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ANYTHING ONE CAN DO, TWO CAN DO TOO - AND IT'S MORE INTERESTING

by

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Department of Chemistry
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All of the reaction chemistry surrounding mononuclear transition metal compounds could just as easily be carried out at a bimetallic center. Indeed, there should be additional types of reactions uniquely associated with the M-M bond. This general premise is discussed in light of the recent reactivity found for dimolybdenum and ditungsten compounds. For a given M_2^{x+} center, the

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preferred coordination geometries, ligand substitution behaviors and dynamical properties (fluxional behavior) are noted. The ability of these compounds to undergo Lewis base association and dissociation reactions, reversible insertions or ligand migrations, oxidative addition and reductive elimination reactions, as well as direct additions across the M-M bond are discussed. Finally, the possible mechanisms for one of these reactions, reductive elimination of alkane and alkene from a dimolybdenum center, is considered in detail.

Introduction

I should like to propose that all the types of reactions which have been established for mononuclear transition metal complexes will also occur for dinuclear transition metal complexes, and furthermore, that the latter will show additional modes of reactivity which are uniquely associated with the metal-metal bond. In this article, I shall support this proposal by illustrations taken from the reactions of dinuclear compounds of molybdenum and tungsten, two elements which enter into extensive dinuclear relationships.[1]

Coordination Numbers and Geometries

For any transition element in a given oxidation state and d^n configuration, there is generally a fairly well defined coordination chemistry. Ligand field stabilization energies are often important, if not dominant, and readily account for the fact that mononuclear complexes of Cr(3+), Co(3+) and Pt(4+) are almost invariably octahedral, while those of Cr(2+) and high spin Co(2+) may be either four or six coordinate. The effect of the charge on the metal and attainment of an 18 valence shell of electrons are also two strong forces in determining preferred coordination numbers. High coordination numbers (7 and 8) are common for the early transition elements in their high oxidation states (4+ and 5+), while the later transition elements in their low oxidation states often have low coordination numbers (2, 3 and 4). Similar factors control the coordination preferences of the dinuclear compounds of molybdenum and tungsten.

$(M\equiv M)^{4+}$ Complexes.[2] In scores of dinuclear molybdenum compounds, and to a lesser extent ditungsten compounds, a central M_2^{4+} unit has a M-M quadruple bond of configuration $\sigma^2\pi^4\delta^2$. The metal atomic orbitals involved in the M≣M bond are d_{z^2} (σ), d_{xz},d_{yz} (π) and d_{xy} (δ). The remaining metal atomic orbitals are available for use in metal ligand bonding giving rise to two types of compounds shown schematically in I and II below.

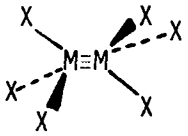
I

II

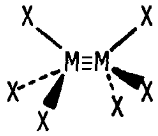
In compounds of type I, four metal ligand bonds are formed in a plane using metal atomic s, p_x, p_y, $d_{x^2-y^2}$ orbitals. The overall geometry about the dimetal center is eclipsed as a result of the formation of the M-M δ bond. In these compounds, the metal atoms attain a 16 valence shell of electrons. In compounds of type II, two additional bonds are formed along the M-M axis. These utilize the p_z atomic orbitals of each metal atom and, in this way, the EAN rule is satisfied. At this time, the majority of compounds are of type I: axial coordination to give II is generally weak as evidenced by long Mo-axial distances in the solid state. An immediate analogy is seen with the coordination chemistry of Pt(II) which is most often square planar with coordination number 4, but sometimes 5 coordination is observed giving 16 and 18 valence shell electronic configurations, respectively. The absence of a M≣M bond between two trigonally coordinated metal atoms, e.g. as is common for compounds with $M\equiv M$ bonds, can be understood: a trigonal field leaves the $d_{x^2-y^2}$ and d_{xy} orbitals degenerate and so a $\sigma^2\pi^4\delta^2$ configuration would be paramagnetic with the two unpaired electrons residing in the δ orbitals.

$(M\equiv M)^{6+}$ Compounds.[3] A large number of compounds containing a central M_2^{6+} unit have recently been synthesized for molybdenum and tungsten in which a central

M≡M bond arises from the formation of a σ bond (d_{z^2}-d_{z^2}) and a degenerate pair of π bonds (d_{xz}-d_{xz}, d_{yz}-d_{yz}).[4] In these compounds, the coordination number of the metal atoms is commonly 3 and 4, but examples of 5 and 6 are also known. For coordination number 3, the three ligand atoms bonded to each metal atom lie in a plane, giving rise to ground state structures which are either staggered, IIIa, or eclipsed, IIIb, depending upon the requirements of the ligands. Similarly for coordination number four, the four ligand atoms bonded to each metal atom lie in a plane, and the conformation about the M-M bond depends on the requirements of the ligands giving rise to staggered IVa, eclipsed IVb (shown below) or intermediate situations.

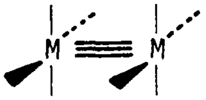


IIIa



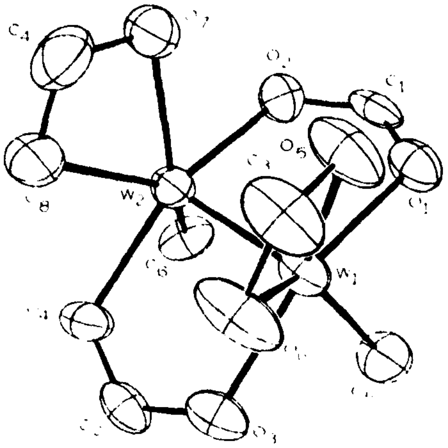
IIIb

IVa

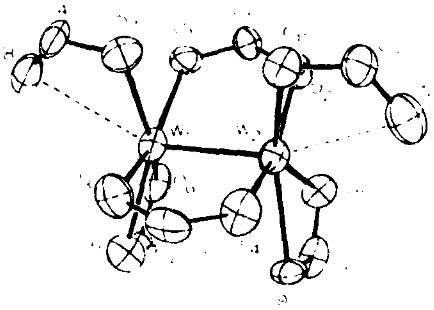


IVb

For coordination numbers 5 and 6, which are less common, the structures of $W_2(O_2CNEt_2)_4Me_2$ and $W_2(O_2CNMe_2)_6$, shown in V and VI below, reveal that five equivalent bonds can readily be formed in a pentagonal plane (using metal s, p_x, p_y, d_{xy} and $d_{x^2-y^2}$ atomic orbitals), but the sixth bond which must be formed along the M-M axis (using the p_z atomic orbital) is formed only weakly.[5]

