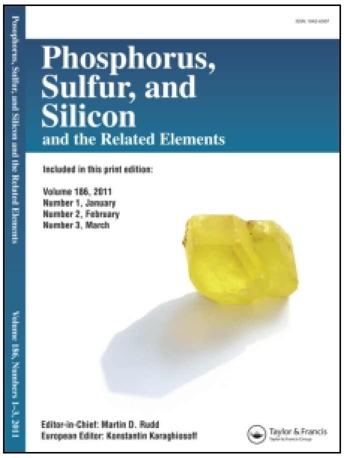

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Ligand Exchange by Halogenation of P^{III}Compounds

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LIGAND EXCHANGE BY HALOGENATION OF P^{III} COMPOUNDS

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Abstract The chlorination of several acyclic and cyclic P^{III} compounds at $0^{o}C$ is discussed. Often a ligand exchange reaction is observed.

The halogenation of P^{III} compounds 1 gives dihalogenophosphoranes 2 or halogenophosphonium halogenides 3. It is known, that the halogene adducts are often unstable; in the case of Y = OAlk they react to the phosphoryl compounds 4 and in the case of Y = Z = OPh to the phosphonium salts 5 under ligand exchange[1].

$$\underset{\mathbf{1}}{Z_2PY} + X_2 \longrightarrow \underset{\mathbf{2}}{Z_2PYX_2} \quad \text{or} \quad \underset{\mathbf{3}}{Z_2PYX^+X^-}$$

$$\mathbf{2} \longrightarrow AlkX + \underset{\mathbf{4}}{Z_2P(O)X} \qquad \mathbf{3} \longrightarrow \underset{\mathbf{5}}{(PhO)_4P^+X^-} + (PhO)_2PX$$

X = Hal; Y = Z = OAlk, OAr, NR_2, Hal

We found, that the chlorination ($0^{o}C$) of the compounds 1a - 1d did not give the halogene adducts 2 or 3, but the phosphonium salts 6a - 6c instead. 6d exchanged the last chlorine of the cation and gave 6f. Furthermore, the phenyl o-phenylene phosphite 1e reacted with chlorine to two phosphoranes and P^{III} chloride.

$$2\ Z_2PY \ + \ 2\ Cl_2 \longrightarrow Z_2PY_2^{+}\ Z_2PCl_4^{-}$$
$$\underline{1} \qquad\qquad\qquad\qquad \underline{6}$$

	a	b	c	d	e
Z_2	2Cl	2Cl	c-$C_6H_4O_2$	PhO/Cl	o-$C_6H_4O_2$
Y	OPh	NMe_2	NMe_2	OPh	OPh

$$(PhO)_4P^{+}PCl_6^{-}$$
$$\underline{6f}$$

$$\underline{1e} \xrightarrow{Cl_2} Z_2P(OPh)Cl_2 \ + \ Z_2P(OPh)_2Cl \ + \ Z_2PCl$$

Our interpretation of these reactions is summarized in the following four equations:

$$\underline{1} + X_2 \longrightarrow \underline{2} \text{ or } \underline{3} \qquad (1)$$
$$\underline{2} \text{ or } \underline{3} + \underline{1} \longrightarrow Z_2PY_2X \text{ or } Z_2PY_2^{+}X^{-} + Z_2PX \qquad (2)$$
$$Z_2PX + X_2 \longrightarrow Z_2PX_3 \qquad (3)$$
$$Z_2PY_2^{+}X^{-} + Z_2PX_3 \longrightarrow \underline{6} \qquad (4)$$
$$X = Cl$$

This assumption, especially equation (2), was proven by the reaction of stable chlorine adducts 7 and 8 with P^{III}compounds. All reactions proceeded under ligand exchange.

$$\underset{\underline{7}}{catPCl_3} \qquad \underset{\underline{8}}{(PhO)_2P(NMe_2)Cl^{+}Cl^{-}} \qquad cat = o\text{-}C_6H_4O_2$$

$$\underline{7} + P(OPh)_3 \longrightarrow catP(OPh)_3 + PCl_3$$
$$\underline{7} + P(NMe_2)_3 \longrightarrow catP(NMe_2)_2^{+}Cl^{-} + Cl_2PNMe_2$$
$$\underline{7} + catPOPh \longrightarrow cat_2POPh + PCl_3$$
$$\underline{8} + \underset{\underline{9}}{(PhO)_2PNMe_2} \longrightarrow \underset{\underline{10}}{(PhO)_2P(NMe_2)_2^{+}Cl^{-}} + (PhO)_2PCl$$

Furthermore, we tested our assumption by the reaction of two moles of P^{III} compounds with one mole of chlorine, the addition of equations (1) and (2). In all cases we found the products expected[2,3].

$$2\ \underline{1b} + Cl_2 \longrightarrow (Me_2N)_2PCl_2{}^+Cl^- + PCl_3$$

$$2\ \underline{1c} + Cl_2 \longrightarrow catP(NMe_2)_2{}^+Cl^- + catPCl$$

$$2\ \underline{9} + Cl_2 \longrightarrow \underline{10} + (PhO)_2PCl$$

$$4\ \underline{1a} + Cl_2 \longrightarrow (PhO)_4P^+Cl^- + 3\ PCl_3 \qquad (5)$$

In contrast to $\underline{1b}$ or $\underline{1c}$, $\underline{9}$ reacted with chlorine (1:1) to $\underline{8}$. In accordance with $\underline{1b}$ or $\underline{1c}$ however, $\underline{9}$ reacted with chlorine (2:1) to $\underline{10}$. With a quarter of chlorine $\underline{1a}$ gave the salt $\underline{5}$ (X=Cl; Eq.(5)). It is a multiple ligand exchange reaction.

We also studied the chlorination of $\underline{1}$ with antimony pentachloride and obtained the chlorophosphonium hexachloroantimonates $\underline{11}$ in good yields[4].

$$\underset{\underline{1}}{Z_2PY} + 2\ SbCl_5 \longrightarrow \underset{\underline{11}}{Z_2PYCl^+SbCl_6{}^-} + SbCl_3$$

$$Z = Y = OPh,\ NMe_2,\ Hal,\ o\text{-}C_6H_4O_2$$

We did not observe a ligand exchange, probably the rate of the formation of hexachloroantimonate is much faster than the rate of the ligand exchange reaction.

$$\underline{1} \xrightarrow[-SbCl_3]{SbCl_5} \underline{3} \qquad \begin{array}{l} \overset{\underline{1}}{\nrightarrow}\ Z_2PY_2{}^+X^- \\ \xrightarrow[SbCl_5]{}\ \underline{11} \end{array}$$

$X = Cl$

REFERENCES

1. Halogenation of derivatives of phosphorous acid (review), J. Gloede, Z. Chem., 28, 352 (1988).
2. J. Gloede and R. Waschke, Z. anorg. allg. Chem., 545, 184 (1987).
3. J. Gloede, H. Groß and R. Waschke, Phosphorus and Sulfur, 34, 15 (1987).
4. The reaction with 1a and 1b was described by J. K. Ruff, Inorg. Chem., 2, 813 (1963).