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Synthesis and characterization of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$, a mixed valence oxo alkyl dimer in which d^0 and d^2 tungsten centers are connected by an asymmetric oxo bridge [1]

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Abstract

Reaction of the ethylene hydride complex $[W(\eta^5\text{-}C_5H_5)_2(CH_2{=}CH_2)H]PF_6$ (**4**PF_6) with mild oxygen atom sources such as dimethyl sulfoxide or propylene oxide gives the terminal oxo ethyl complex $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ (**3**PF_6). Reaction of this with PMe_2Ph gives a strongly colored compound which crystallizes in the monoclinic space group $C2/c$ with $a = 19.483(4)$ Å, $b = 22.397(6)$ Å, $c = 14.289(3)$ Å, $\beta = 133.59(1)°$. A single crystal X-ray diffraction study ($R_F = 5.75\%$, $R_w = 5.31\%$) has established that the compound contains the cationic dimer $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]^+$ (**1**$^+$). Metric parameters support formulation of **1**$^+$ as a mixed valence dimer of W(IV) and W(VI) in which a mono-cyclopentadienyl tungsten oxo alkyl $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$ is coordinated through an oxo ligand to a cationic tungstenocene alkyl "$[W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)]^+$". The oxo bridge is asymmetric, with a double bond (1.78(1) Å) to the mono-cyclopentadienyl tungsten center and a single bond (2.03(1) Å) to the bis-cyclopentadienyl tungsten, while the terminal oxo ligand has a triple bond to tungsten (1.68(1) Å). The strong absorbance of **1**$^+$ at 583 nm is assigned to a metal to metal charge transfer transition. Formation of **1**$^+$ is proposed to involve initial nucleophilic addition of PMe_2Ph to a cyclopentadienyl ligand in **3**$^+$ to give a transient cyclopentadiene ligand which is displaced by the oxo ligand of a second equivalent of **3**$^+$. This sequence is supported by ^1H and ^{31}P NMR studies which establish that there is a single P containing product formulated as the cyclopentadiene-substituted phosphonium salt $[P(C_5H_5)Me_2Ph]^+$ (**5**$^+$), as confirmed by independent synthesis and spectroscopic characterization of **5**$^+$ by addition of C_5H_5I to PMe_2Ph. Photolysis of **1**$^+$ results in dissociation of the monocyclopentadienyl oxo alkyl fragment $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$(**2**), which has been independently characterized, and formation of the alkene hydride $[W(\eta^5\text{-}C_5H_5)_2(CH_2{=}CH_2)H]^+$.

Keywords: Tungsten; Cyclopentadienyl; Oxo; Oxidation; Mixed valence

1. Introduction

The dihalides and dihydrides $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$, $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$, $[W(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ [1] were amongst the first bent metallocene complexes to be prepared, and exploration of their chemistry soon established that these systems provide an unusual combination of reactive sites on the front of the metallocene wedge together with a relatively inert Cp_2M backbone. Derivatives of these compounds have therefore played an important role in the development of our understanding of the reactions of transition metal organometallics, particularly in the hands of Green [3] and his co-workers; important examples include their role in the development of the photochemistry of polyhydride complexes, of C–H activation chemistry, and of insertion reactions of alkene and alkylidene ligands: for contemporaneous reviews which illustrate the development of Malcolm's contributions to this area see Ref. [2]; for comprehensive reviews see Ref. [3].

The formation and reactivity of oxo complexes has been a recurring theme in molybdenocene and tungstenocene chemistry, beginning with the seminal work

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[3] Anyone who has had the privilege of working with Malcolm knows that "in the hands of" can be taken literally.

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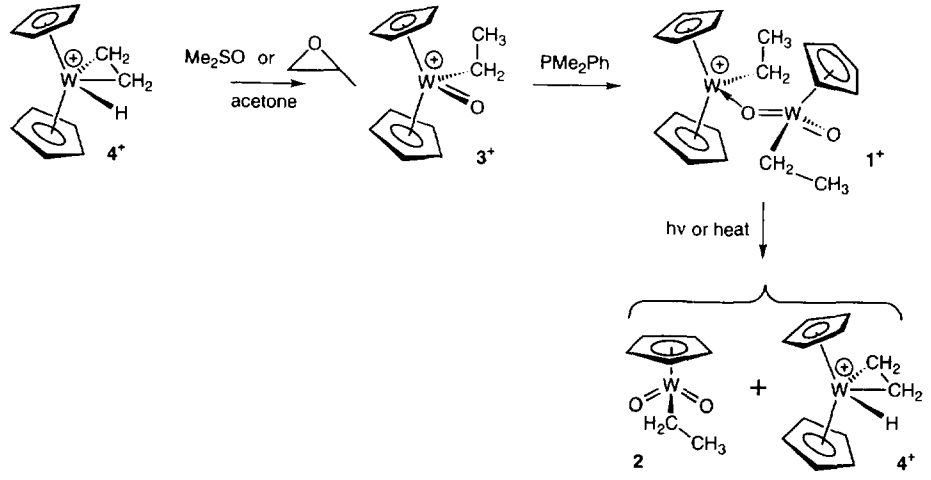


Scheme 1.

of Cousins and Green in which they converted [{Mo(η^5-C_5H_5)(CO)$_3$}$_2$] into [{Mo(η^5-C_5H_5)(O)$_2$}$_2$O], [Mo(η^5-C_5H_5)(O)$_2$Cl], [Mo(η^5-C_5H_5)(O)Cl$_2$], and [Mo(η^5-C_5H_5)Cl$_4$] [4]. These reports provided the first access to the chemistry of monocyclopentadienyl complexes of Mo without carbonyl ligands, and have been extensively used as entry points to this system (for a review of developments up to the early 1980s, see Ref. [5]); however, the lack of convenient syntheses of analogous W compounds for many years limited corresponding exploration of the oxo chemistry of mono-cyclopentadienyl W systems. Recent reports of routes to both oxo and halo mono-cyclopentadienyl (and substituted cyclopentadienyl) W starting materials [6–10] have, however, drastically changed this situation, and there has been rapid development of this area [11].

The oxo chemistry of Mo and W with two cyclopentadienyl ligands is intrinsically more limited because of the restricted ligand environment, although Green et al. [12] discovered routes to the terminal oxo complexes [M(η^5-C_5H_5)$_2$(O)] as early as 1972; see also Ref. [13]. The unusual nature of these materials as sources of electron-rich oxo ligands has recently been recognized [14], and the corresponding oxo chemistry of bis-pentamethylcyclopentadienyl tungsten has been explored by Parkin and co-workers [15,16]. We have recently reported an example of a cationic terminal oxo alkyl complex of tungstenocene [W(η^5-C_5H_5)$_2$(O)(CH_3)]$^+$, and we have also reported the synthesis and structural characterization of [{W(η^5-C_5H_5)$_2$(CH_3)}$_2$(μ-O)]$^{2+}$, a symmetrical oxo-bridged dimer in which two formally d^1 W(V) centers are spin paired through a linear oxo bridge [17,18].

We now wish to report, as summarized in Scheme 1, the synthesis and structural characterization of [{W(η^5-C_5H_5)$_2$(CH_2CH_3)}(μ-O){W(η^5-C_5H_5)(O)(CH_2-CH_3)}]PF_6 (**1**PF_6), an example of a new class of oxo complexes which combines the mono-cyclopentadienyl and bis-cyclopentadienyl ligand environments. The molecule is a mixed valence dimer of W(IV) and W(VI) in which a monocyclopentadienyl tungsten oxo alkyl [W(η^5-C_5H_5)(O)$_2$(CH_2CH_3)] (**2**) is coordinated to a cationic tungstenocene alkyl "[W(η^5-C_5H_5)$_2$(CH_2CH_3)]$^+$" to give a dimer with an asymmetric oxo bridge. The dimer is prepared by an unusual reaction in which nucleophilic addition of a phosphine to a cyclopentadienyl ligand in the previously unreported terminal oxo complex [W(η^5-C_5H_5)$_2$(O)(CH_2CH_3)]PF_6 (**3**PF_6) results in removal of one cyclopentadienyl ligand. The dimer is photosensitive, and the monocyclopentadienyl oxo alkyl fragment **2** has been photolytically removed from the tungstenocene fragment and independently characterized.

