo(NMe_2)_4$.

Clearly the reactivity of compounds containing M-M multiple bonds toward reductive-elimination and oxidative-addition reactions is going to be as complex and is at present even less predictable than analogous reactions involving mononuclear transition metal complexes.^{50,51}

Reactions of the M-M Triple Bond with Small Unsaturated Molecules. $Cp_2M_2(CO)_4$ compounds react in solution under very mild conditions with a large number of unsaturated organic molecules, un, to form 1:1 adducts $Cp_2M_2(CO)_4(un)$. The compounds where M = Mo and un = $PhC \equiv CPh$, $EtC \equiv CEt$, $HC \equiv CH$, $CH_2=C=CH_2$, and Me_2NCN have been characterized by X-ray crystallography.⁵²⁻⁵⁵ In all cases un acts as

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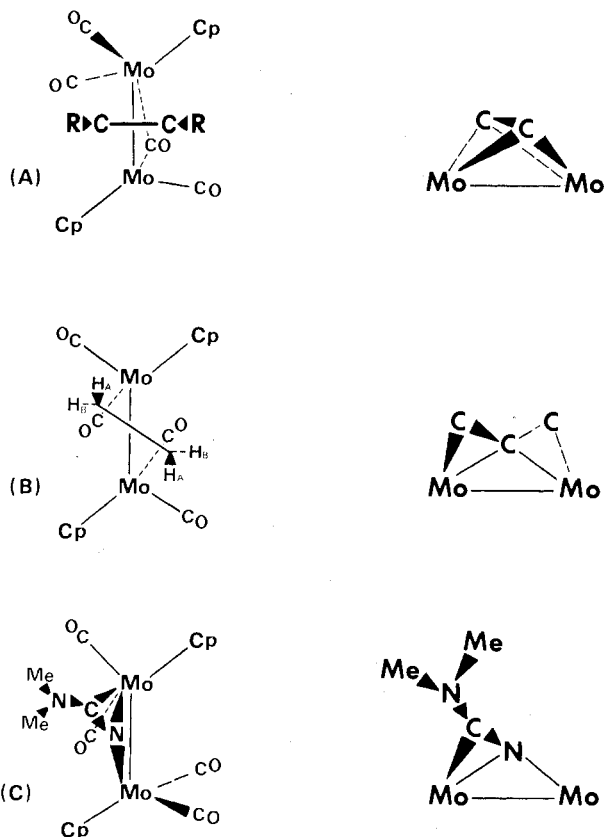


Figure 4. Schematic representations of the $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{un})$ molecular structures; A, un = $\text{RC}\equiv\text{CR}$; B, un = $\text{CH}_2=\text{C}=\text{CH}_2$; C, un = Me_2NCN .

a four-electron donor ligand and spans the Mo_2 bond in the manner shown in Figure 4. The Mo-to-Mo distance increases in length from 2.40 Å in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to 2.974, 3.015, and 3.117 Å when un = $\text{HC}\equiv\text{CH}$, Me_2NCN , and $\text{CH}_2=\text{C}=\text{CH}_2$, respectively.

The acetylene adducts share a common $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{C}_2$ structure. There is a crosswise acetylene bridge (i.e., a pseudo-tetrahedral Mo_2C_2 core), typical of that found in many other dinuclear acetylene complexes.⁵⁶⁻⁶¹ The asymmetry of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ moiety presumably arises from internal steric crowding. In the adducts where un = Me_2NCN and $\text{CH}_2=\text{C}=\text{CH}_2$, the $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ moiety adopts a more relaxed structure having virtual C_2 symmetry.

Allene bridges the Mo-Mo bond obliquely. One of the allenic π orbitals donates a pair of electrons to one

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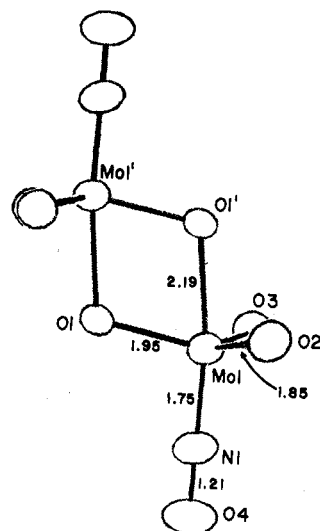
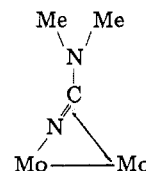


Figure 5. An ORTEP view of the $[\text{MoO}_3\text{NO}]_2$ skeleton of the $[\text{Mo}(\text{OPr-}i)_3\text{NO}]_2$ molecule showing the coordination geometry about molybdenum and average bond distances. The Mo-Mo distance is 3.335 (1) Å.

molybdenum atom while the other orthogonal allenic π orbital interacts with the other molybdenum atom. The bonding of the dimethylcyanide molecule to the Mo_2 group is schematically shown below.



The central NCN angle is 135° and the five nonhydrogen atoms of the Me_2NCN moiety lie in a plane. The bridging Me_2NCN group thus donates a nitrogen lone pair to one molybdenum atom and a CN π -electron pair to the other one.

