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# Reductive carbonylations reactions of primary phosphine mono-$\eta$-cyclopentadienyltungsten (V) compounds [☆]

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## Abstract

The new tungsten (IV) compounds $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(P)(CO)]$ (where $P = H_2PC_3H_5$, $H_2PC_2H_3$ or $PMe_3$) have been prepared from the corresponding tungsten (V) compounds $[W((\eta\text{-}C_5H_4{}^iPr)Cl_4(P)]$ by treatment with $[Fe_2(CO)_9]$ The crystal structures have been determined for the W(IV) compounds with $P = H_2PC_2H_5$ and $PMe_3$.

*Keywords:* Tungsten; Cyclopentadienyl; Phosphines; Carbonyl; Chloride; X-ray diffraction

## 1. Introduction

We have recently reported the synthesis of the paramagnetic tungsten (V) compounds $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(P)]$ ($P = H_2PC_3H_5$ **1** or $H_2PC_2H_3$ **2**) [1]. We have since studied their reactions, and report here an interesting reductive carbonylation reaction with $[Fe_2(CO)_9]$.

## 2. Results and discussion

The compounds $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(H_2PC_3H_5)]$ **1** and $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(H_2PC_2H_3)]$ **2**, were treated with a 1 molar equivalent of $[Fe_2(CO)_9]$ in THF at room temperature; the mixtures turned from green to dark red, and after ca. 20 min orange precipitates separated. Extraction of these into dichloromethane led to isolation of the compounds $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(H_2PC_3H_5)(CO)]$ **3** and $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(H_2PC_2H_3)(CO)]$ **4** as orange microcrystals (Scheme 1). The analytical and spectroscopic data for **3** and **4** are given in Table 1. The IR spectrum of **3** showed characteristic bands at 2398, 1654, and 2015 $cm^{-1}$ assignable to $\nu$(P–H), $\nu$(C=C) and $\nu$(CO), respectively. The corresponding bands for **4** appeared at 2369, 1635 and 2007 $cm^{-1}$, respectively. Both the NMR and the microanalysis indicated the presence of ca. 1/3 of a molecule of THF in **3**. The coupled $^{31}P$ NMR spectra of **3** and **4** showed triplets centered at −42.9 ppm, ($^1J(^{31}P\text{–}^1H)$ 370 Hz) and −43.75 ppm, ($^1J(^{31}P\text{–}^1H)$ 409 Hz), respectively, confirming that two hydrogens remain bound to the phosphorus atoms.

Single crystals of **3** were obtained from $CH_2Cl_2$. The molecular structure of **3** was determined and is shown in Fig. 1. Selected distances and angles are given in Table 2. The most striking feature is that the phosphine ligand occupies an equatorial position and is *cis* to the carbonyl group, whereas in the starting material $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(H_2PC_3H_5)]$ **1** it occupies the axial position. The structure of **3** is discussed further below.

Treatment of **1** with $[Fe_2(CO)_9]$ in toluene or dichloromethane did not yield **3** and this suggests that $[Fe(CO)_4(THF)]$ is the active species in the formation of **3**. It seems likely that a driving force for the reductive carbonylation of **1** is provided by the formation of strong Fe–Cl bonds: a related dehalogenation reaction was used by Pettit et al. to prepare $[Fe(\eta\text{-cyclobutadiene})(CO)_3]$ [2]. The formation of **3** in THF was monitored by IR spectroscopy. Initially a transient band at ca. 1650 $cm^{-1}$ was observed that may indicate the presence of an intermediate with a Fe–CO–W bridge.

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[☆] Dedicated to Professor Fausto Calderazzo in recognition of his outstanding contributions to inorganic chemistry.

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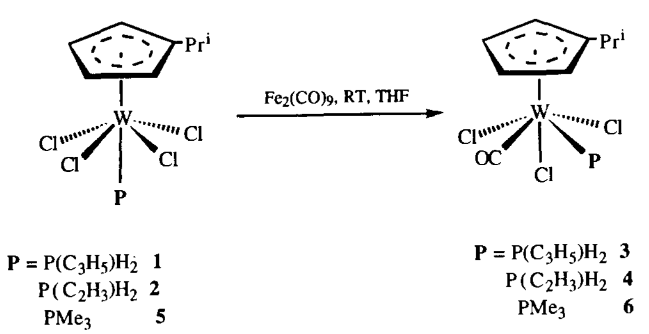

Scheme 1.

