Cyclopentadienyl Molybdenum and Tungsten Dihalides

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1 Introduction

Mono-η-cyclopentadienyl transition metal halide complexes form an important class of precursor in the synthesis of other organometallic compounds.[1] In this class, compounds of the general type $[M(\eta\text{-}C_5R_5)X_2]n$ (X = halogen) are now established for the majority of the transition metals. Until recently, however, reactivity had only been explored in substantial detail for the metal–metal non-bonded Group 9 complexes $[M_2(\eta\text{-}C_5R_5)_2X_2(\mu\text{-}X)_2]$ (M = Rh or Ir).[1] In this article we review the synthesis, structures, and reactivity of the tungsten and molybdenum members of this class.

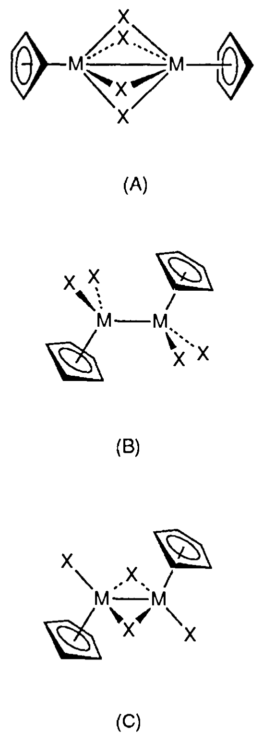
2 Synthesis and Structures

We shall begin by examining the synthesis and molecular structures of the compounds $[M(\eta\text{-}C_5R_5)X_2]_n$ (M = Mo or W, X = halide, $n = 2$ or uncertain). Two extreme geometries (Figure 1; A and B) have been observed for the binuclear derivatives depending both upon the identity of the metal and the substituents on the η-cyclopentadienyl ring. There is a third potential basic geometry (Figure 1; C) which possesses two terminal and two bridging halide ligands. The geometry C has not been observed for M = Mo or W, but in fact is the most common amongst the other $[M(\eta\text{-}C_5R_5)X_2]_2$ derivatives of the transition metals, including the first member of the triad, chromium.[2] Table 1 lists the crystallographically characterized $[M(\eta\text{-}C_5R_5)X_2]_2$ derivatives of Mo and W along with their predicted M–M valence electronic configuration (*vide infra* – Bonding).

Malcolm Green obtained his Ph.D. at Imperial College of Science and Technology in 1959. He moved to Cambridge as a Demonstrator in 1960 and a Fellow of Corpus Christi College (1961). He was appointed Fellow and Tutor in Inorganic Chemistry at Balliol College, Oxford in 1963, and became Professor of Inorganic Chemistry at Oxford University in 1989.

He has been an A. P. Sloan Visiting Professor at Harvard University (1973) and a Sherman Fairchild Visiting Scholar at the California Institute of Technology (1981). His work has been recognized by the award of a Corday–Morgan Medal, a Tilden Lectureship and Prize, the ACS Award for Inorganic Chemistry (1984) and he was elected Fellow of the Royal Society in 1985. He has published 2 books and over 350 articles in the field of organotransition metal chemistry.

Philip Mountford was educated at Hatfield Polytechnic [B.Sc. (Hons., Class 1) and the Smith, Kline, and French prize in applied chemistry, 1986] and Balliol College, Oxford (D. Phil, 1990) where he carried out research with Professor M. L. H. Green into the structures and reactivity of organoditungsten complexes. In 1989 he was elected to a Junior Research Fellowship at Wolfson College, and in 1990 took up the post of Departmental Demonstrator in the Inorganic Chemistry Laboratory, Oxford. He is co-author of over 20 publications and his research interests include the synthesis, reactivity, and electronic and molecular structures of complexes containing metal–metal or metal–ligand multiple bonds.



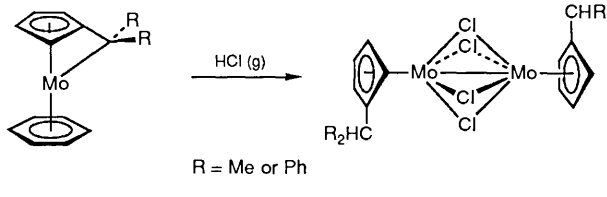
(A)

(B)

(C)

Figure 1 The three basic geometries for η-cyclopentadienyl metal dihalide dimers. No particular bond order is implied by the line between the metal atoms.

The dimolybdenum dimers $[Mo_2(\eta\text{-}C_5H_4CHR_2)_2(\mu\text{-}Cl)_4]$ (R=Me or Ph) were first prepared by treatment of the corresponding η-fulvene complexes $[Mo(\eta^5,\eta^1\text{-}C_5H_4CR_2)(\eta\text{-}C_6H_6)]$ with HCl gas.[3] The molecular structure for R=Me is of the type A (Figure 1), and is shown in Figure 2(a). The complexes $[Mo_2(\eta\text{-}C_5H_4CHR_2)_2(\mu\text{-}Cl)_4]$ were the first examples of dinuclear complexes with four bridging halide ligands, and their diamagnetic nature together with simple electron-counting procedures and a Mo–Mo bond length of 2.607(1) Å (for R=Me) suggested that they possess a molybdenum–molybdenum single bond. Attempted preparation of the tungsten analogues by treatment of $[W(\eta^5,\eta^1\text{-}C_5H_4CR_2)(\eta\text{-}C_6H_6)]$ with HCl gas failed to afford any tractable product.[4]



(1)

Recently, Alt and co-workers found that treatment of $[W_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)_2]$ with HCl gas at low temperature gave a blue, insoluble, carbonyl-free material formulated as $[W(\eta\text{-}C_5H_5)Cl_2]_2$ on the basis of analytical and infra-red data.[5] Previously, Schrock had reported that reduction of $[W(\eta\text{-}C_5Me_5)Cl_4]$ with two equivalents of sodium amalgam or

Table 1 Structure and bonding of crystallographically characterized $[M(\eta\text{-}C_5R_5)Cl_2]_2$ (M = Mo or W) complexes

Compound	Structural type [a]	M−M electronic configuration [b]	M−M bond length (Å)	Reference
$[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$	A	$\sigma^2\delta^{*2}\delta^2$	2.607(1)	*c*
$[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$	B	$\sigma^2\pi^4$	2.3678(8)	*d*
$[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$	A	$\sigma^2\delta^{*2}\delta^2$	2.626(1)	*e*

[a] See Figure 1. [b] J. C. Green, M. L. H. Green, P. Mountford, and M. J. Parkington, *J. Chem. Soc., Dalton Trans.*, 1990, 3407. [c] P. D. Grebenik, M. L. H. Green, A. Izquierdo, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1987, 9. [d] M. L. H. Green, J. D. Hubert, and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3793. [e] C. J. Harlan, R. A. Jones, S. U. Koschmieder, and C. M. Nunn, *Polyhedron*, 1990, **9**, 669.

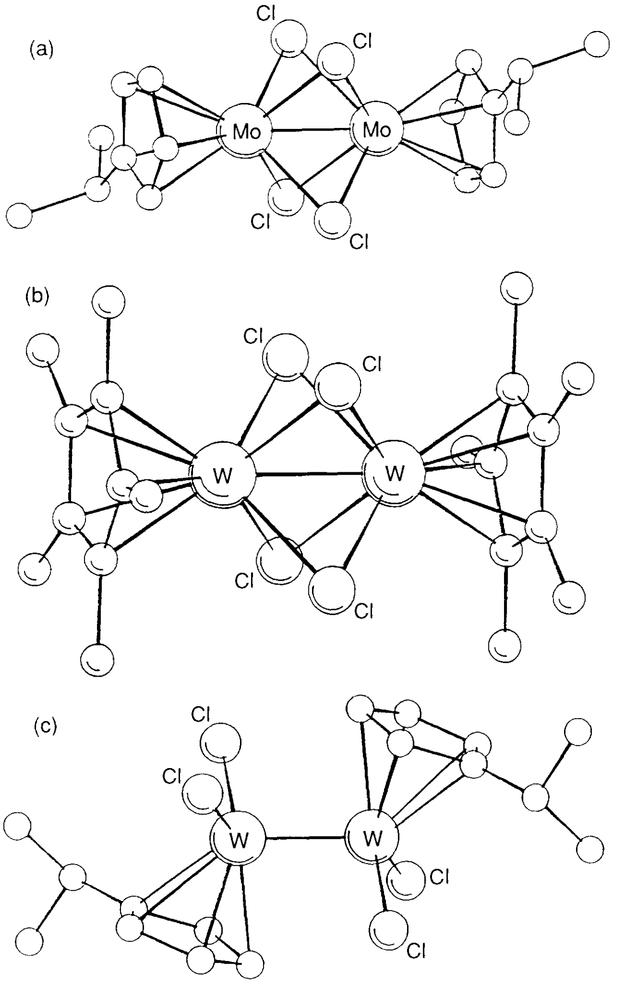
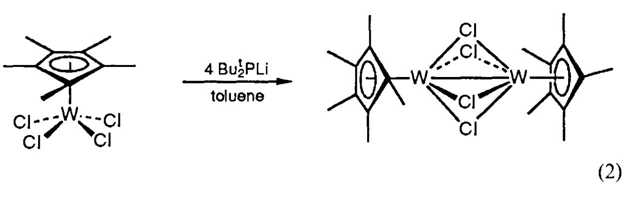


