Tris-N-(N',N',N",N"-tetramethylguanidyl)phosphine Oxide – Synthesis and Reaction with Acids

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The phosphoryl compound (O:)P(TMG)$_3$ (TMG = N',N',N",N"-tetramethylguanidyl) (**6**) was synthesized during attempts to obtain the potentially very basic (but still unknown) compound P(TMG)$_3$ (**1**). Its reaction with HCl resulted in the triply protonated species **7**. The crystal structure of compound **7** was determined; it crystallizes as a bis-dichloromethane solvate. Each protonated nitrogen forms a hydrogen bond to one chloride. A series of protonation experiments was conducted in order to test the behaviour of **6** towards weak acids.

Key words: Tetramethylguanidine, Basicity, Phosphine Oxides

Introduction

In our laboratory, we have investigated a variety of TMG-substituted compounds with phosphorus in various oxidation and bonding states; see, *e. g.* [1 – 3]. Of special interest were TMG-substituted compounds involving trivalent phosphorus, as electron-rich systems, due to their lone electron pairs and concomitant high basicity. After the observation of high basicity in the case of $Ph_3CP(TMG)_2$ [3], this basicity would be expected to be higher still in the case of P(TMG)$_3$ (**1**); *cf.* Fig. 1.

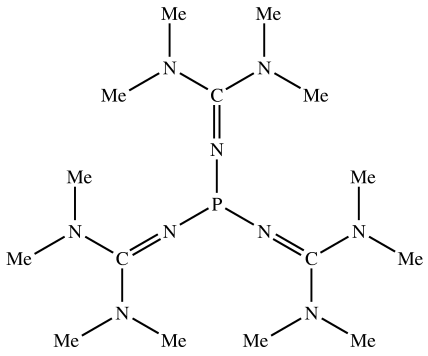

Fig. 1. The hypothetical P(TMG)$_3$ (**1**).

Results and Discussion

The direct reaction of PCl_3 with six equivalents of HTMG (as nucleophilic reagent and HCl-acceptor) gave, because of the basicity of the desired product **1**, only the already known phosphonium salt $[HP(TMG)_3]^+Cl^-$ (**2**), as did the reaction of **1** with LiTMG in the aprotic solvent toluene. Thus, the direct synthesis of **2** in CH_2Cl_2 from PCl_3 and five equivalents of HTMG is easily conducted (Scheme 1).

$$\begin{array}{lllll} PCl_3 & + 6\,HTMG & \rightarrow P(TMG)_3 & + 3\,HTMG\cdot HCl \\ P(TMG)_3 & + HTMG\cdot HCl & \rightarrow [HP(TMG)_3]^+Cl^- & + HTMG \\ \hline PCl_3 & + 5\,HTMG & \rightarrow [HP(TMG)_3]^+Cl^- & + 3\,HTMG\cdot HCl \end{array}$$

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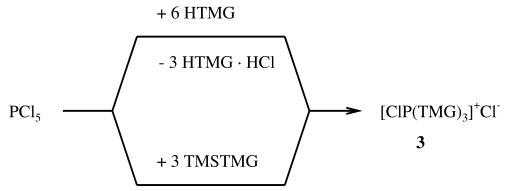
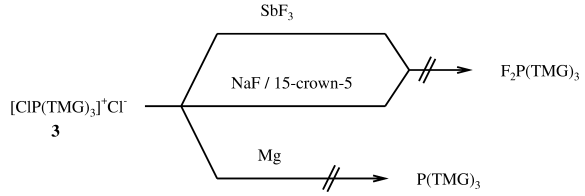
Scheme 1.

Another promising reaction pathway was the reduction of $Cl_2P(TMG)_3$ (**3**). The direct reaction of PCl_5 with six equivalents of trimethylsilyltetramethylguanidine (TMSTMG) in CH_2Cl_2 failed because compound **3** seems to be present as the ionic $[ClP(TMG)_3]^+Cl^-$ in the polar solvent CH_2Cl_2 and could not be separated from the by-product HTMG · HCl. The fluorinated species $F_2P(TMG)_3$ was expected to be covalent and easily separable from HTMG · HCl, but fluorination reactions of **3** with SbF_3 or NaF and 15-crown-5 in acetonitrile were unsuccessful. Finally, pure $[ClP(TMG)_3]^+Cl^-$ could be obtained *via* the reaction of PCl_5 with TMSTMG in CH_2Cl_2 after 1 h in 60% yield, but its reduction with elemental Mg gave an inseparable mixture of several products (Schemes 2 and 3).



