Reactions of [Os$_5$(CO)$_{15}$C] with Diphosphines; Synthesis, Reactivity, and the X-Ray Crystal Structure of [Os$_5$(CO)$_{15}$C{Ph$_2$P(CH$_2$)$_2$PPh$_2$}] †

Brian F. G. Johnson, Jack Lewis, * **Paul R. Raithby, Maria J. Rosales, and Dorothy A. Welch**
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The reaction of [Os$_5$(CO)$_{15}$C] with 1,2-bis(diphenylphosphino)ethane (dppe) in CH$_2$Cl$_2$ under reflux affords the addition product [Os$_5$(CO)$_{15}$C(dppe)] (**1**). An X-ray crystal structure shows that the Os$_5$ square-pyramidal geometry of the parent carbide has opened up to give a 'wingtip-bridged butterfly' arrangement with the carbido-carbon atom lying at the centre of the metal framework. The diphosphine ligand co-ordinates in a unidentate fashion to the Os atom bridging the 'wingtips' of the 'butterfly' leaving the second phosphorus atom pendant. Reaction of complex (**1**) with further [Os$_5$(CO)$_{15}$C] gives a complex which has been tentatively assigned as the adduct [{Os$_5$(CO)$_{15}$C}$_2$(dppe)] (**2**).

The chemistry of the carbido-clusters [M$_5$(CO)$_{15}$C] (M = Ru or Os) with nucleophilic reagents has been extensively studied.[1] These reactions generally involve the formation of an adduct [M$_5$(CO)$_{15}$C(L)] (L = MeCN,[2] I$^-$,[3] pyridine,[4] CO,[5] or PR$_3$[2]) which adopts an open, carbide-centred, 'wingtip-bridged butterfly' metal geometry and may subsequently lose CO to form a substituted product [M$_5$(CO)$_{14}$C(L)] in which the metal framework has re-closed to give the square-based pyramidal geometry. A difference between the reactivity of the ruthenium and osmium systems has been observed and this has been attributed to the greater kinetic lability of the former species.[5]

The reaction of [Ru$_5$(CO)$_{15}$C] with phosphines leads only to the isolation of substitution products[2] [Ru$_5$(CO)$_{15-n}$C(PR$_3$)$_n$] (n = 1—4; for bulky phosphine ligands, n is small) and with diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1—4) the product is [Ru$_5$(CO)$_{13}$C{Ph$_2$P(CH$_2$)$_n$PPh$_2$}]; for n = 2 the diphosphine ligand bridges two adjacent ruthenium atoms,[6] for n = 4 two opposite Ru atoms in the square base are bridged.[7]

We now report the result of the reaction between [Os$_5$(CO)$_{15}$C] and the diphosphine Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe). This particular system was chosen because it was hoped that the relatively kinetically inert osmium cluster would allow the isolation of the intermediate addition product.

Results and Discussion

The complex [Os$_5$(CO)$_{15}$C] reacts with 1,2-bis(diphenylphosphino)ethane (dppe) in a 1:1 molar ratio, in CH$_2$Cl$_2$, under reflux to give the addition product [Os$_5$(CO)$_{15}$C(dppe)] (**1**) in 95% yield after 24 h. The proton-decoupled ^{31}P n.m.r. spectrum of (**1**) consists of two doublets, with one of these resonances unshifted from the free ligand [−154.2 p.p.m. relative to P(OMe)$_3$ which corresponds to −13.2 p.p.m. relative to H$_3$PO$_4$] while the other resonance occurs upfield at −158.9 p.p.m. (−17.9 p.p.m. relative to H$_3$PO$_4$). The phosphorus–phosphorus coupling, ^3J(PP), of 35 Hz is typical of a monoco-ordinated diphosphine and is consistent with the potentially
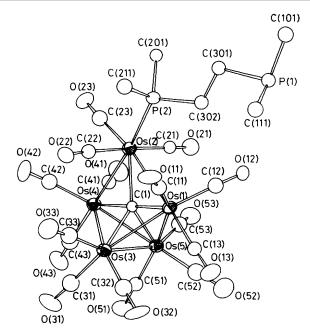
Figure. ORTEP plot of [Os$_5$(CO)$_{15}$C(dppe)] (**1**). Phenyl rings have been omitted for clarity

bidentate ligand co-ordinating to the metal framework through only one P atom.

