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⑥ PROSPECTS FOR DINUCLEAR TRANSITION METAL CHEMISTRY
ILLUSTRATED BY RECENT ADVANCES IN THE CHEMISTRY OF
DIMOLYBDENUM AND DITUNGSTEN.

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PROSPECTS FOR DINUCLEAR TRANSITION METAL CHEMISTRY
ILLUSTRATED BY RECENT ADVANCES IN THE CHEMISTRY OF
DIMOLYBDENUM AND DITUNGSTEN

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Introduction

Dinuclear compounds of general formula M_2L_n , in which two directly bonded metal atoms M are surrounded by n ligands, L, are an important class of non-classical coordination complexes.¹ Synthetic procedures involving non-aqueous solvents and inert atmospheres have led to the discovery of dinuclear compounds for virtually all the transition elements. At this time molybdenum and tungsten show the most prolific dinuclear chemistry; literally hundreds of compounds are known with metal-to-metal bonds of order 1, 2, 3, 3.5, and 4. Recent reviews have dealt with the ground state properties and the electronic structures of compounds containing M-M quadruple and triple bonds.²⁻⁴ In this article the reactions of dinuclear compounds are emphasized. It is this author's view that reaction schemes evolved for mononuclear organotransition metal complexes will be applicable to dinuclear complexes and furthermore, that dinuclear compounds may provide building blocks for the systematic synthesis of new polynuclear and cluster compounds. It is with this prejudice that recent developments in the dinuclear chemistry of molybdenum and tungsten are discussed.

Pertinent to any discussion of a dinuclear compound is an appreciation of the metal-metal interactions, an assignment of M-M bond order, its meaning and significance. A satisfactory qualitative formulation of electronic structure and M-M bond order can generally be obtained by a simple analysis of the symmetry types of orbitals required to form M-L and M-M bonds and a consideration of the symmetry properties of the metal valence shell orbitals. A detailed knowledge of structural parameters is therefore necessary. In the absence of detailed calculations this approach must be considered qualitative and is deemed satisfactory only if the conclusions reached by arguments based on symmetry and electronic configuration are in agreement with the known ground state magnetic and structural properties of the dinuclear compound. A brief survey of structural and bonding considerations in dimolybdenum and ditungsten chemistry

illustrates these considerations.

M-M Bonds of Order Four

There is a large class of compounds containing a central Mo_2X_8 skeleton (X = halide, O, C, N, S) that has D_{4h} symmetry. See Figure 1a. Examples from this class include $\text{Mo}_2\text{Cl}_8^{4-5}$, $\text{Mo}_2(\text{CH}_3)_8^{4-6}$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4^7$, $\text{Mo}_2(\text{N}_2\text{CPh}_3)_4^8$ and $\text{Mo}_2(\text{S}_2\text{COEt})_4^9$. Closely related are compounds of the type $\text{Mo}_2\text{X}_{8-x}\text{Y}_x$. The ligand 2,6-dimethoxyphenyl (DMP) provides an example of the latter class where X = C, Y = O and x = 4, and the compound $\text{Mo}_2(\text{DMP})_4$ has the shortest Mo-to-Mo distance known.¹⁰ [See Table 1 for a comparison of M-M distance in compounds with M-M bonds of order 4.] In general $\text{Mo}_2\text{X}_{8-n}\text{Y}_n$ compounds adopt symmetrical structures in which the electronic configuration of each metal atom is the same.

In all of the above the formal oxidation number of molybdenum is two and each molybdenum atom forms four σ -bonds to ligand atoms using s, p_x , p_y and $d_{x^2-y^2}$ atomic orbitals. The remaining four valence electrons per molybdenum form a M-M quadruple bond: $\sigma^2(d_{z^2}-d_{z^2})$, $\pi^4(d_{xz}-d_{xz}, d_{yz}-d_{yz})$, $\delta^2(d_{xy}-d_{xy})$.

As a result of forming four M-X σ bonds and a M-M quadruple bond each molybdenum attains a 16 valence shell electronic configuration. Attainment of the inert gas structure, 18 valence shell electrons, is often achieved by the axial coordination (along the M-M axis) of neutral donor ligands to give compounds of the type $\text{M}_2\text{X}_8\text{L}_2$ as shown in Figure 1b. These M-L bonds may involve metal p_z atomic orbitals which are not otherwise utilized.

This qualitative description of the bonding, which was originally proposed by Cotton^{12,13} for the isoelectronic $\text{Re}_2\text{Cl}_8^{2-}$ anion, is deemed satisfactory because it accounts for (i) the diamagnetic nature of the compounds (ii) the exceedingly short Mo-Mo distances (see Table 1) and (iii) the eclipsed conformation of the ligands. The latter is required by the formation of the δ bond and is found even when bridging bidentate groups are not present. Recent SCF-X $_{\alpha}$ -SW calculations^{14,15} provide strong support for this picture of the M-M quadruple bond, particularly

when the metals are in low formal oxidation states and the ligands are simple as is the case for $\text{Mo}_2\text{Cl}_8^{4-}$. The metal-metal bonds are comprised mostly of d-d combinations. With higher oxidation states and more complicated ligands such as RCO_2^- a more complex orbital mixing pattern emerges in which M-M bonding interactions are distributed over more than one molecular orbital of the appropriate symmetry type.¹⁶ Nevertheless, the highest occupied molecular orbitals retain a high degree of metal-metal bonding character and for a number of dinuclear compounds which adopt structures akin to those shown in Figure 1 a fairly simple molecular orbital configuration and M-M bond order assignment is possible. For example, the series $\text{Mo}_2(\text{SO}_4)_4^{4-}$, $\text{Mo}_2(\text{SO}_4)_4^{3-}$ and $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ provide examples of compounds containing M-M bonds of order 4, 3.5 and 3 having molecular orbital configurations (HOMOs) M-M $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta^2\delta^{*1}$ and $\sigma^2\pi^4\delta^2\delta^{*2}$, respectively.

Even more recently SCF-X_α-SW calculations on $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$ and $\text{Rh}_2(\text{O}_2\text{CH})_4$ have been used to predict¹⁷ that the Rh-Rh bond order is one in dirhodium compounds, $\text{Rh}_2(\text{O}_2\text{CR})_4$, $\text{Rh}_2(\text{CO}_3)_4^{4-}$ and $\text{Rh}_2(\text{SO}_4)_4^{4-}$, all of which adopt the dimolybdenum tetracetate structure. The M-M MO configuration is predicted to be $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$. This form of bond order assignment has a direct parallel with that for the homo- and heterodinuclear molecules and ions of the first short period of elements, such as, N_2 , NO^+ , NO , NO^- and O_2 . Its success in transition metal chemistry for homodinuclear complexes of the 2nd and 3rd row transition elements, which have geometries of the type shown in Figure 1, follows because M-L σ and σ^* molecular orbitals lie, respectively, lower and higher in energy than the molecular orbitals derived from M-M interactions.

Rather interestingly tungsten has not been found to form W-W quadruple bonded complexes with nearly the same degree of proliferation as its neighbors in the periodic table, molybdenum and rhenium. Indeed, the first compound containing a W-W quadruple bond was only recently characterized structurally despite numerous earlier attempts. The mixed methyl-chloro-

ditungsten anion¹⁸ $W_2Me_{8-x}Cl_x^{4-}$, where $x \sim 2.5$ and the octamethyl-ditungsten anion,¹⁹ $W_2Me_8^{4-}$ were shown to adopt the $Mo_2Me_8^{4-}$ structure. A W-W distance of $2.263(2)\text{\AA}$ was found in the former compound.

Several attempts to prepare the carboxylato compounds $W_2(O_2CR)_4$ failed to yield crystals.^{20,21} Indeed, there must be some doubt that such compounds have ever been made since it has recently been shown that the reactions between $W(CO)_6$ and certain carboxylic acids yield trinuclear complexes which have a common central $[W_3O_2(O_2CR)_6]^{2+}$ unit.^{22,23} There is an equilateral triangle of tungsten atoms ($W-W = 2.75\text{\AA}$) and the two oxygen atoms not belonging to the RCO_2 moieties lie on a 3-fold axis of symmetry above and below the triangle so that the W_3O_2 group of atoms define a trigonal bipyramid.²²

In somewhat related reactions involving $M(CO)_6$ and aryl-formamidines the $M\equiv M$ compounds, $M_2(HC(NR)_2)_4$ were isolated for $M = Cr$ and Mo ²⁴, but for tungsten a rather unexpected and unusual compound was isolated, $W_2(\mu-CO)_2(\mu-CH(NR_2)_2)_2(CH(NR_2)_2)(RNCHN(R)CH_2)$.²⁵

There are also some compounds which may be presumed to have M-M quadruple bonds but which do not adopt structures akin to those in Figure 1. Two such compounds are $Mo_2(allyl)_4$ and $W_2(C_8H_8)_2$.

Molybdenum and chromium form isostructural allyl compounds $M_2(C_3H_5)_4$ which have a pair of bridging allyl groups and a pair of terminally bonded $\eta^3-C_3H_5$ ligands. The M-M distances are $1.97(3)$ and $2.183(2)\text{\AA}$ for $M = Cr$ ²⁶ and Mo ²⁷, respectively. These distances fall in the typical range observed for $M\equiv M$ bonds of these elements (see Table 1). Thus, the short M-M distance, the diamagnetism and the existence of the central M_2^{4+} moiety suggest the likelihood of a M-M quadruple bond in these compounds. Rather interestingly a Re-Re triple bond, $M-M\sigma^2\pi^4\delta^2\delta^*2$, has been proposed²⁸ for $Re_2(allyl)_4$ as a result of a structural characterization and a calculation using the Hartree-Fock-Rootham SCF method in the Fenske Hall approximation. Thus it seems likely that in $Mo_2(allyl)_4$, the basic Mo_2^{4+} unit containing a M-M quadruple bond is present.

In the air-stable compound $W_2(C_8H_8)_3$ there are two terminally

bonded $\eta^4\text{-C}_8\text{H}_8$ ligands (one per tungsten atom) and one bridging C_8H_8 ligand.²⁹ The W-W distance is $2.375(1)\text{\AA}$, which is longer by ca. 0.12\AA than many W-W triple bonded compounds discussed later. Despite the length of the bond a W-W quadruple bond was suggested²⁹ since (i) the diamagnetism requires an even bond order and (ii) a W-W double bond would be expected to be longer (see later). This last compound to be discussed, $\text{W}_2(\text{C}_8\text{H}_8)_3$, obviously has quite a different electronic structure than the M_2X_8 (Figure 1) type compounds.

If the C_8H_8 ligands are considered to carry no formal charge then the formal oxidation number of tungsten is zero. The bonding between two "naked" Group VI transition elements M_2 provides for the potential formation of a sextuple bond: $1\sigma_g^2(d_{z^2}-d_{z^2})$; $1\pi_u^4(d_{xz,yz}-d_{xz,yz})$; $1\delta_g^4(d_{xy,x^2-y^2}-d_{xy,x^2-y^2})$; $2\sigma_g^2(s-s)$. Recent SCF-X $_{\alpha}$ -SW calculations on Mo_2 do predict a sextuple bond of this type having the $2\sigma_g^2$ as the HOMO and contributing little to the net M-M bonding,³⁰ and, a Mo-Mo distance of 2.12\AA was calculated to have minimum energy cf. M-M distances for $\text{Mo}\equiv\text{Mo}$ in Table 1.

By metal atom-argon matrix condensation experiments, Mo_2 has actually been prepared and its U.V.-visible spectral properties recorded.³⁰ An extended Huckel-calculation was also undertaken³⁰ which led to the following orbital configuration $1\sigma_g^2, 1\pi_u^4, 2\sigma_g^2, 1\delta_g^4$. The HOMO $1\delta_g^4$ was considered non-bonding or at least not contributing to the net Mo-Mo bonding and thus a bond order of 4 was considered most appropriate for Mo_2 : cf. bond order 6 above.

M-M Bonds of Order Three

An extensive coordination chemistry surrounds compounds containing M-M triple bonds in which the metals atoms are either in oxidation state +1 or +3, and are coordinated to either 3, 4, 5 or 6 ligand atoms.³² Since the formation of a M-M triple bond requires the use of 3 metal valence orbitals, the total number of metal valence orbitals may vary from 6 to 9 and the number of

metal valence electrons from 12 to 18.

