Synthesis and *X*-ray Crystal Structure of a Tri-iridium Cluster, $[Ir_3(CO)_6(Ph)(\mu_3\text{-}PPh)(\mu\text{-dppm})]$ †

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The reaction between $[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ and $CH(PPh_2)_3$ in the presence of CO and Zn yields $[Ir_3(CO)_6(Ph)(\mu_3\text{-}PPh)(\mu\text{-dppm})]$ (1) (dppm = $Ph_2PCH_2PPh_2$), an uncharacterised product, and $[Ir_4(CO)_9\{CH(PPh_2)_3\}]$. The solid-state structure of (1) has been established by *X*-ray crystallography. Complex (1) crystallises in space group $P2_1/c$ with $a = 11.811(3)$, $b = 22.328(5)$, $c = 17.864(4)$ Å, $\beta = 99.51(2)°$, and $Z = 4$. The structure was solved by direct methods and difference-Fourier syntheses and refined by block-matrix least-squares methods to $R = 0.0476$ ($R' = 0.0511$). The molecule contains a triangular array of iridium atoms capped by a phenylphosphido(2−) group. One edge of the iridium triangle is bridged by a dppm ligand and a phenyl group is σ-bonded to the third iridium atom. In addition, there are two carbonyl ligands terminally bound to each Ir atom.

Our interest in transition-metal cluster complexes stabilised with multidentate phosphine ligands led us to investigate a potentially high-yield route to $[Ir_4(CO)_9\{CH(PPh_2)_3\}]$ using the mononuclear complex $[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ rather than $[Ir_4(CO)_{12}]$ as the source of iridium. $[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ has been shown to react with CO and Zn in the presence of monodentate phosphines, L, to give $[Ir_4(CO)_{11}L]$ and $[Ir_4(CO)_{10}L_2]$,[1] in the presence of bis(diphenylphosphino)methane (dppm) to give $[Ir_4(CO)_{10}(\text{dppm})]$,[2] and in the presence of *trans*-1,2-bis(diphenylphosphino)ethylene to give $[Ir_3(CO)_7\{\mu\text{-}(cis\text{-}PPhCH{=}CHPPh_2)\}]$, the first reported neutral triangular trinuclear iridium cluster.[3] We report here how a similar reaction with the tridentate phosphine ligand $CH(PPh_2)_3$ leads to the formation of $[Ir_3(CO)_6(Ph)(\mu_3\text{-}PPh)(\mu\text{-dppm})]$ (1), thus indicating how such ligands may be used as templates for the synthesis of cluster complexes of unusual nuclearity.

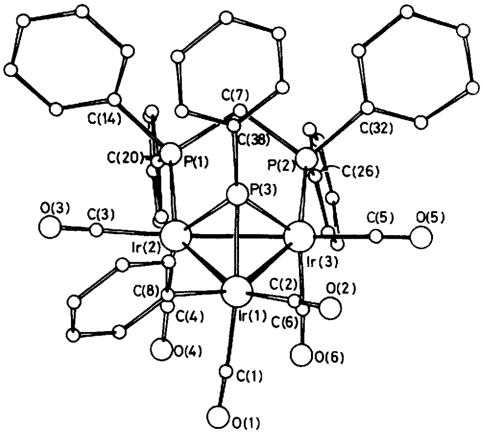

Figure. Molecular geometry of $[Ir_3(CO)_6(Ph)(\mu_3\text{-}PPh)(\mu\text{-dppm})]$ (1), including the atomic numbering scheme

Results and Discussion

$[IrCl(CO)_2(CH_3C_6H_4NH_2\text{-}p)]$ reacts at 90 °C with $CH(PPh_2)_3$ in the presence of Zn, CO (4.5 atm), 2-methoxyethanol, and water to give three products, two of which can be obtained in a pure state by chromatography and fractional crystallisation. Two bands separated on a Florisil column using acetone–light petroleum as eluant. The first band contained a mixture of two products, (1) and (2). Recrystallisation from dichloromethane–light petroleum gave bright yellow needles of (1), but (2) could not be obtained completely free of (1). The i.r. and n.m.r. spectroscopic data for (1) and (2) are given in Table 1. The second band from the chromatography column contained the previously reported[4] $[Ir_4(CO)_9\{CH(PPh_2)_3\}]$ (3), although the yield (5%) is not high enough under the conditions employed to make this an attractive route in comparison with the direct reaction of $[Ir_4(CO)_{12}]$ with $CH(PPh_2)_3$.

