Synthesis of the W≡W Triply Bonded Dimers $[\mathrm{W_2(\eta\text{-}C_5H_4R)_2X_4}]$ (X = Cl, R = Me or Pr^i; X = Br, R = Pr^i) and *X*-Ray Crystal Structures of $[\mathrm{W(\eta\text{-}C_5H_4Pr^i)Cl_4}]$ and $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4}]$ *

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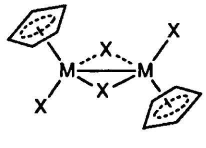
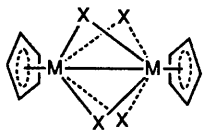
The syntheses of the W≡W triply bonded species $[\mathrm{W_2(\eta\text{-}C_5H_4R)_2X_4}]$ (X = Cl, R = Me or Pr^i; X = Br, R = Pr^i) and of their singly bonded congeners $[\mathrm{Mo_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}X)_4}]$ (X = Cl, R = Me or Pr^i; X = Br, R = Me) are reported along with *X*-ray crystal-structure determinations of $[\mathrm{W(\eta\text{-}C_5H_4Pr^i)Cl_4}]$ and $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4}]$. The molecular structure of $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4}]$ consists of two mutually *trans* $\mathrm{W(\eta\text{-}C_5H_4Pr^i)Cl_2}$ units linked by an unsupported W≡W triple bond [W≡W 2.367 8(6) Å].

The ready availability of useful synthons has been a significant factor in the advancement of organometallic chemistry. One important class of compounds is that of the η-cyclopentadienyl transition-metal dihalide complexes $[\{\mathrm{M(\eta\text{-}C_5R_5)X_2}\}_2]$ (X = Br, Cl, or I). Members of this class of complex are now known for M = Sc,[1] Ti,[2] V,[3] Nb,[4] Ta,[5] Cr,[6] Mo,[7] Re,[8] Ru,[9], Co,[10] Rh,[11] and Ir.[11] For M = Sc or Ti, the complexes appear to be oligomeric in the solid state, but for most of the others dinuclear structures have been established with either two (**A**; M = Cr, Re, Ru, Co, Rh, or Ir) or four (**B**; M = V, Ta, or Mo) halide bridges. The niobium compound $[\{\mathrm{Nb(\eta\text{-}C_5Me_5)Cl_2}\}_2]$ may also possess a quadruply bridged structure as in the vanadium and tantalum congeners.



(A)



(B)

Since the complexes $[\{\mathrm{M(\eta\text{-}C_5R_5)X_2}\}_2]$ have proved to be a widely exploited class of synthons, we were interested to note that the tungsten homologue in this series had not been well established. Our earlier attempts to prepare tungsten analogues of the dimolybdenum species $[\mathrm{Mo_2(\eta\text{-}C_5H_4CHR_2)_2(\mu\text{-}Cl)_4}]$ (R = Me or Ph)[7] *via* treatment of the corresponding η-fulvene complexes $[\mathrm{W(\eta\text{-}C_5H_4CR_2)(\eta\text{-}C_6H_6)}]$ with HCl in a manner used for the preparation of the dimolybdenum species failed to yield any tractable product. More recently, however, Alt *et al.*[12] found that treatment of the $[\mathrm{W_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}H)_2}]$ with HCl in toluene at −78 °C afforded a blue, carbonyl-free, insoluble precipitate which was formulated as $[\{\mathrm{W(\eta\text{-}C_5H_5)Cl_2}\}_2]$ on the basis of microanalytical and i.r. data. In contrast, Schrock and co-workers[13] reported that treatment of $[\{\mathrm{W(\eta\text{-}C_5Me_5)Cl_4}\}_2]$ with 4 equivalents of sodium amalgam afforded an emerald-green compound, but for which no characterising data were presented. It was proposed that this compound 'is $[\{\mathrm{W(\eta\text{-}C_5Me_5)Cl_2}\}_2]$, probably with four bridging chloride ligands.'

Here we report the synthesis and characterisation of the triply bonded ditungsten complexes $[\mathrm{W_2(\eta\text{-}C_5H_4R)_2X_4}]$ (X = Cl, R = Me or Pr^i; X = Br, R = Pr^i), the dimolybdenum complexes $[\mathrm{Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}X)_4}]$ (R = Me, X = Cl or Br), and an alternative synthesis of the previously reported complex $[\mathrm{Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4}]$.[7] Part of this work has been communicated.[14]

Results and Discussion

We set out to explore a reductive dimerisation route analogous to those previously exploited by Messerle[5] and Herrmann and co-workers[8] for other third row $[\{\mathrm{M(\eta\text{-}C_5R_5)X_2}\}_2]$ (M = Ta or Re) complexes. Although the tetrahalide complexes $[\mathrm{Mo(\eta\text{-}C_5H_4R)X_4}]$ (X = Br, R = H; X = Cl, R = H or Me) have been known for many years,[15] the tungsten analogues were described only recently. The compounds $[\{\mathrm{W(\eta\text{-}C_5R_4Bu^t)Cl_4}\}_2]$ (R = Me or Et) were first prepared by treating $[\mathrm{W(\equiv CBu^t)Cl_3(dme)}]$ (dme = 1,2-dimethoxyethane) with an excess of $\mathrm{C_2R_2}$, and were formulated as dimers on the basis of a molecular weight determination for $[\{\mathrm{W(\eta\text{-}C_5Et_4Bu^t)Cl_4}\}_2]$ in $\mathrm{CH_2Cl_2}$.[16] Subsequently it was found that treatment of $[\mathrm{M(\eta\text{-}C_5Me_4R)(CO)_3Me}]$ (M = Mo, R = Me; M = W, R = Me, Et, or Pr^n) with $\mathrm{PCl_5}$ (2.5 equivalents) in $\mathrm{CH_2Cl_2}$ gave the almost insoluble tetrachloride derivatives $[\{\mathrm{M(\eta\text{-}C_5Me_4R)Cl_4}\}_n]$ (M = Mo, n = 1; M = W, n = 2) in >80% yield.[17]

The compounds $[\mathrm{Mo(\eta\text{-}C_5H_4R)(CO)_3Me}]$ (**1a**; R = H) and (**1b**; R = Me),[18] $[\mathrm{Mo_2(\eta\text{-}C_5H_4Me)_2(CO)_6}]$,[19] and $[\mathrm{W(\eta\text{-}C_5H_5)(CO)_3Me}]$ (**2a**)[18] were prepared as described previously. The anionic derivatives $[\mathrm{M(\eta\text{-}C_5H_4R)(CO)_3}]^-$ (M = Mo or W) were prepared by treating $[\mathrm{M(CO)_6}]$ with $\mathrm{Na[C_5H_4R]}$ in refluxing diglyme ($\mathrm{MeOCH_2CH_2OCH_2CH_2OMe}$) for 2—3 h after the method of Manning and co-workers.[19] The mononuclear species $[\mathrm{M(\eta\text{-}C_5H_4R)(CO)_3Me}]$ (**1c**; M = Mo, R = Pr^i), (**2b**; M = W, R = Me), and (**2c**; M = W, R = Pr^i) were obtained by treatment of the anions with methyl iodide. The compounds (**1c**), (**2b**), and (**2c**) have not been described previously and were characterised by elemental analysis and by comparison of their i.r. and n.m.r. spectra with those of the known homologues.