Treatment of $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4(PMe_3)]$ **5**, prepared from $[W(\eta\text{-}C_5H_4{}^iPr)Cl_4]$ and $PMe_3$, with $[Fe_2(CO)_9]$, using the same conditions as described above for **3**, gave $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(PMe_3)(CO)]$ **6** in ca. 20% yields, showing that the presence of the unsaturated C=C groups on the primary phosphine ligands is not essential for the reductive carbonylation reaction.

The compound **6** exhibits spectroscopic characteristics similar to those of **3** and **4**. A single crystal of **6** suitable for X-ray diffraction was obtained from a saturated solution in dichloromethane and the crystals retained a $CH_2Cl_2$ molecule of crystallisation. The molecular structure of **6** is given in Fig. 2 and selected interatomic distances and angles are listed in Table 3.

The geometrical features of the compounds **3** and **6** are very similar. In both of them the tungsten atom have a significantly distorted octahedral coordination, with two *cis*-Cl ligands and a CO and a phosphine ligand in the pseudo-equatorial plane and with the $C_5$-ring centroid (CEN) *trans* to the Cl ligand (Cl(3) in **3** and Cl(1) in **6**). The corresponding CEN–W–Cl angles are 170.9 and 171.2°. The distortions from the ideal angles (90 and 180°) range from 1.2–29.2 for **3** and 0.1–30.9° for **6**. The tungsten atom is displaced out of the equatorial plane towards the $C_5$-ring, by 0.56 Å for **3** and by 0.57 Å for **6**. This reflects the steric pressure of the $C_5$-ring on the equatorial ligands. There is a close contact (3.238(6) Å) between Cl(1) and C(10) of the isopropyl group of **3**; this compares with the sum of the relevant van der Waals radii of 3.50 Å [3]. This close contact may contribute to the displacement of 0.18 Å of the isopropyl group from the plane of the $\eta$-$C_5$-ring and away from the tungsten.

The cyclopentadienyl rings are approximately coplanar with the equatorial plane; the corresponding dihedral angles are 10.1° for **3** and 8.5° for **6**. It is noteworthy that, in contrast to **3** and **6**, in the related molecules $[W(\eta\text{-}C_5Me_4Et)Cl_4(H_2PC_3H_5]$ [1] **7** and $[W(\eta\text{-}C_5Me_5)Cl_4(H_2PPh)]$ **8** [4] the phosphine ligand occupies the *trans*-position relative to the $C_5$-ring. This may be attributed to the greater bulk of the $C_5Me_4Et$ and the $C_5Me_5$ ligands compared with the $C_5H_4{}^iPr$ ligand. Indeed, owing to the greater intramolecular steric pressure, the W–CEN distance is elongated from 2.005 Å to 2.003 Å in **3** and **6** to 2.081 Å in **7**, whereas the displacement of the tungsten atom in **9** is increased to 0.64 Å. We note that in **6** the $PMe_3$ ligand lies essentially *trans* to the isopropyl group whilst the smaller allylphosphine in **3** adopts a near *cis* orientation.

The W–P distances of 2.472(1) Å in **3** and 2.542(1) Å in **6** are well within the wide range of 2.422(2)–2.564(5) Å observed for the mononuclear octahedral tungsten complexes [1,4–6]. Considerable shortening of the W–P bond in **3** in comparison with the values of 2.554(2) Å in **7** and 2.569(5) Å in **8** may be attributed, at least in part, to the *trans* influence of the Cl-ligand

Table 1
Analytical and spectroscopic data

| Compound and analysis (%) | NMR data [a] |
|---|---|
| **3** $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(P(C_3H_5)H_2)(CO)]$.<br>1/3THF [b]<br>Orange<br>C 30.7 (30.6)<br>H 3.9 (3.9)<br>Cl 20.0 (20.3) | $^1H$ NMR: 5.95 (m, 1H, =C*H*R), 5.30 (m, 2H *H*$_2$C=CHR), 4.60 (d, 2H, $C_5H_4$, 4.15 (d, 2H, $C_5H_4$), 3.17 (m, 1H, C*H*$_2$P), 2.95 (sp, 1H, Me$_2$C*H*), 1.3 (q, 6H, (C*H*$_3$)$_2$CH), and bands due to THF<br>$^{31}P$: −42.9 (t, $^1J(^{31}P–^1H)$, 370 Hz) |
| **4** $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(P(C_2H_3)H_2)(CO)]$ [cd]<br>Orange | $^1H$: 6.0 (m, 1H, H$_2$C=C*H*R), 5.4 (m, 2H, *H*$_2$C=CHR), 4.65 (c, 2H, $C_5H_4{}^iPr$), 4.3 (c, 2H, $C_5H_4{}^iPr$), 2.95 (sept, 1H, Me$_2$C*H*), 1.3 (app. q, 2H, (C*H*$_3$)$_2$CH)<br>$^{31}P$: −43.7535 (t, $^1J(^{31}P–^1H)$ 409 Hz) |
| **6** $[W(\eta\text{-}C_5H_4{}^iPr)Cl_3(PMe_3)(CO)]$ [e]<br>Red-brown | $^{31}P$ NMR: −24.318 |

[a] NMR data given as: chemical shift ($\delta$ ppm) [multiplicity, relative intensity, assignment]. In $CD_3CN$.

