The Crystal Structure of $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$; a Phosphine Substituted Iridium Cluster with All-terminal CO Ligands

Jennifer A. Clucas, Marjorie M. Harding, Barry S. Nicholls, and Anthony K. Smith*

Department of Inorganic, Physical, and Industrial Chemistry, University of Liverpool, Liverpool L69 3BX, U.K.

The tridentate phosphine-substituted iridium cluster, $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$, has been shown by *X*-ray crystallography to be the first example of a phosphine-substituted tetranuclear iridium cluster in which the all-terminal CO ligand configuration of the parent $[Ir_4(CO)_{12}]$ is maintained.

Although the parent cluster carbonyl, $[Ir_4(CO)_{12}]$, has an all-terminal CO ligand structure,[1] phosphine substitution to give $[Ir_4(CO)_{12-n}L_n]$ ($n = 1$—4) induces a change to a structure in which three carbonyl groups are edge-bridging around a basal plane (*i.e.* the Ir_4 cluster adopts the C_{3v} structure found in $[Co_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$ and their derivatives).[2] Both electronic[3,4] and steric[5—8] factors have been proposed as providing the major influence on the particular structure adopted by these closely related clusters. However, it is clear from n.m.r. studies of the fluxional behaviour of $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) clusters and their phosphine-substituted derivatives, that the energy differences between the two structural types (*i.e.* all terminal carbonyl T_d and bridging-carbonyl C_{3v} structures) are usually very small and so there will be a delicate balance of factors governing the particular structure adopted.[7]

Since the synthesis of $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$ was first reported in 1980,[9] there has been some doubt about its structure.[9—12] On the basis of i.r. spectroscopy[10] the complex has been assigned the same C_{3v} structure as the cobalt and rhodium analogues, that is, with the ligand capping the carbonyl-bridged basal plane of an Ir_4 tetrahedron. However, it has been suggested[11] that the phosphorus chemical shift of δ −39.1 p.p.m. is more indicative of a structure in which the ligand is chelated to one metal atom, thus forming Ir–P–C–P four membered rings.†

We found no evidence for the presence of bridging carbonyl ligands in $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$ in either the i.r. spectrum (ν_{CO} in CH_2Cl_2: 2060s, 2010vs, 1978w, 1951m cm^{-1}) or the ^{13}C n.m.r. spectrum (see below). Furthermore, we have synthesised a phosphine derivative $[Ir_4(CO)_8\{(Ph_2P)_3CH\}(PPh_3)]$, for which the i.r. spectrum also shows no evidence for bridging carbonyl ligands.[12] We therefore undertook an *X*-ray

---

† The existence of four-membered rings involving the P atoms was postulated on the basis of the $\Delta_R$value (ref. 6) of this complex, using $[Ir_4(CO)_9(PPh_2Me)_3]$ as a comparison. However, it should be noted that the complexes are not isostructural; in the PPh_2Me complex only one phosphine ligand occupies a basal-axial site, the other two occupying basal-equatorial sites (ref. 8).

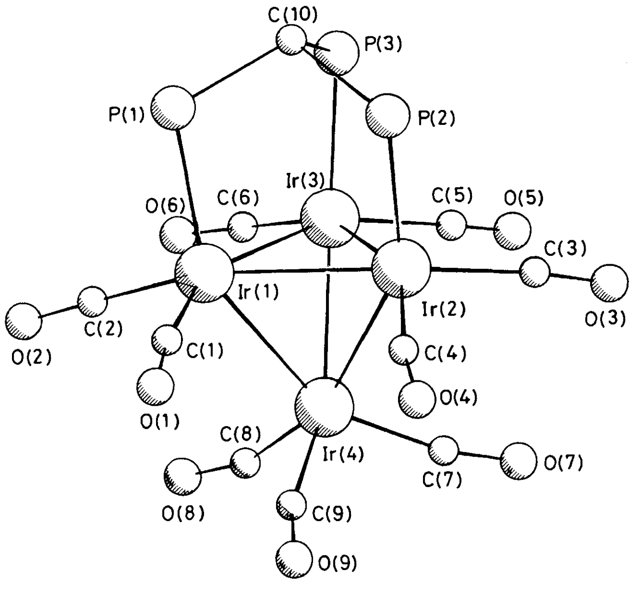

Figure 1. The structure of $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$ with phenyl groups and H atoms omitted. Important bond lengths (Å) and angles (°) averaged for two independent molecules, and assuming C_{3v} symmetry in each: Ir(1)–Ir(2) 2.695(3), Ir(1)–Ir(4) 2.684(4), Ir–P 2.306(15), Ir–C 1.79(6); Ir(2)–Ir(1)–P(1) 96.8(3), Ir(3)–Ir(1)–P(1) 90.8(3), C(1)–Ir(1)–P(1) and C(2)–Ir(1)–P(1) 103(2), Ir(2)–Ir(1)–C(1) and Ir(3)–Ir(1)–C(2) 98.5(1.9), Ir(4)–Ir(1)–C(1) and Ir(4)–Ir(1)–C(2) 97.3(1.9).

crystal structure determination of $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$.‡§ The structure was solved by direct methods and a heavy atom phased Fourier series (SHELX[13]) using 5119 unique reflections with $F > 5\sigma(F)$ collected on a CAD4 diffractometer. Least squares refinement with aniosotropic thermal parameters for Ir and P atoms, constrained phenyl groups, and hydrogens in calculated positions converged to $R = 7.3\%$. In the difference Fourier map there are still peaks of ± 2 e Å^{-3} within 1.2 Å of the Ir positions but no other peaks greater than 1.3 e Å^{-3}.

