The First Square-pyramidal Cluster in the Cobalt Subgroup: Synthesis and Structural Characterization of the Iridium Complex $[Ir_5(CO)_8(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$

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Deprotonation of $[Ir_4(CO)_{11}PPhH_2]$ in the presence of $[M(\eta^5\text{-}C_5Me_5)(MeCN)_3][SbF_6]_2$ (M = Rh or Ir) affords the pentanuclear species $[MIr_4(CO)_{10}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ in high yield; the penta-iridium derivative has been shown by an *X*-ray crystallographic study to possess an unprecedented square-pyramidal arrangement of Ir atoms supported by the phosphinidene ligand.

The synthesis and reactivity of metal carbonyl clusters with phosphinidene (RP) bridges is a fast-growing area which has recently been reviewed.[1] Studies of the reactions of triangular clusters containing a μ_3-PR ligand[2a] and those of μ_4-PR-bridged square planar species[2b] have already demonstrated the crucial role that this ligand may play in holding the metal fragments together, even in the cases where M–M bond breakage occurs during the reaction. Such studies have been restricted to clusters containing up to four metal atoms, mainly owing to the lack of reliable high-yield synthetic routes to larger metal species. Here we report the convenient synthesis of the first pentanuclear, μ_4-PPh-containing clusters of the cobalt subgroup $[MIr_4(CO)_{10}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M = Ir or Rh), obtained by condensation of the dications $[M(C_5Me_5)(MeCN)_3][SbF_6]_2$ (M = Ir or Rh) with the deprotonation product of $[Ir_4(CO)_{11}PPhH_2]$. The tetranuclear substituted carbonyl complexes $[Ir_4(CO)_{11}(PPhHR)]$ (**1a** and **b**) have been synthesized[3] from $[Ir_4(CO)_{11}Br]^-$ (**2**) and PPhHR in the presence of silver salts. Subsequent deprotonation of (**1a**) *in situ* with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN in the presence of $[M(C_5Me_5)(MeCN)_3][SbF_6]_2$ (**3a** or **b**)[4] at room temperature, followed by t.l.c. (3 : 7 CH_2Cl_2–hexane), afforded the dark brown cluster compounds $[MIr_4(CO)_{10}(C_5Me_5)(PPh)]$ (**4a** and **b**) in 50 and 85% yield, respectively, after recrystallization from CH_2Cl_2–hexane. Spectroscopic data suggest that these two compounds are isostructural in solution.†

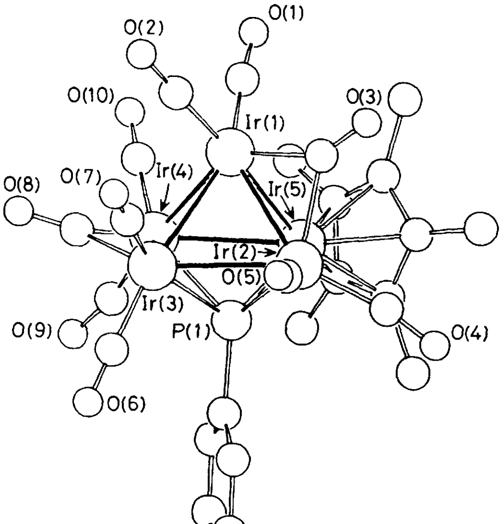

Figure 1. The molecular structure of $[Ir_5(CO)_8(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (**4a**). The C atoms of the CO groups bear the same numbering as the corresponding O atoms. H Atoms of the phenyl and methyl groups are omitted for clarity. Bond distances (Å) for the two independent molecules include: Ir(1)–Ir(2) 2.758(1), 2.752(1); Ir(1)–Ir(3) 2.798(1), 2.784(1); Ir(1)–Ir(4) 2.747(1), 2.754(1); Ir(1)–Ir(5) 2.738(1), 2.764(1); Ir(2)–Ir(3) 2.806(1), 2.817(1); Ir(2)–Ir(5) 2.775(1), 2.790(1), Ir(3)–Ir(4) 2.758(1), 2.735(1); Ir(4)–Ir(5) 2.826(1), 2.801(1); mean Ir(5)–C 2.22(5), 2.22(5); $C\text{–}C_{Me}$ 1.53(1), 1.51(1); $P\text{–}C_{Ph}$ 1.81(2), 1.78(2); $Ir\text{–}C_{CO}$ 1.86(2), 1.86(2); C–O 1.19(2), 1.18(2).

$[Ir_4(CO)_{11}(PPhHR)]$	(**1**)	a; R = H b; R = Ph
$[Ir(CO)_{11}Br]^-$	(**2**)	
$[M(C_5Me_5)(MeCN)_3][SbF_6]_2$	(**3**)	a; M = Ir b; M = Rh
$[MIr_4(CO)_{10}(C_5Me_5)(PPh)]$	(**4**)	a; M = Ir b; M = Rh
$[Ir_4(CO)_{10}PPhH]^-$	(**5**)	

In order to establish unambiguously the molecular structure of (**4a**) an *X*-ray structural determination has been carried out,‡ showing that (**4a**) possesses a square-pyramidal metal framework, a geometry so far observed only for Fe subgroup metal clusters with the exception of the mixed metal species $[Ru_3Rh_2(CO)_{13}(PEt_3)(PPh)]$.[5] The structure of (**4a**) is shown in Figure 1; some relevant bond distances are reported in the

