

## Organometallic chemistry of $d^3-d^3$ dimolybdenum and ditungsten

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### Introduction

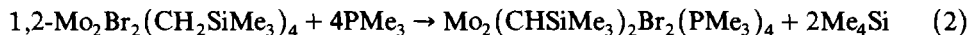
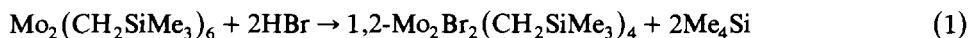
A synthetic organometallic chemist is in certain ways similar to a geographical explorer of the past. In order to finance a foray into new chemistry the appropriate finances must be secured and to secure these the prospects for the discovery of scientific rewards must seem good, at least as judged by the peer review system and the priorities of funding agencies. Herein lies a common irony. Only the value of a past discovery can be assessed with any reasonable accuracy. A truly new discovery provides merely the opportunity for new investment and potential future reward. So too for the explorer. To return with gold and silver was a success which could be immediately measured by weight, while the discovery of a new mineral or land could at best be viewed with optimism. The successful exploration of the organometallic chemistry of the later transition elements during the 1960's spurred several young investigators to the west and the south in the Periodic Table. The success of these investigations became manifest during the 1970's and '80's as the organometallic chemistry of the early transition elements, the lanthanides and actinides came to fruition. Much of the success in these areas came from the use of  $\eta^5$ -cyclopentadienyl ligands as spectator groups. Indeed in this area of the Periodic Table the  $\eta^5$ -C<sub>5</sub>R<sub>5</sub> class of ligands has achieved a role paralleled only by the use of tertiary phosphines for the later transition elements.

As an inorganic chemist trained in the 1960's, I was attracted to the notion that dinuclear compounds of the group 6 transition elements with M–M multiple bonds might provide inorganic templates that could, in part, mimic the chemistry of the later transition elements. Could the general concepts of the 18 electron rule, oxidative-additions, reductive eliminations, migratory insertions, oxidative couplings, etc. [1] that link  $d^8$ -ML<sub>4</sub> and  $d^6$ -ML<sub>6</sub> species be extended to compounds containing M≡M and M<sup>4</sup>–M bonds of valence configuration  $\sigma^2\pi^4$  and  $\sigma^2\pi^4\delta^2$ , respectively? Might not an Mo<sub>2</sub> center serve as a cheap alternative to mononuclear rhodium? Two synthetic strategies were immediately appealing: (1) To investigate the reactions of dinuclear compounds wherein the metal–carbon bonds were introduced by metathetic reactions and were thus present in the “starting material”. (2) To use a coordinatively unsaturated dinuclear compound as a template for

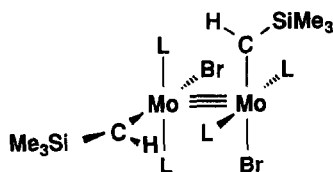
organometallic chemistry by substrate uptake and activation. Both strategies have been scientifically rewarding, though it is clear that neither  $\text{Mo}_2$  nor  $\text{W}_2$  is a substitute for mononuclear Rh or Pt. This account summarizes some of the pertinent findings and ideas that have emerged from these investigations.

### $\text{M}_2\text{X}_6$ compounds containing alkyl ligands

Compounds containing quadruple bonds between molybdenum atoms were amongst the early examples of M–M multiply bonded compounds and those involving tungsten atoms were discovered subsequently [2]. The first M–M triply bonded compounds  $\text{M}_2\text{X}_6$  were prepared by Wilkinson and his coworkers [3,4] from metathetic reactions involving molybdenum and tungsten halides and organolithium or -magnesium reagents involving the  $\beta$ -hydrogen stabilized  $\text{Me}_3\text{SiCH}_2$  ligand. Little reaction chemistry has been developed around these compounds. They are sterically crowded and access to the dinuclear center is limited to all but small molecules such as CO. The tungsten compounds are also formed in conjunction with other organometallic species such as  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  and  $(\text{Me}_3\text{SiCH}_2)_4\text{W}_2(\mu\text{-CSiMe}_3)_2$  which have an interesting chemistry of their own [5]. If two  $\text{Me}_3\text{SiCH}_2$  ligands are replaced by bromide ligands, Eq. 1, a more reactive compound  $1,2\text{-Mo}_2\text{Br}_2(\text{CH}_2\text{SiMe}_3)_4$  is obtained [6]. The latter is reactive toward metathetic reactions involving Br exchange for alkoxide or amide and also towards Lewis base association. Addition of  $\text{PMe}_3$  induces an  $\alpha$ -CH activation at the dinuclear center leading to elimination of  $\text{Me}_4\text{Si}$ , Eq. 2 [7].



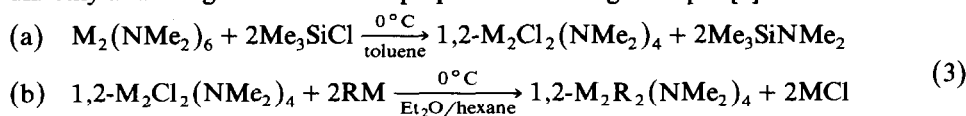
The structure of the bis trimethylsilylmethylidene is shown schematically in A.



A

The bonding in  $\text{Mo}_2\text{Br}_2(\text{CHSiMe}_3)_2(\text{PMe}_3)_4$  may be viewed in terms of two  $d^3\text{-Mo}^{\text{III}}$  fragments that form a M–M triple bond of configuration  $\sigma^2\pi^4$  by the interaction of metal  $d_{z^2}(\sigma)$  and  $d_{xz}, d_{yz}(\pi)$  orbitals. With four ligands lying roughly in a plane (the  $xy$  plane) only one metal  $d$  orbital is available for  $\pi$ -bonding to the  $\text{Me}_3\text{SiCH}$  ligand. This requires that the plane of the  $\text{Mo-C(H)Si}$  atoms lie along the M–M axis as is indeed observed.

A large number of alkyl, benzyl and aryl dinuclear compounds with attendant dimethylamido ligands have been prepared according to Eq. 3 [8].



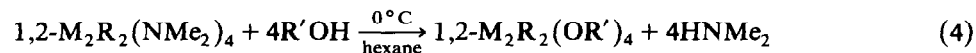
[R = alkyl, allyl, cyclopentadienyl, indenyl, benzyl, aryl; M' = Li or MgCl]

In solution and in the solid state these compounds adopt ethane-like geometries and occur in *gauche*- and *anti*-rotamers. Again the  $d^3-d^3$  center allows for the formation of M–M triple bonds of configuration  $\sigma^2\pi^4$  and here the two dimethylamido ligands  $\pi$ -donate to two metal  $d$  orbitals in the  $xy$  plane, namely the  $x^2-y^2$  and  $xy$  orbitals. This restricts the M–NC<sub>2</sub> planes to be co-linear with the M–M axis as noted in **A** for the methyldene ligand. Barriers to M–N bond rotation have been determined from VT NMR studies and fall in the range 10–14 kcal mol<sup>-1</sup>.

As a result of the M–M triple bond and Me<sub>2</sub>N-to-M  $\pi$  donation the metal atoms in M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds achieve a 16 valence shell of electrons. One might anticipate that these compounds should behave as coordinatively unsaturated species and be susceptible to forming *agostic* M–HC interactions [9] with the attendant alkyl or NMe<sub>2</sub> ligands. This is not so, however. M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds where the R group contains  $\beta$ -H atoms show considerable thermal persistence. They may be sublimed at 80–110 °C, 10<sup>-2</sup> Torr and heated in solution to 80–100 °C for several hours with little decomposition. From the description of the bonding noted above it is evident that the one vacant metal atomic orbital is a  $p_z$  orbital (or  $d_{z^2}-p_z$  hybrid) that lies along the M–M axis. Presumably a CH-to-M interaction in this position is not favored because of the high *trans*-influence/*trans*-effect of the M–M triple bond. It is a general phenomenon for (M≡M)<sup>6+</sup>-compounds: axial ligation (along the M–M axis) is not favored relative to ligation in the  $xy$  plane (with the one exception of **B** noted later).

