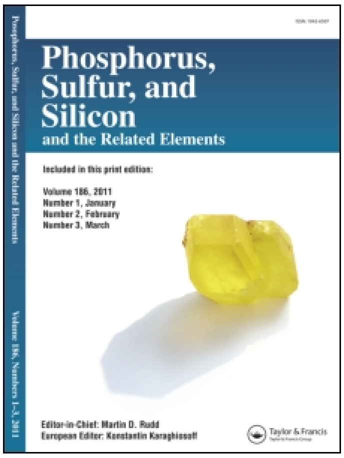

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SYNTHESIS AND NMR INVESTIGATION OF PHOSPHINEIMINOPHOSPHONIUM ORGANOFLUOROPHOSPHATE SALTS

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SYNTHESIS AND NMR INVESTIGATION OF PHOSPHINEIMINOPHOSPHONIUM ORGANOFLUOROPHOSPHATE SALTS

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The reaction of *N*-trimethylsilylphosphineimines, $Me_3SiN{=}PR^1R^2R^3$ (R^1, R^2, and R^3 = hydrocarbon or NMe_2 group) with the fluorophosphoranes, $MePF_4$, $PhPF_4$, and Me_2PF_3 has furnished fluorophosphineiminophosphonium organofluorophosphates, involving the anions, $[RPF_5]^-$ (R = Me, Ph) or $[Me_2PF_4]^-$, respectively. The characterization of these salts by ^1H, ^{19}F, and ^{31}P n.m.r. spectroscopy is described. The n.m.r. parameters are discussed in terms of electronic structure. The $^2J_{PP}$ coupling constant was determined to be positive by triple resonance experiments on two of the compounds.

INTRODUCTION AND DISCUSSION OF SYNTHESES

It has been demonstrated in numerous examples that the cleavage of the nitrogen-$SiMe_3$ linkage by fluorophosphoranes is a useful means of establishing a phosphorus–nitrogen bond, the only other product being the volatile and chemically rather inert fluorosilane, Me_3SiF (cf., e.g. References 1–4, and other references quoted therein). During the reaction the co-ordination number 5 of phosphorus is usually retained although there are exceptions, such as the unusual reaction of *N*-trimethylsilyl-phosphine imines of the type $Me_3SiN{=}PR^1R^2R^3$ with tetra- and trifluorophosphoranes in which not the expected phosphineimino-substituted fluorophosphoranes with λ^5 phosphorus, but their ionic isomers, involving λ^4 (cationic) and λ^6 (anionic) phosphorus are formed,[5,6] i.e.

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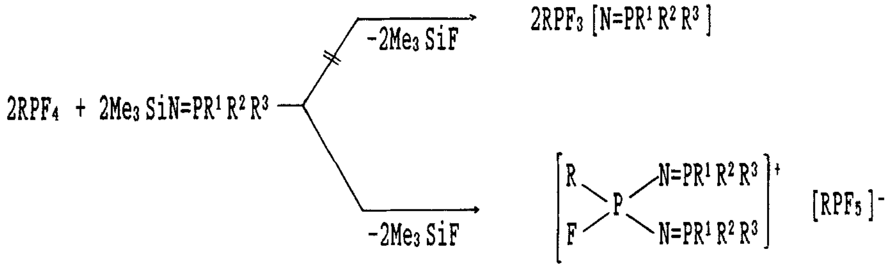

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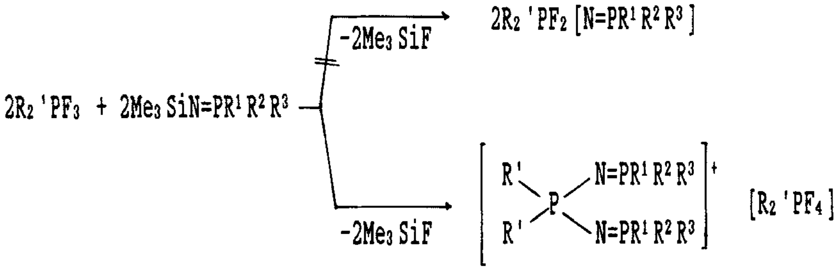
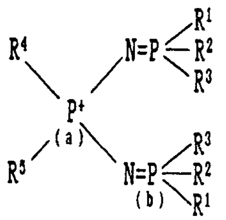


