The Structure of a Five-co-ordinated Complex of Iridium(I)

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A NUMBER of complex compounds have recently been described[1,2] which have the formula $[M(CO)(dp)_2]X$, where dp = $(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)$, $(Ph_2P{\cdot}CH_2{\cdot}PPh_2)$, *etc.* The ease with which these compounds undergo the reaction

$$[M(CO)(dp)_2]^+ \rightleftharpoons [M(dp)_2]^+ + CO$$

varies markedly both with the metal,[2] and with the nature of the chelate ligand.[1] In the absence of any obvious chemical reason, it is probable that the differences in stability between these complexes (and also the differences in their reactivity as hydrogenation catalysts) are determined by differences in their detailed stereochemical structure. We are therefore examining some of these compounds by X-ray methods, and we give here a preliminary description of the complex $[Ir(CO)(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]Cl$.

The crystal unit cell parameters are:— $C_{53}H_{48}ClIrOP_4$; $M = 1052{\cdot}5$; monoclinic, $a = 11{\cdot}27 \pm 0{\cdot}02$, $b = 36{\cdot}33 \pm 0{\cdot}08$, $c = 11{\cdot}78 \pm 0{\cdot}02$ Å, $\beta = 102{\cdot}2° \pm 0{\cdot}1$; $V = 4712{\cdot}6$, $D_m = 1{\cdot}490$ (by flotation), $Z = 4$, $D_c = 1{\cdot}483$, $F_{000} = 2112$; Space group $P2_1/n$ (C^5_{2h}, No. 14). Cu-K_α radiation was used. The crystal dimensions were approximately 0·2 mm., and the linear absorption factor 75 cm.$^{-1}$.

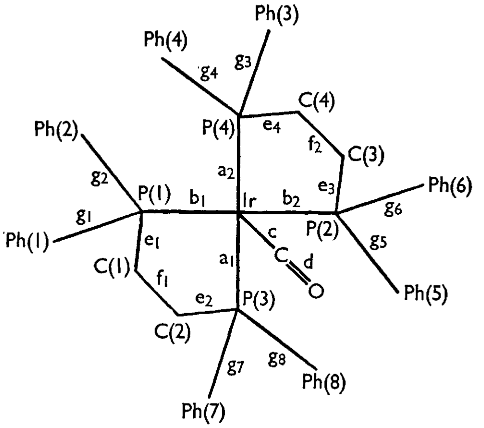

FIGURE 1. *The structure and dimensions of the complex ion, with the estimated standard deviations of the last digit in parentheses.*

Bond-lengths Å
a = b = 2·37 (2)
c = 1·82 (2)
d = 1·16 (3)
e = 1·83 (4)
f = 1·61 (7)
g = 1·83 (7)
Phenyl C–C = 1·41

Bond-angles
b_1c = 143 (2)°
b_2c = 109 (2)°
b_1b_2 = 108 (1)°
a_1a_2 = 176 (1)°
a_1b_1 = a_2b_2 = 83 (1)°
a_1b_2 = a_2b_1 = 97 (1)°
ac = 91 (1)°
cd = 178 (3)°
ae = be = 109 (2)°
ef = 110 (3)°
gg = 102 (4)°
eg = 104 (4)°
ag = bg = 119 (2)°

The structure was solved by three-dimensional Patterson and electron-density syntheses, followed by four cycles of least-squares refinement using isotropic temperature factors. The R-value at this stage is 12·9%, using 4602 independent non-zero structure factors ($hk0$–6 and $0kl$–$2kl$). The crystal contains separate discrete ions $[Ir(CO)(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]^+$ and Cl^-, the interaction between positive and negative ions being purely ionic. The complex ion (see Figure 1) is approximately bipyramidal, but is considerably distorted from the symmetrical trigonal-bipyramidal configuration. The bond-angles in equatorial plane defined by P(1), P(2), and C are 108°, 109°, and 143°. All other bond-angles and bond-lengths fall within the normally accepted range. There are no significant differences between the axial and equatorial Ir–P bond lengths (2·37 Å); and their values suggest that they are single bonds, with little or no π-bonding.

The distorted stereochemistry appears to be dictated, not by the atoms bonded directly to the metal atom, but by the hydrogen atoms in the *ortho*-positions on certain of the phenyl groups. The two diphosphine ligands do not co-ordinate to iridium in the same way; in one there is no obvious relationship between the orientation of the phenyl groups and the co-ordination axes of the iridium atom; but in the other diphosphine, two phenyl groups (3 and 6) are aligned with their planes approximately parallel and perpendicular to the pyramidal axis of the iridium atom. The effect of this is to bring the two *ortho*-hydrogen atoms H(22) and H(36) close to the metal atom (approximately 3·1 and 3·3 Å) within the gap formed by the

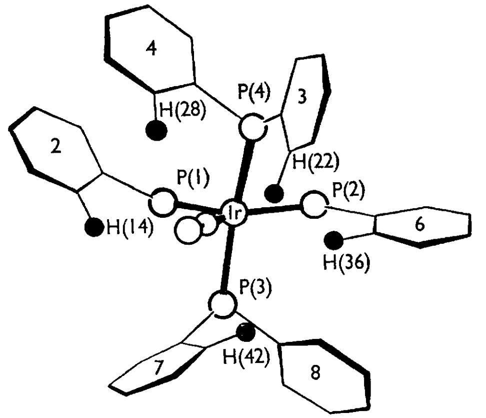

FIGURE 2. *The structure of part of the ion, showing the hydrogen atoms involved in steric interactions*
Distances from iridium: H(22) 3·3 Å, H(36) 3·1Å
distances from carbonyl carbon: H(14) 2·8 Å, H(22) 2·5Å
H(28) 2·8 Å, H(42) 2·8Å

wide P(2)–Ir–C angle; and the nearer of these, H(36), lies in the basal plane very near the centre of the wide angle. Further examination discloses that the carbon atom of the carbonyl group has for its nearest neighbours four hydrogen atoms, H(14), H(22), H(28), and H(42), at distances 2·5—2·8 Å. It appears that the combined steric hindrance effects of these hydrogen atoms are sufficient to distort the molecule into the configuration which is found (see Figure 2).

It is less easy to find a convincing reason why the phenyl groups should adopt this particular configuration rather than any other. We suggest that it is the result of a very delicate balance of forces, of which the key factor is the relatively strong interaction of the metal atom with its nearest hydrogen neighbour, H(36). It is possible that the wide P(2)–Ir–C angle is occupied by a localised electron pair on the metal, which interacts with this hydrogen atom. With the orientation of this phenyl group (6) determined, the mutual steric hindrance of the phenyl groups, the resistance to torsion of the $P-CH_2-CH_2-P$ bridges, and repulsion by the electron pair if it is present, combine to constrain the entire molecule into the configuration which is found.

If this hypothesis is correct, small changes in the nature of the ligands will markedly disturb the balance of repulsive forces, and will produce relatively large changes in the stereochemistry, and the large changes which are observed in the stability and reactivity of the complex ions.

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[1] K. A. Taylor, Brit. Pat. Appl. No. 18327/65.

[2] A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, **1966**, 589.