LEVEL II

DYNAMIC AND STATIC STEREOCHEMISTRY IN DIMOLYBDENUM AND DITUNGSTEN COMPOUNDS CONTAINING A CENTRAL $(M \equiv M)^{6+}$ UNIT

by

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The chemistry of molybdenum and tungsten in oxidation state +3 is now dominated by compounds containing a central $(M \neq M)^{6+}$ core, with metal-to-metal distances in the range of 2.2 to 2.3 Å. The molecular orbital configuration of the triple bond is $\sigma^2\pi^4$ arising from the mutual interaction of metal atomic d_{z^2} (σ) and d_{xz}, d_{yz} (π) orbitals. In compounds containing the central $(M \equiv M)^{6+}$

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20. ABSTRACT continued.

core, the metal atoms may be bonded to three, four, five or six ligand atoms. Examples of each are given and for a given coordination number the preferred geometry is discussed. Low temperature nmr studies support the view that the structures found in the solid state are also present in solution. Variable temperature nmr studies reveal a wealth of knowledge concerning the dynamic behavior of those molecules in solution. For example, (i) $M_2(NR_2)_6$ and $M_2(NR_2)_4Y_2$ molecules (Y = halide, alkyl or alkoxy group) are molecular propellers; (ii) rotational barriers about metal-to-metal triple bonds in $M_2Y_4X_2$ (M≡M) compounds are comparable to those in related $Si_2Y_4X_2$ and P_2Y_4 compounds; the latter contain a central element-element σ-bond of length 2.2 to 2.3 Å; (iii) molecules of the type $L(RO)_3M≡M(OR)_3L'$ contain OR groups which are cis and trans to the neutral ligands L and L'. Site exchange between cis and trans groups occurs on the nmr time scale by a threshold mechanism which does not involve exchange of OR groups between the two metal atoms. This is compared to the fluxional properties associated with MX_5 compounds ($D_{3h} \rightleftharpoons D_{4h}$). Finally, the absence of any complex containing a central M_4^{12+} tetrahedral moiety is noted. The closest approach to such a compound is seen in the tetranuclear complexes $Mo_4(\mu\text{-}F)_4(OBu^t)_8$ and $Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8$ which contain a bisphenoid of molybdenum atoms having two short Mo-Mo distances (2.26 Å) and four long Mo-Mo distances (3.75 Å) corresponding to localized triple and non-bonding interactions, respectively.

Introduction

"There are literally thousands of chromium(3+) complexes which, with very few exceptions, are all hexacoordinate."[1] This is not surprising in view of the fact that ligand field stabilization favors an octahedral geometry for a d^3 ion. Since ligand field stabilization energies increase sizeably in going from the first to the second row and again from the second to the third row within a triad of transition metals, one might have anticipated an abundance of molybdenum(3+) and tungsten(3+) hexacoordinate complexes. Rather interestingly, just the reverse trend is observed: there are but a handful of well authenticated mononuclear molybdenum(3+) complexes and to this author's knowledge, not one mononuclear complex is known for tungsten(3+). Does this mean that the argument based on ligand field stabilization is fallacious? Certainly not. If we consider the d^6 configuration, for example, we find an abundance of six-coordinate octahedral 2nd and 3rd row transition metal complexes, e.g. Ir(3+), Pt(4+) complexes. The main difference between the d^3 and d^6 systems rests with the former being paramagnetic and the latter diamagnetic and, since within any triad of metals for given oxidation state Z+, the effective nuclear charge exerted on the valence electrons decreases down the series, then the d^3 orbitals in an octahedral environment, t_{2g}^3, become more diffuse and available for metal-metal bonding. This is well demonstrated in the structures of the $M_2Cl_9^{3-}$ ions which share a common confacial bioctahedral geometry, D_{3h}, and where the M-M distances change from 3.12 Å (M=Cr) to 2.67 (M=Mo) to 2.41 (M=W).[2,3] Indeed $W_2Cl_9^{3-}$ is diamagnetic and Pauling[4] introduced the canonical structures W=W and W≡W as part of a resonance hybrid description

for the anion. However, the types of compounds described in this account are of a simpler nature in that there are no atoms directly bridging the two metals.

Syntheses

Though this account does not dwell on syntheses or reactivity patterns of the compounds to be described, it is worth noting that the basic M_2X_6 compounds, M = Mo, W, X = R(β-elimination stabilized alkyl) or NMe_2 are derived from metathetic reactions involving either $MoCl_5$, $MoCl_3$, WCl_6 or WCl_4.[5] Though the details of these reactions are now known, we have presented a strong case for the fact that the M_2X_6 compounds are not formed by the coupling of two reactive mononuclear species.[6] The most synthetically useful compounds are the dimethylamido compounds, $M_2(NMe_2)_6$,[7,8] from which literally scores of dinuclear compounds containing the central $(M \equiv M)^{6+}$ have been prepared. Some of these reactions are summarized in Scheme 1.

Solid State Structures

M_2X_6 Compounds (X = R, NR_2 and OR).

