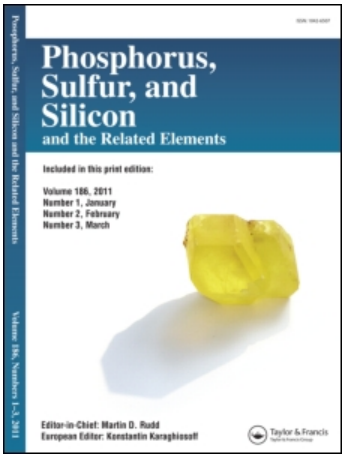

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INTRAMOLECULAR DONOR-ACCEPTOR-INTERACTION IN *N,N,N'*-TRIMETHYL-*N'*-HALOPHOSPHINOETHYLENDIAMINES AND IN *N,N,N'*-TRIMETHYL-*N'*-DIFLUOROARSINOETHYLENDIAMINE

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INTRAMOLECULAR DONOR–ACCEPTOR-INTERACTION IN *N,N,N'*-TRIMETHYL-*N'*-HALOPHOSPHINOETHYLENDIAMINES AND IN *N,N,N'*-TRIMETHYL-*N'*-DIFLUOROARSINOETHYLENDIAMINE

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The reaction of $Me_2NCH_2CH_2N(Me)SiMe_3$ with $MePCl_2$, Bu^tPCl_2, and AsF_3 was found to proceed with formation of the trimethylsilyl halides, Me_3SiX (X = Cl, F), and of the phosphorus-nitrogen (or arsenic-nitrogen)-bonded compounds, $Me_2NCH_2CH_2N(Me)P(Me)Cl$, $Me_2NCH_2CH_2N(Me)P(Bu^t)Cl$, and $Me_2NCH_2CH_2N(Me)AsF_2$, respectively. When PBr_3, Et_2NPCl_2, and Et_2NPBr_2 were allowed to react with $Me_2NCH_2CH_2N(Me)SiMe_3$ the ionic, intramolecularly coordinated compounds, $[Me_2\overline{NCH_2CH_2N(Me)}\overline{P}Br]^+Br^-$, $[Me_2\overline{NCH_2CH_2N(Me)}\overline{P}NEt_2]^+Cl$, and $[Me_2\overline{NCH_2CH_2N(Me)}\overline{P}NET_2]^+ Br^-$ were formed. The high- and low-temperature ^1H- and ^{19}F-n.m.r. spectra of these compounds were investigated. Their interaction with Lewis acids has been shown in the case of some acyclic, covalent phosphorylated derivatives of *N.N.N'*-trimethyl-ethylendiamine to induce intramolecular complexation between phosphorus and the nitrogen of the Me_2N group. The spiro compound, $[(Me_2\overline{NCH_2CH_2N(Me)})_2\overline{P}]^+[BPh_4]^-$, was obtained from the monocyclic product, $[Me_2\overline{NCH_2CH_2N(Me)}\overline{P}Cl]^+ Cl^-$, with $Na[BPh_4]/Me_2NCH_2CH_2N(Me)SiMe_3$.

INTRODUCTION

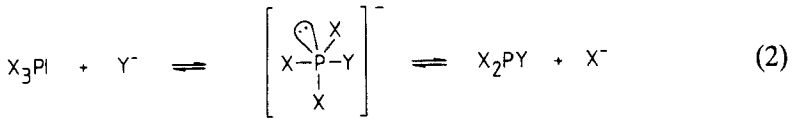
As against the innumerable cases of phosphorus (III) compounds exhibiting donor-properties towards transition-metal[1] or main group acceptors there is a comparatively small number of reports of such compounds functioning as acceptors. Thus some time ago evidence has been presented for the formation of an adduct, $Cl_3P{\cdot}NMe_3$ at low temperatures.[2] At the same time investigations were conducted in order to evaluate the effect of ligands X in PX_3 towards certain Lewis bases. The following sequence, in order of decreasing tendency towards the interaction of PX_3 with nitrogen donor species has been established,[3]

$$Cl_3P > Br_3P \gg Me_3P \qquad (1)$$

Highly electronegative ligands at phosphorus apparently promote the complex formation by decreasing the electron density at phosphorus. Adducts of type $X_3P{\cdot}NR_3$, for example, may be viewed as intermediates in the nucleophilic substitution at phosphorus unless they are to be formulated as ionic compounds, in the sense $[X_2P{\cdot}NR_3]^+ X^-$.