Very recently the compound W<sub>2</sub>(c-Pentyl)<sub>3</sub>(NMe<sub>2</sub>)<sub>3</sub> has been structurally characterized [10]. This has only three dimethylamido ligands so one metal center has two *cyclo*-pentyl ligands and one dimethylamide. With the M–M triple bond and three metal ligand  $\sigma$  bonds there are two orbitals in the  $xy$  plane available for  $\pi$ -bonding. For (Me<sub>2</sub>N)(c-Pentyl)<sub>2</sub>W≡W(c-Pentyl)(NMe<sub>2</sub>)<sub>2</sub> one tungsten has two NMe<sub>2</sub> ligands and is therefore analogous to those in 1,2-M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds. However, the (Me<sub>2</sub>N)(c-Pentyl)<sub>2</sub>W center has a vacant orbital in the  $xy$  plane and this is evidently an active site: one of the cyclopentyl ligands behaves as a chelate ligand forming both a W–C  $\sigma$  bond, 2.12 Å and a CH-to-W bond, W–C $\beta$  = 2.56 Å.

The dimethylamido groups in M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds are labile to alcoholysis reactions and kinetically (but not thermodynamically) it is favorable to replace the NMe<sub>2</sub> groups in preference to the R groups, Eq. 4 [11].



The M–C bonds in the M<sub>2</sub>R<sub>2</sub>(OR')<sub>4</sub> compounds are susceptible to protonolysis and in the presence of R'OH further reaction to give M<sub>2</sub>(OR')<sub>6</sub> compounds can occur with the elimination of RH. This latter reaction is suppressed by steric congestion at the metal and so a judicious balancing of bulk between R and R' is required, e.g. for R = Me, R' must be very bulky as in *t*-Bu but for R = CH<sub>2</sub>-*t*-Bu then R' may be Et. The sterically extremely demanding disyl ligand (Me<sub>3</sub>Si)<sub>2</sub>CH completely suppresses alcoholysis reactions at room temperature [12]. There are complicating reactions that may occur during alcoholysis, Eq. 4, as will be described later.

The compounds of formula M<sub>2</sub>R<sub>2</sub>(OR')<sub>4</sub>, like their parent dimethylamides M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>, are yellow-orange, hydrocarbon-soluble, diamagnetic, air-sensitive,

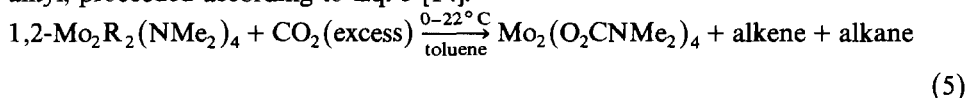
crystalline solids. The  $M_2R_2(OR')_4$  compounds are less thermally robust, and purification by crystallization is preferable to sublimation, which occurs with extensive decomposition. The greater thermal persistence of the  $NMe_2$  supported compounds is probably a consequence of the  $\pi$ -donating order  $Me_2N > OR'$ , though the mechanism of the thermal decompositions of these compounds has not been investigated.

In solution VT NMR studies reveal restricted rotations about the M–M triple bond only for very bulky combinations of R and R', e.g. for R =  $CH_2$ -t-Bu and R' = i-Pr at low temperatures *anti* and *gauche* rotamers are seen [11].

### Reductive-elimination by alkyl group disproportionation

Compounds of formula  $1,2-M_2R_2X_4$  ( $M \equiv M$ ) seemed ideal candidates for reductive elimination to  $M_2X_4(M^4-M)$  compounds by alkyl group disproportionation. This would demonstrate an analogy with mononuclear  $d^6$ - $ML_6$  to  $d^8$ - $ML_4$  transformations. From what was known about the ease of mononuclear reductive elimination [13], it was clear that the inorganic residue  $M_2X_4$  should be thermodynamically stable. A logical synthetic approach seemed to be to convert  $M_2R_2(NMe_2)_4$  compounds to  $M_2(O_2CX)_4$  compounds, of which the carboxylates (X = alkyl or aryl) were well known, several having been structurally characterized [2].

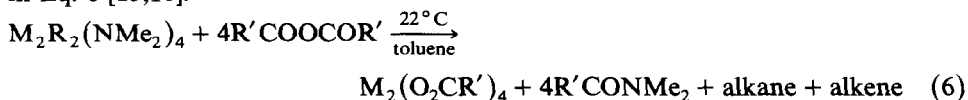
Addition of  $CO_2$  to the  $Mo_2R_2(NMe_2)_4$  compounds where R = a  $\beta$ -H containing alkyl, proceeded according to Eq. 5 [14].



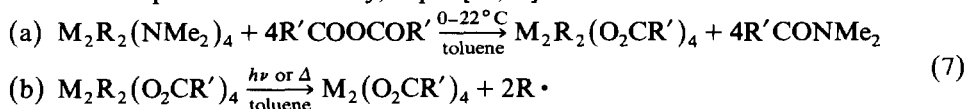
Labelling studies showed that this reaction was intra-molecular and involved the formal transference of a  $\beta$ -H atom from one alkyl ligand to the  $\alpha$ -C atom of the other. This was a very clean reaction, as determined from the use of R =  $CH_2CD_3$  which gave only  $CH_2DCD_3$  and  $CH_2=CD_2$  [14].

The reaction 5 was not applicable for tungsten, and in this and other reactions tungsten exhibits a reluctance to undergo reductive elimination relative to molybdenum:  $d^3-d^3 M^{III}-M^{III} \rightarrow d^4-d^4 M^{II}-M^{II}$ . As we shall see later the converse is also true. Oxidative addition to the  $d^3-d^3 W^{III}-W^{III}$  center is more facile. In this regard dinuclear chemistry parallels the mononuclear chemistry of the 2nd and 3rd row transition elements.

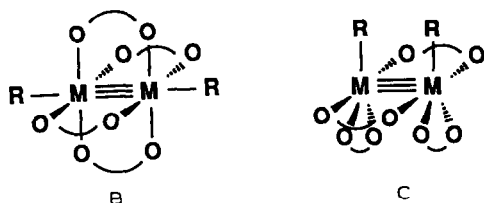
The formation of  $W_2(O_2CR)_4$  compounds can be achieved by the reaction shown in Eq. 6 [15,16].



When  $R_2$  is  $(CH_2)_4$ , i.e. the dimetal center is bridged by four methylene groups to give a 1,2-dimetallacyclohex-1,2-yne, two equivalents of ethylene are eliminated [17]. In the case of R = benzyl, aryl and neopentyl, i.e. groups lacking  $\beta$ -H atoms, the reaction proceeds differently, Eq. 7 [16,17].



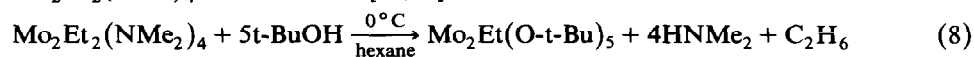
The dialkyltetracarboxylates adopt one of two geometries depicted by **B** and **C** below.



