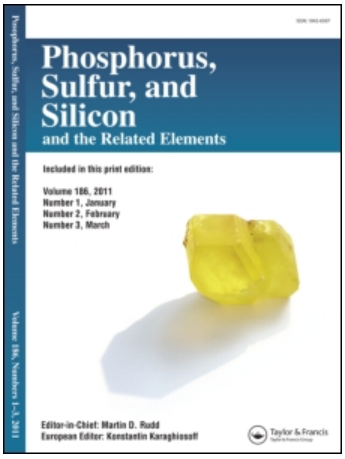

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SYNTHESIS AND STRUCTURE OF TETRAORGANOGUANIDINYL-SUBSTITUTED PHOSPHORUS-HALOGEN COMPOUNDS AND OF TRIS-N-(N',N',N'',N''-TETRAMETHYL) GUANIDINYL-PHOSPHONIUM SALTS

J. Münchenberg[a]; H. Thönnessen[a]; P. G. Jones[a]; R. Schmutzler[a]
[a] Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Germany

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SYNTHESIS AND STRUCTURE OF TETRAORGANOGUANIDINYL-SUBSTITUTED PHOSPHORUS-HALOGEN COMPOUNDS AND OF TRIS-N-(N',N',N'',N''-TETRAMETHYL) GUANIDINYL-PHOSPHONIUM SALTS*

J. MÜNCHENBERG, H. THÖNNESSEN, P.G. JONES and R. SCHMUTZLER

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329. D-38023 Braunschweig, Germany

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The N-(N',N',N",N"-tetraorgano)guanidine-substituted dichlorophosphines **3a - 3c** were prepared by the reaction of phosphorus trichloride with the corresponding guanidine or N-lithiated guanidine. The high-field shift of the $\delta(^{31}P)$ values of **3a - 3c** reflects the strong electron-donating effect of the guanidinyl substituents. Attempts to achieve further substitution of chlorine in PCl_3 by N',N',N",N"-tetramethylguanidine (HTMG) **1a** (employed as such or as its N-trimethylsilyl derivative, TMSTMG, **2**) led to the formation of tris-N-(N',N',N",N"-tetramethyl)guanidinylphosphonium salts such as **4**. A salt containing the same cation was obtained from the reaction of bis-N-(N',N',N",N"-tetramethyl)guanidinyltrichlorophosphorane **5** with magnesium. Difluoro-N-(N',N',N",N"-tetramethyl)guanidinylphosphine **6** was obtained from difluorochlorophosphine and HTMG **1a**. Hydrolysis of **6** led, depending upon the conditions of the reaction, either to N',N',N",N"-tetramethylguanidinium phosphonofluoridate **7** or tris-N-(N',N',N",N"-tetramethyl)guanidinylphosphonium pentafluorophosphate **8**. A single crystal X-ray structure determination of **8** revealed a disordered anion and a cation with short P-N bonds, attributed to $p\pi$-$d\pi$ interaction. Dimethylamino-bis-N-(N',N',N",N"-tetramethyl)guanidinyl-phosphine **9** and the chloro-diorganoamino-N-(N',N',N",N"-tetramethyl)guanidinyl-phosphines **10** and **11** were obtained from the corresponding dichlorodiorganoaminophosphines and HTMG **1a** or N-trimethylsilyl-(N',N',N",N"-tetramethyl)guanidine **2**.

Keywords: N',N',N",N"-Tetramethylguanidine; Phosphine; N-(N',N',N",N"-tetraorgano)-guanidinyl-substituted; Phosphonium salt; N-(N',N',N",N"-tetramethyl)-guanidinyl-substituted; Phosphorane; N-(N',N',N",N"-tetramethyl)-guanidinylsubstituted; Pentafluorophosphate anion; Crystal structure

* Dedicated to Dr. Robert Wolf

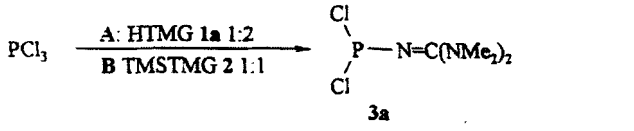
INTRODUCTION

In the course of our studies concerning the synthesis and properties of N-(N',N',N",N"-tetramethyl)guanidinyl-(TMG)-substituted phosphorus compounds we have investigated compounds of type RP(:X)(F)TMG (R = t-Bu, Ph ; X = lone pair, O, S, Se, Te)[1] and RP(:O)(Cl)TMG (R = t-Bu, Ph, Ph_3C)[2]. To the best of our knowledge the only TMG-substituted phosphorus-halogen compound without an organic substituent bonded to phosphorus via carbon is $Cl_2P(:O)TMG$. Attempts to achieve further substitution with TMG to form, e.g., $ClP(:O)(TMG)_2$ or $(TMG)_3P(:O)$ failed[2]. Thus, we were interested in the preparation of phosphorus-halogen compounds (especially phosphorus(III) compounds) containing the TMG or another guanidinyl substituents. Also, attempts at the synthesis of $P(TMG)_3$ were undertaken.

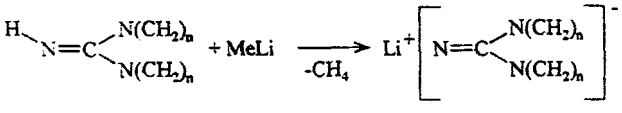
RESULTS

Dichloro-N-(N',N',N",N"-tetramethyl)guanidinyl-phosphine **3a** was readily accessible in the same way as most other TMG-substituted phosphorus(III)-compounds[3], by reacting PCl_3 with HTMG in a 1:2 molar ratio. HTMG acted as the base removing HCl from the reaction mixture [Eq. (1a)].

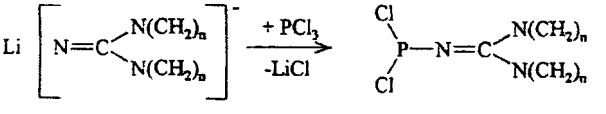
Bispyrrolidinomethyleneimide **1b** and bispiperidinomethyleneimide **1c**, prepared according to the standard method of synthesis of substituted guanidines estab-



3a (1a)



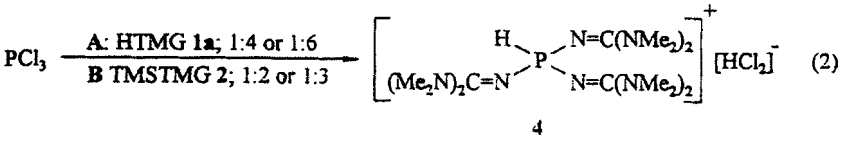
1b (n = 4)
1c (n = 5) (1b)



3b (n = 4)
3c (n = 5)

lished by J.v. Braun[4], were lithiated with methyllithium and then allowed to react with PCl_3 in a 1:1 molar ratio, furnishing dichloro-(bispyrrolidinomethyleneimino)-phosphine **3b** and dichloro-(bispiperidinomethyleneimino)-phosphine **3c** [Eq. (1b)].

