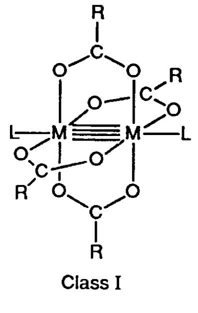
Tertiary Phosphine Adducts of $[W_2(\mu\text{-}O_2CBu^t)_4]$. Crystal Structure of $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ ‡

Philip Mountford *,† **and J. A. Gareth Williams**
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

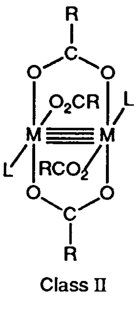
Treatment of the quadruply bonded ditungsten complex $[W_2(\mu\text{-}O_2CBu^t)_4]$ with phosphines PMeRR' (R = R' = Me or Ph; R = Me, R' = Ph) affords bis(adducts) which have the general formula $W_2(O_2CBu^t)_4{\cdot}2PMeRR'$. Each adduct possesses a different arrangement of the PMeRR' and O_2CBu^t ligands. The complex $[W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2]$ contains two equatorially bound phosphine ligands per dimeric unit whereas in $[W_2(\mu\text{-}O_2CBu^t)_4(PMePh_2)_2]$ both phosphine ligands are axially co-ordinated. The crystallographically characterised complex $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ has a novel geometry in which one axially and one equatorially co-ordinated PMe_2Ph ligand is present. The compound $[W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2]$ reacts with carbon monoxide or chlorotrimethylsilane to afford mononuclear $[W(O_2CBu^t)_2(CO)_3(PMe_3)_2]$ or dinuclear $[W_2(\mu\text{-}O_2CBu^t)_2Cl_2(PMe_3)_2]$ respectively.

The study of the synthesis, structure, bonding and reactivity of complexes containing metal–metal multiple bonds is an area that continues to attract much attention.[1] The tetrakis(carboxylato)dimolybdenum(II) species $[Mo_2(\mu\text{-}O_2CR)_4]$ (R = H, alkyl or aryl) are arguably the most important class of dimers that contain a Mo–Mo quadrupole bond and members of this group have been known since the early 1960s.[1c] They are key starting materials in Mo_2^{4+} chemistry and have been the focus of numerous synthetic, physical and theoretical studies.[1] In contrast, the congeneric tungsten(II) dimers $[W_2(\mu\text{-}O_2CR)_4]$ (R = H, Me, Et, CF_3, Bu^t or $C_6H_2Me_3$-2,4,6)[2–7] or their solvated adducts (R = Ph or C_6H_4OMe-4)[4] were prepared only relatively recently and their chemistry remains largely unexplored.

Of particular relevance to the work described herein is the preparation of a large number of adducts of the general formula $Mo_2(O_2CCF_3)_4{\cdot}2L$ (L = tertiary monophosphine or phosphite; 2L = tertiary diphosphine).[8–10] Several tertiary phosphine adducts of $[W_2(\mu\text{-}O_2CCF_3)_4]$ and one of $[W_2(\mu\text{-}O_2CBu^t)_4]$ have also been reported.[3,6] The structurally characterised bis(tertiary phosphine) derivatives of $[M_2(\mu\text{-}O_2CR)_4]$ (M = Mo or W) have been divided into two categories denoted 'Class I' and 'Class II'[6] according to the mode of co-ordination of the phosphine and carboxylato ligands.



Class I



Class II

The Class I adducts have two axially bound phosphines and four bridging carboxylato ligands; the crystallographically characterised Class II adducts have two equatorially bound phosphine ligands, two bridging carboxylato groups and two monodentate carboxylato groups held *trans* to the phosphine ligands (other isomers of the Class II structure shown above may exist in solution[8]). A combination of ligand size and basicity was invoked to account for the class of geometry favoured by a particular phosphine.[8]

We were interested to develop the chemistry of $[W_2(\mu\text{-}O_2CBu^t)_4]$. To our knowledge the only reported phosphine derivative of this species is the Class I complex $[W_2(\mu\text{-}O_2CBu^t)_4(PPh_3)_2]$. We describe here some new phosphine adducts together with the reactions of one of them with carbon monoxide and chlorotrimethylsilane.

Results and Discussion

When a solution of $[W_2(\mu\text{-}O_2CBu^t)_4]$ in diethyl ether was treated with two equivalents of trimethylphosphine an immediate colour change from pale yellow to purple was observed. Subsequent work-up afforded air- and moisture-sensitive purple crystals of the bis(phosphine) adduct $[W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2]$ **1** in 40% yield. Characterising data for **1** and all the other new compounds described herein are presented in Table 1 and the reactions and proposed structures are shown in Scheme 1. Small quantities of a second, green complex **2** were also isolated, and by carrying out the above reaction in toluene an improved yield of the green compound was obtained. The nature of **2** will be discussed shortly.

Elemental analysis for complex **1** was consistent with the stoichiometry $W(O_2CBu^t)_2{\cdot}PMe_3$. Bands at 1589 and 1562 cm^{-1} in the IR spectrum of **1** [assignable to $\nu_{asym}(CO_2)$] are consistent with the presence of monodentate carboxylato ligands. The ^1H NMR spectrum of **1** showed two singlet and one doublet [^2J(HP) = 8.4 Hz] resonances with intensities in the ratio 1 : 1 : 1 assignable to the methyl groups of two types of a O_2CBu^t moiety and one type of PMe_3 ligand. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1** is consistent with this interpretation. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet resonance at δ 0.3 (the resonance for PMe_3 in the same solvent occurs at δ −65.5) flanked by ^{183}W satellites from which ^1J(P–W) = 341.8 and ^3J(P–P) = 21.5 Hz could be obtained. The large chemical shift difference between free and co-ordinated phosphine is highly

