

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

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The reaction of $[\text{Os}_5(\text{CO})_{15}\text{C}]$ with 1,2-bis(diphenylphosphino)ethane (dppe) in CH_2Cl_2 under reflux affords the addition product $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (**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 $[\text{Os}_5(\text{CO})_{15}\text{C}]$ gives a complex which has been tentatively assigned as the adduct $\{[\text{Os}_5(\text{CO})_{15}\text{C}]_2(\text{dppe})\}$ (**2**).

The chemistry of the carbido-clusters $[\text{M}_5(\text{CO})_{15}\text{C}]$ ($\text{M} = \text{Ru}$ or Os) with nucleophilic reagents has been extensively studied.¹ These reactions generally involve the formation of an adduct $[\text{M}_5(\text{CO})_{15}\text{C}(\text{L})]$ ($\text{L} = \text{MeCN}$,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 $[\text{M}_5(\text{CO})_{14}\text{C}(\text{L})]$ 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 $[\text{Ru}_5(\text{CO})_{15}\text{C}]$ with phosphines leads only to the isolation of substitution products² $[\text{Ru}_5(\text{CO})_{15-n}\text{C}(\text{PR}_3)_n]$ ($n = 1-4$; for bulky phosphine ligands, n is small) and with diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) the product is $[\text{Ru}_5(\text{CO})_{13}\text{C}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$; 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 $[\text{Os}_5(\text{CO})_{15}\text{C}]$ and the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (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 $[\text{Os}_5(\text{CO})_{15}\text{C}]$ reacts with 1,2-bis(diphenylphosphino)ethane (dppe) in a 1:1 molar ratio, in CH_2Cl_2 , under reflux to give the addition product $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (**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 $\text{P}(\text{OMe})_3$ which corresponds to -13.2 p.p.m. relative to H_3PO_4] while the other resonance occurs upfield at -158.9 p.p.m. (-17.9 p.p.m. relative to H_3PO_4). The phosphorus-phosphorus coupling, $^3J(\text{PP})$, of 35 Hz is typical of a monocoordinated diphosphine and is consistent with the potentially

[†] [1,2-Bis(diphenylphosphino)ethane-*P*]- μ_5 -carbido-cyclo-pentakis(tricarbonylosmium)(7Os-Os).

Supplementary data available (No. SUP 56401, 6 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

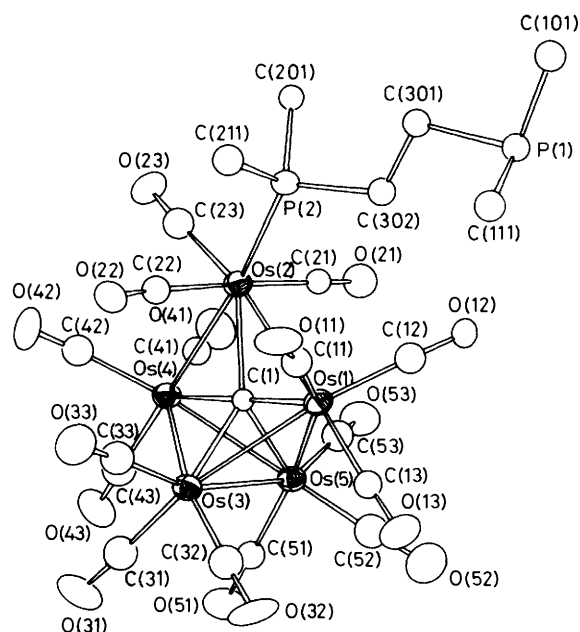


Figure. ORTEP plot of $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (**1**). Phenyl rings have been omitted for clarity

