Synthesis of Stable *N′,N′,N′′,N′′*-Tetramethylguanidine-Substituted σ^4(P)- and σ^3(P)-Organophosphorus Compounds with *N*-Protonated P–N Bonds The First σ^3-Phosphorus-Substituted Ammonium Salts☆

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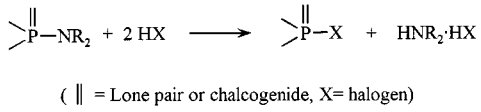
Received December 15, 1997

Keywords: *N′,N′,N′′,N′′*-Tetramethylguanidine / Triphenylmethyl / Phosphorus-substituted ammonium salts / Steric hindrance / Cleavage reactions

The dependence of the protolytic decomposition rate of phosphorus amides on the substituents at phosphorus is decribed. On treatment with HCl, the *N′,N′,N″,N″*-tetramethylguanidine(= TMG)-substituted σ^4(P) compounds **5** and **9** formed salts that were protonated at the imino nitrogen atoms and were completely stable in the solid state, and surprisingly stable in solution. Even with a large excess of HCl, only the imino nitrogen atom underwent protonation, with formation of HCl_2^- as a counter anion, without cleavage of the P–N bond. The basicity of the imino nitrogen atom also protected σ^3(P) species from electrophilic attack, and the ionic compounds **12**, **14**, and **20c** were formed, providing examples of the first stable σ^3(P) amides with one or two protonated P-N bonds. Such unusual stability is associated with steric protection by the Ph_3C (= trityl) group and charge delocalization over the TMG-moiety. In contrast, $MeP(TMG)_2$ was unstable towards HCl, whereas treatment with $HSbF_6$ led to the phosphonium salt **24**, where protonation had occurred at phosphorus. The same result was obtained when triphenylmethylphosphonous dichloride **1** was allowed to react with 3 equivalents of HTMG, forming the stable phosphonium salt **19**, soluble in water, which was converted to the bicationic species **20c** upon treatment with HCl. – The basicity of the tritylated phosphorus compounds was found to increase in the order **5** < **2** < **19** < **13** < HTMG < **21**; the basic centre is the phosphorus atom in **21** and the imino nitrogen atom in all other compounds. The fluorinating agent $Et_3N \cdot 3$ HF caused rapid conversion of compound **6** to **25**, the nucleophilic attack of fluoride ion at phosphorus could not be prevented by the stabilizing effects mentioned. – All compounds were investigated by ^{1}H- and ^{31}P-NMR spectroscopy. The crystal structures of compounds **5**, $Ph_3CP(=O)$-(H)TMG,and **6**, [**5** · 2 HCl], were determined; **6** is protonated at the imino nitrogen, leading to a longer P–N bond [**5**: 161.6(2), **6**: 168.7(2) pm], and the counterion is HCl_2^-. In the structure of **20c**, $[Ph_3CP(TMG)_2] \cdot 3$ HCl, the cation is protonated at both imino N atoms and the counterions are Cl^- and HCl_2^- (one of each).

Introduction

The bond between phosphorus and nitrogen is particularly susceptible to attack by acids; this is exploited in a general method of forming phosphorus halides from the corresponding phosphorus amides (Eq. 1). The hydrolytic cleavage of the P−N bond is complex and takes place under mild conditions to give an ammonium salt and the corresponding phosphorus halide[1][2].



(1)

(‖ = Lone pair or chalcogenide, X= halogen)

Because alkyl groups are the most widely used substituents at nitrogen, and in connection with our own studies on *N′,N′,N′′,N′′*-tetramethylguanidine (TMG)-derivatives[3], we wished to apply the method to TMG-substituted phosphorus compounds. In particular, we wanted to prepare the monochloride of (triphenylmethyl)phosphonous acid **8**, which could, in principle, be formed by the process described in Eq. 1, via compound **5**.

In contrast to expectation, the reaction of **5** with HCl furnished the ionic compound **6**, an intermediate that was reasonably stable in solution and completely stable in the solid state.

Such cases of protonation of the nitrogen atom with preservation of the P−N bond are scarce in the literature. However, a few examples of compounds are known in which the P−N bond was not affected by protonic acids; e.g., Riess et al. were able to isolate stable ammonium salts with tetra- and penta-coordinated phosphorus[4]. Furthermore, Schmidpeter et al. have investigated 5-membered ring systems containing −P=N− moieties, from which stable ammonium salts could also be obtained[6]. However, σ^3(P) compounds with protonated phosphorus-nitrogen single bonds have only been postulated as reaction intermediates[7][8][9][10]. Most reactions of phosphorus amides with protonic acids proceed via protonation at phosphorus, which is due mainly to the nucleophilic character of the phosphorus atom; a few examples of such phosphonium salts with various counterions have been reported[11][12].

Thus, the intermediates formed by HCl attack on TMG-substituted phosphanes need to be identified and investi-

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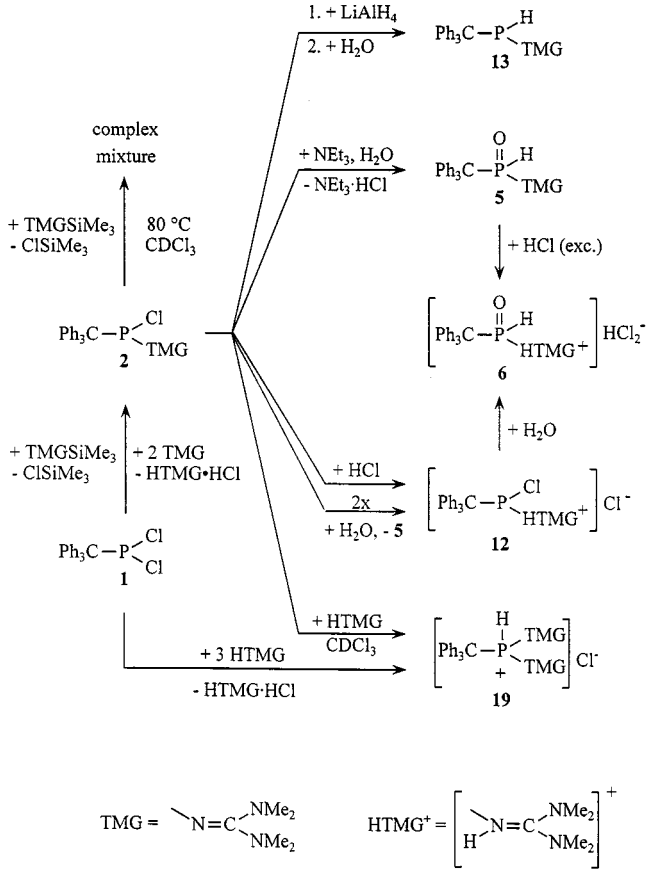
gated with regard to their stability (e.g., by varying the environment of the phosphorus atom). The protolytic stability of the P−N bond must be determined by electronic (a conjugative delocalization of the cationic charge on phosphorus or at TMG) and steric factors (shielding of the phosphorus atom by a bulky substituent). In our investigations we used trityl-TMG substituted phosphorus compounds, which proved suitable in forming intermediates of interest, especially in the acid-catalysed nucleophilic substitution at σ^3(P) amides[8][12][13].

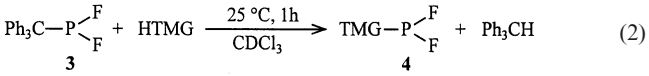
Results and Discussion

The phosphonous dichloride **1**, which has been known since 1933[14], was used as starting material for the preparation of compounds containing the trityl-moiety bonded to phosphorus. It reacted vigorously with 2 equivalents of HTMG, forming compound **2** (Scheme 1).

Scheme 1

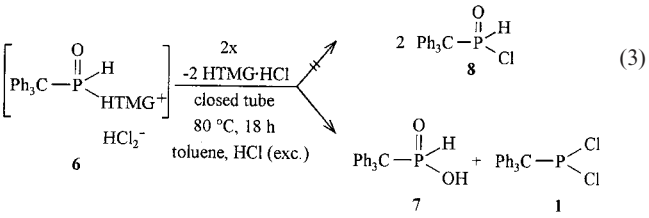


Using the less reactive agent Me_3SiTMG (Scheme 1) partial aminolysis of **1** was also effected. The reaction of triphenylmethylphosphonous difluoride **3** and HTMG, however, involved an unusual preferential cleavage of the phosphorus−carbon rather than the phosphorus−fluorine bond, with formation of the known phosphonous difluoride **4**[15] (Eq. 2); this interesting phenomenon had previously been observed by Nixon in connection with aminolysis reactions of Cl_3CPF_2[16].