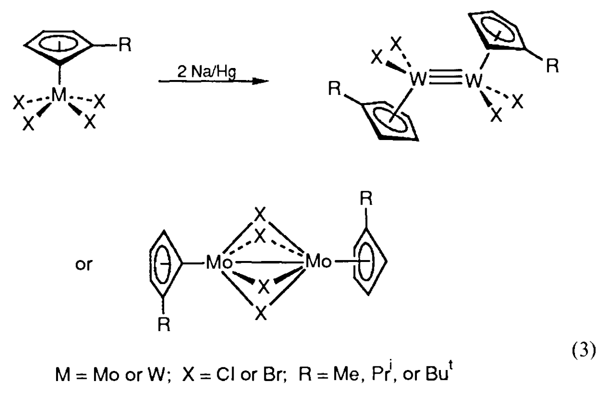
Figure 2 The molecular structures of (a) $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$, (b) $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$, and (c) $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$. Hydrogen atoms are omitted for clarity.[3,7,8]

$LiBEt_3H$ afforded an emerald green material for which no characterizing data were presented, but which was described as $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ with a structure analogous to those of the dimolybdenum complexes described above.[6] This compound was later crystallographically characterized [Figure 2(b)] as its $[P_2Bu^t_4]$ co-crystallate (obtained from the reduction of $[W(\eta\text{-}C_5Me_5)Cl_4]$ with $LiPBu^t_2$) and has the type A tetrachloride-bridged structure $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ with no unusual contacts between the $[P_2Bu^t_4]$ and ditungsten molecules.[7]



(2)

Reduction of the mono-ring-substituted tetrahalide complexes $[W(\eta\text{-}C_5H_4R)X_4]$ (R = Me or Pr^i, X = Br or Cl) with two equivalents of sodium amalgam gave the corresponding green complexes $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ in 40—60% yield.[8] An *X*-ray crystal structure determination of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ [Figure 2(c)] revealed a dimer with an unsupported W≡W triple bond, in striking contrast to the structure of its dimolybdenum congener [Figure 2(a)] and the pentamethylcyclopentadienyl analogue, $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$. An analogous reductive dimerization route may also be used to prepare the dimolybdenum compounds $[Mo_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ or $[Mo_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}X)_4]$ (R=Me, Pr^i, or Bu^t; X = Br or Cl) from the tetrahalides $[Mo(\eta\text{-}C_5R_5)X_4]$,[8] and is thus the best general route into these dimer systems.



(3)

Unfortunately, the analogous ring-unsubstituted homologues $[M(\eta\text{-}C_5H_5)X_2]_n$ cannot be prepared cleanly using sodium amalgam because of their insolubility and consequent contamination with the sodium halide by-product. However, Poli has shown that the use of zinc as a reducing agent with $[Mo(\eta\text{-}C_5H_5)Cl_4]$ in thf solution affords an insoluble, golden-yellow, crystalline material formulated as $[M(\eta\text{-}C_5H_5)Cl_2]$ and which is thought to be oligomeric in the solid state.[9] Very recently, the cationic μ-iodo species $[Mo_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}I)_4]^+$ has been prepared and shows reversible oxidation and reduction waves in its cyclic voltammogram.[10]

3 Bonding

The bonding in the two different geometries found for the $[M(\eta\text{-}C_5R_5)X_2]_2$ (M = Mo or W) dimers has been the subject of a detailed study using gas-phase He-I and He-II photoelectron (PE) spectroscopy and extended-Hückel molecular orbital calculations.[11] The model complexes studied were $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)_4]$ (type A) and $[W_2(\eta\text{-}C_5H_5)_2Cl_4]$ (type B) idealized to C_{2h} symmetry; the interaction diagrams are given in Figures 3 and 4 respectively.

The type A structure possesses a $\sigma^2\delta^{*2}\delta^2$ configuration for the Mo−Mo interaction amounting to a net metal–metal single bond which agrees with formal electron-counting procedures (note that although the symmetry of these molecules is lower than cyclindrical, the classification of metal-based orbitals according to the σ, π, and δ notation is nevertheless a useful distinction based on predominant orbital type). The σ-bonding orbital ($1a_g$) arises from overlap of the metal valence d_{z^2} orbitals

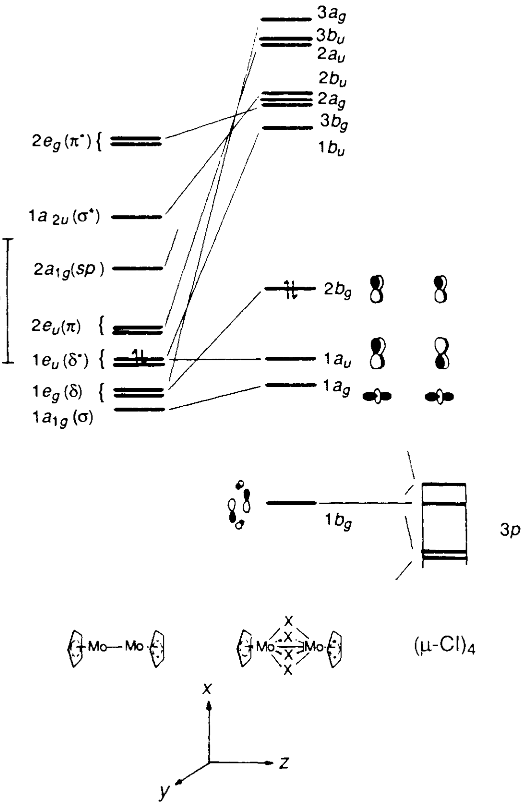


Figure 3 Interaction diagram for $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)_4]$. (Reproduced by permission from reference 11.)

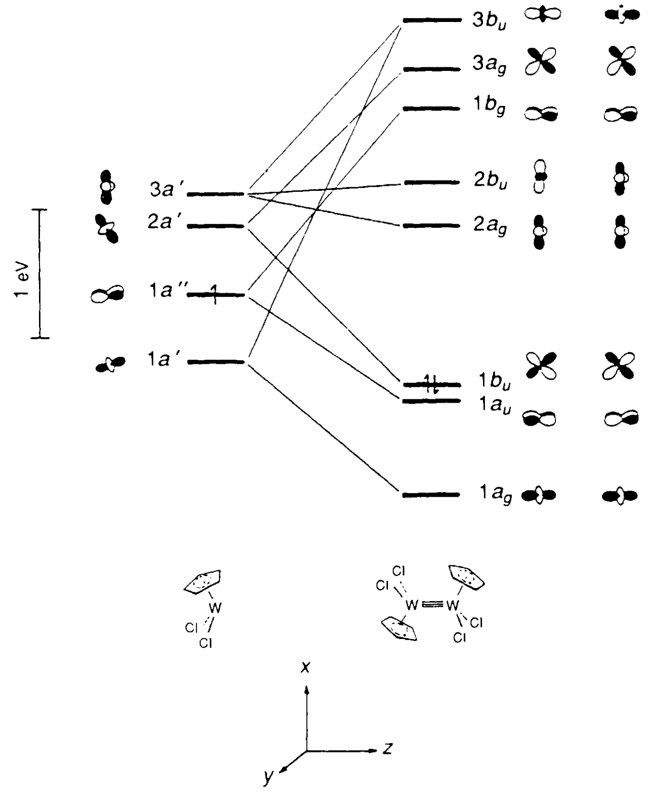


Figure 4 Interaction diagram for $[W_2(\eta\text{-}C_5H_5)_2Cl_4]$. (Reproduced by permission from reference 11.)

and the δ ($2b_g$) and δ* ($1a_u$) levels are the in- and out-of-phase combinations respectively of the *dxy* orbitals. The remaining 4*d* orbitals of molybdenum (d_{xz}, d_{yz}, $d_{x^2-y^2}$) are involved in Mo–(μ-Cl) framework bonding and are thus raised high in energy.