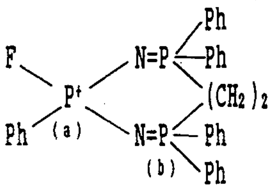
The groups R^1, R^2, and R^3 at phosphorus may be either the same or different; if some or all of these groups are NMe_2 no change in the course of this reaction is observed. If may further be noted that the type of product obtained depends on the stoichiometric ratio in which fluorophosphorane and silylated phosphine imine are allowed to react, and the following has been observed, for example, for the reaction of RPF_4 (R = Me, Ph) with $Me_3SiN{=}PMe_2Ph^5$,

The reaction is noteworthy, not only because it furnishes the novel phosphinimine-substituted phosphonium cations but also because it provides easy access to derivatives of the hexafluorophosphate ion of type $[R_nPF_{6-n}]^-$ (n = 1, 2), especially the novel $[Me_2PF_4]^-$.

We are now describing work on a number of systems (Table I), including an extension of the synthetic work, with discussion of further N-trimethylsilylphosphine imines whose reactions with fluorophosphoranes have not previously been studied, and which have furnished new and/or unusual salts (compounds **II/III**, **V**, **VI**, and **VII**—see Table I and structures **A** and **B**). Especially noteworthy here is the bis(N-trimethylsilyl)phosphineimine,



A



B

TABLE I

The phosphineiminophosphonium compounds discussed (see Structure **A**)

Cation	R^4	R^5	R^1	R^2	R^3	Anion
I[a]	Me	Me	Me	Me	Me	$[Me_2PF_4]^-$
II[b]	F	Me	Me	Me	Me	$[MePF_5]^-$
III[b]	$N{=}PMe_3$	Me	Me	Me	Me	$[MePF_5]^-$
IV[c]	F	Me	Pr^i	Pr^i	Pr^i	$[MePF_5]^-$
V	F	Ph	NMe_2	NMe_2	NMe_2	$[PhPF_5]^-$[d]
VI[e]	F	Ph	Ph	Ph	$—CH_2—$	$[PhPF_5]^-$
VII[f]	$N{=}PMe_2Ph$	Ph	Me	Me	Ph	$[PhPF_5]^-$
VIII	F	Ph	Me	NMe_2	NMe_2	$[PhPF_5]^-$
IX[g]	Me	Me	Pr^i	Pr^i	Pr^i	$[Me_2PF_4]^-$
X[g]	Me	Me	Me	Me	Ph	$[Me_2PF_4]^-$
XI[g]	F	Ph	Pr^i	Pr^i	Pr^i	$[PhPF_5]^-$

[a] Compound **I** of Reference 5.

[b] **II** and **III** were present in the same sample with a common anion.

[c] Compound **VI** of Reference 5.

[d] The sample used for some measurements had undergone degradation of the anion to give $PhP(O)F_2$, HF and F^-.

[e] **VI** had the cyclic structure B. There was some degradation of the anion to give $PhP(O)F_2$.

[f] Compound **V** of Reference 5.

[g] Reference 5, compound not studied in the present work.

$Me_3SiN{=}P(Ph_2){—}CH_2CH_2{—}P(Ph)_2{=}NSiMe_3$, and its reaction with phenyltetrafluorophosphorane to give the unusual fluorophosphonium phenylpentafluorophosphate, **VI**. The precursor, ethylenebis-(diphenyl)phosphine, has been described previously;[7] its reaction with two equivalents of trimethylsilyl azide was conducted according to published methods.[8] The synthesis of the new *N*-trimethylsilylphosphineimine, $Me_3SiN{=}P(Me)(NMe_2)_2$ was also accomplished, using the reaction of the phosphine, $P(Me)(NMe_2)_2$ with trimethylsilyl azide.[5,7,8] As in the case of the trimethylsilyl azide reaction with $P(NMe_2)_3$,[9] a significant side reaction has been observed for the system $P(Me)(NMe_2)_2/Me_3SiN_3$. The overall reaction may be described by the following equation:

$$3P(Me)(NMe_2)_2 + 3Me_3SiN_3 \rightarrow 3N_2 + Me_3SiN{=}P(Me)(NMe_2)_2$$
$$+ Me_2NSiMe_3 + (Me)(NMe_2)_2P{=}N{—}P(Me)(NMe_2){=}NSiMe_3$$