Treatment of $[\mathrm{Mo(\eta\text{-}C_5H_4R)(CO)_3Me}]$ (R = H, Me, or Pr^i) with $\mathrm{PCl_5}$ (2.5 equivalents) in $\mathrm{CH_2Cl_2}$, followed by refluxing for 8 h, afforded purple-red $[\mathrm{Mo(\eta\text{-}C_5H_4R)Cl_4}]$ (**3a**; R = H), (**3b**; R = Me), and (**3c**; R = Pr^i) in *ca.* 60—80% yield. The air- and water-sensitive compounds (**3a**) and (**3b**) have been described previously.[15] The isopropyl

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* Tetrachloro(η-isopropylcyclopentadienyl)tungsten and *trans*-bis[dichloro(η-isopropylcyclopentadienyl)tungsten] (3*W*–*W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

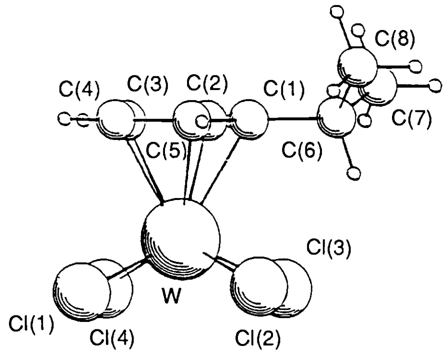

Figure 1. Molecular structure of [W(η-$C_5H_4Pr^i$)Cl_4] (**4c**)

Table 1. Bond lengths (Å) and angles (°) for [W(η-$C_5H_4Pr^i$)Cl_4] (**4c**) with estimated standard deviations (e.s.d.s) in parentheses. Cp_{cent} refers to the computed η-$C_5H_4Pr^i$ ring centroid

W–Cl(1)	2.339(1)	W–Cl(2)	2.346(1)
W–Cl(3)	2.347(1)	W–Cl(4)	2.339(1)
W–C(1)	2.326(4)	W–C(2)	2.315(4)
W–C(3)	2.340(5)	W–C(4)	2.348(5)
W–C(5)	2.304(5)	C(1)–C(2)	1.420(6)
C(1)–C(5)	1.421(7)	C(1)–C(6)	1.506(6)
C(2)–C(3)	1.390(7)	C(3)–C(4)	1.388(8)
C(4)–C(5)	1.421(7)	C(6)–C(7)	1.519(7)
C(6)–C(8)	1.520(7)	Cp_{cent}–W	1.992

Cl(2)–W–Cl(1)	82.28(5)	Cl(3)–W–Cl(1)	137.15(6)
Cl(3)–W–Cl(2)	82.81(5)	Cl(4)–W–Cl(1)	82.62(5)
Cl(4)–W–Cl(2)	139.29(5)	Cl(4)–W–Cl(3)	83.10(5)
C(1)–W–Cl(1)	131.4(1)	C(1)–W–Cl(2)	87.3(1)
C(1)–W–Cl(3)	87.5(1)	C(1)–W–Cl(4)	130.0(1)
C(2)–W–Cl(1)	137.6(1)	C(2)–W–Cl(2)	121.6(1)
C(2)–W–Cl(3)	83.6(1)	C(2)–W–Cl(4)	94.4(1)
C(2)–W–C(1)	35.6(2)	C(3)–W–Cl(1)	103.9(1)
C(3)–W–Cl(2)	139.9(1)	C(3)–W–Cl(3)	113.3(1)
C(3)–W–Cl(4)	80.6(1)	C(3)–W–C(1)	58.6(2)
C(3)–W–C(2)	34.8(2)	C(4)–W–Cl(1)	81.0(1)
C(4)–W–Cl(2)	111.8(1)	C(4)–W–Cl(3)	141.7(1)
C4)–W–Cl(4)	102.8(1)	C(4)–W–C(1)	59.4(2)
C(4)–W–C(2)	58.3(2)	C(5)–W–Cl(1)	95.7(1)
C(5)–W–Cl(2)	82.0(1)	C(5)–W–Cl(3)	121.5(1)
C(5)–W–Cl(4)	137.1(1)	C(5)–W–C(1)	35.7(2)
C(5)–W–C(2)	58.8(2)	C(4)–W–C(3)	34.5(2)
C(5)–W–C(3)	58.1(2)	C(5)–W–C(4)	35.6(2)
C(2)–C(1)–W	71.7(3)	C(5)–C(1)–W	71.3(3)
C(5)–C(1)–C(2)	105.8(4)	C(6)–C(1)–W	123.5(3)
C(6)–C(1)–C(2)	127.0(4)	C(6)–C(1)–C(5)	127.2(4)
C(1)–C(2)–W	72.6(2)	C(3)–C(2)–W	73.6(3)
C(3)–C(2)–C(1)	108.7(4)	C(2)–C(3)–W	71.6(3)
C(4)–C(3)–W	73.1(3)	C(4)–C(3)–C(2)	109.7(4)
C(3)–C(4)–W	72.5(3)	C(5)–C(4)–W	70.5(3)
C(5)–C(4)–C(3)	106.7(4)	C(1)–C(5)–W	73.0(2)
C(4)–C(5)–W	73.9(3)	C(4)–C(5)–C(1)	109.0(4)
C(7)–C(6)–C(1)	112.1(4)	C(8)–C(6)–C(1)	111.8(4)
Cp_{cent}–W–Cl(1)	110.40	Cp_{cent}–W–Cl(2)	110.18
Cp_{cent}–W–Cl(3)	111.47	Cp_{cent}–W–Cl(4)	110.31

homologue (**3c**) was characterised by elemental analysis and by comparison of its i.r. spectrum with those of [Mo(η-C_5H_4R)Cl_4] (R = H or Me).

The tungsten analogues [W(η-C_5H_4R)Cl_4] (**4a**; R = H), (**4b**; R = Me), and (**4c**; R = Pr^i) were similarly obtained as red, air- and water-sensitive materials in 60—90% yield by treatment of the appropriate precursors [W(η-C_5H_4R)$(CO)_3Me$] with PCl_5 in CH_2Cl_2, and were characterised by elemental analysis and i.r. spectroscopy. In general, their i.r. spectra were similar to those of the corresponding molybdenum congeners, but the bands assignable to ν(M–Cl) modes were shifted to slightly lower frequency for the tungsten complexes. The similarity of the i.r. data for the molybdenum and tungsten derivatives suggests that their solid-state structures are also very similar.

Table 2. Fractional atomic co-ordinates (× 10^4) for [W(η-$C_5H_4Pr^i$)Cl_4] (**4c**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	3 003.0(1)	1 518.3(3)	5 885.5(1)
Cl(1)	4 919(1)	2 746(2)	5 939.6(9)
Cl(2)	3 201(1)	3 462(2)	7 146.1(8)
Cl(3)	1 098(1)	2 948(2)	5 632.1(9)
Cl(4)	2 840(1)	2 101(3)	4 433.3(8)
C(1)	2 283(4)	−1 239(7)	6 591(3)
C(2)	2 014(4)	−1 679(7)	5 710(3)
C(3)	3 060(5)	−1 986(8)	5 429(3)
C(4)	4 008(5)	−1 720(8)	6 098(4)
C(5)	3 532(4)	−1 230(8)	6 822(3)
C(6)	1 422(4)	−933(8)	7 168(3)
C(7)	213(5)	−1 809(11)	6 786(4)
C(8)	1 883(5)	−1 833(11)	8 046(3)

The tetrachloro complexes [M(η-C_5H_4R)Cl_4] (M = Mo or W) are only moderately soluble in CH_2Cl_2 and tetrahydrofuran (thf); their solubility increases in the order R = H < Me < Pr^i. Single crystals of [W(η-$C_5H_4Pr^i$)Cl_4] (**4c**) suitable for an *X*-ray structure analysis were grown by cooling a concentrated dichloromethane solution. The molecular structure of (**4c**) is shown in Figure 1, selected bond lengths and angles are listed in Table 1, and final fractional atomic co-ordinates in Table 2.