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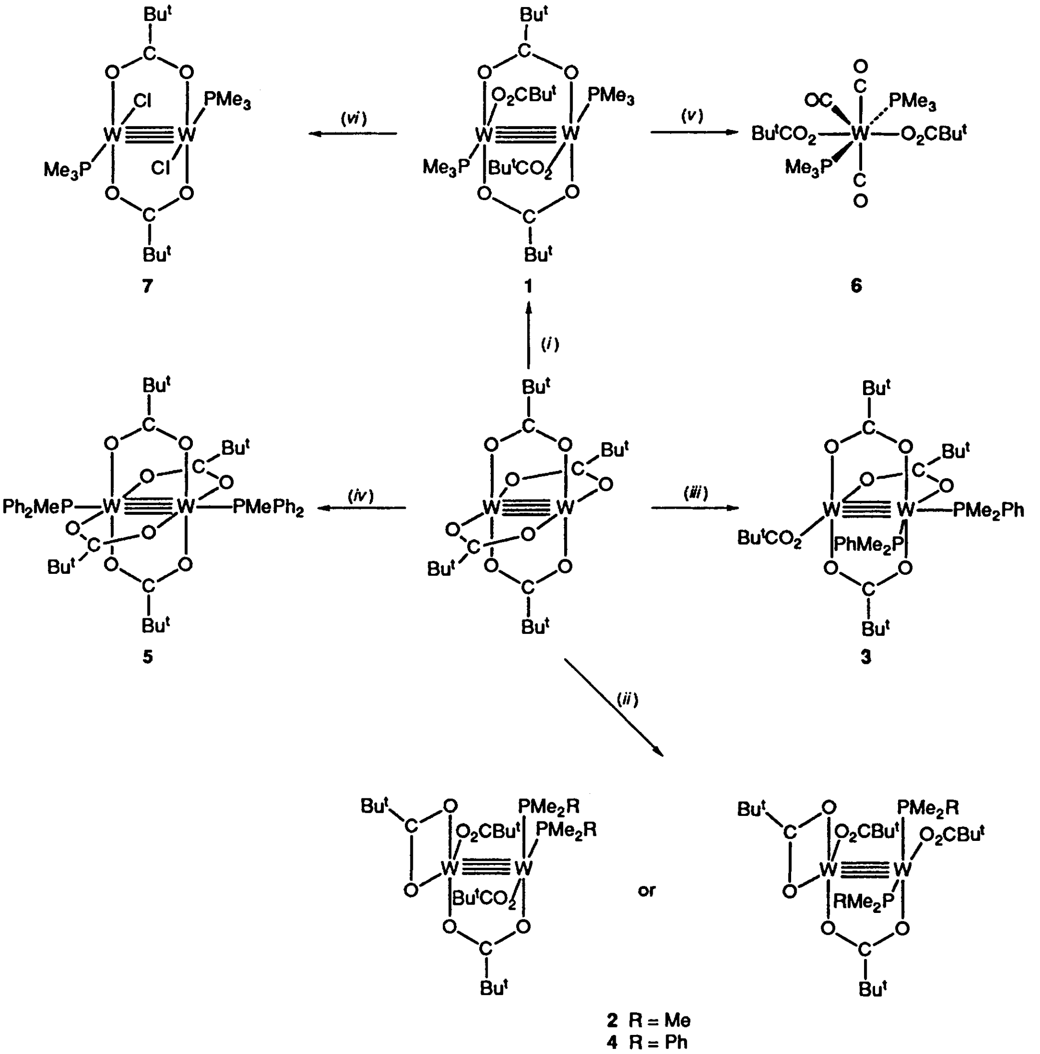
† *Present address:* Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: atm = 101 325 Pa.



Scheme 1 (*i*) PMe$_3$ (2 equivalents), Et$_2$O, room temperature (r.t.), 30 min, 40%; (*ii*) PMe$_3$ (2 equivalents), toluene, r.t., 2 h, 33% (for **2**) or PMe$_2$Ph (2 equivalents), Et$_2$O, r.t., 2 h, 21% (for **4**); (*iii*) PMe$_2$Ph (2 equivalents), Et$_2$O, r.t., 2 h, 33%; (*iv*) PMePh$_2$ (2 equivalents), Et$_2$O, r.t., 3 h, 17%; (*v*) PMe$_3$ (2 equivalents), CO (8 atm), Et$_2$O, r.t., 2.5 h, 46%; (*vi*) Me$_3$SiCl (2 equivalents), toluene, 140 °C, 24 h, 42%

suggestive of equatorially bound PMe$_3$ ligands. Taken together, the data for **1** are consistent with the Class II geometry illustrated in Scheme 1. The proposed structure of **1** is analogous to that of the crystallographically characterised trifluoroacetato species [W$_2$(μ-O$_2$CCF$_3$)$_2$(O$_2$CCF$_3$)$_2$(PBu$^n{}_3$)$_2$] reported by Sattelberger and co-workers.[6]

The elemental analysis for the second (green) product **2** of the reaction between [W$_2$(μ-O$_2$CBu^t)$_4$] and PMe$_3$ was also consistent with the stoichiometry W(O$_2$CBu^t)$_2$·PMe$_3$. However, although the IR spectrum of **2** also shows bands consistent with the presence of monodentate O$_2$CBu^t ligands the ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra (Table 1) now indicate that four inequivalent O$_2$CBu^t ligands and two inequivalent PMe$_3$ ligands are present. The two PMe$_3$ ligands appear as mutually coupled doublets [^2J(P–P) = 9.3 Hz] with ^{183}W satellites [^1J(P–W) = 262 and 283 Hz] in the ^{31}P-{^{1}H} NMR spectrum. The chemical shifts for the PMe$_3$ ligands (δ −38.7 and −39.5) are at higher field than those for the PMe$_3$ ligands in **1**, but are substantially different from that of free PMe$_3$. These ^{31}P data suggest that the PMe$_3$ ligands are most likely equatorially bound to the W$_2$ unit since axially bound ligands appear to be only ever weakly co-ordinated; one would not *a priori* expect to observe P–P or P–W coupling or indeed a substantial difference in ^{31}P chemical shift between that of the bound PMe$_3$ ligands in **2** and that of free PMe$_3$ in the same solvent if one or both of the PMe$_3$ ligands were axially co-ordinated.[6,8]

