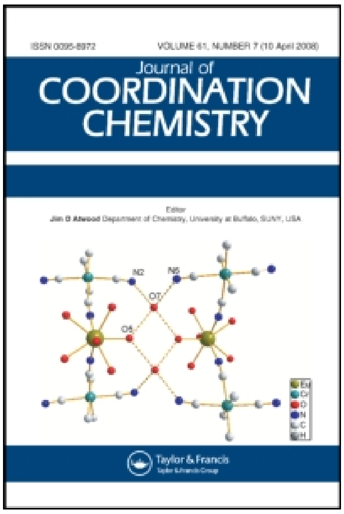

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SHORT COMMUNICATIONS

The Crystal and Molecular Structure of Chlorocarbonyltris (Phenyldimethylphosphine) Iridium (I). Chemical Implications of a Long Iridium-Chlorine Bond

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Sir:

We have recently reported that the addition of excess PMe_2Ph to a solution of $IrCl(CO)(PMe_2Ph)_2$ resulted in spectral changes which were interpreted in terms of the formation of the tris(phosphine) complex, $IrCl(CO)(PMe_2Ph)_3$ (**1**).[1] The further observation[1] that the apparent rate of oxidative addition of H_2 to **1** was higher than to $IrCl(CO)(PMe_2Ph)_2$ was unexpected in view of prior demonstrations that other five-coordinate d^8 complexes are intrinsically unreactive toward H_2 and related substrates, the oxidative additions of such molecules generally being accomplished through mechanisms involving prior dissociation to reactive four-coordinate complexes.[2-4] One possible interpretation of this unusual reversal of reactivity is that depicted by equation (1) according to which **1** is in equilibrium, through dissociation of the Cl^- ligand, with a highly reactive four-coordinate ion pair $[Ir(CO)(PMe_2Ph)_3]^+Cl^-$.[5] In the light of these considerations the isolation of **1** and the determination of its structure by single crystal X-ray diffraction were clearly of interest.

$$\underset{\mathbf{1}}{IrCl(CO)(PMe_2Ph)_3} \rightleftarrows [Ir(CO)(PMe_2Ph)_3]^+Cl^- \xrightarrow{H_2} [IrH_2(CO)(PMe_2Ph)_3]^+Cl^- \tag{1}$$

Yellow brick-shaped crystals of **1**, having the correct elemental analysis, were prepared by addition of a large excess of hexane to a hot benzene solution containing 0.02 M $IrCl(CO)(PMe_2Ph)_2$ and 0.02 M PMe_2Ph followed by slow cooling. The X-ray analysis was performed on a crystal of approximate dimensions, 0.1 × 0.2 × 0.3 mm. *Crystal data*: $M = 670.1$; monoclinic; space group $P2_{1/c}$; $a = 16.25(2)$, $b = 10.38(1)$, $c = 30.07(5)$ Å, $\beta = 147.30(3)°$; $V = 2740(12)$ Å^3; $Z = 4$; $D = 1.624$; $D_m = 1.62$ g cm^{-3}.

Three dimensional intensity data were collected on a Picker FACS I diffractometer with a graphite monochromater (Mo–K_α radiation, 0.71069 Å) out to $2\theta = 40°$. 1331 reflections with intensities $> 2\sigma$ were used in the refinement. After the measured intensities were corrected for Lorentz, polarization, and absorption effects, the structure was solved by Patterson and Fourier techniques. Full-matrix least square refinement, treating the phenyl groups as rigid bodies, and varying the thermal parameters of Ir, Cl and P anisotropically, led to final values of $R = 0.033$ and $R_W = 0.045$.

The structure of $IrCl(CO)(PMe_2Ph)_3$ is depicted in Figure 1. The Ir atom is clearly five-coordinated in the solid state, with a distorted trigonal-bipyramidal arrangement of ligand atoms corresponding to two P ligands (P_2 and P_3) in axial positions and the remaining P (P_1), together with the Cl and CO ligands, in the equatorial plane. The Ir atom is displaced by only 0.017 Å from the latter plane. The principal distortions from idealized trigonal-bipyramidal geometry are reflected in the axial P_2–Ir–P_3 angle of 165.1(2)° and in the unequal angles between the equatorial ligands: P_1–Ir–Cl, 96.3(2); P_1–Ir–C, 134.1(6); Cl–Ir–C, 129.5(6)°.

