Reactions Involving the Triple Bond in Dimolybdenum and Ditungsten Hexa-alkoxides and C–C, C–N, and C–O Triple Bonds

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1 Introduction

The ability of transition metals to form multiple bonds with themselves is now a well recognized and accepted aspect of chemistry.[1] Based on bond length, conformation, electronic and vibronic absorption spectroscopy, theoretical considerations employing sophisticated calculations and, above all, an internal consistency, the evidence for a M–M multiple bond in certain compounds is overwhelming. Such is the case for the quadruple bond in the $Mo_2Cl_8^{4-}$ anion and the triple bond in $Mo_2(OCH_2Bu^t)_6$, for example. However, not all cases are so clear cut since there may be extensive mixing of metal–metal and metal–ligand bonding such that the significance and validity of a M–M bond order or its assignment is questionable. Whenever there are bridging ligand atoms bonded to both metal atoms, then, in particular, problems arise concerning the detailed nature of the metal–metal interactions.

In the first decade following Cotton's discovery[2,3] of the quadruple bond in the $Re_2Cl_8^{2-}$ anion the scope of the field became apparent and our understanding of the electronic structure of M–M multiple bonds matured. It was not, however, until the mid to late 1970s that chemists started to explore the reactivity of M–M multiple bonds in a systematic manner. The initial findings were exciting and exposed a wide variety of reactivity patterns.[4,5] It became apparent that general rules concerning additions and eliminations of the type well established in organic chemistry could not naively be extended to M–M multiple bonds. Triple bonds between molybdenum atoms may have a variety of electronic configurations, $\sigma^2\pi^4$, $\sigma^2\pi^2\delta^2$, $\pi^4\delta^2$, and even $\sigma^2\pi^4\delta^2\delta^{*2}$, and the reactivity of the Mo≡Mo bond reflects this. By contrast the C≡C bond is always of configuration $\sigma^2\pi^4$ leading to a more uniform reactivity.

Our group has been developing the chemistry of the triple bond in dimolybdenum and ditungsten hexa-alkoxides, compounds of formula $M_2(OR)_6$.[6] These compounds are members of an extensive group of d^3–d^3 dimers which

[1] F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms', Wiley, 1982.
[2] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, R. Robinson, and J. S. Wood, *Science*, 1964, 145, 1305.
[3] F. A. Cotton, *Inorg. Chem.*, 1965, 4, 334.
[4] 'Reactivity of Metal-Metal Bonds', ed. M. H. Chisholm, ACS Symp. Ser., 1981, vol. 155.
[5] M. H. Chisholm and I. P. Rothwell, *Prog. Inorg. Chem.*, 1982, 29, 1.
[6] M. H. Chisholm, *Polyhedron*, 1983, 2, 681.
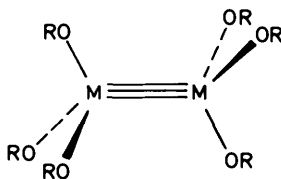
(1)

adopt a staggered 'ethane-like' geometry in the ground state depicted by (1) above. The triple bond (1) has a configuration $\sigma^2\pi^4$ derived from the metal d^3–d^3 interaction.[7] Taking the M–M axis to be the z axis, the metal atomic d_{z^2} orbitals interact to form σ and σ^* orbitals and the degenerate d_{xz}, d_{yz} atomic orbitals form $\pi_{x,y}$ and $\pi_{x,y}{}^*$ molecular orbitals. The triple bond is cylindrical and these molecules are inorganic analogues of alkynes. He(I) and He(II) photoelectron spectroscopy reveals that the first ionization (lowest energy) is from the filled M–M π orbitals; the second ionization comes from the M–M σ orbital while the third, at still higher ionization energy, is from oxygen lone pairs.[8,9] Roughly 0.5 eV separates the filled M–M π and σ orbitals. $M_2(OR)_6$ compounds are yellow to reddish-orange and this colour arises from an electronic absorption at the low energy end of the u.v. which tails into the visible region of the spectrum. This absorption can reliably be assigned to the HOMO $\longrightarrow$ LUMO transition. The former is M–M π and the latter is an orbital of e symmetry, being a mix of M–M δ^* and π^*.
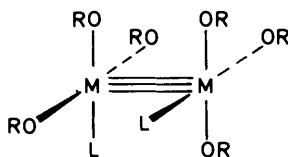
These compounds are co-ordinatively unsaturated and can, if steric factors permit, co-ordinate Lewis bases such as pyridine and PMe_3 to form adducts of formula $M_2(OR)_6L_2$.[6] In forming a new metal–ligand σ bond there is a loss in oxygen-to-metal π bonding. The geometry of these adducts is indicated in (2) below. Each metal atom is in a roughly square planar co-ordination environment and is united to the other metal atom by a triple bond of configuration $\sigma^2\pi^4$. The latter does not impose any conformational restrictions and eclipsed and staggered geometries have been found for $M_2(OR)_6L_2$ compounds depending only upon the ligand–ligand interactions across the M–M bond.

The M–M distances in compounds (1) and (2) span a narrow range, 2.2 to 2.4 Å, with the W–W distance being roughly 0.1 Å longer than the Mo–Mo distance in pairs of otherwise identical molecules. The M–M distances are sensitive to steric

[7] The $X_3M{\equiv}MX_3$ molecules have been the subject of numerous theoretical studies: K. W. Dobbs, M. H. Francl, and W. J. Hehre, *Inorg. Chem.*, 1984, **23**, 24; T. Ziegler, *J. Am. Chem. Soc.*, 1983, **105**, 7543; R. A. Kok and M. B. Hall, *Inorg. Chem.*, 1983, **22**, 728; B. E. Bursten, F. A. Cotton, J. C. Green, E. A. Seddon, and G. Stanley, *J. Am. Chem. Soc.*, 1980, **102**, 4579; M. B. Hall, *J. Am. Chem. Soc.*, 1980, **102**, 2104; A. Dedieu, T. A. Albright, and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3141; T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.*, 1977, **100**, 7736.

[8] F. A. Cotton, G. G. Stanley, B. Kalbacher, J. C. Green, E. Seddon, and M. H. Chisholm, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 3109.

[9] E. M. Kober and D. L. Lichtenberger, results to be published.

$$\begin{array}{c}
\text{RO} \quad \text{RO} \quad \text{OR} \quad \text{OR} \\
\text{RO}{-}\text{M}{\equiv}\text{M}{-}\text{OR} \\
\text{L} \quad \text{L} \quad \text{OR}
\end{array}$$

(2)

factors *cf.* W–W = 2.296(2) Å in $W_2(OEt)_6(L-L)$, where L–L = *N,N'*-dimethyl-ethylenediamine, and W–W = 2.397(1) Å in $W_2(OBu^t)_6(py-4-Me)_2$.

These compounds have been found to enter into a wide variety of reactions including oxidative additions[10,11] and reductive eliminations[12,13] wherein the M–M bond order is changed in a stepwise manner downward $[(M{\equiv}M)^{6+} \longrightarrow (M{=}M)^{8+} \longrightarrow (M{-}M)^{10+}]$ and upward $[(M{\equiv}M)^{6+} \longrightarrow (M{\equiv}M)^{4+}]$, respectively. This article deals with a group of reactions involving the M–M triple bond in $M_2(OR)_6$ compounds and $C{\equiv}C$, $C{\equiv}N$, and $C{\equiv}O$ bonds. These may be viewed as a special class of oxidative-addition reactions in which electron density is removed from the $M{\equiv}M$ bond to form metal–ligand bonds. The dinuclear centre achieves a reactivity not seen in mononuclear chemistry.

2 Reactions Involving Alkynes
Alkynes react with $M_2(OR)_6$ compounds or their adducts $M_2(OR)_6L_2$ in hydrocarbon solvents at <25 °C to give a wide variety of products. Small sterically unencumbered alkynes, such as HCCH, MeCCH, and MeCCMe, are very rapidly polymerized. By careful control of reaction stoicheiometry and conditions, these same alkynes and others also produce new organometallic complexes. The organometallic compounds isolated and characterized include ten simple alkyne adducts stabilized by pyridine ligation, six of which have been characterized by single crystal *X*-ray crystallography.[14–17]

Alkyne Adducts.—Alkyne adducts of formula $M_2(OR)_6(R'CCR')(py)_n$, where $n = 1$ or 2, adopt one of three structures depicted by (3), (4), and (5) below. Two compounds of each structural type have been characterized by crystallography and these are underlined while the assignment of structure for the other four rests on low temperature limiting n.m.r. spectroscopic data.