Clearly these data are not consistent with either a Class I or Class II structure for **2**. Nor are any of the isomers of Class II postulated by Andersen and co-workers[8] possible since each contains at least one symmetry element (other than the identity operation) that would give only two inequivalent O$_2$CBu^t ligands and one type of PMe$_3$ ligand in the NMR spectra. Unfortunately we have not been able to obtain crystals of **2** suitable for a diffraction analysis, but we believe that the examples of possible structures shown in Scheme 1 for **2** are consistent with the data in Table 1. For instance, co-ordination of both PMe$_3$ ligands to the same tungsten atom would be expected to give a greater shielding of the ^{31}P nuclei than a 1,2-mode of ligation to the W$_2$ unit (*cf.* that in **1**); the observed phosphorus–phosphorus coupling constant is in the range expected for ^2J(P–P) in mutually *cis*-PR$_3$ ligands. Note that other structures, *e.g.* with mutually *trans*-PMe$_3$ ligands, are also possible, although characteristic virtual coupling effects would be expected in the ^{1}H NMR spectra for such species. Dinuclear species containing both a bridging and a non-bridging bidentate carboxylato ligand have been crystallographically characterised for tungsten[11,12] and for other transition metals.[13]

We were not able to achieve the conversion of [W$_2$(μ-O$_2$CBu^t)$_2$(O$_2$CBu^t)$_2$(PMe$_3$)$_2$] **1** into [W$_2$(μ-O$_2$CBu^t)(O$_2$CBu^t)$_3$(PMe$_3$)$_2$] **2** (or likewise of **2** into **1**) in solution. Both species lose PMe$_3$ on heating in the solid state to return the yellow [W$_2$(μ-O$_2$CBu^t)$_4$] starting material. We considered the

Table 1 Analytical and spectroscopic data

		Analyses[a]		
Compound	Colour	C	H	NMR[b]
1[c]	Purple	33.6 (33.8)	5.75 (5.8)	^1H: 1.48 (s, 18 H, O_2CBu^t), 1.41 [d, 18 H, $^2J(^1H-^{31}P)$ 8.4, PMe_3], 1.25 (s, 18 H, O_2CBu^t) $^{13}C-\{^1H\}$: 190.1, 182.6 (2 × $O_2\mathit{C}Bu^t$), 40.5 (overlapping 2 × $O_2C\mathit{C}Me_3$), 29.6, 28.0 (2 × $O_2CC\mathit{Me}_3$), 15.7 (virtually coupled m, PMe_3) $^{31}P-\{^1H\}$: 0.3 [s, $^1J(^{31}P-^{183}W)$ 341.8, $^3J(^{31}P-^{31}P)$ 21.5, PMe_3]
2[d]	Green	33.4 (33.8)	5.9 (5.8)	^1H: 1.81, 1.55 [d, 9 H, $^2J(^1H-^{31}P)$ 8.7, PMe_3], 1.50, 1.48, 1.42, 1.04 (s, 9 H, O_2CBu^t) $^{13}C-\{^1H\}$: 186.4 (2 signals overlapping), 184.4, 182.2 ($O_2\mathit{C}Bu^t$), 41.1, 40.5 (3 signals overlapping) ($O_2C\mathit{C}Me_3$), 28.8, 28.5, 28.4, 27.6 ($O_2CC\mathit{Me}_3$), 24.8 [d, $^1J(^{13}C-^{31}P)$ 28.7, PMe_3], 23.1 [d, $^1J(^{13}C-^{31}P)$ 28.1, PMe_3] $^{31}P-\{^1H\}$: −38.7 [d, 1 P, $^2J(^{31}P-^{31}P)$ 9.3, $^1J(^{31}P-^{183}W)$ 262, PMe_3] −39.5 [d, 1 P, $^2J(^{31}P-^{31}P)$ 9.3, $^1J(^{31}P-^{183}W)$ 283, PMe_3]
3[e]	Burgundy	41.1 (41.2)	5.5 (5.5)	$^{31}P-\{^1H\}$: 10.2 (s), 0.7 (s), −39.0 (br s, signal collapses on cooling)
4[f]	Green	40.7 (41.2)	5.6 (5.5)	^1H: 7.50–7.40, 7.20–7.10 (m, partially obscured by residual protio solvent, $PMe\mathit{Ph}_2$) 2.43, 2.35, 1.85, 1.67 [d, 3 H, $^2J(^1H-^{31}P)$ 7.5, $P\mathit{Me}_2Ph$], 1.60, 1.50, 1.36, 1.10 (s, 9 H, O_2CBu^t) $^{13}C-\{^1H\}$: 186.7, 185.9, 182.7, 181.7 ($O_2\mathit{C}Bu^t$), 146.6 [d, $^1J(^{13}C-^{31}P)$ 39.0, *ipso*-C of Ph], 145.7 [d, $^1J(^{13}C-^{31}P)$ 40.7, *ipso*-C of Ph], 131.1, 130.7 (CH of Ph, remaining CH resonance obscured by solvent C_6D_5 resonances), 40.4, 39.7 (2 signals overlapping), 38.3 ($O_2C\mathit{C}Me_3$), 25.0 [d, $^1J(^{13}C-^{31}P)$ 27.1, $P\mathit{Me}_2Ph$], 18.7 [d, $^1J(^{13}C-^{31}P)$ 27.2, $P\mathit{Me}_2Ph$] (remaining $P\mathit{Me}_2Ph$ and $O_2CC\mathit{Me}_3$ resonances obscured by CD_3 resonance of solvent) $^{31}P-\{^1H\}$: −40.6 [d, 1 P, $^2J(^{31}P-^{31}P)$ 9.2, PMe_2Ph] −35.2 [d, 1 P, $^2J(^{31}P-^{31}P)$ 9.2, PMe_2Ph]
5	Red	46.8 (47.1)	5.2 (5.3)	^1H: 7.38 (m, 8 H, *m*-H of Ph), 7.05 (m, partially obscured by residual protio solvent, *o*- and *p*-H of Ph), 1.42 (s, 36 H, O_2CBu^t), 1.40 [d, 6 H, $^2J(^1H-^{31}P)$ 1.5, $P\mathit{Me}Ph_2$] $^{13}C-\{^1H\}$: 188.3 ($O_2\mathit{C}Bu^t$), 139.0 (*ipso*-C of Ph), 132.8, 132.5 (CH of Ph, remaining CH resonance obscured by solvent C_6D_5 resonances), 40.2 ($O_2C\mathit{C}Me_3$), 29.9 ($O_2CC\mathit{Me}_3$), 11.6 [d, $P\mathit{Me}Ph_2$, $^1J(^{13}C-^{31}P)$ 11.6] $^{31}H-\{^1H\}$: −30.0 ($PMePh_2$)
6[g]	Yellow	37.9 (37.7)	6.4 (6.1)	^1H:[h] 1.38 [d, 18 H, $^2J(^1H-^{31}P)$ 8.9, PMe_3], 1.30 (s, 18 H, O_2CBu^t) $^{13}C-\{^1H\}$:[i] 243.0 [t, $^2J(^{13}C-^{31}P)$ 25, CO], 188.4 ($O_2\mathit{C}Bu^t$), 40.6 ($O_2C\mathit{C}Me_3$), 28.0 ($O_2CC\mathit{Me}_3$), 15.7 (virtually coupled m, PMe_3) $^{31}P-\{^1H\}$:[h] 2.81 [s, $^1J(^{31}P-^{183}W)$ 173, PMe_3]
7[j]	Purple	23.5 (24.2)	4.4 (4.5)	^1H: 1.48 (s, 18 H, O_2CBu^t), 1.30 [d, 18 H, $^2J(^1H-^{31}P)$ 8.7, PMe_3] $^{13}C-\{^1H\}$:[h] 191.1 ($O_2\mathit{C}Bu^t$), 40.4 ($O_2C\mathit{C}Me_3$), 29.5 ($O_2CC\mathit{Me}_3$), 13.3 (virtually coupled m, PMe_3) $^{31}P-\{^1H\}$: −3.3 [s, $^1J(^{31}P-^{183}W)$ 331, $^3J(^{31}P-^{31}P)$ 17.9, PMe_3]