[b] Ir ($cm^{-1}$). 2398 br ($\nu$ P–H), 2015 w,sh ($\nu$ CO), 1654s ($\nu$ C=C).

[c] Ir ($cm^{-1}$) 2369 w, sh ($\nu$ P–H), 2007 br ($\nu$ CO), 1635 s ($\nu$ C=C).

[d] Satisfactory analysis not obtained due to sensitivity in air.

[e] Ir ($cm^{-1}$): 2015 s ($\nu$ CO). Satisfactory analysis not obtained due to loss of $CH_2Cl_2$.

in the former compound (the shortening of the W–P bond *trans* to the chlorine of 0.03–0.06 Å is common for tungsten compounds [6]. Steric effects have also been used to account for the lengthening of the W–P bond to 2.629(6) Å in $[W(PPh_3)_2Cl_4]$ [7] and 2.686(4) Å in $[W(CO)_5P^tBu_3]$ [8] compared with 2.516(2) Å in $[W(CO)_5PMe_3]$ [9].

The W–Cl bond lengths of 2.448–2.489(1) Å, av. 2.565 Å in **3** and 2.467–2.469(1) Å in **6** are significantly longer than the corresponding values of 2.3200–2.410 Å found for the molecules **7**, **8**, $[W(PH_2{}^tBu)_2Cl_4]$ [4] and $[W(PPh_3)_2Cl_4]$ [7], which have four chlorine substituents. However, they are similar to those found for tungsten complexes with three or fewer chlorine ligands [5,6,10].

In conclusion we have described the reductive carbonylation of tungsten (V) monomers to the tungsten (IV) compounds by treatment with $[Fe_2(CO)_9]$. This reaction, shown in the scheme, provides an entry to the study of the relatively poorly explored chemistry of the η-cyclopentadienyl trichloridetungsten (IV) complexes.

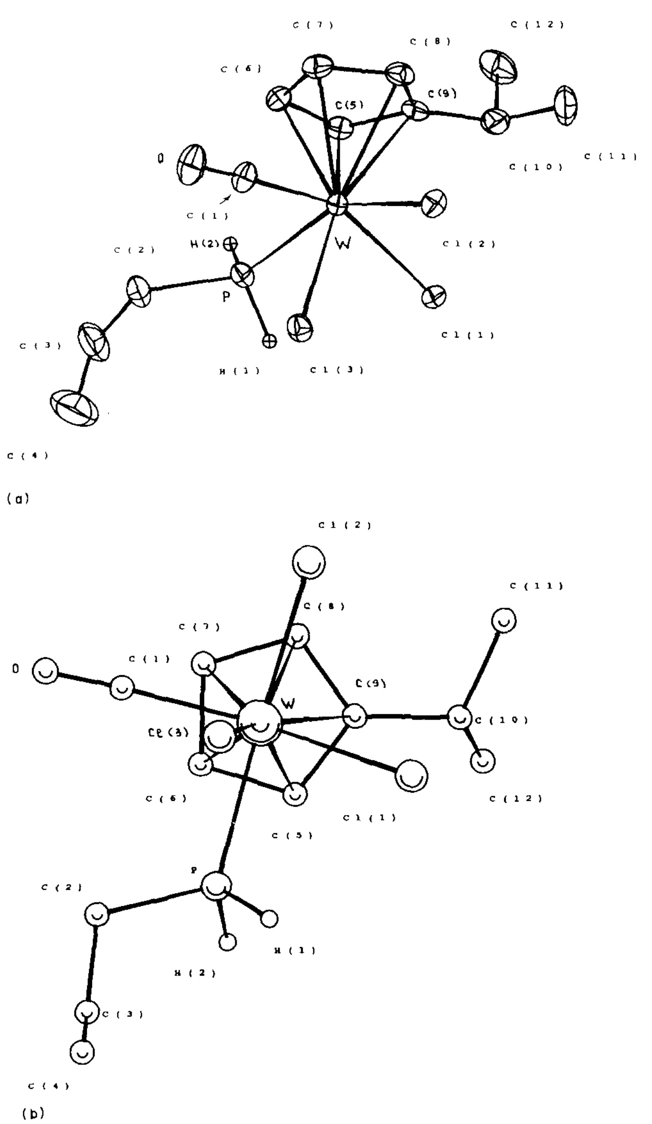

Fig. 1.

