Oxidative Addition of $Ph_3PCHCHO$ at a Triosmium Cluster with Cleavage of C–H Bonds: Crystal Structures of Two Isomers containing the New Ligands Ph_3PCCHO and Ph_3PCHCO, respectively

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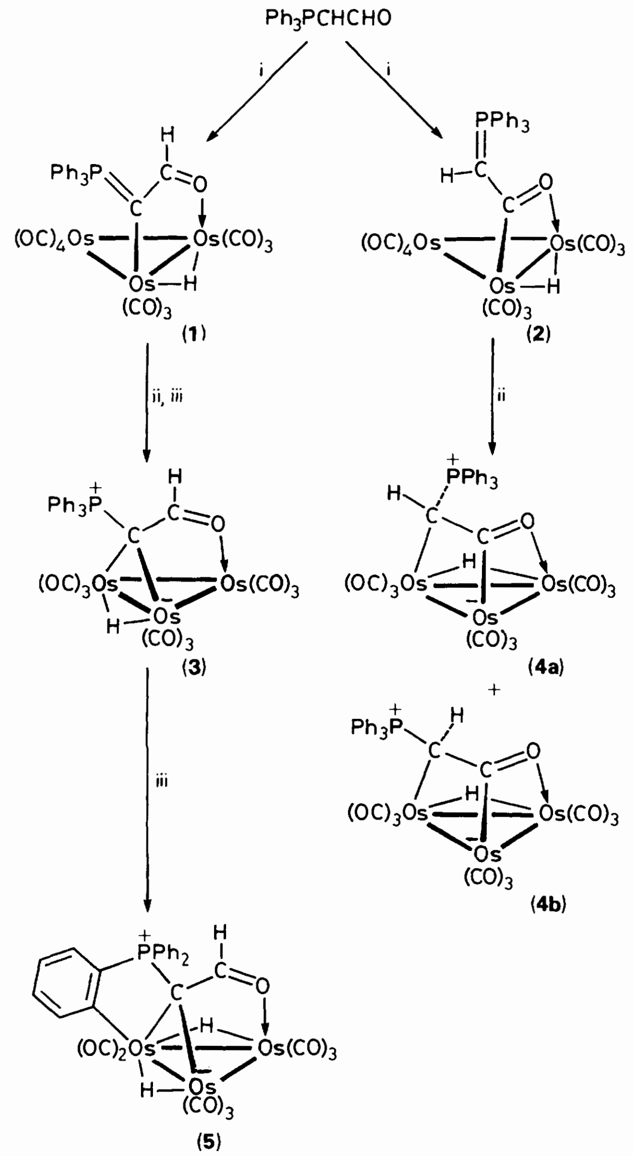
Rapid oxidative addition of $Ph_3PCHCHO$ at $[Os_3(CO)_{10}(MeCN)_2]$ gives the isomers $[Os_3H(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ (**1**) and $[Os_3H(\mu\text{-}Ph_3PCHCO)(CO)_{10}]$ (**2**) (*X*-ray structures reported) which decarbonylate to give the clusters containing triply-bridging ligands: $[Os_3H(Ph_3PCCHO)(CO)_9]$ (**3**), $[Os_3H_2(C_6H_4PPh_2CCHO)(CO)_8]$ (**5**), and $[Os_3H(Ph_3PCHCO)(CO)_9]$ (**4**) (as two isomers).

The cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with many molecules of type HX to give the clusters $[Os_3H(\mu\text{-}X)(CO)_{10}]$ and often CH bonds are cleaved.[1] Initial co-ordination before the oxidative addition step seems necessary since pyridine, alkenes, and aldehydes react with decreasing rates in this order but alkanes do not react. (Triphenylphosphoranylidene)ethanal, $Ph_3PCHCHO$, has dipolar character with significant negative charge at oxygen and positive charge at the phosphorus. The oxygen atom should be a good donor and indeed $Ph_3PCHCHO$ reacts rapidly (within 1 min) with $[Os_3(CO)_{10}(MeCN)_2]$ in CH_2Cl_2 at room temperature to give the isomers $[Os_3H(Ph_3PCCHO)(CO)_{10}]$ (**1**) (35%) and $[Os_3H(Ph_3PCHCO)(CO)_{10}]$ (**2**) (35%). Since both compounds are light-sensitive, the reaction, TLC on silica, and isolation of products were carried out in the dark. The reaction rate is very much greater than for simple aldehydes, RCH_2CHO, which give acyl clusters $[Os_3H(\mu\text{-}RCH_2CO)(CO)_{10}]$.[2] The unsaturated aldehydes $RCH{=}CHCHO$ (R = Me or Ph) also undergo slow oxidative addition in this case at two sites, the 1- and 3-positions,[3] in contrast to oxidative addition at the 1- and 2-positions of $Ph_3PCHCHO$.

Scheme 1 shows the formation of (**1**) and (**2**) and their subsequent decarbonylations. Dichloromethane solutions of (**1**) and (**2**) in visible light (*e.g.* daylight) gave (**3**) (80%) and an inseparable mixture of (**4a**) and (**4b**) (70% in total), respectively. Thermolysis of cluster (**1**) in toluene at 100 °C gave (**3**), which decarbonylates further to (**5**) (76%), whereas (**2**) does not decarbonylate in the dark at this temperature. The structures shown for (**1**)—(**5**) are based on IR and NMR



Scheme 1. i, $[Os_3(CO)_{10}(MeCN)_2]$, CH_2Cl_2, 20 °C; ii, visible light, CH_2Cl_2, 20 °C; iii, toluene, 100 °C or heptane, 96 °C.

spectroscopy† and *X*-ray crystallography. Cluster (**4**) exists as two isomers which could not be separated in bulk and spectra given correspond to mixtures. However, on one occasion isomerically pure crystals were successfully grown and an *X*-ray structure of one of these, (**4a**), was obtained. On the basis of this structure, we believe that the other isomer, (**4b**), has the structure shown with inversion at carbon. The organic ligands in (**1**)—(**5**) have apparently not been observed previously.

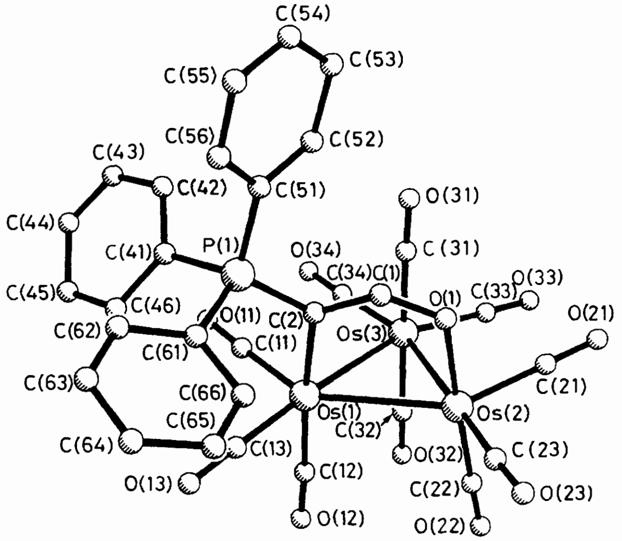


Figure 1. Molecular structure of the cluster $[Os_3H(Ph_3CCHO)(CO)_{10}]$ (**1**). Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.933(1), Os(1)–Os(3) 2.928(1), Os(2)–Os(3) 2.871(1), Os(1)–C(2) 2.21(1), Os(2)–O(1) 2.11(1), C(1)–O(1) 1.32(2), C(1)–C(2) 1.38(2), C(2)–P(1) 1.73(1), Os(1)–C(2)–C(1) 122(1), Os(2)–O(1)–C(1) 124(1), Os(1)–C(2)–P(1) 123.6(8), P(1)–C(2)–C(1) 113(1), C(2)–C(1)–O(1) 126(1).