The apparently curious ordering of the δ* and δ metal-based orbitals ($1a_u$ and $2b_g$ respectively in Figure 3) has been attributed to the different extent of their interactions with the appropriate symmetry-adapted combinations of the bridging ligand orbitals. Similar reversals of δ* and δ metal-based orbitals have been proposed for other dimetallic complexes.[12]

In contrast, the type B structure (Figure 4) possesses a W≡W triple bond of valence electronic configuration $\sigma^2\pi^4$. In this case the metal–metal σ bond ($1a_g$) also arises from overlap of the d_{z^2} orbitals, but removal of the bridging ligands allows the d_{xz} and d_{yz} metal orbitals to come down in energy and form the two virtually isoenergetic components of the π system ($1a_u$ and $1b_u$). At relatively low energy are vacant δ ($2a_g$, LUMO) and δ* ($2b_u$) molecular orbitals formed from the in- and out-of-phase combinations of the $5d_{x^2-y^2}$ atomic orbitals. The green colour of the $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ complexes has been tentatively ascribed to $\sigma \rightarrow \delta^*$ and/or $\pi \rightarrow \delta$ transitions.[11] The electronic structure of $[W_2(\eta\text{-}C_5H_5)_2Cl_4]$ is broadly similar to those of the related metal–metal triply-bonded d^3–d^3 dimers $[X_3M{\equiv}MX_3]$ (M = Mo or W; X = NR_2, OR, alkyl).[13,14]

The PE spectra of the type A complexes $[Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}Br)_4]$[11] and $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$[15] are consistent with the molecular orbital description outlined above, showing ionizations assignable to excitations from three separate metal-based orbitals. The first vertical ionization energy for the dimolybdenum complex (6.29 eV) is substantially higher than that of the pentamethylcyclopentadienyl ditungsten complex (5.74 eV) indicating that the latter is more electron-rich. The relatively narrow band width of the σ-ionizations (approximately equal to those of the δ and δ* ionizations) in these complexes has been discussed in terms of the inflexibility of the $M_2(\mu\text{-}X)_4$ core. Thus the anticipated lengthening of the M–M bond in the ^2A_g ion state formed on removing an electron from the σ orbital may be countered by increased Cl–Cl lone pair repulsions in the $(\mu\text{-}Cl)_4$ bridge as the $Mo_2(\mu\text{-}Cl)_4$ unit elongates along the Mo–Mo vector.[11]

The He I and He II PE spectra for $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ showed only one, symmetrical metal-based ionization at 6.48 eV, whereas two might have been expected both from the extended-Hückel calculations and from a general anticipation of a stronger σ-bonding than π-bonding interaction on valence orbital overlap criteria.[11] However, assuming Koopmans' theorem, the PE spectra suggest that the σ and π levels are isoenergetic. Similar phenomena have been noted in other metal–metal multiply-bonded dimers[14,16] and have been attributed to the relatively close approach of the two metal centres in such complexes.[13] This leads to a substantial unfavourable overlap between the valence nd_{z^2} orbital of one metal atom with the outer core *ns* or np_z orbital of the other, and to a destabilization of the metal–metal valence σ-interaction. The first ionization energy (6.48 eV) for $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ suggests that this complex is more electron-rich than the related metal–metal triply-bonded carbonyl complexes, $[M_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (M = Cr, Mo, or W; 1st i.e. = 7.25—7.36 eV)[17] and most of the $[M_2X_6]$ complexes of Chisholm and Cotton.[13,14]

The different ground state molecular geometries of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ and $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ has been rationalized in terms of the extent of metal–metal overlap afforded in the type B geometry for the two metals.[11] The quadruply-bridged structure A clearly favours metal–ligand bonding whereas the type B geometry emphasizes metal–metal bonding. Extended-Hückel molecular orbital calculations predict a larger total metal–metal overlap population for M = W than for M = Mo in the type B complex $[M_2(\eta\text{-}C_5H_5)_2Cl_4]$. It was concluded that 'there exists a delicate balance between metal–metal and metal–ligand bonding' in these complexes.[11] This statement is underscored by the structure of $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ for which a quadruply-bridged type A geometry presumably minimizes η-C_5Me_5–chloride ligand steric interactions at the expense of direct metal–metal bonding. However, the importance of metal–metal bonding in setting the basic geometries of Group 6 metal complexes is further emphasized by the structures of the dichromium complexes $[Cr_2(\eta\text{-}C_5R_5)_2X_2(\mu\text{-}X)_2]$ (R = H or Me; X = Cl, Br, or I) which are paramagnetic, of the structural type C and contain no metal–metal bond.[2]

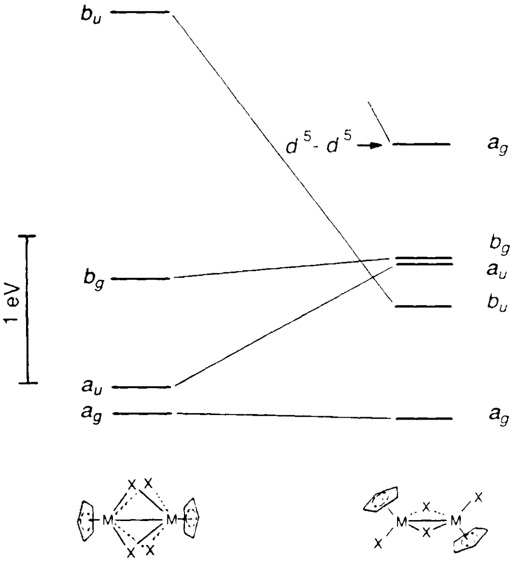


Figure 5 Correlation diagram for the opening of a quadruply-bridged dimer (type A) to a doubly-bridged dimer (type C). (Reproduced by permission from reference 11.)

The possibility of a metal–metal bonded type C (doubly-bridged) geometry intermediate between the two extremes A and B for the molybdenum or tungsten complexes has been probed using extended-Hückel calculations which gave the correlation diagram reproduced in Figure 5. For a d^3–d^3 electron count, a quadruply-bridged (type A) structure is favoured over the doubly-bridged one both in terms of metal-based orbital energetics and an unfavourably small HOMO–LUMO gap in the type C geometry.[11]

4 Reactivity

The two very different alternative geometries (*i.e.*, either a quadruply-bridged or unsupported metal–metal bond) found for the $[M(\eta\text{-}C_5R_5)X_2]_2$ complexes, might, at first sight, lead one to anticipate that their reactions would be clearly partitioned according to individual ground-state structures. However, there appears to be relatively little energy difference between the two extreme geometries, which are sensitive to changes in metal or cyclopentadienyl ligand substituents, and a solution equilibrium situation [type A↔type B] lying well to one side or the other could be envisaged. Moreover, a recent study of the symmetry-allowed 'opening-up' process, $[M_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)_4]$ (type A) → $[M_2(\eta\text{-}C_5H_5)_2Cl_4]$ (type B) using extended-Hückel procedures for M = Mo or W predicted no significant energy barrier (in the absence of steric effects) along the reaction coordinate for a d^3–d^3 dimer.[18]

It is found in fact that the reactions of the bridged and non-bridged $[M(\eta\text{-}C_5H_5)X_2]_2$ complexes have some features in common, but in other instances differ substantially according not only to the basic ground-state geometry of the dimer, but also to the nature of X.

4.1 Lewis Base Addition Reactions

The reactions of $[M(\eta\text{-}C_5R_5)X_2]n$ with Lewis bases are summarized in Scheme 1 and fall broadly into two categories depending on whether the products obtained are dinuclear or mononuclear. The formation of mononuclear compounds may be accompanied by a change in formal oxidation state giving M^{II} or M^{IV} derivatives.

Addition of chloride ions to the molybdenum or tungsten complexes $[M(\eta\text{-}C_5H_4R)Cl_2]_n$ gives the binuclear, anionic derivatives $[M_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)]^-$ (M = Mo, R = H or Me; M = W, R = Me or Pr^i).[9,19] A crystal structure determination for M = Mo, R = H revealed a metal–metal bond length of 2.413(1) Å, and Fenske-Hall molecular orbital calculations suggest that this molecule contains a Mo≡Mo triple bond.[9] The anions are labile at room temperature and the fluxional process can be interpreted as one involving effective rotation of the μ-chloride ligand around the metal–metal vector.[19]

The anion $[Mo_2(\eta\text{-}C_5H_4Me)_2Cl_4(\mu\text{-}Cl)]^-$ reacts with HCl gas returning the quadruply-bridged precursor $[Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}Cl_4)]$ in quantitative yield, presumably *via* the intermediate Mo^{IV} dimer $[Mo_2(\eta\text{-}C_5H_4Me)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ which might then reductively eliminate HCl. In support of this hypothesis the corresponding ditungsten anion is readily protonated to give the stable μ-hydrido complex $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$.[19] The differing reactivities of Mo and W illustrate the accepted view that W has a greater ability than Mo to support higher oxidation states.