M_2X_6 compounds ($X = R$,^{33,34} NR_2 ^{35,36} and OR ³⁷⁻³⁹) adopt staggered ethane-like geometries; the central M_2E_3 skeleton ($E = C, N, O$) has D_{3d} symmetry and the M-M-E angles are ca. 104° . Figure 2 shows two views of the $Mo_2(NMe_2)_6$ molecule which is representative of this class of compounds. A number of closely related derivatives of general formula $M_2X_2(NR_2)_4$ where $X = Cl, Br, I, CH_3, C_2H_5$ and CH_2SiMe_3 , $R = Me$ or Et , have been made and have been shown to adopt 1,2 disubstituted ethane-like geometries.³³ From hydrocarbon solutions they crystallize in the anti-conformation but in solution both anti- and gauche-rotamers may be present. Figure 3 shows a view of the $W_2Cl_2(NEt_2)_4$ molecule which is representative of the $M_2X_2(NR_2)_4$ class of compounds. The central $W_2Cl_2N_4$ skeleton has C_{2h} symmetry.

In both the M_2X_6 and $M_2X_2(NR_2)_4$ classes of compounds there are triple bonds between metal atoms that are coordinated to only 3 ligand atoms. As a result of M-X σ -bonding and the formation of the M-M triple bond, the metal atoms use only 6 metal valence orbitals and achieve only a 12 valence shell electronic configuration. When $X = OR$ and NR_2 ligand to metal π -bonding is also possible and allows the metal atoms to increase their number of valence shell electrons. Direct evidence for ligand-to-metal π -bonding is seen by the short M-N and M-O distances and, in the case of $X = NR_2$, by the planarity of the M-NC₂ units.⁴⁰

In $Mo_2(OSiMe_3)_6(HNMe_2)_2$ ⁴¹ and $Mo_2(O_2COBu^t)_2(OBu^t)_4$ there are M-M triple bonds between molybdenum atoms that are coordinated to four ligand atoms in an approximately square planar manner. A view of the $Mo_2(OSiMe_3)_6(HNMe_2)_2$ molecule is shown in Figure 4. Note the partially staggered conformation of ligand atoms. A triple bond composed of one σ plus two equivalent π components [$\sigma(d_{z^2}-d_{z^2}), \pi(d_{xz}, d_{yz} - d_{xz}, d_{yz})$] places no restriction on conformation cf. $Mo_2Cl_8^{4-}$ and related molecules and ions where one δ -bond is formed by a specific $d_{xy}-d_{xy}$ interaction. In $Mo_2(O_2COBu^t)_2(OBu^t)_4$, however, there are bridging O_2COBu^t ligands which lead to an eclipsed Mo_2O_8 conformation.⁴²

The compounds $W_2Me_2(O_2CNet_2)_4$ and $W_2(O_2CNMe_2)_6$ have been shown⁴³ to adopt closely related structures having virtual C_{2v} symmetry and provide examples of compounds containing M-M triple bonds between metal atoms that are coordinated to 5 and 6 ligand atoms, respectively. The central $W_2C_2(O_2C)_4$ skeleton of the $W_2Me_2(O_2CNet_2)_4$ molecule is shown in Figure 5 and the $W_2(O_2C)_6$ skeleton of the $W_2(O_2CNMe_2)_6$ molecule is shown in Figure 6. In both molecules there are two bridging dialkylcarbamato ligands, $R_2NCO_2^-$, 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 non-bridging carbamato ligand, one oxygen atom from each of the two bridging carbamato groups and either an oxygen atom from a carbamato ligand in $W_2(O_2CNMe_2)_6$ or a methyl carbon atom in $W_2Me_2(O_2CNet_2)_4$. In $W_2(O_2CNMe_2)_6$ the second oxygen atoms from the non-bridging carbamato ligands which are axially aligned coordinate weakly along an extension of the W-W triple bond.

In all of the above 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 leads to a satisfactory qualitative formulation of structure.

The M-M triple bond is formed primarily by overlap of metal d_{z^2} orbitals to give a σ -component and metal d_{xz} , d_{yz} orbitals to give the π -components. This assumption has been supported by SCF-X $_{\alpha}$ -SW calculations on the molecules $Mo_2(OH)_6$, $Mo_2(NH_2)_6$ and $Mo_2(NMe_2)_6$.⁴⁴ For the M_2X_6 molecules the M-L σ -bonds may use metal s , p_x and p_y orbitals. Ligand to metal π -bonding, which is important when $X = OR$ and NR_2 , involves the metal d_{xy} and $d_{x^2-y^2}$ atomic orbitals.⁴⁴ In $Mo_2(OSiMe_3)_6(HNMe_2)_2$ and $Mo_2(O_2COBu^t)_2(OBu^t)_4$ the four quasi-square-planar M-L σ -bonds use s , p_x , p_y and $d_{x^2-y^2}$ metal orbitals. In the $W_2Me_2(O_2CNet_2)_4$ and $W_2(O_2CNMe_2)_6$ molecules the five quasi-coplanar bonds to the ligand atoms may use s , p_x , p_y , d_{xy} and $d_{x^2-y^2}$ orbitals. In the case of $W_2(O_2CNMe_2)_6$ the tungsten p_z atomic orbitals may also

be employed in the formation of the weak axial W-O σ -bonds.

In addition to the aforementioned compounds which involve triple bonds between metal atoms in their formal oxidation state +3, there are the compounds $(C_5R_5)_2M_2(CO)_4$, where $M = Cr, Mo, W$ and $R = H$ and Me , which involve metal atoms in a formal oxidation state +1 and may be considered to have M-M triple bonds on the basis of (i) their diamagnetism (ii) attainment of an 18 valence shell electronic configuration by the metal atoms and (iii) the short M-M distances.^{45, 46} Compare, for example, the Mo-Mo distances of 2.448(1) and 3.235(1) Å which are found in $Cp_2Mo_2(CO)_4$ ⁴⁶ and $Cp_2Mo_2(CO)_6$,⁴⁷ respectively. The M-M distances in these compounds are, however, longer than those found in the compounds containing M-M triple bonds when the metals ($M = Mo, W$) are in their formal oxidation state +3.

M-M Bonds of Order Two

At this time M-M bonds of order of two are relatively rare. Indeed, no compounds are known which have M-M double bonds unbridged by ligand atoms.⁴⁸ The compounds $Mo_2(OBu^t)_6(CO)$ ⁴⁹ ($Mo-Mo = 2.498(1) \text{ \AA}$) and $Mo_2(OPr^i)_8$ ⁵⁰ ($Mo-Mo = 2.523(1) \text{ \AA}$) have been structurally characterized and their geometries are shown in Figures 7 and 8, respectively. In both molecules the molybdenum atoms are coordinated to five ligand atoms. In $Mo_2(OBu^t)_6(CO)$ the geometry closely approaches that of a square based pyramid with the carbonyl carbon at the apical position while in $Mo_2(OPr^i)_8$ each molybdenum atom is at the center of a distorted trigonal bipyramid. The Mo-Mo distances fall between those of Mo-Mo triple bonds (see Table 2) and those of Mo-Mo single bonds,⁵¹ which together with the observed diamagnetism (this requires a M-M bond of even order) suggests a M-M bond of order two.

Certainly there is a metal-to-metal bond in $Mo_2(OPr^i)_8$. This is quite evident when a comparison is made between the closely related compounds $Mo_2(OPr^i)_8$ and $Mo_2(OPr^i)_6(NC)_2$.⁵² See Figure 8. In both compounds there is essentially trigonal bipyramidal coordination about each molybdenum atom and there is a

pair of bridging OPr^{i} ligands which form alternately long (axial) and short (equatorial) Mo-O bonds. The most striking differences between the two structures are (i) the Mo-to-Mo distances (see Figure 8) and the angles of the planar $\text{Mo}_2(\mu\text{-O})_2$ moieties. These differences are readily accounted for by simple ligand field considerations. For a five coordinate transition metal ion in a trigonal bipyramidal environment the metal atomic orbitals of lowest energy are the d_{xz} and d_{yz} atomic orbitals; these are not involved in M-L σ -bonding. For $\text{Mo}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$, which in a formal sense may be considered to have molybdenum atoms in an oxidation state of +2 (a linear M-N-O moiety may be viewed as $\text{M}^- \leftarrow (\text{NO}^+)$) there are four electrons in the (d_{xz}, d_{yz}) orbitals. These have the correct symmetry to bond to the $\text{NO}\pi^*$ orbitals and are extensively used in this back bonding as is indicated by the low value of $\nu(\text{N-O}) = 1630 \text{ cm}^{-1}$ and the short Mo-N distance $1.754(7) \text{ \AA}$.⁵³ In $\text{Mo}_2(\text{OPr}^{\text{i}})_8$, the formal oxidation number of molybdenum is +4. Each molybdenum atom has two 4d valence electrons which by $d_{xz}-d_{xz}$ and $d_{yz}-d_{yz}$ internuclear interactions may form a M-M double bond.

The tungsten compound $\text{W}_2(\mu\text{-CH}(\text{NR})_2)(\mu\text{-CO})_2(\text{CH}(\text{NR})_2)(\text{CH}_2\text{NRCHNR})$ has a W-W distance of $2.464(3) \text{ \AA}$.²⁵ The short W-W distance, together with the observed diamagnetism (which implies a M-M bond of even order, 0, 2, 4) suggests a W-W bond order of two. However, there must always be room for speculation about M-M bond order when there are atoms bridging both metals. This is particularly apparent in the chemistry of Mo-Mo single bonds which vary greatly in length depending upon oxidation state number and the character of the ligands present.⁵¹ Whenever bridging groups are present it is not possible to distinguish unequivocally between the direct coupling of electron spins (M-M bonding) and indirect coupling through the bridges.

M-M Bond Strengths

It is likely that there is at least a reasonable correlation between M-M bond length and bond strength, $D(\text{M-M})$. Compounds containing long unbridged M-M single bonds are known to react by homolytic or heterolytic M-M cleavage. For example, the M-M

distance in $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ are $3.138(3)$ (Fe-Fe)⁵⁴ and $3.235(1)\text{\AA}$ (Mo-Mo) and the enthalpies of M-M dissociation, $D(\text{M-M})$ are 56 kJ mol^{-1} ⁵⁴ and ca. 125 kJ mol^{-1} ,⁵⁵ respectively. For compounds with M-M quadruple bonds which have very short M-M distances there have been varying discordant estimates of $D(\text{M-M})$ ranging from the exceedingly large⁵⁶ to the surprisingly low.⁵⁷

To date, however, there has only been one estimate based on thermochemical arguments. For the compounds $(\text{Me}_2\text{N})_3\text{M}\equiv\text{M}(\text{NMe}_2)_3$ the heats of formation, $\Delta H_f^\circ(\text{g})$, were determined to be $(\pm 5 \text{ kJ mol}^{-1})$ 133.9 (M = Mo) and $137.5 \text{ kJ mol}^{-1}$ (M = W). The bond enthalpy of the triple bond, $D(\text{M}\equiv\text{M})$, can only be determined from these values if $\bar{D}(\text{M-N})$ is known and herein lies the rub. A "reasonable guess" can be made based on the known values of $\bar{D}(\text{M-N})$ for mononuclear compounds $\text{Mo}(\text{NMe}_2)_4$ and $\text{W}(\text{NMe}_2)_6$ for which $\bar{D}(\text{Mo-N}) = 255 \pm 5 \text{ kJ mol}^{-1}$ and $\bar{D}(\text{W-N}) = 226 \pm 5 \text{ kJ mol}^{-1}$. Using these values directly one obtains an estimated $D(\text{Mo}\equiv\text{Mo}) = 393 \text{ kJ mol}^{-1}$ and $D(\text{W}\equiv\text{W}) = 945 \text{ kJ mol}^{-1}$. Certainly it is most unlikely that the strengths of these triple bonds differ by so much, which merely points to the problem of taking even a "reasonable guess" at the value of $\bar{D}(\text{M-N})$ in $\text{M}_2(\text{NMe}_2)_6$ compounds. Nevertheless, it does seem that $D(\text{M}\equiv\text{M})$ are large in $\text{M}_2(\text{NMe}_2)_6$ compounds, though probably not as strong as the strongest of homonuclear bonds $D(\text{N}\equiv\text{N}) = 946 \text{ kJ mol}^{-1}$.

Solution Behavior

There is abundant spectroscopic evidence to support the view that dinuclear compounds with M-M multiple bonds exist in solution as discrete molecules or ions and, furthermore, that their configurations are essentially the same as those determined crystallographically. The Mo_2^{4+} unit ($\text{M}\equiv\text{M}$) even seems to exist as an aquo ion $\text{Mo}_2(\text{aq})^{4+}$ under certain conditions.⁵⁹ Since all dinuclear compounds with M-M bonds of non fractional order are diamagnetic their solution behavior may be investigated by nmr techniques.