[10] M. H. Chisholm, C. C. Kirkpatrick, and J. C. Huffman, *Inorg. Chem.*, 1981, **20**, 871.
[11] M. H. Chisholm, J. C. Huffman, and A. L. Ratermann, *Inorg. Chem.*, 1983, **22**, 4100.
[12] M. H. Chisholm, J. C. Huffman, and R. J. Tatz, *J. Am. Chem. Soc.*, 1983, **105**, 2075.
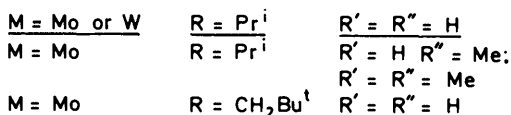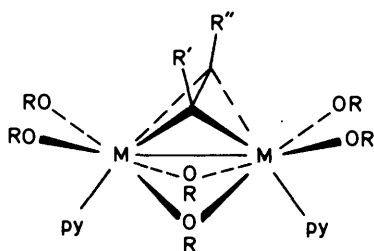[13] M. H. Chisholm, K. Folting, J. C. Huffman, and R. J. Tatz, *J. Am. Chem. Soc.*, 1984, **106**, 1153.
[14] M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 4389.
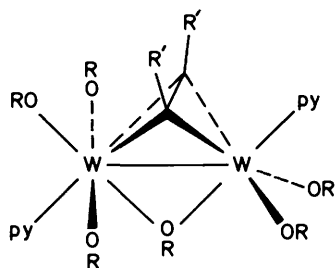[15] M. H. Chisholm, K. Folting, D. M. Hoffman, J. C. Huffman, and J. Leonelli, *J. Chem. Soc., Chem. Commun.*, 1983, 589.
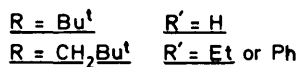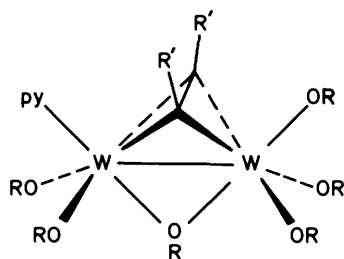[16] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6794.
[17] M. H. Chisholm, B. Conroy, D. M. Hoffman, and J. C. Huffman, results to be published.

M = Mo or W   R = Pr^i R′ = R″ = H
M = Mo   R = Pr^i R′ = H R″ = Me;
                             R′ = R″ = Me
M = Mo   R = CH$_2$Bu^t R′ = R″ = H

(3)

R = CH$_2$Bu^t R′ = H or Me

(4)

R = Bu^t R′ = H
R = CH$_2$Bu^t R′ = Et or Ph

(5)

Each structural type has a central pseudo-tetrahedral M_2C_2 unit. In (3) there are two alkoxy bridges while in (4) and (5) there is only one. If the bridging alkyne is considered to occupy a single co-ordination site, (3) represents a confacial bioctahedral geometry while in (4) one metal has octahedral co-ordination but the other is only five co-ordinate. The bridging alkyne and the bridging alkoxide occupy, respectively, equatorial and axial positions of a distorted trigonal bipyramid about the five co-ordinate tungsten in (4). In (5), which has only one molecule of ligated pyridine, each tungsten atom is in a distorted trigonal bipyramidal environment with the bridging alkyne and bridging alkoxide in equatorial and axial sites, respectively.

What factors favour the adoption of one structure over another? Bulky combinations of R, R′, and R″ favour (5) while molybdenum has only been found to adopt structural type (3), the confacial bioctahedron. Alkynes bind to the ditungsten centre more tightly, which may account for tungsten's ability to adopt

structures of type (4) and (5). In solution several of these alkyne adducts are fluxional, showing rapid bridge-terminal OR group site-exchange and reversible dissociation of pyridine. With the exception of compound (3) M = Mo, R′ = R″ = Me, there is no evidence for reversible dissociation of the μ_2-alkyne ligand. For compounds of type (5) one must also consider what structures might be present in solution when the pyridine ligand has dissociated.

Table 1   *Selected bond distances (Å) for $M_2(OR)_6(py)_n(\mu\text{-}C_2R'_2)$ compounds of molybdenum and tungsten (n = 1 or 2)*

Compound	Structure Type[a]	M–M	C–C	M–C (averaged)	Ref.
$Mo_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)$	(3)	2.544(1)	1.37(1)	2.09	b
$W_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)$	(3)	2.567(1)	1.39(2)	2.09	c
$W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2H_2)$	(4)	2.610(2)	1.39(3)	2.14	d
$W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2Me_2)$	(4)	2.602(1)	1.37(2)	2.14	c
$W_2(OCH_2Bu^t)_6(py)(\mu\text{-}C_2Et_2)$	(5)	2.572(1)	1.40(2)	2.14	d
$W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$	(5)	2.665(1)	1.44(1)	2.10	c

[a] (3), (4), and (5) refer to the schematic drawings given in the text. [b] M. H. Chisholm, K. Folting, J. C. Huffman, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 4389. [c] M. H. Chisholm, K. Folting, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6794. [d] M. H. Chisholm, B. K. Conroy, K. Folting, D. M. Hoffman, and J. C. Huffman, results to be published.

The M–M, M–C, and C–C distances of the central M_2C_2 units in (3), (4), and (5) are given in Table 1. The C–C distances are slightly longer than those typically found in perpendicular alkyne metal complexes which span a small range 1.32—1.38 Å.[18] For a comparison one might note the C–C double bond distance in ethylene, 1.337(3) Å, and the typical C–C single bond distances of 1.54 Å and 1.46 Å for C_{sp^3}–C_{sp^3} and C_{sp^2}–C_{sp^2}, respectively.[19] The C–C distance in $Gd_5Cl_9C_2$, 1.46 Å, formally C_2^{6-}, is also worthy of note, since it is a limiting value for a C–C single bond in C_2 carbides.[20]

Some ^{13}C n.m.r. data for the bridging C_2H_2 ligand in compounds of type (3), (4), and (5), together with related data for a μ_2 and μ_4-C_2H_2 in cobalt carbonyl complexes are given in Table 2.

The values of $^1J_{^{13}C^{-1}H}$ are reduced from *ca.* 250 Hz in C_2H_2 and are approaching that in ethylene, 156 Hz. More remarkable are the extremely small values of $^1J_{^{13}C^{-13}C}$ which in the case of $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ and $W_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)$ have not been resolved. This places their magnitude at less than 15 Hz. For comparison the values of $^1J_{^{13}C^{-13}C}$ in ethyne, ethylene, and ethane are 171.5, 67.6, and 34.6 Hz, respectively, while that observed for the η^2-C_2H_2 ligand in $W_2(OPr^i)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$, a compound discussed later, is

[18] For an extensive listing of C–C distances in perpendicular $M_2(\mu\text{-}C_2R_2)$ containing complexes see: D. M. Hoffman, R. Hoffmann, and C. R. Fisel, *J. Am. Chem. Soc.*, 1982, **104**, 3858.
[19] K. Kuchitsu, *MTP Int. Rev. Sci. Phys. Chem. Ser. One*, 1972, **11**, 221.
[20] A. Simon, E. Warkentin, and R. Masse, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1013.