(2)

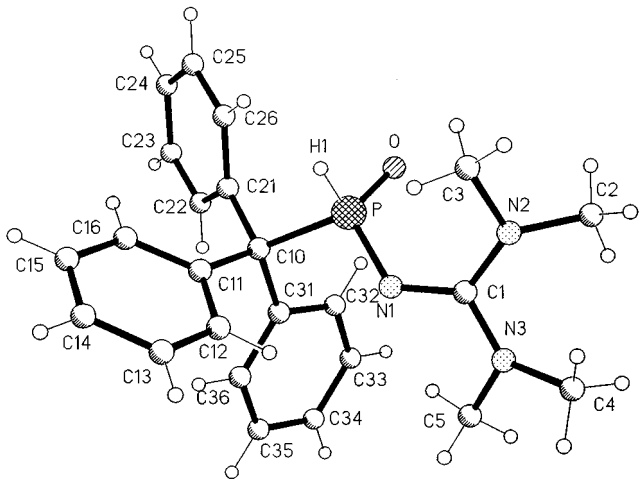
Treatment of **2** with H_2O and NEt_3 led spontaneously to triphenylmethylphosphonous *N′,N′,N′′,N′′*-tetramethylguanidinide **5** (Scheme 1). The attempted preparation of the monochloride of triphenylmethylphosphonous acid **8** using excess HCl led to the hydrogendichloride **6** (formally **5**·2 HCl), which was stable at room temperature and was converted to Ph_3CPCl_2 **1** and $Ph_3CPH(O)OH$ **7** upon heating in excess HCl at 80°C (Eq. 3).



(3)

This result is at variance with the observation that organo(chloro)phosphonous acids are usually stable when they contain sterically demanding substituents[17].

Figure 1. Structure of **5** in the crystal. The solvent has been omitted for clarity[a]

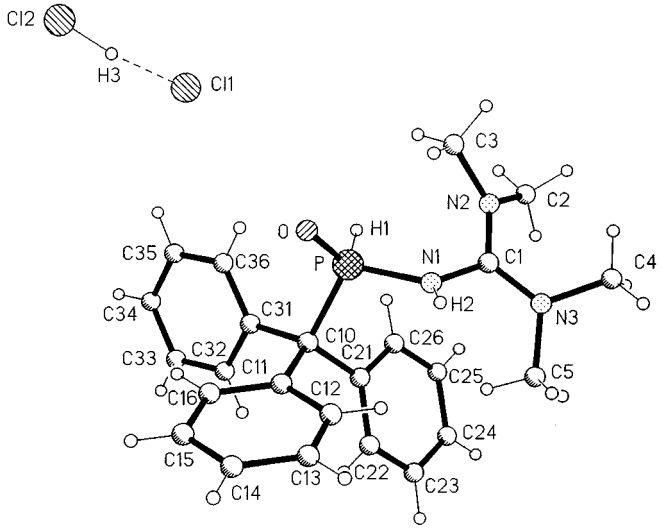


[a] Selected bond lengths [pm] and angles [°]: P−O 148.1(2), P−H(1) 136(2), P−N(1) 161.6(2), P−C(10) 187.5(2), N(1)−C(1) 131.5(3), N(2)−C(1) 137.3(3), N(2)−C(3) 145.5(3), N(2)−C(2) 145.5(3), N(3)−C(1) 134.5(3), N(3)−C(5) 145.0(4), N(3)−C(4) 146.6(4), O−P−N(1) 117.35(11), O−P−C(10) 114.13(11), N(1)−P−H(1) 107.6(9), C(10)−P−H(1) 101.7(9), O−P−H(1) 110.0(9), N(1)−P−C(10) 104.76(11), C(1)−N(1)−P 126.8(2), C(1)−N(2)−C(3) 120.4(2), C(1)−N(2)−C(2) 121.8(2), C(3)−N(2)−C(2) 114.8(2), C(1)−N(3)−C(5) 120.0(2), C(1)−N(3)−C(4) 122.9(2), C(5)−N(3)−C(4) 115.7(2), N(1)−C(1)−N(3) 119.4(2), N(1)−C(1)−N(2) 124.8(2), N(3)−C(1)−N(2) 115.7(2).

Discussion of the X-Ray Structures of 5 and 6

Compound **5** crystallises with half a molecule of dichloromethane (disordered over an inversion centre) in the asymmetric unit. The hydrogen atom H2 of the cation of **6**

Figure 2. Structure of **6** in the crystal[a]



[a] Selected bond lengths [pm] and angles [°]: P−O 147.2(2), P−N(1) 168.7(2), P−C(10) 186.0(2), P−H(1) 132(2), N(1)−C(1) 137.8(3), N(1)−H(2) 90(3), N(2)−C(1) 133.0(3), N(2)−C(3) 145.8(3), N(2)−C(2) 146.7(3), N(3)−C(1) 132.2(3), N(3)−C(4) 145.8(3), N(3)−C(5) 146.6(3), Cl(1)−H(3) 187(3), Cl(2)−H(3) 135(3), O−P−N(1) 112.38(10), O−P−C(10) 113.61(10), N(1)−P−C(10) 108.25(11), O−P−H(1) 114.9(8), N(1)−P−H(1) 103.3(8), C(1)−N(1)−P 126.3(2), C(1)−N(1)−H(2) 114.5(1.7), P−N(1)−H(2) 118.6(1.7), C(1)−N(2)−C(3) 123.5(2), C(1)−N(2)−C(2) 121.2(2), C(3)−N(2)−C(2) 115.2(2), C(1)−N(3)−C(4) 121.6(2), C(1)−N(3)−C(5) 123.1(2), C(4)−N(3)−C(5) 114.9(2), N(3)−C(1)−N(2) 121.6(2), N(3)−C(1)−N(1) 118.8(2), N(2)−C(1)−N(1) 119.6(2), Cl(1)−H(3)−Cl(2) 173(2).

was located at the imino nitrogen N1; this hydrogen and all other non-C-bonded hydrogen atoms of **5** and **6** were refined freely.

The P−O, P−C, and P−H bonds are marginally shorter in **6** than in **5** [**5**: P−O 148.1(2), P−C10 187.5(2), P−H1 136(2) pm; **6**: P−O 147.2(2), P−C10 186.0(2), P−H1 132(2) pm]. The increase in coordination number at the imino nitrogen leads, as expected, to a marked increase in the P−N bond length [**5**: P−N 161.6(2), **6**: P−N 168.7(2) pm]. In compound **5** the imino N−C bond [N1−C1 131.5(3) pm] is naturally shorter than the amino N−C bonds [N2−C1 137.3(3), N3−C1 134.5(3) pm]. In compound **6** the N1−C1 bond [137.8(3) pm] is about 5 pm longer than N2−C1 [133.0(3) pm] and N3−C1 [132.2(3) pm]; this indicates that the positive charge is delocalized over the two dimethylamino groups. The average $N-C_{methyl}$ bond lengths differ insignificantly [**5**: 145.6, **6** 146.22 pm].

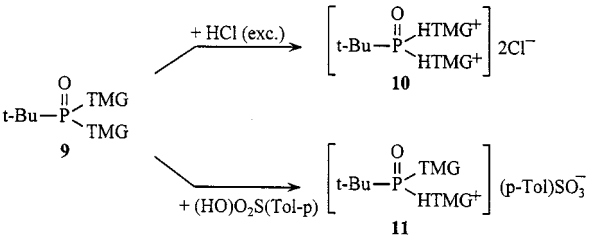
The phosphorus atom, as expected, displays somewhat distorted tetrahedral coordination geometry, with the largest angles involving the doubly bonded O atom. In the case of **5** O−P−N1 [117.35(11)°] is the largest, C10−P−H1 [101.7(9)°] the smallest angle; in **6** O−P−H1 [114.9(8)°] and C10−P−H1 [103.5(8)°].

The counteranion in compound **6** is the hydrogendichloride anion. The angle at H3 is 173(2)°. One Cl−H bond is significantly longer than the other [Cl1−H3 187(3), Cl2−H3 135(3) pm], so the negative charge is mainly located at Cl1. The Cl−Cl distance is 320.8(1) pm, which is normal for hydrogendichloride anions (cf. [(4-$CH_3OC_6H_4$)$(CH_3)PCl_2$] [ClHCl]: Cl···Cl 321.0(3) pm; [(4-$C_2H_5OC_6H_4$)PCl_3] [ClHCl]: Cl···Cl 318.9(1) pm)[18].

The H2 atom forms a hydrogen bond to Cl1 at [1.5 − x, 0.5 + y, −0.5 − z], with the following dimensions: H2···Cl1 237(3) pm, N1···Cl1 321.9(2) pm and N1−H2···Cl1 157(2)°. The H1 atom is linked to O [at 1.5 − x, 0.5 + y, 0.5 − z] via short contacts that may be interpreted as hydrogen bonds [H1···O 255(2), P···O 386.6(2) pm, P−H1···O 170.4(1.2)°].

The formation of compounds **1** and **7** from **6** would appear to be the result of the conversion of $Ph_3CPH(=O)Cl$ **8**, formed as an intermediate by nucleophilic attack of chloride anion on **6**. This process is complex and will be discussed in a subsequent publication.

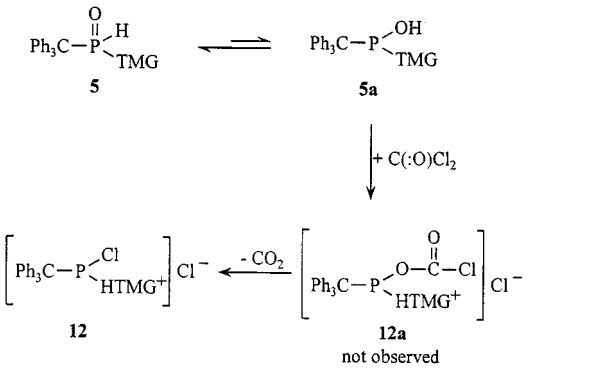
The unusual stability of **6** is caused by the kinetically stabilizing effect of the trityl group[19], and the possibility of charge delocalisation in TMG-substituted phosphorus compounds[3]. The latter might be the reason for the possibility of the isolation of compound **10**, a doubly protonated species whose formation was concluded from analytical data (Eq. 4).