^1H , ^{13}C and ^{31}P nmr studies of the neutral compounds $\text{Mo}_2\text{X}_4\text{L}_4$, where X = a halide or alkyl group and L = PR_3 or $\text{P}(\text{OR})_3$, show that in solution these compounds may be present in various isomers which result in the geometric arrangements of the two MoX_2L_2 units.^{60,61} The ethane-like compounds $\text{M}_2(\text{NR}_2)_3$ and $\text{M}_2\text{X}_2(\text{NR}_2)_4$ ($\text{M} \equiv \text{M}$) display interesting dynamic solution behavior. They are molecular propellers⁶² with each NC_2 unit acting as a blade. On the nmr time scale rotations about M-N bonds are fast and slow at high and low temperatures, respectively. The high and low temperature limiting ^1H nmr spectra for $\text{W}_2\text{Cl}_2(\text{NEt}_2)_4$ are shown in Figure 9 and are illustrative of this point. The low temperature spectrum is entirely consistent with the freezing on the nmr time scale of the structure found in the crystalline state which is shown in Figure 3. There are two types of N-Et groups, namely proximal and distal ethyl groups which, lying over and away from the metal-to-metal triple bond, are deshielded and shielded, respectively.⁶³ On raising the temperature these two ethyl groups interconvert more rapidly until the spectrum corresponds to the time averaged proximal \approx distal exchange resonances. At both high and low temperatures the $\text{Et } ^1\text{H}$ spectra correspond to ABX_3 spectra since the methylene protons are diastereotopic. From this and other observations on related compounds it has been argued that the only reasonable mechanism for proximal \approx distal exchange involves rotations about M-N bonds.⁶⁴

While the ^1H and ^{13}C nmr spectra of $\text{M}_2\text{X}_2(\text{NR}_2)_4$ compounds, where X = a halide, are consistent with the presence of only the anti-rotamer in solution, the dialkyl compounds ($\text{X} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) exist in solution in both anti and gauche conformers. In the gauche conformation the central $\text{M}_2\text{C}_2\text{N}_2\text{N}_2$ skeleton has C_2 symmetry with nitrogen atoms which are either mutually anti or anti-to-carbon atoms. The low temperature limiting ^{13}C nmr spectrum of $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ is shown in Figure 10 and illustrates this point. This spectrum can only be reconciled with the existence in solution of a mixture of anti and gauche conformers of $(\text{Et})(\text{Me}_2\text{N})_2\text{Mo} \equiv \text{Mo}(\text{NMe}_2)_2(\text{Et})$.⁶⁵ At higher temperatures the

proximal and distal N-Me resonances coalesce but anti \rightleftharpoons gauche isomerization remains slow on the nmr time scale. For $W_2(CH_2SiMe_3)_2(NEt_2)_4$ the energy of activation for anti-to-gauche isomerization was determined to be $100 \pm 8 \text{ kJ mol}^{-1}$.⁶⁶ The compounds $Mo_2Me_2(OBu^t)_4$ and $Mo_2Et(OBu^t)_5$ show variable temperature nmr spectra which are consistent with the view that rotation about the $Mo \equiv Mo$ bond is rapid on the nmr time scale, even at -80°C .⁶⁵ A significant difference between the dialkylamido and alkoxy compounds is the cogging effect of the NC_2 units in the former. Certainly as the bulkiness of the ligands decreases in these M_2X_6 compounds the barrier to $M \equiv M$ rotation is expected to get lower. Indeed calculations by Albright and Hoffman,⁶⁷ which ignore steric effects, predict eclipsed ground state geometries for the molecules M_2H_6 and M_2Cl_6 .

REACTIONS

Little is known about the pathways which lead to the formation of dinuclear compounds with $M-M$ multiple bonds. They may be formed by either the coupling of two mononuclear species or by the elimination of a dinuclear species from a cluster. The formation of $Mo_2(O_2CR)_4$ compounds ($M \equiv M$) in the reaction between $Mo(CO)_6$ and RCO_2H is an example of the former and the formation of $W_2(NMe_2)_6$ ($W \equiv W$) in the reaction between $[WCl_4]_x$ is an example of the latter.⁶⁸ Dinuclear compounds having $M-M$ multiple bonds are often readily accessible via reactions involving other $M-M$ multiple bonded compounds.

Ligand Substitutions.

Some of the reactions associated with the Mo_2^{4+} moiety ($Mo \equiv Mo$) are shown in Scheme 1. Analogous reactions involving the W_2^{4+} unit are not established. In Scheme 2 a number of reactions involving the M_2^{6+} ($M \equiv M$) unit are shown. Here an extensive dinuclear chemistry has been established for both molybdenum and tungsten, though differences do exist between the reactivity patterns of these elements.

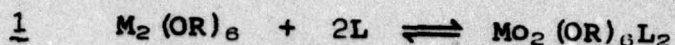
Two types of ligand substitution reactions are shown in

Schemes 1 and 2. The first involves the reaction of an M-X bond with an organic substrate containing an active hydrogen atom and is exemplified by the reaction of $M_2(NMe_2)_6$ compounds with alcohols which yield $M_2(OR)_6$ compounds with the elimination of amine. The second involves the nucleophilic displacement of one ligand by another which may or may not be accompanied by an overall change in charge of the complex. No doubt future syntheses along these lines will yield an even larger number of triple and quadruple M-M bonded compounds.

Little is known about the detailed mechanism of ligand substitution reactions at these dinuclear centers and this is clearly an important area for future research. It was 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 once formed slowly isomerizes to the gauche rotamer.^{68,69} 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 groups in square planar platinum(II) chemistry.⁷⁰ Such a general effect in dinuclear chemistry remains to be established, however.

Lewis Base Association and Dissociation

Certain compounds containing the central Mo_2^{4+} moiety ($M \equiv M$) will reversibly coordinate two neutral ligands along the axis of the Mo-Mo bond.⁴ This interconverts compounds of the type shown in Figure 1a with those in Figure 1b. The Mo-to-axially coordinated ligand atom distances are long and have little effect on the Mo-to-Mo distances. Similarly a number of alkoxy compounds containing the central M_2^{6+} moiety ($M \equiv M$) will reversibly add donor ligands according to the general eq. 1. The equilibrium position



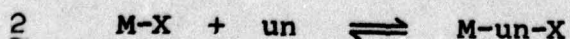
in 1 depends largely on the steric properties of R and L, the adducts being favored by less bulky R and L groups.³⁹

The compounds $Mo_2(OSiMe_3)_6(HNMe_2)_2$ ⁴¹ and $W_2(OPr^i)_6(py)_2$ ⁷¹ have been structurally characterized. In both compounds there are unbridged $M \equiv M$ bonds whose distances are within the range found for other compounds containing the central M_2^{6+} moiety. See Table 2. The MO_3N units are square based pyramids and the orientation of the metal-ligand bonds with respect to the M-M bond is partially staggered as shown in Figure 4.

In contrast to the above, where coordination of donor ligands occurs without disruption of the M-M multiple bond, the compounds $Cp_2M_2(CO)_4$ react with donor ligands (PR_3, CO) to form $Cp_2M_2(CO)_4L_2$ compounds with a great increase in metal-to-metal distance. Compare, for example, the Mo-to-Mo distances of 2.448(1) and 3.235(1) Å found in $Cp_2Mo_2(CO)_4$ ⁴⁶ and $Cp_2Mo_2(CO)_6$ ⁴⁷, respectively. The change in Mo-to-Mo distance may readily be accounted for by considerations of the electronic configuration of the metal atoms. In $Cp_2Mo_2(CO)_4$ each molybdenum attains an 18-valence shell electronic configuration as a result of forming a metal-to-metal triple bond. Addition of four electrons to the central $M \equiv M$ moiety and the formation of two M-L bonds reduces the M-M bond order to one in the adducts $Cp_2M_2(CO)_4L_2$. In this way an 18 valence shell configuration for each molybdenum atom is maintained.

Insertion Reactions

M-C (alkyl),⁷² M-N (dialkylamide)⁴⁰ and M-O (alkoxide)⁷³ bonds are known to undergo a large number of insertion reactions which may be represented by the general eq. 2, where $X = R, NR_2$ and OR



and un = an unsaturated molecule.

Thus far only the reactivity of M_2X_6 compounds ($X = R, NR_2,$ and OR) towards CO_2 has been investigated in detail. Insertion into $M-NR_2$ and $M-OR$ bonds occurs readily, but no reaction is observed for $M-R$ bonds. This is clearly seen in the reaction between $W_2Me_2(NEt_2)_4$ and CO_2 which gives $W_2Me_2(O_2CNEt_2)_4$.⁴³

Insertion into $M-NR_2$ bonds is irreversible and proceeds via an amine catalyzed sequence: $HNR_2 + CO_2 \rightleftharpoons HO_2CNR_2$; $M-NR_2 + HO_2CNR_2 \rightarrow M-O_2CNR_2 + HNR_2$.⁷⁴ Insertion into $M-OR$ bonds in the reaction between $M_2(OR)_6$ and CO_2 to give $M_2(OR)_4(O_2COR)_2$ compounds is readily reversible and occurs by a direct mechanism.⁴²

Reductive Elimination

A reductive elimination of an $X-Y$ group across a metal-to-metal bond of order n could yield a compound containing a metal-to-metal bond of order $n + 1$. Several of the compounds described previously should serve as excellent models for this type of reaction. For example, when the compound $Mo_2Et_2(NMe_2)_4$ reacts with CO_2 equimolar amounts of ethane and ethylene are liberated.⁶⁵ The molybdenum containing product was formulated as $Mo_2(O_2CNMe_2)_4$ ($M \equiv M$) on the basis of analytical and spectroscopic data. Thus it appears⁷⁵ that the reaction with CO_2 to give the carbamate ligand, $Me_2NCO_2^-$ promotes a β -hydrogen elimination reaction, $Et-M \equiv M-Et \rightarrow Et-M \equiv M-H + C_2H_4$, which is followed by a C-H reductive elimination across the $M-M$ bond, $Et-M \equiv M-H \rightarrow M \equiv M + Et-H$.

It has also been noted that both $Mo_2(CH_2SiMe_3)_6$ ³⁴ and $Mo_2(OPr^i)_6$ ⁷⁶ react with acetic acid to yield upon sublimation $Mo_2(OAc)_4$. Here a $M-M$ triple to quadruple bond transformation is unequivocally achieved (both of the starting compounds and the product have been structurally characterized by X-ray crystallography) but the detailed reaction pathway and the nature of the eliminated organic compounds are not yet known.

Oxidative Addition

The addition of an $X-Y$ substrate across a $M-M$ multiple bond of order n could yield a compound having an $M-M$ bond order $n - 1$. There are at present very few structurally characterized examples

of this type of conversion and in those that are known there is always an introduction of bridging atoms: an intramolecular Lewis Base association reaction accompanies or follows the oxidative addition process. A rationale for this observation may well rest in the fact that oxidative addition increases the effective positive charge on the metal atoms and that this is compensated for by an intramolecular Lewis Base association reaction. Since the formation of metal-ligand-metal bridges changes both the number of metal atom valence shell electrons and the hybridization of the metal atoms changes in M-M bond order from n to $n - x$ where $x = 1, 2, \dots, n$ are possible.

Addition of HX to the anion $\text{Mo}_2\text{X}_8^{4-}$, where $X = \text{Cl}$ or Br , has been shown under certain conditions to yield the anions $\text{Mo}_2(\text{H})\text{X}_8^{3-}$ which adopt structures akin to that of the $\text{Mo}_2\text{Cl}_9^{3-}$ anion, having a bridging hydrogen atom and a pair of bridging X groups. The anions $\text{Mo}_2(\text{H})\text{X}_8^{3-}$ are diamagnetic and have short Mo-to-Mo distances (for $X = \text{Cl}$, $\text{Mo-Mo} = 2.380(1)\text{\AA}$). The reaction can be considered to bring about a M-M quadruple to triple bond transformation, though the triple bond is obviously quite different from that previously described for the unbridged M_2X_6 compounds containing the central M_2^{6+} moiety.