2. Experimental details

2.1. Materials and methods

All transformations and manipulations were performed using a Vacuum Atmospheres drybox or standard Schlenk tube and cannula inert atmosphere techniques under an atmosphere of prepurified nitrogen unless otherwise noted. Glassware was washed by soaking in saturated KOH in isopropanol overnight, rinsed with de-ionized water and flame dried under vacuum before use.

Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and then distilled from sodium–benzophenone under nitrogen. Dichloromethane was distilled from calcium hydride under a calcium sulfate drying tube. Acetone was distilled from potassium carbonate under a calcium sulfate drying tube. Dimethylsulfoxide (Mallinckrodt) was reagent grade and was used as-received. Distilled water was degassed for 30 min before use.

The ethylene complex [W(η^5-C_5H_5)$_2$-(CH_2=CH_2)H]PF_6 was prepared from [W(η^5-

$C_5H_5)_2Cl_2$] [19] by literature procedures [20]. The following reagents were used as-received from the supplier indicated: PMe_2Ph (Strem), NH_4PF_6 (Alfa), KPF_6 (Alfa), $AgPF_6$ (Alfa), propene oxide (Alfa), $Tl(C_5H_5)$ (Alfa), I_2 (Mallinckrodt), Celite 545 and Alumina AbsorptionR (Fisher A-540).

NMR spectra were recorded on AM-300 or WM-300-WB (^1H, 300 MHz; ^{13}C, 75.5 MHz; ^{31}P 121.5 MHz) spectrometers at ambient temperature unless otherwise noted. Perdeutero-solvents were 99.9 + at.% pure and were used as-received from either Cambridge Isotopes or Merck, Sharpe, and Dohme. In some cases ^{13}C and ^{31}P spectra were recorded in protio solvents with the addition of a sealed capillary tube containing a deuterated solvent to provide a locking signal (a 'locker-tube'). ^1H NMR chemical shifts are reported in parts per million downfield of TMS using the residual protons of the solvent as an internal standard. The shifts of these standards were assigned to the following values relative to TMS (δ): acetone, 2.04; benzene, 7.15; dichloromethane, 5.32. ^{13}C NMR chemical shifts are reported in parts per million using the ^{13}C chemical shift of the deuterated solvent as an internal standard. These were assigned the following values (δ): acetone, 29.5; benzene, 128.0; dichloromethane, 53.8. ^{13}C and ^{31}P spectra were recorded with broad band ^1H decoupling unless otherwise noted. ^{31}P NMR chemical shifts are reported in parts per million downfield of idealized external H_3PO_4 using the PF_6^- ion as an internal standard (defined as $\delta - 142.7$).

Infrared spectra were obtained as Nujol mulls on CsI plates on a Perkin–Elmer 683 grating infrared spectrometer. The 1601 cm^{-1} band of polystyrene was used as an external reference. Ultraviolet–visible (UV–vis) spectra were obtained on a Perkin–Elmer 552 instrument using a matched set of 1.0 cm cells, one of which could be sealed airtight. Electron impact (EI) mass spectra were recorded on an AEI MS-9 double-focusing spectrophotometer using a direct insertion probe with an ionizing voltage of 40 eV. Fast atom bombardment (FAB) and field desorption (FD) mass spectra were performed by the MIT mass spectral laboratory under the direction of Cathy Costello. The ions which exhibited a tungsten isotope pattern are reported as the values of m/z which correspond to the species containing the ^{184}W isotope. Analytical services were provided as indicated by the Schwarzkopf Microanalytical Laboratory (Woodside, NY) or Galbraith Laboratories (Knoxville, TN).

2.2. Synthesis of $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ ($3PF_6$)

2.2.1. Dimethylsulfoxide route

A saturated solution of 0.525 g (1.08 mmol) of $[W(\eta^5\text{-}C_5H_5)_2(CH_2{=}CH_2)H]PF_6$ in 3 ml of dimethylsulfoxide was heated to 40 °C for 18 h. Addition of 20 ml of a saturated aqueous NH_4PF_6 solution to the resulting dark red solution precipitated a gray flocculent solid. The supernatant was discarded and the residue was washed with 1 × 10 ml of distilled water and extracted into acetone (3 × 20 ml). Distilled water (8 ml) was added to the filtered red solution and acetone was removed under reduced pressure to yield a yellow microcrystalline solid which was collected and extracted into acetone. The slightly cloudy solution was filtered through a 1 × 8 cm column of Celite 545 and concentrated to 3 ml. Slow addition of 20 ml of diethyl ether precipitated 0.330 g (0.65 mmol, 61% yield) of yellow microcrystalline $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$. IR (Nujol mull) cm^{-1}: 3130 (m, $\eta^5\text{-}C_5H_5$), 3100 (sh), 1431 (w, sh on Nujol, $\eta^5\text{-}C_5H_5$), 1200 (m), 1133 (w), 1105 (w, br), 1080 (w, br), 1060 (w, br), 1035 (w, br), 975 (w, br), 900 (w, sh), 885 (s, W=O), 850 (m, sh), 830 (s, $[PF_6]^-$), 745 (vw), 725 (vw), 555 (s, $[PF_6]^-$), 355 (vw). ^1H NMR (300 MHz, acetone-d_6): δ 6.87 (s, 10, ($\eta^5\text{-}C_5H_5$)), 3.55 (q, $J = 7.2$ Hz, satellites $^2J_{W-H} = 8.3$ Hz, 2, CH_2), 2.32 (t, $J = 7.2$ Hz, 3, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 114.4 (s, d in gated decoupled spectra, $^1J_{C-H} = 185$ Hz, ($\eta^5\text{-}C_5H_5$)), 24.3 (s, q in gated decoupled spectra, $^1J_{C-H} = 127$ Hz, CH_3), 23.0 (s, t in gated decoupled spectra, $^1J_{C-H} = 136$ Hz, satellites $^1J_{W-C} = 77$ Hz, WCH_2). MS (FAB, based on ^{184}W) 359 $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]^+$ m/z. Anal. Found (Galbraith): C, 28.78; H, 2.96. $C_{12}H_{15}F_6OPW$. Calc.: C, 28.59; H, 3.00%.

2.2.2. Propylene oxide route

A solution of 0.103 g (0.21 mmol) of $[W(\eta^5\text{-}C_5H_5)_2(CH_2{=}CH_2)H]PF_6$ in 10 ml of acetone and 10 ml of propylene oxide was heated overnight at 40 °C. The solution was concentrated to saturation and the crude product was precipitated by the addition of diethyl ether. The product was collected and extracted into acetone, and the resulting solution was filtered and concentrated to saturation. Slow addition of diethyl ether precipitated 0.93 g (0.185 mmol, 88% yield) of the microcrystalline pale yellow product. ^1H NMR and IR spectra were identical to those of authentic $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ as reported above. UV–vis (THF) 600 nm ($\varepsilon = 20$ l mol^{-1} cm^{-1}). Mol. wt. (Schwarzkopf, dimethylformamide) 237 g mol^{-1} of particles (expected 504/2 = 252 g mol^{-1}).