The coordination geometries of other five-coordinate iridium(I) complexes of known structure include both square-pyramidal (e.g., $IrCl_2(NO)(PPh_3)_2$,[7] $IrCl(NO)(CO)(PPh_3)_2{}^+$,[8] $IrCl(CO)(SO_2)(PPh_3)_2$[9]) and trigonal-bipyramidal (e.g.,

$IrCl(CO)_2(PPh_3)_2$,[10] $IrH(NO)(PPh_3)_3{}^+$,[11]) ligand arrangements. The only distinctive feature of the structure of $IrCl(CO)(PMe_2Ph)_3$ in this context is the location of two of the phosphine ligands in axial positions, whereas in other related tris(phosphine) d^8 complexes such as $IrH(NO)(PPh_3)_3{}^+$,[11] and $RhH(CO)(PPh_3)_3$[12] all three phosphine ligands are in the equatorial positions. With one important exception that is discussed below (namely the long Ir-Cl bond), the metal-ligand bond lengths, as well as the intra-ligand bond lengths and angles, are all within the normal ranges of typical corresponding values in other complexes.

The strikingly exceptional feature of the structure of $IrCl(CO)(PMePh)_3$ is the abnormally long Ir—Cl bond, i.e., 2.619(6) Å. This is at least 0.2 Å longer than the Ir—Cl bond lengths in all other known five-coordinate iridium complexes which (in agreement with the sum of the covalent radii, i.e., 2.35 Å) range from 2.34 Å in $IrCl(NO)(CO)(PPh_3)_2{}^+$,[8] to 2.41 Å in $IrCl(CO)_2(PPh_3)_2$.[10] This result supports our earlier suggestion that the unexpectedly high reactivity of $IrCl(CO)(PMe_2Ph)_3$ toward oxidative addition of H_2 is due to the facile dissociation of the Cl^- ligand to form the highly reactive $Ir(CO)(PMe_2Ph)_3{}^+$ ion.[1] The marked weakening and lengthening of the Ir—Cl bond in $IrCl(CO)(PMe_2Ph)_3$ probably reflect accumulation of electron density on the Ir atom due to the three strongly basic phosphine ligands. This is also implied by the extremely low C—O stretching frequency of the compound, i.e., 1885 cm^{-1} which is well below the values typical of other neutral carbonyls [e.g., 1960 cm^{-1} in the corresponding bis(phosphine) complex, $IrCl(CO)(PMe_2Ph)_2$]. The implications of this apparent connection between the structure and reactivity of $IrCl(CO)(PMe_2Ph)_3$, for the reactivities of other d^8 complexes are clearly such as to warrant further attention.

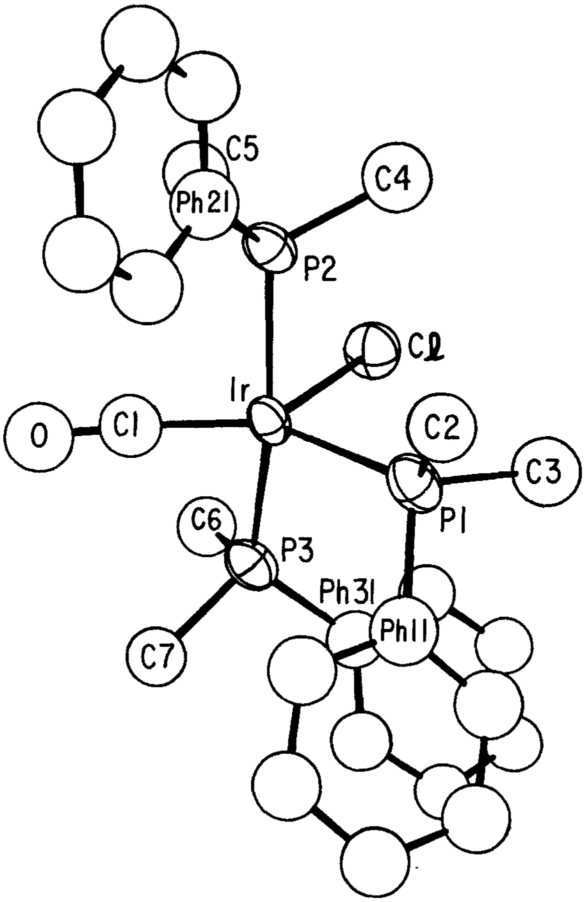

FIGURE 1 The structure of $IrCl(CO)(PMe_2Ph)_3$. Principal bond lengths: $Ir-P_1 = 2.342(5)$; $Ir-P_2 = 2.320(6)$; $Ir-P_3 = 2.330(6)$; $Ir-C_1 = 1.77(2)$; $Ir-Cl = 2.619(6)$; $C_1-O = 1.20(2)$ Å. Principal bond angles: $P_2-Ir-P_3 = 165.1(2)$; $C_1-Ir-Cl = 129.5(6)$; $Cl-Ir-P_1 = 96.3(2)$; $C_1-Ir-P_2 = 89.5(6)$; $C_1-Ir-P_3 = 86.4(6)$; $Cl-Ir-P_2 = 84.0(2)$; $Cl-Ir-P_3 = 87.6(2)$; $P_1-Ir-P_2 = 96.9(2)$; $P_1-Ir-P_3 = 96.2(2)$; $Ir-C_1-O = 172(2)$°.

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