The conversion of $\text{Mo}_2(\text{OPr}^i)_6$ to $\text{Mo}_2(\text{OPr}^i)_8$ (Figure 8) may be viewed as a metal-to-metal triple to double bond transformation, though as previously noted there must always be some room for speculation about M-M bond order in the presence of bridging ligand atoms. The reactions between $\text{Mo}_2(\text{S}_2\text{COEt}_2)_4$ ($\text{M} \equiv \text{M}$) and the halogens I_2 and Br_2 yield $\text{Mo}_2\text{X}_2(\text{S}_2\text{COEt})_4$ compounds ($X = \text{I}$ or Br).⁷⁸ The structure of the oxidative-addition products is shown in Figure 11. Each half of the centrosymmetric dinuclear molecule consists of a planar $\text{Mo}(\text{S}_2\text{CO})$ unit with a halogen atom bonded perpendicular to the mean MoS_4 plane. The two halves of the molecule are joined with each molybdenum atom lying over one of the S_2C groups of the other half of the molecule so that it is bonded to both S atoms (mean $\text{Mo-S} = 2.44\text{\AA}$) and the C atom ($\text{Mo-C} = 2.302\text{\AA}$). This side-on S_2C group may be viewed as a 4 electron π -donor. Attainment of an

18-electron valence shell configuration for each molybdenum atom is achieved by formation of a metal-to-metal single bond. The observed Mo-to-Mo distance, 2.720 (3) Å, is well within the range observed for Mo-Mo single bonds. The change in M-M bond order, four to one, which accompanies the reaction could not have been predicted but may be rationalized with judicious hindsight: (1) The structural characterizations of $\text{Mo}_2\text{X}_2(\text{S}_2\text{COEt})_4$ compounds provide the first examples of π -bonded S_2COEt group. (2) The structure of a number of closely related $\text{M}_2\text{X}_2(\text{O}_2\text{CNR}_2)_4$ compounds are believed to adopt the $\text{W}_2\text{Me}_2(\text{O}_2\text{CNET}_2)_4$ ($\text{M} \equiv \text{M}$) structure⁶⁶ shown in Figure 5. (3) The rationale must lie in the different nature of the O_2CNR_2 and S_2COR ligands and their ability to respond to the needs of the M_2^{4+} and M_2^{6+} dinuclear centers. There must, however, be a delicate balance between M-L and M-M interactions in these M_2^{6+} systems. Further it may be noted that attempts to prepare $\text{Mo}_2(\text{S}_2\text{CNET}_2)_4$ ($\text{M} \equiv \text{M}$) by the reaction of $\text{Mo}_2\text{Cl}_8^{4-}$ with $\text{NaS}_2\text{CNET}_2$ yielded a dimer having the expected empirical formula but having the structure shown schematically in Figure 12.⁷⁹ Although the detailed mechanism leading to the formation of this product is not known it may be viewed as a formal C = S addition to the M-M quadruple bond. Here a really very surprising difference is seen between the xanthate, S_2COR and the dithiocarbamate ligand, S_2CNR .

Clearly the reactivity of compounds containing M-M multiple bonds towards oxidative addition reactions is going to be as complex and is at present much less predictable than analogous reactions involving mononuclear transition metal complexes. This is particularly apparent from the unusual modes of bonding and reactivity of S_2CX ligands discussed above.

Reactions of M-M Multiple Bonds with Small Unsaturated Molecules

$\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds react in solution under very mild conditions with a large number of unsaturated organic molecules, un, to form 1:1 adducts $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{un})$, where $\text{M}=\text{Mo}$ and W . The compounds where $\text{M} = \text{Mo}$ and un = $\text{PhC}\equiv\text{CPh}$,⁸⁰ $\text{EtC}\equiv\text{CEt}$,⁸⁰ $\text{HC}\equiv\text{CH}$,⁸⁰ $\text{CH}_2=\text{C}=\text{CH}_2$ ⁸¹ and Me_2NCN ⁸² have been characterized by X-ray

crystallography. In all cases un acts as a four electron donor ligand and spans the Mo_2 bond in a manner shown schematically in Figure 13. The Mo-to-Mo distance increases in length from $2.448(1)\text{\AA}$ in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to $2.974(1)$, $3.015(1)$ and $3.117(1)\text{\AA}$ in the adducts $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{un})$, when $\text{un} = \text{HC}\equiv\text{CH}$,⁸⁰ Me_2NCN ⁸² and $\text{CH}_2=\text{C}=\text{CH}_2$,⁸¹ respectively. This is tantamount to a M-M triple to single bond transformation.

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

Allene bridges the Mo-Mo bond obliquely, a manner which allows one of the allene π -orbitals to donate an electron pair to one molybdenum while the other orthogonal allenic π -orbital interacts with the other molybdenum atom.

In the dimethylcyanamide adduct the central NCN angle is 135° and the five non-hydrogen 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.

In a recent communication Stone and his co-workers⁸³ have shown that the reaction between $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds ($\text{M} \equiv \text{M}$, $\text{M} = \text{Cr}$, Mo) and acetylenes proceed in a manner shown in Scheme 3 under more forcing conditions. Here the oligomerization of acetylenes about a dinuclear metal center is seen to proceed in a sequential manner: $\text{M}_2\text{C}_2 \longrightarrow \text{M}_2\text{C}_4 \longrightarrow \text{M}_2\text{C}_6 \longrightarrow \text{M}_2\text{C}_8$ and the metal-metal interactions are seen to change in response to the binding requirements of the hydrocarbon unit: an 18 valence shell electronic configuration is maintained by the metal atoms.

The alkoxides $\text{Mo}_2(\text{OR})_6$, where $\text{R} = \text{Bu}^t$ and Pr^i , have also been found to react rapidly at room temperature with acetylenes, allenes and cyanimides but at this time no structural data is available on the products of addition.⁷⁶ Some interesting differences might be

expected here since the nature of the M-M triple bonds in the compounds $\text{Cp}_2\text{M}_2(\text{CO})_4$ and $\text{M}_2(\text{OR})_6$ differ markedly.

$\text{Mo}_2(\text{OR})_6$ compounds ($\text{R} = \text{Bu}^t$ and Pr^i) react readily with carbon monoxide to give $\text{Mo}(\text{CO})_6$ and oxidized molybdenum alkoxides.⁷⁰ The reaction between $\text{Mo}_2(\text{OBu}^t)_6$ and CO has been shown to proceed via an initial reversible step involving addition of CO across the M-M bond to give $\text{Mo}_2(\text{OBu}^t)_6\text{CO}$,⁴⁹ the structure of which is shown in Figure 7. This is a carbene-like addition and brings about a metal-to-metal triple to double bond transformation, $\text{M}\equiv\text{M} + \text{X}$:

$\rightarrow \begin{array}{c} \text{X} \\ \diagup \quad \diagdown \\ \text{M} = \text{M} \end{array}$, which could be a general reaction for a number of X: substrates eg X: = RNC, R_2C and organometallic carbene-like molecules such as $\text{Fe}(\text{CO})_4$ and PtL_2 .⁸⁴

$\text{Cp}_2\text{M}_2(\text{CO})_4$ and $\text{Mo}_2(\text{OR})_6$ react with nitric oxide to yield 2 $\text{CpM}(\text{CO})_2\text{NO}$ ⁸⁵ and $\text{Mo}_2(\text{OR})_6(\text{NO})_2$ ⁵² compounds, respectively. Nitric oxide cleaves the $\text{M}\equiv\text{M}$ bond. In a formal sense, these reaction of M-M triple bonds with NO to give two M-NO groups correspond to the replacement of the $\text{Mo}\equiv\text{Mo}$ bond (a σ bond plus two π -bonds) by two $\text{Mo}\equiv\text{N}-\text{O}$ bonds. Again there is a σ -electron pair and two π -electron pairs shared by a molybdenum atom and its partner, which is now a nitrogen atom instead of another molybdenum atom. The values of $\nu(\text{NO})$ in $\text{Mo}_2(\text{OR})_6(\text{NO})_2$ compounds ca. 1630 cm^{-1} are indicative of extensive molybdenum to nitrogen π -bonding.

The structure of $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ is shown in Figure 8 where a comparison is made to the related dinuclear compound $\text{Mo}_2(\text{OPr}^i)_6$ ($\text{Mo} = \text{Mo}$). The bonding in these compounds was previously discussed. The absence of any significant M-M bonding in the nitrosyl compound is not only evident from the Mo-Mo distance, 3.325 \AA , but also from the chemical reactivity of $\text{Mo}_2(\text{OR})_6(\text{NO})_2$ compounds with donor ligands such as pyridine which yield dinuclear complexes $\text{Mo}(\text{OR})_3(\text{NO})(\text{L})$.⁷⁶ The related compound $\text{Mo}_2(\text{OBu}^t)_6(\text{NO})(\text{py})$ has recently been structurally characterized.⁸⁶ Again there is trigonal bipyramidal coordination about tungsten with the nitrogen atoms of the nitrosyl and pyridine ligands forming, respectively, short and long axial bonds.

Building Blocks for Clusters

The factors which lead to the formation of dinuclear compounds containing M-M bonds of multiple order rather than to the formation of polynuclear or cluster compounds in which the metal atoms form a greater number of σ -bonds, both M-M and M-L through the agency of bridging ligand atoms is not well understood. The size of the ligands and their ability to form bridges are, however, clearly two important factors and this is illustrated in the following.

1. Cl-for-NMe-groups substitution in $M_2(NMe_2)_6$ compounds yield ultimately cluster compounds $[MCl_3]_x$, though the initial steps involve dinuclear compounds of the ethane-like type eg. $M_2Cl_2(NMe_2)_4$ compounds.⁸⁷

2. Alkoxides of Mo(III) and W(III) exist in the dinuclear M-M triple bonded form only when the R group is bulky.³⁹ For molybdenum the neopentoxide exists in both the dinuclear and polymeric forms. The ethoxide is tetrameric and diamagnetic in solution and shows ions $Mo_4(OEt)_{12}^+$, and $Mo_3(OEt)_9^+$ in the mass spectrometer.³⁹ For tungsten only the very bulky triethylsiloxy and t-butoxy ligands give dinuclear compounds. The less bulky isopropoxy and neopentoxy groups give tetranuclear compounds.⁸⁸ A black crystalline tetranuclear compound has been structurally characterized⁸⁸ and the W_4O_{14} skeleton is shown in Figure 14.

Originally this compound was believed to be $W_4(OPr^i)_{12}(HOPr^i)_2$ having one of the Pr^iOH ligands coordinated to each of the terminal tungsten atoms.³² Viewed in this manner the compound provides a model for the first step of the polymerization of $W_2(OPr^i)_6$, a process which is in this cases halted by the coordination of Pr^iOH to the terminal tungsten atoms. However, recent studies cast doubt about the validity of this view. There is no direct spectroscopic evidence for the presence of the hydroxyl group.⁸⁸ Furthermore, addition of pyridine, even dissolving the compound in pyridine does not lead to the expected displacement of isopropanol and formation of $W_2(OPr^i)_8(py)_2$. The latter is formed in the reaction between $W_2(NMe_2)_6$ and Pr^iOH in pyridine and has been shown⁷¹ to

adopt a structure akin to that of $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$ (see Figure 4) which has a $\text{M} \equiv \text{M}$ unbridged by ligand atoms.

A plausible rationale for the above and for the observed $\text{W}(2)-\text{W}(1)$ distance of 2.46 \AA , which is longer than any other $\text{W} \equiv \text{W}$ bond distance (see Table 2), is that the tetranuclear compound is a product of oxidative addition of a $\text{Pr}^i\text{O}-\text{H}$ group to a $\text{W} \equiv \text{W}$ bond: $\text{W}_2(\text{OPr}^i)_6 + \text{Pr}^i\text{O}-\text{H} \longrightarrow [\text{W}_2(\mu\text{-H})(\text{OPr}^i)_7]_2$. The centrosymmetric molecule would then contain tungsten atoms in their formal oxidation state 4; each tungsten atom would be in a six coordinate environment and the hydrogen atoms would bridge $\text{W}(2)-\text{W}(1)$ and $\text{W}(1)'\text{-W}(2)'$ in positions which are respectively trans to the long terminal Pr^iO ligands $\text{O}(2)$ and $\text{O}(2)'$. The presence of the bridging hydrogen atoms remains to be established, however.

A very recent report by McCarley and his co-workers⁸⁹ describes the dimerization of two $\text{M}-\text{M}$ quadruply bonded units to give tetrametal analogue of cyclobutadiyne: $2 \text{Mo}_2\text{X}_4(\text{PR}_3)_2(\text{MeOH})_2 \longrightarrow \text{Mo}_4\text{X}_8(\text{PR}_3)_4 + 4 \text{MeOH}$, see scheme 4.