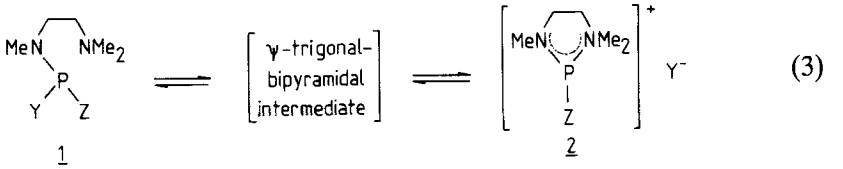
With certain anions, Y^- as nucleophiles, an intermediate with anionic, tetra-coordinated phosphorus may be obtained in a crystalline state from

phosphorus (III) compounds, in the presence of large cations. These species have trigonal-bipyramidal structures whose axial bonds are, in some cases, extremely dissimilar, illustrating the different extent of the displacement of X in PX_3 as X^- through the nucleophile Y^-,[4]



(2)

In compounds of type **1** a possibility has been found to exist of an intramolecular donor–acceptor-interaction, with formation of ionic compounds of type **2**,



1 2 (3)

The compound with Y = Z = Cl could be shown unambiguously to exist as an intramolecular complex of type **2**.[5] No intramolecular interaction at room temperature was apparent in the case Y = Cl and Z = Ph[5] whereas the ^1H n.m.r. spectrum did indicate an interaction upon cooling.[5]

We are now describing attempts at the synthesis of *N.N.N'*-trimethylethylendiamine-substituted halophosphines, and we have extended our studies to include a related *N*-AsF_2 derivative. We were hoping to obtain some information on how the substituents at P(III) or As(III) will affect the intramolecular coordination, in accord with Equation (3). Furthermore, the effect of temperature changes and of the addition of Lewis acids on the equilibrium (3) has been investigated.

RESULTS AND DISCUSSION

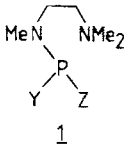
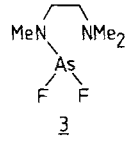
As described in a previous report[5] the reaction of the trimethylsilyl derivative, $Me_2NCH_2CH_2N(Me)SiMe_3$, **5**, with the appropriate dihalophosphines was employed in the synthesis of compounds **1c** and **2f** (Tables I and II). The other compounds in Table I and II were synthesized in the same manner (Equation (4); X and Y = Cl or Br; Z is another ligand, e.g. Me, Br, and NEt_2).

This reaction, proceeding with the loss of trimethylhalosilane, is known to lead to the formation of a covalent phosphorus-nitrogen linkage.[6]

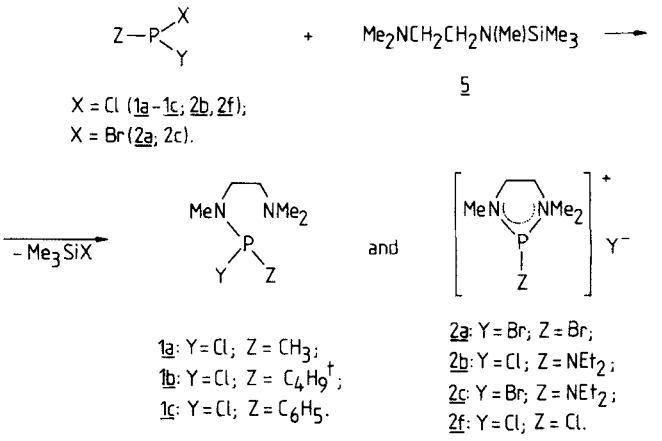
The analogous difluoroarsino derivative, $Me_2NCH_2CH_2N(Me)AsF_2$, **3**, could be synthesized from **5** and arsenic trifluoride in an analogous fashion, as outlined in.[7] Compound **1b** (Table I) was obtained directly in the reaction of *N.N.N'*-trimethylethylenediamine with t-butyldichlorophosphine in the presence of triethylamine. The formation of aminophosphines in the reaction of phosphorus (III) halides with amines has been reported, c.f., e.g.[8]

TABLE I

^1H, ^{19}F, and ^{31}P n.m.r. data of the *N.N.N'*-trimethyl-*N'*-phosphinoethylendiamines, **1a–1c**, and of *N.N.N'*-trimethyl-*N'*-difluoroarsinoethylendiamine, **3**.

