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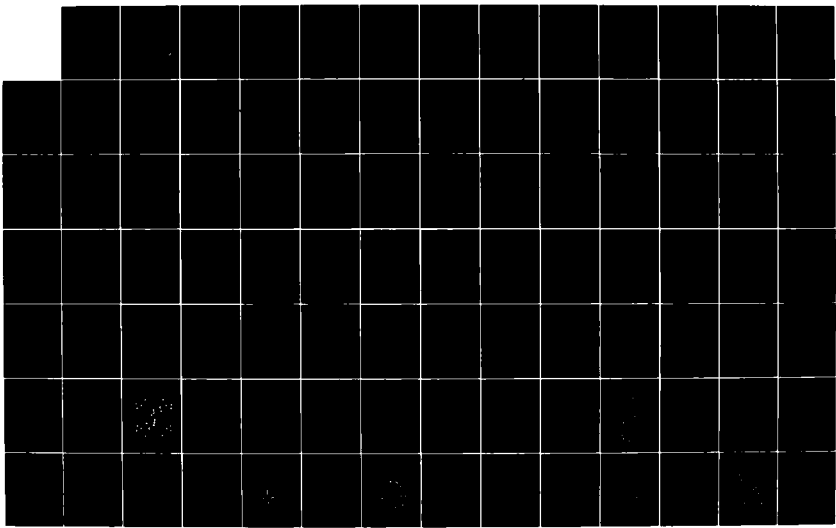
METAL-METAL BONDS AND METAL CARBON BONDS IN THE
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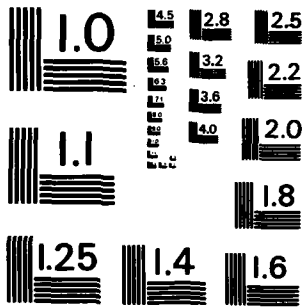
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METAL-METAL BONDS AND METAL CARBON BONDS
IN THE CHEMISTRY OF MOLYBDENUM AND TUNGSTEN ALKOXIDES

by

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Prepared for Publication

in

Polyhedron

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Metal-metal bonds are found in alkoxides of molybdenum and tungsten when the metal atoms are in oxidation states 2 through 5. Metal-metal bonds may be localized and multiple or single in order, or may be delocalized in cluster molecular orbitals. The structures of these metal alkoxides are quite different from those seen previously. Metal-metal bonds provide a reservoir of electrons		

for redox reactions: the reservoir may be tapped in oxidative-addition reactions and filled in reductive-elimination reactions. Alkoxide ligands are shown to support an extensive organometallic chemistry. Alkoxide ligands may act as four or two electron donor ligands and may readily change between terminal and bridging (μ_2 and μ_3) sites. This allows for the facile interconversion of saturated and unsaturated metal centers. As strong σ -donor ligands, they can enhance backbonding to π -acid ligands on the same metal. By π -donating to vacant metal d orbitals, they may suppress metal-hydride abstraction from coordinated alkyl, alkylidene and alkylidyne ligands and they stabilize metals in high oxidation states. A variety of steric control can be engineered by choice of alkyl (RO) groups and this may greatly influence structure, M-M bonding and reactivity of coordinated ligands.

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METAL-METAL BONDS AND METAL CARBON BONDS
IN THE CHEMISTRY OF MOLYBDENUM AND TUNGSTEN ALKOXIDES

Malcolm H. Chisholm

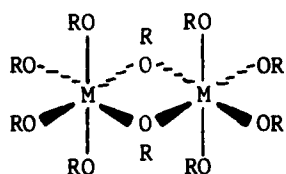
Department of Chemistry, Indiana University,
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Introduction

Simple binary alkoxides of formula $M(OR)_n$ are known for most electro-positive metals and the majority of the transition elements and lathanides. Mixed metal alkoxides are known for a variety of metals and some of these have quite remarkable properties. For example, the lanthanide elements and aluminum form an extensive series of isopropoxides of formula $MA_3(OPr^i)_{12}$ which are volatile solids or liquids.

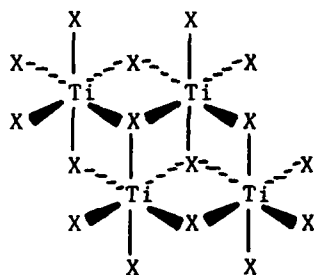
A characteristic feature of an alkoxy ligand is its ability to readily form bridges between two or even three metal atoms. Such oligomerization proceeds in order to satisfy the metal atom's desire to attain a preferred coordination geometry. Oligomerization may be suppressed by the use of sterically bulky alkoxy ligands and, in this way, unusual coordination numbers and geometries may be imposed. Many examples could be used to illustrate these simple concepts. I shall mention but a few.

(1) Alkoxides of niobium and tantalum in the +5 oxidation state exist as dimers when the alkoxy group is not too sterically demanding, e.g. MeO and EtO, as shown in I below. However, with bulky alkoxides, such as Bu^tO , monomeric five coordination is imposed.



I

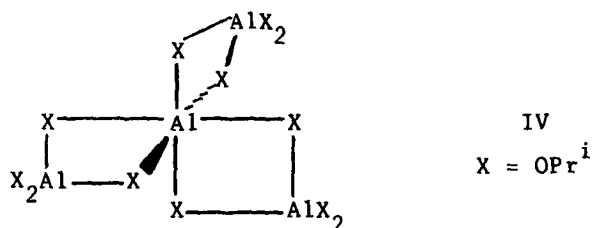
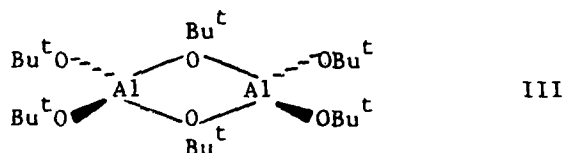
(2) The ethoxides and methoxides of titanium (+4) adopt a tetrameric structure in the solid state, II, whereby each metal atom achieves an octahedral environment. In benzene solution, the titanium ethoxide dissociates to trimers, while with the bulky Bu^tO ligand, a monomeric $\text{Ti}(\text{OBu}^t)_4$ is found.



II

X = OMe, OEt

(3) Aluminum-tert-butoxide is a dimer, III, while the isopropoxide is a trimer when freshly distilled and a tetramer in the solid state, and when aged in solution, IV. Chromium(III), which is a similar size to aluminum(III), has a greater propensity for forming octahedral complexes because of the crystal field stabilization energy arising from the t_{2g}^3 orbital configuration in an O_h field. Cr(III) forms a non-volatile, non-hydrocarbon soluble isopropoxide $[\text{Cr}(\text{OPr}^i)_3]_n$ and based upon electronic spectral and magnetic properties, it is formulated as having a polymeric $\text{Cr}(3+)\text{O}_6$ lattice structure.



It should also be emphasized that alkoxide ligands may act as π -donor ligands, $RO \rightarrow M$. This capability will have maximum effect for terminal alkoxy ligands and for transition metals in high oxidation states with vacant d orbitals of appropriate symmetry to receive π -electrons.

Metal alkoxides are in general a highly reactive group of complexes. The metal atoms are commonly susceptible to nucleophilic attack and the oxygen atoms are susceptible to electrophilic attack. Common reactions involving substrates with acidic hydrogens include hydrolysis with water, alcohol exchange with other alcohols or silanols, substitution reactions with organic acids or acid anhydrides, acyl halides, β -diketones, β -ketoesters, β -ketoamines and Schiff bases. Insertion reactions also occur with unsaturated molecules such as CO_2 , CS_2 and $ArNCO$.

The preparations, physico-chemical properties and chemical reactions of metal-alkoxides have been extensively reviewed within the past few years.^{1,2} The scope of this report is confined to the alkoxide chemistry of molybdenum and tungsten. Except in the oxidation state +6, where the metal

atoms have no valence d electrons, the alkoxide chemistry of these elements is markedly different from that anticipated by Bradley's early theories for metal alkoxide polymers.^{3,4} In all the lower oxidation states, the d^n valence electrons on the metal atoms are used to form metal-metal bonds which may be localized single or multiple bonds or delocalized into cluster bonding molecular orbitals. The formation of metal-metal bonds may modify or totally change the structural ground state of a molecule from that anticipated for a d^0 metal complex. Furthermore, metal-metal bonds provide a reservoir for electrons which may be "tapped" for oxidative-addition reactions or "filled" in reductive-elimination reactions.

One other area of chemistry that is emphasized concerns the use of alkoxy ligands in organometallic chemistry. Alkoxy ligands, which are strong π -donors and may readily interchange bonding modes between terminal and bridging (μ_2 and μ_3), are clearly very different from the now "classical" ligands in organometallic chemistry, such as tertiary phosphines, carbonyl, cyclopentadienes and olefins, all of which are soft and π -acceptors. We see a new facet of organometallic chemistry emerging in the area of early transition metal organoalkoxide chemistry.

Classes of Compounds

d^3-d^3 Dimers with M-M Triple Bonds. The addition of alcohols to hydrocarbon solutions of $\text{Mo}_2(\text{NMe}_2)_6$ ⁵ leads to an extensive series of dinuclear alkoxides $\text{Mo}_2(\text{OR})_6$, where $\text{R} = \text{Bu}^t, \text{Pr}^i, \text{CH}_2\text{Bu}^t, \text{CH}(\text{Me})\text{Ph}, \text{SiMe}_3$ and SiEt_3 .⁶ Polymeric compounds $[\text{Mo}(\text{OR})_3]_n$ are obtained for sterically unencumbered alkoxy ligands such as OEt and OMe, but little is yet known

about these compounds. The dinuclear alkoxides, $\text{Mo}_2(\text{OR})_6$ are yellow-orange, hydrocarbon soluble, crystalline compounds. They sublime in vacuo in the temperature range 70 to 120°C at 10^{-4} torr. In the mass spectrometer, they yield strong molecular ions, together with an extensive series of Mo_2 -containing ions. They are diamagnetic and show only one type of alkoxy or trialkylsiloxy group in their ^1H and ^{13}C NMR spectra, independent of temperature. Only one compound, the neopentoxide, has been fully characterized by a single crystal X-ray study and its molecular structure is shown in Figure 1. There is an unbridged Mo-Mo triple bond of distance 2.22 Å and the central Mo_2O_6 skeleton has virtual D_{3d} symmetry. There can be little, if any, doubt that the other alkoxides of formula $\text{Mo}_2(\text{OR})_6$ adopt similar structures and, as such, are members of an extensive series of compounds containing M-M triple bonds (M = Mo, W) between tri-ligated metal atoms.⁷

Rather interestingly, alcoholysis reactions involving $\text{W}_2(\text{NMe}_2)_6$ ⁸ do not lead to an extensive series of compounds of formula $\text{W}_2(\text{OR})_6$.⁹ Only $\text{W}_2(\text{OBu}^t)_6$ has been isolated, though amine adducts $\text{W}_2(\text{OR})_6(\text{HNMe}_2)_2$ have been obtained for $\text{R} = \text{Pr}^i$ and CH_2Bu^t .¹⁰ Tungsten appears to differ from molybdenum in three important respects with regard to the formation and stability of $\text{M}_2(\text{OR})_6$ compounds. (1) Tungsten binds Lewis bases more tightly for a given alkoxy group, e.g. as in the isolation of $\text{W}_2(\text{OR})_6(\text{HNMe}_2)_2$ noted above. (2) Tungsten is more readily oxidized to W(4+) alkoxides. Both of these points will be elaborated upon further in this article. (3) Whereas $\text{Mo}_2(\text{OR})_6$ compounds readily sublime when heated in vacuo, $\text{W}_2(\text{OBu}^t)_6$ and the amine adducts $\text{W}_2(\text{OR})_6(\text{HNMe}_2)_2$, where $\text{R} = \text{SiMe}_3$, Pr^i and CH_2Bu^t , decompose when heated in vacuo above 80°C.⁹ In the mass spectrometer, however, $\text{W}_2(\text{OR})_6^+$ ions are observed.⁹

Some mixed amido- or alkyl-alkoxy compounds containing M≡M bonds have been prepared. For example, treatment of 1,2-Mo₂X₂Y₄ (M≡M), where X = Br and Y = CH₂SiMe₃ or X = Cl and Y = NMe₂, with LiOR (2 equivalents) yields compounds of formula 1,2-Mo₂(OR)₂Y₄ where R = Bu^t and Prⁱ. The molecular structure of 1,2-Mo₂(OBu^t)₂(CH₂SiMe₃)₄ deduced from a single crystal X-ray study reveals the anti-conformation.¹¹ See Figure 2. Rather interestingly, the 1,1-isomer, (Bu^tO)₂(Me₃SiCH₂)Mo≡Mo(CH₂SiMe₃)₃, is obtained from the addition of Bu^tOH to 1,1-Mo₂(NMe₂)₂(CH₂SiMe₃)₄.¹¹

Alcoholysis reactions involving 1,2-Mo₂R₂(NMe₂)₄ proceed via elimination of HNMe₂ to give 1,2-Mo₂R₂(OR')₄ compounds [R = Me, R' = Bu^t; R = CH₂SiMe₃, CH₂CMe₃ and R' = Bu^t, Prⁱ, CH₂CMe₃ and Et], but when R contains β-hydrogens, elimination of one equivalent of alkane results in Mo₂R(OR')₅ compounds [R = Et and Pr; R' = Bu^t and Prⁱ]. The mechanistic aspects of these reactions are discussed later.

The most striking feature of the aforementioned compounds of formula M₂(OR)₆ and M₂X_n(OR)_{6-n} is the presence of the M-M triple bond, unsupported by bridging alkoxide ligands. Evidently the bridged Al₂(OR)₆ structure, III, is considerably higher in energy since compounds of formula X₂YM≡MY₃ and XY₂M≡MXY₂ do not readily isomerize in hydrocarbon solvents, even at +100°C.¹¹

From calorimetric studies, it has been estimated that the formation of a pair of bridging OR ligands from two terminal OR ligands, 2Mo-OR → Mo₂(μ-OR)₂, is favored by 10-15 Kcal mol⁻¹.¹² That bridges are not seen in these compounds, and that isomerizations which would be possible if bridged intermediates were energetically accessible, imply that the energy difference between (RO)₃Mo≡Mo(OR)₃ and (RO)₂Mo(μ-OR)₂Mo(OR)₂

must be quite large and at least greater than ca. 30 Kcal mol⁻¹. This in turn must reflect upon the relative strengths of Mo-Mo bonds in the bridged and non-bridged structures.

The strength of D(Mo≡Mo) in Mo₂(OPrⁱ)₆ has been estimated to be 90 Kcal mol⁻¹ from calorimetric studies wherein the heat of formation of Mo₂(OPrⁱ)₆ is determined.¹² However, it is impossible to separate D(Mo-OR) and D(Mo≡Mo) in such calculations and thus an error in the assumption of D(Mo-OR) is magnified six-fold in D(Mo≡Mo). Since D(Mo-OR) can be determined for a large number of mononuclear compounds, a reasonable estimate of D(Mo-OR) in Mo₂(OR)₆ compounds can be obtained to ±5 Kcal mol⁻¹. The strength of the Mo≡Mo bond may therefore be determined to lie within the range 60-120 Kcal mol⁻¹, and so a value of 90-100 Kcal mol⁻¹ seems most plausible.

A simple bonding picture for M₂(OR)₆ compounds can be constructed as follows. Letting the z axis be coincident with the M-M axis, the metal atomic d_{z²} orbitals may interact to form σ and σ* M-M molecular orbitals and d_{xz} and d_{yz} may form π and π* orbitals. In oxidation state +3, each metal has the d³ configuration and thus a M-M triple bond of configuration σ²π⁴ can be formed. Each metal may use s, p_x and p_y atomic orbitals to form three σ bonds with the OR ligands, and metal d_{xy}, d_{x²-y²} and p_z atomic orbitals have the appropriate symmetry to form π-bonds with oxygen filled p atomic orbitals. It is clear from considerations of the short Mo-OR bond distances that there is considerable multiple bond character. (See also Physical Evidence for RO-to-M Multiple Bonding.)

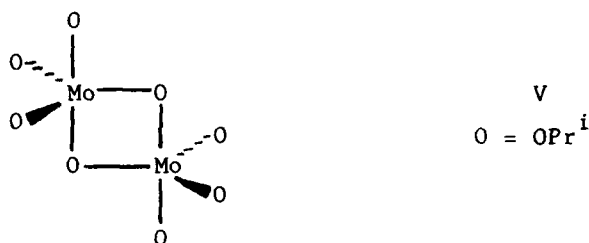
This qualitative bonding scheme finds support from detailed calculations employing the SCF X_α-SW technique on Mo₂(OH)₆.¹³ The orbital energies

so calculated correlate well with the data obtained from He(I) and He(II) photoelectron spectroscopic studies. For $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6$, the first ionization occurs at ca. 7.2 eV and the second at 8.0 eV, corresponding to ionizations from M-M π and σ bonding orbitals, respectively.

The electronic absorption spectra of $\text{M}_2(\text{OR})_6$ compounds have recently been examined.¹⁴ There are no absorption maxima in the visible region of the spectra: the colors (yellow or orange) are derived from higher energy absorptions tailing into the visible. The first absorption maximum, ν_1 , occurs at 360 nm (ϵ ca. 1400) for $\text{Mo}_2(\text{OPr}^i)_6$ and can be assigned to a M-M π -to-M-L π^* transition (M-M π -to-M-M δ). The second absorption maximum, ν_2 , occurs at 210.5 nm (ϵ ca. 22,400) and is assigned to the M-M π -to- π^* transition. The spectrum of $\text{W}_2(\text{OBu}^t)_6$ is very similar with ν_1 at 380 nm (ϵ ca. 1600) and ν_2 at 210 nm (ϵ ca. 13,000). The spectrum of $\text{W}_2(\text{OBu}^t)_6$ also shows quite pronounced shoulders to low energy of these absorption maxima which can be assigned to the spin forbidden transitions to triplet states: $\nu'_1 = 460$ nm (ϵ ca. 500) and $\nu'_2 = 250$ nm (ϵ ca. 6,800). The electronic absorption spectra of $\text{Mo}_2(\text{OPr}^i)_6$ and $\text{W}_2(\text{OBu}^t)_6$ are compared in Figure 3.

d^2-d^2 Dimers with M-M Double Bonds. The addition of alcohols to $\text{Mo}(\text{NMe}_2)_4$ leads to an extensive series of compounds of formula $[\text{Mo}(\text{OR})_4]_n$.¹⁵ The bulky tert-butoxide appears to be monomeric in benzene, but its structure is not known in the solid state. It is weakly paramagnetic, which contrasts with the diamagnetic monomeric four-coordinate compounds, MoX_4 , where $X = \text{NMe}_2$ ¹⁶ and SBU^t .¹⁷ $\text{Mo}(\text{OBu}^t)_4$ is clearly a molecule worthy of further attention. The isopropoxide is dimeric and diamagnetic in hydrocarbon solutions, but in the presence of pyridine, a paramagnetic species, believed to be $\text{Mo}(\text{OPr}^i)_4(\text{py})_2$ akin to $\text{Mo}(\text{OSiMe}_3)_4(\text{HNMe}_2)_2$,¹⁵ is

formed. In the solid state, an interesting dimeric structure is found.¹⁸ Each molybdenum atom is in a distorted trigonal bipyramidal geometry. The two halves of the molecule share a common axial equatorial edge through the agency of alkoxy bridges as shown schematically in V below.



An ORTEP view of this molecule is shown in Figure 4. The Mo-O distances show the expected and general trend that terminal M-O distances are shorter than bridging ones, but we also find that the axial bonds are longer than the equatorial bonds within each set of terminal and bridging ligands. This also turns out to be a general trend in what is now quite an extensive series of dimeric molybdenum compounds whose structures are based on fused trigonal bipyramids.

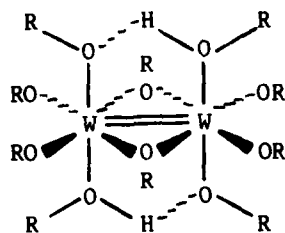
The diamagnetism and the shortness of the Mo-Mo distance, 2.523(1) Å, are readily rationalized by the presence of a Mo-Mo double bond. This may be formulated in the following manner. Let the z axis be coincident with the axial O-Mo-O groups of each metal. Then the formation of five σ bonds to oxygen may use s, p_x , p_y , p_z and d_{z^2} atomic orbitals. This leaves two doubly degenerate d orbitals (d_{xz} , d_{yz}) and ($d_{x^2-y^2}$, d_{xy}) with the former lying lower in energy in a simple trigonal bipyramidal field. If we then choose the y axis to be coincident with the Mo-O (equatorial)

bridging ligands, then the d_{yz} atomic orbitals can form M-M σ and σ^* orbitals; the $d_{xz}-d_{xz}$ interaction will yield π and π^* orbitals. This simple picture predicts a M-M bonding configuration $\sigma^2 \pi^2$ for a d^2-d^2 dimer. Note the degeneracy of the M-M π bonds, which is present in $X_3M=MX_3$ compounds, is removed for a dimer of type V.

The M-M distances in the molecules $Mo_2(OPr^i)_8$ and $Mo_2(OPr^i)_6(NO)_2$ make an interesting comparison. The latter compound adopts a structure similar to that shown in V in which two axial OR groups are replaced by linear Mo-N-O groups.¹⁹ If for the purposes of electron counting we use the formalism that a linear M-N-O group is equivalent to $M^-(NO^+)$, then the formal oxidation state of molybdenum is +2 in $Mo_2(OPr^i)_6(NO)_2$, resulting in a d^4-d^4 dimer. In terms of M-M bonding, this would lead to a totally non-bonding configuration $\sigma^2 \pi^2 \pi^*2 \sigma^*2$ and the Mo-to-Mo distance, 3.335(2) Å, precludes an M-M bond. In fact, the d^4 electrons on each molybdenum reside in the (d_{xz}, d_{yz}) orbitals and are extensively used in backbonding to the NO π^* orbitals, as evidenced by the low $\nu(N-O)$ value, 1640 cm^{-1} .

Other alkoxides of Mo(4+) derived from alcoholysis reactions involving $Mo(NMe_2)_4$ are less well characterized. With decreasing size of the alkoxide ligand, there is a tendency to associate further in solution. For example, a cryoscopic molecular determination on the ethoxide gave a value close to that expected for a trimer, $[Mo(OEt)_4]_3$. In view of the tetranuclear structure of the tungsten analogue (discussed later), further studies of these $[Mo(OR)_4]_n$ compounds should be undertaken.

Dinuclear tungsten(IV) alkoxides of formula $W_2(OR)_8$ are presently not known. However, it seems that routes to such compounds should be forthcoming, even though $W(NMe_2)_4$ is not a known compound. For example, oxidative-addition reactions involving $RO-OR$ and $W_2(OR)_6$ compounds might prove effective. The only simple d^2-d^2 dinuclear tungsten alkoxides are the green compounds of formula $W_2Cl_4(OR)_4(HOR)_2$.²⁰ These were first prepared by Wentworth and Clark from the reactions of $[Bu_4N]_3W_2Cl_9$ with alcohols and were incorrectly formulated as tungsten(III) compounds, $W_2Cl_4(OR)_2(HOR)_4$.²¹ Later work, however, showed that these compounds could be prepared by a variety of routes including alcoholysis of WCl_4 and that they were in fact tungsten(IV) dimers.²² The structure of $W_2Cl_4(OEt)_4(HOEt)_2$ was determined by a single crystal study and revealed the edge-shared octahedral geometry shown in VI.²⁰



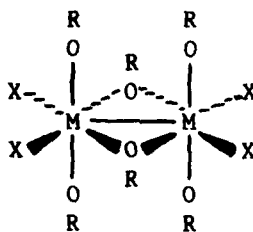
VI

The fusing of two octahedral units along a common edge allows the metal t_{2g} atomic orbitals to interact to form one σ , one π and one δ bonding and anti-bonding set of molecular orbitals. The d^2-d^2 dimer thus provides a double bond of configuration $\sigma^2\pi^2$, which is compatible with the W-W distance of 2.479(1) Å.

There are a number of other dinuclear alkoxides of molybdenum and tungsten which are formed by addition reactions involving $M_2(OR)_6$ compounds that can be considered to have M-M double bonds. These are discussed later.

d^1-d^1 Dimers with M-M Single Bonds. The only homoleptic M(5+) compound that is known for molybdenum and tungsten is $W(OPh)_5$, formed by the reduction of $W(OPh)_6$ with molecular hydrogen and Raney nickel.²³ In solution, a molecular weight determination yielded a value greater than a monomer, but less than a dimer. In view of the structural characterization of $M_2Cl_4(OR)_6$ compounds, it is possible that the phenoxide has an edge-shared W_2O_{10} moiety.

There are a number of reports in the early literature concerning compounds of empirical formula $WCl_2(OR)_3$ formed from reactions of WCl_6 with alcohols and under electrolysis. It is not clear that the early workers were correct in their formulations since various colors and magnetic properties were attributed to these compounds. However, more recently Cotton and Walton²⁴ have prepared an extensive series of $W_2Cl_4(OR)_6$ compounds by the oxidation of $W_2Cl_4(OR)_4(HOR)_2$ compounds using molecular oxygen or Ag^+ as oxidants.²⁴ Addition of halogens to $Mo_2(OPr^i)_6$ leads to $Mo_2X_4(OPr^i)_6$ compounds, where $X = Cl, Br$ and I .²⁵ All of these compounds are orange crystalline solids. They are diamagnetic and show two types of OR ligands, consistent with the maintenance in solution of the structure found in the solid state, depicted by VII, for $Mo_2(OPr^i)_6X_4$ where $X = Cl$ and Br ²⁵ and for $W_2(OEt)_6Cl_4$.²⁴



VII

In all of the structurally characterized compounds of formula $M_2Cl_4(OR)_6$, the M-M distance is close to 2.71 Å, which is roughly 0.8 Å less than that of a M-M non-bonding distance found for the d^0-d^0 compound $[Nb(OMe)_5]_2$.²⁶

A compilation of bond distances and assigned bond orders for a number of simple dinuclear alkoxides and their adducts or derivatives is given in Table I. A fairly consistent picture emerges. Triple bonds of configuration $\sigma^2\pi^4$ have distances in the range 2.2 to 2.3 Å; double bonds, $\sigma^2\pi^2$, are all close to 2.5 Å; single bonds, σ^2 , are close to 2.7 Å, while non-bonding distances for $M_2(\mu-OR)_2$ -containing compounds are all greater than 3 Å, typically in the range 3.3 to 3.5 Å.

Trinuclear Alkoxides. Since some of the alkoxides of molybdenum(IV) appear trimeric in solution, it is interesting to speculate that triangulo Mo_3 structures might be found for certain $[Mo(OR)_4]_n$ compounds. The six metal valence electrons not used in M-OR bonding could be used to form M-M bonds: $a^2 + e^4$. This situation is seen for $Mo_3O(OR)_{10}$ compounds, where R = Prⁱ and CH₂Bu^t.²⁷ An ORTEP view of the central skeleton of the $Mo_3O(OCH_2Bu^t)_{10}$ molecule is shown in Figure 5. The structure is closely related to a large group of triangulo Mo_3 - and W_3 -containing complexes with capping

(μ_3^-) oxo, sulfido and carbyne ligands.²⁸ In solution, the ^1H NMR spectra indicate that the solid state structure is maintained. Four types of alkoxy ligands are seen in the integral ratio 3:3:3:1, indicating that the molecule is not fluxional on the NMR time-scale.

Tetranuclear Alkoxides. Addition of ethanol or methanol to hydrocarbon solutions of $\text{W}_2(\text{NMe}_2)_6$ yields the tetranuclear alkoxides $\text{W}_4(\text{OR})_{16}$.^{29,30} The structure of the ethoxide has been determined by an X-ray study and is shown in Figure 6. The structure is of type II which is found for $[\text{Ti}(\text{OR})_4]_4$ compounds where $\text{R} = \text{Me}$ and Et ,³¹ but the $\text{W}---\text{W}$ distances are all shorter than the analogous $\text{Ti}---\text{Ti}$ distances. Evidently in $\text{W}_4(\text{OEt})_{16}$, the eight tungsten valence electrons are used to form delocalized $\text{M}-\text{M}$ bonds.