Potential Catalytic Reactions

The ability of compounds containing $\text{M}-\text{M}$ multiple bonds to enter into reactions well documented in mononuclear organotransition metal chemistry suggests that they may prove of catalytic significance. Indeed certain catalytic sequences are already suggested. For example, the ability of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to coordinate unsaturated molecules that are four-but not two-electron donors raises the potential for selective hydrogenation catalysis: $\text{Cp}_2\text{Mo}_2(\text{CO})_4 + \text{un} \longrightarrow \text{Cp}_2\text{Mo}_2(\text{CO})_3(\text{un})$; $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{un}) + \text{H}_2 \longrightarrow \text{Cp}_2\text{Mo}_2(\text{CO})_4 + \text{unH}_2$. In the absence of molecular hydrogen and under slightly more forcing conditions catalytic cyclooligomerizations may prove possible. This is suggested by the reaction sequences shown in Scheme 3 where $\text{un} = \text{RC}\equiv\text{CR}$.

Conclusions

1. Dinuclear compounds containing $\text{M}-\text{M}$ multiple bonds undergo reaction of the type well documented in mononuclear transition metal chemistry. However, at a dinuclear center multistep processes

are more often triggered. This is well exemplified by oxidative addition reactions, $\text{Mo}_2^{4+} \rightarrow \text{Mo}_2^{6+}$, which occur with Lewis Base association via intramolecular metal-ligand-metal bridge formation.

2. Reactions which lead to stepwise changes in M-M bond order are known and may involve either a change in oxidation state or coordination number of the metal, or both. At present it is not possible to predict generalized reactions which will yield such changes in M-M bond order because of the uncertainties that surround accompanying ligand rearrangements.

3. Little detailed mechanistic information is currently available about reactions at dinuclear centers. This clearly is an important area for future research.

4. Small unsaturated molecules ($\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{C}=\text{C}$, $\text{C}=\text{O}$) react readily with M-M multiple bonds. Often, but not exclusively, the unsaturated molecule coordinates to the dinuclear center in a manner which is quite different from that observed in mononuclear chemistry eg. as shown in Figure 12. The potential for carrying out catalytic reactions involving these unsaturated molecules has been recognized.

5. The formation of new cluster or polynuclear compounds from dinuclear M-M multiply bonded precursors has been recognized and indeed shown to occur when steric factors permit association. The potential for heteronuclear cluster synthesis by metathetic reactions involving organometallic anions and dinuclear complexes containing substitutionally labile ligands such as Cl remains to be explored.

6. Finally it should be noted that this account has dealt exclusively with homodinuclear compounds of molybdenum and tungsten. Synthetic routes to mixed metal dimers such as $\text{MoW}(\text{O}_2\text{CCMe}_3)_4^{90}$ ($\text{Mo} \equiv \text{W}$) are becoming known. It seems likely that in the near future heterodinuclear compounds containing more exotic combinations of metals will be prepared. The recent isolation by Wilkinson and his co-workers⁹¹ of $(\text{Me}_3\text{SiCH}_2)_2\text{M}(\text{CH}_2-\text{S}(\text{Me})_2\text{CH}_2)-\text{M}(\text{PR}_3)_3$ ($\text{M} \equiv \text{Mo}$, 2.16 Å) shows that a M-M quadruple bond can be

supported between two molybdenum atoms which differ in both oxidation state (Mo^{I} , Mo^{III}) and coordination number (4, 3). The formation of isoelectronic series of dinuclear transition complexes involving say $\text{W} \equiv \text{W}$ and $\text{Ta} \equiv \text{Re}$ centers (cf $\text{N} \equiv \text{N}$ and $\text{C} \equiv \text{O}$) seems very likely.

Acknowledgements

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Table 1. Metal-Metal Distances in Some Compounds Containing M-M Quadruple Bonds (M = Mo, W)

Compound	M-M Å	Ref.
Mo ₂ (2,6-C ₆ H ₃ (OMe) ₂) ₄	2.065 (1)	a
Mo ₂ (O ₂ CH) ₄	2.091 (2)	b
Mo ₂ (O ₂ CCMe ₃) ₄	2.088 (1)	c
Mo (O ₂ CCF ₃) ₄	2.090 (4)	d
K ₂ Mo ₂ Cl ₈ ·2H ₂ O	2.139 (4)	e
Li ₄ Mo ₂ Me ₈ ·4THF	2.147 (3)	f
K ₄ Mo ₂ (SO ₄) ₄ ·2H ₂ O	2.110 (3)	g
Mo ₂ (S ₂ COEt) ₄ ·2THF	2.125 (1)	h
Mo ₂ (allyl) ₄	2.183 (2)	i
MoW (O ₂ CCMe ₃) ₄	2.080 (1)	j
Li ₄ W ₂ Cl _x Me _{8-x} ·4THF	2.261 (2)	k
W ₂ (C ₈ H ₈) ₃	2.375 (1)	l

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Table 2. Lengths of M-M Triple Bonds in Compounds of the Types M_2L_6 , $M_2L_4X_2$ and Some of their Adducts

Compound	M-M, Å	
	M = Mo	M = W
$M_2(CH_2SiMe_3)_6$	2.167 (?) ^a	2.255 (2) ^b
$M_2(NMe_2)_6$	2.214 (3) ^c	2.294 (2) ^d
$M_2(OCH_2CMe_3)_6$	2.222 (2) ^e	---
$M_2(OSiMe_3)_6(NHMe_2)_2$	2.242 (1) ^f	---
$M_2(OPr^i)_6(py)_2$	---	2.300 (1) ^g
$M_2(OBu^t)_4(O_2COBu^t)_2$	2.241 (1) ^h	---
$M_2(O_2CNMe_2)_6$	---	2.279 (1) ⁱ
$M_2Me_2(O_2CNET_2)_4$	---	2.272 (1) ⁱ
$M_2Me_2(NMe_2)_4$	2.201 (1) ^j	---
$M_2Me_2(NEt_2)_4$	---	2.291 (1) ^k
$M_2Cl_2(NMe_2)_4$	2.201 (2) ^l	2.285 (2) ^l
$M_2Cl_2(NEt_2)_4$	---	2.301 (1) ^m
$M_2Br_2(NEt_2)_4$	---	2.301 (2) ⁿ
$M_2I_2(NEt_2)_4$	---	2.300 (4) ⁿ

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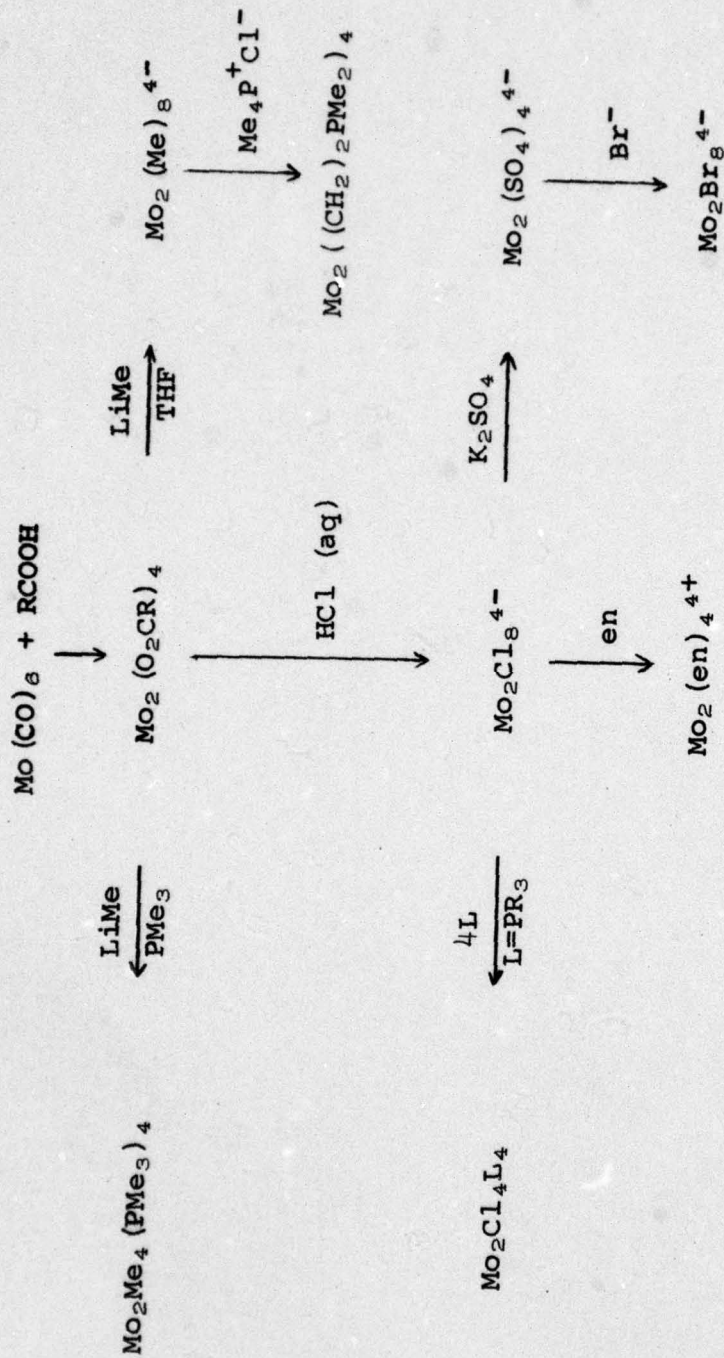
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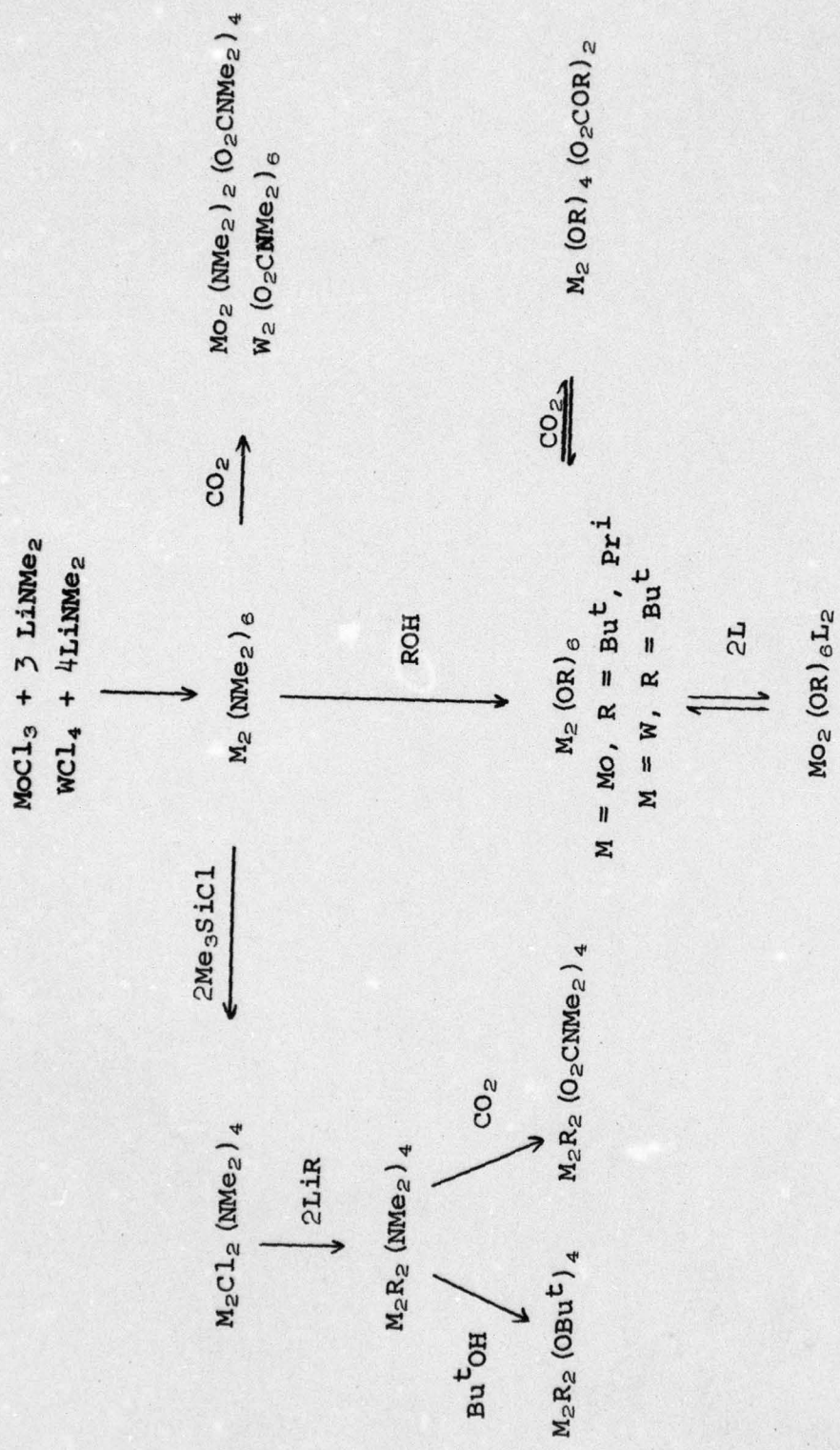
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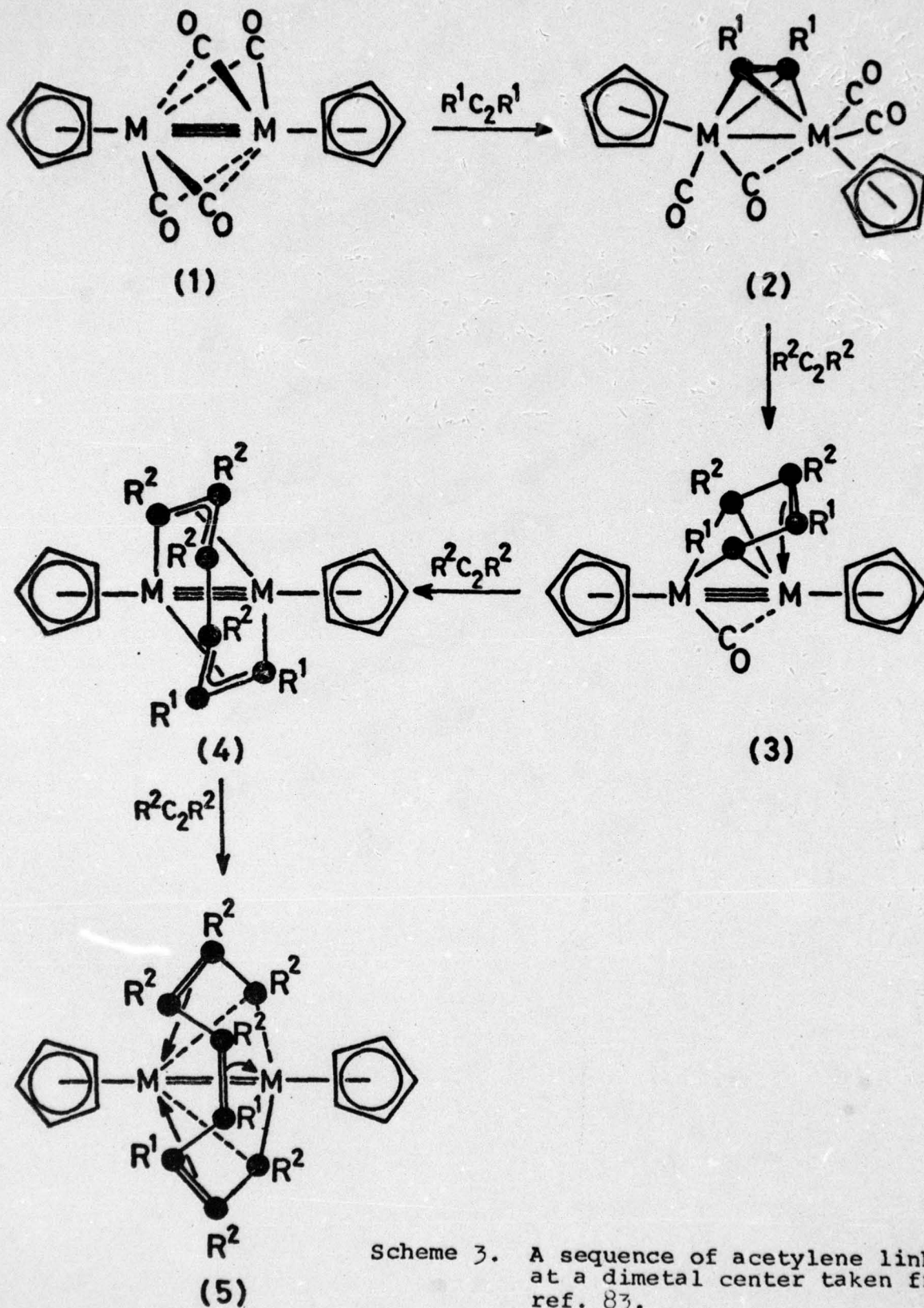
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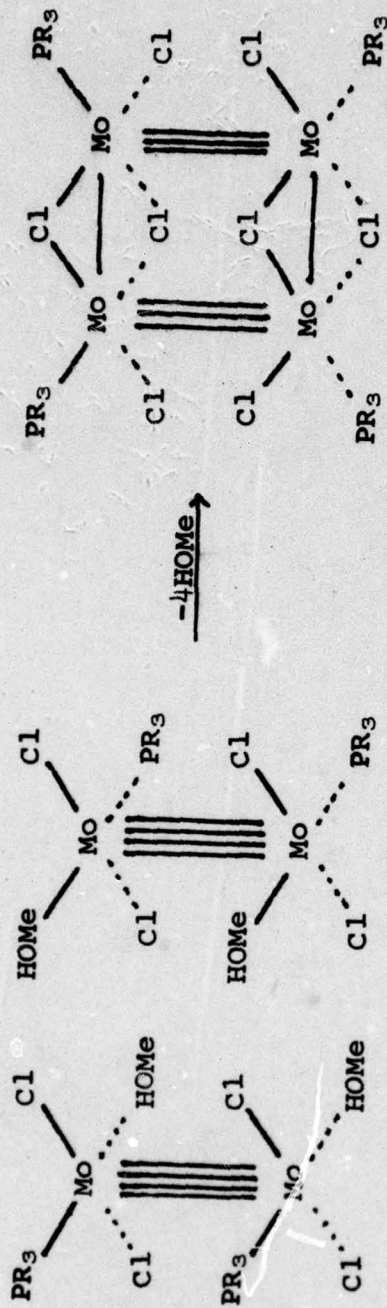
Scheme 1. Reactions Leading to and Interconverting Dimolybdenum Compounds Containing M-M Quadruple Bonds.



