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Analogies between Alkoxides and Oxide Structures in the Chemistry of Molybdenum and Tungsten*

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In all but oxidation state +6, the available valence electrons in molybdenum and tungsten alkoxides and oxides are used to form M–M bonds. This, together with the desire of the metal atom to achieve an octahedral environment with respect to oxygen binding, leads to many similarities in the structures of molecular metal alkoxide clusters and cluster units found within the extended lattices of macromolecular oxide structures. Metal–metal bonding may take the form of localized multiple bonding or may be delocalized over M_3, M_4, or M_6 units. These general principles are illustrated by several specific examples of each class. The choice of alkyl group in the synthesis of the metal alkoxides allows for steric control of coordination number and geometry at the metal. Thus, coordinative unsaturation can be engineered and used in the activation of small organic molecules. A possible analogy with surface effects on metal oxides exists. A model for the splitting of C≡O to surface carbide and oxide is presented, along with recent findings concerning the coupling of W≡W and C≡C/C≡N bonds.

Introduction

In this paper I should like to draw attention to four general topics. (1) The structural analogies between metal alkoxides and metal oxides: the central metal–oxygen units in $[M(OR)_x]_n$ compounds often resemble subunits in the extended array or lattices of metal oxides. (2) The variety of alkoxide clusters: these include compounds with localized M–M multiple bonds and delocalized cluster M–M bonds. (3) The fascinating physicochemical properties of these alkoxide clusters: specifically, new experimental data are presented for oxo-capped triangulo clusters of formula $Mo_3O(O\text{-i-}Pr)_{10}$ and the mixed metal cluster $Mo_2WO(O\text{-i-}Pr)_{10}$. (4) The extensive organometallic chemistry supported by alkoxide ligands: particular interest arises here because metal alkoxides may provide hydrocarbon soluble models for heterogeneous catalysts. Specific attention will be given to recent findings concerning the reactions of $W_2(OR)_6$ compounds with C≡O, $R'C{\equiv}CR'$, and $R'C{\equiv}N$.

General Considerations about Metal Alkoxide Structures

It has long been known that metal alkoxides of empirical formula $M(OR)_x$ tend to oligomerize both in solution and in the solid state to give compounds of formula

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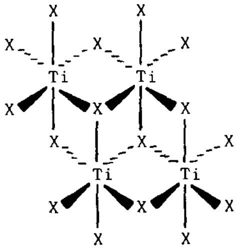
$[M(OR)_x]_n$ (*1*). The association is driven by the metal atom's desire to attain its prefered coordination number, most often 6, and is achieved by forming additional M–O bonds (6-x) through the agency of bridging (μ_2 or μ_3) OR ligands. Entropy opposes these associative, enthalpy-driven reactions and the degree of oligomerization found in the solid and solution may vary quite significantly. Molecular weight determinations carried out cryoscopically and ebullioscopically generally differ. Bulky alkyl groups and polar coordinating solvents favor monomeric or lower oligomers.

Based on these considerations and careful molecular weight determinations and infrared studies, Bradley (*2*, *3*), was able to build a workable and understandable theory for metal alkoxide polymers. Many of the early considerations are well exemplified by the studies of titanium(IV) alkoxides. The skeletal structure of the compounds $[Ti(OR)_4]_4$, where R = Me and Et, deduced from X-ray studies (*4*), is shown schematically in **I** below. Here through the agency of μ_2 and μ_3-OR bridges each titanium atom achieves an octahedral environment. In benzene solution, however, there is evidence for a trimer ⇄ tetramer equilibrium. More bulky alkoxy groups suppress oligomerization and $Ti(O{-}t{-}Bu)_4$ is a monomeric distillable liquid (60°C, 10^{-2} Torr) (*1*).



I

Mixed oxo-alkoxides often show higher degrees of oligomerization as seen, for example, in the structures of $Ti_7O_4(OEt)_{20}$ (*5*) and $Nb_8O_{10}(OEt)_{20}$ (*6*). These compounds bridge the gap between oligomeric alkoxides, $[M(OR)_x]_n$, and macromolecular oxides, $[M_aO_b]_\infty$ (*3*).

During the early considerations of metal alkoxide structures little or no thought was given to structure modification by M–M bonding, since this was either not possible, e.g., for d^0 or d^{10} metal compounds, or just not observed, e.g., for the d^n alkoxides of the first-row transition metal ions and the f^n-lanthanoids. However, the recent work with alkoxides of molybdenum and tungsten show that M–M bonding may indeed be of paramount importance in determining structure (*7*).

Classes of Mo and W Alkoxides

There are simple dinuclear alkoxides having multiple bonds between the metal atoms. These include M–M quadruple bonds in $Mo_2(O{-}i{-}Pr)_4(HOPr)_4$ (*8*) and $Mo_2(OCH_2{-}t{-}Bu)_4(PMe_3)_4$ (*8*) and M–M triple bonds in $M_2(OR)_6$ and $M_2(OR)_6L_2$ compounds (L = neutral donor ligand such as py or PMe_3) (*7*). The former adopt structures based on the well-established eclipsed D_{4h} template for M–M quadruple-bonded compounds (*9*), e.g., as in the $Re_2Cl_8^{2-}$ anion, while the latter are trigonal or square planar with respect to the ligand to metal binding. The overall conformation reflects the internal forces operating within the molecule, e.g., $Mo_2(OR)_6$ compounds adopt a staggered ethane-like geometry, typical of many $X_3M{\equiv}MX_3$ compounds (*10*) but in $W_2(O{-}i{-}Pr)_6(HNMe_2)_2$ the existence of hydrogen bonds across the M–M triple bond, N–H ---- OR, leads to a virtually eclipsed geometry in the solid state. The point to note is that the M–M triple bond of configuration $\sigma^2\pi^4$ is cylindrical and does not, unlike the quadruple bond of configuration $\sigma^2\pi^4\delta^2$, impose any restraint with respect to conformation. There are M–M double bonds in compounds such as $Mo_2(O{-}i{-}Pr)_8$