The products could be separated by fractional distillation. Both the expected "normal" Staudinger product, and the by-product were characterized by elemental analysis, and by n.m.r. spectroscopy. The reaction of tris(diethylamino)phosphine with trimethylsilylazide proceeds in a notably different fashion from that of the related $(Me_2N)_3P$[9] in that the sole product is the Staudinger-type compound $Me_3SiN{=}P(NEt_2)_3$, no side reactions being observed. This preparation constitutes a significant improvement over the literature procedure of Flindt *et al.*[10]

The characterization of our phosphineimine-substituted fluorophosphates rests largely on their n.m.r. spectra,[5,6] and it was a main objective of the present work to study the n.m.r. of the previously reported compounds,[5,6] **I**, **IV**, **VI**, **VII**, and **IX–XI** in detail. An n.m.r. investigation of compounds **II**/**III**, **V**, and **VII** is also described. Some n.m.r. data have been reported previously.[5] However, proton decoupling was not used, (P, P) coupling constants were not measured, and some of the phosphorus chemical shifts were not obtained. The results from phosphorus, fluorine and proton n.m.r. spectra of eight such cations are reported here, including data obtained from $^{31}P\text{-}\{^1H\}$ and $^{19}F\text{-}\{^1H\}$ double resonance. There is particular interest in the variation of phosphorus chemical shifts and (P, P) coupling constants with the substituent R.

EXPERIMENTAL: SYNTHETIC WORK

All experiments were conducted with rigorous exclusion of moisture in an atmosphere of dry nitrogen. All glass apparatus had been carefully baked out in vacuo. No attempt was made, normally, to quantitatively determine the amount of trimethylfluorosilane formed in the reactions between *N*-trimethylsilylphosphine imines and fluorophosphoranes.

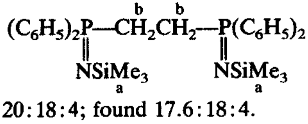
Starting materials. The fluorophosphoranes, $MePF_4$, Me_2PF_3, and $PhPF_4$ were synthesized according to literature procedures.[11–13] Published procedures were also employed in the synthesis of *N*-trimethylsilylphosphine imines, $Me_3SiN{=}PR^1R^2R^3$, from the appropriate phosphines and trimethylsilyl azide;[7,14] e.g. for $Me_3SiN{=}PMe_3$,[5] $Me_3SiN{=}P(NMe_2)_3$[9] and $Me_3SiN{=}P(Ph_2)CH_2CH_2(Ph_2)P{=}NSiMe_3$.[9a] The dimethylamino-substituted compound, $Me_3SiN{=}PMe(NMe_2)_2$, is new.

N-Trimethylsilyl-methylbis(dimethylamino)phosphine imine. Trimethylsilyl azide[14] (27.3 g; 0.24 mole) was placed in a two-necked flask, fitted with a reflux condenser and a pressure-equalizing dropping funnel. Methylbis(dimethylamino)phosphine (3.18 g; 0.24 mole) was added dropwise with magnetic stirring over 2 h at 100°. The addition was accompanied by vigorous evolution of nitrogen. Stirring at 100° was continued for 16 h. All volatile products were then removed at room temperature in vacuo (0.13 mbar), and were condensed in a trap at −196°C. The product was found to consist, largely, of Me_2NSiMe_3 (^1H n.m.r.). The less-volatile products were fractionally distilled in vacuo:

(i) $\overset{a}{Me_3}SiN{=}P\overset{b}{Me}(N\overset{c}{Me_2})_2$, 24 g (45%), b.p. 40°C (0.13 mbar). Anal. $C_8H_{24}N_3PSi$ (221.36), found: C, 43.32; H, 10.99; P, 13.19; calc.: C, 43.41; H, 10.93; P, 13.99. δ_P 17.5; ^1H n.m.r.: δ_a 0.19 (s); δ_b 1.39 (d); (J_{PH} 13.7 Hz); δ_c 2.54 (d; J_{PH} 10.1 Hz). Integration, calc. 9:3:12 (=3:1:4), found 3:1:3.8.