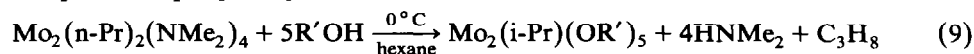
In **B** there is axial ligation of the R groups which generates a M–M triple bond of valence configuration  $\pi^4\delta^2$ . The evidence for the filled  $\delta$  orbital being the HOMO is seen in electronic spectral data, photoelectron spectroscopy and electrochemical studies [16]. In **C** the M–M triple bond is of the more conventional form  $\sigma^2\pi^4$ . In solution an equilibrium between the geometric isomers **B** and **C** is seen for  $M = W$ ,  $R = \text{CH}_2\text{Ph}$  and  $R' = \text{Et}$ . It seems likely that this is general for  $W_2R_2(O_2CR')_4$  compounds and an orbital analysis of a Walsh diagram indicates that the interconversion of isomers **B** and **C** is a symmetry allowed process [18].

The thermally and photochemically induced reductive elimination, reaction 7b, occurs more readily for  $M = \text{Mo}$  than  $M = W$  consistent with the general trend in metal ligand bond strengths that lie in the order 3rd row > 2nd row for the transition metals. Indeed it is difficult to isolate  $\text{Mo}_2R_2(O_2CR')_4$  compounds due to facile reductive elimination by Mo–C bond homolysis when  $R =$  a non- $\beta\text{H}$  stabilized alkyl. For tungsten on the other hand, it is possible to obtain  $\beta$ -hydrogen containing compounds of formula  $W_2(i\text{-Bu})_2(O_2CR')_4$ . Presumably the latter are stabilized by the presence of only one  $\beta\text{-H}$  atom and by conformational preferences that do not favor the planar M–C–C–H four center transition state necessary for  $\beta\text{-H}$  abstraction. The elimination of isobutane and isobutylene is achieved at room temperature, however, to yield  $W_2(O_2CR')_4$  compounds.

From the above it should be understood that the detailed mechanism of the reductive eliminations are not yet understood and further studies are clearly warranted. There are, in fact, numerous examples wherein CH activation at these dinuclear centers occur and in many instances would have gone unnoticed but for a labelling study or an unexpected isomerization. For example, the reaction between 1,2- $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  and  $t\text{-BuOH}$  proceeds according to the stoichiometry shown in Eq. 8. Even when only 4 equiv. of  $t\text{-BuOH}$  are employed the compound  $\text{Mo}_2\text{Et}_2(\text{OBu}^t)_4$  is not formed [11,19].



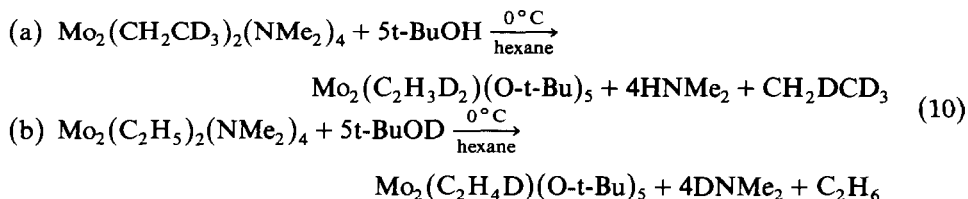
In the reaction between  $\text{Mo}_2(\text{n-Pr})_2(\text{NMe}_2)_4$  and  $R'\text{OH}$  a mono isopropyl derivative is the kinetic product and this only slowly isomerizes to the  $n$ -propyl compound, Eq. 9 [11,19].



[ $R' = t\text{-Bu}$  and  $i\text{-Pr}$ ]

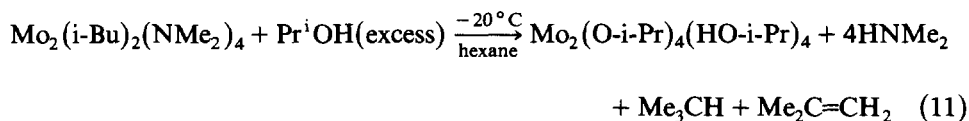
Labelling studies revealed that the liberated alkane in reaction 8 was not formed by protolysis but rather by a  $\beta\text{-H}$  to  $\text{C}_\alpha$  transfer, Eq. 10a, and that the resultant

alkyl ligand was formed from the elements of alkene and the hydroxyl hydrogen of the alcohol, Eq. 10b.



In the  $\text{Mo}_2(\text{C}_2\text{H}_4\text{D})(\text{O-t-Bu})_5$  formed in Eq. 10b the D atom is initially on the C $\beta$  carbon of the ethyl ligand but with time is scrambled over both  $\alpha$  and  $\beta$  carbon atoms.

The reactions 10a and 10b suggest a complex reaction sequence involving t-BuO for  $\text{NMe}_2$  exchange and reductive elimination/oxidation addition. Again the detailed reaction pathway is not understood but the notion of a "reduced"  $\text{Mo}_2^{\text{II,II}}$  reactive intermediate gains support from the finding that alcoholysis reactions employing the isobutyl ligand lead to  $d^4$ - $d^4$  compounds with elimination of isobutylene and isobutane, Eq. 11 [20].

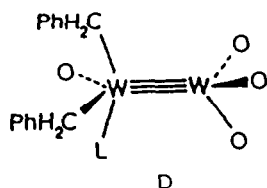


The compound  $\text{Mo}_2(\text{O-i-Pr})_4(\text{HO-i-Pr})_4$  contains an eclipsed  $\text{Mo}_2\text{O}_8$  skeleton with O-H $\cdots$ O bonds spanning the Mo<sup>4</sup>-Mo bond. This compound is extremely reactive. Addition of neutral ligands yields  $\text{Mo}_2(\text{O-i-Pr})_4\text{L}_4$  compounds where L = pyridine or  $\text{PMe}_3$ , and addition of ethylene gives initially  $\text{Mo}_2\text{Et}(\text{O-i-Pr})_5$  which in the presence of the excess i-PrOH reacts further to give  $\text{Mo}_2(\text{O-i-Pr})_6$  and ethane by protolysis. Evidently in the reaction involving  $\text{Mo}_2(\text{i-Bu})_2(\text{NMe}_2)_4$  and i-PrOH, the bulky isobutylene ligand competes inefficiently for coordination to the  $d^4$ - $d^4$  Mo<sup>II</sup>-Mo<sup>II</sup> center.

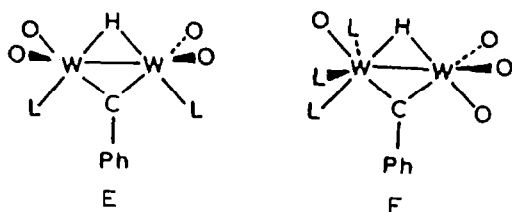
### Alkyl group transfer and $\alpha$ -CH activation

In ethane-like  $\text{M}_2\text{X}_2\text{Y}_4$  compounds it is known that alkyl group transfer is kinetically a slow process. For example, 1,2 and 1,1- $\text{Mo}_2(\text{NMe}_2)_2(\text{CH}_2\text{SiMe}_3)_4$  isomers do not interconvert either in the solid state or in solution ( $T < 80^\circ\text{C}$ ) [6,21]. However, when the coordination number at the metal increases it seems that bridge formation becomes more facile. This could represent an important first step leading to C-H bond activation in the reactions previously described.