[a] Calculated values in parentheses. [b] At 298 K in $[^2H_8]$ toluene unless otherwise stated. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (in Hz) and assignment; for ^1H NMR spectra *J* refers to the $^1H-^1H$ coupling constant; for ^{13}C NMR spectra *J* refers to the $^{13}C-^1H$ coupling constant unless otherwise stated. [c] ν_{assym} for O_2CBu^t 1589, 1562 cm^{-1}. [d] ν_{assym} for O_2CBu^t 1631, 1585 cm^{-1}. [e] ν_{assym} for O_2CBu^t 1616, 1562 cm^{-1}. [f] ν_{assym} for O_2CBu^t 1627, 1582 cm^{-1}. [g] Analysis for **6**·0.33 Et_2O; mass spectrum: $[M]^+$ 622, $[M - CO]^+$ 594, $[M - 2CO]^+$ 566, $[M - 3CO]^+$ 538; ν_{assym} for O_2CBu^t 1618, 1515 cm^{-1}. [h] In $[^2H_6]$benzene. [i] At 193 K. [j] Cl 10.8 (8.95%).

possibility that **1** or **2** might be an oxidation or hydrolysis product. However, treatment of complex **1** with one equivalent of O_2 or H_2O did not give **2** (and likewise **2** did not react with O_2 or H_2O to give **1**). The formation of two different isomeric adducts from the addition of the same phosphine to a tetrakis(carboxylato)dimetal molecule has been reported previously. Thus $Mo_2(O_2CCF_3)_4 \cdot 2PMePh_2$ possesses either a Class I or a Class II structure depending on the solvent used in its preparation.[9,10]

Treatment of a diethyl ether solution of $[W_2(\mu-O_2CBu^t)_4]$ with two equivalents of PMe_2Ph afforded a dark red solution from which the red and green compounds $[W_2(\mu-O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ **3** and $[W_2(\mu-O_2CBu^t)(O_2CBu^t)_3(PMe_2Ph)_2]$ **4** respectively could be isolated in modest yield. Elemental analysis for both compounds are consistent with the stoichiometry $W(O_2CBu^t)_2 \cdot PMe_2Ph$ and their IR spectra indicate the presence of monodentate carboxylato ligands (Table 1). Crystals of compound **3** were suitable for an X-ray diffraction analysis; the molecular structure is shown in Fig. 1, selected bond lengths and angles are listed in Table 2 and fractional atomic parameters for all non-hydrogen atoms are given in Table 3.

The structure of **3** is very unusual and appears to be unprecedented in tetrakis(carboxylato)dimetal chemistry. The

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ **3**

W(1)–W(2)	2.2345(9)	W(1)–P(1)	2.487(5)
W(1)–P(2)	2.839(5)	W(1)–O(1)	2.16(1)
W(1)–O(3)	2.08(1)	W(1)–O(5)	2.04(1)
W(2)–O(2)	2.12(1)	W(2)–O(4)	2.02(1)
W(2)–O(6)	2.01(1)	W(2)–O(7)	2.15(1)
O(1)–C(1)	1.28(2)	O(2)–C(1)	1.26(2)
O(3)–C(2)	1.24(2)	O(4)–C(2)	1.32(2)
O(5)–C(3)	1.26(2)	O(6)–C(3)	1.26(2)
O(7)–C(4)	1.26(2)	O(8)–C(4)	1.24(2)

P(1)–W(1)–W(2)	96.0(1)	P(2)–W(1)–W(2)	162.4(1)
P(2)–W(1)–P(1)	97.8(2)	O(1)–W(1)–W(2)	87.8(4)
O(1)–W(1)–P(1)	89.8(4)	O(1)–W(1)–P(2)	103.2(4)
O(3)–W(1)–W(2)	87.3(3)	O(3)–W(1)–P(1)	174.5(4)
O(3)–W(1)–P(2)	79.9(4)	O(3)–W(1)–O(1)	85.9(5)
O(5)–W(1)–W(2)	87.7(3)	O(5)–W(1)–P(1)	91.7(4)
O(5)–W(1)–P(2)	80.9(4)	O(5)–W(1)–O(1)	175.4(5)
O(5)–W(1)–O(3)	92.9(5)	O(2)–W(2)–W(1)	91.7(4)
O(4)–W(2)–W(1)	92.2(4)	O(4)–W(2)–O(2)	87.2(5)
O(6)–W(2)–W(1)	91.9(4)	O(6)–W(2)–O(2)	176.4(5)
O(6)–W(2)–O(4)	92.0(5)	O(7)–W(2)–W(1)	112.2(4)
O(7)–W(2)–O(2)	87.5(6)	O(7)–W(2)–O(4)	155.1(5)
O(7)–W(2)–O(6)	91.8(5)	C(1)–O(1)–W(1)	120.3(12)
C(1)–O(2)–W(2)	119.0(12)	C(2)–O(3)–W(1)	122.2(11)
C(2)–O(4)–W(2)	118.3(10)	C(3)–O(5)–W(1)	120.1(11)
C(3)–O(6)–W(2)	117.5(12)	C(4)–O(7)–W(2)	115.4(11)
O(2)–C(1)–O(1)	121.0(16)	C(11)–C(1)–O(1)	119.1(20)
C(11)–C(1)–O(2)	119.8(19)	O(4)–C(2)–O(3)	120.0(13)
C(21)–C(2)–O(3)	122.7(16)	C(21)–C(2)–O(4)	117.3(16)
O(6)–C(3)–O(5)	122.9(16)	C(31)–C(3)–O(5)	118.1(18)
C(31)–C(3)–O(6)	118.8(19)	O(8)–C(4)–O(7)	123.0(16)
C(41)–C(4)–O(7)	119.8(18)	C(41)–C(4)–O(8)	117.2(19)

