DALTON PERSPECTIVE

Ditungsten hexaalkoxides: templates for organometallic chemistry and catalysis *

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The reactions between $W_2(OR)_6$ compounds and carbon monoxide, ethene, acetylene, allene, 1,3-dienes, ketones, aldehydes and eneones are described. The selection of R allows for control of steric access to the $(W{\equiv}W)^{6+}$ centre and the relative reducing power of the W–W π electrons and Lewis acidity of the W atoms. With CO, $W_2(OBu^t)_6$ gives $W_2(OBu^t)_6(\mu\text{-CO})$, $\tilde{\nu}(CO) = 1575\ cm^{-1}$, while $W_2[OCMe_2(CF_3)]_6$ yields $W_2[OCMe_2(CF_3)]_6(CO)_2$ with $\tilde{\nu}(CO) = 2081$ and $2050\ cm^{-1}$. Similarly, whereas MeCN and $W_2(OBu^t)_6$ react rapidly in hydrocarbons to yield products of metathesis $(Bu^tO)_3W{\equiv}N$ and $(Bu^tO)_3W{\equiv}CMe$, $W_2[OCMe_2(CF_3)]_6$ reversibly forms the Lewis-base adduct $W_2[OCMe_2(CF_3)]_6(NCMe)_2$. Allene and $W_2(OBu^t)_6$ react to give a 1:1 adduct having a μ-C–C–C fragment that is parallel to the W–W axis and a 2:1 adduct wherein one allene forms a metallaallyl that is η^1 bound to one W atom and η^3 to the other. Novel modes of binding to the dinuclear centre lead to novel modes of substrate activation. Examples include the reductive cleavage of ketone and aldehyde C–O bonds which forms the basis of an olefination reaction. Also co-ordination of 1,3-dienes as a μ-η^1:η^4 carbon fragment to the dinuclear centre facilitates the specific hydrogenation to give 3-enes.

Whilst with hindsight our past may be viewed with 20:20 vision, the future is always veiled by the mist of uncertainty. It is from this vantage point that we carry out research. Modern co-ordination chemistry can reasonably be traced to the foundations laid by Alfred Werner and his followers but with each ensuing discovery of a new complex or reaction only time allowed an accurate assessment of its impact. Within this context we can now look back to some of the significant trends in the development of organotransition-metal chemistry which deals by definition with the chemistry of the transition metal to carbon bond.[1]

Two points are really striking. First, the importance of the inorganic template and its valence configuration (its frontier molecular orbitals) and secondly, the role of the ancillary or spectator ligands. The latter may be used judiciously to control the stereochemistry about the metal centre and also the relative energetics of the frontier orbitals.

For the later transition metals the square-planar d^8 ML_4 and the octahedral d^6 ML_6 complexes are of particular note along with their respective more reactive and electron-deficient d^8 T-shaped ML_3 and d^6 square-pyramidal ML_5 fragments. It is from these templates that we witnessed the development of the hydrogenation of olefins by rhodium complexes and subsequent extensions to hydrosilylation and hydroformylation. Of similar importance was the development of the d^{10} tetrahedral ML_4 and trigonal ML_3 complexes and their interconversions with d^8 square-planar ML_4 species. From this chemistry emerged the DuPont synthesis of adiponitrile, one of the two monomers that are employed in the synthesis of nylon, by hydrocyanation of butadiene.[2]

For the early transition elements the use of the now ubiquitous family of cyclopentadienyl ligands was all important and probably the most significant fragment was that of the bent $(C_5H_5)_2M$ moiety for the Group 4, 5 and 6 metals. The chemistry that has emerged over the past two decades employing bent $(C_5R_5)_2M$ as a template, where C_5R_5 encompasses the full family of cyclopentadienyl ligands, is truly amazing. α-Olefin polymerization carried out by carefully designed C_2-symmetric, cationic, bent sandwich compounds of zirconium promises to supplant all previous Ziegler–Natta processes because of the control of stereoregularity and molecular weight distribution.[3]

The chemistry of metal carbonyls also represents one of the most significant chapters in organometallic chemistry being intimately linked with homogeneous hydroformylation catalysis employing cobalt and the conversion of synthesis gas (H_2 + CO) into methanol by nickel.[2] The stepwise loss of a carbonyl ligand allows for substrate uptake and in many cases for cluster formation. Higher-nuclearity clusters of Ru, Os, Ni, Pd and Pt are truly remarkable with respect to their structural chemistry and also for the way in which hydrocarbon fragments may bind.[4] The study of these clusters and the organometallic chemistry of surfaces has enjoyed a fruitful symbiotic relationship.[5]

The potential organometallic chemistry of dinuclear molybdenum and tungsten was particularly attractive to me since compounds of molybdenum and tungsten with multiple metal–metal bonds of order four, M_2^{4+}, and three, M_2^{6+}, have eight and six electrons, respectively, and therefore posed a potential relationship with the then established organometallic chemistry of d^6 and d^8 mononuclear metal complexes.[6]

There are several ways in which to explore this type of chemistry. In the first instance it is always possible to introduce metal–carbon bonds by metathetical reactions as in the formation of $M_2(C_3H_5)_4$, $M_2Me_8^{4-}$, $M_2(CH_2R)_6$, where R = Bu^t, SiMe$_3$ or Ph, and in mixed ligated compounds such as $M_2R_2(NMe_2)_4$ and $M_2R_2(OR^1)_4$. However, an alternative approach is to take an M_2L_n template that lacks any M–C bond and use this in what may be viewed as an analogous manner to starting with NiL_3 or NiL_2, where L = a tertiary phosphine or phosphite ligand. In this article I restrict my observations to the development of the chemistry of $W_2(OR)_6$ compounds which are members of the now well known family of so-called d^3–d^3 ethane-like dimers, **I**.[7]

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* Dedicated to Lord Lewis, Professor of Inorganic Chemistry, 1970–1995, Cambridge University, on the occasion of his retirement, and based in part on a lecture presented at the Dalton Symposium, Metal–Metal Bonds in Chemistry, 14–15th September, 1995, Cambridge, UK.

Non-SI units employed: eV $\approx 1.60 \times 10^{-19}$ J, cal = 4.184 J, atm = 101 325 Pa.

$W_2(OR)_6$ Compounds

Compounds of type I are readily prepared from $W_2(NMe_2)_6$ by an alcoholysis reaction (1).[8] Alternatively the compound

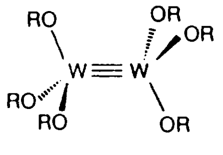
$$W_2(NMe_2)_6 + 6ROH \xrightarrow[\text{hexane}]{22\,^\circ\text{C}} W_2(OR)_6 + 6NHMe_2 \qquad (1)$$

$$NaW_2Cl_7 + 6NaOBu^t \xrightarrow[\text{hexane, thf}]{22\,^\circ\text{C}} W_2(OBu^t)_6 + 7NaCl \qquad (2a)$$

$$W_2(OBu^t)_6 + ROH\ (\text{excess}) \xrightarrow[\text{hexane}]{22\,^\circ\text{C}} W_2(OR)_6 + 6Bu^tOH \qquad (2b)$$

$W_2(OBu^t)_6$ can be made by reaction (2a)[9] (see footnote 5 in ref. 9, also ref. 10) and subsequent alcohol exchange (2b) may yield I; thf = tetrahydrofuran.

Compounds of type I are restricted to bulky R groups, *e.g.* Bu^t, Pr^i, CH_2Bu^t, cyclohexyl, $SiMe_2Bu^t$, $CMe_2(CF_3)$, $CMe(CF_3)_2$ and $2,6\text{-}Me_2C_6H_3$. With less sterically demanding groups such as CH_2Pr^i, cyclopentylmethyl and CH_2Bu^t, $W_4(OCH_2R)_{12}$ compounds are formed.[11] For R = Pr^i the equilibrium (3) exists in solution.[12]



I

$$2W_2(OPr^i)_6 \rightleftharpoons W_4(OPr^i)_{12} \qquad (3)$$

During the alcoholysis reaction (1) or (2b) it is possible to introduce a Lewis base such as pyridine (py), PMe_3 or a chelating ligand, *e.g.* $MeHNCH_2CH_2NHMe$, and trap the $W_2(OR)_6$ fragment as in the isolation and characterization of $W_2(OEt)_6(MeHNCH_2CH_2NHMe)_2$.[13] However, here the chelating amine is too tightly bound to make the $W_2(OEt)_6$ molecule available for reaction in solution. In the case of $W_2(OCH_2Bu^t)_6(py)_2$ the pyridine ligands bind reversibly in solution, equation (4), affording access to $W_2(OCH_2Bu^t)_6$

$$W_2(OCH_2Bu^t)_6(py)_2 \xrightleftharpoons[\text{benzene, hexane}]{22\,^\circ\text{C}} W_2(OCH_2Bu^t)_6 + 2py \qquad (4)$$

which in hydrocarbon solutions then only slowly dimerizes to give irreversible formation of $W_4(OCH_2Bu^t)_{12}$.