The crystal structure determination shows that (**4c**) is monomeric in the solid state with no intermolecular contacts closer than the sum of the appropriate van der Waals radii. Compound (**4c**) has a typical 'four-legged piano-stool' geometry with the methyl groups of the isopropyl group directed away from the WCl_4 fragment, possibly to minimise non-bonding interactions with the basal chloride ligands, although crystal-packing effects could be equally important. The tungsten atom lies 0.83 Å above the plane containing the four chloride ligands. Although it has been proposed previously that the more extensively ring-substituted species [{W(η-C_5R_4R')Cl_4}$_2$] (R = Me, R′ = Me, Et, or Pr^n; R′ = Bu^t, R = Me or Et)[16,17] adopt dimeric structures in solution, it is clearly possible that these species also have monomeric structures in the solid state.

Further studies showed that the oxidative route could be extended to the synthesis of the analogous tetrabromo derivatives [M(η-C_5H_4R)Br_4] (**5**; M = Mo, R = Me) and (**6**; M = W, R = Pr^i). Thus treatment of [Mo_2(η-C_5H_4Me)$_2(CO)_6$] or [W(η-$C_5H_4Pr^i$)$(CO)_3Me$] with PBr_5 (4 and 2.5 equivalents respectively) in CH_2Cl_2 followed by reflux of the mixtures for 12 h gave the tetrabromide derivatives [Mo(η-C_5H_4Me)Br_4] and [W(η-$C_5H_4Pr^i$)Br_4] in 82 and 62% yield respectively. The compounds (**5**) and (**6**) were characterised by elemental analysis and i.r. spectroscopy.

When a red suspension of [W(η-C_5H_4R)Cl_4] (R = Me or Pr^i) in toluene or thf was treated with Na–Hg (2 equivalents) over 2 h at room temperature, an emerald-green solution was formed. Filtration (to remove NaCl) and subsequent crystallisation from toluene gave green crystals of a material analysing as [W_2(η-C_5H_4R)$_2Cl_4$] in 45%, (**7a**; R = Me), and 60%, (**7b**; R = Pr^i), yield. Typically, 10 g of [W(η-C_5H_4R)Cl_4] afforded 5—6 g of [W_2(η-C_5H_4R)$_2Cl_4$]. Similarly, reduction of purple-brown [W(η-$C_5H_4Pr^i$)Br_4] in thf gave dark green microcrystals of [W_2(η-$C_5H_4Pr^i$)$_2Br_4$] (**8**) in *ca.* 35% yield. In contrast, when [W(η-C_5H_5)Cl_4] was treated with Na–Hg in a similar fashion a

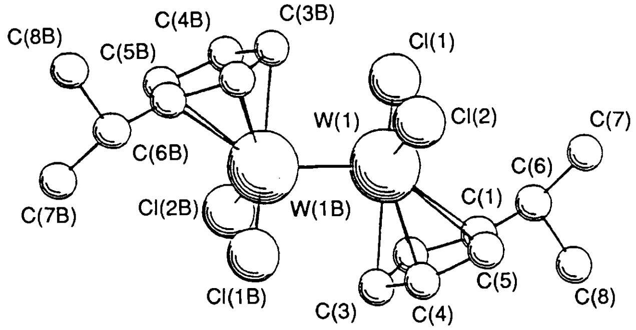

Figure 2. Molecular structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ (**7b**). The molecule lies across a crystallographic inversion centre. Atoms labelled B are related to their counterparts by the symmetry operator $-x, -y, -z$. Hydrogen atoms omitted for clarity

Table 3. Bond lengths (Å) and angles (°) for $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ (**7b**) with e.s.d.s in parentheses. Cp_{cent} refers to the computed $\eta\text{-}C_5H_4Pr^i$ centroid

W(1)–W(1B)	2.367 8(6)	W(1)–Cl(1)	2.321(2)
W(1)–Cl(2)	2.312(2)	W(1)–C(1)	2.492(8)
W(1)–C(2)	2.342(8)	W(1)–C(3)	2.287(8)
W(1)–C(4)	2.302(8)	W(1)–C(5)	2.456(8)
C(1)–C(2)	1.41(1)	C(1)–C(5)	1.42(1)
C(1)–C(6)	1.49(1)	C(2)–C(3)	1.44(1)
C(3)–C(4)	1.37(1)	C(4)–C(5)	1.40(1)
C(6)–C(7)	1.51(1)	C(6)–C(8)	1.54(1)
Cp_{cent}–W(1)	2.054		

Cl(1)–W(1)–W(1B)	100.25(6)	Cl(2)–W(1)–W(1B)	100.30(6)
Cl(2)–W(1)–Cl(1)	110.99(9)	C(1)–W(1)–W(1B)	140.0(2)
C(1)–W(1)–Cl(1)	86.5(2)	C(1)–W(1)–Cl(2)	114.1(2)
C(2)–W(1)–W(1B)	106.5(2)	C(2)–W(1)–Cl(1)	89.4(2)
C(2)–W(1)–Cl(2)	142.7(2)	C(2)–W(1)–C(1)	33.7(3)
C(3)–W(1)–W(1B)	86.5(2)	C(3)–W(1)–Cl(1)	123.0(2)
C(3)–W(1)–Cl(2)	123.3(2)	C(3)–W(1)–C(1)	58.0(3)
C(3)–W(1)–C(2)	36.1(3)	C(4)–W(1)–W(1B)	105.3(2)
C(4)–W(1)–Cl(1)	142.7(2)	C(4)–W(1)–Cl(2)	90.7(2)
C(4)–W(1)–C(1)	56.6(3)	C(4)–W(1)–C(2)	57.6(3)
C(4)–W(1)–C(3)	34.9(3)	C(5)–W(1)–W(1B)	139.3(2)
C(5)–W(1)–Cl(1)	114.6(2)	C(5)–W(1)–Cl(2)	86.7(2)
C(5)–W(1)–C(1)	33.3(3)	C(5)–W(1)–C(2)	56.1(3)
C(5)–W(1)–C(3)	57.5(3)	C(5)–W(1)–C(4)	34.1(3)
C(2)–C(1)–W(1)	67.3(5)	C(5)–C(1)–W(1)	72.0(5)
C(5)–C(1)–C(2)	106.3(8)	C(6)–C(1)–W(1)	126.9(6)
C(6)–C(1)–C(2)	125.9(8)	C(6)–C(1)–C(5)	127.7(8)
C(1)–C(2)–W(1)	79.0(5)	C(3)–C(2)–W(1)	69.9(5)
C(3)–C(2)–C(1)	109.6(8)	C(2)–C(3)–W(1)	74.0(5)
C(4)–C(3)–W(1)	73.2(5)	C(4)–C(3)–C(2)	105.6(8)
C(3)–C(4)–W(1)	72.0(5)	C(5)–C(4)–W(1)	79.0(5)
C(5)–C(4)–C(3)	110.8(8)	C(1)–C(5)–W(1)	74.7(5)
C(4)–C(5)–W(1)	66.9(5)	C(4)–C(5)–C(1)	107.7(8)
C(7)–C(6)–C(1)	114.6(8)	C(8)–C(6)–C(1)	109.7(8)
C(8)–C(6)–C(7)	110.3(8)	Cp_{cent}–W(1)–Cl(1)	112.5
Cp_{cent}–W(1)–Cl(2)	113.0	Cp_{cent}–W(1)–W(1B)	118.6