The addition of  $\text{PMe}_3$  (2 equiv.) to a hydrocarbon solution of 1,2- $\text{Mo}_2(\text{CH}_2\text{Ph})_2(\text{O-i-Pr})_4$  yields, at low temperatures, a bis-ligated compound  $\text{Mo}_2(\text{CH}_2\text{Ph})_2(\text{O-i-Pr})_4\text{L}_2$  (L =  $\text{PMe}_3$ ) which upon warming leads to an isolatable crystalline compound of formula  $\text{Mo}_2(\text{CH}_2\text{Ph})_2(\text{O-i-Pr})_4\text{L}$  and structure D [22]. One Mo center is ligated by three O-i-Pr ligands, the other by two benzyl ligands, one alkoxide and one  $\text{PMe}_3$  ligand.

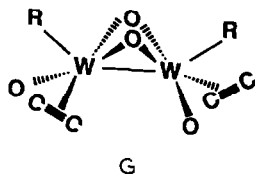


The analogous reaction involving  $W_2(CH_2Ph)_2(O-i-Pr)_4$  takes an entirely different course, though at low temperature the formation of a symmetrical adduct is observed,  $W_2(CH_2Ph)_2(O-i-Pr)_4L_2$ . Upon warming to room temperature phosphine dissociation occurs and toluene (1 equiv.) is eliminated. The hydrido benzyldiene  $W_2(H)(\mu-CPh)(O-i-Pr)_4L_2$  of structure E is the thermodynamic product though a tris-ligated hydridobenzyldiene, F, is the kinetic product [23].

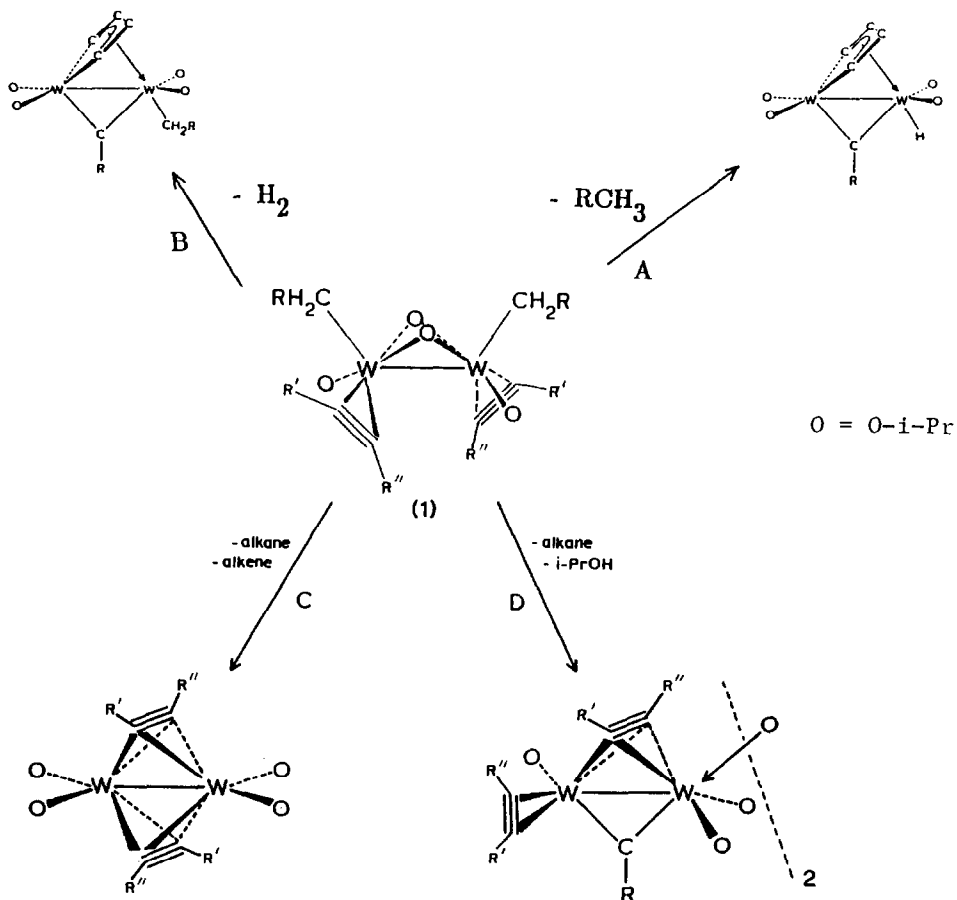


It seems likely that a phosphine promoted benzyl migration facilitates the  $\alpha$ -CH activation process. If  $\alpha$ -CH activation at a  $[W(CH_2Ph)_2(O-i-Pr)L]$  center occurred to give  $W(=CHPh)(O-i-Pr)L$ , the product could be obtained by oxidative addition of the  $W=CHPh$  group across the  $W\equiv W$  bond. Again an analogy is seen with the mononuclear chemistry of  $W(CH_2CMe_3)_3(\equiv C-t-Bu)$  which with neat  $PMe_3$  and upon heating yielded, by  $\alpha$ -CH activation, the first example of a compound containing an alkyl, an alkylidene and an alkylidyne ligand  $W(CH_2-t-Bu)(=CH-t-Bu)(\equiv C-t-Bu)(PMe_3)_2$  [24].

In another study the reactions between  $1,2-W_2R_2(O-i-Pr)_4$  compounds and alkynes were examined [25]. Again subtle factors associated with the bulkiness of the groups were important. When  $R = CH_2-t-Bu$  reactions involving  $MeC\equiv CMe$  or  $EtC\equiv CEt$  gave alkylidyne complexes  $[(i-PrO)_2(t-BuCH_2)W\equiv CR']_2$  where  $R' = Me$  or  $Et$  but for less sterically demanding R, e.g.  $R = Ph, CH_2Ph, i-Pr$ , the initial products were bisalkyne adducts  $W_2(CH_2R)_2(O-i-Pr)_4(\eta^2-C_2R'_2)_2$  where  $R' = Me$  or  $Et$  of structural type G.



The bis-alkyne adducts, however, react further at ambient conditions to give by  $\alpha$ -CH activation alkylidyne-hydrides  $W_2(\mu-CR)(\mu-C_4R'_4)(H)(O-i-Pr)_4$  when the alkyl ligand lacks  $\beta$ -H atoms. There is a minor product derived from loss of  $H_2$ , namely an alkyl-alkylidyne  $W_2(\mu-CR)(\mu-C_4R'_4)(CH_2R)(O-i-Pr)_4$ . When the attendant ligands contain  $\beta$ -H atoms the major products are the bis- $\mu$ -alkyne adducts  $W_2(\mu-$



Scheme 1

$C_2R'_2)_2(O-i-Pr)_4$ , derived from formal reductive elimination of alkane and alkene. However,  $\alpha$ -CH activation competes with  $\beta$ -CH activation, and the  $\alpha$ -CH activation process leads, by elimination of alkane and alcohol, to alkyne-alkyldiene complexes,  $[W_2(\mu-CR)(\mu-C_2R'_2)(O-i-Pr)_3(\eta^2-C_2R'_2)]_2$ . These reactions are summarized in Scheme 1 and plausible reaction pathways have been discussed in the light of various kinetic and labelling studies. The potentially important role of alkyl group migration between the two tungsten centers is underscored by the low temperature isolation of a 1,1-dimethyl derivative  $W_2Me_2(O-t-Bu)_4(\mu-C_2Me_2)_4(py)$  formed in the reaction between  $1,2-W_2Me_2(O-t-Bu)_4(py)_2$  and  $MeC\equiv CMe$  in pentane solutions at or below  $0^\circ C$  [25].