The compounds $W_2(OR)_6$ are electronically unsaturated with each metal having only a 12 valence-electron count as a result of forming three W–O σ bonds and a W–W triple bond. By oxygen p_π donation, the RO ligands may compensate in part for this electron deficiency. The RO p_π to W d_π donation has two effects: (1) it influences the energy of the M≡M π orbitals by a filled–filled interaction as shown schematically in Fig. 1; (2) it influences the Lewis acidity of the metal acceptor orbitals (which are formally the W–O π^* orbitals having W–W δ symmetry). The photoelectron ionization energies from the W≡W π orbitals for R = Bu^t, $CMe_2(CF_3)$ or $CMe(CF_3)_2$ are, respectively, 6.27, 7.31 and 8.14 eV.[14] This reveals the marked influence of introducing CF_3 groups in place of Me groups on the highest occupied molecular orbital (HOMO). The lowest unoccupied molecular orbitals (LUMOs) of $W_2(OR)_6$ compounds are the metal-centred M–O π^* orbitals as shown in Fig.

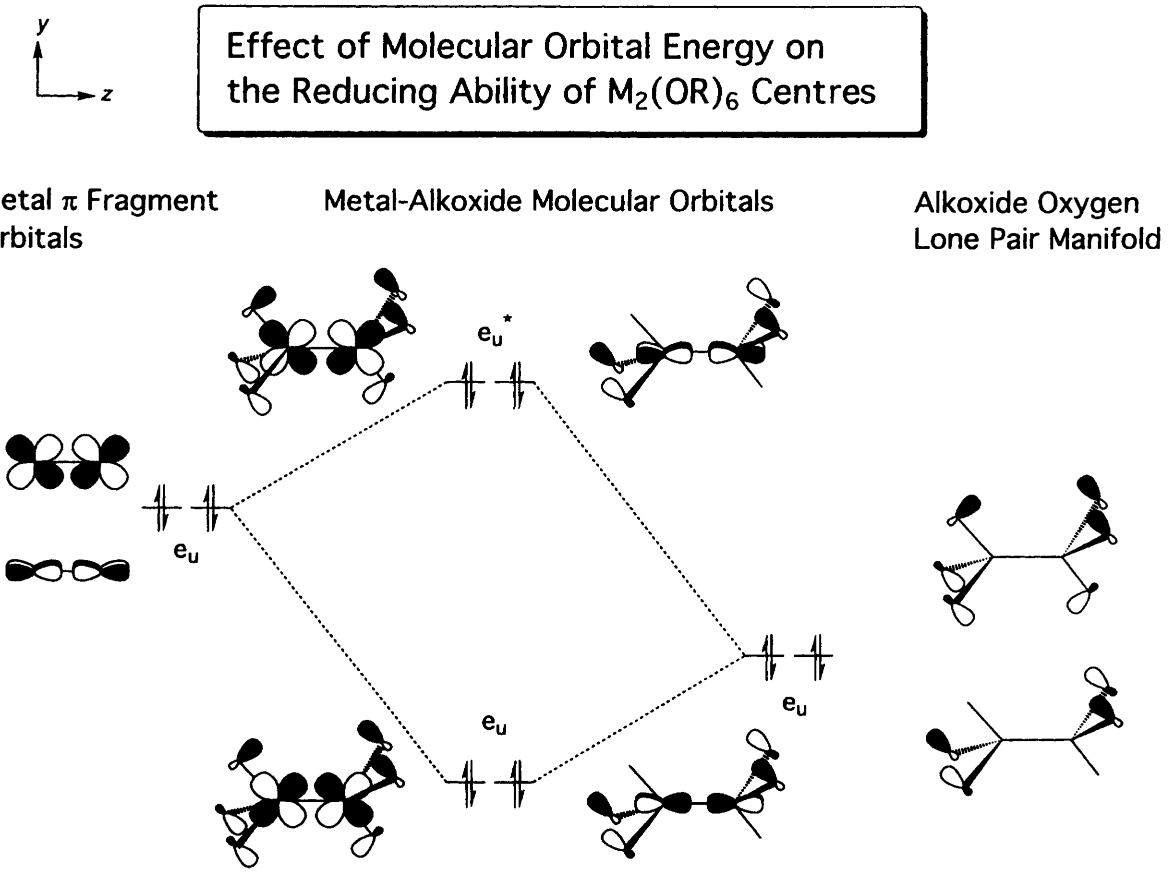


Fig. 1 A schematic molecular orbital interaction diagram showing how oxygen p_π to metal d_π interactions raise the energy of the M–M π orbitals

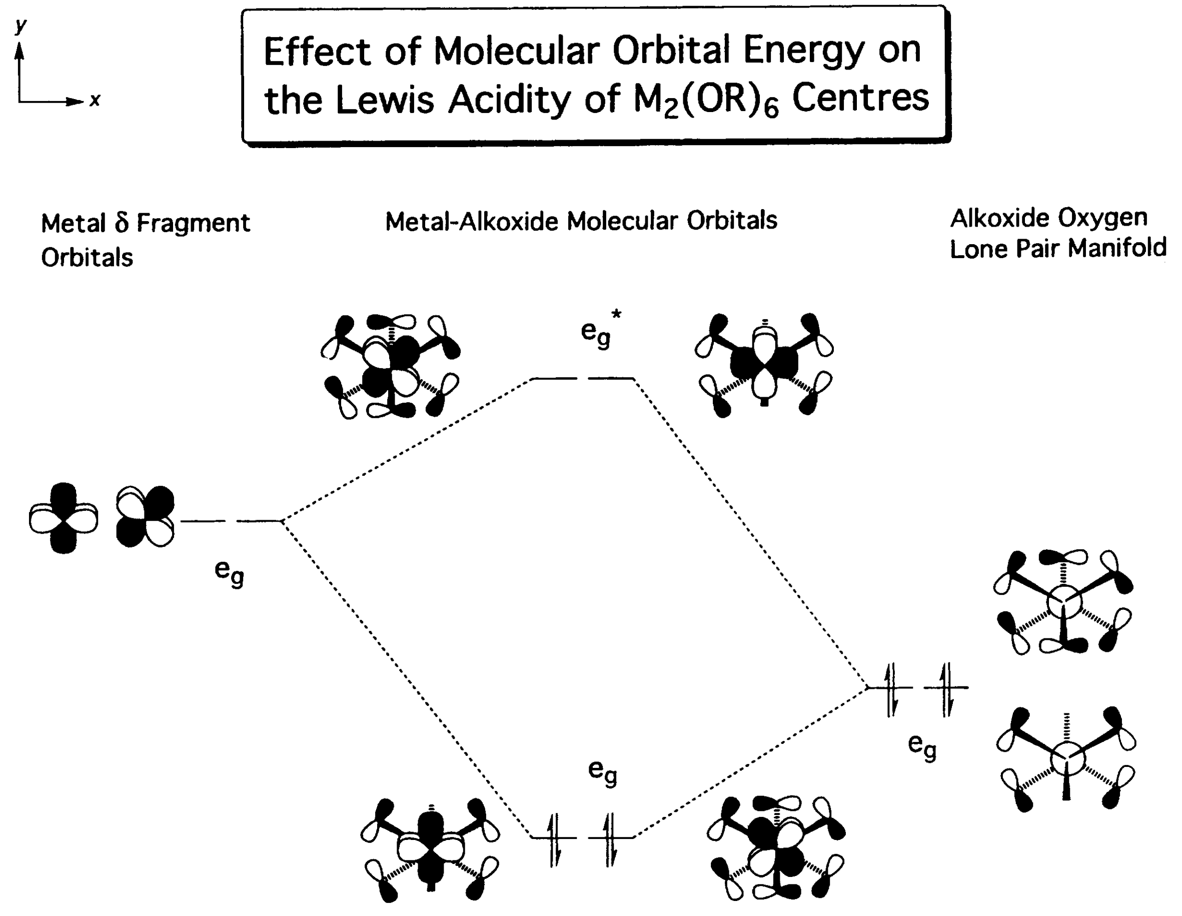


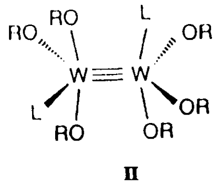
Fig. 2 A schematic molecular orbital interaction diagram showing how oxygen p_π to metal d_π interactions influence the metal-centred δ and δ* empty orbitals

2. These have M–M δ/δ* symmetry. The weaker the RO p_π-to-M d_π bonding the lower in energy are the metal-centred M–O π* orbitals and thus the more Lewis acidic are the metal centres. The σ-donor ability of the RO^- ligands also influences the energy of the M–M π and δ/δ* orbitals in a similar manner but due to isotropic effects (electronegativity) rather than the specific d_π–p_π orbital interactions noted in Figs. 1 and 2.