colour change from scarlet to brown was observed, but no product could be isolated.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for $[W_2(\eta\text{-}C_5H_4\text{-}Pr^i)_2Cl_4]$ (**7b**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	4 567.6(4)	4 941.5(3)	998.4(3)
Cl(1)	2 387(3)	3 621(2)	436(2)
Cl(2)	6 970(3)	4 137(2)	2 328(2)
C(1)	2 710(10)	5 953(7)	2 213(8)
C(2)	2 537(11)	6 371(7)	935(9)
C(3)	4 122(11)	6 857(7)	812(9)
C(4)	5 245(11)	6 673(7)	1 997(9)
C(5)	4 428(11)	6 145(8)	2 877(9)
C(6)	1 323(11)	5 448(8)	2 752(8)
C(7)	1 918(16)	4 583(10)	3 823(12)
C(8)	315(12)	6 397(10)	3 231(11)

Table 5. Comparison of M≡M bond lengths in some M_2L_6 systems

Complex	M≡M (Å)	Ref.
$[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ (**7b**)	2.367 8(6)	*a*
$[W_2(\eta^3\text{-}C_9H_7)_2(NMe_2)_4]$	2 334(1)	21
$[Mo_2(NMe_2)_6]$	2.214(3)	*b*
$[W_2(NMe_2)_6]$	2.294(1)	*c*
$[W_2Cl_2(NMe_2)_4]$	2.285(2)	*d*
$[Mo_2(OCH_2CMe_3)_6]$	2.222(2)	*e*
$[W_2(CH_2SiMe_3)_6]$	2.255(2)	*f*

[a] This work. [b] M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichart, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 4469. [c] M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 4477. [d] M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, 1977, **16**, 2407. [e] M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, 1977, **16**, 1801. [f] M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *Inorg. Chem.*, 1976, **15**, 2252.

A single-crystal *X*-ray structure determination of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ (**7b**) was carried out. The molecular structure is shown in Figure 2, selected bond lengths and angles are listed in Table 3, and final fractional atomic co-ordinates are given in Table 4. The molecular structure of (**7b**) consists of two $W(\eta\text{-}C_5H_4Pr^i)Cl_2$ fragments united in a staggered *anti* conformation with no bridging chloride ligands. The relatively short W–W separation [2.367 8(6) Å] is indicative of substantial metal–metal bonding which, together with the d^3—d^3 valence electron count,* suggests a formal W≡W triple bond. An investigation of the electronic structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ using extended-Hückel computational techniques and gas-phase photoelectron spectroscopy has been reported[20] and found a $\sigma^2\pi^4$ description of the W≡W triple bond, consistent with formal electron-counting procedures.

As discussed above, all previously reported structurally characterised complexes of the general class $[\{M(\eta\text{-}C_5R_5)X_2\}_2]$ have either two or four bridging halide ligands. Clearly the compounds $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ represent a new structural variation. Especially startling are the dramatic structural differences between the chromium,[6] molybdenum,[7] and tungsten congeners which have two, four, or no μ-Cl bridges respectively. Factors which may be important in selecting the structural type adopted by a particular complex $[\{M(\eta\text{-}C_5R_5)X_2\}_2]$ (*i.e.* no, two, or four μ-halide linkages) have been elaborated by us elsewhere.[20]

The compounds $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ are also members of the general class of d^3–d^3 dimers M_2L_6. A number of other examples of this class have been structurally characterised. Table 5 compares the W≡W bond length in compound (**7b**) with the M≡M bond lengths of some other M_2L_6 systems. It is the longest reported to date for a d^3–d^3 complex with an unsupported metal–metal triple bond. This may be attributable to the electronegative nature of Cl and its poor π-donor ability compared to OR and NR_2.

Of the other M_2L_6 systems listed in Table 5, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ is most closely related to the η^3-indenyl complex

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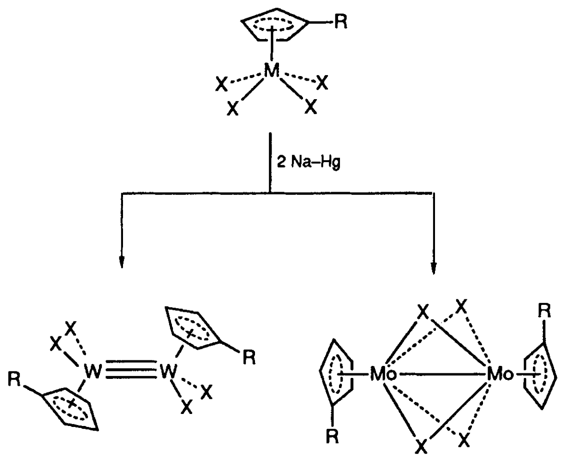
* Here were use the usual d^n–d^n notation where '*n*' refers to the number of electrons from each ML_x fragment available for primary metal–metal bonding.



(7) X = Cl; R = Me,(a), or Pr^i, (b) (9) X = Cl; R = Me,(a), or Pr^i, (b)
(8) X = Br, R = Pr^i (10) X = Br, R = Me

Scheme. A general route to η-cyclopentadienyl dihalide dimers of Mo and W

$[\mathrm{W_2(\eta^3\text{-}C_9H_7)_2(NMe_2)_4}]$ recently reported by Chisholm *et al.*[21] That the indenyl moiety is only η^3-bound to tungsten suggests that in this complex $\mathrm{N}(p_\pi)\rightarrow\mathrm{W}(d_\pi)$ bonding is preferred to η^5 co-ordination of the indenyl $\mathrm{C_5}$ ring. In contrast, for (**7b**), Cl is a relatively poor π donor and accordingly the isopropylcyclopentadienyl ring adopts a pentahapto co-ordination. However, the $\mathrm{C_5}$ ring of the indenyl ligand is well known to slip easily from η^5 to η^3 co-ordination, and for (**7b**) the W(1)–C(1) and W(1)–C(5) bond lengths [2.492(8) and 2.456(8) Å respectively] are significantly longer than the other three tungsten–cyclopentadienyl ring carbon distances [W(1)–C(2) 2.342(8), W(1)–C(3) 2.287(8), W(1)–C(4) 2.302(8) Å]. Unfortunately, although the simple cyclopentadienyl complex $[\mathrm{W_2(\eta\text{-}C_5H_5)_2(NMe_2)_4}]$ was also reported,[21] crystals suitable for an *X*-ray diffraction analysis could not be obtained, and the reported ^{1}H and ^{13}C n.m.r. data alone do not uniquely define the nature of the W–η-$\mathrm{C_5H_5}$ bonding beyond the fact that there are five time-averaged equivalent H and C atoms (at −80 °C in [$^2\mathrm{H_8}$]toluene).[21]

