

Developing the reactivity of multiple bonds between metal atoms: inorganic functional groups

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Abstract - The dinuclear chemistry of molybdenum and tungsten in oxidation states +3 and +4 is compared and contrasted with that of mononuclear chemistry. Specific attention is given to coordination geometries, electronic ground state structure, redox reactions, template reactions and polymer synthesis.

INTRODUCTION

Cotton's discovery of the M-M quadruple bond in 1964 heralded a new chapter in coordination chemistry.¹ It was not that compounds containing metal-metal bonds were unknown prior to 1964 for there were examples both in inorganic and organometallic chemistry. However, in the now famous structure of the $\text{Re}_2\text{Cl}_8^{2-}$ anion we saw for the first time the importance of multiple bonds between metal atoms. Cotton immediately recognized that, in order to account for the unique shortness of the Re-Re distance and the eclipsed geometry of the two ReCl_4^- units, there had to be a strong metal-metal bond and by symmetry and electron counting this had to be comprised of one σ , two π and one δ components. The latter was responsible for the eclipsed geometry and was before that time an unrecognized feature in bonding.

Although compounds with M-M multiple bonds are non-classical coordination complexes in the Wernerian sense, their chemistry has developed as a natural outgrowth of mononuclear chemistry. This is because they lend themselves to investigations of synthesis, structure, bonding and reactivity that parallel those of mononuclear chemistry. For a complex of formula $\text{L}_2\text{M}^n\text{ML}_2$ there is a group of $2x$ ligands, L, surrounding a dinuclear center M_2^n . A number of important questions are raised: What is the favored disposition of ligands? What is the nature of the M-M interaction? What is the electronic structure of the complex and how does this account for its observed spectroscopies? How does it react? Is it substitutionally labile or inert? In what way is the dinuclear center redox active? Can it participate in dinuclear oxidative additions or reductive eliminations? Can the dinuclear center be used as a template to do coupling reactions? The questions go on but soon one realizes that all the basic chemistry available to mononuclear complexes could still be possible for dinuclear systems and there should be more, namely that chemistry which is unique to dinuclear complexes.

It is with these questions in mind and with this philosophy that my group has been investigating the dinuclear chemistry of molybdenum and tungsten for the past 10-15 years. We have restricted our attention to the chemistry of these two elements for two reasons. 1) There is a rich and diverse dinuclear chemistry involving molybdenum and tungsten in their oxidation states +2 to +5. 2) We have not been in a position to claim that we understand the principles of the dinuclear chemistry of these elements (beyond a knowledge of ground state structure and bonding) and to look elsewhere would be to ignore the problems in our laboratory.

In this lecture I shall outline some of the general principles and highlight some recent developments concerning the dinuclear chemistry of molybdenum and tungsten in their oxidation states +3 and +4.

d^3-d^3 AND d^4-d^4 GROUND STATE STRUCTURES AND BONDING

I have recently reviewed² the ground state coordination chemistry of d^3-d^3 dimers of molybdenum and tungsten and I mention here only the important general features. The preferred coordination geometry about a M_2^{5+} unit ($M = Mo, W$) reflects the subtle interplay that exists between maximizing metal-metal and metal-ligand bonding. So, for example, unlike the mononuclear coordination chemistry of Rh^{3+} that is dominated by six coordinate octahedral complexes, the coordination chemistry of W^{3+} , which is principally that of W_2^{6+} , is extremely diverse with respect to coordination number and geometry.

Figure 1 shows diagrammatically the types of geometries that are involved. There is the extensive family of so-called ethane-like dimers $X_3M=MX_3$, where X = a bulky ligand such as CH_2SiMe_3 , OBu^t , S-mesityl, NMe_2 , Se-mesityl, and seemingly innumerable compounds of the type $X_2YM=MX_2Y$ where X is one of the afore-mentioned ligands and Y is a halide, phosphide, etc.³ Closely related are compounds wherein two four coordinate metal ions are united by M-M triple bonds, e.g. $M_2(OR)_6(py)_2$ compounds.⁴ Compounds such as $(Pr^tO)_3Mo=Mo(CH_2Ph)_2(OPr^t)(PMe_3)$ provide examples of triple bonds uniting three and four coordinate metal atoms.⁵ In the structures of $W_2Me_2(O_2CNET_2)_4$ ⁶ and $W_2(O_2CX)_6$ compounds ($X = NMe_2$ or Bu^t)⁷ we see M-M triple bonds uniting metal atoms that are either 5 coordinate or 6 coordinate. In the latter case there is a weak (as evidenced by long M-O bond distances of ca 2.6 Å) axial to metal interaction.

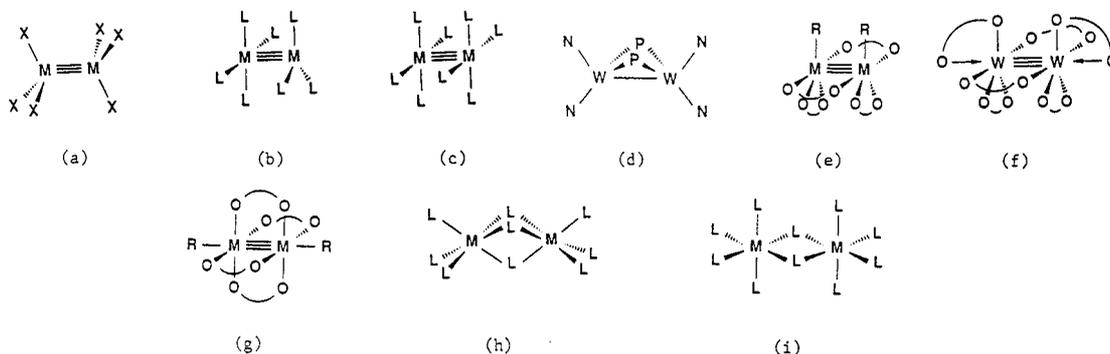


Fig. 1

The coordination geometries of d^4-d^4 dimers are much less varied being dominated by two planar four coordinate metal ions united by a quadruple bond. The two ends of the molecule ion are eclipsed as required for the formation of the M-M δ bond. There are relatively few exceptions to this type of geometry and the exceptions arise from either the introduction of bridging ligands, e.g. as in $Mo_2(allyl)_4$ ⁸ and $Mo_2(PBu^t_2)_4$ ⁹ or because chelating phosphine or arsine ligands span the M-M bond in such a way as to introduce a non-eclipsed geometry of the two four coordinate metal ions.¹⁰ The bonding in the dinuclear compounds can in all instances be easily formulated from the combining of two L_nM fragments. In general the triple bonds are of configuration $\sigma^2\pi^4$ and the quadruple bonds are $\sigma^2\pi^4\delta^2$. The M-M distances for triple bonds lie in the range 2.2 ($M = Mo$) to 2.3 Å ($M = W$) and the quadruple bonds are roughly 0.1 Å shorter.

The compounds of formula $W_2R_2(O_2CR')_4$ ¹¹ are unique amongst d^3-d^3 dimers in that they have M-M distances comparable to those of the d^4-d^4 $W_2(O_2CR')_4$ complexes. They are also exceptions to the rule that axial ligation to a M-M multiple bond is weak. The two structures are closely related as is shown diagrammatically in I and II below.



The compound I may be converted to II either thermally ($R = Bu^t, PhCH_2$) or photochemically ($R = CH_2Bu^t$) and it is instructive to consider the bonding in I as a derivative of that in II wherein two alkyl radicals are brought up along the M-M axis.¹² This is shown in Fig. 2.