2.3. Synthesis of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$ ($1PF_6$)

A solution of 180 μl (1.30 mmol) of PMe_2Ph in 5 ml of THF was added to a stirred suspension of 0.530 g (1.05 mmol) of $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ in 10 ml of THF. After an induction period of a few seconds a blue suspension formed. The suspension was kept in the dark and shaken occasionally over the next 40 min. Diethyl ether was then added to precipitate a

crystalline product which was collected, rinsed with THF (2 × 5 ml) and placed under vacuum for 30 min. The purple solid was extracted into acetone and the solution was filtered and concentrated to saturation. Slow addition of diethyl ether yielded 0.380 g (0.48 mmol, 91% yield) of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$ as clusters of purple-red platelets. IR (Nujol mull) cm^{-1}: 3136 (sh, η^5-C_5H_5), 3120 (mw, η^5-C_5H_5), 2720 (vw), 1300 (vw, br), 1260 (vw, br), 1176 (m), 1115 (vw), 1070 (w), 1020 (w, sh), 1008 (m, br), 952 (m, sh), 940 (m), 873 (w, sh), 850 (vs, W=O), 830 (vs, $[PF_6]^-$), 775 (w), 740 (vw), 720 (vw), 550 (s, $[PF_6]^-$), 510 (w), 465 (vw), 375 (m), 355 (w). ^{1}H NMR (300 MHz, acetone-d_6): 6.72 (s, 5, W1(η^5-C_5H_5)), 5.76 (s, 5, W2(η^5-C_5H_5)), 5.56 (s, 5, W2(η^5-C_5H_5)), 2.43 (m, 1, diastereotopic H of W1CH_2), 2.28 (m, 1, diastereotopic H of W1CH_2), 1.85 (t, J = 7.3 Hz, 3, CH_3 of W1Et), 1.54 (t, J = 7.3 Hz, 3, CH_3 of W2Et), 0.95 (m, 1, diastereotopic H of W2CH_2), 0.48 (m, 1, diastereotopic H of W2CH_2). Homonuclear ^{1}H-decoupling NMR (300 MHz, acetone-d_6): irradiation of the resonance at δ 0.95 changed the triplet at δ 1.54 into a doublet while the multiplet at δ 0.48 became narrower; irradiation of the triplet at δ 1.54 changed the multiplets at δ 0.95 and 0.48 into distorted doublets. The corresponding series of experiments on the other ethyl resonances gave equivalent results. ^{13}C NMR (75.5 MHz, acetone-d_6): δ 109.99 (s, d in gated decoupled spectra, $^1J_{C-H}$ = 181.3 Hz, W1(η^5-C_5H_5)), 97.12 (s, d in gated decoupled spectra, $^1J_{C-H}$ = 184.3 Hz, W2(η^5-C_5H_5)), 96.25 (s, d in gated decoupled spectra, $^1J_{C-H}$ = 183.8 Hz, W2(η^5-C_5H_5)), 31.67 (s, t in gated decoupled spectra, $^1J_{C-H}$ = 128.8 Hz, satellites with $^1J_{W-C}$ = 127 Hz, W1CH_2), 21.60 (s, q in gated decoupled spectra, $^1J_{C-H}$ = 124.3 Hz, CH_3), 18.32 (s, q in gated decoupled spectra, $^1J_{C-H}$ = 126.6 Hz, CH_3), 1.78 (s, t in gated decoupled spectra, $^1J_{C-H}$ = 125 Hz, satellites with $^1J_{W-C}$ = 59 Hz, W2CH_2). UV–vis (THF) 584 nm (ε = 3100 l mol^{-1} cm^{-1}), 320 nm (ε = 2701 mol^{-1} cm^{-1}); UV–vis (acetone) 583 nm (ε = 7400 l mol^{-1} cm^{-1}). MS (FAB, based on ^{184}W), 653 ($[W_2(\eta^5\text{-}C_5H_5)_3(CH_2CH_3)_2O_2]^+$, 53%), 359 ($[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]^+$, 100%), 343 ($[W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)]^+$, 40%) m/z, very weak (< 5%) ion at 863 ($\{[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]_2[PF_6]\}^+$) m/z; MS (FD, based on ^{184}W) 588 ($[W_2(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)_2O_2]^+$), 444, 363, 343 ($[W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)]^+$), 310 ($[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]^+$) m/z. Anal. Found (Galbraith): C, 28.46; H, 3.36; P, 3.65. $C_{19}H_{25}F_6O_2PW_2$. Calc.: C, 28.59; H, 3.16; P, 3.88%.

2.4. Synthesis of $[PMe_2Ph(C_5H_5)]I$

A stirred slurry of 0.500 g (1.9 mmol) of TlC_5H_5 in 10 ml of THF was treated with a solution of 0.23 g (0.93 mmol) of I_2 in 20 ml of THF, added dropwise at 0 °C. The reaction mixture was stirred for 30 min and filtered into a Schlenk reaction vessel pre-cooled to −78 °C. A white powder precipitated upon standing, and the resulting C_5H_5I solution was used immediately without further purification [21]. A solution of 0.154 g (1.1 mmol) of PMe_2Ph in 10 ml of THF at −78 °C was added and the reaction mixture was allowed to warm slowly (30 min) to room temperature. A whitish-yellow precipitate formed, and the yellow residue of $[PMe_2Ph(C_5H_5)]I$ was collected by filtration, rinsed with 1 × 5 ml THF, and placed under vacuum for 3 h. IR (Nujol mull) cm^{-1}: 3050 (w, C_5H_5), 3018 (vw, sh on Nujol), 1592 (w), 1568 (w, Ph), 1488 (sh), 1475 (w, sh on Nujol), 1439 (m, sh on Nujol), 1363 (w, sh on Nujol), 1352 (s), 1320 (w), 1310 (vw), 1300 (w), 1280 (vw), 1245 (vw), 1195 (vw), 1160 (w), 1122 (s), 1109 (s), 1008 (ms), 1001 (w, sh), 973 (s), 940 (s), 925 (w, sh), 885 (s), 856 (vw), 814 (m), 780 (m), 752 (s), 743 (w, sh), 711 (ms), 692 (ms), 520 (vw), 480 (s), 420 (s). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.1–7.9 (c, 2H, HC(2) of C_5H_5 + p-CH of Ph), 7.81 (m, 2H, o-CH), 7.73 (m, 2H, m-CH), 7.18 (m, 1H, HC(3) of C_5H_5), 6.84 (m, 1H, HC(4) of C_5H_5), 3.67 (m, 2H, CH_2), 2.69 (d, $^2J_{P-H}$ = 14.5 Hz, 6H, P(CH_3)$_2$); ^{31}P{1H} NMR (121.5 MHz, THF, acetone-d_6 locker tube, KPF_6 added as an internal standard): δ 14.6 (s, $[P(C_5H_5)Me_2Ph]^+$), −142.7 (septet, $[PF_6]^-$).

2.5. Synthesis of $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$ (2)

An intensely blue solution of 0.20 g (0.25 mmol) of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$ in 25 ml of acetone was maintained at 23 °C and illuminated with a 75 W General Electric high intensity sunlamp placed 20 cm away for 4.5 h, during which time the solution color bleached to a pale orange. The solution was concentrated to dryness and the residue was extracted with diethyl ether (3 × 15 and 1 × 5 ml), leaving a reddish tan solid which was shown to be $[W(\eta^5\text{-}C_5H_5)_2(CH_2{=}CH_2)H]PF_6$ (0.114 g, 0.24 mmol, 94% yield) by comparison of its ^{1}H NMR and IR spectra with those of an authentic sample. The combined colorless filtrates were concentrated to saturation and slowly cooled to −78 °C, to precipitate 0.054 g (0.17 mmol, 70% yield) of long colorless needles of $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$. IR (Nujol mull) cm^{-1}: 3100 (m, η^5-C_5H_5), 3080 (sh), 1420 (w, η^5-C_5H_5), 1370 (w, sh on Nujol), 1193 (mw), 1032 (mw), 1010 (sh), 1003 (mw), 955 (m, sh), 950 (s, W=O), 910 (sh), 905 (s, W=O), 888 (w, sh), 850 (m, C_5H_5), 830 (m, C_5H_5), 722 (w, br), 520 (w), 362 (w). ^{1}H NMR (300 MHz, benzene-d_6): δ 5.43 (s, 5H, (η^5-C_5H_5)), 2.08 (q, J = 7 Hz, 2H, CH_2), 1.93 (t, J = 7 Hz, 3H, CH_3); ^{1}H NMR (80 MHz, acetone-d_6): δ 6.54 (s, 5H, (η^5-C_5H_5)), 2.27 (q, J = 7 Hz, CH_2), 1.83 (t, J = 7 Hz,

CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 110.72 (s, (η^5-C_5H_5)), 26.46 (s, satellites with 13% total intensity, $^1J_{W-C}$ = 142 Hz, CH_2), 21.51 (s, CH_3); ^{13}C (gated decoupled) NMR (75.5 MHz, CCl_2D_2): δ 110.07 (d of quin, $^1J_{C-H}$ = 179.0 Hz, $^nJ_{C-H}$ = 6.6 Hz (n = 2,3), (η^5-C_5H_5)), 29.53 (t of q, $^1J_{C-H}$ = 129.4 Hz and $^2J_{C-H}$ = 4.9 Hz, CH_2), 21.53 (q of t, $^1J_{C-H}$ = 127.1 Hz and $^2J_{C-H}$ = 3.8 Hz, CH_3). MS (EI, based on ^{184}W) 310 [(W(η^5-C_5H_5)(CH_2CH_3)O_2]$^+$, 11%), 282 ([W(η^5-C_5H_5)O_2H]$^+$, 100%), 200 ([WO]$^+$, < 2%), 184 ([W]$^+$, < 2%) m/z. Anal. Found (Galbraith): C, 27.13; H, 3.30. $C_7H_{10}O_2W$. Calc.: C, 27.12; H, 3.26%.

2.6. X-ray diffraction study of [{W(η^5-C_5H_5)$_2$(CH_2CH_3)}(μ-O){W(η^5-C_5H_5)(O)(CH_2CH_3)}]-PF_6

Intensely colored purple-red blocks of [{W(η^5-C_5H_5)$_2$(CH_2CH_3)}(μ-O){W(η^5-C_5H_5)(O)(CH_2CH_3)}]-PF_6 suitable for X-ray analysis were grown by vapor-diffusion over 3 weeks at 0 °C in the dark of diethyl ether into a CH_2Cl_2 solution of the title compound. A crystal of dimensions 0.22 × 0.20 × 0.10 mm^3 mounted in a 0.3 mm glass capillary tube under nitrogen was used for the diffraction study. Data were collected on a Nicolet R3 diffractometer using graphite monochromatized Mo Kα radiation (50 kV, 30 mA). Data collection was controlled by the Nicolet P3 program [22] and the structure was solved and refined using SHELXTL [23]. Diffractometer data were processed with FOXTAPE, a local modification of the Nicolet program XTAPE. Empirical absorption corrections were performed by the program XEMP (Nicolet) while drawings were generated by the program SNOOPI (part of the Oxford University CHEMGRAF Suite package) [24] or by XPLOT (Nicolet). All molecular calculations were performed with the aid of the program XP (Nicolet). Atomic scattering factors were based on literature values [25]. Weights were taken as $[\sigma^2(F) + gF^2]^{-1}$. Crystal data, details of the data collection, and final agreement parameters are summarized in Table 1.

The unit cell was indexed using 15 reflections obtained from a rotation photograph. Two angles were near 90°, and a lattice determination using both the P3 program and TRACER [26] yielded a monoclinic C cell. A trial data collection revealed systematic absences which indicated the space group to be either Cc (No. 9) or $C2/c$ (No. 15). Axial photographs confirmed that only the B axis had axial symmetry. Final unit cell parameters were obtained by a least squares refinement of the angles obtained from 12 selected Friedel pairs in the range $20 \leq 2\theta \leq 30°$.

The intensities of three check reflections were measured after every 60 reflections. A minor (less than 3σ) decay was observed and a linear decay correction was applied during processing of the raw data. A semi-empirical absorption correction (based on ψ scans from eight reflections in the range $8 < 2\theta < 48°$ and optimized to yield the minimum merging R), Lorentz and polarization corrections were applied to the data.

Table 1
Crystal data, data collection parameters, and agreement factors for [{W(η^5-C_5H_5)$_2$(CH_2CH_3)}(μ-O){W(η^5-C_5H_5)(O)(CH_2CH_3)}]PF_6

Crystal data	
Molecular formula	$C_{19}H_{25}F_6O_2PW_2$
Molecular weight (g mol^{-1})	798.06
Space group	$C2/c$ (#15)
a (Å)	19.483 (4)
b (Å)	22.397 (6)
c (Å)	14.289 (3)
β (deg)	133.59 (1)
V (Å^3)	4516 (2)
Z	8
d_c (g ml^{-1})	2.35
d_o (g ml^{-1})	2.34
Data collection	
μ (cm^{-1})	105.4
T (°C)	23
λ (Å)	0.71069
Scan type	$2\theta-\theta$
Max 2θ (deg)	55
Min 2θ (deg)	3
Scan range (deg)	1.8 (symmetrical)
Scan speed (deg min^{-1})	3.5–20
Background/scan ratio	0.50
Total reflections	4430
Unique reflections ($I > 3\sigma(I)$, $F > 3\sigma(F)$)	3249
Agreement factors	
Final R (%) [a]	5.75
Final R_w (%) [b]	5.31
Number of parameters	276
Goodness of fit (GOF) [c]	1.116
g value	0.00111

[a] $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$.
[b] $R_w = \Sigma|(w)^{1/2}(F_{obs} - F_{calc})|/\Sigma|(w)^{1/2}F_{obs}|$.
[c] GOF = $[\Sigma w(|F_{obs}| - |F_{calc}|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

The average of the absolute values of $(E^2 - 1)$ was 0.98, indicating that the unit cell of the crystal is centrosymmetric [27], and the structure was therefore solved in the centrosymmetric space group $C2/c$. Examination of the Patterson map readily revealed the two tungsten positions. The PF_6^- counterions were found on two special positions (0, y,0.25 and 0, y,0.75) and were refined as fixed octahedrons, allowing the P–F distance to refine as a free variable. Blocked cascade least squares refinement of the available parameters was continued until the remaining non-hydrogen atoms were located in the difference maps. All non-hydrogen atoms were made anisotropic and allowed to refine for several cycles, then hydrogen atoms were placed in calculated positions (U_{iso}(H) = 1.2U_{iso}(C); d_{C-H} = 0.96 Å) and the refinement was continued.

It soon became apparent that considerable disorder was present in the (η^5-C_5H_5) ligand designated as C21–C25. This ligand was fixed as a planar pentagon

(d_{C-C} = 1.36 Å) and the structure was refined until it converged ($\Delta(\max)/\sigma < 0.2$) at which point these restraints were removed and the refinement was continued until convergence was achieved ($\Delta(\max)/\sigma < 0.1$). An extinction free variable was introduced which refined to zero, consistent with the lack of systematic extinction ($F_{obs} < F_{calc}$) of the most intense structure factors. The weighting scheme employed was $w = [\sigma^2(F) + gF^2]^{-1}$. The value of the F^2 multiplier was manually adjusted so that a normal probability plot [28] gave a slope as close to 1.0 as possible (1.001).

There were 19 peaks in the final difference map with electron densities greater than 1.0 e^- Å^{-3}, mostly within 1.0 Å of tungsten or associated with the methyl and PF_6^- groups. It was not possible to locate enough suitable peaks near C21–C25 or in the PF_6^- groups to attempt to model the apparent disorder and, given the overall noise level in the structure, it was felt that the effect of such modeling on the structure would have been insignificant and modeling efforts were abandoned. Final atomic coordinates, site occupancy factors (SOF), and isotropic displacement coefficients for the non-hydrogen atoms are listed in Table 2.