The compounds $W_2(OR)_6$ are inorganic analogues of alkynes having cylindrical triple bonds of electronic configuration $\sigma^2\pi^4$ since with D_{3d} symmetry the π_x and π_y orbitals are degenerate. The d^3 $W(OR)_3$ fragment is isolobal with $Co(CO)_3$, $(C_5H_5)W(CO)_2$ and, of course, CR.[15] The $W_2(OR)_6$ molecules have therefore an analogy with $M_2(C_5H_5)_2(CO)_4$ (M≡M) compounds (M = Mo or W) and the hypothetical molecule $Co_2(CO)_6$. However, whereas addition of Lewis bases to give $Co_2(CO)_6L_2$ or $M_2(C_5H_5)_2(CO)_4L_2$ (*e.g.* for L = CO, CNR or PMe_3) generates M–M single-bonded compounds, because the $(C_5H_5)M(CO)_3$ and $Co(CO)_3L$ fragments are isolobal with $H^•$ and $CH_3^•$, the formation of $W_2(OR)_6L_2$ compounds occurs with retention of the M–M triple bond. [The d^3 $W(OR)_3L$ fragment still has frontier orbitals of σ and π symmetry: d_{z^2}, d_{xz} and d_{yz}. With lower symmetry the *xz* and *yz* orbitals are no longer degenerate but have similar energy.] The generalized equilibrium (5), for which (4) is a specific example, is influenced

$$W_2(OR)_6 + 2L \overset{K_{eq}}{\rightleftharpoons} W_2(OR)_6L_2 \qquad (5)$$

by the nature of R by electronic and steric factors. As noted above the introduction of CF_3 for Me increases the Lewis acidity of the metal centre and thus increases K_{eq} as defined in equation (5). Steric factors associated with both R and L may also be very important in determining the magnitude of K_{eq} and in some instances only one ligand L may bind to the M_2^{6+} centre if the steric pressure is great.[16]



II

Reactions

With nitriles. From the above it becomes apparent that, by judicious choice of R, a $W_2(OR)_6$ compound may be substrate selective. An interesting example of this type of selectivity is seen in reactions involving acetonitrile. As noted by Schrock and co-workers[17] some ten years ago, $W_2[OCMe_2(CF_3)]_6$ reacts reversibly with MeCN to give a bis(acetonitrile) adduct. Though not structurally characterized this compound shows spectroscopic properties that are entirely consistent with the adoption of a structure typical of that now seen for several structurally characterized $M_2(OR)_6L_2$ compounds and represented schematically by **II**.[18] In solution there is rapid rotation about the W–W bond but for certain $M_2(OR)_6L_2$ compounds this can be frozen out at low temperatures on the NMR timescale.

As part of a study aimed at obtaining thermodynamic and activation parameters for equilibria (5) we have determined for R = $CMe_2(CF_3)$ and L = MeCN that $\Delta H^\circ = -26$ kcal mol^{-1} and $\Delta S^\circ = -78$ cal K^{-1} mol^{-1}, $\Delta H^\ddagger = 24$ kcal mol^{-1} and $\Delta S^\ddagger = -38$ cal K^{-1} mol^{-1}.[19] These data were obtained from variable temperature ^{15}N NMR studies in $[^2H_8]$toluene.

In contrast, $W_2(OBu^t)_6$ and MeCN react in benzene, toluene and hexane at room temperature (and below) to give products of the reductive cleavage of the C≡N moiety as shown in equation (6).[19] We attribute this notable difference to electronic

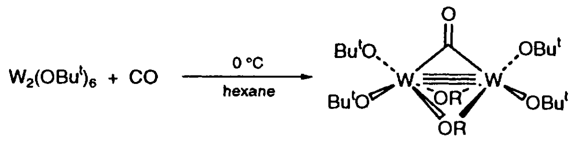
$$W_2(OBu^t)_6 + MeCN \xrightarrow[\text{hexane}]{22\,^\circ C} (Bu^tO)_3W{\equiv}N + (Bu^tO)_3W{\equiv}CMe \quad (6)$$

$$Mo_2(OCH_2Bu^t)_6 + (p\text{-}XC_6H_4)_2C{=}S \xrightarrow[\text{benzene}]{T/^\circ C} Mo_2(\mu\text{-}S)(OCH_2Bu^t)_6[{=}C(C_6H_4X)_2] \quad (7)$$

factors and from studies of a related reductive cleavage of $(p\text{-}XC_6H_4)_2C{=}S$, equation (7) have noted the marked influence of the X group (electron donating, OMe, to electron withdrawing, CF_3) on the activation parameters.[16] The activation parameters reflect the difference in orbital energies of the M≡M HOMO, the filled π orbital, and the substrate π* orbitals. It seems likely that similar factors are operative in the cleavage of the C≡N bond in nitriles since $W_2[OCMe_2(CF_3)]_6$ and PhCN react in benzene to give the trimeric nitride $\{WN[OCMe_2(CF_3)]_3\}_3$ which has a central planar W_3N_3 core with alternating short and long W-N distances.[20] The rates of cleavage in $p\text{-}XC_6H_4C{\equiv}N$ substrates are markedly dependent upon the nature of X following the order X = Cl > H > OMe.[19]

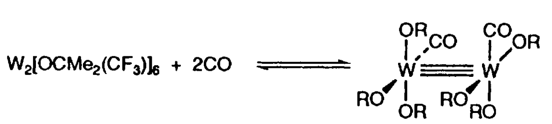
A plausible structure for a reactive intermediate on the pathway leading to cleavage of the C≡N bond in nitriles is seen in the structurally characterized compound $Mo_2(OCH_2Bu^t)_6(\mu\text{-}NCNMe_2)$ **III**.[21] A similar $\mu\text{-}\eta^1{:}\eta^2\text{-}SCPh_2$ ligand was seen in the complex $Mo_2(C_5H_5)_2(CO)_4(\mu\text{-}SCPh_2)$ formed by the addition of $Ph_2C{=}S$ to $Mo_2(C_5H_5)_2(CO)_4$ (M≡M).[22]

With carbon monoxide. Compounds $W_2(OR)_6$ readily react with carbon monoxide and again we observe a marked difference in the nature of products as a function of R. For R = Bu^t a 1:1 adduct is formed according to equation (8)[23]



(8)

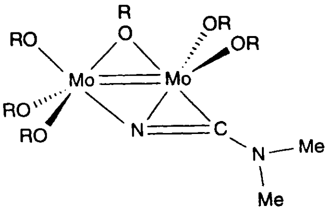
ν̃(CO) = 1575 cm⁻¹



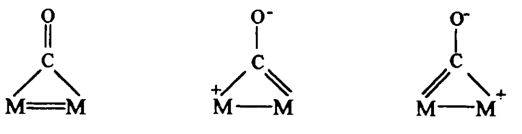
(9)

ν̃(CO) = 2081, 2050 cm⁻¹

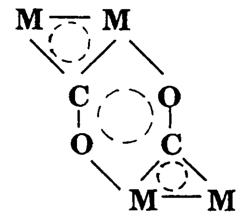
whereas for the weaker π-donating and less electron-releasing Bu^tMe_2SiO and $(CF_3)Me_2CO$ ligands, bis carbonyl adducts are formed, equation (9).[24] The latter are formed reversibly and although a monocarbonyl adduct must be involved in this reaction none is detected in solution by either ^{13}C NMR or infrared spectroscopy. The compound $W_2(OBu^t)_6(\mu\text{-}CO)$ shows a remarkably low value for ν̃(CO), namely 1575 cm^{-1}. This is well below the range seen for μ-CO ligands in organometallic chemistry, typically 1850–1750 cm^{-1}.[25] There are two important factors influencing the unusual nature of the μ-CO moiety in $W_2(OBu^t)_6(\mu\text{-}CO)$. First the addition of C≡O across the W≡W bond leads to the formation of an inorganic analogue of a cyclopropenone. These are known to have rather reduced ketonic groups (relative to $R_2C{=}O$ compounds) because the presence of the C=C bond allows a mixing with the C–O π* orbital in the C_3 plane.[26] Thus for the central $W_2(\mu\text{-}CO)$ moiety we can write the resonance forms shown in **IV**. The second important factor is that the filled oxygen p_π orbitals are capable of interacting with the filled tungsten d_π orbitals that are involved in W to CO π* back bonding. Thus, in $W_2(OBu^t)_6(\mu\text{-}CO)$ one π-acceptor ligand enjoys the presence of six Bu^tO π-donor ligands.[27]



III



IV



V

In contrast the carbonyl ligands in $W_2[OCMe_2(CF_3)]_6(CO)_2$ interact with a less electron-rich metal centre and the values of ν̃(CO), 2081 and 2050 cm^{-1}, are not greatly reduced from the value of free carbon monoxide, 2143 cm^{-1}, suggesting that the CO 5σ donation to the W_2^{6+} centre is supplemented by relatively modest W d_π to CO π* back bonding.

