Preparation and Structure of Trichlorotris(dimethylphenylphosphine)tungsten(III), the First Structurally Characterised Neutral Mononuclear Complex of Tungsten(III)†

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A mononuclear complex of tungsten(III) has been obtained by the zinc reduction of [$WCl_4(PMe_2Ph)_3$]. This product, [$WCl_3(PMe_2Ph)_3$], has an octahedral, meridional configuration, and crystallises in the space group $P2_1/c$, with $a = 16.177(2)$, $b = 10.350(1)$ and $c = 18.079(2)$ Å, $\beta = 113.81(6)°$. It can be used to prepare other mononuclear tungsten(III) compounds. Its structural relationship with other complexes, [$MCl_3(PMe_2Ph)_3$] (M = Re, Os or Ir), is discussed.

Some years ago[1] we described the synthesis of compounds [$WCl_4(PR_3)_2$] (PR_3 = tertiary phosphine) by reduction of WCl_6 with Zn in CH_2Cl_2 in the presence of the phosphine. Further reduction of the tungsten(IV) species in the presence of phosphine under dinitrogen yielded dinitrogen complexes,[2] and the only intermediates we detected were of tungsten(II), such as [$WCl_2(Ph_2PCH_2CH_2PPh_2)_2$].[3] Certainly we observed no tungsten(III) species, and mononuclear tungsten(III) complexes are rather rare. In fact the best characterised by far are dinuclear complexes with bridges or metal–metal multiple bonds.[4] In this paper we describe the preparation and structure of the new mononuclear tungsten(III) complex [$WCl_3(PMe_2Ph)_3$], and only the second to be characterised structurally apart from [$(C_5H_4MeN)_2H$][$WBr_4(C_5H_4MeN)_2$].[5]

Results

The complex [$WCl_3(PMe_2Ph)_3$] is prepared by zinc reduction of [$WCl_4(PMe_2Ph)_3$] in the absence of any added phosphine. This synthetic route appears to require the availability of a seven-co-ordinate tungsten(IV) precursor, of a type not available for phosphines more sterically demanding than PMe_2Ph. The identity of this low-spin complex ($\mu_{eff} = 1.74\ \mu_B$) was confirmed by X-ray structure analysis. The isolation of this material, and the earlier reports of species such as [$WCl_3(py)_3$] (py = pyridine),[6] confirms that ligands such as tris(pyrazolyl)borate (L), as suggested for the molecule [$WLCl_3$]$^-$,[7] are not necessary for the stabilisation of mononuclear tungsten(III) compounds, even if they help it. The conditions of preparation are clearly also important.

X-Ray Crystal Structure of mer-[$WCl_3(PMe_2Ph)_3$].—The compound forms discrete mononuclear molecules with octahedral, meridional arrangements of phosphine and chloride ligands (Fig. 1). Atomic coordinates and molecular dimensions are given in Tables 1 and 2. There are no intermolecular approaches shorter than the appropriate van der Waals contacts. The W–P bond lengths are similar (see Table 2) and of the expected magnitudes, though the unique bond opposite to chloride is marginally shorter. This is as expected. However, the W–Cl bonds are significantly different, and the shortest of the three, W–Cl(3), is *trans* to a chlorine. It is difficult to believe that this is an electronic effect, and it may be due to crystal packing. The angles about tungsten do not differ much from the ideal 90°, though Cl(1) and Cl(3) are bent slightly towards the phosphorus atom P(5), and P(6) and P(4) are bent marginally more towards Cl(2). These distortions are presumably related to ligand bulk.

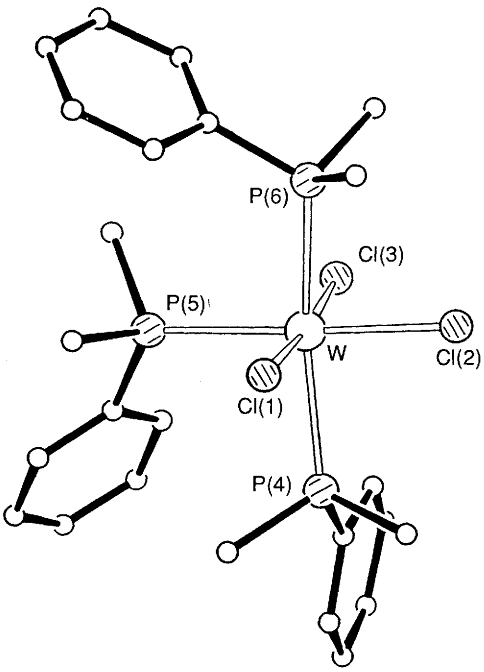

Fig. 1 Molecular structure of *mer*-[$WCl_3(PMe_2Ph)_3$], showing the atom numbering scheme