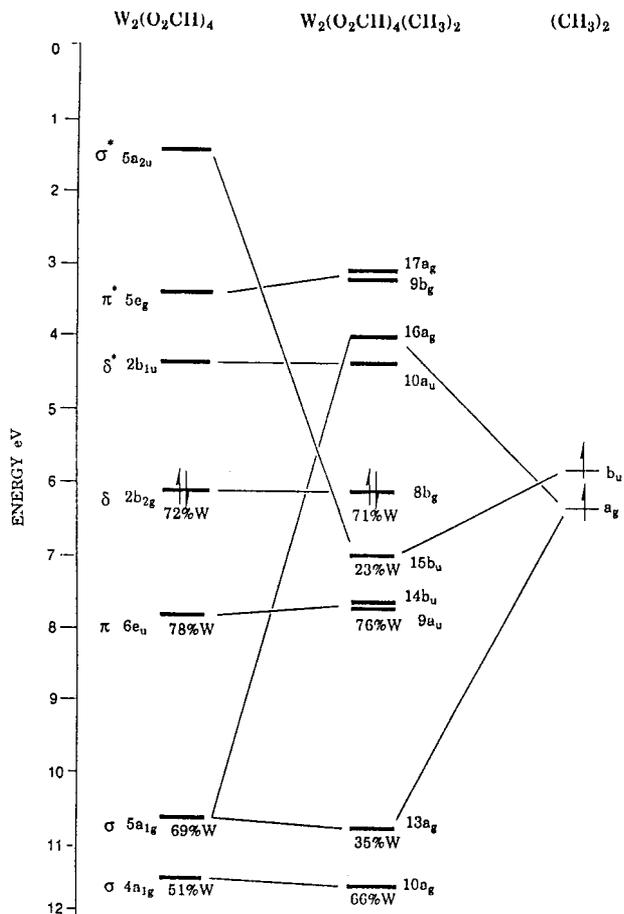


Fig. 2. This diagram shows the correlation of the M-M bonding orbitals in $W_2(O_2CH)_4$ with two CH_3 fragments in the formation of $W_2(O_2CH)_4(CH_3)_2$. The HOMOs are denoted by spin paired arrows. In $W_2(O_2CH)_4$ there are two σ type bonding orbitals, $4a_{1g}$ and $5a_{1g}$, having W $6s$ and Wd_{z^2} character, respectively. Both have some M-O bonding component. The $6e_u$ and $2b_{2g}$ are the M-M π and δ orbitals, respectively. In forming two new bonds to the CH_3 groups the M-M π and δ orbitals are perturbed little. The two lower energy σ orbitals are stabilized slightly while the new σ orbitals $15b_u$ is principally W-C bonding and only slightly W-W antibonding.

Although it is typical to denote the quadruple bond in $M_2(O_2CR)_4$ compounds ($M = Mo, W$) with the notation $\sigma^2\pi^4\delta^2$ only the δ and π orbitals are predominantly metal d in character. Thus for the M-M σ bond there is a mixing with M-O bonding. Both the W $6s$ and the W $5d_{z^2}$ can form M-M σ interactions and M-O σ/σ^* interactions. So it is not appropriate to assign the M-M σ bond to one specific M.O. Two M.O.'s make significant contributions to M-M σ bonding. Now the introduction of two alkyl radicals along the M-M axis will mix with M-M σ and σ^* orbitals. The in-phase radical combination, a_g , will mix with M-M σ orbitals and the out-of-phase combination, b_u , will mix with M-M σ^* as shown in Fig. 2. Two M-M σ orbitals are stabilized and one new orbital, $15b_u$ in Fig. 2, is occupied. Though this has M-M σ^* character, it is principally metal-carbon bonding. Consequently the sum of M-M σ bonding is roughly the same in the d^3-d^3 and d^4-d^4 complexes of type I and II.

The striking feature of complexes of type I is that their HOMO is δ^2 and their M-M M.O. configuration is formally $\pi^4\delta^2$ for the d^3-d^3 interaction. The electronic spectra, photoelectron spectra and the cyclic voltametric studies all support this assignment.¹¹

The mixing of M-M σ bonding with metal-ligand bonding is a common problem in inorganic chemistry but it is in no way unique to metal containing complexes. For example, although it is convenient to talk of a C-C σ bond in ethane or ethylene and to visualize this in a fragment MO approach there is in reality extensive mixing of C-C σ/σ^* and C-H σ interactions.¹³

Finally, with respect to the coordination chemistry of d^3-d^3 dinuclear complexes, I should note that confacial and edge-shared octahedra are common, e.g. as in $M_2X_9^{3-}$ ions ($X = \text{halide}$)¹⁴ and $W_2Cl_6(py)_4$,¹⁵ respectively. More recently we have established the existence of $X_4M_2(\mu-PR_2)_2$ compounds where $X = O\text{Bu}$ ¹⁶ or NMe_2 .¹⁷ The latter may be viewed as derivatives of two fused tetrahedra sharing a common edge, e.g. as in a distorted Al_2Cl_6 structure. Two fused tetrahedra would yield a M-M M.O. configuration $\sigma^2\delta^2\delta^{*2}$ and clearly this is not favored relative to the ethane-like geometry that yields the $\sigma^2\pi^4$ triple bond. However, the formation of the phosphine

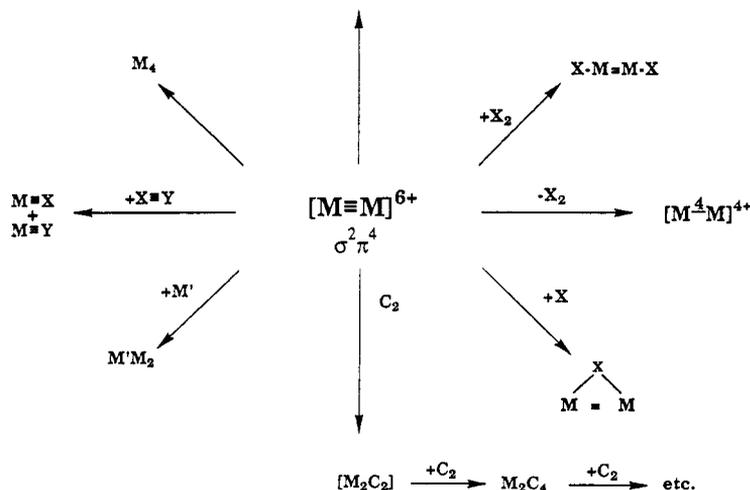
bridges compensates for the weakening of the M-M bond. Open and closed (μ -PR₂) isomers of W₂(NMe₂)₄(PHex^c)₂ have been structurally characterized.¹⁷ In the unbridged isomer the M-M distance is 2.31Å whereas in the bridged isomer this distance is 2.57 Å. In the latter there is a puckered W₂P₂ (butterfly) core (Fig. 1d) that in solution can be seen to invert, E_{act} ca 14 kcal mol⁻¹ from VT NMR studies. The puckering of the W₂P₂ unit enhances the M-M bonding relative to that in the planar structure.

REACTIONS

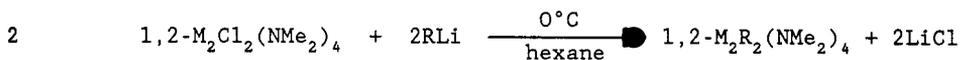
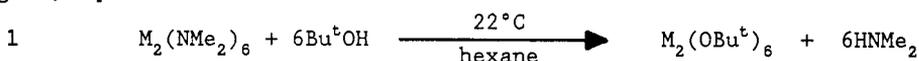
Scheme 1 shows the types of reactions that we have studied for the X₃M=MX₃ compounds of M-M M.O. configuration, $\sigma^2\pi^4$.