The central centrosymmetric M_4X_{16} unit formed by four fused octahedral units appears quite common in coordination compounds and in ternary metal oxides. A mixed oxo-alkoxy-pyridine compound, $\text{Mo}_4(\mu_3-\text{O})_2(\mu_2-\text{O})_2(\text{O})_4-(\mu_2-\text{OPr}^i)_2(\text{OPr}^i)_2(\text{py})_4$, has been structurally characterized.³⁰ $\text{Ag}_8\text{W}_4\text{O}_{16}$ ³² and $\text{Ba}_{1.14}\text{Mo}_8\text{O}_{16}$ ³³ also have Mo_4O_{16} subunits. The molybdenum oxide contains two types of M_4 units differing most significantly in the $\text{M}-\text{M}$ distances. This difference can be correlated with the number of bonding cluster electrons: 8 versus 10. The M_4X_{16} framework has been found to accommodate 0, 4, 8 and 10 cluster bonding electrons. The changes in $\text{M}-\text{M}$ distances as a function of the number of cluster electrons are summarized in Table II. It is clear that molybdenum and tungsten use their d^n electrons to form $\text{M}-\text{M}$ bonds. The nature of the $\text{M}-\text{M}$ bonding in the 8 and 10 electron clusters has recently been the subject of a Fenske-Hall calculation by Cotton and Fang.³⁴ They rationalized the elongation of two $\text{M}---\text{M}$ distances, which

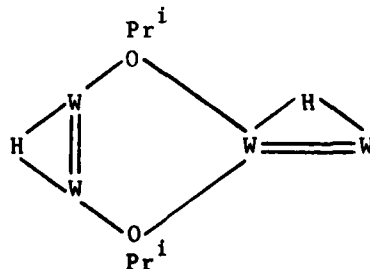
accompanies the change from the 10 electron to the 8 electron cluster, in terms of a second order Jahn-Teller distortion.

Aside from the solid state structural parameters, the presence of M-M cluster bonding electrons drastically alters the solution behavior of $M_4(OR)_{16}$ compounds. Whereas $[Ti(OEt)_4]_4$ dissociates in benzene solution to trimers, the tungsten compound retains its tetranuclear nature as evidenced by cryoscopic molecular weight determinations. Also, the 1H NMR spectrum of $W_4(OMe)_{16}$ shows eight sharp resonances of equal intensity, which is exactly what is predicted by a consideration of the centrosymmetric solid state structure of $W_4(OEt)_{16}$.

From reactions between $W_2(NMe_2)_6$ and Pr^iOH , a most intriguing hydrido-alkoxide, $W_4(\mu-H)_2(OPr^i)_{14}$, has been isolated and characterized.³⁵ The central $W_4(\mu-H)_2O_{14}$ skeleton of this molecule is shown in Figure 7. The molecule is centrosymmetric and the eight electrons available for M-M bonding are evidently used to form two localized M-M double bonds: $W(1)-W(2) = W(1)'-W(2)' = 2.446(1) \text{ \AA}$. The central distance, $W(1)---W(1)' = 3.407(1) \text{ \AA}$, is typical of a non-bonding distance in $M_2(\mu_2-OR)_2$ -containing compounds (see Table I). The molecule may thus be viewed as a dimer of dinuclear compounds: $[W_2(\mu-H)(OPr^i)_7]_2$. It is interesting to speculate why $W_4(\mu-H)_2(OPr^i)_{14}$ adopts a chain structure rather than a cluster based on the $W_4(OEt)_{16}$ structure in which a pair of μ_2 or μ_3 OEt ligands are replaced by hydrides.

A cryoscopic molecular weight determination in benzene indicates that a tetranuclear structure is maintained in solution. However, in contrast to

the rigid (NMR timescale) structure of $W_4(OR)_{16}$ compounds ($R = Me$ and Et), $W_4(\mu-H)_2(OPr^i)_{14}$ is highly fluxional. In the 1H NMR spectrum, only one type of OPr^i ligand is observed in the temperature range -60° to $+80^\circ C$. Evidently some fluxional process rapidly scrambles all the OPr^i ligands. This process also exchanges the two types of tungsten atoms, which are in formal oxidation states $+4\frac{1}{2}$ and $+3\frac{1}{2}$, since the hydride resonance at $\delta = 7.87$ ppm shows only one coupling to ^{183}W , $I = \frac{1}{2}$, 14.5 natural abundance. From the relative intensities of the satellites to the central hydride resonance, it is evident that the hydride ligand bridges two equivalent tungsten atoms; the hydride ligands are not scrambled over all four tungsten atoms. One can readily accommodate these observations by a fluxional process in which the molecule essentially "turns itself inside-out". A cleavage of one of the central $W(1)-\mu-OR$ bridges could be followed by a succession of bridge \rightleftharpoons terminal OPr^i exchanges to give an intermediate of the type shown in VIII below. From such an intermediate, a return to the chain structure could occur with exchange of $W(1)$ and $W(2)$. It is, however, still quite remarkable that $W_4(\mu-H)_2(OPr^i)_{14}$ is so labile to OPr^i scrambling.



VIII

Three further types of tetranuclear alkoxides have recently been found for compounds of formula $\text{Mo}_4\text{X}_4(\text{OR})_8$, where $\text{X} = \text{F}, \text{Cl}$ and Br . These are described later since they are formed in X-for-OR exchange reactions involving $\text{Mo}_2(\text{OR})_6$ compounds. It should be noted, however, that each of these structures is possible for a compound of formula $\text{Mo}_4(\text{OR})_{12}$ and, since the $\text{Mo}_2(\text{OR})_6$ ($\text{M} \equiv \text{M}$) structure is only realized with bulky R groups, the structures of the polymeric compounds $[\text{Mo}(\text{OEt})_3]_n$ and $[\text{Mo}(\text{OMe})_3]_n$ are clearly worthy of investigation.

Hexanuclear Alkoxides. In methanol as solvent, molybdenum(II) halides react with NaOMe to give $\text{Na}_2\text{Mo}_6\text{X}_8(\text{OMe})_6$ compounds, where $\text{X} = \text{Cl}$ and Br .³⁶ Based on spectroscopic data, these compounds can reasonably be formulated as $\text{Mo}_6(\mu_3\text{-X})_8^{4+}$ -containing clusters in which six OMe ligands are terminally bonded to each molybdenum atom and radiate from the center of an idealized Mo_6 -octahedral unit. Under more forcing conditions (150°C , NaOMe melt), a yellow-brown crystalline compound of formula $\text{Na}_2\text{Mo}_6(\text{OMe})_{14}$ is obtained.³⁶ This compound is pyrophoric in air and shows two types of OMe ligands in the ^1H NMR spectrum in the integral ratio 3:4, which is consistent with a cube-octahedral relationship for a $\text{Mo}_6(\mu_3\text{-OMe})_8^{4+}$ moiety with six terminal OMe ligands. A full structural study seems warranted for this 24-electron Mo_6 cluster compound.

Physical Evidence for RO-to-M π -Bonding. Direct evidence for RO-to-M multiple bonding can be seen in a large number of structural studies. For terminal alkoxy ligands, the $\text{C}_{\text{sp}^3}\text{-O}$ distances average $1.44(2) \text{ \AA}$. Given that this is a single bond distance and that the radius of C_{sp^3} is 0.77 \AA , then

the covalent radius of oxygen (single bond) is placed at 0.67 Å. The covalent radius of molybdenum or tungsten may be reasonably estimated from M-C_{sp} distances. For example, in compounds of formula 1,2-M₂R₂(NMe₂)₄³⁷ or 1,2-Mo₂(OBu^t)₂(CH₂SiMe₃)₄,³⁸ where the M-C_{sp} distances are 2.17(2) Å, the single bond covalent radius for M is determined to be 1.40 Å. This then sets d_(Mo-O) = r_M + r_O = 2.06 Å. This value is in fact typical of M-μ-OR distances, but considerably longer than any seen for terminal M-OR groups which fall in the range 1.80-1.96 Å. In Mo₂(OCH₂Bu^t)₆, the average Mo-O distance is 1.88(2) Å.⁶ In this molecule, it is the metal δ-type orbitals, d_{xy} and d_{x²-y²}, which are primarily involved in π-bonding and an average Mo-O bond order of 1.66 is thus expected to correlate with this distance. Upon addition of another ligand, one of the in-plane orbitals becomes used in π-bonding. Typically in M₂(OR)₆L₂ compounds, the M-O distances are in the range 1.90-1.96 Å, consistent with a net decrease in π-bonding. On the other hand, in 1,2-Mo₂(OBu^t)₂(CH₂SiMe₃)₄, where each alkoxy group may be fully involved in π-bonding, the Mo-O distance is shorter. A listing of terminal and bridging M-OR bond distances is given in Table III.

Of course, many factors may influence an individual M-O distance, particularly the oxidation state of the metal, the trans-ligand and steric and electronic properties of adjacent ligands.³⁹ It is, however, safe to say terminal RO-to-Mo or -W distances are always shorter than would be expected from considerations of single bond radii.

The influence of RO-to-M π-bonding may be shown in the spectroscopic properties of adjacent ligands. (1) In Mo(OBu^t)₂(py)₂(CO)₂,⁴⁰ the low values of ν(CO), 1906 and 1776 cm⁻¹, arise because π-donor ligands enhance t_{2g}⁴ backbonding to carbonyl π* orbitals. (2) In MoO₂(OPrⁱ)₂(bpy),⁴¹ which

contains the cis-Mo(6+)O₂ moiety and a pair of mutually trans OPrⁱ ligands, the oxo and OPrⁱ ligands compete to fill (π-donate with) the vacant Mo t_{2g} orbitals. There is an abundance of π-electrons to do this job. An oxo group may be a six electron donor and usually a cis-Mo(6+)O₂ group will contain two Mo-O groups of bond order 2.5. It has been noted that Mo-O bond distance, Mo-O bond order and ¹⁷O chemical shifts correlate linearly for terminal Mo-O groups.⁴² In MoO₂(OPrⁱ)₂(bpy), the Mo-O (oxo) distances, 1.71(1) Å (averaged), and the ¹⁷O chemical shift value of 878 ppm are longer and lower, respectively, than the values anticipated for a cis-Mo(6+)O₂ function in octahedral complexes. The maximum Mo-O π bond order of 1.5 is evidently not attained because some RO-to-Mo π-bonding occurs. The latter, however, is relatively small as evidenced by the rather long Mo-OPrⁱ distances, 1.93(1) Å (averaged).⁴¹

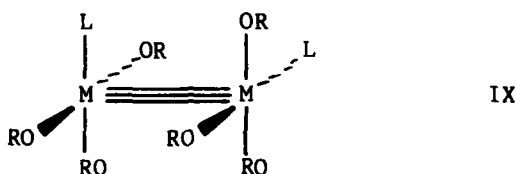
Chemical Reactions

By far the most extensively studied group of alkoxides of molybdenum and tungsten are the dinuclear compounds of formula M₂(OR)₆ (M≡M). Their reactions are discussed in detail and, where appropriate, related reactions involving other alkoxides are noted.

Lewis Base Association Reactions. In hydrocarbon solutions, M₂(OR)₆ compounds (M≡M) react with N and P donor ligands, L, according to the equilibrium reaction 1 shown below.^{6,9,10,43,44}



The position of equilibrium is very sensitive to the nature of R and L and for related compounds $K_W > K_{Mo}$. Also, tungsten prefers to coordinate P donors relative to N donors, provided steric factors permit coordination. Several adducts have now been structurally characterized. All structures are based on conformations of IX.



Each metal atom is coordinated to four atoms which lie roughly in a plane; the two metal atoms are united by a triple bond and the two halves of the molecule adopt a conformation which is determined by ligand-ligand interactions across the M-M bond. In general, steric repulsive interactions favor staggered conformations, but for $W_2(OPr^i)_6(HNMe_2)_2$, a near eclipsed geometry is found. In the latter case, N-H---OR hydrogen bonding occurs across the M-M bond similar to that found in $W_2Cl_4(OR)_4(HOR)_2$ compounds.²⁰ Some pertinent structural data for these Lewis base adducts are given in Table IV.

The equilibrium 1 may be monitored by NMR spectroscopy as a function of temperature. At room temperature in toluene- d_8 , $Mo_2(OPr^i)_6$ and pyridine react rapidly and reversibly to give $Mo_2(OPr^i)_6(py)_2$. On lowering the temperature, the equilibrium position shifts in favor of the adduct and pyridine dissociation-association becomes slow on the NMR time-scale. The spectrum of the adduct at ca. $-25^\circ C$, 220 MHz, indicates two types of OPr^i

ligands in the integral ratio 2:1, consistent with cis and trans $\text{Pr}^i\text{O-W-py}$ groups. At this temperature, rotation about the M-M bond is rapid, but at lower temperatures and at higher magnetic field strengths (below -50°C , 360 MHz), three OPr^i ligands are seen in the integral ratio 1:1:1. The spectrum is thus consistent with the adoption of a structure having C_2 symmetry akin to that found in the solid state.⁴³ For some compounds, e.g. $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6(\text{py})_2$, low temperature spectra have been obtained indicative of freezing out two conformations, each having C_2 symmetry for the $\text{M}_2\text{O}_6\text{N}_2$ skeleton; furthermore, restricted rotations about Mo-L bonds are observed.⁴³

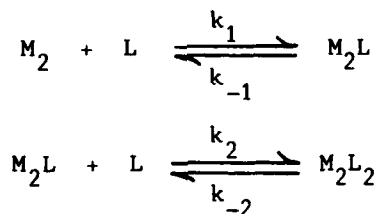
For P donor ligands (PMe_3 , PMe_2Ph , PPh_3 , $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), the equilibrium 1 may also be monitored by ^{31}P NMR spectroscopy. For specific combinations of alkoxide and P donor ligands, it is possible to observe high temperature limiting spectra corresponding to free phosphine and low temperature spectra corresponding to the adducts. This is because the favorable enthalpy of binding in 1 may be offset at higher temperatures by the negative entropy of binding. The ^{31}P chemical shifts of free and coordinated phosphines differ by ca. 25 ppm. At intermediate temperatures, a single broadened resonance is observed. The position of this resonance is dependent upon the relative concentrations of coordinated and free phosphine and the line shape is influenced by the rate of exchange. The ^{31}P NMR spectra of the ditungsten adducts show interesting satellite features due to couplings (one and two bond) to ^{183}W , $I = \frac{1}{2}$, 15% natural abundances (see Figure 8).

The equilibrium 1 may also be monitored by U.V.--visible spectroscopy. All the adducts of formula $\text{M}_2(\text{OR})_6\text{L}_2$ are more intensely colored than the parent $\text{M}_2(\text{OR})_6$ compounds. On adduct formation, the lowest energy transition

of the $M_2(OR)_6$ compounds, ν_1 , which corresponds to M-M π -to-M-L π^* , (d_{xy} , $d_{x^2-y^2}$) splits into two bands. One band moves to higher energy and the other to lower energy: it is the latter which is responsible for absorption in the visible region.

One other intriguing aspect to emerge from studies of 1 is the finding that $M_2(OR)_6L$ species are unstable with respect to disproportionation to $M_2(OR)_6$ and $M_2(OR)_6L_2$. This leads to a cooperative phenomenon. For the sequence depicted by 2, where M_2 represents $M_2(OR)_6$ and M_2L_2 represents $M_2(OR)_6L_2$, both of which are in equilibrium, the second addition of L occurs more rapidly than the first, $k_2 > k_1$. Similarly in the dissociation reaction, the second loss of L is more rapid than the first, $k_{-1} > k_{-2}$.

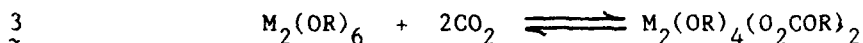
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This observation is quite contrary to what would be expected from simple considerations of both steric factors and Lewis acid-Lewis base concepts. The origin of the relative instability of $M_2(OR)_6L$ compounds must be electronic, but at present it is not clearly understood.

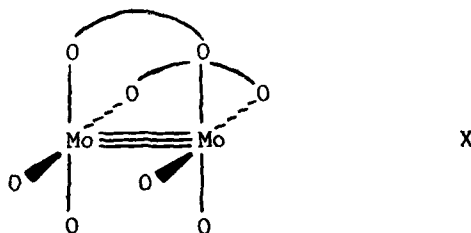
In contrast to Lewis base association reactions involving $M_2(OR)_6$ compounds which retain the $M \equiv M$ bond, $Mo_2(OPr^i)_8$ ($M=M$) reacts with Lewis bases to give $Mo(OPr^i)_4L_2$ compounds. The latter are paramagnetic and are most likely related to the $Mo(OSiMe_3)_4(HNMe_2)_2$ molecule which has a central MoO_4N_2 skeleton of octahedral geometry in the solid state¹⁵ as is shown in Figure 9.

M-OR Bond Insertion Reactions. $M_2(OR)_6$ compounds react rapidly and reversibly with CO_2 , both in hydrocarbon solutions and in the solid state, to give mixed alkoxide-alkylcarbonato compounds according to equation 3.^{45,46}



The mechanism of CO_2 insertion in 3 involves a direct pathway: it does not require a catalyst such as ROH.⁴⁶ The alkylcarbonato compounds, $M_2(OR)_4(O_2COR)_2$ are quite stable at room temperature, but readily and reversibly lose CO_2 when heated to 60-80°C. In solution, however, the alkylcarbonato compounds readily lose CO_2 according to 3 and must be maintained under an atmosphere of CO_2 (25°C) if the equilibrium is to favor the insertion product.

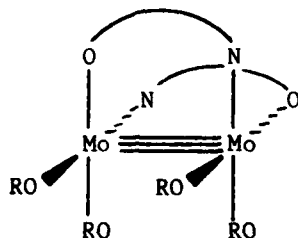
The solid state molecular structure of $Mo_2(OBu^t)_4(O_2COBu^t)_2$ was determined by an X-ray study and revealed the cis-bridged geometry depicted by X. The presence of a pair of bridging O_2CX groups imposes a near eclipsed conformation as is shown in Figure 10.



The 1H NMR spectra of $M_2(OR)_4(O_2COR)_2$ compounds ($R = CHMe_2$ and CH_2CMe_3) are consistent with the presence of a cis-bridged O_2COR structure in solution. Specifically, for the Mo-OR ligands, the methyl groups are

diastereotopic for the isopropoxy compound, giving rise to a pair of doublets, and the methylene protons are diastereotopic for the neopentoxide, which gives rise to an AB quartet.

$M_2(OR)_6$ compounds have also been found to react with alkyl- and aryl-cyanates, $R'NCO$, to give insertion products $M_2(OR)_4(OC(OR)NR')_2$. This insertion reaction is irreversible and the products are quite stable in solution. The 1H NMR spectra are generally consistent with the cis-bridged, head-to-tail structure found for $Mo_2(O_2CH_2CMe_3)_4(OC(OCH_2CMe_3)NPh)_2$ in the solid state,⁴⁷ which is represented by XI below.



XI

Ligand Exchange Reactions. A number of closely related compounds to those depicted by X and XI have been obtained from protolysis reactions in which a bidentate ligand is substituted for an OR group. For example, the reactions between 1,3-diaryltriazines and $Mo_2(OR)_6$ compounds give $Mo_2(OR)_4(ArN_3Ar)_2$ compounds and related reactions involving 2-hydroxypyridine yield $Mo_2(OR)_4(O-N)_2$ where O-N is the dianion derived from deprotonation of 2-hydroxypyridine.⁴⁸ The structural characterization of $Mo_2(OPr^i)_4(O-N)_2$ revealed the cis-bridged, head-to-tail geometry depicted by XI in the solid state and 1H NMR studies are consistent with this structure being maintained in solution.

Bidentate ligands generally bridge the Mo≡Mo bond when formation of a five-membered ring is achieved, e.g. as is found for RCOO⁻, ArNNNAr⁻ and R'NC(OR)O⁻ ligands. However, reactions between M₂(OR)₆ compounds and 2,4-pentanedione, acacH, proceed to give M₂(OR)₄(acac)₂ derivatives in which the acac ligands are bidentate, but are chelated to each metal. The structure of Mo₂(OCH₂CMe₃)₄(acac)₂ found in the solid state is shown in Figure 11. Presumably the formation of the six-membered ring is favored relative to the seven-membered ring which would be required if acac⁻ were to span the Mo≡Mo bond. Using unsymmetrically substituted acac⁻ ligands which form A-B-type chelates, three geometric isomers are possible, each having an enantiomer. However, in solution we have only been able to observe two isomers, probably because extremely facile rotation about the Mo≡Mo bond rapidly interconverts two isomers on the ¹H NMR time-scale.

Halide-for-Alkoxide Exchange. From the reaction between Mo₂(OBu^t)₆ and PF₃ in hydrocarbon solvents, a black crystalline product of empirical formula MoF(OBu^t)₂ was isolated.⁴⁹ During one such preparation, crystals suitable for an X-ray study were obtained and, when this was undertaken, the unit cell was found to contain a mixture of molecules Mo₄F₄(OBu^t)₈ and Mo₄F₃(OBu^t)₈(NMe₂) in the ratio 1:2. The presence of the NMe₂ group, which was not anticipated, can reasonably be traced to incomplete alcoholysis in the preparation of Mo₂(OBu^t)₆ from Mo₂(NMe₂)₆. The structure of the Mo₄F₄(OBu^t)₈ molecule is shown in Figure 12. The central Mo₄ unit is a bisphenoid with two short Mo-Mo distances, 2.24 Å, and four long Mo-Mo distances, ca. 3.75 Å. The molecule may be viewed as two Mo≡Mo units

brought together through the agency of fluoride bridges. Each $\text{Mo}_2(\text{OBU}^t)_4-(\mu\text{-F})_2$ unit (M≡M) has a geometry very similar to that found in $\text{Mo}_2(\text{OBU}^t)_4-(\text{O}_2\text{COBU}^t)_2$.⁴⁶ The $\text{Mo}_4\text{F}_3(\text{OBU}^t)_8(\text{NMe}_2)$ molecule has one $\mu\text{-NMe}_2$ group in place of a $\mu\text{-F}$ group, but this produces a negligible effect on the M-M distances in the Mo_4 moiety.

In search of a more general route to mixed halide-alkoxide compounds, we have initiated studies of the reactions between $\text{Mo}_2(\text{OPr}^i)_6$ and acetyl halides.⁵⁰ In hexane, $\text{Mo}_2(\text{OPr}^i)_6$ and CH_3COX ($\text{X} = \text{Cl}$ and Br) produce black crystalline compounds of empirical formula $\text{Mo}_4\text{X}_3(\text{OPr}^i)_9$. These compounds are only very sparingly soluble in hexane, but are appreciably soluble in toluene. ^1H NMR spectra recorded in toluene- d_8 and benzene- d_6 are consistent with that expected for a $\text{Mo}_4(\mu_2\text{-X})_3(\mu_2\text{-OPr}^i)(\text{OPr}^i)_8$ structure akin to that described above for $\text{Mo}_4\text{F}_3(\text{NMe}_2)(\text{OBU}^t)_8$.

A further reaction between $\text{Mo}_4\text{X}_3(\text{OPr}^i)_9$ and CH_3COX or a direct reaction between $\text{Mo}_2(\text{OPr}^i)_6$ and CH_3COX (2 equiv) in toluene yield black crystalline compounds of empirical formula $\text{MoX}(\text{OPr}^i)_2$. These compounds are only very sparingly soluble in toluene and little is known about their solution properties. The solid state molecular structures are fascinating, however. For the chloride,⁵⁰ there is a square of molybdenum atoms with eight bridging (μ_2) OPr^i ligands, four lying above and four lying below the Mo_4 plane. The Mo-Cl bonds are terminal and radiate from the center of the Mo_4 -square (see Figure 13). The central $\text{Mo}_4\text{O}_8\text{Cl}_4$ unit has virtual D_{4h} symmetry. The Mo-Mo distance of 2.37 Å implies strong Mo-Mo bonding. The compound is diamagnetic and, in a formal sense, may be viewed as an inorganic analogue of cyclobutadiene formed by the coupling of two Mo=Mo units.

Quite remarkably, the structure of the bromide, $\text{Mo}_4\text{Br}_4(\text{OPr}^i)_8$, is different from that of the chloride just discussed. The bromide contains a butterfly or opened-tetrahedron of molybdenum atoms with five relatively short Mo-Mo distances, ca. 2.5 Å, and one long distance, 3.1 Å.⁵⁰ The Mo-Br groups are all terminal, but the Mo-OPrⁱ groups are terminal (2) and doubly (4) and triply (2) bridging as shown in Figure 14.

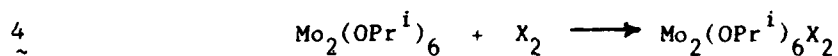
The $\text{Mo}_4\text{X}_4(\text{OPr}^i)_8$ structures, where X = Cl and Br, may be viewed as subunits of the well known $\text{Mo}_6(\mu_3\text{-X})_8^{4+}$ unit.⁵¹⁻⁵³ In both of the alkoxide structures, the oxygen atoms lie roughly at the corners of an idealized O_8 cube. The four molybdenum atoms occupy positions at four faces of the cube such that two opposite faces are vacant (X = Cl) or two adjacent faces are vacant (X = Br) relative to the $\text{Mo}_6(\mu_3\text{-X})_8^{4+}$ geometry.

It seems likely that the $\text{Mo}_4\text{X}_4(\text{OPr}^i)_8$ molecules will be reactive toward further association reactions: $\text{M}_2 + \text{M}_4 + \text{M}_6$, etc. It may ultimately be possible to systematically interconvert M_2 (multiple bond), M_4 (cluster) and M_6 (octahedral) complexes. It should also be noted that McCarley and coworkers⁵⁴ have coupled two $\text{Mo}\equiv\text{Mo}$ bonds to form a rectangular Mo_4^{8+} containing compound: $2\text{Mo}_2\text{Cl}_4(\text{PR}_3)_2(\text{HOMe})_2 + \text{Mo}_4\text{Cl}_4(\mu_2\text{-Cl})_4(\text{PR}_3)_4 + 4\text{MeOH}$. The M-M distances are alternating long and short, indicative of single and triple bonds, respectively, in a simple valence bond description.

At this point, it is worth noting the variety of M_4 -alkoxide structures that have been found for molybdenum and tungsten: $\text{Mo}_4\text{F}_4(\text{OBu}^t)_8$,⁴⁹ $\text{Mo}_4\text{Cl}_4(\text{OPr}^i)_8$,⁵⁰ $\text{Mo}_4\text{Br}_4(\text{OPr}^i)_8$,⁵⁰ $\text{W}_4(\text{OEt})_{16}$ ³⁰ and $\text{W}_4(\mu\text{-H})_2(\text{OPr}^i)_{14}$.³⁵ In each structure, M-M bonding is clearly important, but it is not clear what factors are responsible for the adoption of one geometry relative to

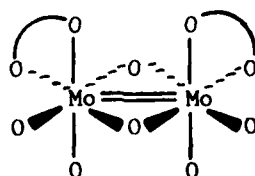
another. Why do the $\text{Mo}_4\text{X}_4(\text{OR})_8$ structures differ for $\text{X} = \text{F}, \text{Cl}$ and Br , and why are two localized $\text{W}=\text{W}$ bonds found in $\text{W}_4(\mu\text{-H})_2(\text{OPr}^i)_{14}$, rather than an 8-electron W_4 cluster of the type seen in $\text{W}_4(\text{OEt})_{16}$? These questions provide the stimulus for further studies in the area.

Oxidative-Addition Reactions. Compounds with M-M multiple bonds have a source of electrons which may be tapped for oxidative processes. A number of simple stepwise M-M bond order transformations have been observed.⁵⁵ Oxidative-addition reactions involving $\text{Mo}_2(\text{OPr}^i)_6$ ($\text{M}=\text{M}$) have been noted to give $(\text{Mo}=\text{Mo})^{8+}$ -containing compounds as shown in equation 4.



where $\text{X} = \text{Pr}^i\text{O}^{11}$ or $\text{PhCOO}^{41,56}$

The structure and bonding in $\text{Mo}_2(\text{OPr}^i)_8$ has already been discussed. The structure of $\text{Mo}_2(\text{OPr}^i)_6(\text{O}_2\text{CPh})_2$ has not been determined by a single crystal study, but NMR characterization suggests the edge-shared octahedral geometry shown in XII.