Discussion

This new complex extends the series of complexes [$MCl_3(PMe_2Ph)_3$], the structures of which have been described in preliminary form for M = Re, Os or Ir.[8] A complete description of *mer*-[$IrCl_3(PMe_2Ph)_3$] was published subsequently, but the data for Re and Os have never been expanded.[9]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Final atomic coordinates (fractional × 10^4) for *mer*-$[WCl_3(PMe_2Ph)_3]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
W	7 810.2(1)	5 027.2(2)	3 190.7(1)
Cl(1)	6 682(1)	3 933(1)	2 026.7(8)
Cl(2)	8 106(1)	6 591(1)	2 316.2(9)
Cl(3)	8 938(1)	5 887(2)	4 317(1)
P(4)	6 453.2(9)	6 395(1)	3 088.3(8)
C(41)	6 532(4)	7 609(5)	3 855(3)
C(42)	5 755(4)	8 085(6)	3 909(4)
C(43)	5 801(5)	8 946(7)	4 485(4)
C(44)	6 612(5)	9 321(6)	5 057(4)
C(45)	7 391(5)	8 909(7)	4 996(4)
C(46)	7 340(4)	8 051(6)	4 379(4)
C(47)	5 460(4)	5 430(7)	2 993(4)
C(48)	6 015(5)	7 317(7)	2 153(4)
P(5)	7 551(1)	3 381(1)	4 097.1(8)
C(51)	7 020(4)	3 950(5)	4 763(3)
C(52)	7 365(5)	5 055(5)	5 216(4)
C(53)	6 997(5)	5 507(8)	5 741(4)
C(54)	6 326(7)	4 857(7)	5 834(5)
C(55)	5 978(5)	3 757(8)	5 395(5)
C(56)	6 328(4)	3 295(6)	4 866(4)
C(57)	8 576(4)	2 645(7)	4 835(4)
C(58)	6 875(5)	1 998(6)	3 585(5)
P(6)	8 970.1(9)	3 726(1)	2 894.8(8)
C(61)	9 152(4)	2 044(5)	3 192(3)
C(62)	9 914(4)	1 615(6)	3 843(4)
C(63)	9 990(6)	301(7)	4 064(5)
C(64)	9 316(6)	−551(7)	3 653(5)
C(65)	8 588(7)	−144(6)	3 023(6)
C(66)	8 482(4)	1 144(6)	2 767(4)
C(67)	10 083(4)	4 459(7)	3 318(5)
C(68)	8 709(5)	3 620(6)	1 821(3)

Table 2 Selected molecular dimensions (lengths in Å, angles in °) in *mer*-$[WCl_3(PMe_2Ph)_3]$ with e.s.d.s in parentheses (angles marked * have e.s.d.s less than 0.05°)

(*a*) In the tungsten co-ordination sphere			
W–Cl(1)	2.437(1)	W–P(4)	2.555(1)
W–Cl(2)	2.441(1)	W–P(5)	2.514(1)
W–Cl(3)	2.295(2)	W–P(6)	2.536(1)
Cl(1)–W–Cl(2)	91.3*	Cl(2)–W–P(6)	82.0*
Cl(1)–W–Cl(3)	175.0(1)	Cl(3)–W–P(4)	101.6(1)
Cl(1)–W–P(4)	82.7*	Cl(3)–W–P(5)	88.1(1)
Cl(1)–W–P(5)	89.1*	Cl(3)–W–P(6)	90.1(1)
Cl(1)–W–P(6)	86.0*	P(4)–W–P(5)	93.3*
Cl(2)–W–Cl(3)	91.4(1)	P(4)–W–P(6)	165.0*
Cl(2)–W–P(4)	88.5*	P(5)–W–P(6)	96.3*
Cl(2)–W–P(5)	178.2*		
(*b*) In the phosphine ligands			
P(4)–C(41)	1.837(5)	P(5)–C(58)	1.812(6)
P(4)–C(47)	1.839(6)	P(6)–C(61)	1.810(5)
P(4)–C(48)	1.818(6)	P(6)–C(67)	1.814(6)
P(5)–C(51)	1.835(5)	P(6)–C(68)	1.815(5)
P(5)–C(57)	1.823(6)		
W–P(4)–C(41)	121.9(2)	C(51)–P(5)–C(57)	100.5(3)
W–P(4)–C(47)	113.5(2)	C(51)–P(5)–C(58)	104.1(3)
W–P(4)–C(48)	111.0(2)	C(57)–P(5)–C(58)	103.1(4)
C(41)–P(4)–C(47)	103.6(3)	W–P(6)–C(61)	119.6(2)
C(41)–P(4)–C(48)	103.0(3)	W–P(6)–C(67)	112.5(2)
C(47)–P(4)–C(48)	101.5(3)	W–P(6)–C(68)	112.6(2)
W–P(5)–C(51)	117.1(2)	C(61)–P(6)–C(67)	105.2(3)
W–P(5)–C(57)	114.7(2)	C(61)–P(6)–C(68)	101.5(3)
W–P(5)–C(58)	115.3(2)	C(67)–P(6)–C(68)	103.8(3)

