Reactions of Chlorophosphenium Salts with 1,1,3,3-Tetraalkyl-2-trimethylsilylguanidines. Molecular Structures of New Heterocyclic Systems: [R2NPN{C(NR2)2}]2²⁺ and [R2NP{N[C(NR2)2]}]2AlCl3

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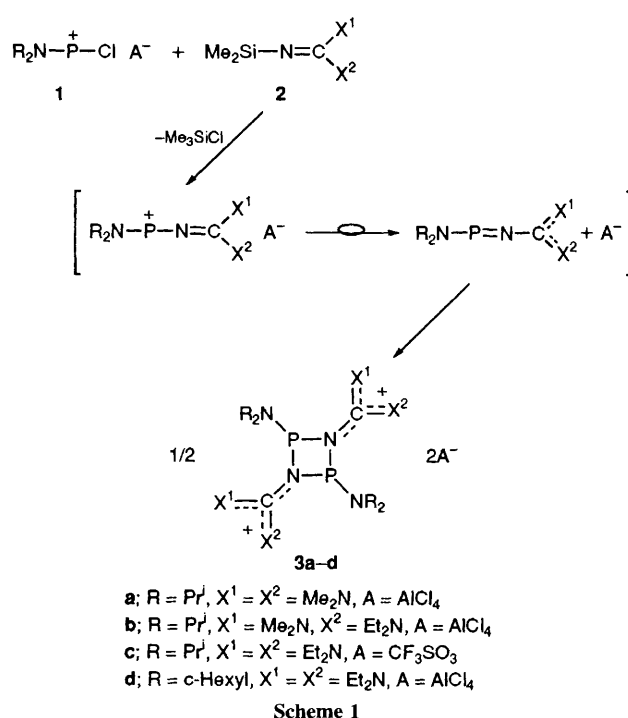
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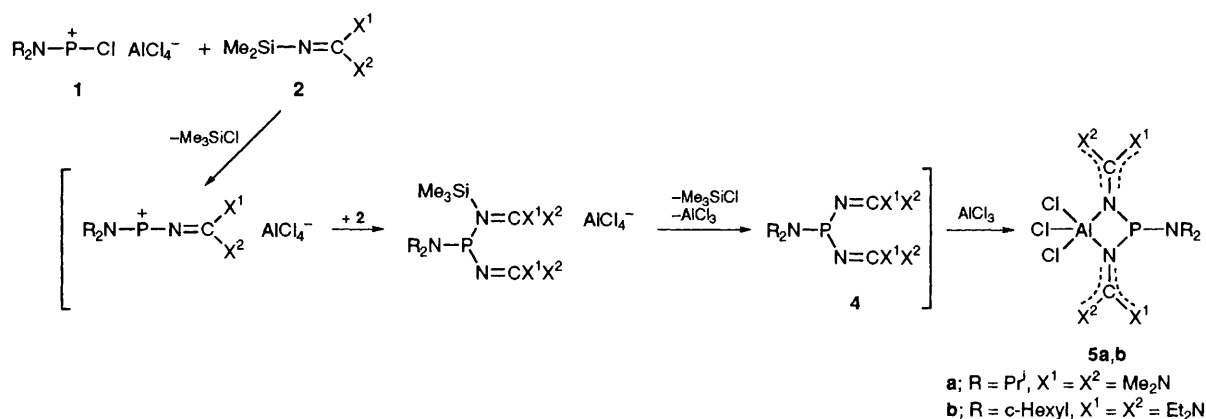
The reactions of phosphenium salts (Cl–P⁺–NR2)A⁻ (A = AlCl4, CF3SO3) 1 with guanidines (R2N)2C=NSiMe3 2 afford dicationic 1,3-bis[bis(dialkylamino)methylene]-1,3-diazonia-2λ³, 4λ³-diphosphacyclobutanes 3 or 1,3-bis[bis(dialkylamino)methylene]-1,3-diazonia-2λ³-phospha-4,4,4-trichloroaluminacyclobutanes 5, depending on the experimental conditions.

P-Functionalized phosphenium salts (X–P⁺–NR2)A⁻ have attracted considerable attention during the last few years, owing to their versatile reactivity.[1] Functionalized phosphenium cations of the type [R$_m$E=E¹(R$_n$)P⁺–NR2] (E, E¹ = main group elements) are particularly interesting because they can exist in two discrete states: as phosphenium ions and as cationic phosphorus-element double-bond species, [R$_m$E⁺-(R$_n$)E¹=P–NR2]. However, despite the intense activity on low-coordinate phosphorus chemistry, there is little information on reactivity of such molecular systems.[2–5]

We now report the first examples of the reactions in which the [X¹X²C=N–P–NR2]⁺ species, generated in situ by the treatment of the P-chlorophosphenium salts 1 with the 2-trimethylsilylguanidines 2 act both as phosphenium ions and as λ³-iminophosphines, to provide access to rare types of molecules containing bis(dialkylamino)methylene-substituted azaphosphacyclobutanes 3.