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† *Spectroscopic data*: ν_{CO}(hexane) for (**3a**) and (**3b**) 2072m, 2040s, 2026vs, 2010vw, 1994w, 1981w, 1855w, and 1832vw cm^{-1}; ^1H n.m.r. (CD_2Cl_2) (**3a**) δ 2.08 [d, C_5Me_5, *J*(P–H) 1.6 Hz] and 7.11—7.33 (*m*, PPh); (**3b**) δ 1.82 [d of d, C_5Me_5, *J*(P–H) 2.2, *J*(Rh–H) 0.2 Hz] and 7.16—7.34 (m, PPh); $^{31}P\text{-}\{^1H\}$ n.m.r. (CD_2Cl_2) (**3b**) δ 130.4 [d, PPh, *J*(P–Rh) 105.4 Hz]; *m/z* (**3a**) 1488, (**3b**) 1398 [electron impact and fast atom bombardment m.s. using nitrobenzyl alcohol as matrix] [calc. ^{193}Ir (**3a**) 1488, (**3b**) 1398].

‡ *Crystal data* for (**4a**): $C_{26}H_{20}Ir_5O_{10}P$, triclinic, space group $P\bar{1}$, a = 14.511(5), b = 15.366(8), c = 13.962 Å, α = 89.99(3), β = 93.94(2), γ = 86.15(3)°, U = 3098.8 Å^3, Z = 4, $F(000)$ = 2623, $\mu(\text{Mo-}K_\alpha)$ = 207.2 cm^{-1}, θ range 2.5—25°, final *R* value 0.050 (R_w = 0.057) for 6965 of 11 457 independent reflections [$I > 2.5\sigma(I)$], collected at room temperature with an Enraf-Nonius CAD4 diffractometer (ω–2θ scan method, scan width 0.75°). Absorption correction was applied by Walker and Stuart's method[9] (correction range 0.66—1.00). Ir and P Atoms were allowed to vibrate anisotropically, C and O atoms isotropically. The H atoms of the phenyl and methyl groups were added in calculated positions [C–H 1.08 Å] and refined 'riding' on their respective C atoms. Because of the presence of two independent molecules in the asymmetric unit all structural parameters are reported as pairs of corresponding mean values in the two molecules. The phenyl group of the μ_4-PPh ligand in one of the two molecules was found to be affected by disorder, adopting two almost orthogonal orientations (50% occupancy?) underneath the cluster square base. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

caption. The square base of the Ir_5 core is supported by a μ_4-PPh ligand, while the C_5Me_5 ligand co-ordinates the basal Ir atom [Ir(5)] which does not bear CO ligands. The remaining Ir atoms are bound to two terminal CO ligands each, and are involved in one interaction with the two bridging CO groups. These latter span one basal edge and one non-contiguous apical edge, respectively. In this way, each Ir atom of the polyhedron receives a formal five-electron contribution either from the C_5Me_5 or from the CO ligands. If we assume a four-electron contribution from the μ_4-PPh ligand to the basal atoms, all Ir atoms formally possess 18 electrons. The resulting molecular electron count for (**4a**) of 74 electrons is in agreement with the effective atomic number (EAN) rule, and has been observed for all the other square pyramidal cluster species fully characterized to date.[5—7] It is worth noting that the CO-bridged metal–metal bonds do not show any appreciable shortening with respect to the unbridged bonds, in agreement with the behaviour observed for most Ir clusters when bridging CO groups are present.[8]

The mechanism of formation of compounds (**4a** and **b**) is not clear. Deprotonation of (**1a**), but in the absence of (**3a** or **b**), is rapid and gives a mixture of highly unstable mono anions, including $[Ir_4(CO)_{10}PPhH]^-$ (**5**), in low yields,[3] as well as hydride-containing species {probably $[HIr_4(CO)_nPPh]^-$ (n = 9—11}. If (**3a**) or (**3b**) is then added to this mixture, (**4a**) and (**4b**), respectively, are obtained only in low yields (below 2%) along with decomposition products.

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References

1 G. Huttner and K. Knoll. *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 743.

2 (a) G. Huttner, J. Schneider, H.-D. Muller, G. Mohr, J. von Seyerl, and L. Wohlfahrt, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 76; (b) H. Vahrenkamp and D. Walters, *Organometallics*, 1982, **1**, 874; T. Jaeger, S. Aime, and H. Vahrenkamp, *ibid.*, 1986, **5**, 245.

3 J. N. Nicholls, P. R. Raithby, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1986, 1617.

4 P. M. Maitlis, *Acc. Chem. Res.*, 1978, **11**, 301.

5 M. J. Mays, P. R. Raithby, P. L. Taylor, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 959.

6 (a) E. H. Braye, L. F. Dahl, W. Hubel, and D. L. Wampler, *J. Am. Chem. Soc.*, 1962, **84**, 4633; (b) C. R. Eady, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Organomet. Chem.*, 1971, **32**, C49; (c) P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 546.

7 R. D. Adams, I. T. Horvath, B. E. Segmuller, and L. W. Yang, *Organometallics*, 1983, **2**, 1301.

8 D. Braga and F. Grepioni, *J. Organomet. Chem.*, 1987, **336**, C9.

9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.