Table 3 presents comparable data for all four complexes *mer*-$[MCl_3(PMe_2Ph)_3]$. It can be seen that there is a drop in M–P distances, whether P *trans* P or P *trans* Cl, from tungsten to iridium, whereas the corresponding M–Cl distances are effectively constant. This has been ascribed to an anisotropy in the radii of the elements, and has also been observed for metal(IV) species. However, it has not been adequately explained why M–P bond variations should be consistent with the expected trends in radii of the metal(III) species, whereas there is no reflection of this in the M–Cl bonds. However, we have already noted,[10] in the context of Fe–Cl and Fe–P bond lengths, that the phosphorus bond lengths are very sensitive to the iron spin states, whereas the chlorine bond lengths do not vary sensibly. It may be that this is related to the greater ionic character of bonds to chlorine as compared to bonds to phosphorus, but that hardly seems to provide an explanation. The π-bonding abilities of Cl and P should not be so very different.

It has been shown[11] that a common form of tungsten(III) complex is dinuclear, with octahedral co-ordination around each tungsten, and octahedra paired by edge- or face-sharing, with additional W–W bonds. An example is the equilibrium between $[W_2Cl_6(PEt_3)_4]$ (edge sharing) and $[W_2Cl_6(PEt_3)_3]$ (face sharing).[12] Accordingly, it seemed worthwhile to determine whether our complex might not also give rise to similar equilibria (Scheme 1), but with an extension to include the mononuclear species.

$$2[WCl_3(PR_3)_3] \underset{+2PR_3}{\overset{-2PR_3}{\rightleftharpoons}} [W_2Cl_6(PR_3)_4] \underset{+PR_3}{\overset{-PR_3}{\rightleftharpoons}} [W_2Cl_6(PR_3)_3]$$

Mononuclear Binuclear, edge-shared Binuclear, face-shared

Scheme 1

The ^1H NMR spectrum of $[WCl_3(PMe_2Ph)_3]$ shows sharp, shifted peaks which we could not assign, and certainly there are no facile equilibria as observed for other tungsten and molybdenum[13] phosphine complexes. The $^{31}P-\{^1H\}$ NMR spectrum shows two singlets in the ratio 2:1 at δ −155.19 and −164.62 with respect to $P(OMe)_3$, with tungsten satellites on each, J_{WP} = 170 and 216 Hz, respectively.

Prolonged heating of $[WCl_3(PMe_2Ph)_3]$ in toluene at 130 °C produced a mixture with a complex ^{31}P NMR spectrum which we were unable to analyse. Considerable decomposition seems evident. An alternative approach would be to synthesise $[WCl_3(PEt_3)_3]$ to study this. However, although $[WCl_4(PMe_3)_3]$[14] is known, all our attempts to synthesise $[WCl_4(PEt_3)_3]$ were unsuccessful, and we were only ever able to isolate $[WCl_4(PEt_3)_2]$.

The new complex $[WCl_3(PMe_2Ph)_3]$ may be used to synthesise other mononuclear tungsten(III) compounds. As examples, we describe here the syntheses and characterization of $[WCl_3(PMe_2Ph)(Ph_2PCH_2CH_2PPh_2)]$, $[WCl_3(PMe_2Ph)_2(py)]$ and of $[WCl_3(PMe_2Ph)(bipy)]$ (bipy = 2,2′-bipyridine). Doubtless many other complexes would be obtainable from this source.

Experimental

All manipulations were carried out using the Schlenk-tube technique under dry dinitrogen. NMR spectra were obtained using a JEOL GSX270 spectrometer. The magnetic moments were measured in solution in $CDCl_3$ by the Evans method.[15] Microanalyses were by Mr. C. J. Macdonald, Nitrogen Fixation Laboratory. The complex $[WCl_4(PMe_2Ph)_3]$ was prepared by the literature method.[16] Molecular weights were determined by use of a vapour-pressure osmometer.

