

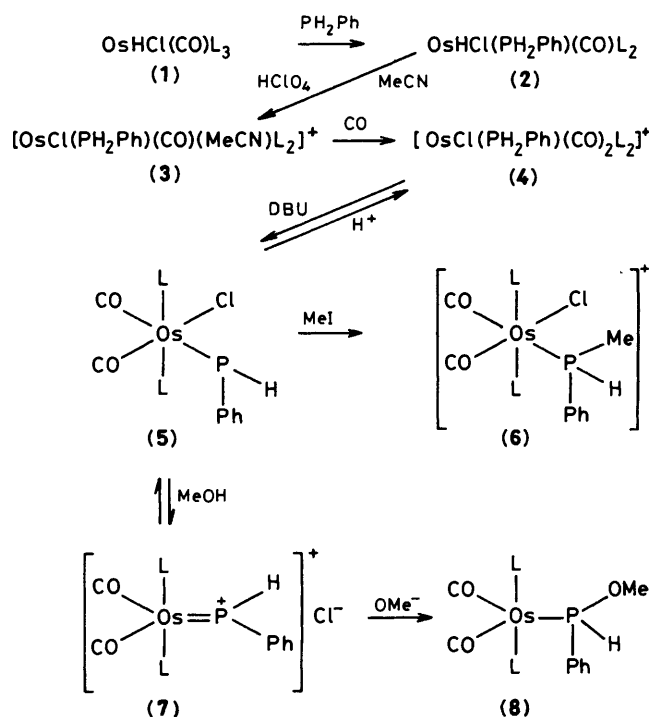
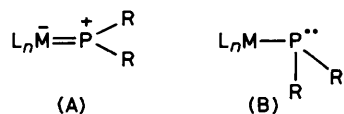
Reactivity Patterns associated with Pyramidal and Planar Phosphido-Ligand Geometries; Synthesis and Structure of $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ and of $[\text{Os}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]$

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Deprotonation of $[\text{OsCl}(\text{PH}_2\text{Ph})(\text{CO})_2(\text{PPh}_3)_2]^+$ gives the terminal phosphido-complex, $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, which has pyramidal geometry at P and associated nucleophilic properties, *e.g.*, protonation and methylation at P, but $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ also reacts with methoxide to form the zerovalent compound $[\text{Os}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]$ suggesting the intermediacy of the planar phosphido-complex $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]^+$.

Structural studies indicate that a terminal phosphido-ligand in the complex $\text{L}_n\text{M}-\text{PR}_2$ can have one of two possible geometries: either a planar phosphorus geometry, with a short M-P bond length and a large (approx. 130°) M-P-R bond angle;¹⁻⁴ or a pyramidal phosphorus geometry with a long M-P bond and a small ($<114^\circ$) M-P-R bond angle.^{1,5} A simple bonding scheme distinguishes these two conformations as shown by (A) and (B) *i.e.*, the PR_2 -ligand is either planar and a $3e$ -donor as in (A) or pyramidal and a $1e$ -donor as in (B). The nucleophilic properties normally associated with phosphido-ligands are explained by (B) but the formal charges present in (A) suggest possible electrophilic character for the planar phosphido-ligand. Although few reports^{1,6} detail this reactivity pattern a preliminary account⁷ of the related arsenic complex, $[\text{CpW}(\text{CO})_2(\text{AsBu}^t_2)]$, ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) reveals electrophilicity associated with the As atom. In this communication we report (i) synthesis of the terminal phenylphosphido-complex $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, (ii) a crystal structure determination of this molecule, (iii) methoxide addition to the phenylphosphido-ligand to give the zerovalent complex $[\text{Os}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]$, and (iv) a crystal structure determination of this zerovalent complex.



Scheme 1. $\text{L} = \text{PPh}_3$.

The phenylphosphine cationic complex, (4),[†] (see Scheme 1) is readily prepared in three steps from $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$, (1), via rapid phenylphosphine substitution to give (2) followed by cleavage of the hydride ligand with perchloric acid to give (3), and slow carbonylation with CO (40 p.s.i., 8 h, 25 °C) to give (4).

A benzene suspension of (4) reacts instantly with base, e.g. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), to give a yellow solution from which $[\text{Os}(\text{PPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, (5), is obtained in 95% yield. The nucleophilic character of (5) is displayed by the reversibility of the deprotonation reaction and by methylation to give $[\text{OsCl}(\text{PHMePh})(\text{CO})_2(\text{PPh}_3)_2]^+$, (6). However, the pyramidal phosphido-complex also reacts with nucleophiles and when (5) is treated with methoxide in methanol the zerovalent complex (8) is produced from methoxide addition to the phosphorus centre (Scheme 1).

The structure of (5) was established by a single crystal X-ray diffraction study[‡] (Figure 1). A long Os–P bond length, 2.523(7) Å, is found for the phenylphosphido-ligand, the usual range for Os–P(PR₃) bond lengths being 2.32–2.45 Å. Although the phosphorus-bound hydrogen was not located the pyramidal geometry of the phosphido-ligand is implied by the small Os–P(1)–C(11) angle of 113.4(6)°. A short W–P(PHPh) bond length, 2.291(1) Å, was found in $[\text{W}(\equiv\text{CCMe}_3)(\text{PHPh})\text{Cl}_2(\text{PEt}_3)_2]$,³ the only other phenylphosphido-complex to be structurally characterised. A large, 140.0(2)°, W–P–C(phenyl) bond angle was also found for this planar phenylphosphido-ligand and the contrast with (5) provides further evidence for the amphoteric character of the phosphido-ligand.