		Y	Z	δ(P)	δ(N(CH$_3$)$_2$)	δ(NCH$_3$)	δ(NCH$_2$CH$_2$)	δ(H of ligand Z)	
 1	**1a**	Cl	CH_3	+149.8[a]	218;S	2.70;D; ^3J(HP) = 10.6;	2.4–3.3;M	1.67;D; ^3J(HP) = 11.6	a
	1b	Cl	$C_4H_9^t$	+160.9[c]	2.25;S	2.78;D; ^3J(HP) = 7.0;	2.2–3.4;M;	1.18;D; ^3J(HP) = 15.0	b
	1c[5]	Cl	C_6H_5	+144.5[b]	2.14;S;	2.54;D; ^3J(HP) = 9.7;	2.3;M and 3.1;M;	7.4;M	b
 3	**3**	δ(F)	−70.0; S(broad)[a]		2.35;S;	2.85;S;	2.65;M and 3.21;M		c

^1H: 60 MHz; CH_2CH_2 (δ + 5.35 p.p.m., relative to Si(CH$_3$)$_4$) int. ref.; ^{31}P: 24.3 MHz; H_3PO_4 ext. ref.; ^{19}F: 56.4 MHz; CCl_3F ext. ref.; solvents: dichloromethane;[a] chloroform-d;[b] neat.[c]
S: singlet; D: doublet; M: multiplet.



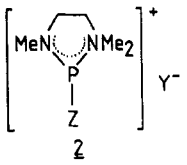
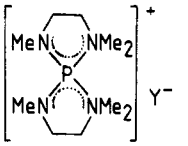
(4)

The compounds obtained at room temperature were present either as liquid, distillable *N.N.N'*-trimethyl-*N'*-phosphinoethylendiamines, **1**, or as ionic phospholidines of type **2** (c.f., Tables I and II). The structures of type **1** or **2** could readily be distinguished by their ^1H n.m.r. spectra. Thus, only a singlet resonance was observed for the protons of the N(CH$_3$)$_2$ group in **1** while the same lines in compounds of type **2** were split into doublets, as a result of ^3J(HP) coupling. The values of ^3J(HP) observed were characteristically smaller than for ^3J(HP) of the NCH$_3$ resonances in the same compounds. The δ_P values for **1a–1c** are similar to those of other amino-phosphines. Thus for $Me_2NP(Me)Cl$ (similar to **1a**) δ_P + 151 has been reported.[9]

The difluoroarsine, **3** was obtained as a distillable, covalent liquid. The ^1H and ^{19}F n.m.r. data (Table I) are comparable to those of the related diethylaminodifluoroarsine, Et_2NAsF_2.[7]

TABLE II

^1H and ^{31}P n.m.r. data of the phospholidinium salts, **2a–2f** and for the spiro compounds, **4a–4c**.

		Y	Z	δ(P)	δ(N(CH$_3$)$_2$)	δ(NH$_3$)	δ(NCH$_2$CH$_2$)	δ(H of ligand Z)	
	**2a**	Br	Br	+173.4[b,+]	2.90;D; ^3J(HP) = 5.0;	3.03;D; ^3J(HP) = 14.0;	3.29;M and 3.92;M		b, +
	2b	Cl	NEt_2	+153.9[c]	2.93;D; ^3J(HP) = 8.2;	2.73;D; ^3J(HP) = 11.5;	3.53;M;	δ(CH$_2$CH$_3$): 1.17;T; ^3J(HH) = 7.0; δ(CH$_2$CH$_3$): 3.21; D(Q); ^3J(HP) = 9.7: ^3J(HH) = 7.0	c
	2c	Br	NEt_2	+154.9[a]	2.86;D; ^3J(HP) = 8.0;	2.76;D; ^3J(HP) = 12.0;	3.50;M;	δ(CH$_2$CH$_3$): 1.12;T; ^3J(HH) = 7.0; δ(CH$_2$CH$_3$): 3.24; D(Q); ^3J(HP) = 10.5; ^3J(HH) = 7.0	c
	2d	[AlCl$_4$] δ(Al):+99.2[c]	CH_3	+179.7[c]	2.97;D; ^3J(HP) = 7.9;	2.87;D; ^3J(HP) = 13.5;	3.55;M;	1.47;D; ^2J(HP) = 7.5	c
	2e	[AlCl$_4$]	C_6H_5	+165.0[a]	2.87;D; ^3J(HP) = 7.6;	3.00;D; ^3J(HP) = 12.6	3.40;M;	7.5;M	b
	2f[5]	Cl	Cl	+160.3[c]	3.30;D; ^3J(HP) = 5.2;	3.09;D; ^3J(HP) = 13.1 2.72;D;	3.86;M		b
	**4a**	Cl		+153.9[a]	2.53;D; ^3J(HP) = 4.0;	^3J(HP) = 12.0;	2.9–3.5;M		c
	4b	Br		+154.9[b]	2.70;D; ^3J(HP) = 4.0;	2.82;D; ^3J(HP) = 9.0;	3.0–3.6;M		b
	4c	[BPh$_4$]		+154.1[c,+]	2.38;D; ^3J(HP) = 3.8;	2.60;D; ^3J(HP) = 7.8;	2.7;M and 3.26; M;	δ([B(C$_6$H$_5$)$_4$]$^-$): 7.19;M; 7.00; M; and 7.28;M	c, +