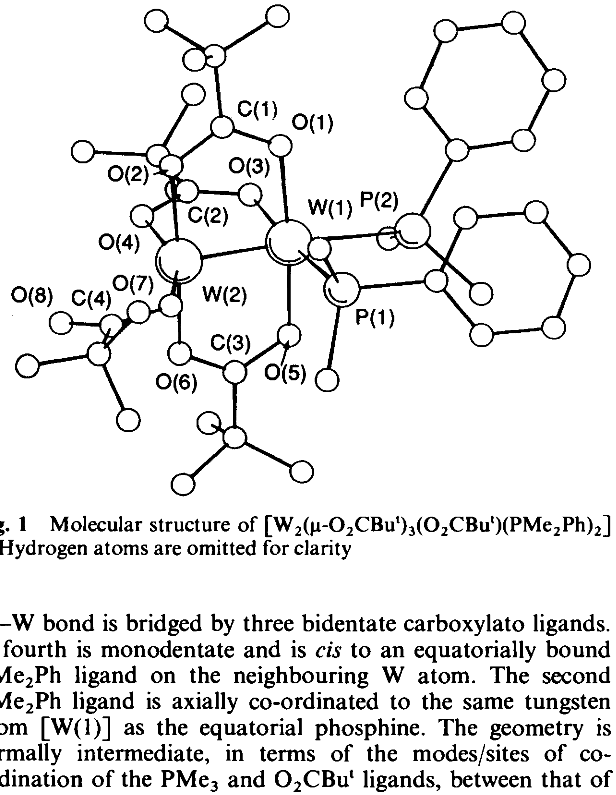


Fig. 1 Molecular structure of $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ **3**. Hydrogen atoms are omitted for clarity

W–W bond is bridged by three bidentate carboxylato ligands. A fourth is monodentate and is *cis* to an equatorially bound PMe_2Ph ligand on the neighbouring W atom. The second PMe_2Ph ligand is axially co-ordinated to the same tungsten atom [W(1)] as the equatorial phosphine. The geometry is formally intermediate, in terms of the modes/sites of co-ordination of the PMe_3 and O_2CBu^t ligands, between that of Class I and Class II. The W–W bond length [W(1)–W(2) 2.2345(9) Å] is typical for an axially ligated W_2 species with a metal–metal quadruple bond.[1a,b] As expected, the axially co-ordinated phosphine ligand is less tightly bound [W(1)–P(2) 2.839(5) Å] than the equatorially co-ordinated one [W(1)–P(1) 2.487(5) Å]. This type of variation has been found in comparing metal–phosphorus bond lengths in Class I and Class II complexes. In general, axially bound ligands compete with the metal–metal σ-bonding electrons for the same metal orbital combination, invariably resulting in a relatively weak metal–donor interaction. Equatorially co-ordinated ligands can bond through a strong interaction with a metal sp_2d hybrid orbital. The W(1)–P(1) distance in **3** is very close to that [2.489(3) Å] in the Class II complex $[W_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(PBu^n{}_3)_2]$.[6] For the Class I isomer of $Mo_2(O_2CCF_3)_4{\cdot}2PMePh_2$ the average Mo–P(axial) bond length is 2.988 Å,[10] whereas for the Class II isomer the Mo–P(equatorial) bond length is 2.511(3) Å.[9]

The compound $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ exists as a mixture of isomers in solution and its NMR spectra are very complex. Only the $^{31}P\text{-}\{^1H\}$ NMR data are reported in Table 1. At 298 K three singlets are observed at δ 10.2, 0.7 and −39 in the $^{31}P\text{-}\{^1H\}$ spectrum of a single crystal of **3** dissolved in $[^2H_8]$toluene. On cooling the sample, the two lowest-field resonances remain unchanged whereas the high-field resonance has a very temperature-dependent chemical shift, and eventually broadens into the baseline. Several new resonances appear on cooling the sample further, indicating the presence of more than one interconverting species. That **3** has such an unusual structure may be due to the sterically congested nature of the complex. The isolation of the particular isomer shown in Fig. 1 (rather than any of the other species present in solution) is presumably a consequence of relative solubilities of the various isomers present in solution.

The crystals of the green species $[W_2(\mu\text{-}O_2CBu^t)(O_2CBu^t)_3(PMe_2Ph)_2]$ **4** were not suitable for diffraction studies and were characterised by elemental analysis and spectroscopic data alone. The NMR spectra (Table 1) are very similar to those of **2** and show four types of O_2CBu^t ligand and two inequivalent, diastereotopic PMe_2Ph ligands. The phosphines appear as a pair of mutually coupled doublets at δ −35.2 and −40.6 (free PMe_2Ph in $[^2H_8]$toluene appears at δ −49.4) in the $^{31}P\text{-}\{^1H\}$ NMR spectrum $[^2J(P\text{–}P) = 9.2\ Hz]$ but without observable ^{183}W satellites. The absence of observed coupling to ^{183}W and the smaller difference in δ for free and bound phosphine suggest that PMe_2Ph binds less tightly to the W_2 core in **4** than the PMe_3 ligands do in **2**.