Depending on the ratio of reactants and the order of mixing, the coupling reactions between 1 and 2 give various products. Slow addition of 1 equiv. of 2 to a CH2Cl2 solution of 1 at −78 °C under an argon atmosphere results in 3 which was isolated as colourless crystalline solid in up to 75% yield. Because the P-chlorophosphenium ions were shown to be very reactive toward compounds with an N–Si bond,[3] the transient formation of the methyleneamino-substituted phosphenium ions and their transformations into λ³-iminophosphines must be postulated in these reactions (Scheme 1).

a; R = Pr^i, X¹ = X² = Me2N, A = AlCl4
b; R = Pr^i, X¹ = Me2N, X² = Et2N, A = AlCl4
c; R = Pr^i, X¹ = X² = Et2N, A = CF3SO3
d; R = c-Hexyl, X¹ = X² = Et2N, A = AlCl4

Scheme 1

Scheme 2

a; R = Pr^i, X^1 = X^2 = Me$_2$N
b; R = c-Hexyl, X^1 = X^2 = Et$_2$N

Compounds **3**† have been characterized by their ^{1}H, ^{31}P and ^{27}Al (or ^{19}F) NMR spectra and the structure **3c** has been determined by single crystal X-ray diffraction analysis. Crystalline **3c** consists of discrete cation and (CF$_3$SO$_3$)$^-$ anion, with no significant interactions between the ions. The cation (Fig. 1)‡ is crystallographically centrosymmetric in consequence of which P$_2$N$_2$ ring is strictly planar; Pr$^i_2$N groups are in *trans* position to each other. The P atom has a pyramidal configuration [the bond angles sum, 289.7(3)°], while all eight N atoms and two carbon atoms [(C(7), C(7)'] are trigonal planar within experimental error. The dihedral angles between the plane of the N$_2$P$_2$ ring and N(2)C(1)C(4), C(7)N(3)N(4) planes are 89.1(3) and 33.2(5)°, respectively. All C–N bonds [1.340–1.361(4) Å] are significantly shorter than usual C(sp^2)–N(sp^2) bond (1,45 Å)^6 indicating that the
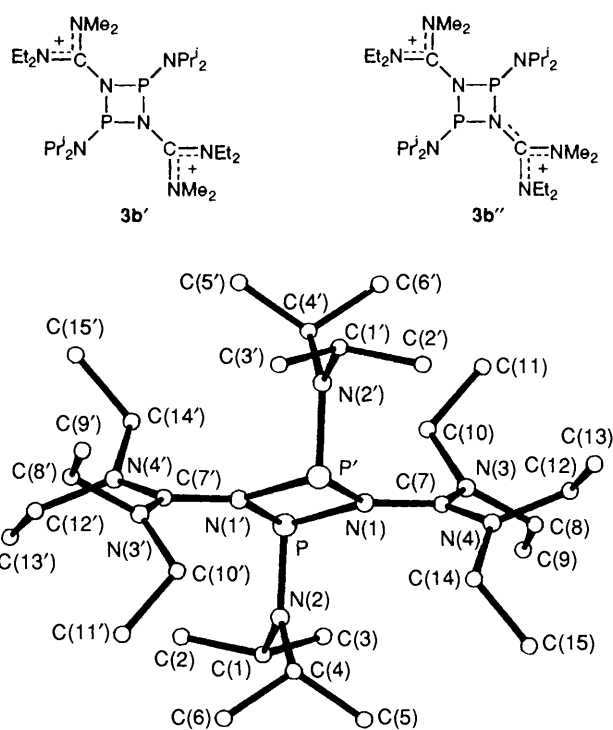

3b'   **3b''**

Fig. 1 Molecular structure of the cation **3c**. Selected bond lengths (Å) and angles (°): P–N(1) 1.780(3), P–N(1') 1.784(3), P–N(2) 1.647(3), N(1)–C(7) 1.361(3), N(2)–C(1) 1.500(3), N(2)–C(4) 1.482(3), N(3)–C(7) 1.340(3), N(4)–C(7) 1.352(4); N(1)–P–N(1') 77.3(1), N(1)–P–N(2) 106.5(1), N(1')–P–N(2) 105.9(1), P–N(1)–P' 102.7(2), P–N(1)–C(7) 129.1(2), P'–N(1)–C(7) 128.3(2), N(1)–C(7)–N(3) 119.9(3), N(1)–C(7)–N(4) 119.7(3), N(3)–C(7)–N(4) 120.5(2).