When R = Pr^i or CH_2Bu^t, $W_2(\mu\text{-}CO)$-containing compounds are also formed but these need to be trapped by the presence of a donor ligand such as pyridine, *e.g.*[28] as in $W_2(OPr^i)_6(py)_2(\mu\text{-}CO)$. These compounds are closely related to the $W_2(OBu^t)_6(\mu\text{-}CO)$ molecule discussed above having similarly low ν̃(CO) values (≈1570 cm^{-1}) and py ligands *trans* to the W–C bond of the μ-CO moiety. In solution the pyridine ligands are labile to dissociation allowing the formation of the dimer of dimers $[W_2(OR)_6(\mu\text{-}CO)(py)]_2$[29] where the ionic forms of the resonance structures shown in **IV** are realized. Simply replacing OBu^t by OPr^i by the alcoholysis reaction (10) leads to

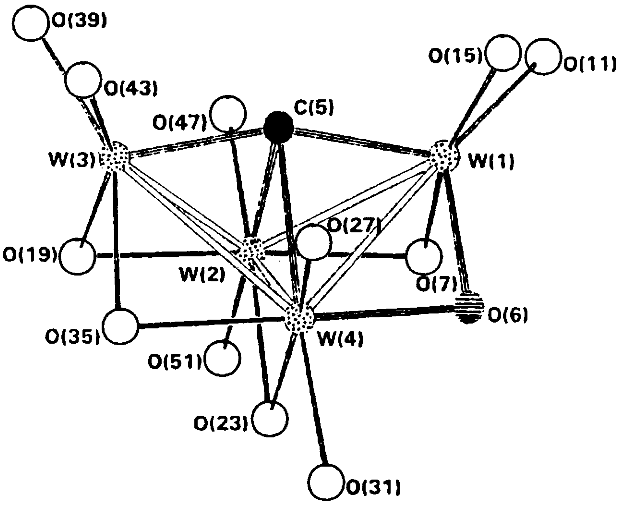
$$2[W_2(OBu^t)_6(\mu\text{-}CO)] + Pr^iOH\ (\text{excess}) \xrightarrow[\text{hexane}]{22\,^\circ C} [W_2(OPr^i)_6(\mu\text{-}CO)]_2 + 12Bu^tOH \quad (10)$$

$[W_2(OPr^i)_6(\mu\text{-}CO)]_2$ whose central core is depicted by **V**.[23] Of particular note in the structure of $[W_2(OPr^i)_6(\mu\text{-}CO)]_2$ are (*i*) the lengthening of the M–M and the carbonyl C–O bond distances and (*ii*) the shortening of the M–C distance relative to those in $W_2(OBu^t)_6(\mu\text{-}CO)$. Also the O-to-W distance within the planar central moiety shown in **V** is 1.96 Å, typical of an RO-to-W distance.[18] In the infrared spectrum the band associated, at least in part, with $\tilde{\nu}$(CO) occurs at 1240 cm^{-1} based on ^{13}C labelling which causes a *ca.* 20 cm^{-1} shift to lower frequency. The CO ligand in $[W_2(OPr^i)_6(CO)]_2$ is being reduced by two effects: (*i*) W d_π to CO π^* donation and (*ii*) CO oxygen p_π to W d_π bonding. The former reduces the C–O bond order by occupation of π^* antibonding orbitals and the latter by removing electron density from the filled C–O 1π molecular orbital. Clearly both are required if C–O bond cleavage is to be achieved and typically in surface science one observes C–O cleavage for the early and middle transition elements that have 'half' filled bands.[30] Elements like Pd and Cu that have filled d bands merely adsorb CO in a carbon-bonded fashion and when cleavage occurs, as in the Boudard reaction on a nickel surface, CO_2 is evolved and surface-bound graphitic carbon is formed.[31]

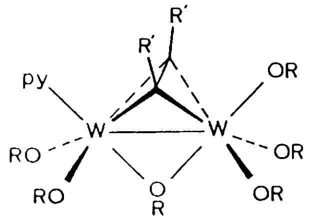
We have shown that CO can be cleaved to give carbide and oxide ligands when *one* equivalent of CO is taken up by the tetranuclear clusters, $W_4(OCH_2R)_{12}$, where R = Pr^i, cyclopentyl or cyclobutyl.[32] Also in the alcoholysis reactions (11), CO cleavage occurs but here there are competing side

$$W_2(OBu^t)_6(\mu\text{-CO}) + W_2(OBu^t)_6 \xrightarrow[\text{hexane, 22 °C}]{+\text{ROH (excess)}} W_4(\mu_4\text{-C})O(OR)_{12} \tag{11}$$

reactions wherein $[W_2(OR)_6(CO)]_2$ and $W_4(OR)_{12}$ compounds are formed.[32] A common structural motif for all of these carbido clusters is a butterfly of tungsten atoms and a μ_4-C ligand of the type shown in **VI**.



VI



VII

With alkynes. Schrock and co-workers[9] in their original report of the reductive cleavage of nitriles, equation (6), also noted a similar cleavage, or metathesis reaction, involving alkynes and $W_2(OBu^t)_6$, equation (12) where R = Me, Et or

$$W_2(OBu^t)_6 + RC{\equiv}CR \xrightarrow[\text{hexane}]{0\,°\text{C}} 2(Bu^tO)_3W{\equiv}CR \tag{12}$$

Pr^n. This reaction is also very sensitive to the nature of the alkoxide ligands on tungsten and the substituents R on the C≡C bond.[33] With less sterically demanding OPr^i and OCH$_2$Bu^t ligands μ-alkyne adducts and products derived from the coupling of alkynes may be obtained, *e.g.* $W_2(OPr^i)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$.[34] The reaction between ethyne and $W_2(OBu^t)_6$ also leads to an ethyne adduct which may be isolated as a pyridine adduct with the structure **VII**.[35] The μ-ethyne ligand in $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py)$ is greatly reduced as evidenced by a long C–C bond, 1.44 Å, and the W–W distance of 2.67 Å. In many ways this may be viewed as a dimetallatetrahedrane and this is supported by the small value of $^1J(^{13}C\text{-}^{13}C) \approx 10$ Hz. The C–C distance and *J*(C–C) coupling constant are similar to those for the tetrahedrane $Bu^t_4C_4$.[36]

In solution there is clear evidence for the existence of the equilibrium (13) and mixing the μ-$^{13}C_2H_2$ and μ-C_2D_2 labelled

$$W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py) \rightleftharpoons 2(Bu^tO)_3W{\equiv}CH + py \tag{13}$$

ethyne adducts generates the μ-H^{13}CCD-containing compound by way of equilibrium (13).[35] Similarly in the reaction between Bu^{n}C≡CH and $W_2(OBu^t)_6$, which yields $(Bu^tO)_3W{\equiv}CBu^n$, in the presence of pyridine one can detect $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py)$ by NMR spectroscopy.[35]

If the strong N-donor quinuclidine (qncd) is added to a solution containing the $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py)$ compound the equilibrium is shifted in favour of the methylidyne complex $(qncd)(Bu^tO)_3W{\equiv}CH$. However, if the π-acceptor CO ligand is added the μ-C_2H_2 ligand is trapped as $W_2(OBu^t)_6(\mu\text{-}C_2H_2)$(CO). Thus, it is clear that the electron density at the metal is important in determining the position of the equilibrium involving the dinuclear ethyne adduct and the mononuclear methylidyne complex. Evidence for the generality of this conclusion was found in the reactions involving CO and each of $(Bu^tO)_3W{\equiv}CMe$ and $(Bu^tO)_3W{\equiv}C(CH_2)_nC{\equiv}W(OBu^t)_3$, equations (14)[37] and (15) (*n* = 4 or 5).[38] In both instances the μ-alkyne adducts were structurally characterized.

$$2(Bu^tO)_3W{\equiv}CMe + CO \xrightarrow[\text{hexane}]{22\,°\text{C}} W_2(OBu^t)_6(\mu\text{-}C_2Me_2)(CO) \tag{14}$$

$$(Bu^tO)_3W{\equiv}C(CH_2)_nC{\equiv}W(OBu^t)_3 + CO \xrightarrow[\text{hexane}]{22\,°\text{C}} W_2(OBu^t)_6[\mu\text{-}C_2(CH_2)_n](CO) \tag{15}$$