If PMe_2Ph does indeed induce behaviour in this system that is intermediate between Class I and Class II, then the use of a slightly bulkier phosphine ought to favour a change of structural type to Class I. Treatment of an ether solution of $[W_2(\mu\text{-}O_2CBu^t)_4]$ with two equivalents of $PMePh_2$ gave a colour change from yellow to orange-red. Subsequent work-up afforded a modest yield of $[W_2(\mu\text{-}O_2CBu^t)_4(PMePh_2)_2]$ **5** for which elemental analysis suggests the stoichiometry $W(O_2CBu^t)_2{\cdot}PMePh_2$ (Table 1). The IR spectra show no evidence for the presence of monodentate O_2CBu^t ligands. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra show only one type of O_2CBu^t ligand environment and the $^{31}P\text{-}\{^1H\}$ chemical shift (δ −30, no ^{183}W satellites observed) is close to that of free $PMePh_2$ (δ −38.4). Thus **5** has the Class I axially ligated geometry illustrated in Scheme 1 and is presumably isostructural with the crystallographically characterised bis(triphenylphosphine) adduct $[W_2(\mu\text{-}O_2CBu^t)_4(PPh_3)_2]$.[3]

Reactivity Studies of $[W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2]$ **1**.—Treatment of **1** with H_2 (8 atm) in diethyl ether gave no reaction. The compound did react readily with Me_2S_2 (one equivalent) but unfortunately although a large number of products were formed, none could be isolated in a pure form. Studies of the oxidative addition reactions of $[W_2(\mu\text{-}O_2CBu^t)_4]$ with Br_2 or I_2 were reported to give a complex mixture of products involving facile scrambling of the O_2CBu^t ligands.[12] The reaction of **1** with carbon monoxide (8 atm) in diethyl ether, however, resulted in a low yield of the mononuclear complex

Table 3 Fractional atomic coordinates with e.s.d.s in parentheses for $[W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.329 84(3)	0.159 69(3)	0.058 1(6)	C(23)	0.514(2)	−0.055(2)	0.087(4)
W(2)	0.406 52(3)	0.157 66(4)	0.194 0(6)	C(24)	0.494(3)	−0.021(3)	−0.089(3)
P(1)	0.263 9(3)	0.264 8(3)	0.121 1(7)	C(32)	0.562(2)	0.315(2)	0.017(3)
P(2)	0.270 0(3)	0.150 5(3)	−0.150 2(7)	C(33)	0.479(2)	0.329(2)	−0.119(3)
O(1)	0.262 2(7)	0.093 3(7)	0.154(1)	C(34)	0.556(2)	0.224(2)	−0.102(4)
O(2)	0.339 4(7)	0.092 8(8)	0.287(1)	C(42)	0.347(3)	0.299(3)	0.504(5)
O(3)	0.375 7(6)	0.067 0(6)	0.005(1)	C(43)	0.430(2)	0.372(2)	0.434(4)
O(4)	0.451 7(6)	0.068 6(7)	0.140(1)	C(44)	0.473(2)	0.298(2)	0.556(4)
O(5)	0.400 0(6)	0.220 8(6)	−0.023(1)	C(101)	0.188 4(8)	0.285 7(9)	0.037(2)
O(6)	0.475 0(6)	0.218 1(7)	0.113(1)	C(102)	0.315(1)	0.346(1)	0.126(2)
O(7)	0.386 9(7)	0.239 7(7)	0.309(1)	C(103)	0.220(1)	0.259(1)	0.253(2)
O(8)	0.488 8(8)	0.212(1)	0.382(1)	C(104)	0.177(1)	0.352 1(9)	−0.007(2)
C(1)	0.282(1)	0.072(1)	0.246(2)	C(105)	0.121(1)	0.366(1)	−0.075(2)
C(2)	0.426 5(9)	0.039 8(8)	0.052(2)	C(106)	0.075(1)	0.314(1)	−0.093(2)
C(3)	0.458(1)	0.237(1)	0.019(2)	C(107)	0.086(1)	0.248(1)	−0.056(2)
C(4)	0.434(1)	0.247(1)	0.380(2)	C(108)	0.140(1)	0.233(1)	0.012(2)
C(11)	0.239(1)	0.016(1)	0.304(2)	C(201)	0.194(1)	0.092 2(9)	−0.167(2)
C(21)	0.459(1)	−0.028 8(9)	0.015(2)	C(202)	0.247(1)	0.230(1)	−0.221(2)
C(31)	0.511 5(9)	0.276(1)	−0.048(2)	C(203)	0.335(1)	0.109(1)	−0.237(2)
C(41)	0.423(1)	0.300(1)	0.469(2)	C(204)	0.188(1)	0.041(1)	−0.093(2)
C(12)	0.280(2)	−0.047(2)	0.330(4)	C(205)	0.132(2)	−0.010(2)	−0.101(3)
C(13)	0.176(2)	−0.004(2)	0.245(3)	C(206)	0.085(1)	−0.004(2)	−0.182(4)
C(14)	0.221(2)	0.046(2)	0.408(3)	C(207)	0.092(1)	0.051(2)	−0.254(4)
C(22)	0.408(2)	−0.081(2)	−0.020(3)	C(208)	0.145(1)	0.097(1)	−0.241(3)

$[W(O_2CBu^t)_2(CO)_3(PMe_3)_2]$ **6** which has been characterised by elemental analysis, IR and NMR spectroscopy and mass spectrometry (Table 1). The product **6** clearly possesses a W : PMe_3 ratio of 1 : 2 whereas in the starting dimer **1** this ratio is 1 : 1 and so the reaction is deficient in PMe_3. When the reaction between **1** and CO was repeated in the presence of an additional two equivalents of PMe_3 per equivalent of **1** the yield was substantially increased.