† **3a**: m.p. 133–135 °C; yield 76%; NMR data: ^{1}H (CD$_3$OD, int. SiMe$_4$) δ 1.24 [d, ^3J(HH) 6.6 Hz, Me$_2$C], 1.50 [d, ^3J(HH) 6.6 Hz, 6 H, Me$_2$C], 3.14 (s, 6 H, Me$_2$N), 3.38 (s, 6 H, Me$_2$N), 3.77 (m, 1 H, CH), 4.15 (m, 1 H, CH); ^{31}P (MeCN, 85% H$_3$PO$_4$) δ 170.8; ^{27}Al [MeCN, Al(H$_2$O)$_3^{3+}$] δ 103.6. **3b**: m.p. 114–118 °C; yield 62%; **3b'**: ^{31}P (MeCN) δ 168.9; ^{27}Al (MeCN) δ 103.6; **3b''**: ^{31}P (MeCN)AB-spin system, δ 168.0 [d, ^2J(P^{A}P^B) 24 Hz, P^A], 169.2 [d, ^2J(P^{A}P^B) 24 Hz, P^B]; ^{27}Al (MeCN) δ 103.6. **3c**: m.p. 150–152 °C; yield 75%; ^{31}P (MeCN): 170.5; ^{19}F (CD$_3$CN, CCl$_3$F) δ −77. **3d**: m.p. 165–168 °C; yield 72%, ^{31}P (MeCN) δ 171.4; ^{27}Al (MeCN) δ 103.6. **5a**: m.p. 177–178 °C; yield 95%; NMR data: ^{1}H (CD$_3$CN, int. SiMe$_4$) δ 1.17 [d, ^3J(HH) 6.6 Hz, 12 H, Me$_2$C], 2.92 (s, 6 H, Me$_2$N), 2.95 (br, s, 6 H, Me$_2$N), 3.18 (br s, 6 H, Me$_2$N), 3.30 (s, 6 H, Me$_2$N), 3.75 (m, 2 H, CH); ^{31}P (CH$_2$Cl$_2$) δ 90.0; ^{27}Al (MeCN) δ 52.1, Δv$_{1/2}$ 272 Hz. **5b**: m.p. 165–168 °C; yield 80%; NMR data: ^{31}P (MeCN) δ 96.5; ^{27}Al(MeCN) δ 52.1, Δv$_{1/2}$ 804 Hz. Satisfactory analytical data have been obtained for compounds **3** and **5**.

‡ *Crystal data* for **3c**: C$_{32}$H$_{68}$F$_6$N$_8$O$_6$P$_2$S$_2$, M = 901.0, monoclinic, a = 9.645(3), b = 11.661(5), c = 21.536(7) Å, β = 101.58(3)°, V = 2372.8 Å^3, Z = 2, D_c = 1.26 g cm^{-3}, space group $P2_1/n$, μ = 2.4 cm^{-1} F(000) = 960, 4853 unique reflection, R = 0.085, R_w = 0.110, GOF = 3.45.

Crystal data for **5b**: C$_{30}$H$_{62}$AlCl$_3$N$_7$P, M = 685.2, monoclinic, a = 15.547(8), b = 19.365(5), c = 26.333(9) Å, β = 101.03 (4)°, V = 7781.6 Å^3, Z = 8 (two independent molecules), D_c = 1.17 g cm^3, space group $P2_1/c$, μ = 3.3 cm^{-1}, F(000) = 2960, 11 632 unique reflection, R = 0.077, R_w = 0.098, GOF = 2.83.

Data were collected on a CAD-4 diffractometer at ambient temperature (18 ± 2 °C) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares calculations. The weighting scheme w = (σ^2F + 0.0016F^2)$^{-1}$ was used. All hydrogen atoms were included in the final refinements with the fixed positional and thermal parameters. Correction for the Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package.^{10} Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

unsaturation is delocalized into the N$_2$CN fragments. Consistent with X-ray data are ^{1}H and ^{31}P NMR spectra which show that the rotation of the X^{1}X^{2}C groups about the P$_2$N–C bonds is hindered at 300 K, and two isomers **3b'** and **3b''** exist at room temp. in a 1 : 1 molar ratio [**3b'** δ(^{31}P) 168.9; **3b''** δ(^{31}P) 168.0 and 169.2; ^2J(PP) 24 Hz].