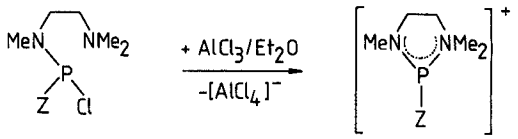
^1H: 60 MHz and 400 MHz[+]; CH_2Cl_2 (δ + 5.35 p.p.m., relative to Si(CH$_3$)$_4$) int. ref.; ^{31}P: 24.3 MHz and 162 MHz[+]; H_3PO_4 ext. ref.; solvents: dichloromethane;[a] chloroform-d;[b] acetonitrile-d_3;[c] neat.[d]
S: singlet; D: doublet; T: triplet; Q: quartet; M: multiplet.

The δ_P values of the salts, **2a–2e** and **2f**,[5] are listed in Table II. They are characteristic of three-coordinate phosphorus.

During the second step of the reaction, according to Equation (3) a phosphorus-chlorine bond (for Y = Cl) is broken while a nitrogen-phosphorus donor–acceptor bond is formed. A value of 289 ± 42 kJ/mole has been reported as the average dissociation enthalpy of the P-Cl bond[10] while for the N–P donor–acceptor bond in trimethylamine-phosphorus trihalide complexes values of <30 kJ/mole have been reported for the dissociation enthalpy.[3] The transformation of **1** into **2** should, therefore, be accompanied by a marked increase in entropy, through a chelate effect which has also been noted in the complexation of metallic centres through polydentate ligands.[11]

The compounds, **1a** and **1c**, are of special interest. They were formed in the reaction, according to Equation (4) as the acyclic isomers. The intramolecular complexation, with formation of the phospholidinium salts, **2d** and **2e**, could be induced by aluminum trichloride (Equation (5)).

The identity of **2d** as a tetrachloroaluminate could be confirmed by its ^{27}Al n.m.r. spectrum (Table II). A value of +101.9 p.p.m. (relative to $Al(H_2O)_6^{3+}$) has been reported for the ion, $[AlCl_4]^-$, in $POCl_3$ solution.[12] In compound, **2e**, E.I. mass spectrometry allowed the observation of the cation while the F.A.B.



(5)

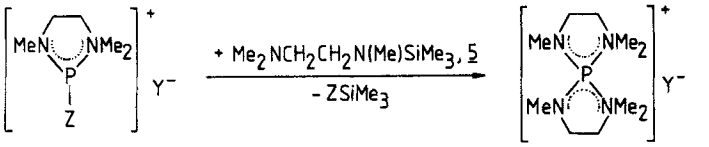
1a: Z = CH_3;
1c: Z = C_6H_5.

2d: Z = CH_3;
2e: Z = C_6H_5.

(negative) mass spectrum revealed the presence of the anion, $[AlCl_4]^-$, with the expected isotope pattern.

