Bis(triphenylphosphine)carbonatoplatinum(II)

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Further studies on what was believed[1] by analogy with the carbon disulphide and carbonyl sulphide complexes, *e.g.*, $(Ph_3P)_2PtCS_2$,[1,2] to be a carbon dioxide complex have shown that, in fact, in the complete absence of oxygen (or air), tris(triphenylphosphine)platinum(0) in diethyl ether or benzene solution does not react with carbon dioxide at 25°. On admission of oxygen, a rapid reaction occurs and white to pale yellow crystals of a hitherto unknown type of carbonate-complex, $(Ph_3P)_2PtCO_3$ are precipitated according to the stoicheiometric equation:

$$(Ph_3P)_3Pt + O_2 + CO_2 = (Ph_3P)_2PtCO_3 + Ph_3PO$$

The complex can be crystallised from various solvents but with benzene, dichloromethane, chloroform, and acetone, one molecule of solvent is tightly held in the lattice. The benzene-containing complex, whose composition and structure has been determined by *X*-ray diffraction[3] has, after crystallisation from benzene solutions containing excess PPh_3, m.p., 202—205° [Found: C, 58·3; H, 4·5; O, 4·9 (direct); CO_2, 5·4 (direct); P, 5·9; Pt, 23·0. $(Ph_3P)_2PtCO_3,C_6H_6$ requires C, 60·2; H, 4·2; O, 5·6; CO_2, 5·1; P, 7·2; Pt, 22·7%]. The chloroform adduct is similar [*M* (in $CHCl_3$), found 838, required 899]. The infrared spectra show bands at 1680, 980, 1180, 875, and 760 cm.$^{-1}$ in agreement with those established for chelate carbonato-complexes.[4]

That the oxidation occurs *via* the intermediate orange-cream oxygen complex, m.p., 135°, ν_{O-O} 830 cm.$^{-1}$ [Found: C, 56·3; H, 3·9; O, 4·3. $(Ph_3)_2PtO_2$ requires C, 57·5; H, 4·0; O, 4·2%] is shown by direct interaction of this complex, obtained as a precipitate by the action of oxygen on concentrated solutions of $(Ph_3P)_3Pt$ in benzene, with carbon dioxide when the carbonato-complex is obtained.

Oxidations by molecular oxygen of Ph_3P [5,6] and $C_6H_{11}NC$ [5] using $(Ph_3M)_4M$ (M = Pd, Pt) have been reported and the existence of oxygen compounds of Ni,[5] Pd,[4,5] and Pt [4,5] have been mentioned; although analytical data was not given, the infrared band of the co-ordinated oxygen agrees with our value.

The i.r. spectrum of $(Ph_3P)_2PtCO_3$, appeared to be identical with that of a sample of the "hydrido" species $(Ph_3P)_2PtH_2$,[7,8] prepared in these laboratories some years ago by the original procedure. We have established the identity of the complexes by analysis, spectra, and mass spectra. Further we have shown that $(Ph_3P)_3Pt$ does not react with hydrogen (400 atm./50°) and that the "hydrido" species gives no high-field n.m.r. lines at concentrations far in excess of those where authentic hydrido-complexes give substantial signals. The carbonato-complex was hence obtained[7,8] by adventitious carbon dioxide and oxygen present in solvents.

Finally, the direct interaction of $(Ph_3P)_2PtCl_2$ with silver carbonate in acetone, chloroform, or benzene also gives $(Ph_3P)_2PtCO_3$ solvent, whose *X*-ray powder pattern is identical[3] with that of the product obtained by oxidation. A corresponding palladium complex can be obtained.

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