Treatment of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ or $[Mo(\eta\text{-}C_5H_5)Cl_2]$ with monodentate or certain bidentate tertiary phosphines (Scheme 1) affords the paramagnetic, mononuclear Mo^{III} derivatives $[Mo(\eta\text{-}C_5H_4R)Cl_2(PR'_3)_2]$.[3,20–22] The crystal structures for R = Pr^i, $(PR'_3)_2$ = dppe,[20] and for R = H, R′ = Me[23] have been reported and confirm the 'four-legged piano stool' geometry depicted in Scheme 1. The complexes $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_2(PR'_3)_2]$ are precursors to the Mo^{IV} trihydrido derivatives $[Mo(\eta\text{-}C_5H_4Pr^i)H_3(PR'_3)_2]$, some of which are H–D exchange catalysts.[3]

In contrast, $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ reacts with dmpe to afford the Mo^{II} derivative $[Mo(\eta\text{-}C_5H_4Pr^i)(dmpe)_2]^+$ which is readily protonated to give the hydrido cation, $[Mo(\eta\text{-}C_5H_4Pr^i)(dmpe)_2H]^{2+}$.[3] On treatment of $[Mo(\eta\text{-}C_5H_5)Cl_2]$ with dmpe, the first intermediate observed by ESR spectroscopy gives a quintet resonance indicative of a complex containing a $Mo(dmpe)_2$ unit and again no evidence for a mono-dmpe adduct was reported.[22] The differing reactivity of dmpe compared to that of the other mono- and bi-dentate phosphines described above has been discussed in terms of a smaller Tolman cone angle for the dmpe ligand.[3] Addition of bipyridyl to $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ gives mononuclear Mo^{III} complexes analogous to those described above for the reactions with phosphines.[20]

In contrast to the behaviour of the dimolybdenum complexes, treatment of the W≡W triply-bonded complex $[W_2(\eta\text{-}C_5H_4Me)_2Cl_4]$ with dmpe gave the diamagnetic, dinuclear complex $[W_2(\eta\text{-}C_5H_4Me)_2Cl_2(\mu\text{-}Cl)_2(dmpe)]$ (Figure 6) for which a structure determination revealed a relatively long W–W bond [W–W = 3.196(1) Å].[24] The isolation of a dimeric complex for tungsten may reflect a greater strength of W–W *versus* Mo–Mo bonds. The corresponding reaction of $[W_2(\eta\text{-}C_5H_4Me)_2Cl_4]$ with PMe_3 afforded no tractable product.[25]

The nuclearity of the products obtained from treating $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ (R = Me or Pr^i, X = Br or Cl) with carbon monoxide (Scheme 1) depends critically on the identity of X and further highlights the delicate balance of factors at work in setting the reaction pathways of these complexes. For X = Cl, the dinuclear species $[W_2(\eta\text{-}C_5H_4R)_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ analogous to $[W_2(\eta\text{-}C_5H_4Me)_2Cl_2(\mu\text{-}Cl)_2(dmpe)]$ are obtained. The complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$ exist as a *ca.* 2:1 mixture of isomers in solution. The major isomer has been crystallographically characterized and possesses the C_2 geometry shown in Scheme 1. Its solution NMR spectra show one diastereotopic η-C_5H_4R and CO ligand environment. The second isomer cannot be separated from the major one, and although it is known that it contains two types of diastereotopic η-C_5H_4R and CO ligands in its NMR spectra it is not possible unambiguously to assign a molecular structure.[19]

For X = Br, only the mononuclear W^{IV} derivative *fac*-$[W(\eta\text{-}C_5H_4Pr^i)Br_3(CO)_2]$ was isolated. This complex has also been crystallographically characterized.[19] Presumably the longer W–W bond required in the $W_2(\mu\text{-}X)_2$ core for X = Br makes the

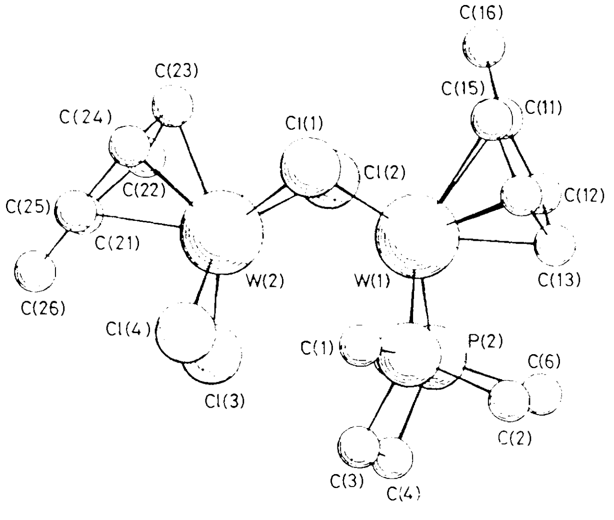


Figure 6 Molecular structure of $[W_2(\eta\text{-}C_5H_4Me)_2Cl_2(\mu\text{-}Cl)_2(dmpe)]$. Hydrogen atoms are omitted for clarity.
(Reproduced by permission from reference 24.)

formation of a dinuclear derivative unfavourable. The quadruply-bridged, pentamethylcyclopentadienyl species $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ also reacts with CO and gives the corresponding dinuclear product $[W_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$.[18]

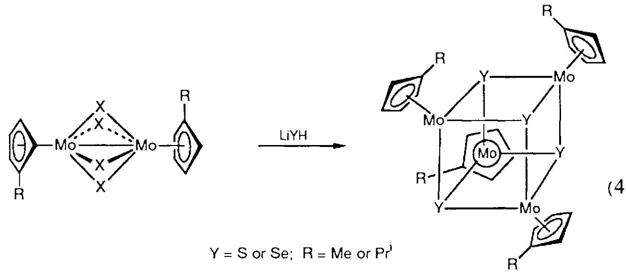
Treatment of $[W_2(\eta\text{-}C_5H_4R)_2Cl_4]$ (R = Me or Pr^i) with Bu^tNC does not give analogues of either of the carbonyl complexes described above. The reaction leads instead to complexes which contain both a terminal and bridging t-butylisocyanide ligand on the basis of their IR and NMR spectra.[19] A structure consistent with the spectral data is $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)(Bu^tNC)\{\mu\text{-}(\sigma + \pi)\text{-}Bu^tNC\}]$ (see Scheme 1).

4.2 Ligand Exchange Reactions

Treatment of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ with LiSR (R = Me, Ph, or adamantyl) affords in modest yields the corresponding tetra-μ-thiolato derivatives $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}SR)_4]$ which have been crystallographically characterized for R = Me and Ph.[20] With $LiSBu^t$ the mixed μ-sulphido-μ-thiolato complexes *cis,anti*- and *trans,syn*-$[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}S)_2(\mu\text{-}SBu^t)_2]$ were formed. The reaction of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ with $EtSSiMe_3$ gave a mixture of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}SEt)_4]$ and *cis,anti*- and *trans,syn*-$[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}S)_2(\mu\text{-}SEt)_2]$.

The yield of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}SMe)_4]$ from the reaction with LiSMe can be substantially increased by the addition of a four-fold excess of $FeCl_2$ to the tetrachloride dimer before addition of the LiSMe. This modified route may proceed *via* an anionic intermediate such as $[Fe(SMe)_4]^{2-}$ and we note that treatment of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ with $[NEt_4]_2[Fe(S\text{-}p\text{-}tol)_4]$ affords a small yield (< 2%) of the μ-S-*p*-tol species, $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}S\text{-}p\text{-}tol)_4]$.[20]

The electron-rich sulphur- or selenium-molybdenum cubane-like complexes $[Mo_2(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}Y)_4]$ (R = Pr^i, Y = S or Se; R = Me, Y = S) may be prepared in reasonable yields from $[Mo_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}Cl)_4]$ and LiYH. The *X*-ray structure for R = Pr^i, Y = S has been reported.[26,27] A second product of the reaction for R = Me, Y = S was $[Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$; it is not known if this is a side product of the reaction or an intermediate in the formation of the cubane itself.[26] The mixed sulphur/selenium cubanes $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_x(\mu_3\text{-}Se)_{4-x}]$ (x = 0—4) can be prepared as a mixture of compounds from $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ and LiSH/LiSeH, but unfortunately they cannot be separated by column chromatography.[28]