XII
 $\text{O} = \text{OR}$
 $\text{O} \text{ O} = \text{PhCO}_2$

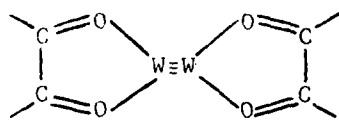
The direct addition of halogens X_2 , where $\text{X} = \text{Cl}, \text{Br}$ and I , to hydrocarbon solutions of $\text{Mo}_2(\text{OPr}^i)_6$ gives edge-shared octahedral complexes

with Mo-Mo single bonds, $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$, VII.²⁵ Attempts to prepare $\text{Mo}_2(\text{OPr}^i)_6\text{X}_2$ (M=M) compounds by the careful addition of an equivalent of the halogen were unsuccessful and there is evidence that such compounds are unstable with respect to disproportionation to $\text{Mo}_2(\text{OR})_6$ and $\text{Mo}_2(\text{OR})_4\text{X}_2$ compounds. However, from the reaction between $\text{Mo}_2(\text{OR})_6$ and $\text{C}_6\text{H}_5\text{NO}_2$ in hexane/pyridine solvent mixtures, compounds of formula $\text{Mo}_2(\text{OR})_6(\text{C}_6\text{H}_5\text{NO}_2)_2$ have been isolated.⁵⁷ The neopentoxide has been shown to have an interesting confacial bioctahedral geometry involving two μ_2 -OR and one μ_3 -OR bridge (see Figure 15). The Mo-Mo distance, 2.534(1) Å, is consistent with the presence of a $(\text{Mo}=\text{Mo})^{8+}$ unit. However, in a formal sense, the oxidation states of the two molybdenum atoms differ, $\text{Mo}(4\frac{1}{2}^+)$ and $\text{Mo}(3\frac{1}{2}^+)$. The EPR spectra in toluene- d_8 are consistent with the maintenance of this structure in solution.

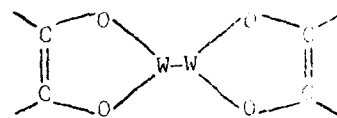
A number of other substrates react with $\text{M}_2(\text{OR})_6$ compounds to give adducts which may be viewed as products of redox reactions. For example, orthoquinone ligands can behave as neutral, -1 (semiquinones) or -2 (catecholate) ligands.⁵⁸ The adducts with $\text{M}_2(\text{OR})_6$ compounds, either 1:1 or 2:1, are often highly colored, presumably due to low energy charge transfer, either MLCT or LMCT. Tetrachloroorthoquinone, which is known to be a good oxidizing agent, $\text{C}_6\text{Cl}_4\text{O}_2 + 2e^- = \text{C}_6\text{Cl}_4\text{O}_2^{2-}$, -0.78 V, has been found to react with $\text{Mo}_2(\text{OR})_6$ compounds to give 2:1 adducts $\text{Mo}_2(\text{OR})_6(\text{O}_2\text{C}_6\text{Cl}_4)_2$, which may best be viewed as d^1-d^1 dimers. The structure of the isopropoxide is shown in Figure 16. From a consideration of the Mo-Mo, Mo-O and C-O (quinone) distances, this is clearly a Mo_2^{10+} -containing compound.

$\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ also reacts with benzil and 2,3-butanedione to give 2:1 adducts of formula $\text{W}_2(\text{OR})_6(\text{R}_2'\text{C}_2\text{O}_2)_2$. The structures of the compounds

where $R = \text{Pr}^i$ and $R' = p\text{-tolyl}$ and methyl have been determined in the solid state.⁶⁰ The structure of the 2,3-butanedione derivative is shown in Figure 17. Once again, the W-W, W-O and C-C distances (2,3-butanedione ligand) are indicative of a d^1-d^1 , W_2^{10+} -containing molecule. Most notably, the C-C double bond is evidenced by the 1.33(1) Å bond distance which demonstrates the importance of the resonance form XIIIb relative to XIIIa.



XIIIa



XIIIb

In these reactions which oxidize the $(M \equiv M)^{6+}$ unit, it is interesting to note that oxidation occurs more readily for tungsten than molybdenum. This is seen, for example, in the alcoholysis reactions of $M_2(\text{NMe}_2)_6$ compounds. Whereas molybdenum forms an extensive series of $\text{Mo}_2(\text{OR})_6$ compounds, tungsten is readily oxidized to the +4 oxidation state as in the formation of $W_4(\mu\text{-H})_2(\text{OPr}^i)_{14}$ ³⁵ and $W_4(\text{OEt})_{16}$.³⁰ The oxidation of the $(W \equiv W)^{6+}$ unit may be blocked by strongly coordinating ligands such as pyridine, $\text{MeN}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ and PMe_3 which give adducts $W_2(\text{OR})_6\text{L}_2$ or $W_2(\text{OR})_6(\text{L-L})$ when alcoholysis of $W_2(\text{NMe}_2)_6$ is carried out in their presence.¹⁰ The oxidative-addition step presumably proceeds through an unsaturated and reactive intermediate of the form $W_2(\text{OR})_6(\text{HOR})$. This type of oxidative-addition finds a parallel in the recent work of Brown and Nubel:⁶¹ $1,2\text{-Re}_2(\text{CO})_8(\text{X-H})_2 + \text{Re}_2(\text{CO})_8(\text{X-H}) + \text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-X})$ where $\text{X-H} = \text{H}_2\text{O}$ and $\text{C}_6\text{H}_5\text{N}$ (pyridine).

A number of other reactions with unsaturated organic molecules (π -acceptors such as CO, $RC\equiv CR$) lead to adducts which may be viewed as oxidative-addition products. These are discussed later.

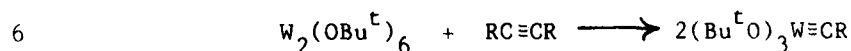
M-M Cleavage Reactions. $M_2(OR)_6$ compounds react with NO (2 equiv) in hydrocarbon solvents to cleave the $M\equiv M$ bond. In a formal sense, the $M-M$ σ and π bonds are broken to form two $M-N$ σ bonds and four $M-N$ π bonds (Md -to-NO π^*) as shown in equation 5.



The molecular structure of $[Mo(OPr^i)_3NO]_2$ deduced from an X-ray study¹⁹ is shown in Figure 18. Each molybdenum atom is in a distorted trigonal bipyramidal geometry. The molecule is centrosymmetric with linear terminal Mo-N-O groups which occupy axial positions. The two halves of the molecule are joined along a common equatorial axial edge by a pair of μ -OPrⁱ ligands. The Mo-to-Mo distance is 3.335 Å, typical of a non-bonding M---M distance spanned by a pair of μ -OR ligands (see Table I). The lack of any M-M bond in $M_2(OR)_6(NO)_2$ compounds can also be seen in their reactions with donor ligands such as pyridine, which leads to $M(OR)_3(NO)(py)$ compounds.⁶² The structure of the $W(OBu^t)_3(NO)(py)$ ⁶³ molecule is shown in Figure 19. Again, the local trigonal bipyramidal geometry is seen and extensive $W(d_{xz}, d_{yz})^4$ -to-NO π^* bonding is evident from the extremely short W-NO distance and the low value of $\nu(NO)$, 1555 cm^{-1} . For a series of related $M_2(OR)_6(NO)_2$ compounds, the $\nu(NO)$ values fall ca. 1720 (M = Cr), 1640 (M = Mo) and 1550 (M = W), which reflects the relative ability of the

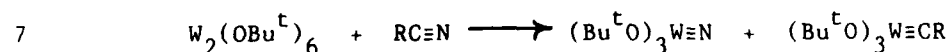
group 6 metals to backbond to the π -acceptor NO ligand in their oxidation state 3+ (or 2+ if we count $M^+ + (NO^+)$ for a linear M-N-O group).

Another cleavage of the M=M bond has recently been reported by Schrock and coworkers⁶⁴ in the reaction between $W_2(OBu^t)_6$ and alkynes as shown in equation 6.



where R = Me, Et, Pr

The reaction appears to be specific to $W_2(OBu^t)_6$: other alkoxides of W_2^{6+} and related dimolybdenum compounds give different products as will be discussed later. Also, the cleavage of the W=W bond in $\underline{6}$ is not observed in reactions with ethyne. Closely related to $\underline{6}$ is the cleavage of the W=W bond in reactions involving nitriles, eq. $\underline{7}$.⁶⁴



where R = Me, Ph and PhCH₂

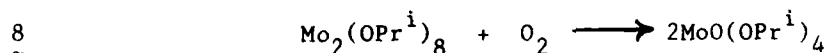
If the alkylidyne ligand is counted as a 3- ligand like nitride N^{3-} , then reactions $\underline{6}$ and $\underline{7}$ may be viewed as oxidative-cleavages of the M=M bond.

Other $W_2(OR)_6$ compounds will react with nitriles to give nitrides, i.e. the reaction is not specific to the Bu^tO ligand, but we have not been able to use $\underline{7}$ to prepare other $(RO)_3W\equiv CR'$ compounds. It appears that the alkylidynes may themselves react with nitriles to give nitrides and alkynes. $Mo_2(OR)_6$ compounds do not react with nitriles to give nitrides.

Once again the greater reactivity of the $W \equiv W$ bond, relative to $Mo \equiv Mo$, is seen with respect to oxidation.

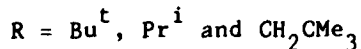
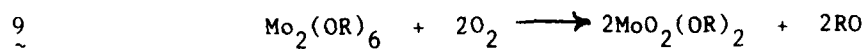
The molecular structures of the $(Bu^tO)_3W \equiv X$ compounds, where $X = CMe$ and N , have been determined in the solid state and are shown in figures 20 and 21, respectively.⁶⁵ A comparison with the structures of $[Mo(OPr^i)_3NO]_2$ and $W(OBu^t)_3(NO)(py)$, shown in figures 18 and 19, is most interesting. $(Bu^tO)_3W \equiv N$ crystallizes in the hexagonal space group $P6_3cm$ yielding a beautiful view down the C axis, as shown in Figure 22.

Closely related to 6 and 7 is the cleavage of a $M=M$ bond by reaction with O_2 to give two $M=O$ bonds, eq. 8.^{27,41}



Reaction 8 is extremely rapid and quantitative. However, addition of molecular oxygen to $M_2(OR)_6$ compounds leads to a variety of products, depending on the metal and the steric properties of the alkoxy ligands.

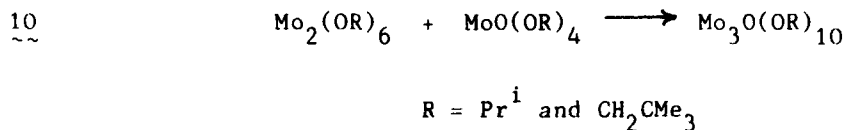
For molybdenum, the overall reaction proceeds according to 9, but many intermediates may be detected or isolated where $R = Pr^i$ and CH_2-CMe_3 .^{66,41}



The compound $MoO_2(OBu^t)_2$ is monomeric; the related isopropoxy and neopentoxy compounds are oligomers $[MoO_2(OR)_2]_n$ of, as yet, unknown struc-

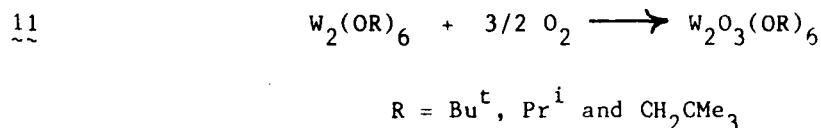
tures. A clean synthesis of the latter compounds involves the addition of excess of ROH ($R = \text{Pr}^i, \text{CH}_2\text{CMe}_3$) to $\text{MoO}_2(\text{OBu}^t)_2$. Addition of pyridine or 2,2'-bipyridine to $[\text{MoO}_2(\text{OR})_2]_n$ compounds yields monomeric octahedral complexes. The molecular structure of $\text{MoO}_2(\text{OPr}^i)_2(\text{bpy})$ in the solid state reveals the cis- MoO_2 group with mutually trans OPr^i ligands as shown in Figure 23.⁴¹

The addition of molecular oxygen to $\text{Mo}_2(\text{OR})_6$ compounds, where $R = \text{Pr}^i$ and CH_2CMe_3 , leads initially to green solutions containing the triangulo $\text{Mo}_3\text{O}(\text{OR})_{10}$ compounds (see Figure 5). A clean, direct synthesis of these compounds is by the addition of $\text{MoO}(\text{OR})_4$ to $\text{Mo}_2(\text{OR})_6$ compounds, eq. 10. This simple redox reaction redistributes the six electrons available for metal-metal bonding from $\sigma^2 \pi^4$ in $\text{M} \equiv \text{M}$ to $a^2 + e^4$ in the triangulo Mo_3^{12+} unit.



Further reaction of $\text{Mo}_3\text{O}(\text{OR})_{10}$ with O_2 leads to cleavage of the Mo_3 unit and elimination of RO^\bullet which abstracts H from solvent. A hexanuclear chain compound $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ has been isolated and structurally characterized.⁶⁷ A view of this fascinating molecule is shown in Figure 24. The average oxidation state of molybdenum is +5.33. Four electrons are available for metal-metal bonding and these are used to form two localized Mo-Mo single bonds, as is evidenced by the two short Mo-Mo distances, 2.585(1) Å, compared to the four long distances, 3.3 Å. These electrons are reactive toward further oxidation by molecular oxygen: $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12} + \text{O}_2 \rightarrow 6\text{MoO}_2(\text{OPr}^i)_2$.

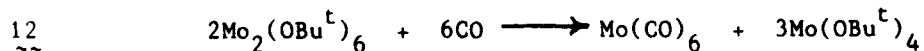
For tungsten, the story is much simpler, but quite different from molybdenum as is shown in equation 11.⁴¹



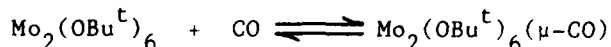
The structures of W₂O₃(OR)₆ compounds are not known and, in solution, only one OR group is seen in the NMR spectra. A cryoscopic molecular weight determination in benzene indicated that W₂O₃(OBu^t)₆ is extensively (60%) dissociated, presumably to WO₂(OBu^t)₂ and WO(OBu^t)₄. The mass spectra of W₂O₃(OR)₆ compounds show only mononuclear ions and may be viewed as a superimposition of fragments derived from WO(OR)₄ and WO₂(OR)₂. A plausible structure for W₂O₃(OR)₆ compounds can be based on a confacial bioctahedral unit with two bridging OR ligands and one bridging oxo group.

Metal-Carbon Bonds

Reactions with Carbon Monoxide. Carbon monoxide reacts rapidly with hydrocarbon solutions of M₂(OR)₆ compounds at 1 Atmos, 25°C. In some cases, the reactions produce M(CO)₆ compounds and oxidized metal containing species, i.e. CO induces disproportionation. The detailed course of the reaction depends upon the metal, M versus W, and on the steric properties of the alkoxy ligand. In the case of Mo₂(OBu^t)₆, the stoichiometric reaction 12 has been established and has been shown to proceed via an initial reversible reaction 13.⁶⁸



13

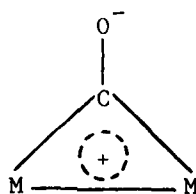


The dark purple crystalline compound $\text{Mo}_2(\text{OBu}^t)_6(\mu\text{-CO})$ adopts a structure in which each molybdenum atom is in a square based pyramidal geometry. The two halves of the molecule are joined by a $\mu_2\text{-CO}$ ligand which occupies the apical position and a pair of $\mu_2\text{-OBu}^t$ ligands which are basal with respect to the fused square based pyramids. The central skeleton of this beautiful molecule is shown in Figure 25.

Since the bridging carbonyl ligand can be counted as a one-electron donor to each metal, the addition of CO transforms a $d^3\text{-}d^3$ dimer to a $d^2\text{-}d^2$ dimer and thus a M-M triple to a double bond. The Mo-Mo distance, 2.498(1) Å is consistent with this assignment. The C-O triple bond is also reduced to a C-O double bond: $(\text{M}\equiv\text{M})^{6+} + \text{CO} + (\text{M}=\text{M})^{8+}(\mu\text{-CO}^{2-})$.

In the presence of donor ligands, such as pyridine, it is possible to isolate an extensive series of compounds of formula $\text{M}_2(\text{OR})_6\text{L}_2(\mu\text{-CO})$ from reactions between $\text{M}_2(\text{OR})_6$ compounds and CO.⁶⁹ These compounds are closely related to $\text{Mo}_2(\text{OBu}^t)_6(\mu\text{-CO})$, having a donor ligand trans to the M-C bond of the bridging CO ligand. In solution, the donor ligands are labile to reversible dissociation and, on the NMR time-scale, bridge \rightleftharpoons terminal OR group exchange is rapid. However, at low temperature and high magnetic field strengths, low temperature limiting spectra are obtained which are consistent with the structures observed in the solid state. The donor ligands serve the important role of suppressing the kinetically facile disproportionation reactions which occur in the presence of excess CO. Also, CO dissociation from $\text{Mo}_2(\text{OR})_6(\mu\text{-CO})$ is blocked when the dimer is ligated.

These μ_2 -CO compounds show anomalous spectroscopic properties (see Table V). The values of $\nu(\text{CO})$ are unprecedentedly low for μ_2 -CO ligands in neutral molecules. Also, the ^{13}C carbonyl chemical shifts appear below 300 ppm, which is out of the range of bridging carbonyl ligands in organometallic compounds. From simple symmetry considerations, it can be seen that the M-M π bond can interact strongly with the C=O π^* orbital. These molecules are inorganic analogues of cyclopropenones and show a significant contribution of the resonance shown in XIV.

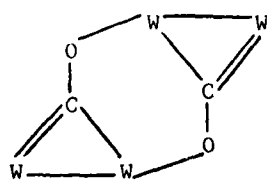


XIV

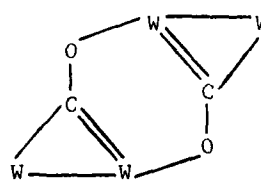
The resonance form XIV is equivalent to an oxycarbyne ligand bridging two metal atoms and suggests that the μ -CO ligand might behave as a good Lewis base. This has actually been demonstrated in the isolation of a molecule of formula $\text{W}_4(\text{OPr}^i)_{12}(\text{py})_2(\text{CO})_2$ formed in the reaction between CO and $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$.⁷⁰ This intriguing complex may be viewed as a dimer of dimers formed by the loss of one pyridine from $\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$: $2\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO}) + \text{W}_4(\text{OPr}^i)_{12}(\text{py})_2(\text{CO})_2 + 2\text{py}$. Figure 26 shows the essential details of this molecule.⁷⁰

Four points should be noted. (1) The W-W distance of 2.654(1) Å is close to that of a single bond distance found in edge-shared octahedral complexes of W(5+), e.g. 2.715(1) Å in $\text{W}_2(\text{OEt})_6\text{Cl}_4$ and certainly longer than the W=W bond in $\text{W}_2(\text{OEt})_4(\text{HOEt})_2\text{Cl}_4$ ²⁴ and $\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$. (2) The

W-O (carbonyl) distance of 2.02 \AA is much shorter than would be expected for a simple donor $O \rightarrow W$ distance. The W-O distance is approaching a W-OR terminal distance. (3) The C-O bond distance of 1.32 \AA is close to that expected for a $C_{(sp^2)}-O$ single bond distance. (4) The W-C (carbonyl) distance is shorter by ca. 0.1 \AA than it is in the $W_2(OPr^i)_6(py)_2(\mu-CO)$ molecule. All four points are indicative of the importance of the resonance forms XVa and XVb.



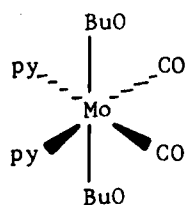
XVa



XVb

Thus, in a simple sequence, the $W \equiv W$ and $C \equiv O$ bonds are transformed to single bonds, W-W and C-O, respectively. In a further reaction with $W_2(OPr^i)_6$, it appears that an additional two-electron reduction of the CO ligand occurs to give carbido and oxotungsten clusters. It is not yet clear how this proceeds: the stoichiometry of the reaction is not known. The structural characterization of $W_4(OPr^i)_{12}(NMe)(C)$, a molecule derived from the degradation of $W_2(OPr^i)_6(HNMe_2)_2$, reveals⁷¹ the butterfly W_4C unit shown in Figure 27 and bears a striking resemblance to the "iron-butterfly", $Fe_4(C)(CO)_{13}$.⁷²

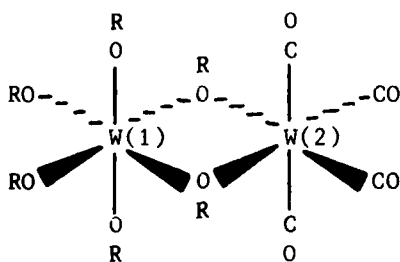
In the presence of excess CO, two other carbonyl compounds have been isolated and structurally characterized. $Mo(OBu^t)_2(py)_2(CO)_2$ is formed in the reaction between $Mo_2(OBu^t)_6$ and CO, in the presence of pyridine, and has a distorted octahedral geometry based on XVI.⁴⁰



XVI

This molecule is characterized by unusually low $\nu(\text{CO})$ values, 1906 and 1776 cm^{-1} , for cis dicarbonyl $\text{Mo}(2+)$ containing compounds. In part, this may be understood in terms of the RO π -donating ability of the RO ligands. The C-Mo-C angle is also unusually small, 72° , and this presumably influences the magnitude of the CO coupling which is exceedingly large, $\Delta = 140 \text{ cm}^{-1}$.

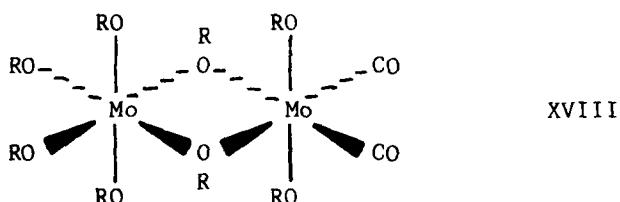
Cotton and Schwotzer⁷⁰ have isolated a compound of formula $\text{W}_2(\text{OPr}^i)_6(\text{CO})_4$ from the reaction between $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ and CO. This molecule has the edge-shared octahedral geometry shown in XVII.



XVII

The W-W distance is greater than 3 \AA , too long to indicate any W-W bonding. Also, the W-O distances associated with the $\text{W}_2(\mu_2\text{-OPr}^i)_2$ group are asymmetric, averaging 1.92 \AA and 2.10 \AA to W(1) and W(2), respectively. The compound may be viewed as a $\text{W}(6+)$ - $\text{W}(0)$ dimer in which a pair of alkoxy groups act as neutral ligands to a $\text{W}(\text{CO})_4$ group. It is easy to see how

$W(CO)_6$ and $W(OPr^i)_6$ could be derived by the further reaction with two equivalents of CO. In the reaction between CO and $Mo_2(OPr^i)_8$, an adduct, $Mo_2(OPr^i)_8(CO)_2$, was isolated⁴⁰ and was proposed to have the similar structure shown in XVIII based on the appearance of two CO bands at 1940 and 1820 cm^{-1} .



If for the sake of electron counting we split the bridge asymmetrical-ly, this may be viewed as a $Mo(6+)---Mo(2+)$ dimer. $Mo_2(OPr^i)_8(CO)_2$ would then be related to $Mo(OBu^t)_2(py)_2(CO)_2$, XVI.

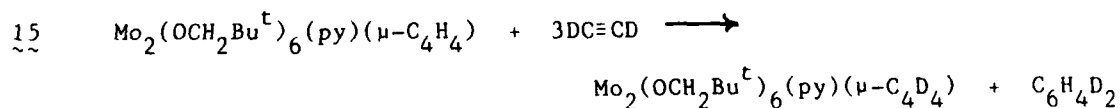
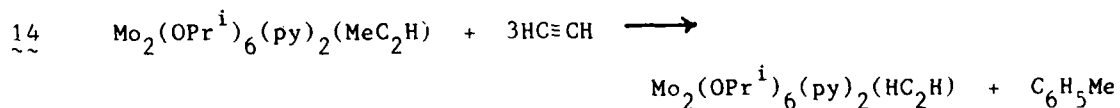
Addition of Alkynes. Hydrocarbon solutions of $Mo_2(OR)_6$ compounds ($R = Bu^t, Pr^i$ and CH_2Bu^t) react rapidly with the sterically unencumbered alkynes, $CH\equiv CH$, $MeC\equiv CH$ and $MeC\equiv CMe$. Ethyne produces an insoluble polymer of grey-black metallic appearance; propyne yields a yellow powdery material and but-2-yne gives a rubbery material. The detailed nature of these polymers are not known at present. The polymerization processes are very rapid at room temperature and, in an attempt to moderate these reactions and investigate the mechanism of polymerization, we carried out alkyne additions in the presence of donor ligands such as pyridine. This approach yielded a number of interesting compounds containing alkyne or alkyne fragments. For the isopropoxy ligand, compounds of formula $Mo_2(OPr^i)_6(py)_2-$

($\mu\text{-C}_2\text{RR}'$) were isolated ($\text{R} = \text{R}' = \text{H}$, Me and $\text{R} = \text{Me}$, $\text{R}' = \text{H}$). The structure of $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ is shown in Figure 28, wherein a close resemblance can be seen to the $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$ molecule. In solution, these molecules are fluxional and show rapid reversible dissociation of pyridine on the NMR time scale.

With the less sterically demanding neopentoxo ligand, flyover compounds are formed and a view of the structurally characterized compound $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6(\text{py})(\mu\text{-C}_4\text{H}_4)$ is shown in Figure 29. A number of interesting points emerge from a consideration of this structure. Whereas it is possible to view the $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ molecule as a $d^3\text{-}d^3$ dimer with the bridging alkyne acting as a four-electron donor, in the $\mu\text{-C}_4\text{H}_4$ compound, the dimolybdenum center has clearly been oxidized. The Mo-Mo distance, $2.69(1) \text{ \AA}$, is approaching that of a single bond distance. If the $\mu\text{-C}_4\text{H}_4$ ligand is counted as a 2- ligand with respect to Mo(1) and merely a η^4 -diene to Mo(2), then the formal oxidation state of Mo(1) is $+4\frac{1}{2}$ and that of Mo(2) is $+3\frac{1}{2}$. The Mo(1)- $\mu\text{-O}$ distance, $2.06(2) \text{ \AA}$, is notably shorter than the Mo(2)- $\mu\text{-O}$ distance, $2.17(2) \text{ \AA}$, and the Mo(1)-N(pyridine) distance, $2.15(3) \text{ \AA}$, is significantly shorter than those in $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ which average $2.31(1) \text{ \AA}$. In solution (toluene- d_8), the molecule is not fluxional on the NMR time scale and the pyridine ligand does not exchange with free pyridine. Only at $+90^\circ\text{C}$ do these processes become sufficiently rapid to cause line broadening.

The nature of the formation of the $\mu\text{-C}_4\text{H}_4$ ligand is evidently a simple coupling process since the ^1H NMR spectrum of the $\mu\text{-C}_4\text{H}_2\text{D}_2$ ligand formed from the addition of C_2H_2 to $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$, is an AX spectrum, whereas that of the protio ligand $\mu\text{-C}_4\text{H}_4$ is an AA'XX' spectrum at 220 MHz.

The possible role of these compounds in alkyne polymerization was investigated by a variety of labelling studies which showed that they were only involved in alkyne trimerization to give benzenes, e.g. as in equations 14 and 15.⁷³



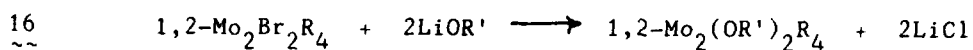
The catalytically active species in the polymerization process, which is kinetically more rapid than cyclotrimerization, is not yet known. It could conceivably be a carbene, vinylidene or carbyne function,⁷⁴ all of which could be derived from an alkyne.