(*11*) and $W_2Cl_4(OEt)_4(HOEt)_2$ (*12*) and M–M single bonds in simple dinuclear compounds, e.g., $M_2X_4(OR)_6$ compounds (*13, 14*) and in extended chains such as $Mo_6O_{10}(O\text{–i-Pr})_{12}$ (*15*). There are also M–M multiple bonds in higher nuclearity species. For example, $Mo_4F_4(O\text{–t–Bu})_8$ contains a bisphenoid of molybdenum atoms with two short Mo–Mo distances, 2.26 Å, and four long Mo–Mo distances, 3.75 Å, corresponding to M–M triple and M–M nonbonding distances, respectively (*16*).

Triangulo metal alkoxides are found for $M_3(\mu_3\text{-}O)(OR)_{10}$ compounds. These have six electrons available for metal–metal bonding, a^2e^4, to give an equilateral M_3 triangle (*15, 17, 18*).

A wide variety of tetranuclear structures has been found. In $Mo_4Cl_4(O\text{–i-Pr})_8$ there is a Mo_4-square while in $Mo_4Br_4(O\text{–i-Pr})_8$ there is a Mo_4-butterfly or opened tetrahedron (*19*). Both of these cluster units have 12 electrons available for M–M bonding, as does $Mo_4F_4(O\text{–t-Bu})_8$ though as noted before the latter compound is best viewed as a dimer of Mo≡Mo bonded compounds: $[Mo_2(\mu_2\text{-}F)_2(O\text{–t-Bu})_4]_4$. The compound $W_4(OEt)_{16}$ (*20*) adopts the $[Ti(OEt)_4]_4$ structure, **I**, but the presence of eight cluster electrons (two from each W(4+) center) leads to a greatly contracted W_4 unit. The compound $W_4(H)_2(O\text{–i-Pr})_{14}$ also has eight electrons available for M–M bonding but here they are used to form double bonds leading to an interesting four-W-atom chain structure $[W_2(H)(OPr)_7]_2$ having consecutively short–long–short W–W distances (*21*).

To my knowledge no M_5-alkoxide clusters have been reported. However, the first Mo_6-cluster was reported as long ago as 1968 by Nannelli and Block (*22*). From the reaction between $MoCl_2$ and NaOMe, they obtained salts containing the anions $Mo_6Cl_8(OMe)_6^{2-}$ and $Mo_6(OMe)_{14}^{2-}$. They formulated these as members of the octahedral Mo_6-face shared, $(\mu_3\text{-}X)_8$, clusters and recently this has been confirmed by X-ray studies (*23*). These are 24-electron clusters.

Alkoxide–Oxide Structural Analogies

Though multiple bonds between metal atoms are not commonly seen in metal oxide structures there are known examples. The first example of a Mo═Mo bond was seen in one form of MoO_2 which has a distorted rutile structure wherein the Mo(4+) ions occupy adjacent octahedral holes throughout the lattice (*24*). The octahedra are distorted with short Mo–Mo distances, 2.51 Å, comparable to the Mo–Mo double-bond distance in $Mo_2(O\text{–i-Pr})_8$, 2.523(1) Å (*11*). The ternary oxide $La_4Re_2O_{10}$ has a fluorite-type structure in which O^{2-} is substituted for F^- and four of the five Ca^{2+} sites are occupied by the large La^{3+} ions. The remaining Ca^{2+} site is occupied by a $(Re{\equiv}Re)^{8+}$ unit with an Re–Re distance of 2.52(1) Å (*25*). Though M–M multiple bonds are not commonly seen in extended lattice structures they may well occur more commonly on or near the surfaces where the coordination numbers of the metal atoms are lower.

Triangulo Mo_3 cluster units are seen in the ternary oxide $Zn_2Mo_3O_8$ which contains Mo(4+) ions (*26, 27*). The Mo–Mo distance 2.524(2) Å (averaged) in the oxide is essentially identical to that in the oxo-capped alkoxide cluster $Mo_3O(O\text{–i-Pr})_{10}$, 2.535(2) Å (averaged) (*15*) though the coordination geometry of each cluster is not the same. The oxide structure has the M_3X_{13} structure with one capping oxo and three bridging oxo groups. The same structure is seen in aqueous solutions of Mo(4+) which contain the $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3^{4+}$ ion (*28–30*). The alkoxide structure has both a capping oxo and a capping alkoxide together with three μ_2-OR groups. In this way the M_3X_{11} unit and the M_3X_{13} unit both allow for octahedral coordination about molybdenum. We have just discovered yet another

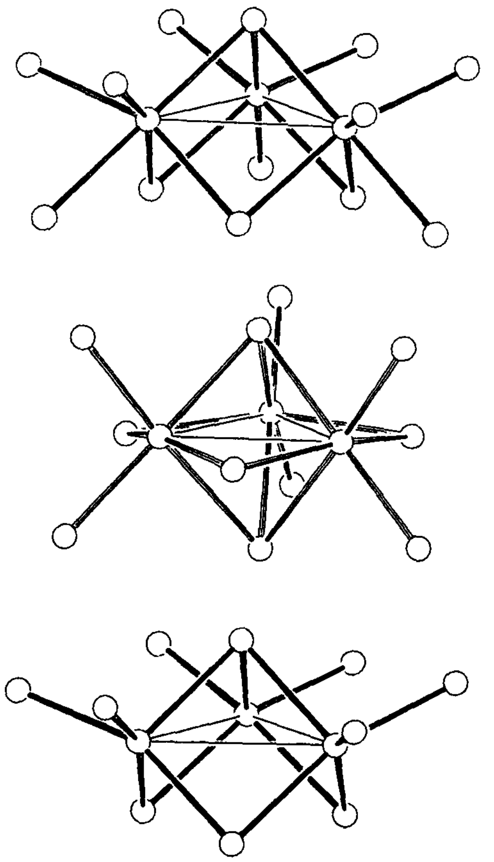


FIG. 1. Comparison of the M_3X_{13}, M_3X_{11}, and M_3X_{10} structures as seen in the molecular structures of $Zn_2Mo_3O_8$, $M_3O(OR)_{10}$, where M = Mo and W and R = i-Pr and CH_2–t-Bu, and $W_3(CMe)(O\text{–i-Pr})_9$, respectively.