Since the spectroscopic properties of (1) did not allow its molecular structure to be determined, a single-crystal *X*-ray diffraction study was carried out. Since (2) could not be obtained in a pure state, it remains incompletely characterised.

The molecular structure of (1) is shown in the Figure. Selected bond parameters are given in Table 2. The molecule contains a triangular array of iridium atoms capped by a phenylphosphido(2−) group. One edge of the iridium triangle is bridged by dppm, and a phenyl group is σ-bonded to the third iridium atom. In addition, there are two carbonyl ligands terminally bound to each Ir atom. Thus, the initial tridentate phosphine ligand, $CH(PPh_2)_3$, has undergone $HC{-}PPh_2$ bond cleavage followed by protonation of the central carbon atom to give dppm and PPh_2. The PPh_2 moiety has undergone P−Ph bond cleavage leading to a μ_3-PPh ligand and the formation of an Ir−Ph σ bond. Significantly, all the fragments of the phosphine are co-ordinated on the same side of the iridium triangle. This suggests that $CH(PPh_2)_3$ has acted as a template for the formation of the triangular array of Ir atoms. Under the reaction conditions the iridium atoms presumably are reduced to the zero oxidation state and then ligand breakdown occurs, by an intramolecular mechanism to give an iridium(I) cluster, in order to satisfy the electronic requirements of the Ir atoms.

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† 2,3-μ-[Bis(diphenylphosphino)methane]-1,1,2,2,3,3-hexacarbonyl-1-phenyl-μ_3-phenylphosphido-*triangulo*-tri-iridium(I).

Supplementary data available (No. SUP 23598, 33 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 atm = 101 325 Pa.

Table 1. Spectroscopic data for complexes (1) and (2)

Complex	ν(CO)/cm^{-1} [a]	^{31}P-{^{1}H} N.m.r. (δ/p.p.m.) [b,c]	^{1}H N.m.r. (δ/p.p.m.) [b,d]
[$Ir_3(CO)_6$(Ph)(μ_3-PPh)(μ-dppm)] (1)	2 043s, 2 019s, 1 990s, 1 968br (sh)	128.1 [t, *J*(PP) 183, PPh] −24.1 [d, *J*(PP) 183, PPh_2]	6.7—7.7 (m, Ir–Ph and P–Ph) 3.15 [q, *J*(PH) 26, CH_2]
(2)	2 034w, 2 011m, 1 995s, 1 974w, 1 917w	225.8 [d, *J*(PP) 14.6], −46.4 [d, *J*(PP) 75.6], −52.4 [dd, *J*(PP) 14.6, *J*(PP′) 75.6]	

[a] In CH_2Cl_2. [b] In CD_2Cl_2, coupling constants in Hz. [c] Relative to 85% H_3PO_4. [d] Relative to $SiMe_4$.