A single crystal X-ray diffraction study of (8)[‡] confirms the presence of the unusual PH(OMe)Ph ligand (Figure 2). The

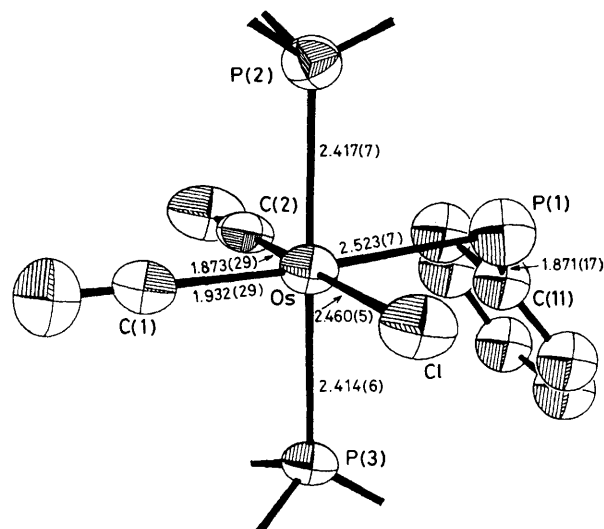


Figure 1. Molecular structure of $[\text{Os}(\text{PHPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, (5), (phenyl rings omitted for clarity). Bond lengths are given in Å. The Os–P(1)–C(11) angle is 113.4(6)°.

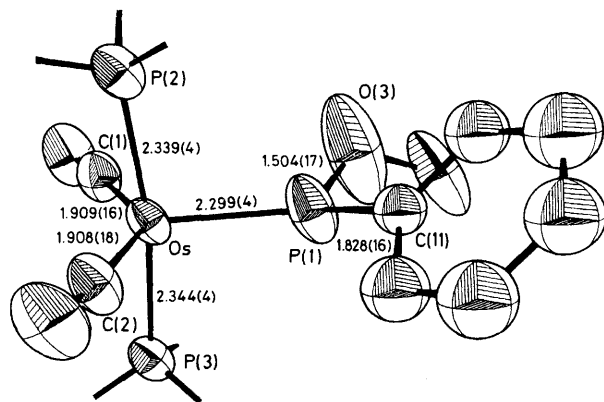


Figure 2. Molecular structure of $[\text{Os}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]$, (8), (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are: P(2)–Os–P(3) 170.7(1), C(1)–Os–C(2) 134.2(6), P(1)–Os–P(2) 95.6(2), P(1)–Os–P(3) 93.7(2), Os–P(1)–O(3) 119.8(6), Os–P(1)–C(11) 124.1(5)°.

[†] New compounds (2)–(6) and (8) have all given satisfactory elemental analyses. Important i.r. absorptions (ν , cm^{-1}) are as follows: (2) 1930 (CO); (3) 1968 (CO); (4) 2032, 1996 (CO); (5) 2018, 1953, (CO), 2264, (PH); (6) 2056, 1995, (CO); (8) 1932, 1904, 1847, (CO).

[‡] Crystal data for (5): $\text{C}_{44}\text{H}_{36}\text{O}_2\text{OsP}_3 \cdot \text{C}_7\text{H}_6\text{O}$, $M = 925.1$, monoclinic, space group $P2_1/n$, $a = 10.369(1)$, $b = 17.823(11)$, $c = 22.598(3)$ Å, $\beta = 97.30(1)^\circ$, $U = 4143.5$ Å³, $D_c = 1.48$ g cm^{-3} for $Z = 4$, $F(000) = 1856$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\beta(\text{Mo-K}\alpha) = 31.37$ cm^{-1} , 3306 observed [$F > 3\sigma(F)$] reflections were measured on a CAD4 diffractometer. Owing to crystal decomposition in the X-ray beam it was necessary to use four crystals for the data collection; corrections for decomposition and absorption were applied to each crystal before the data were combined. Separate scale factors were applied to each crystal. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least squares (all atoms anisotropic except for phenyl carbon and hydrogen atoms) to $R = R_w = 0.070$. The lattice contains an ethanol of solvation.

Crystal data for (8): $\text{C}_{45}\text{H}_{39}\text{O}_3\text{OsP}_3$, $M = 910.1$, triclinic, $P\bar{1}$, $a = 12.774(2)$, $b = 13.292(4)$, $c = 12.171$ Å, $\alpha = 105.14(2)$, $\beta = 95.42(2)$, $\gamma = 85.28(2)^\circ$, $U = 1982.1$ Å³, $D_c = 1.52$ g cm^{-3} for $Z = 2$, $F(000) = 908$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu(\text{Mo-K}\alpha) = 32.17$ cm^{-1} , 3858 observed [$F > 3.0\sigma(F)$] reflections were collected on a CAD4 diffractometer and corrections for crystal decomposition applied. The structure was solved by Patterson and difference Fourier techniques and refined by full matrix least squares (all atoms anisotropic except for phenyl carbon and hydrogen atoms) to $R = R_w = 0.053$. The methoxy group shows considerable anisotropy which may be indicative of some disorder.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

free phosphine, $\text{PH}(\text{OMe})\text{Ph}$, is unstable towards rearrangement to cyclopolyphosphine and methanol,⁸ and has been prepared only in the co-ordination sphere of a metal.⁹ The overall structure of (8) is a distorted trigonal bipyramid with a strongly-bound equatorial $\text{PH}(\text{OMe})\text{Ph}$ -ligand.

To account for nucleophilic addition of methoxide to the phenylphosphido-ligand it is suggested that a cationic, planar, phenylphosphido-species, (7), is an intermediate (undetected) in the synthesis of (8) and the formation of (7) is favoured in the polar solvent, methanol. Thus the reactivity of a terminal phosphido-ligand depends upon the geometry it adopts, which in turns depends upon the number and nature of accompanying ligands.

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