Scheme 1

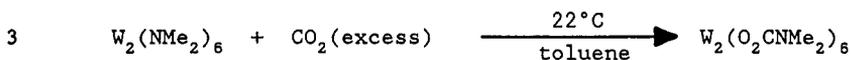
Coordination Chemistry: Substitution Reactions



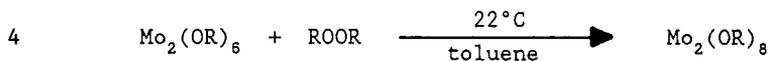
1. There is a vast area of substitution chemistry wherein ligands are interchanged at the dinuclear center. These may proceed with retention of geometric form, e.g. in the alcoholysis reaction, eq. 1,¹⁸ or in the replacement of a chloro group by an alkyl ligand, eq. 2.¹⁹



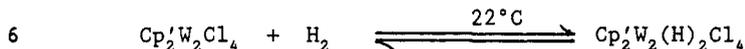
Alternatively, the replacement of a monodentate ligand by a bidentate ligand, as in the formal insertion reaction, eq. 3,⁶ may maintain the triple bond of M-M M.O. configuration $\sigma^2\pi^4$ but change the structural type from (a) to (f) in Fig. 1.



2. Oxidative addition reactions involving Mo₂(OR)₆ compounds and dialkylperoxides or halogens to give Mo₂(OR)₈ and Mo₂(OR)₆X₄ compounds (X = halide) were the first examples of reactions wherein a M-M triple bond was converted to a M-M double bond, $\sigma^2\pi^2$, and a M-M single bond, σ^2 , respectively, eqs. 4 and 5.²⁰

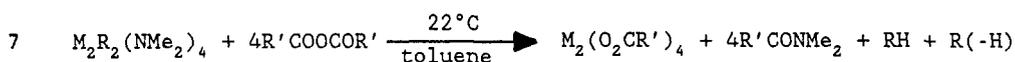


Oxidative-addition of alkyl halides to these dinuclear centers has not been observed. The more reactive organic halides, e.g. benzyl bromide and allyl chloride, act as halogenating reagents. In this regard the dinuclear centers do not show reactivity comparable to that of the later d^8 -transition metal complexes. Similarly oxidative addition of H_2 is not commonly observed though at least one example of the reversible addition of H_2 across a $M=M$ bond is known, eq. 6.²²



The compound $Cp'_2W_2Cl_4$ has an unbridged $W=W$ bond and may be considered as a member of the $X_2YM=MYX_2$ compounds of type (a) in Fig. 1 where $Cp' = \eta^5-C_5H_4Pr^1$ substitutes for a monodentate Y group.

3. Reductive-eliminations from the dinuclear center have been extensively studied for alkyl group disproportionation reactions of type 7.²³ These have been shown to be intramolecular and to involve the transference of the β -hydrogen atom from one alkyl ligand to the α -carbon atom of the other.



Reductive eliminations can be brought about with other ligand sets but only under more forcing conditions. For example, treatment of the $W_2Cl_4(THF)_2$ anion²⁴ with Na/Hg in THF (THF = tetrahydrofuran) in the presence of PMe_3 will convert a W_2^{6+} moiety (structural type h in Fig. 1) to W^{4+} with formation of $W_2Cl_4(PMe_3)_4$.²⁵ In general reductive eliminations $M_2^{6+} \rightarrow M_2^{4+}$ are more favorable for $M = Mo$ than for $M = W$ and the opposite is true of oxidative-addition reactions. This parallels the general trends in mononuclear chemistry. Compare, for example, the organometallic chemistry of Pd^{2+}/Pd^{4+} with Pt^{2+}/Pt^{4+} .

The stepwise changes in M-M bond order brought about by oxidative-addition and reductive elimination reactions have a parallel in the organic chemistry of C-C bonds. One is naturally led to the question of how dinuclear oxidative-additions and reductive eliminations proceed. Do they occur directly across the M-M bond or do they involve reactions at one metal center that are followed or preceded by ligand migrations across the M-M bond?

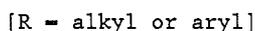
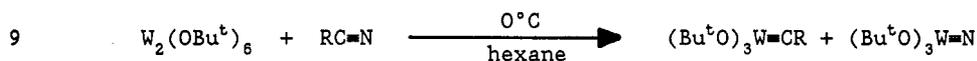
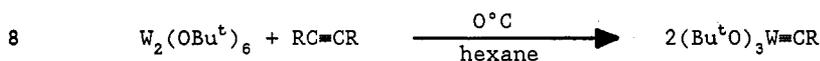
There are reasons to believe that the latter is operative. 1) From an orbital analysis, Hoffman²⁶ has shown that the simple addition of an X-X bond across a M-M bond is forbidden by symmetry. 2) We have found examples of ligand migrations for $M = Mo$ that could model the first step in an elimination reaction observed for $M = W$. For example, the addition of PMe_3 to $1,2-Mo_2(CH_2Ph)_2(OPr^i)_4$ brings about a facile 1,2- to 1,1-benzyl migration at room temperature with the formation of $(Pr^iO)_3Mo=Mo(OPr^i)(CH_2Ph)_2(PMe_2)$, a compound of structure type b in Fig. 1.⁵ A similar addition of PMe_3 to $1,2-W_2(CH_2Ph)_2(OPr^i)_4$ brings about an elimination of toluene and the formation of a hydrido-benzylidyne complex.²⁷ The kinetic product, III, contains three PMe_3 ligands bound to one tungsten atom and three OPr^i ligands attached to the other. The thermodynamic product, IV, which is formed by PMe_3 dissociation from III is the more symmetrically substituted compound having two OPr^i ligands and one PMe_3 attached to each tungsten.



4. The dinuclear center acts as a redox active template for the activation of small molecules and unsaturated organic groups. Carbene-like additions across the M-M bond by groups such as CO ²⁸ and RNC ²⁹ are facile and sometimes reversible, e.g.³⁰ for Co and $Mo_2(OBu^t)_6$. Carbon-carbon coupling reactions involving the reactions between $M_2(OR)_6$ compounds and alkynes³¹ and ethylene³² have been extensively studied. Alkyne adducts contain a central $M_2(\mu-C_2R_2)$ moiety that may be considered as a dimetallatetrahedrane with M-M, M-C and C-C single bond distances.³³ The reaction

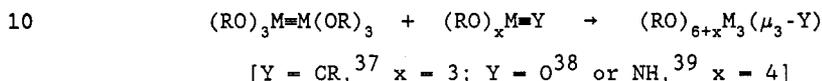
between the M=M bond and the C=C bond may be viewed as a complementary redox reaction. The M=M bond contains the configuration $\sigma^2\pi^4$ and is a potential six electron reductant. The alkyne with empty C-C π^* and σ^* orbitals is a potential six electron oxidant. The dimetallatetrahedrane formally represents a four electron exchange. Of course, this is only a formalism in electron counting as indeed is the assignment of oxidation states. We have found examples wherein the alkyne adducts, the dimetallatetrahedranes, are in equilibrium with the alkylidyne complexes.³⁴ These represent internal redox reactions and the position of equilibrium can be tuned by the ancillary ligands present at the metal center.