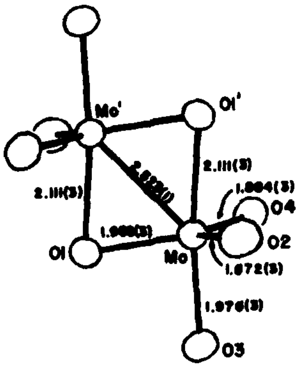


V



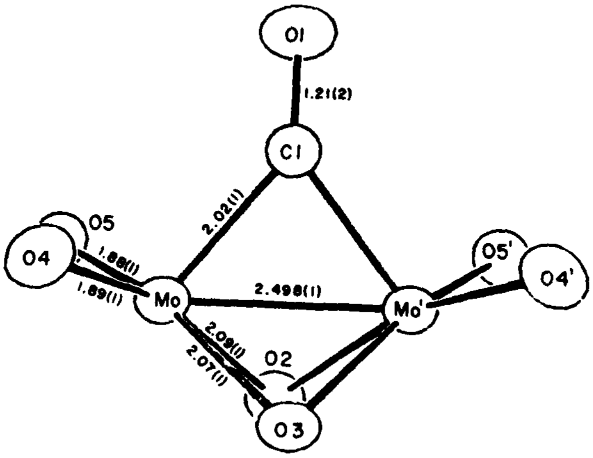
VI

<u>$(M{=}M)^{8+}$ Compounds</u>.[6] Compounds containing M=M bonds are at present not common. The coordination number of five is, however, seen in both $Mo_2(OPr^i)_8$[7] and $Mo_2(OBu^t)_6(CO)$,[8] which have, with respect to each metal atom, trigonal bipyramidal and square based pyramidal structures, respectively. See VII and VIII below.



VII

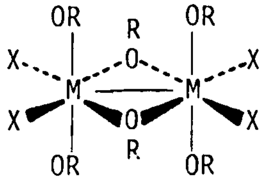
0 = OPr^i



VIII

0 = OBu^t

$(M\text{-}M)^{10+}$ Compounds. Single M-M bonds formed by molybdenum and tungsten in the +5 oxidation state are dependent on the nature of the bridging ligands.[9] For example, Mo_2Cl_{10} is paramagnetic[10] and does not show structural evidence[11] for a M-M bond. Oxygen ligands, however, appear to favor the M-M bond[12] as is seen in the recent structural characterizations of $Mo_2X_4(OPr^i)_6$ compounds which have the structure shown in IX below[13] with Mo-to-Mo distances of 2.73 Å.



X = Br or Cl

IX

The coordination number six is seen in IX. The M-M bond arises from the interactions of metal d orbitals which have their lobes directed inbetween the bridging ligands. An octahedral geometry for each metal is thus well suited for this type of d^1-d^1 M-M single bond.

For the sake of brevity, I have restricted my attention here to M-M bonds of integral order and have considered only the cases where all the available d^n electrons are used to form M-M bonds. There are, however, dinuclear compounds having M-M bonds of fractional order[14] and dinuclear compounds in which not all the available d^n electrons contribute to M-M bonding. Well known examples of the latter are $Cp_2Mo_2(CO)_4$ (M≡M)[15] and $Cp_2Mo_2(CO)_6$ (M-M)[16] compounds which both contain molybdenum atoms in oxidation state number +1 (formally they are d^5-d^5 dimers), but by considerations of the EAN rule and the observed M-M distances (2.448(1) and 3.235(1) Å) are commonly considered to have M-M triple and single bonds, respectively.

Ligand Substitution Reactions[17]

Mononuclear compounds can be broadly classified as kinetically labile or inert toward ligand substitution reactions: e.g. Cr(3+), Co(3+) and Pt(4+) are inert while Cr(2+), high spin Co(2+) are labile. These dramatic differences in kinetic lability are easily rationalized by ligand field considerations. Other factors which are important in determining rates of ligand substitution are the size of the ligands, the formal positive charge and the number of valence electrons on the metal. Many complexes which satisfy the EAN rule are substitutionally "inert" and undergo substitution by an initial loss of a ligand. Group 6 transition metal carbonyl compounds provide good examples of the latter phenomenon. On the other hand, the coordinatively unsaturated square planar complexes of the group 8 transition elements react by ligand association reactions (S_N2). The labilizing effect of a group in the trans position to the group which is undergoing substitution, the trans-effect phenomenum, is well documented for square planar and octahedral complexes and can allow kinetic control in the isolation of isomers of octahedral and square planar compounds.

All of these considerations carry over into the dinuclear chemistry of molybdenum and tungsten. Ligand substitution reactions around the $(\mathrm{M}≣\mathrm{M})^{4+}$ and $(\mathrm{M}{\equiv}\mathrm{M})^{6+}$ moieties are well documented.[6] Kinetically, they are slower than the nmr time-scale. Thus, $Mo_2R_4(PMe_3)_4$ compounds $(\mathrm{M}≣\mathrm{M})$ will not exchange coordinated with excess PMe_3 to give a single PMe_3 resonance, but addition of a different phosphine will lead to rapid scrambling on the synthetic time-scale.

In the reaction between anti-$W_2Cl_2(NEt_2)_4$ and alkyllithium reagents LiR (2 equiv), substitution of Cl-by-R occurs with retention of configuration.[18] Kinetically anti-$W_2R_2(NEt_2)_4$ is formed which then isomerizes to a mixture of anti and gauche rotamers, with the latter being the favored rotamer. This substitution reaction can be viewed as an example of an S_F2 process in which the new bond is formed as the old bond is broken within a square plane.[19] Formation of the anti rotamer arises because the cogging effect of NR_2 groups produces an energy barrier to rotation about the M≡M bond (E_{Act} ~24 Kcal mol^{-1}).[20] Ligand substitution is thus kinetically faster than anti $\rightleftharpoons$ gauche isomerization. Another example of kinetic control in ligand substitution at a dimolybdenum center is seen in the following. Hexane solutions of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ (M≡M) react with $LiNMe_2$ and $HNMe_2$ to give 1,1- and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, respectively, which once formed do not isomerize readily.[21] Addition of Bu^tOH to 1,1- and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ yields 1,1- and 1,2-$Mo_2(OBu^t)_2(CH_2SiMe_3)_4$, respectively, whereas with CO_2 (1 atmos, 25°C), the 1,1-isomer yields 1,1'-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$, while the 1,2-isomer does not react. Clearly, a rich substitution chemistry surrounds these dinuclear compounds and remains to be explored and exploited.