The NMR spectra of $[W(O_2CBu^t)_2(CO)_3(PMe_3)_2]$ **6** show only one PMe_3 and O_2CBu^t environment even at 193 K; at this temperature the CO ligands still appear as a triplet [^2J(C–P) 25 Hz] at δ 243.0. The NMR data are consistent with either a symmetrical pentagonal bipyramidal geometry (having C_{2v} symmetry) or a monocapped octahedral geometry (as illustrated in Scheme 1) which is still rapidly fluxional on the NMR time-scale at low temperature (seven-co-ordinate transition-metal complexes are frequently highly fluxional). We favour the latter possibility though cannot discount a static pentagonal bipyramidal structure. There is only one example of a crystallographically characterised compound of the type $[MX_2(CO)_3L_2]$ (where X is a univalent ligand and L a neutral two-electron donor) having a pentagonal bipyramidal structure, namely $[WI_2(CO)_3(dppm)]$ [dppm = bis(diphenylphosphino)methane]. In this species the small 'bite' angle of the bidentate phosphine is thought to favour the pentagonal bipyramidal structure.[14] In all of the other crystallographically characterised cases, for example $[WCl_2(CO)_3(PEt_3)_2]$, the structures are based on a capped octahedron.[15]

A number of examples of the cleavage of metal–metal multiple bonds by π-acceptor ligands such as CO, NO and RNC are known.[1] A particularly relevant example of such a reaction is that of the quadruply bonded $[M_2Cl_4(PR_3)_4]$ (M = Mo or W, R = Et or Bu^n) with CO (1 atm) at 70 °C to afford the complexes $[MCl_2(CO)_3(PR_3)_2]$ and *trans*-$[M(CO)_4(PR_3)_2]$.[16]

We were interested in attempting to replace two of the O_2CBu^t groups in $[W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2]$ **1** by Cl. For example treatment of $[Mo_2(\mu\text{-}O_2CR)_4]$ (R = Me or Bu^t) with $SiMe_3Cl$ in the presence of a variety of donor ligands L [L = tetrahydrofuran (thf), Me_2S or PR'_3] yielded the binuclear compounds $[Mo_2(\mu\text{-}O_2CR)_2Cl_2L_2]$ or $[Mo_2Cl_4L_4]$.[17,18] Treatment of a toluene solution of **1** with two equivalents of chlorotrimethylsilane at 140 °C for 24 h resulted in a green-purple solution from which purple microcrystals of $[W_2(\mu\text{-}O_2CBu^t)_2Cl_2(PMe_3)_2]$ **7** were isolated in 42% yield. Small amounts of the tetrachloroditungsten complex $[W_2Cl_4(PMe_3)_4]$[19] were also formed in this reaction. This side-product proved difficult to separate completely from the main product. The NMR and mass spectral data for **7** are consistent with the C_{2h} structure illustrated in Scheme 1, although an analogous structure with C_2 symmetry and the PMe_3 ligands mutually gauche cannot be discounted on the basis of the NMR data alone. Notably the compound $[Mo_2(\mu\text{-}O_2CBu^t)_2Cl_2(PEt_3)_2]$ exists as either a C_2 or a C_{2h} isomer (both crystallographically characterised) depending on the method of preparation.[18] Compound **7** is also analogous to the dimolybdenum species $[Mo_2(\mu\text{-}O_2CMe)_2Cl_2(PR_3)_2]$ (R = Bu^n or Ph).[17] Interestingly, an attempt to prepare $[W_2Cl_4(dppm)_2]$ from $[W_2(\mu\text{-}O_2CPh)_4]$ and dppm in the presence of $SiMe_3Cl$ failed to afford any tractable product.[20] A quadruply bonded species related to **7** was proposed to be an intermediate in the formation of $[W_2(\mu\text{-}O_2CPh)_2(\mu\text{-}Cl)(\mu\text{-}H)Cl_2(PBu^n{}_3)_2]$ from $[W_2Cl_4(PBu^n{}_3)_4]$ and $PhCO_2H$ but was not isolated.[21] The paramagnetic anion $[W_2I_4(\mu\text{-}O_2CBu^t)_2]^-$ has two carboxylato ligands bridging in a bidentate manner a W_2 core.[12]

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, unless stated otherwise. Celite 545 filtration aid (Koch-Light) was pre-dried at 80 °C before use. All solvents were pre-dried over molecular sieves and refluxed over appropriate drying agents {sodium (toluene), potassium (tetrahydrofuran), Na/K alloy [light petroleum (b.p. 40–60 °C), pentane, diethyl ether], P_2O_5 (C_6H_5Cl)} under an atmosphere of dinitrogen and collected by distillation. [$^2H_6$]Benzene and [$^2H_8$]toluene were dried over potassium at 70 °C, degassed and stored under N_2 in Young's ampoules. All NMR samples were prepared in the dry-box in screw-top tubes (Wilmad) or sealed under vacuum at liquid-nitrogen temperature.

Proton, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded on a Brüker AM-300 spectrometer at 300.0, 75.47 or 121.49 MHz respectively. The ^{1}H and ^{13}C-{^{1}H} spectra were referenced internally to residual protio-solvent resonances and are reported relative to tetramethylsilane (δ 0). The ^{31}P-{^{1}H} spectra were referenced externally relative to trimethyl phosphate in $\mathrm{D_2O}$. All chemical shifts (δ) are quoted in ppm and coupling constants in Hz. High-frequency shifts are reported as being positive in each case. The IR spectra were recorded on either Mattson Polaris or Perkin-Elmer 1710 Fourier-transform spectrometers in the range 4000–400 cm^{-1}. Samples were prepared as Nujol mulls between KBr plates. All data are quoted in cm^{-1}. Electron impact ionisation mass spectra were recorded on an AEI MS 302 mass spectrometer updated with an MSS data handling system; quoted peaks had the appropriate isotope patterns. Elemental analyses were carried out by the Analysis Department of the Inorganic Chemistry Laboratory, Oxford, or by Analytische Laboratorien, Gummersbach, Germany.

The compounds $\mathrm{WCl_4}$ and $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$ were prepared according to the literature methods.[22,23]

Preparations.—$[\mathrm{W_2(\mu\text{-}O_2CBu^t)_2(O_2CBu^t)_2(PMe_3)_2}]$ **1**.—The complex $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$ (0.51 g, 0.66 mmol) was dissolved in diethyl ether (25 cm^3) and $\mathrm{PMe_3}$ (1.2 cm^3 of a 10% solution in diethyl ether, 2 equivalents) was added with stirring. A deep purple solution was immediately formed from which the volatiles were removed under reduced pressure after 30 min. The purple residue was extracted into pentane (2 × 15 cm^3; a small amount of **2** remained undissolved). On cooling the purple pentane solution to −25 °C, purple crystals of **1** were obtained which were isolated by filtration, washed with cold (−25 °C) pentane (2 × 5 cm^3) and dried *in vacuo*. Yield 0.24 g (40%).