Scheme 2. Some Reactions leading to and Interconverting Dinuclear Compounds Containing M-M Triple Bonds (M = Mo and W).



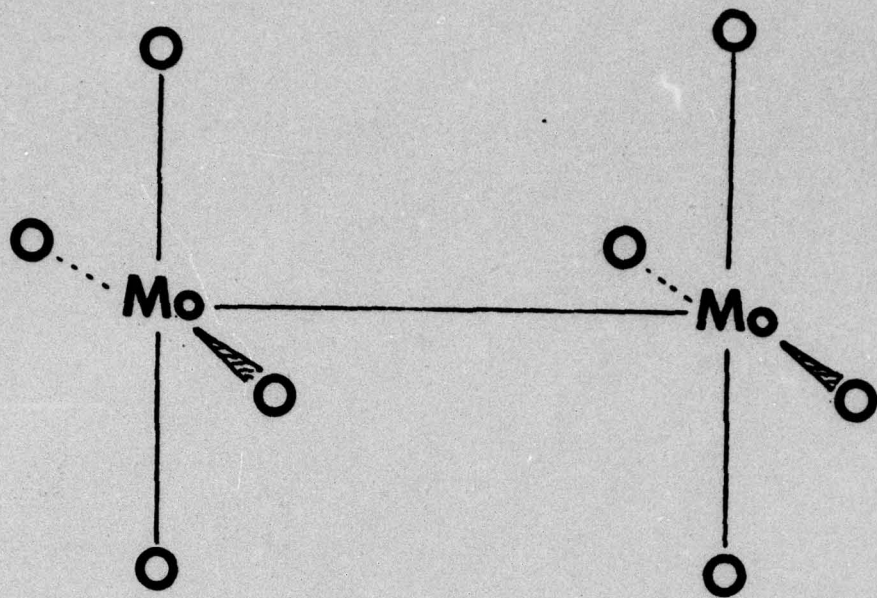
Scheme 3. A sequence of acetylene linking at a dimetal center taken from ref. 83.



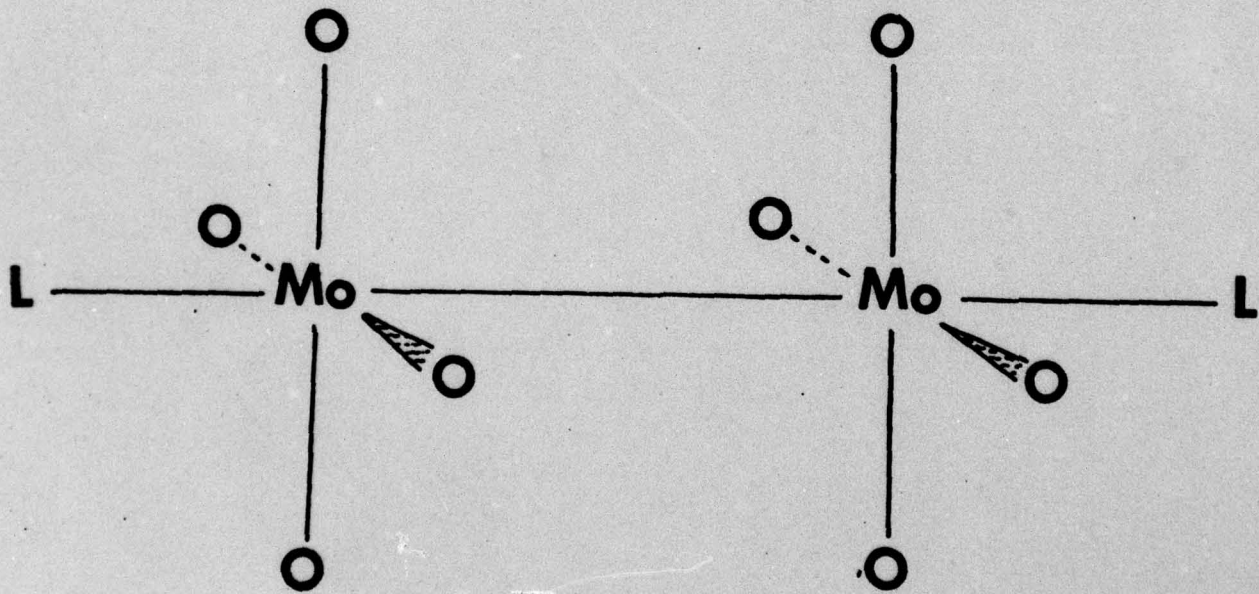
Scheme 4. Dimerization of $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_2(\text{HOME})_2$ ($\text{Mo} \equiv \text{Mo} = 2.143(1)\text{\AA}$) to give $\text{Mo}_4\text{Cl}_8(\text{PR}_3)_4$ ($\text{Mo} \equiv \text{Mo} = 2.211(3)\text{\AA}$; $\text{Mo} - \text{Mo} = 2.901(2)\text{\AA}$) by elimination of MeOH and formation of chloro bridges.

