Journal of Organometallic Chemistry, 408 (1991) C18–C21
Elsevier Sequoia S.A., Lausanne
JOM 21783PC

Preliminary communication

Oxidative addition of phenylphosphole: X-ray crystal structures of two ring-opened products $[Os_3(\mu_3\text{-}PhPC_4H_4)(CO)_x]$ where $x = 8$ or 9

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(Received February 12th, 1991)

Abstract

The phenylphosphole complex $[Os_3(PhPC_4H_4)(CO)_{11}]$ decarbonylates in refluxing octane to yield the oxidative addition product $[Os_3(\mu_3\text{-}PhPC_4H_4)(CO)_9]$ (**1**) in which ring-opening of both the triosmium and the five-membered phosphole rings has occurred, while further thermal decarbonylation to the cluster $[Os_3(\mu_3\text{-}PhPC_4H_4)(CO)_8]$ (**2**) leads to metal ring closure and a major reorganisation of the coordination of the 8-electron donating $PhPC_4H_4$ ligand.

Some five-membered heterocyclic ligands (furan [1], thiophene [2], pyrrole [3]) undergo oxidative addition with C–H bond cleavage on reaction with $[Os_3(CO)_{10}(MeCN)_2]$ to give $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_3X)(CO)_{10}]$ (X = O, S, or NR), whereas others (selenophene [2], tellurophene [2]) ring open to give the clusters $[Os_3(\mu\text{-}C_4H_4X)(CO)_{10}]$ (X = Se or Te). We have now examined another member of this class of heterocycles, phenylphosphole, and find that simple substitution compounds $[Os_3(PhPC_4H_4)_x(CO)_{12-x}]$ ($x = 1$ or 2) are formed initially with the heterocycle η^1-co-ordinated through the P atom, which is the commonly found mode of co-ordination for phospholes [4]. The only other known type of co-ordination is η^1 through phosphorus to one metal atom and η^4 through carbon atoms to another metal atom [5]. However, oxidative addition does occur subsequently, since a solution of $[Os_3(PhPC_4H_4)(CO)_{11}]$ in refluxing octane leads to $[Os_3(PhPC_4H_4)(CO)_9]$ (**1**) and to $[Os_3(PhPC_4H_4)(CO)_8]$ (**2**) (respective yields 50 and 15% after 3 h and 18 and 25% after 10 h). Isolated cluster **1** was separately shown to convert thermally to cluster **2**. The ^1H NMR spectrum * indicates that cluster **1** does not contain a hydride ligand and that the C_4 chain is still intact but is bonded to the phosphorus atom at one end only. However, a single-crystal X-ray structure **

(Fig. 1) was needed to establish the mode of bonding. The $PhPC_4H_4$ ligand is bonded to the three metal atoms as an 8-electron donor which makes cluster **1** a 50-electron cluster with only two Os–Os bonds as expected for this count. The coordination can be analysed in terms of a μ-phosphido (three-electron donor) and a μ-alkylidene (two-electron donor) bridge linking the bonded Os(1)–Os(2) edge and an η^3-allyl (three-electron donor) group bonded to Os(3). The five-membered phosphole ring has been expanded to a six-membered ring by insertion of an Os atom. This relates to our previously observed ring opening of selenophene and tellurophene except that products in those cases, $[Os_3(\mu\text{-}C_4H_4X)(CO)_{10}]$ (**3**) (X = Se or Te), have doubly bridging six-electron donating bridges. It is very likely that the initial product from $[Os_3(PhPC_4H_4)(CO)_{11}]$ is the ring-opened cluster $[Os_3(\mu\text{-}PhPC_4H_4)(CO)_{10}]$ (**3**) (X = PPh) with structure closely related to that of $[Os_3(SeC_4H_4)(CO)_{10}]$ but this species must readily decarbonylate to cluster **1** and is not observed (Scheme 1).

On decarbonylation of cluster **1** to give cluster **2**, it appears from the ^1H NMR spectrum * that the $PhPC_4H_4$ ligand remains intact but there are large changes in the chemical shifts and coupling constants which indicate that there is a total reorganisation in the way the ligand is coordinated. The single-crystal X-ray structure ** of **2** shows that the $PhPC_4H_4$ ligand is indeed intact (Fig. 2) and is still an eight-electron donor. The loss of CO in this process is compensated for by the formation of a new Os–Os bond with closure of the metal triangle. This change in cluster shape has necessitated a major change in the way the organic ligand is co-ordinated. The μ-phosphido component to the bonding remains but the C_4 chain is now co-ordinated through a σ-bond [Os(1)–Os(4)] and an η^4-diene co-ordination to Os(3). In effect one Os–C σ-bond and an η^3-allyl bond is replaced by an η^4-diene bond to metal.