Replacing the Bu^{t}O ligands by Bu^{t}Me$_2$Si ligands at the W_2^{6+} centre also dramatically alters the nature of the reaction. The compound $W_2(OSiMe_2Bu^t)_6$ has been structurally characterized and shown to be as in **I**.[39] Further, in hydrocarbon solutions ethyne forms a 1 : 1 adduct which has been structurally characterized as its pyridine adduct and shown to be analogous to $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py)$ **VII**. However, in solution, there is no evidence for an equilibrium of type (13) involving a methylidyne complex. In contrast, the compound is labile toward the elimination of HOSiMe$_2$Bu^t according to equation (16). The $W_2(OSiMe_2Bu^t)_5(\mu\text{-}C_2H)$ complex has the structure

$$W_2(OSiMe_2Bu^t)_6(\mu\text{-}C_2H_2)(py) \xrightarrow[\text{hexane}]{22\,°\text{C}} W_2(OSiMe_2Bu^t)_5(\mu\text{-}C_2H) + py + Me_2Bu^tSiOH \tag{16}$$

shown in Fig. 3 and is evidently formed irreversibly as the

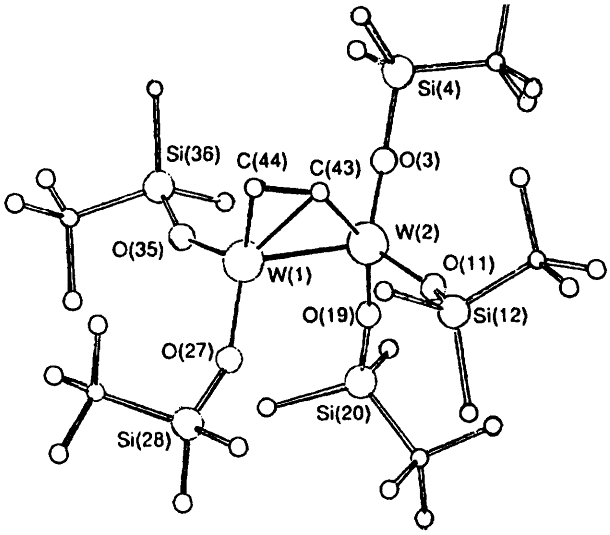


Fig. 3 A ball-and-stick drawing of the $W_2(OSiMe_2Bu^t)_5(\mu\text{-}CCH)$ molecule

presence of Me_2Bu^tSiOD does not lead to exchange of the μ-C_2H proton.[39] Interestingly, the eliminated Me_2Bu^tSiOH from reaction (16) does react with the μ-C_2H_2 complex to give a μ-$CHCH_2$ complex and a μ-CMe complex as shown in equations (17) and (18), respectively.[39] The μ-$CHCH_2$ and μ-CMe

$$\mathrm{W_2(OSiMe_2Bu^t)_6(\mu\text{-}C_2H_2)(py) + Me_2Bu^tSiOH \xrightarrow[\text{hexane}]{22\,^{\circ}C} W_2(OSiMe_2Bu^t)_7(\mu\text{-}CHCH_2) + py} \quad (17)$$

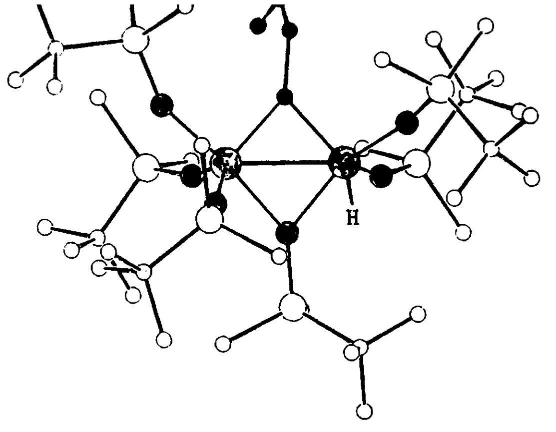
$$\mathrm{W_2(OSiMe_2Bu^t)_6(\mu\text{-}C_2H_2)(py) + Me_2Bu^tSiOH \xrightarrow[\text{hexane}]{22\,^{\circ}C} W_2(OSiMe_2Bu^t)_7(\mu\text{-}CMe) + py} \quad (18)$$

complexes are isomers, being related by a 1,2 H-atom shift, and they do not interconvert. Therefore they must be formed by separate pathways. Evidence for this is clearly seen in the fact that when $W_2(OSiMe_2Bu^t)_6(\mu\text{-}C_2H_2)(py)$ is allowed to react in the presence of Me_2Bu^tSiOD all the protons of the μ-CMe group are exchanged (slowly) to give CCD_3 whereas the μ-CHCHD ligand is inert to this type of exchange. One can but speculate why this should be. The most plausible explanation to this author is that the μ-CHCHD ligand arises from reaction of Me_2Bu^tSiOH with the μ-C_2H_2 complex whereas the formation of the μ-CMe ligand proceeds from the reversible protonation of a μ-vinylidene complex with the latter being derived in an irreversible manner from the μ-C_2H_2 complex.

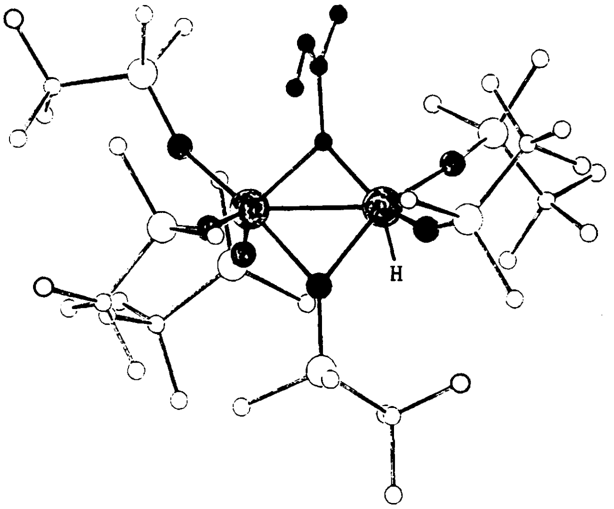
Yne–ene couplings. Although $W_2(OBu^t)_6(\mu\text{-}C_2H_2)(py)$ is labile in solution according to equation (13), it does not react with C–C double bonds. However, $W_2(OSiMe_2Bu^t)_6(\mu\text{-}C_2H_2)(py)$, which does not show an equilibrium related to (13), does react with ethene and allene in a most interesting and stereospecific manner to give products derived from carbon–carbon bond formation.[40] It should be emphasized that the C–C coupling reaction must be carried out at low temperature, −20 °C or below, in order to avoid reaction (16). In the coupling of ethene with the μ-ethyne ligand labelling studies have provided insight concerning the bonds being formed and broken as shown in equation (19).[40] The structure of the

$$\mathrm{W_2(OSiMe_2Bu^t)_6(\mu\text{-}^{13}C_2H_2)(py) + C_2D_4 \xrightarrow[\text{hexane}]{-20\,^{\circ}C} W_2H(OSiMe_2Bu^t)_6(\mu\text{-}^{13}C^{13}CH{=}CDCD_3) + py} \quad (19)$$

hydrido alkylidyne complex is shown in **VIII**. Note the hydrogen atom from the μ-$^{13}C_2H_2$ ligand forms the hydride ligand and the ^{13}C–^{13}C connectivity is maintained with one carbon being bonded to the metal.



VIII



IX

With the coupling of allene and the μ-ethyne ligand the situation is reversed as shown in equation (20). An allene

$$\mathrm{W_2(OSiMe_2Bu^t)_6(\mu\text{-}^{13}C_2H_2)(py) + CH_2{=}C{=}CH_2 \xrightarrow[\text{hexane}]{-20\,^{\circ}C} W_2H(OSiMe_2Bu^t)_6(\mu\text{-}CC{=}CH_2{}^{13}CH{=}^{13}CH_2)} \quad (20a)$$

$$\mathrm{W_2(OSiMe_2Bu^t)_6(\mu\text{-}^{13}C_2D_2)(py) + CH_2{=}C{=}CH_2 \xrightarrow[\text{hexane}]{-20\,^{\circ}C} W_2H(OSiMe_2Bu^t)_6(\mu\text{-}CC{=}CH_2CD{=}CHD)} \quad (20b)$$

trans

proton is used to form the hydride ligand and the μ-$^{13}C_2H_2$ moiety is removed from direct contact with the dinuclear centre.[40] The structure of the μ-ethyne–allene coupled product is shown in **IX**. It should perhaps be mentioned that the location of the hydride ligand was not determined crystallographically but is known to be terminal based on the magnitude of the satellites of the coupling constants involving ^{183}W, $I = \frac{1}{2}$, 14.5% natural abundance. Its position can reasonably be proposed, as shown in the ball-and-stick drawings **VIII** and **IX**, from the hydride-locating program XHYDEX.[41] The specificity of the bonds broken and formed in reactions (19) and (20), which is truly remarkable, can be rationalized based on the formation of $W_2(\mu\text{-}C_4)$ containing complexes which then undergo β- and α-H activation processes. These possible reaction pathways have been discussed elsewhere[40] and though plausible remain unverified.