Analogous reactions involving $\text{W}_2(\text{OR})_6\text{L}_2$ compounds with C_2H_2 have led to the isolation of simple adducts $\text{W}_2(\text{OR})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ where $\text{R} = \text{Bu}^t$ and Pr^i .⁴³ The isopropoxide is isostructural with its molybdenum analogue and shows similar solution behavior. However, its reactivity is somewhat different. Addition of more ethyne leads to $\text{W}_2(\text{OPr}^i)_6(\mu\text{-C}_4\text{H}_4)(\text{C}_2\text{H}_2)$ presumably via an intermediate $\text{W}_2(\text{OPr}^i)_6(\text{py})(\mu\text{-C}_4\text{H}_4)$ analogous to $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6(\text{py})(\mu\text{-C}_4\text{H}_4)$. Similarly, addition of 2-butyne to $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ proceeds ultimately to give $\text{W}_2(\text{OPr}^i)_6(\mu\text{-C}_4\text{Me}_4)(\text{C}_2\text{Me}_2)$. The solid state structures of the compounds $\text{W}_2(\text{OPr}^i)_6(\mu\text{-C}_4\text{R}_4)(\text{C}_2\text{R}_2)$ where $\text{R} = \text{H}$ and Me have been determined by X-ray studies and their dynamic solution behavior investigated by variable temperature NMR studies. An ORTEP view of the $\text{W}_2(\text{OPr}^i)_6(\mu\text{-C}_4\text{H}_4)$ -

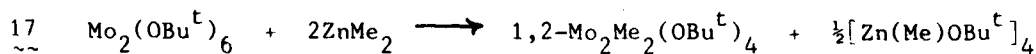
(C₂H₂) compound is given in Figure 30 which provides the basis for a comparison with the Mo₂(OCH₂Bu^t)₆(py)(μ-C₄H₄) molecule. The W-W distance is 2.877(1) Å, indicative of a relatively weak M-M bond. This distance is ca. 0.2 Å longer than that in Mo₂(OCH₂Bu^t)₆(py)(μ-C₄H₄), consistent with the view that metal d electrons are effectively tied up in backbonding to the π-acceptor ligands. Tungsten, relative to molybdenum, is more easily oxidized and, in this instance, is reluctant to eliminate a benzene molecule.

As noted earlier, W₂(OBu^t)₆ reacts with 2-butyne to give (Bu^tO)₃-W≡CMe.⁶⁴ Cotton and Schwotzer⁷⁰ have characterized [(Bu^tO)₂W(μ-CPh)]₂ and W₂(OBu^t)₄(μ-C₂Ph₂)₂ compounds from reactions involving W₂(OBu^t)₆ and PhC≡CPh. The structure of the former compound is similar to that observed for [(Me₃SiCH₂)₂W(μ-CSiMe₃)]₂,⁷⁶ while the latter contains a planar W₂O₄ moiety with terminal OBU^t ligands with two skewed bridging μ-acetylene ligands. It is evident that a wide variety of products are derived from reactions involving alkynes and M₂(OR)₆ compounds and that steric and electronic factors and reaction conditions are critical in controlling the course of the reaction.

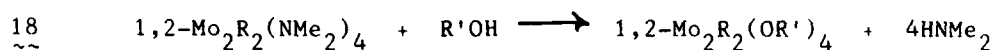
Alkyl-Alkoxides of Dimolybdenum (M≡M). Two approaches to the synthesis of mixed alkyl-alkoxides of dimolybdenum (M≡M) have been taken. One involves metathetic reactions wherein an alkyl ligand or an alkoxy ligand is introduced to the dimetal center, e.g. as in 16¹¹ and 17.⁷⁷



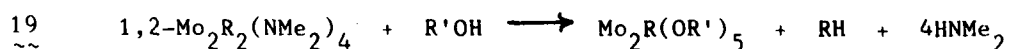
where $\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{R}' = \text{Bu}^t$ or Pr^i



The other approach involves the alcoholysis of $1,2\text{-Mo}_2\text{R}_2(\text{NMe}_2)_4$ compounds. The latter reaction yields products dependent on the nature of the alkyl ligand as is shown in 18 and 19.⁷⁸



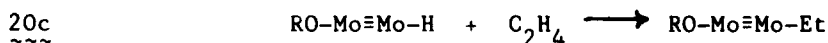
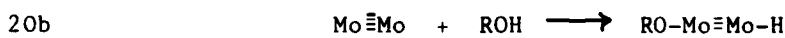
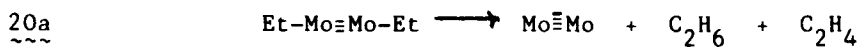
where $\text{R} = \text{Me}$, $\text{R}' = \text{Bu}^t$; $\text{R} = \text{CH}_2\text{CMe}_3$, CH_2SiMe_3
and $\text{R}' = \text{Bu}^t$, Pr^i , CH_2CMe_3 and Et



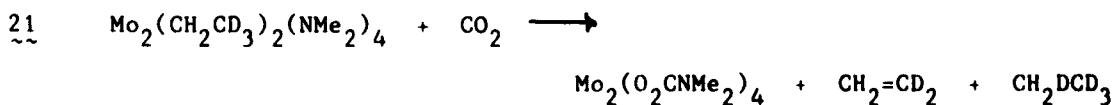
where $\text{R} = \text{Et}$ and Pr ; $\text{R}' = \text{Bu}^t$ and Pr^i

The rate of alcoholysis is dependent on the steric factors of R and R', being much slower for bulky combinations. Alcoholysis is faster for Mo-NMe₂ groups than for Mo-R groups, but the thermodynamically favored products in 18 and 19 are Mo₂(OR')₆ compounds, and these are ultimately formed under prolonged alcoholysis. For example, while Mo₂Me₂(NMe₂)₄ reacts rapidly with Bu^tOH to give Mo₂Me₂(OBu^t)₄, further reaction to give Mo₂Me(OBu^t)₅ and Mo₂(OBu^t)₆ occurs more slowly.

The failure to isolate or even detect $\text{Mo}_2\text{R}_2(\text{OR}')_4$ compounds, where $\text{R} = \text{Et}$ and Pr and $\text{R}' = \text{Bu}^t$ and Pr^i , suggested a β -hydrogen elimination pathway was involved. This was confirmed and delineated in the following reactions.⁷⁸ (1) When $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$ and $\text{Mo}_2(\text{CH}(\text{CD}_3)_2)_2(\text{NMe}_2)_4$ were allowed to react with Bu^tOH , the eliminated alkanes were CH_2DCD_3 and $\text{CD}_3\text{CHDCD}_3$, respectively. (2) When $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ was allowed to react with Bu^tOD , the resulting ethyl complex was $\text{Mo}_2(\text{CH}_2\text{CH}_2\text{D})(\text{OBu}^t)_5$. Evidently the elimination of alkane involves the transference of a β -hydrogen (or deuterium) from one alkyl group to the α -carbon of the other, and the resultant ethyl ligand is formed from the hydrogen atom (deuterium) of the hydroxyl group of the alcohol and a coordinated alkene. A reductive-elimination and oxidative-addition sequence of the type schematically represented by 20a, b and c is implicated.



Each step has precedence in the dinuclear chemistry of molybdenum and tungsten. (1) Reductive elimination by alkyl group disproportionation has been observed in the reactions between $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ and CO_2 , reaction 21.⁷⁹



(2) Oxidative-addition of ROH to a W-W triple bond is seen in the formation of $W_4(\mu-H)_2(OPr^i)_{14}$.³⁵ (3) Insertion of alkenes into metal hydrides is, of course, well documented in organometallic chemistry and $W_2(\mu-H)_2(OPr^i)_{14}$ reacts reversibly with ethylene.³⁵

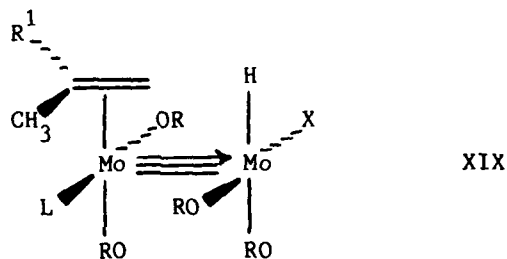
Further evidence for the sequence in 20 is seen in the observation that $Mo_2Bu^i_2(NMe_2)_4$ reacts with Pr^iOH to give an intense blue solution which by 1H NMR can be seen to contain a Mo_2 -hydride, $\delta = 6.7$ ppm. This probably is a confacial bioctahedral compound: $Mo_2(OPr^i)_3(\mu-H)(\mu-OPr^i)_2(HNMe_2)_3$. Addition of ethylene gives $Mo_2Et(OPr^i)_5$.

One other interesting feature of 19 concerns the insertion step forming the alkyl. In reactions involving $Mo_2R_2(NMe_2)_4$ with Bu^tOH , where $R = Pr^i, Pr^n$ and Bu^i , the products are $Mo_2Pr^i(OBu^t)_5$ and $Mo_2Bu^t(OBu^t)_5$. In the reaction between $Mo_2Pr^n_2(NMe_2)_4$ and Pr^iOH , the initially formed compound is $Mo_2Pr^i(OPr^i)_5$ which, in the absence of donor ligands such as $HNMe_2$, is quite stable. However, upon addition of donor ligands, $HNMe_2$ or py , isomerization to $Mo_2Pr^n(OPr^i)_5$ is observed. It is apparent that (1) the insertion of the alkyl ligand occurs with kinetic control and (2) that isomerization of the alkene ligand by a β -hydrogen elimination process does not readily occur for $Mo_2R(OR')_5$ compounds, but that this may be promoted by a Lewis base association reaction.

It is possible to rationalize these observations in the following way. (1) The metal-hydride insertion step occurs across the M-M bond and thus the conformational preference for alkene coordination with its alkyl substituent(s) distal to the M-M bond will generate, upon hydride insertion, the most highly substituted carbon being σ -bonded to molybdenum. (2) The strongly π -donating RO ligands will effectively tie up empty molybdenum

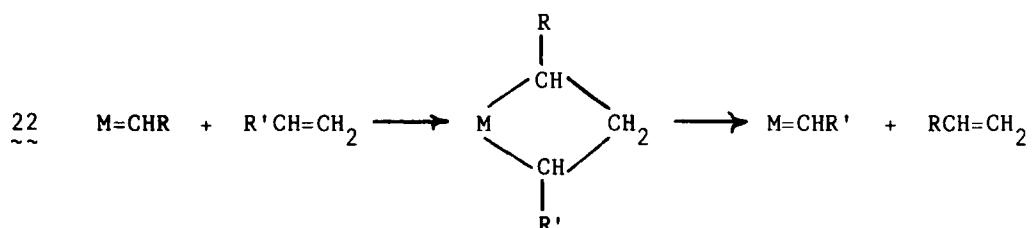
atomic orbitals which would otherwise be available for M---H-C interactions leading to M-H and alkene. This stabilization of β -hydrogen containing alkyls has been discussed in detail in connection with $M_2R_2(NMe_2)_4$ compounds.³⁷ (3) In the presence of donor ligands, the coordination of a ligand to one metal activates the other toward β -hydrogen abstraction. This may be viewed as another aspect of the cooperative binding of $M_2(OR)_6$ compounds, reaction 2, discussed previously.

A common intermediate of the type shown in XIX can be envisaged.

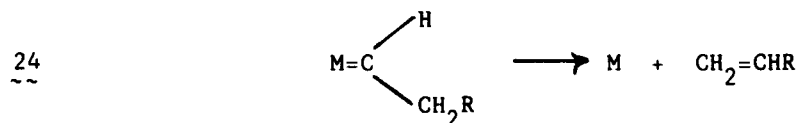
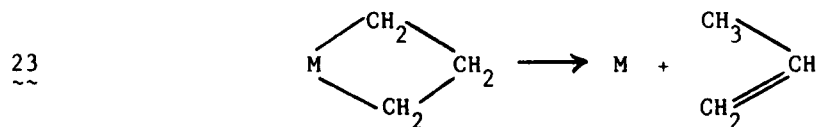


When $X = R$ (alkyl), elimination of alkane occurs. When $X = OR$, insertion will lead to $Mo_2(CH(CH_3)R')(OR)_5$, where $R' = H$ or Me . A subsequent isomerization of the alkyl ligand may occur in the presence of L providing the alkene can ultimately gain access to a position with the alkyl group(s) over the M-M bond. Alternatively, if the Lewis base coordinates to the $Mo(OR)_3$ end of the molecule, β -hydrogen abstraction followed by an insertion to give the isomerized alkyl may occur at the other metal. Clearly more work is required to delineate the intricacies of these reactions.

Olefin- and Acetylene-Metathesis Reactions. One of the most fascinating reactions to capture the minds of organic and organometallic chemists within recent years is the olefin metathesis reaction.^{80,81} There is now a large body of evidence to support the intimate mechanism originally proposed by Chauvin⁸² which is depicted by 22.



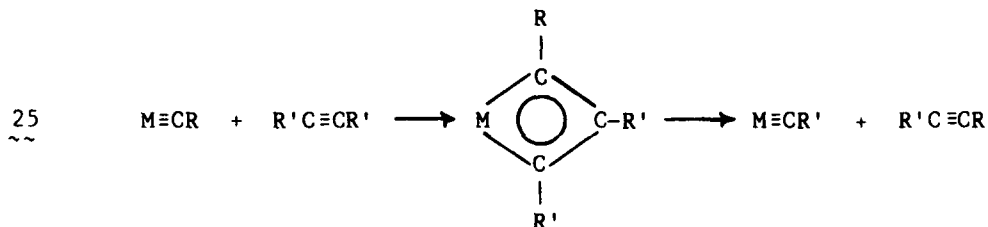
Schrock and coworkers⁸³ have shown that niobium and tantalum alkylidene complexes can indeed promote olefin metathesis. One of the terminating steps and break down in the catalytic cycle involves a β -hydrogen elimination step either from the metallacycle or from the alkylidene complex as shown in 23 and 24.



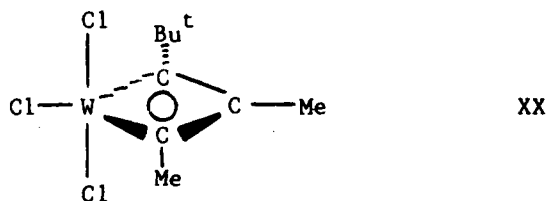
In both 23 and 24, β -hydrogen abstraction is followed by reductive elimination of alkene by C-H bond formation. The net effect is a 1,2-H atom shift. Schrock and coworkers have shown that these competing β -hydrogen

abstraction reactions can be greatly suppressed by replacing Cl by RO ligands.⁸⁴ Tungsten(VI) oxo, imido and alkoxy alkylidene complexes are amongst the best homogeneous olefin metathesis catalysts known.⁸³ The role of the ancillary π -donor ligands in the olefin metathesis reaction has recently been the subject of a theoretical study: the so-called spectator group effect.⁸⁵

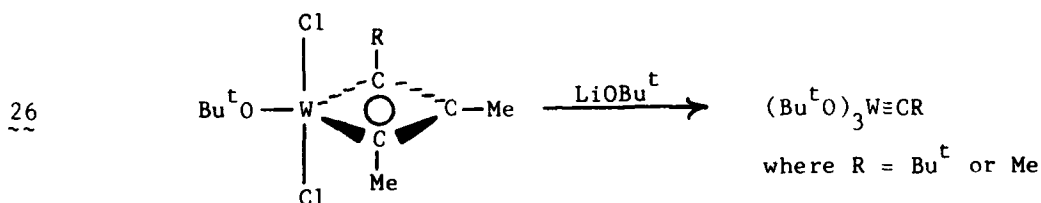
The alkoxy-alkylidyne complexes $(\text{Bu}^t\text{O})_3\text{W}\equiv\text{CR}$ are efficient alkyne metathesis catalysts. There is good evidence to support the view that alkyne metathesis proceeds via the intermediacy of a tungstenacyclobutadiene as shown in eq. 25.



When chloride ligands are on tungsten, a tungstencyclobutadiene complex, XX, has been isolated and structurally characterized⁸⁶ and found to have a trigonal bipyramidal geometry with one W-Cl and two W-C bonds in the equatorial plane.



Further reaction with another molecule of dimethylacetylene gives $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{WCl}_3$: tungsten is reduced from +6 to +4. However, when alkoxy ligands are present, the alkylidyne complex is stabilized relative to the metallacyclobutadiene and the ultimate formation of the π -cyclopentadiene $\text{W}(4+)$ complex is not observed. Interestingly, one Bu^tO ligand can be introduced into the equatorial site replacing Cl in XX, but a further Bu^tO for Cl substitution reforms the alkylidyne complex, eq. 26.



The Bu^tO ligands favor the alkylidyne ligand, relative to the metallacyclobutadiene; they suppress β -hydrogen elimination and favor the oxidation state +6 for tungsten.

Concluding Remarks

Metal-metal bonds are pervasive in the chemistry of molybdenum and tungsten alkoxides. They may modify structures found for d^0 metal alkoxides as is seen for $\text{W}_4(\text{OEt})_{16}$ or may provide for totally new geometries as is seen for the $\text{M}_2(\text{OR})_6$ compounds. Metal-metal bonds provide a reservoir of electrons for redox chemistry: the reservoir may be tapped in oxidative-addition reactions and may be filled in reductive-elimination processes. Alkoxide ligands may act as four- or two-electron donors and may readily change between terminal and bridging positions. This allows for the facile

interconversion of saturated and unsaturated metal centers. As π -donor ligands, they can enhance backbonding to π -acid ligands on the same metal; they can tie up vacant metal d orbitals and suppress metal-hydride abstraction from coordinated alkyl ligands and they stabilize metals in high oxidation states. A variety of steric control may be engineered by suitable choice of alkyl group and this may greatly influence structure, M-M bonding and the reactivity of coordinated ligands. This is well illustrated in the reactions of $\text{MeC}\equiv\text{CMe}$ with $\text{W}_2(\text{O}^t\text{Bu})_6$ and $\text{W}_2(\text{O}^i\text{Pr})_6$ which lead to $(\text{Bu}^t\text{O})_3\text{-W}\equiv\text{CMe}$ and $\text{W}_2(\text{O}^i\text{Pr})_6(\mu\text{-C}_4\text{Me}_4)(\text{MeC}_2\text{Me})$. It is now clear that an extensive organometallic chemistry can be supported in the absence of ligands commonly employed in organometallic chemistry.

Acknowledgements

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Table I. Metal-Metal Distances and Metal-Metal Bond Orders in Representative Dinuclear Alkoxides of Molybdenum and Tungsten.

Compound	Bridging Ligands	M-M Distance (Å)	Bond Order	Ref
$\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6$	none	2.222(2)	3	6
$\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2$	none	2.250(2)	3	47
$\text{W}_2(\text{OPr}^i)_6(\text{py})_2$	none	2.334(1)	3	9
$\text{Mo}_2(\text{OBu}^t)_6(\text{CO})$	$2\text{OBu}^t, \text{CO}$	2.498(1)	2	68
$\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$	$2\text{OPr}^i, \text{CO}$	2.486(2)	2	69
$\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$	$2\text{OPr}^i, \text{CO}$	2.499(3)	2	69
$\text{Mo}_2(\text{OPr}^i)_8$	2OPr^i	2.523(1)	2	16
$\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6\text{Br}_2(\text{py})$	$2\text{OR}, \text{Br}$	2.534(1)	2	47
$\text{W}_2\text{Cl}_4(\text{OEt})_4(\text{HOEt})_2$	2OEt	2.483(1)	2	20
$[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$	$\text{H}, 2\text{OPr}^i$	2.446(1)	2	35
$\text{Mo}_2\text{Cl}_4(\text{OPr}^i)_6$	2OPr^i	2.731(1)	1	25

Table I. Continued.

Compound	Bridging Ligands	M-M Distance (Å)	Bond Order	Ref
$W_2Cl_4(OEt)_6$	2OEt	2.715(1)	1	24
$[Mo_4(OPr^i)_3(NO)]_2$	2OPr ⁱ	3.335(2)	0	19
$[W_2(H)(OPr^i)_7]_2$	2OR	3.407(1)	0	35
$[W(OMe)_4NPh]_2$	2OMe	3.47(1)	0	a

^aA.J. Nielson and J.M. Waters. *Polyhedron* 1982, 1, 561.

Table II. M-M Distances (Å) Found in Compounds which are Structurally Related to $W_4(OEt)_{16}$.^a

Compound	M(2)-M(1)'	M(1)-M(2)	M(1)-M(1)'	Number of M ₄ Cluster Electrons	Ref.
$[Ti(OEt)_4]_4$	3.34	3.50	3.42	0	31
$Ag_8W_4O_{16}$	3.32	3.23	3.49	0	32
$Mo_4O_8(OPr^i)_4(py)_4$	3.47	2.60	3.22	4	30
$Mo_4Cl_4O_6(OPr^n)_6$	3.43	2.67	not given	4	b
$W_4(OEt)_{16}$	2.65	2.94	2.76	8	30
$Ba_{1.14}Mo_8O_{16}$	2.54	2.84	2.56	8	33
$Ba_{1.14}Mo_8O_{16}$	2.61	2.57	2.58	10	33

(a) Distances are quoted to ± 0.01 Å; the labelling scheme for M(1), M(2) and M(1)' is shown below and is such that M(1) and M(2) have, respectively, two and three terminal groups. (b) S.A. Koch and S. Lincoln, *Inorg. Chem.* 1982, 21, 2904.



Table III. Representative M-O Distances (Å) in Molybdenum and Tungsten Alkoxides.^a

Compound	M-O (terminal)	Mo-O (μ_2)	Mo-O (μ_3)	Ref
$\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6$	1.905(6) 1.867(6) 1.855(6)			6
$\text{Mo}_2\text{Cl}_4(\text{OPr}^i)_6$	1.815(3) 1.808(3) 1.819(3) 1.814(3)	2.020(3) 2.013(3) 2.014(3) 2.016(3)		25
$\text{W}_2\text{Cl}_4(\text{OEt})_6$	1.820(4) 1.828(4)	2.011(4) 2.013(4)		24
$\text{Mo}_2(\text{OPr}^i)_8$	1.976(3) (axial) 1.884(3) (eq) 1.872(3) (eq)	2.111(3) (axial) 1.958(3) (eq)		16
$\text{Mo}_3\text{O}(\text{OCH}_2\text{Bu}^t)_{10}^a$	1.94(2) (trans to O) 1.85(2) (trans to OR)	2.02(3)	2.21(3)	27
$\text{Mo}_4\text{Cl}_4(\text{OPr}^i)_8^a$		1.981(4) 2.078(4)		50
$\text{Mo}_4\text{Br}_4(\text{OPr}^i)_8^a$	1.84(1)	2.02(2)	2.15(1)	50
$\text{W}_4(\text{OEt})_{16}^a$	1.93(3)	2.04(3)	2.18(2)	30

Table III. Continued.

Compound	M-O (terminal)	Mo-O (μ_2)	Mo-O (μ_3)	Ref
$\text{Mo}_2(\text{O}^t\text{Bu})_6(\text{CO})$	1.88(1) 1.89(1)	2.09(1) 2.07(1)		68
$\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$	1.909(6) 1.920(5)	2.098(6) 2.113(6)		69
$\text{W}_2(\text{OPr}^i)_6(\text{py})_2(\text{CO})$	1.91(2) 1.92(2)	2.12(2) 2.15(2)		69
$[\text{W}(\text{OMe})_4\text{NPh}]_2$	1.92(1) 1.97(1) 2.02(1)	2.04(1) (trans to OMe) 2.14(1) (trans to NPh)		b

^aAveraged where appropriate.

^bA.J. Nielson and J.M. Waters, Polyhedron 1981, 1, 561.

Table IV. Comparison of M-M, M-N, M-O Bond Distances (Å) and Relevant Bond Angles (°) in Selected $M_2(OR)_6L_2$ Compounds. ^a

Compound	M-M	M-N(av)	M-M-L(av)	L-M-M-L	M-O ^t	M-M-O ^t	M-O ^c (av)	M-M-O ^c (av)	Ref
$W_2(OPr^i)_6(HNMe_2)_2$	2.339(1)	2.28	90.6	95.0	1.90	110.1	1.96	100	43
$W_2(OPr^i)_6(py)_2$	2.334(1)	2.27	91.8	58.6	1.92	105.7	1.94	102	9
$W_2(OCH_2Bu^t)_6(pyMe-4)_2$	2.328(2)	2.27	97.4	127.2	1.94	99.2	1.92	107	43
$W_2(OEt)_6(DMEDA)$	2.296(2)	2.28	90.0	48.3	1.89	106.8	1.94	102	43
$W_2(OCH_2Bu^t)_6(PMe_3)_2$	2.362(2)	2.52	90.2	114.0	1.95	113.3	1.96	104	b
$Mo_2(OPr^i)_6(py)_2$	2.250(2)	2.32	92.7	56.5	1.90	104.3	1.95	104	43
$Mo_2(OCH_2Bu^t)_6(py)_2$	2.222(1)	2.31	95.1	44.5	1.96	105.8	1.94	103	43
$Mo_2(OSiMe_3)_6(HNMe_2)_2$	2.242(1)	2.28	94.6	110.0	1.94	101.6	1.95	103	c
$Mo_2(OCH_2Bu^t)_6(DMEDA)$	2.218(1)	2.31	91.1	51.3	1.92	101.6	1.96	102	43

^a Abbreviations are as follows: py = pyridine; pyMe-4 = 4-methylpyridine; DMEDA = $Me_2NCH_2CH_2NMe_2$; O^t = oxygen trans to L; O^c = oxygens cis to L. ^b M.J. Chetcuti, M.H. Chisholm and J.C. Huffman, results to be published. ^c M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, *J. Am. Chem. Soc.* 1978, 100, 153.

Table V. Some Characterization Data for the $M_2(OPr^i)_6(py)_2(\mu-CO)$ Compounds.^a

	M = Mo	M = W
$\nu(CO) \text{ cm}^{-1}$	1655	1555
$\nu(^{13}CO) \text{ cm}^{-1}$	1637	1532
$\delta(^{13}CO) \text{ ppm}$	325.7	310.4 $J_{^{183}W-^{13}C} = 170 \text{ MHz}$
$d(C-O) \text{ \AA}$	1.19(1)	1.22(2)
$d(M-CO) \text{ \AA}$	2.06(1)	2.04(2)
$d(M-N) \text{ \AA}$	2.486(2)	2.490(3)

^aAll data taken from ref. 69.

Figure 1. An ORTEP view of the centrosymmetric $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6$ molecule. Pertinent distances (\AA) and angles ($^\circ$) are: Mo-Mo = 2.222(2); Mo-O(1), -O(2), -O(3) = 1.905(6), 1.867(6), 1.855(6); Mo'-Mo-O(1), -O(2), -O(3) = 98.3(2), 105.5(2), 105.4(2).

