An Iridium Complex of 5-Co-ordinated Phosphorus

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The 5-co-ordinate phosphorus complex $Ir(CO)Cl_2(PEt_3)_2PCl_4$ has been prepared by the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with dichlorine.

Metal complexes of 5-co-ordinated P, As, or Sb are very rare.[1] We have recently prepared[2] the complex $Ir(CO)Cl_2(PEt_3)_2P'Cl_2$ (**1**) by oxidative addition of PCl_3 to $Ir(CO)Cl(PEt_3)_2$, and it has been characterised by analysis, by mass spectrometry, and by *X*-ray crystallography. The chemical shift† of P′ is 304 p.p.m. Treatment of a solution of (**1**) in chloroform with dichlorine

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† Positive to high frequency of 85% H_3PO_4.

leads to the disappearance of the n.m.r. signals due to **(1)** and to the appearance of new peaks in the P{H} spectrum at +7.6 p.p.m. (t; J 17.7 Hz) and −8.6 p.p.m. (d; J 17.7 Hz). The product has been isolated as a white powder; analysis for C, H, and Cl is consistent with the formulation of the compound as $Ir(CO)Cl_2(PEt_3)_2PCl_4$ (Cl, found 31.3; calc. 30.4%). The solution in nitromethane is non-conducting, and the n.m.r. spectrum in that solvent is not significantly different from that in dichloromethane. Attempts to obtain the mass spectrum gave molecular ion peaks due to $Ir(CO)Cl_2(PEt_3)_2P(OH)_2Cl_2$ and $Ir(CO)Cl_2(PEt_3)_2POCl_2$, but the analytical data are not consistent with either of these formulations. Treatment of our product with triethylphosphine in dichloromethane gave **(1)** and a compound with a singlet P{H} resonance at 111.9 p.p.m. (found[3] for Et_3PCl_2 112.2 p.p.m.) in essentially quantitative yield; reaction between our product and $Ir(CO)Cl(PEt_3)_2$ gave **(1)** and $Ir(CO)Cl_3(PEt_3)_2$ in high yield. These observations establish the identity of our product (Scheme 1).

$$\begin{tikzcd}
\underset{\textbf{(1)}}{Ir(CO)Cl_2(PEt_3)_2PCl_2} \arrow[d, "Cl_2"] & \\
Ir(CO)Cl_2(PEt_3)_2PCl_4 \arrow[r, "Et_3P"] \arrow[d, "Ir(CO)Cl(PEt_3)_2"] & \textbf{(1)} + Et_3PCl_2 \\
\textbf{(1)} + Ir(CO)Cl_3(PEt_3)_2 &
\end{tikzcd}$$

Scheme 1

The compound appears to hydrolyse very slowly if it is left to stand at room temperature, and it decomposes on sublimation. So far all our attempts to grow single crystals have failed, and so we do not know the stereochemical relationships of the groups round P′ or Ir, except that the Et_3P groups are mutually *trans*.

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References

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2 E. A. V. Ebsworth, N. T. McManus, N. J. Pilkington, and D. W. H. Rankin, to be published.

3 E. A. V. Ebsworth and N. J. Pilkington, unpublished results. The value given by R. Appel and H. Schöler, *Chem. Ber.*, 1977, **110**, 2382, seems to be based on the opposite sign convention for chemical shifts.