In all of these compounds, there is a central staggered ethane-like M_2C_6, M_2N_6 or M_2O_6 group having virtual D_{3d} symmetry.[5] Two views of the $Mo_2(NMe_2)_6$ are shown in Figure 1. The $M-NC_2$ planes are aligned with the Mo-Mo-N planes thus maintaining D_{3d} symmetry and giving rise to six proximal N-methyl groups, those lying over the metal-metal bond, and six distal N-methyl groups. There is also a large class of $M_2X_2(NR_2)_4$ compounds e.g. X = halide, alkyl or alkoxide group.[5,9] These may be viewed as 1,2-disubstituted

ethane-like molecules. The halides all crystallize in the anti-rotamer and maintain this in hydrocarbon solutions.[10,11] Figure 2 shows the molecular structure of $W_2Cl_2(NEt_2)_4$:[10] again the N-ethyl groups are arranged in proximal and distal sets. The solid state structures of $W_2Me_2(NEt_2)_4$[12] and $Mo_2Me_2(NMe_2)_4$[13] also show the anti-rotamer.

$M_2X_6L_2$ Compounds.

$Mo_2(OSiMe_3)_6(HNMe_2)_2$[14] and $W_2(OPr^i)_6(py)_2$[15] are two examples of nitrogen donor adducts to M_2X_6-type molecules. The geometry about each metal is essentially square planar and the two MO_3N units are joined in such a manner that they are partially staggered with respect to each other. A view down the W-W bond of the $W_2O_6N_2$ skeleton of the $W_2(OPr^i)_6(py)_2$ molecule is shown in Figure 3.

In the $Mo_2(OBu^t)_4(O_2COBu^t)_2$ molecule, there are a pair of <u>cis</u> O_2COBu^t ligands which bridge the Mo-Mo triple bond.[16] This imposes a virtually eclipsed geometry on the $Mo_2O_4O_4'$ skeleton.

In the $W_2(NMe_2)_4(PhN_3Ph)_2$ molecule, the diphenyltriazenido group is bidentate but does not bridge the W-W triple bond.[17] An ORTEP view of the molecule is shown in Figure 4: note that the molecule has a C_2 axis of symmetry.

Irrespective of the nature of the groups present, we have found that when four atoms are coordinated to each metal in an $(M \equiv M)^{6+}$ compound, the four atoms lie at least roughly at the corners of a square plane. Typically the M-M distance is <u>ca</u> 0.02 Å longer in these compounds than in the simple M_2X_6 compounds.[18]

What about five atoms coordinating to each metal? Where will the fifth ligand position be? Well, we only have one structurally characterized example, so it is certainly premature to claim a general trend. The central skeleton of the $W_2(CH_3)_2(O_2CNEt_2)_4$ molecule is shown in Figure 5. There are a pair of bridging O_2CNEt_2 ligands which impose an eclipsed geometry with respect to each end of the molecule.[19] There are also a pair of bidentate O_2CNEt_2 ligands and the carbon atom of the methyl group makes up a pentagonal coordination for each tungsten.

Although one cannot generalize from a single case, the structure of $W_2(O_2CNMe_2)_6$[19] is so closely related to that of $W_2(CH_3)_2(O_2CNEt_2)_4$ that it is at least tempting to say that a pattern is beginning to emerge. The central $W_2(O_2C)_6$ skeleton is shown in Figure 6. The relationship between the structure of $W_2(CH_3)_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ is most striking: the methyl carbon is replaced by an oxygen atom of an axially aligned O_2CNMe_2 group. The other oxygen forms a weak/long bond in the axial position.

Thus it appears that the central $(M \equiv M)^{6+}$ unit upon expanding the coordination number of each metal from 3, to 4, to 5 goes from trigonal, to square planar to pentagonal planar, and only reluctantly will accept a sixth ligand atom in the axial position (axial with respect to the M-M bond).

Remarks on Bonding

In all the compounds, a simple analysis of the symmetry types of orbitals required to form M-M and M-L bonds and a considration of the symmetry properties of the metal valence shell orbitals leads to a satisfactory formulation of electronic structure.

We may assume that the M-M triple bond is formed primarily by overlap of metal d_{z^2} orbitals to give the σ component and metal d_{xz} and d_{yz} orbitals to give the π-components. This is in accord with the assumption originally made and subsequently supported by SCF Xα calculations[20] for the quadruple bond in $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$. Furthermore, the detailed electronic structure of Mo_2X_6 compounds (X = R, NMe_2 and OH) was the subject of recent SCF Xα SW calculation and here the calculated and observed PE spectra were in good agreement.

Then in M_2X_6 molecules the metal may use sp^2 or sd^2 hybrids to form the three trigonal bonds. When X = NR_2 or OR, ligand to metal π-bonding may also occur to two of the metal orbitals not used in σ-bonding. The maximum M-N bond order is, therefore, $1^{2/3}$ in $M_2(NMe_2)_6$ compounds and each metal attains a valence shell of 16 electrons.[7,8]

In $M_2X_4L_2$ molecules, the four planar bonds may use s, p_x, p_y, $d_{x^2-y^2}$-hybrids. In $W_2(Me)_2(O_2CNEt_2)_4$ the five quasi planar bonds may use tungsten s, p_x, p_y, $d_{x^2y^2}$ and d_{xy} atomic orbitals and in $W_2(O_2CNMe_2)_6$, the additional use of the tungsten p_z orbital may be employed to form the weak axial W-O bond (2.67 Å).

Such a qualitative picture may be viewed as satisfactory to the extent that it readily accounts for the observed diamagnetic nature of the compounds and the short nature of the Mo-Mo distances which are only ca 0.1 Å longer than those found in compounds containing Mo≡Mo bonds.[22] Furthermore, all the compounds are yellow or orange resulting from a tailing into the visible of higher energy (U.V.) charge transfer bands.