Table 2 N.m.r. data for the bridging ethyne moiety in selected transition-metal complexes

Compound	Structure Type[a]	δ^b	$J_{W–C}{}^c$	$^1J_{C–H}$	$^2J_{C–H}$	$J_{C–C}$	$^3J_{H–H}$	Ref.
$Mo_2(OPr^i)_6(py)_2(C_2H_2)$	(3)	166.7 (−65 °C, C_7D_8)	—	201.4	4.7	26.9	~0	f
$W_2(OCH_2Bu^t)_6(py)_2(C_2H_2)$	(4)	133.2 (−20 °C, C_7D_8)	44.8 / 32.8	189.7	1.0	19.0	2.9	f
$W_2(OPr^i)_6(py)_2(C_2H_2)$	(3)	166.3 (−40 °C, C_7D_8)	41.6	~192	~0	<15	~0	g
$W_2(OBu^t)_6(py)(C_2H_2)$	(5)	120.1 (−40 °C, C_7D_8)	41.4^d	~184	~0	<15	~0	g
$W_2(OBu^t)_6(CO)(C_2H_2)$	(5)	125.5 (−40 °C, C_7D_8)	38 / 25	191.9	−1.7	15.8	5.4	g
$Co_2(CO)_6(C_2H_2)$	μ_2-η^2	e	—	209.8	15.7	55.9	~0	h
$Co_4(CO)_{10}(C_2H_2)$	μ_4-η^2	e	—	174.7	4.5	21	~0	h

^{a} (3), (4), and (5) refer to structural types defined in the text. ^{b} Chemical shift in p.p.m. relative to Me_4Si. Temperature and solvent in brackets. ^{c} All coupling constants are in Hz. ^{d} $J_{W–C} \simeq J_{W_2–C}$. ^{e} Not reported: data obtained from ^1H n.m.r. spectra recorded at −50 °C, $CDCl_3$ solvent. ^{f} M. H. Chisholm, B. K. Conroy, K. Folting, D. M. Hoffman, and J. C. Huffman, results to be published. ^{g} M. H. Chisholm, K. Folting, D. M. Hoffman, and J. C. Huffman, J. Am. Chem. Soc., 1984, **106**, 6794. ^{h} S. Aime, D. Osella, E. Giamello, and G. Granozzi, J. Organometal. Chem., 1984, **262**, C1

54.5 Hz. Only in small organic rings such as cyclopropane has $^{1}J_{^{13}C-^{13}C} \sim 10$ Hz been previously noted.[21]
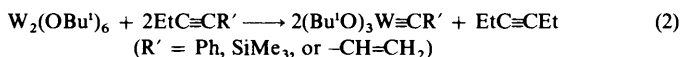
In summary, compounds of the type (3), (4), and (5) may be viewed as dimetallatetrahedranes having M–M and C–C and four M–C bonds, all of roughly order unity.

It was noted earlier that bulky combinations of R, R′, and R″ favour the adoption of structure (5). However, this is only to a point. Beyond this increasing steric pressure causes C–C bond scission of the co-ordinated alkyne.

Alkyne Scission.—Schrock and co-workers[22] first noted the remarkable metathesis reaction shown in equation 1, wherein a W≡W bond and a C≡C bond are cleaved to form two W≡C bonds.

$$W_2(OBu^t)_6 + R'C{\equiv}CR' \longrightarrow 2(Bu^tO)_3W{\equiv}CR' \qquad (1)$$
$$(R' = Me, Et, or Pr)$$
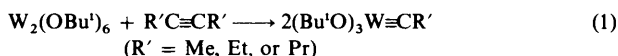
The compounds $(Bu^tO)_3W{\equiv}CR'$ are alkyne metathesis catalysts[23,24] which allowed Schrock to extend the synthesis of alkylidyne compounds as shown in equation 2.[22]

$$W_2(OBu^t)_6 + 2EtC{\equiv}CR' \longrightarrow 2(Bu^tO)_3W{\equiv}CR' + EtC{\equiv}CEt \qquad (2)$$
$$(R' = Ph, SiMe_3, or -CH{=}CH_2)$$

The reactions shown in equations (1) and (2) are rapid at 25 °C in benzene which contrasts with the reported scission of co-ordinated alkynes in cluster carbonyl compounds.[25,26] The latter require much more forcing conditions.

The compounds $(Bu^tO)_3W{\equiv}CR'$, where $R' = Me$[27] and NMe_2,[28] have been shown to be weakly associated dimers in the solid state as shown in (6) below. Through the agency of a pair of alkoxy bridges two trigonal bipyramidal tungsten atoms are united along a common equatorial–axial edge. The W–O axial bonds are much longer, 2.42(1) Å, than the equatorial bridging W–O bonds, 1.95(1) Å. The W–C distances are 1.77(2) Å and the W-to-W distance is *ca.* 3.5 Å; the latter is a non-bonding distance. In solution ^{13}C n.m.r. signals at *ca.* 250 p.p.m. with large values of $J_{^{183}W-^{13}C}$, *ca.* 300 Hz, are characteristic of the W≡C moiety.

During our characterization of the ethyne adduct $W_2(OBu^t)_6(\mu\text{-}{*}C_2H_2)(py)\cdot\frac{1}{2}py$, where *C represents 90 atom % ^{13}C, we discovered a ^{13}C signal which could most

[21] For listing of C–C and C–H couplings see: J. L. Marshall, 'C–C and C–H NMR Couplings' in *Methods in Stereochemical Analysis*, vol 2, Verlag Chemie Intl., 1983; J. B. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972; H. Gunther, *Angew. Chem., Int. Ed. Engl.*, 1972, 11, 861.

[22] R. R. Schrock, M. L. Listemann, and L. G. Sturgeoff, *J. Am. Chem. Soc.*, 1982, 104, 4291.

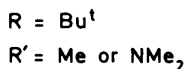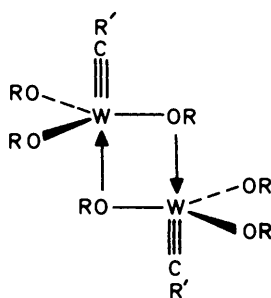[23] J. Sancho and R. R. Schrock, *J. Mol. Catal.*, 1982, 15, 75.

[24] R. R. Schrock, *ACS Symp. Ser.*, 1983, 211, 369.

[25] J. T. Park, J. R. Shapley, M. R. Churchill, and C. Bueno, *J. Am. Chem. Soc.*, 1983, 105, 6182.

[26] N. T. Allison, J. R. Fritch, K. C. P. Vollhardt, and E. Walborsky, *J. Am. Chem. Soc.*, 1983, 105, 1384, 4501.

[27] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Inorg. Chem.*, 1983, 22, 2903. Professor F. A. Cotton has informed us that the molecular structure of $(Bu^tO)_3W{\equiv}CPh$ is monomeric in the solid state, being essentially one half of the dimer shown in structure (6).

[28] M. H. Chisholm, J. C. Huffman, and N. S. Marchant, *J. Am. Chem. Soc.*, 1983, 105, 6162.

$$R'$$
$$C$$
$$\text{III}$$

$$RO{\diagdown}$$
$$W{\longrightarrow}OR$$
$$RO{\diagup}$$

$$RO{\longrightarrow}W{\diagup}{\text{-}}OR$$
$$\phantom{RO{\longrightarrow}W}OR$$
$$\text{III}$$
$$C$$
$$R'$$

$$R = Bu^t$$

$$R' = Me \text{ or } NMe_2$$

(6)

reasonably be assigned to the methylidyne complex $(Bu^tO)_3W{\equiv}CH$: $\delta(W{\equiv}C) = 252.4$ p.p.m. with $J_{^{183}W-^{13}C} = 289$ Hz and $J_{^{13}C-H} = 150$ Hz.[16] The existence of such a compound is not surprising in view of Schrocks findings,[22] equation 1, but just how such a species is formed upon dissolution of a crystalline sample of $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2).\frac{1}{2}py$ is of interest. One plausible explanation is that the alkylidyne and the alkyne adduct are in equilibrium, equation 3.

$$W_2(OBu^t)_6(\mu\text{-}C_2H_2) \rightleftharpoons [(Bu^tO)_3W{\equiv}CH]_2 \qquad (3)$$
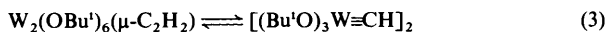
Consistent with expectations based on equation 3 , we find that when equimolar quantities of crystalline samples of $W_2(OBu^t)_6(py)(\mu\text{-}*C_2H_2).\frac{1}{2}py$ and $W_2(OBu^t)_6(py)(\mu\text{-}C_2D_2).\frac{1}{2}py$ are dissolved in $[^2H_8]$toluene at 25 °C and within 30 min the ^{13}C spectrum is recorded at -60 °C, there is evidence for the formation of $W_2(OBu^t)_6(py)(\mu\text{-}H*CCD)$ in the statistically expected ratio: $\mu\text{-}*C_2H_2:\mu\text{-}H*CCD = 1:2$. Also when hex-1-yne (1 equiv) is added to a $[^2H_8]$toluene solution of $W_2(OBu^t)_6$ in the presence of pyridine ($\frac{3}{2}$ equiv) the ^1H n.m.r. spectrum recorded at -60 °C clearly shows the presence of $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ along with other signals. These findings are all consistent with equation 3 but do not unequivocally establish this equilibrium. One of the difficulties in working with solutions of $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ is that samples decompose over a 24 h period at room temperature and this decomposition becomes much more rapid at elevated temperatures. [The carbonyl adduct, $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(CO)$ (discussed later) is more thermally stable but does not show evidence of methylidyne formation.] The decomposition involves Bu^tO ligand breakdown to give $Me_2C{=}CH_2$, Bu^tOH, and W-oxo bond formation.

