A Ditertiary Phosphine Complex of Cobalt(0)

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THE product of the reaction between $[CoBr_2 \{C_2H_4(PPh_2)_2\}_2]$ and sodium borohydride, previously described as a derivative of cobalt(0),¹ was shown to be a hydrido-complex of cobalt(I), $[CoH \{C_2H_4(PPh_2)_2\}_2]$.²

In order to obtain a well-characterised cobalt(0) derivative, we have investigated the reaction between the above cobalt(II) complex and several reducing agents. The cobalt(0) complex, $[Co \{C_2H_4(PPh_2)_2\}_2]$, is best obtained by treating the cobalt(II) complex with 2M-potassium

hydroxide in aqueous ethanol under nitrogen atmosphere. The reaction takes about 8 days for completion in aqueous solution, and about 3 days in 95% ethanolic solution at room temperature. The reducing agent is in this case the phosphine itself, and the reaction takes place according to the equation $[DP = C_2H_4(PPh_2)_2]$:

 $5\mathrm{CoBr}_{2}(\mathrm{DP}_{2}) + 10\mathrm{KOH} = 4\mathrm{Co}(\mathrm{DP})_{2} +$

 $2\text{DPO}_2 + \text{Co(OH)}_2 + 10\text{KBr} + 4\text{H}_2\text{O}.$

¹ J. Chatt, F. A. Hart, and D. T. Rosevear, J. Chem. Soc., 1961, 5504.

² A. Sacco and R. Ugo, J. Chem. Soc., 1964, 3274.

The red precipitate can be crystallized from benzene, by addition of ethanol, to give paramagnetic dark red crystals, m.p. $227-230^{\circ}$, which are very rapidly oxidised by air. The i.r. spectrum is identical with that of the corresponding nickel(0) complex in the 4000-600 cm.⁻¹ range. In benzene it has a dipole moment of 1.2 D, assuming $_{A}P = 0$, or 0.0 D, assuming $_{A}P \simeq 0.10 _{B}P$.

The cobalt(0) complex in benzene solution quickly reduces hydrogen at room temperature and atmospheric pressure giving the cobalt(I) hydrido-complex,² and at once reduces anhydrous stannous chloride to metallic tin.

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