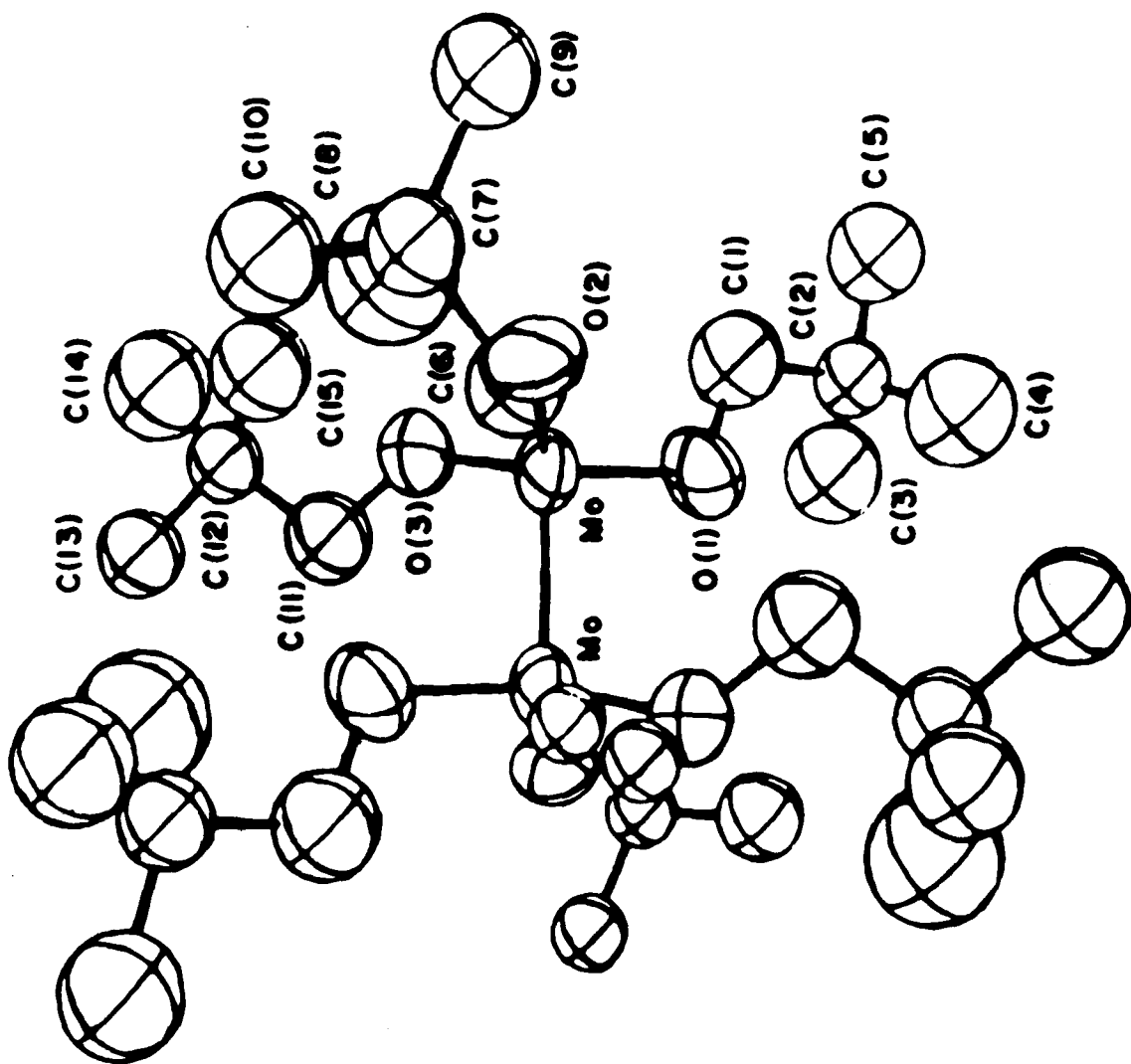


Figure 2. An ORTEP view of the centrosymmetric $1,2\text{-Mo}_2(\text{OBu}^t)_2(\text{CH}_2\text{SiMe}_3)_4$ molecule. Pertinent distances (\AA) and angles ($^\circ$) are: $\text{Mo}(1)\text{-Mo}(1)' = 2.209(2)$; $\text{Mo}(1)\text{-O}(2), \text{-C}(7), \text{-C}(12) = 1.865(8), 2.13(1), 2.14(1)$; $\text{Mo}(1)'\text{-Mo}(1)\text{-O}(2), \text{-C}(7), \text{-C}(12) = 110.7(2), 100.0(3), 100.2(4)$.

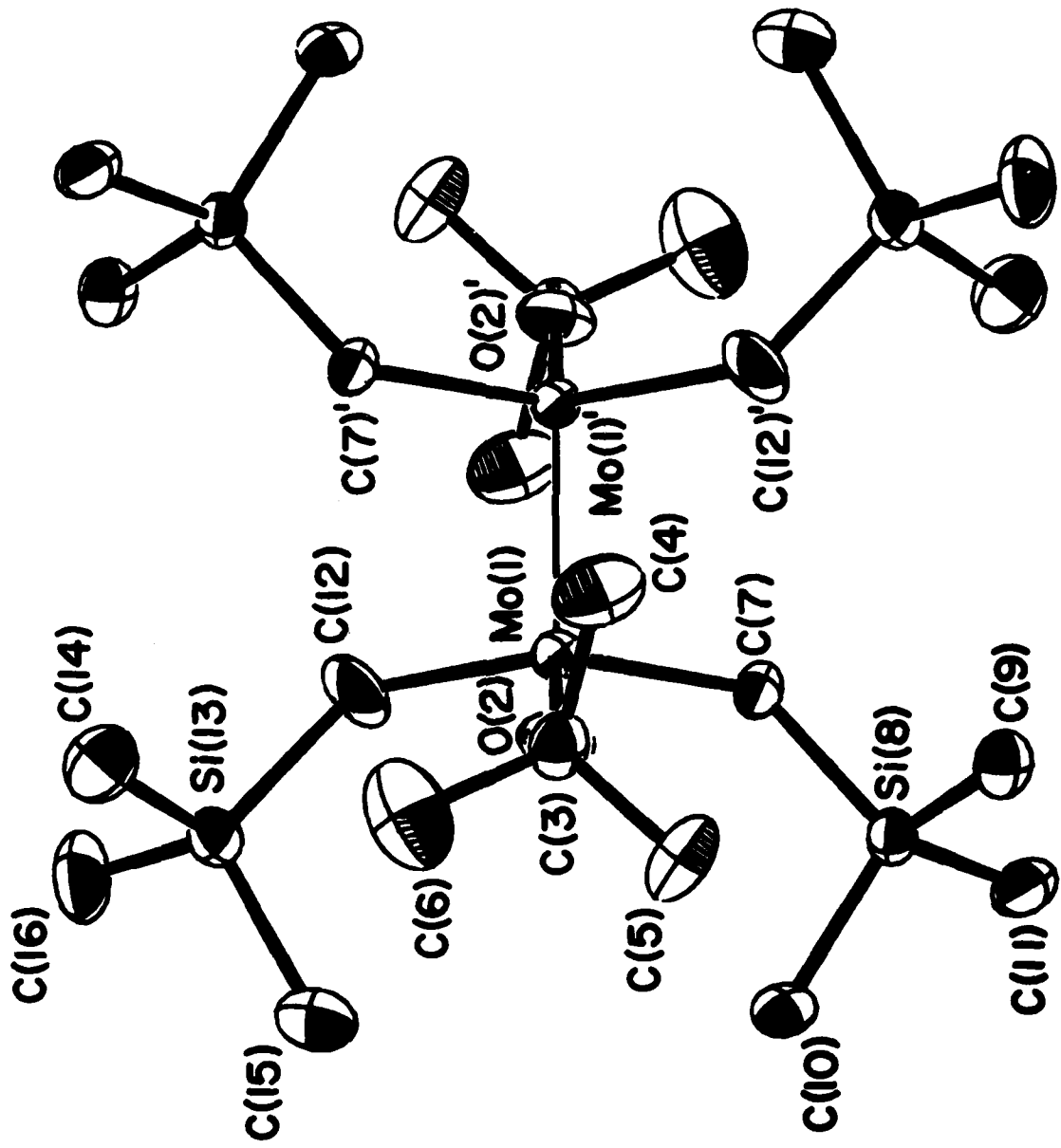


Figure 3. Comparison of the electronic absorption spectra of $\text{Mo}_2(\text{OPr}^i)_6$ and $\text{W}_2(\text{O}^t\text{Bu})_6$ in hexane solutions.

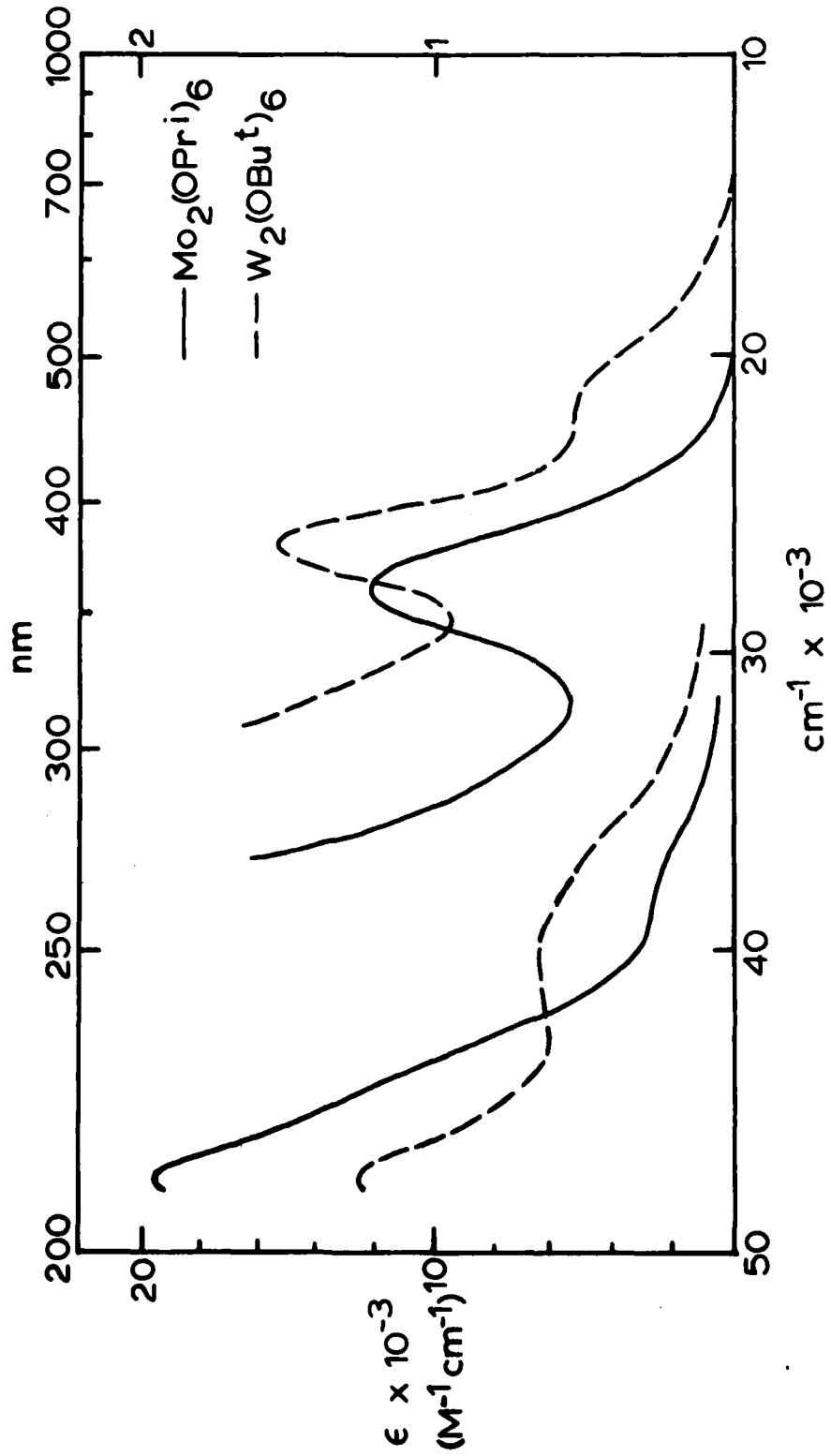


Figure 4. An ORTEP view of the centrosymmetric $\text{Mo}_2(\text{OPr}^i)_8$ molecule. Pertinent distances are given in comparison with the $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ molecule in Figure 18.

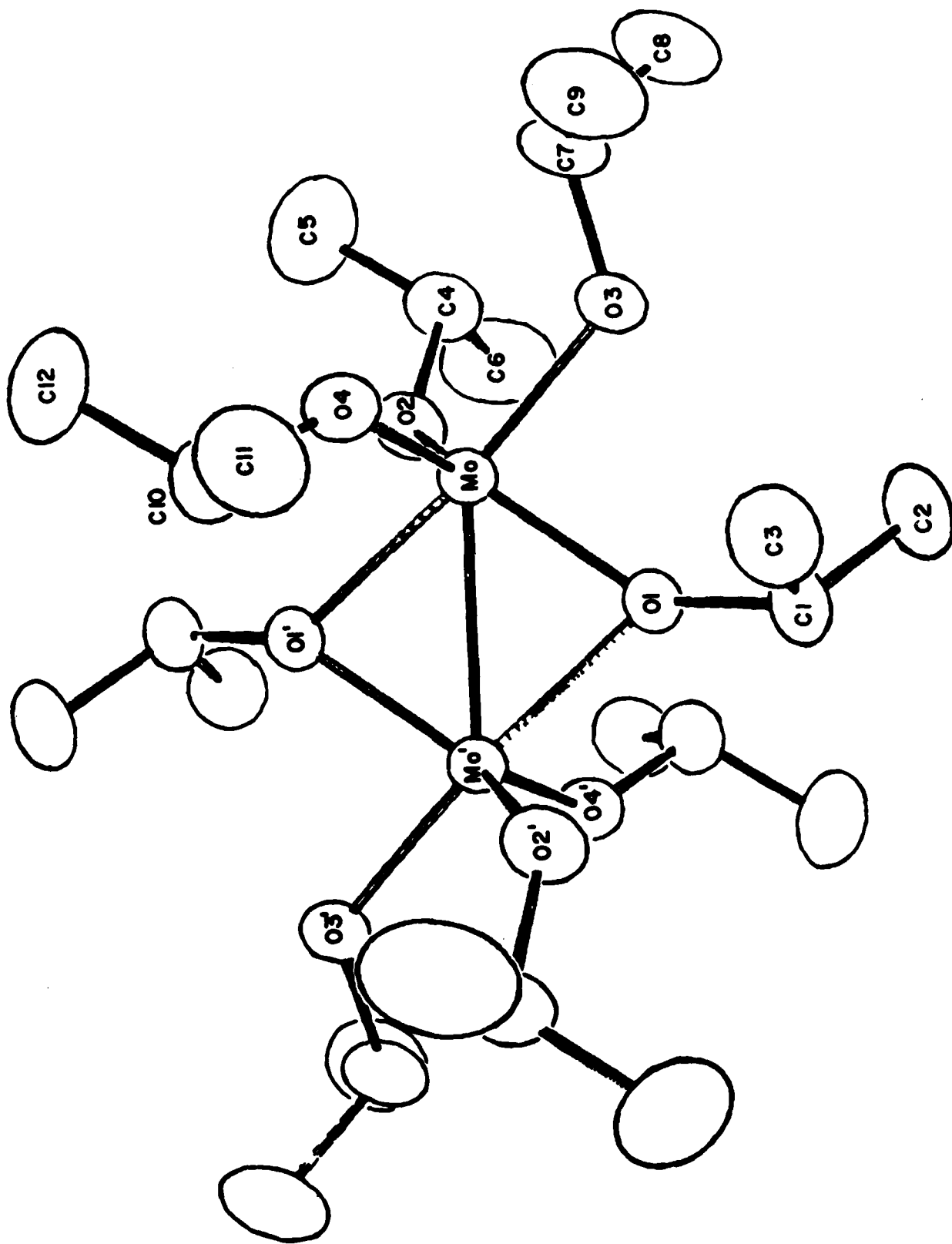


Figure 5. An ORTEP view of the central $\text{Mo}_3\text{O}(\text{OC})_{10}$ skeleton of the $\text{Mo}_3\text{O}(\text{OCH}_2\text{Bu}^t)_{10}$ molecule. All atoms are assigned arbitrary thermal parameters. Each molybdenum atom is in a distorted octahedral environment with respect to six directly bonded oxygen atoms. Pertinent bond distances in Å (averaged) are: Mo-Mo = 2.529(9), Mo- $\mu_3\text{O}(\text{oxo})$ = 2.03(3), Mo- μOR = 2.21(3), Mo- $\mu_2\text{OR}$ = 2.02(3), Mo-OR(terminal) trans to O(4) = 1.94(2), Mo-OR(terminal) trans to $\mu_3\text{OR}$ = 1.85(3).

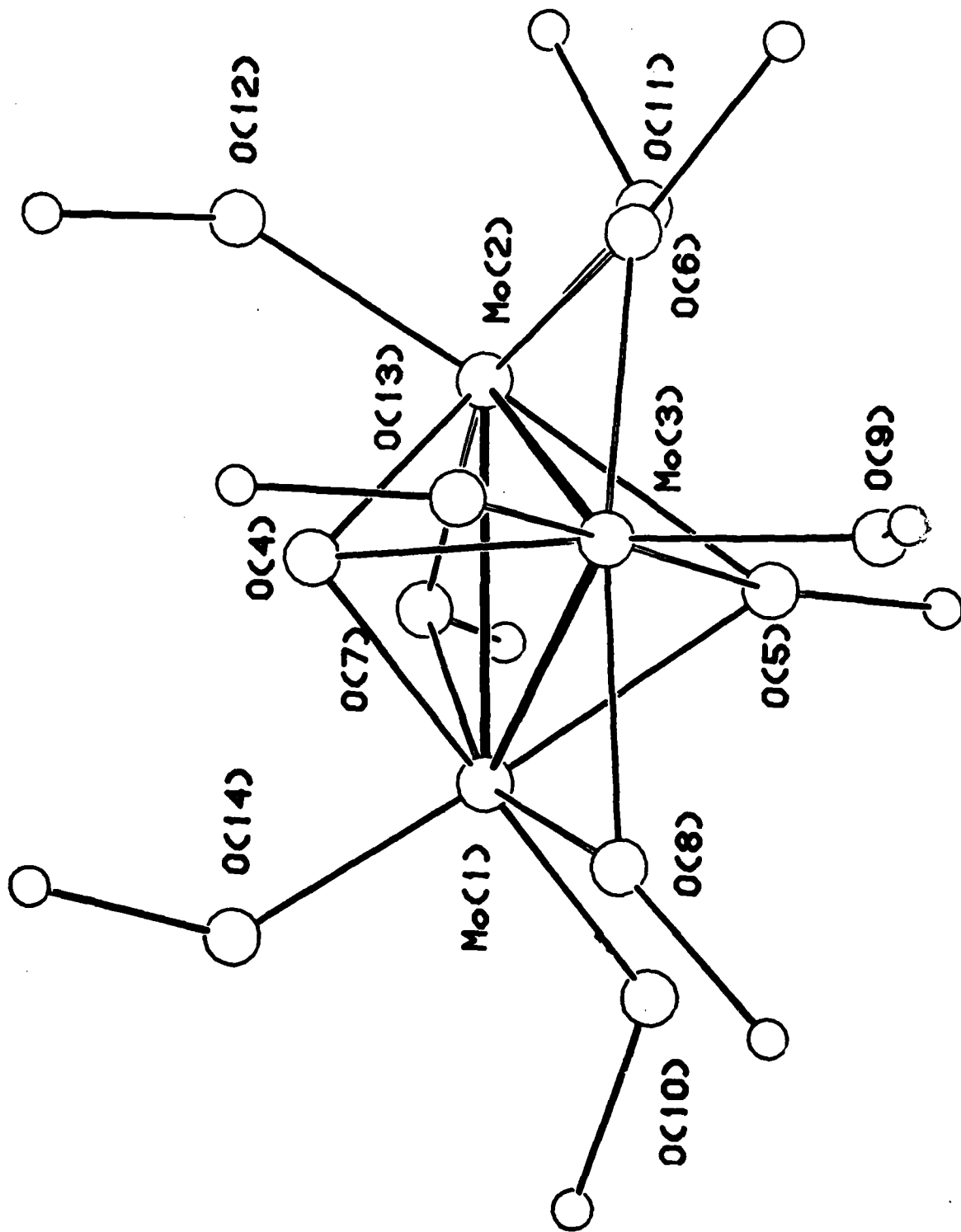


Figure 6. An ORTEP view of the centrosymmetric $W_4(OEt)_{16}$ molecule emphasizing the local WO_6 octahedral geometry for each tungsten atom. Pertinent W-W and W-O distances are given in Tables II and III, respectively.

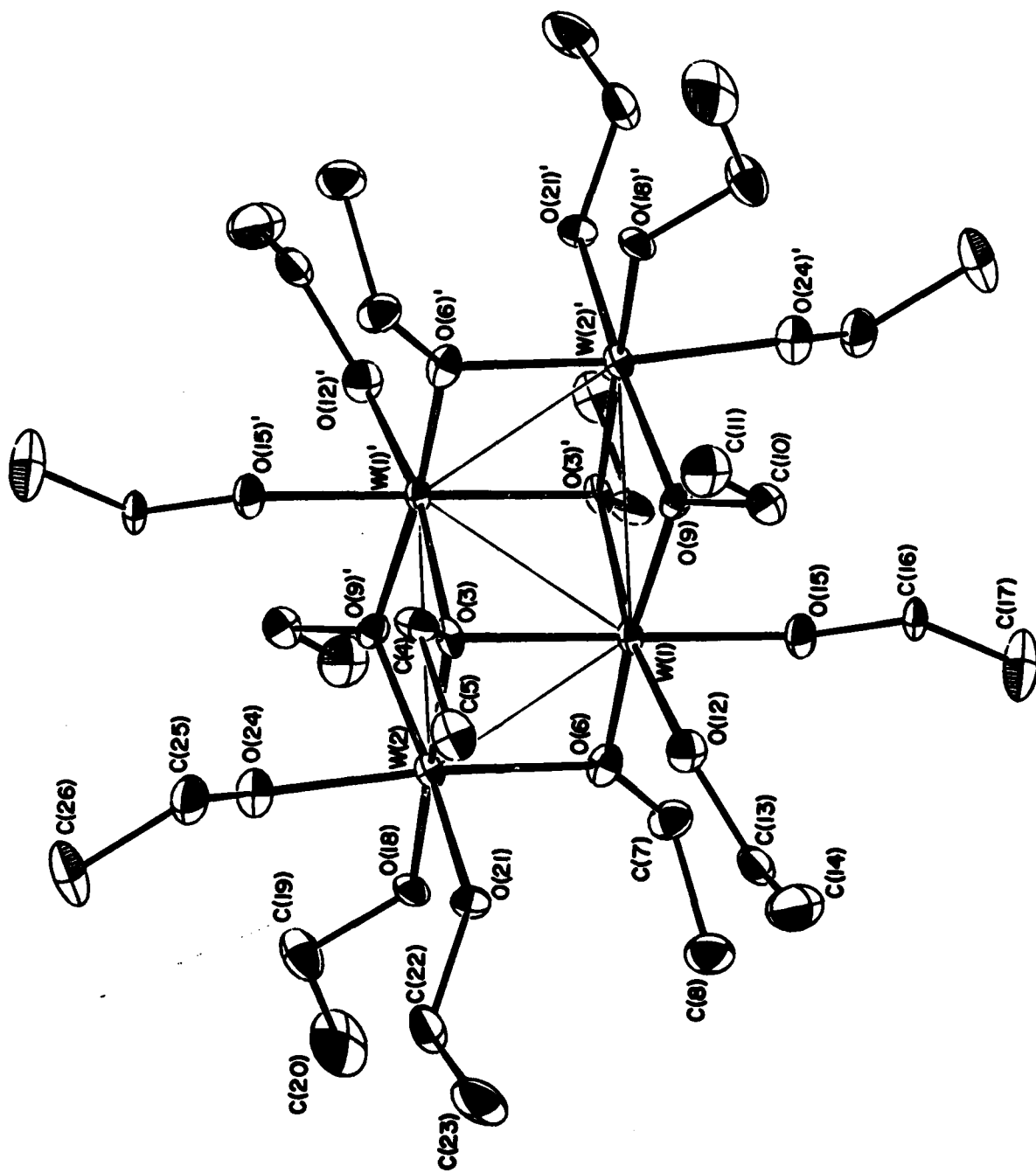
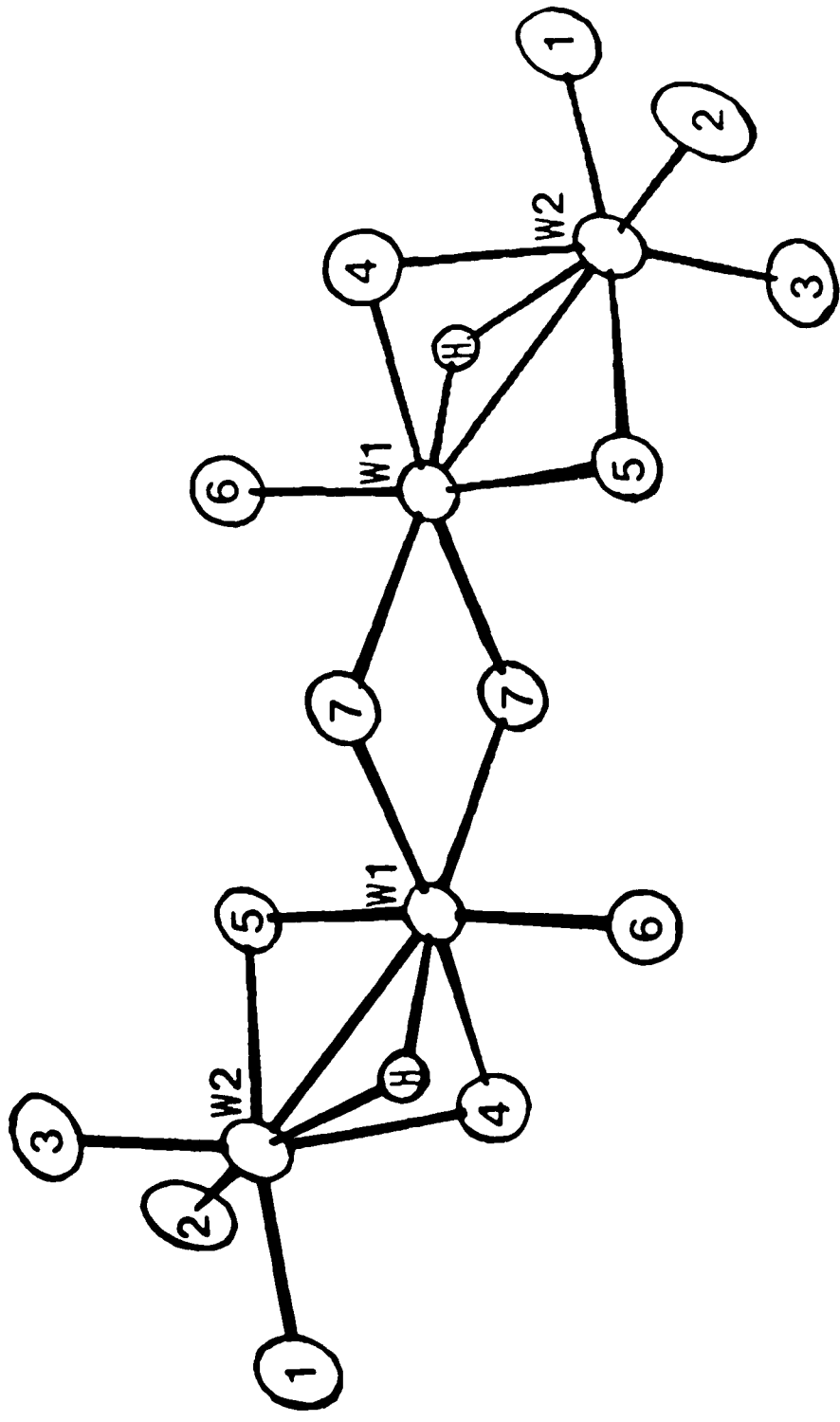


Figure 7. An ORTEP view of the central skeleton of the centrosymmetric $W_4(\mu-H)_2(OPr^i)_{14}$ molecule. Some pertinent distances (Å) and angles (°) are: $W(1)---W(1)' = 3.407(1)$, $W(1)-W(2) = 2.446(1)$ and $W(2)-W(1)-W(1)' = 142$. The W-OR distances are within the range reported in Table III for terminal and μ_2 -OR ligands.



10/10/10

Figure 8. ^{31}P NMR spectrum (40.5 MHz, 25°C, toluene- d_8 solvent) of $\text{W}_2(\text{OCH}_2\text{-Bu}^t)_6(\text{PMe}_3)_2$. Chemical shift $\delta \approx 1.5$ ppm relative to external H_3PO_4 (85% aq); $^1\text{J}_{\text{W-}^{31}\text{P}} = 240$ Hz, $^2\text{J}_{\text{W-}^{31}\text{P}} = 20$ Hz and $^3\text{J}_{\text{P-}^{31}\text{P}} = 5.4$ Hz.