The two independent molecules in the asymmetric unit are not significantly different. The tridentate phosphine ligand caps a triangular face of the Ir_4 tetrahedron and all the CO ligands are terminally bonded (Figure 1). The molecular symmetry is approximately C_{3v}, the only significant deviations from this are in the orientation of the phenyl rings. Small deviations of the Ir–C–O angles from linearity are barely significant (range 163—179°, e.s.d.'s 4—8°); but such deviations are quite understandable since the bending force constant of the Ir–C–O angles is small and minor adjustments of oxygen positions may greatly improve the packing of molecules in the crystal.

The molecule is therefore unique with respect to carbonyl ligand distribution in phosphine substituted tetranuclear (M = Co, Rh, Ir) clusters. The reason for the adoption of an all-terminal CO ligand structure is not clear. It may be significant that the tridentate phosphine ligand is constrained to co-ordination at axial sites in the basal plane of the Ir_4 tetrahedron, whereas in the analogous $[Ir_4(CO)_9(PPh_2Me)_3]$, which adopts the carbonyl-bridging C_{3v} structure, the phosphine ligands occupy one basal-axial and two basal-equatorial sites. However, the complex $[Ir_4(CO)_9\{(Et_2P)_3SiMe\}]$, which also has a tridentate phosphine ligand capping the basal plane of the Ir_4 tetrahedron at axial sites,[14] adopts the carbonyl-bridging structure. Thus the steric effect of the bulky phenyl groups on $(Ph_2P)_3CH$ compared to less bulky ethyl groups on $(Et_2P)_3SiMe$ may also play an important role in structure determination. Some evidence for this is provided by the low temperature ^{13}C n.m.r. spectrum of the complex [in CD_2Cl_2, at 25 °C: δ 166.5s (CO basal), 156.4q p.p.m. (CO apical, J_{CP} 13.6 Hz); at −91 °C, δ 167.2t (CO basal, J_{CP} 5.2 Hz), 166.6s (CO basal), 157.2m p.p.m. (CO apical)]. The basal CO ligands are seen to be fluxional at 25 °C (presumably a 'merry-go-round' process *via* a bridged intermediate), but at −91 °C the bulky phenyl groups of the phosphine ligand appear to adopt a configuration such that the basal carbonyls become inequivalent.

We thank Dr. R. O. Gould of Edinburgh University for the diffraction data collection, and Dr. N. Walker of Queen Mary College, London, for the absorption corrections, and the S.E.R.C. (B. S. N.) for financial support.

Received, 8th December 1983; Com. 1597

References

1 M. R. Churchill and J. P. Hutchinson, *Inorg. Chem.*, 1978, **17**, 3528.
2 G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.*, 1977, **99**, 607.
3 V. G. Albano, G. Ciani, and S. Martinengo, *J. Organomet. Chem.*, 1974, **78**, 265.
4 D. L. Kepert and S. C. Williams, *J. Organomet. Chem.*, 1981, **217**, 235.
5 B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.*, 1976, 211.
6 B. F. G. Johnson and R. E. Benfield, *J. Chem. Soc., Dalton Trans.*, 1978, 1554.
7 R. E. Benfield and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1980, 1743.
8 R. E. Benfield and B. F. G. Johnson, *Transition Met. Chem.*, 1981, **6**, 131.
9 A. A. Arduini, A. A. Bahsoun, J. A. Osborn and C. Voelker, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 1024
10 A. A. Bahsoun, J. A. Osborn, C. Voelker, J. J. Bonnet, and G. Lavigne, *Organometallics*, 1982, **1**, 1114.
11 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
12 D. F. Foster, J. Harrison, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1983, **248**, C29.
13 G. M. Sheldrick, SHELX program for crystal structure determination, University Chemical Laboratory, Cambridge, 1976.
14 D. F. Foster, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1983, **244**, 159.

---

‡ *Crystal data* for $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$, $C_{46}H_{31}Ir_4O_9P_3$, $M = 1589.4$, triclinic, space group $P\bar{1}$, $a = 13.013(3)$, $b = 17.201(8)$, $c = 22.921(4)$ Å, $\alpha = 93.73(3)$, $\beta = 100.31(2)$, $\gamma = 78.15(3)°$, $U = 4934.6$ Å^3, Mo-K_α, $\lambda = 0.7107$ Å, $D_m = 2.3$ g cm^{-3}, $Z = 4$, $D_c = 2.14$ g cm^{-3} (two independent molecules in the asymmetric unit), μ(Mo-K_α) = 104.9 cm^{-1}.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.