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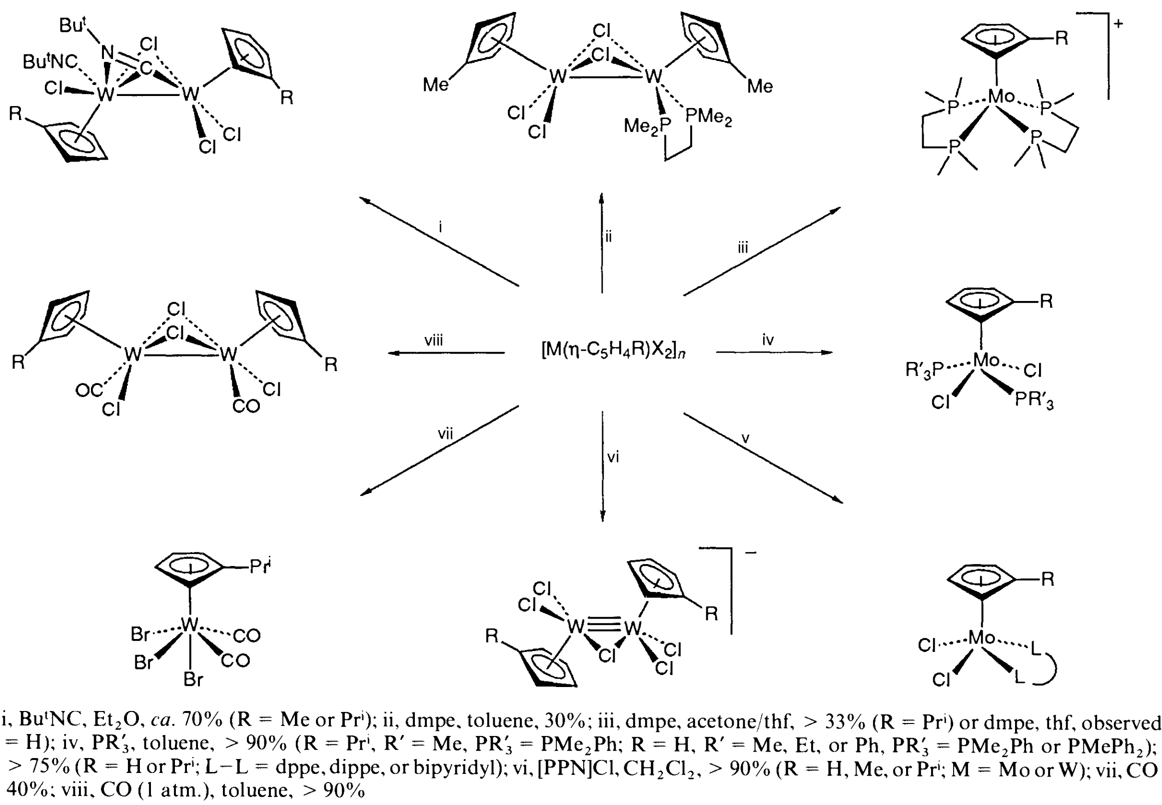
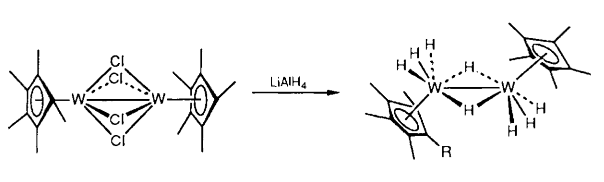
In contrast, treatment of the quadruply-bridged tungsten complex $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ with LiSH under reflux in



Reagents: i, Bu^tNC, Et_2O, *ca.* 70% (R = Me or Pr^i); ii, dmpe, toluene, 30%; iii, dmpe, acetone/thf, > 33% (R = Pr^i) or dmpe, thf, observed by ESR only (R = H); iv, PR'_3, toluene, > 90% (R = Pr^i, R′ = Me, $PR'_3 = PMe_2Ph$; R = H, R′ = Me, Et, or Ph, $PR'_3 = PMe_2Ph$ or $PMePh_2$); v, L−L, toluene, > 75% (R = H or Pr^i; L−L = dppe, dippe, or bipyridyl); vi, [PPN]Cl, CH_2Cl_2, > 90% (R = H, Me, or Pr^i; M = Mo or W); vii, CO (1 atm.), toluene, 40%; viii, CO (1 atm.), toluene, > 90%

Scheme 1 Reactions of $[M(\eta\text{-}C_5H_4R)X_2]_n$ with Lewis bases.

toluene gave a mixture of the previously-reported dimeric sulphido complexes $[W_2(\eta\text{-}C_5Me_5)_2S_2(\mu\text{-}S)_2]$ and $[W_2(\eta\text{-}C_5Me_5)_2S_2(\mu\text{-}S_2)]$.[18] In another ligand replacement reaction of $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$, Schrock has found that treatment with $LiAlH_4$ affords, on cold methanolysis work-up, the perhydro complex $[W_2(\eta\text{-}C_5Me_5)_2H_6(\mu\text{-}H)_2]$ in 40—50% yield.[6]



(5)

4.3 Oxidative Addition Reactions

The complexes $[M(\eta\text{-}C_5H_4R)X_2]_n$ undergo a number of oxidative addition reactions, some of which are illustrated in Scheme 2.

Poli has recently shown that $[Mo(\eta\text{-}C_5H_5)Cl_2]$ reacts with $PhICl_2$ to give $[Mo(\eta\text{-}C_5H_5)Cl_3]$ which is a useful precursor to other Mo^{IV} complexes.[29] The compound $[Mo(\eta\text{-}C_5H_5)Cl_3]$ may also be prepared by valence comproportionation of $[Mo(\eta\text{-}C_5H_5)Cl_2]$ and $[Mo(\eta\text{-}C_5H_5)Cl_4]$, or by reducing the latter with $TiCl_3$.

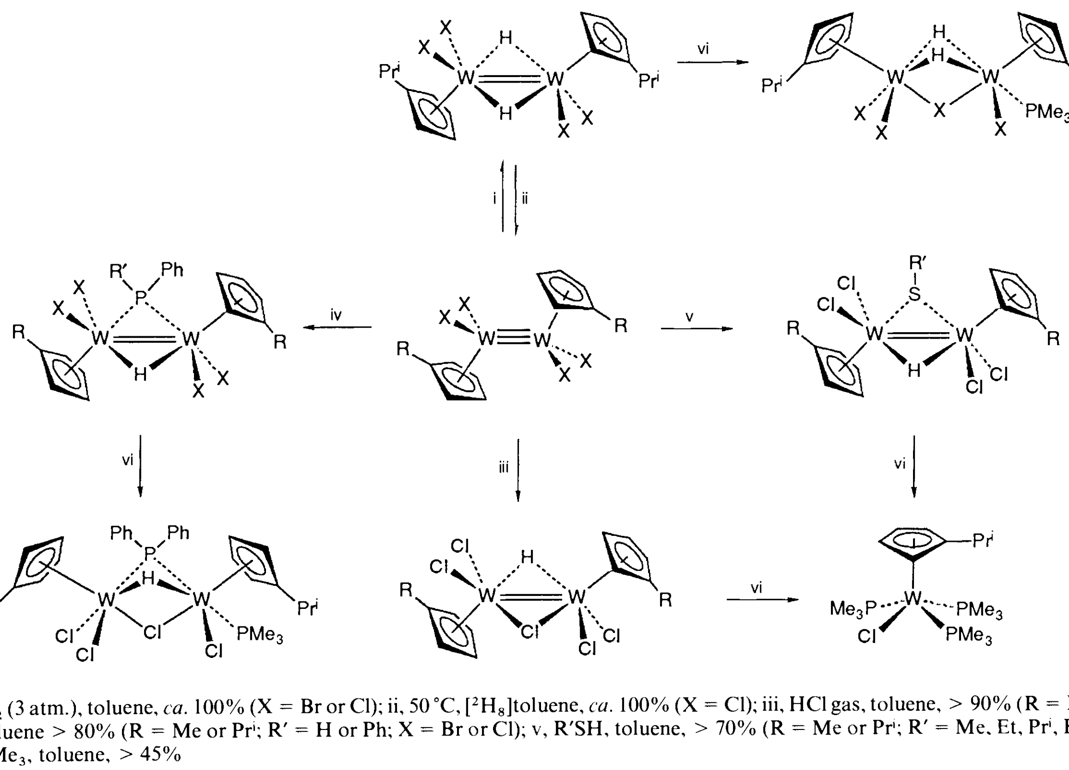
Treatment of the complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4]$ with dihydrogen (2—3 atm.) affords the corresponding μ-dihydro derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}H)_2]$ (Scheme 2). The bridging nature of the hydride ligands was inferred from the magnitude of the ^{183}W satellites (*ca* 26% by area of total signal; ^{183}W, 14.5% natural abundance, $I = \frac{1}{2}$). A bridging molecular dihydrogen $[W_2(\mu\text{-}H_2)]$ representation of the bonding was discounted by the low-temperature T_1 value for the hydride ligands (*ca.* 1.2 s at −90 °C) and by the magnitude of the one-bond hydrogen–tungsten coupling constant ($^1J[^1H-^{183}W] = 112$—116 Hz).[30]

