New Mode of 'Benzyne' Co-ordination. Crystal and Molecular Structure of $Os_3(CO)_9(PEt)(C_6H_4)$

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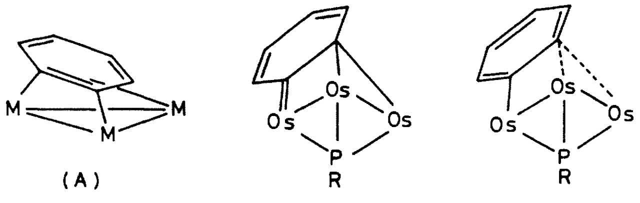
Summary The benzyne ligand in $Os_3(CO)_9(PEt)(C_6H_4)$ is shown by *X*-ray crystallography to be asymmetrically bound with one carbon atom σ-bonded to one osmium while a second bridges the two other metal atoms; a low energy process interchanges these two sites in solution.

We report that thermolysis of $Os_3(CO)_{11}PPh_2R$ (R = Me, Et, and Ph) affords a series of complexes, $Os_3(CO)_9(PR)(C_6H_4)$ [(**1**), R = Me; (**2**), R = Et, and (**3**), R = Ph] which possess a new type of benzyne co-ordination.

Synthesis of the air-stable, yellow, crystalline solids (**1**), (**2**), and (**3**) is effected readily by refluxing the appropriate $Os_3(CO)_{11}PPh_2R$ derivative in n-nonane for 1 h (70–80% yield). Complex (**2**) [ν_{CO} (cyclohexane) 2086w, 2064vs, 2050wsh, 2041s, 2010s, 2007s, 1991s, 1989msh, 1982w, and 1976w cm^{-1}] has been most studied, but the mass, i.r., and



(A) (B) (C)

(1) R = Me
(2) R = Et
(3) R = Ph

Carbonyl groups not shown

^{1}H n m r spectra of (**1**) and (**3**) indicate that they are entirely analogous At 30 °C, the ^{1}H n m r spectrum of (**2**) ($CDCl_3$) contains the A and B parts of an AA′BB′X system centred at δ 7·60 and 7·00 with small *J*(PH) values and its {^{1}H}^{13}C spectrum ($C_6D_5CD_3$) includes three aromatic resonances δ 147·8 [d, *J*(PC) 5·4 Hz], 146·8 [d, *J*(PC) 4·0 Hz], and 128·5 p p m (s) This is apparently consistent with a symmetrically co-ordinated benzyne ligand Since the other ligands were expected to provide local C_{3v} symmetry [with a μ_3-PR and three $Os(CO)_3$ groups], an *X*-ray crystal structure determination of (**2**) was undertaken to establish the mode of benzyne co-ordination under these circumstances

Crystal data $C_{17}H_9O_9Os_3P$, triclinic, space group $P\bar{1}$, $a = 8{\cdot}385(2)$, $b = 9{\cdot}391(4)$, $c = 14{\cdot}900(9)$ Å, $\alpha = 94{\cdot}57(4)$, $\beta = 94{\cdot}05(4)$, $\gamma = 68{\cdot}60(3)°$, $Z = 2$, $U = 1087{\cdot}9(9)$ Å^3, Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å), μ(Mo-K_α) = 169 0 cm^{-1}, F(000) = 852 The structure was solved by heavy-atoms methods and the refinement at present gives $R = 0{\cdot}079$ (141 parameters refined) for 2783 independent reflections [$I_0 > 2{\cdot}5\sigma(I)$ and $2{\cdot}9 < 2\theta < 50°$, collected on a Syntex *P*3 four-circle diffractometer] †

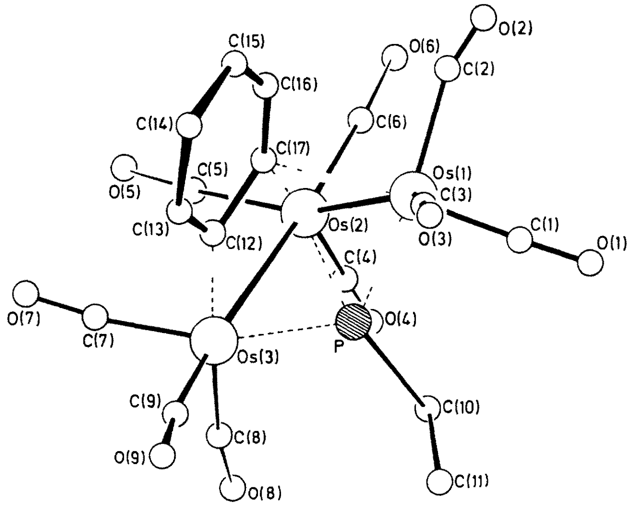


FIGURE 1 Molecular structure of $Os_3(CO)_9(C_6H_4)(PC_2H_5)$ Bond lengths Os(1)–Os(2) 2 789(2), Os(2)–Os(3) 2 929(2), Os(1)–C(17) 2·31(3), Os(2)–C(17) 2·17(3), Os(3)–C(12) 2 13(3), C(12)–C(17) 1·53(5), Os(1)–P 2·335(8), Os(2)–P 2·415(9), Os(3)–P 2·306(9), P–C(10) 1·86(4), and Os(1) Os(3) 4·008(2) Å Bond angles Os(1)–Os(2)–Os(3) 89 0(1)° Benzyne–Os_3 interplanar angle 58·9°