The reaction of aminochlorophosphines with aluminum trichloride with formation of low-valent, cationic phosphorus species has been described.[13] The reaction of the difluoroarsino compound, **3**, with acceptor fluorides, was expected to follow the same course, and was attempted with boron trifluoride etherate, and with phosphorus pentafluoride. The exact nature of the products could not be established, however. It appears that the As-F bond in the products is quite unstable. Thus, the ^{19}F n.m.r. resonance for the arsenic-bonded fluorine in the product obtained from the reaction of **3** with $F_3B{\cdot}OEt_2$, dissolved in acetonitrile, was found to disappear upon heating the solution to 50°C. For the product, obtained from **3** and PF_5, only the $[PF_6]^-$ resonance, but no signal for fluorine bonded to arsenic could be observed.

Some of the phospholidinium salts, **2**, contain functional groups at phosphorus. Their reaction with **5** was studied, therefore, as providing an approach to the synthesis of the novel spiro compounds of type **4** (Equation (6)),



(6)

2a: Y = Br; Z = Br;
2c: Y = Br; Z = NEt_2;
2f: Y = Cl; Z = Cl;
2g: Y = [BPh_4]; Z = Cl.

4a: Y = Cl;
4b: Y = Br;
4c: Y = [BPh_4].

Thus reaction of **2f** with Na[BPh_4], followed by reaction of the tetraphenylborate salt, **2g** (without prior isolation) with one equivalent of **5**, led to the formation of the spiro compound, **4c**. The identity of **4c** has been established from its ^1H and ^{31}P n.m.r. data (Table II) and by elemental analysis.

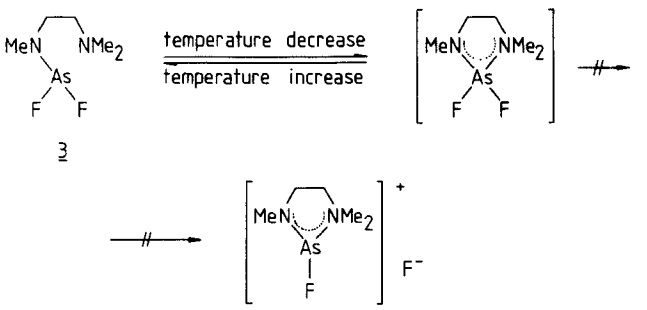
The ^1H and ^{31}P n.m.r. data of the spiro compounds, **4a** and **4b**, obtained from **2a**, **2c**, and **2f**, in accord with Equation (6), are also included in Table II. The nearly identical values of δ_H, δ_P, and $^3J(HP)$ serve to confirm the identity of **4a** and **4b**. Isolation of **4a** and **4b** was found impossible. It may be noted that compound **4b** is formed not only from **5** and PBr_3, but also from **2c**, via elimination of Me_3SiNEt_2 and formation of a P—N bond. The formation of the chelate system in **4b** apparently provides the driving force for this reaction.

The central structural feature in the compounds of type **4** with a ψ-pentacoordinate P(III) atom may be regarded as a model of a stable intermediate of

the nucleophilic substitution at three-coordinate phosphorus, in analogy to the recently described tetrahalo- and tetracyano-phosphorus(III) anions.[4] It is to be expected that in a ψ-trigonal-bipyramidal structure the apical positions at phosphorus are occupied by the two donor nitrogen atoms whereas the other two nitrogen atoms and the lone pair of electrons are suggested to be located in equatorial sites. The same pattern is suggested, considering the effect of the two five-membered rings (decrease in ring strain). The small value of ^3J(HP) (4 Hz) for the $N(CH_3)_2$-protons is thought to confirm the increase in length of the apical, relative to the equatorial bonds. For $[PCl_4]^-$ δ_P 201.5 p.p.m. has been reported[4] which may be compared to 155 p.p.m., observed for **4a**.

In accord with the equilibrium formulated in Equation (3) low temperature should favour the intramolecular complex, **2** whereas at higher temperatures the weak donor–acceptor interaction is expected to break, and structure **1** should be preferred. This could be demonstrated for **1c**[5] (Table I). Neither for the phospholidinium salts, **2a–2e**, nor for the spiro compound, **4b**, was the donor–acceptor bond found to break upon increase of the temperature. The highest temperatures which could be reached while ^{1}H n.m.r. spectra were recorded were the boiling points of the solvents employed ($CHCl_3$-*d*, CH_3CN-d_3). In all compounds the coupling, ^3J(HP) of the $N(CH_3)_2$ protons was retained in the temperature region accessible. Significant changes in chemical shifts or coupling constants were not observed, either. In the case of **2c** the appearance of the ^{1}H n.m.r. resonance for the NCH_2CH_2N groups was found to change above +50°C. A broad multiplet observed at room temperature was found to change reversibly when the temperature was raised, in that the peak sharpened up and increased in height.