Schrock³⁵ and coworkers have made extensive use of the metathesis reactions, eq. 8 and 9, wherein the dinuclear center is used in the one step synthesis of mononuclear complexes containing metal-ligand triple bonds.



Reactions of type 8 and 9 are remarkable in that thermodynamically strong bonds ($> 200 \text{ kcal mol}^{-1}$) are cleaved with kinetic facility. I shall comment on these factors later in this lecture.

5. As a final class of reactions, I mention the use of M=M bonds in cluster forming reactions. An unsaturated ML_n moiety may add to the M=M bond in a similar manner to the way in which M-C multiple bonds have been used by Stone³⁶ and coworkers in the assembly of organometallic clusters. Reactions of the type described by the generalized eq. 10 may also be viewed as conproportionation redox reactions: $2M^{3+} + M^{6+} \rightarrow 3M^{4+}$.

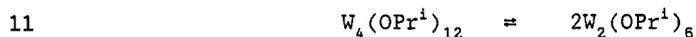


Many of the alkoxide supported small clusters of molybdenum and tungsten bear a striking similarity to carbonyl clusters of the later transition elements, e.g. $W_3(OR)_9(\mu_3-Y)$ and $Co_3(CO)_9(\mu_3-Y)$ where $Y = CR^{37}$ or P^{40} . It is often useful, both in terms of bonding and reactivity, to look to the isolobal relationships⁴¹ that are present in these systems. For example, the $d^3-M(OR)_3$ fragment is isolobal with CR , P and $Co(CO)_3$ which readily accounts for the similarity of the carbonyl and alkoxide clusters noted above.⁴² There are, however, important differences between the alkoxide and carbonyl clusters. Thus whereas the 18 electron rule is generally satisfied in small metal carbonyl clusters, the molybdenum and tungsten alkoxide clusters are electron deficient. Also, whereas the triply bonded molecule $(CO)_3Co\equiv Co(CO)_3$ is hypothetical, the $(RO)_3M\equiv M(OR)_3$ compounds are isolable because of the steric factors imposed by the alkyl ligands.

For a long time we were tantalized by the nature of $M_4(OR)_{12}$ compounds. For sterically less demanding alkyl groups, e.g. $R = \text{Et, } CH_2Pr^i, CH_2Bu^c, CH_2Pen^c$ and even Pr^i for $M = W$, we knew from cryoscopic molecular weight determinations that the degree of oligomerization n for the compound $[M(OR)_3]_n$ was approximately four. However, all attempts at a crystallographic determination of structure were unsuccessful because of problems of disorder or twinning. The NMR data were too complex to allow for any unique solution of structure. Finally, David Clark obtained crystals of $[W(OPr^i)_3]_n$ from DME (1,2-dimethoxyethane) that did diffract satisfactorily and revealed that within the unit cell there was a 1:1 mixture of $W_2(OPr^i)_6$ and its dimer, the 12-electron cluster $W_4(OPr^i)_{12}$.⁴³ The former is not surprisingly a member of the ethane-like dimers with $W-W = 2.315(1) \text{ \AA}$, $W-O = 1.87(1)$ and $W-W-O = 107(1)^\circ$. The $W_4(OPr^i)_{12}$ molecule is centrosymmetric with a planar $W_4(\mu-O)_4$ unit. The metal skeleton corresponds to a distorted rhombus with alternating short, $2.502(1) \text{ \AA}$, and long, $2.733(1) \text{ \AA}$, metal-metal distances corresponding formally

to M-M double and single bonds, respectively, based on M-M distances.⁴ Of course, within the cluster there is considerable delocalization of M-M bonding and the diagonal W-W distance 2.807(2) Å is still within a M-M bonding distance. Above and below the W_4 plane there are eight terminal alkoxide ligands, two bound to each tungsten atom. The four bridging OPrⁱ ligands whose oxygen atoms lie in the W_4 plane are of two types, those bridging the long W-W bonds and those bridging the short W-W bonds. The latter are asymmetric and could be viewed as semi-bridging groups,⁴⁴ being principally bonded to the wing-tip W atoms. The distortion from a symmetrical rhombus was traced to a 2nd order Jahn-Teller distortion.⁴³

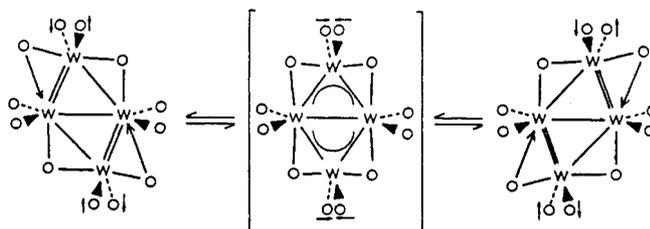
In toluene- d_8 solution two dynamic processes were observed, one involving solely the cluster and the second the equilibrium between the cluster and the dinuclear compound, eq. 11.⁴⁵



A careful analysis of the intramolecular cluster dynamics led us to propose that the cluster oscillates about a symmetrical rhomboidal core. In this way the alternating short and long W-W distances are exchanged as are the two types of bridging OPrⁱ ligands. Accompanying this rocking of the W_4O_4 moiety there is a proximal and distal isopropyl group exchange of the OPrⁱ ligands attached to two of the tungsten atoms, namely the wing-tip tungsten atoms - those that are furthest apart in the rhombus. The combined operations of the rocking of the rhombus and the correlated rotations about the OPrⁱ ligands were termed "the Bloomington Shuffle" for obvious local sentiments. Schematically these are shown in Scheme 2.

Scheme 2

"THE BLOOMINGTON SHUFFLE"



Schematic representation of the intramolecular dynamic exchange of the $W_4(\mu-O)_4(O)_8$ core of $W_4(O-i-Pr)_{12}$ together with methine vector reorientation about a time-averaged symmetrical (D_{2h}) rhomboidal framework of tungsten atoms.

It is important to recognize that this cluster motion does not involve a square W_4 intermediate for this would lead to the observation that all the terminal groups were exchanged. This is clearly not happening. The bridging groups are made equivalent and so are the terminal groups on the wing-tip tungsten atoms but these do not exchange with those attached to the back-bone W atoms.

An interesting analogy with cyclobutadiene is seen. The latter also avoids the square D_{4h} - C_4H_4 geometry and adopts a rectangular ground state geometry. Calculations indicate that cyclobutadiene would oscillate from one rectangular geometry to the other by way of a rhombus and thereby avoid the square.⁴⁶ For both the $W_4(\text{OPr}^i)_{12}$ and cyclo- C_4H_4 , the D_{4h} geometry is predicted to be a diradical and a molecule of lower symmetry is stabilized by what is commonly called a 2nd order Jahn-Teller distortion.⁴⁷ Why for cyclo- C_4H_4 this should be a rectangle and for $W_4(\text{OPr}^i)_{12}$ a rhombus probably reflects the nature of p-p and d-d π -type interactions within the E_g framework. Clearly the rhomboidal ground state for $W_4(\text{OPr}^i)_{12}$ allows some back-bone W-W bonding at a distance of 2.8 Å.