(4)

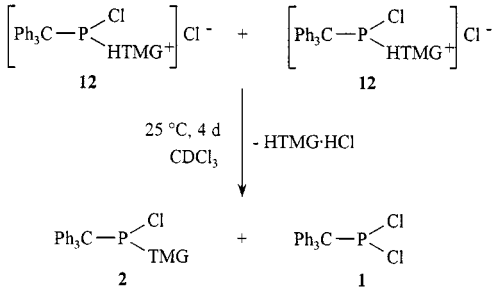
The possibility of rearrangement of the dichloride **10** to the hydrogendichloride in the solid state was considered, in the mass spectrum, from the observation of only the monoprotonated parent ion. The cation **11** was formed in good yield by treatment of **9** with *p*-tolylsulfonic acid. This counterion, of low nucleophilicity, gave rise to additional stabilization, compared to the chloride ion.

The displacement of halogen by water was of particular importance and led, as mentioned above, to compound **5** in the presence of NEt_3, or to a mixture of **5** and **12**, in which a second molecule of **2** acted as a scavenging agent for the HCl liberated (Scheme 1). In the presence of excess water the same treatment afforded compound **6**. Compound **12** was also formed by reaction of **2** with HCl (Scheme 1) and **5** with phosgene (Eq. 5), respectively.



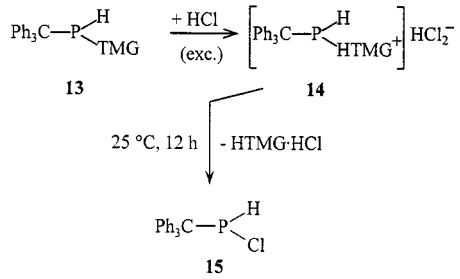
(5)

The latter reaction was preceded by the formation of the tautomeric parent acid **5a**, where the proton was more strongly acidic than in **5**, and the reaction with $C(=O)Cl_2$ took place rapidly. The assumed intermediate **12a** was unstable and was transformed to **12**. This salt was stable as a solid, but in solution slowly decomposed to **1**, **2**, and HTMG·HCl (Eq. 6).



(6)

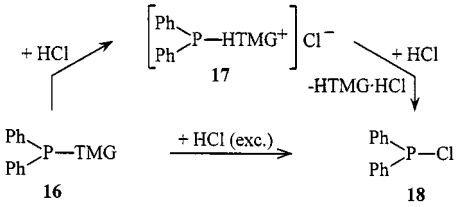
To define the effects causing the unusual stability of **12**, further investigations were conducted that involved variation of the nucleophilicity and steric congestion at the phosphorus atom. Thus, the nucleophilicity of the tritylated phosphorus compounds should increase if the chlorine atom in **2** were substituted by hydrogen. This was realized when **2** was allowed to react with $LiAlH_4$ (Scheme 1). The isolation of **13** was not possible because Ph_3CH was also formed and could not be separated from the reaction mixture. A toluene solution of the resulting crude product was, therefore, treated with excess HCl, and the colourless solid precipitated was identified as the hydrogendichloride **14**, where protonation had occurred at the imino nitrogen atom (Eq. 7).



(7)

The identity of **14** was established by analytical and NMR spectral data, and by its decomposition to triphenylmethylphosphonous chloride **15**. Compounds like **15** are sufficiently stable only in the presence of bulky groups, and only a few examples, mainly referred to as intermediates, are mentioned in the literature[20][21][22]. Compound **15**, which is completely stable, will be described elsewhere in connection with alternative synthetic routes and further investigations.

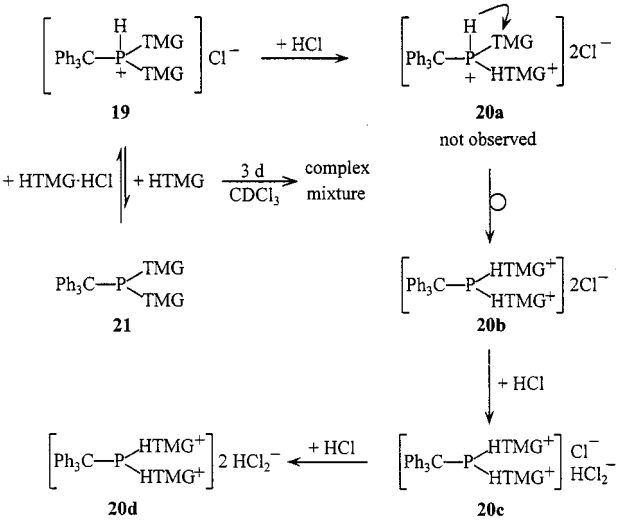
To exclude the steric hindrance effect of the trityl group, the protonation reaction was repeated with compound **16** where, moreover, the nucleophilicity of phosphorus should be higher than in both **2** and **13** (Eq. 8).



(8)

The reaction pathway is not clear. The solid that precipitated from toluene consisted of HTMG·HCl and a phosphorus compound separated that could not be isolated (in a 1:1 ratio). The product soluble in toluene was characterized by ^{31}P NMR as diphenylphosphinous chloride **18**, which was formed as shown (Eq. 8). The precise location of the proton in **17** could not be established, because the ^{1}H NMR resonance of the proton bonded to phosphorus or nitrogen was not observed.

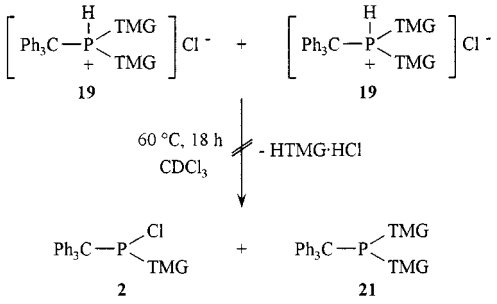
Scheme 2



When the reaction of HTMG with **1** was carried out in a molar ratio 3:1, the final product was the phosphonium salt **19**, which was also obtained when **2** was allowed to react with HTMG (Scheme 1). In both cases, the strongly basic properties of the phosphorus atom of $Ph_3C-P(TMG)_2$ **21** were evident (based on ^{31}P NMR studies). The equilibrium between **19** and **21** was established spontaneously (molar ratio **19/21** = 6:4). After removing the volatile products, the phosphonium salt **19** was isolated.

The isolation of **21** from this equilibrium mixture was, however, not possible. After the components were left in solution in $CDCl_3$ for 3 d, a complex mixture was obtained (Scheme 2). The attempted preparation of **21** via reaction of **2** with Me_3SiTMG was also unsuccessful because under the reaction conditions (temperature ca. 80°C), decomposition with formation of an oily product took place (Scheme 1). The above-mentioned acid-base equilibrium could not be observed when **19** was treated with excess NEt_3. This provides additional evidence of the high basicity of **21**. The basic properties of the phosphorus atom in amino-substi-

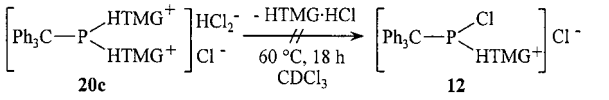
tuted phosphorus compounds are well known[23][24]. However, it should be noted that in the preparation of $RP(TMG)_2$ (R = Me, *t*Bu, and Ph) by treatment of $RPCl_2$ with HTMG (molar ratio: 1:4) these compounds could be obtained readily and in good yield by distillation of the corresponding crude products[3]. The formation of **19** took place quantitatively, but the separation from HTMG·HCl by washing with H_2O resulted in low yields, because **19** also showed hydrophilic properties. The phosphorus atom in $Ph_3C-P(TMG)_2$ seemed to be more basic than the imino nitrogen atom in HTMG and, therefore, **19** showed (in contrast to the conversion of compounds **12** and **14**) no decomposition to the chlorinated compound **2** and the unprotonated species **21**, respectively (Eq. 9).



(9)

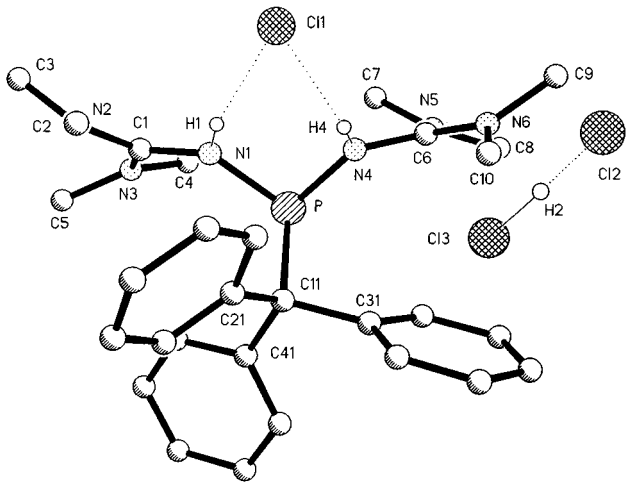
The TMG moieties in $[Ph_3C-PH(TMG)_2]^+$ also were found to display basic properties at the imino nitrogen atoms and additional HCl should lead to a doubly protonated species. Surprisingly, the product resulting from the reaction of **19** with HCl was, instead of the expected compound **20a**, the σ^3(P) compound **20b**, where both imino nitrogen atoms were protonated (Scheme 2).