The ^{19}F n.m.r. spectrum of the difluoroarsine, **3**, in dichloromethane revealed a dramatic sharpening of the very broad AsF_2 resonance upon lowering the temperature. This effect is reversible; it became noticeable at −10°C and seemed to be most pronounced at −40°C. Fluoride ion could not be observed in the n.m.r. spectrum at temperatures down to −70°C. These observations suggest that the displacement of F^- (Equation (7)), in analogy to (3), does not proceed beyond



(7)

an intramolecular interaction. While the phosphorus analogue of **3** could not be isolated, **3** is stable in solution in dichloromethane over several weeks at −20 °C. The solutions were found to assume a yellow coloration when exposed to light.

EXPERIMENTAL

All experiments were conducted with exclusion of air and moisture in sealed vessels. Solvents were dried by standard procedures.[14]

NMR spectra: Spectrometer Perkin-Elmer R 24 B (^{1}H at 60 MHz); JEOL JNMC-60 HL (^{1}H at 60 MHz; ^{31}P at 24.3 MHz; ^{19}F at 56.4 MHz); Bruker AM-300 and WM-400, Gesellschaft für Biotechnologische Forschung mbH, Braunschweig-Stöckheim (^{1}H at 300 and 400 MHz; ^{31}P at 162 MHz).

Tetramethylsilane (^{1}H), CCl_3F (^{19}F), and 85% H_3PO_4 ext. (^{31}P) were used as references. Dichloromethane ($\delta + 5.35$[15]) for ^{1}H and $P(OCH_3)_3$ ($\delta + 141.0$[16]) for ^{31}P were employed as internal (^{1}H) and external (^{31}P) standards. Hexafluorobenzene, C_6F_6 ($\delta - 163.0$[17]) served as a further external reference for ^{19}F n.m.r. spectra. All chemical shift values are listed in p.p.m. High field shifts have negative, low field shifts positive sign. The integration of all ^{1}H n.m.r. spectra was consistent with the structure.

Mass spectra in the E.I. and F.A.B. mode were recorded on a Finnigan MAT 8430 spectrometer (70 eV).

Starting materials: *N.N.N'*-trimethyl-*N'*-trimethylsilylethylendiamine, **5**, was synthesized in accord with ref.[18] Arsenic trifluoride and methyldichlorophosphine were supplied by Dr. W. E. White, Pennwalt Chemical Corporation, Tulsa, Oklahoma, U.S.A., and Dr. W. Klose, Hoechst AG, Werk Knapsack, Knapsack bei Köln, respectively. t-Butyldichlorophosphine,[19] diethylaminodichlorophosphine,[20] and diethylaminodibromophosphine[21] were synthesized by the literature procedures indicated.

Reacttion of **5** *with methyldichlorophosphine: synthesis of* $Me_2NCH_2CH_2N(Me)P(Me)Cl$, **1a**. Compound **5** (40.0 g; 0.23 mole) was added dropwise with magnetic stirring during 15 min. to a solution of 26.85 g (0.23 mole) of methyldichlorophosphine in 50 ml of dichloromethane, cooled with ice-water. Stirring at room temperature was continued for 2 h. Volatile products were removed by pumping in vacuo (50 mm) at room temperature. The higher boiling reside was fractionally distilled through a 10 cm Vigreux column. The product, **1a**, was obtained as a colorless liquid of b.p. 70°C (4 mm); yield 30.7 g (73%).

$C_6H_{16}ClN_2P$ (182.64)
Anal. found: C, 39.60; H, 8.63
calc.: C, 39.46; H, 8.83.

Reaction of **5** *with t-butyldichlorophosphine: Preparation of* $Me_2NCH_2CH_2N(Me)P(Bu^t)Cl$; **1b**. *N.N.N'*-Trimethylethylene diamine (3.40 g; 0.033 mole) was added dropwise with magnetic stirring over 10 min. to a solution of 5.29 g (0.033 mole) of t-butyldichlorophosphine and 10.20 g (0.1 mole) of triethylamine in 50 ml of carbon tetrachloride, cooled with ice-water. After stirring had been continued at room temperature for 1 h the hydrochloride precipitate was removed by filtration, and was washed with three 20 ml portions of carbon tetrachloride. The filtrate was concentrated by pumping in vacuo (50 mm/1 h) at room temperature. Fractional distillation of the higher-boiling product through a 10 cm Vigreux column gave 4.52 g (60%) of **1b** of b.p. 63°C (0.8 mm).