Cotton and Schwotzer also have studied the reactions between $W_2(OBu^t)_6$ and each of $PhC{\equiv}CPh$[29] and $EtC{\equiv}CEt$[30] in hot toluene solutions (50—75 °C) and in

[29] F. A. Cotton, W. Schwotzer, and E. S. Shamshoum, *Organometallics*, 1983, **2**, 1167.

[30] F. A. Cotton, W. Schwotzer, and E. S. Shamshoum, *Organometallics*, 1983, **2**, 1340.

varying ratios of W_2:alkyne from 3:1 to 1:1. A variety of crystalline products have been identified including those of alkyne scission, $W_2(OBu^t)_4(\mu\text{-}CPh)_2$, $(Bu^tO)_3W\equiv CPh$ and $[W_3(OBu^t)_5(\mu\text{-}O)(\mu\text{-}CEt)O]_2$. The latter compound again is indicative of Bu^tO ligand decomposition.
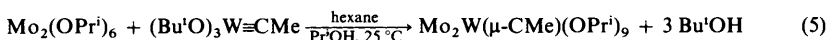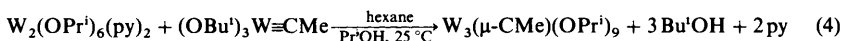
It is important to note that these scissions of the $C\equiv C$ bond do not occur in reactions involving $Mo_2(OBu^t)_6(Mo\equiv Mo)$, nor for other compounds such as $M_2(NMe_2)_6$ and $M_2(CH_2SiMe_3)_6(M\equiv M)$. The reactions appear to be unique to tungsten but are not exclusively limited to the Bu^tO ligand. Other alkoxy groups will give this type of cleavage but the compounds $[(RO)_3W\equiv CR']_n$ are not known. The evidence for $C\equiv C$ scission is, however, overwhelming. For example, in the reaction between $W_2(OPr^i)_6(py)_2$ and $MeC\equiv CMe$ (1 equiv), the triangulo-complex $W_3(\mu_3\text{-}CMe)(OPr^i)_9$ is formed.[31] The structure of the alkylidyne-capped cluster is shown in (7) below. Averaged distances are $W–W = 2.74(1)$ Å and $W–C = 2.06(1)$ Å.

Propylidyne and benzylidyne analogues of (7) are formed in reactions involving $W_2(OPr^i)_6(py)_2$ and $EtC\equiv CEt$ and $PhC\equiv CPh$, respectively.[32] We believe the $W_3(\mu_3\text{-}CR')$ formation is understandable in terms of a conproportionation of $W_2(OPr^i)_6$ and $(Pr^iO)_3W\equiv CR'$. This has a parallel in the preparation of the oxo-capped triangulo-compounds $M_3(\mu_3\text{-}O)(OPr^i)_{10}$ by reaction between $M_2(OPr^i)_6$ and $MO(OPr^i)_4$.[33,34] Further support for this suggestion comes from the essentially quantitative preparation of (7) by the reaction shown in equation 4 and

R = Pr^i X = CMe
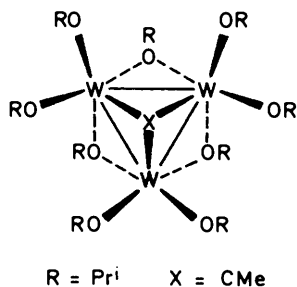
(7)

the successful synthesis of a mixed-metal cluster, which is isomorphous and isostructural with (7), by the reaction shown in equation 5.[35] We have also noted
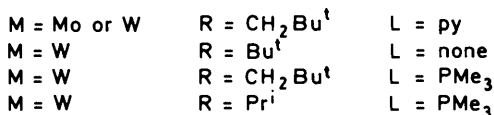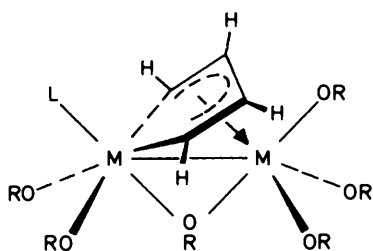
$$W_2(OPr^i)_6(py)_2 + (OBu^t)_3W\equiv CMe \xrightarrow[\text{Pr}^i\text{OH, 25 °C}]{\text{hexane}} W_3(\mu\text{-}CMe)(OPr^i)_9 + 3\,Bu^tOH + 2\,py \quad (4)$$

$$Mo_2(OPr^i)_6 + (Bu^tO)_3W\equiv CMe \xrightarrow[\text{Pr}^i\text{OH, 25 °C}]{\text{hexane}} Mo_2W(\mu\text{-}CMe)(OPr^i)_9 + 3\,Bu^tOH \quad (5)$$

[31] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Inorg. Chem.*, 1984, **23**, 3683.
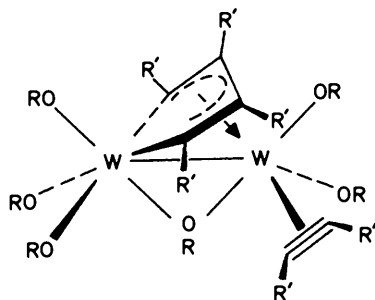[32] M. H. Chisholm and B. Conroy, results to be published.
[33] M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.
[34] M. H. Chisholm, J. C. Huffman, E. M. Kober, *Inorg. Chem.*, 1985, **24**, xxx.
[35] M. H. Chisholm, K. Folting, J. A. Heppert, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1985, **107**, xxx.

M = Mo or W	R = CH_2Bu^t	L = py
M = W	R = Bu^t	L = none
M = W	R = CH_2Bu^t	L = PMe_3
M = W	R = Pr^i	L = PMe_3

(8)

R = Pr^i	R′ = H or Me
R = CH_2Bu^t	R′ = H or Me

(9)

that in the reaction between $W_2(OPr^i)_6(py)_2$ and $BuC\equiv CH$ or $MeC\equiv CH$ (1 equiv), the ethyne adduct, $W_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)$ is formed.[17] Thus we conclude that alkyne scission is not limited to Bu^tO ligands but that with the less bulky alkoxy-groups products other than $[(RO)_3W\equiv CR']_n$ may be formed.

Alkyne Coupling Reactions.—Whenever it has been possible to isolate an alkyne adduct it has been possible to show that these are labile towards C–C coupling reactions upon further addition of alkyne. In many instances new compounds are

M≡M + H*C≡*CH ⟶

↓ DCCD

← DCCD
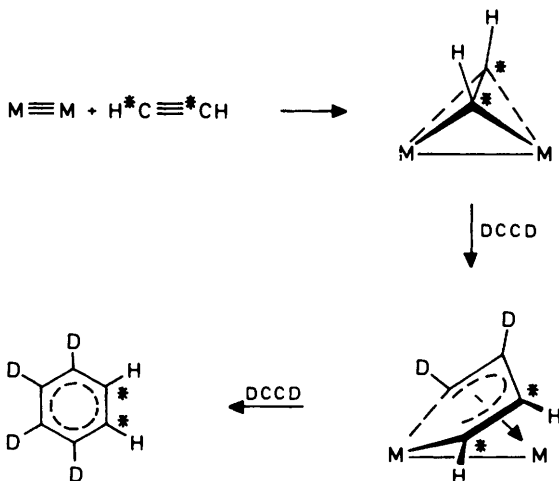
Scheme *The cyclotrimerization of ethyne molecules at the dinuclear centre. The specific combination of labels shown here involved* $Mo_2(OCH_2Bu^t)_6(py)_2$ *in* $[^2H_8]$*toluene at room temperature*

formed containing either two or three alkyne fragments bonded to the dimetal centre as shown in (8) and (9) above.[14,15,36]

In the case of molybdenum the alkyne adducts, (3), and the μ-C_4H_4 compound, (8), were shown to be involved in the catalytic cyclotrimerization of alkynes to give benzenes.[14] Labelling studies have shown that C–C bonds are not broken during the cyclotrimerization (see Scheme). Though not isolated for molybdenum, compounds analogous to those shown for (9) are almost certainly involved in the cyclotrimerization reaction. Interestingly, the ditungsten compounds are reluctant to release the co-ordinated coupled alkynes.