The migration of the proton in **20a** is caused by the electron-withdrawing effect of the $HTMG^+$ moiety, which is comparable to that of a chlorine atom. The electron density at the phosphorus atom in **20b** is comparable to that in **12**, and a decreasing tendency of electrophilic attack was established by treatment of **20b** with excess hydrogen chloride, leading to HCl_2^- as counter anion. There was no protonation at the phosphorus atom. Treatment of **19** with HCl (ratio 1:1) led to the ionic species **20b** with chloride as counterion. Compound **20b** was insoluble in $CDCl_3$, whereas the corresponding hydrogendichloride **20d** was well soluble in chlorinated solvents and, as expected from its structure, insoluble in nonpolar solvents. The crystals, obtained from the reaction mixture (in CH_2Cl_2/Et_2O, ratio: 7:1) at room temperature by treatment of **19** with HCl (ratio: 1:3), contained both chloride and hydrogendichloride anions (see below). The solubility of this compound (**20c**) lies between that of **20b** and **20d**. Surprisingly, the attempted conversion of **20c** did not afford the expected compounds **12** and HTMG·HCl, and reflected the increasing influence of steric congestion by the second $HTMG^+$ moiety (Eq. 10). Thus, in contrast to **12** and **14**, nucleophilic attack at the phosphorus atom was not possible, even on raising the temperature (60 °C).



(10)

Figure 3. Structure of **20c** in the crystal. Methyl and phenyl hydrogen atoms and solvent have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: P−N(4) 171.7(3), P−N(1) 173.4(2), P−C(11) 195.8(3), N(1)−C(1) 135.4(4), N(1)−H(1) 81.9(40), N(2)−C(1) 133.9(4), N(2)−C(2) 146.1(4), N(2)−C(3) 146.8(4), N(3)−C(1) 133.4(4), N(3)−C(4) 146.1(4), N(3)−C(5) 146.5(4), N(4)−C(6) 135.9(4), N(4)−H(4) 74.4(36), N(5)−C(6) 133.7(4), N(5)−C(7) 146.1(4), N(5)−C(8) 146.8(4), N(6)−C(6) 133.0(4), N(6)−C(10) 145.8(4), N(6)−C(9) 146.3(4), Cl(2)−H(2) 170.1(54), Cl(3)−H(2) 145.5(54), N(4)−P−N(1) 93.07(12), N(4)−P−C(11) 104.53(12), N(1)−P−C(11) 105.30(12), C(1)−N(1)−P 130.2(2), P−N(1)−H(1) 114(3), C(1)−N(1)−H(1) 115(3), C(1)−N(2)−C(2) 121.7(3), C(1)−N(2)−C(3) 120.7(3), C(2)−N(2)−C(3) 115.4(3), C(1)−N(3)−C(4) 123.4(2), C(1)−N(3)−C(5) 121.8(3), C(4)−N(3)−C(5) 114.7(3), C(6)−N(4)−P 124.8(2), P−N(4)−H(4) 119(3), C(6)−N(4)−H(4) 115(3), C(6)−N(5)−C(7) 122.1(2), C(6)−N(5)−C(8) 122.8(3), C(7)−N(5)−C(8) 114.9(2), C(6)−N(6)−C(10) 121.5(2), C(6)−N(6)−C(9) 123.2(3), C(10)−N(6)−C(9) 114.9(2), N(3)−C(1)−N(2) 120.0(3), N(3)−C(1)−N(1) 122.2(3), N(2)−C(1)−N(1) 117.7(3), N(6)−C(6)−N(5) 121.8(3), N(6)−C(6)−N(4) 118.1(3), N(5)−C(6)−N(4) 120.1(3), Cl(2)−H(2)−Cl(3) 177(4).

Discussion of the X-ray Structure of 20c

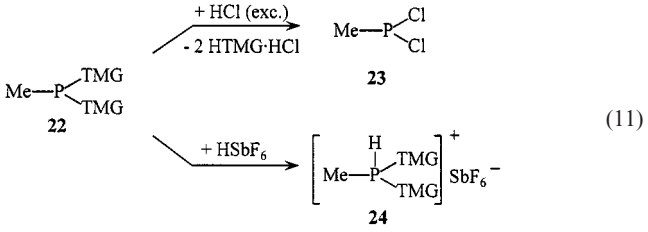
Compound **20c** crystallises as a dichloromethane solvate. All three non-C-bonded hydrogen atoms were refined freely.

The P−N bonds in **20c** [P−N1 173.4(2), P−N4 171.7(3) pm] are longer than those of $Ph_2P(TMG)$ **A**[25] [P−N1 169.6(3) pm]. The N1−C1 [135.4(4) pm] and N4−C6 [135.9(4) pm] bonds are about 5 pm longer [**A**: P−N1 129.3(4) pm], but the amino N−C bonds [133.0(4) (N6−C6) to 133.9(4) (N2−C1) pm] are much shorter than those of **A** [N2−C1 138.2(4), N3−C1 136.4(4) pm]. In compound **20c** the formal imino N−C double bond is longer than the amino N−C bonds, which means that the positive charge is effectively delocalized via π bonding to N2, N3, N5, and N6. The N−methyl bond lengths vary from 145.8(4) pm (N6−C10) to 146.8(4) pm (N2−C2 and N5−C8).

The phosphorus atom displays a pyramidal configuration, lying 82 pm out of the plane of its α-substituents. The smallest angle at phosphorus is between the two TMG substituents [N1−P−N4 93.07(12)°], the angles involving C11 of the triphenylmethyl group are 105.30(12)° (N1−P−C11) and 104.53(12)° (N4−P−C11), respectively. The P−C11 bond [195.8(3) pm] is extremely long.

The hydrogendichloride anion displays dimensions of 145(5) pm (Cl3−H2), 170(5) pm (Cl2−H2), 177(4)° (Cl2−H2−Cl3). The distance between Cl2 and Cl3 is 315.5(1) pm. The other counterion is a chloride ion, which forms hydrogen bonds to both N−H groups; the Cl···H distances are 247(4) pm (Cl1···H1) and 237(4) pm (Cl1···H4).

In compound **22** the steric hindrance effect of the organic group was essentially absent, and treatment with excess HCl afforded the chlorinated product **23**, with no P- or N-protonated intermediates being observed (Eq. 11).



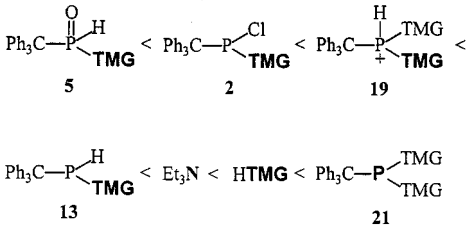
(11)

The ^{31}P-NMR spectrum of the adduct between **22** and $HSbF_6$ also suggested that electrophilic attack on the polar P−N bond led to the phosphonium cation, an intermediate that was stable in combination with weakly nucleophilic anions but not in the presence of chloride ions.

A measure of the relative basicity of compounds **2**, **5**, **13**, and **19** was obtained through the acid-base reactions outlined in Scheme 3.

The basicity of the tritylated compounds increased in the order shown in Figure. 4 (in comparison to HTMG and NEt_3) and, in agreement with this, the acidity of the corresponding acids (**6**, **12**, **20**, **14**, and **19**) increased in the reverse order, as was evident from ^{1}H NMR studies.

Figure 4. The relative basicities of tritylated *N′,N′,N″,N″*-tetramethylguanidino-substituted phosphorus compounds in comparison to NEt_3 and HTMG (**bold print**: main basic centres)



Increasing acidity effects an increasing tendency to proton exchange and influences the observed ^{1}H NMR spectra. Figure. 5 shows the ^{1}H-NMR spectra of **5** observed after interaction with HCl in various ratios (employing the corresponding mixtures of **5** and **6**).

The ^1J(PH) values may be considered as diagnostic of the extent of the protonation of compound **5**, and of the deprotonation of **6**. These values lay between 494 Hz (sharp doublet, compound **5**) and 550 Hz (broad doublet, compound **6**). If the ratio of HCl to **5** was increased to 1:1, HCl_2^- was formed and because of proton exchange processes δ(^{1}H)(P*H*) and ^1J(PH) could not observed. A dynamic phenomenon that can be explained by a fast bond exchange, relative to the NMR time scale, also led to the averaging of the NMR signals in the ^{31}P-NMR spectra and caused the absence of the N*H* proton resonance in the ^{1}H NMR. In contrast, in the ^{31}P-NMR spectra ^1J(PH)-coupling of the phosphorus nuclei of **5** was observed, even in the presence of HCl. The δ(^{31}P) values observed for mixtures of **5** and HCl showed a linear relationship, and ranged between δ = 24.8 (compound **5**) and δ = 27.4 (compound **6**) (Figure. 6).

