Salts of the Dimethyltetrafluorophospate, $[Me_2PF_4]^-$, Anion

By W. STADELMANN, O. STELZER, and R. SCHMUTZLER*

(*Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstrasse* 4, 33 *Braunschweig, Germany*)

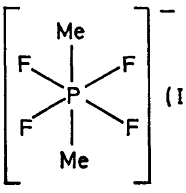
Summary Stable phosphiniminophosphonium salts of the hitherto unknown dimethyltetrafluorophosphate anion, $[Me_2P(N{=}PR_3)_2]^+[Me_2PF_4]^-$, have been prepared in the reaction of dimethyltrifluorophosphorane with several *N*-trimethylsilylphosphine imines.

THE spontaneous rearrangement of certain dialkylaminotrifluorophosphoranes, $R^1PF_3NR^2_2$, with formation of the ionic products, $[R^1PF(NR^2_2)_2][RPF_5]$, has been established *in a num*ber of instances.[1–3] The fluoro-anions, $[RPF_5]^-$ ($R = Me, Me_2N, Ph$) and $[R^1R^2PF_4]^-$ ($R^1 = R^2 = Ph$ or $R^1 = Me$, $R^2 = Ph$), could also be obtained by the addition of caesium fluoride to the appropriate fluorophosphoranes, RPF_4 and $R^1R^2PF_3$,[4] or by the aminolysis of RPF_4 (in the case of $[RPF_5]^-$).[5] Formation of the anion $[Me_2PF_4]^-$ has not been observed, however, either in the aminolysis of Me_2PF_3 or by addition of caesium fluoride to Me_2PF_3.[4] In the course of a systematic study of the cleavage reactions of silicon–nitrogen compounds with fluorophosphoranes we have now investigated the reaction of Me_2PF_3 with *N*-trimethylsilylphosphine imines. The reactions proceeded readily, with release of 1 mole of trimethylfluorosilane per mole of $Me_3SiN{=}PR_3$, in accord with equation (1). We

$$2\,Me_3SiN{=}PR_3 + 2\,Me_2PF_3 \rightarrow 2\,Me_3SiF + [Me_2P(N{=}PR_3)_2]^+[Me_2PF_4]^- \qquad (1)$$

have thus obtained three salts containing the dimethyltetrafluorophosphate ion, sufficiently stabilized to be isolated by the following cations $[Me_2P(N{=}PR_3)_2]^+$ ($R_3 = Me_3$, Me_2Ph, or Pr^i_3). There was no evidence for the formation of a fluorophosphorane, $Me_2PF_2N{=}PR_3$, that might be expected.

The formation of salts of the dimethyltetrafluorophosphate anion has been established from ^{19}F and ^1H n.m.r. evidence (spectra were recorded on solutions in dichloromethane). ^{19}F: doublet of septets, with $^1J_{P-F}$ 856; $^3J_{F-H}$ 10 Hz; δ_F (internal CCl_3F reference) $+20{\cdot}9$ p.p.m. ^1H: doublet of quintets, with $^2J_{P-H}$ 20·5 Hz; $^3J_{F-H}$ 9·5 Hz; δ_H (internal CH_2Cl_2 reference) $+4{\cdot}23$ p.p.m. These data are consistent with the octahedral structure (I) but the possibility is not excluded that the observed spectrum is the result of a positional exchange process within the fluoro-anion. Such equilibration of fluorine environments has been observed in the octahedral fluorotitanate complexes, $[F_4Ti{\cdot}2B]$.[6] Because of the limited solubility of our dimethyltetrafluorophosphate salts at low temperature we have been unable, so far, to check the temperature dependence of the ^{19}F n.m.r. spectra.



(I)

Attempts to obtain ^{31}P n.m.r. spectra of the dimethyltetrafluorophosphates have been unsuccessful, presumably due to the limited solubility of the salts and the expected high multiplicity which will give rise to weak signals.

The same type of reaction as with dimethyltrifluorophosphorane could also be realized between *N*-trimethylsilylphosphine imines and tetrafluorophosphoranes. In this case, a series of phosphiniminoorganophosphonium salts of the corresponding pentafluorophosphate anions was obtained and fully characterized by analysis and ^1H, ^{19}F, and ^{31}P n.m.r. spectroscopy. Either reaction (2) or (3) was observed.

$$2\,Me_3SiN{=}PR^1_3 + 2\,R^2PF_4 \rightarrow 2\,Me_3SiF + [R^2(F)P(N{=}PR^1_3)_2]^+[R^2PF_5]^- \qquad (2)$$

$$3\,Me_3SiN{=}PR_3 + 2\,RPF_4 \rightarrow 3\,Me_3SiF + [RP(N{=}PR_3)_3]^+[RPF_5]^- \qquad (3)$$

The observed stability of the phosphinimino-phosphonium cations and their ability to stabilize anions such as $[Me_2PF_4]^-$ are probably related to the extensive delocalization of the positive charge possible in these cations.

(*Received, July* 16*th*, 1971; *Com.* 1231.)

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