$\text{Cp}_2\text{M}_2(\text{CO})_4$ and $\text{Mo}_2(\text{OPr-}i)_6$ react with nitric oxide (2 equiv) to yield $2\text{CpMo}(\text{CO})_2\text{NO}$ ⁶² and $[\text{Mo}(\text{OR})_3\text{NO}]_2$ ⁶³ compounds, respectively. The structure of the isopropoxy compound $[\text{Mo}(\text{OPr-}i)_3\text{NO}]_2$ has been determined by X-ray crystallographic studies;⁶³ the immediate coordination about the metal atoms in this centrosymmetric molecule is shown in Figure 5. Each molybdenum atom is in a trigonal-bipyramidal environment having a terminal NO and a long Mo-O bond of a bridging OPr-*i* ligand in the axial positions. The Mo-Mo separation of 3.335 (2) Å signifies an absence of metal-to-metal bonding.

In a formal sense, these reactions of M-M triple bonds with NO to give two Mo-NO groups correspond to the replacement of the $\text{Mo}\equiv\text{Mo}$ bond (a σ bond plus two π bonds) by two $\text{Mo}=\text{N}-\text{O}$: bonds. Again, there is a σ -electron pair and two π -electron pairs shared by the Mo atom and its partner, which is now a nitrogen atom instead of another molybdenum atom. The low values of $\nu(\text{NO})$ in $[\text{Mo}(\text{OR})_3\text{NO}]_2$ compounds, ca. 1630

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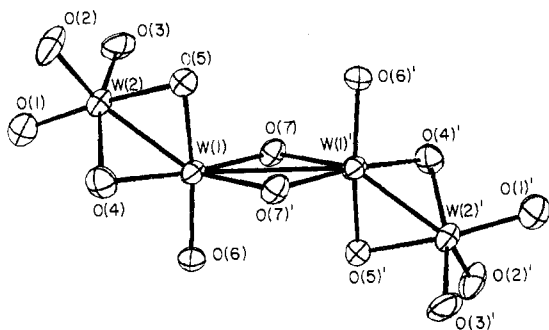


Figure 6. An ORTEP view of the $W_4(OPr-i)_{12}(HOPr-i)_2$ molecule showing only the W_4O_{14} skeleton. The molecule has C_2 symmetry. Some important parameters are: $W(1)-W(2) = 2.46 \text{ \AA}$; $W(1)-W(1)' = 3.80 \text{ \AA}$; $W(2)-W(1)-W(1)'$ angle = 140° .

cm^{-1} , are indicative of extensive molybdenum to NO π^* bonding.

The dinuclear alkoxides are also extremely reactive toward carbon monoxide and acetylenes.⁶⁴ With 2 equiv of CO, $Mo_2(OPr-i)_6$ yields a polymeric black crystalline compound of empirical formula $Mo(OPr-i)_3(CO)$ which shows $\nu(CO)$ at 1960, 1880, 1840, and 1820 cm^{-1} . Upon heating in vacuo, this compound, yields $Mo(CO)_6$ and $Mo_2(OPr-i)_8$ by sublimation and an as yet uncharacterized residue.

Polynuclear Complexes. The factors which lead to the formation of dinuclear compounds containing M–M bonds of multiple order n rather than to the formation of polynuclear or cluster compounds in which the metal atoms form n σ bonds with each other are not well understood. The size of the ligands is one important factor, and this is illustrated in the following.

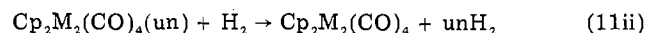
Alkoxides of Mo(III) and W(III) exist in the dinuclear M–M triple-bonded form only when the R group is bulky. For molybdenum, the neopentoxide exists in both dinuclear and polymeric forms. The ethoxide is tetrameric and diamagnetic in solution and shows ions $Mo_4(OEt)_{12}^+$, $Mo_3(OEt)_9^+$, and $Mo_2(OEt)_6^+$ in the mass spectrum.²⁷ For tungsten only the very bulky triethylsiloxy and *tert*-butoxy ligands give dinuclear

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compounds.²² The less bulky isopropoxy and neopentoxy groups give tetranuclear complexes. A black crystalline tetranuclear compound, $W_4(OPr-i)_{12}(HOPr-i)_2$, has been structurally characterized (see Figure 6) and is believed to have one of the two Pr-*i*-OH ligands coordinated at each terminal tungsten.⁶⁵ Formation of $W_4(OPr-i)_{12}(HOPr-i)_2$ may be viewed as the first step in a polymerization of $W_2(OPr-i)_6$ which is halted in this instance by the coordination of the Pr-*i*-OH ligands.

Since the chloro ligands in $M_2Cl_2(NR_2)_4$ compounds are substitutionally labile, reactions involving organometallic anions might allow for the synthesis of new polynuclear and cluster compounds incorporating the unsaturated M_2 moiety. This is an area of current investigation.

Potential Catalytic Reactions. The ability of compounds containing M–M triple bonds to enter into reactions well documented in mononuclear organometallic chemistry suggests that they may prove of catalytic significance. Indeed, one catalytic sequence (eq 11) is already suggested by the ability of the $Cp_2M_2(CO)_4$ compounds to coordinate unsaturated molecules that are four- but not two-electron donors.



Our attempts to hydrogenate the acetylene in $Cp_2Mo_2(CO)_4(HC_2H)$ in benzene at 25 and 70° C proved unsuccessful, though at 100° C ethylene is apparently formed.⁶⁶ The potential of $Cp_2M_2(CO)_4$ compounds for selective hydrogenation catalysis should be examined further.

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