Stereochemical Lability

Three types of stereochemical lability have been observed: (1) rotations about M-M bonds, (2) cis $\rightleftharpoons$ trans isomerizations at each metal center and (3) bridge $\rightleftharpoons$ terminal ligand exchange processes.

Rotations about the M≣M bond are not observed (on the nmr time-scale) and are not expected since this would rupture the δ bond. In compounds containing the central $(M≡M)^{6+}$ moiety, which have the $\sigma^2\pi^4$ configuration, rotation appears to be only restricted by the steric properties of the ligands. The compounds 1,1- and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ show E_{Act} for M-M rotation of ca. 15 Kcal mol. For $Mo_2Me_2(CHSiMe_3)_4$, the barrier is less than 8 Kcal mol^{-1} and conformers have not been frozen out on the nmr time-scale.[22]

The compounds $Mo_2(OR)_6L_2$, where R = alkyl or $SiMe_3$ and L = a neutral nitrogen donor ligand, contain three oxygen atoms and one nitrogen atom coordinated to each molybdenum atom.[23,24] Thus, there are a pair of mutually trans OR ligands and one which is trans to the N atom. At low temperatures in toluene-d_8, the ^1H nmr spectra are consistent with the expected 2:1 ratio of OR ligands described above. Upon raising the temperature, all the OR ligands become equivalent on the nmr time-scale. For $Mo_2(OPr^i)_6(NCNMe_2)$, the molybdenum atoms are different because of an asymmetric central $Mo_2(\mu\text{-}NCNMe_2)$ moiety.[26] Here the low temperature limiting spectrum reveals four types of OR ligands in the expected integral ratio 1:1:2:2. Upon raising the temperature, there is a collapse of a pair of these signals to give at ca. +35°, and 220 MHz, three OPr^i resonances in the integral ratio 3:2:1, consistent with the view that cis $\rightleftharpoons$ trans OPr^i exchange is rapid at one molybdenum, but not at the other. These exchange processes have been shown to be intramolecular and thus, parallel the common lability associated with five coordinate mononuclear complexes.[27] For the dinuclear compounds, however, the fifth coordination site is the other metal atom.

The compounds $Mo_2(OPr^i)_8$ (M=M)[7] and $Mo_2(OBu^t)_6(\mu\text{-}CO)$ (M=M),[8] which contain bridging OR ligands, show rapid bridge $\rightleftharpoons$ terminal group exchange on the nmr time-scale. Similarly, the compounds $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ show exchange between bridging and terminal carbamato ligands on the nmr time-scale.[5]

Organometallic Reactions

Tolman[28] has suggested that all commonly occuring organometallic reactions, including those that are important in catalysis, can be classified by five named reactions, each with its microscopic reverse: (1) Lewis base association and dissociation, (2) Lewis acid association and dissociation, (3) insertion and deinsertion (ligand migration reactions), (4) oxidative addition and reductive elimination and (5) oxidative coupling and reductive decoupling. With the exception of the simple Lewis acid association-dissociation reactions, we have studied examples of all of the aforementioned reactions.

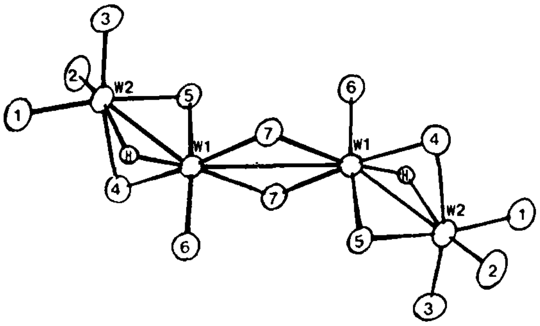
Lewis Base Association and Dissociation. The dinuclear alkoxides $M_2(OR)_6$ reversibly add donor ligands to give $M_2(OR)_6L_2$ compounds:[23,24] the position of equilibrium is dependent on the bulkiness of R and L. In these reversible Lewis base addition reactions, the M-M distances are essentially unchanged, c.f.[23,24] Mo-to-Mo = 2.222(1) Å in $Mo_2(OCH_2CMe_3)_6$ with Mo-to-Mo = 2.242(1) Å in $Mo_2(OSiMe_3)_6(HNMe_2)_2$, since the metal atoms do not attain an 18 valence shell electronic configuration. However, for compounds containing $M{\equiv}M$ bonds in which the metal atoms have a completed valence shell of electrons, e.g. $Cp_2M_2(CO)_4$ compounds (M = Mo and W), the formation of two new metal-ligand bonds will occur only with a reduction in M-M bond order, from three to one, c.f. the Mo-to-Mo distances of 2.448(1) Å[15] and 3.235(1) Å[16] found for $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$, respectively.

Insertion-Deinsertion Reactions. An example of a facile reversible insertion-deinsertion reaction is seen in the reactions between $M_2(OR)_6$ compounds and CO_2 which give $M_2(OR)_4(O_2COR)_2$ compounds.[29] These reactions were shown to proceed by a direct insertion mechanism (i.e. not by an indirect mechanism involving catalysis by traces of alcohols) with energies of activation of not greater than 20 Kcal mol^{-1}.

Oxidative-Addition Reactions. Chuck Kirkpatrick has been studying oxidative additions to $Mo_2(OPr^i)_6$ ($M{\equiv}M$).[30] Addition of Pr^iOOPr^i leads to

$Mo_2(OPr^i)_8$ (M≡M).[7] Addition of each of the halogens Cl_2, Br_2 and I_2 proceeds to give the compounds $Mo_2(OPr^i)_6X_4$ (M-M) where X = Cl, Br or I. In these oxidative-additions, a stepwise change in M-M bond order, from three to two to one, is achieved. A large number of related additions have been noted, but await detailed structural characterizations.

