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Reversible skeletal substitution reactions involving group 13 heterophosphazenes

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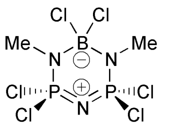
The cyclic boratophosphazene, N(PCl$_2$NMe)$_2$BCl$_2$ 1, reacts with two equivalents of AlMe$_3$ to give the aluminatophosphazene heterocycle, N(PCl$_2$NMe)$_2$AlClMe 4. The unprecedented reverse skeletal substitution (Al for B) was accomplished by treating 4 with Ag[BF$_4$] to form the fluorinated boratophosphazene N(PCl$_2$NMe)$_2$BF$_2$ 5.

Heterocycles which incorporate main group elements within the ring framework are of widespread interest as they often exhibit unusual bonding and structural arrangements,[1] and consequently, novel chemical behaviour.[2] For example, main group heterocycles are attracting attention as potential catalysts,[3] as ligands for transition metals,[4] and as polymer precursors *via* ring-opening polymerization (ROP) processes.[5,6] The development of new and versatile synthetic methods which allow the skeletal structure of inorganic rings to be controlled are therefore of clear importance.

As part of our previous work concerning the ROP of inorganic rings[7] we have explored the chemistry of the boratophosphazene **1**.[8] During the course of our investigations some unusual reactivity was observed.[9] For example, reaction of **1** with halide acceptors (ECl$_3$, E = B, Al and Ga) generated novel planar borazine–phosphazene hybrid cations **2**.[10] Furthermore, the reaction of **1** with silver(I) salts with AsF$_6^-$ and SbF$_6^-$ counter ions resulted in the formation of new heterophosphazenes **3** in which the boron atom in **1** was replaced by arsenic and antimony.[11] Although, examples of such skeletal substitution processes for boron-containing rings are extremely rare,[12] the general synthetic importance of such transformations in organic[13] and inorganic[14] chemistry is clearly evident.



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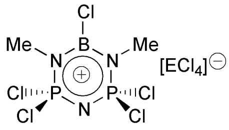

E = B, Al and Ga

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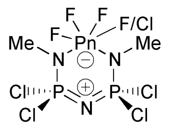

Pn = As and Sb

3

To further explore the scope of the skeletal substitution chemistry of **1**, this species was treated with one equivalent of AlMe$_3$ in toluene. The ^{31}P NMR spectrum of the resulting mixture showed complete conversion of **1** (δ 28.2) to two new products (1 : 1) with upfield-shifted resonances at δ 23.6 and 25.3. As all attempts to separate this mixture were unsuccessful, we subsequently reacted **1** with two equivalents of AlMe$_3$ and observed the appearance of a single resonance in the ^{31}P NMR spectrum at δ 23.6.[15] Removal of the volatiles followed by recrystallization from toluene gave highly air- and moisture-sensitive colorless crystals which did not give a ^{11}B NMR signal,[16] consistent with the absence of boron in this product. The ^{1}H NMR spectrum showed a singlet resonance at δ −0.57 along with a complex multiplet signal centered at δ 2.85, with an integration ratio of 3:6. A similar multiplet is observed for the NMe signal in the boratophosphazene **1** [δ 3.23 (m)][10] and suggested a heterophosphazene ring structure was retained along with the incorporation of an added methyl group. Based on this data, we assigned the structure of the new heterocycle as the aluminatophosphazene **4**. Confirmation of the formation of **4**† was obtained from elemental analysis, mass spectrometry and a single-crystal X-ray diffraction study (Fig. 1).§