If for the sake of electron counting the μ-C_4R_4 and η^2-C_2R_2 ligands are counted as 2-ligands, being a part of metallacyclopentadienyl and metallacyclopropenyl rings, respectively, then the average oxidation state of tungsten in (9) is $+5$. Of course, oxidation states in compounds of type (9) are rather arbitrary. The main point we wish to emphasize is that in forming new metal–ligand bonds the W–W bond order has been reduced to at most a single bond, consistent with the observed distances W–W = 2.86 Å in (9).[15,36]

C–C coupling is favoured over C–C scission providing steric factors permit. Addition of MeC≡CMe (>3 equiv) to $W_2(OPr^i)_6(py)_2$ yields[36] $W_2(OPr^i)_6(\mu$-$C_4Me_4)(C_2Me_2)$ in essentially quantitative yield despite the fact that the simple alkyne adduct cannot be isolated and there is strong evidence for the formation of $(Pr^iO)_3W≡CMe$. Similarly addition of C_2H_2 (1 equiv) to a solution of $W_2(OBu^t)_6$ in $[^2H_8]$toluene or $[^2H_6]$benzene leads to a 50–50 mixture of $W_2(OBu^t)_6$ and $W_2(OBu^t)_6(\mu$-$C_4H_4)$.[36] $W_2(OBu^t)_6(\mu$-$C_4H_4)$ is presumably formed by the reaction between C_2H_2 and $W_2(OBu^t)_6(\mu$-$C_2H_2)$ with the latter being an exceedingly

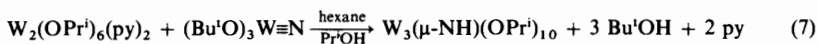[36] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6806.

R = Pr^i X = NH   Y = OPr^i
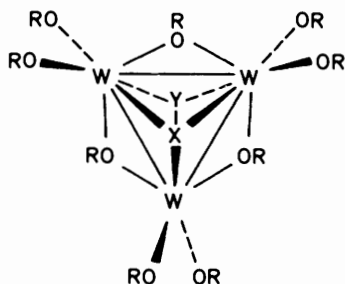
(10)

reactive molecule in the absence of an additional co-ordinated py or CO ligand. The direct addition of C_2H_2 to a solution of $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)\cdot\frac{1}{2}py$ leads to $W_2(OBu^t)_6(\mu\text{-}C_4H_4)$, quantitatively.

3 Reactions Involving RC≡N

$W_2(OBu^t)_6$ reacts with nitriles in hydrocarbon solvents at room temperature according to equation 6.[22] The nitrido-compound has an interesting linear polymeric structure involving alternating short, 1.74(1) Å, and long, 2.66(1) Å, W–N distances corresponding to W–N triple bonds and weak dative single bonds respectively.[27] The nitrido-compound is only very sparingly soluble in hexane and Schrock and co-workers[22] have used reaction 6 to prepare alkylidyne derivatives not easily prepared by reactions 1 and 2.

$$W_2(OBu^t)_6 + R'C\equiv N \longrightarrow (Bu^tO)_3W\equiv N + (Bu^tO)_3W\equiv CR' \qquad (6)$$

$$R' = Ph \text{ or } Me$$
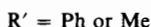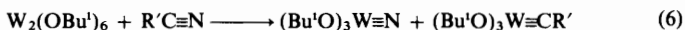
Reactions involving other ditungsten alkoxides and nitriles lead to $[(RO)_3W\equiv N]_x$ compounds ($R = Pr^i$ and CH_2Bu^t) which may be isolated by vacuum sublimation. The fate of the presumably-formed alkylidyne compound $[(RO)_3W\equiv CR']_x$ is not certain though in the reaction between $W_2(OPr^i)_6(py)_2$ and $MeC\equiv N$ compound (7) is formed. This once again provides evidence for the formation of the reactive species $(Pr^iO)_3W\equiv CMe$. If the reaction between $W_2(OPr^i)_6(py)_2$ and $MeC\equiv N$ is carried out in the presence of Pr^iOH then an imido-capped compound $W_3(\mu_3\text{-NH})(OPr^i)_{10}$, (10), is also formed.[37] The imido-compound is isomorphous with the oxo-capped compound $W_3(\mu_3\text{-O})(OPr^i)_{10}$.[34] A direct synthesis of (10) is by the reaction outlined in equation 7.[37]

$$W_2(OPr^i)_6(py)_2 + (Bu^tO)_3W\equiv N \xrightarrow[Pr^iOH]{hexane} W_3(\mu\text{-NH})(OPr^i)_{10} + 3 \text{ Bu}^tOH + 2 \text{ py} \qquad (7)$$

[37] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, results to be published.
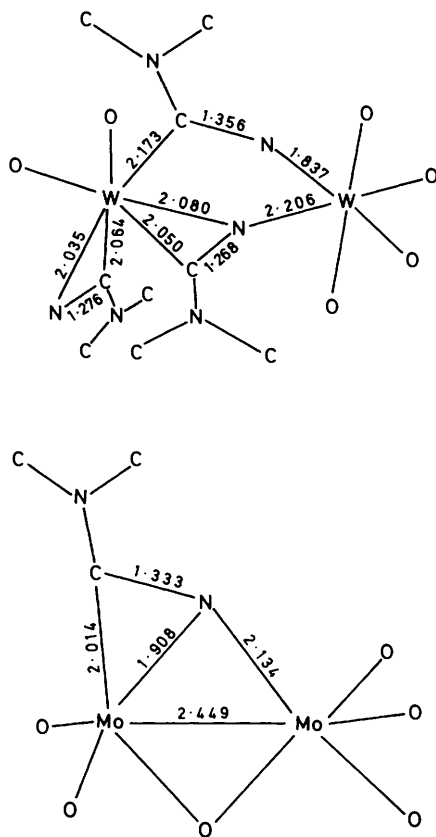
Figure 1 *Comparison of the* Me$_2$NCN-*to-metal bonding in* W$_2$(OCH$_2$Bu^i)$_6$(NCNMe$_2$)$_3$ *and* Mo$_2$(OCH$_2$Bu^i)$_6$(NCNMe$_2$). *The positions of the alkoxy-ligands are denoted by* O

While there is evidence that ditungsten hexa-alkoxides react with alkyl or arylnitriles, R'C≡N, to give products derived from scission of the W≡W and C≡N bonds, no parallel reactions are found for Mo$_2$(OR)$_6$ compounds. The latter do not even co-ordinate nitriles as *N*-donor adducts of type (2).

This is quite a remarkable difference in the reactivity of triple bonds between molybdenum and tungsten atoms. We believe, however, that it is easily understood in terms of the relative ease of oxidation of the metals (W > Mo) and the relative reducing power of their M≡M bonds. The reactions shown in equations 1,2, and 6 can be viewed as oxidative cleavages of the (W≡W)$^{6+}$ moiety to give two W(6+) centres.

Though Mo$_2$(OR)$_6$ compounds show little or no affinity towards simple alkyl or aryl nitriles they do form 1:1 adducts with dimethyl- and diethylcyanamide, R'$_2$N-C≡N, and a comparison of the reactivity with W$_2$(OR)$_6$ compounds is

81

particularly pertinent. The spectroscopic characterization of $Mo_2(OR)_6(NCNR_2)$ compounds, where $R = Bu^t$, Pr^i, or CH_2Bu^t and $R' = Me$ or Et, leads us to believe they are all similar in structure and bonding.[38] Only for $R = Bu^t$ and $R' = Me$ or Et do we see reversible binding of the cyanamide in solution. The molecular structure of the compound where $R = CH_2Bu$ and $R' = Me$, deduced from X-ray studies, reveals that the Me_2NCN ligand spans the Mo–Mo bond of distance 2.449(1) Å.[27] The Mo–Mo distance together with Mo–C, Mo–N, and C–N distances allow one to formulate the adduct in terms of a Me_2NCN^{2-} ligand bonding to a $(Mo\textrm{=}Mo)^{8+}$ centre (see Figure 1).