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 $[\text{Os}_5(\text{CO})_{16}\text{C}]^5$ and $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{I})]^{-3}$ 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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{I})]^{-3}$ and $[\text{Os}_5(\text{CO})_{16}\text{C}]^5$ 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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (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) | 0.026 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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{L})]$ when $\text{L} = \text{dppe}$ this ligand occupies a co-ordination site *trans* to an Os—Os bond, while when $\text{L} = \text{I}^-$ 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 CH_2Cl_2 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 CH_2Cl_2 , to reflux with 1 equivalent of $[\text{Os}_5(\text{CO})_{15}\text{C}]$ a yellow, insoluble product is obtained. This insolubility precludes the use of ^{31}P 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 $[\text{Os}_5(\text{CO})_{15}\text{C}]$ persist for up to 48 h, but those of $[\text{Os}_5(\text{CO})_{15}\text{C}]$ then slowly disappear. The remaining species then possess a carbonyl environment similar to that of $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$. On this evidence the yellow complex is

tentatively assigned the formula $[\{\text{Os}_5(\text{CO})_{15}\text{C}\}_2(\text{dppe})]$ (2) where the dppe ligand links two ' $\text{Os}_5(\text{CO})_{15}\text{C}$ ' fragments via the two P donor atoms.

Experimental

The cluster $[\text{Os}_5(\text{CO})_{15}\text{C}]$ was obtained as a minor product in the sealed-tube pyrolysis of $[\text{Os}_3(\text{CO})_{12}]$.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 $\text{P}(\text{OMe})_3$ 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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (1).—A mixture of $[\text{Os}_5(\text{CO})_{15}\text{C}]$ and dppe (1 equivalent) in dichloromethane was heated, under reflux, until the i.r. spectrum showed disappearance of the $\nu(\text{CO})$ 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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (95%); R_f 0.6. Infrared spectrum: $\nu(\text{CO})$ (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 $[\text{Os}_5(\text{CO})_{15}\text{C}(\text{dppe})]$ (^{192}Os) with subsequent loss of 56 mass units to give $[\text{Os}_5(\text{CO})_{13}\text{C}(\text{dppe})]^+.$

Reaction of Complex (1) with $[\text{Os}_5(\text{CO})_{15}\text{C}]$.—A mixture of complex (1) and 1 mol equivalent of $[\text{Os}_5(\text{CO})_{15}\text{C}]$ was refluxed in dichloromethane, under N_2 , and the reaction followed by i.r. spectroscopy [$\nu(\text{CO})$]. After 48 h, peaks due to $[\text{Os}_5(\text{CO})_{15}\text{C}]$ had disappeared and a yellow, powdery material had precipitated at the bottom of the flask. Infrared spectrum: $\nu(\text{CO})$ (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. $\text{C}_{42}\text{H}_{24}\text{O}_{15}\text{Os}_5\text{P}_2$, $M = 1781$, monoclinic, $a = 10.313(3)$, $b = 16.949(5)$, $c = 25.786(8)$ Å, $\beta = 95.23(2)^\circ$, $U = 4488.5$ Å³ (by least-squares refinement on diffractometer angles for 54 automatically centred reflections at $\pm 2\theta$, $\lambda = 0.71069$ Å), space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 2.601$ g cm^{-3} , $F(000) = 3224$ electrons, crystal dimensions $0.51 \times 0.46 \times 0.16$ mm, $\mu(\text{Mo-K}_\alpha) = 142.22$ 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. 8404 Reflections measured ($5 \leq \theta \leq 25^\circ$, $\pm h - k - l$), empirical absorption correction applied using 300 azimuthal scan data, 6986 data with $F_o > 2\sigma(F_o)$. No significant crystal decomposition or movement during data collection.

Structure analysis and refinement. Automatic centrosymmetric 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 $w^{-1} = \sigma^2(F_o) + 0.004256 F_o^2$. 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 ($U_H = 0.08$ Å²). Refinement (6986 data, 339 variables) converged at $R = 0.0810$, $R_g [= \sqrt{(\Sigma \Delta^2 w) / \Sigma w F^2}] = 0.1067$. Complex neutral scattering factors¹¹ 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

We thank the Universidad Nacional Autónoma de Mexico (M. J. R.) and the S.E.R.C. for financial support during the period of this research.

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Received 2nd May 1985; Paper 5/724