(ii) $(\overset{a}{Me})(\overset{c}{Me_2}N)_2\overset{A}{P}{=}N{-}\overset{B}{P}(N\overset{d}{Me_2})(\overset{b}{Me}){=}N{-}Si\overset{e}{Me_3}$, 8.0 g (0.0246 mole), b.p. 85°C (0.13 mbar) $C_{11}H_{33}N_5P_2Si$ (325.45), found: C, 39.72; H, 9.95; P, 18.53; calc.: C, 40.60; H, 10.22; P, 19.03. δ_P (A) 30.4; δ_P (B) 6.7, J_{PP} 21 Hz. ^1H n.m.r.: δ_a 1.60 (J_{PH} 14.3 Hz); δ_b 1.22 ($^2J_{PH}$ 14.3 Hz, $^4J_{PH}$ 1.4); δ_c 2.58 (J_{PH} 10.1 Hz); δ_d 2.54 (J_{PH} 14.3 Hz); δ_e 0.15. Integration, calc. 6:18:9 (=2:6:3), found 2:6:3.1. It would appear that the latter compound is slightly contaminated by the former.

Bis-N(trimethylsilyl)-ethylenebis(diphenylphosphine)imine (cf. Reference 9a). A mixture of 10.0 g (0.025 mole) of ethylene-bis(diphenyl-phosphine)[7] and 5.8 g (0.05 mole) of trimethylsilyl azide was stirred for 1 h at 100°C. The reaction mixture solidified on cooling to room temperature, and the product was obtained in analytical purity (13.9 g; 97%). $C_{32}H_{42}N_2P_2Si_2$ (572.80), found: C, 67.0; H, 7.4; N, 4.3; P, 10.7; calc.: C, 67.1; H, 7.4; N, 4.3; P, 10.7. $\delta_P + 6.22$. ^1H n.m.r. spectrum



$$(C_6H_5)_2\underset{\underset{NSi\underset{a}{Me_3}}{\|}}{P}{-}\overset{b}{CH_2}\overset{b}{CH_2}{-}\underset{\underset{NSi\underset{a}{Me_3}}{\|}}{P}(C_6H_5)_2$$

δ_a (CH_2Cl_2) 5.1; $\delta_b + 2.8$ (N_{PH} 3.0). Integration, $H_{arom}:H_a:H_b =$ 20:18:4; found 17.6:18:4.

Preparation of phosphineimino-phosphonium fluorophosphates. The synthesis of compounds **I**, **IV**, **VII**, and **IX–XI** has previously been described.[5] The remaining compounds have been synthesized either by Bartsch[15] or by Stadelmann:[16]

Reaction of N(trimethylsilyl)trimethylphosphine imine with methyltetrafluorophosphorane (synthesis of a mixture of II and III). The *N*-trimethylsilyl-phosphine imine (12.9 g; 0.08 mole) was placed in a three-necked flask, fitted with a dry-ice cooled condenser and an internal thermometer. Methyltetra fluorophosphorane (4.9 g; 0.04 mole) was added through a condenser, held at −10°C, with magnetic stirring. The reaction commenced instantaneously, and formation of a white precipitate was observed, which disappeared again after about half of the fluorophosphorane had been added. Towards the end of the addition of the fluorophosphorane, precipitation of the crystalline product was seen. This was filtered, washed with *n*-pentane, and dried in vacuo.

The n.m.r. data (Tables II and III) indicated that a mixture of **II** and **III** in a ratio 1:1.4 had been formed.

Reaction of N-trimethylsilyltris(dimethylaminophosphine)imine with phenyltetrafluorophosphorane (synthesis of **V***).* A mixture of 5.28 g (0.021 mole) of the phosphine imine and 3.92 g (0.021 mole) of phenyltetrafluorophosphorane in 20 cm^3 of methylcyclohexane was refluxed for 24 h. After cooling to room temperature, the supernatant liquid was decanted from the product. The latter was washed with three 20 cm^3 portions of *n*-pentane. After pumping in vacuo (1 mbar/20°C) **V** was obtained as a viscous oil which did not crystallize. The yield was 6.25 g (86%). $C_{24}H_{46}F_6N_8P_4$ (684.57), found: C, 42.2; H, 6.1; F, 16.4; N, 16.5; P, 18.5. calc.: C, 42.1; H, 6.7; F, 16.6; N, 16.3; P, 18.1.