Studies of the equilibrium reaction, eq. 11, revealed the thermodynamic parameters $\Delta H^\circ = +21(2)$ kcal mol⁻¹ and $\Delta S^\circ = +61(6)$ eu. Enthalpically the cluster is favored relative to the triple bonded molecule $W_2(\text{OPr}^i)_6$ but this is opposed by entropic factors. From studies of the rate of approach to equilibrium as a function of temperature we obtained the following activation parameters. (1) For the dissociation $W_4 \rightarrow W_2$: $\Delta H^\ddagger = +30(2)$ kcal mol⁻¹, $\Delta S^\ddagger = +18(6)$ eu and for the coupling reaction, $2W_2 \rightarrow W_4$: $\Delta H^\ddagger = +10(1)$ kcal mol⁻¹ and $\Delta S^\ddagger = -39(3)$ eu. Collectively these data provide a comprehensive picture of the equilibrium, eq. 11, and show that the coupling of two M-M triple bonds has a small enthalpy of activation.

Stimulated by these findings, we looked at the reversible coupling of two hypothetical $W_2(OH)_6$ molecules to give $W_4(OH)_{12}$ along a reaction coordinate maintaining C_{2h} symmetry by carrying out Fenske-Hall calculations at 10 intermediate steps of the reaction. See Fig. 3. A detailed analysis of the orbital mixing during this reaction revealed that the reversible coupling of two M-M triple bonds in this system is not forbidden by symmetry in the Woodward-Hoffmann⁴⁸ sense and thus the M-M triple bonds in $W_2(OR)_6$ compounds differ from C-C triple bonds in alkynes.

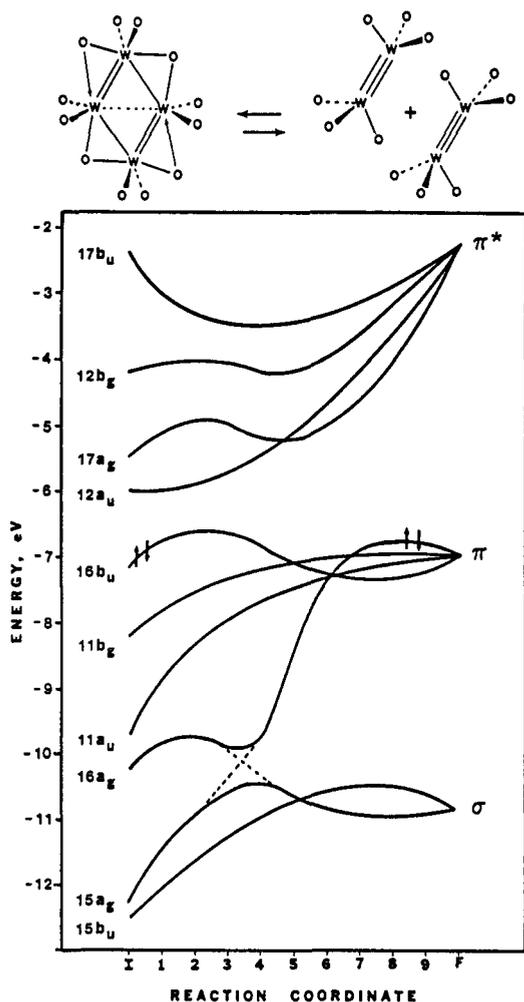
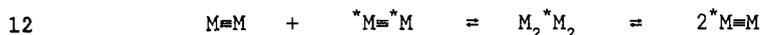


Fig. 3. A Walsh diagram for the concerted $[\pi^2_s + \pi^2_s]$ cycloreversion process. The predominantly metal-based orbitals of the Jahn-Teller distorted $C_{2h}W_4(\mu-OH)_4(OH)_8$ molecules are shown at left, and those of two molecules of $W_2(OH)_6$ are shown at right.

The combined operations of the Bloomington Shuffle and the equilibrium, eq. 11, should bring about a metathesis of the metal atoms in the M=M bond, eq. 12.



The reaction 12 can only be followed by an isotopic labelling of the metal atoms in $W_2(OPr^i)_6$ and this experiment has yet to be carried out.

SUBSTITUTIONAL LABILITY OF DINUCLEAR COMPLEXES

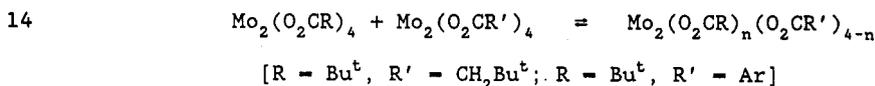
From the above brief description of the reactions of M-M triple bonded compounds it is clear that they are reactive species. In part this has to do with thermodynamics - they are high energy compounds as would be expected for reactions of type 8 and 9 where strong bonds are being broken. Of course, stronger metal-ligand multiple bonds are being formed, otherwise these reactions would not be favored. However, it is important to realize that these reactions proceed under mild conditions because the complexes are substitutionally labile. The compounds $X_3M=MX_3$ do not dissociate their ligands X in hydrocarbon solvents but are labile because the metal ions can increase their coordination numbers. Thus the equilibrium reaction 13, that interconverts

structural types (a) and (c) in Fig. 1, occurs sufficiently fast to cause line broadening on the ^{31}P NMR time-scale. This is reminiscent of the facile exchange

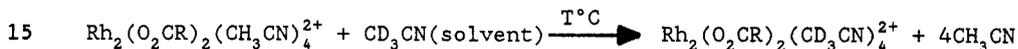


involving $\text{M}(\text{PR}_3)_4$ and $\text{M}(\text{PR}_3)_3$ complexes with free phosphines ($\text{M} = \text{Pd}$ or Pt).⁴⁹ The $\text{X}_3\text{M}=\text{MX}_3$ compounds may be viewed as coordinatively unsaturated and are substitutionally labile to associative, A , and associative-interchange, I_a , reactions.

There is reason to believe that dinuclear complexes containing M-M multiple bonds can be classified as substitutionally labile or inert based on their M-M M.O. configurations. The $\text{X}_3\text{M}=\text{MX}_3$ compounds, M-M $\sigma^2\pi^4$, have low lying empty metal based δ , δ^* and π^* orbitals and are thus labile to reactions involving associative or I_a processes. This is also true for M-M quadruply bonded complexes with M-M M.O. configuration $\sigma^2\pi^4\delta^2$. For example, $\text{Mo}_2(\text{O}_2\text{CR})_4$ complexes are labile to ligand exchange reactions, eq. 14,⁵⁰ though this is not rapid on the NMR time scale.



The solvated cation $\text{Mo}_2(\text{O}_2\text{CR})_2(\text{CH}_3\text{CN})_4^{2+}$ dissolves in CD_3CN at -46°C with rapid CD_3CN for CH_3CN exchange. By contrast the $\text{Rh}_2(\text{O}_2\text{CR})_4$ compounds are inert to ligand exchange of the type shown for molybdenum in eq. 14 and the solvated cation $\text{Rh}_2(\text{O}_2\text{CR})_2(\text{CH}_3\text{CN})_4^{2+}$ is indefinitely persistent with respect to CD_3CN for CH_3CN exchange in acetonitrile- d_3 at room temperature. From ^1H NMR studies of the $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$ exchange reaction, eq. 15, we find that $t_{1/2}$ for exchange is ca 4 hr at 100°C and that the activation parameters are $\Delta\text{H}^\ddagger = +33(1)$ kcal mol⁻¹ and $\Delta\text{S}^\ddagger = +11(3)$ eu.⁵⁰

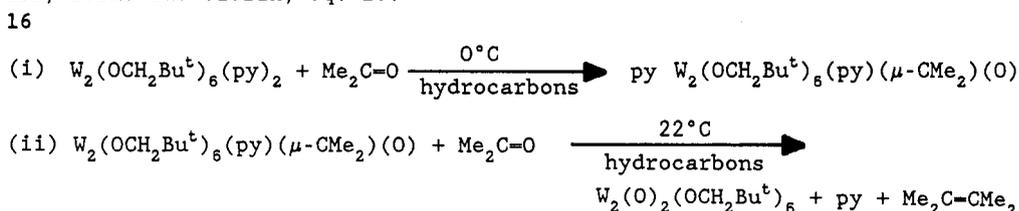


The M-M M.O. configuration of $\sigma^2\pi^4\delta^2\delta^*\pi^*\pi^*$ provides no metal based orbital (other than σ^* which is directed along the M-M axis) for nucleophilic attack. Thus the Rh_2^{4+} center is substitutionally inert (relative to M_2^{6+} and M_2^{4+} where $\text{M} = \text{Mo}, \text{W}$) and reacts via an I_a mechanism.