Table 2
Fractional atomic coordinates ($\times 10^4$), SOF, and isotropic displacement coefficients (U_{iso}; Å$^2 \times 10^3$) for the non-hydrogen atoms of [{W(η^5-C_5H_5)$_2$(CH_2CH_3)}(μ-O){W(η^5-C_5H_5)(O)(CH_2CH_3)}]PF_6

Atom	x	y	z	SOF	U_{iso}
W1	7306.2(0.5)	213.7(0.3)	2916.9(0.6)	1.0	40.4(0.4)
W2	6418.2(0.4)	1736.5(0.3)	1375.7(0.5)	1.0	31.9(0.3)
O1	7004(7)	973(5)	2423(9)	1.0	41(7)
O2	6306(9)	−185(6)	1844(13)	1.0	84(10)
P1	0	1497(2)	2500	0.5	41(4)
F11	102(7)	1494(4)	1510(8)	1.0	76(10)
F12	0	808(5)	2500	0.5	240(63)
F13	0	2183(5)	2500	0.5	260(77)
F14	1073(5)	1493(4)	3633(8)	1.0	204(18)
P2	0	1447(3)	7500	0.5	57(5)
F21	36(10)	1445(4)	8618(10)	1.0	111(16)
F22		2137(5)	7500	0.5	123(27)
F23	1099(5)	1447(4)	8509(12)	1.0	150(14)
F24	0	759(4)	7500	0.5	125(25)
C11	5010(10)	2171(8)	415(16)	1.0	56(12)
C12	5123(10)	1665(10)	1078(16)	1.0	62(11)
C13	5060(11)	1154(9)	441(17)	1.0	55(13)
C14	4964(11)	1363(9)	−564(16)	1.0	58(11)
C15	4950(11)	1964(8)	−573(14)	1.0	51(10)
C21	7780(12)	2204(12)	2143(26)	1.0	123(15)
C22	7952(19)	2036(12)	3124(22)	1.0	150(22)
C23	7405(22)	2310(13)	3223(25)	1.0	137(34)
C24	6858(15)	2676(9)	2123(29)	1.0	145(18)
C25	7116(18)	2589(11)	1471(20)	1.0	115(22)
C31	9002(12)	364(9)	4146(23)	1.0	70(17)
C32	8536(18)	131(14)	2953(25)	1.0	92(23)
C33	8244(21)	−461(16)	2910(24)	1.0	124(26)
C34	8494(14)	−555(9)	4070(20)	1.0	71(17)
C35	8953(12)	−50(9)	4812(17)	1.0	64(13)
C4	6786(11)	1231(8)	407(14)	1.0	48(11)
C5	6522(15)	1503(11)	−777(18)	1.0	73(16)
C6	7334(13)	283(9)	4455(16)	1.0	60(14)
C7	6374(16)	492(16)	3943(26)	1.0	129(25)

Tables listing the anisotropic displacement coefficients for the non-hydrogen atoms and calculated fractional coordinates and isotropic displacement coefficients for the hydrogen atoms have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis of the terminal oxo complex [W(η^5-C_5H_5)$_2$(O)(CH_2CH_3)]PF_6 (3PF_6)

The terminal ethyl oxo complex [W(η^5-C_5H_5)$_2$(O)(CH_2CH_3)]PF_6 (3PF_6) was prepared by a reaction related to that used to make the methyl oxo complex [W(η^5-C_5H_5)$_2$(O)(CH_3)]PF_6 [17,18]. This preparation involves photolysis of [W(η^5-C_5H_5)$_2$($NCCH_3$)(CH_3)]PF_6 in air, a reaction which presumably involves photodissociation of acetonitrile to generate an intermediate 16-electron methyl complex "[W(η^5-C_5H_5)$_2$(CH_3)]$^+$" which is then oxidized to the d^0 oxo complex. The analogous 16-electron ethyl intermediate is accessible by insertion of the coordinated alkene into the metal hydride linkage in [W(η^5-C_5H_5)$_2$(CH_2=CH_2)H]PF_6 (4PF_6; insertion is a process which we have previously demonstrated is rapid and reversible in room temperature solutions of this hydride [29] and of the corresponding propene complex [W(η^5-C_5H_5)$_2$(CH_2=$CHCH_3$)H]PF_6 [30]), and aerial oxidation of 4PF_6 in acetone provides access to the ethyl oxo complex 3PF_6.

We have, however, found it more convenient to prepare 3PF_6 by oxidation of 4PF_6 with mild oxidizing agents like dimethylsulfoxide and propylene oxide. Both act as sources of oxygen atoms (as confirmed in the DMSO case by observation of the characteristic odor of dimethylsulfide over the reaction mixture), and a convenient high yield route to 3PF_6 involves heating 4PF_6 with propylene oxide in acetone for several hours and then pumping away the volatiles to yield pure 3PF_6.

The ethyl oxo complex 3PF_6 forms a pale yellow microcrystalline solid which is light-, air- and water-stable. It is stable for months in acetone, acetonitrile, or dimethylsulfoxide solution and does not react with I_2, dilute acids, or methylfluorosulfonate.

^{1}H and ^{13}C NMR spectra established the presence of the (η^5-C_5H_5) ligands and of the metal bound ethyl group (^{183}W satellites were observed on the carbon resonance of the methylene group with $^1J_{W-C}$ = 77 Hz). The presence of an oxo group is established by the FAB mass spectrum of the salt, which contains the molecular ion corresponding to [W(η^5-C_5H_5)$_2$(O)(CH_2CH_3)]$^+$. The stoichiometry of the salt was confirmed by combustion analysis, and formulation as a monomer (rather

than a dimer with two bridging oxo groups) is supported in the solid state by the presence of a strong IR band in Nujol mulls at 885 cm^{-1} which can be assigned to a terminal oxo group and in solution by a determination of the molecular weight in dimethylformamide as 237 g mol^{-1} (predicted value for a monomer 252 g mol^{-1}, predicted value for a dimer 336 g mol^{-1}).

Attempts to grow crystals of $\mathbf{3}PF_6$ suitable for an X-ray diffraction study were unsuccessful. Approaches examined included recrystallization from acetone–ether (layer and vapor diffusion), acetonitrile–ether (layer), and slowly cooled acetone and THF solutions. Similarly unsuccessful attempts to grow crystals of the PF_6^- salt of the corresponding methyl complex $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_3)]^+$ were circumvented by metathesis to form a crystallizable iodide salt [17], but this strategy was unsuccessful with $\mathbf{3}^+$ since the PF_6^- and I^- salts of $\mathbf{3}^+$ have nearly identical solubilities.

3.2. Reaction of $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ with PMe_2Ph: preparation, structural characterization and formulation of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$

The terminal oxo complex $\mathbf{3}^+$ reacts readily with PMe_2Ph in THF. The reaction has a distinct induction period of between a few seconds and 1 min before an intense blue color develops. The solution then deposits intensely colored red-purple platelets; precipitation is completed by addition of diethyl ether and the material is recrystallized from acetone–diethyl ether. The compound is light and heat sensitive, and decomposes rapidly in nucleophilic solvents such as acetone, acetonitrile, dimethylsulfoxide, and water. Solutions in THF and CH_2Cl_2 are stable in the dark, but cannot be heated above room temperature without significant decomposition.

The ^1H and ^{13}C NMR spectra of the material established that the new compound contained cyclopentadienyl ligands with three distinct chemical shifts (as confirmed at the field strength of an 80 MHz spectrometer as well as that of the 300 MHz instrument for which data are reported) and two distinct ethyl ligands, both of which had diastereotopic methylene groups. It was improbable that such a diversity of ligand environments could arise from a mononuclear structure, and a single crystal X-ray diffraction study was undertaken, as described in Section 2.6, to determine the structure of the complex. This established that the complex is $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)\text{-}CH_2CH_3)\}]PF_6$ ($\mathbf{1}PF_6$), formed in 91% yield, with the molecular structure shown in Fig. 1 in which two tungsten centers are connected by a bent oxo bridge. Selected bond lengths and angles are listed in Tables 3 and 4 respectively; Table 4 also includes some angles involving vectors from the metal centers to the ring centroids to clarify the geometries of the metal centers.