The n.m.r. spectra of $[\mathrm{W_2(\eta\text{-}C_5H_4R)_2X_4}]$ show one set of η-$\mathrm{C_5H_4R}$ ring signals and are thus consistent with their proposed solid-state structures. Variable-temperature ^{1}H n.m.r. studies of (**7b**) from 213 to 343 K show one η-$\mathrm{C_5H_4Pr^i}$ ring environment over this temperature range. Thus it appears that the *anti* rotamer persists in solution and that there is no evidence for the alternative *gauche* rotamer which would be expected to possess a diastereotopic η-$\mathrm{C_5H_4Pr^i}$ moiety, readily distinguishable by n.m.r. spectroscopy. The large observed chemical shift difference (*ca.* 2.1 to 2.4 p.p.m.) between the AA′ and XX′ parts of the η-$\mathrm{C_5H_4R}$ ring spin system in the ^{1}H n.m.r. spectra is suggestive of the magnetic anisotropy commonly associated with metal–metal multiple bonds.[22] For the η-$\mathrm{C_5H_4Pr^i}$ rings in the singly bonded complex $[\mathrm{Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4}]$ the chemical shift difference between the AA′ and XX′ parts in the ^{1}H n.m.r. spectrum is <0.1 p.p.m.[7]

Interestingly, after this work was completed, Jones and co-workers[23a] reported the *X*-ray crystal structure of the co-crystallate $[\mathrm{W_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_4}]\cdot\mathrm{2Bu^t_2P\text{-}PBu^t_2}$ in which there are no close contacts between ditungsten and diphosphine species.[23a] The former adopts a quadruply bridged structure, an observation which may be driven by the steric relief afforded by axial co-ordination of the bulky pentamethylcyclopentadienyl ligands and which clearly indicates a delicate balance between steric influences and metal–metal bonding in the $[\{\mathrm{W(\eta\text{-}C_5R_5)Cl_2}\}_2]$ systems.

The quadruply bridged dimolybdenum compounds $[\mathrm{Mo_2(\eta\text{-}C_5H_4CHR_2)_2(\mu\text{-}Cl)_4}]$ (R = Me or Ph) were first prepared by treatment of the corresponding fulvene complexes $[\mathrm{Mo(\eta\text{-}C_5H_4CR_2)(\eta\text{-}C_6H_6)}]$ with HCl gas in light petroleum.[7] It was of interest to determine if such complexes could also be prepared *via* a reductive route from the corresponding tetrachloro precursors.

Reduction of $[\mathrm{Mo(\eta\text{-}C_5H_4R)Cl_4}]$ (R = Me or Pr^i) with Na–Hg (2 equivalents) in thf, followed by crystallisation from toluene, gave dark brown crystals of $[\mathrm{Mo_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}Cl)_4}]$ (**9a**; R = Me) and (**9b**; R = Pr^i) in 70—85% yield. The isopropyl analogue (**9b**) was characterised by comparison of its ^{1}H n.m.r. and i.r. spectra with those previously reported. Interestingly, the earlier method of preparation gave $[\mathrm{Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4}]$ as a pink solid, whereas the reductive route afforded dark brown crystals. However, it is noteworthy that in the earlier synthesis the initial (pink) material was recrystallised from hot (80 °C) petroleum (b.p. 100—120 °C) giving brown crystals. These were then subsequently characterised by *X*-ray diffraction studies and ^{1}H n.m.r. and i.r. spectroscopy. Consequently, the identity of the initially formed pink material is uncertain. Attempted preparation of the ring-unsubstituted compound $[\mathrm{Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)_4}]$ *via* the sodium amalgam reduction of $[\mathrm{Mo(\eta\text{-}C_5H_5)Cl_4}]$ did not prove successful. We note, however, that Poli and Rheingold[23b] have recently obtained a material formulated as $[\mathrm{Mo(\eta\text{-}C_5H_5)Cl_2}]$ from the reduction of $[\mathrm{Mo(\eta\text{-}C_5H_5)Cl_4}]$ with zinc powder (1 equivalent).

The bromide-supported analogue, $[\mathrm{Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}Br)_4}]$ (**10**), could also be prepared *via* a reductive route. Thus reduction of $[\mathrm{Mo(\eta\text{-}C_5H_4Me)Br_4}]$ (**5**) with Na–Hg (2 equivalents) in thf gave a red-brown solution. Extraction with toluene, filtration, and subsequent crystallisation at −80 °C afforded orange-brown crystals of (**10**) in *ca.* 40% yield which were characterised by elemental analysis and by ^{1}H n.m.r. and i.r. spectroscopy. The ^{1}H n.m.r. spectrum of $[\mathrm{Mo_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}Br)_4}]$ was very similar to those of $[\mathrm{Mo_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}Cl)_4}]$, and its photoelectron spectrum was very different from that of $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4}]$.[20] It is therefore proposed that (**10**) has a quadruply bridged Mo–Mo single bond analogous to that of $[\mathrm{Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4}]$.

Conclusion

We have shown that the route first described by Schrock for the preparation of ring pentasubstituted η-cyclopentadienyl tetrahalide complexes of Mo and W may also be used to prepare the less extensively ring-substituted analogues, and have extended the route to the preparation of the bromide-supported homologues. Subsequent reduction of the ring-substituted complexes $[\mathrm{M(\eta\text{-}C_5H_4R)X_4}]$ affords dinuclear $(\mathrm{M^{III}})_2$ derivatives in good yield and in gram quantities. The syntheses and structures proposed for the compounds (**7**)—(**10**) are shown in the Scheme.

Experimental

All manipulations of air- and moisture-sensitive materials were performed using either standard Schlenk-line techniques under an atmosphere of dinitrogen, which had been purified by passage over a BASF catalyst and 4-Å molecular sieves, or in an inert-atmosphere dry-box containing dinitrogen. Solvents were pre-dried by standing over 4-Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentoxide (dichloromethane), sodium (toluene), potassium–benzophenone (thf), or sodium–potassium alloy (1:3 w/w) (light petroleum, b.p. 40–60 °C). Deuteriated solvents for n.m.r. studies were stored in a Youngs ampoule under an atmosphere of dinitrogen over sodium–potassium alloy ([$^2H_6$]benzene) or molecular sieves ([^{2}H]chloroform).

Proton and ^{13}C n.m.r. spectra were recorded on a Brüker WH 300 spectrometer (^{1}H, 300 MHz) or a Brüker AM 300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz). Carbon-13 n.m.r. spectra were recorded using a gated sequence to give nuclear Overhauser enhancement. Spectra were referenced internally using the residual protio solvent (^{1}H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0 p.p.m.). All chemical shifts are quoted in δ (p.p.m.) and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, spt = septet, m = multiplet), coupling constant, relative integration, and assignment.

Unless stated otherwise, i.r. spectra were recorded as Nujol mulls of CsI plates using either a Perkin-Elmer 1510 FT interferometer or, in the region 250—400 cm^{-1}, a Perkin-Elmer 457 grating spectrometer. Data are expressed as wavenumber (cm^{-1}) with relative intensity in parentheses (s = strong, m = medium, w = weak, sh = shoulder).

Elemental analyses were performed by the analytical department of this laboratory and are expressed as found (required) in % w/w. The compound [$Mo_2(\eta$-$C_5H_4Me)_2(CO)_6$] was prepared as described previously.[19]

Preparations.—Isopropylcyclopentadiene.[24]—To a stirred solution of Na[C_5H_5] (88.1 g, 1 mol) in liquid ammonia (1 000 cm^3) at −78 °C was added isopropyl iodide (100 cm^3, 1 mol) slowly over 1.5 h. A colourless precipitate was observed and the ammonia allowed to evaporate overnight (14 h). In a well ventilated fume hood, water (250 cm^3) was carefully added and the mixture extracted with light petroleum (500 cm^3). The combined extracts were dried over anhydrous magnesium sulphate, concentrated using a rotary-film evaporator, and distilled under reduced pressure. Fractions distilling in the range 21—30 (40) and 31—34 °C (30 mmHg) were collected and characterised by ^{1}H n.m.r. spectroscopy as a *ca.* 1:1 mixture of 1-isopropylcyclopenta-1,3-diene and 2-isopropylcyclopenta-1,3-diene. Yield 46.1 g (43%).