The aluminatophosphazene **4** adopts a boat conformation with the tetrahedral Al and two coordinate N(2) atom displaced out of the P$_2$N$_2$ plane by 0.523(2) and 0.265(2) Å, respectively. The P–N bond lengths which flank N(2) [1.563(2) Å av.] are similar to the remaining P–N(Me) bond lengths [1.575(2) Å av.] and suggest some π-bonding occurs throughout the N–P–N–P–N moiety. For comparison, typical P–N bond lengths in [Cl$_3$P=N=PCl$_3$]$^+$ are in the range of 1.51–1.56 Å.[17] The Al–N bond lengths within **4** were identical [1.889(2) Å] and consistent with the presence of Al–N single bonds.[18] The Al–Cl bond, which occupies an axial position, appears to be elongated [2.1613(10) Å] with respect to the Al–Cl distances within most four-coordinate Al species (Al–Cl bond lengths within AlCl$_4^-$ generally range from 2.12 to 2.14 Å).[19] Consequently, abstrac-

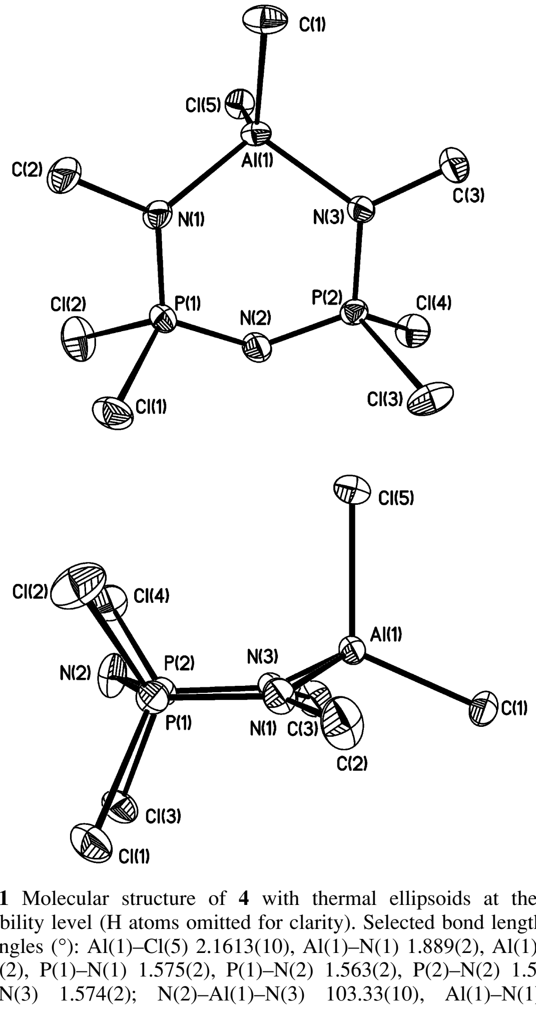

Fig. 1 Molecular structure of **4** with thermal ellipsoids at the 30% probability level (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Al(1)–Cl(5) 2.1613(10), Al(1)–N(1) 1.889(2), Al(1)–N(3) 1.889(2), P(1)–N(1) 1.575(2), P(1)–N(2) 1.563(2), P(2)–N(2) 1.562(2), P(2)–N(3) 1.574(2); N(2)–Al(1)–N(3) 103.33(10), Al(1)–N(1)–P(1) 121.14(13), N(1)–P(1)–N(2) 115.08(12), P(1)–N(2)–P(2) 130.18(16), N(2)–P(2)–N(3) 114.89(12), P(2)–N(3)–Al(1) 121.58(13), C(1)–Al(1)–Cl(5) 114.00(10).

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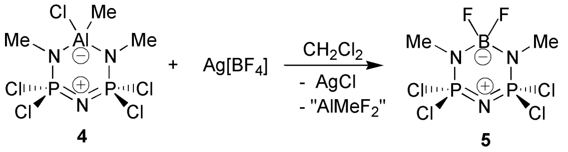

Scheme 1

tion of chlorine from the aluminium center in **4** in a similar manner to the conversion of **1** to **2** seemed feasible.