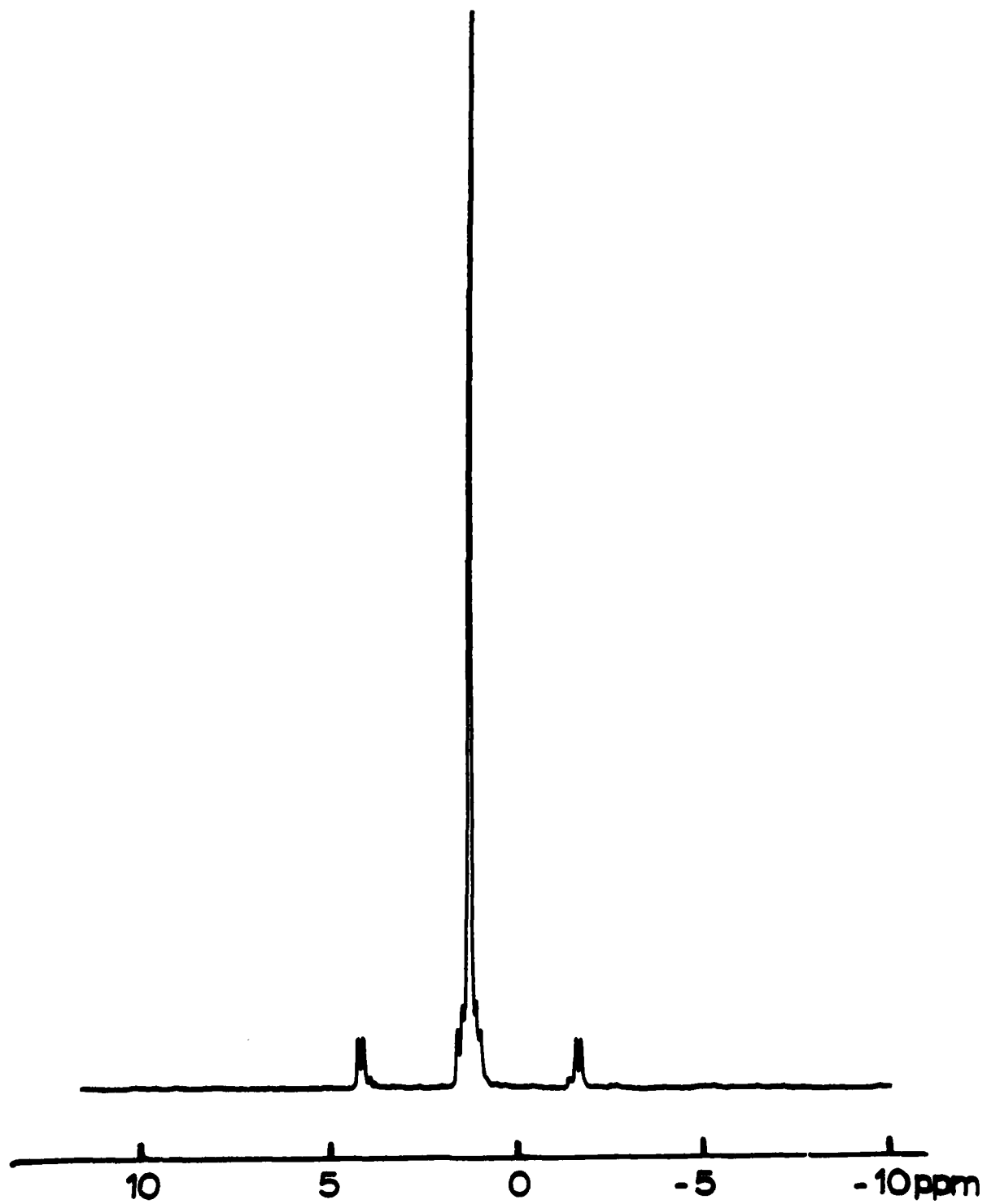


Figure 9. An ORTEP view of the centrosymmetric $\text{Mo}(\text{OSiMe}_3)_4(\text{HNMe}_2)_2$ molecule showing the trans octahedral geometry of the MoO_4N_2 skeleton. Pertinent distances (\AA) and angles ($^\circ$) are: $\text{Mo}-\text{O}(1)$, $-\text{O}(2)$, $-\text{N}(1)$ = 1.950(4), 1.951(4), 2.219(4); $\text{O}(1)-\text{Mo}-\text{O}(1)'$, $-\text{O}(2)$, $-\text{O}(2)'$, $-\text{N}(1)$, $-\text{N}(1)'$ = 180.0(3), 89.2(1), 90.8(1), 94.6(1), 85.4(1); $\text{Mo}-\text{O}(1)-\text{Si}(1)$ = 170.8(2); $\text{Mo}-\text{O}(2)-\text{Si}(2)$ = 174.2(2).

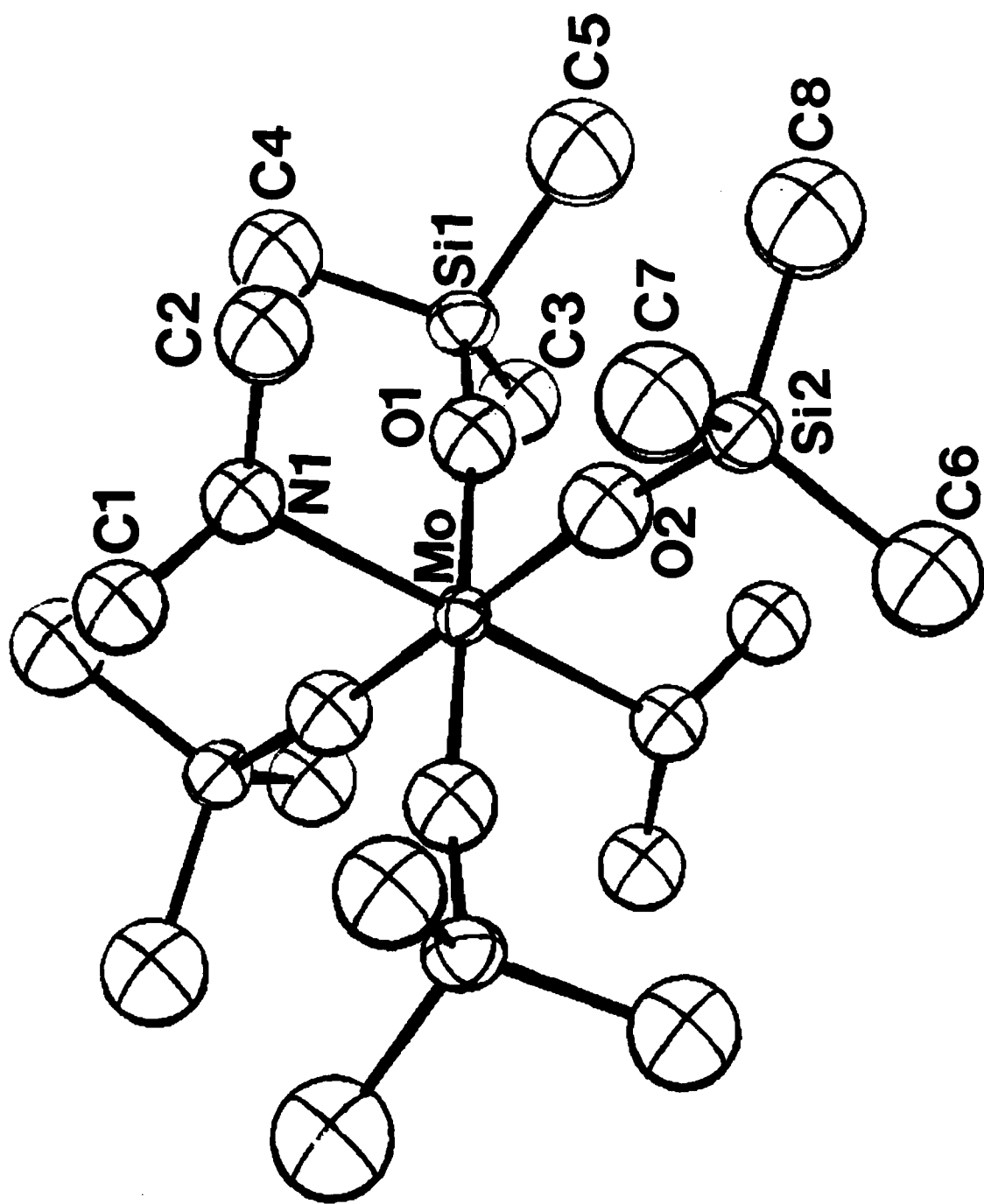


Figure 10. An ORTEP view of the central skeleton of the $\text{Mo}_2(\text{OBu}^t)_4(\text{O}_2\text{C}-\text{OBu}^t)_2$ molecule viewed down the Mo-Mo bond showing the near eclipsed geometry caused by the presence of the cis-bridging O_2COR ligands. Some pertinent distances (\AA) are: Mo-Mo = 2.241(1); Mo- OBu^t = 1.88(2), Mo-O-(alkylcarbonate) = 2.12(2).

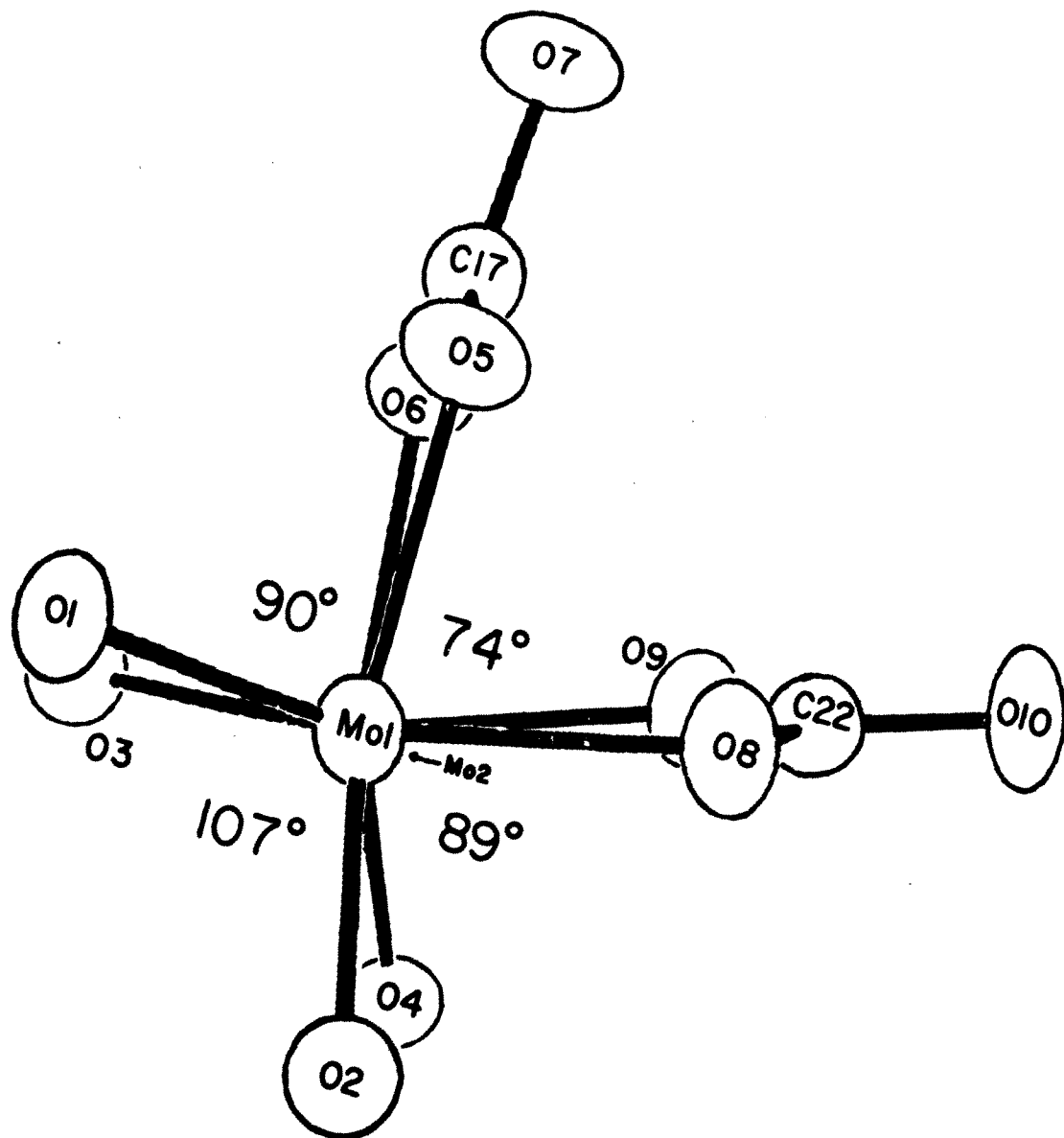


Figure 11. an ORTEP view of the $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_4(\text{acac})_2$ molecule looking down the Mo-Mo bond showing the staggered conformation. Some pertinent distances (\AA) are Mo-Mo = 2.237(1), Mo-OR = 1.89(1) (averaged) and Mo-O-(acac) = 2.08(2) (averaged). The Mo-Mo-O angles fall in the range 97-104°.

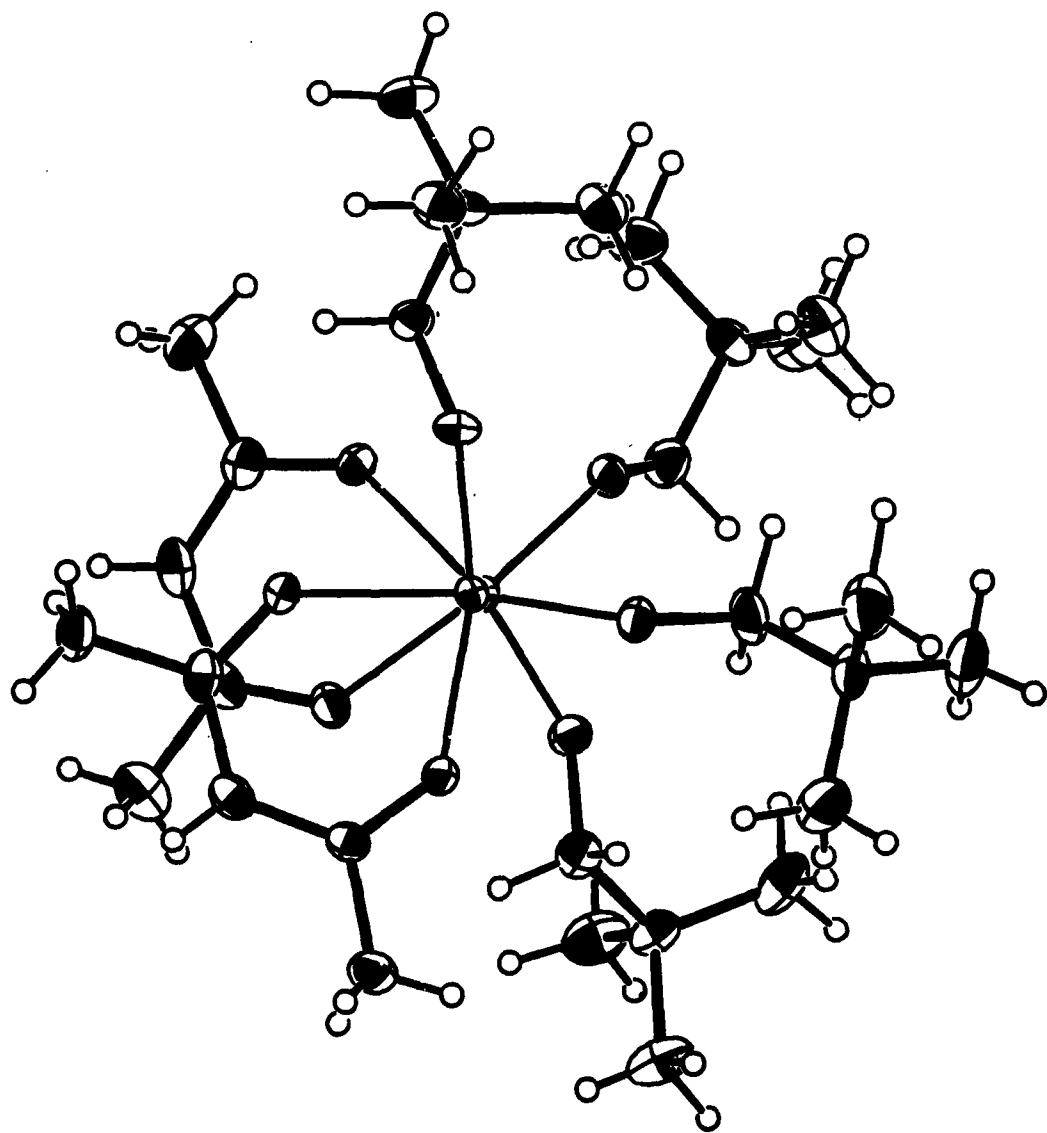


Figure 12. An ORTEP view of the central skeleton of the $\text{Mo}_4(\text{OBU}^t)_8(\mu_2\text{-F})_4$ molecule. Pertinent distances (\AA) are: $\text{Mo}(1')\text{-Mo}(2') = 2.262(2)$, $\text{Mo}(3')\text{-Mo}(4') = 2.63(2)$, $\text{Mo}(1')\text{-Mo}(3') = 3.743(2)$, $\text{Mo}(1')\text{-Mo}(4') = 3.730(2)$, $\text{Mo}(2')\text{-Mo}(3') = 3.713(2)$, $\text{Mo}(2')\text{-Mo}(4') = 3.700(2)$, $\text{Mo}\text{-}\mu\text{-F} = 2.10(2)$ (averaged) and $\text{Mo}\text{-O} = 1.94(2)$ (averaged).

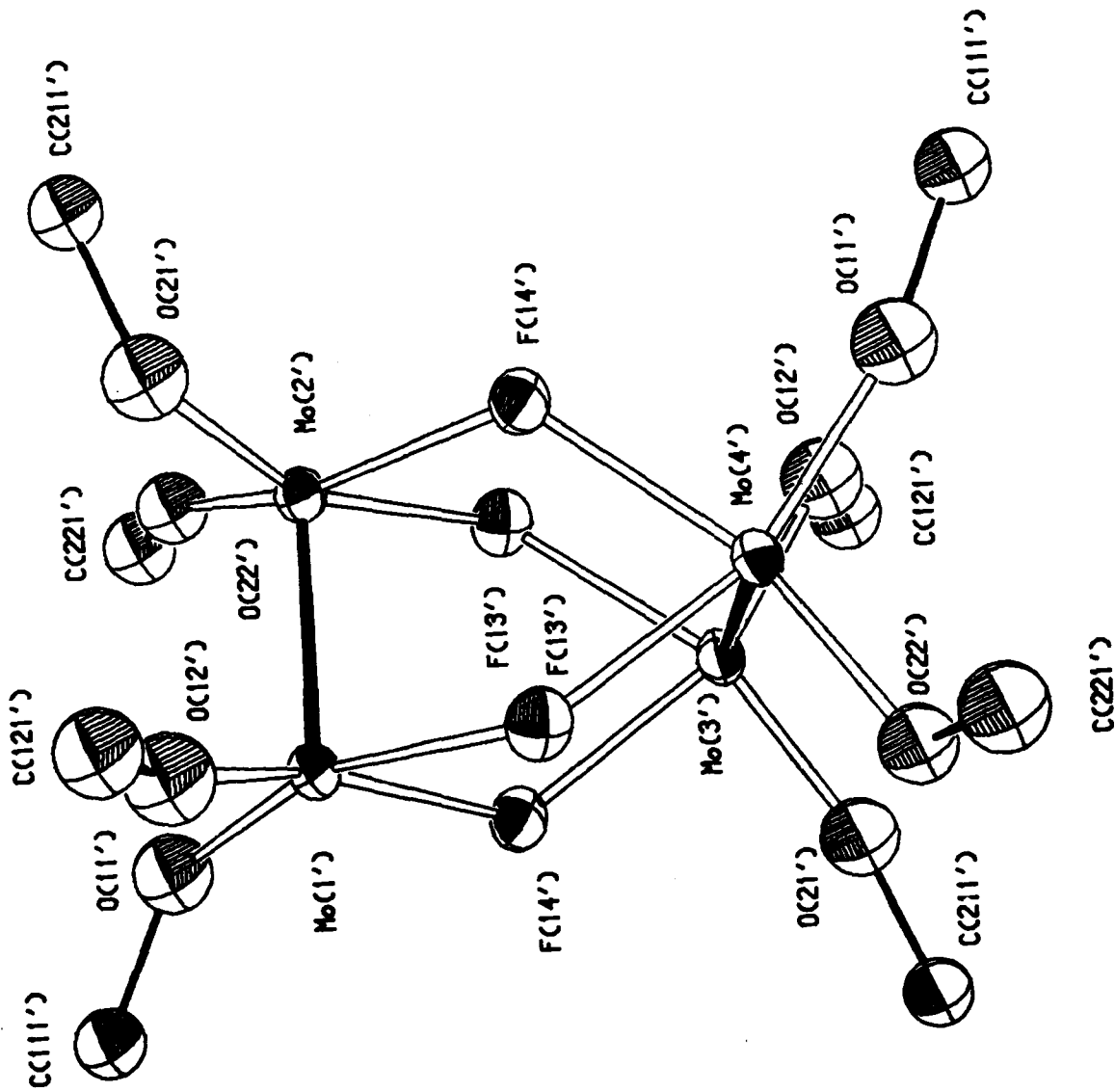
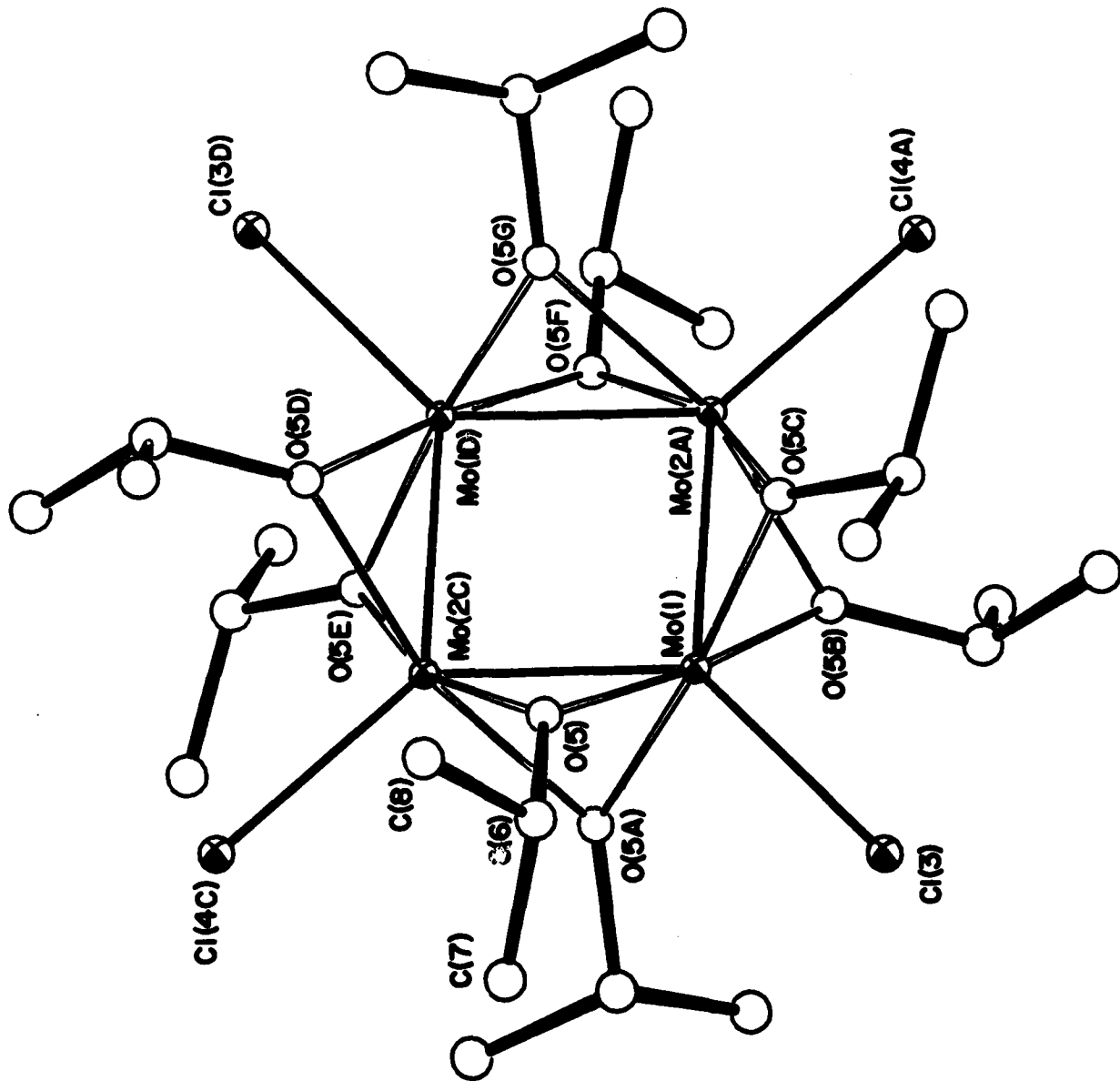


Figure 13. An ORTEP view of the $\text{Mo}_4\text{Cl}_4(\text{OPr}^i)_8$ molecule. The molecule has a crystallographically imposed C_2 axis, which contains Cl(3)-Mo(1)-Mo(1D)-Cl(3D), and a mirror plane, which contains Cl(4C)-Mo(2C)-Mo(2A)-Cl(4A) and relates atoms O(5) and O(5D), O(5A) and O(5E), etc. Pertinent bond distances (\AA) and angles are: Mo(1)-Mo(2C) = 2.378(2), Mo(1)-Cl(3) = 2.442(5), Mo(1)-O(5) = 1.981(4), Mo(2C)-O(5) = 2.078(4); Mo(2C)-Mo(1)-Mo(1D) = 91.4(1); Mo(1)-Mo(2C)-Mo(1D) = 88.5(1); Cl(3)-Mo(1)-O(5) = 93.3(1).



100
 100
 100

Figure 14. An ORTEP view of the $\text{Mo}_4\text{Br}_4(\text{OPr}^i)_8$ molecule which has C_{2v} symmetry. Some pertinent distances (\AA) and angles ($^\circ$) are: $\text{Mo}(1)\text{-Mo}(2) = 2.513(1)$, $\text{Mo}(2)\text{-Mo}(1)' = 2.516(1)$; $\text{Mo}(2)\text{-Mo}(2)' = 2.481(1)$; $\text{Mo}(1)\text{-Br}(3) = 2.596(1)$; $\text{Mo}(2)\text{-Br}(4) = 2.568(1)$; $\text{Mo-OR} = 1.84(1)$ (terminal), $2.02(1)$ (μ_2) and $2.15(1)$ (μ_3) (averaged); $\text{Mo}(1)\text{-Mo}(2)\text{-Mo}(1)' = 81.6(1)$; $\text{Mo}(1)\text{-Mo}(2)\text{-Mo}(2)' = 60.5(1)$.