type of triangulo alkoxide cluster in $W_3(\mu\text{-CMe})(\mu_2\text{-O–i-Pr})_3(\text{O–i-Pr})_6$ (*31*). This has a M_3X_{10} central unit with a capping alkylidyne and three μ_2–OR groups. This structure allows each molybdenum atom to be in a square-based pyramidal geometry. This structure can be viewed as a derivative of that seen for $Zn_2Mo_3O_8$, namely, one in which the ligand sites trans to the capping group are absent. These structural types involving M_3X_{13}, M_3X_{11}, and M_3X_{10} units are shown in Fig. 1.

Possibly the best analogy between oxide and alkoxide clusters is seen in the M_4X_{16} unit which is common to $[Ti(OEt)_4]_4$, $W_4(OEt)_{16}$, the mixed oxo-alkoxide $Mo_4O_8(\text{O–i-Pr})_4(py)_4$ (*15*), and the oxides $Ag_8W_4O_{10}$ (*32*) and $Ba_{1.14}Mo_8O_{16}$ (*33*). In the latter oxide there are two types of M_4X_{16} units differing principally in their M–M distances and, based on electron counting, these can reliably be established as 8- and 10-electron M_4 units. The central M_4 unit is shown to accommodate 0, 4, 8, and 10 electrons, and these are seen to be used in M–M bonding as reflected in the M–M distances for the M_4 unit. See Table I.

Physicochemical Properties

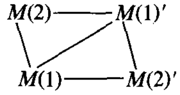
The physicochemical properties of these alkoxide clusters are of interest for a number of reasons. (1) Where the alkoxide cluster represents a subunit of a metal-oxide structure the electronic properties of the latter may involve localized cluster units and may thus resemble the former or may be quite different because of interactions between the cluster subunits. (2) The influence of the alkoxide ligand on the properties of a basic cluster unit are of interest. Gray and co-workers (*34, 35*) have discovered interesting redox chemistry and long-lived photoexcited states for the $Mo_6(\mu_3\text{-}X)_8X_6^{2-}$ ions (X = Cl, Br). The effect of substituting X = Cl, Br by OR, which are strong π-donor ligands, is of fundamental interest. (3) The small cluster units lend themselves toward theoretical studies (calculations) concerning the nature of the M–M bonding. A comparison of experimental data with that predicted by theory is always interesting with the two enjoying a synergistic relationship. Cotton and Fang (*36*) explained the distortions in going from the M_4X_{16} 10e to 8e clusters in terms of a second-order Jahn–Teller distortion and predicted that $W_4(OEt)_{16}$ should be susceptible to electrochemical reduction. Experimen-

TABLE I

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	*4*
$Ag_8W_4O_{16}$	3.32	3.23	3.49	0	*32*
$Mo_4O_8(OPr^i)_4(py)_4$	3.47	2.60	3.22	4	*20*
$W_4(OEt)_{16}$	2.65	2.94	2.76	8	*20*
$Ba_{1.14}Mo_8O_{16}$	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 labeling 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.



tally a reversible one-electron reduction was found subsequently (*37*).

$M_3O(OR)_{10}$ Compounds

A convenient synthesis of these compounds involves the comproportionation reaction

$$(RO)_3M\equiv M(OR)_3 + (RO)_4M\equiv O \rightarrow M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6 \quad (1)$$

where R = i-Pr and CH_2–t-Bu. This was originally noted for M=Mo (*15*) and has now been extended to M=W (*18*).

The synthesis of the mixed metal cluster $Mo_2WO(O\text{–}i\text{-}Pr)_{10}$ was achieved (*18*) from a reaction employing $Mo_2(O\text{–}i\text{-}Pr)_6$ and $(i\text{-}PrO)_4WO$, but the attempted synthesis of the related MoW_2 compound failed because oxo group transfer from Mo to W gives $(i\text{-}PrO)_4W\equiv O$ and $MoW(O\text{–}i\text{-}Pr)_6$.

Cotton and co-workers (*38*) have made extensive studies of triangulo M_3 clusters of the early transition elements (M = Nb, Mo, W) and have performed calculations employing the Fenske–Hall method on $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3(OH)_6$ (*17*) and other M_3-cluster types. The former serves as a model for the real molecules $Mo_3O(OR)_{10}$, where R = i-Pr and CH_2–t-Bu. The calculations predict that the HOMO is an *e* orbital and that it is principally M–M bonding resulting from the Mo *d*–*d* interactions. The LUMO is of *e* symmetry. It is of π-Mo–Mo bonding type but antibonding with respect to Mo–O interactions. The LUMO is also principally of metal *d* character. The calculated HOMO–LUMO gap is small, ca. 1.5 eV. Qualitatively, a similar orbital picture is expected for the W_3 and Mo_2W clusters, though in the mixed metal cluster the degeneracy of the *e* orbitals will be removed. The splitting of energy levels is expected to be small because of the close similarity of the metals Mo and W.

Expectations based on the calculations are in remarkable harmony with the experimentally observed physicochemical properties of the molecules.