With ethene. At room temperature and 1 atm pressure ethene hydrocarbon solutions of each of $W_2(OBu^t)_6$, $W_2(OSiMe_2Bu^t)_6$ and $W_2[OCMe_2(CF_3)]_6$ fail to react. It is therefore not possible to make a comparison between steric or electronic factors that may be responsible for this lack of reactivity although it seems likely that steric factors are important in the case of $W_2(OBu^t)_6$ since the related but less sterically constrained $W_2(OCH_2Bu^t)_6$ and $W_2(OPr^i)_6$ compounds show reactivity.[42] The neopentoxide reversibly forms a bis(ethene) adduct according to equation (21). The structure of the

$$W_2(OCH_2Bu^t)_6 + 2CH_2{=}CH_2 \rightleftharpoons W_2(OCH_2Bu^t)_6(\eta^2\text{-}C_2H_4)_2 \quad (21)$$

bis(ethene) adduct is depicted in **X**. There is a co-operative binding of ethene and no evidence for a monoethene adduct is seen. The binding of ethene to one tungsten must activate the other to substrate uptake and conversely the loss of one ethene facilitates the loss of the other. The structural parameters and NMR data for $W_2(OCH_2Bu^t)_6(\eta^2\text{-}C_2H_4)_2$ strongly support the view that the metal–olefin interaction may be considered as a metallacyclopropane with W–C 2.21, C–C 1.42 Å and ^1J(C–C) = 34 Hz. Also the disposition of the C_2 axes with respect to the M–M axis is consistent with a d^2 W–η^2-C_2H_4 moiety and the presence of a d^1–d^1 W–W single bond.[42d]

The compound $W_2(OPr^i)_6$ and ethene also react reversibly at room temperature, 1 atm, equation (22), but here the product is

$$W_2(OPr^i)_6 + 3C_2H_4 \rightleftharpoons W_2(OPr^i)_6(CH_2)_4(\eta^2\text{-}C_2H_4) \quad (22)$$

$W_2(OPr^i)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, whose structure is depicted in **XI**.[42b] Presumably a bis(ethene) adduct akin to **X** is an intermediate in the formation of **XI** but we have never been able to prove this beyond a reasonable doubt. The metallacyclobutane is formed reversibly by the coupling of two ethene ligands but we cannot be sure that the C–C coupling involves a bis(ethene) adduct of type **X**. However, we can show in the reversible reaction (22) that the η^2-C_2H_4 ligand is labile to scrambling with added ethene. This is easily seen from a labelling experiment of the type shown in equation (23).[42b]

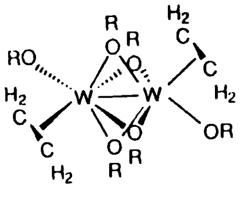
$$W_2(OPr^i)_6(CH_2)_4(\eta^2\text{-}C_2H_4) + {}^{13}C_2H_4 \rightleftharpoons W_2(OPr^i)_6(CH_2)_4(\eta^2\text{-}{}^{13}C_2H_4) + C_2H_4 \quad (23)$$

The final product in the reaction between $W_2(OR)_6$ compounds (R = Pr^i or CH_2Bu^t) and ethene is $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ which is formed by α-hydrogen-atom transfer from the metallacyclopentane ring to the co-ordinated ethene ligand, equation (24). The structure of the μ-alkylidyne-bridged metallacyclic compound is shown in **XII**.[42b]

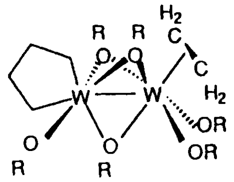
$$W_2(OPr^i)_6(CH_2)_4(\eta^2\text{-}C_2D_4) \xrightarrow[\text{hexane}]{22\,^\circ C} W_2(OPr^i)_6(\mu\text{-}CCH_2CH_2CH_2) + C_2D_4H_2 \quad (24)$$

The three structures shown in **X**–**XII** reveal the flexibility of $W_2(OR)_6$ as a template. Bridging alkoxides readily open and close as is evident from the existence of four, three and one bridge, in **X**, **XI** and **XII**, respectively.

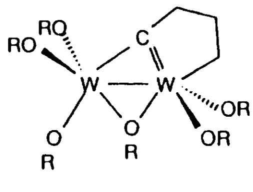
With aldehydes and ketones. Aldehydes and ketones react with $W_2(OPr^i{}_6)(py)_2$ in hydrocarbon solvents at room temperature according to equation (25). The rate-limiting step



X



XI



XII

$$W_2(OPr^i)_6(py)_2 + Me_2C{=}O \xrightarrow[\text{benzene}]{22\,^\circ C} W_2(OPr^i)_6(\mu\text{-}CMe_2)O(py) + py \quad (25)$$

$$W_2(OPr^i)_6(\mu\text{-}CRR^1)O(py) + R^2R^3C{=}O \xrightarrow[\text{benzene}]{22\,^\circ C} W_2(OPr^i)_6O_2 + RR^1C{=}CR^2R^3 \quad (26)$$

is the dissociation of pyridine since unligated $W_2(OPr^i)_6$ reacts in $[^2H_8]$toluene at −80 °C to give an oxo-μ-prop-2-ylidene complex as evidenced by ^1H and ^{13}C NMR studies employing $Me_2{}^{13}C{=}O$. The presence of pyridine in reaction (25) is important in stabilizing (trapping) the μ-alkylidene complex which is labile to further C–C coupling and, indeed, forms the basis of an olefination reaction (26).[43] There are limitations to the generality of this reaction, some of which we have already noted,[44] and some of which are still under investigation.

The first reaction, (25), bears a striking resemblance to the cleavage of diaryl thiones noted before, equation (7), but the ultimate position of the alkylidene and sulfide/oxide ligands differs. In reaction (7) the sulfide is bridging and the alkylidene is terminal, whereas in (25) the oxo is terminal and the alkylidene bridging. It is also worth noting in passing that $Mo_2(OPr^i)_6$ and rigorously dry acetone fail to react, a fact that we attribute to electronic factors associated with the cleavage of C–X multiple bonds by M≡M bonded complexes.

There are a number of limitations to the generality of reaction (25). First, steric factors are important and neither $Bu^t{}_2C{=}O$ nor $(Bu^t)MeC{=}O$ enter into this cleavage. Also esters and amides $RCONMe_2$, fail to react while acetyl chloride gives Pr^iO_2CMe and W–Cl bond formation. Although the cleavage reaction of simple aldehydes and ketones is very fast, occurring rapidly at −80 °C as determined by NMR studies, the reactions with α,β-unsaturated aldehydes and ketones can lead to products of ring closure (1,4 addition).[45] The products that were structurally characterized from these reactions are summarized in Fig. 4.[45] Of note here is the formation of the bis (η^2-aldehyde-*C,O*) complex for OCH=CHMe. Evidently the first addition of the α,β-unsaturated aldehyde causes ring

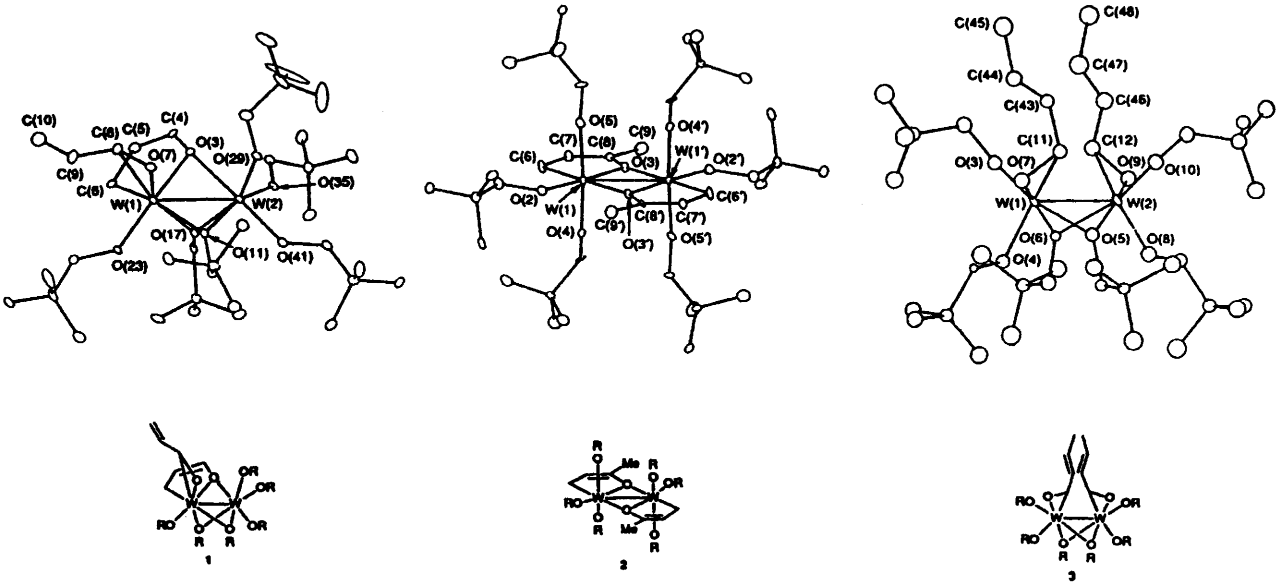
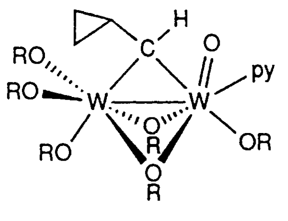
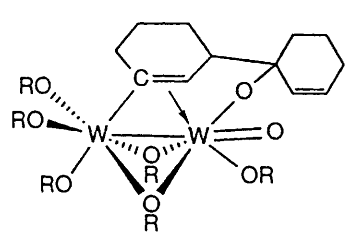


Fig. 4 The acrylaldehyde **1**, methyl vinyl ketone **2** and the crotonaldehyde **3** adducts of W$_2$(OCH$_2$Bu^t)$_6$



XIII



XIV

closure (1,4 adition) which is either reversible or opened upon the second addition of substrate. The substrate O=C(Me)-CH=CMe$_2$ is, however, too sterically demanding to allow for 1,4 addition and the reaction proceeds to give cleavage of the C–O double bond.

