The Adducts formed by Phosphorus Tricyanide with Some Aluminium Compounds

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LITTLE is known about the ability of phosphorus tricyanide[1] to form co-ordination compounds. The *X*-ray data show that it possesses a pyramidal structure in which there is some interaction between the phosphorus atom and neighbouring nitrogen atoms of other molecules.[2] The intermolecular bonding survives dissolution in organic solvents since phosphorus tricyanide is tetrameric in nitromethane and dimeric in acetonitrile, dioxan, and benzene.[3]

To assess the ability of phosphorus tricyanide to form co-ordination compounds initial studies have been made to determine donor–acceptor relationships in diethyl ether solutions of aluminium compounds. Thus addition of an ether solution of phosphorus tricyanide (1·09 g.) to an ether solution of aluminium hydride (0·3 g.) results in the immediate precipitation of a buff-coloured solid which was separated by filtration under nitrogen and pumped for some hours at $1{\cdot}0 \times 10^{-2}$ mm. pressure at room temperature. The solid had a composition corresponding to $AlH_3,P(CN)_3,0{\cdot}8(C_2H_5)_2O$.

On mixing an ether solution of phosphorus tricyanide (1·09 g.) and aluminium trichloride (1·33 g.) at room temperature, a white precipitate is formed which accounts for about 10% of the material present in the reaction mixture. Filtration under nitrogen followed by removal of the ether at reduced pressure yields a 1 : 1 complex corresponding to the composition $AlCl_3,P(CN)_3,(C_2H_5)_2O$. Heating the adduct to 100° results in removal of the ether and elimination of cyanogen chloride to give a white solid corresponding to the empirical formula AlCl,PCN.

A similar addition of phosphorus tricyanide (1·09 g.) to an ether solution of aluminium bromide (2·67 g.) results in the precipitation of a white

solid which accounts for most of the reactant concentration in solution. The solid is presumably formed by an elimination process which occurs at room temperatures since the composition of the solid corresponds to the empirical formula AlBr,-PCN,1·4$(C_2H_5)_2O$. Heating to 100° results in removal of some of the ether to give AlBr,PCN,-$(C_2H_5)_2O$.

Finally the reaction of phosphorus tricyanide with aluminium tricyanide was studied. In this case aluminium tricyanide which is insoluble in ether (or any other suitable solvent) was shaken with an ether solution of phosphorus tricyanide. However, no evidence for adduct formation was obtained. Studies on the nature of the thermal elimination products are in progress and will be reported later.

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