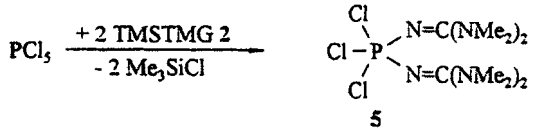
The reaction of PCl_3 with HTMG **1a** in a 1:4 or 1:6 molar ratio, as well as the reaction of PCl_3 with TMSTMG **2** in a 1:2 or 1:3 molar ratio led to the phosphonium salt **4**, instead of $ClP(TMG)_2$ or $(TMG)_3P$ [Eq. (2)].



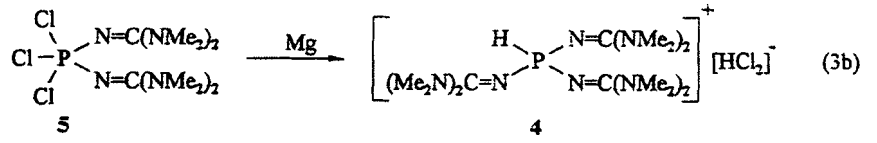
4 (2)

The deprotonation of **4** with methyllithium was attempted. Depending on the conditions, either no appreciable reaction or decomposition was observed.

Phosphorus pentachloride reacted with three equivalents of TMSTMG **2** with formation of bis-N-(N',N',N",N"-tetramethyl)guanidinyltrichlorophosphorane **5**, instead of the expected tris-N-(N',N',N",N"-tetramethyl)guanidinyldichlorophosphorane [Eq. (3a)].



5 (3a)

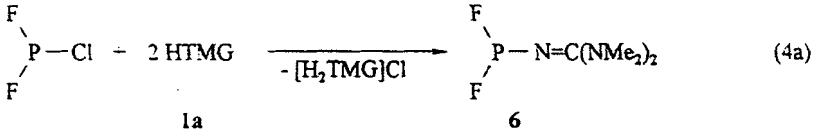


5 4 (3b)

Reduction of **5**, by dechlorination with an active metal, should furnish $ClP(TMG)_2$. The reaction of **5** with magnesium led to a phosphonium salt containing the cation of **4** [Eq. (3b)], instead of the expected product. This compound was not isolated, and it could not be established with certainty if the product contained the chloride or the hydrogen dichloride anion.

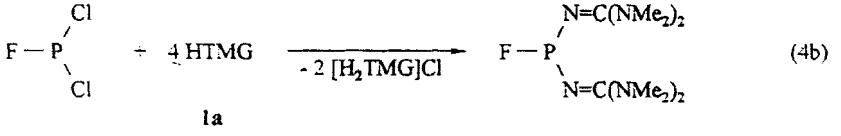
From difluorochlorophosphine and HTMG **1a**, difluoro-N-(N',N',N",N"-tetramethyl)-guanidinyl-phosphine **6** was obtained [Eq. (4a)]. The same reaction conducted with fluorodichlorophosphine furnished only traces of fluoro-bis-N-(N',N',N",N"-tetramethyl)guanidinylphosphine, besides an ionic product containing the same cation as **4** and several by-products [Eq. (4b)].

Hydrolysis of **5** with excess water furnished the guanidinium phosphonofluoridate **7** as the main product [course **A** in Eq. (5)]. Slow hydrolysis with a sub-



(4a)

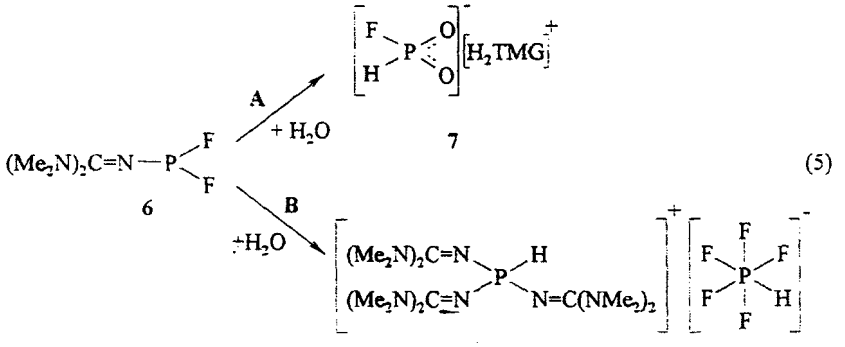
1a **6**



(4b)

1a

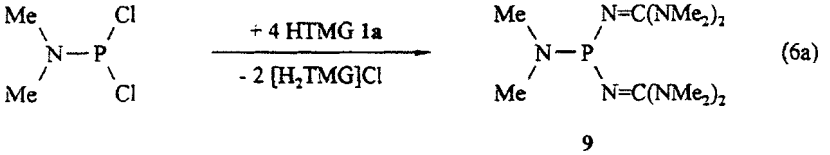
stoichiometric amount of water led to the phosphonium pentafluorophosphate **8** [course **B** in Eq. (5)].



(5)

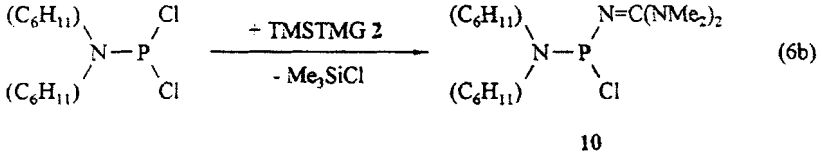
6 **7** **8**

In the reaction of diorganoaminodichlorophosphines with HTMG **1a** or TMSTMG **2**, dimethylamino-bis-N-(N',N',N",N"-tetramethyl)-guanidinyl-phosphine **9**, and the chloro-diorganoamino-N-(N',N',N",N"-tetramethyl)guanidinyl-phosphines **10** and **11** were obtained [Eq. (6a) - (6c)].