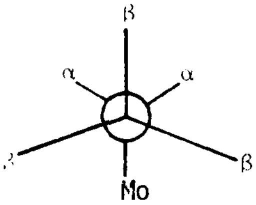
The formation of $W_4(\mu\text{-}H)_2(OPr^i)_{14}$ in the reaction between $W_2(NMe_2)_6$ and Pr^iOH (excess) can also be viewed as an oxidative-addition: $W_2(OPr^i)_6 + Pr^iO\text{-}H \rightarrow \frac{1}{2}[W_4(\mu\text{-}H)_2(OPr^i)_7]_2$.[31] An ORTEP view of the central $W_4(\mu\text{-}H)_2O_{14}$ skeleton is shown below. The molecule is centrosymmetric with alternating short (2.446(1) Å) and long (3.407(1) Å) W-to-W distances consistent with the presence of alternating W-to-W double and non-bonding distances.



Curtis and coworkers[32] have also documented a number of oxidative-addition reactions in their studies of the reactivity of $Cp_2Mo_2(CO)_4$.

Reductive Eliminations. The synthesis of an extensive series of $1,2\text{-}M_2R_2(NMe_2)_4$ compounds[33,34] from the reaction between $1,2\text{-}M_2Cl_2(NMe_2)_4$ (M≡M) and alkyllithium reagents, LiR (2 equiv), where R = CH_3, Et, i-Pr, n-Bu, sec-Bu, t-Bu, CH_2CMe_3 and CH_2SiMe_3, affords the opportunity of studying the decomposition pathways of alkyl groups coordinated to dimetal centers. Some particularly interesting comparisons can be made with mononuclear σ-alkyl complexes of the transition elements, which have been the subject of much investigation.[35]

The structure of the $Mo_2Et_2(NMe_2)_4$ molecule is shown in Figure 1.[34] This view emphasizes the virtual C_2 axis of symmetry which exists for gauche $1,2\text{-}M_2X_2(NMe_2)_4$ compounds. All the hydrogens were located and refined, and in Figure 2 a stereoview of the molecule is shown which shows the orientations of the C-H bonds. Two important points can be seen: (1) the conformation about the C-C bonds of the ethyl groups is, within the limits of experimental error, perfectly staggered. Thus, as is shown in the Newman projection below, two β-hydrogen atoms are equidistant from the molybdenum



atom to which the ethyl ligand is σ-bonded. The β-H-to-Mo distances are 3.25(5) Å, which, taken together with the staggered conformation about the C-C bond, indicates the absence of any significant β-H---Mo interaction.[36] (2) The $MoNC_2$ units, which are planar, are aligned along the M-M axis and one hydrogen atom from each methyl group is contained within this plane. This introduces relatively short CH---Mo distances as is shown in Figure 3. The shortest distances are between the molybdenum atoms and the hydrogen atoms on the distal methyl groups, but only a little longer are the distances involving proximal methyl hydrogens and the other molybdenum atoms across the

$Mo\equiv Mo$ bond. This leads one to wonder "what are the closest natural CH---Mo distances in molecules of this type". This question is readily answered: keeping the central $Mo_2N_4C_2$ unit rigid, but allowing rotations about Mo-N, Mo-C, and C-C bonds produces CH---Mo distances of 2.3 to 2.4 Å, as shown in Figure 4, between the methyl protons of the ethyl ligand and the molybdenum atom to which it is not directly bonded. The methyl groups of the ethyl ligands thus provide β and γ hydrogens to the two molybdenum atoms and the γH---Mo distances across the $Mo\equiv Mo$ bond are the shortest.

Although the $Mo_2R_2(NMe_2)_4$ compounds are thermally stable below +100°C, the addition of a number of substrates will cause reductive elimination of alkanes and alkenes, when R = Et, Pr, and Bu. This type of reductive disproportionation of two alkyl ligands is fairly common in dialkylmononuclear chemistry, e.g.[37] $(PPh_3)_2Pt(Bu^n)_2 \rightarrow [(PPh_3)_2Pt]_x$ + 1-butene + butane. The addition of CO_2 and PhNNNHPh give the M-M quadruply bonded compounds $Mo_2(O_2CNMe_2)_4$ and $Mo_2(PhN_3Ph)_4$[38] as the molybdenum containing products. When R = CH_2CD_3, only CH_2=CD_2 and CD_3CH_2D are formed and it has been shown by use of the appropriate cross-over experiments that this elimination process is intramolecular.

The reaction between $Mo_2(CH_2CH_3)_2(NMe_2)_4$ and CO_2 in toluene-d_8 has been followed at -30°C by ^1H nmr spectroscopy. The build-up of an intermediate, namely $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ can be seen. The spectrum corresponding to this intermediate is shown in Figure 5 and is entirely consistent with the view that the molecule has a virtual C_2 axis of symmetry passing through the mid-point of the Mo-Mo bond, i.e. as is found[29] for $Mo_2(OBu^t)_4(O_2COBu^t)_2$. The reaction pathway following the formation of the intermediate $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ poses two interesting possibilities. The slow step in the reaction could be involved in the reductive-elimination of ethane and ethylene from $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ which would then generate a species "$Mo_2(NMe_2)_2(O_2CNMe_2)_2$" highly reactive to further reaction with CO_2. Alternatively, the slow step could involve CO_2 insertion into the Mo-NMe_2 bonds of $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$ to give say $Mo_2Et_2(O_2CNMe_2)_4$, c.f.[5] the structurally characterized compound $W_2Me_2(O_2CNEt_2)_4$, which then rapidly eliminates ethane and ethylene.