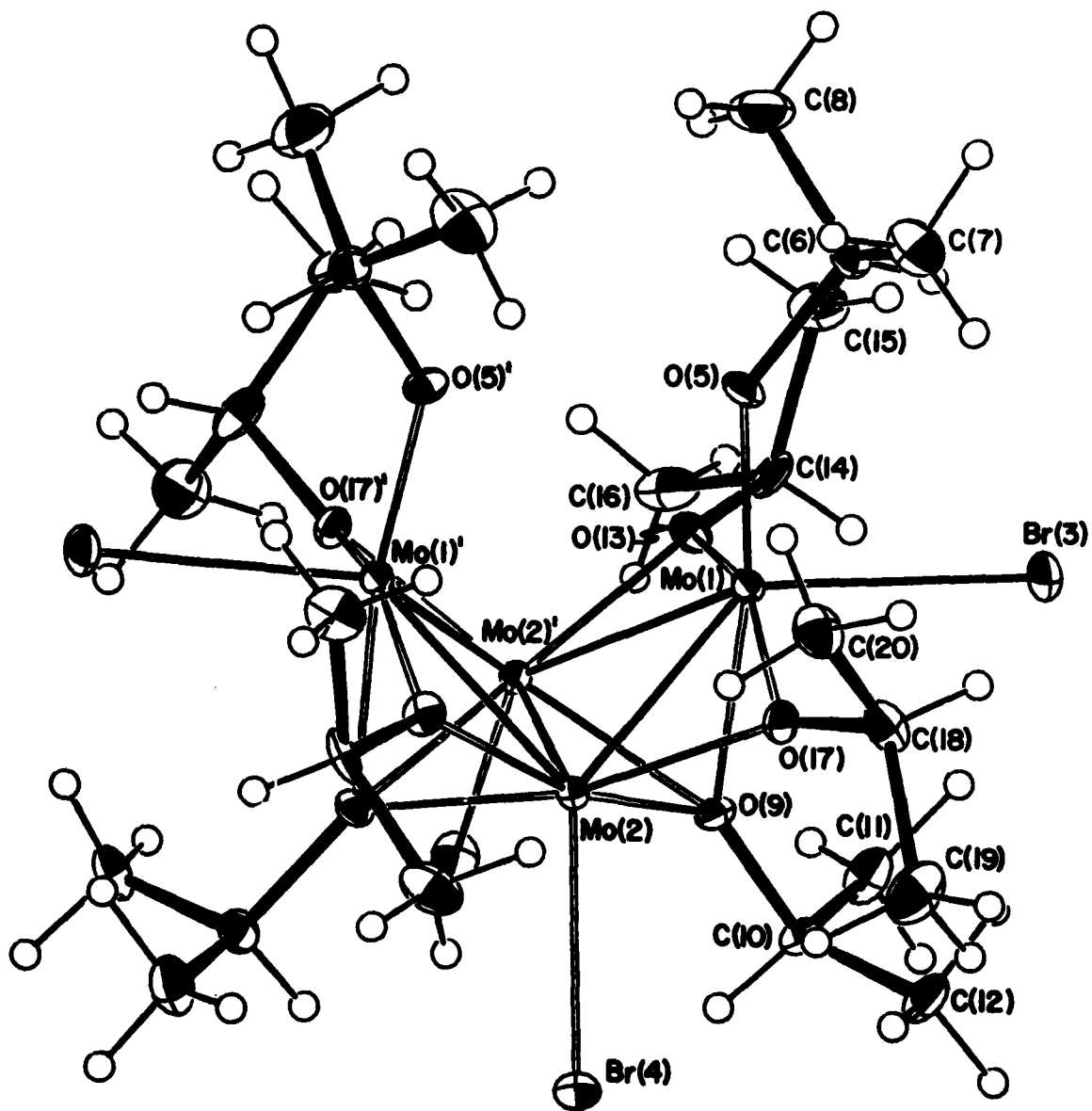


Figure 15. An ORTEP view of the $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6\text{Br}_2(\text{py})$ molecule showing the confacial bioctahedral geometry. Some pertinent distances (\AA) are: Mo-Mo = 2.534(1), Mo-Br (terminal) = 2.584(1), Mo-Br (μ_2) = 2.73(1) (averaged), Mo-N = 2.257(6). The Mo-O distances are all within the range commonly found for terminal and μ_2 ligands as shown in Table III.

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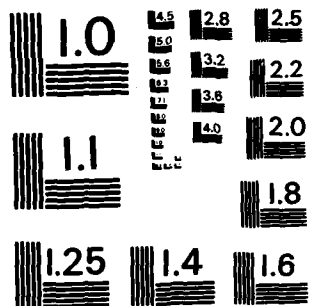
METAL-METAL BONDS AND METAL CARBON BONDS IN THE
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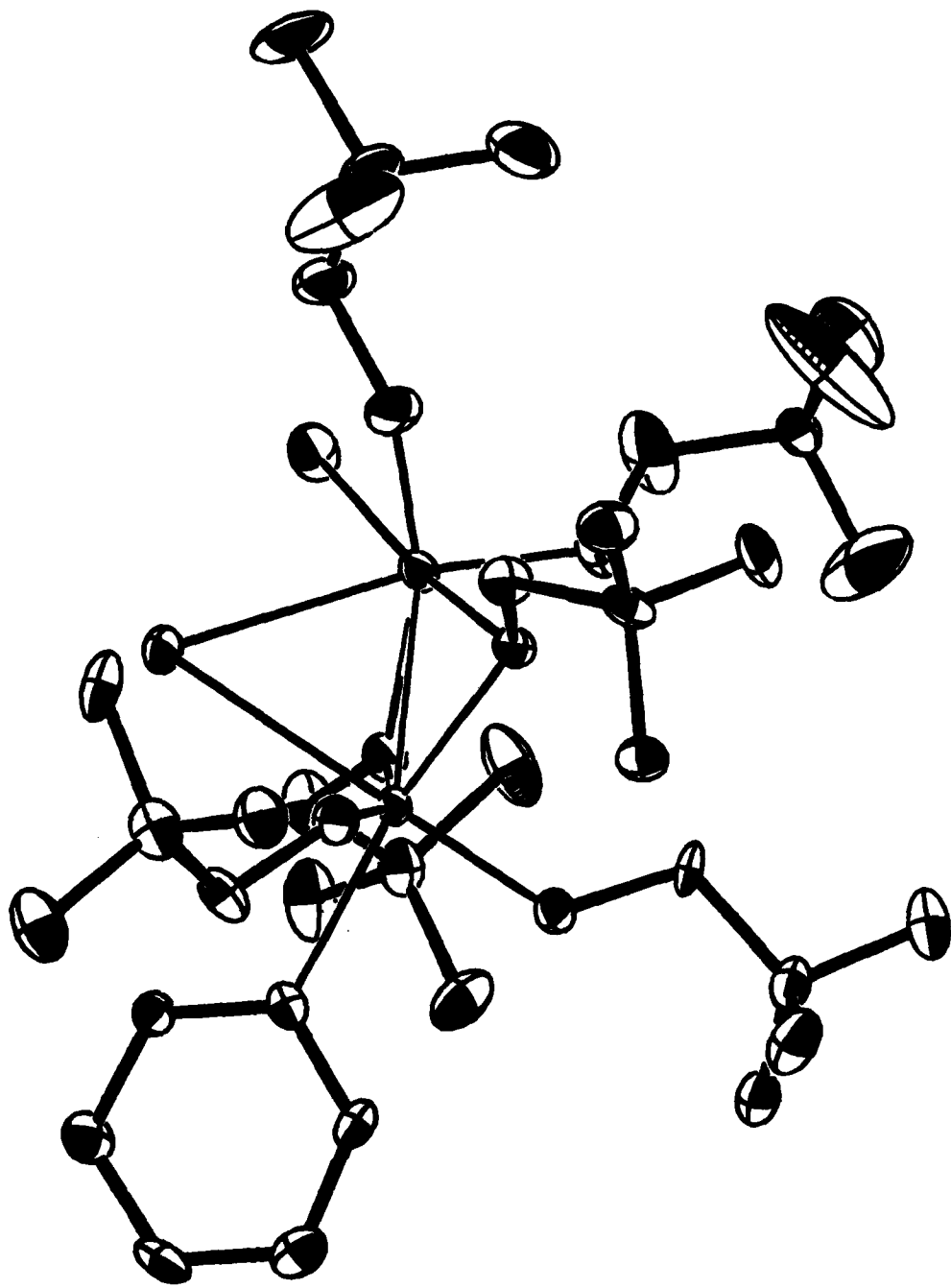


Fig. 1

Figure 16. An ORTEP view of the $\text{Mo}_2(\text{OPr}^i)_6(\text{O}_2\text{C}_6\text{Cl}_4)_2$ molecule emphasizing the edge-shared octahedral geometry. The Mo-Mo distance is 2.754(2) Å and the Mo-O distances (averaged) are 1.83(1) (terminal OR), 2.01(1) (μ -OR) and 2.02(1) Å ($\text{O}_2\text{C}_6\text{Cl}_4$).

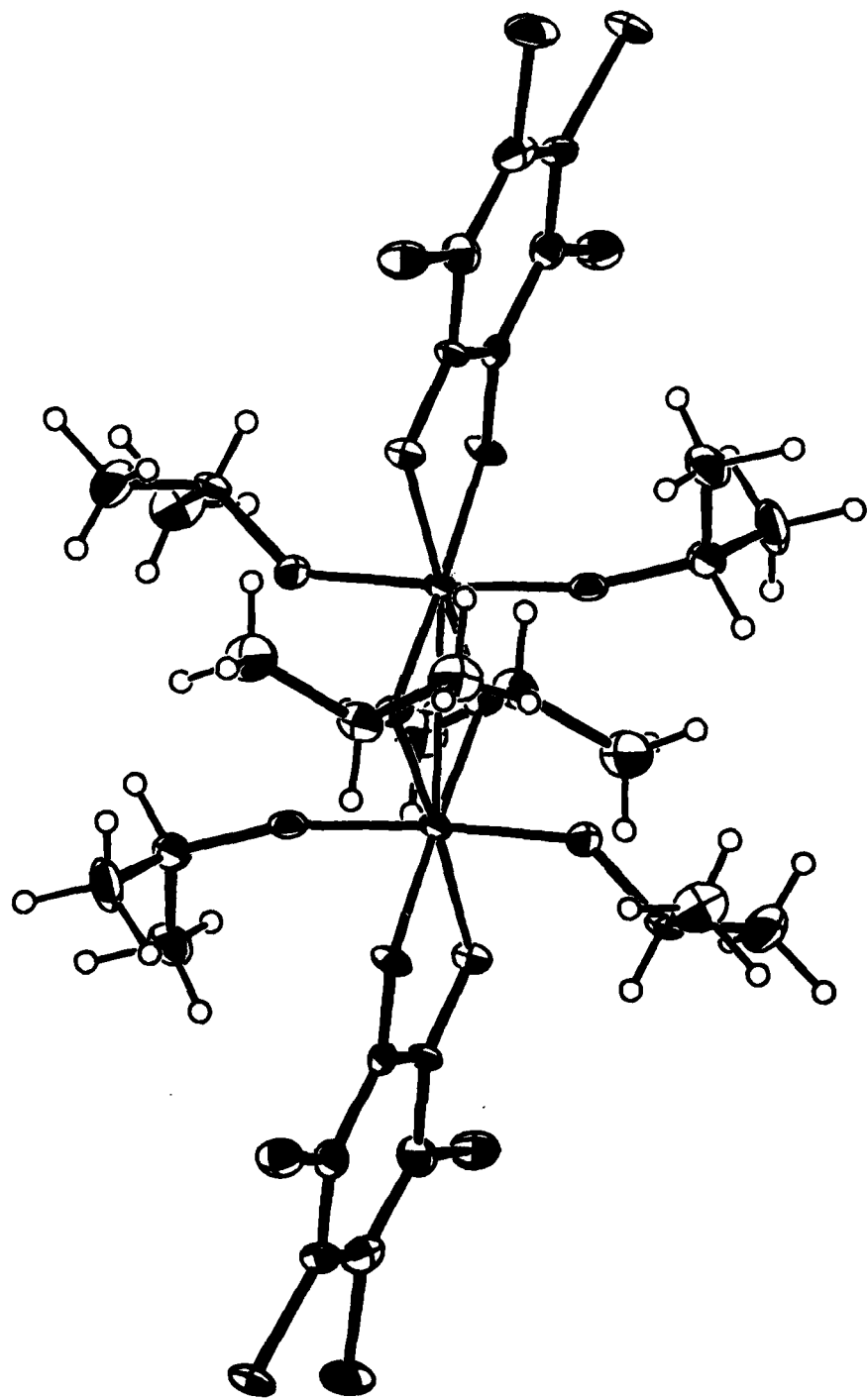


Figure 17. An ORTEP view of the $W_2(OPr^i)_6(O_2C_2Me_2)_2$ molecule. The W-W distance is 2.754(1) Å and the distances (Å) associated with the $W-O_2C_2Me_2$ moiety are: (averaged) W-O = 1.94(4), C-O = 1.34(2); C-C (central) = 1.35(1).

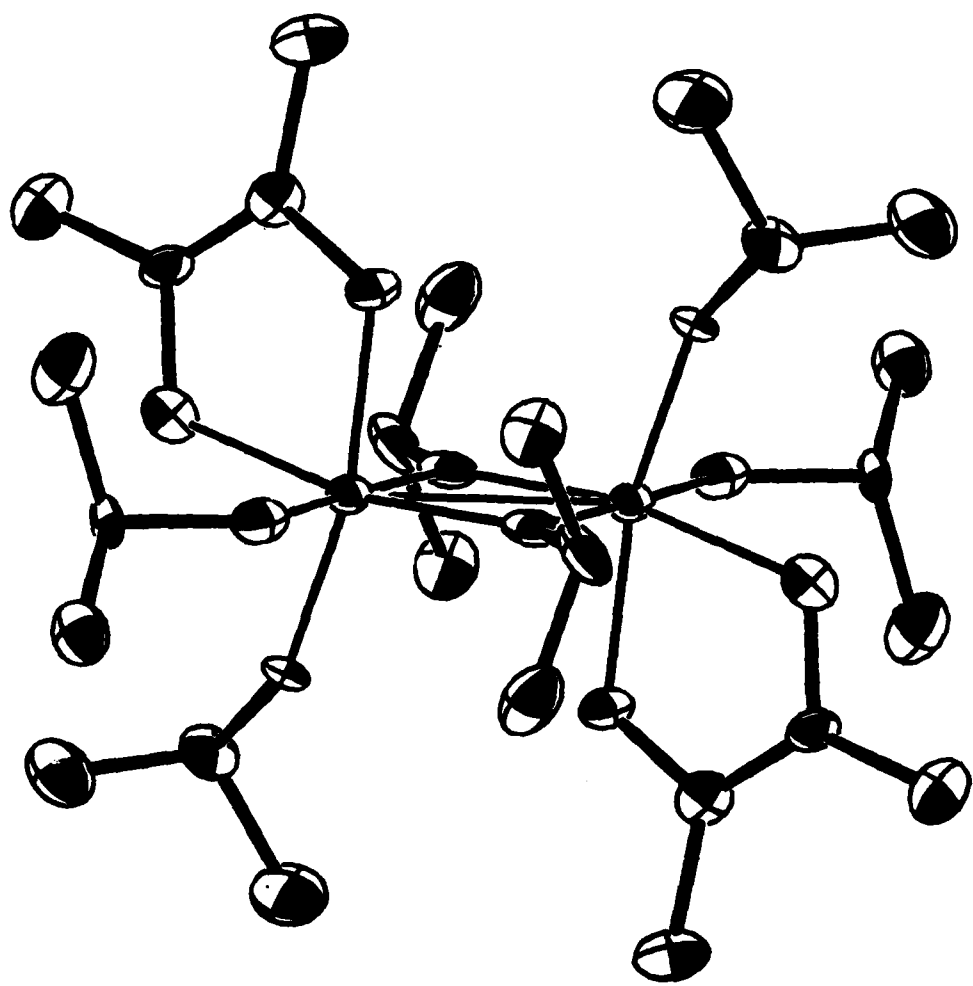
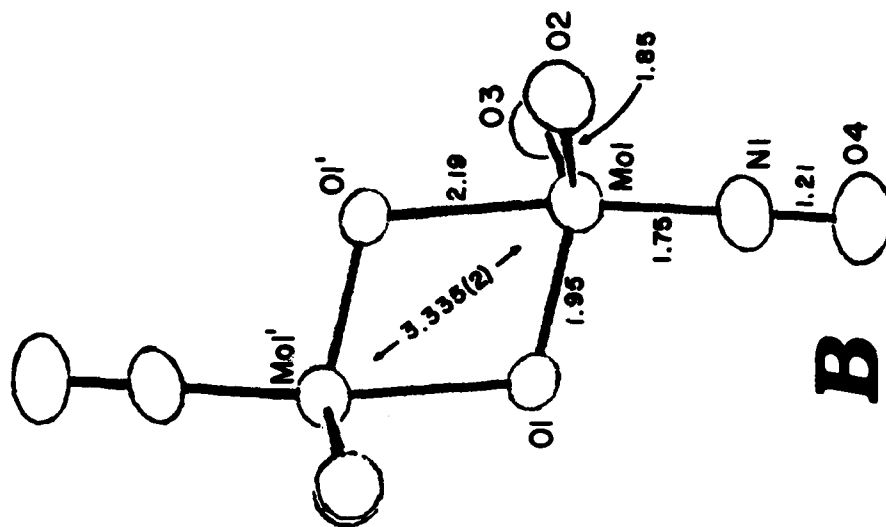
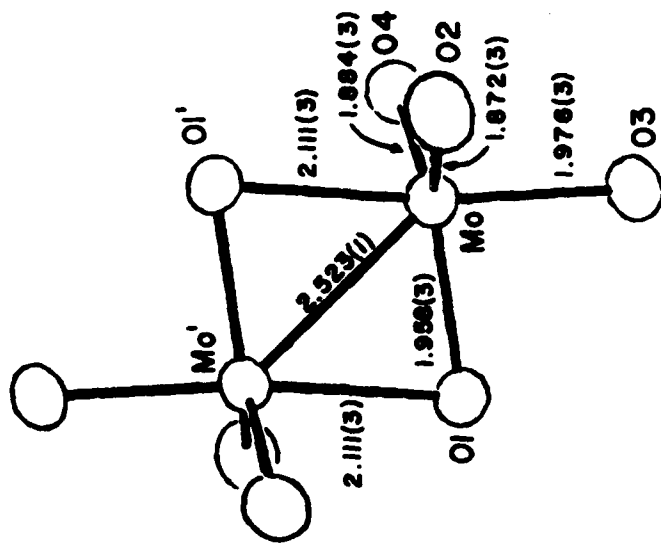


Figure 18. Comparison of some structural parameters for the centrosymmetric molecules $\text{Mo}_2(\text{OPr}^i)_8$ and $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$.



B

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



A

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

Figure 19. An ORTEP view of the $W(OBu^t)_3(NO)(py)$ molecule. Some pertinent distances (\AA) and angles ($^\circ$) are $W-NO = 1.732(8)$, $W-N(py) = 2.323(7)$, $W-O = 1.88(1)$ (averaged); $W-N-O = 179.2(8)$, $N-W-N = 177.0(3)$, $O-W-N(NO) = 100(1)$ (averaged).

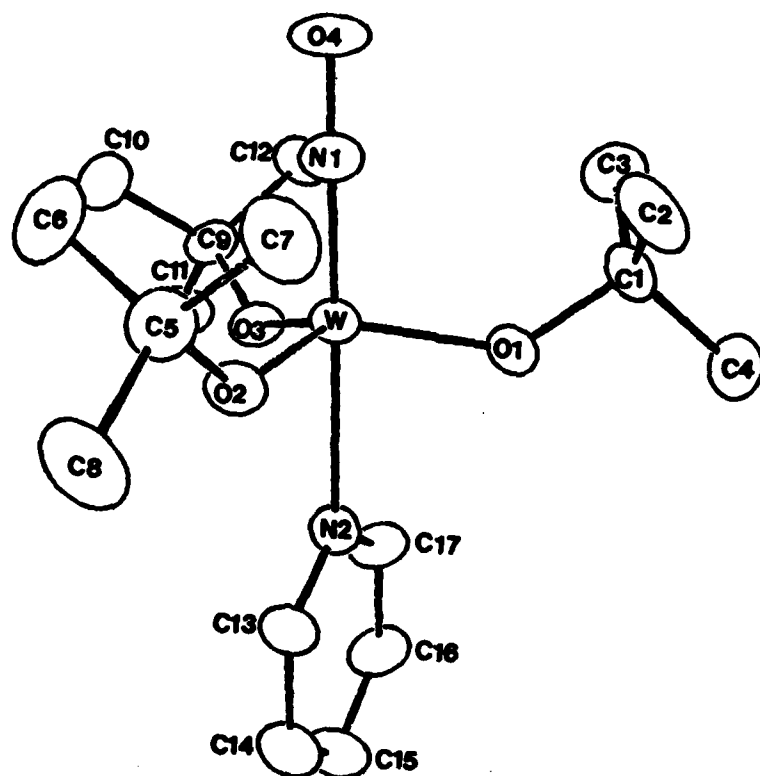


Figure 20. An ORTEP view of the centrosymmetric $[(\text{Bu}^t\text{O})_3\text{W}=\text{CMe}]_2$ molecule. Pertinent bond distances (\AA) and angles ($^\circ$) are: $\text{W}(1)-\text{O}(4)$, $-\text{O}(9)$, $-\text{O}(14)$, $-\text{C}(2) = 1.886(4)$, $1.897(4)$, $1.934(4)$ and $1.759(6)$; $\text{W}(1)'\text{-O}(14) = 2.484(4)$; $\text{C}(2)-\text{W}(1)$, $-\text{O}(4)$, $-\text{O}(9)$, $-\text{O}(14) = 102.3(2)$, $101.2(2)$ and $102.8(2)$; $\text{W}(1)-\text{C}(2)-\text{C}(3) = 179.8(6)$.

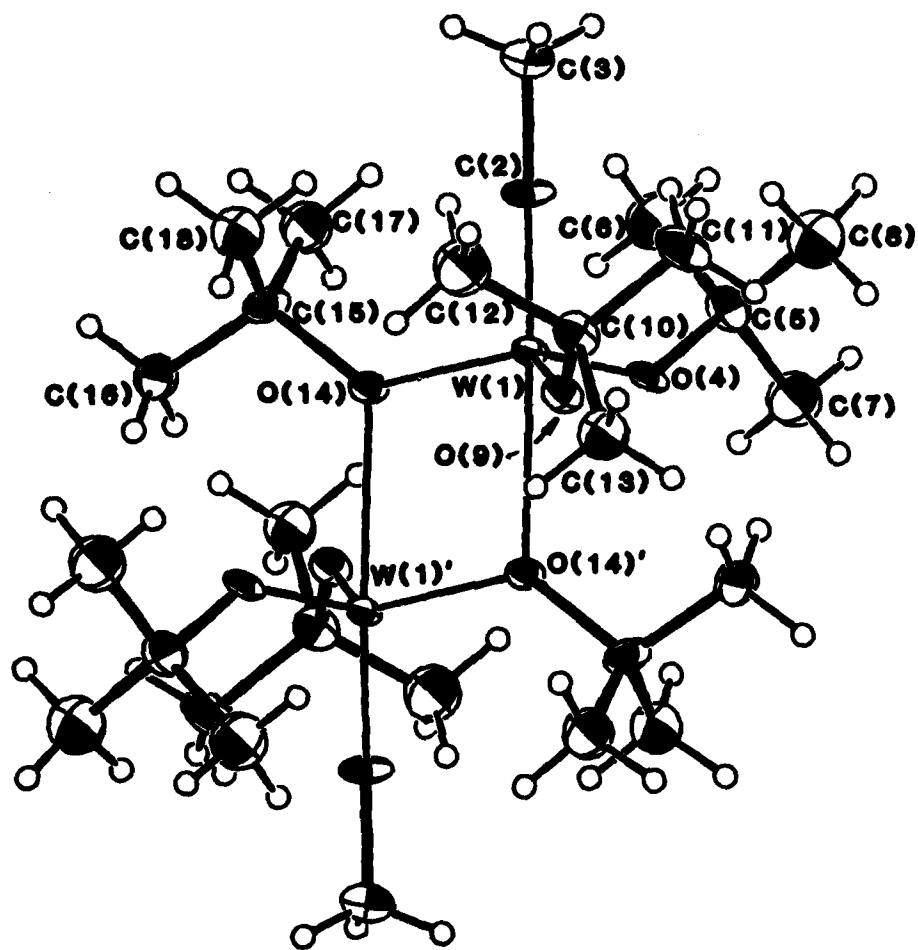


Figure 21. An ORTEP view of the repeating unit along the C axis in the $[(\text{Bu}^t\text{O})_3\text{WN}]_x$ polymer. Pertinent distances (\AA) and angles ($^\circ$) are: $\text{W}(1)\text{-N}(2) = 1.740(15)$; $\text{W}(1)\text{-O}(3) = 1.872(7)$; $\text{W}(1)\text{-N}(2)' = 2.661(15)$; $\text{N}(2)\text{-W}(1)\text{-O}(3) = 101.6(2)$; $\text{W}(1)\text{-O}(3)\text{-C}(4) = 136.6(8)$.

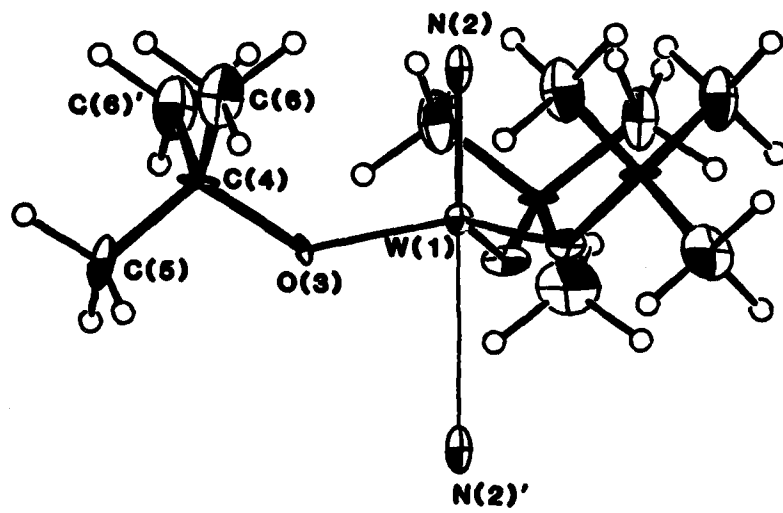


Figure 22. View of the $[\text{W}(\text{O}^t\text{Bu})_3\text{N}]_x$ polymer viewed down the C axis from a point at $x = 1/3$, $y = 2/3$. Five cells along the C axis are shown. Hydrogen atoms have been omitted. In the space group $P6_3cm$, there is a hexagonal network of tungsten atoms perpendicular to the C axis.

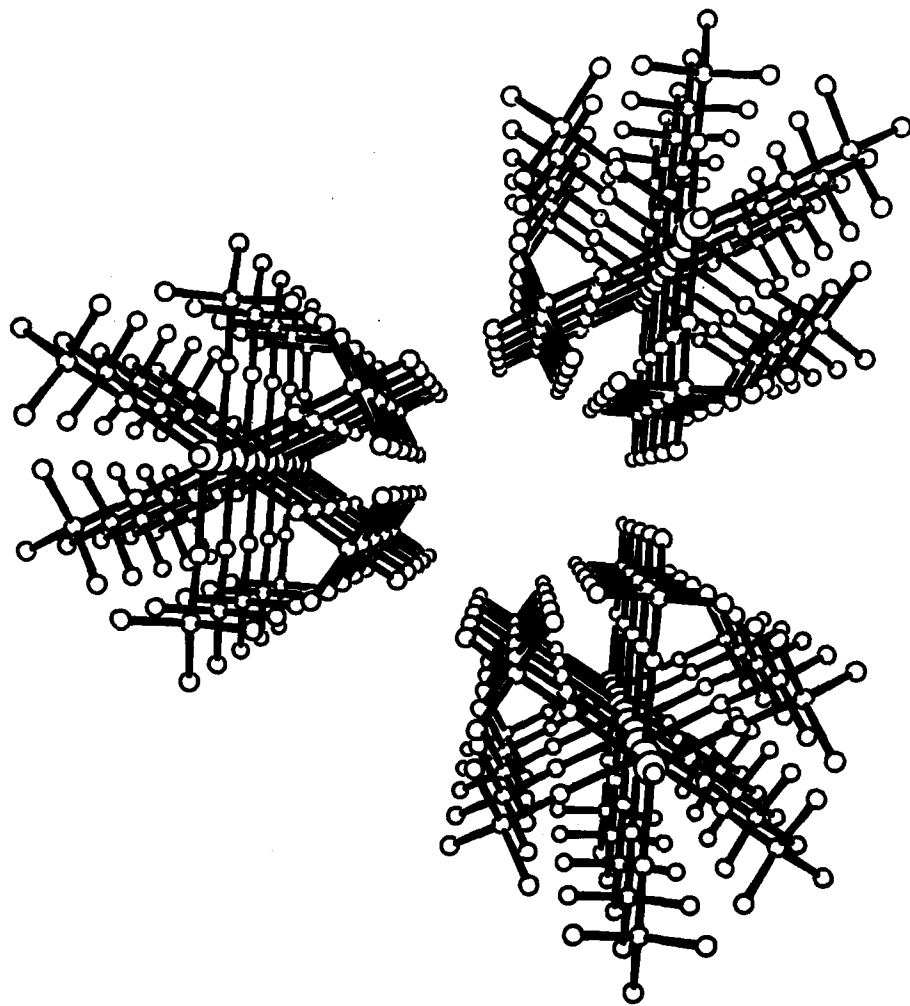


Fig. 1

Figure 23. An ORTEP view of the $\text{MoO}_2(\text{OPr}^i)_2(\text{bpy})$ molecule. Some pertinent bond distances (\AA) and angles ($^\circ$) are: $\text{Mo}(1)\text{-O}(14)$, $\text{-O}(15)$, $\text{-O}(16)$, $\text{-O}(20)$ $\text{-N}(2)$, $\text{-N}(13)$ = 1.69(1), 1.72(1), 1.91(1), 1.94(1), 2.37(1) and 2.35(1); $\text{O}(14)\text{-Mo}(1)\text{-O}(15)$ = 108.0(3), $\text{O}(14)\text{-Mo}(1)\text{-O}(16)$ = 96.6(3), $\text{O}(14)\text{-Mo}(1)\text{-O}(20)$ = 96.7(3), $\text{O}(16)\text{-Mo}(1)\text{-O}(20)$ = 160.9(3), $\text{N}(2)\text{-Mo}(1)\text{-N}(13)$ = 69.2(3).