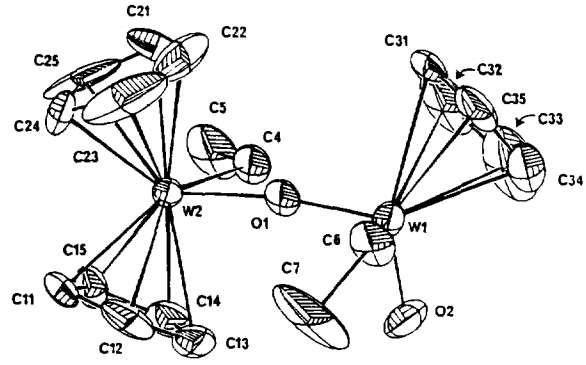


Fig. 1. Molecular structure of the $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]^+$ cation (50% probability ellipsoids; hydrogen atoms have been omitted for clarity).

The tungsten centers in $\mathbf{1}^+$ have an average oxidation state of +1 and it was initially unclear how to interpret the bonding in the complex, particularly since the electronic absorption of $\mathbf{1}^+$ at 583 nm is reminiscent (albeit at somewhat lower energy) of the bands in the range of 500 to 520 nm which are a characteristic feature of d^1–d^1 metal dimers connected by a linear oxo bridge which spin pairs the metal centers [17,18,31]. A similar interpretation of the bonding in $\mathbf{1}^+$ would not, however, be consistent with the bend in the oxo bridge (W1–O1–W2 = 164(1)°), and is ruled out by the marked asymmetry in the lengths of the $W\text{–}O_{bridging}$ bond lengths with W1–O1 = 1.78(1) Å and W2–O1 = 2.03(1) Å.

This asymmetry in the bridge argues in favor of a mixed valence interpretation in which W1 is a d^0/W(VI) center with a double bond to the bridging oxo ligand, which is acting as a donor ligand to W2, a d^2/W(IV) center as shown in Scheme 1. The remaining oxygen atom is then a conventional terminal oxo ligand with a triple bond to a W(VI) center, as supported by comparison of the W1–O2 bond length of 1.68(1) Å with the average value of 1.700 Å calculated for such bonds in a recent statistical analysis of metal–oxygen multiple bond lengths [32]; the observed bond length is well within a

Table 3
Selected bond lengths (Å) within $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$

W1–C31	2.47(2)	W2–C11	2.27(2)	W2–C21	2.31(3)
W1–C32	2.37(4)	W2–C12	2.26(2)	W2–C22	2.31(2)
W1–C33	2.38(4)	W2–C13	2.37(2)	W2–C23	2.31(3)
W1–C34	2.40(2)	W2–C14	2.36(1)	W2–C24	2.24(2)
W1–C35	2.45(1)	W2–C15	2.28(1)	W2–C25	2.29(3)
C11–C12	1.39(3)	C21–C22	1.25(5)	C31–C32	1.37(4)
C12–C13	1.41(3)	C22–C23	1.31(6)	C32–C33	1.43(5)
C13–C14	1.39(4)	C23–C24	1.40(4)	C33–C34	1.38(5)
C14–C15	1.35(3)	C24–C25	1.35(6)	C34–C35	1.38(3)
C15–C11	1.41(4)	C25–C22	1.26(3)	C35–C31	1.38(4)
W1–C6	2.17(4)	W1–O1	1.78(1)	W1–O2	1.68(1)
W2–C4	2.25(3)	W2–O1	2.03(4)		
C6–C7	1.54(4)	C4–C5	1.52(4)		

Table 4
Selected bond angles (deg) within $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$

W1–C6–C7	112(2)	O2–W1–C6	100(1)	O–W1–C6	96(1)
W2–C4–C5	119(2)	O2–W1–O1	107(1)	O–W2–C4	77(1)
W1–O1–W2	164(1)				
C11–C12–C13	109(2)	C21–C22–C23	112(3)		
C12–C13–C14	106(2)	C22–C23–C24	101(4)		
C13–C14–C15	110(2)	C23–C24–C25	110(3)		
C14–C15–C11	109(2)	C24–C25–C21	104(3)		
C15–C11–C12	106(2)	C25–C21–C22	113(4)		
C31–C32–C33	108(3)	C32–C33–C34	107(3)		
C33–C34–C35	108(3)	C34–C35–C31	110(2)		
C35–C31–C32	108(2)				
Cp1 [a]–W2–C4	104	Cp3 [a]–W1–O1	120		
Cp2 [a]–W2–C4	104	Cp3–W1–O2	123		
Cp1–W2–O1	108	Cp3–W1–C6	106		
Cp2–W2–O1	106				
Cp1–W2–Cp2	139				

[a] Cp1 is the centroid of the cyclopentadienyl ligand containing C11 to C15. Cp2 and Cp3 are similarly defined for C21 to C25 and C31 to C35 respectively.

standard deviation (0.05 Å) of the average value. The terminal oxo ligand gives rise to an IR stretching absorption at an unexceptional frequency of 850 cm^{-1}, but no bands in the 200–800 cm^{-1} region can be unambiguously assigned to the W–O–W group.

If the bonding interpretation in Scheme 1 is correct, the W1–O1 and W2–O1 bond lengths should be close to W/O double and single bonds respectively, but it is difficult to find sets of comparison data which themselves represent unambiguous bonding situations. One approach to identifying simple metal/O double bonds without π-donor contributions has been suggested by Mayer and co-workers [32], who pointed out that factrioxo complexes should have simple double bonds because the d_{xy}, d_{xz}, and d_{yz} orbital are locked up in the π bonding framework, and some crystallographically characterized examples of such complexes have recently become available [33–36]. One of the structures (that of $[WO_3$(1,4,7,-triazacyclononane-*N*,*N*′,*N*″)] [33] contains one anomalously long W=O bond (1.851 Å), differing by more than 4σ from other members of the set, and data from this structure have been treated as outliers and excluded from statistical analysis [37]; this leaves a set of 21 experimentally determined W=O bond lengths which average 1.758 Å (standard deviation 0.014 Å). The significance of this average is restricted since the structures cover a limited set of ligand environments, but these are weighted towards environments related to the mono-cyclopentadienyl side of $\mathbf{1}^+$ since no less than 12 of the values derive from structural studies of three different salts of $[WO_3(\eta^5\text{-}C_5Me_5)]^-$ [36]. This average W=O bond length is surprisingly long relative to the value of 1.726 Å (standard deviation 0.041 Å) for the corresponding Mo distance, but is remarkably close to the W1–O1 bond length of 1.78(1) Å. This agreement provides strong support for formulation of W1–O1 as a double bond.

The problems with identifying an appropriate set of comparison data are even more severe in the case of the W2–O1 bond, since no obvious structural models such as η^1-ketone complexes of tungsten have been reported, but in this case we can make an internal comparison with the W–alkyl bond length of 2.25(3) Å. Two corrections can be used to derive a prediction of the W–O single bond length in this environment; both treat the interaction as a covalent bond, and one is subtraction of 0.098 Å to correct for the difference in the covalent radii of C and O (this is the difference between average C_{sp^3}–C_{sp^3} and C_{sp^3}–O bond lengths) [38], and the second involves subtraction of an additional 0.058 Å as an estimate of the probable difference in the covalent radii of sp^3 and sp O (this was done because of the 164.4° bond angle at O1; the value corresponds to the difference between average C_{sp^3}–C_{sp^3} and C_{sp^3}–C_{sp} bond lengths). Comparison of the predicted W–O single bond length of 2.09 Å with the experimental W2–O1 length of 2.03(1) Å establishes that this is essentially a single bond, but that it may be somewhat shortened, suggesting that the interaction is supplemented by some π-donation from O1. The bond is, however, much longer than the average W=O double bond (1.758 Å; see above) and is also much longer than the 1.70(1) Å terminal W=O bond in the closely related cationic tungstenocene oxo complex $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_3)]^+$ [17]. Interestingly, the W2–O1 bond length is remarkably close to that predicted by an extremely simple model in which the W^{4+} and O^{2-} ionic radii [39] are summed to give a predicted bond length of 2.01 Å.