There are many known examples of co-ordinated phospholes, all bonded through the phosphorus atom to the metal but this appears to be the first example of an

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* *Selected spectroscopic data for clusters 1 and* **2**: IR data (cm^{-1}) for cyclohexane solutions; ^1H NMR data (300 MHz, J values in Hz) for acetone-d_6 solutions at room temperature. *Cluster 1*: ν(CO): 2082w, 2065sh, 2059vs, 2045m, 2030s, 2012s, 1999m, 1988m, 1981s, 1964w, 1955w. ^1H NMR: δ 7.48 (m, Ph), 6.15 (m, H^x), 5.62 (dd, H^y), 4.84 (ddd, H^w), 3.40 (dd, H^z) ($J(H^x-H^y)$ 8.6, $J(H^x-H^w)$ 6.6, $J(H^x-H^z)$ 0.4, $J(H^y-H^z)$ 7.6, $J(H^w-P)$ 20.7, $J(H^x-P)$ 3.5, $J(H^y-P)$ 12.8, $J(H^z-P)$ 7.6). *Cluster* **2**: ν(CO): 2080m, 2048s, 2014vs, 1990m, 1964m, 1949w. ^1H NMR: δ 10.56 (ddd, H^z), 7.85 (dd, H^y), 7.50 (m, Ph), 6.35 (dddd, H^x), 4.63 (dd, H^w) ($J(H^y-H^z)$ 8.3, $J(H^x-H^z)$ 1.0, $J(H^x-H^y)$ 6.6, $J(H^w-H^x)$ 10.0, $J(H^w-P)$ 7.6, $J(H^x-P)$ 21.1, $J(H^z-P)$ 4.3).

** *Crystal structure determinations.* Both structures: Nicolet R3v/m diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å) at 23°c, SHELXTL-PLUS [7]. *Cluster 1*: yellow crystal, $C_{19}H_9O_9Os_3P$, $M = 982.85$, triclinic, space group $P\bar{1}$, a 8.831(2), b 8.824(2), c 14.521(3) Å, α 85.31(2), β 80.49(2), γ 79.33(2)°, U 1094.9(5) $Å^3$, $Z = 2$, μ(Mo-K_α) 175.0 cm^{-1}, $F(000) = 876$. Direct methods, 3075 unique absorption-corrected intensity data between $5 \leqslant 2\theta \leqslant 50°$ and with $I_o \geqslant 3\sigma(I_o)$ in refinement, 289 parameters (all non-H atoms anisotropic, H-atoms in idealised positions), final $R = 0.0546$ and $R_w = 0.0541$ where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$. *Cluster* **2**: yellow crystal, $C_{18}H_9O_8Os_3P$, $M = 954.84$, monoclinic, space group $P2_1/n$, a 12.548(4), b 10.470(4), c 17.084(4) Å, β 112.65(3)°, U 2071(1) $Å^3$, $Z = 4$, μ(Mo-K_α) 185.0 cm^{-1}, $F(000) = 1696$. Direct methods, 2504 unique absorption-corrected data between $5 \leqslant 2\theta \leqslant 50°$ and with $I_o \geqslant 3\sigma(I_o)$ in refinement, 266 parameters (all non-H atoms except C(21) anisotropic, H-atoms in idealised positions), final $R = 0.0635$ and $R_w = 0.0655$ where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.0022F_o^2]$. A list of atom coordinates and a complete list of bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

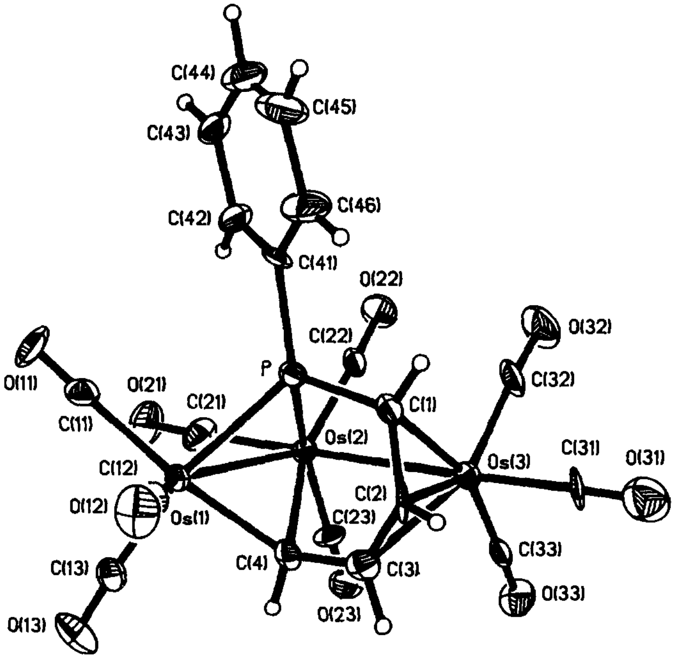
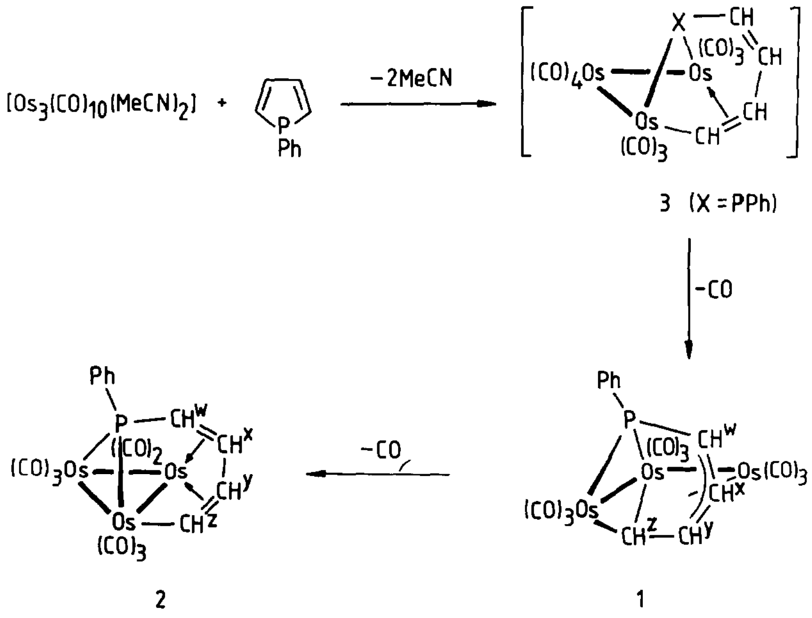


