

# Synthesis and Structure of a *P*-Metallated Phospha-alkene, $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$

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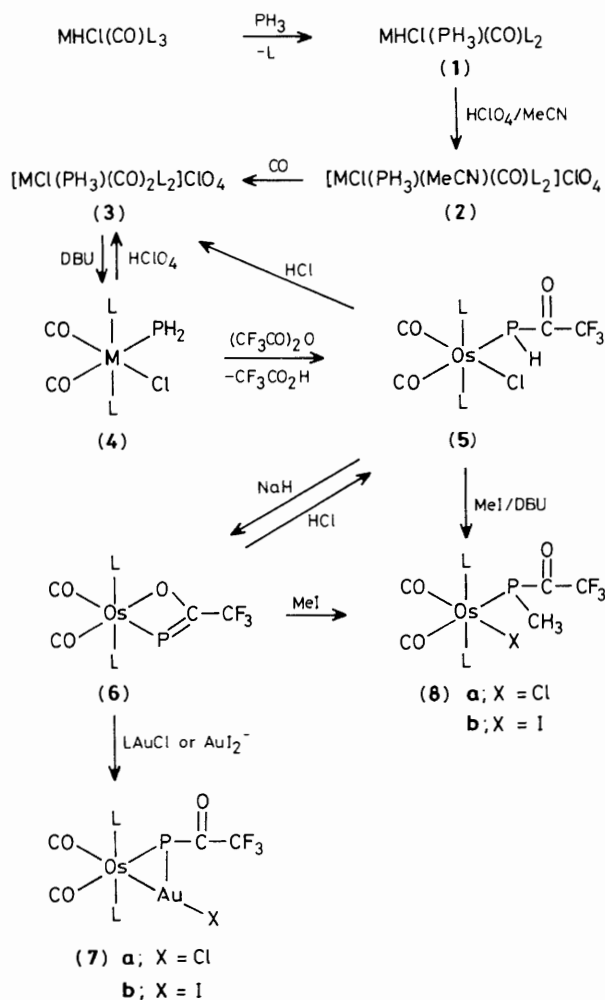
The terminal  $\text{PH}_2$ -complex,  $[\text{Os}(\text{PH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ , when treated with  $(\text{CF}_3\text{CO})_2\text{O}$  gives  $[\text{Os}\{\text{PH}(\text{C}[\text{O}]\text{CF}_3)\}\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$  and this compound is dehydrochlorinated by NaH in tetrahydrofuran yielding the putative phosphinidene species,  $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$  which ring-closes to the title compound the solid-state structure of which is proved by X-ray crystallography.

Transition metal phosphinidene complexes,  $\text{L}_n\text{M}=\text{PR}$ , have been implicated as reaction intermediates in trapping experiments<sup>1-3</sup> but a stable example remains elusive. We have demonstrated that zero-valent osmium and ruthenium fragments with the steric protection provided by a pair of *trans* triphenylphosphine ligands can engage in multiple bond formation to carbon and yield stable complexes like  $[\text{Os}(\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ <sup>4</sup> and  $[\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2]$ .<sup>5</sup> In the light of these findings we have begun seeking stable molecules with phosphinidene ligands bound to zero-valent osmium and a typical target molecule for synthesis is  $[\text{Os}(\text{P}=\text{R})(\text{CO})_2(\text{PPh}_3)_2]$ . We describe herein (i) a terminal  $\text{PH}_2$ -complex,  $[\text{Os}(\text{PH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$  (4) which is a ver-

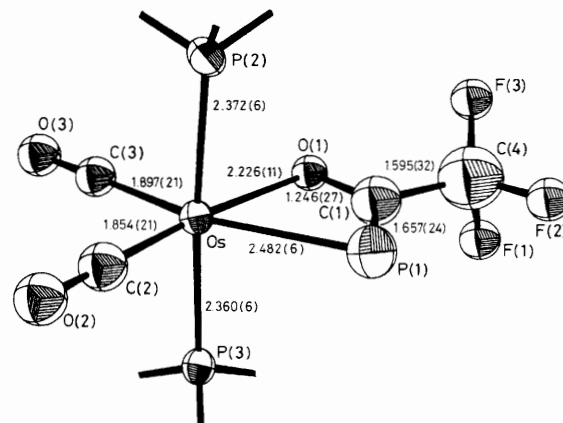
satile intermediate, (ii) the derived acylphosphido-complex,  $[\text{Os}\{\text{PH}(\text{C}[\text{O}]\text{CF}_3)\}\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$  (5) where the P-H bond is sufficiently acidic to permit dehydrochlorination by NaH in tetrahydrofuran (THF) to give not  $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$  but the *P*-metallated phospha-alkene complex,  $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$  (6), and (iii) reactions of (6) which suggest some phosphinidene character associated with this molecule.