### $M_2(OR)_6$ compounds as templates

The dinuclear  $d^3-d^3$  center in an  $M_2X_6$  compound offers a redox active and coordinatively unsaturated template for substrate activation. It offers an entry point to organometallic chemistry akin to that of a  $d^{10}-ML_n$  compound where  $M = Ni, Pd, Pt$  and  $L =$  tertiary phosphine and  $n = 2$  or  $3$ . The restrictions are based on



steric factors, orbital energetics and symmetry. Alkoxides provide a particularly good class of ancillary ligands for the  $(M\equiv M)^{6+}$  center [26]. The selection of a given RO ligand can influence solubility, steric pressure at the metal center and the frontier orbital energies. The  $d^3$ - $M(OR)_3$  fragment is isolobal with  $d^9$ - $Co(CO)_3$  and  $d^5$ - $CpM(CO)_2$ , where  $M = Mo$  or  $W$ , which in turn are isolobal with CR [27]. The hypothetical molecule  $Co_2(CO)_6$  and the organometallic compounds  $Cp_2M_2(CO)_4$  ( $M = Mo$  or  $W$ ) and the alkoxides  $M_2(OR)_6$  are all related in having M–M triple bonds. The reactivity of the groups have some similarities but also several differences. For example, addition of two neutral ligands to  $Co_2(CO)_6$  or  $Cp_2M_2(CO)_4$  results in formation of M–M single bonds in compliance with the 18 electron rule. The  $Co(CO)_3L$  and  $CpM(CO)_2L$  fragments are 17 electron fragments and their frontier orbitals are isolobal with  $CH_3\cdot$  or  $H\cdot$ . Addition of neutral donor ligands such as  $PMe_3$  or pyridine to  $M_2(OR)_6$  compounds establishes an equilibrium, Eq. 12, wherein the M≡M bond is retained in the Lewis base adducts. The  $d^3$ - $M(OR)_3$  and  $d^3$ - $M(OR)_3L$  frontier orbitals are isolobal.



How can this be? The  $M_2(OR)_6$  compounds have M–M  $\pi^4$  as the HOMO and M–M  $\delta/\delta^*$  as the LUMO. To the extent that RO-to-M  $\pi$  bonding is important the latter, the  $\delta/\delta^*$  orbitals (of which there are *two* at each metal center being derived from  $d_{xy}$  and  $d_{x^2-y^2}$  metal atomic orbitals) can be viewed as M–O  $\pi^*$  orbitals. Upon formation of a bond to pyridine or  $PMe_3$  one M–OR  $\pi$ -bond is sacrificed as one new metal–ligand  $\sigma$  bond (M–N or M–P) is formed. The equilibrium reaction 12 is thus internally buffered by RO-to-M  $\pi$ -bonding and does not influence the M–M triple bond. The M–M distances of  $M_2(OR)_6$  and  $M_2(OR)_6L_2$  compounds are essentially the same (within 0.02 Å) while the six M–O distances each increase by ca. 0.06 Å [28].

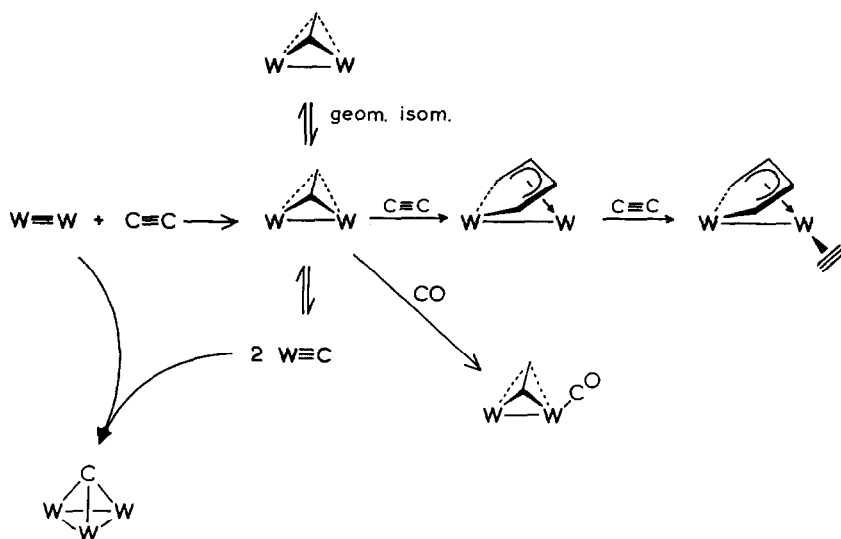
If the substrate is both a Lewis base and a  $\pi$ -acid then the M–M  $\pi$ -bonds become involved in metal–ligand  $\pi$ -back bonding. In general metal–ligand bonding is stronger than M–M bonding and so the M–M bond order is reduced from 3.

### Reactions with alkynes

Addition of alkynes to  $M_2(OR)_6$  compounds leads to a variety of interesting reactions and products as outlined in Scheme 2. This area of chemistry has been reviewed recently [29] and only some of the general factors will be commented on here.

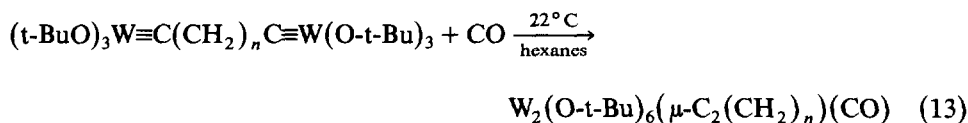
The 1 : 1 alkyne adducts can be viewed as dimetallatetrahedranes with M–M and C–C single bonds. In general C–C coupling is favored to C–C cleavage. The metathesis of  $M\equiv M$  and  $C\equiv C$  is favored for bulky alkoxides, e.g. *t*-Bu, and for tungsten over molybdenum [30].

These alkyne addition reactions can be viewed as a type of oxidative addition in as much as electron density is removed from M–M bonding to M–C bonding. Oxidation states can be assigned as  $W^V$  in the  $W_2(OR)_6(\mu-C_2R_2)$  compounds and  $W^{VI}$  in the  $(RO)_3W\equiv CR'$  compounds. The equilibrium between a  $W_2(OR)_6(\mu-C_2R_2)$  compound and its alkylidyne counterpart  $(RO)_3W\equiv CR'$  can be viewed as an internal redox reaction. This type of redox activity is commonly encountered in inorganic compounds containing non-innocent ligands such as quinones, dithiolenes and in di-



Scheme 2

or polysulfides where S–S bond cleavage and formation can occur. Addition of a  $\pi$ -acid ligand such as CO or indeed another equivalent of alkyne may drain off the equilibrium in favor of products containing or derived from the  $\mu$ - $C_2R'_2$  adduct. Recently we have employed this technique in the synthesis of  $\mu$ -cycloalkyne compounds from polymethylene bridged alkyldiyne compounds, Eq. 13 [31].

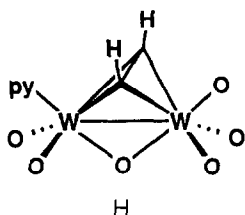


[ $n = 4$  and  $5$ ]

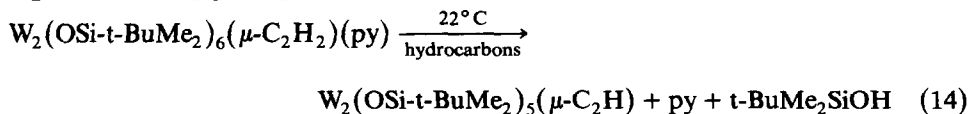
Many of the products derived from the reactions between alkynes and  $M_2(\text{OR})_6$  compounds bear testimony to the value of the isolobal principle that relates  $d^3\text{-M}(\text{OR})_3$  with  $\text{Co}(\text{CO})_3$  and  $\text{CpM}(\text{CO})_2$ ;  $(t\text{-BuO})_3W\equiv\text{CR}'$  and  $\text{CpW}(\text{CO})_3(\equiv\text{CR}')$ ;  $(\text{RO})_6M_2(\mu\text{-}C_2R'_2)$ ,  $\text{Cp}_2M_2(\text{CO})_4(\mu\text{-}C_2R'_2)$ , and  $\text{Co}_2(\text{CO})_6(\mu\text{-}C_2R'_2)$ ;  $W_3(\mu_3\text{-CR}')(\text{O-}i\text{-Pr})_9$  and  $\text{Co}_3(\mu\text{-CR}')(\text{CO})_9$  [26b].