Sodium cyclopentadienide salts. The general method used for the preparation of ether-free Na[C_5H_4R] (R = H, Me, or Pr^i) was as follows. Sodium (2.5 g, 0.11 mol) was placed in a three-necked round-bottom flask (500 cm^3), immersed in a CO_2–acetone bath and equipped with a CO_2–acetone condenser and a side-arm tap, into which ammonia (*ca.* 200 cm^3) was condensed. The cyclopentadiene monomer (0.15 mol) was titrated dropwise, with efficient stirring, until the blue colour changed to pale grey (*ca.* 1.5 h). The cold bath was removed and the ammonia allowed to evaporate. Residual volatiles were removed under reduced pressure (60—70 °C) to afford white Na[C_5H_4R] (*ca.* 100% based on Na).

[$M(\eta$-$C_5H_4R)(CO)_3Me$] [M = Mo, (**1**) *or* W, (**2**) R = H, (**a**), Me, (**b**) *or* Pr^i, (**c**). The compounds [$M(\eta$-$C_5H_4R)(CO)_3Me$] (M = Mo, R = H or Me; M = W, R = H) were prepared as described previously.[18]

[$W(\eta$-$C_5H_4Me)(CO)_3Me$]. A mixture of Na[C_5H_4Me] (10.4 g, 0.1 mol) and [$W(CO)_6$] (30 g, 0.085 mol) in thf (25 cm^3) was refluxed for 12 h and then stirred at room temperature (r.t.) for 12 h. Excess of methyl iodide was added and a precipitate formed. Removal of volatiles under reduced pressure followed by extraction with light petroleum (5 × 100 cm^3) and filtration afforded a pale yellow solution. Removal of solvent under reduced pressure afforded (**2b**) as a spectroscopically pure yellow solid which could be used in further reactivity studies without additional purification {14.3 g, 46% based on [$W(CO)_6$]}. An analytically pure sample of compound (**2b**) was obtained by sublimation of the crude product *in vacuo* (150 °C; 10^{-4} mbar, 10^{-2} Pa). Elemental analysis for $C_{10}H_{10}O_3W$: C, 33.5 (33.2); H, 2.7 (2.8). Proton n.m.r. data ([^{2}H]chloroform): 5.22 [virtual t, 2 H, $J(HH)_{app}$ 2.5, η-C_5H_4Me], 5.15 (virtual t, 2 H, $J(HH)_{app}$ 2.5, η-C_5H_4Me], 2.01 (3 H, s, η-C_5H_4Me), and 0.39 [s 3 H, J(HW) 3.3, WMe]. Selected i.r. data: ν(C≡O) 2 014 and 1 919.

[$M(\eta$-$C_5H_4Pr^i)(CO)_3Me$]. In a typical preparation, Na[$C_5H_4Pr^i$] (18.5 g, 0.142 mol) and [$M(CO)_6$] (0.142 mol) were heated (130—140 °C) together in diglyme (230 cm^3) for 4 h in a large Schlenk tube equipped with an air-cooled condenser. The [$M(CO)_6$] sublimed out and was periodically returned to the reaction mixture. The mixture was cooled to *ca.* 30 °C and excess of methyl iodide (*ca.* 0.4 mol) added. After 3 h the volatiles were removed under reduced pressure and the residues extracted with hot light petroleum (3 × 120 cm^3), filtered through a bed of Celite, and reduced to a red (M = W) or orange-yellow (M = Mo) mobile oil. Residual diglyme was removed under reduced pressure to afford analytically pure [$M(\eta$-$C_5H_4Pr^i)(CO)_3Me$]. Yield 80—90%.

Elemental analysis for $C_{12}H_{14}MoO_3$, (**1c**): C, 47.45 (47.7); H, 4.9 (4.7). N.m.r. data ([$^2H_6$]benzene): ^{1}H, 4.48 [virtual t, 2 H, $J(HH)_{app}$ 2.5, η-$C_5H_4Pr^i$], 4.44 [virtual t, 2 H, $J(HH)_{app}$ 2.5, η-$C_5H_4Pr^i$], 2.10 [spt, 1 H, J(HH) 7, C*H*Me$_2$], 0.83 [d, 6 H, J(HH) 7, CH*Me*$_2$], and 0.44 (s, 3 H, MoMe); ^{13}C, 241.1 [s, *trans* (*C*O)MoMe], 227.7 [s, *cis* (*C*O)$_2$MoMe], 123.0 (s, *C*Pr^i), 91.1 [d, J(CH) 181, CH of η-$C_5H_4Pr^i$], 91.0 [d, J(CH) 181, CH of η-$C_5H_4Pr^i$], 27.3 [d, J(CH) 128, *C*HMe$_2$], 23.8 [q, J(CH) 126, CH*Me*$_2$], and −20.5 [q, J(CH) 137, MoMe]. Selected i.r. data (thin film): ν(C≡O) 2 017 and 1 925.

Elemental analysis for $C_{12}H_{14}O_3W$, (**2c**): C, 36.7 (36.95); H, 3.5 (3.6). N.m.r. data ([$^2H_6$]benzene): ^{1}H, 4.44 [virtual t, 2 H, $J(HH)_{app}$ 2.5, η-$C_5H_4Pr^i$], 4.41 [virtual t, 2 H, $J(HH)_{app}$ 2.5, η-$C_5H_4Pr^i$], 2.09 [spt, 1 H, J(HH) 7, C*H*Me$_2$], 0.80 [d, 6 H, J(HH) 7, CH*Me*$_2$], and 0.53 [s, 3 H, J(HW) 1.9, WMe]; ^{13}C, 230.9 [s, J(CW) 132, *trans* (*C*O)WMe], 217.7 [s, J(CW) 158, *cis* (*C*O)$_2$WMe], 121.2 (s, *C*Pr^i), 89.9 [d, J(CH) 180, *C*H of η-$C_5H_4Pr^i$], 27.3 [d, J(CH) 125, *C*HMe$_2$], 23.7 [q, J(CH) 126, CH*Me*$_2$], and −33.3 [q, J(CH) 125, J(CW) 29, WMe]. Selected i.r. data (thin film): ν(C≡O) 2 011 and 1 908.

[$M(\eta$-$C_5H_4R)Cl_4$] [M = Mo, (**3**), *or* W, (**4**); R = H, (**a**), Me, (**b**), *or* Pr^i (**c**)]. These compounds were prepared using a similar method to that described by Schrock and co-workers[17] for [$M(\eta$-$C_5Me_5)Cl_4$] (M = Mo or W).

A typical preparation was as follows. A solution of [$M(\eta$-$C_5H_4R)(CO)_3Me$] (0.1 mol) in dichloromethane (200 cm^3) was added dropwise to a stirred solution/suspension of phosphorus pentachloride (0.25 mol) in dichloromethane (200 cm^3) over 1 h with evolution of a colourless gas (presumably CO). The mixture was refluxed (6 h), cooled, and concentrated to *ca.* 100 cm^3. The supernatant was decanted and the red (M = W) or burgundy (M = Mo) microcrystalline product washed with dichloromethane (3 × 30 cm^3) and dried *in vacuo*. Yield 60—90%.