$[\mathrm{W_2(\mu\text{-}O_2CBu^t)(O_2CBu^t)_3(PMe_3)_2}]$ **2**. To a stirring solution of $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$ (0.51 g, 0.66 mmol) in toluene (30 cm^3) was added $\mathrm{PMe_3}$ in toluene (1.2 cm^3 of a 10% solution, 2 equivalents). After 2 h the toluene was removed under reduced pressure at room temperature and the residue extracted into light petroleum, giving a purple solution and leaving behind some yellow-green solid subsequently shown by NMR to be $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$. The petroleum solution was reduced in volume and cooled to −80 °C for 20 h, to give compound **2** as a green solid, which was washed with cold petroleum (2 × 10 cm^3) and dried *in vacuo*. Yield 0.20 g (33%).

$[\mathrm{W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2}]$ **3** *and* $[\mathrm{W_2(\mu\text{-}O_2CBu^t)(O_2CBu^t)_3(PMe_2Ph)_2}]$ **4**. To a solution of $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$ (0.51 g, 0.66 mmol) in diethyl ether (25 cm^3) was added $\mathrm{PMe_2Ph}$ in diethyl ether (1.9 cm^3 of a 10% solution, 2 equivalents) to give a dark red solution. After 2 h the solution was reduced in volume and cooled to −25 °C and then −80 °C for 24 h giving large, dark burgundy crystals of compound **3**. The supernatant was filtered off and the red solid washed with cold (−80 °C) diethyl ether and dried *in vacuo*. Yield 0.23 g (33%).

Removal of the solvent from the supernatant under reduced pressure and recrystallisation of the resulting residue from pentane gave compound **4** as an analytically pure green-brown microcrystalline solid. Yield 0.15 g (21%).

$[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4(PMePh_2)_2}]$ **5**. The complex $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_4}]$ (0.47 g, 0.61 mmol) was dissolved in diethyl ether (25 cm^3) and $\mathrm{PMePh_2}$ was added (2.3 cm^3 of a 10% solution in diethyl ether, 2 equivalents of $\mathrm{PMePh_2}$) giving an orange-red solution. After 3 h the solvent was removed under reduced pressure and the residue extracted into light petroleum. Crystallisation occurred on cooling to −80 °C. The supernatant was filtered off and the solid washed with a small amount of cold light petroleum and dried *in vacuo* at room temperature. The resulting red material was found to be very oily. It was therefore recrystallised carefully from pentane at −80 °C and the resulting red microcrystalline solid dried *in vacuo* at −40 °C. Yield 0.12 g (17%).

Table 4 Crystal data, data collection and processing parameters for $[\mathrm{W_2(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)(PMe_2Ph)_2}]$ **3**

Formula	$\mathrm{C_{36}H_{58}O_8P_2W_2}$
M	1048.49
Crystal size/mm	0.40 × 0.45 × 0.70
Crystal system	Tetragonal
Space group	$P4_1$
a/Å	19.016(7)
c/Å	12.456(5)
U/Å^3	4504.12
Z	4
D_c/g cm^{-3}	1.546
μ/cm^{-1}	53.24
F(000)	2064
2θ limits/°	3–50
ω scan width (+0.35 tan θ)/°	0.80
Total data collected	5521
Total unique data	4470
Number of observations [$I > 3\sigma(I)$]	3213
R(merge)	0.029
Number of variables	374
Observations/variables	8.6
Weighting coefficients	17.73, −14.58, 11.26
Maximum, minimum peak in final difference map/e Å^{-3}	2.1 [1.00 Å from W(1)], −0.02
R $(\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.041
R' $\{[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$	0.047

$[\mathrm{W(O_2CBu^t)_2(CO)_3(PMe_3)_2}]$ **6**. To a solution of **1** (0.39 mmol, prepared *in situ*) in diethyl ether (20 cm^3) in a Fischer–Porter bottle was added $\mathrm{PMe_3}$ (2 equivalents) and carbon monoxide to a pressure of 8 atm giving a colour change from purple to green after 30 min. The mixture was stirred for a further 2 h at room temperature. The solution was filtered and the solvent removed under reduced pressure. The residue was washed with light petroleum (3 × 10 cm^3) giving compound **6** as a yellow solid which contained (by ^{1}H NMR) $\frac{1}{3}$rd of a mole of diethyl ether per formula unit. Yield 0.23 g (46%).

$[\mathrm{W_2(\mu\text{-}O_2CBu^t)_2Cl_2(PMe_3)_2}]$ **7**. To a solution of **1** (0.51 g, 0.66 mmol) in toluene (50 cm^3) was added chlorotrimethylsilane (1.6 cm^3 of a 10% solution in toluene, 2 equivalents). The solution was heated at 140 °C under reduced pressure for 24 h resulting in a change of colour to purple-green. The volatiles were removed under reduced pressure and the residue extracted into light petroleum, giving a purple solution and leaving behind a solid, shown by ^{1}H NMR spectroscopy to contain $[\mathrm{W_2Cl_4(PMe_3)_4}]$.[19] Cooling the purple light petroleum solution to −80 °C gave compound **7** as a dark purple solid, which was isolated by filtration, washed with cold light petroleum (2 × 10 cm^3) and dried *in vacuo*. Yield 0.22 g (42%).

X-Ray Crystal Structure Determination of **3**.—Crystal data, data collection and processing parameters are given in Table 4. A crystal of **3** was sealed in a Lindemann glass capilliary under $\mathrm{N_2}$ and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 reflections. Three reflections were chosen as intensity standards and were measured every 3600s 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[24] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The tungsten atom positions were determined by direct methods. Subsequent Fourier difference syntheses revealed the positions of all other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures with the exception of the methyl groups of the

O_2CBu^t ligands which were refined isotropically. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.3 × the isotropic, or equivalent isotropic, thermal parameter of the carbon atom to which they were bonded) and refined riding their supporting carbon atoms. A Chebyshev weighting scheme[25] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[26]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS[27] suite on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral atom scattering factors were taken from the usual sources.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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