Scheme 2.



Scheme 3.

Because it was known that weaker nucleophiles at phosphorus can be displaced by stronger ones, a solution of $P(NEt_2)_3$ was refluxed with an excess of TMG in toluene, but after 2 h only the mono-substituted compound **4** could be identified as a main product *via* ^{31}P NMR spectroscopy (eq. (1)). After 1 d a multitude of products were observed with ^{31}P NMR signals in the region -10 to -100 ppm.

$$P(NEt_2)_3 + HTMG \rightarrow (TMG)P(NEt_2)_2 + HNEt_2 \qquad (1)$$

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In analogy to the known compounds of type $RP(TMG)_2$ with R = Me, *t*-Bu and Ph, the corresponding trityl-substituted compound $Ph_3CP(TMG)_2$ should be accessible from Ph_3CPCl_2 and HTMG, because it is known that in some cases the Ph_3C group can be substituted by the anion of a free base such as HTMG *via* nucleophilic substitution. In the case of $Ph_3CP(TMG)_2$ the basicity of phosphorus was found to be stronger than that of the free base HTMG, so only the phosphonium salt **5**, protonated at phosphorus, was obtained, and a substitution was impossible (eq. (2)).

$$Ph_3CPCl_2 + 3\,HTMG \rightarrow [Ph_3CP(H)(TMG)_2]^+Cl^- + [HTMG]Cl \qquad (2)$$

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In the course of these studies we have, however, obtained the new compound, tris-N(N',N',N",N"tetramethyl)guanidyl phosphine oxide, $(O:)P(TMG)_3$, **6** in the reaction of $P(:O)Cl_3$ with HTMG in dichloromethane (eq. (3)).

$$P(:O)Cl_3 + 6\,HTMG \rightarrow (O:)P(TMG)_3 + 3\,[HTMG]Cl \qquad (3)$$

6

In order to obtain **1**, the reduction of **6** was attempted with $Cl_3SiSiCl_3$, known as a good deoxygenating agent for phosphine oxides, and with $LiAlH_4$, but in both cases only the phosphonium salt $[HP(TMG)_3]^+Cl^-$ could be identified through ^{31}P NMR spectroscopy, among a multitude of products.

Table 1. Hydrogen bonding for **7** [pm, °]; D refers to the donor, A to the acceptor atom.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1···Cl1	84(3)	221(3)	304.8(3)	174(4)
N4-H4···Cl2	85(2)	230(3)	309.3(3)	156(3)
N7-H7···Cl3	84(2)	226(3)	304.9(3)	157(3)
C99-H99A···Cl2	99	260	353.5(4)	157.8
C2-H2A···Cl3	98	272	363.3(4)	154.8
C3-H3A···Cl1$^{\#1}$	98	278	371.1(4)	159.8
C5-H5C···Cl1$^{\#1}$	98	274	362.6(4)	151.0
C99-H99B···Cl1$^{\#2}$	99	274	367.2(4)	158.0

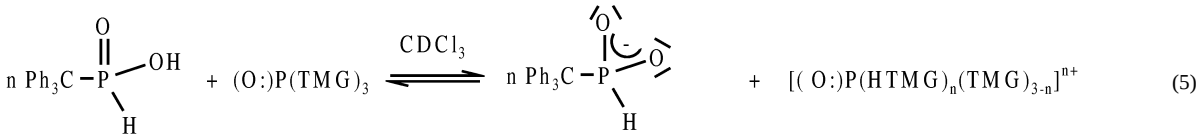
Symmetry transformations for the equivalent atoms: $^{\#1}$ $x, -y+1/2, z+1/2$; $^{\#2}$ $x-1, -y+1/2, z-1/2$.