For X = Cl the dihydrogen addition reaction is reversible, and warming a toluene solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)_2]$ to 60 °C under reduced pressure, returned the precursor $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ in quantitative yield as the first example of the reversible addition of H_2 to a metal–metal multiple bond. In contrast, the bromide-supported analogue $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}H)_2]$ is stable up to *ca.* 100 °C in toluene. Treatment of a toluene solution of the pentamethylcyclopentadienyl analogue, $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$, with dihydrogen (10 atm.) gave no reaction.[18] This latter observation contrasts with the behaviour of the ditantalum analogue, $[Ta_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$, which reacts with H_2 (3 atm.) to give the μ-hydrido derivative, $[Ta_2(\eta\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H_2)]$.[31]

The W≡W triply-bonded dimers readily insert into P–H, S–H, and Cl–H bonds, but do not undergo insertion into N–H or O–H bonds, presumably due to the greater bond strengths of the latter. The primary and secondary phosphines PPhR′H (R′ = H or Ph) react readily with the complexes $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ to afford the corresponding μ-phosphido derivatives $[W_2(\eta\text{-}C_5H_4R)_2X_4(\mu\text{-}H)(\mu\text{-}PPhR')]$ (R = Me or Pr^i; R′ = H or Ph; X = Br or Cl) in good yield.[30] The metal–metal bond length of 2.6556(7) Å found for $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}PPh_2)]$ is consistent with the W–W double bond expected from simple electron-counting procedures. A qualitative molecular orbital interpretation of the metal–metal bonding suggested a valence electronic configuration of $\sigma^2\pi^2$.[30]

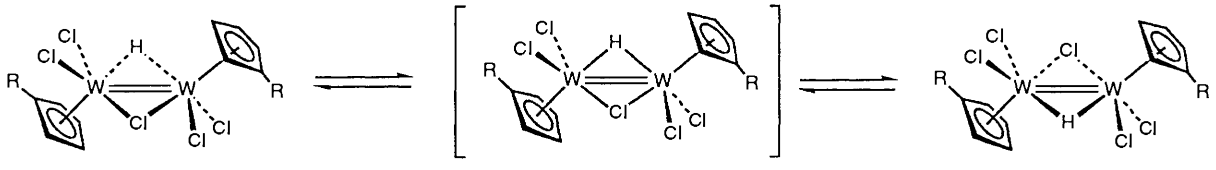
Treatment of $[W_2(\eta\text{-}C_5H_4R)_2Cl_4]$ with HCl gas in toluene gives the μ-chloro-μ-hydrido compounds $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ in > 90% yield.[30] These latter complexes may also be prepared by protonation of the μ-chloride anions $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)]^-$. The corresponding molybdenum species $[Mo_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ cannot be prepared by either route.[19,32]

The compounds $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ are fluxional and at room temperature their ^1H NMR spectra show an AA′BB′ spin system for the η-cyclopentadienyl ring protons, whereas at low temperature an ABCD spin system is observed. $\Delta G^\ddagger$ values of 12.5 ± 0.15 (at 263 K) and 12.3 ± 0.15 kcal mol^{-1} (at 268 K) were measured for $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ (R = Pr^i and Me respectively). The mechanism illustrated below, involving an equilibrium between edge-sharing square-based pyramidal and trigonal bipyramidal structures, has been proposed to account for the fluxional behaviour of these complexes.[30] Similar behaviour has been suggested for the μ-phosphido carbonyl complexes, $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)(\mu\text{-}PPhR)]$ (R = H or Ph).[33]



Reagents: i, H_2 (3 atm.), toluene, *ca.* 100% (X = Br or Cl); ii, 50 °C, $[^2H_8]$toluene, *ca.* 100% (X = Cl); iii, HCl gas, toluene, > 90% (R = Me or Pr^i); iv, PHPhR′, toluene > 80% (R = Me or Pr^i; R′ = H or Ph; X = Br or Cl); v, R′SH, toluene, > 70% (R = Me or Pr^i; R′ = Me, Et, Pr^i, Bu^t, or Ph); vi excess of PMe_3, toluene, > 45%

Scheme 2 Oxidative addition reactions of $[W_2(\eta\text{-}C_5H_4R)_2X_4]$.



R = Me of Pr^i

(6)

A series of μ-arene- and μ-alkane-thiolato derivatives $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}SR')(\mu\text{-}H)]$ (R = Pr^i or Me; R′ = Me, Et, Pr^i, Bu^t, or Ph) have been prepared (Scheme 2) and are also fluxional on the NMR timescale.[30] In the high temperature (fast exchange) limit the $\eta\text{-}C_5H_4R$ ring protons appear as a single ABCD spin system, whereas in the low temperature (slow exchange) limit they appear as two inequivalent ABCD spin systems. For R′ = Me or Bu^t the fast and slow ring exchange limits respectively could not be observed. A fluxional process analogous to that postulated above for $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)]$ was rejected since the μ-SPh complexes are fluxional at room temperature whilst the closely-related μ-phosphido complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}PPhH)(\mu\text{-}H)]$ are static up to at least 90 °C in toluene-d_8.

The free energies of activation for the fluxional process in the complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}SR')(\mu\text{-}H)]$ (R′ = Me, Et, Pr^i, or Ph) [see Figure 7(a)] show that $\Delta G\ddagger$ clearly decreases with *increasing* steric demands of the μ-SR′ moiety. The mechanism shown in Figure 7(b) involves lone pair inversion at the μ-S atom. $\Delta G\ddagger$ decreases with steric bulk because the two ground-state geometries [at left and right in Figure 7(b)] are more sensitive to the steric demands of the bridging ligand than is the postulated transition state (at centre) in which the R′ group is orientated directly away from the $W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}H)$ fragment. Therefore as R′ increases in size the ground state geometry is destabilized *relative* to the transition state and so $\Delta G\ddagger$ decreases.[30]

The oxidative addition products $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}H)(\mu\text{-}Y)]$ (Y = H, SR′, PPhR′, or Cl) react with PMe_3 (Scheme 2). For Y = SR′ or Cl (X = Cl), only the mononuclear product $[W(\eta\text{-}C_5H_4Pr^i)(PMe_3)_3Cl]$ could be isolated. For Y = H (X = Cl or Br) or PPh_2(X = Cl), however, the dinuclear Lewis base adducts, $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_3(\mu\text{-}X)(\mu\text{-}H)(\mu\text{-}Y)(PMe_3)]$ were obtained and the solid state structure for Y = PPh_2 has been determined.[30]

4.4 Alkyne Addition and Related Reactions

The W≡W triply bonded complexes $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ react with one or two equivalents of alkyne in a manner similar to that found for the related metal–metal triply-bonded complexes $[M_2(OR)_6(py)_n]$ (M = Mo or W; n = 0—2) and $[M_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (M = Cr, Mo or W).[34] The pentamethylcyclopentadienyl analogue $[W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4]$ does not react with but-2-yne, and the dimolybdenum complex $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$ gives intractable products.[26] The alkyne addition and coupling reactions of $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ are shown in Scheme 3.

Addition of one equivalent of C_2R_2 to $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4]$ affords the corresponding mono-μ-alkyne derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}C_2R_2)]$ (X = Br, R = Me or Ph; X = Cl, R = Et or $SiMe_3$) in 40—70% yield.[32,35] A preliminary crystal structure determination for X = Br, R = Ph revealed a distorted dimetallatetrahedrane geometry for the W_2C_2 core (Figure 8) whereby the projection of the alkyne C–C vector is not mutually orthogonal with respect to the W–W vector (deviation *ca.* 26°). The C–C and W–W bond lengths [1.41(4) and 2.795(3) Å respectively] in $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}C_2Ph_2)]$ are consistent with substantial back-donation of electron density from metal–metal bonding orbitals to the π^* orbitals of the μ-alkyne ligand.