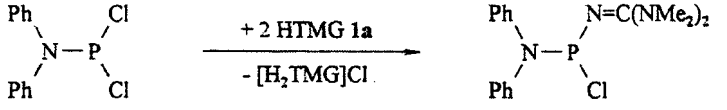
(6a)

9



(6b)

10

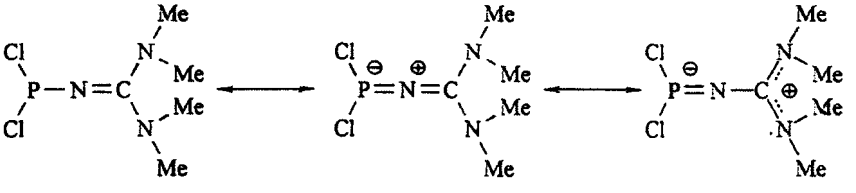


(6c)

11

DISCUSSION

The $\delta(^{31}P)$ values of **3a, 3b** and **3c** (Table I) were observed at higher field than those of most diorganoaminodichlorophosphines. This is caused by the strong electron-donating effect of the tetraorganoguanidine substituent, leading to increased $d\pi$-$p\pi$-interaction between phosphorus and the imino nitrogen (Scheme 1). Thus, the effect of the electronegativity of nitrogen, leading to a downfield shift of the $\delta(^{31}P)$ value, is compensated. The same ^{31}P-NMR spectroscopic properties were observed for dichloro(1,3-dimethyl-2-imidazol-2-ylidenimino)phosphine ($\delta(^{31}P)$ = 128.09 ppm)[5]. The $\delta(^{31}P)$ value of **3b** lay at higher field than the values of **3a** and **3c**, indicating the better ability of the pyrrolidino moiety to stabilise a positive charge.



SCHEME 1

The $\delta(^{31}P)$ value and the $^{1}J(PF)$ coupling constant of the fluorine compound **6** (Table 1) lay in the range typical of diorganoaminodifluorophosphines[6]. In contrast, the $\delta(^{19}F)$ value of **6** was -48.79 ppm, whereas the $\delta(^{19}F)$ values of other diorganoaminodifluorophosphines lay between -60 and -70 ppm[6]. The fluorine atoms are more strongly deshielded by the TMG-substituent than by diorganoamino substituents at phosphorus.

The $\delta(^{31}P)$ value of **5** at high field indicates that the phosphorus atom is pentacoordinated (whereas, because of the strong electron-donating effect of the TMG-substituent, a chlorophosphonium salt was expected). In the ^{1}H-NMR spectrum of **5** one signal with a $^{5}J(PH)$ coupling constant of 2.18 Hz was observed. This coupling constant is slightly larger than the coupling constants

previously observed for TMG-substituted species involving pentacoordinated phosphorus[3].

TABLE I Selected NMR data for compounds **3a - 12.**

	$\delta(^{31}P)$	$\delta(^{1}H)$	$\delta(^{13}C)$	
		$[N(C\underline{H}_3)_2]$	$[N(\underline{C}H_3)_2]$	$N=\underline{C}<$
3a[a]	131.84	2.97	41.09	157.41
3b	117.39	3.13[b]	-	-
3c	135.93	3.25[b]	-	-
4	-17.12[c]	3.02	39.99	161.72
5	-27.89	2.68[d]	40.27	159.35
6	140.85[e]	2.71	39.91	162.22
8	-16.76[f]	2.97	-	-
9	98.99[g]	2.70[a,h]	-	-
10[g]	157.32	2.57	39.78	161.33
11[g]	146.74	2.26	-	-

a: recorded in CD_3CN; b: $N(C\underline{H}_2)_2(CH_2)_n$, n = 3, 4 c: $^1J(PH)$ = 539.35 Hz; d: $^5J(PH)$ = 2.18 Hz; e: $^1J(PF)$ = 1215.90 Hz; f: $^1J(PH)$ = 538.6 Hz; g: recorded in C_6D_6; h: in C_6D_6 four signals were observed: δ = 2.570, 2.573, 2.67 and 2.72 ppm.

The $\delta(^{31}P)$ value of **9** lay at higher field than the values of tris-(diorganoamino)-phosphines, illustrating the electron-donating effect of the TMG-substituent. The $\delta(^{31}P)$ values of the chloro compounds **10** and **11** were observed at lower field, in the high field part of the range where most $\delta(^{31}P)$ values of bis-(diorganoamino)-chlorophosphines lie. The ^1H-NMR spectrum of **9**, recorded in CD_3CN, exhibited one signal for the protons of the TMG-substituent. In the ^1H-NMR spectrum recorded in C_6D_6 four signals were observed for these protons. It would appear that the rotation around the PN_{TMG}-bond is hindered in C_6D_6 at room temperature, leading to nonequivalence of the dimethylamino groups of the TMG-substituents.

The $\delta(^1H)$ values of the TMG-substituents of **10** and **11** were observed at unusually high field ; a shift of such magnitude has not previously been observed for this type of protons in phosphorus compounds.

In the ^{31}P-NMR-spectrum of the hydrolysis product **7** a doublet at δ = 0.07 ppm [$^1J(PF)$ = 966.17 Hz] was observed. This was split into a doublet of dou-

blets in the proton-coupled spectrum [^{1}J(PH) = 663.55 Hz]. In the ^{1}H-NMR-spectrum a signal from the dimethylamino groups (δ = 2.82 ppm), and a doublet of doublets, caused by the proton directly bonded to phosphorus (δ = 6.74 ppm, ^{1}J(PH) = 663.49 Hz, ^{2}J(FH) = 127.78 Hz) were observed. In addition, a broad signal at δ = 8.26 ppm was observed, which was attributed to the protons at the imino nitrogen atom of the N',N',N",N"-tetramethylguanidinium cation. Compared to the $\delta(^{31}P)$-value of phosphonofluoridic acid, H(F)P(:O)(OH)[7] the $\delta(^{31}P)$ value of **7** (δ = 0.07 ppm) was shifted slightly to lower field. The coupling constants of **7** [^{1}J(PF) = 966.17, ^{1}J(PH) = 663.55] were smaller than those of phosphonofluoridic acid [^{1}J(PF) = 1032 Hz, ^{1}J(PH) = 785 Hz[7].

The $\delta(^{31}P)$ values of the cations of **4** and **8** were nearly identical, as were the ^{1}J(PH) coupling constants (Table I). The small differences observed arise from the different anions. The $\delta(^{31}P)$ values of triarylphosphonium compounds lie in the same range[8] whereas the $\delta(^{31}P)$ values of diorganoaminophosphonium compounds $[R_2NP(H)R'_2]^+$, comparable to the cations of **4** and **8**, lie at lower field[9,10]. The ^{1}J(PH) coupling constants observed for diorganoaminophosphonium $[R_2NP(H)R'_2]^+$ and for triarylphosphonium compounds are of the same order of magnitude[8-10]. The $\delta(^{31}P)$ value of **4** showed the solvent dependence expected for an ionic species [-17.12 ppm in $CDCl_3$ and -15.1 ppm in CD_3CN].