We have as yet been unable to distinguish between these pathways, though we are inclined toward favoring the former pathway based on the analogy with the reactions observed with triazenes shown in 1, 2 and 3 below. The

$$Mo_2(NMe_2)_6 + \text{ArNNNHAr (excess)} \rightarrow Mo_2(NMe_2)_4(ArN_3Ar)_2 \ (\text{M}{\equiv}\text{M}) + Me_2NH \qquad (1)$$

$$Mo_2R_2(NMe_2)_4 + \text{ArNNNHAr (excess)} \rightarrow Mo_2R_2(NMe_2)_2(ArN_3Ar)_2 \ (\text{M}{\equiv}\text{M}) + Me_2NH \qquad (2)$$

$$Mo_2R_2(NMe_2)_4 + \text{ArNNNHAr (excess)} \rightarrow Mo_2(ArN_3Ar)_4 \ (\text{M≣M}) + \text{alkane} + \text{1-alkene} + HNMe_2 \qquad (3)$$

difference between (2) and (3) rests solely on the nature of R. When R = CH_3 or CH_2CMe_3, reaction 2 occurs. When R = Et and Bu^n, reaction 3 occurs. The molecular structure of the compound $Mo_2Me_2(NMe_2)_2(ArN_3Ar)_2$, where Ar = p-tolyl, is shown in Figure 6. The molecule has a crystallographically imposed C_2 axis of symmetry relating the two four-coordinated molybdenum atoms. It is not unreasonable to suppose that reaction 3 proceeds via initial formation of the $Mo_2R_2(NMe_2)_2(ArN_3Ar)_2$ compounds, which then undergo elimination of alkane and alkene generating the coordinatively unsaturated molecules $Mo_2(NMe_2)_2(ArN_3Ar)_2$ which react rapidly with the excess triazine to give $Mo_2(ArN_3Ar)_4$ (M≣M).

At this time, nothing definitive can be said concerning the intimate mechanism of elimination beyond noting the facts: it is intramolecular, quantitative and irreversible - no scrambling of labels is observed.

A plausible interpretation of these results is that elimination occurs by a rate determining step which is akin to a cyclometallation reaction across the M-M bond. This is suggested by the close CH---Mo distance shown in Figure 4. Once the Mo-H bond is formed, elimination of alkane is rapid. Rather interestingly, the elimination of alkene from the dinuclear center may then be a slower final step: analogous reactions involving $W_2R_2(NMe_2)_4$ and either CO_2 or triazines yield 1 mole of alkane and as yet uncharacterized tungsten compounds which retain the elements of the alkene.

It is clear from this brief summary that dinuclear reductive elimination sequences have pathways which arise uniquely from the presence of the dimetal center, in addition to those accessible to mononuclear complexes.

Oxidative-Coupling and Reductive-Decoupling. Examples of oxidative-coupling and reductive-decoupling of ligands about a dimetal center are seen in the work of Stone, Knox and their coworkers[40] and are not discussed here.

Direct Attack on the M-M Multiple Bond

A number of small unsaturated molecules or functional groups have been found to add across the M-M triple bond in $Cp_2Mo_2(CO)_4$ to give adducts $Cp_2Mo_2(CO)_4(un)$, where un = acetylenes,[41] allenes,[42] cyanamides,[43] and thioketones.[44] In all of these adducts, the unsaturated fragments act as four electron donors to the dimetal center, thus reducing the M-M bond order from three to one.

The same group of unsaturated molecules have been found to react with $Mo_2(OPr^i)_6$, but as yet none of the adducts has been characterized by a full

X-ray study. The spectroscopic data observed[45] for $Mo_2(OPr^i)_6(NCNMe_2)$ are entirely consistent, however, with a mode of addition directly analogous to that observed above.

Carbon monoxide has been shown[8] to reversibly add across the M≡M bond of $Mo_2(OBu^t)_6$ to give $Mo_2(OBu^t)_6(\mu\text{-CO})$ (M=M). See VIII before. We have previously speculated[46] that this carbene-like addition to a M≡M bond could be one of general class of reactions that are common to dinuclear compounds. Similar additions of CO across Pd-Pd and Pt-Pt bonds have been reported.[47] Recently, Raterman has shown[48] that aryl azides react with $Mo_2(OBu^t)_6$ to give diamagnetic compounds of formula $Mo_2(OBu^t)_6(\mu\text{-NAr})_2$, where Ar = Ph and p-tolyl. A single crystal study of the tolyl derivative is currently in progress. Since aryl azides often act as a source of nitrenes, RN:, by the ready elimination of dinitrogen upon coordination to a transition metal,[49] this reaction could be viewed as a double carbene-like addition to the M≡M bond and a Mo-Mo single bond is expected in the product $Mo_2(OBu^t)_6(\mu\text{-NAr})_2$.

Addition of nitric oxide to $M_2(OR)_6$ compounds give $[M(OR)_3NO]_2$ compounds. The latter do not contain M-M bonds: the structure of $[Mo(OPr^i)_3NO]_2$ is closely related to that of $Mo_2(OPr^i)_8$, shown in VII, but has a Mo-to-Mo distance of 3.325(1) Å.[50] In a formal sense, the M≡M bond in $Mo_2(OPr^i)_6$ has been replaced by two metal-ligand triple bonds ($M{\equiv}N{\rightarrow}O$). The absence of any direct M-M bond in $[M(OR)_3NO]_2$ compounds is also supported (in addition to the structural evidence cited above) by the fact that the alkoxy bridged dimers are readily cleaved by donor ligands such as pyridine. This has been structurally confirmed for $W(OBu^t)_3(NO)(py)$.[51]

Walton and coworkers[52] have found that compounds containing M≣M bonds are also cleaved by the addition of certain unsaturated molecules, such as isocyanides.

Conclusions

The time is ripe for truly exciting developments in the reactivity of dinuclear transition metal compounds. The potential for cyclic sequences of reactions, as is required for catalytic reactions, has already been realized. (1) Muetterties, et al.[53] have shown that alkynes can be selectively hydrogenated to alkenes (cis 2H-addition) by $Cp_2Mo_2(CO)_4$: the rate determining step involves CO dissociation from the acetylene adducts $Cp_2Mo_2(CO)_4(R_2C_2)$. (2) We have found that $W_4(\mu\text{-}H)_2(OPr^i)_{14}$ will isomerize olefins: it selectively takes 1-butene to cis-2-butene, for example.[54] While one can but speculate about the ultimate impact of dinuclear transition metal chemistry, it is surely fair to say that the elucidation of the intimate mechanisms of reactions at dinuclear metal centers will prove more challenging and fascinating than did their analogues at mononuclear centers.

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Captions to Figures

Figure 1. An ORTEP view of the $Mo_2Et_2(NMe_2)_4$ molecule emphasizing the virtual C_2 axis of symmetry. Pertinent structural parameters are Mo-to-Mo ($M \equiv M$) = 2.206(1) Å, Mo-N = 1.96 Å (av), Mo-C = 2.18 Å (av), Mo-Mo-N angle = 103° (av) and Mo-Mo-C angle = 101° (av).