It was known that TMG-substituted phosphorus compounds are stable towards protonic acids, in that they undergo protonation at the imino nitrogen atoms, rather than the (more common) PN cleavage reaction [5, 6]. This observation was confirmed in the case of **6**; to a solution of **6** in toluene were added two equivalents of a solution (1M) of HCl in diethyl ether (eq. (4)).

$$(O:)P(TMG)_3 + 3\,HCl \rightarrow (O:)P(H^+TMG)_3 \cdot 3Cl^- \qquad (4)$$

6 **7**

Within three days colourless crystals were formed and were characterized by a single crystal X-ray determination (Fig. 2). The crystalline product consisted of $(O:)P(TMG)_3$, protonated at all three imino nitrogen atoms, with three chloride ions (**7**) and two equivalents of dichloromethane per formula unit of **7**. This observation allows the conclusion that the triply protonated species, which was readily precipitated, even when less than the stoichiometrically required amount of HCl was employed, is the most stable in the system. The mother liquor was not investigated further. The hydrogen atoms at the imino nitrogen atoms are involved in hydrogen bonding to the chloride ions. Details of these hydrogen bonds, together with some short non-classical C-H···Cl contacts, are listed in Table 1. The bonds between the imino nitrogen atoms and carbon [N1-C1: 137.0(4) pm, N4-C6: 138.2(4) pm, N7-C11: 138.2(4) pm] are longer than the bonds of the amino nitrogen atoms to the sp^2-hybridized carbon atoms [131.1 4) pm (N9-C11) to 133.2(4) pm (N3-C1)]. This shows that the positive charges are delocalized over the amino nitrogen atoms. The environment at phosphorus is tetrahedral as expected. The largest bond angles involve the doubly bonded oxygen atom [O-P-N1: 111.18(13)°, O-P-N4: 114.70(13)°, O-P-N7:



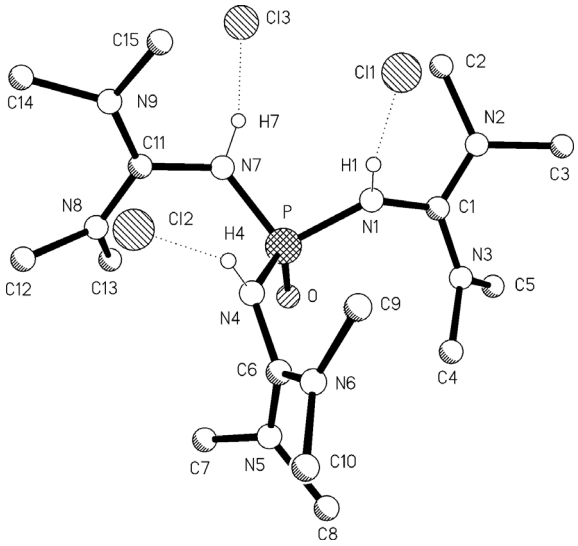


Fig. 2. The structure of compound **7** in the crystal. Solvent molecules and methyl hydrogen atoms are omitted for clarity. The N-H···Cl contacts are dotted. Selected bond lengths (pm) and angles (°):(°): P-O 145.7(2), P-N7 165.8(3), P-N4 166.5(3), P-N1 167.1(3), N1-C1 137.0(4), N2-C1 132.4(4), N3-C1 133.2(4), N4-C6 138.2(4), N5-C6 133.2(4), N6-C6 131.2(4), N7-C11 138.2(4), N8-C11 133.0(4), N9-C11 131.1(4); O-P-N7 120.22(13), O-P-N4 114.70(13), N7-P-N4 100.27(13), O-P-N1 111.18(13), N7-P-N1 100.14(13), N4-P-N1 108.80(14), C1-N1-P 127.1(2), C6-N4-P 126.0(2), C11-N7-P 126.7(2).

120.22(13)°]; the angle N1-P-N7, 100.14(13)°) is the most compressed.

A series of experiments was conducted involving tritylphosphonous acid (**8**) in $CDCl_3$, and monitored by ^{31}P NMR spectroscopy, in order to establish if this relatively weak acid would suffice to protonate the imino nitrogen atoms of **6**, as in the case of HCl (eq. (5)).

The electron-donating TMG group, through the protonation, changes to the electron-accepting $HTMG^+$ group. Therefore, a change is caused in the electronic situation of the molecule, in that the basicity of the remaining TMG group is reduced, possibly to such an extent that it is insufficient to deprotonate the tritylphosphonous acid. During the acid-base reaction tritylphosphonous acid is in equilibrium with the base, $(O:)P(TMG)_3$. The ratio of **8** to deprotonated **8** is revealed through the $^1J_{PH}$ coupling constant in the proton coupled ^{31}P NMR spectrum. This is inversely related to the degree of deprotonation of the acid, allowing conclusions as to the protonation of **6**. The coupling constants vary between 506 Hz (for the completely deprotonated species) and 570 Hz (for the free acid). Table 2 illustrates that it is impossible to stoichiometrically protonate **6** with tritylphosphonous acid.