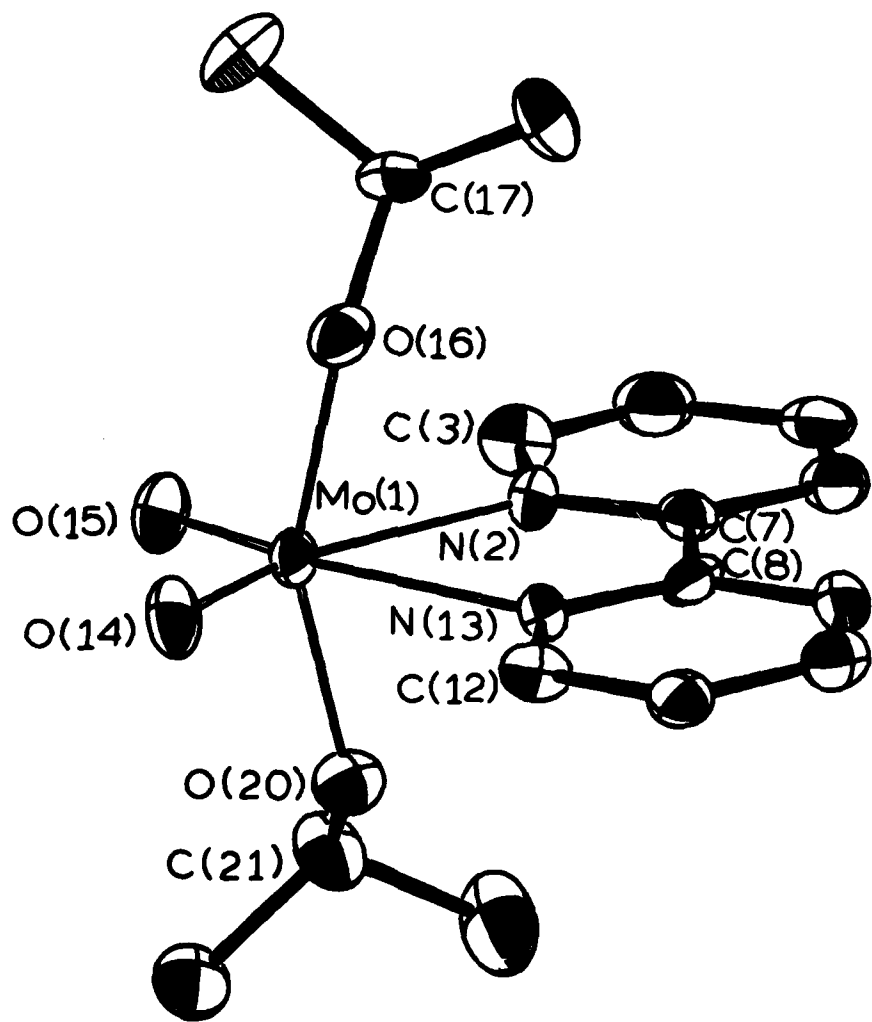


Figure 24. An ORTEP view of the centrosymmetric molecule $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$. Some pertinent bond distances (\AA) and bond angles ($^\circ$) are: $\text{Mo}(1)\text{-Mo}(2) = \text{Mo}(1)'\text{-Mo}(2)' = 2.585(1)$; $\text{Mo}(1)\text{-Mo}(1)' = 3.353(1)$, $\text{Mo}(2)\text{-Mo}(3) = \text{Mo}(2)'\text{-Mo}(3)' = 3.285(1)$, $\text{Mo}(1)'\text{-Mo}(1)\text{-Mo}(2) = 146.5(1)$, $\text{Mo}(1)\text{-Mo}(2)\text{-Mo}(3) = 134.3(1)$; $\text{Mo-oxo (terminal)} = 1.68$ (averaged); $\text{Mo-oxo } (\mu_2) = 1.93$ (averaged); $\text{Mo-OR (terminal)} = 1.86$ (averaged), $\text{Mo-OR } (\mu_2) = 2.05\text{-}2.19$.

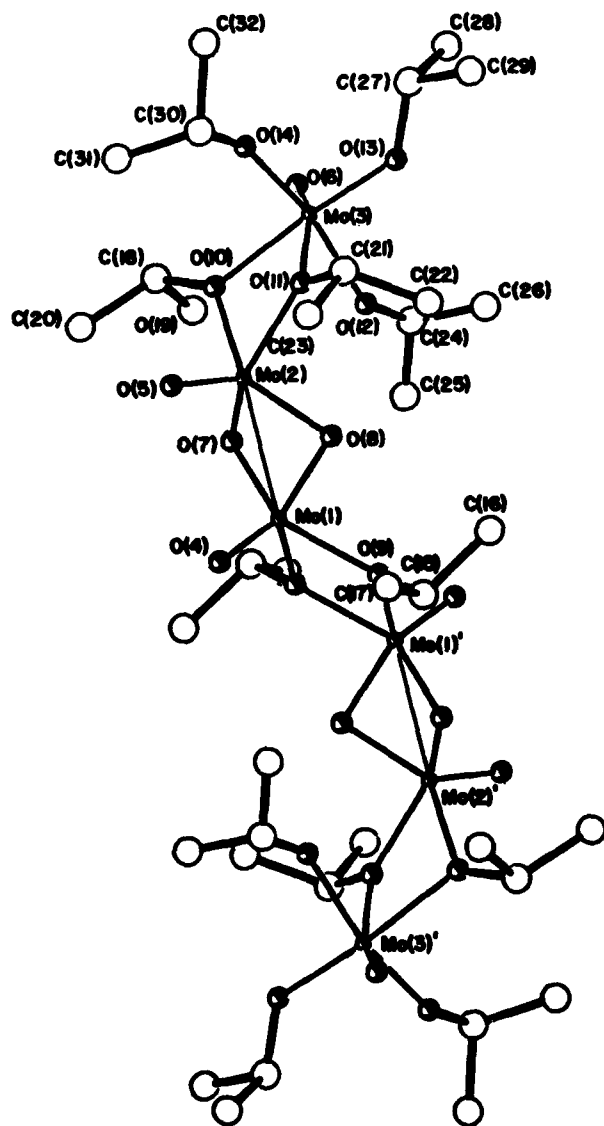


Figure 25. Central skeleton of the $\text{Mo}_2(\text{OBu}^t)_6(\mu\text{-CO})$ molecule showing some of the pertinent distances.

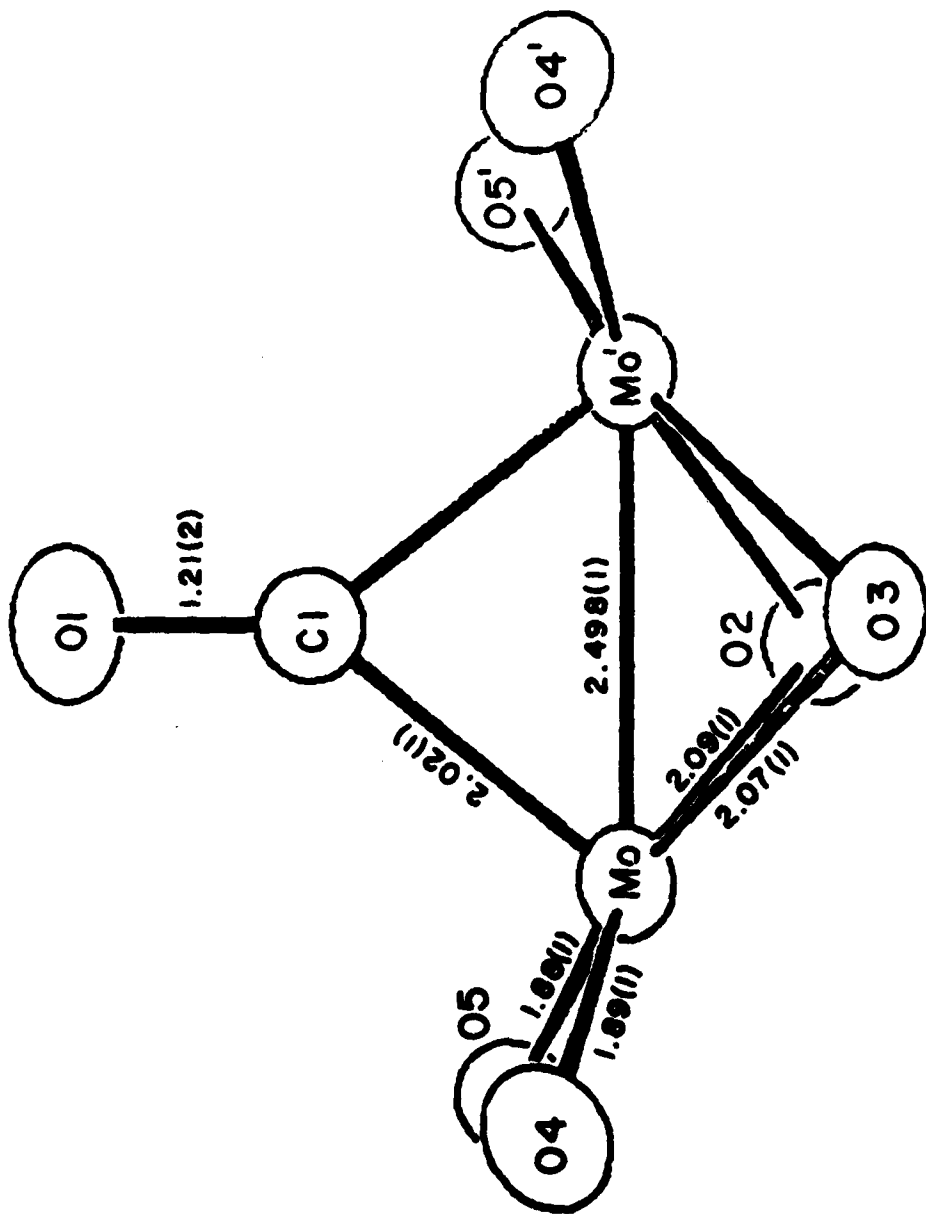


Figure 26. An ORTEP view of the central $W_4O_{12}(CO)_2N_2$ skeleton of the centrosymmetric $W_4(OPr^i)_{12}(py)_2(CO)_2$ molecule. Some key bond distances are: $W(1)-W(2) = 2.654(1)$, $W(1)-C(1) = 2.00(3)$, $W(2)-C(1) = 1.91(3)$, $C(1)-O(1)' = 1.33(3)$ and $W(2)-O(1) = 2.01(1)$ Å.

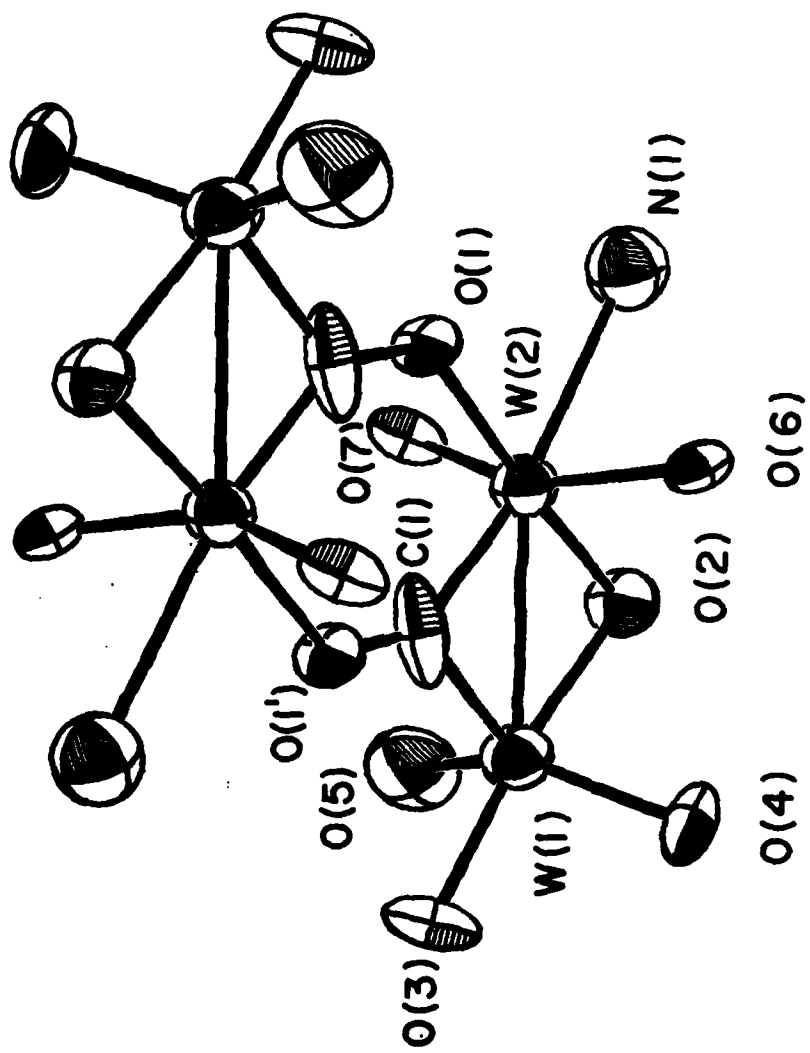


Figure 27. ORTEP view of the central $W_4(C)(N)O_{12}$ skeleton of $W_4(\mu_4-C)-(\mu_2-NMe)(OPr^i)_{12}$. Some pertinent bond distances (\AA) are: $W(1)-W(3) = 2.799(2)$, $W(1)-W(4) = 2.814(2)$, $W(2)-W(3) = 2.822(1)$, $W(2)-W(4) = 2.747(2)$, $W(3)-W(4) = 2.795(2)$, $W(1)-C = 1.91(1)$, $W(2)-C = 1.96(1)$, $W(3)-C = 2.25(1)$, $W(4)-C = 2.24(1)$, $W-O$ (terminal OR) = 1.90 (averaged), $W-\mu_2O$ (bridging OR) = 2.05 (averaged), $W-\mu-N = 1.94$ (averaged).

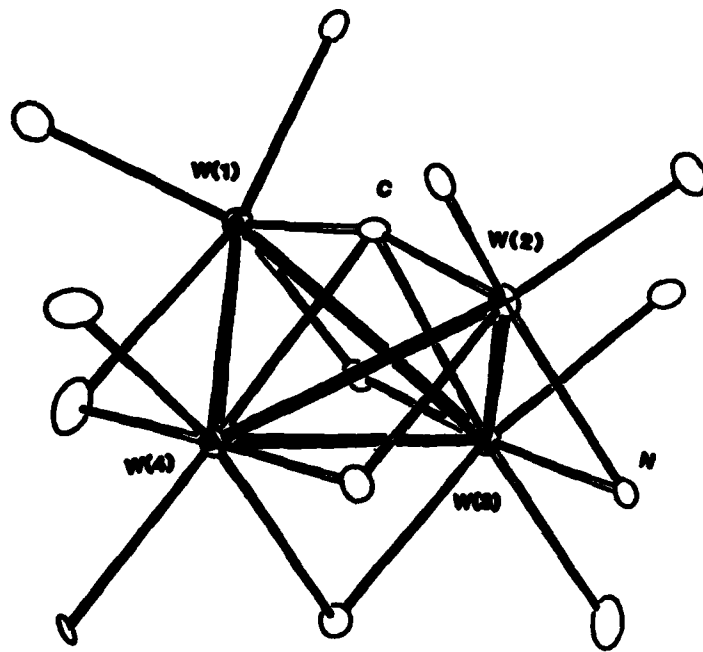


Figure 28. An ORTEP view of the central $\text{Mo}_2\text{O}_6\text{N}_2(\mu\text{-C}_2\text{H}_2)$ skeleton of the $\text{Mo}_2(\text{OPr}^i)_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ molecule. Some bond distances (\AA) (averaged where appropriate) are: Mo-Mo = 2.554(1), Mo-O (terminal) = 1.94(2), Mo-O (μ_2) = 2.15(1), Mo-N = 2.31(1), Mo-C = 2.09(1) and C-C ($\mu\text{-C}_2\text{H}_2$) 1.368(6).

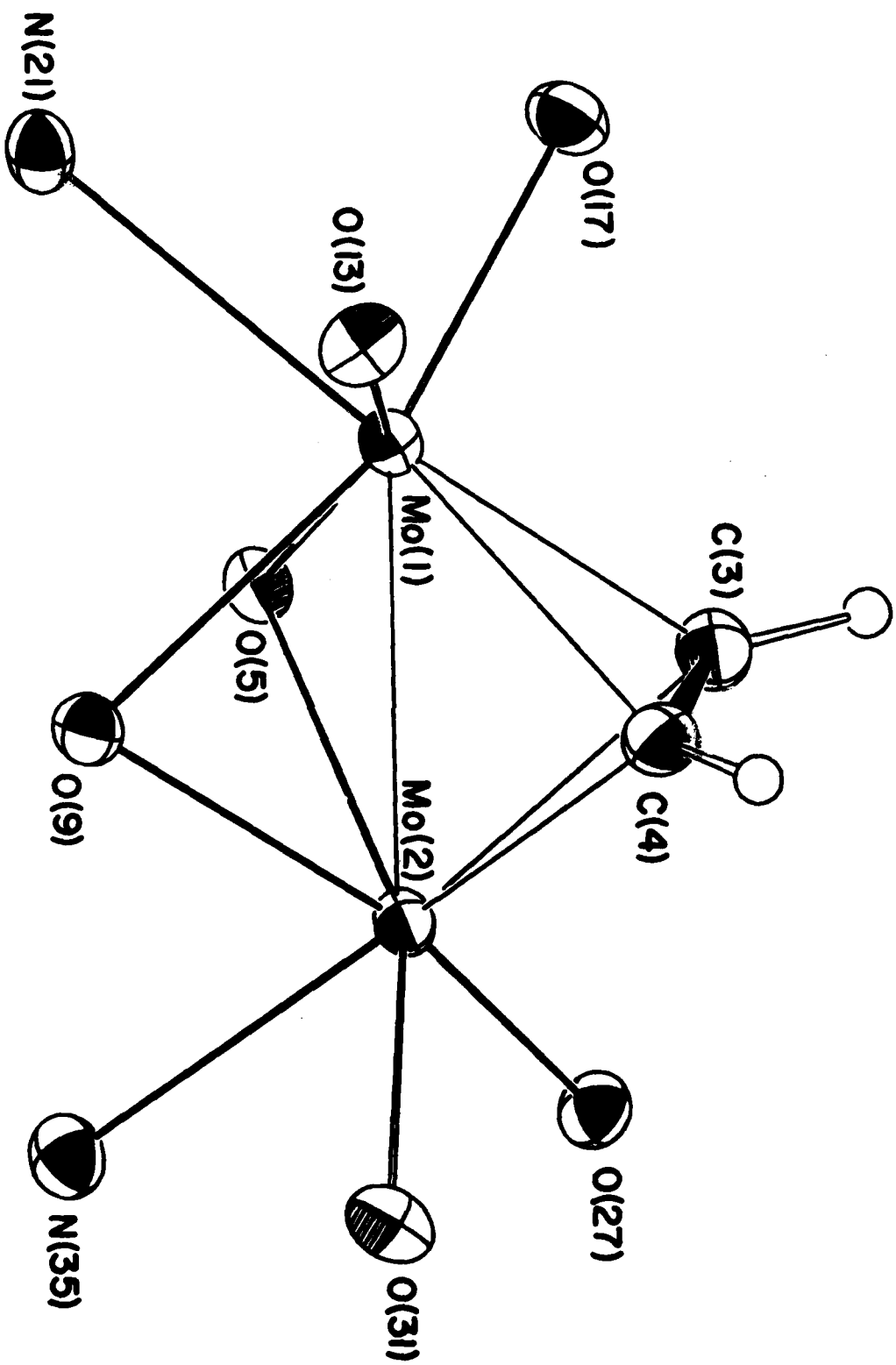


Figure 29. An ORTEP view of the $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ molecule. Some pertinent bond distances (\AA) (averaged where appropriate) are: Mo-Mo = 2.69(1), Mo-O = 1.92(2), Mo-O (μ_2) = 2.15(2), Mo-N = 2.15(1), Mo-C (σ) = 2.12(2), Mo-C (π) = 2.37(2); C-C ($\mu\text{-C}_4\text{H}_4$) = 1.45(2).

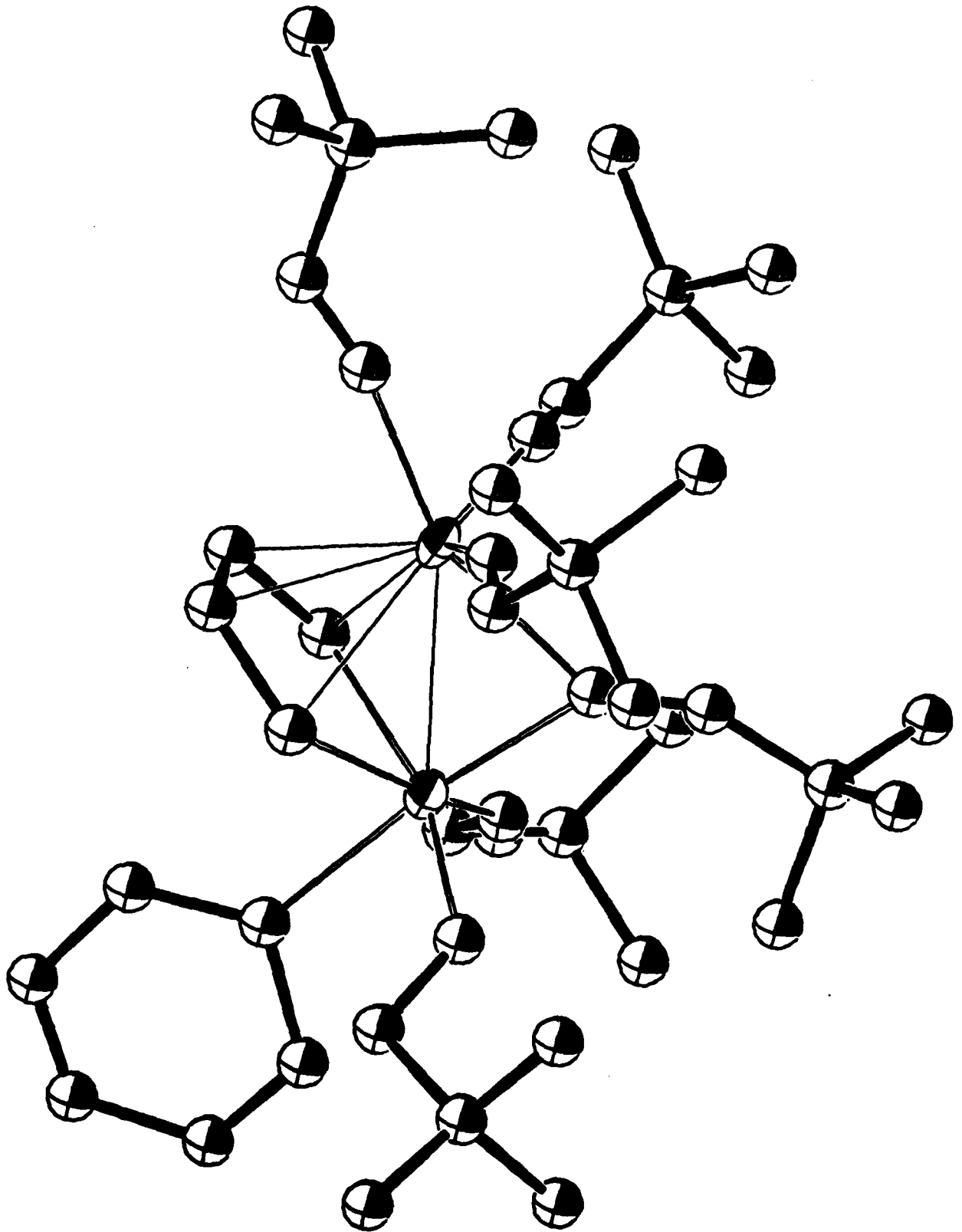
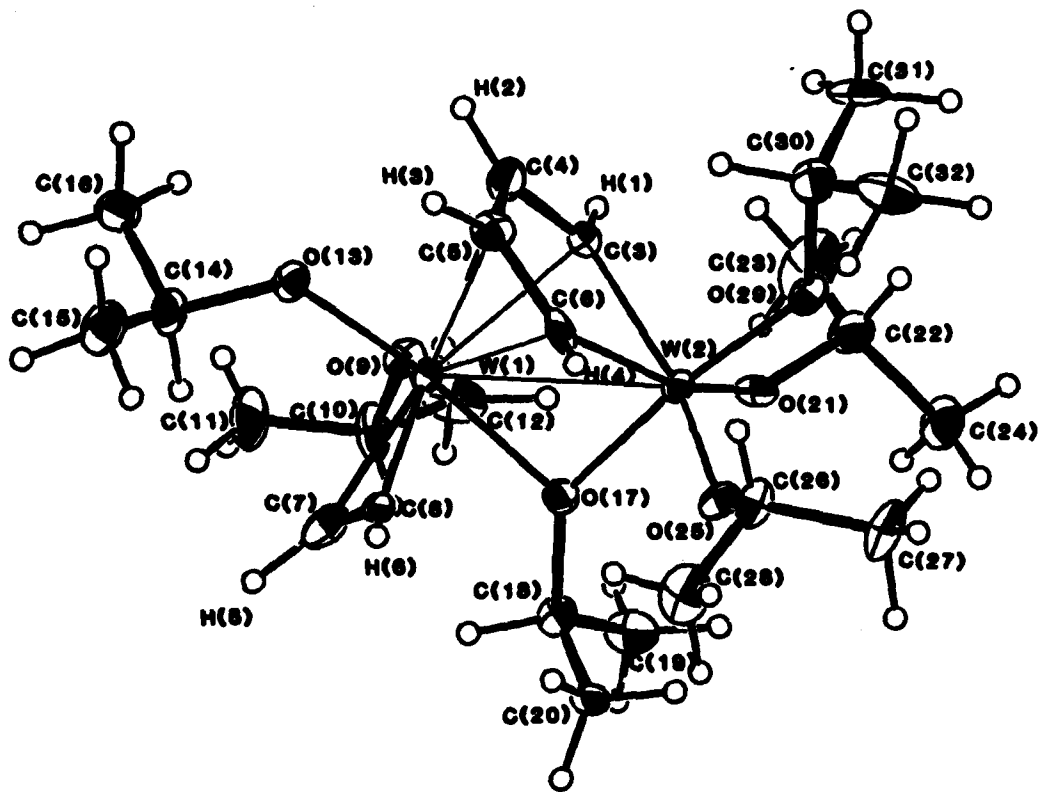


Figure 30. An ORTEP view of the $W_2(OPr^i)_6(\mu-C_4H_4)(C_2H_2)$ molecule. Some pertinent bond distances (\AA), averaged where appropriate, are: $W(1)-W(2) = 2.877(1)$, $W(2)-C(3), -C(6) = 2.11(1), 2.14(1)$; $W(1)-C(3), -C(4), -C(5), -C(6) = 2.42(1), 2.42(1), 2.40(1), 2.37(1)$; $W(2)-C(7), -C(8) = 2.09(1), 2.06(1)$. The W-O distances fall within the range of W-OR terminal and μ_2 reported in Table III.



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