The Structure of Bis(triphenylphosphine)carbonatoplatinum(II)

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THE slow separation of a white complex from benzene solutions of tetrakistriphenylphosphine and tristriphenylphosphineplatinum has been interpreted as due to the formation of the hydrido-complex, $PtH_2(PPh_3)_2$;[1,2] the suggestion was apparently confirmed[2] by the more rapid formation of the complex under 200 atm of hydrogen. However, while *X*-ray studies of this material were in progress Nyman *et al.*,[3] showed that there is no reaction of tris(triphenylphosphine)platinum with pure hydrogen and that this complex interacts with carbon dioxide in presence of oxygen. The observation[2] must therefore be attributed to the presence of adventitious oxygen and to the use of commercial-grade hydrogen known to contain carbon dioxide.

The complex separates from a benzene solution of bistriphenylphosphineplatinum[4] in several hours only, while crystals of bistriphenylphosphineplatinum transform over a period of a few months if kept in a sealed tube under a partial pressure of air of 1—5 mm. Hg.

The nature and structure of the complex was completely determined by a single-crystal *X*-ray analysis. The crystals are triclinic with $a = 12{\cdot}49$, $b = 15{\cdot}70$, $c = 10{\cdot}56$ Å, $\alpha = 110{\cdot}9°$, $\beta = 70{\cdot}0°$, $\gamma = 98{\cdot}1°$; space group $P\bar{1}$. Intensities of more than 3500 independent reflexions with $F^2/\sigma F_0^2 \geqslant 3{\cdot}0$ have been measured on a 'Pailred' automatic diffractometer. The Patterson synthesis could be directly interpreted for all atomic positions (excluding hydrogens) and immediately showed the complex to be bis(triphenylphosphine)carbonatoplatinum(II). Three block-diagonal least-squares cycles of refinement of atomic positional and isotropic Debye factors have been carried out on the 1200 independent reflexions for which $F_0^2/\sigma F_0^2 \geqslant 10$ and the present discrepancy index for these reflexions is 0·057. The platinum(II) ion has distorted square-planar co-ordination symmetry with mean bond lengths Pt–P 2·24, Pt–O 2·07, C–O 1·28 Å, and P–Pt–P 98·2°, O–Pt–P 98·8°, and O–Pt–O 64·0°. We have further confirmed the nuclear magnetic resonance and infrared spectroscopic findings of Nyman *et al.*,[3] and the bands extending from 1180 cm.$^{-1}$ to 760 cm.$^{-1}$ have also been examined in the deuterated phosphine complex, $Pt[P(C_6D_5)_3]CO_3$.

The carbonato-complex forms *cis*-$PtCl_2(PPh_3)_2$ and *cis*-$Pt(NO_3)_2(PPh_3)_2$[m.p., 223—227°. Found: C, 51·3; H, 3·4; N, 3·5. Calc.: C, 51·3; H, 3·6; N, 3·4%] on treatment with hydrochloric and nitric acids, respectively.

The formation of the carbonato-species is very dependent on the nature of the phosphine ligand. Benzene solutions of the complexes PtL_3 [L = (*p*-tolyl)$_3$P, or (*p*-chlorophenyl)$_3$P] give only very poor yields of the carbonate in the case of the tris-*p*-tolylphosphine and none in the case of tris-*p*-chlorophenylphosphine.

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