The $\delta(^1H)$ values of the TMG-substituents of **4** and **8** were identical (Table I). The $\delta(^1H)$ value of the proton directly bonded to phosphorus in **4** displayed only a small solvent dependence (7.79 ppm in $CDCl_3$ and 7.82 ppm in CD_3CN). In the ^{1}H-NMR spectrum of **4** the signal of the proton of the $[HCl_2]^-$ ion could be observed only in $CDCl_3$at δ = 8.75 ppm. The $\delta(^1H)$ value observed depends upon the dissociation of the anion into Cl^- and HCl. This dependency is nearly linear, showing that about 40 % of the anion are dissociated in $CDCl_3$ solution[11].

In the FAB mass spectrum of **4** a peak, originating from the cation, was observed in the positive part (m/z = 374) while in the negative part only an adduct of the chloride anion and the solvent nitrobenzylalcohol (NBA) and not the $[HCl_2]^-$ ion (or an adduct of the $[HCl_2]^-$ ion with NBA) were observed.

TABLE II NMR data for the pentafluorophosphate anion.

	$\delta(^{31}P)$	$^1J(PF_{eq})$	$^1J(PF_{ax})$	$^1J(PH)$	$^2J(FH)$	*Ref.*
8	-139.7 ppm	833.6 Hz	735.6 Hz	953.2 Hz	127.5 Hz	–
$[Et_3NH][HPF_5]$	-141.5 ppm	820 Hz	730 Hz	945 Hz	-	12
$[Et_4N][HPF_5]$	-123 ppm	825.9 Hz	736.9 Hz	946.9 Hz	122.9 Hz	13

The NMR data observed for the pentafluorophosphate anion of **8** are shown in Table II, together with some literature data. There are some large differences, especially in the $\delta(^{31}P)$ values, which might be explained by differences in the solvents employed and in the cations. The presence of the pentafluorophosphate anion in **8** is proved by the ^{31}P-and ^{1}H-NMR spectra and by the base peak in the negative FAB mass spectrum (m/z = 127)

Structure of 8

The single crystal X-ray structure analysis of **8** showed an extensively disordered anion (the identity of which was, however, clear from the NMR and the FAB mass spectra). The following discussion is thus restricted to the cation.

The P1-H bond [131(3) pm] of **8** is insignificantly different from that in $[t\text{-}Bu_2P(H)(N(CH_2)_4)]^+$ [128 (4) pm][10], one of the very few nitrogen-substituted

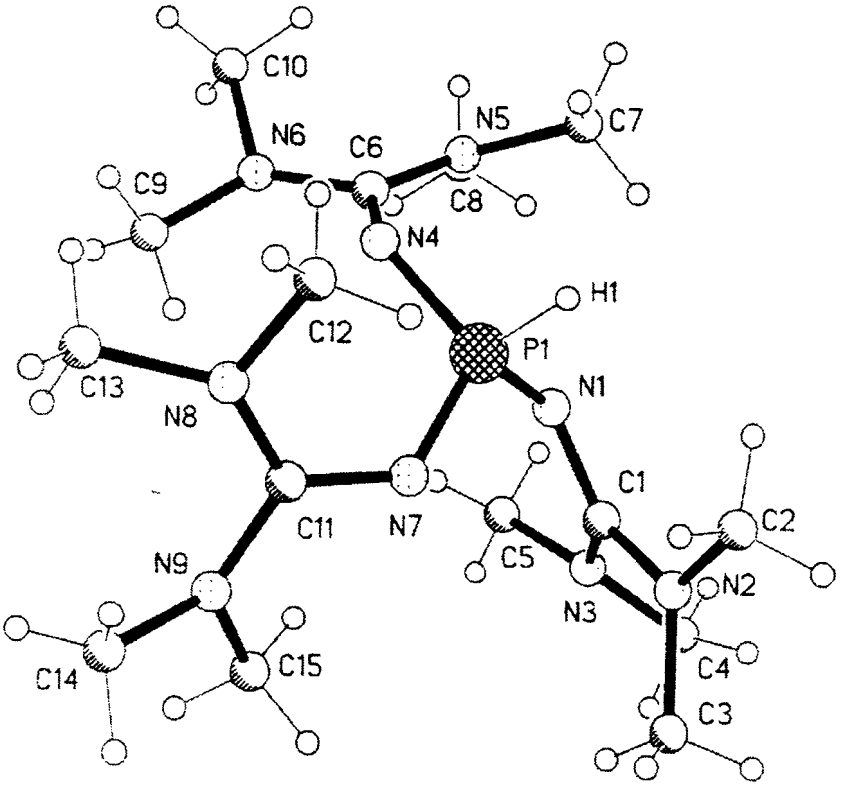


FIGURE 1 Molecular structure of the cation of **8**

phosphonium salts studied by X-ray diffraction. The phosphorus atom in the cation of **8** displays only slight deviation from the tetrahedral coordination, as found in most phosphonium compounds[14]. The angles at phosphorus involving hydrogen [H1-P1-N1: 108.1(12)°, H1-P1-N4 107.1(12)°, H1-P1-N7: 108.1(12)°] are slightly smaller, the other angles [N1-P1-N4: 111.20(12)°, N1-P1-N7: 109.91(12), N4-P1-N7: 112.14(12)°] slightly larger than the ideal tetrahedral angle.

The P-N bond lengths lie between 160.5(2) pm [P1-N7] and 161.5(2) pm [P1-N1]. This is considerably shorter than the P-N bond length in TMG-substituted phosphines [Ph_2P(TMG): 169.6(3) pm][3]. The P-N bond in [t-$Bu_2P(H)(N(CH_2)_4)]^+$ [166.7 pm] was only slightly shorter than the value of the corresponding phosphine[10]. The P-N bonds in TMG-substituted thiophosphoryl compounds [between 162.37(14) and 163.51(13) pm] are longer[3] than in **8**; in TMG-substituted phosphoryl compounds[2,5] the P-N bond lengths [between 159 and 164.9(4) pm] are about the same as in **8**. The P-N-C angles in **8** [P1-N1-C1 and P1-N4-C6: 128.1(2)° and P1-N7-C11: 128.9(2)°] are greater than the expected angle of 120° for sp^2-hybridised nitrogen. The average absolute P-N-C-N torsion angle of 43.8° represents a major deviation from the expected planar geometry at the N-C double bond. The N-C double bond lengths of **8** [average: 131.6 pm] are comparable to the value in Ph_2PTMG [129.3(4) pm][3] but longer than the "standard" double bond length [127.9 pm][16]. The remaining C-N bonds at the imino carbon atoms [average: 135.2 pm] are considerably shorter than a "standard" C-N single bond [141.6 pm][16].