Reaction of bis-N(trimethylsilyl)ethylenebis(diphenylphosphine)-imine with phenyltetrafluorophosphorane (synthesis of **VI***).* To a solution of the phosphine imine (11.2 g; 0.02 mole) in 50 cm^3 of *o*-xylene was added 7.4 g (0.04 mole) of phenyltetrafluorophosphorane with magnetic stirring at 90°C. After stirring had been continued for 1 h the reaction mixture was allowed to cool to room temperature. The crystalline product, **VI**, was collected by filtration, and was pumped dry in vacuo. The product was obtained in analytical purity (13.9 g; 92%). $C_{38}H_{34}F_6N_2P_4$ (758.63) found: C, 60.2; H, 4.7; F, 14.7; N, 3.6; P, 16.0; calc.: C, 60.3; H, 4.5; F, 15.1; N, 3.7; P, 16.4.

Reaction of N-trimethylsilyl-methylbis(dimethylamino)phosphine imine with phenyltetrafluorophosphorane (synthesis of **VIII***).* As described for the preceding experiment, a mixture of the phosphine imine (4.64 g; 0.021 mole) and phenyltetrafluorophosphorane (3.90 g; 0.021 mole) in 20 cm^3 of methylcyclohexane was refluxed for 24 h at 110°C. Upon removal of liquid volatile products, a viscous oil was left which did not crystallize. The material was pumped dry in vacuo. $C_{22}H_{40}F_6N_6P_4$ (626.49) found: C, 42.31; H, 6.56; F, 18.40; calc.: C, 42.18; H, 6.44; F, 18.20.

Reaction of tris(diethylamino)phosphine with trimethylsilylazide (preparation of N-trimethylsilyltris(diethyl)aminophosphine imine[16]*).* As described for the reaction of $(Me_2N)_2PMe$ with Me_3SiN_3,[9] 42.2 g (0.37 mole) of Me_3SiN_3 was placed in a two-necked flask, fitted with a pressure-equalizing dropping funnel, and a reflux condenser, topped by a drying tube. To the azide, heated to 100°C 87.8 g (0.36 mole) of $(Et_2N)_3P$ (0.36 mole) was added dropwise during 2 h, with magnetic stirring. Vigorous evolution of nitrogen was noted and the reaction mixture was stirred overnight at 100°C. Distillation produced the *N*-trimethylsilylphosphine imine, of b.p. 95°C (0.13 mbar); yield 92.4 g (75%). Anal. $C_{15}H_{39}N_4PSi$ (334.56); found: C, 53.85; H, 11.86; P, 9.07; calc.: C, 53.85; H, 11.75; P, 9.26. ^1H n.m.r. spectrum: $\delta_H(CH_3{-}Si)$ 0.5; $\delta_H(CH_3)$ 1.10; J_{HH} 7.2 Hz; $\delta_H(CH_2)$ 3.06; J_{HP} 12.7 Hz. Integration, calc. for $(CH_3)_3SiN{=}P[N(C_2H_5)_2]_3$: 9:12:18 = 3:4:6; found: 3:4.2:5.8. ^{31}P n.m.r.: δ_P 8.45.

EXPERIMENTAL: NUCLEAR MAGNETIC RESONANCE DETAILS

The n.m.r. data reported above were obtained using a JEOL 60HL spectrometer operating at 60.0, 56.4 and 24.3 MHz for ^1H, ^{19}F and ^{31}P respectively. The accurate n.m.r. spectra reported in Tables II and III were recorded at ambient probe temperature (35–37°C) in the CW or FT mode using a Varian XL100-15 spectrometer for phosphorus (40.5 MHz), a Varian HA100 (94.1 MHz) or a JEOL FX100 (93.7 MHz) spectrometer for fluorine, and the HA100 for proton (99.9 MHz) resonances. The phosphorus spectra were proton noise-decoupled, and multiscan or multipulse averaging was used where necessary to improve the signal-to-noise ratio. In some cases proton-coupled spectra were recorded to obtain phosphorus-proton coupling constants in order to clarify analysis of the proton spectra. Proton decoupling of some of the fluorine HA100 spectra was carried out using a Schlumberger frequency generator and a double-tuned matching network described elsewhere.[17] Proton-noise-decoupling was used for the FX100 fluorine spectra.