However, addition of **4** to a solution of Ag[BF$_4$]‡ led to a surprising reaction. Rather than producing the aluminium analogue of the cation in **2**, we observed quantitative formation of the previously known[10] fluorinated boratophosphazene **5** by ^{31}P [δ 28.8 (m)], ^{11}B [δ 0.06 (heptet)] and ^{19}F NMR [δ −147.4 (s)] spectroscopy (Scheme 1). In addition, the resulting white solid possessed ^{1}H and ^{13}C NMR resonances attributable to the formation of **5**. Although no intermediates could be detected when the reaction was monitored by NMR, we have not ruled out the possible formation of an aluminatophosphazene cation and are currently trying to isolate such a species. The above mentioned replacement of B for Al represents, to our knowledge, the first reversible skeletal substitution process for an inorganic ring involving main group elements.

In summary, we have extended the scope of the skeletal substitution chemistry of the boratophosphazene **1** to include the insertion of aluminium for boron to form the novel aluminatophosphazene **4**. Moreover, we report an unprecedented reversible skeletal replacement of B by Al. Studies of the mechanisms of these reactions are in progress.

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Notes and references

† *Synthesis and selected spectroscopic data* for **4**: under strictly anhydrous and anaerobic (N$_2$) conditions, AlMe$_3$ (10.3 mL, 20.6 mmol, 2.0 M solution in toluene) was added dropwise to **1** (3.66 g, 10.2 mmol) in 100 mL of toluene at 0 °C to give a colorless solution. The mixture was allowed to warm to room temperature and was stirred for 5 h. Removal of the volatiles *in vacuo* afforded a white residue. Recrystallization from toluene (2 mL, −30 °C, 12 h) produced large colorless blocks of **4** (2.14 g, 59%). ^{1}H NMR (300 MHz, CDCl$_3$): δ −0.57 (s, AlCH$_3$, 3H) and δ 2.85 (m, NCH$_3$, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 31.1 (m, NCH$_3$); no AlCH$_3$ resonance was observed. ^{31}P NMR (121 MHz, CDCl$_3$): δ 23.6 (s). ^{11}B NMR (96 MHz, CDCl$_3$): no signal detected. MS EI, 70 eV (*m*/*z*, %): 319 (M$^+$ − Cl, 100). mp 66–68 °C. Anal. Calc. for C$_3$H$_9$AlCl$_5$N$_3$P$_2$ (353.3): C, 10.20; H, 2.57; N, 11.89. Found: C, 9.58; H, 2.43; N, 11.51%.

§ *Crystal data* for **4**: C$_3$H$_9$AlCl$_5$N$_3$P$_2$, M = 353.30, monoclinic, space group $P2_1/c$, a = 9.6405(6), b = 7.8844(5), c = 19.1001(12) Å, β = 102.851(3)°, U = 1415.43(15) Å^3, Z = 4, D_c = 1.658 Mg m^{-3}, μ = 1.282 mm^{-1}, F(000) = 704, T = 150(1) K, λ(Mo-Kα) = 0.71073 Å, crystal size 0.40 × 0.30 × 0.30 mm, 3200 independent reflections, 3433 collected. Goodness-of-fit on F^2 = 1.136, final R indices [$I > 2\sigma(I)$], R_1 = 0.0365, wR_2 = 0.0795. Refinement was by full-matrix least squares on F^2 using all data. All hydrogen atoms were included in calculated positions and refined isotropically.

CCDC reference number 179588. See http://www.rsc.org/suppdata/cc/b2/b201582j/ for crystallographic data in CIF or other electronic format.

‡ *Synthesis* of **5**: in the absence of light, **4** (0.094 g, 0.27 mmol) in 1 mL of CH$_2$Cl$_2$ was added to a suspension of Ag[BF$_4$] (0.054 g, 0.28 mmol) in 3 mL of CH$_2$Cl$_2$. The immediate formation of a white precipitate was observed and the reaction mixture was stirred for 16 h. The mixture was filtered and removal of the volatiles provided a white solid (0.050 g, 57%) which was identified as **5** based on NMR spectroscopy.[10]

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