Scheme 3

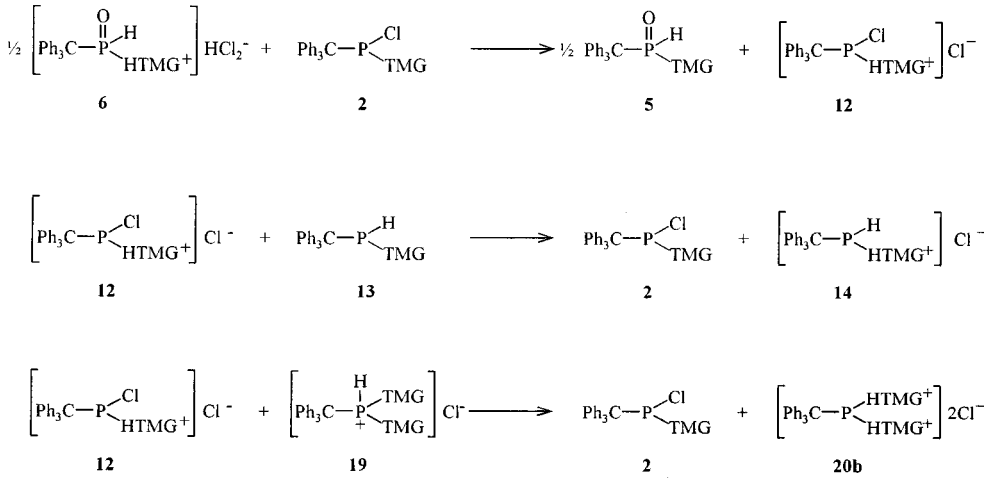


Figure 5. ^{1}H NMR spectra of mixtures of **5** with various ratios of HCl

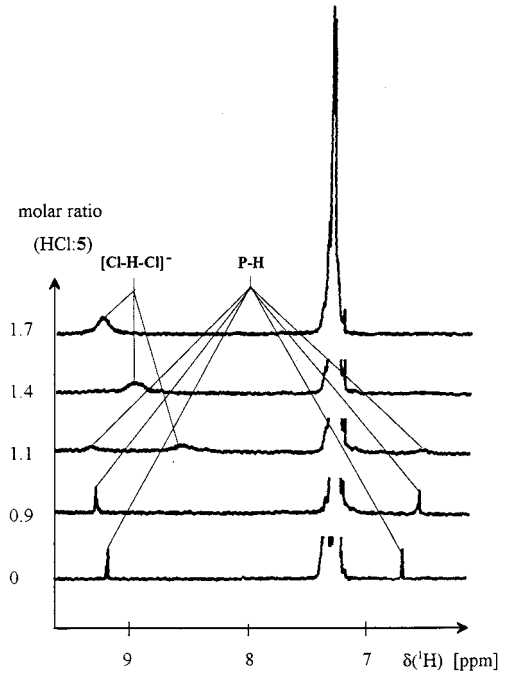
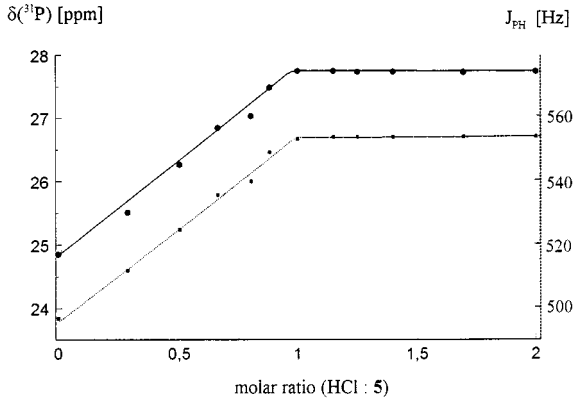


Figure 6. Dependence of $\delta(^{31}P)$ (upper curve) and $^1J(PH)$ (lower curve) of **5** on the degree of protonation at the imino nitrogen atom



The ^{1}H NMR signal of the HCl_2^- proton moved significantly downfield when the proportion of HCl was increased (broad hump at room temperature).

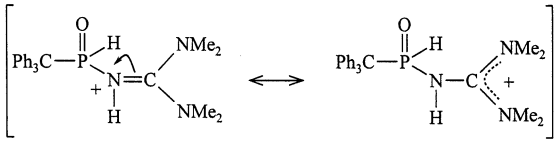
The ^{1}H-NMR spectra of compounds **10**, **11**, and **17** were also influenced by such dynamic phenomena, whereas the NMR spectra of **12** and **14** were more informative, and clear evidence for the presence of hydrogen atoms in both compounds came from ^{1}H-NMR spectra. The increasing basicity in the series led to restricted proton interactions, and the NMR spectra of **12**, **14**, and **20c** exhibited broadened singlets, caused by the protons bonded to the imino nitrogen atoms. Furthermore, in **14** the resonance of the P*H* proton was observed as a broad doublet of doublets, making the accurate determination of $^1J(PH)$ and $^3J(HH)$ impossible. However, the observed value of $J(PH)$ (ca. 235 Hz) is typical of $\sigma^3(P)$ compounds[26], and suggested the structure proposed for **14**.

The restricted proton exchange (as concluded from the ^{1}H-NMR spectra) was also proved by ^{31}P-NMR spectroscopy. Mixtures of compounds **2** and **13** with the corresponding protonated species (**12** and **14**) did not give rise to single averaged peaks. Furthermore, both systems (**2/12**; **13/14**) showed, in contrast to the system **5/6**, separate resonances for the protonated and unprotonated species.

For TMG·HCl, the signals of the $N(CH_3)_2$ protons of all protonated compounds (**6**, **10**, **11**, **12**, **14**, **17**, and **20c**) were shifted downfield, compared to those of the related unprotonated species. All the spectra exhibited sharp singlets, and demonstrated the chemical equivalence of the $N(CH_3)_2$ groups, caused by a three step isomerisation via, a: deprotonation, b: inversion of configuration at the imino nitrogen atom, and c: reprotonation; a mechanism that was reported previously for other TMG-substituted compounds[27][28][29].

In addition to structural parameters (see X-ray studies), the ^{31}P-NMR data also could be used as a sensitive probe to evaluate the electronic structure of the C=N double bond. Surprisingly, the ^{31}P-NMR signals of the protonated $\sigma^3(P)$ species (**12**, **14**, **20c**) were markedly shifted to high field, relative to the corresponding unprotonated compounds (**2**, **13**, **21**). This phenomenon can be rationalized as a consequence of the delocalisation of the positive charge along the $P-N=C(NMe_2)_2$ grouping (Figure. 7).

Figure. 7. Possible charge delocalisation over the TMG moiety (illustrated for molecule **6**)



6

Thus, the ^{31}P-NMR data of the protonated species should generally be comparable to those of the corresponding amino-substituted phosphorus compounds. A compilation of such data is shown in Table 1, supporting this assumption through similar $\delta(^1H)$ values of corresponding N(H)−*t*Bu-substituted phosphorus compounds.

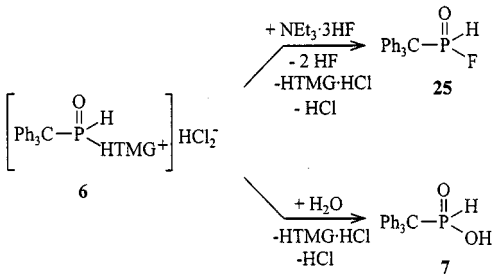
Table 1. $\delta(^{31}P)$ values of unprotonated and protonated tritylated *N′,N′,N″,N‴*-tetramethylguanidino-substituted phosphorus compounds, compared to those of the corresponding *tert*-butyl derivatives

R =	TMG	HTMG⁺	-N(H)t-Bu [30]
$Ph_3C-P(Cl)R$	154.7 ppm **2**	122.1 ppm **12**	129.1 ppm
$Ph_3C-P(=O)(H)R$	24.7 ppm **5**	27.7 ppm **6**	26.3 ppm
$Ph_3C-P(H)R$	33.1 ppm **13**	15.4 ppm **14**	18.7 ppm
Ph_3C-PR_2	114.3 ppm **21**	83.5 ppm **20**	-

The observation that the resonance of the phosphorus atom in **17** was shifted downfield, in the direction of the unprotonated precursor **16**, cannot be explained. Compounds **19** and **24** were characterized from their ^1J(PH) values, which were typical of σ^4(P) compounds[26].

Reactivity of Protonated Compounds

Because of the protonation at the imino nitrogen atom of aminosubstituted trityl-phosphane compounds, the phosphorus becomes more electrophilic and thus more susceptible to nucleophilic attack (e.g. by H_2O). In agreement with this it has been found that the chemical behaviour of protonated species is similar to that of the corresponding halogenated compounds. Thus **6** reacted slowly with H_2O, forming triphenylmethylphosphonous acid **7** (Eq. 12), whereas hydrolysis of the unprotonated compound **5** was not observed.



(12)

However, the sensitivity to nucleophilic attack at the protonated P−N bond of these species appeared to be lower than at the P−Cl bond, because hydrolysis of **12** initially led to the displacement of the chlorine atom (Scheme 1).

The bis(TMG)-substituted phosphorus compound **19** was attacked by H_2O to a lesser extent, forming **6** and additional phosphorus compounds that could not be characterized (decomposition of **19** after 7d at room temperature in dichloromethane and excess H_2O: ca. 10%). Unexpectedly, **20c** was soluble in water, and showed no conversion to the expected compounds (**6** or **7**, and HTMG · HCl). This must be due to steric congestion.

On changing the counterion to F^-, the displacement of $HTMG^+$ took place rapidly. For instance, the reaction of **6** with $NEt_3 \cdot 3$ HF in a 1:1 molar ratio spontaneously led to triphenylmethylphosphonous fluoride **25** (Eq. 12), providing an alternative convenient synthesis to that reported previously[19].