Table 2. Selected bond distances (Å) and angles (°)

Ir(1)–Ir(2)	2.768(1)	Ir(3)–C(6)	1.871(18)
Ir(1)–Ir(3)	2.779(1)	P(1)–C(7)	1.843(17)
Ir(2)–Ir(3)	2.769(1)	P(2)–C(7)	1.850(15)
Ir(1)–P(3)	2.256(5)	P(1)–C(14)	1.806(13)
Ir(1)–C(1)	1.926(15)	P(1)–C(20)	1.819(13)
Ir(1)–C(2)	1.819(22)	P(2)–C(26)	1.838(13)
Ir(1)–C(8)	2.084(16)	P(2)–C(32)	1.823(14)
Ir(2)–P(1)	2.323(5)	P(3)–C(38)	1.790(13)
Ir(2)–P(3)	2.278(5)	C(1)–O(1)	1.094(21)
Ir(2)–C(3)	1.915(17)	C(2)–O(2)	1.131(27)
Ir(2)–C(4)	1.923(19)	C(3)–O(3)	1.111(22)
Ir(3)–P(2)	2.309(5)	C(4)–O(4)	1.144(25)
Ir(3)–P(3)	2.285(5)	C(5)–O(5)	1.096(25)
Ir(3)–C(5)	1.883(19)	C(6)–O(6)	1.145(23)
Ir(1)–Ir(2)–Ir(3)	60.2(1)	C(8)–Ir(1)–P(3)	101.3(4)
Ir(2)–Ir(3)–Ir(1)	59.9(1)	P(1)–Ir(2)–P(3)	96.4(2)
Ir(3)–Ir(1)–Ir(2)	59.9(1)	P(2)–Ir(3)–P(3)	99.2(2)

Experimental

Infrared spectra were recorded as dichloromethane solutions in 0.5-mm NaCl cells on a Perkin-Elmer 681 spectrometer. Hydrogen-1 and phosphorus-31 n.m.r. spectra were recorded on FT-NMR Bruker WM250 and JEOL FX-90Q instruments. Microanalysis was carried out by Elemental Micro-Analysis Ltd. (Devon). [$IrCl(CO)_2(CH_3C_6H_4NH_2$-*p*)] was prepared by a published method.[5]

Reaction of [$IrCl(CO)_2(CH_3C_6H_4NH_2$-*p*)] *with* $CH(PPh_2)_3$.—[$IrCl(CO)_2(CH_3C_6H_4NH_2$-*p*)] (1.14 g, 2.9 mmol), $CH(PPh_2)_3$ (0.54 g, 0.8 mmol), zinc (washed with dilute HCl, then H_2O, and 2-methoxyethanol; 9 g), 2-methoxyethanol (150 cm^3), and water (6 cm^3) were stirred together under CO (4.5 atm) at 90 °C for 1 h in a glass pressure vessel. The vessel was then cooled, vented, and the orange-brown solution filtered and evaporated to dryness under reduced pressure. The residue was chromatographed on a Florisil column using acetone–light petroleum (b.p. 60—80 °C) (1 : 8) as eluant. Two yellow bands separate. The first band contains a mixture of (1) and (2). Recrystallisation from dichloromethane–light petroleum gave bright yellow needles of (1) (5%) (Found: C, 39.65; H, 2.6. $C_{43}H_{32}Ir_3O_6P_3$ requires C, 39.3; H, 2.45%). Compound (2) could not be obtained in an analytically pure state. The second yellow band contained the compound [$Ir_4(CO)_9\{CH(PPh_2)_3\}$] (5%).

Crystal Data.—$C_{43}H_{32}Ir_3O_6P_3$, $M = 1\,314$, Monoclinic, space group $P2_1/c$, $a = 11.811(3)$, $b = 22.328(5)$, $c = 17.864(4)$ Å, $\beta = 99.51(2)°$, $U = 4\,646$ Å^3, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $F(000) = 2\,452$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu = 83.8$ cm^{-1}.