It should be noted that electron withdrawing alkynes such as  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  and  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  do not react with  $M_2(\text{OR})_6$  compounds. Presumably the electron donating properties of the alkyne are at least as important as the  $\pi$ -acceptor properties.

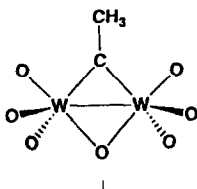
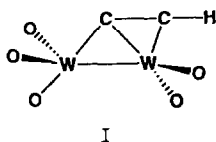
Recently we have started [32] to investigate the reactivity of closely related trialkyl siloxy derivatives of which the compound  $W_2(\text{OSi-}t\text{-BuMe}_2)_6$  is in many ways similar to  $W_2(\text{O-}t\text{-Bu})_6$  in terms of the steric pressure at the metal center. In the presence of pyridine, hexane solutions of  $W_2(\text{OSi-}t\text{-BuMe}_2)_6$  and ethyne yield a 1 : 1 adduct  $W_2(\text{OSi-}t\text{-BuMe}_2)(\mu\text{-}C_2H_2)(\text{py})$ . Spectroscopically and structurally this is very similar to  $W_2(\text{O-}t\text{-Bu})_6(\mu\text{-}C_2H_2)(\text{py})$  [33] and the common  $W_2O_6(\mu\text{-}C_2)N$  skeleton is depicted by H.



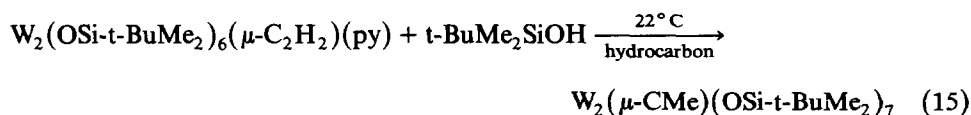
The  $\mu$ -ethyne siloxy derivative is reactive in solution and in a unimolecular reaction eliminates  $t\text{-BuMe}_2\text{SiOH}$  with the formation of the  $\mu\text{-C}_2\text{H}$  derivative,  $\text{W}_2(\text{OSi-}t\text{-BuMe}_2)_5(\mu\text{-C}_2\text{H})$ , of structure I, Eq. 14.



The silanol that is liberated in reaction 14 back reacts slowly with the starting alkyne adduct to give the  $\mu$ -ethylidyne compound  $\text{W}_2(\mu\text{-CMe})(\text{OSi-}t\text{-BuMe}_2)_7$ , which by analogy with the structurally characterized compound  $\text{W}_2(\mu\text{-CMe})(\mu\text{-O-}t\text{-Bu})(\text{O-}i\text{-Pr})_6$  [34], we propose adopts the structure J.



The formation of the  $\mu$ -ethylidyne is obtained (at the expense of the  $\mu\text{-C}_2\text{H}$  compound) by the addition of excess  $t\text{-BuMe}_2\text{SiOH}$  to the  $\mu\text{-C}_2\text{H}_2$  compound, Eq. 15.



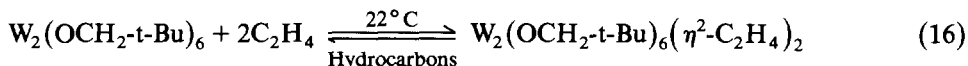
A  $\sigma, \pi$ -vinyl containing compound, presumably  $\text{W}_2(\mu\text{-CHCH}_2)(\text{OSi-}t\text{-BuMe}_2)_7$ , is detected as an intermediate in the reaction shown in Eq. 15.

The H atom transfers involving  $\mu\text{-C}_2\text{H}_2$ ,  $\mu\text{-C}_2\text{H}$ ,  $\mu\text{-CHCH}_2$  and  $\mu\text{-CCH}_3$  in reactions 14 and 15 occur under extremely mild conditions and parallel reactions on certain metal surfaces [35]. In the dinuclear organo-metallic chemistry of carbonyl-containing compounds these H atom transfers are brought about by superhydride sources or strong acids such as  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  [36].

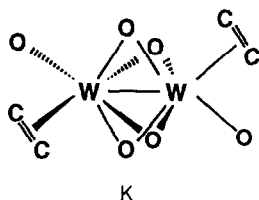
### Reactions between $\text{W}_2(\text{OR})_6$ compounds and carbon-carbon double bonds

The reactions between  $\text{M}\equiv\text{M}$  and  $\text{R}'\text{C}\equiv\text{CR}''$  or  $\text{R}'\text{C}\equiv\text{N}$  may be viewed as complementary redox reactions. The dinuclear metal center is potentially a 6 electron reducing agent and the alkyne or nitrile is a potential 6 electron reductant. When six electrons are so transferred then a metathesis of  $\text{M}\equiv\text{M}$  and  $\text{C}\equiv\text{N}$  occurs with formation of  $\text{M}\equiv\text{C}$  and  $\text{M}\equiv\text{N}$  bonds. Within this framework the reaction

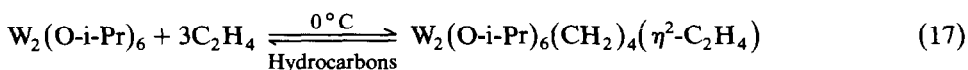
involving an olefin and a  $M_2(OR)_6$  compound may be viewed as a non-complementary reaction and indeed it is found that  $W_2(OCH_2-t-Bu)_6$  reacts reversibly with two equivalents of ethylene, Eq. 16 [37].



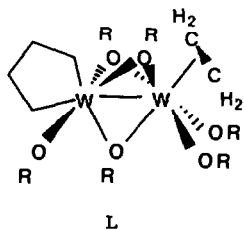
The structure of the bis ethylene adduct is depicted by **K** and has  $C_2$  molecular symmetry [38]. In solution there is restricted rotation about the  $W-C_2$ (olefin) axis and this and the observed structure can be understood in terms of the joining of two pseudo-tetrahedral  $d^3-W(OR)_3(C_2H_4)$  fragments. In a tetrahedral environment the  $e$  type orbitals ( $z^2$  and  $x^2-y^2$ ) lie below the  $t_2$ . The former are used to form the  $Wd_{\pi}$ -to-olefin  $\pi^*$  bond and  $W-W$   $\sigma$ -bond and it is the mutual competition between  $M-M$  and  $M$ -olefin bonding that leads to the observed structure **K**.



The bis-olefin adduct reacts further with ethylene to give an alkylidyne bridged complex by way of an intermediate metallacyclopentane ethylene complex [37]. In the reaction between  $W_2(O-i-Pr)_6$  and ethylene the latter is formed reversibly, Eq. 17, and may be isolated at  $0^\circ C$ . It has been structurally characterized and found to



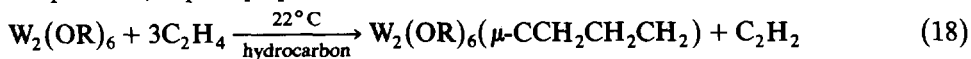
adopt the geometry depicted by **L** in the solid-state. In solution it is fluxional though low temperature  $^1H$  and  $^{13}C$  NMR spectra are consistent with expectations based on **L**. Labelling studies show that Eq. 17 does not involve  $C-C$  (ethylene) bond cleavage or isomerization of *cis*, *trans*- and *gem*- $C_2H_2D_2$ .