We are grateful to *BASF AG, Bayer AG* and *Hoechst AG* for generous supplies of chemicals used in this research, and to *Fonds der Chemischen Industrie* for financial assistance.

Experimental Section

All experiments were carried out with exclusion of air and moisture; solvents were purified and dried according to the usual methods[31][32]. – NMR spectra were recorded in $CDCl_3$ (unless otherwise noted) at 298 K, using a Bruker AC-200 instrument at 200.1 MHz (^{1}H), 81.3 MHz (^{31}P) and 50.3 MHz (^{13}C) and referenced internally to residual solvent resonances. – Electron impact mass spectra were recorded on solid samples, using a Finnigan MAT 8430 (70 eV) instrument. – Melting points were taken in sealed capillaries and are uncorrected (Instrument: Büchi 510). – IR spectra were recorded on a BIO-RAD IR-165 instrument. – The abbreviation "in vacuo" indicates a pressure of 0.1 mm Hg.

The following compounds were synthesized according to the literature: Ph_3CPCl_2[14], Ph_3CPF_2[19], (*t*Bu)P(=O)(TMG)$_2$[33], Ph_2P(TMG) and MeP(TMG)$_2$[3], Me_3SiTMG[34]. All other compounds were obtained commercially.

Reactions which were investigated solely by ^{31}P-NMR spectroscopy in $CDCl_3$ are not described in the Experimental Section, because the products were synthesized by alternative methods reported in the present work, and also in previous publications.

Chloro Triphenylmethylphosphonous N′,N′,N″,N″-Tetramethylguanidinide (**2**). – *Method A: Reaction of Triphenylmethylphosphonous Dichloride* **1** *with HTMG:* HTMG (1.80 g, 15.64 mmol) was added dropwise with stirring over 10 min at room temperature to a solution of **1** (2.70 g; 7.82 mmol) in 30 ml of dichloromethane. The solvent was evaporated and toluene (50 ml) was added to the residue. The precipitate was filtered off and the solvent from the filtrate was removed in vacuo. The residue was dissolved in 15 ml of dichloromethane and the product was obtained as an amorphous, colourless solid. Yield 2.1 g (63.3%); m.p. 145°C (dec.). – ^{1}H NMR: δ = 2.59 (s, 12 H, N(CH$_3$)$_2$), 7.16−7.37 (m, 15 H, Ph_3C). $C_{24}H_{27}ClN_3P$ (423.92): calcd. C 68.00, H 6.42, N 9.91; found C 67.70, H 6.64, N 9.91.

Method B: From **1** *and* Me_3SiTMG: To a solution of 1.0 g (2.9 mmol) **1** in 7 ml of toluene, 543 mg (2.9 mmol) of Me_3SiTMG was added at room temperature. After 3 h the precipitate was filtered off, washed with 5 ml of diethyl ether and dried in vacuo. Yield 1.03 g (83.9%); m.p. 143°C (dec.).

Triphenylmethylphosphonous N′,N′,N″,N″-Tetramethylguanidinide (**5**): *N′,N′,N″,N″*-Tetramethylguanidine (1.6 g; 13.9 mmol) was added dropwise with stirring over 10 min at room temperature to a solution of **1** (2.40 g, 6.95 mmol) in 40 ml of toluene. To this solution a solution of H_2O (0.5 g; 27.76 mmol) in HTMG (0.8 g; 6.95 mmol) was added with stirring at 0°C during 30 min. The reaction mixture was allowed to reach room temperature and the precipitate was filtered off. The solvent was removed from the filtrate in vacuo, and the product was left as a colourless solid. Yield 2.4 g (85.1%); m.p. 175°C (dec.). – ^{1}H NMR: δ = 2.61 [s, 12 H, N(CH$_3$)$_2$], 7.18−7.35 (m, 15 H, Ph_3C), 7.92 [d, ^1J(PH) = 493.7 Hz, 1 H, PH]. – ^{13}C NMR: δ = 39.73 (s, CH$_3$), 62.96 [d, ^1J(PC) = 90.7 Hz, Ph_3C], 143.25 [d, ^2J(PC) = 3.1 Hz, C_6H_5], 130.73 [d, ^3J(PC) = 6.5 Hz, C_6H_5], 127.88 (s, C_6H_5), 126.45 [d, ^5J(PC) = 2.0 Hz, C_6H_5], 162.58 (s, C=N). – ^{31}P NMR: δ = 24.8 (s). – IR (KBr): ν = 1339 (P=O), 2307 (P−H). – $C_{24}H_{28}N_3OP$ (405.48): calcd. C 71.09, H 6.96, N 10.36; found C 70.53, H 6.91, N 10.04.

[Triphenylmethylphosphonous N′,N′,N″,N″-Tetramethylguanidinide] · 2 HCl (**6**): To a solution of $Ph_3CPH(O)$TMG **5** (1.01 g; 2.5 mmol) in 10 ml of toluene were added at room temperature 3 equivalents of HCl (7.5 ml of a 1 M solution in diethyl ether; 7.5 mmol HCl). The precipitate was filtered off and the product was obtained as a colourless solid. Yield 1.12 g (95.6%); m.p. 220°C (dec.). – ^{1}H NMR: δ = 2.88 [s, 12 H, N(CH$_3$)$_2$], 7.13−7.32 (m, 15 H, Ph_3C), 9.58 (s, 1 H, HCl_2^-), no resonances for P*H* and N*H* were observed. – ^{13}C NMR: δ = 41.65 (s, CH$_3$), 63.32 [d, ^1J(PC) = 77.7 Hz, Ph_3C], 139.12 [d, ^2J(PC) = 2.4 Hz, C_6H_5], 130.38 [d, ^3J(PC) = 7.3 Hz, C_6H_5], 129.02 (s, C_6H_5), 128.04 [d, ^5J(PC) = 2.6 Hz, C_6H_5], 159.65 (s, C=N). – ^{31}P NMR: δ = 27.7 (s). – IR (KBr): ν = 1291 (P=O), 2340 (P−H). – $C_{24}H_{30}Cl_2N_3OP$ (478.40): calcd. C 60.25, H 6.32, N 8.78; found C 60.33, H 6.21, N 8.82.

6 (*Preparation of Crystals*): A solution of $Ph_3CPH(=O)$TMG **5** (1.01 g; 2.5 mmol) in 10 ml of toluene was combined with a solu-

tion of 2 equivalents of HCl (5.0 ml; 5 mmol HCl of a 1 M solution in diethyl ether) in toluene (20 ml). After 4 d the resulting colourless crystals were filtered off. Yield 1.15 g (98.1%).

Decomposition of **6**; *Formation of* **1** *and* **7**: A solution of **5** (1.0 g; 2.5 mmol) in toluene (20 ml) was treated with gaseous hydrogen chloride for (ca.) 2 min but the precipitate (**6**) formed instantaneously was found to be dissolved again after prolonged action of HCl. This solution was heated in a sealed tube for 18 h at 80°C. The solvent was removed in vacuo and the products were characterized by ^{31}P NMR spectroscopy. The data were identical to those of **1** and **7**[19].

[tert-Butylphosphonic Bis(N′,N′,N′′,N′′-tetramethylguanidinide)] · 2 HCl (**10**): Addition of 2 equivalents of HCl (4.52 ml of a 1 M solution in diethyl ether; 4.52 mmol) to a stirred solution of **9** (0.75 g; 2.26 mmol) in toluene (20 ml) at room temperature resulted in a yellow oil. After decanting the solvent the oil was washed with n-hexane (2× 10 ml), was dried in vacuo and **10** was obtained as a colourless solid. Yield 0.89 g (97.3%); m.p. 79°C (dec.). − ^{1}H NMR: δ = 1.42 [d, ^3J(PH) = 18.72, 9 H, PC(CH$_3$)$_3$], 3.21 [s, 24 H, N(CH$_3$)$_2$], no resonance for N(*H*)=C< was observed. − ^{31}P NMR: δ = 31.70 (s). − FAB-MS chemical ionization with nitrobenzyl alcohol (= NBA)]: positive *m/z* (%): 666 (2) [(*t*BuP(=O)(TMG)$_2$·H)$_2$]$^+$, 333 (78) [*t*BuP(=O)(TMG)$_2$·H]$^+$, 218 (100) [*t*BuP(=O)TMG]$^+$, 71 (12) [HNCNMe$_2$]$^+$; negative (*m/z*) (%): 188 (100) [Cl$^-$·NBA]$^-$. − IR (KBr): ν = 1253 (P=O). − $C_{14}H_{35}Cl_2N_6OP$ (405.35): calcd. C 41.48, H 8.70, N 20.73; found: C 41.60, H 8.73, N 20.46.

tert-Butylphosphonic Bis(N′,N′,N′′,N′′-tetramethylguanidinide)] · (p-Tol)SO$_3$H (**11**): A solution of a mixture of **9** (0.45 g; 1.35 mmol) and *p*-toluenesulphonic acid (0.25g; 1.31 mmol) in 10 ml of toluene was stirred at room temperature for 16 h. The oily precipitate formed was separated from the solvent and after washing with n-hexane (two 5 ml portions) **11** was obtained as a colourless solid. Yield 0.62 g (94.5%); m.p. 135°C (dec.). − ^{1}H NMR: δ = 1.23 [d, ^3J(PH) = 16.85, 9 H, PC(CH$_3$)$_3$], 2.31 (s, 12 H, *Me*C$_6$H$_4$SO$_3^-$), 2.98 [s, 12 H, N(CH$_3$)$_2$], 7.10/7.74 [m (AA′XX′), 4 H, MeC$_6$*H*$_4$SO$_3^-$]. − ^{31}P NMR: δ = 20.28 (s). − FAB-MS (NBA): positive *m/z* (%): 333 (86) [*t*BuP(=O)(TMG)$_2$·H]$^+$, 218 (100) *t*BuP(=O)TMG]$^+$, 71 (14) [HNCNMe$_2$]$^+$; negative (*m/z*) (%): 324 (16) [MeC$_6$H$_4$SO$_3$·NBA]$^-$, 171 (100) [MeC$_6$H$_4$SO$_3$]$^-$. − $C_{21}H_{37}N_6O_4PS$ (500.60): calcd. C 50.39, H 7.45, N 16.79, S 6.40; found: C 50.02, H 8.07, N 16.53, S 6.21.