Table 2
Selected interatomic distances (Å) and angles (°) in **3** [a]

| | |
|---|---|
| W–Cl(1) | 2.457(1) |
| W–Cl(2) | 2.489(1) |
| W–Cl(3) | 2.448(1) |
| W–P | 2.472(1) |
| W–C(1) | 2.025(5) |
| W–C(5) | 2.280(4) |
| W–C(6) | 2.257(5) |
| W–C(7) | 2.298(5) |
| W–C(8) | 2.396(5) |
| W–C(9) | 2.427(5) |
| W–CEN | 2.005 |
| P–C(2) | 1.816(6) |
| P–H(1) | 1.23(5) |
| P–H(2) | 1.28(5) |
| O–C(1) | 1.114(7) |
| C(2)–C(3) | 1.45(1) |
| C(3)–C(4) | 1.16(1) |
| Cl(1)–W–Cl(2) | 84.81(4) |
| Cl(1)–W–Cl(3) | 80.57(5) |
| Cl(2)–W–Cl(3) | 79.74(5) |
| Cl(1)–W–P | 82.26(4) |
| Cl(2)–W–P | 150.84(5) |
| Cl(3)–W–P | 72.43(5) |
| Cl(1)–W–C(1) | 153.1(2) |
| Cl(2)–W–C(1) | 91.2(2) |
| Cl(3)–W–C(1) | 72.6(2) |
| P–W–C(1) | 88.7(2) |
| Cl(1)–W–CEN | 107.8 |
| Cl(2)–W–CEN | 104.6 |
| Cl(3)–W–CEN | 170.7 |
| P–W–CEN | 104.2 |
| C(1)–W–CEN | 99.0 |
| W–P–C(2) | 120.1(2) |
| W–P–H(1) | 109.8(25) |
| W–P–H(2) | 115.9(24) |
| C(2)–P–H(1) | 106.4(24) |
| C(2)–P–H(2) | 100.5(24) |
| H(1)–P–H(2) | 102.1(35) |
| W–C(1)–O(1) | 177.5(6) |
| P–C(2)–C(3) | 113.1(7) |
| C(2)–C(3)–C(4) | 135.3(14) |

[a] CEN denotes the centroid of the ring C(5)–C(9).

## 3. Experimental details

All manipulations and reactions were carried out either by use of standard Schlenk-vessel and vacuum-line techniques under an dinitrogen (which had been purified by passage over MnO (or a BASF catalyst) and 4 Å molecular sieves), or in a dry-box containing dinitrogen. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under dinitrogen from phosphorus pentoxide (dichloromethane) potassium (tetrahydrofuran), sodium (toluene, triglyme), sodium-potassium alloy (1:3 w/w), [light petroleum ether (b.p. 40–60°C), diethyl ether, pentane]. Deuterated solvents (Aldrich) for NMR studies were stored in Young's ampoules under dinitrogen over sodium/potassium alloy ([$^2H_6$] benzene) or dried over calcium hydride ($CD_2Cl_2$) and transferred by vacuum distillation. Proton, $^{13}$C and $^{31}$P spectra were recorded using a Bruker AM 300 ($^1$H 300 MHz, $^{13}$C 75.5 MHz, $^{31}$P 121.6 MHz). $^{13}$C NMR spectra were recorded using a gated sequence to give nuclear Overhauser enhancement. Spectra were referenced internally using residual protio solvent resonances ($^1$H and $^{13}$C) relative to tetramethylsilane ($d = 0$ ppm) or externally using trimethylphosphate in $D_2O$ ($^{31}$P). All chemical shifts are quoted in *d* (ppm) and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constant, relative integration and assignment. IR spectra were recorded on a Perkin-Elmer 1510 FT interferometer or, in the region below 400 cm$^{-1}$, on a Perkin-Elmer 457 grating spectrometer. Elemental analyses were performed in the Microanalytical Department of this laboratory. The compounds [W(η-$C_5H_4{}^iPr$)$Cl_4$(P)] (P = $H_2PC_3H_5$ **1**, $H_2PC_2H_3$ **2**) are prepared as described [1].