The reactions between $W_2(OR)_6$ compounds and dialkylcyanamides are quite different. With the bulky Bu^tO ligand the products are those predicted by equation 6, where $R' = Me_2N$ or Et_2N,[27] but with $R = CH_2Bu^t$ the 1:3 adduct $W_2(OCH_2Bu^t)_6(NCNMe_2)_3$ has been isolated at low temperatures.[39] Here three different modes of Me_2NCN to W bonding are seen in the same molecule (see Figure 1). Each Me_2NCN ligand may again be viewed as a dianion and an analogy with the bonding of η^2-acyl ligands[40] is seen. Of course, assignment of oxidation states in such a molecule is somewhat arbitrary. However, the W-to-W distance of 3.85 Å clearly shows that the W≡W bond has been cleaved and the ability of $W_2(OCH_2Bu^t)_6$ to react with three molecules of Me_2NCN relative to $Mo_2(OCH_2Bu^t)_6$, which forms only a 1:1 adduct, testifies to the greater reactivity of the W≡W bond and its desire to transfer electron-density to metal–ligand bonding.

4 Reactions with Carbon Monoxide
Kelly first discovered that hydrocarbon solutions of $Mo_2(OBu^t)_6$ and C≡O react rapidly at room temperature and 1 atm according to the stoicheiometry shown in equation 8.[41]

$$2Mo_2(OBu^t)_6 + 6CO \longrightarrow Mo(CO)_6 + 3Mo(OBu^t)_4 \qquad (8)$$

The first step in equation 8 is the reversible formation of $Mo_2(OBu^t)_6(\mu\textrm{-}CO)$, (11).[41] Carbonylation of $Mo_2(OPr^i)_6$ proceeds similarly to give $Mo(CO)_6$ and in the presence of pyridine an initial carbonyl adduct, $Mo_2(OPr^i)_6(py)_2(\mu\textrm{-}CO)$ can be isolated.[42,43] The latter compound adopts the structure shown in (12) which is closely related to (11) having a Mo–N bond *trans* to the Mo–C bond thereby completing the octahedral co-ordination of each metal atom.

In the case of the carbonylation of $Mo_2(OPr^i)_6$, the oxidized form of molybdenum is $Mo_2(OPr^i)_8(CO)_2$ which is believed to have the edge-shared bioctahedral structure shown in (13).[44]

Carbonylation of $W_2(OR)_6$ compounds also leads to $W(CO)_6$ under very mild

[38] M. H. Chisholm and R. L. Kelly, *Inorg. Chem.*, 1979, **18**, 2266.
[39] M. H. Chisholm, J. C. Huffman, and N. S. Marchant, *Polyhedron*, 1984, **3**, 1033.
[40] M. D. Curtis, K. B. Shiu, and W. M. Butter, *Organometallics*, 1983, **2**, 1475 and references therein.
[41] M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, 1979, **101**, 7645.
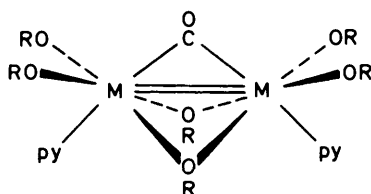[42] M. H. Chisholm, J. C. Huffman, J. Leonelli, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 7030.
[43] F. A. Cotton and W. Schwotzer, *Inorg. Chem.*, 1983, **22**, 387.
[44] M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *J. Am. Chem. Soc.*, 1979, **101**, 7615.

M = Mo or W   R = Bu^t

(11)

M = Mo or W   R = Pr^i or CH$_2$Bu$^{\bullet}$
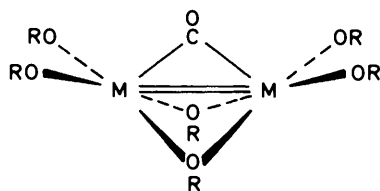
(12)

conditions but the details of the reaction pathways differ from those of molybdenum in two important respects. (*a*) The oxidized form of tungsten is W(6+) and (*b*) at low CO to W$_2$ ratios, where analogues of (11) and (12) are formed, the CO ligand is not readily lost from the dinuclear centre.

Cotton and Schwotzer[45] isolated a compound of formula W$_2$(OPr^i)$_6$(CO)$_4$

M = Mo   R = Pr^i
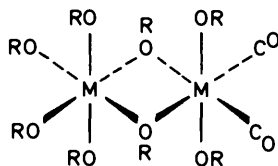
(13)

[45] F. A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, 1983, 105, 5639.

R = Pr^i

(14)
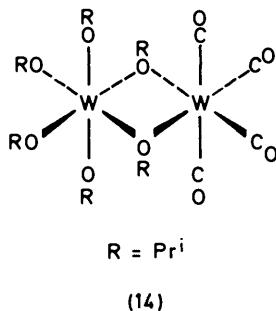
during their studies of the reaction between $W_2(OPr^i)_6$ and CO. The structure of this interesting molecule is indicated by (14) above.

The alkoxy-bridges are very asymmetric in (14) implying that a $W(OPr^i)_6$ molecule is ligated to a $W(CO)_4$ fragment. The stepwise conversion of (1) to (11) to (13) to (14) and finally to $W(OR)_6$ and $W(CO)_6$ by CO uptake and CO and OR group migrations is easy to envisage.

As indicated earlier the CO ligand binds more tightly to the W_2 centre in (11) and (12) compounds than to the Mo_2 centre and some interesting data comparing the molybdenum and tungsten compounds are given in Table 3.[46] The following points are worthy of particular note. (*a*) The M–M and C–O (carbonyl ligand) distances (2.5 and 1.2 Å) are comparable to double bond distances in $(M=M)^{8+}$-containing compounds and ketones, respectively. (*b*) The values of $v(CO)$ are exceptionally low for bridging carbonyl ligands (μ_2-CO) in neutral molecules which normally appear in the range 1 700—1 860 cm^{-1}.[47] (*c*) The value of $v(CO)$ is lower, by *ca.* 70—80 cm^{-1}, for compounds where M = W relative to M = Mo. (*d*) The chemical shifts of the bridging-carbonyl carbon atoms are below 300 p.p.m., which is downfield of the range commonly observed for μ-CO ligands.[48]

All these points are understandable in terms of the mixing of M–M π and C–O π^* orbitals. These molecules are inorganic analogues of cyclopropenones and the simple VB (Valence Bond) structure (15) will have a significant contribution from the ionic resonance forms 15*a* and 15*b*.

(15)   (15*a*)   (15*b*)
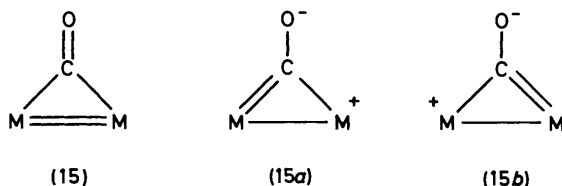
[46] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Organometallics*, 1985, **4**, xxx.
[47] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, 4th Edn., 1980, p. 1072.
[48] M. H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, 1976, **20**, 299.

Table 3 Selected i.r. and ^{13}C n.m.r. data for the $M_2(\mu\text{-CO})$ and $[W_2(\mu\text{-CO})]_2$ containing compounds (M = Mo or W)

Compound	$\nu_{CO}{}^{a}(cm^{-1})$	$\nu^{13}_{CO}(cm^{-1})$	$\delta(^{13}CO)(p.p.m.)^{b}$	$^{1}J_{^{183}W-^{13}C}(Hz)$	^{13}C N.m.r. Temperature/ Solvent	Ref.
$W_2(OBu^t)_6(\mu\text{-CO})$	1 598 (1 605)^{c}	1 559	291.0	192.9	21 °C/C_6D_6	h
$Mo_2(OBu^t)_6(\mu\text{-CO})$	1 670	N.R.^{d}	272.5	—	—	i
$W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-CO})$	1 587 1 579 1 567 (1 595)^{c}	1 546 1 538	321.6	150.3	−60 °C/C_7D_8	h
$Mo_2(OCH_2Bu^t)_6(py)_2(\mu\text{-CO})$	1 660	N.R.	323.6	—	20 °C/C_6D_6	j
$W_2(OPr^i)_6(py)_2(\mu\text{-CO})$	1 570 1 579 (1 298)^{c}	1 533 (1 271)^{c}	341^{e}	—	—	h
$Mo_2(OPr^i)_6(py)_2(\mu\text{-CO})$	1 655	1 618	331.5	—	25 °C/C_6D_6	j
$[W_2(OPr^i)_6(\mu\text{-CO})]_2$	1 272	1 243	305.5	188.9^{f} 164.0	−55 °C/C_7H_8	h
$[W_2(OPr^i)_6(py)(\mu\text{-CO})]_2$	1 305 (1 298)^{c}	1 265	310.4	170.0^{g}	34 °C/C_7D_8	h (i.r.) j,k (n.m.r.)