REDUCTIVE COUPLING OF KETONES/ALDEHYDES TO OLEFINS AT DITUNGSTEN CENTRES

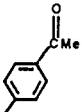
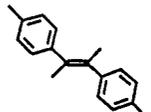
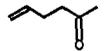
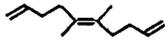
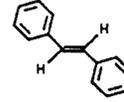
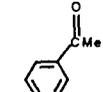
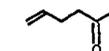
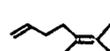
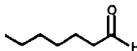
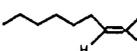
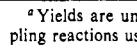
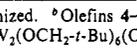
In 1984, we noted⁵¹ that $\text{W}_2(\text{OPr}^i)_6(\text{py})_2$ and acetone react to give $\text{W}_4(\text{O})_2(\text{OPr}^i)_{12}$, a compound of novel structure, and tetramethylethylene. However, it was not until 1989 when Jeff Klang initiated a thorough investigation of the reactions involving $\text{W}_2(\text{OR})_6$ compounds and ketones or aldehydes that we became aware of how this reductive coupling occurred. Initially we supposed that the reaction proceeded via a pinacolate intermediate and as such provided a molecular model for the McMurry⁵² reaction that employs reduced titanium halides. It was known from the work of Cotton, Walton and their coworkers⁵³ that pinicol coupling occurred in related reactions between W_2^{8+} centers and ketones.

Klang⁵⁴ showed that the reaction between $\text{W}_2(\text{OCH}_2\text{Bu}^t)_6(\text{py})_2$ and acetone in hydrocarbon solvents proceeds as a two step reaction. The first step occurs at ca 0°C and leads to an oxo- μ -propylidene complex and the second step, which occurs at room temperature, forms the olefin, eq. 16.⁵⁴



The two step process, eq. 16, allows for the selective cross coupling of ketones/aldehydes not heretofore possible. The products of some of these reactions are given in Table 1.

Table I. Alkenes Formed by Reductive Coupling or Cross-Coupling of Ketones/Aldehydes by $W_2(OCH_2-t-Bu)_6py_2^a$

aldehyde/ketone	olefin	yield ^a (%)
		51
		1
		21
		2
		3
		b
		b
		b

^a Yields are unoptimized. ^b Olefins 4-7 were formed by cross-coupling reactions using $W_2(OCH_2-t-Bu)_6(O)(CMe_2)(py)$

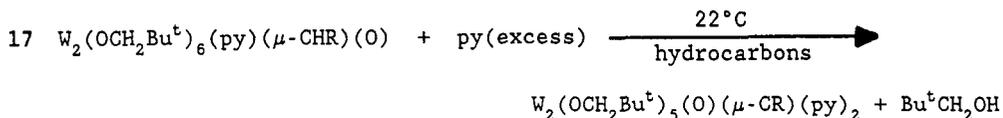
The low yields reported for some of the reactions given in Table 1 were the cause of some concern to me. As isolated yields (not yields determined by gc or NMR) there was room for physical loss of products during workup since these reactions were typically carried out on ca 500 mg of $W_2(CH_2Bu^t)_6(py)_2$ and workup involved destroying the tungsten complex in aqueous media and separating the organic compounds by chromatography.

Aron Sousa and Eric Lucas have investigated these reactions by a variety of NMR studies employing various ketones and aldehydes labelled at the ketonic carbon. Their findings are summarized as follows⁵⁵

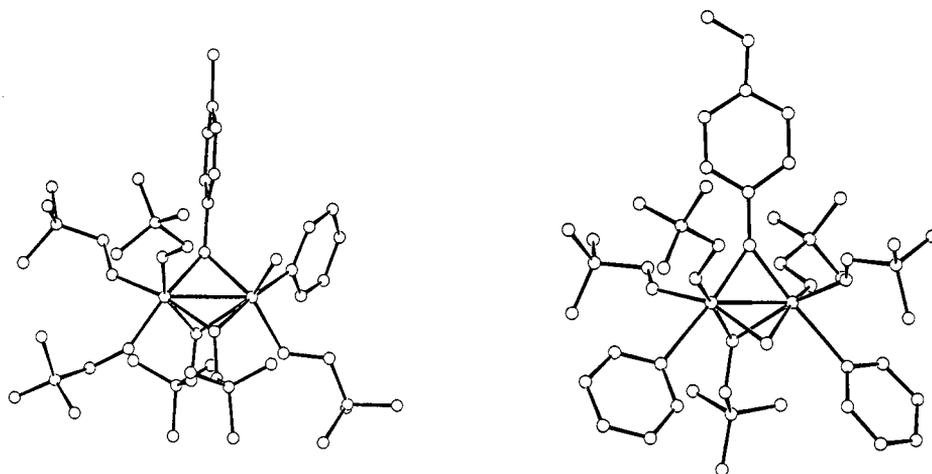
1. When the reaction between unligated $W_2(OCH_2Bu^t)_6$ and a ketone or aldehyde is carried out at low temperature, ca $-78^\circ C$, the only detectable ^{13}C labelled signal associated with the ketonic carbon is that of a $W_2(\mu-CRR')$ carbon (aside from that of the free ketone or aldehyde). By contrast the reaction between $W_2(OCH_2Bu^t)_6(py)_2$ and an aldehyde or ketone does not show any evidence for $W_2(\mu-CRR')$ formation until pyridine dissociation occurs at ca $-15^\circ C$.

This emphasizes that the rate of cleavage of the C=O bond in 16(i) is limited by pyridine dissociation. In the reaction involving $W_2(OCH_2Bu^t)_6$, which is coordinatively unsaturated, uptake of the ketone or aldehyde is rapid at $-78^\circ C$ and the C=O bond cleavage is so fast that no simple 1:1 adduct can be detected.

2. While the first step in the reaction, eq. 16 (i) appears to be clean and straight forward for aldehydes and ketones, the second step shows complicating side reactions. For example, μ -alkylidenes and μ -arylidene derived from aldehydes react with excess pyridine to give alkylidynes, eq. 17.