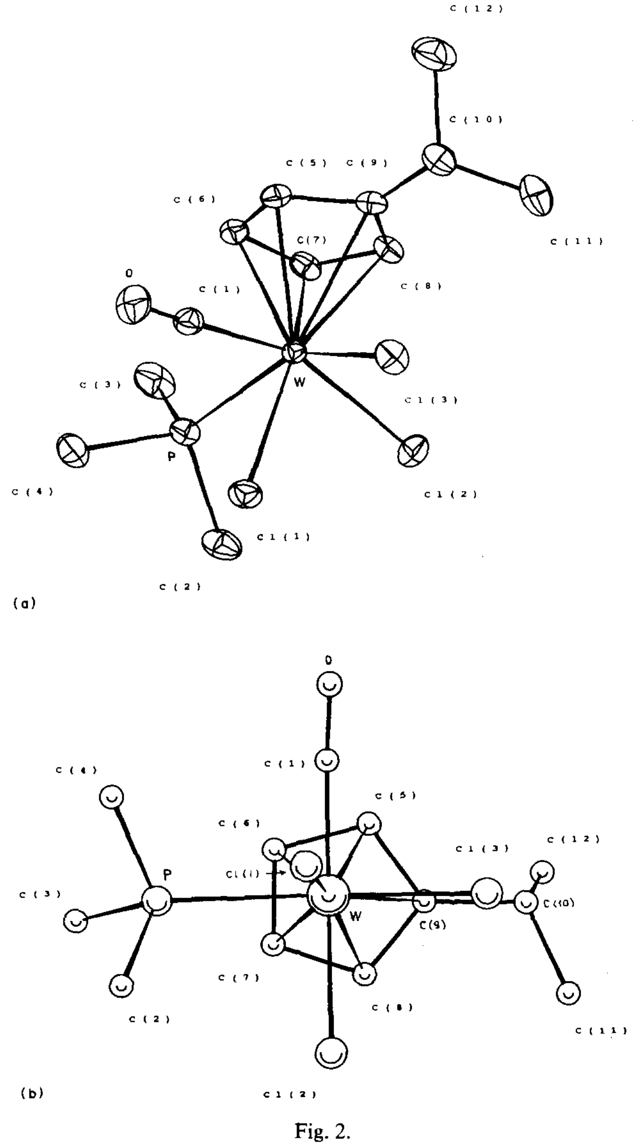

Fig. 2.

Table 3
Selected interatomic distances (Å) and angles (°) for **6** [a]

| | |
|---|---|
| W–Cl(1) | 2.4683(9) |
| W–Cl(2) | 2.4692(9) |
| W–Cl(3) | 2.467(1) |
| W–P | 2.542(1) |
| W–C(1) | 2.022(4) |
| W–C(5) | 2.319(4) |
| W–C(6) | 2.250(4) |
| W–C(7) | 2.252(4) |
| W–C(8) | 2.379(4) |
| W–C(9) | 2.474(3) |
| W–CEN | 2.003 |
| P–C(2) | 1.812(5) |
| P–C(3) | 1.820(5) |
| P–C(4) | 1.819(5) |
| O–C(1) | 1.116(5) |
| Cl(1)–W–Cl(2) | 82.70(4) |
| Cl(1)–W–Cl(3) | 77.59(3) |
| Cl(2)–W–Cl(3) | 83.38(4) |
| Cl(1)–W–P | 72.27(3) |
| Cl(2)–W–P | 86.15(3) |
| Cl(3)–W–P | 149.08(3) |
| Cl(1)–W–C(1) | 72.6(1) |
| Cl(2)–W–C(1) | 155.0(1) |
| Cl(3)–W–C(1) | 87.6(1) |
| P–W–C(1) | 89.9(1) |
| Cl(1)–W–CEN | 171.2 |
| Cl(2)–W–CEN | 105.9 |
| Cl(3)–W–CEN | 104.9 |
| P–W–CEN | 105.9 |
| C(1)–W–CEN | 98.9 |
| W–P–C(2) | 115.0(2) |
| W–P–C(3) | 120.4(2) |
| C(2)–P–C(3) | 100.6(3) |
| W–P–C(4) | 113.5(2) |
| C(2)–P–C(4) | 104.3(2) |
| C(3)–P–C(4) | 100.7(3) |
| W–C(1)–O | 177.0(4) |

[a] CEN denotes the centroid of the ring C(5)–C(9).