^{a} I.r. spectra were recorded for Nujol mulls between CsI plates except when noted. ^{b} In p.p.m. relative to TMS. ^{c} I.r. spectrum recorded for a toluene solution. ^{d} N.R. = not reported. ^{e} Magic-angle ^{13}C n.m.r. value. Solution value from *ref. j* below is incorrect. ^{f} Consistent with the solid-state structure, there are two $^{183}W-^{13}C$ coupling constants. ^{g} Only one $^{183}W-^{13}C$ coupling constant reported. ^{h} M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Organometallics*, submitted. ^{i} M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, 1979, **101**, 7645. ^{j} M. H. Chisholm, J. C. Huffman, J. Leonelli, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 7030. ^{k} F. A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, 1983, **105**, 4955

(16*a*)   (16*b*)
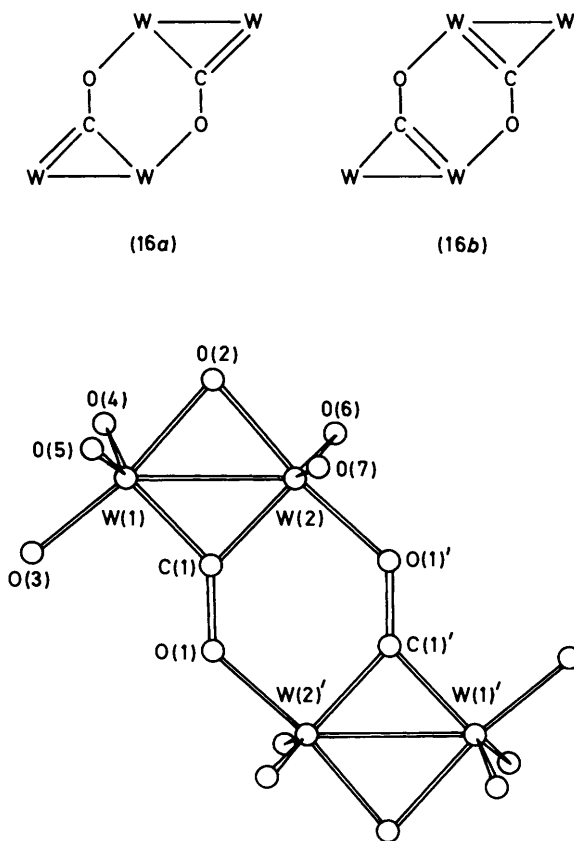
Figure 2 *A ball and stick drawing of the central* $[W_2(\mu\text{-}CO)O_6]_2$ *skeleton of the* $[W_2(OPr^i)_6(\mu - CO)]_2$ *molecule showing the trigonal bipyramidal co-ordination at each tungsten atom. Pertinent distances are given in the text*

The lower values of $\nu(CO)$ for $M = W$ relative to $M = Mo$ reflect the greater reducing power of the $W{\equiv}W$ bond and the greater W to C–O π^* bonding.

The bonding picture presented by (15) and its ionic resonance forms, leads to the prediction that the oxygen atom of the μ-CO ligand should be nucleophilic and the metal centre electrophilic. This prediction was realized experimentally by Cotton and Schwotzer[49] who, in attempting to prepare $W_2(OPr^i)_6(py)_2(\mu\text{-}CO)$ isolated instead $W_4(OPr^i)_{12}(CO)_2(py)_2$. The closely related molecule $W_4(OPr^i)_{12}(CO)_2$, which has the central $W_4O_{12}(CO)_2$ skeleton shown in Figure 2, is made by the addition of Pr^iOH to $W_2(OBu^i)_6(\mu\text{-}CO)$.[46] The formation of $W_4(OPr^i)_{12}(CO)_2$ or its pyridine adduct arises from the dimerization of two molecules of (11) or (12). The

[49] F. A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, 1983, **105**, 4955.

essential feature of the dimerization is the coupling of two units of (15) to give the resonance isomers shown in (16*a*) and (16*b*).

Of note in the structural characterization of $W_4(OPr^i)_{12}(CO)_2$ is that the W–W and C–O distances increase from those in (11) and (12) to W–W = 2.66(1) Å and C–O = 1.35(1) Å. These are W–W and C_{sp^2}–O single-bond distances, respectively. On the other hand the W–C distances, 1.95(1) Å (averaged) are shorter than those in (11) and (12).

The stepwise reaction involving $W{\equiv}W + C{\equiv}O \longrightarrow W_2(\mu\text{-}CO)$ followed by $2W_2(\mu\text{-}CO) \longrightarrow [W_2(\mu\text{-}CO)]_2$ converts W–W and C–O triple bonds first into double bonds and then into single bonds. Formally the ditungsten centre is oxidized $(W{\equiv}W)^{6+} \longrightarrow (W{=}W)^{8+} \longrightarrow (W{-}W)^{10+}$ and the carbonyl ligand reduced. We believe that the reaction does not stop here but rather by a further reaction between $W_2(OPr^i)_6$ and $W_4(OPr^i)_{12}(CO)_2$ (note the metal atoms are only five co-ordinate in the latter molecule—see Figure 2) the C–O bond of the former carbon monoxide molecule is cleaved to give carbido, C^{4-}, and oxide, O^{2-} tungsten alkoxide clusters. The reduction of $C{\equiv}O$ to C^{4-} and O^{2-}, a six-electron process, requires the co-operative effects of two or more $(W{\equiv}W)^{6+}$ units which contrasts with the cleavage of $C{\equiv}C$ and $C{\equiv}N$ bonds described before. Further work is required to establish these important matters and at present the evidence for $C{\equiv}O$ cleavage to carbide and oxide is speculative. However, we have observed a facile C=O bond cleavage reaction, equation 9,[50] and also have isolated the carbido butterfly-cluster $W_4(\mu_4\text{-}C)(OPr^i)_{12}(\mu_2\text{-}NMe)$ from a thermal decomposition of $W_2(OPr^i)_6(HNMe_2)_2$.[6]

$$2W_2(OPr^i)_6(py)_2 + 2Me_2C{=}O \longrightarrow W_4O_2(OPr^i)_{12} + Me_2C{=}CMe_2 \qquad (9)$$

5 Reactions with N–N Triple Bonds

The facile cleavage of $C{\equiv}C$ and $C{\equiv}N$ bonds, the reactions with $C{\equiv}O$ leading to C–O single bonds and possibly carbide and oxide lead one to ask: What about $N{\equiv}N$? All the chemistry described thus far has been carried out under an atmosphere of N_2 and we have found no evidence for N_2 activation. Professor Schrock also informed us that he and his group had looked for a possible reaction between $W_2(OBu^t)_6$ and N_2 at high pressures and moderately elevated temperatures but found none.[51]

A plausible explanation for this lack of reactivity may lie in the poor ligating properties of the N_2 molecule. It is possible that the reaction between $W_2(OBu^t)_6$ and N_2 to give $(Bu^tO)_3W{\equiv}N$ is thermodynamically favourable but has a high kinetic barrier imposed by the low affinity of the weak Lewis base to the $(W{\equiv}W)^{6+}$ centre.

This leads one to speculate whether or not a transition-metal dinitrogen complex[52] might serve as a carrier of a more active N_2 molecule to the $(W{\equiv}W)^{6+}$ centre. In this regard we note that diaryl-substituted diazomethanes react very

[50] T. P. Blatchford, M. H. Chisholm, K. Folting, and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1984, 1295.
[51] Personal communication.
[52] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.

