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Preliminary communication

TRIDENTATE DIMETALLATED PHOSPHITEIRIDIUM COMPLEXES. THE CRYSTAL STRUCTURE OF $[IrCl\{P(OC_6H_3CH_3)_2(OC_6H_4CH_3)\}(\gamma\text{-PICOLINE})_2]$

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Summary

$[Ir_2Cl_2\{P(O\text{-}o\text{-tolyl})_3\}_3]$ has been prepared from $[CODIrCl]_2$ and *o*-tolylphosphite in boiling xylene, and shown to be a novel precursor for a series of neutral and cationic tridentate dimetallated phosphite iridium(III) complexes.

Although many compounds having internal metal—carbon bonds are known there is only one example [1] to date of a complex containing a dimetallated tridentate ligand. During our studies [2] on cationic iridium(I) systems we observed that the neutral compound $[CODIr\{P(OC_6H_4)(OC_6H_5)_2\}\{P(OC_6H_5)_3\}]$ precipitated from hot ethanol solutions containing $[CODIrCl]_2$ and triphenylphosphite [3]. We now find that if $[CODIrCl]_2$ is treated with *o*-tolylphosphite in boiling xylene a yellow product (I) of unknown structure results and for which a stoichiometry of $[Ir_2Cl_2\{P(O\text{-}o\text{-tolyl})_3\}_3]$ is inferred from microanalytical and molecular weight data. During efforts to fully characterise I it became apparent that this complex is very reactive to a large range of ligands and addenda molecules producing a series of neutral and cationic dimetallated tridentate phosphite iridium(III) complexes.

Thus treatment of I with CO in boiling benzene gave an insoluble white complex of stoichiometry $[IrCl(CO)\{P(O\text{-}o\text{-tolyl})_3\}]_x$ (II) with a single $\nu(CO)$ absorption in the IR at 2075 cm^{-1}. II further reacted with γ-picoline to give the soluble monomeric compound $[IrCl(CO)\{P(O\text{-}o\text{-tolyl})_3\}(\gamma\text{-picoline})]$ (III) ($\nu(CO)$ 2045 cm^{-1}; yield 80%) in a typical halogen bridge fission reaction and from which, taking into account the insoluble nature of II, we deduce that $x = 2$. The reaction of I with the σ-donor ligands L (L = pyridine, γ-picoline,

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PPh_3, PMe_2Ph, $PMePh_2$) gave the monomeric complexes [$IrClL_2${P(O-*o*-tolyl)$_3$}] (IV), whereas in boiling acetonitrile I formed the cation [$Ir(CH_3CN)_3${P(O-*o*-tolyl)$_3$}]$^+$ (V) which was characterised as the PF_6 and BPh_4 salts. If the reaction solution of V containing ethanol is boiled for a prolonged period (24 h) the dimer [IrHCl{P($OC_6H_3CH_3$)($OC_6H_4CH_3$)$_2$}-(CH_3CN)]$_2$ is formed and this gave [IrHCl{P($OC_6H_3CH_3$)($OC_6H_4CH_3$)$_2$}-(pyridine)$_2$] on treatment with an excess of pyridine. Except for I these compounds were fully characterised by elemental analysis, molecular weight, conductivity, IR and ^{1}H NMR data. Complexes II—V are white in colour which precludes their formulation as square planar iridium(I) species, and so we suspected that the single *o*-tolylphosphite ligand was a tridentate dimetallated group. To confirm this the preliminary structure of [IrCl{P(O-*o*-tolyl)$_3$}-(γ-picoline)$_2$] has been determined.

The white needle-shaped crystals obtained are monoclinic, of space group $P2_1/c$, with a 9.12(2), b 17.36(2), c 20.65(2) Å; β 90.5(1)°, $Z = 4$; $\mu = 28.25$ cm^{-1}. 2583 observed reflection intensities were measured on a four-circle diffractometer, and the molecular structure was determined from Patterson and Fourier syntheses after the usual corrections (including absorption) to the data were applied. Isotropic full-matrix refinement of the atomic parameters has reduced the residual value to 0.076 and the refinement is still continuing. The iridium atom has distorted octahedral coordination (Fig. 1), and the two internal metal carbon bonds are in *cis* position to each other and in *trans* position to the two γ-picoline ligands. One molecule of H_2O per compound was identified in the crystal structure.

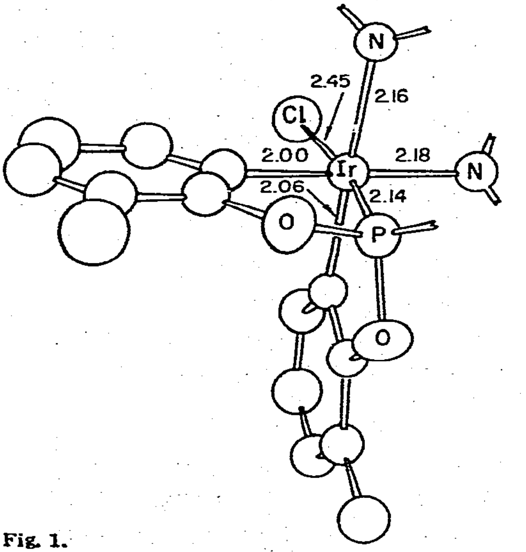

Fig. 1.

Significant bond distances are Ir—P 2.14(1) Å; Ir—Cl 2.45(1) Å; Ir—N 2.16(2) Å (mean); Ir—C 2.00(2) and 2.06(2) Å. Observed bond angles are; P—Ir—C 80(1)°; P—Ir—Cl 170.6(3)°; N—Ir—C 178(0) and 179(2)°, the distortion probably being due to the steric requirements of chelate ring formation. A comparison of bond lengths with those observed [4] in the crystal structure of $[\overline{\mathrm{IrCl\{P(OC}}_6H_4)(OC_6H_5)_2\}_2\{P(OC_6H_5)_3\}]$ indicates that our shorter mean Ir—C value of 2.03 Å (cf. Ir—C 2.10 Å) may be due to a weaker structural *trans* effect of the γ-picoline groups compared to the phosphorus of the triphenylphosphite group. We cannot explain our long Ir—Cl bond (cf. 2.41 Å) and short Ir—P bond (cf. 2.25 Å).

Reactions of I with SO_2, CS_2 and acetylenes have given crystalline products which are not yet fully characterised.

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