Lastly it should be noted that a triple bond consisting of a σ component and two equivalent π-components has cylindrical symmetry and imposes no

restriction upon geometry [cf. $Re_2Cl_8^{2-}$ where the δ component of the M-M bond imposes an eclipsed geometry of the two $ReCl_4^-$ units]. The observed geometries for all of the aforementioned compounds appear to be totally dominated by the steric requirements of the ligands. All the M_2X_6 and $M_2X_6L_2$ compounds adopt staggered geometries because steric repulsive interactions dominate. Only in $Mo_2(OBu^t)_4(O_2COBu^t)_2$, $W_2(Me)_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$, which contain bridging OCO groups, are the geometries eclipsed.

Dynamical Solution Behavior

Since all the compounds are diamagnetic, their dynamical solution behavior is readily investigated by variable temperature NMR spectroscopy. The dialkylamido compounds reveal the expected, but rarely before observed, diamagnetic anisotropy associated with a triple bond. Variable temperature NMR studies reveal that these molecules are "cheerleader" molecules: they whirl as they twirl.[23] Detailed descriptions concerning the rotations that occur around the M-N bonds and the $M \equiv M$ bonds have been presented elsewhere, as has the assignment of proximal and distal resonances.[5a] It is sufficient here to exemplify the phenominum.

Figure 7 shows the high temperature and low temperature limiting ^{1}H NMR spectrum of $W_2Cl_2(NEt_2)_4$ in toluene-d_8. At high temperatures, >130°C, proximal $\rightleftharpoons$ distal ethyl exchange is rapid on the NMR time scale, while at low temperatures, <-16°C, proximal and distal resonances are frozen out. Three further points are noteworthy. (1) The high-temperature limiting spectrum corresponds to an ABX_3 spectrum and the low-temperature limiting spectrum to two ABX_3 spectra. Evidently the mechanism of proximal $\rightleftharpoons$ distal exchange does not remove the diastereotopic nature of the methylene protons.

(2) The spectra correspond to the presence of only the anti rotamer in solution. This is the rotamer found in the solid state; see Figure 2.

(3) There is a large chemical shift separation between proximal and distal methylene proton resonances, ca. 2.5 ppm. The separation between proximal and distal methylene carbon resonances is much larger, ca 30 ppm.

The variable temperature NMR spectra of $M_2R_2'(NR_2)_4$ compounds, R' = Me, Et, i-Pr, n-Bu, CH_2CMe_3 and CH_2SiMe_3, and R = Me and Et, are more complex because both anti and gauche rotamers exist in equilibria in solution.[12,24,25] A gauche $M_2R_2'(NR_2)_4$ molecule has C_2 symmetry and thus has two types of NR_2 groups: two are anti to R' and two are mutually anti. The low temperature limiting ^{1}H NMR spectrum for $W_2(CH_2CMe_3)_2(NMe_2)_4$ in toluene-d_8 is shown in Figure 8. Note: (1) The gauche-rotamer predominates, (2) the methylene protons of CH_2CMe_3 ligands are diastereotopic and form an AB pattern. (3) The chemical shift separation of the H_a and H_b protons is now exceedingly large (cf. the $N(CH_2CH_3)_2$ spectra shown in Figure 7). The latter presumably reflects the fact that in the gauche rotamer, the pair of bulky CMe_3 groups impose a prefered conformation in which the methylere protons occupy sites which are quite different with respect to the $M \equiv M$ triple bonds diamagnetic anisotropy.

Since the $M_2R_2(NR_2)_4$ molecules apparently prefer to crystallize in the anti-rotomeric form, it has been possible to measure the energy of activation for anti-to-gauche isomerization in these molecules. This is slow on the NMR time scale and can be followed by monitoring the approach to equilibrium: E_{Act} falls in the range 20 to 24 kcal mol^{-1}, depending upon specific R and R' combinations.[5a]

A point which now naturally arises is by what mechanism does anti ⇌ gauche isomerization occur: a simple rotation about the M ≡ M bond or by an intramolecular mechanism in which NR_2 groups are transfered from one metal atom to the other by way of the formation of dialkylamido bridges cf.[26] metal carbonyl site exchange in cluster metal carbonyls? This question is best answered by the examination of a molecule of the formula M_2X_5Y. Here the X groups naturally fall into three classes as shown below.
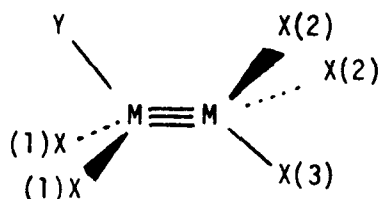
If rotation about the M ≡ M bond is frozen out on the NMR time scale, then one should observe 3 different X signals. If rotation is fast on the NMR time scale, then X(2) and X(3) become equivalent but remain distinct from X(1). Finally, if exchange of X groups between the two metal atoms occurs rapidly, then all X groups become equivalent.

