Group Exchange on Phosphorus *via* Co-ordination to Platinum

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Summary Prolonged heating of an excess of dialkyalmino-difluorophosphines with $PtCl_2$ gives the corresponding bis(dialkylamino)fluorophosphine complex and PF_3.

RECENTLY we described the synthesis of some tetrakis-(fluorophosphine) complexes of zerovalent platinum, PtL_4, [L = CF_3PF_2; $(CF_3)_2PF$; PF_3] by direct reaction between platinum(II) chloride and the fluorophosphine ligand.[1] Dialkylaminodifluorophosphines R_2NPF_2 (R = Me, Et, R_2 = cyclo-C_5H_{10}), on the other hand, react with platinum chloride at 60° to afford high yields of the square-planar Pt^{II} complex *cis*-$(R_2NPF_2)_2PtCl_2$ (I) [Eq. (1)]. Furthermore, prolonged heating with an excess of ligand at the same temperature unexpectedly leads to a redistribution of groups attached to phosphorus, affording the corresponding bis(dialkylamino)fluorophosphine complex *cis*-$[(R_2N)_2PF]_2$-$PtCl_2$ (II) with evolution of trifluorophosphine [(Eq. (2)].

$$2R_2NPF_2 + PtCl_2 \rightarrow cis\text{-}(R_2NPF_2)_2PtCl_2 \qquad (1)$$

$$4R_2NPF_2 + PtCl_2 \rightarrow cis\text{-}[\{(R_2N)_2PF\}_2]PtCl_2 + 2PF_3 \qquad (2)$$

The combining ratios of $PtCl_2 : R_2NPF_2 : PF_3$ were always very close to that expected from Eq. (2).

In the absence of the platinum salt no significant exchange of groups on phosphorus was observed under analogous conditions.

The identity of the products was confirmed by elemental analyses and the *cis*-stereochemistry established by far-i.r. and ^{19}F n.m.r. studies. The n.m.r. spectra are of the $X_2AA'X_2'$ or $XAA'X'$ type (X = fluorine, A = phosphorus), and as discussed elsewhere[2,3] these can be easily analysed to give accurate values of the phosphorus–phosphorus coupling constant $^2J_{PMP'}$ because $^1J_{PF} >> {}^2J_{PMP'}$. The resulting small values (25—37 c./sec.) are characteristic of *cis*-complexes.[4]

The dialkylaminodifluorophosphine complex (I; R = Me) was shown to be the reaction intermediate in Eq. (2) by its essentially quantitative conversion into (II; R = Me) when heated (60°) with an excess of dialkylaminodifluorophosphine [Eq. (3)].

$$cis\text{-}(Me_2NPF_2)_2PtCl_2 + 2Me_2NPF_2 \rightarrow cis\text{-}[\{(Me_2N)_2PF\}_2PtCl_2] + 2PF_3 \qquad (3)$$

Similar reactions have been observed using platinum(II) bromide, where it appears that group exchange occurs more readily than in the chloro-complexes.

The mechanism of these unusual redistribution reactions presumably involves initial co-ordination of a third molecule of the dialkylaminodifluorophosphine to the square planar Pt^{II} complex forming a five-co-ordinated intermediate which then undergoes group exchange with subsequent loss of trifluorophosphine. We have found no evidence for a similar exchange of groups on phosphorus during studies of related square-planar rhodium(I) dialkylaminodifluorophosphine complexes.

We thank the S.R.C. for a Research Studentship (for M.D.S.).

(*Received, May 30th,* 1969; *Com.* 761.)

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