The structural characterization of the μ -tolylidene complex, $W_2(OCH_2Bu^t)_6(py)-(C(H)C_6H_4-p-Me)(O)$ and that of the μ -anisylidyne complex $W_2(OCH_2Bu^t)_5(py)_2(\mu-C_6H_4-p-OMe)(\mu-O)$ are shown in Fig. 4.⁵⁶

Fig. 4: $W_2(ONp)_6(O)(py)(\mu-CHAr)$

W-W	2.655
W-C	2.147, 2.164

 $W_2(ONp)_5(\mu-O)(py)_2(\mu-CAr)$

W-W	2.451
W-C	1.971, 1.990

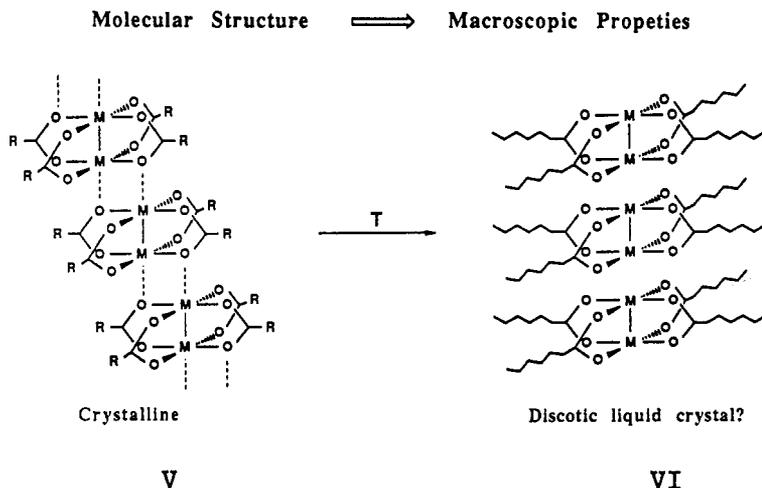
3. Lucas and Sousa⁵⁵ have followed the reactions of the labelled benzylidene compound $W_2(OCH_2Bu^t)_6(py)(\mu-^{13}C(H)Ph)(O)$ with unlabelled PhCHO and shown that the μ -benzylidene carbon label is found exclusively in the olefinic resonance of stilbene. When unlabelled $W_2(OCH_2Bu^t)_6(py)(\mu-C(H)Ph)(O)$ is allowed to react with Ph¹³CHO, there are (in addition to the olefinic ¹³C signal of stilbene) other ¹³C signals derived from Ph¹³CHO - probably arising from the diolate group $WO_2C_2H_2Ph_2$.

Further studies are planned to delineate the details of this interesting reaction sequence and to explore its utility in selective organic transformations. What is already clear is that the dinuclear center affords the opportunity of combining two well known reactions in the mononuclear chemistry of the early transition elements, (1) The reductive cleavage of a ketonic C=O group to oxo and alkylidene ligands⁵⁷ and (2) the metathesis reaction between a high valent metal-alkylidene and a ketone to give a metal-oxo group and an olefin.⁵⁸

M-M MULTIPLE BONDS IN ORDERED ASSEMBLIES

The macromolecular chemistry of M-M multiple bonds remains to be discovered. There is the potential for the synthesis of new materials with interesting optical, electronic and magnetic properties. As a starting point in this area we have begun to investigate the synthesis and properties of materials derived from dimetal tetracarboxylates, $M_2(O_2CR)_4$ compounds. These are known for a variety of metals with varying M-M M.O. configurations, e.g. quadruple bonds $\sigma^2\pi^4\delta^2$ for M = Mo, double bonds, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ for M = Ru.¹ The M_2 center is redox active and the ease of oxidation or reduction can be tuned by the choice of substituents R and the metal. There is also reason to believe that charge transfer can be photochemically induced to an acceptor ligand in a similar way to that which is commonly observed for a Mt_{2g}^6 -to- $L\pi^*$ charge transfer in mononuclear transition metal chemistry.

In the solid state unligated $M_2(O_2CR)_4$ compounds form ladder structures wherein an oxygen atom of a carboxylate ligand from one dinuclear center binds axially to the M_2 unit of its neighbor, as in V.⁵⁹ It seemed reasonable to suppose, that for certain substituents R, compounds of this type might show thermotropic discotic liquid crystalline phases wherein these axial O-to-M interactions were broken, VI. There is an obvious analogy with the stacking of square-planar d^8 metal complexes that have been shown to exhibit discotic behavior when appropriate organic substituents are present.⁶⁰

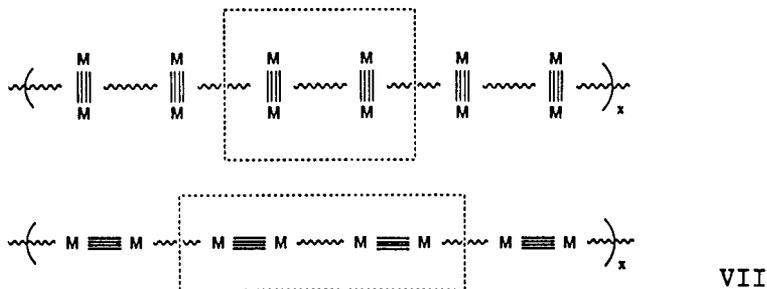


Roger Cayton prepared a series of $\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CH}_3)_4$ compounds and examined these by DSC and microscopy. Under a N_2 atmosphere the compounds where $n = 2$ to 10 show reversible behavior, involving crystalline, discotic liquid-crystalline and isotropic liquid phases as a function of temperature.⁶¹

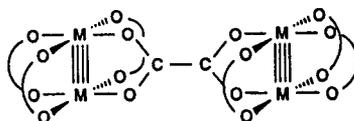
French workers had previously found that $\text{Cu}_2(\text{O}_2\text{CR})_4$ compounds⁶² and the laureate ($n = 6$) and stearate ($n = 16$) for Rh_2^{4+} showed⁶³ a crystalline to discotic mesophase transition. They also determined⁶³ by X-ray crystallography the intercolumnar separations for the various values of n .

One notable difference for the $\text{Rh}_2(\text{O}_2\text{CR})_4$ compounds is that the liquid crystalline phase persisted to higher temperature than for the Mo_2 analogues. Indeed, the $\text{Rh}_2(\text{O}_2\text{CR})_4$ compounds decomposed $>300^\circ\text{C}$ before melting. We were puzzled by these differences since it did not fit with the model of the crystalline = discotic phase change based on $\text{V} = \text{VI}$. With the assistance of Jodi Wesemann, Roger Cayton examined various octanoates of the related Cr_2^{4+} , W_2^{4+} and Ru_2^{4+} ions. The tungsten compound shows only a crystal-to-isotropic liquid phase change whereas the Cr_2^{4+} and Ru_2^{4+} containing compounds show only the crystal and liquid crystal phases up to their decomposition temperatures, ca $>270^\circ\text{C}$. It is known that the axial binding to the dinuclear center follows the order $\text{Cr} \gg \text{Mo} > \text{W}$ and also $\text{Rh} > \text{Mo}$.^{1,64} Thus it appears that it is the intermolecular $[-\text{M}_2-\text{O}-\text{M}_2-\text{O}-]$ interactions that are responsible for the order in the discotic liquid crystalline phase.

Roger Cayton has also initiated a program aimed at the synthesis of 1-D polymers incorporating multiple bonds between metal atoms. Two limiting types of polymers are envisaged wherein the M_2 units are united covalently by ligands so that the M-M axis is either perpendicular or parallel to the axis of polymer propagation, as shown in VII below.