Since all the cations gave first-order spectra, with only small deviations for **V**, the coupling constants and chemical shifts were measured directly. The phosphorus chemical shifts were calculated by measuring the frequency of the relevant signal relative to the deuterium frequency of the lock

TABLE II

Data obtained for the phosphineiminophosphonium cations from ^{31}P or ^{19}F spectra[a]

	$\delta(P_a)$ (ppm)	$\delta(P_b)$ (ppm)	$^2J_{P_aP_b}$ (Hz)	$\delta(F)$ (ppm)	$^1J^b_{P_aF}$ (Hz)	$^3J^c_{P_bF}$ (Hz)
I	22.24	22.28	3.0	—	—	—
II	27.30	25.99	+4.3	−48.28	−964[b]	2.0[c]
III	13.62	18.11	11.5	—	—	—
IV	14.41	44.60	+9.7	−41.15	−955[b]	6.6[c]
V	−18.8	22.2	51.0	−54.72	−947[b]	~0
VI	22.45	25.56	10.0	−42.56	−964[b]	3.5[c]
VII	5.57	14.31	6.4	—	—	—
VIII	7.7	33.1	35.4	−56.06	−950[b]	~10
IX	5.8	38.9	—	—	—	—
X	20.7	16.3	—	—	—	—
XI	3.3	45.3	—	−51.2	−961[b]	—

[a] The chemical shifts are reported to ±0.05 ppm, and J_{PP} to ±0.5 Hz. The signs of coupling constants are only given where assumed ($^1J_{PF}$) or measured (two cases of $^2J_{PP}$).

[b] From ^{19}F spectra; ±1 Hz.

[c] From ^{19}F spectra; ±0.1 Hz.

signal and referencing this to the Ξ-value[18] for 85% orthophosphoric acid, 40480740 Hz. Fluorine and proton chemical shifts were measured from internal CCl_3F and TMS, respectively.

The relative signs of $^1J_{PF}$ and $^2J_{PP}$ were determined for **II** and **IV**, which showed AM_2X spectra when proton decoupled. The M region (P_b) was observed whilst the high (or low) frequency moiety of the fluorine spectrum (separated by $^1J_{PF}$) was irradiated. It was found that the low (or high)

TABLE III

Proton data[a,b] obtained for the phosphineimino-phosphonium cations

	$\delta(H_a)$ (ppm)	$\delta(H_b)$ (ppm)	$\lvert^2J_{P_aH}\rvert$ (Hz)	$\lvert^2J_{P_bH}\rvert$ (Hz)	$\lvert^4J_{P_aH}\rvert$ (Hz)	$\lvert^4J_{P_bH}\rvert$[c] (Hz)	$\lvert^3J_{H_aF}\rvert$ (Hz)
I	1.54	1.38	13.6	13.2	0.2	0.7	—
II	1.66	1.71	17.2	13.8	0.8	0.5	6.0
III	1.42	1.36	13.2	13.3	—	—	—
IV	1.77	2.94[d] 1.29[e]	17.5	10.8[d] 15.9[e]	—	—	5.7[f]
V	—	2.42	—	10.0[g]	—	—	—
VI	not recorded						
VII	—	1.71	—	13.1	—	—	—
VIII	not recorded						
IX	h	h	13	10.5[d] 15.5[e]	—	—	—
X	h	h	13.6	13.2	0.8	—	—
XI	—	h	—	10.5[d] 16[e]	—	—	—

[a] Excluding phenyl protons.

[b] Chemical shifts are given to ±0.01 ppm, coupling constants to ±0.1 Hz.

[c] To protons of groups attached to P_b.

[d] Involving the methine proton of the isopropyl groups. In the case of compounds **IV** and **IX** there are errors in this parameter in Reference 5.

[e] Refers to ^3J involving the methyl protons of the isopropyl groups.

[f] $^3J(HCPF)$.

[g] $^3J(P_bNCH)$.

[h] Reference 5 gives shifts with respect to the signal for CH_2Cl_2.

frequency doublet of the phosphorus signal caused by $^3J_{PF}$ was affected. Since $^1J_{PF}$ may be assumed to be negative,[19] this result shows $^2J_{PP}$ to be positive. This experiment required triple resonance, since both proton decoupling and fluorine tickling were used. The two irradiating frequencies were supplied by the XL100 spectrometer gyrocode (100 MHz) and a Schlumberger frequency generator (94.1 MHz) respectively. They were mixed in a Varian heteronuclear double resonance matching network normally used for F-{H} experiments.[19] Unfortunately, determination of the sign of $^2J_{PP}$ for **V** and **VIII** was not possible because $^3J_{PF}$ is too small to be resolved.