In order to confirm the pendant bonding mode of the dppe ligand to establish the geometry of the metal framework, a single-crystal X-ray analysis was undertaken. The molecular structure of complex (**1**) is shown in the Figure together with the atom numbering scheme adopted. The final atomic co-ordinates are presented in Table 1 while selected bond length and angle data are in Table 2. The cluster geometry resembles that in [Os$_5$(CO)$_{16}$C][5] and [Os$_5$(CO)$_{15}$C(I)]$^-$,[3] and may be described as a 'wingtip-bridged butterfly,' the 'butterfly' being defined by the atoms Os(1), Os(3), Os(4), and Os(5). The variation in metal–metal distances in complex (**1**) follows those in [Os$_5$(CO)$_{15}$C(I)]$^-$[3] and [Os$_5$(CO)$_{16}$C][5] in that the Os(3)–Os(5) 'hinge' bond distance is the shortest. In all three clusters the Os(wingtip)–Os(hinge) distances are shorter than the

Table 1. Fractional co-ordinates of atoms with standard deviations in parentheses for [Os₅(CO)₁₅C(dppe)] (1)

Atom	x	y	z	Atom	x	y	z
Os(1)	0.558 20(7)	0.283 73(4)	−0.003 21(3)	C(51)	0.663 2(20)	0.318 4(12)	−0.171 4(8)
Os(2)	0.782 98(7)	0.178 50(4)	0.025 76(2)	O(51)	0.691 4(20)	0.356 1(11)	−0.206 4(6)
Os(3)	0.740 09(7)	0.384 66(4)	−0.051 08(3)	C(52)	0.438(3)	0.293 5(14)	−0.125 8(9)
Os(4)	0.881 29(7)	0.240 47(4)	−0.070 00(3)	O(52)	0.325 8(20)	0.303 6(11)	−0.138 7(7)
Os(5)	0.613 50(8)	0.267 40(4)	−0.110 32(3)	C(53)	0.590 7(24)	0.158 5(14)	−0.135 9(9)
C(1)	0.717 8(15)	0.261 1(8)	−0.037 1(5)	O(53)	0.576 3(21)	0.102 4(8)	−0.153 2(7)
P(1)	0.329 0(5)	0.094 3(3)	0.163 27(19)	C(301)	0.510 4(17)	0.088 0(10)	0.163 7(6)
P(2)	0.723 9(4)	0.132 7(3)	0.108 27(16)	C(302)	0.546 9(18)	0.123 9(10)	0.114 2(7)
C(11)	0.575 5(19)	0.324 7(11)	0.066 8(7)	C(102)	0.174 3(10)	0.055 7(9)	0.241 0(5)
O(11)	0.593 6(19)	0.352 9(8)	0.105 1(5)	C(103)	0.144 5(10)	0.029 5(9)	0.289 8(5)
C(12)	0.435 8(20)	0.199 6(12)	0.003 7(7)	C(104)	0.243 4(10)	0.002 6(9)	0.326 0(5)
O(12)	0.365 3(14)	0.143 9(9)	0.002 6(6)	C(105)	0.372 1(10)	0.001 8(9)	0.313 4(5)
C(13)	0.418 4(18)	0.354 1(11)	−0.022 9(7)	C(106)	0.401 8(10)	0.028 0(9)	0.264 5(5)
O(13)	0.331 8(17)	0.395 3(10)	−0.031 9(7)	C(101)	0.302 9(10)	0.054 9(9)	0.228 4(5)
C(21)	0.676 6(18)	0.097 7(10)	−0.011 8(7)	C(112)	0.266 2(15)	0.245 6(7)	0.130 7(4)
O(21)	0.620 1(18)	0.048 9(9)	−0.034 8(7)	C(113)	0.261 5(15)	0.327 8(7)	0.133 2(4)
C(22)	0.880 4(20)	0.262 6(11)	0.062 3(7)	C(114)	0.308 9(15)	0.366 7(7)	0.178 7(4)
O(22)	0.928 0(17)	0.315 9(8)	0.084 3(6)	C(115)	0.361 0(15)	0.323 5(7)	0.221 7(4)
C(23)	0.942 4(22)	0.115 4(12)	0.032 2(8)	C(116)	0.365 8(15)	0.241 4(7)	0.219 2(4)
O(23)	1.029 3(15)	0.076 3(10)	0.035 9(7)	C(111)	0.318 3(15)	0.202 4(7)	0.173 7(4)
C(31)	0.832 9(25)	0.439 3(14)	−0.099 8(9)	C(202)	0.818 4(13)	0.018 5(7)	0.182 4(3)
O(31)	0.891 9(24)	0.472 4(10)	−0.129 3(7)	C(203)	0.838 4(13)	−0.059 2(7)	0.199 1(3)
C(32)	0.613 0(23)	0.462 4(14)	−0.057 7(8)	C(204)	0.817 0(13)	−0.121 3(7)	0.163 8(3)
O(32)	0.530 2(18)	0.510 2(11)	−0.063 3(7)	C(205)	0.775 6(13)	−0.105 7(7)	0.111 8(3)
C(33)	0.834 8(22)	0.434 4(12)	0.005 8(8)	C(206)	0.755 6(13)	−0.028 0(7)	0.095 1(3)
O(33)	0.883 7(21)	0.470 8(11)	0.040 3(7)	C(201)	0.776 9(13)	0.034 0(7)	0.130 4(3)
C(41)	0.897 5(21)	0.131 6(12)	−0.095 4(7)	C(212)	0.924 2(9)	0.199 9(8)	0.174 5(5)
O(41)	0.900 3(20)	0.071 1(8)	−0.109 8(7)	C(213)	0.977 4(9)	0.254 3(8)	0.211 0(5)
C(42)	1.050 6(24)	0.254 3(13)	−0.029 9(9)	C(214)	0.896 1(9)	0.305 5(8)	0.235 4(5)
O(42)	1.140 9(17)	0.267 3(15)	−0.007 7(7)	C(215)	0.761 6(9)	0.302 3(8)	0.223 1(5)
C(43)	0.949(3)	0.288 0(14)	−0.132 4(10)	C(216)	0.708 4(9)	0.247 9(8)	0.186 6(5)
O(43)	0.983 9(19)	0.310 1(11)	−0.168 1(6)	C(211)	0.789 7(9)	0.196 7(8)	0.162 2(5)