Scheme 1 outlines the chemistry to be described.† Complexes of  $\text{PH}_3$  are still unusual<sup>6</sup> but  $\text{PH}_3$  readily replaces one  $\text{PPh}_3$  (*trans* to H) in  $\text{MHCl}(\text{CO})(\text{PPh}_3)_3$  to give (1). The cationic complexes (2) and (3) are prepared by acid cleavage of the hydride ligand followed by carbonylation (80 psi, 18 h, 70 °C). Deprotonation of (3) leads to the air-stable (4) with a pyramidal  $\text{PH}_2$ -ligand (*cf.* the production of a  $\text{PPhPh}$ -ligand from a  $\text{PH}_2\text{Ph}$  complex<sup>7</sup>). The phosphorus atom in (4) is readily acylated with trifluoroacetic anhydride and spontaneous loss of  $\text{H}^+$  yields (5). In the presence of the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) the trifluoroacetylphosphido-ligand is readily methylated with iodomethane to give (8) ( $\text{X} = \text{Cl}$ ). However, in the presence of HCl, (5) eliminates the trifluoroacetyl group resulting in the re-formation of the cationic  $\text{PH}_3$ -complex (3).

The trifluoroacetylphosphido-ligand in (5) is deprotonated by either DBU or NaH in a THF solution heated under reflux

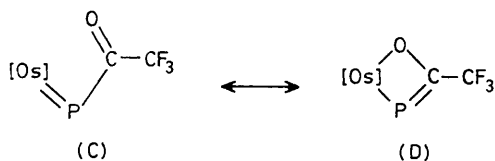
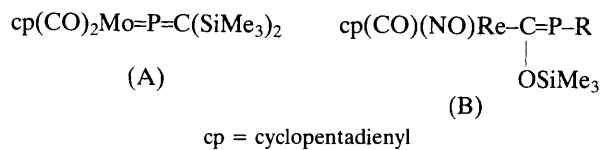


**Scheme 1.** Synthesis and reactions of  $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$  ( $\text{L} = \text{PPh}_3$ ,  $\text{M} = \text{Ru}$  or  $\text{Os}$ ,  $\text{X} = \text{Cl}$  or  $\text{I}$ ).



**Figure 1.** Molecular structure of  $[\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2]$  (6) (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are:  $\text{P}(1)\text{-Os-O}(1)$  67.3(4),  $\text{Os-P}(1)\text{-C}(1)$  73.6(8),  $\text{P}(1)\text{-C}(1)\text{-O}(1)$  128.2(1.6),  $\text{Os-O}(1)\text{-C}(1)$  90.8(1.2)°.

† New compounds (1)–(7) have all given satisfactory elemental analyses. Important i.r. absorptions ( $\nu$ ,  $\text{cm}^{-1}$ ) are as follows: (1) 1942 (CO), 2332 (PH); (2) 1961 (CO); (3) 2064, 2004 (CO); (4) 2030, 1962 (CO), 2260 (PH); (5) 2040, 1976 (CO), 1620 (acyl CO), 2320 (PH); (6) 2012, 1943 (CO); (7a) 2024, 1952 (CO), 1649 (acyl CO); (7b) 2023, 1960 (CO), 1646 (acyl CO); (8a) 2034, 1975 (CO), 1512 (acyl CO); (8b) 2030, 1972 (CO), 1512 (acyl CO).



forming the phospho-alkene (6). A single crystal X-ray diffraction study of (6)<sup>‡</sup> reveals the structure shown in Figure 1. Phospha-alkenes (RP=CR'<sub>2</sub>) have a diverse co-ordination chemistry<sup>8</sup> but examples where either R or R' are metal substituents are restricted to the phosphavinylidene (A)<sup>9</sup> with a linear Mo-P-C arrangement and the C-metallated compound (B).<sup>10</sup>

Compounds (A) and (6) appear to be the only two reported compounds with two-co-ordinate phosphorus donor atoms. § However, (6) differs from (A) in having a very bent arrangement at the phosphorus atom, the Os-P-C angle is 73.6(8)°. The bonding can be considered in terms of (C)  $\longleftrightarrow$  (D).

<sup>‡</sup> Crystal data (6): C<sub>40</sub>H<sub>30</sub>F<sub>3</sub>O<sub>3</sub>OsP<sub>3</sub>, *M* = 898.2, monoclinic, space group *C2/c*, *a* = 19.555(13), *b* = 13.168(3), *c* = 28.888(15) Å, β = 103.83(4)°, *U* = 7223(6) Å<sup>3</sup>, *D<sub>c</sub>* = 1.65 g cm<sup>-3</sup> for *Z* = 8, *F*(000) = 3535, λ(Mo-K<sub>α</sub>) = 0.71069 Å, μ(Mo-K<sub>α</sub>) = 35.62 cm<sup>-1</sup>. 3184 Observed reflections [*F* > 3σ(*F*)] were collected on a Syntex diffractometer at -90 °C. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least squares (all atoms anisotropic except phenyl carbon and hydrogen atoms) to *R* 0.071 (*R<sub>w</sub>* = 0.064). The atomic co-ordinates 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.

§ But see ref. 11

The weak Os-O interaction, 2.226(11) Å, is evident from comparison with other Os-O distances, *e.g.*, for the chelate carbonate ligand in [Os(OC(O)O)Cl(NO)(PPh<sub>3</sub>)<sub>2</sub>] the Os-O distances are 2.034(5) and 2.060(5) Å.<sup>12</sup> Also the C-O bond is short at 1.246(27) Å. These facts suggest a contribution to the bonding from (C) and some reactions of (6) are compatible with this. Compound (6) forms a 1:1 adduct with gold(I) fragments (AuX), and a structure, not yet confirmed crystallographically, but compatible with i.r. data is given as (7) (see Scheme 1).

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