Captions to Figures

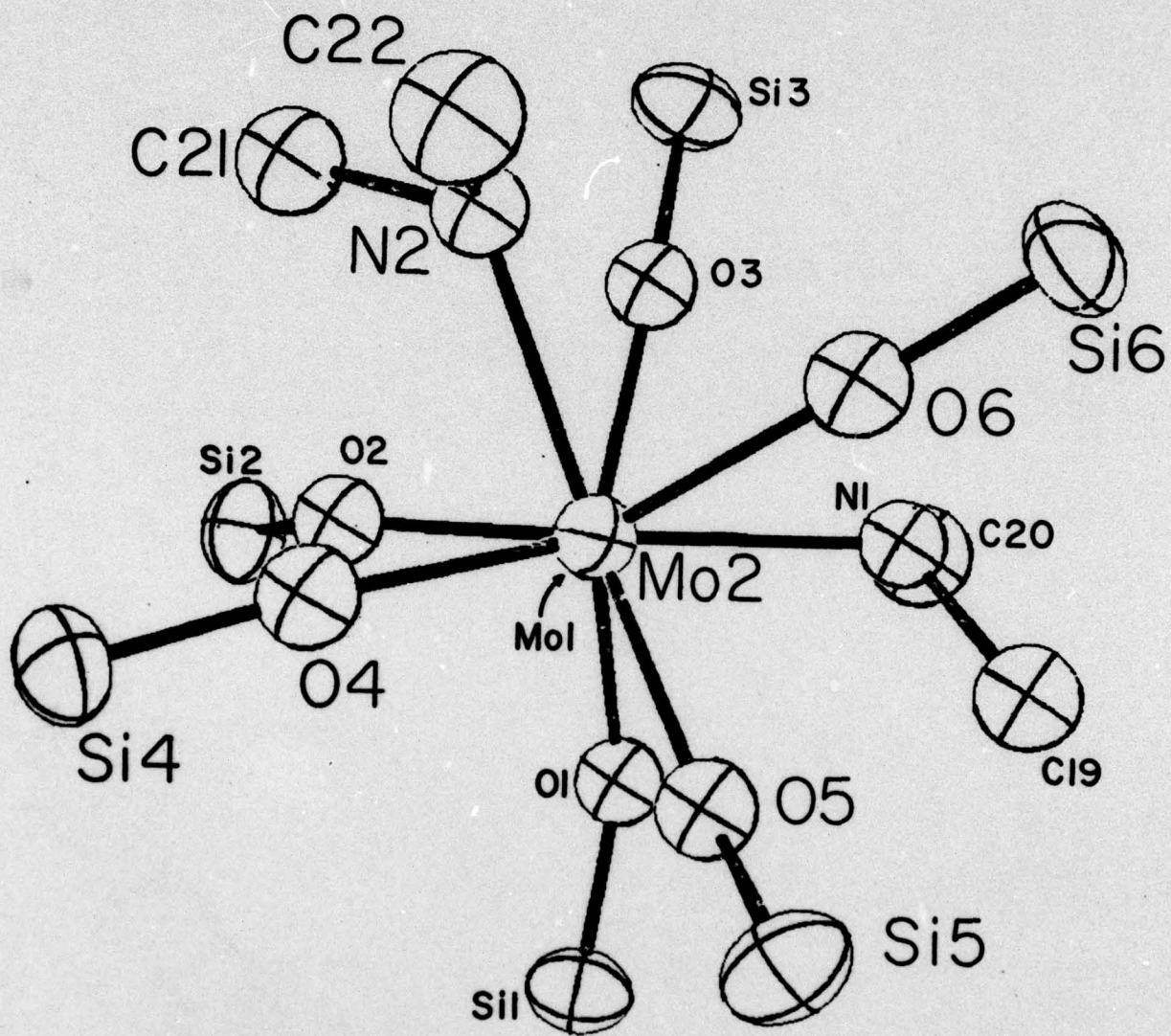
- Figure 1.** Schematic representations of the two geometries commonly found for Mo_2^{4+} containing compounds ($\text{Mo} \equiv \text{Mo}$) having D_{4h} symmetry.
- Figure 2.** Two ORTEP views of the $\text{Mo}_2(\text{NMe}_2)_6$ molecule showing how the $\text{Mo}_2(\text{NC}_2)_6$ moiety has virtual D_{3d} symmetry.
- Figure 3.** An ORTEP view of the $\text{W}_2\text{Cl}_2(\text{NEt}_2)_4$ molecule. The central $\text{W}_2\text{Cl}_2\text{N}_4$ group has C_{2h} symmetry.
- Figure 4.** The $\text{Mo}_2(\text{OSi})_6(\text{NC}_2)_2$ skeleton of the $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$ molecule viewed down the Mo-Mo triple bond showing the partially staggered conformation of the ligand atoms.
- Figure 5.** The central $\text{W}_2\text{C}_2(\text{O}_2\text{C})_4$ skeleton of the $\text{W}_2(\text{CH}_3)_2(\text{O}_2\text{CNMe}_2)_4$ molecule which has virtual C_{2v} symmetry.
- Figure 6.** The central $\text{W}_2(\text{O}_2\text{C})_6$ skeleton of the $\text{W}_2(\text{O}_2\text{CNMe}_2)_6$ molecule with some pertinent bond distances.
- Figure 7.** The $\text{Mo}_2(\text{O})_6(\text{CO})$ skeleton of the $\text{Mo}_2(\text{OBu}^t)_6(\text{CO})$ molecule together with some pertinent bond distances.
- Figure 8.** The central skeletons of the $\text{Mo}_2(\text{OPr}^i)_6$ and $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ molecules together with some pertinent bond distances. These views emphasize how each molybdenum atom is in a distorted trigonal bipyramidal environment.
- Figure 9.** The high and low temperature limiting ^1H nmr spectra of anti- $\text{W}_2\text{Cl}_2(\text{NET}_2)_4$ in toluene- d_8 recorded at 100 MHz.
- Figure 10.** The low temperature limiting ^1H decoupled ^{13}C nmr spectrum of anti and gauche $\text{Mo}_2(\text{Et})_2(\text{NMe}_2)_4$ obtained at -60°C in toluene- d_8 at 270 MHz.
- Figure 11.** An ORTEP view of the $\text{Mo}_2\text{I}_2(\text{S}_2\text{COEt})_4$ molecule viewed perpendicular to the Mo - Mo bond.
- Figure 12.** Structural representation of the compound once thought to be $\text{Mo}_2(\text{S}_2\text{CNPr}_2)_4$ ($\text{Mo} \equiv \text{Mo}$) but shown by X-ray crystallography to be $[(\text{Pr}_2\text{NCS}_2)(\text{Pr}_2\text{NCS})(\mu\text{-S})\text{Mo}]_2$.
- Figure 13.** Schematic representations of the $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{un})$ molecules where A, un = $\text{RC} \equiv \text{CR}$; B, un = allene and C, un = Me_2NCN emphasizing the coordination of the central $\text{Mo}_2(\text{un})$ group.
- Figure 14.** An ORTEP view of the W_4O_{14} skeleton of the $\text{W}_2(\text{OPr}^i)_{14}(\text{H})_2$ molecule. The molecule has C_i symmetry. The locations of the hydride groups are not known but are believed to be bridging $\text{W}(2)\text{-W}(2)$ trans to $\text{W}(2)\text{-O}(2)$ and $\text{W}(1)'\text{-W}(2)'$ trans to $\text{W}(2)'\text{-O}(2)'$. Some pertinent distances and angles are $\text{W}(1)\text{-W}(2) = 2.46\text{\AA}$, $\text{W}(1)\text{-W}(1)' = 3.30\text{\AA}$ and $\text{W}(1)\text{-W}(1)'\text{-W}(2)'$ angle = 140° .

