Metal-atom Clusters in Iridium Carbonyl–Triphenylphosphine Complexes

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L. Malatesta and G. Caglio have recently obtained[1] iridium complexes containing a metal atom cluster attached to carbon monoxide and substituted phosphine molecules. The compounds have been formulated as $[Ir_4(CO)_{10}(PPh_3)_2]$ (I), $[Ir_4(CO)_9(PPh_3)_3]$ (II), $[Ir_4(CO)_8(PPh_2Et)_4]$ (III), and $[Ir_4(CO)_6(Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2)_2]$ (IV).

The complexes can be obtained as diamagnetic yellow-orange crystals which are soluble in benzene and acetone as monomeric species.

Crystal structure analysis has given information about the composition (which is difficult to establish chemically), cluster geometry, and bonding type of these polynuclear co-ordination compounds.

Infrared spectra of these complexes show C–O stretching frequencies which are peculiar to bridged carbonyls, while Dahl[2] has recently found that $Ir_4(CO)_{12}$ has a tetrahedral cluster of metal atoms with carbonyl groups attached linearly to the apices of the iridium polyhedron.

Crystal data of compounds (I) and (II) are given in the Table.

Almost 700 observable reflections were collected for (I), using Cu-K_α radiation and multiple films integrated by Weissenberg method, and 720 reflections for (II), using Mo-K_α and standard precession technique. The intensities were measured with a microdensitometer, corrected for the usual Lorentz polarisation factor and scaled; anomalous dispersion has been taken into account.

Three-dimensional Patterson analysis showed clearly a tetrahedron of iridium atoms together with the relative position of the metal polyhedron in the unit cell. Fourier synthesis with coefficients phased by cluster atoms gave the phosphorus positions but no information about the light atoms.

Consequently in both analyses, iridium and phosphorus atoms were preliminarily refined by the least-squares method, followed by a rigid-body treatment of the three phenylphosphine groups using a method of minimum residual programmed for IBM 7040 computer.[3]

Difference Fourier, executed at this stage,

TABLE

Complex		a (Å)	b (Å)	c (Å)	α	β
(I) $[Ir_4(CO)_{10}(PPh_3)_2]$	Monoclinic	$14 \cdot 15 \pm 1$	$17 \cdot 88 \pm 1$	$17 \cdot 82 \pm 1$		$90°50' \pm 10'$
(II) $[Ir_4(CO)_9(PPh_3)_3]$	Triclinic	$13 \cdot 31 \pm 1$	$20 \cdot 91 \pm 2$	$12 \cdot 77 \pm 1$	$97°21' \pm 10'$	$104°09' \pm 10'$

Complex		γ	S.G.	Z	D_c(g./cm.³)	D_m(g./cm.³)
(I) $[Ir_4(CO)_{10}(PPh_3)_2]$	Monoclinic		$P2_1/c$	4	$2 \cdot 31$	$2 \cdot 35$
(II) $[Ir_4(CO)_9(PPh_3)_3]$	Triclinic	$110°57' \pm 10'$	$P\bar{1}$	2	$2 \cdot 00$	$2 \cdot 10$

showed clearly the unresolved carbonyl peaks which enabled the number of CO ligands and their approximate positions to be ascertained. To refine ligand geometry, the method of minimum residual was again applied to both kinds of carbonyl groups: one co-linear with apical metal atoms, and the other bridged and co-planar to the iridium edges. The values of the residual were computed as a function of the rotational and translational parameters of these two kinds of rigid groups and the geometry of the two complexes corresponding to the minimum residual was found.

The configuration of carbonyl and phosphorus atoms around iridium cluster is shown in Figures 1
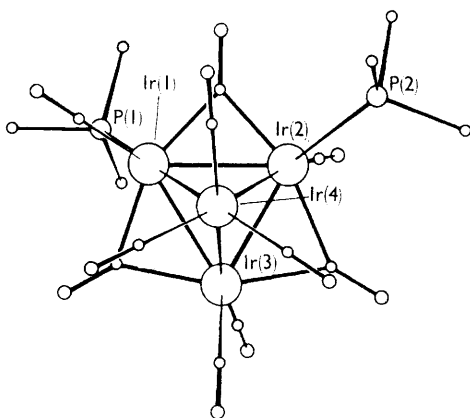

FIGURE 1. *Projection of the molecule* $Ir_4(CO)_{10}(PPh_3)_2$ *on the basal iridium plane. Only one carbon atom of the phenyl groups is shown.*

and 2. The present stage of refinement corresponds to residual $R_I = 0.110$ for the structural analysis of compound (I), and $R_{II} = 0.134$ for the complex (II).

Thus, the structures can be outlined:

(i) Iridium atoms are arranged at apices of a tetrahedron with an edge of 2.73 Å.

(ii) Three carbonyl groups are bridged to basal iridium atoms which have three phenyl-phosphine as ligands. These carbonyl groups are not more than 10° out of basal

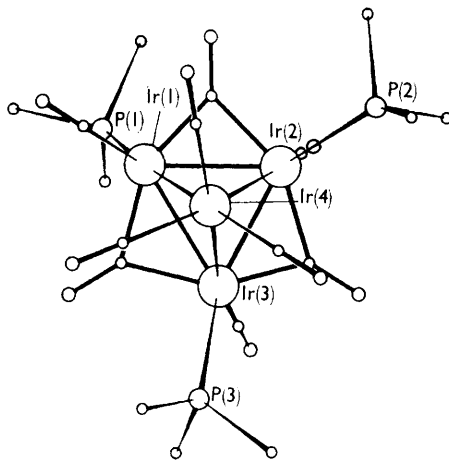iridium plane. The average Ir–P distance is 2.36 Å and Ir–C (bridged) 2.1 Å.

FIGURE 2. *Projection of the molecule* $Ir_4(CO)_9(PPh_3)_3$ *on the basal iridium plane. Only one carbon atom of the phenyl groups is shown.*

(iii) One apical iridium atom is linearly bound to three carbonyl groups, at the average distance Ir–C (linear) 1.85 Å.

(iv) No relevant differences have been detected in bond distances between iridium atoms having bridged- or linearly-bonded carbonyl groups.

(v) Configuration around apical iridium atom is trigonal antiprismatic, corresponding to a slightly distorted octahedron.

(vi) The compound (I) has no relevant molecular symmetry, while the complex (II) shows a pseudosymmetry plane containing atoms P(1)–Ir(1)–Ir(4). The i.r. spectra of the compounds in solid and solution present many bands in agreement with these low symmetries.

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[1] L. Malatesta and G. Caglio, *Chem. Comm.*, 1967, **420**.
[2] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821.
[3] V. Albano, P. L. Bellon, F. Pompa and V. Scatturin, *Rend. Istituto Lombardo Sci.*, 1966, *A*, **100**, 337.