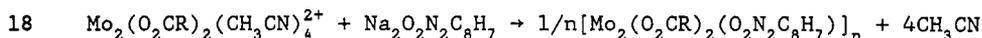


Again employing the $\text{M}_2(\text{O}_2\text{CR})_4$ compounds as the inorganic polymer building block, the polymers can be prepared by condensation reactions with one equivalent of a dicarboxylic acid. In reactions between $\text{M}_2(\text{O}_2\text{CR})_4$ and one half equivalent of $\text{HO}_2\text{C}-\text{R}'-\text{CO}_2\text{H}$ covalently linked dimers can be prepared and provide models for the subunits within the polymers VII. If the dicarboxylic acid is oxalic acid or para- $\text{C}_6\text{F}_4(\text{COOH})_2$ then the M_2 units are linked in the perpendicular sense, VIII.⁶⁵

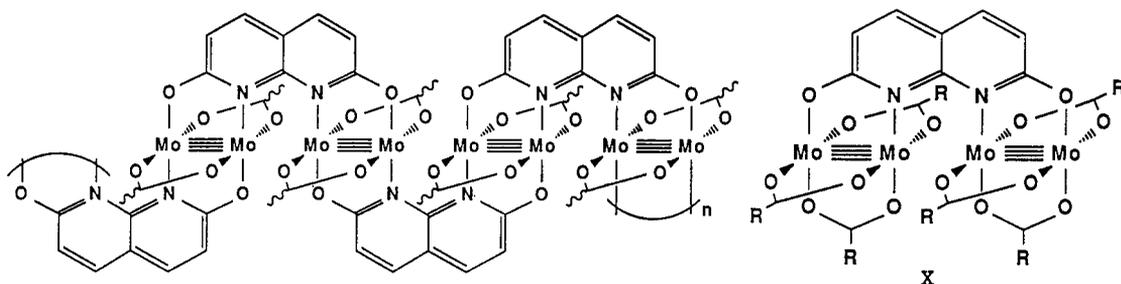


VIII

The use of 1,8-anthracene-dicarboxylic acid aligns the M_2 units, at least approximately, in the parallel mode with respect to the polymer chain.⁶⁵ Another example of a parallel polymer is based on the use of a ligand derived from 2,7-dihydroxy-1,8-naphthyridine. See eq. 18 and IX below.⁶⁶



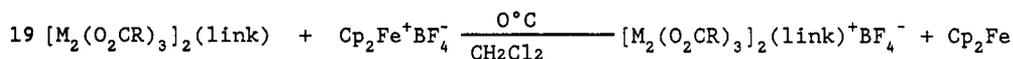
Solubility in toluene and THF can be imparted to the polymer by the use of long chain carboxylates, e.g. dodecanoates. Molecular studies have been carried out on the covalently linked dimers $[Mo_2(O_2CBut)_3]_2O_2N_2C_8H_7$, X.⁶⁶



IX

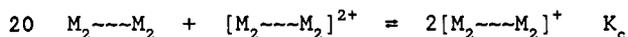
It should be mentioned that we have as yet no X-ray structure on X and, although we are confident of our formulation of this as a parallel linked dimer, we do not wish to imply by our drawing X that the M-M-M-M axis is strictly linear. It is most likely to be ruffled as in, for example, some of the Pt_4 chain compounds prepared by Lippard *et al.*⁶⁷ as models for the Pt-blues.

We have characterized these covalently linked dimers of dimers by a number of physical and spectroscopic techniques along with their oxidized radical cations.^{65,66} The latter are generally accessible from the reaction between the neutral dimer of dimers and ferrocinium salts, eq. 19.



In the oxalate and naphthyridine bridged compounds the dinuclear centers are strongly coupled. The extent of the coupling can be determined from electrochemical studies where the comproportionation constant for the equilibrium reaction shown in eq. 20 is estimated from the separation between the 1st and 2nd oxidation potentials of the

covalently linked dimers:⁶⁸ $K_c = \exp\left(\frac{\Delta E_{1/2}}{25.69}\right)$.



The values of K_c for $[M_2(O_2CBut)_3]_2(\mu\text{-oxalate})$ are ca 10^6 and 10^{12} for $M = Mo$ and W , respectively. To put these into a more established context, the electronic coupling is comparable to that in the Creutz-Taube ion, $(H_3N)_5Ru\text{-pyrazine-Ru}(NH_3)_5^{2+/3+}$ and its osmium analogue⁶⁹ for molybdenum and tungsten, respectively. The greater coupling for the 3rd row transition metal ions arises from their relative orbital energies and more favorable overlap with the ligand π^* system.

Roger Cayton⁶⁶ has carried out Fenske-Hall M.O. calculations on $[M_2(O_2CH)_3]_2$ (μ -oxalate) molecules with atomic parameters taken from a typical $M_2(O_2CR)_4$ compound linked by a planar oxalate group. The origin of the electronic mixing between the two dinuclear centers is clearly seen to arise from the M-M δ and $C_2O_4^{2-}$ HOMO-LUMO interactions. See Fig. 5.

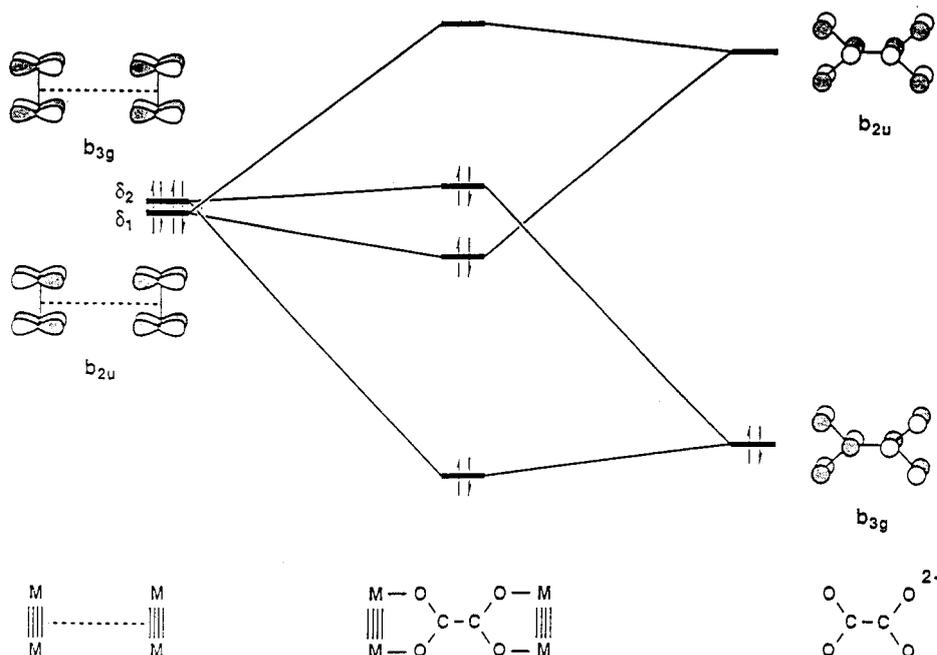


Fig. 5 Interaction of μ - C_2O_4 π Orbitals with the M-M δ Orbitals

From the orbital interaction (Fig. 5) diagram we can anticipate the growth of the δ -oxalate band in the perpendicular polymer.

The oxalate bridge dimers are red (M = Mo) and purple (M = W) whereas the $M_2(O_2CR)_4$ compounds are yellow. The lowest energy electronic transition in the dimer of dimers can be seen to arise from a M-M δ to $C_2O_4^{2-}$ π^* transition (Fig. 5). The purple color for M = W is an indication of the relatively higher energy δ orbitals. The $W_2(\mu$ -oxalate) polymer is black.

CONCLUDING REMARKS

Compounds with multiple bonds between metal atoms form an important class of inorganic complexes within the greater field of modern coordination chemistry. Their chemistry has thus far proved rewarding in terms of developing concepts in bonding and spectroscopy. Their reactions are sometimes quite different from those of mononuclear complexes and this offers promise for the development of new reagents for synthesis. Similarly the tuneability of M-M M.O. configuration suggests that a macromolecular chemistry based on dinuclear subunits should be an interesting field for future endeavor.

Acknowledgements

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