Formulation of W2 as a W(IV) center is further supported by the observed O1–W2–C4 bond angle of 77°; this is in the range previously established to be characteristic of d^2 tungstenocene complexes as a consequence of the steric influence of the non-bonding pair of electrons, and is below the range characteristic of d^0

tungstenocene complexes (72 to 82° for d^2 complexes, 85 to 94° for d^1 complexes, and 94 to 105° for d^0 complexes [40,41]). The steric influence of the non-bonding pair of electrons on W2 may also be responsible for the large W2–C4–C5 bond angle of 118(2)°, which is indistinguishable from the 117(1)° value for the corresponding angle in the d^2 ethyl complex $[Mo(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)Cl]$ [40].

Formulation of $\mathbf{1}^+$ as a W(VI)–W(IV) oxo-bridged dimer allows it to be classified as an asymmetric (i.e. with a difference in oxidation states greater than one) homonuclear inner sphere mixed valence compound [42]. There is a heavy emphasis in the extensive mixed valence literature of the past 30 years on symmetric homonuclear complexes, particularly those containing Ru(II) and Ru(III) [43], but there are also many classic examples of asymmetric systems ranging back as far as Werner's observations of intense colors in systems containing both Pt(IV) and Pt(II) ([44] as discussed in Ref. [42]). More recently, the extensive development of the synthetic chemistry of higher nuclearity coordination and organometallic complexes has provided a wide range of other examples of both asymmetric and symmetric mixed valence complexes, in many of which the valencies are trapped because the two metal centers differ in their ligand environment (as in the present case) and in some of which the metals are connected by bridging oxides. Nevertheless, a thorough recent review of mixed-valence complexes of the early transition metals [45] identified only one other class containing W(IV) and W(VI) centers. In this group of complexes the metal centers are connected by two bridging sulfides, and examples include two interesting dimers prepared by Green and co-workers by reaction of $[Cp_2WCl_2]$ ($Cp = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5H_4Me$) with WS_4^{2-} to give $[Cp_2W^{IV}(\mu\text{-}S)_2W^{VI}S_2]$ complexes [46] and some related trimers with $[S_2W(\mu\text{-}S)_2WE(\mu\text{-}S)_2WS_2]^{2-}$ cores [47]. Interesting structural comparisons can also be made with $[\{W(\eta^5\text{-}C_5Me_5)(CO)_3\}\{W(\eta^5\text{-}C_5Me_5)(O)_2\}]$ [48], a W(I)–W(V) dimer with a metal–metal bond; the average WO bond length of 1.73(2) Å in this dimer, for example, is intermediate between the two W1–O bond lengths in $\mathbf{1}^+$ since there will be some π-donation from both oxygen atoms to the tungsten center.

There is some evidence in the structural parameters that the metal centers are somewhat sterically congested. For example, the angle between the W2–O1 vector and the plane defined by W2 and the centroids of its two cyclopentadienyl ligands is 32.2° while the corresponding W2–C4 angle is 44.9°, suggesting a shifting of W2 and O1 towards the open end of the W2 sandwich to minimize steric interactions between the cyclopentadienyl ligands on W2 and the substituents on W1.

A number of features of $\mathbf{1}^+$ could give rise to electronic transitions in the visible region of the spectrum, including d–d transitions on W2, MLCT transitions involving W2, and LMCT transitions involving W1, but we prefer to assign the strong absorbance of $\mathbf{1}^+$ at 583 nm to a metal to metal charge transfer (MMCT) transition. A definitive assignment would require more detailed spectroscopic work than we have undertaken, but there is nothing resembling this feature in the spectra of cationic $[W(\eta^5\text{-}C_5H_5)_2(L)X)]^+$ complexes in which the metal centers resemble W2 (e.g. $\mathbf{4}^+$ is colorless, $[W(\eta^5\text{-}C_5H_5)_2(PMe_2Ph)(CH_3)]^+$ is orange [49], $[W(\eta^5\text{-}C_5H_5)_2(NCCH_3)(CH_3)]^+$ is orange-brown [17]), nor in the spectrum of free $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$ (colorless—see below). MMCT transitions are one of the most distinctive features of mixed valence complexes [4] [42], and the association of the 583 nm absorbance of $\mathbf{1}^+$ with the presence of both the W(IV) and W(VI) centers offers a strong argument for a significant MMCT component in the transition from which it arises. This assignment would establish $\mathbf{1}^+$ as a Class II mixed valence complex [50].

3.3. Comments on NMR spectra of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$

Both tungsten centers in $\mathbf{1}^+$ approximate tetrahedral geometries: in addition to the shared oxo ligand the coordination sphere of W1 is completed by two η^5-cyclopentadienyl ligands and an ethyl group while that of W2 is completed by one η^5-cyclopentadienyl ligand, a terminal oxo group, and a second ethyl group. This renders the monocyclopentadienyl tungsten center chiral, and provided exchange of the bridge and terminal oxo ligands on W1 is slow on the NMR time scale, the prochiral cyclopentadienyl ligands on W1 and the hydrogens in both methylene groups will be diastereotopic, as is observed in both ^1H and ^{13}C NMR spectra.

The pair of cyclopentadienyl resonances in ^1H spectra at δ 5.76 and 5.56 are assigned to the diastereotopic cyclopentadienyl ligands on W2; they are at the lower field end of the region in which we have previously observed cyclopentadienyl resonances of cationic d^2 bent tungstenocene complexes (e.g. see Refs. [17,30,49]) and have a separation similar to the chemical shift differences that we have previously observed between diastereotopic cyclopentadienyl resonances in such complexes (cf. δ 5.62 and 5.55 in acetone-d_6 for the endo isomer of $[W(\eta^5\text{-}C_5H_5)_2(CH_2CHCH_3)H]^+$ [30]; cyclopentadienyl resonances of cationic d^2 bent tung-

[4] These are also commonly termed intervalence transfer (IT) or intervalence charge transfer (IVCT) transitions. We prefer MMCT in the present context because of the differing ligand environments at the two metal centers.

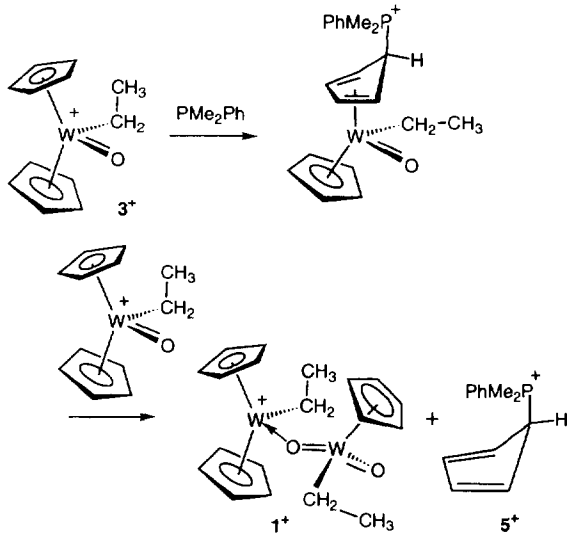
stenocene complexes range from this region up ca. δ 5, as in the δ 5.12 resonance of $[W(\eta^5\text{-}C_5H_5)_2(PMe_2Ph)(CH_3)]^+$) [49]. The resonance at δ 6.72 is assigned to the cyclopentadienyl ligand on W1; this low field position is similar to that of the cyclopentadienyl ligand of **2** in acetone-d_6 (δ 6.54).

Selective decoupling experiments (see Section 2.3) established that the lower field pair of resonances arising in ^{1}H spectra from diastereotopic methylene hydrogens (average δ 2.36) were bonded to each other and to the lowest field CH_3 resonance (δ 1.85), and these were assigned to the ethyl ligand on the mono-cyclopentadienyl end of the molecule (cf. δ 2.27 and 1.83 for the CH_2 and CH_3 resonances of **2**). The remaining pair of resonances arising from diastereotopic methylene hydrogen resonances (average δ 0.72) and the corresponding methyl resonance (δ 1.54; the connectivity was again confirmed by selective decoupling) were assigned to the ethyl group on the tungstenocene end of the molecule (cf. δ 1.34 and 0.90 for $[W(\eta^5\text{-}C_5H_5)_2(NCCH_3)(CH_2CH_3)]^+$ in acetonitrile-d_3 [51]). The strong parallels between the ^{1}H spectra of **2** and of the W1 ligands in $\mathbf{1}^+$ suggested that the ^{13}C shifts of the methylene and methyl resonances in **2** (δ 26.5 and 21.5) could be used as the basis for assignment of the ^{13}C resonances of $\mathbf{1}^+$ with the appropriate ^{1}H couplings at δ 31.7 and 21.6 to $W1CH_2CH_3$, leaving the remaining methylene and methyl resonances at δ 1.8 and 18.3 to be assigned to $W2CH_2CH_3$.