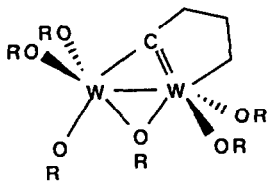
The compounds  $W_2(OCH_2-t-Bu)_6(\eta^2-C_2H_4)_2$  and  $W_2(O-i-Pr)_6(CH_2)_4(\eta^2-C_2H_4)$  have relatively long  $W-W$  and  $C-C$  distances ca. 2.6 and 1.44 Å, respectively [37,38]. For the sake of electron counting the  $W-C_2$  olefin group can be termed a metallacyclopropane and the ditungsten center  $W_2^{10+}$  ( $M-M$ ).

In solution at room temperature  $W_2(O-i-Pr)_6(CH_2)_2(\eta^2-C_2H_4)$  reacts to give  $W_2(O-i-Pr)_6(\mu-CCH_2CH_2CH_2)$  (structure **M**) and ethane. These are the ultimate products in the reactions between many  $W_2(OR)_6$  compounds and ethylene at room

temperature, Eq. 18 [37].

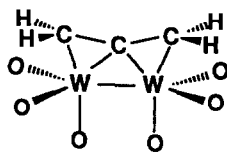


[R = *c*-Hex, *c*-Pent, *i*-Pr, CH<sub>2</sub>-*t*-Bu]

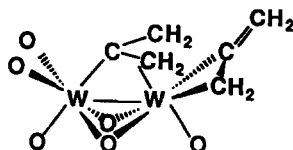


M

Only the sterically encumbered W<sub>2</sub>(O-*t*-Bu)<sub>6</sub> and ethylene fail to react in hydrocarbon solvents at room temperature. It seems likely that steric factors disfavor the formation of a monoethylene adduct sufficiently to prevent attainment of a bis-ethylene complex supported by six alkoxide ligands. Support for this notion comes from the fact that allene forms a bis-allene adduct by way of a stabilized μ-parallel mono-allene complex W<sub>2</sub>(O-*t*-Bu)<sub>6</sub>(μ-C<sub>3</sub>H<sub>4</sub>) of structure N wherein the allene has been rehybridized. The bis allene complex has the structure shown in O involving a μ-metallaallyl and a η<sup>2</sup>-allene ligand [39].



N

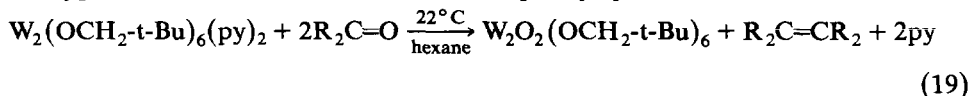


O

In the μ-parallel allene adduct the W–W distance, 2.58 Å, the C–C distances 1.47 Å, the W–C distance 2.10(2) Å (av) and the C–C–C angle, 141°, all emphasize the importance of Wd<sub>π</sub>-to-allene π\* back bonding [39]. The allene is acting as a four electron donor to tungsten and also as a four electron acceptor. In the bis allene adduct the combined Wd<sub>π</sub>-to-allene π\* back bonding is sufficient to lengthen and essentially destroy the M–M bond, W–W = 2.86 Å.

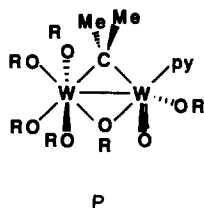
### Reactions involving carbon–oxygen double bonds

Reactions involving W<sub>2</sub>(OCH<sub>2</sub>-*t*-Bu)<sub>6</sub>(py)<sub>2</sub> and ketones or aldehydes in hydrocarbon solvents at room temperature yield olefins by a reductive coupling and deoxygenation of the C–O double bonds, Eq. 19 [40].

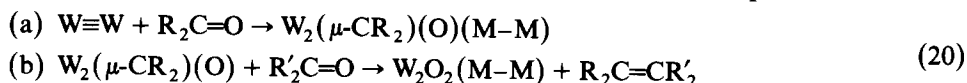


Initially it was believed that this reaction provided a model for the McMurry reaction [41] which is known to proceed via a two step reaction sequence: (1) C–C bond formation to give pinacolate ligands and (2) C–O bond cleavage with liberation of olefin. However, this is not the case. Studies of reaction 19 show that a two step mechanism is operative but the first step involves C–O bond cleavage to

give dinuclear  $\mu$ -alkylidene oxo compounds. The  $\mu$ -propylidene and  $\mu$ -benzylidene compounds  $W_2(OCH_2-t-Bu)_6(\mu-CR'R^2)(O)(py)$  have been isolated from reactions carried out at  $0^\circ C$  and a derivative has been structurally characterized by an X-ray study. The proposed structure of the  $\mu-CR'R^2$  containing compounds is shown in P.



The second step in the reaction generates the C–C bond and by C–O bond cleavage liberates the olefin. It is therefore possible to carry out the reaction between  $W_2(OCH_2-t-Bu)_6(py)_2$  and one ketone or aldehyde at  $0^\circ C$ , isolate the  $\mu$ -alkylidene compound and allow this to react with a second ketone or aldehyde to achieve a selective cross-coupling of different ketones/aldehydes. The overall sequence is a four electron oxidation of the W–W triple bond, Eq. 20.



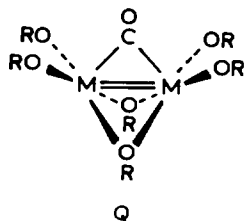
In the reaction sequence 20, the ditungsten center combines two well known mononuclear reactions: (1) the cleavage of the  $R_2C=O$  bond by lower valent tungsten complexes, e.g. [42]  $WCl_2(PMe_3)_4$  and (2) the reaction between an early transition metal alkylidene and a ketone or aldehyde to give a metal oxo group and an olefin [43].

Currently studies are underway to explore the potential utility of these reductive coupling reactions and to compare functional group tolerances and selectivities with related reactions involving the McMurry reagents and Wittig reagents.

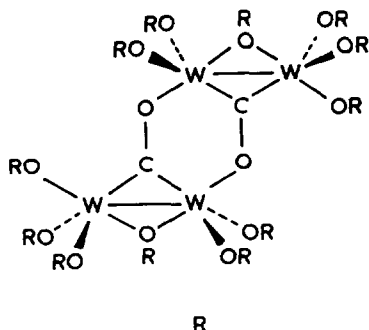
### Activation of carbon monoxide

$Mo_2(OR)_6$  compounds fail to show comparable reactivity with C–C and C–O double bonds. This difference between  $M=Mo$  and  $W$  reflects the relative orbital energetics of the  $M \equiv M$  bond and emphasizes the greater reducing ability of the  $W \equiv W$  bond. This is clearly evident in the reactions involving carbon monoxide.

The tert-butoxides  $M_2(O-t-Bu)_6$  react with CO (1 equiv.) in hydrocarbon solutions to give mono carbonyl adducts of structure type Q [44].