We have been able to synthesize molecules of this form. For example, when $Mo_2(C_2H_5)_2(NMe_2)_4$ is treated with tert-butanol in benzene, the fascinating reaction shown below occurs:[24,27]

$$Mo_2(C_2H_5)_2(NMe_2)_4 + Bu^tOH \xrightarrow[25°C]{PhH} Mo_2(C_2H_5)(OBu^t)_5 + C_2H_6$$
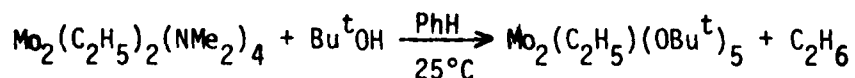
Examination of the ^{1}H NMR spectrum of $Mo_2(C_2H_5)(OBu^t)_5$ at -65°C and 270 MHz shows two types of OBu^t groups in the integral ratio 2:3. This is consistent with the view that rotation about the W ≡ W bond is still rapid on the NMR time

scale and furthermore that alkoxy group exchange between metal atoms is slow. Further support for facile rotation about the $M \equiv M$ is seen in the low temperature ^1H NMR spectra of $M_2Me_2(OBu^t)_4$ compounds.[28] Here we have not yet been able to freeze out anti ⇌ gauche isomerization on the NMR time scale even using high field spectrometers. We attribute the difference in E_{Act} to rotation about the $M \equiv M$ bond in compounds of the form $M_2R_2'(NR_2)_4$ and $M_2R_2'(OBu^t)_4$ to the cogging effect of the NR_2 groups in the former. The compounds $M_2(NR_2)_6$ and $M_2X_2(NR_2)_4$, which we refer to as cheerleader molecules, are stereochemically correspondent to 1,1,2,2-tetraaryl substituted ethane and in solution behave as molecular propellers. When the blades are removed as in $M_2R_2(OBu^t)_4$ and $M_2R(OBu^t)_5$ compounds, then rotation about the $M \equiv M$ bond becomes much more facile, $E_{Act} < 7$ kcal mol^{-1}. Indeed the rotational barriers appear closely related to tetraalkyl silanes $R_2HSi-SiHR_2$ and tetraaryl diphosphines R_2P-PR_2, which in solution also prefer the gauche conformation.[30] This comparison is all the more impressive when one recognizes that the Si-Si σ-bond distance is ca 2.3 Å (Mo $\equiv$ Mo is 2.2 Å) and the P-P σ-distance is 2.2 Å (W $\equiv$ W is 2.3 Å). Thus we believe that our work has provided the first experimental demonstration that for a non-linear molecule containing a triple bond composed of one σ and two equivalent π-components, the rotational barrier is limited only by the steric factors associated with the substituents on the two elements which are united by the triple bond.

Molecules of the type $M_2(OR)_6L_2$ contain two types of OR groups on each metal atom, namely those which are cis and trans with respect to the ligand L. In all cases which we have examined thus far, the low temperature limiting NMR spectra reveal two types of OR groups in the integral ratio 2:1. Perhaps

even more fascinating is our observation that the low temperature limiting ^{13}C NMR spectrum of the $W_2(OPr^i)_6(py)_2$ molecule shows three methyne carbon signals, $OCH(CH_3)_2$, in the integral ratio 1:1:1 which is just what is expected for a $W_2O_6N_2$ skeleton that has virtual C_2 symmetry, namely the pyridine ligands are adjacent to each other as shown in Figure 3. Although in the crystal there are six distal oxygen atoms, it is easy to see that a slight twisting about the $W \equiv W$ bond which brings about a time averaged molecule with an apparent C_2 axis of symmetry thereby making the oxygen atoms fall into three sets (O1, O5), (O3, O7) and (O2, O6). It then follows that there should be three sets of methyne carbon atoms.

At room temperature on the NMR time scale, all $M_2(OR)_6L_2$ molecules show only one type of OR group. This is consistent with rapid (NMR time scale) cis $\rightleftharpoons$ trans isomerization. Once again, however, one would like to answer the question "How is this achieved?" In order to probe such an intriguing matter one must design a molecule of the form $M_2(OR)_6L_1L_2$ in which L_1 and L_2 are two different donor ligands: then each end of the molecule is effectively labelled M(1) and M(2). One must also design a molecule where it is possible to show that L_1 and L_2 do not hop between the two metal atoms, either by an intra or intermolecular mechanism. In this regard ligand dissociation must be ruled out, otherwise, M(1) and M(2) would become equivalent.

We think we have been fortunate enough to obtain such a molecule. Crystallographically we have shown that acetylenes,[31] allenes[32] and dialkylamino-cyanimides[33] add across the $M \equiv M$ bonds in the $Cp_2Mo_2(CO)_4$[34] compound in the manner shown in Figure 9. Now it so happens that $Mo_2(OR)_6$ compounds also react with all of the above. Unfortunately, at this time, no crystallographic data