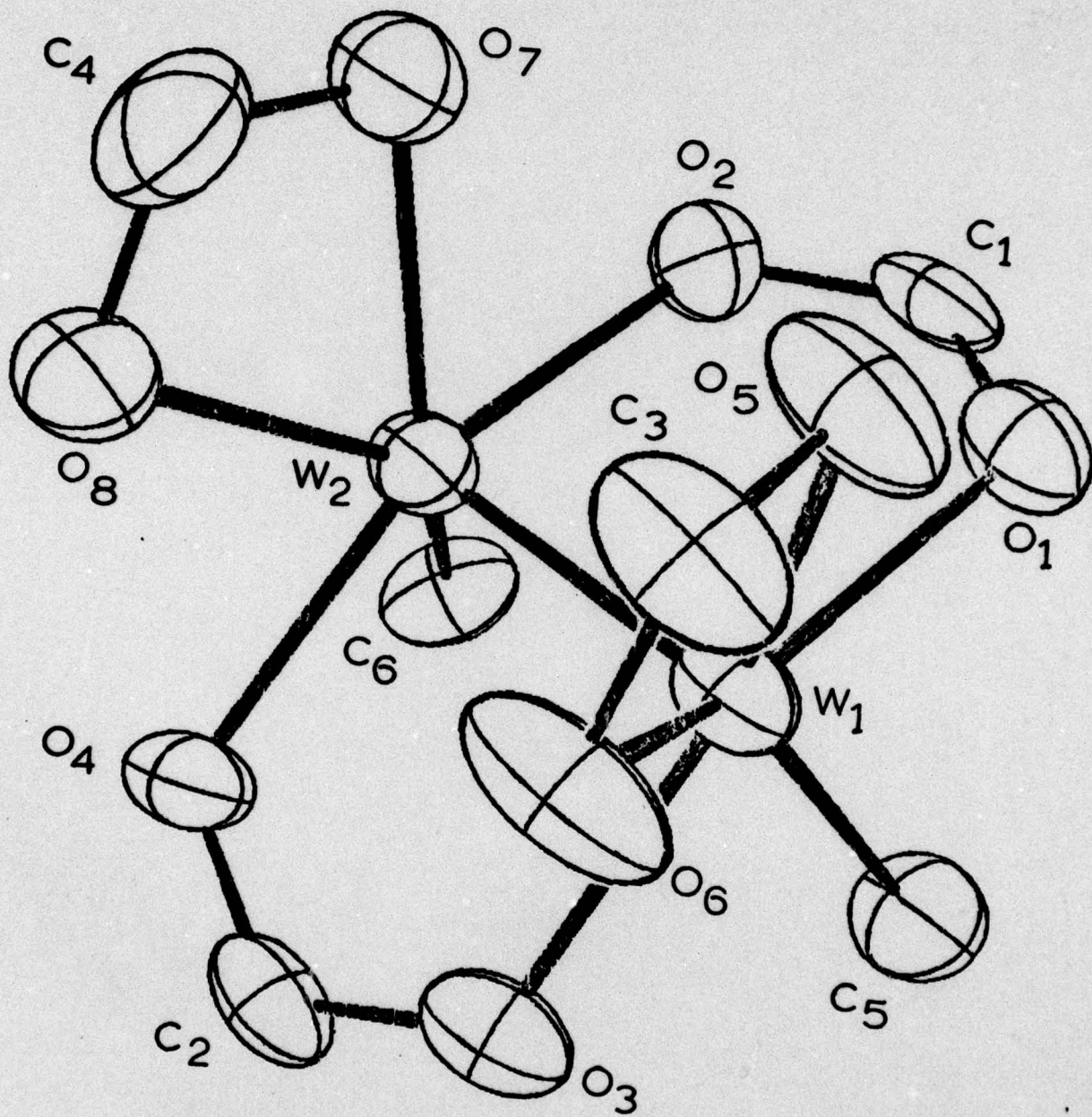


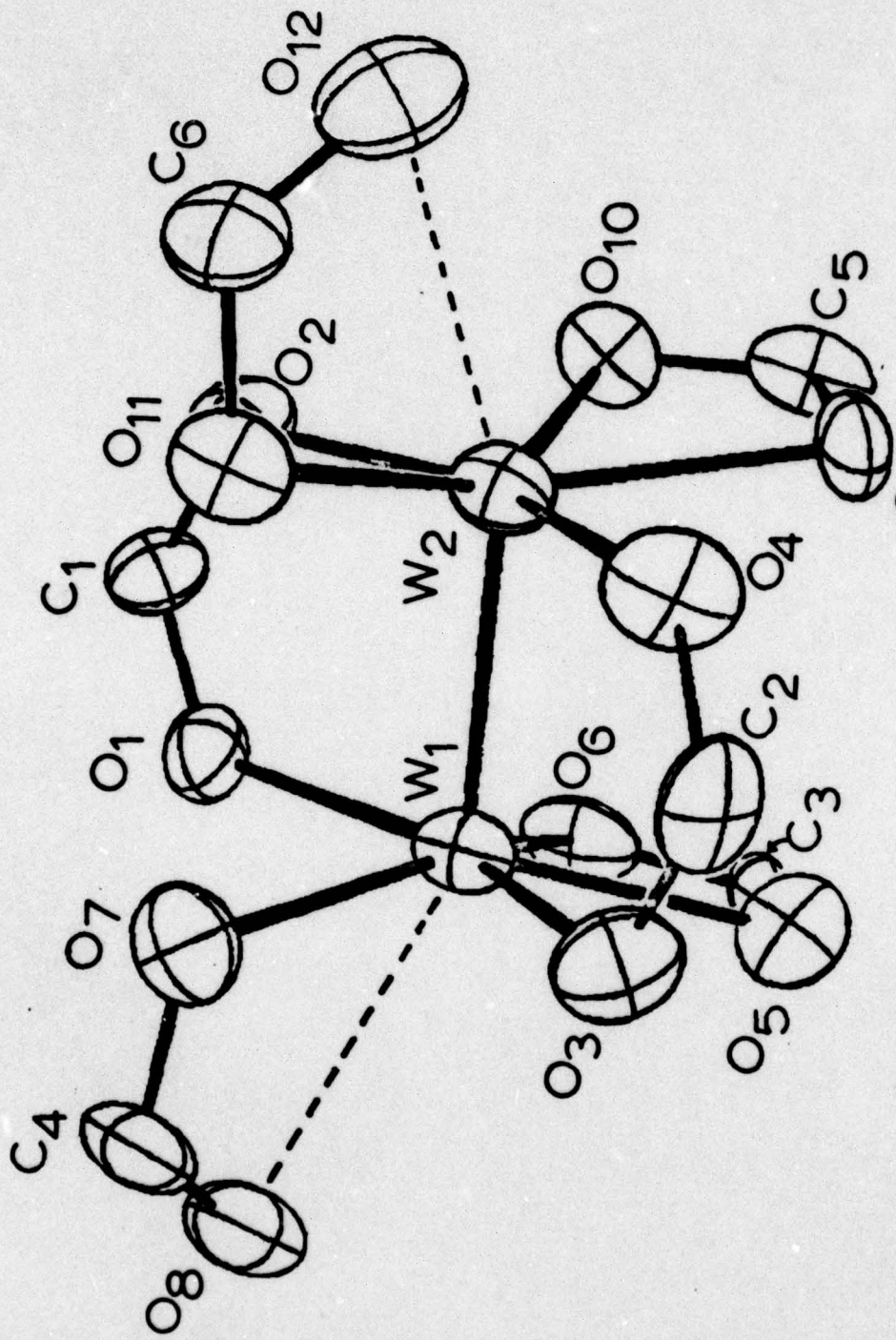
✓
A



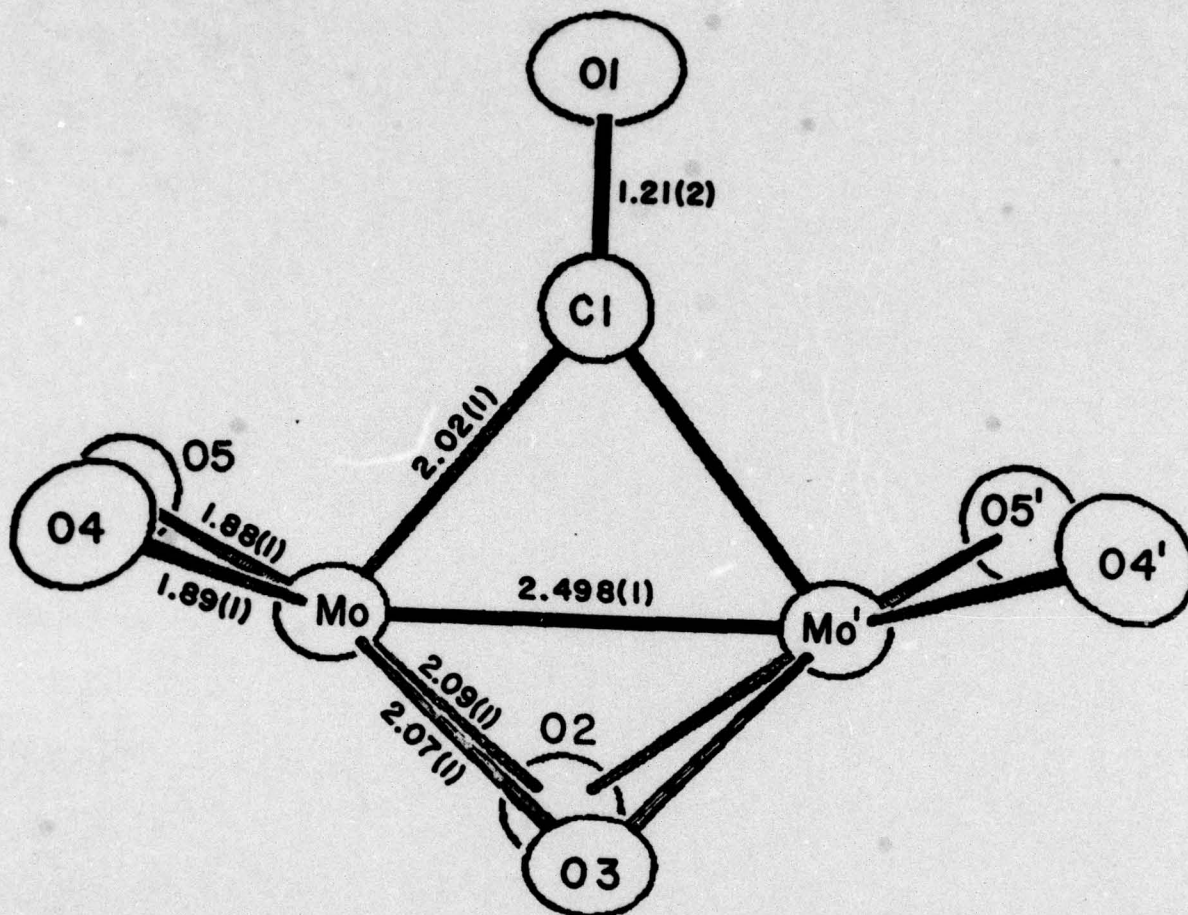
B



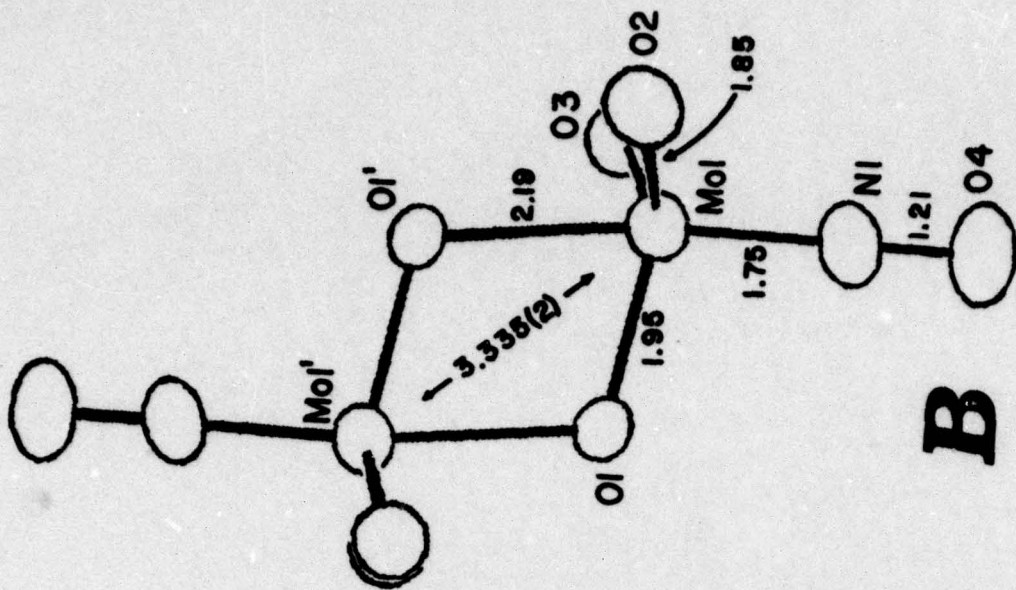




$W_2(O_2C)_6$ skeleton in $W_2(O_2CNMe_2)_6$: $W-W = 2.28 \text{ \AA}$,
 $W-O = 2.07$ (bridging); $2.15/2.04, 2.68 \text{ \AA}$ (terminal).

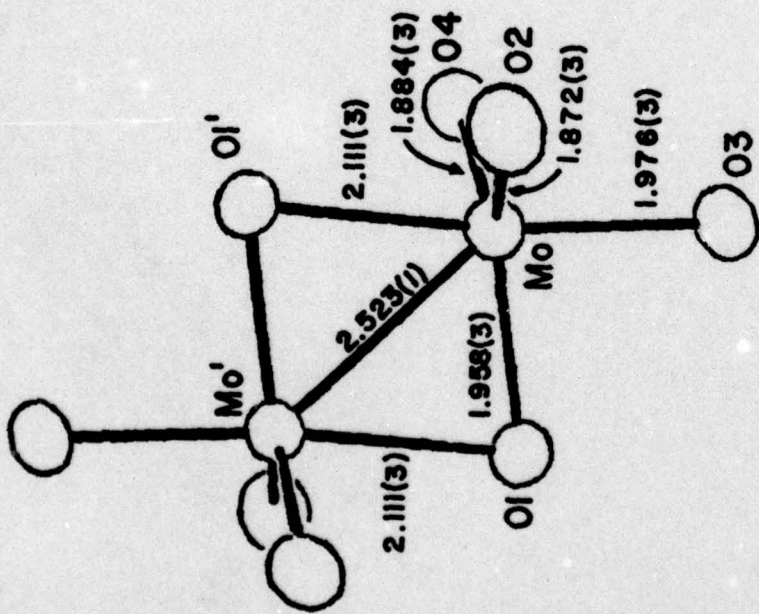


Mo₂O₆(CO) Skeleton of
Mo₂(O-t-Bu)₆(CO)



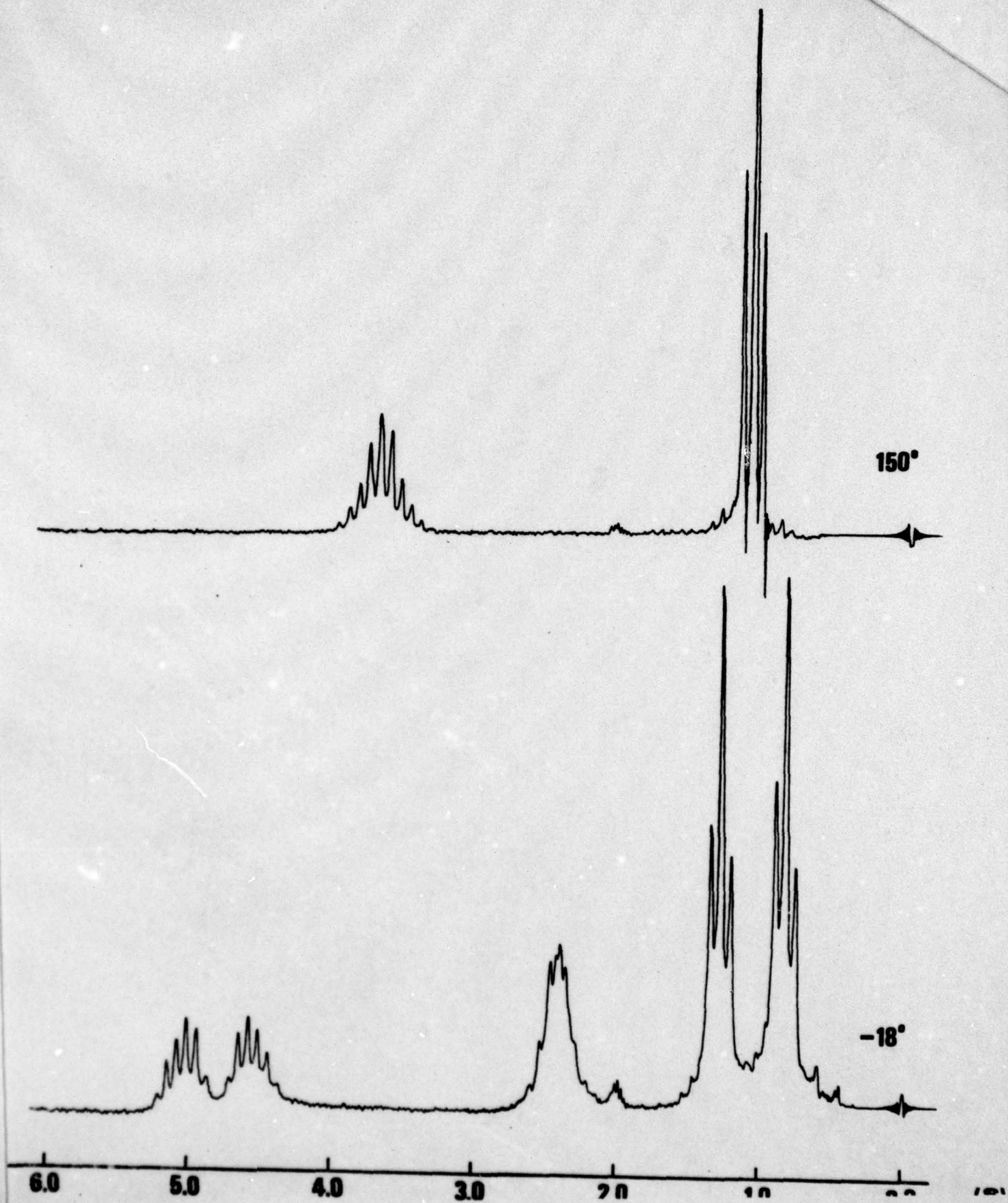
B

$\text{Mo}_2(\text{O-i-Pr})_6(\text{NO})_2$
Skeleton



A

$\text{Mo}_2(\text{O-i-Pr})_8$
Skeleton



^{13}C

(*) anti & gauche — $\text{Mo}_2(\sigma\text{-C}_2\text{H}_5)_2(\text{NMe}_2)_4$