The *X*-ray structures of (**1**) and (**2**)‡ are reported here (Figures 1 and 2) and those of (**3**), (**4a**), and (**5**) will be reported later. In clusters (**1**) and (**2**) the organic ligand bridges two metal atoms through C and O atoms. In these and each of the derivatives we have synthesised from $Ph_3PCHCHO$ (see Scheme 1), there are Os–O bonds and we believe that this is the first metal–ligand bond to be formed. $Ph_3PCHCHO$ exists as isomers *cis* and *trans* about the central C–C bond and likewise (**1**) and (**2**) are *trans* and *cis* in this respect. We do not know, however, whether (**1**) is formed from *trans*-$Ph_3PCHCHO$ and (**2**) from the *cis* isomer. Bonding descriptions (**A**) and (**C**) correspond with those of known compounds without phosphorus centres, *e.g.* $[Os_3H(RCH{=}CCHO)(CO)_{10}]$ and $[Os_3H(RCH{=}CHCO)(CO)_{10}]$ (R = Me or Ph).[3,4] However, the phosphorane nature of (**1**) and (**2**) allows contributions from the zwitterionic forms (**B**) and (**D**).[5] As a result the ν_{CO} wavenumbers for (**1**) are lower by 3—13 cm^{-1} than for the corresponding absorptions for the

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† *Key spectroscopic data:* IR ν_{CO}/cm^{-1}: (**1**) (CH_2Cl_2) 2097m, 2058s, 2042s, 2009s, 2003s, 1980m, 1956sh; (**2**) (hexane) 2097m, 2055s, 2046s, 2012s, 2007s, 1994m, 1984sh, 1979m, 1974sh, 1964m; (**3**) (CH_2Cl_2), 2071m, 2036vs, 2015s, 1985m, 1955m; mixture of (**4a**) and (**4b**) (CH_2Cl_2) 2078s, 2047vs, 2011s, 1995m, 1981m; (**5**) (heptane) 2082s, 2044s, 2013vs, 1992s, 1973m, 1944s. ^1H NMR (200 MHz, $CDCl_3$): (**1**) δ −12.85 (s, OsH), 7.5—7.7 (Ph), 8.10 (d, *J* 14.8 Hz, CCHO); (**2**) δ −14.45 (s, OsH), 4.20 (d, *J* 29.3 Hz, CHCO), 7.4—7.6 (Ph); (**3**) δ −12.71 (s, OsH), 7.1—7.8 (Ph), 10.65 (d, *J* 7.0 Hz, CCHO); mixture of (**4a**) and (**4b**) δ −15.50 (t, *J* 1.1 Hz, OsH), −12.92 (s, OsH), 2.90 (d, *J* 17.7 Hz, CHCO), 3.07 (dd, *J* 14.8, 1.1 Hz, CHCO), 7.3—7.7 (Ph); (**5**) δ −12.69 (s, OsH), −11.64 (d, *J* 5.3 Hz, OsH), 8.22 (m, *ortho*-H, C_6H_4), 6.9—7.9 (Ph + C_6H_4), 10.73 (dd, *J* 6.8, 1.3 Hz, CCHO).