is available on the adducts. Nevertheless, if we make the assumption that in the $Mo_2(OPr^i)_6(NCNMe_2)$ molecule,[35] one molybdenum atom receives a lone pair of electrons from the terminal nitrogen atom while the other molybdenum atom receives a pair of electrons from the C=N π-bond and, furthermore, that this causes the $NCNC_2$ unit to become planar with a fairly high energy barrier (NMR time scale) to rotation about the central C-N bond, then we are home and dry. This may seem like too much to assume, but the amazing fact is that the low temperature ^1H NMR spectrum shown in Figure 10 is entirely consistent with these assumptions. There are four methyne proton resonances, labelled A, B, C and D in Figure 10, respectively. The methyl region of the OPr^i ligands is more complex and consists of three well separated doublets marked E, F and G and three overlapping sets marked H in Figure 10. Six methyl resonances are indeed expected according to our assumption since (i) each molybdenum atom is labelled, (ii) there are cis and trans OPr^i ligands with respect to the $NCNMe_2$ ligand and (iii) the methyl groups of the cis-OPr^i ligands are diastereotopic. There are also two signals of equal intensity for the N-methyl protons which is expected for a planar C_2NCN moiety with restricted rotation about the central N-C bond. (This latter observation is directly analogous to the low temperature limiting spectrum observed for $Cp_2Mo_2(CO)_4(NCNMe_2)$.[33] The only other resonances seen in the spectrum (Figure 10) are assignable to (i) small amounts of $Mo_2(OPr^i)_6$ which is present as an impurity and (ii) residual protons in the toluene-d_8 solvent.

On raising the temperature, the methyne proton resonances B and D start to broaden and then coalesce as do three of the methyl doublets, namely the

doublets indicated by F, G and one from H in Figure 10. At this temperature site exchange of three of the OPr^i ligands is fast while the other three are still frozen out on the NMR time scale. There are still two signals of equal intensity for the N-methyl protons which implies that the $Mo_2(NCNC_2)$ unit is <u>not</u> fluxional. We believe the most reasonable interpretation of the dynamic behavior of the molecule at +16°C is that alkoxy group exchange is occurring rapidly at one molybdenum atom but not at the other one. Furthermore, it is reasonable to suppose that the rapid site exchange involves the alkoxy groups which are coordinated to the least sterically crowded molybdenum atom, namely the one which receives a nitrogen lone pair.

On raising the temperature above 16°C site exchange between the other set of OPr^i ligands sets in and finally (>80°C) all OPr-i ligands become equivalent and the N-methyl resonances collapse to a single resonance. This is consistent with the view that the Mo_2NCNC_2 unit becomes fluxional in a manner which equilibrates both molybdenum atoms: this was found for $Cp_2Mo_2(CO)_4(NCNMe_2)$. All these temperature dependent processes do not involve free $Mo_2(OPr-i)_6$, which is present in solution, and are thus considered intramolecular processes.

Indeed a very plausible explanation for the above and indeed all the $M_2(OR)_6L_2$ compounds is that the ends of the molecules undergo facile square-based pyramidal $\rightleftharpoons$ trigonal bipyramidal interconversions of the type well known for mononuclear ML_5 complexes.[36] The only major difference is that for the dinuclear compounds $M \equiv M$ there seems to be a marked preference for the square-based pyramid and thus the triginal bipyramidal form is either a relatively unstable intermediate or a transition state for <u>cis</u> $\rightleftharpoons$ <u>trans</u> isomerization shown below.
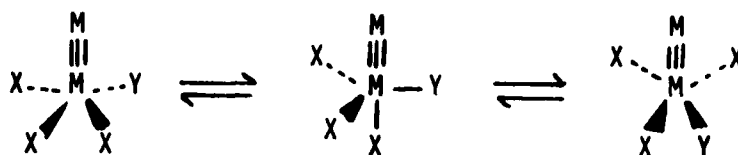
The $W_2(O_2CNMe_2)_6$ molecule displays a particularly fascinating dynamical solution behavior.[19] Each O_2CNC_2 unit is planar and one can reasonably assume[37] that E_{Act} for rotation about the central C-N bond is ca 16 kcal mol^{-1}. Thus the carbon resonances of the methyl groups can be used to monitor the motions of the oxygen atoms. Furthermore, by using $^{13}CO_2$ in the preparation of the compound (see Scheme 1) one can readily monitor the three types of carboxylic carbon atoms.[38] Three distinct chemical processes can be detected which are in increasing order of energy of activation: (1) the exchange of O(12) and O(11) sites. This is tantamount to an intramolecular substitution reaction in which an entering axially aligned ligand, O(12), substitutes one of the ligands in the pentagonal plane, O(11); (2) Exchange of terminally bonded carbamate groups, i.e. ^{13}C resonances associated with C(5) and C(6) coalesce and (3) finally above room temperature exchange between bridging and terminally bonded carbamate ligands become fast on the NMR time scale.

The dynamic behavior of $W_2Me_2(O_2CNEt_2)_4$ also parallels that of $W_2(O_2CNMe_2)_6$ in solution but here there are only two types of carbamato ligands: bridging and terminal. Below room temperature, the solid state structure (Figure 5) is frozen out on the NMR time scale. However, above 50°C, rapid exchange of bridging and terminal ligands occurs.[19]