All three compounds show reversible one-electron reductions in CH_2Cl_2 or THF solutions (*17, 18*). The peak separations for the oxidative and reductive waves are all larger than the 60-mV ideal separations for one-electron processes. With our experimental setup, reversible couples such as ferrocene/ferrocenium exhibit peak separa-

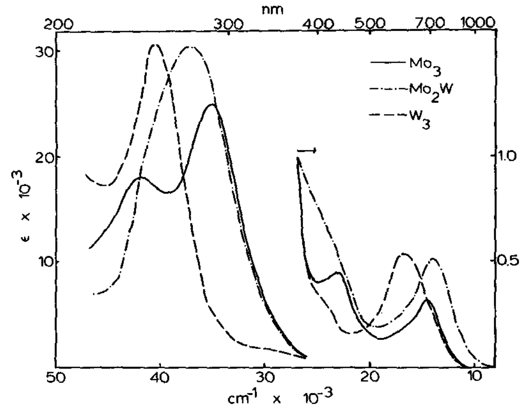


FIG. 2. Comparison of the uv–visible electronic absorption spectra of the $M_3O(O\text{-i-Pr})_{10}$ and $Mo_2WO(O\text{-i-Pr})_{10}$ compounds, where M = Mo and W. Spectra were obtained from hexane solutions at room temperature.

tions of 90–120 mV indicating that part of the large separation is due to uncompensated internal resistance. Also there may be a problem of slow electron transfer to and from these molecules because the Mo_3 center has a hydrocarbon shield. Moreover, the LUMO has M–M bonding and M–O antibonding character, which may impose a significant barrier because the equilibrium structures of the neutral and reduced species may differ significantly. Suffice it to say that reductive coulometry has established that the first reduction is a one-electron process and the reduced species $Mo_3O(O\text{–i-Pr})_{10}^-$ is stable for hours in THF or CH_2Cl_2 allowing its spectroscopic characterization. The $M_3O(OR)_{10}$ compounds are also oxidized but this is an irreversible process.

Electrochemical data for the three triangulo clusters are presented in Table II. The data show rather interesting trends. In comparing the Mo_3 and W_3 complexes, it is seen that both the oxidation and reduction processes occur at significantly more negative potentials for the W_3 complex. This is consistent with the generally observed phenomenon that, for medium-to-high oxidation states, third-row transition metal ions are easier to oxidize and harder to reduce than their second-row analogs. This is also in accord with the calculations which predict that both the HOMO and LUMO are predominantly metal-centered.

The couples for the Mo_2W species occur at intermediate potentials though not at values that would be predicted on pure statistical grounds. The reduction couples occur at only a slightly more negative value than that for the Mo_3 complex. The implication is that the reduction is more heavily centered on the Mo centers than on W. The value for the oxidation of the Mo_2W complex is much closer to that for the W_3 complex which implies that the oxidation process is predominantly W-centered. This is consistent with the general behavioral differences between Mo and W noted above. Presumably the Mo–W bonds are polarized in the fashion $Mo^{\delta-}$–$W^{\delta+}$.

A comparison of the UV–visible spectra is shown in Fig. 2. Qualitatively, the spectra are similar. For each compound there is a low-energy band at 600–700 nm in the visible region of the spectrum with a molar absorption coefficient, ε, of ca. 500 liters mole^{-1} cm^{-1}. This band is responsible for the blue–green color of the complexes. In addition there are intense bands ($\varepsilon > 20{,}000$ liters mole^{-1} cm^{-1}) in the ultraviolet region. We can assign the former to the HOMO → LUMO transition and the latter to ligand (oxygen p) to metal charge transfer.

TABLE II

ELECTROCHEMICAL DATA FOR TRIANGULO OXO CAPPED METAL ALKOXIDES[a]

$M_3O(O\text{–i-Pr})_{10}$	$E_{1/2}$(red) (V)	$\Delta E_{1/2}$ (mV)	E_p(ox) (V)
Mo_3	−1.46	110	0.48
Mo_2W	−1.57	175	0.20
W_3	−2.16	140	0.09

[a] THF solution, 0.01 F $AgNO_3(CH_3CN)/Ag$ reference electrode.

Both the energy and the intensity of the lowest energy transitions are in accord with expectations based on the calculations which predict the HOMO and LUMO to be predominantly metal *d* in character with a gap of 1.5 eV. The trends in λ_{max} for this absorption are also interesting: 690 (Mo_3), 718 (Mo_2W), and 600 (W_3). The shift to higher energy $W_3 > Mo_3$ is consistent with a slightly stronger metal–metal interaction for the tungsten complex. A possible cause for the shift to lower energy for the Mo_2W complex could be traced to the expected splittings of the *e*-type orbitals (both for the HOMO and LUMO).

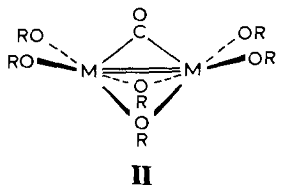
A comparison of the high-energy bands shows a shift to higher energy on going from the Mo_3 to the W_3 complex with the Mo_2W complex exhibiting transitions at intermediate energy. Since the W_3 complex is found to be 0.7-V harder to reduce electrochemically than the Mo_3 complex, this is exactly the type of behavior expected for an O → *M* LMCT transition. This would place the oxygen lone pairs of the alkoxide ligands approximately 2 eV lower in energy than the metal-centered HOMO which is again in good agreement with the MO calcuations.