The values of  $\bar{\nu}(CO)$  are unprecedentedly low for  $\mu_2$ -CO ligands in neutral molecules: ca.  $1640\text{ cm}^{-1}$  ( $M = Mo$ ) and  $1570\text{ cm}^{-1}$  ( $M = W$ ). The fact that the



$\bar{\nu}(\text{CO})$  values for  $M = \text{W}$  is  $70 \text{ cm}^{-1}$  lower than that for  $M = \text{Mo}$  reflects the greater degree of  $\text{W}_2$ -to-CO back bonding. In a formal sense these compounds are inorganic analogues of cyclopropenones having  $M-M$  and  $C-O$  double bonds. Quite remarkably  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  is formed reversibly and at room temperature under a  $\text{N}_2$  purge or a vacuum  $\text{Mo}_2(\text{O}-t\text{-Bu})_6$  is regenerated.

The  $\text{W}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  compound reacts in hydrocarbon solvents with  $i\text{-PrOH}$  ( $\geq 6$  equiv.) at room temperature to give  $\text{W}_4(\mu\text{-CO})_2(\text{O}-i\text{-Pr})_{12}$  which has the central skeleton depicted by **R** [44].

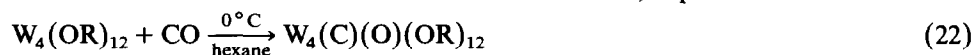
In  $\text{W}_4(\mu\text{-CO})_2(\text{O}-i\text{-Pr})_{12}$  the  $\text{W}-\text{W}$  distance,  $2.67 \text{ \AA}$ , and  $\text{C}-\text{O}$  (carbonyl) distance  $1.35 \text{ \AA}$  are approaching single bond distances while the  $\text{W}-\text{C}$  and  $\text{W}-\text{O}$  (carbonyl) distances of  $1.95-1.96 \text{ \AA}$  are indicative of some double bond character. The bonding in the  $\text{M}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  and  $\text{W}_4(\mu\text{-CO})_2(\text{O}-i\text{-Pr})_{12}$  molecules has been the subject of a theoretical study [45].

The  $(\text{W}\equiv\text{W})^{6+}$  center, which is capable of a six-electron reduction of certain  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{N}$  bonds is not capable of a cleavage of  $\text{C}\equiv\text{O}$  to the elements  $(\text{RO})_2\text{WC}$  and  $\text{WO}(\text{OR})_4$  but a stepwise reaction process does ultimately lead to cleavage of the  $\text{C}-\text{O}$  bond. Two strategies have been explored. In the first, a  $\text{W}_2(\mu\text{-CO})$  compound is allowed to react with a  $\text{W}\equiv\text{W}$  containing compound, Eq. 21. This parallels the reductive cleavage of ketones, Eq. 20a.

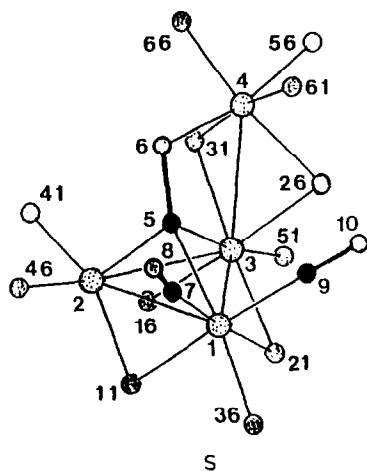


The problems with reaction 21 arise from the selection of the attendant alkoxide ligands. Steric factors dictate that a  $\text{W}_2(\text{OR})_6(\mu\text{-CO})$  compound must be able to react with its precursor  $\text{W}_2(\text{OR})_6$ . When this is so, it is also possible to form the compounds  $\text{W}_4(\mu\text{-CO})_2(\text{OR})_{12}$  and the tetranuclear clusters  $\text{W}_4(\text{OR})_{12}$  [47]. Thus the carbido- $\text{W}_4$  cluster is formed in competition with two other tetranuclear species.

The second approach involves the use of a tetranuclear alkoxide formed from the irreversible coupling of two  $\text{W}_2(\text{OR})_6$  compounds:  $2\text{W}_2(\text{OR})_6 \rightarrow \text{W}_4(\text{OR})_{12}$  [47]. The tetranuclear alkoxide is then allowed to react with  $\text{CO}$ , Eq. 22.



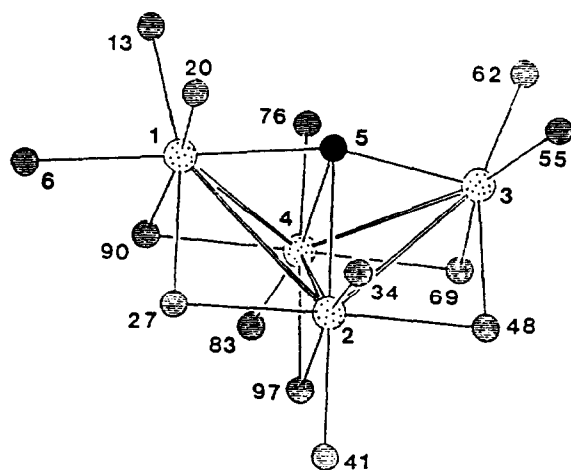
The latter approach is also not without complications. (1) The  $\text{W}_4(\text{OR})_{12}$  clusters are capable of picking up three  $\text{CO}$  ligands to give  $\text{W}_4(\mu_4\text{-CO})(\text{CO})_2(\text{OR})_{12}$  compounds [46,48]. The central skeleton of the structure of the iso-butoxide is shown in **S** and contains a spiked triangle of tungsten atoms. The  $\mu_4$ -carbonyl ligand can be



viewed as a metallaoxycarbyne  $M-O-C\mu_3-W_3$  and the C-O bond distance 1.37 Å is again indicative of a single bond.

The tricarbonyl compound does not react directly to give a  $W_4(\mu_4-C)$ -containing compound though its structure is suggestive of how a  $W_4(\mu_4-CO)$  compound (lacking additional carbonyl ligands) might appear prior to the act of C-O bond cleavage [49].

A second complication in reaction 22 arises from oxo group transfer reactions that yield  $W_4(\mu_4-C)(OR)_{14}$  compounds. The structure of the  $\mu_4$ -carbide where R = cyclo-pentyl has been determined and its  $W_4(C)(O)_{14}$  skeleton is shown in T



T



below. The fate of the oxo group is presently not known. It is possible that an intermolecular reaction involving  $W_4(\mu_4\text{-CO})(\text{OR})_{12}$  or  $W_4(\mu_4\text{-C})(\text{O})(\text{OR})_{12}$  and the unreacted cluster  $W_4(\text{OR})_{12}$  yields  $W_4(\text{C})(\text{OR})_{14}$  and  $W_4\text{O}(\text{OR})_{10}$ . A compound of the latter formula has been characterized for  $R = i\text{-Pr}$  [50].

Studies of reactions 21 and 22 have involved extensive use of  $^{13}\text{C}$  NMR spectroscopy and 60:40 mixtures of double labelled carbon monoxide  $^{13}\text{C}^{18}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ . With high resolution  $^{13}\text{C}$  NMR spectroscopy, the cleavage of the C–O bond can be detected by the small isotope chemical shift  $\Delta C(^{18}\text{O}-^{16}\text{O})$  [51].

### Concluding remarks

The dinuclear  $d^3-d^3$   $M\equiv M$  center has provided a fertile inorganic template for the development of organometallic chemistry. Over the past decade many of the reactions well known in mononuclear chemistry have been observed and in several instances new chemistry, that which is distinct from mononuclear chemistry, has emerged. It seems that the  $(M\equiv M)^{6+}$  center may be used for selective C–C bond forming reactions in a manner of potential use in organic synthesis. Further explorations seem well justified.

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