Fig. 1. Molecular structure of $[Os_3(PhPC_4H_4)(CO)_9]$ (1); selected bond lengths (Å) and angles (°): Os(1)–Os(2), 2.813(1); Os(2)–Os(3), 2.948(1); Os(1)...Os(3), 4.510(1); Os(1)–P, 2.353(5); Os(2)–P, 2.380(5); Os(1)–C(4), 2.10(2); Os(2)–C(4), 2.25(2); Os(3)–C(1), 2.22(2); Os(3)–C(2), 2.21(2); Os(3)–C(3), 2.34(2); P–C(1), 1.79(2); C(1)–C(2), 1.40(3); C(2)–C(3), 1.44(3); C(3)–C(4), 1.44(3); P–C(1)–C(2), 121(1); C(1)–C(2)–C(3), 117(2); C(2)–C(3)–C(4), 129(2); Os(1)–P–Os(2), 72.9(1); Os(1)–C(4)–Os(2), 80.4(7).



Scheme 1

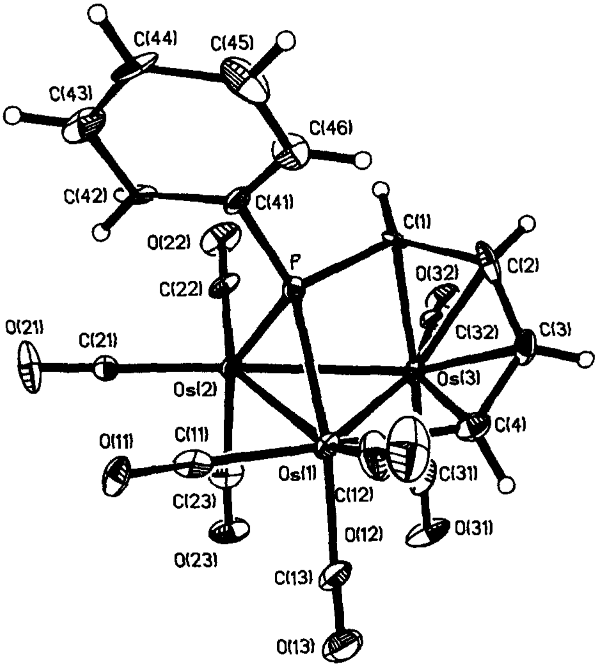


Fig. 2. Molecular structure of $[Os_3(PhPC_4H_4)(CO)_8]$ (2); selected bond lengths (Å) and angles (°): Os(1)–Os(2), 2.863(2); Os(2)–Os(3), 2.768(2); Os(1)–Os(3), 2.861(2); Os(1)–P, 2.339(7); Os(2)–P, 2.331(7); Os(3)...P, 2.874(6); Os(3)–C(1), 2.32(3); Os(3)–C(2), 2.28(3); Os(3)–C(3), 2.27(3); Os(3)–C(4), 2.14(3); Os(1)–C(4), 2.14(3); P–C(1), 1.77(3); C(1)–C(2), 1.40(3); C(2)–C(3), 1.39(5); C(3)–C(4), 1.40(5); P–C(1)–C(2), 134(3); C(1)–C(2)–C(3), 124(3); C(2)–C(3)–C(4), 126(2); C(3)–C(4)–Os(1), 131(2); Os(1)–P–Os(2), 75.6(2).

oxidative addition with a metal atom inserted into a P–C bond. Indeed in other cases the reverse (ring-closure) reaction occurs as in the reaction of μ-phosphido ligands with acetylenes to give phosphole-type rings [6].

Acknowledgements. We thank the SERC for a studentship (for N.I.P.) and for a grant towards the diffractometer.

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