Organometallic Chemistry Supported by Alkoxide Ligands

Within the last few years there has been a resurgence of interest in the field of metal alkoxides and aryloxides. Schrock and coworkers (*39*) in their beautiful work with *M*–C double- and triple-bonded compounds have found that alkoxides can be valuable supporting ligands. By suppressing α and β hydrogen abstraction reactions, for example, $M{=}CRR'$ and $M{\equiv}CR$ functions may have exceedingly high activity toward olefin and alkyne metathesis reactions, respectively. The work of Rothwell (*40*) with the bulky aryloxide ligand derived from 2,6-di-t-butylphenol and the early transition elements, particularly Ta, has revealed new insights into C–H bond activation by d^0 metal centers. Our own interests stem from the recognition that in heterogeneous catalysis metal oxides form an extremely important group of catalysts for a wide variety of hydrocarbon and small organic molecules (oxygenates). Presumably *M*–C and *M*–H bonds are at work with oxo groups (terminal and bridging) as the other supporting ligands. This drew our attention to simple alkyl and hydrido alkoxides such as $R_2Mo_2(OR')_4$ (*41*), $RMo_2(OR')_5$ (*41*), and $W_4(\mu\text{-}H)_2(O\text{–}i\text{-}Pr)_{14}$ (*42*). As has been noted before, reduced molybdenum and tungsten alkoxides and oxides (*43*), that is to say all other than *M*(6+) alkoxides and oxides, form *M–M* bonds and these provide a reservoir of electrons which may be used for reducing substrate molecules. Probably unique amongst this group of reactions are those involving $W_2(OR)_6(M{\equiv}M)$ compounds and alkynes, nitriles, and carbon monoxide. Here the reducing power of the W≡W bond and the differing requirments of the C≡C, C≡N, and C≡O groups lead to some fascinating reactions and new compounds.

Activation of Carbon Monoxide

Hydrocarbon solutions of $W_2(O\text{–}t\text{-}Bu)_6$ react with CO rapidly at room temperature to give $W_2(O\text{–}t\text{-}Bu)_6(\mu\text{-}CO)$ (*44*), the structure of which is



II

The molybdenum analog is also known and is isostructural (*45*). In both compounds there are formally *M–M* double bonds, *M–M* = 2.49 Å, and C–O double bonds, C–O = 1.21 Å. The ν(CO) stretching frequencies are remarkably low: 1598 cm^{-1} (M = W) and 1670 cm^{-1} (M = Mo). Formally these compounds are inorganic analogs of cyclopropenone and the lowering of the C–O stretching frequency can be understood in terms of bonding between the M–M π bonding orbital and the C–O π^* orbital. The fact that the C–O stretching frequency is lower by ca. 70 cm^{-1} in the tungsten compound than in the molybdenum compound is another reflection of the greater reducing power of W(3+) relative to Mo(3+) in related compounds. The extremely low C–O stretching frequency and analogy with cyclopropenone lead one to suspect that the oxygen atom should be nucleophilic. This was first realized by Cotton and Schwotzer (*46*) who, in attempting to prepare $W_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ (*47*), actually isolated $W_4(O\text{-}i\text{-}Pr)_{12}(CO)_2(py)_2$ in which the C–O ligand bridged three tungsten atoms. A consideration of the W–W,

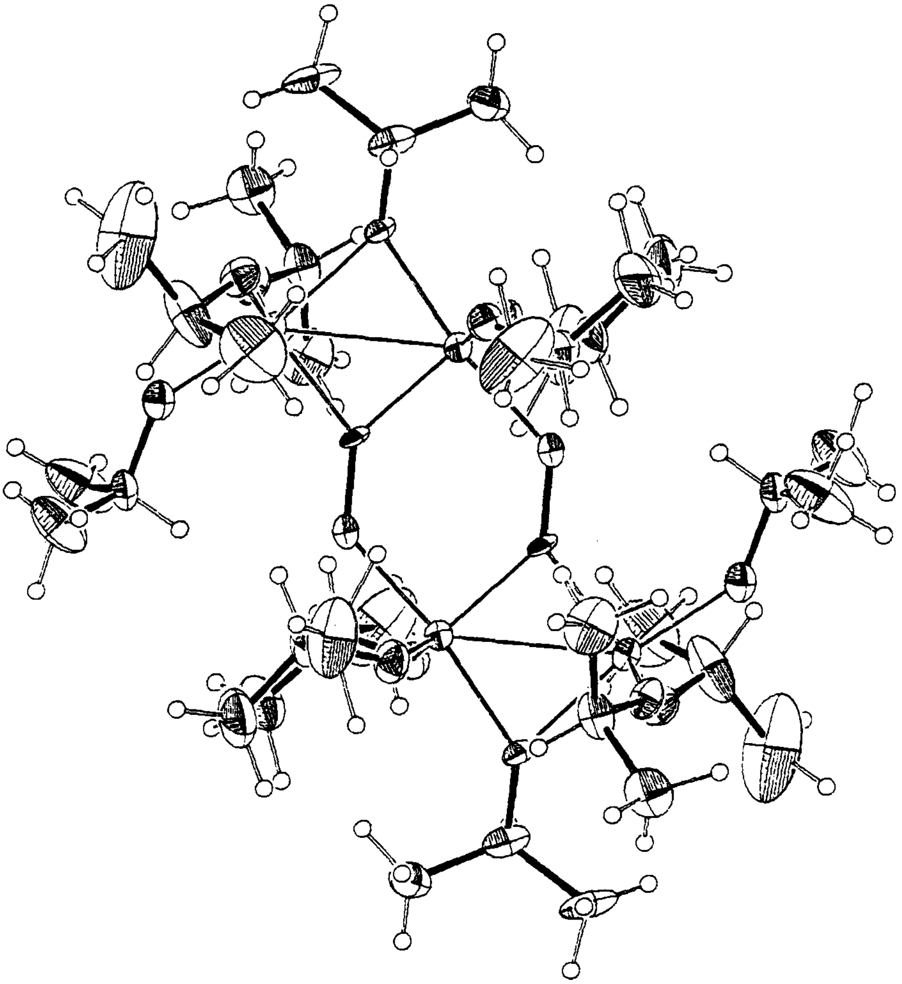
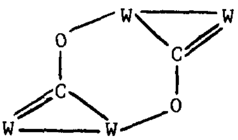
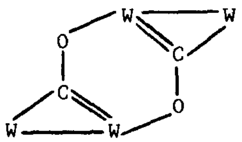


