Oxidative fluorination of substituted phosphines with sulphur chloride pentafluoride

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ALKYL- and aryl-fluorophosphoranes are conveniently prepared by oxidative fluorination of the appropriate chlorophosphine with arsenic or antimony trifluorides or sulphur tetrafluoride[1]. We wish to report that chlorophosphines are oxidatively fluorinated to fluorophosphoranes by sulphur chloride pentafluoride in an exothermic reaction carried out under very mild conditions (Table 1).

Chlorophosphine	Reaction conditions	Identified products
PhPCl ₂	1 : 1 mole ratio −30°C	PhPF ₄ * SCl ₂ †
Ph₂PCI	1 : 1 mole ratio -30°C	$Ph_2PF_3^* SCl_2^\dagger$
		[SF ₄ † formed with excess of Ph ₂ PCl]
MePCl ₂	l : 1 mole ratio -60°C	$MePF_4^* SCl_2^\dagger$

Table 1. Reactions of SF₅Cl with chlorophosphines

*By i.r. and ¹H and ¹⁹F N.M.R. spectroscopy. E. L. Muetterties,

W. Mahler, and R. Schmutzler, inorg. Chem. 2, 613 (1963).

†By i.r. spectroscopy by comparison with the spectra of authentic samples.

EXPERIMENTAL

Volatile materials were handled in a conventional vacuum system and involatile materials in a dry box. I.r. spectra were recorded using a Perkin-Elmer 457 spectrometer and NMR spectra using a Perkin-Elmer R.10 instrument at 60 MHz (¹H) or 56.4 MHz (¹⁹F). Sulphur chloride pentafluoride (a gift from I.C.1. Ltd., Mond Division) was dried over P_2O_5 and purified by vacuum distillation. Its i.r. spectrum indicated the presence of some SF₆ but no SF₄. Methyldichlorophosphine (a gift from Albright and Wilson Ltd.) and other substituted phosphines (commercial samples) were redistilled before use and dried over Na or molecular sieves as appropriate.

Reactions were performed by allowing mixtures of reactants contained in glass or metal ampoules to warm from -196° C until reaction occurred, the products being separated by fractional distillation. In addition to the reactions summarised in the Table 1, the behaviour of SF₅Cl towards trimethyl phosphite and tris(dimethylamino)phosphine was investigated. In both cases vigourous reaction occurred below 20°C to give SF₄ (identified by i.r. spectroscopy), but the phosphorous products were not identified.

DISCUSSION

Sulphur chloride pentafluoride has previously been shown to behave as an oxidative fluorinating agent towards tetrakis(dimethylamino)diboron[2] and transition metal carbonyl derivatives and their complexes[3, 4]. The present reactions occur at low temperatures, indicating low activation energies,

- 1. For a review of synthetic routes to fluorophosphoranes see R. Schmutzler, *Halogen Chemistry* 2, 31 (1967).
- 2. A. G. Massey and N. R. Thompson, J. inorg. nucl. Chem. 25, 175 (1963).
- 3. A. G. Massey and K. J. Packer, J. chem. Soc. 5554 (1961).
- 4. R. D. W. Kemmitt, R. D. Peacock and J. Stocks, Chem. Comm. 554 (1969).

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Notes

and in contrast to sulphur hexafluoride, the chloride pentafluoride is quite reactive. Sulphur dichloride and traces of sulphur and chlorine were isolated in addition to the fluorophosphoranes, and oxidation of phosphorus(III) to phosphorus(V) is probably by direct reaction with sulphur chloride pentafluoride but any chlorine liberated could well take part in the oxidation step.

The reactions between sulphur chloride pentafluoride and the halogen free derivatives, tris-(dimethylamino)phosphine and trimethylphosphite, give products that were not identified but which, from their i.r. and NMR spectra, contain phosphorus(V)-fluorine groups. Sulphur tetrafluoride is also a product and it appears that reduction of sulphur(VI) does not proceed to sulphur(II) or sulphur-(0) in contrast to the reactions with chlorophosphines.

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Metal-halogen stretching frequencies of transition metal complexes*

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THE INFRA-RED (i.r.) active ν (M-Cl) of ten complexes of Mn⁺³, Co⁺², Cr⁺³, Zn⁺², Cd⁺² and Fe⁺³ with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) can be used to diagnose the oxidation state and coordination number of the metal ions in complexes.

EXPERIMENTAL

The Mn⁺³ complexes were prepared as reported[1]. Other complexes were prepared by mixing concentrated solutions of respective metal chlorides in 10N hydrochloric acid (the strength of the acid was, however, 5N for the Fe⁺³ complexes) and ligands in acetone in equimolar ratio, except in the case of Cr⁺³ and Fe⁺³ complexes where the molar ratios were 1:3 and 1:2 respectively. The precipitates obtained after frequent stirring of the resultant solutions, were filtered and dried under vacuum in a desiccator for 48 hr. Elemental microanalyses were carried out in duplicate for carbon, hydrogen, nitrogen, chlorine and in some cases metals by the Alfred Bernhardt Micro-analytical laboratory, West Germany. The results of the analyses were within ±2 per cent for carbon and chlorine and within ±5 per cent for others of the theoretical values[2]. The i.r. spectra in nujol mull were recorded on a Beckman I.R. 9 in the 700-200 cm⁻¹ region. Melting points (only for new complexes) and magnetic moments for Fe⁺³ complexes were also determined.

RESULTS AND DISCUSSION

The assignment of ν (M-Cl) in the spectra of the complexes are based on published results on related complexes [2, 3]. The metal-chlorine bands are generally strong and broad and can be identified easily in the spectra of the complexes.

*This work is a part of Ph.D. thesis submitted by the author to the Graduate School, University of Hawaii, Honolulu, U.S.A. in 1967.

- 1. H. A. Goodwin and R. A. Sylva, Aust. J. Chem. 18, 1743 (1965).
- 2. S. N. Ghosh, Ph.D. Thesis, University of Hawaii, Honolulu, 1968.
- 3. R. J. H. Clark, Record Chem. Progr. 26, 269 (1965).

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