These values imply that the hybridisation of the imino nitrogen atoms lies between sp and sp^2, and that the P-N bond has partial double bond character. The positive charge of the cation is delocalised over the three TMG-substituents.

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere, employing standard vacuum and inert gas techniques. The solvents were dried by standard procedures and were freshly distilled before use. The ^1H (200.1 MHz), ^{13}C (50.3 MHz), ^{19}F (188.3 MHz) and ^{31}P (80.1 MHz) NMR spectra were recorded on a Bruker AC-200 spectrometer using, unless indicated otherwise, $CDCl_3$ as a solvent. All shifts are reported relative to TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F) and H_3PO_4 (^{31}P). The EI and the FAB mass spectra were recorded on a Finnigan MAT 8430 spectrometer at 70 eV. The abbreviation "i.v." refers to a pressure of 0.1 mm Hg.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **8**

	x	*y*	*z*	*U(eq)*
P(1)	2843.6(5)	8741.2(8)	811.1(3)	27.6(2)
N(1)	3392(2)	10337(3)	641.1(9)	32.0(5)
N(2)	1947(2)	11577(3)	-4 8(10)	37.9(6)
N(3)	3317(2)	13009(3)	572.9(10)	37.7(6)
N(4)	3682(2)	7870(3)	1309.3(10)	36.2(6)
N(5)	5517(2)	8558(3)	1241.2(11)	40.1(6)
N(6)	5090(2)	8162(4)	2086.5(11)	48.1(7)
N(7)	1653(2)	9115(3)	952.5(9)	33.8(5)
N(8)	1226(2)	7033(3)	1495.9(10)	37.3(6)
N(9)	717(2)	9571(3)	1639.5(10)	38.7(6)
C(1)	2879(2)	11585(3)	406.7(10)	29.2(6)
C(2)	1632(3)	10188(4)	-339.1(12)	52.1(9)
C(3)	1069(3)	12760(5)	-52(2)	57.6(9)
C(4)	3315(3)	14306(4)	193.3(15)	48.4(8)
C(5)	4177(3)	13118(4)	1076.2(15)	56.6(9)
C(6)	4739(2)	8206(3)	1526.4(12)	34.5(6)
C(7)	5386(3)	8084(5)	668.5(14)	53.5(9)
C(8)	6430(3)	9656(5)	1433(2)	61.7(10)
C(9)	4267(4)	8121(6)	2422(2)	71.5(12)
C(10)	6206(3)	7583(5)	2354(2)	69.8(11)
C(11)	1226(2)	8561(3)	1358.3(11)	31.5(6)
C(12)	1386(3)	5819(4)	1113.8(15)	45.5(8)
C(13)	1322(3)	6507(5)	2063.4(14)	58.6(10)
C(14)	-240(3)	9131(5)	1872.1(13)	52.4(9)
C(15)	930(3)	11238(4)	1618(2)	59.5(10)
P(2)	2110.3(8)	9269.7(12)	3596.9(4)	58.6(3)
F(1)	2099(4)	11010(4)	3802.5(14)	143(2)
F(2)	2036(5)	7552(5)	3393(2)	193(3)
F(3)	2576(11)	8509(7)	4149(2)	149(5)
F(4)	2810(12)	9223(17)	3232(5)	224(8)
F(5)	889(5)	9184(9)	3314(3)	117(3)
F(3')	1757(6)	10138(7)	2992(2)	91(2)
F(4')	1283(6)	9090(10)	4021(4)	150(4)
F(5')	3191(7)	9310(23)	3898(9)	356(15)

TABLE IV Bond lengths [pm] and angles [°] for the cation of **8**

P(1)-H(1)	131(3)	N(5)-C(8)	145.4(4)
P(1)-N(7)	160.5(2)	N(5)-C(7)	145.8(4)
P(1)-N(4)	160.6(2)	N(6)-C(6)	136.7(4)
P(1)-N(1)	161.5(2)	N(6)-C(9)	144.7(4)
N(1)-C(1)	130.6(3)	N(6)-C(10)	146.4(4)
N(2)-C(1)	135.4(3)	N(7)-C(11)	132.4(3)
N(2)-C(2)	145.1(4)	N(8)-C(11)	134.8(4)
N(2)-C(3)	145.9(4)	N(8)-C(12)	144.9(4)
N(3)-C(1)	135.5(3)	N(8)-C(13)	146.3(4)
N(3)-C(5)	145.0(4)	N(9)-C(11)	134.8(4)
N(3)-C(4)	145.6(4)	N(9)-C(15)	144.9(4)
N(4)-C(6)	131.8(4)	N(9)-C(14)	146.6(4)
N(5)-C(6)	134.2(4)		
H(1)-P(1)-N(1)	108(1)	C(6)-N(6)-C(10)	121.5(3)
H(1)-P(1)-N(4)	107(1)	C(9)-N(6)-C(10)	115.3(3)
H(1)-P(1)-N(7)	108(1)	C(11)-N(7)-P(1)	128.9(2)
N(7)-P(1)-N(4)	112.14(12)	C(11)-N(8)-C(12)	121.1(2)
N(7)-P(1)-N(1)	109.91(12)	C(11)-N(8)-C(13)	122.5(3)
N(4)-P(1)-N(1)	111.20(12)	C(12)-N(8)-C(13)	115.0(3)
C(1)-N(1)-P(1)	128.1(2)	C(11)-N(9)-C(15)	120.1(3)
C(1)-N(2)-C(2)	120.7(3)	C(11)-N(9)-C(14)	122.9(3)
C(1)-N(2)-C(3)	122.6(3)	C(15)-N(9)-C(14)	115.6(3)
C(2)-N(2)-C(3)	115.0(3)	N(1)-C(1)-N(2)	125.1(3)
C(1)-N(3)-C(5)	118.9(2)	N(1)-C(1)-N(3)	118.4(2)
C(1)-N(3)-C(4)	122.6(2)	N(2)-C(1)-N(3)	116.5(2)
C(5)-N(3)-C(4)	114.2(3)	N(4)-C(6)-N(5)	125.3(3)
C(6)-N(4)-P(1)	128.1(2)	N(4)-C(6)-N(6)	118.0(3)
C(6)-N(5)-C(8)	123.6(3)	N(5)-C(6)-N(6)	116.6(3)
C(6)-N(5)-C(7)	121.3(3)	N(7)-C(11)-N(9)	118.4(3)
C(8)-N(5)-C(7)	114.2(3)	N(7)-C(11)-N(8)	124.2(3)
C(6)-N(6)-C(9)	119.4(3)	N(9)-C(11)-N(8)	117.4(2)

The following compounds were prepared according to published methods: bis-pyrrolidinomethyleneimine **1b** and bispiperidinomethyleneimine **1c**[4], TMSTMG **2**[17], difluorochlorophosphine and dichlorofluorophosphine[18], dimethylaminodichlorophosphine and dicyclohexylaminodichlorophosphine[19], diphenylaminodichlorophosphine[20]. Other reagents were commercially available.