[Chloro Triphenylmethylphosphonous N′,N′,N′′,N′′-Tetramethylguanidinide] · HCl (**12**): − *Method A : Treatment of* **5** *with Phosgene:* A solution of C(=O)Cl$_2$ (0.27 g; 2.7 mmol) in toluene (1.4 ml) was added to a solution of **5** (1.1 g; 2.7 mmol) in toluene (20 ml) at room temperature. After 10 min the evolution of CO_2 had ceased, and the solid product was separated and washed with diethyl ether (10 ml). The product was dried in vacuo and the product was obtained as an amorphous solid. Yield 1.0 g (80.0%); m.p. 168°C (dec.). − ^{1}H NMR: δ = 2.95 [s, 12 H, N(CH$_3$)$_2$], 7.13−7.41 (m, 15 H, Ph$_3$C), 7.85 (s, 1 H, NH$^-$). − $C_{24}H_{28}Cl_2N_3P$ (460.4): calcd. C 62.61, H 6.13, N 9.13; found: C 62.80, H 6.29, N 8.94.

Method B: Treatment of **2** *with HCl:* To a solution of **2** (1.0 g, 2.36 mmol) in 10 ml of toluene was added at room temperature 1 equivalent of HCl (2.36 ml of a 1 M solution in diethyl ether; 2.36 mmol HCl). After 5 min the colourless precipitate of **12** was collected by filtration, washed with diethyl ether (5 ml), and dried in vacuo. Yield 1.0 g (91.7%), m.p. 167°C (dec.).

Method C: Via Hydrolysis of **2**: To a solution of **2** (1.0 g; 2.36 mmol) in 10 ml of toluene were added at room temperature 0.5 equivalents of H_2O (21 mg; 1.18 mmol). After 15 min the colourless precipitate of **12** was collected by filtration, washed with diethyl ether (5 ml), and dried in vacuo. Yield 0.48 g (88.4%), m.p. 166°C (dec.).

Triphenylmethylphosphonous N′,N′,N′′,N′′-Tetramethylguanidinide (**13**): To a solution of 1.3 g (3.1 mmol) of **2** in 20 ml of diethyl ether 0.2 g (5.3 mmol) of LiAlH$_4$ were added at 0°C with stirring. The mixture was allowed to warm up to room temperature and stirring was continued for another hour. The reaction was quenched by addition of water (20 ml), using a water bath for cooling. The precipitate was filtered off and the solvent was removed from the filtrate in vacuo. To the residue 10 ml of diethyl ether was added and the product was obtained as a colourless amorphous substance, containing small amounts of Ph$_3$CH (4%), on cooling this solution to −20°C. Yield 0.81 g (67.8%); m.p. 118°C (dec.). − ^{1}H NMR: δ = 2.55 [s, 12 H, N(CH$_3$)$_2$], 7.25 (s, 15 H, Ph$_3$C), 5.67 (d, ^1J(PH) = 188.4 Hz, 1 H, PH).

[Triphenylmethylphosphonous N′,N′,N′′,N′′-Tetramethylguanidinide]·2 HCl (**14**): To a solution of Ph$_3$CPH(TMG) **13** (0.6 g; 1.5 mmol) in 10 ml of toluene were added at room temperature 3 equivalents of HCl (4.5 ml of a 1 M solution in diethyl ether; 4.5 mmol HCl). The precipitate was filtered off and the product was obtained as a colourless solid. Yield 0.51 g (71.6%); m.p. 145°C (dec.). − ^{1}H NMR: δ = 2.84 [s, 12 H, N(CH$_3$)$_2$], 7.09−7.43 (m, 15 H, Ph$_3$C), 5.81 [dd, 1 H, J(PH) = 235.6 Hz, J(HH) = 4.6 Hz, P-H], 7.99 (m, 1 H, NH), 10.60 (s, 1 H, HCl$_2^-$). − $C_{24}H_{30}Cl_2N_3P$ (462.4): calcd. C 62.34, H 6.54, N 9.08; found C 62.49, H 6.52, N 8.96.

Decomposition of **14**: A 60 mg (0.13 mmol) sample of **14** was dissolved in CDCl$_3$ (0.5 ml) and placed into a 5-mm NMR tube, capped with a rubber septum. The decomposition was monitored by ^{31}P NMR; it was complete after 18 h. Product **15** was characterized by comparison of its ^{1}H and ^{31}P NMR data to those of an authentic sample[30].

[Diphenylphosphinous N′,N′,N′′,N′′-Tetramethylguanidinide] · HCl (**17**): A solution of **16** (0.61 g; 2.01 mmol) in toluene (30 ml) was treated with gaseous hydrogen chloride until precipitation of a colourless solid commenced. The solid product was separated by filtration and investigated by ^{31}P- and ^{1}H-NMR spectroscopy. The spectra indicated a mixture of **17** and HTMG·HCl. In the ^{31}P-NMR spectrum of the filtrate a signal was observed which was due to Ph$_2$PCl [δ(^{31}P) in C$_6$D$_6$ = 82.2[35]]. − ^{1}H NMR: δ = 2.98 [s, 12 H, N(CH$_3$)$_2$], 7.12−7.79 (m, 5 H, C$_6$H$_5$); no resonance for N(*H*)=C< was observed. − ^{31}P NMR: δ = 41.2 (s).

Bis(N′,N′,N′′,N′′-tetramethylguanidino) Triphenylmethyl Phosphonium Chloride (**19**): *N′,N′,N′′,N′′*-Tetramethylguanidine (2.0 g; 17.4 mmol) was added dropwise with stirring over 10 min at room temperature to a solution of **1** (2.0 g, 5.80 mmol) in 20 ml of dichloromethane. After stirring for 0.5h at room temperature the reaction mixture was washed with water (10 ml) and was cooled to 0°C. The dichloromethane layer was separated from the mixture and dried over Na$_2$SO$_4$ (5.0 g). The solvent was removed in vacuo, and the residue was washed with 10 ml of diethyl ether, resulting in a colourless, amorphous substance. Yield 1.59 g (50.9%); m.p. 146°C (dec.). − ^{1}H NMR: δ = 2.70 [s, 24 H, N(CH$_3$)$_2$], 7.05−7.25 (m, 15 H, Ph$_3$C), 8.23 [d, ^1J(PH) = 471.5 Hz, 1 H, PH]. − ^{31}P NMR: δ = 5.1. − $C_{29}H_{40}ClN_6P$ (539.1): calcd. C 64.61, H 7.48, N 15.59; found C 62.19, H 7.63, N 14.24.

[Triphenylmethylphosphonous Bis(N′,N′,N′′,N′′-tetramethylguanidinide)] · 3 HCl (**20c**): To a solution of [Ph$_3$CPH-(TMG)$_2$]$^+$Cl$^-$ (**19**) (0.5 g; 0.93 mmol) in 10 ml of dichloromethane were added at room temperature 3 equivalents of HCl (2.8 ml of a

Table 2. Crystal data of **5**, **6**, and **20c**

	5·0.5 CH_2Cl_2	**6**	**20c**·CH_2Cl_2
Formula	$C_{24.5}H_{29}ClN_3OP$	$C_{24}H_{30}Cl_2N_3OP$	$C_{30}H_{44}Cl_5N_6P$
M_r	447.93	478.38	696.93
Crystal habit	colourless prism	colourless prism	colourless prism
Crystal size (mm)	0.60 x 0.40 x 0.30	0.60 x 0.45 x 0.20	0.80 x 0.65 x 0.20
Temperature (°C)	-130	-100	-130
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Cell constants			
a (pm)	883.9(2)	1271.2(2)	881.6(2)
b (pm)	937.5(2)	913.18(12)	1248.9(3)
c (pm)	1465.4(3)	2134.6(3)	1624.3(3)
α (°)	80.99(3)	90	72.51(2)
β (°)	85.76(3)	95.734(8)	87.95(2)
γ (°)	77.87(3)	90	85.81(2)
U (nm^{-3})	1.1716(4)	2.4656(6)	1.7010(6)
Z	2	4	2
D_X (Mg m^{-3})	1.270	1.289	1.361
μ (mm^{-1})	0.253	0.349	0.504
$F(000)$	474	1008	732
$2\theta_{max}$ (°)	50	50	50
absorption correction	none	none	psi-scans
min. and max. transmission			0.794 and 0.906
No. of refins.:			
measured	4415	4375	8507
independent	4130	4338	6013
R_{int}	0.018	0.034	0.019
$wR(F^2$, all refl.)	0.121	0.090	0.135
$R(F,>4\sigma(F))$	0.049	0.040	0.054
No. of parameters	297	296	399
S	1.04	0.89	1.02
max. Δ/σ	< 0.001	< 0.001	< 0.001
max. $\Delta\rho$ (e nm^{-3})	296	368	1843