### 3.1. Preparation of [W(η-$C_5H_4{}^iPr$)$Cl_3$($H_2PC_3H_5$)(CO)] 3

The compound [W(η-$C_5H_4{}^iPr$)$Cl_4$($H_2PC_3H_5$)] (0.5 g $1 \times 10^{-3}$ moles) was mixed with 1 equivalent of [$Fe_2(CO)_9$] (0.375 g, $1 \times 10^{-3}$ moles) under dinitrogen. THF (30 cm$^3$) was added and the solution was stirred for 6 h or until all the [$Fe_2(CO)_9$] had reacted. A colour change from green to dark red was observed and was accompanied by precipitation of an orange solid which was filtered off and recrystallised from $CH_2Cl_2$ to give orange crystals. A further crop was obtained when the filtrate was concentrated and then kept at −25°C for 24 h. Yield, 110 mg 27%.

### 3.2. Preparation of [W(η-$C_5H_4{}^iPr$)$Cl_4$($H_2PC_2H_3$)(CO)] 4

A solution of [W(η-$C_5H_4{}^iPr$)$Cl_4$($H_2PC_2H_3$)] (0.5 g, $1 \times 10^{-3}$ mole) in THF (20 $cm^3$) was treated with 1 equivalent of [$Fe_2(CO)_9$] (0.375 g, $1 \times 10^{-3}$ mole) and the mixture was stirred until all the [$Fe_2(CO)_9$] had reacted. The colour changed from green to dark red and an orange solid separated. The solid was filtered off and recrystallised from $CH_2Cl_2$. A further crop was obtained when the filtrate had been concentrated and kept at −25°C for 24 h. Yield, 110 mg (24%).

### 3.3. Preparation of [W(η-$C_5H_4{}^iPr$)$Cl_4$($PMe_3$)] 5 and [W(η-$C_5H_4{}^iPr$)$Cl_4$($PMe_3$)(CO)] 6

The compound [W(η-$C_5H_4{}^iPr$)$Cl_4$] (0.4 g) in THF (30 $cm^3$) was treated with 1 equivalent of trimethylphosphine (0.7 g in THF). There was an immediate colour change from red to dark green. The solution was stirred for 15 min, the volatiles were then removed under reduced pressure, and the residue was extracted into toluene to give an olive green solution. This was cooled to give analytically pure olive green microcrystals of [W(η-$C_5H_4{}^iPr$)$Cl_3$($PMe_3$)] **5** (yield, > 70%). Some of compound **5** (0.5 g, $1 \times 10^{-3}$ mole) was mixed with [$Fe_2(CO)_9$] (0.365 g, $1 \times 10^{-3}$ mole) under dinitrogen, THF (40 $cm^3$) was added, and the mixture was stirred vigorously until all the [$Fe_2(CO)_9$] had reacted, colour changing from olive-green to a dark dichroic red-green. The solid that separated was filtered off, dried under reduced pressure, and extracted into dichloromethane to give a red-brown solution, which was concentrated and set aside at room temperature for five days to give air-sensitive red-brown crystals of **6**. Yield, 0.1 g, 20%.

Table 4
Crystal and data reduction details for **3** and **6**

| | **3** | **6** |
|---|---|---|
| Formula | $C_{12}H_{18}Cl_3OPW$ | $C_{12}H_{20}Cl_3OPW \cdot CH_2Cl_2$ |
| M | 499.5 | 586.4 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | *Pbca* |
| *a* (Å) | 11.234(2) | 20.755(6) |
| *b* (Å) | 12.775(4) | 16.728(3) |
| *c* (Å) | 12.531(3) | 11.310(5) |
| β (°) | 111.80(2) | 90.0 |
| *U* ($Å^3$) | 1669.6(8) | 3927(2) |
| *Z* | 4 | 8 |
| $D_c$ (g $cm^{-3}$) | 1.99 | 1.98 |
| μ ($cm^{-1}$) | 76.3 | 67.8 |
| *F*(000) | 952 | 2256 |
| ω scan width (°) | 0.81 + 0.34tan | 0.74 + 0.34tan |
| ω scan speed (°$min^{-1}$) | 1.3–6.7 | 1.3–10.1 |
| Lattice segment | $-h,h,-l,k-l,l$ | $-l,h,-l,k,-l,l$ |
| Crystal size ($mm^3$) | 0.10 × 0.25 × 0.37 | 0.10 × 0.16 × 0.50 |
| $\theta_{max}$ (°) for data | 28 | 27 |
| No. of reflections: | | |
| Total | 4520 | 4753 |
| Unique | 3708 | 4065 |
| In refinement | 2878 | 2935 |
| $R_{merge}$ | 0.031 | 0.020 |
| No. of variables | 171 | 278 |
| Obs./variabl. | 16.8 | 10.6 |
| Weighting coeff. | 10.4, −6.4, 8.3 | 5.5, −3.7, 4.3 |
| Max, min peaks in the final difference maps (e $Å^{-3}$) | 1.10, −0.35 | 0.50, −0.24 |
| *R* | 0.026 | 0.019 |
| $R_w$ | 0.031 | 0.021 |