Reaction of phosphorus trichloride with TMSTMG 2; Synthesis of dichloro-N-(N',N',N'',N''-tetramethyl)guanidinyl-phosphine 3a:

A solution of 1.34 g (9.8 mmol) of PCl_3 in 20 ml of n-hexane was added at 0°C to a solution of 1.84 g TMSTMG **2** in 30 ml of n-hexane. The mixture was refluxed for 2.5 h. The solution was decanted from the oily residue and the solvent was removed i.v. The remaining solid was dissolved in 40 ml of diethyl ether and was cooled to -20°C for 16 h. The precipitate was filtered off and dried i.v. Yield: 1.56 g (73.9 %), colourless solid, mp.: 38°C.

^{1}H-NMR (CD_3CN): δ = 2.97 (s, $N(CH_3)_2$). ^{13}C-NMR (CD_3CN): δ = 41.09 (s, $N(\underline{C}H_3)_2$); δ = 157.41 (s, N=$\underline{C}$<). ^{31}P-NMR (CD_3CN): δ = 131.84 (s). EI-MS: m/z (%): 215 (2) $[M]^+$, 180 (10) $[M - Cl]^+$, 171 (3) $[Cl_2PNCNMe_2]^+$, 136 (36) $[PCl_3]^+$, 110 (4) $[ClPNMe_2]^+$ 101 (100) $[PCl_2]^+$, 71 (4) $[HNCNMe_2]^+$ 44 (4) $[NMe_2]^+$· $C_5H_{12}Cl_2N_3P$ (216.05); calc.: C 27.80, H 5.60, N 19.45; found: C 27.85, H 5.95, N 19.35.

General procedure for the reaction of lithiated guanidines with phosphorus trichloride:

At 0°C 30 ml of a 1.6 M solution of methyllithium in n-hexane (48 mmol of methyllithium) were added to a solution of 20.0 mmol of the guanidine in 50 ml of diethyl ether. The mixture was refluxed for 2 h. The solvent was evaporated to 1/4 of its volume and the precipitate was filtered off. The solid was washed twice with 10 ml of n-hexane and was dried i.v. Yield : (65 - 75 %). The lithiated compound was allowed to react with PCl_3 without further purification.

A solution of 2.2 g (16.0 mmol) of PCl_3 in 20 ml of diethyl ether was added at 0°C to a suspension of 14 mmol of lithiated guanidine in 30 ml of diethyl ether. The mixture was stirred at room temp. for 2 h and the precipitate was filtered off. The solvent was removed i.v. and the residue was recrystallised from n-hexane (**3b**) or a toluene-n-hexane 1:4 mixture (**3c**).

Dichloro-(bispyrrolidinomethyleneimino)-phosphine 3b:

Yield: 0.87 g (22.7 %), colourless solid, mp.: 76°C. ^{1}H-NMR: δ = 1.34 (m, 8 H, N($CH_2C\underline{H}_2)_2$); δ = 3.13 (m, 8 H, N($C\underline{H}_2CH_2)_2$). ^{31}P-NMR: δ = 117.39 (s). $C_9H_{16}Cl_2N_3P$ (268.13); calc.: C 40.32, H 6.01, N 15.67; found: C 39.44, H 5.95, N 14.98.

Dichloro-(bispiperidinomethyleneimino)-phosphine 3c:

Yield: 0.98 g (22.2 %), colourless solid, mp.: 103°C.

^{1}H-NMR: δ = 1.60 (s, br, 12 H, N($CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_2$)); δ = 3.25 (s, br, 8 H, N($C\underline{H}_2CH_2CH_2CH_2C\underline{H}_2$)) ^{31}P-NMR: δ = 135.93 (s). $C_{11}H_{20}Cl_2N_3P$ (296.18); calc.: C 44.61, H 6.81, N 14.19; found: C 44.62, H 6.86, N 14.11.

Reaction of phosphorus trichloride with TMSTMG 2; Synthesis of tris-N-(N',N',N'',N''-tetramethyl)guanidinylphosphonium hydrogen dichloride 4:

A solution of 2.27 g (16.5 mmol) of PCl_3 in 20 ml of THE was added over 3 h at 0°C to a solution of 11.37 g (60.6 mmol) of TMSTMG **2** in 30 ml of THF. The mixture was stirred for 30 min, the precipitate was filtered off, washed with 5 ml of THF and dried i.v. Yield: 4.24 g (57.56 %), colourless solid, mp.: 83°C (dec.).

^{1}H-NMR: δ = 3.02 (d, ^{5}J(PH) = 0.54, 36 H, N($C\underline{H}_3)_2$); δ = 7.79 (d, ^{1}J(PH) = 539.96, 1 H, P$\underline{H}$); δ = 8.75 (s, br, 1 H, Cl-$\underline{H}$-Cl$^-$). ^{13}C-NMR: δ = 39.99 (s, N($\underline{C}H_3)_2$); δ = 161.72 (s, N=$\underline{C}$<). ^{31}P-NMR: δ = -17.12 (d, ^{1}J(PH) = 539.4). FAB-MS: m/z (%); pos.: 374 (100) $[HP(TMG)_3]^+$, 259 (21) $[P(TMG)_2]^+$, 189 (12) $[Me_2NP(TMG)]^+$, 116 (53) $[H_2TMG]^+$, 71 (23) $[NCNMe_2]^+$, 44 (5) $[NMe_2]^+$; neg.: 188 (100) $[NBA{\cdot}Cl]^-$. $C_{15}H_{38}Cl_2N_9P$ (446.41); {$[C_{15}H_{37}N_9P]^+$ (374.50) $[HCl_2]^-$ (71.91)}; calc. C 40.36, H 8.58, N 28.24; found: C 39.89, H 8.64, N 28.00.

Reaction of phosphorus pentachloride with TMSTMG 2; Formation of bis-N-(N',N',N'',N'''-tetramethyl)guanidinyltrichlorophosphorane 5:

A solution of 4.50 g (24.0 mmol) of TMSTMG **2** in 20 ml of diethyl ether was added at 0°C over 15 h to a suspension of 1.67 g (8.0 mmol) of PCl_5 in 20 ml of diethyl ether. The mixture was stirred for 2 h at 0°C. The precipitate was filtered off, washed with 10 ml of diethyl ether and dried i.v. Yield: 1.96 g (67.0 %), colourless solid, mp.: 114°C. ^{1}H-NMR: δ = 2.68 (s, N($C\underline{H}_3)_2$). ^{13}C-NMR: δ = 40.27 (s, N($\underline{C}H_3)_2$); δ = 159.35 (d, ^{2}J(PC) = 4.14, N=$\underline{C}$<). ^{31}P-NMR: δ = -27.89 (s).