The molecule (Figure 1) consists of a bent chain of three osmium atoms, each co-ordinated by three carbonyl groups The plane of the three osmium atoms is co-ordinated on one side by a face bridging ($P–C_2H_5$) ligand and on the opposite side by a benzyne ligand The Os(1)–Os(2) and Os(2)–Os(3) bond lengths are consistent with metal–metal bonding The benzyne ligand is bound asymmetrically to the chain with one carbon atom linked to Os(3) only [C(12) Os(2) 3·04 Å] and the adjacent carbon atom bonded to both Os(1) and Os(2) In the benzyne ligand the C(12)–C(17) distance is lengthened to a value consistent with a single carbon–carbon bond [1·53(5) Å], while the other carbon–carbon distances in the ring are closer to those normally found in a benzene ring (average 1·39 Å) This contrasts with the situation for the previously reported bonding mode to a trinuclear cluster (A) in $Os_3(CO)_7(PPh_2)_2(C_6H_4)$,[1] $HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$,[2] and $HOs_3(CO)_7(PPh_2)(PPhC_6H_4C_6H_3)$[2] in which little deviation from a mean of 1·42 Å was observed Two bonding descriptions appear plausible The C_6H_4 ligand acts as a 4-electron donor in the first (B), allowing the cluster to comply with the 18-electron rule However, the mean Os–C(17) distance of 2·24 Å is *ca* 0·1 Å longer than the metal–carbon bond lengths to the bridging carbenes in $H_2Os_3(CO)_9(CH_2)$[3] and $H_2Os_4(CO)_{12}(CHCH_2Ph)$[4] Indeed, the osmium–carbon distances suggest that the ligand is acting as a terminal, C(12), and bridging, C(17), aryl group (C) This would make the aryne a 2-electron donor, rendering the cleavage of the Os(1)–Os(3) bond problematical Taking the bond lengths as a whole, the ring is best described as an *o*-phenylene ligand with some carbenoid character, *i e* contributions from (B) and (C)

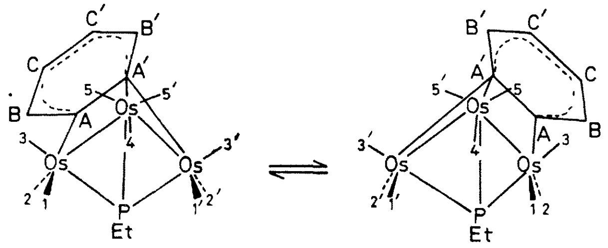


FIGURE 2 Aryne rocking of (**2**).

{^{1}H}^{13}C N m r spectra of a ^{13}CO-enriched sample of (**2**) have been recorded between −132 and 95 °C From −80 to −60 °C, the carbonyl region exhibits four resonances assigned as follows (Figure 2) δ (CD_2Cl_2–$CHFCl_2$) 183·4 [d, *J*(PC) 66 Hz, C-3 and C-3′], 179·6 [d, *J*(PC) 9 Hz, C-1 and C-1′ or C-2 and C-2′], 179·2 [d, *J*(PC) 8 Hz, C-4, C-5, and C-5′], and 173·4 p p m (s, C-1 and C-1′ or C-2 and C-2′) At −100 °C, the resonance at δ 179 2 p p m broadens and by −132 °C, it splits into two broad resonances at δ 180·4

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† 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

[d, J(PC) *ca* 11 Hz, C-5 and C-5′] and 178 0 p p m (s, C-4) This is consistent with a fast exchange process which still gives an apparent molecular symmetry plane at −132 °C (Figure 2) At −132 °C, localised scrambling begins to exchange C-4 with C-5 and C-5′ At 15 °C, rotation of the two end $Os(CO)_3$ groups becomes evident as the three resonances at δ 183 4, 179 6, and 173 4 p p m broaden By 95 °C ($C_6D_5CD_3$) they form a broad, averaged resonance, but even at this temperature there is no evidence of exchange between carbonyl environments on the central and terminal osmium atoms, indicating a rigid metal frame The aryne rocking process (Figure 2), involving the making and breaking of Os(2)–carbon bonds, evidently has a much lower activation energy than previously reported examples of acetylene oscillation on the face of a triosmium cluster, *e g* $Os_3(CO)_7(PMe_2)_2(C_6H_4)$[5] and $H_2Os_3(CO)_9(MeCCMe)$[6]

Phosphine degradation has progressed further than usual to form (**1**), (**2**) and (**3**) {An exception is the isolation of $Os_5(CO)_{15}[P(OMe)]$ from $Os_3(CO)_{11}P(OMe)_3$ under more vigorous conditions[7]} Cleavage of aryl–phosphorus bonds is evidently preferred since, under similar conditions, all P–C bonds in $Os_3(CO)_{11}PEt_3$[8] are retained and only the aryl group is lost from phosphorus in $Os_3(CO)_{11}PMe_2Ph$ to yield $HOs_3(CO)_9(PMe_2)(C_6H_4)$[5] The single pyrolysis product from $Os_3(CO)_{11}PPh_3$ contrasts with the plethora of products obtained by heating hydrocarbon solutions of $Os_3(CO)_{12}$ and PPh_3[1,2,9] All those metallated products are derived from $Os_3(CO)_{10}(PPh_3)_2$

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