‡ *Crystal data* for $[Os_3H(Ph_3PCCHO)(CO)_{10}]$ (**1**): yellow crystal, $C_{30}H_{17}O_{11}Os_3P$, M = 1155.04 g mol^{-1}, monoclinic, $P2_1/n$, a = 12.526(3), b = 14.926(5), c = 16.908(6) Å, β = 95.79(2)°, U = 3145(1) Å^3, Z = 4, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 122.1 cm^{-1}, $F(000)$ = 2112. Final R and R_W values 0.0627 and 0.0665 for 4428 absorption-corrected data [$5 \leqslant 2\theta \leqslant 50°$] with $F_o \geqslant 3\sigma(F_o)$. $[Os_3H(Ph_3PCHCO(CO)_{10}]$ (**2**): yellow crystal, $C_{30}H_{17}O_{11}Os_3P$, M = 1155.04, triclinic, $P\bar{1}$, a = 10.730(2), b = 12.989(5), c = 13.002(4) Å, α = 66.58(2), β = 86.96(2), γ = 83.26(2)°, U = 1651.5(8) Å^3, Z = 2, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 116.3 cm^{-1}, $F(000)$ = 1056. Final R and R_W values 0.0491 and 0.0484 for 4571 absorption-corrected data [$5 \leqslant 2\theta \leqslant 50°$] with $F_o \geqslant 3\sigma(F_o)$. Both compounds: Nicolet R3v/m diffractometer, direct methods, all non-H atoms anisotropic, no H-atoms in the models. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

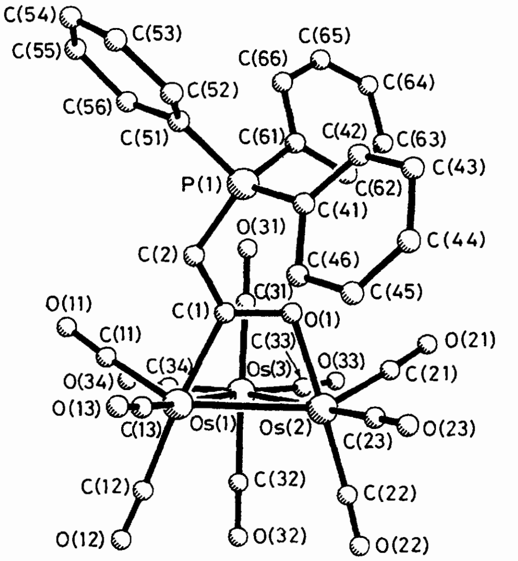
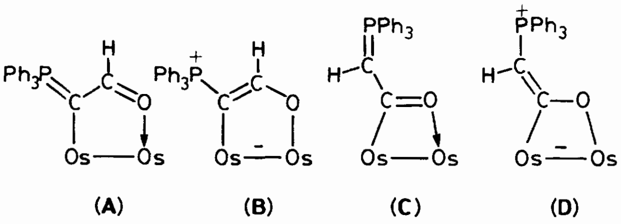


Figure 2. Molecular structure of the cluster $[Os_3H(Ph_3CHCO)(CO)_{10}]$ (**2**). Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.890(1), Os(1)–Os(3) 2.858(1), Os(2)–Os(3) 2.856(1), Os(1)–C(1) 2.10(1), Os(2)–O(1) 2.104(8), C(1)–O(1) 1.32(2), C(1)–C(2) 1.36(2), C(2)–P(1) 1.75(1), Os(1)–C(1)–O(1) 114.1(7), Os(1)–C(1)–C(2) 127.0(8), Os(2)–O(1)–C(1) 109.8(6), O(1)–C(1)–C(2) 119(1), C(1)–C(2)–P(1) 121.7(9).

non-phosphorus containing compound $[Os_3H(PhCH{=}CCHO)(CO)_{10}]$, and for (**2**) lower by 7—17 cm^{-1} relative to those of $[Os_3H(PhCH{=}CHCO)(CO)_{10}]$, representing small contributions of (**B**) and (**D**) to the basic structures (**A**) and (**C**), respectively. On the other hand, the Ph_3P groups in compounds (**3**)—(**5**) are linked through tetrahedral carbon atoms to the clusters and there is much closer to a complete negative charge at the metal atoms and a more fully developed phosphonium centre. Consequently ν(CO) for (**3**) are 41—48 cm^{-1} lower than the corresponding absorptions for $[Os_3H_2(CHCHO)(CO)_9]$,[6] which has a very similar μ_3-ligand but without the phosphonium centre.



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