$R = \Sigma(|F_0 - F_c|)/\Sigma|F_0|$; $R_w = \{\Sigma w(|F_0 - F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$

Table 5
Fractional atomic coordinates and equivalent isotropic (isotropic for H) temperature factors ($Å^2$) for **3**

| Atom | *x* | *y* | *z* | $U_{(eq)}$ |
|---|---|---|---|---|
| W | 0.72507(2) | 0.23704(1) | 0.81762(1) | 0.0383 |
| Cl(1) | 0.5963(1) | 0.36834(9) | 0.6796(1) | 0.0489 |
| Cl(2) | 0.5983(1) | 0.10736(9) | 0.6712(1) | 0.0529 |
| Cl(3) | 0.5294(1) | 0.2301(1) | 0.8600(1) | 0.0595 |
| P | 0.7386(1) | 0.3780(1) | 0.9569(1) | 0.0513 |
| O | 0.7700(5) | 0.0761(4) | 1.0180(4) | 0.0818 |
| C(1) | 0.7545(6) | 0.1314(4) | 0.9454(5) | 0.0585 |
| C(2) | 0.7456(7) | 0.3458(6) | 1.1002(5) | 0.0695 |
| C(3) | 0.737(1) | 0.437(1) | 1.1661(8) | 0.1108 |
| C(4) | 0.657(1) | 0.475(1) | 1.190(1) | 0.1597 |
| C(5) | 0.9051(4) | 0.3255(4) | 0.8272(4) | 0.0447 |
| C(6) | 0.9394(5) | 0.2468(4) | 0.9118(5) | 0.0544 |
| C(7) | 0.9146(6) | 0.1498(4) | 0.8519(6) | 0.0602 |
| C(8) | 0.8716(5) | 0.1710(4) | 0.7354(5) | 0.0547 |
| C(9) | 0.8677(5) | 0.2785(4) | 0.7180(5) | 0.0480 |
| C(10) | 0.8408(7) | 0.3345(7) | 0.6056(6) | 0.0731 |
| C(11) | 0.789(1) | 0.2632(9) | 0.5027(7) | 0.0961 |
| C(12) | 0.9629(9) | 0.3885(7) | 0.6100(8) | 0.0891 |
| H(1) | 0.648(5) | 0.439(4) | 0.916(5) | 0.06(1) |
| H(2) | 0.835(5) | 0.439(4) | 0.981(5) | 0.05(1) |

### 3.4. Crystal structure determination of compounds 3 and 6

Crystal data and details of the data collection and refinement are given in Table 4. The general procedure was as follows. A crystal was mounted under dinitrogen in a Lindeman tube (0.7 mm), which was then sealed with a small flame and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were calculated from the setting angles of 24 strong, high-angle carefully-centred reflections. Three reflections were choosen as intensity standards and were measured at 1 h intervals and three orientation control reflection were measured every 200 reflections. The data were collected at room tempera-

Table 6
Fractional atomic coordinates and equivalent isotropic (isotropic for H) temperature factors (Å$^2$) for **6**

