

Synthesis and Structural Characteristics of Planar Iridium(II) Complexes

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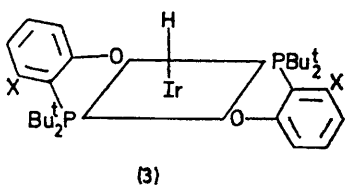
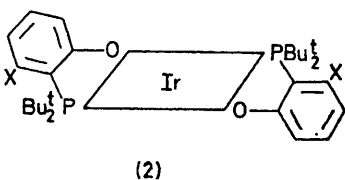
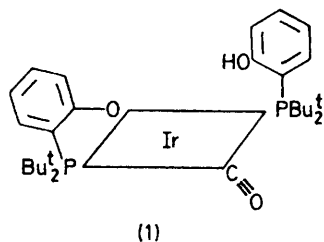
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Summary The syntheses and structures of two iridium(II) complexes, *trans*- $[\text{Ir}(\text{Bu}_2\text{PC}_6\text{H}_4\text{O})_2]$ and *trans*- $[\text{Ir}\{\text{Bu}_2\text{PC}_6\text{H}_3(\text{OMe})\}_2]$, are described. No definite example of a stable mononuclear complex of iridium(II) is known^{†1,2} although there is evidence for the existence of transient iridium(II) species in some oxidative addition reactions of iridium(I) to iridium(III) complexes.^{4,5}

[†] The nitrosyl complex $[\text{IrBr}_3(\text{NO})(\text{PPh}_3)_2]$ could be regarded as a complex of iridium(II) but this depends on assigning a positive charge to the nitrosyl ligand.³

We now find that the divalent state can be stabilised by *OP*-bidentate chelates.

Bubbling carbon monoxide through a boiling propan-2-ol solution of (2-methoxyphenyl)di-*t*-butylphosphine and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (prepared *in situ* from chloroiridic acid) provides the yellow iridium(I) complex $[\text{Ir}(\text{CO})(\text{PBu}_2^t\text{C}_6\text{H}_4\text{O})(\text{PBu}_2^t\text{C}_6\text{H}_4\text{OH})]$ (**1**) *i.e.* demethylation has occurred. A benzene or xylene solution of (**1**) in air rapidly becomes blood red and gives carbon dioxide and the deep red iridium(II) complex $[\text{Ir}(\text{PBu}_2^t\text{C}_6\text{H}_4\text{O})_2]$ (**2**) ($\text{X} = \text{H}$) (*ca.* 50%) together with a few percent of the purple iridium(III) hydride $[\text{IrH}(\text{PBu}_2^t\text{C}_6\text{H}_4\text{O})_2]$ (**3**) ($\text{X} = \text{H}$). The iridium(II) complex is paramagnetic, μ_{eff} (300 K) = 1.76 B.M., the crystals belonging



to the space group $P2_1/c$ with $a = 8.111$, $b = 11.926$, $c = 15.669$ Å, $\beta = 108.52^\circ$; $Z = 2$, $D_m = 1.53$, and $D_c = 1.54$ g cm $^{-3}$. The stereochemistry, shown in Figure 1, has been defined by an X-ray analysis based on 1851 reflection intensities [$\text{Mo-K}\alpha$; automatic four-circle diffractometry; $I_{\text{obs}} > 3\sigma(I_{\text{obs}})$] with least-squares convergence to $R = 0.06$ on refinement of positional and isotropic thermal parameters only. The complex has exact C_2 symmetry and is rigorously planar.

Treatment of iridium trichloride with di-*t*-butyl-2,6-dimethoxyphenylphosphine in propan-2-ol gives the purple iridium(III) hydride, (**3**) ($\text{X} = \text{OMe}$). A dichloromethane solution of this hydride is rapidly converted by aerial oxidation into the red iridium(II) complex (**2**) ($\text{X} = \text{OMe}$). The room temperature magnetic moment is again 1.78 B.M.

and the crystals are triclinic with $a = 8.285$, $b = 8.791$, $c = 12.066$ Å, $\alpha = 102.30^\circ$, $\beta = 88.43^\circ$, $\gamma = 110.66^\circ$; $Z = 1$, $D_m = 1.45$, and $D_c = 1.45$ g cm $^{-3}$. The integrated intensities of 3039 observed independent reflections, measured

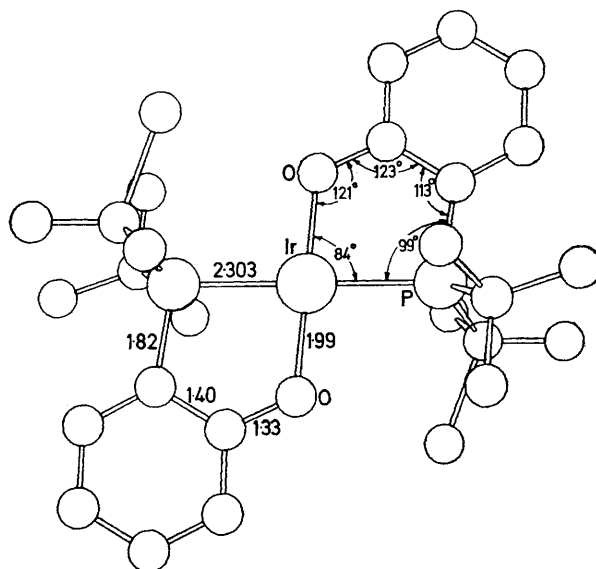


FIGURE 1. $\text{Ir}[\text{P}(\text{C}(\text{Me})_3)_2\text{C}_6\text{H}_4\text{O}]_2$; bond lengths (Å) and bond angles in the chelate ring. E.s.d.'s in the bond lengths are 0.004 (Ir—P), 0.01 (Ir—O) and an average of 0.01 $_6$ Å for the remainder.

on an automatic four-circle diffractometer using $\text{Cu-K}\alpha$ radiation, have formed the basis of an X-ray analysis. Isotropic least-squares refinement in space group $P\bar{1}$ has reached $R = 0.067$; the complex, shown in Figure 2, again has C_2 symmetry.

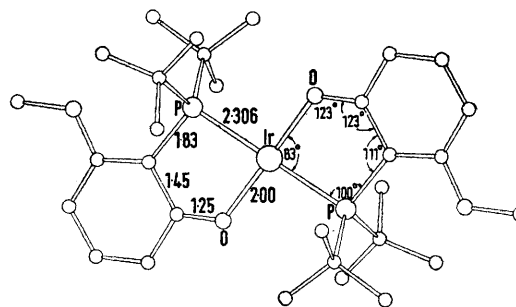


FIGURE 2. $\text{Ir}[\text{P}(\text{C}(\text{Me})_3)_2\text{C}_6\text{H}_3(\text{OMe})\text{O}]_2$; bond lengths (Å) and bond angles in the chelate ring. E.s.d.'s in the bond lengths are 0.003 (Ir—P), 0.01 (Ir—O) and an average of 0.01 $_6$ Å for the remainder.

The complexes, characterized also by microanalytical, molecular weight, *i.r.*, and ^1H and ^{31}P n.m.r. data, react

readily with small molecules. For example, the iridium(II) complex (2) (X = OMe) takes up oxygen reversibly to give a purple adduct and all complexes of types (2) and (3) take up carbon monoxide readily. These reactions are being investigated.

We thank the S.R.C. for support, I.C.I. Ltd. for a fellowship (H.C.E.), and Engelhard Industries Ltd. for the loan of iridium trichloride.

(Received, 3rd May 1974; Com. 503.)

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