FIG. 3. An ORTEP view of the centrosymmetric $W_4(CO)_2(O\text{-}i\text{-}Pr)_{12}$ molecule emphasizing the central planar $[W_2(\mu\text{-}CO)]_2$ unit. Pertinent distances (Å) are W–W = 2.657(1), W–C = 1.95(1) (averaged), C–O = 1.35(1), W–O = 1.974(8) (carbonyl), W–O = 1.90(2) (averaged) (terminal O*R*), W–O = 2.04(3) (averaged) (bridging O*R*).

W–C, and W–O and C–O distances leads one to represent the core of this tetranuclear compound in the valence bond description resonance forms shown in **IIIa** and **IIIb** below.

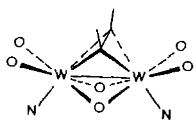


IIIa

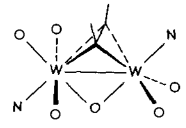


IIIb

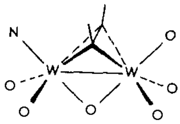
A simple route to an unligated form of the molecule involves the alcoholysis reaction: $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO) + 6\ i\text{-}PrOH \rightarrow \frac{1}{2}[W_4(\mu\text{-}CO)_2(O\text{-}i\text{-}Pr)_{12}] + 6t\text{-}BuOH$ (*44*). An ORTEP showing the molecular structure of this molecule is given in Fig. 3. From ^{13}CO labeling studies we can identify ν(C–O) for the bridging carbonyl ligand: $\nu(^{12}C\text{–}O) = 1272\ cm^{-1}$ and $\nu(^{13}C\text{–}O) = 1243\ cm^{-1}$. The ^{13}C NMR spectrum at room temperature shows, for the "fixed" CO ligand, a signal at $\delta = 305.5$ ppm with satellites due to coupling to two inequivalent ^{183}W nuclei, $J_{W\text{-}C} = 189$ and 164 Hz. In two steps we have gone from W≡W + C≡O to W═W and C═O to W—W and C—O, while the W—C bond order has increased with each step. We believe that this provides a model for the reductive cleavage of C≡O to surface-bound carbide and oxide and we are currently looking at reactions aimed at completing the C–O cleavage to give alkoxy tungsten clusters bearing carbide and oxide ligands starting from compounds such as $W_4(CO)_2(O\text{-}i\text{-}Pr)_{12}$.



$W_2(OPr^i)_6(py)_2(\mu\text{-}HCCH)$



$W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}MeCCMe)$



$W_2(OBu^t)_6(py)(\mu\text{-}HCCH)$

FIG. 4. Structural types seen for alkyne adducts of ditungsten hexaalkoxides of formula $W_2(OR)_6(\mu\text{-}C_2R_2')(py)_n$, where $n = 1$ or 2. O represents alkoxy ligands and N represents coordinated pyridine.

Alkyne and Nitrile Activation

Alkynes and nitriles have been found to react with $W_2(OR)_6$ (W≡W) compounds to give a wide variety of products. Schrock and co-workers (*48*) discovered the metathesis reactions involving $W_2(O\text{-}t\text{-}Bu)_6$ and C≡C and C≡N bonds shown in

$$W_2(O\text{-}t\text{-}Bu)_6 + RC{\equiv}CR \xrightarrow{[R = Me,\ Et,\ Pr]} 2(t\text{-}BuO)_3W{\equiv}CR \quad (2)$$

$$W_2(O\text{-}t\text{-}Bu)_6 + RC{\equiv}N \xrightarrow{[R = Me,\ Ph]} (t\text{-}BuO)_3W{\equiv}N + (t\text{-}BuO)_3W{\equiv}CR \quad (3)$$

Cotton and co-workers (*49*) found under somewhat different conditions that PhC≡CPh gave $(t\text{-}BuO)_4W_2(\mu\text{-}CPh)_2$ and $(t\text{-}BuO)_4W_2(\mu\text{-}C_2Ph)_2$ along with very small quantities of $(t\text{-}BuO)_3W{\equiv}CPh$.

We have found that it is possible to prepare alkyne adducts of ditungsten hexaalkoxides and that these fall into one of three structural types. These are shown in Fig. 4. Obviously steric factors are very important in determining both the structure and the course of reaction. In the case of the ethyne adduct of $W_2(O\text{-}t\text{-}Bu)_6$ and the 2-butyne adduct of $W_2(O\text{-}i\text{-}Pr)_6$ we have found evidence for an equilibrium between the dimetallatetrahedrane and the alkylidyne complex (*50, 51*).