R = Bu^t Ar = *p* - tolyl
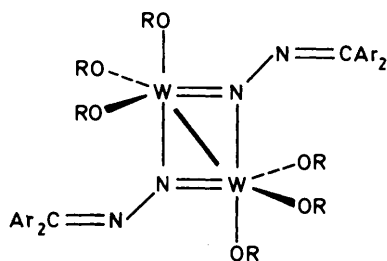
(17)

rapidly with $W_2(OR)_6$ compounds in hydrocarbon solvents even at -78 °C. The molecular structure of the adduct $W_2(OBu^t)_6(N_2CAr_2)_2$ is shown schematically in (17).[53]

The geometry depicted by (17) is based on two fused trigonal bipyramids sharing a common equatorial–axial edge. The W–W distance is 2.675(1) Å and the N–N distance is 1.41(1) Å, typical of single-bond distances. In the reaction between $W_2(OBu^t)_6$ and N_2CAr_2, the $(W{\equiv}W)^{6+}$ unit has been oxidized to $(W{-}W)^{10+}$ and the diazoalkane reduced to $Ar_2CN_2^{2-}$, a hydrazido $2-$ ligand.[54–56]

6 Reactions of Alkyne Adducts with Nitriles and Carbon Monoxide

The observation of facile C–C coupling in the reactions of alkyne adducts, (3), (4), and (5) with additional equivalents of alkyne led us to investigate their reactivity toward CO and RCN molecules.

We have found no evidence for C–C bond formation in reactions of alkyne adducts, compounds (3), (4), and (5), or the μ-C_4R_4-containing compounds, (8), with carbon monoxide at room temperature, 1 atm. Simple 1:1 adducts of the type shown in (18), (19), and (20) below have been isolated.[57]

However, nitriles and the alkyne adducts of tungsten react rapidly to give dinuclear compounds containing fused heterocyclic rings.[58] The driving force for these reactions appears to be the formation of both C–C and W–N bonds.

$W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2).\tfrac{1}{2}py$ reacts at room temperature with $R'C{\equiv}N$ (1 equiv), where $R' = Me$ and Ph to give (21). The VB description is based on the bond distances: W–W = 2.674(1) Å, W=C = 1.980(6) Å, W=N = 1.903(5) Å, W–N = 2.041(5) Å and C=C = 1.36(1) Å.[59] The geometry about each tungsten atom

[53] M. H. Chisholm, J. C. Huffman, and A. L. Ratermann, *Inorg. Chem.* 1984, **23**, 2303.
[54] J. R. Dilworth, *Coord. Chem. Rev.*, 1976, **21**, 29.
[55] J. Chatt, R. A. Head, P. B. Hitchcock, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, 1977, **133**, Cl.
[56] J. Chatt, G. J. Leigh, and R. A. Head, *J. Chem. Soc., Dalton Trans.*, 1980, 1129.
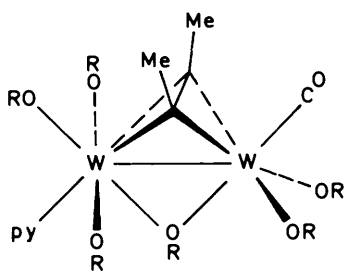[57] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, results to be published.
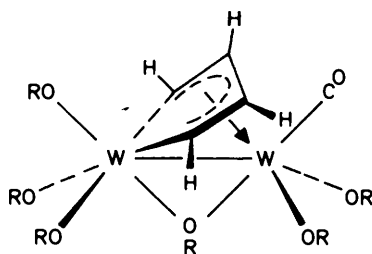[58] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6815.
[59] For a discussion of M–N bond distances and bond order assignments see W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

R = Bu^t

(18)

R = CH$_2$Bu^t

(19)

R = Bu^t
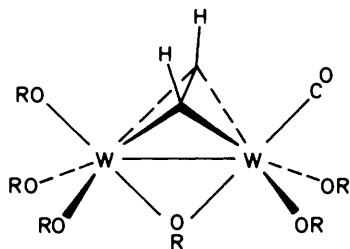
(20)

corresponds to a distorted trigonal-bipyramid in which the W=C and W=N bonds occupy equatorial positions.

The compound W$_2$(OCH$_2$Bu^t)$_6$(py)$_2$(μ-C$_2$Me$_2$) reacts with MeC≡N (> 2 equiv) to give W$_2$(OCH$_2$Bu^t)$_6${N(CMe)$_4$N}(py). In this molecule each tungsten atom is six co-ordinate and the local geometry is a distorted octahedron. The two tungsten atoms share a face formed by two OR ligands and the nitrogen atom of the metallacycle shown in (22). Again the VB depiction is based on observed W–W, W–N, C–N, and C–C distances. It is reasonable to assume that a molecule analogous to (21) is an intermediate in the reaction to form (22).

7 Concluding Remarks

The reactions described in this account show that the (M≡M)$^{6+}$ unit in M$_2$(OR)$_6$ compounds, (1), provides both a source of electrons and a template for C≡C, C≡N, and C≡O groups. These reactions may be viewed as a special class of oxidative additions in which electron density is removed from M–M bonds to form metal–ligand bonds. It is the availability of the empty π^* orbitals of the C≡C, C≡N, and

89

$$W_2(OBu^t)_6\{\mu\text{-}CHCHC(R)N\}$$
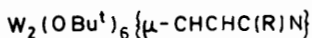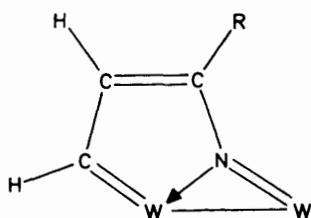
(21)

$C\equiv O$ groups that leads to the mutal reduction in M–M and C–X bond order (X = C, N, or O). The W≡W bond is a more powerful reducing agent than the Mo≡Mo bond leading in certain cases to remarkable oxidative cleavage reactions, equations 1 and 6. The latter are dependent upon steric factors. Whenever possible the formation of more metal–ligand bonds is favoured over cleavage of C–C or C–N bonds.

The role of alkyne adducts in the metathesis reactions (equation 1) is also of interest. What reaction pathway leads from the pseudo-tetrahedral M_2C_2 unit in $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ to the alkylidyne $(Bu^tO)_3W\equiv CH$? Are 1,2 or 1,3-dimetallacyclobutadiene intermediates, (23) or (24), involved?

Also what part do bridging alkoxy-ligands play in the pathway leading to C–C cleavage? If we consider the proposed equilibrium shown in equation 3, it is easy to anticipate that it could be close to thermochemical neutrality. The dimetallatetrahedrane has six σ-bonds, four W–C bonds, one C–C, and one W–W bond while two alkylidyne–tungsten moieties have two W–C σ-bonds and four W–C π-bonds. It

$$W_2(OCH_2Bu^t)_6\{\mu\text{-}N(CMe)_4N\}(py)$$

(22)

(23)   (24)
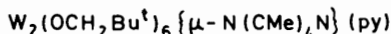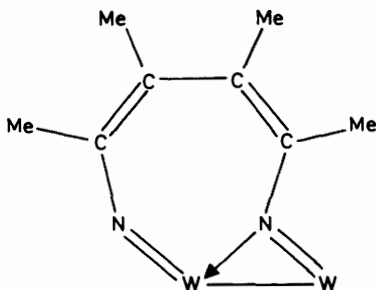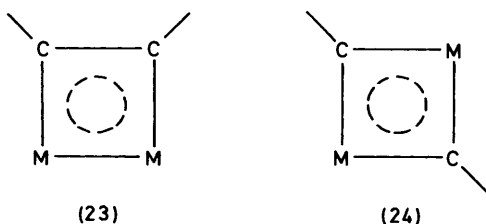
has been estimated [60] that the conversion of two terminal M–OR bonds into four M–OR bridging bonds, 2 M–OR $\longrightarrow$ M$_2$(μ-OR)$_2$, is enthalpically favoured by 10—15 kcal mol^{-1}. Consequently steric factors which permit alkoxide bridge formation might favour the dimetallatetrahedrane while bulky substituents could cause sufficient internal steric pressure to break the μ-OR bridges and favour C–C scission.

While the present findings raise still many unanswered questions they indicate many avenues for future research and the great potential that compounds with M–M multiple bonds offer toward multi-electron redox reactions.

Note Added in Proof
Schrock and co-workers have recently reported [61] the cleavage of the Mo≡Mo bond in the reaction between Mo$_2$(OBu^t)$_6$ and PhC≡CH (15 equiv) and the full details [62] of their studies of the reactions between alkynes and W$_2$(OBu^t)$_6$.

[60] K. J. Cavell, J. A. Connor, G. Pilcher, M. A. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, H. A. Skinner, Y. Virmani, and M. T. Zafaram-Moattar, *J. Chem. Soc., Faraday Trans.*, 1981, **77**, 1585.
[61] H. Strutz and R. R. Schrock, *Organometallics*, 1984, **3**, 1600.
[62] M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74.