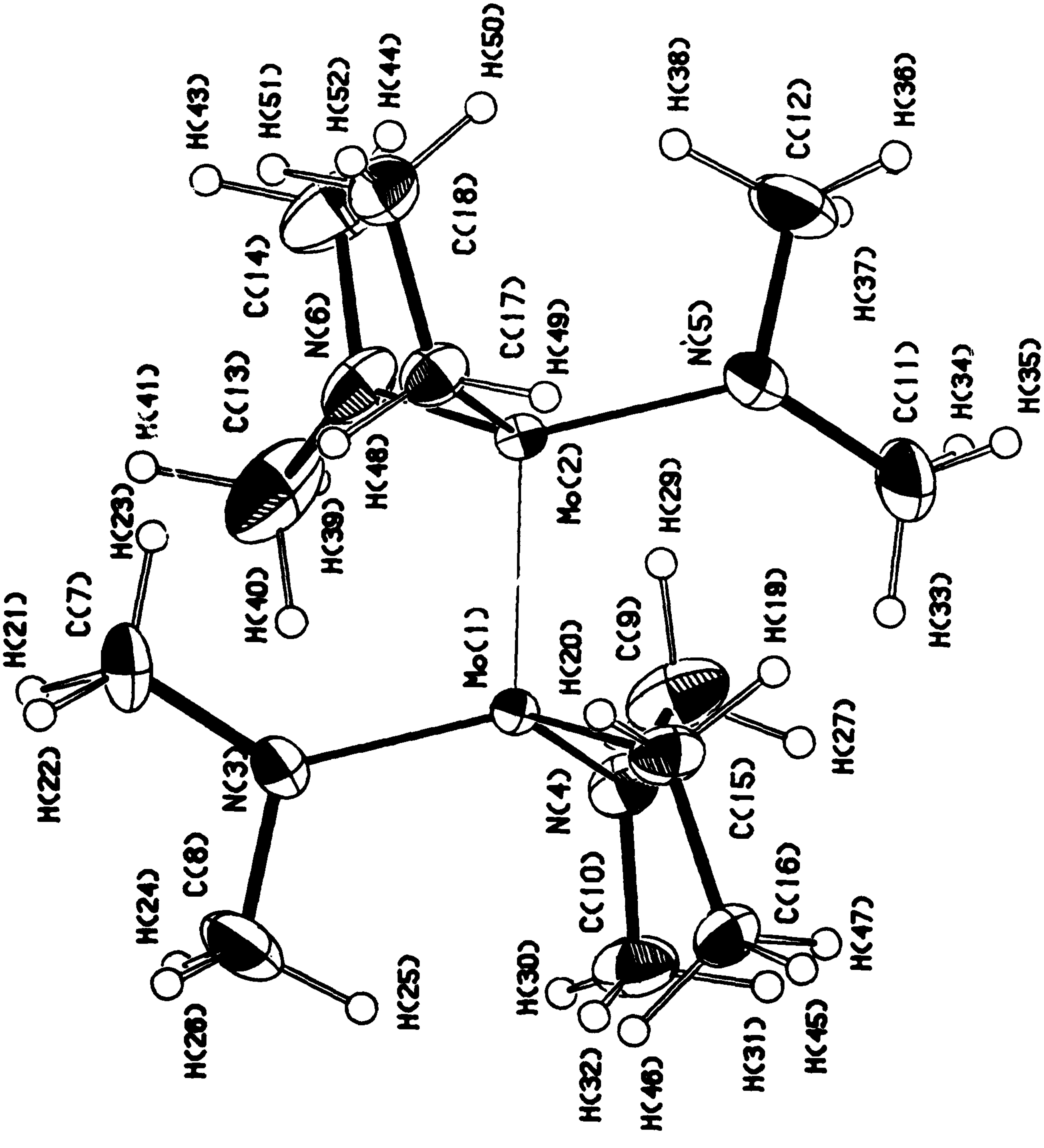
Figure 2. Stereoview of the $Mo_2Et_2(NMe_2)_4$ molecule looking down the Mo-Mo bond. This stick view of the molecule emphasizes the positions of all the hydrogen atoms.

Figure 3. A line drawing of one Mo_2NC_2 fragment showing the Mo---HC distances which arise to the two hydrogen atoms which are confined in the plane of the $Mo-NC_2$ unit.

Figure 4. A line drawing of one Mo_2-ethyl fragment showing the short CH---Mo distance which arises from rotations about Mo-C and C-C bonds.

Figure 5. ^1H nmr spectrum recorded at -30°C, 100 MHz, during the reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2, showing the formation of the intermediate $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, along with the products C_2H_4 and C_2H_6 and $Mo_2(O_2CNMe_2)_4$. The solvent is toluene-d_8 and the protio impurities are indicated by *. The signal noted by ** corresponds to $Mo_2(O_2CNMe_2)_4$ which, because of its very low solubility, is mostly precipitated as it is formed.