Table 2. Selected bond lengths (Å) and angles (°) for [Os₅(CO)₁₅C(dppe)] (1) with estimated standard deviations in parentheses

Os(1)–Os(2)	2.996(1)	Os(2)–C(1)	2.20(1)	Os(3)–Os(4)	2.909(1)	Os(4)–C(41)	1.97(2)
Os(1)–Os(3)	2.897(1)	Os(2)–P(2)	2.395(4)	Os(3)–Os(5)	2.761(1)	Os(4)–C(42)	1.96(2)
Os(1)–Os(5)	2.884(1)	Os(2)–C(21)	1.96(2)	Os(3)–C(1)	2.14(1)	Os(4)–C(43)	1.98(3)
Os(1)–C(1)	1.97(1)	Os(2)–C(22)	1.94(2)	Os(3)–C(31)	1.89(3)	Os(5)–C(1)	2.09(1)
Os(1)–C(11)	1.93(2)	Os(2)–C(23)	1.96(2)	Os(3)–C(32)	1.86(2)	Os(5)–C(51)	1.91(2)
Os(1)–C(12)	1.92(2)	P(2)–C(302)	1.85(2)	Os(2)–C(33)	1.89(2)	Os(5)–C(52)	1.87(3)
Os(1)–C(13)	1.91(2)	P(1)–C(301)	1.87(2)	Os(4)–Os(5)	2.897(1)	Os(5)–C(53)	1.97(2)
Os(2)–Os(4)	2.947(1)	C(301)–C(302)	1.49(2)	Os(4)–C(1)	1.99(1)		