3.4. Mechanism of the conversion of $[W(\eta^5\text{-}C_5H_5)_2(O)(CH_2CH_3)]PF_6$ into $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]PF_6$

The loss of a cyclopentadienyl ligand during the conversion of $\mathbf{3}^+$ to $\mathbf{1}^+$ is most unusual. We have, however, recently reported some examples of the preparation of tungstenocene derivatives with functionalized cyclopentadienyl ligands in which the first step was addition of a nucleophile to a cyclopentadienyl ligand in the cationic tungstenocene complex $[W(\eta^5\text{-}C_5H_5)_2(SEt_2)Br]^+$ to give a complex with a reactive cyclopentadiene ligand [52]. Those reactions involved anionic nucleophiles, but $\mathbf{3}^+$ should be even more electrophilic than $[W(\eta^5\text{-}C_5H_5)_2(SEt_2)Br]^+$ since it contains a highly electronegative oxo ligand and also contains d^0 W(VI) rather than d^2 W(IV); formation of $\mathbf{1}^+$ could reasonably involve initial nucleophilic addition of PMe_2Ph to a cyclopentadienyl ligand in $\mathbf{3}^+$ to give a transient cyclopentadiene ligand which is then displaced by the (relatively) nucleophilic oxo ligand of a second equivalent of $\mathbf{3}^+$ to give the observed product (Scheme 2).

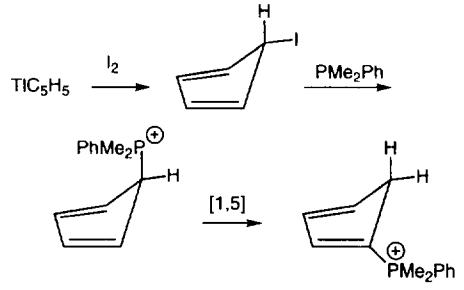
Monitoring of the reaction of $\mathbf{3}^+$ with excess PMe_2Ph in acetone-d_6 by ^{1}H NMR provided no evidence for the formation of identifiable intermediates in the reaction.



Scheme 2.

Cations $\mathbf{1}^+$ and $\mathbf{3}^+$ were the only cyclopentadienyl tungsten complexes observable by ^{1}H NMR, indicating that the intermediate cyclopentadiene complex does not persist under the reaction conditions. Dissociation of the cyclopentadiene ligand is unusual but reasonable; in most cases in which we have previously proposed the formation of intermediate cyclopentadiene ligands the endo-hydride then migrates to the metal center, but, unlike the present case, those reactions all involve an oxidizable d^2 tungsten center. The cyclopentadiene ligand in the intermediate in Scheme 2 would also be expected to be more substitutionally labile in a d^0 species than in the isolable d^4 cyclopentadiene complex $[W(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5CCl_3)(CO)Cl]$ [53] because of the absence of back donation from the metal center into the diene π-acceptor orbitals.

Support for the mechanistic sequence proposed in Scheme 2 was obtained by monitoring the reaction of $\mathbf{3}^+$ with excess PMe_2Ph in acetone-d_6 by ^{31}P NMR. The spectra contained resonances assignable to excess PMe_2Ph (s, δ −44.8) and PF_6^- (septet, δ −142.7) together with a singlet at δ 14.6. This was tentatively assigned to the cyclopentadiene-substituted phosphonium salt $[P(C_5H_5)Me_2Ph]^+$ ($\mathbf{5}^+$) as confirmed by independent synthesis of $\mathbf{5}^+$ from thallium cyclopentadienide via C_5H_5I, as shown in Scheme 3 and described in Section 2.4. The material is not stable in solution for more than a few hours, and attempts to isolate the PF_6^- salt by exchanging the iodide with $AgPF_6$, $TlPF_6$ or aqueous KPF_6 resulted in decomposition. Spectroscopic characterization of **5I** did, however, establish (^{1}H NMR) that the sequence in Scheme 3 had led to $\mathbf{5}^+$, although the isomer of $\mathbf{5}^+$ anticipated from addition of C_5H_5I to PMe_2Ph, in which the P is attached to the sp^3 carbon in the ring, had isomerized to an isomer with P on an sp^2 carbon. The observed isomer is likely to be the more



Scheme 3.

stable, and could readily be formed from the anticipated kinetic product by a suprafacial 1,5 sigmatropic shift which is symmetry allowed and which should be facile in this cyclic hydrocarbon [54]. The same isomer is the only phosphorus-containing product of the reaction of 3^+ with PMe_2Ph (^{31}P NMR) in strong support of the proposal in Scheme 2.

3.5. Thermolysis and photolysis of $[\{W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)\}(\mu\text{-}O)\{W(\eta^5\text{-}C_5H_5)(O)(CH_2CH_3)\}]\text{-}PF_6$; synthesis of $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$ (2)

Acetone and acetonitrile solutions of 1^+ decompose upon standing to 4^+ and $[W(\eta^5\text{-}C_5H_5)(O)_2(CH_2CH_3)]$ (**2**). The rates of conversion are slow ($t_{1/2}$ ca. 24 h) when the solutions are left at ambient temperatures in the dark, but are rapid when the solutions are illuminated with a sunlamp. The products are easily separated by removal of the solvent and trituration of **2** into diethyl ether to leave insoluble $4PF_6$. The alkene hydride was characterized by comparison of ^1H NMR and IR spectra with those of an authentic sample, and these techniques did not identify the presence of any other materials (although the red color indicates the presence of minor impurities; pure 4^+ is colorless).

Pure samples of **2** were obtained as long colorless needles in ca. 70% yield by slow cooling of a saturated diethyl ether solution to −78 °C. NMR spectra contained features diagnostic of the presence of the cyclopentadienyl ligand and the tungsten-bound ethyl group within **2**. Bands assignable to symmetric and antisymmetric absorptions of the two terminal oxo ligands were observed at 950 and 905 cm^{-1}, consistent with formulation as a monomer rather than an oxo-bridged dimer. The molecular ion was observed in EI mass spectra (11% intensity), although the most intense ion is that corresponding to $[W(\eta^5\text{-}C_5H_5)(O)_2H]^+$, the product of β-elimination of ethylene from 2^+. The complex is analogous to two other $[W(\eta^5\text{-}C_5R_5)O_2(alkyl)]$ oxo alkyls for which monomeric structures have been established crystallographically [15,55].

Complex **2** is remarkably stable. It is air-, light-, water-, and heat-stable, and does not react with dilute acid or PMe_2Ph at room temperature. It is particularly notable that it shows no tendency towards β-elimination of ethylene despite its formally 16-electron nature: this reflects both the d^0 nature of the metal center, which could not contribute to β-elimination by back-donation to an incipient alkene ligand, and the importance of π-donation from the terminal oxo ligand in reducing unsaturation at the metal center.

Photolysis to give **2** and 4^+ is entirely consistent with formulation of 1^+ as a complex in which **2** acts as a donor ligand to the 16-electron "$[W(\eta^5\text{-}C_5H_5)_2(C_2H_5)]^+$" cation. Photodissociation of **2** from 1^+ is then photodissociation of a donor ligand from a $[W(\eta^5\text{-}C_5H_5)_2(L)R]^+$ complex, a process which we previously observed in related complexes like $[W(\eta^5\text{-}C_5H_5)_2(NCCH_3)(CH_3)]^+$ [17], and this is followed by rapid β-elimination within the coordinatively unsaturated ethyl cation to form 4^+.

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