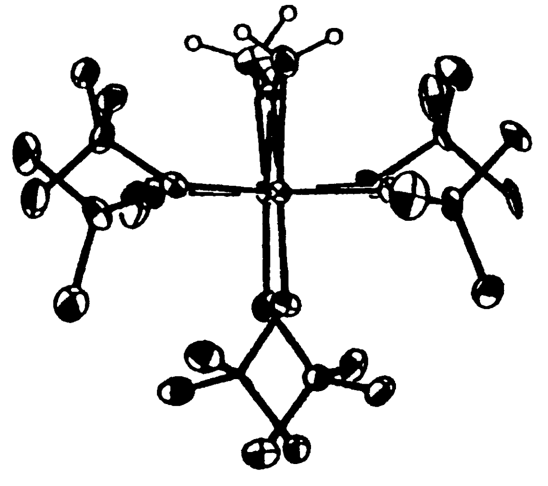
The nature of the C–O double-bond cleavage was probed by use of cyclopropanecarbaldehyde and the product shown in **XIII** was obtained and structurally characterized.[46] The fact that the cyclopropyl ring did not open is a strong indication that neither radical nor significant positive charge build-up occurred on the ketonic carbon during the C–O bond cleavage. The cleavage reaction can therefore be envisaged as a skeletal rearrangement of the 2 + 2 addition product, W$_2$(μ-η^1 : η^2-OC), and as with the cleavage of the C=S bond in Ph$_2$C=S [equation (7)] and nitriles, equation (6), a plausible structural intermediate is of the type shown in **III**. [Note reactions employing Me$_2$NCN and W$_2$(OBu^t)$_6$ give products of cleavage of the C≡N bond as in equation (6);[21] only Mo$_2$(O$_2$CH$_2$Bu^t)$_6$ forms a 1 : 1 adduct.]

The second step of the reaction involves C–C bond formation between the alkylidene carbon and the entering ketonic or aldehyde carbon. This would generate a dimetallaoxirane and by subsequent elimination of olefin the W$_2$(OPr^i)$_6$O$_2$ product. While we have found no direct evidence of the dimetallaoxirane we have noted that the use of cyclohexenone, which first produces the β-unsaturated μ-alkylidene, gives rise to the product of vinyligous coupling.[46] The structure of this complex is shown in **XIV** and the vinyligous coupling reaction supports our contention that the olefin is formed in a bimolecular reaction involving the second equivalent of ketone/aldehyde and the dinuclear μ-alkylidene complex.

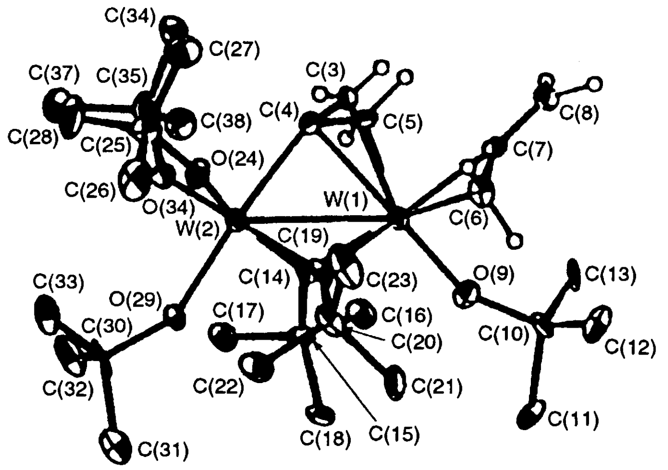
With allene. Allene (1 equivalent) and W$_2$(OBu^t)$_6$ react at 0 °C and below in hydrocarbon solvents to give green solutions of a 1 : 1 adduct which has been structurally characterized.[47] The drawing **XV** is a view of the molecule looking down the W–W axis. The complex is most unusual, indeed unprecedented, in showing a V-shaped C–C–C unit co-ordinated parallel to the W–W axis. Also the four hydrogen atoms of the allene lie in a plane. From theoretical studies it has been estimated that the transition state for enantiomerization of RCH=C=CH$_2$ would have this type of geometry.[48] A simple MO bonding scheme depicting the principal interactions of the bent CH$_2$CCH$_2$ fragment and W$_2$(OR)$_6$ is shown in Fig. 5. From this it is seen that the allene acts as a four-electron donor to the W$_2$$^{6+}$ centre which back donates four electrons. The latter is unique to dinuclear chemistry and the importance of this back bonding undoubtedly underscores the rather long C–C bond distances in the μ-allene ligand, 1.46 Å, which are comparable to those expected for C$_{sp^2}$–C$_{sp^2}$ single-bond distances.[49] The 1 : 1 allene adduct, **XV**, is thermally unstable above 0 °C [yielding products derived from W$_2$(OBu^t)$_6$ and MeC≡CH] but does form a thermally stable compound upon the addition of a second equivalent of allene. The structure of the latter compound W$_2$(OBu^t)$_6$[μ-C(CH$_2$)$_2$](η^2-CH$_2$CCH$_2$) is shown in **XVI**.[47]

Thus within the structures **XV** and **XVI** we see two modes of bonding that are unique to dinuclear chemistry, namely the μ-parallel mode in **XV** and the metallaallyl mode, M$_2$[μ-η^1 : η^3-C(CH$_2$)$_2$] in **XVI**. The terminal η^2-CH$_2$=C=CH$_2$ mode is common in mononuclear chemistry and the C–C double bonds remain orthogonal.[50]

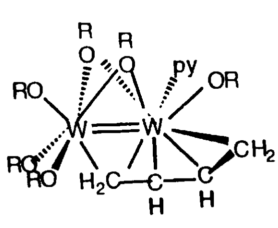
With 1,3-dienes. Buta-1,3-diene reacts reversibly with W$_2$(OCH$_2$Bu^t)$_6$(py)$_2$ in hydrocarbon solutions according to equilibrium (27).[51] The 1 : 1 butadiene adduct is blue and



XV



XVI



XVII

$$W_2(OCH_2Bu^t)_6(py)_2 + CH_2{=}CH{-}CH{=}CH_2 \rightleftharpoons W_2(OCH_2Bu^t)_6(\mu\text{-}\eta^1{:}\eta^4\text{-}C_4H_6)(py) + py \qquad (27)$$

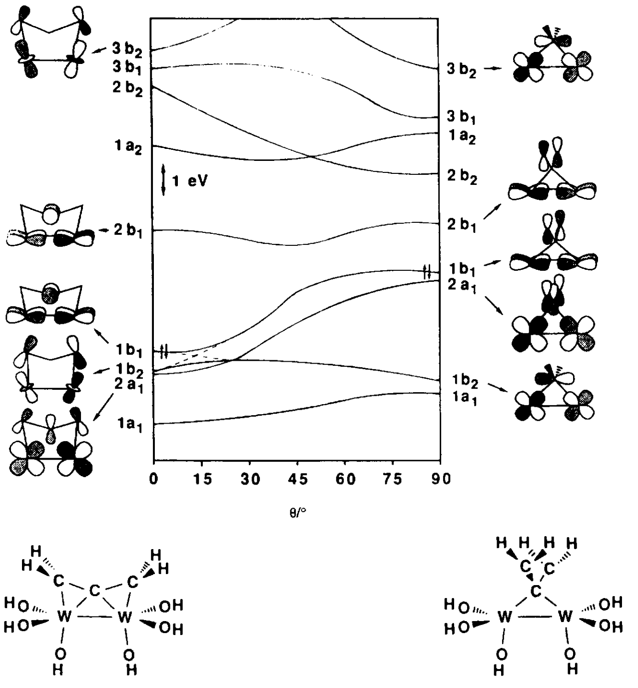


Fig. 5 An orbital-interaction diagram for the bent allene fragment interacting with the $W_2(OH)_6$ molecule in a parallel (left) and perpendicular manner (right)