Molecular Structure Determination of (1).—A crystal of the complex was mounted on a glass fibre with ' shellac ', and

Table 3. Atomic co-ordinates (× 10^4) for [$Ir_3(CO)_6$(Ph)(μ_3-PPh)(μ-dppm)] (1)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir(1)	1 494(1)	968(1)	7 698(1)
Ir(2)	1 546(1)	923(1)	6 156(1)
Ir(3)	3 235(1)	1 544(1)	7 107(1)
C(1)	2 091(17)	175(6)	7 939(10)
O(1)	2 407(13)	−281(7)	8 059(10)
C(2)	1 617(20)	1 311(10)	8 632(12)
O(2)	1 684(16)	1 509(7)	9 220(10)
C(3)	40(15)	635(10)	5 755(9)
O(3)	−837(12)	473(8)	5 522(9)
C(4)	2 369(15)	178(9)	6 196(10)
O(4)	2 833(16)	−274(6)	6 251(10)
C(5)	3 847(21)	2 015(10)	7 951(10)
O(5)	4 226(17)	2 275(7)	8 450(10)
C(6)	4 146(15)	859(8)	7 312(11)
O(6)	4 641(11)	420(7)	7 438(9)
P(1)	1 864(4)	1 448(2)	5 087(2)
P(2)	3 788(4)	2 086(2)	6 127(2)
P(3)	1 311(4)	1 742(2)	6 876(3)
C(7)	2 579(13)	2 172(7)	5 332(9)
C(8)	−216(13)	724(5)	7 668(9)
C(9)	−1 021(13)	1 131(5)	7 855(9)
C(10)	−2 159(13)	954(5)	7 833(9)
C(11)	−2 492(13)	370(5)	7 623(9)
C(12)	−1 687(13)	−37(5)	7 437(9)
C(13)	−549(13)	140(5)	7 459(9)
C(14)	583(11)	1 666(5)	4 448(7)
C(15)	66(11)	2 224(5)	4 493(7)
C(16)	−949(11)	2 362(5)	4 006(7)
C(17)	−1 448(11)	1 942(5)	3 473(7)
C(18)	−931(11)	1 384(5)	3 428(7)
C(19)	84(11)	1 247(5)	3 915(7)
C(20)	2 736(10)	1 139(4)	4 431(6)
C(21)	2 850(10)	1 461(4)	3 778(6)
C(22)	3 631(10)	1 272(4)	3 320(6)
C(23)	4 296(10)	762(4)	3 514(6)
C(24)	4 182(10)	440(4)	4 167(6)
C(25)	3 402(10)	629(4)	4 625(6)
C(26)	4 997(10)	1 812(5)	5 693(7)
C(27)	5 220(10)	2 080(5)	5 028(7)
C(28)	6 161(10)	1 895(5)	4 705(7)
C(29)	6 878(10)	1 442(5)	5 049(7)
C(30)	6 655(10)	1 174(5)	5 715(7)
C(31)	5 714(10)	1 359(5)	6 037(7)
C(32)	4 219(9)	2 860(6)	6 334(7)
C(33)	3 534(9)	3 346(6)	6 055(7)
C(34)	3 925(9)	3 929(6)	6 213(7)
C(35)	5 002(9)	4 026(6)	6 650(7)
C(36)	5 688(9)	3 541(6)	6 929(7)
C(37)	5 296(9)	2 958(6)	6 771(7)
C(38)	417(11)	2 391(5)	6 698(8)
C(39)	−753(11)	2 323(5)	6 425(8)
C(40)	−1 446(11)	2 828(5)	6 256(8)
C(41)	−969(11)	3 399(5)	6 361(8)
C(42)	200(11)	3 467(5)	6 634(8)
C(43)	893(11)	2 963(5)	6 803(8)

unit-cell dimensions and space group were determined from Weissenberg and precession photographs. Intensity data were recorded on a CAD-4 diffractometer. Of the 6 687 unique absorption corrected reflections, 4 541 with $F_o > 3\sigma(F_o)$ were used in the structure solution and refinement. The structure was solved by direct methods and difference-Fourier syntheses and refined by block-matrix least-squares methods, with Ir, P, O, and non-phenyl C atoms assigned anisotropic thermal parameters, to $R = 0.0476$ ($R' = 0.0511$), using the program SHELX.[6] The atomic fractional co-ordinates are listed in Table 3.

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