RESULTS AND DISCUSSION

The parameters obtained from ^{31}P, ^{19}F and ^1H spectra of cations **I–VIII** are given in Tables II and III, together with some data for related systems published earlier.[5] Results for the gegenions are unremarkable and are not reported in detail. With proton decoupling, the phosphorus spectra showed the expected first order patterns—AX_2 for **I**, AX_3 for **III** and **VII** and AMX_2 for **II**, **IV**, **V**, **VI**, and **VIII**. The spectrum for **V** showed slight second-order effects due to the large value of $^2J_{PP}$, and these were taken into account in deriving the data presented in Table II.

The proton spectra of the cations were quite complex, with several overlapping peaks in the methyl region of those samples containing $[MePF_5]^-$ as the anion. However, analysis was possible using data for (P, H) and (F, H) coupling constants obtained from ^{31}P and ^{19}F spectra. The aromatic regions of the proton spectra for **V**, **VI**, **VII** and **VIII** were not analysed due to their complexity, and no proton spectra were recorded for **VI** or **VIII** as in these cases the anion had partially decomposed to $PhP(O)F_2$, HF and F^- via hydrolysis.

Stadelmann *et al.*[5] studied compound **I** and found only one phosphorus signal, which they explained by the delocalisation of the positive charge within the P—(N=P)$_2$ system to give three equivalent phosphorus atoms. The delocalisation was also suggested[6] as a reason for the stability of this type of compound. Complete delocalisation of the charge in the P—N=P bonds would be expected in the symmetrical cations[20,21] $[Cl_3PNPCl_3]^+$ and $[Et_3PNPEt_3]^+$ which show only one phosphorus signal, but for **I** we have observed two distinct signals (for P(a) and P(b)), showing that the distribution of electronic charge is not equal. Our measurements demonstrate the advantages of observing ^{31}P spectra under conditions of proton noise decoupling.

Interpretation of the phosphorus chemical shifts in simple terms of substituent electronegativity is not possible since it is thought that paramagnetic shielding is important, due to the availability of p and d orbital electrons. The fluorine substituent on P(a) in **II**, **IV**, **V**, **VI**, **VII** and **VIII** would be expected to give a large shift to high frequency if diamagnetic shielding was the dominant screening term, as it is for protons.

Steric effects, causing a change in bond angles and hybridisation, could be responsible for the high chemical shifts of P(b) in **IV**, and the substantial variation in $\delta(P_a)$ with substitution at P(b) may be a consequence of delocalisation. No further interpretations of the phosphorus chemical shifts can be made at this stage. The relative importance of the contributions from terms such as hybridisation, bond angles, d_π–p_π bonding, and electronegativity is still undefined.

The P_a–N–P_b coupling constants of six of the cations lie within the same region, 3–12 Hz, the exceptions being **V** where $^2J_{PP}$ is 51 Hz and **VIII** where it is 35.4 Hz. Surprisingly, replacement of a methyl group at the central phosphorus in **I** by fluorine (**II**) only changes $^2J_{PP}$ slightly (if the sign of $^2J_{PP}$ is positive throughout the series), but $^2J_{P_aH}$ is increased by 3.6 Hz. This would indicate that the s orbital character of P(a) is directed towards the methyl group rather than the more electronegative N=PR$_3$ groups, and this is to be expected if Bent's rule[22] is followed (the s orbital character is concentrated in bonds to more electropositive groups). Extended conjugation to further N=P groups, as for **III** and **VII**, does not appear to have a marked effect on $^2J_{PP}$.

The substantial rise in J_{PP} for **V** and **VIII** is remarkable; it may presumably be attributed to the two or three relatively electronegative NMe$_2$ groups attached to each terminal P atom (all the other compounds have only carbon as the bonding element in R^1, R^2 and R^3). It is not clear why the effect of substitution at P_b is so much more pronounced than for changes at the central P atom. However, similar effects of amino substituents on $^2J_{PP}$ have been observed[18] for the related series of cations $[R^1_3P—N—PR^2_3]^+$. The larger value of $|J_{PP}|$ in **V** does seem to be attributable to the electronegativity of the dimethylamino groups on P_b, rather than to steric effects, since the isopropyl substituents in **IV** would alter the coupling constant by a similar amount if steric factors were important. Cyclisation, as for **VI**, does not appear to have any very great effect on $^2J_{PP}$.

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