Table 3 Comparison of structural data for complexes *mer*-$[MCl_3(PMe_2Ph)_3]$

	M–P/Å		M–Cl/Å		
M	P *trans* P	P *trans* Cl	Cl *trans* Cl	Cl *trans* P	Ref.
W	2.545(9)	2.514(1)	2.37(7)	2.441(1)	
Re	2.458(6)	2.401(6)	2.353(6)	2.454(6)	8
Os	2.408(6)	2.350(5)	2.347(6)	2.439(6)	8
Ir	2.373(5)	2.280(2)	2.363(2)	2.437(2)	9

Trichlorotris(dimethylphenylphosphine)tungsten(III).—Zinc (0.30 g, 4.59 mmol) was added to a solution of $[WCl_4(PMe_2Ph)_3]$ (2.91 g, 3.9 mmol) in tetrahydrofuran (thf) (40 cm^3) and the resulting mixture stirred at room temperature for 2 h. After this time the solution was filtered through Celite and the filtrate was taken to dryness. The residue was taken up in thf (10 cm^3) and layered with hexane. Crystallisation of the product occurred upon refrigeration at 0 °C overnight. The complex was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 1.38 g, 50%). It was recrystallised from thf–hexane as brown crystals (Found: C, 41.1; H, 4.80. $C_{24}H_{33}Cl_3P_3W$ requires C, 41.0; H, 4.70%).

(2,2′-Bipyridine)trichloro(dimethylphenylphosphine)tungsten(III).—2,2′-Bipyridine (0.17 g, 1.1 mmol) was added to a solution of $[WCl_3(PMe_2Ph)_3]$ (0.76 g) in thf (20 cm^3). The mixture was stirred at reflux temperature for 3 h. A black solid was obtained, which was filtered off, washed with thf and dried under vacuum. The product was recrystallised from CH_2Cl_2–ether–hexane (20:10:30) as black crystals. Yield 42% (Found: C, 37.5; H, 3.45; N, 4.35. $C_{18}H_{19}Cl_3N_2P_3W$ requires C, 37.0; H, 3.25; N, 4.80%). $\mu_{eff} = 1.92\ \mu_B$, $M = 826$ (800).

[1,2-Bis(diphenylphosphino)ethane]trichloro(dimethylphenylphosphine)tungsten(III).—The diphosphine (0.56 g, 1.42 mmol) was added to a solution of $[WCl_3(PMe_2Ph)_3]$ (0.5 g) in thf (20 cm^3). The mixture was heated at reflux for 0.5 h. Then the solution was reduced to dryness and the residue taken up in CH_2Cl_2, layered with hexane and cooled to −30 °C. The product was obtained as black crystals. Yield: 60% (Found: C, 49.6; H, 4.15. $C_{32}H_{37}Cl_3P_3W$ requires C, 49.4; H, 4.25%). $\mu_{eff} = 2.11\ \mu_B$, $M = 584$ (552).

Trichlorobis(dimethylphenylphosphine)(pyridine)tungsten(III).—To $[WCl_3(PMe_2Ph)_3]$ (0.64 g, 0.91 mmol) in thf (20 cm^3) was added an excess of py (0.22 cm^3, 2.73 mmol). The mixture was heated at reflux for 2 h and a red solution was obtained. This was taken to dryness and the residue was solidified with ether to yield an orange-brown solid. The product was recrystallised from thf–hexane. Yield: 36% (Found: C, 39.1; H, 4.20; N, 1.75. $C_{21}H_{27}Cl_3NP_2W$ requires C, 39.0; H, 4.20; N, 2.10%). $\mu_{eff} = 1.81\ \mu_B$, $M = 645$ (623).

Crystal Structure Analysis of mer-$[WCl_3(PMe_2Ph)_3]$.—*Crystal data.* $C_{24}H_{33}Cl_3P_3W$, $M = 704.7$, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.177(2)$, $b = 10.350(1)$, $c = 18.079(2)$ Å, $\beta = 113.81(6)°$, $U = 2769(5)$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1388$, μ(Mo-Kα) = 47.4 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

The complex forms long, rectangular prismatic needles. One, *ca.* 0.33 × 0.17 × 1.57 mm, was mounted (in air) on a glass fibre. After preliminary photographic examination, the crystal was moved to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) where accurate cell parameters were refined from the goniometer settings of 24 strong reflections with θ *ca.* 14.5°, each of which was centred in four orientations. Diffraction intensities were measured to $\theta_{max} = 25°$. During processing, these data were corrected for Lorentz polarisation effects, crystal decomposition, absorption (using empirical ψ-scan methods; maximum, minimum transmission 1.00, 0.60) and to ensure no negative nett intensities (using Bayesian statistics).

4858 Unique reflections were entered into the SHELX[17] program system, whence the position of the tungsten atom was found from a Patterson synthesis. Subsequent electron-density and Fourier difference syntheses yielded the positions of all other non-hydrogen atoms. Refinement by full-matrix least-squares methods was completed with $R = 0.045$, $R' = 0.045$ for all data, weighted $w = 1.4005/\sigma^2(F)$.

In the final cycles of refinement all non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were placed in ideal positions (methyl groups staggered) with isotropic thermal parameters allowed to refine freely. In a final difference electron-density map the strongest peaks were all in the immediate vicinity of the tungsten atom. Scattering factors for neutral atoms were taken from ref. 18. All computer programs used have been noted above or in ref. 19 and were run on a MicroVAX-II machine in this Laboratory.

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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