Figure 6. An ORTEP view of the $Mo_2Me_2(NMe_2)_2(C_7H_8N_3C_7H_8)_2$ molecule (C_7H_8 = p-tolyl) viewed down the $Mo \equiv Mo$ bond emphasizing the C_2 axis of molecular symmetry which relates the two four coordinate molybdenum atoms. The Mo-to-Mo distance is 2.175(1) Å and Mo-C = 2.193(4) Å.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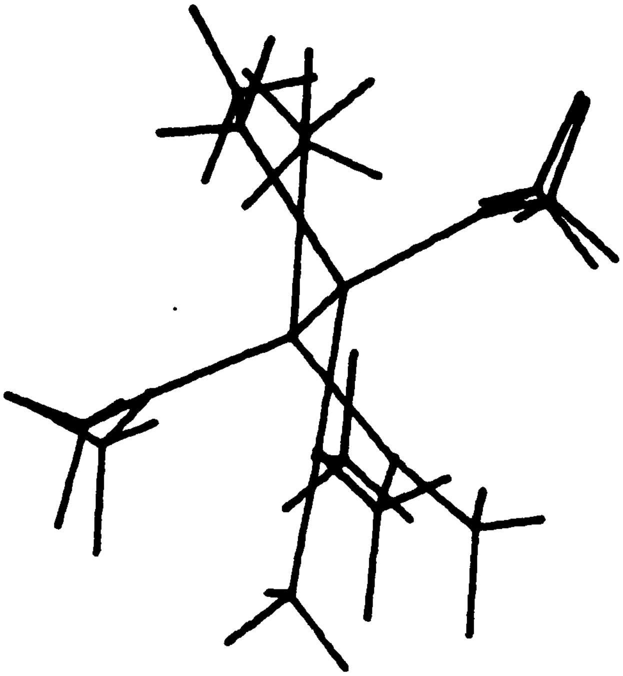
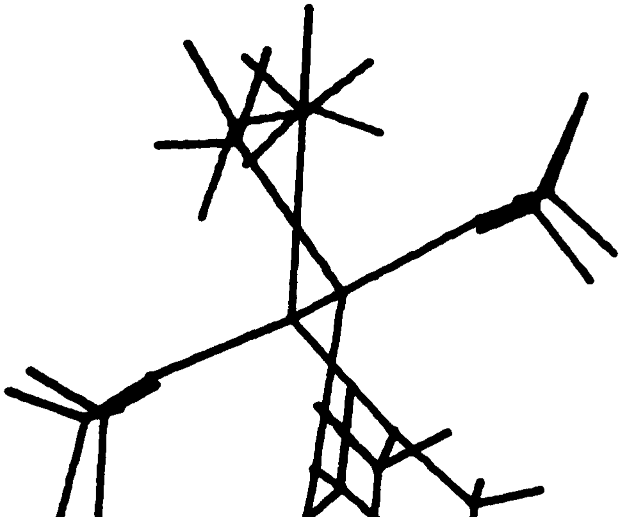
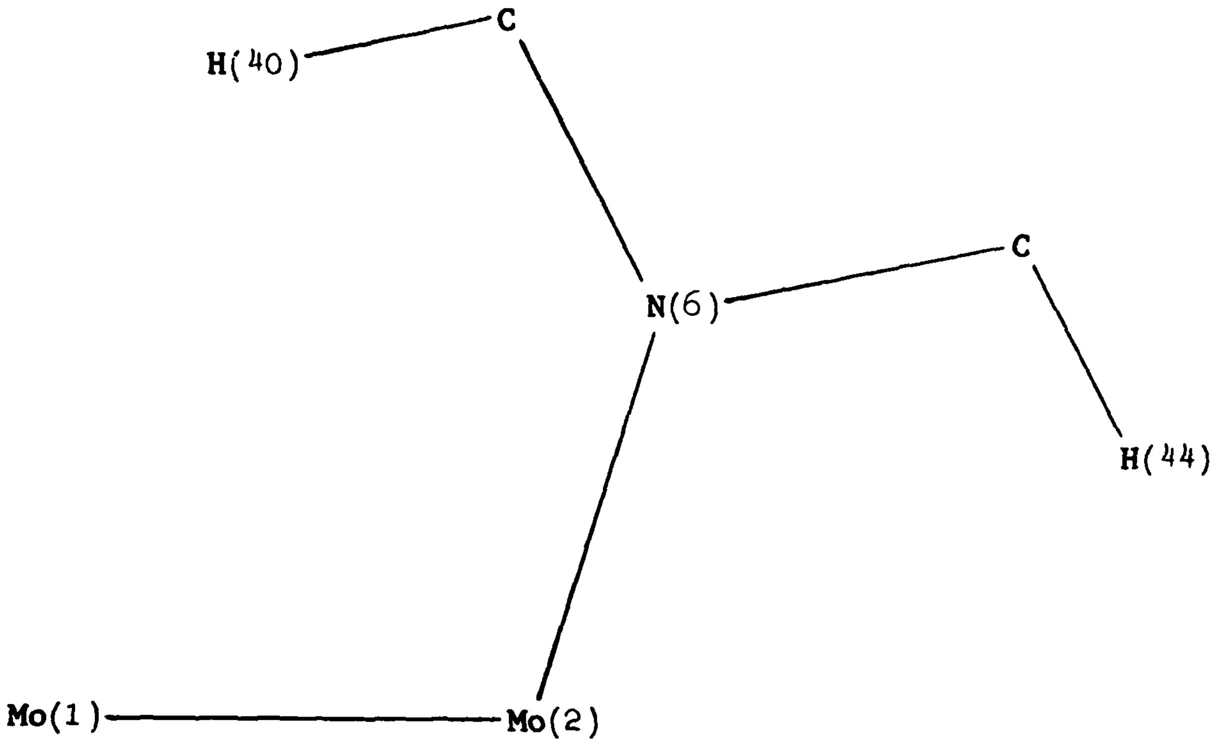