crystallizes from solution (hexane or benzene) with ligation of one molecule of pyridine. The central skeleton of the complex is shown in **XVII**. The binding of the butadiene to the W–W triple bond is not as for a Diels–Alder addition but reflects the trend that the hydrocarbon substrate makes the maximum number of ligand atom to metal interactions. In some ways the structure may be viewed as a μ-alkyl–π-allyl complex and this is reflected in the C–C distances, C–H coupling constants and the values of $^{1}J(^{183}W{-}C)$. The bridging carbon appears at *ca.* δ 40 in the ^{13}C NMR spectrum and has $^{1}J(C{-}H) \approx 123$ and $J(W{-}C) \approx 30$ Hz. The π-allyl fragment is more weakly bonded as judged by shorter C–C distances *ca.* 1.39 Å, $J(C{-}H) \approx 150{-}170$ Hz and small values of $J(W{-}C)$. The formation of this butadiene adduct is favoured at low temperature as is evident from the colour change, brown to blue, that occurs with its formation. Isoprene evidently binds in a similar manner and though there are presently no crystal structural data for this adduct the NMR data lead us to suggest that the terminal $CH_2{=}CH$ functionality occupies the μ-C position. By ^{1}H NMR spectroscopy there is no evidence for the binding of other acyclic or cyclic 1,3-dienes.[52]

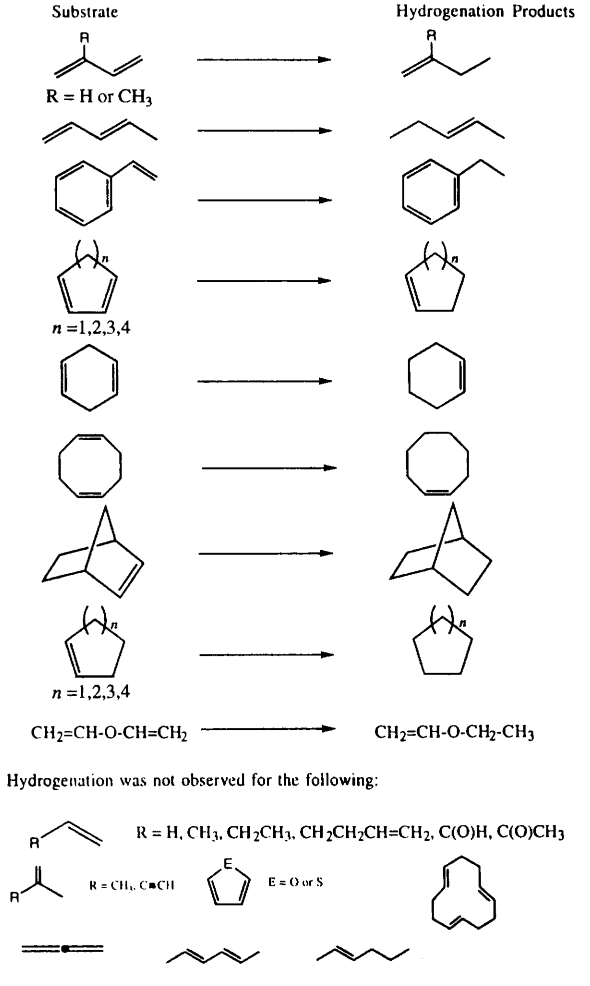
Hydrogenation. Hydrogen does not oxidatively add to the W≡W bond of $W_2(OR)_6$ compounds where R = Bu^t, Pr^i or CH_2Bu^t at 22 °C, 1 atm. However, it is known to add reversibly to the W≡W triple bonds of $W_2(C_5H_4Pr^i)_2Cl_4$[53] and $W_2H_2(OSiBu^t)_4$.[54] Thus for the equilibrium (28) we would expect

$$W_2(OR)_6 + H_2 \rightleftharpoons W_2H_2(OR)_6 \qquad (28)$$

relatively small but positive ΔG° values and, given the lability of substrate binding to the W_2^{6+} centre supported by OR ligands, the $\Delta G^\ddagger$ values should also be modest. The values for ΔG° (and $\Delta H^\ddagger$) should be tuneable by selection of R. Thus, the reversible binding of a number of unsaturated substrates to the W_2^{6+} centre and the facility with which C–C bonds may be formed pose the possibility of a number of catalytic cycles.

In our initial foray into this field we have discovered that the carbide in $W_4(\mu_4\text{-}C)$-containing compounds supported by OR ligands is not hydrogenated at 80 °C, 5 atm, nor is the $\mu\text{-}C_4R_4$ fragment derived from the coupling of two alkyne units in $W_2(OR^1)_6(\mu\text{-}C_4R_4)(\eta^2\text{-}C_2R_2)$ compounds. Since related tantalum μ-alkylidyne fragments can be hydrogenated under somewhat more forcing conditions,[55] similar success at the ditungsten centre is expected if we can work with more thermally robust OR groups. [Typically $W_2(OR)_6$ compounds, where R = alkyl, decompose over a period of time in solution at temperatures between 60 and 100 °C.][56]

We have, however, found that 1,3-dienes may be selectively hydrogenated to the 3-enes at room temperature, 1 atm of H_2, by $W_2(OCHBu^t)_6(py)_2$.[57] In view of the known structure of $W_2(OCH_2Bu^t)_6(\mu\text{-}C_4H_6)(py)$ and its equilibrium (27), it is easy to envisage that the initial mode of activation involves pyridine dissociation followed by uptake of H_2 and hydrogenation of the $\mu\text{-}CH_2CH$ bonds leading to the α-olefin, but-1-ene, which is not activated by $W_2(OCH_2Bu^t)_6$. Reactions employing D_2 gas



Scheme 1 Selective hydrogenation of polyenes catalysed by $W_2(OCH_2Bu^t)_6(py)_2$

show that buta-1,3-diene and isoprene are hydrogenated to $CH_2DCHDCH{=}CH_2$ and $CH_2{=}CMeCHDCH_2D$, respectively.

A summary of the hydrogenations of dienes is presented in Scheme 1.[57] The turnover rates at 22 °C, 1 atm H_2, are very modest, 2–5 h^{-1}. From Scheme 1 it is seen that hydrogenation of conjugated acyclic dienes is limited to 1,3-dienes while for cyclic dienes, presumably as a result of the chelate effect, both conjugated and unconjugated dienes may be hydrogenated.

Cyclic monoenes are more slowly hydrogenated to the cyclic alkanes. It seems that *cis* double bonds may be *very* slowly hydrogenated but we have yet to see any reactivity with *trans* C–C double bonds. Nor has any reactivity been seen toward benzene and the quasi-aromatic thiophene and furan. The hydrogenation of styrene to ethylbenzene and diallyl ether to allyl propyl ether are attributed to the chelate effect that is possible with the neighbouring double bonds.

Further studies concerning the mechanism and potential for selective hydrogenation reactions are underway. Hydridoalkoxides such as $W_2(\mu\text{-}H)(OR)_7$ have been the subject of a recent review.[58] These are known to react with α-olefins to give olefin isomerization products and in the presence of H_2 they act as hydrogenation catalysts. However, such species cannot be responsible for the conversions noted in Scheme 1 since with 1,3-dienes complicated reactivity is observed due to the formation of π-allyl species. Thus, the selectivity observed in the hydrogenation catalysis by $W_2(OCH_2Bu^t)_6(py)_2$ in hydrocarbon solution is believed to result from the initial uptake of the hydrocarbon substance followed by hydrogenolysis.

Conclusion

In retrospect, many of the conditions now expected for a template suitable for organometallic chemistry are met by $W_2(OR)_6$ compounds: (1) the W_2^{6+} centre is electronically unsaturated; (2) it is redox active and undergoes relatively facile oxidation to W_2^{8+} and W_2^{10+} (even oxidative cleavage to two W^{6+} centres is possible); (3) the π-buffering effects of the alkoxide ligands may be tuned by choice of R; (4) steric factors associated with R, together with their electronic effects [(3)] allow the W_2^{6+} centre to be substrate selective and (5) the presence of the dinuclear centre allows for novel modes of substrate binding and activation.

With these factors in mind it is easy to rationalize the observed organometallic chemistry that has been described in this article, including the limited examples of catalysis. The possible future developments are, of course, less certain but would seem to be limited largely by the creativity and imagination of the researchers who chose to explore this field. Limitations on thermal stability should be overcome by judicious choice of OR groups. The use of chiral W_2^{6+} templates remains an area largely to be explored[59] as does that involving the use of sterically selective and functionalized alcohols (diols[60] and triols[61] with specific modes of binding). So some twenty years after the first synthesis of $W_2(OR)_6$ compounds the exploration of their chemistry and, in particular, their use as templates for organometallic chemistry and catalysis remains a fertile field for future endeavours.

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