In contrast to the carbamato complexes which readily exchange bridging and terminal groups, the $W_2(NMe_2)_4(PhN_3Ph)_2$ (see Figure 4) molecule appears

relatively rigid in solution.[17] The molecule contains a C_2 axis of symmetry
and may be considered as a member of the class of gauche-$M_2X_2(NMe_2)_4$ molecules,
only with X = the bidentate triazenido group. There are therefore two types
of NMe_2 groups and at -45°C and 220 MHz, the ^{1}H NMR spectrum clearly shows
four N-methyl resonances of equal intensity: two proximal (downfield) and
two distal (upfield). On raising the temperature there is a pair-wise
collapse to give ultimately two lines at 100°C which means that even though
rotations about the M-N bonds become fast on the NMR time scale the C_2 axis
of symmetry is maintained.[17] Enantiomerization involving either gauche to
gauche or gauche to anti to gauche transformations does not occur rapidly
on the NMR time scale. This could have been caused either by a simple
rotation about the W≡W bond or by the formation of an intermediate in
which the two 1,3-diphenyltriazenido ligands bridged the M≡M bond, cf. the
structure of $Mo_2(OBu^t)_4(O_2COBu^t)_2$.[16] The difference in both the static and
dynamic stereochemistry of the $Mo_2(OBu^t)_4(O_2COBu^t)_2$ and $W_2(NMe_2)_4(PhN_3Ph)_2$
molecules is once again determined by the steric demands of the ligands bonded
to the central $(M≡M)^{6+}$ unit. The M-NC_2 units in $M_2X_2(NMe_2)_4$ compounds are
effectively cogged in such a way that even though rotations about M-N bonds
may be fast on the NMR time scale, rotation about the M≡M is hindered. This
fact can be used to advantage in investigating the mechanisms of substitution
reactions at these dinuclear centers. For example, the observation that
anti-$W_2Cl_2(NEt_2)_4$ reacts with $LiCH_2SiMe_3$ (2 equiv) in benzene to give
anti-$W_2(CH_2SiMe_3)_2(NEt_2)_4$ which then slowly isomerizes to a mixture of anti
and gauche-$W_2(CH_2SiMe_3)_2(NEt_2)_4$ indicates that the alkyl-for-chloride ligand
exchange must proceed with retention of stereochemistry at tungsten.[39]

M_4^{12} Clusters

For some time now we have been trying to establish that the dimerization of two $(M \equiv M)^{6+}$ containing compounds can lead to M_4^{12+} cluster compounds containing a central tetrahedral M_4 unit. Indeed it seemed that for a given ligand X or combination of X, Y ligands, there should be an equilibrium of the type shown below.[6]

$$2X_nM \equiv MX_n \quad \rightleftharpoons \quad \left[\begin{array}{c} M \\ M \cdots M \cdots M \\ M \end{array} \right] X_{4n}$$
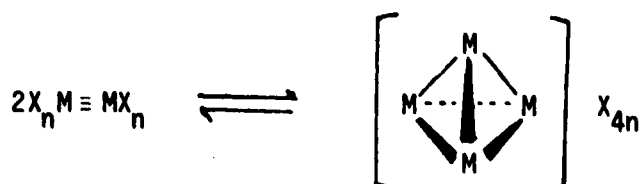
As the steric bulk of an alkoxy-ligand is reduced polynuclear, $[Mo(OR)_3]_n$, compounds are formed, e.g. for R = Et and Me.[40] These are diamagnetic which indicates the existance of metal-metal bonds but as yet no X-ray structural information is available.

The closest approach to a tetrahedral M_4^{12+} cluster was recently found in the reaction between $Mo_2(OBu^t)_6$ and PF_3 (2 equiv) which leads to a black compound of empirical formula $Mo(F)(OBu^t)_2$. In one preparation of this compound, crystals suitable for detailed X-ray work were obtained. The unit cell was found to contain one molecule of $Mo_4(\mu-F)_4(OBu^t)_8$ and two molecules of $Mo_4(\mu-NMe_2)(\mu-F)_3(OBu^t)_8$.[41] The latter compound was a total surprise to us and we attribute the presence of the dimethylamido ligand to incomplete alcoholysis in the preparation of the startirg material $Mo_2(OBu^t)_6$ (see Scheme 1). ORTEP views of the $Mo_4(\mu-F)_4(OBu^t)_8$ and $Mo_4(\mu-NMe_2)(\mu-F)_3(OBu^t)_8$ molecules are shown in Figures 11 and 12 respectively.

In both molecules the Mo_4 unit is a bisphenoid having two short Mo-to-Mo distances, 2.26 Å (averaged), and four long Mo-to-Mo distances, 3.75 Å (averaged). Evidently a fluoride-for-tert-butoxide reaction induces a Lewis base association reaction by the formation of metal-ligand bridges. While substitution of the small and more electronegative fluoride ligand might well be expected to promote a Lewis base association reaction[40], the choice of bridging ligands which is established, namely $F > NMe_2 > OBu^t$, is surprising to us. It seems as if the localized $M \equiv M$ units (2.26 Å) are held apart by the fluoride bridges - though we have no way of knowing at this time whether these molecules are formed under kinetic or thermodynamic control. Finally, however, it should be noted that the geometries about the $Mo_2F_4O_4$ and $Mo_4NF_3O_4$ units ($M \equiv M$) are virtually identical to the local $Mo_2O_4O_4'$ skeleton of the $Mo_2(OBu^t)_4(O_2COBu^t)_2$ ($M \equiv M$) molecule. There are two molybdenum atoms held together by a metal-to-metal triple bond (no bridging groups) and each molybdenum atom is coordinated to four ligands which lie roughly in a square plane.