$C_{10}H_{24}Cl_3N_6P$ (365.67); calc.: C 32.85, H 6.62, N 22.98; found: C 32.66, H 7.06, N 22.38.

Reaction of bis-N-(N',N',N'',N''-tetramethyl)guanidinyltrichlorophosphorane 5 with magnesium; Formation of the tris-N-(N',N',N'',N''-tetramethyl)guanidinylphosphonium cation as in 4:

To a suspension of 0.83 g (2.3 mmol) of **5** in 15 ml of THE were added 1 g (41.1 mmol) of magnesium turnings. After 3 h stirring **5** had dissolved and the solution become dark. In the reaction mixture the only phosphorus-containing compound detectable by ^{31}P-NMR was a phosphonium salt, containing the cation of **4**. This salt could not be isolated. ^{31}P-NMR (THF/CH_3CN) : δ = -16.60 (d, $^1J(PH)$ = 541.8)

Reaction of difluorochlorophosphine with HTMG 1a; Synthesis of difluoro-N-(N',N',N'',N''-tetramethyl)guanidinyl-phosphine 6:

A solution of 42.16 g (0.37 mol) HTMG **1a** in 50 ml of diethyl ether was added at -80°C over 3 h to a solution of 19.11 g (0.18 mol) of difluorochlorophosphine in 150 ml of diethyl ether. The mixture was stirred and allowed to warm up to room temperature over a period of 2 h. The precipitate was filtered off and was washed three times with 50 ml of diethyl ether. The solvent was distilled off, and the remaining oil was fractionated at reduced pressure. Yield: 26.7 g (81.0 %), colourless liquid, bp.: 116°C / 9 mm Hg. ^{1}H-NMR: δ = 2.71 (s, $N(C\underline{H}_3)_2$. ^{13}C-NMR: δ = 39.91 (d, $^4J(PC)$ = 3.66, $N(\underline{C}H_3)_2$); δ = 162.22 (m, $N=\underline{C}<$). ^{19}F-NMR: δ = -48.79 (d, $^1J(PF)$ = 1216.29). ^{31}P-NMR: δ = 140.85 (d, $^1J(PF)$ = 1215.9). $C_5H_{12}F_2N_3P$ (183.14); calc.: C 32.79, H 6.60, N 22.94; found: C 33.65, H 6.86, N 23.82.

Reaction of fluorodichlorophosphine with HTMG 1a; Attempted synthesis of fluoro-bis-N-(N',N',N'',N''-tetramethyl)guanidinyl-phosphine

A solution of 4.07 g (0.03 mol) of $PFCl_2$ in 10 ml of diethyl ether was added at -80°C to a solution of 15.5 g (0.13 mol) of **1a** in 30 ml of diethyl ether. The mixture was stirred for 4 h at -80°C and was then allowed to warm up to room temp. over a period of 1 h. The precipitate was filtered off, washed three times with 10 ml portions of diethyl ether and the solvent was removed i.v. In the remaining oil only traces of fluoro-bis-N-(N',N',N'',N''-tetramethyl)guanidinyl-phosphine could be found.

^{31}P-NMR (Toluene) : δ = 135.98 (d, ^{1}J(PF) = 1221.38).

Hydrolysis of difluoro-N-(N' N',N'',N''-tetamethyl)guanidinyl-phosphine 6:

*Reaction of difluoro-N-(N',N,N'',N''-tetramethyl)guanidinylphosphine **6** with excess water; Formation of N',N',N'',N''-tetramethylguanidinium phosphonofluoridate **7**:* To a solution of 0.60 g (3.28 mmol) of **6** in 10 ml of toluene were added 0.5 g (27.8 mmol) of water. The mixture was stirred for 16 h at room temperature. Then the solvent was removed i.v., and the colourless residue was dissolved in 2 ml of CH_2Cl_2. The precipitate that formed after addition of 10 ml of n-hexane was filtered off and was dried i.v. Yield: 0.3 g (45.9 %), colourless solid, mp.: 168 - 174 °C.

^{1}H-NMR: δ = 2.82 (s, 12 H, N(C$\underline{H}_3$)$_2$); δ = 6.74 (dd, ^{1}J(PH) = 663.49, ^{2}J(FH) = 127.78, 1 H, P$\underline{H}$); δ = 8.26 (s, 2 H, $\underline{H}_2$N=C). ^{31}P-NMR: δ = 0.07 (dd, ^{1}J(PF) = 966.2, ^{1}J(PH) = 663.6). $C_5H_{15}FN_3O_2P$ (199.16)

*Hydrolysis of difluoro-N-(N',N',N'',N''-tetramethyl)guanidinyl-phosphine **6** with a substoichiometric amount of water; Formation of tris-N-(N',N',N'',N''-tetramethyl) guanidinylphosphonium pentafluorophosphate **8**:*

A solution of 1.45 g (13.4 mmol) of **6** in 40 ml of toluene was placed in a flask connected via a glass tube to another flask containing a mixture of 2 ml of water and 30 ml of toluene. The crystals that formed after 14 d at room temperature were collected by filtration and were dried i.v. Yield: 0.82 g (36.6 %), colourless crystals, mp.: >85°C (dec.).

^{1}H-NMR: δ = 2.97 (d, ^{5}J(PH) = 0.55, 36 H, N(C$\underline{H}_3$)$_2$); δ = 7.91 (d, ^{1}J(PH) = 538.50, (TMG)$_3$P$\underline{H}$); δ = 5.95 (dquin, ^{1}J(PH) = 953.39, ^{2}J(HF$_{eq}$)*= 127.50, 1 H, $\underline{H}$PF$_5$). ^{31}P-NMR: δ = -16.76 (d, ^{1}J(PH) = 538.6, (TMG)$_3$$\underline{P}$H); δ = -139.70 (ddquin, ^{1}J(PF$_{eq}$)* = 833.6, ^{1}J(PF$_{ax}$)* = 735.6, ^{1}J(PH) = 953.2, H$\underline{P}$F$_5$). FAB-MS: m/z (%) pos.: 374 (100) [HP(TMG)$_3$]$^{+}$, 259 (18) [P(TMG)$_2$]$^{+}$, 189 (17) [Me$_2$NP(TMG)]$^{+}$, 119 (9) [P(NMe$_2$)$_2$]$^{+}$, 116 (9) [H$_2$TMG]$^{+}$, 71 (3) [NCNMe$_2$]$^{+}$, neg.: 127 (100) [HPF$_5$]$^{-}$. $C_{15}H_{38}F_5N_9P_2$ (501.46) {[$C_{15}H_{37}N_9P$]$^{+}$ (374.50) [HPF$_5$]$^{-}$(126.96)} *) F$_{eq}$: F cis to H; F$_{ax}$: F trans to H.