In the case of C≡N activation we have

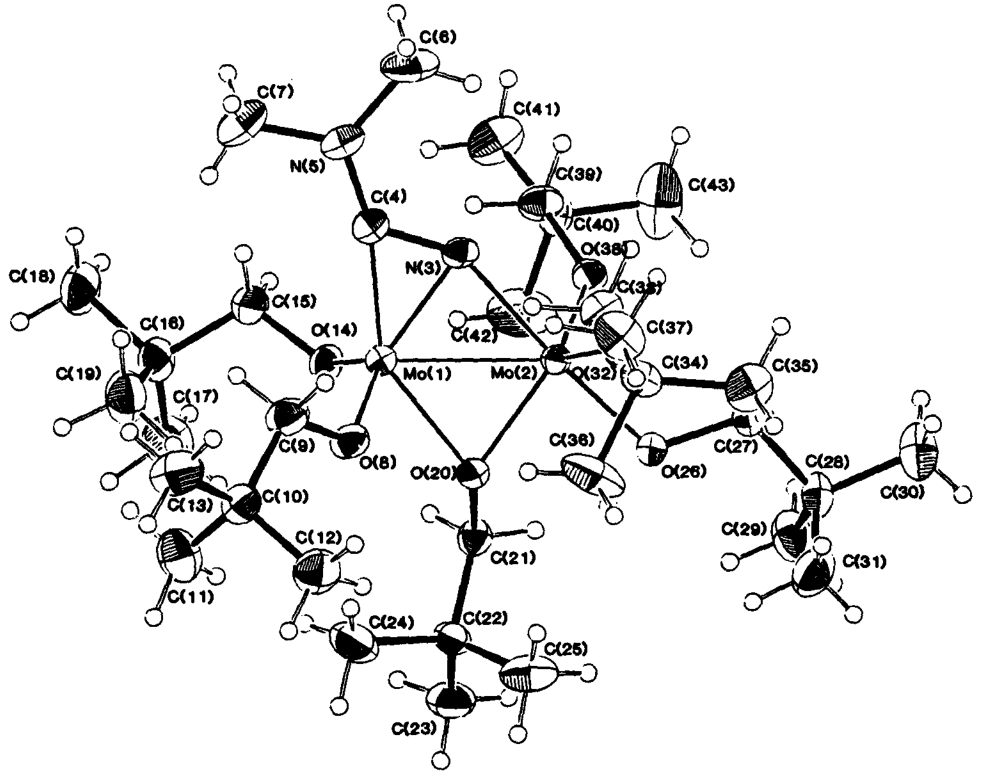


FIG. 5. An ORTEP view of the $Mo_2(OCH_2\text{–t-Bu})_6(\mu\text{-NCNMe}_2)$ molecule. Selected bond distances (Å) associated with the central $Mo_2(CN)$ moiety are Mo–Mo = 2.449(1), Mo–C = 2.014(4), Mo(1)–N = 1.908(3), Mo(2)–N = 2.134(2).

isolated (*52*) $Mo_2(OR)_6(\mu\text{-NCNMe}_2)$ compounds and the structure of the neopentoxy compound has been determined (*53*). This has the structure shown in Fig. 5. The five non-hydrogen atoms of the Me_2NCN ligand all lie in a plane and this plane also contains the two metal atoms. From a consideration of C–N and Mo–Mo distances it is reasonable to view adduct formation akin to a two-electron redox reaction yielding a $(Mo{=}Mo)^{8+}$ center and a $RC{=}N^{2-}$ ligand. Reactions involving $W_2(OR)_6$ compounds proceed differently reflecting the greater reducing power of the W≡W bond but once again the role of steric factors is important in determining the nature of the product. The t-BuO compounds reacts to give $(t\text{-BuO})_3W{\equiv}N$ and $[(t\text{–BuO})_3W{\equiv}CNMe_2]_2$ (*53*) in a manner akin to that found by Schrock [Ref. (*48*); see also Eq. (3)]. However, with the less-bulky neopentoxide ligands the six electrons of the W≡W bond are used to reduce three Me_2NCN ligands for which three different modes of bonding are seen in the structure of $W_2(OCH_2\text{–t-Bu})_6(NCNMe_2)_3$ (*54*). Each Me_2NCN ligand may be viewed as a 2-ligand and with a W-to-W distance of 3.85 Å it is certain that there is no *M*–*M* bond. A comparison of pertinent bond distances associated with the Me_2NCN adducts of the neopentoxy compounds of molybdenum and tungsten is shown in Fig. 6.

The alkyne adducts of $W_2(OR)_6$ are reactive toward further additions of alkynes and nitriles. With alkynes, compounds of for-

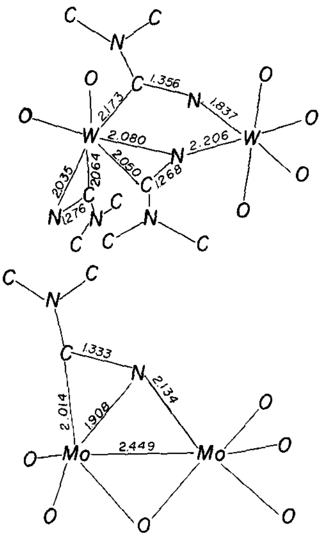


FIG. 6. Comparison of the central skeletons of the $Mo_2(OCH_2\text{-t-Bu})_6(NCNMe_2)$ and $W_2(OCH_2\text{-t-Bu})_6(NCNMe_2)_3$ molecules showing pertinent bond distances in Ångstroms. ESDs are 0.005 Å for C–C and C–N distances and 0.002 Å for M–C/N.

mula $W_2(OR)_6(\mu\text{-}C_4R'_4)(\eta^2\text{-}C_2R'_2)$ have been isolated (R = i-Pr and CH_2-t-Bu, R' = H, Me) (*55, 56*). In the case of the bulky t-butoxy compound there is apparently no room for an $\eta^2\text{-}C_2H_2$ ligand and $W_2(O\text{-t-Bu})_6(\mu\text{-}C_4H_4)$ is formed (*56*).