$C_9H_{22}ClN_2P$ (224.72)
Anal. found: C, 47.80; H, 9.73
calc.: C, 48.10; H, 9.87.

Reaction of **5** *with phosphorus tribromide: synthesis of* $[Me_2\overbrace{NCH_2CH_2N(Me)P}Br]^+ Br^-$, **2a**. The silylated amine, **5** (14.02 g; 0.08 mole) was added dropwise with stirring over 45 min. to an ice-cooled solution of 21.76 g (0.08 mole) of PBr_3 in 50 ml of dichloromethane. Precipitation of a faintly yellow solid was noted, and the reaction mixture was stirred for a further 2 d at room temperature. The precipitate was removed by filtration, was washed with three 20 ml portions of petroleum ether (b.r. 30–40°C), and was dried in vacuo by pumping at room temperature (0.1 mm; 5 h); yield of **2a**, 14.02 g (80%). Unlike the analogous chlorine compound **2a** could not be sublimed without decomposition. On account of its poor solubility, even in acetonitrile, **2a** could not be recrystallized, either.

$C_5H_{13}Br_2N_2P$ (291.98)
Anal. found: C, 20.70; H; 5.02; P, 10.51
calc.: C, 20.57; H, 4.49; P, 10.61.

Reaction of **5** *with diethylaminodichlorophosphine: synthesis of* $[Me_2\overbrace{NCH_2CH_2N(Me)P}(NEt_2)]^+ Cl^-$, **2b**. The silylated amine **5** (7.51 g; 0.043 mole) was added dropwise with magnetic stirring to a solution of 7.49 g (0.043 mole) of diethylaminodichlorophosphine in 20 ml of diethyl ether during

45 min. After another 30 min. stirring period at room temperature the product, formed as a colorless solid, was collected by filtration, washed with three 15 ml portions of petroleum ether (b.r. 30–40°C), and dried in vacuo (0.1 mm; 5 h) at room temperature. Compound **2b** was obtained in 83% yield (8.55 g).

$C_9H_{23}ClN_3P$ (239.73)
Anal. found: C, 45.06; H, 9.79; P, 12.97
calc: C, 45.09; H, 9.67; P, 12.92.

Reaction of **5** *with diethylaminodibromophosphine: synthesis of* $[Me_2\overline{NCH_2CH_2N(Me)}\overline{P(NEt_2)}]^+Br^-$, **2c**. The silylated amine, **5** (10.61 g; 0.061 mole) was added dropwise with stirring during 30 min. to an ice-cooled solution of 16.06 g (0.061 mole) of Et_2NPBr_2 in 100 ml of CCl_4. After the ice-bath had been removed stirring at room temperature was continued for 16 h. As described for **2b** product **2c** was isolated as a colorless solid. Yield 14.65 g (90%); m.p. 74°C.

$C_9H_{23}ClN_3P$ (248.19)
Anal. found: C, 37.46; H, 8.35; P, 10.77
calc.: C, 38.04; H, 8.16; P, 10.90

Reaction of **1a** *with aluminum chloride: synthesis of* $[Me_2\overline{NCH_2CH_2N(Me)}\overline{PCH_3}]^+$ $[AlCl_4]^-$, **2d**. A solution of 1.9 g (0.014 mole) of $AlCl_3$, sublimed in vacuo (0.1 mm; 120°C), in 10 ml of diethyl ether was added dropwise with stirring during 30 min. to an ice-cooled solution of 2.55 g (0.014 mole) of **1a** in 15 ml of diethyl ether. A colorless solid was found to be precipitated. While the reaction was in progress another 20 ml of diethyl ether was added. After the ice-bath had been removed the reaction mixture was stirred at room temperature for 45 min., and refluxed for 5 min. The solid product was removed by filtration, washed with 20 ml of diethyl ether, and dried by pumping in vacuo at room temperature (0.1 mm) during 5 h. Yield 2.86 g (65%). The product was found to be soluble in acetonitrile or sulpholane, less soluble in chloroform, dichloromethane and non-polar solvents.