1 M solution in diethyl ether; 2.79 mmol HCl). After leaving the resulting solution at room temperature for 18 h the product was obtained as colourless crystals. Yield 0.55 g (84.8%); m.p. 146°C (dec.). – ^{1}H NMR: δ = 2.92 [s, 24 H, $N(CH_3)_2$], 7.06–7.41 (m, 15 H, Ph_3C), 8.55 (s, 2 H, NH), 12.2 (s, 1 H, HCl_2^-). – ^{31}P NMR [a striking solvent effect on δ(^{31}P) was noted]: δ ($CDCl_3$) = 83.5, δ (D_2O) = 61.4, δ (CD_3OD) = 72.5. – $C_{29}H_{42}Cl_3N_6P \cdot CH_2Cl_2$ (696.96): calcd. C 51.70, H 6.36, N 12.06; found C 52.96, H 6.55, N 12.65.

Attempted Preparation of [Methylphosphonous Bis(N′,N′,N″,N″-tetramethylguanidinide)] · 4 HCl; Formation of Methylphosphonous Dichloride (**23**): The reaction was carried out in a manner similar to that for **17**, using $MeP(TMG)_2$ (0.5 g; 1.82 mmol) in toluene (30 ml). The ^{31}P-NMR spectrum of the filtrate exhibited one signal only, which was due to **23** [δ(^{31}P) in C_6D_6 = 191.2][36].

Methyl Bis(N′,N′,N″,N″-tetramethylguanidino)phosphonium Hexafluoroantimonate (**24**): Addition of $HSbF_6$ (0.50 g, 2.11 mmol) to a stirred solution of **22** (0.54 g; 1.97 mmol) in n-hexane (10 ml) at room temperature resulted in a colourless oil. After removal of the solvent, the oil was redissolved in dichloromethane (5 ml) and reprecipitated by addition of *n*-hexane (10 ml). This process was repeated twice, giving only a mixture of **24** and $HSbF_6$. – ^{1}H NMR: δ = 0.81 (s, br, 3 H, PCH_3), 2.61 [s, br, 24 H, $N(CH_3)_2$], 6.82 [d, 1 H, J(PH) = 483 Hz, PH]. – ^{31}P NMR: δ = 17.43 (s).

Attempted Preparation of [Triphenylmethylphosphonous N′,N′,N″,N″-Tetramethylguanidinide] · 2 HF; Formation of Triphenylmethylphosphonous Fluoride (**25**): $Et_3N \cdot 3$ HF (337 mg; 2.1 mmol) was added dropwise with stirring over 2 min at room temperature to a solution of **6** (1.0 g, 2.1 mmol) in 10 ml of dichloromethane. The solvent was evaporated in vacuo, and toluene (20 ml) was added to the residue. The precipitate was filtered off and the solvent from the filtrate was removed in vacuo. The product was obtained as an amorphous, colourless solid. Yield 0.6 g (92.5%); m.p. 159°C (dec.)[19].

Determination of Crystal Structures – Data Collection and Reduction: Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 for **5** and **20c**, Siemens P4 for **6**, both with LT-2 low temperature attachment). The cell constants for **5** and **20c** were refined from ±ω angles of 52 reflections in the 2θ range 20–23°. The orientation matrix for **6** was refined from setting angles of 62 reflections in the 2θ range 5–25° (monochromated Mo-K_α radiation).

Structure Solution and Refinement: The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M.Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups, except for P–H, N–H and Cl–H hydrogens, which were refined freely. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ were employed, with $P = (F_o^2+2F_c^2)/3$. Full details of the crystal structure determinations (except structure factors) have been deposited under the number 100815 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ [Telefax: Int. +44 (0)1223/336–033; E-mail: fileserv@chemcrys.cam.ac.uk.]

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

[1] A. B. Burg, P. J. Slota, *J. Am. Chem. Soc.* **1958**, *80*, 1107–1109.
[2] K. Issleib, W. Seidel, *Chem. Ber.* **1959**, *92*, 2681–2694.
[3] J. Münchenberg, O. Böge, A.K. Fischer, P.G. Jones, R. Schmutzler, *Phosphorus, Sulfur, and Silicon* **1994**, *86*, 103–121.
[4] J. Febvay, F. Casabianca, J. G. Riess, *J. Am. Chem. Soc*. **1984**, *106*, 7985–7986.
[5] F. Bouvier, J.-M. Dupart, J. G. Riess, *Inorg. Chem*. **1988**, *27*, 427–430.
[6] J. H. Weinmaier, J. Luber, A. Schmidpeter, S. Pohl, *Angew. Chem*. **1979**, *91*, 442–443; *Angew. Chem., Int. Ed. Engl*. **1979**, *18*, 412–413.
[7] T. A. van der Knaap, F. Bickelhaupt, *Phosphorus and Sulfur* **1984**, *21*, 227–236.
[8] E. E. Nifantyev, M. K. Gratchev, S. Yu. Burmistrov, L. K. Vasyanina, M. Yu. Antipin, Yu. T. Struchkov, *Tetrahedron* **1991**, *47*, 9839–9860.
[9] A. N. Pudovik, E. S. Batyeva, V.A. Al′fonsov, *Phosphorus, Sulfur, and Silicon* **1990, 49/50**, 221–214.
[10] O. Dahl, *Tetrahedron Lett*. **1982**, *23*, 1493–1496.
[11] E. E. Nifantyev, M. K. Gratchev, S. Yu. Burmistrov, *Phosphorus, Sulfur, and Silicon* **1992**, *70*, 159–174.
[12] E. E. Nifantyev, M. K. Gratchev, *Phosphorus, Sulfur, and Silicon* **1990**, *49/50*, 203–206.
[13] E. E. Nifantyev, M. K. Gratchev, *Uspekh. Khim*. **1994**, *63*, 602–637.
[14] H.H. Hatt, *J. Chem. Soc*. **1933**, 776–786.
[15] J. Münchenberg, unpublished results.
[16] J.F. Nixon, *J. Chem. Soc*. **1964**, 2469–2471.
[17] A.G. Cook, *J. Org. Chem*. **1965**, *30*, 1262–1263.
[18] D. Mootz, W. Poll, H. Wunderlich, H.-G. Wussow, *Chem. Ber*. **1981**, *114*, 3499–3504.
[19] V. Plack, J. R. Goerlich, A. Fischer, H. Thönnessen, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem*. **1995**, *621*, 1080–1092.
[20] C. Couret, J. Escudie, H. Ranaivonjatovo, J. Satge, *Organometallics* **1986**, *5*, 113–117.

  1434–1948/98/0606–0865 $ 17.50+.50/0

[21] J. Satge, J. Escudie, C. Couret, H. Ranaivonjatovo, M. Andrianarison, *Phosphorus and Sulfur* **1986**, *27*, 65−74.
[22] J. Escudie, C. Couret, H. Ranaivonjatovo, J. Satge, *J. Chem. Soc., Chem. Commun.* **1984**, *24*, 1621−1622.
[23] R. D. Kroshefsky, J. G. Verkade, *Inorg. Chem*. **1975**, *14*, 3090−3095.
[24] R. G. Pearson, H. Sobel, J. Songstad, *J. Am. Chem. Soc*. **1968**, *90*, 319−326.
[25] J. Münchenberg, Dissertation, Technische Universität, Braunschweig **1996**.
[26] S. Berger, S. Braun and H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen;* Georg Thieme Verlag, Stuttgart-New York **1994**, Vol. 3, p. 126.
[27] H. Kessler, D. Leibfritz, *Tetrahedron Lett*. **1969**, 427−430.
[28] V. J. Bauer, W. Fulmor, G. O. Morton, S. R. Safir, *J. Am. Chem. Soc*. **1968**, *90*, 6846−6847.
[29] K. Kanamori, J. D. Roberts, *J. Am. Chem. Soc*. **1983**, *105*, 4698−4701.
[30] V. Plack, unpublished results.
[31] Autorenkollektiv, *Organikum*, Reprint of the 15th ed.; VEB Deutscher Verlag der Wissenschaften, Berlin **1977**, p. 783.
[32] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 3rd edn.; Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Paris, Braunschweig, **1988**.
[33] J. Münchenberg, J.R. Goerlich, A.K. Fischer, P.G. Jones and R. Schmutzler, *Z. Anorg. Allg. Chem*. **1996**, *622*, 348−354.
[34] S.C. Chaudhry, D. Kummer, *J. Organomet. Chem*. **1988**, *339*, 241−252.
[35] D. G. Gorenstein, *Progr. NMR Spectrosc***. 1983,** *16*, 1.
[36] D. Houalla, T. Mouheich, M. Sanchez, R. Wolf, *Phosphorus* **1975**, *5*, 229−240.

[97306]