| Atom | $x$ | $y$ | $z$ | $U_{(eq)}$ |
|---|---|---|---|---|
| W | 0.707470(6) | 0.100845(7) | 0.02915(1) | 0.0260 |
| Cl(1) | 0.63865(5) | 0.01893(6) | −0.10124(9) | 0.0418 |
| Cl(2) | 0.64148(5) | 0.21096(6) | −0.05130(9) | 0.0436 |
| Cl(3) | 0.76336(5) | 0.11111(7) | −0.16281(9) | 0.0448 |
| Cl(4) | 0.55664(7) | 0.04321(9) | −0.3971(1) | 0.0699 |
| Cl(5) | 0.52311(7) | 0.19401(9) | −0.2888(1) | 0.0738 |
| P | 0.60774(5) | 0.06150(6) | 0.14590(9) | 0.0356 |
| O | 0.7587(2) | −0.0755(2) | 0.0397(3) | 0.0551 |
| C(1) | 0.7398(2) | −0.0130(2) | 0.0389(3) | 0.0372 |
| C(2) | 0.5321(2) | 0.0964(3) | 0.0847(5) | 0.0492 |
| C(3) | 0.5987(3) | 0.0924(4) | 0.2993(5) | 0.0548 |
| C(4) | 0.5972(3) | −0.0460(3) | 0.1598(5) | 0.0499 |
| C(5) | 0.8032(2) | 0.0960(2) | 0.1346(4) | 0.0361 |
| C(6) | 0.7491(2) | 0.0989(3) | 0.2128(3) | 0.0365 |
| C(7) | 0.7197(2) | 0.1742(2) | 0.1947(3) | 0.0355 |
| C(8) | 0.7567(2) | 0.2168(2) | 0.1110(3) | 0.0347 |
| C(9) | 0.8094(2) | 0.1706(2) | 0.0764(4) | 0.0340 |
| C(10) | 0.8661(2) | 0.1963(3) | 0.0027(4) | 0.0442 |
| C(11) | 0.8531(3) | 0.2718(4) | −0.0689(6) | 0.0594 |
| C(12) | 0.9230(3) | 0.2076(5) | 0.0873(6) | 0.0667 |
| C(13) | 0.5864(3) | 0.1358(3) | −0.3436(5) | 0.0559 |
| H(21) | 0.502(3) | 0.070(3) | 0.123(5) | 0.07(2) |
| H(22) | 0.527(2) | 0.155(3) | 0.102(5) | 0.07(2) |
| H(23) | 0.530(3) | 0.073(4) | 0.010(5) | 0.07(2) |
| H(31) | 0.557(3) | 0.073(3) | 0.324(5) | 0.08(2) |
| H(32) | 0.634(3) | 0.069(3) | 0.342(4) | 0.06(1) |
| H(33) | 0.595(3) | 0.151(4) | 0.306(5) | 0.09(2) |
| H(41) | 0.557(3) | −0.052(4) | 0.205(6) | 0.10(2) |
| H(42) | 0.632(3) | −0.065(3) | 0.198(5) | 0.07(2) |
| H(43) | 0.593(2) | −0.072(3) | 0.089(4) | 0.05(1) |
| H(51) | 0.834(2) | 0.053(3) | 0.139(4) | 0.04(1) |
| H(61) | 0.741(2) | 0.059(2) | 0.264(3) | 0.03(1) |
| H(71) | 0.683(2) | 0.195(2) | 0.239(4) | 0.04(1) |
| H(81) | 0.748(2) | 0.270(3) | 0.086(4) | 0.04(1) |
| H(101) | 0.876(2) | 0.151(2) | −0.054(3) | 0.029(9) |
| H(111) | 0.887(3) | 0.289(4) | −0.115(5) | 0.09(2) |
| H(112) | 0.848(2) | 0.317(3) | −0.020(4) | 0.06(1) |
| H(113) | 0.817(3) | 0.265(3) | −0.126(5) | 0.07(2) |
| H(121) | 0.960(3) | 0.210(4) | 0.043(5) | 0.08(2) |
| H(122) | 0.929(3) | 0.162(3) | 0.134(5) | 0.06(2) |
| H(123) | 0.917(3) | 0.241(4) | 0.150(6) | 0.09(2) |
| H(131) | 0.602(3) | 0.160(4) | −0.403(6) | 0.10(2) |
| H(132) | 0.613(2) | 0.127(3) | −0.274(5) | 0.06(1) |

ture using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71069$ Å) and an $\omega$-$2\theta$ scan mode (the ratio of the scanning rates $\omega/\theta = 1.2$). Neither significant crystal decay nor movement was noted.

All data were corrected for Lorentz and polarization effects. Both structures were solved by direct methods. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures (in the refinement were used reflections with $I > 3\sigma(I)$). An empirical absorption correction using the DIFABS [11] program was applied after isotropic convergence. In **3** the hydrogen atoms were placed in calculated positions and included in the final refinement with the fixed positional and thermal parameters. Only the H(1) and H(2) atoms attached to the phosphorus were located in the difference Fourier map and refined isotropically. In **6** all hydrogen atoms were located and refined in the isotropic approximation. A Chebyshev weighting scheme [12] was applied and the data were corrected for the effects of anomalous dispersion. All crystallographic calculations were performed using the CRYSTALS program package [13] on MicroVAX 3800 computer. Neutral atom scattering factors were taken from the usual sources [14]. Fractional atomic coordinates of non-hydrogen atoms are listened in Tables 5 and 6. Tables of H-atom coordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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