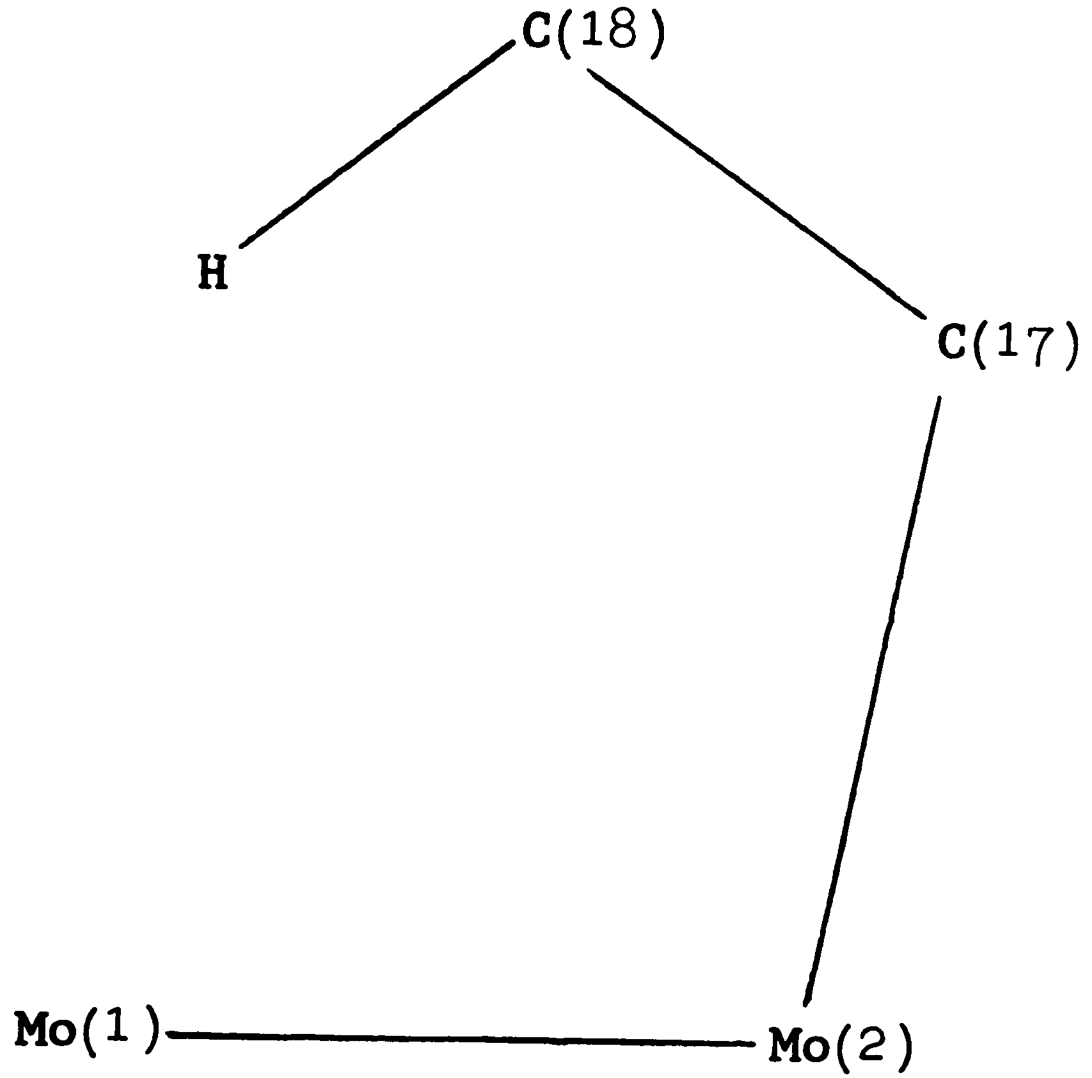




Mo(2) -- H(44) 2.77 Å

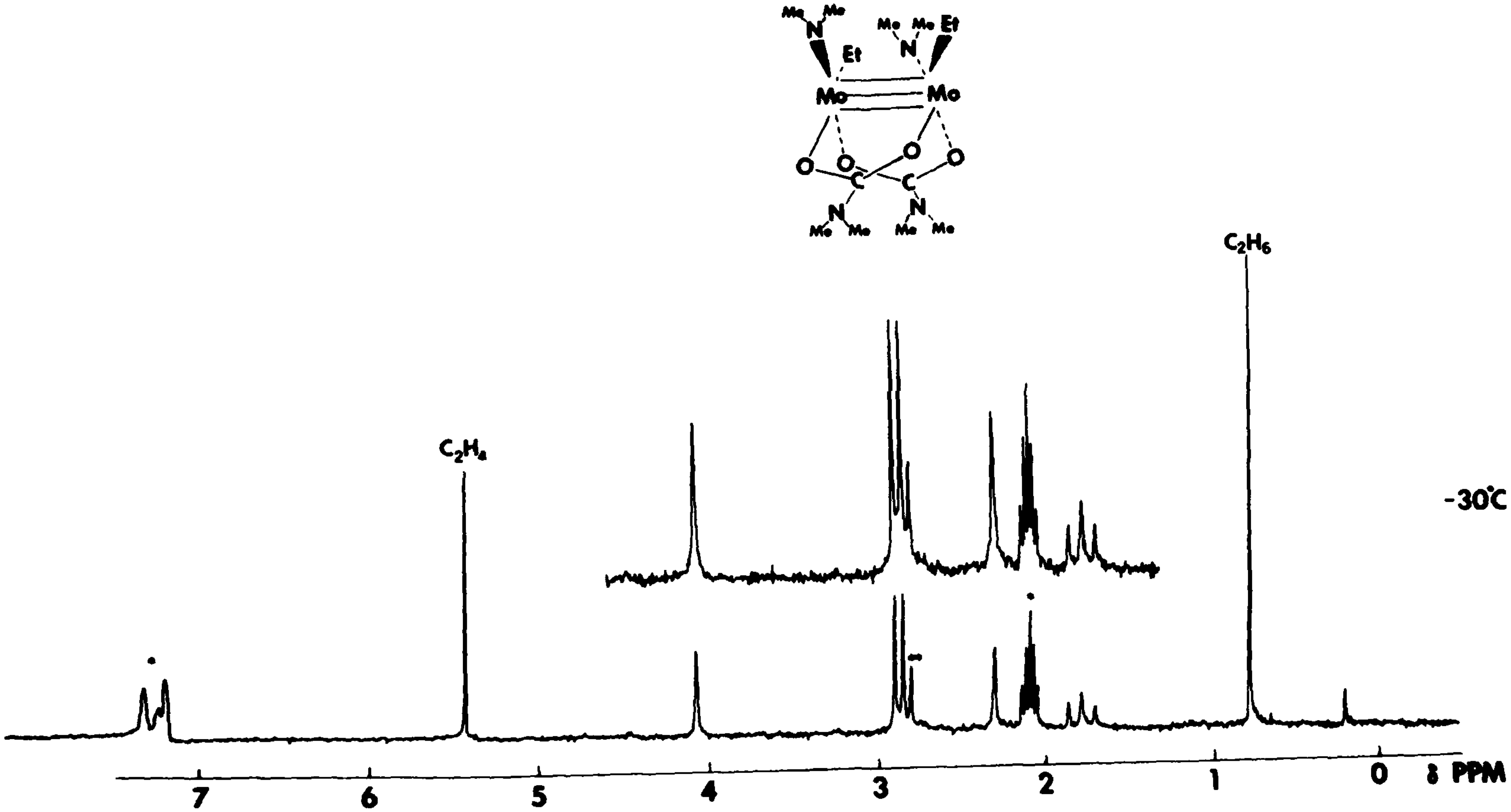
Mo(2) -- H(40) 3.18 Å

Mo(1) -- H(40) 2.96 Å



Mo(1) --- H 2.36 Å

Mo(2) --- H 2.97 Å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