Os(2)–Os(1)–Os(3)	86.6(1)	Os(1)–C(1)–Os(2)	90.5(6)	Os(2)–Os(4)–Os(3)	86.7(1)	Os(3)–C(1)–Os(5)	81.5(5)
Os(2)–Os(1)–Os(5)	88.0(1)	Os(1)–C(1)–Os(3)	89.5(6)	Os(2)–Os(4)–Os(5)	88.1(1)	Os(4)–C(1)–Os(5)	90.6(6)
Os(3)–Os(1)–Os(5)	57.1(1)	Os(1)–C(1)–Os(4)	178.4(8)	Os(3)–Os(4)–Os(5)	56.8(1)	Os(2)–P(2)–C(302)	115.6(6)
Os(1)–Os(2)–Os(4)	84.0(1)	Os(1)–C(1)–Os(5)	90.5(6)	Os(1)–Os(5)–Os(3)	61.7(1)	Os(2)–P(2)–C(201)	118.6(4)
Os(1)–Os(3)–Os(4)	85.9(1)	Os(2)–C(1)–Os(3)	135.7(7)	Os(1)–Os(5)–Os(4)	86.4(1)	C(302)–P(2)–C(201)	99.8(7)
Os(1)–Os(3)–Os(5)	61.2(1)	Os(2)–C(1)–Os(4)	89.3(6)	Os(3)–Os(5)–Os(4)	61.8(1)	C(302)–P(2)–C(211)	106.4(7)
Os(4)–Os(3)–Os(5)	61.4(1)	Os(2)–C(1)–Os(5)	142.8(7)	Os(3)–C(1)–Os(4)	89.5(6)	C(201)–P(2)–C(211)	102.9(6)

Os(wingtip)–Os(bridge) distances. It is interesting that for the cluster [Os₅(CO)₁₅C(L)] when L = dppe this ligand occupies a co-ordination site *trans* to an Os–Os bond, while when L = I⁻ the ligand occupies a site *trans* to a carbonyl ligand. This may reflect the relative donor/acceptor properties of dppe compared to I⁻.

The carbido-carbon remains at the centre of the 'bridged-butterfly.' As in related carbide-centred clusters,[3,5] there are small differences in Os–C(carbide) distances. The shortest Os–C(1) distances involve the wingtip metal atoms and the longest the bridging Os(2) atom.

When complex (1) is heated in CH₂Cl₂ at 40 °C no reaction occurs. This is in contrast to the analogous ruthenium system

which closes up to give the substitution product with the square-based pyramidal metal geometry under these reaction conditions.[2] However, when (1) is heated, in CH₂Cl₂, to reflux with 1 equivalent of [Os₅(CO)₁₅C] a yellow, insoluble product is obtained. This insolubility precludes the use of ³¹P n.m.r. spectroscopy to investigate the phosphorus environments, and the mass spectrum failed to give a clear molecular ion. When the reaction is monitored by i.r. spectroscopy in the carbonyl region (2 150—1 700 cm⁻¹) the initial peaks due to complex (1) and [Os₅(CO)₁₅C] persist for up to 48 h, but those of [Os₅(CO)₁₅C] then slowly disappear. The remaining species then possess a carbonyl environment similar to that of [Os₅(CO)₁₅C(dppe)]. On this evidence the yellow complex is

tentatively assigned the formula $[\{Os_5(CO)_{15}C\}_2(dppe)]$ (2) where the dppe ligand links two '$Os_5(CO)_{15}C$' fragments *via* the two P donor atoms.

Experimental

The cluster $[Os_5(CO)_{15}C]$ was obtained as a minor product in the sealed-tube pyrolysis of $[Os_3(CO)_{12}]$.[8] Infrared spectra were recorded as solutions in 0.5-mm CaF_2 cells on a Perkin-Elmer 983 spectrometer. Mass spectra were obtained using an AEI MS 12 instrument at an ionising potential of 70 eV (1.12×10^{-17} J). The ^{31}P n.m.r. spectra were recorded on a Bruker WH400 spectrometer (400 MHz) using CD_2Cl_2 as solvent and $P(OMe)_3$ as a reference. Thin-layer chromatography was carried out on 20×20 cm glass plates (Merck) coated with a 0.25-mm layer of silica gel.