$C_6H_{16}AlCl_4N_2P$ (315.98)
Anal. found: C, 22.35; H, 5.51; Cl, 45.21; N, 8.41
calc.: C, 22.81; H, 5.10; Cl, 44.87; N, 8.87.

Reaction of **1c** *with aluminum chloride: synthesis of* $[Me_2\overline{NCH_2CH_2N(Me)}\overline{PC_6H_5}]^+$ $[AlCl_4]^-$, **2e**. A solution of 1.12 g (0.009 mole) of $AlCl_3$ in 15 ml of diethyl ether was added dropwise with magnetic stirring during 15 min. to a solution of 2.34 g (0.009 mole) of **1c** in 4 ml of dichloromethane. When stirring had been discontinued a clear oil of higher density than the organic solvents was seen to separate. The oily product was suspended four times in 10–15 ml portions of diethyl ether which was removed quickly by pumping in vacuo (0.1 mm) with magnetic stirring. A colorless solid was obtained, eventually, which was suspended in 20 ml of diethyl ether and collected by filtration through a sintered-glass disc, and was washed with four 10 ml portions of diethyl ether. The solid product thus obtained was pumped dry in vacuo (0.1 mm; 5 h). Yield: 1.58 g (45%); m.p. 80–82°C.

$C_{11}H_{18}AlCl_4N_2P$ (378.03)
Anal. found: C, 35.13; H, 5.02; P, 8.42
calc.: C, 34.95; H, 4.80; P, 8.19.
Ms (E.I.): 209 (cation; 6%); 182/180/178 ($C_6H_5PCl_2^+$; 45%); 145/143 ($C_6H_5PCl^+$; 100%); 58 ($Me_2NCH_2^+$); 50%).
Ms (F.A.B., negative; sulpholane matrix):
175/173/171/169/167 ($[AlCl_4]^-$; 100%).

Reaction of **5** *with* AsF_3: *synthesis of* $Me_2NCH_2CH_2N(Me)AsF_2$, **3**. The silyl amine, **5** (11.4 g; 0.067 mole) was added dropwise with magnetic stirring to a solution of 10.74 g (0.081 mole) of AsF_3 in 20 ml of dichloromethane, held at −15 °C. Stirring was continued for 16 h at room temperature. The product remaining after removal of volatiles at 5 mm/1 h was fractionally distilled through a 10 cm Vigreux column; b.p. 75°C (2 mm); m.p. −25°C; yield 11.17 g (78%)

$C_5H_{13}AsF_2N_2$ (214.09)
Anal. found: C, 28.42; H, 6.09
calc.: C, 28.05; H, 6.12.

Reaction of **2f** *with sodium tetraphenylborate and* **5**: *synthesis of the spiro compound,* $[(Me_2\overline{NCH_2CH_2N(Me)})_2\overline{P}]^+[BPh_4]^-$, **4c**. A solution of 7.41 g 0.022 mole) of $Na[BPh_4]$ in 20 ml of acetonitrile was added dropwise with magnetic stirring over 15 min. to a solution of 4.40 g (0.022 mole) of **2f**[5] in 80 ml of dichloromethane. A colorless precipitate, consisting of sodium chloride and, presumably, of **2g** was formed. No attempt was made to isolate the poorly soluble **2g**. To this suspension, cooled with ice-water, were added 3.84 g (0.022 mole) of silylamine, **5**, dissolved in 5 ml

of dichloromethane during 10 min. with magnetic stirring. The solid, except for the sodium chloride, was dissolved. The remaining solid was separated by centrifugation (7000 r.p.m.) over 10 min. The volume of the filtrate was reduced by pumping in vacuo (0.1 mm) until copious quantities of a colorless solid were precipitated. This product was subsequently recrystallized by warming the magnetically stirred solution up to 60°C. After standing at room temperature during 5 h, the product crystallized as small needles. The crystallization was completed when the reaction mixture was kept at 0°C for 15 h. The product was collected by filtration, washed with two 10 ml portions of acetonitrile, and dried in vacuo (0.1 mm/5 h). Yield, 6.23 g (52%).

$C_{34}H_{46}BN_4P$ (552.56)

Anal. found: C, 73.87; H, 8.37; P, 5.51
calc.: C, 73.91; H, 8.39; P, 5.60.

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