Reaction of dimethylaminodichlorophosphine with HTMG 1a; Formation of dimethylamino-bis-N-(N',N',N'',N''-tetramethyl)guanidinylphosphine 9.

A solution of 5.82 g (0.04 mol) of dimethylaminodichlorophosphine in 50 ml of n-hexane was added over 30 min at 0°C to a solution of 18.3 g (0.16 mol) of HTMG **1a** in 100 ml of n-hexane. The mixture was refluxed for 3 h. After cooling to room temperature the precipitate was filtered off and was washed three times with 20 ml portions of n-hexane. The solvent was removed i.v. and the remaining oil was fractionated twice i.v. Yield: 5.59 g (46.1 %), colourless oil,

bp.: 83°C / 0.6 mm Hg. ^{1}H-NMR (C_6D_6): δ = 2.43 (d, ^{3}J(PH) = 8.84, PN(C$\underline{H}_3$)$_2$); δ = 2.570 (s, br, 6 H, N(C$\underline{H}_3$)$_2$); δ = 2.573 (s, br, 6 H, N(C$\underline{H}_3$)$_2$); δ = 2.67 (s, br, 6 H, N(C$\underline{H}_3$)$_2$); δ = 2.72 (s, br, 6 H, N(C$\underline{H}_3$)$_2$); ^{1}H-NMR (CD_3CN): δ = 2.43 (d, ^{3}J(PH) = 8.84, PN(C$\underline{H}_3$)$_2$); δ = 2.70 (s, 24 H, N(C$\underline{H}_3$)$_2$); ^{31}P-NMR (C_6D_6): δ = 98.99 (s). $C_{12}H_{30}N_7P$ (303.39); calc.: C 47.51, H 9.97, N 32.32; found: C 46.04, H 10.06, N 31.16.

Reaction of dichlorodicyclohexylaminophosphine with TMSTMG 2; Synthesis of chloro-dicyclohexylamino-N-(N',N',N'',N''-tetramethyl)guanidinylphosphine 10:

A solution of 3.25 g (11.5 mmol) of dicyclohexylaminodichlorophosphine in 20 ml of toluene was added at room temperature to a solution of 2.40 g (12.8 mmol) of **2** in 20 ml of toluene. The mixture was stirred for 1 h at room temperature. A small amount of precipitate was filtered off. The solvent was removed i.v. and the oily residue was stirred with 5 ml of n-hexane. The solid thus formed was collected by filtration and was dried i.v. Yield: 2.98 g (71.4 %), colourless solid, mp.: 63°C.

^{1}H-NMR (C_6D_6): δ = 1.02 - 2.13 (m, 22 H, N(C$_6$H$_{11}$)$_2$); δ = 2.57 (s, 12 H, N(C$\underline{H}_3$)$_2$). ^{13}C-NMR (C_6D_6): δ = 26.16 (s, -$\underline{C}$H$_2$-); δ = 27.11 (s, -$\underline{C}$H$_2$-); δ = 39.78 (s, N($\underline{C}$H$_3$)$_2$); δ = 54.64 (s, N-$\underline{C}$H); δ = 161.33 (d, ^{2}J(PC) = 12.84, N=$\underline{C}$<). ^{31}P-NMR (C_6D_6): δ = 157.32 (s). $C_{17}H_{36}ClN_4P$ (362.93); calc.: C 56.58, H 9.50, N 15.52; found: C 56.35, H 9.78, N 15.42.

Reaction of diphenylaminodichlorophosphine with HTMG 1a; Synthesis of chloro-diphenylamino-N-(N',N',N'',N''-tetramethyl)guanidinylphosphine 11:

A solution of 13.4 g (0.05 mol) of diphenylaminodichlorophosphine in 30 ml of toluene was added at room temperature to a solution of 12.05 g (0.1 mol) of **1a** in 70 ml of toluene. The mixture was stirred for 60 h at room temperature. The precipitate thus formed was collected by filtration and was washed with 10 ml of toluene. The solvent was removed i.v. and the oily residue was stirred with 20 ml of n-hexane. The solid thus formed was filtered off, and dried i.v. Yield: 13.56 g (77.8 %), colourless solid, mp.: 48°C.

^{1}H-NMR (C_6D_6): δ = 2.26 (s, 12 H, N(C$\underline{H}_3$)$_2$); δ = 6.92 - 7.61 (m, 10 H, C$_6$H$_5$). ^{31}P-NMR (C_6D_6): δ = 146.74 (s). $C_{17}H_{22}ClN_4P$ (348.81); calc.: C 58.54, H 6.36, N 16.06; found: C 58.32, H 6.66, N 15.41.

X-Ray Structure Determination of 8;

Crystal data of the cation of 8:

$C_{15}H_{37}F_5N_9P_2$, M = 500.48, monoclinic, space group $P2_1/c$, a = 1223.45(10), b = 853.02(8), c = 2492.4(2) pm, β = 102.846(6)°, U = 2.5360(4), Z = 4, D_x = 1.311 $Mg \cdot m^{-3}$, $\lambda(MoK_a)$ = 71.0173 pm, μ = 0.23 mm^{-1}, F(000) = 1060, T = -100°C.

Data collection and reduction:

A colourless prism 0.9 × 0.5 × 0.5 was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 with Siemens LT-2 low temperature attachment). In the 2θ range 6-50° 5468 intensities were registered, of which 4446 were independent (R_{int}=0.013). The cell constants were refined from setting angles of 63 reflections in the 2θ range 6-25°.

Structure solution and refinement:

The structure was solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M.Sheldrick, Universität Göttingen). H atoms were included using a riding model or rigid methyl groups (except PH freely refined). Weighting schemes of the form $w^{-1} = [\sigma^2(F_O^2) + (aP)^2 + bP]$ with $P = (F_O^2 + 2F_c^2)/3$. The final R(F) value was 0.058 with $wR(F^2)$ = 0.184 for all reflections. S = 1.10; max $\Delta/\sigma < 0.001$; max $\Delta\rho$ = 597 $e.nm^{-3}$. The anion was severely disordered and the substituents at P2 were refined as eight (some partially occupied) positions; all significant residual electron density was in the anion region.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 405998.

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