The dimers $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ react with but-2-yne to give the flyover bridge complexes *cis*-$[W_2(\eta\text{-}C_5H_4R)_2X_4(\mu\text{-}C_4Me_4)]$ (Scheme 3), the NMR data for which show the $\eta\text{-}C_5H_4R$ ligands to be equivalent (note that the NMR data alone do not allow discrimination between isomers with $\eta\text{-}C_5H_4R$ ligands either *cis* or *trans* to the μ-hydrocarbyl moiety and only the former is illustrated in Scheme 3). The *cis* complexes convert in solution (or, for X = Cl, in the solid state at *ca.* 200 °C!) to the corresponding *trans* isomers (Scheme 3) which show two $\eta\text{-}C_5H_4R$ ring environments in their NMR spectra, the resonances due to the $\mu\text{-}C_4Me_4$ moiety remaining virtually indistinguishable from those of the *cis* isomers. The *X*-ray crystal structure of *trans*-$[W_2(\eta\text{-}C_5H_4Me)_2Cl_4(\mu\text{-}C_4Me_4)]$ revealed a symmetrically-bridging $\mu\text{-}C_4Me_4$ ligand perpendicular to the plane containing the W–W bond. The complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}C_4Me_4)]$ are the second examples of flyover bridge complexes in which the $\mu\text{-}C_4R_4$ moiety coordinates symmetrically to each metal centre in a η^4-fashion. The energy of activation for the *cis*→*trans* isomerization for X = Cl, R = Pr^i in solution is 23.6 ± 0.2 kcal

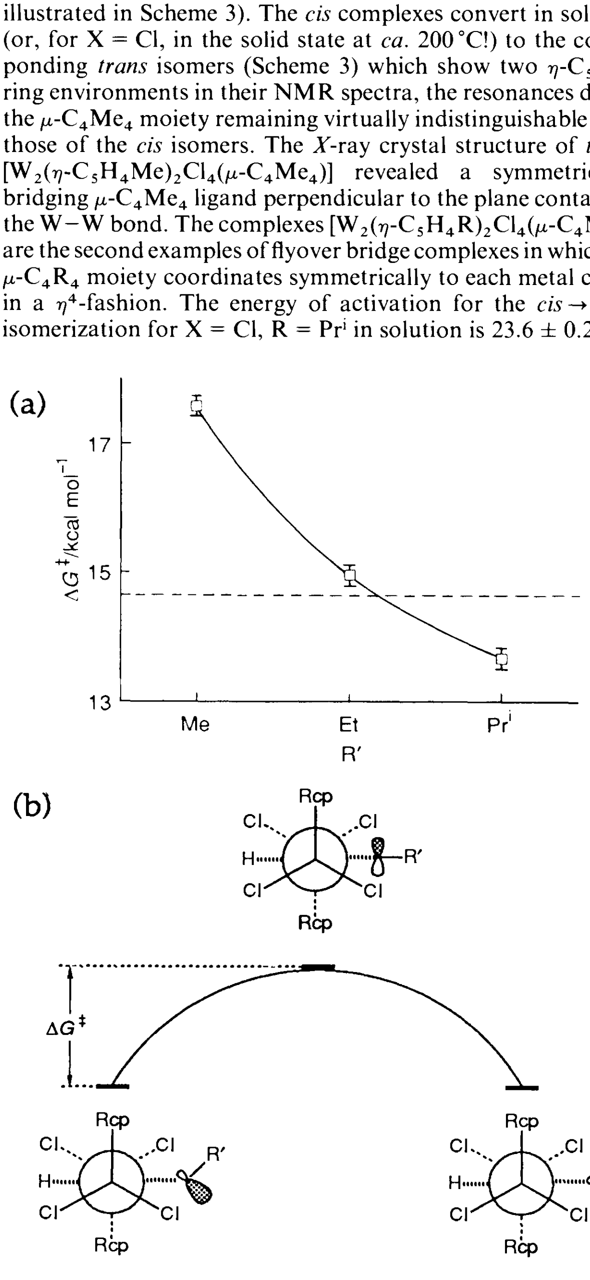


Figure 7 (a) Plot of $\Delta G\ddagger$ (320 K) against R′ group for the fluxional process in $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}SR')]$ (R′ = Me, Et, Pr^i, or Ph). The value for R = Ph is indicated by the horizontal dashed line. The line joining the data points for R′ = Me, Et, and Pr^i was fitted by simple interpolation.
(b) Proposed fluxional process for $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}H)(\mu\text{-}SR')]$ (R = Me or Pr^i; R′ = Me, Et, Pr^i, Bu^t, or Ph). The molecule is viewed as a Newman projection along the W–W vector where Rcp represents $\eta\text{-}C_5H_4R$.
(Reproduced by permission from reference 30.)

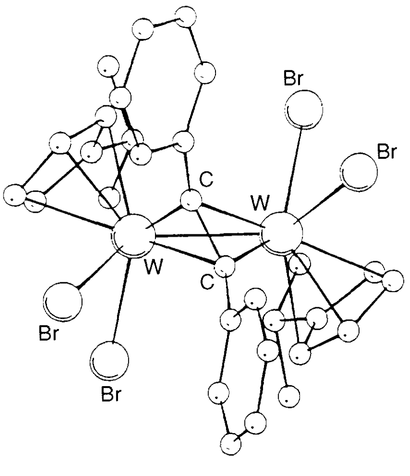


Figure 8 Molecular structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}C_2Ph_2)]$ viewed along the molecular C_2 axis. Hydrogen atoms are omitted for clarity.[32]

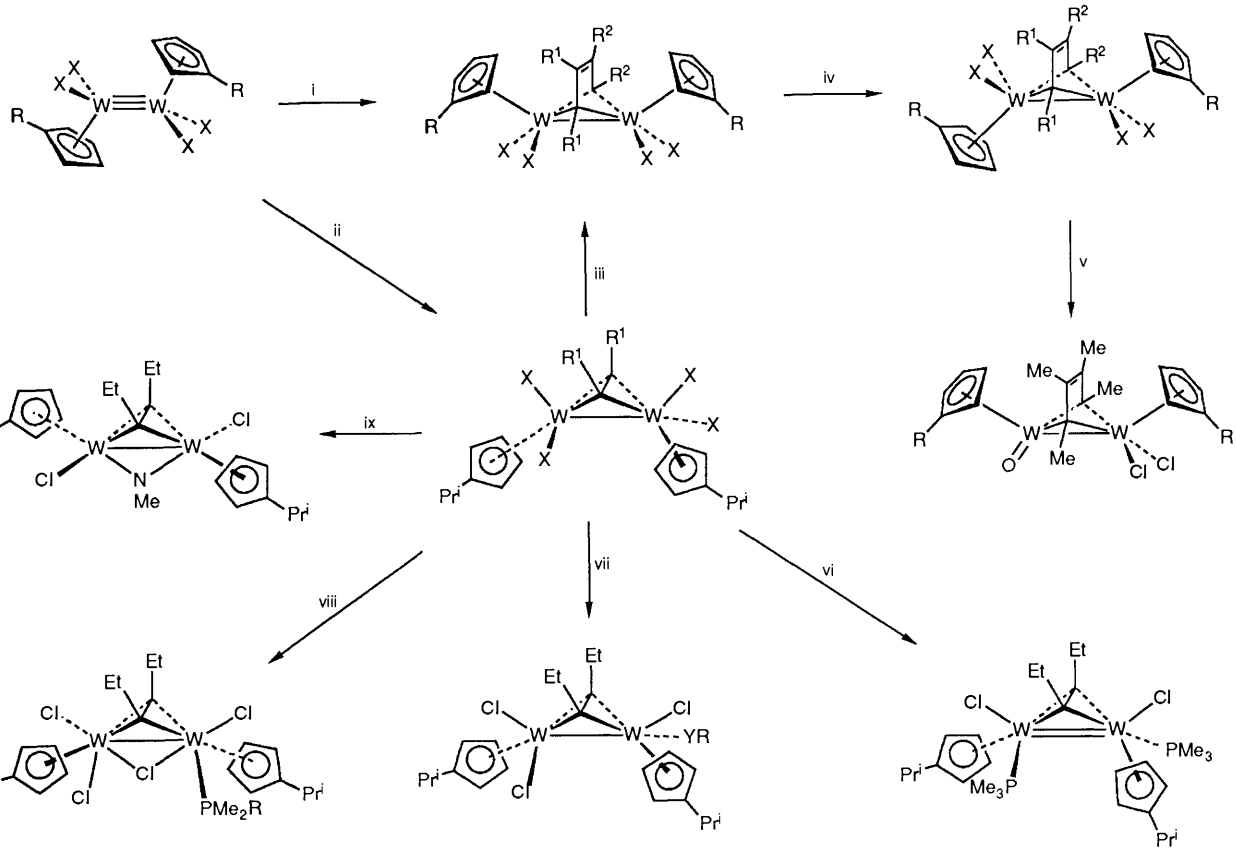
mol^{-1}, and the rates at 336 K for this process increase in the order $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}C_4Me_4)]$ (X = Br < Cl) < $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}C_4Et_2Me_2)]$.[32,35]