Acknowledgements

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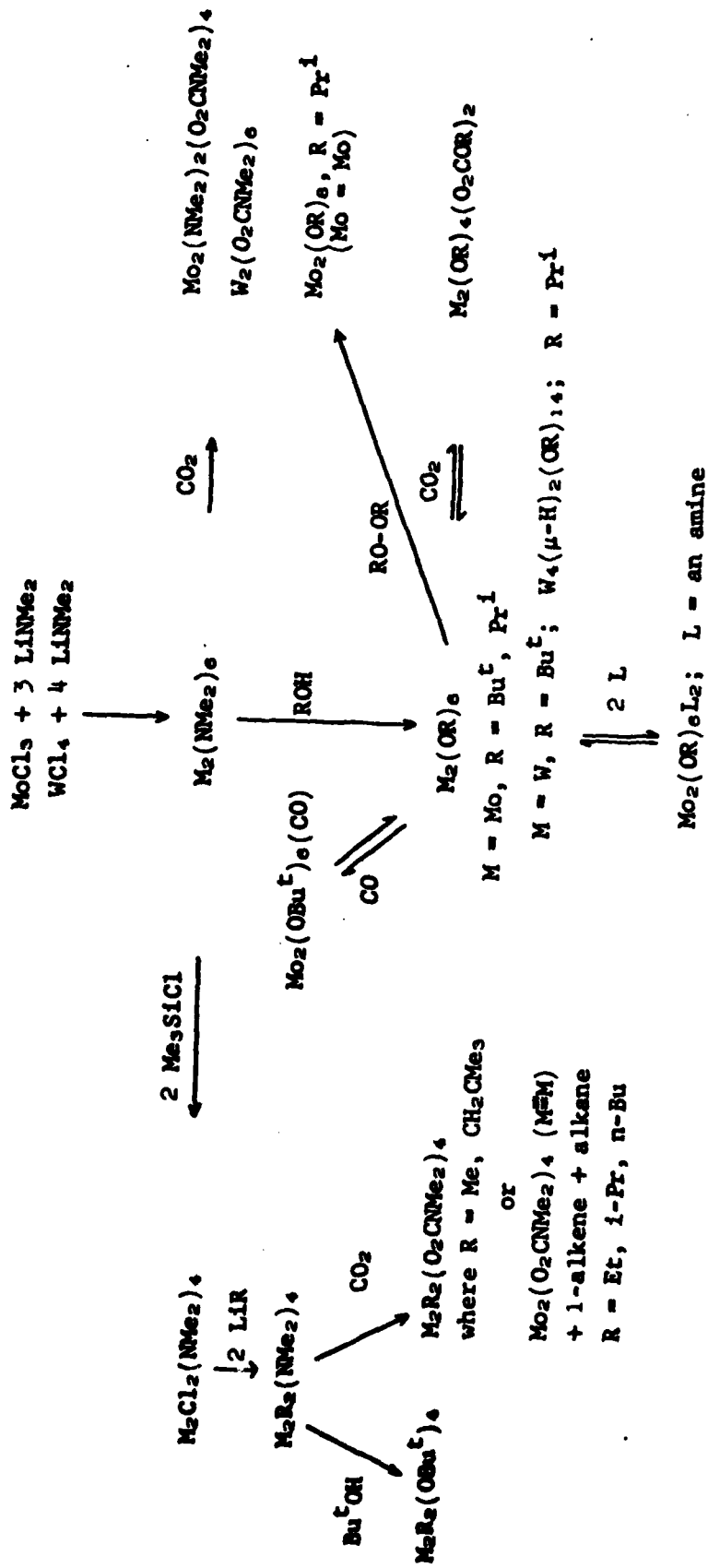
Scheme 1. Some Reactions Leading to and Interconverting Dinuclear Compounds Containing M-M Triple Bonds (M = Mo and W).

Captions to Figures

Figure 1. Two ORTEP views of the $Mo_2(NMe_2)_6$ molecule. In this and in all other structural figures, thermal ellipsoids are drawn at the 50% probability level.

Figure 2. An ORTEP view of the $W_2Cl_2(NEt_2)_4$ molecule. Note the central $W_2Cl_2N_4$ skeleton has virtual C_{2v} symmetry.

Figure 3. The $W_2O_6N_2$ skeleton of the $W_2(OPr^i)_6(py)_2$ molecule viewed down the metal-metal bond.

Figure 4. An ORTEP view of the $W_2(NMe_2)_4(PhN_3Ph)_2$ molecule emphasizing the C_2 axis of the symmetry.

Figure 5. The central $W_2C_2(O_2C)_4$ skeleton of the $W_2(Me)_2(O_2CNEt_2)_4$ molecule emphasizing that the molecule has virtual C_{2v} symmetry.

Figure 6. The central $W_2(O_2C)_6$ skeleton of the $Mo_2(O_2CNMe_2)_6$ molecule emphasizing that the molecule has virtual C_{2v} symmetry.

Figure 7. High (top) and low (bottom) temperature limiting ^1H NMR spectra of anti-$W_2Cl_2(NEt_2)_4$ obtained in toluene-d_8 at 100 MHz.

Figure 8. Low temperature limiting ^1H NMR spectrum of a mixture of anti and gauche $W_2(CH_2CMe_3)_2(NMe_2)_4$ obtained at -65°C and 270 MHz. Note the relative concentrations of gauche to anti rotamers are ca 10:1 and that the methylene protons of the neopentyl ligand are an AB quartet in which the chemical shift separation of the H_a and H_b protons is very large.

Figure 9. Schematic representations of the $Cp_2Mo_2(CO)_4(un)$ molecules where A, un = $RC \equiv CR$; B, un = allene and C, un = Me_2NCN, emphasizing the coordination of the central $Mo_2(un)$ group.