Preparation $[Os_5(CO)_{15}C(dppe)]$ (1).—A mixture of $[Os_5-(CO)_{15}C]$ and dppe (1 equivalent) in dichloromethane was heated, under reflux, until the i.r. spectrum showed disappearance of the $v(CO)$ of the starting material (about 24 h). The solution was concentrated, applied to t.l.c. plates, and eluted with a 50% solution of dichloromethane in n-hexane to yield $[Os_5(CO)_{15}C(dppe)]$ (95%); R_f 0.6. Infrared spectrum: $v(CO)$ (dichloromethane solution) at 2 114w, 2 075s, 2 053vs, 2 041s, 2 027s, 2 016m, 1 994m, and 1 967w cm^{-1}. Molecular ion at m/e 1 790 corresponding to $[Os_5(CO)_{15}C(dppe)]$ (^{192}Os) with subsequent loss of 56 mass units to give $[Os_5(CO)_{13}C(dppe)]^{\cdot+}$.

Reaction of Complex (1) *with* $[Os_5(CO)_{15}C]$.—A mixture of complex (1) and 1 mol equivalent of $[Os_5(CO)_{15}C]$ was refluxed in dichloromethane, under N_2, and the reaction followed by i.r. spectroscopy $[v(CO)]$. After 48 h, peaks due to $[Os_5(CO)_{15}C]$ had disappeared and a yellow, powdery material had precipitated at the bottom of the flask. Infrared spectrum: $v(CO)$ (dichloromethane solution) at 2 114w, 2 075s, 2 053vs, 2 041s, 2 027s, 2 016m, 1 994m, and 1 967w cm^{-1}.

Crystallography.—Crystals of complex (1) were prepared by slow evaporation of a dichloromethane solution and mounted on glass fibres. Crystal singularity was established by preliminary photography [oscillation and zero- and first-level (equi-inclination) Weissenberg; Cu-K_α X-radiation].

Crystal data. $C_{42}H_{24}O_{15}Os_5P_2$, $M = 1$ 781, monoclinic, $a = 10.313(3)$, $b = 16.949(5)$, $c = 25.786(8)$ Å, $\beta = 95.23(2)°$, $U = 4$ 488.5 Å^3 (by least-squares refinement on diffractometer angles for 54 automatically centred reflections at $\pm 2\theta$, $\bar{\lambda} = 0.710$ 69 Å), space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 2.601$ g cm^{-3}, $F(000) = 3$ 224 electrons, crystal dimensions $0.51 \times 0.46 \times 0.16$ mm, $\mu(Mo-K_\alpha) = 142.22$ cm^{-1}.

Data collection and processing. Stoe four-circle diffractometer, graphite-monochromated Mo-K_α X-radiation, 24-step ω—θ scans with step width 0.05°. On-line profile-fitting scheme:[9] 52

strong reflections used as models for ideal profiles of intensity counts which were then used in data collection. 8 404 Reflections measured ($5 \leqslant \theta \leqslant 25°$, $\pm h - k - l$), empirical absorption correction applied using 300 azimuthal scan data, 6 986 data with $F_o > 2\sigma(F_o)$. No significant crystal decomposition or movement during data collection.

Structure analysis and refinement. Automatic centro-symmetric direct methods (SHELX:EEES)[10] for osmium atoms followed by Fourier difference synthesis to locate remaining non-hydrogen atoms. Blocked-cascade least-squares refinement with osmium, phosphorus, oxygen, and carbido-carbon atoms anisotropic. The F_o moduli were weighted according to $w^{-1} = \sigma^2(F_o) + 0.004\ 256\ F_o^2$. Phenyl rings refined as rigid, planar hexagons (C–C 1.395 Å), their hydrogen atoms idealised (C–H 1.08 Å) and allowed to ride on the respective carbon atom ($U_H = 0.08$ Å^2). Refinement (6 986 data, 339 variables) converged at $R = 0.0810$, $R_g\ [= \sqrt{(\Sigma\Delta^2 w)/\Sigma w F^2}] = 0.1067$. Complex neutral scattering factors[11] were employed throughout the structure solution and refinement; computations performed on the University of Cambridge IBM 370/165 computer. The molecular plot was drawn using the ORTEP package.[12]

Acknowledgements

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