Treatment of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ with an excess of EtC_2Me affords the mixed-alkyne flyover bridge derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4\{\mu\text{-}(1,3)\text{-}C_4Et_2Me_2\}]$ and $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4\{\mu\text{-}(1,4)\text{-}C_4Et_2Me_2\}]$ where the numbering in the flyover bridge refers to the positions of the ethyl substituents. Derivatives with a μ-(1,2)- or a (2,3)-$C_4Et_2Me_2$ linkage were not observed. However, addition of but-2-yne to the pre-formed mono-alkyne adduct $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ gave the $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4\{\mu\text{-}(1,2)\text{-}C_4Et_2Me_2\}]$ isomer exclusively, suggesting that the alkyne linking mechanism in this instance involves simple insertion of the second equivalent of alkyne into the W–C(alkyne) bond of the mono-alkyne adduct.[35]

The alkyne coupling reactions of $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ for X = Br do not appear to proceed in the same manner as for X = Cl. The dinuclear monoalkyne adducts $[W(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}C_2R_2)]$ (R = Me, Et, or Ph) do not undergo alkyne coupling reactions. However, poorly-understood labile intermediates with the repeat formula $[W_2(\eta\text{-}C_5H_4Pr^i)Br_2(CR)]_{3x}$ (x = 1 or 2) have been isolated from the reaction of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4]$ with C_2R_2. These complexes, which slowly convert to the corresponding dimers $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}C_2R_2)]$ in solution, react with added butyne to give the flyover bridge derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4\{\mu\text{-}(1,2)\text{-}C_4R_2Me_2\}]$ (R = Me or Et).[32]

The flyover bridge complexes *cis-* and *trans-*$[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}C_4Me_4)]$ react with aqueous acetone to give the red, pentane-soluble mono-oxo derivatives $[W_2(\eta\text{-}C_5H_4R)_2Cl_2(O)(\mu\text{-}C_4Me_4)]$. The *X*-ray crystal structure for R = Me shows that the strong *trans* influence of oxygen results in a 7° deviation of the μ-C_4Me_4 linkage from the ideal perpendicular geometry found for the otherwise identical tetrachloro species, *trans*-$[W_2(\eta\text{-}C_5H_4Me)_2Cl_4(\mu\text{-}C_4Me_4)]$.[35]

Some further reactions of the mono-alkyne adduct, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ have been explored (Scheme 3).[36] Addition of alkali metal thiolates or alkoxides allows replacement of one chloride ligand only, even in the presence of excess reagent, to give the complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(YR)(\mu\text{-}C_2Et_2)]$ (YR = SMe or OEt). Two chloride ligands in $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ may be replaced by treatment with $(Me_3Si)_2NMe$ to give the structurally characterized μ-imido derivative $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NMe)(\mu\text{-}C_2Et_2)]$, whereas reduction with two equivalents of sodium amalgam in the presence of PMe_3 forms the bis(phosphine) derivative $[W_2(\eta\text{-}$

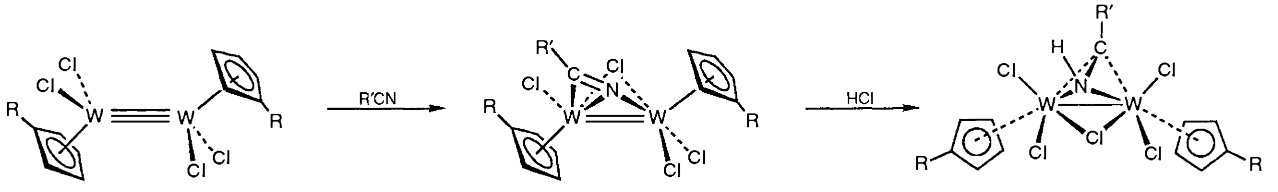


Reagents: i, C_2Me_2, toluene, > 60% (R = Me or Pr^i, $R^1 = R^2$ = Me, X = Br or Cl); ii, $C_2R^1_2$, toluene, 40—70% (R^1 = Me, Et, Ph, or $SiMe_3$; X = Br or Cl); iii, C_2Me_2, thf, 70% (R = Pr^i, R^1 = Et, R^2 = Me, X = Cl); iv, thf, 1—2 d, *ca.* 100% (R = Me or Pr^i, R^1 = Me or Et, R^2 = Me, X = Br or Cl); v, H_2O/acetone, 80% (R = Me or Pr^i, $R^1 = R^2$ = Me); vi, PMe_3, 2 Na/Hg, thf, 40%; vii, M^1YR, thf, 60% (M^1YR = NaOEt or LiSMe); viii, PMe_2R, thf, 70% (R = Me or Ph); ix, $MeN(SiMe_3)_2$, thf, 60%

Scheme 3 Alkyne addition and related reactions of $[W_2(\eta\text{-}C_5H_4R)_2X_4]$.

$C_5H_4Pr^i)_2Cl_2(PMe_3)_2(\mu\text{-}C_2Et_2)]$. Addition of tertiary phosphine PMe_2R to $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ affords the eighteen-electron complexes, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(\mu\text{-}C_2Et_2)(\mu\text{-}Cl)(PMe_2R)]$ (R = Me or Ph). The crystal structure for R = Me has been determined.[36]

Included in this section is the reaction of $[W_2(\eta\text{-}C_5H_4R)_2Cl_4]$ (R = Me or Pr^i) with nitriles R′CN (R′ = Me, Et, or Ph) which give the highly moisture-sensitive, brown μ-(σ + π)-nitrile derivatives $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)\{\mu\text{-}(\sigma+\pi)\text{-}R'CN\}]$.[37] A crystal structure determination for R = Me, R′ = Et confirmed the basic geometry illustrated below. This structure is reminiscent of that proposed for the isocyanide complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)(Bu^tNC)\{\mu\text{-}(\sigma+\pi)\text{-}Bu^tNC\}]$ (*vide supra*), except that the latter have an additional terminal donor ligand.



R = Me or Pr^i
R′ = Me, Et, or CH_2Ph

(7)

Treatment of the nitrile complexes with HCl in toluene affords the purple μ-η^2:η^2-iminoacyl derivatives $[W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}R'CNH)]$. The crystal structure for R = Pr^i, R′ = Et (Figure 9) confirmed the μ-η^2:η^2 mode of coordination of the R′CNH ligand and showed it to be the first example of this type of ligation for the iminoacyl moiety. The N–H proton could not be located crystallographically, but its presence was indicated by IR and NMR deuterium labelling studies.[37] The iminoacyl derivatives are clearly related to the μ-alkyne complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)(PMe_2R)]$ (see Scheme 3) with which they are valence isoelectronic.

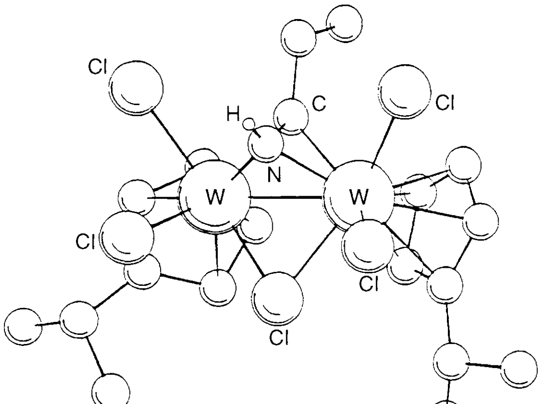


Figure 9 Molecular structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}EtCNH)]$. Hydrogen atoms bonded to carbon are omitted for clarity.[37]

An orange intermediate of identical empirical formula to that of the final, crystallographically characterized purple complex (Figure 9) may be isolated in the reaction of the μ-nitrile complexes $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)\{\mu\text{-}(\sigma+\pi)\text{-}R'CN\}]$ with HCl. These intermediate species readily convert to the corresponding purple isomers in solution, and on the basis of their IR and NMR spectra, have tentatively been assigned analogous structures with a *trans* arrangement of the η-C_5H_4R ligands.[19]

5 Concluding Remarks

We have shown in this article that the molybdenum and tungsten complexes $[M(\eta\text{-}C_5R_5)X_2]_n$ have a rich and diverse reaction chemistry which has obvious potential for further study and development. Complexes with apparently dramatically different ground state structures (*viz à viz* either terminal or bridging halide ligands) may sometimes give rise to parallel chemistry, while a seemingly minor change from Cl to Br can sometimes lead to a quite different reaction pathway. Further studies of the chemistry of these dinuclear complexes are clearly required in order to evaluate the subtle factors which moderate the various structures and pathways of reactivity.

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