Figure 10. Low temperature limiting ^1H NMR spectrum of $Mo_2(OPr^i)_6(NCNMe_2)$ obtained at -45°C, 220 MHz in toluene-d_8. The methyne proton resonances are indicated A, B, C and D and the methyl resonances E, F, G and H. The signals marked with an asterisk are due to $Mo_2(OPr^i)_6$ ($M \equiv M$).

Figure 11. The central skeleton of the $Mo_4(\mu-F)_4(OBu^t)_8$ molecule.

Figure 12. The central skeleton of the $Mo_4(\mu-NMe_2)(\mu-F)_3(OBu^t)_8$ molecule.
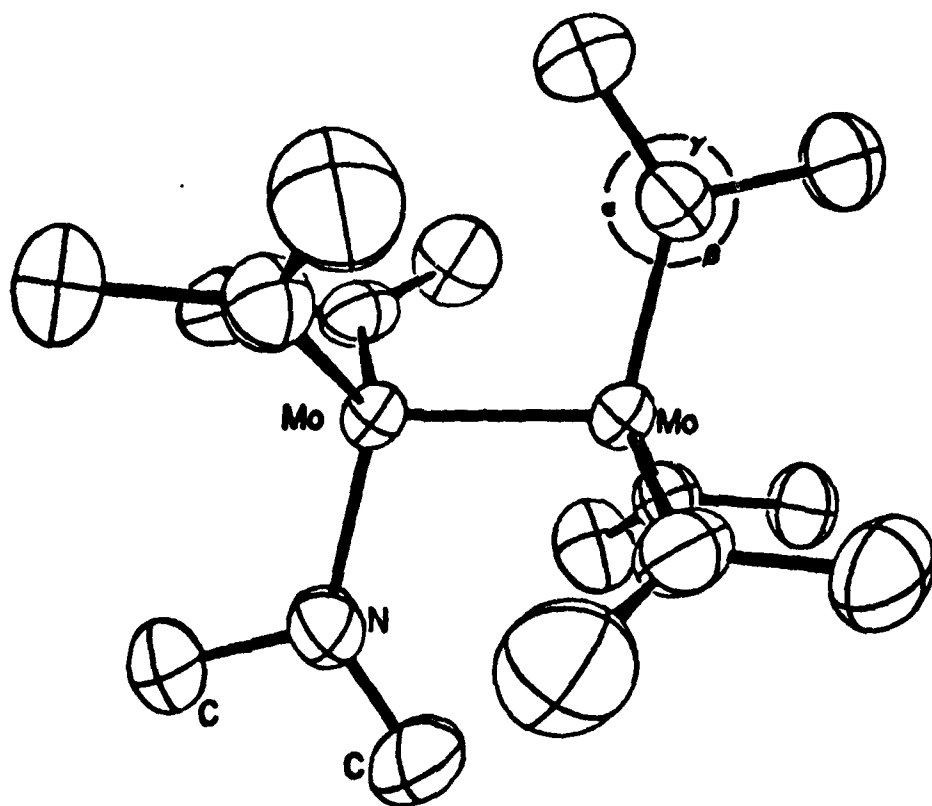
ORTEP view of $MO_2(NMe_2)_6$ viewed nearly perpendicular to the Mo-Mo axis.
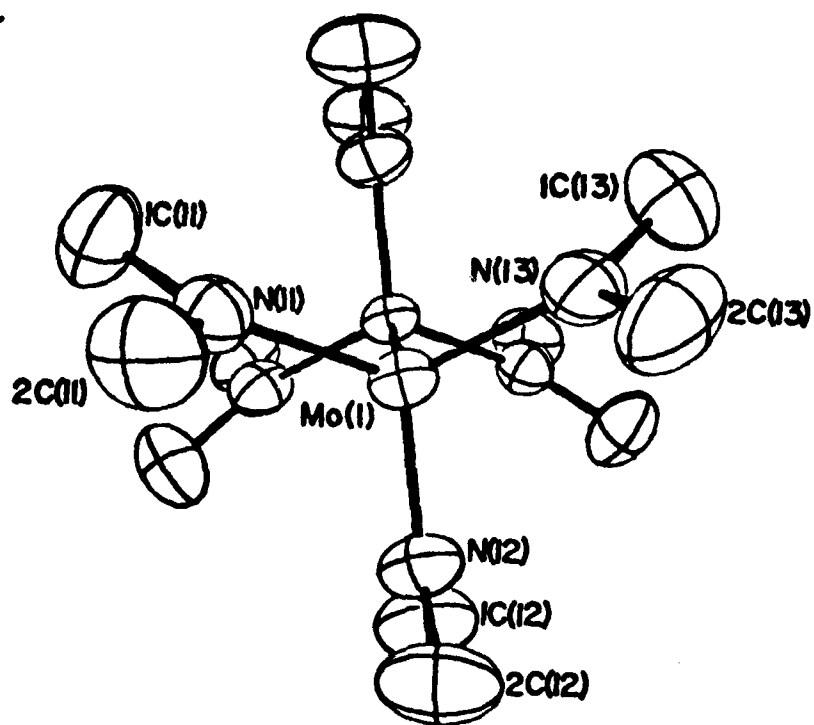
ORTEP view of $Mo_2(NMe_2)_6$ viewed nearly along the Mo-Mo axis.

150°

−18°

(A)

(B)

(C)