Table 2. Protonation of **6** with tritylphosphonous acid in different stoichiometric ratio.

Ratio Base	Ratio Acid	^1J(PH) coupling constant (Hz) in the ^{31}P NMR spectra	Degree of deprotonation of $Ph_3CP(:O)(H)(OH)$ (%)	Average number of protonated imino-N-atoms per molecule of **6**
1	1	506.24	100	1
1	2	514.06	88	1.76
1	3	524.76	72	2.16

Experimental Section

Reaction of $P(:O)Cl_3$ with HTMG: formation of **6**

At 0 °C, six equivalents (4.5 g, 39 mmol) of HTMG were added dropwise to a solution of $P(:O)Cl_3$ (1.0 g, 6.5 mmol) in 15 ml of dichloromethane. After 3 h of stirring (magnetic stirrer) at room temperature volatile products were removed *in vacuo* (0.1 mm Hg) from the reaction mixture, the residue was dissolved in toluene. The remaining tetramethylguanidinium hydrochloride was removed by filtration. Removal of the solvent *in vacuo* left 1.8 g of **6** as a colourless solid of m. p. 110 °C.

Yield: 71%. – ^1H NMR: $\delta = 2.75$ (s). ^{31}P NMR: −11.4 (s). EI-MS: *m/z* (%): 389 (100) $[M]^+$, 346 (24) $[M\text{-}Me_2NH]^+$, 275 (20) $[O{=}P(TMG)_2]^+$, 161 (58) $[O{=}P(TMG)]^+$. – $C_{15}H_{36}N_9OP$ (389.49): calcd. C 46.26, H 9.32, N 32.37; found C 47.37, H 9.58, N 31.67.

Reaction of $(O:)P(TMG)_3$ with HCl

A 1 M solution of HCl in diethyl ether (5.1 ml; *ca.* 5.1 mmol of HCl) was added to a solution of 1.0 g (2.56 mmol) of **6** in 10 ml of toluene at room temperature. After 3 d, **7** crystallized from the reaction mixture as colourless needles.

Yield: 0.78 g (60%), m. p. 123 °C (dec.). – ^{1}H NMR: $\delta = 8.81$ (s (br), 3 H, NH), 3.2 (s, 36 H, CH_3). ^{31}P NMR: -15.2 (s). – $C_{15}H_{39}Cl_3N_3OP$ (498.87).

X-ray structure determination of compound **7**

Crystal data: $C_{15}H_{39}Cl_3N_9OP$. 2 CH_2Cl_2, $M = 668.72$, crystal size $0.70 \times 0.40 \times 0.20$ mm, monoclinic, $P2_1/c$, $a = 1123.7(2)$, $b = 2210.5(4)$, $c = 1375.6(3)$ pm, $\beta = 108.44(2)^\circ$, $U = 3.2417(10)$ nm^3, $Z = 4$, $\mu = 0.689$ mm^{-1}, $F(000) = 1400$, $D_x = 1.370$ Mg/m^3, $T = -130$ °C. Reflexions: total 6841 to $2\theta 50^\circ$, unique 5710; R_{int} 0.0364. Final *wR*2 for all reflections 0.1226, $R1(I > 2\sigma(I))$ 0.0491 for 358 parameters and 10 restraints; S1.031, max. $\Delta\rho$ 510 e nm^{-3}.

Data collection and reduction: The crystal was mounted on a glass fibre in inert oil and transferred to the cold gas stream of the diffractometer (STOE Stadi-4 with LT-2 low temperature attachment; monochromated Mo-K_α radiation).

Structure solution and refinement: The structure was solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-97, G. M. Sheldrick, University of Göttingen). Compound **7** crystallizes with two molecules of CH_2Cl_2, one of them disordered over two positions, in the asymmetric unit.

H atoms were included using a riding model or rigid methyl groups, except for the N-H hydrogen atoms, which were found and refined freely. Full details (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Rd., GB-Cambridge CB2 1EZ, under the number 232375. Copies may be obtained free of charge on application to the Director (Telefax: Int. +12 23 33 60 33; e-mail: deposit@ccdc.cam.ac.uk).

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