With nitriles novel dinuclear compounds containing 5- or 7-membered heterocyclic rings are formed (*57, 58*). In $W_2(O\text{-t-Bu})_6(CHCHC(Ph)N)$, which is formed in the reaction between $W_2(O\text{-t-Bu})_6(\mu\text{-}C_2H_2)(py)$ and $PhC{\equiv}N$ (1 equiv), each tungsten atom is in a distorted trigonal bipyramidal environment. The two halves of the molecule are joined along a common equatorial–axial edge through the agency of an alkoxy ligand and the nitrogen atom of the heterocyclic ligand formed by the coupling of the alkyne and nitrile. Formally this ligand can be counted as a 4-ligand with terminal alkylidene and imido groups: $W{=}CH{-}CH{=}C(Ph){-}N{=}W$, where $W{=}C$ = 1.980(6) Å and $W{-}N$ = 2.041(5) Å and $W{=}N$ = 1.903(5) Å. The W–W distance is 2.674(1) Å, indicative of a single bond. $W_2(O\text{-t-Bu})_6(CHCHC(Ph)N)$ reacts with isopropanol to give $W_2(O\text{-i-Pr})_7(CH_2CHC(Ph)N)$, which is the product of the combined reactions of alcoholysis and alcohol addition across the tungsten–carbon double bond: $W{=}CH{-} + ROH \rightarrow RO{-}W{-}CH_2{-}$. In $W_2(O\text{-i-Pr})_7(CH_2CHC(Ph)N)$ each tungsten atom is in a distorted octahedral environment and the two metal atoms share a face formed by two bridging OR ligands and the nitrogen atom of the metallacycle which is now formally a 3-ligand having imido and alkyl attachments to tungsten: W–C = 2.174(8) Å, W–N = 1.980(6) and 1.962(7) Å and W–W = 2.585(1) Å. A comparison of the bond distances associated with the W_2C_3N metallacycles is shown in Fig. 7.

The metallacycle formed by coupling one $RC{\equiv}CR$ and one $RC{\equiv}N$ group contains a $W{=}C$ bond and is labile toward further insertion reactions. In $W_2(OCH_2\text{-t-Bu})_6(N(CMe)_4N)(py)$, which is formed in

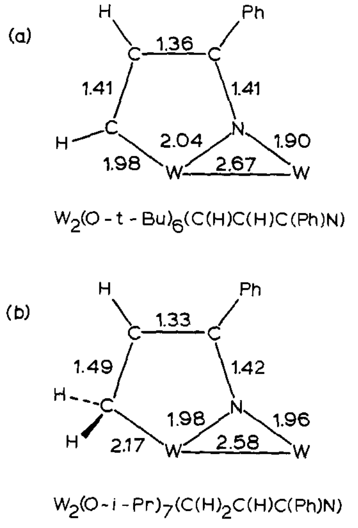


FIG. 7. Comparison of pertinent bond distances (Å) within the W_2-heterocycles in (a) $W_2(O\text{-t-Bu})_6(CHCHCPhN)$ and (b) $W_2(O\text{-i-Pr})_7(CH_2CHCPhN)$. ESDs are 0.005 Å for C–C and C–N distances and 0.002 Å for W–C and W–N distances.

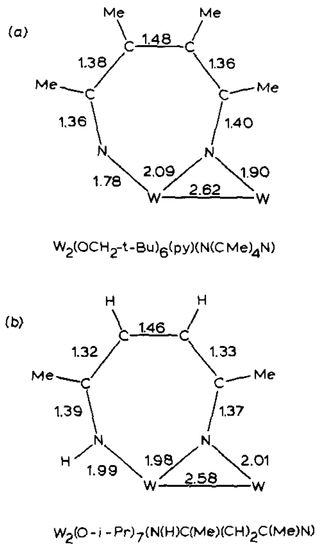


FIG. 8. Pertinent bond distances (Å) for the W_2-7-membered heterocycles in (a) $W_2(OCH_2\text{–t-Bu})_6(N(CMe)_4N)(py)$ and (b) $W_2(O\text{–i-Pr})_7(N(H)C(Me)(CH)_2C(Me)N)$. ESDs are 0.005 Å for C–C and C–N distances and 0.002 Å for W–N distances.

the reaction between $W_2(OCH_2\text{–t-Bu})_6(py)_2(\mu\text{-}C_2Me_2)$ and $MeC{\equiv}N$ (>2 equiv), there is a 7-membered metallacycle which incorporates the 4-ligand derived from 1,4-diamino-1,2,3,4-tetramethyl-1,3-butadiene. The connectivity involves one terminal imido group, W–N = 1.78(1) Å, and one bridging imido group, W–N(μ) = 1.90(1) and 2.09(1) Å. Each tungsten atom is in a distorted octahedral environment and the W–W distance 2.617(1) Å corresponds to a *M–M* single bond. The compound $W_2(O\text{–i-Pr})_7(NHC(Me)CHCHC(Me)N)$, is closely related to $W_2(OCH_2\text{–t-Bu})_6(NCMe)_4N)(py)$ being formed in the reaction between $W_2(O\text{–i-Pr})_6(py)_2(\mu\text{-}C_2H_2)$ and $MeC{\equiv}N$ (>2 equiv) in the presence of i-PrOH. The 7-membered metallacycle now has a terminal amido group (1-) and a bridging imido (2-) function and the addition of *R*OH across the W=N bond parallels the conversion of W=CH*R* to W—CH$_2$*R* noted above. W–N (amido) = 1.986(8) Å, W–N (μ-imido) = 1.983(8) and 2.007(8) Å. Each tungsten is in a distorted octahedral environment with the W–W distance = 2.576(1) Å. A comparison of the bond distances associated with the W_2-7-membered heterocyclic groups is shown in Fig. 8.

Concluding Remarks

In this short discourse I hope to have highlighted some of the points of current interest in the rapidly developing field of alkoxide chemistry of molybdenum and tungsten. Central to all areas of this chemistry is metal–metal bonding. Whether or not the analogies with metal oxide chemistry are valid, this notion has prompted us to look further toward the use of alkoxides as supporting ligands for organometallic chemistry. This promises to be a most fruitful development in early transition metal chemistry.

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