If the phosphenium salt **1** is slowly added to the guanidine **2**, the reaction proceeds in a molar ratio of 1 : 2 and results in the formation of **5**, which was isolated in the form of air- and thermally-sensitive crystals. Typically, 5 mmol of **1**, dissolved in 10 cm^3 of CH$_2$Cl$_2$, was added at −78 °C to 10 mmol of **2** in 5 cm^3 CH$_2$Cl$_2$. After 3 h, the solvent was removed under vacuum and the residue was purified by recrystallization. The formation of **5** may be interpreted by Scheme 2. The multi-step process apparently involves the preliminary generation of the methyleneaminophosphenium ion, followed by
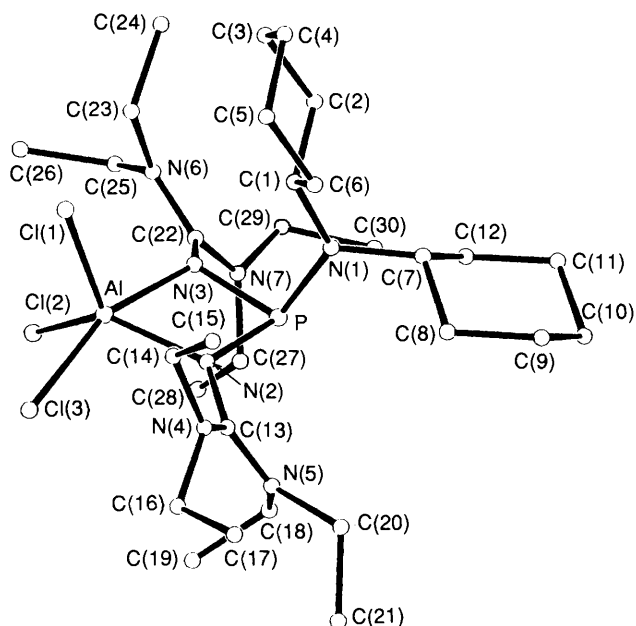
Fig. 2 Molecular structure of one of two crystallographically independent molecules of **5b**. Selected distances (Å) and angles (°) for both molecules: P–N(1) 1.688(5)/1.670(5), P–N(2) 1.747(6)/1.734(5), P–N(3) 1.729(5)/1.741(5), N(2)–C(13) 1.359(8)/1.371(8), N(3)–C(22) 1.337(8)/1.335(8), C(13)–N(4) 1.320(8)/1.311(8), C(13)–N(5) 1.301(8)/1.373(8), C(22)–N(6) 1.353(8)/1.343(9), C(22)–N(7) 1.351(7)/1.373(8), Al–N(2) 1.945(6)/1.937(5), Al–N(3) 2.012(5)/1.963(6), N(2)–P–N(3) 84.3(3)/82.4(3), P–N(2)–Al 102.7(3)/103.2(3), P–N(3)–Al 100.6(3)/101.8(3), N(2)–Al–N(3) 72.2(2)/71.8(2), Cl(3)–Al–N(3) 159.7(2)/151.0(2).

nucleophilic attack of the second equivalent of guanidine on the phosphenium centre and cyclisation of **4** by action of AlCl₃.

The constitution of **5** follows from their NMR data and also from an X-ray structure determination. Although several structures have been reported where the aluminium atom is five-coordinate,[7] the compounds **5** are the first representatives of the PN₂Al cyclic systems with a five-coordinate Al-centre. In the two crystallographically independent molecules of **5b** the PN₂Al rings are folded with dihedral angles of 5 and 10° about N(2)···N(3); otherwise the two cations are essentially identical in structure.

The geometry at Al atom can be described as intermediate between square pyramidal and trigonal bipyramidal. The Al–Cl(3) and Al–N(3) bonds occupy a pseudoaxial position and noticeably elongated as compared with the corresponding pseudoequatorial Al–Cl(1,2) and Al–N(2) bonds. By analogy with **3c** in the molecule **5b** the carbon atoms C(13) and C(22) are sp²-hybridized, as reflected in a planar coordination sphere; the N–C distances reveal a partial double-bond character [1.301–1.373(8) Å, average 1.337 Å]. This finding,

together with the observation that the exocyclic P–N(1) bond is shorter than the intracyclic P–N(2) and P–N(3) bonds indicate a exocyclic delocalization of the positive charge.[8] The ²⁷Al chemical shifts for **5a, b** (δ 52) lie in a range typical for five-coordinate aluminium derivatives.[9]

Finally, it is to be noted that the participation in the reactions under consideration the highly reactive intermediates [(R₂N)₂C=N–P⁺–NR₂] is supported by the fact that attempts of preparing **5** by a stepwise procedure including synthesis of **4** starting from R₂NPCl₂ and **2** followed by treatment of the product with AlCl₃, failed. Even at room temperature the reaction of R₂NPCl₂ with 2 equiv. of **2** proceeded slowly and stopped at the stage of the formation of the corresponding monochlorophosphite; (R₂N)₂C=N–P(Cl)–NR₂; subsequent reaction with AlCl₃ lead to **3** instead of the expected **5**.

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