Elemental analysis for $C_8H_{11}Cl_4Mo$, (**3c**): C, 27.6 (27.8); H, 3.4 (3.1); Cl, 38.4 (41.1). I.r. data: 3 104m, 1 409m, 1 398m, 1 233w, 1 154m, 1 094m, 1 050w, 919w, 900w, 875s, 838w, 650w, 405w, 349s, 330s, 319 (sh), 295 (sh), and 280 (sh).

Elemental analysis for $C_5H_5Cl_4W$, (**4a**): C, 15.7 (15.4); H, 1.4 (1.3); Cl, 33.9 (36.3). I.r. data: 3 088m, 1 610m, 1 305m, 1 148s, 1 075m, 1 015s, 967m, 881s, 863s, 772m, 643w, 615w, 579m, 350s, 320s, 300 (sh), and 280 (sh).

Elemental analysis for $C_6H_7Cl_4W$, (**4b**): C, 17.6 (17.8); H, 1.9 (1.7); Cl, 32.4 (35.0). I.r. data: 3 092m, 1 241m, 1 155m, 1 075m, 1 059m, 1 044m, 1 029s, 989m, 924m, 887s, 839m, 590m, 350s, 320s, 300 (sh), and 280 (sh).

Elemental analysis for $C_8H_{11}Cl_4W$, (**4c**): C, 22.4 (22.2); H, 2.5 (2.6); Cl, 32.2 (32.8). I.r. data: 3 106m, 1 233m, 1 155m, 1 096s, 1 073m, 1 051m, 1 018w, 929w, 896m, 880s, 842m, 658w, 579w, 355s, 320s, 300 (sh), and 280 (sh).

[$M(\eta$-$C_5H_4R)Br_4$] (**5**; M = Mo, R = Me) *and* (**6**; M = W, R = Pr^i). These compounds were prepared in a similar manner to the tetrachloride analogues.

[Mo(η-C$_5$H$_4$Me)Br$_4$]. The compound [Mo$_2$(η-C$_5$H$_4$Me)$_2$(CO)$_6$] (4 g, 7.7 mmol) in dichloromethane (25 cm^3) was added dropwise to a stirred solution/suspension of phosphorus pentabromide (13.3 g, 31 mmol) in dichloromethane (50 cm^3) over 1 h with evolution of gas. The mixture was refluxed (17 h) and the cooled, black, supernatant decanted. The purple-black microcrystals of compound (**5**) were washed with dichloromethane (3 × 20 cm^3) and dried *in vacuo*. Yield 6.3 g (82%). Elemental analysis for C$_6$H$_7$Br$_4$Mo: C, 14.9 (14.6); H, 1.4 (1.4); Br, 64.4 (64.6). I.r. data: 3 083w, 1 071s, 1 022s, 875m, 584w, 522w, 467w, 408w, and 260s.

[W(η-C$_5$H$_4$Pr^i)Br$_4$]. The compound [W(η-C$_5$H$_4$Pr^i)(CO)$_3$Me] (11.3 g, 0.029 mol) in dichloromethane (25 cm^3) was added dropwise over 0.5 h to a stirred solution/suspension of phosphorus pentabromide (32 g, 0.074 mol) in dichloromethane (150 cm^3) with evolution of gas. The dark red solution was refluxed (11 h), cooled to r.t., and the supernatant decanted. The purple-brown microcrystals of compound (**6**) were washed with dichloromethane (2 × 25 cm^3) and dried *in vacuo*. Yield 11 g (62%). Elemental analysis for C$_8$H$_{11}$Br$_4$W: C, 15.4 (15.75); H, 2.0 (1.8); Br, 52.8 (53.3). I.r. data: 3 091w, 1 084s, 1 020s, 878m, 610w, 570w, and 475w.

[W$_2$(η-C$_5$H$_4$Me)$_2$Cl$_4$] (**7a**). To a stirred solution/suspension of [W(η-C$_5$H$_4$Me)Cl$_4$] (5 g, 12.3 mmol) in toluene (120 cm^3) was added sodium amalgam (0.59 g, 25.6 mmol Na, *ca.* 0.5% w/w) over 2 h from a pressure-equalising dropping funnel to give a green solution and a grey precipitate. The solution was filtered through a bed of Celite and the residues washed thoroughly with toluene (3 × 40 cm^3). Subsequent reduction in volume to *ca.* 60 cm^3 and cooling to −80 °C afforded dark green microcrystals of compound (**7a**) (1.85 g, 45%). Elemental analysis for C$_{12}$H$_{14}$Cl$_4$W$_2$: C, 21.7 (21.6); H, 2.1 (2.1); Cl, 21.2 (21.2). N.m.r. data ([^{2}H$_6$]benzene): ^{1}H, 7.07 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.3, η-C$_5H_4$Me], 5.22 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.3, η-C$_5H_4$Me], and 1.47 (s, 6 H, η-C$_5$H$_4Me$); ^{13}C, 125.4 (s, *C*Me), 108.2 [d, J(CH) 176, CH], 104.1 [d, J(CH) 178, CH], and 12.6 [q, J(CH) 129, Me].

[W$_2$(η-C$_5$H$_4$Pr^i)$_2$Cl$_4$] (**7b**). To a stirred solution of [W(η-C$_5$H$_4$Pr^i)Cl$_4$] (12 g, 0.028 mol) in thf (200 cm^3) in a round-bottom flask was added sodium amalgam (1.2 g, 0.056 mol Na, *ca.* 0.5% w/w) over 1 h. Stirring was continued for 5 h, the green supernantant was decanted, and the residues washed with thf (2 × 50 cm^3). The solutions were combined and volatiles removed under reduced pressure. The brown-green residues were extracted with hot toluene (3 × 80 cm^3) and subsequent filtration, reduction of volume to *ca.* 60 cm^3 (when dark green crystals started to appear), and cooling to −80 °C afforded dark green microcrystals of compound (**7b**) (6 g, 60%). Elemental analysis for C$_{16}$H$_{22}$Cl$_4$W$_2$: C, 26.7 (26.55); H, 3.2 (3.1); Cl, 19.35 (19.6). N.m.r. data ([^{2}H$_6$]benzene): ^{1}H, 7.42 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.3, η-C$_5H_4$Pr^i], 5.15 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.3, η-C$_5H_4$Pr^i], 2.21 [spt, 2 H, J(HH) 6.9, C*H*Me$_2$], and 0.70 [d, 12 H, J(HH) 6.9, CH*Me*$_2$]; ^{13}C, 136.6 (s, *C*Pr^i), 106.8 [d, J(CH) 181, CH of η-C$_5$H$_4$Pr^i], 103.7 [d, J(CH) 179, CH of η-C$_5$H$_4$Pr^i], 26.9 [d, J(CH) 130, *C*HMe$_2$], and 22.1 [q, J(CH) 126, CH*Me*$_2$].

[W$_2$(η-C$_5$H$_4$Pr^i)$_2$Br$_4$] (**8**). To a stirred solution of [W(η-C$_5$H$_4$Pr^i)Br$_4$] (5 g, 8.2 mmol) in thf (200 cm^3) was added sodium amalgam (0.39 g, 16.9 mmol Na, *ca.* 0.5% w/w) from a pressure-equalising dropping funnel over 1.5 h to give a green-brown solution and a grey precipitate. The supernatant was decanted and the residues washed with thf (2 × 40 cm^3). The solutions were combined and the volatiles removed under reduced pressure. Extraction of the residues with hot toluene (3 × 80 cm^3) and subsequent filtration, reduction of volume to 75 cm^3, and cooling to −25 °C afforded dark green crystals of compound (**8**) (1.5 g, 35%). Elemental analysis for C$_{16}$H$_{22}$Br$_4$W$_2$: C, 21.0 (21.3); H, 2.7 (2.5); Br, 36.2 (34.45). N.m.r. data ([^{2}H$_6$]benzene): ^{1}H, 7.58 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.4, η-C$_5H_4$Pr^i], 5.18 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.4, η-C$_5H_4$Pr^i], 2.29 [spt, 2 H, J(HH) 6.9, C*H*Me$_2$], and 0.79 [d, 12 H, J(HH) 6.9, CH*Me*$_2$]; ^{13}C, 136.5 (s, *C*Pr^i), 107.5 [d, J(CH) 175, CH of η-C$_5$H$_4$Pr^i], 103.8 [d, J(CH) 184, CH of η-C$_5$H$_4$Pr^i], 27.4 [d, J(CH) 128, *C*HMe$_2$], and 22.3 [q, J(CH) 128, CH*Me*$_2$].

[Mo$_2$(η-C$_5$H$_4$Me)$_2$(μ-Cl)$_4$] (**9a**). To a stirred solution of [Mo(η-C$_5$H$_4$Me)Cl$_4$] (6.97 g, 0.022 mol) in thf (300 cm^3) was added sodium amalgam (1.1 g of Na, 0.046 mol, *ca.* 0.5% w/w) over 1 h. The initial deep red colour turned brown after 30 min and a grey precipitate was observed. The mixture was stirred for 24 h, filtered, and the residues extracted with thf (125 cm^3). The volatiles were removed under reduced pressure and the dark brown solid extracted with hot toluene (700 cm^3). Subsequent filtration and concentration, followed by cooling to −80 °C for 12 h, afforded dark brown crystals. These were washed with cold toluene (25 cm^3) and cold light petroleum (2 × 25 cm^3) and dried *in vacuo*. The combined washings and mother-liquors were concentrated and a second crop of brown crystals was obtained. Total yield 3.9 g (72%). Elemental analysis for C$_{12}$H$_{14}$Cl$_4$Mo$_2$: C, 29.5 (29.3); H, 2.9 (2.9); Cl, 28.4 (28.8). ^{1}H N.m.r. data ([^{2}H$_6$]benzene): 5.99, 5.82 (m, m, 2 H, 2 H, C$_5H_4$Me), and 1.47 (s, 3 H, Me).

Alternative synthesis of [Mo$_2$(η-C$_5$H$_4$Pr^i)$_2$(μ-Cl)$_4$] (**9b**).[7] To a stirred solution of [Mo(η-C$_5$H$_4$Pr^i)Cl$_4$] (8.45 g, 0.024 mol) in thf (400 cm^3) was added sodium amalgam (1.26 g, 0.055 mol Na, *ca.* 0.5% w/w) from a pressure-equalising dropping funnel over 2 h to give a brown solution and grey precipitate, which was then stirred for 24 h. The supernatant was decanted and the residues washed with thf (3 × 50 cm^3). The solutions were combined and the volatiles removed under reduced pressure. Extraction of the residues with hot toluene (3 × 150 cm^3) and subsequent filtration, reduction of volume to *ca.* 130 cm^3, and cooling to −80 °C afforded dark brown crystals of compound (**9b**) (5.8 g, 86%).

[Mo$_2$(η-C$_5$H$_4$Me)$_2$(μ-Br)$_4$] (**10**). To a stirred solution of [Mo(η-C$_5$H$_4$Me)Br$_4$] (3 g, 6.1 mmol) in thf (150 cm^3) was added sodium amalgam (0.28 g, 13 mmol Na, *ca.* 0.5% w/w) from a pressure-equalising dropping funnel over 45 min to afford a brown solution and a grey precipitate. Stirring was continued for 18 h, the supernatant was decanted, and the residues washed with thf (3 × 25 cm^3). The solutions were combined and the volatiles removed under reduced pressure. Extraction of the residues with hot toluene (3 × 60 cm^3), filtration (twice), reduction in volume to *ca.* 80 cm^3, and cooling to −25 °C afforded compound (**10**) as golden-brown microcrystals (0.75 g, 40%). Elemental analysis for C$_{12}$H$_{14}$Br$_4$Mo$_2$: C, 21.2 (21.5); H, 2.2 (2.1); Br, 46.8 (47.7). ^{1}H N.m.r. data ([^{2}H$_6$]benzene): 5.69 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.4, η-C$_5H_4$Me], 5.57 [virtual t, 4 H, J(HH)$_{\text{app}}$ 2.4, η-C$_5H_4$Me], and 1.62 (s, 6 H, Me).

X-Ray Crystal-structure Determinations of Compounds (**4c**) *and* (**7b**).—Crystal data and collection and processing parameters are given in Table 6. A crystal was sealed in a Lindemann glass capillary and transferred to the goniometer head of an Enraf-Nonius CAD-4 diffractometer interfaced to a PDP 11/23 and LSI minicomputer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3 600 s of *X*-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[25] based on an azimuthal scan was applied. Equivalent reflections were merged and systematically absent reflections rejected. The heavy-atom

Table 6. Crystallographic data[a] for $[W(\eta-C_5H_4Pr^i)Cl_4]$ (**4c**) and $[W_2(\eta-C_5H_4Pr^i)_2Cl_4]$ (**7b**)

	$[W(\eta-C_5H_4Pr^i)Cl_4]$ (**4c**)	$[W_2(\eta-C_5H_4Pr^i)_2Cl_4]$ (**7b**)
Formula	$C_8H_{11}Cl_4W$	$C_{16}H_{22}Cl_4W_2$
M	432.84	723.86
Crystal size/mm	0.10 × 0.35 × 0.40	0.20 × 0.25 × 0.30
Colour	Red	Emerald green
a/Å	11.599(2)	8.021(1)
b/Å	6.325(2)	11.788(2)
c/Å	16.115(3)	10.515(2)
β/°	101.50(1)	103.62(1)
U/Å^3	1 158.6	972.0
Z	4	2
D_c/g cm^{-3}	2.481	2.473
μ/cm^{-1}	110.69	126.35
F(000)	804	668
2θ limits/°	3—48	3—50
Scan angle/°	0.80 + 0.35 (tanθ)	0.60 + 0.35 (tanθ)
Absorption (min., max.)	1.0, 4.68	1.0, 1.82
Total data collected	2 772	2 433
No of observations [$I > 3\sigma(I)$]	1 602	1 286
No. of variables	121	103
Observations/ variables	13.24	12.48
Weighting scheme	Chebyshev	Unit weights
Weighting coefficients	6.510, −4.159, 4.630	1
Largest residual peak in final difference map/e Å^{-3}	0.08	0.10
R (merge)	0.023	0.034
R^b	0.019	0.024
R'^c	0.021	0.025

[a] Details in common: monoclinic; space group $P2_1/c$; Mo-K_α radiation (λ = 0.710 69 Å); scan mode ω—2θ; horizontal aperture 2.5 mm; zone $+h$, $+k$, $+l$. [b] $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

position(s) were determined from a Patterson synthesis. Subsequent Fourier difference syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by least-squares procedures. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) and refined riding on their supporting carbon atoms. For compound (**4c**) a Chebyshev weighting scheme[26] was applied. The data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[27]) in the final stages of refinement.

All crystallographic calculations were performed using the CRYSTALS suite[28] on a VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford. Scattering factors were taken from the usual sources.[29]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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