Communications to the Editor

Skeletal Substitution as a Route to New Inorganic Heterocycles: The Unexpected Replacement of Boron in a Borazine-like Environment

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Inorganic rings are of considerable interest due to their intriguing molecular and solid-state structures, bonding, and function as precursors to polymers via ring opening polymerization and to ceramics via pyrolysis.[1–3] Borazines and phosphazenes are among the most well-studied classes of inorganic heterocycles, and both have been found to possess robust ring skeletons. For example, halogenated derivatives permit facile and efficient side-group substitution reactions.[4,5] We recently reported[6] the synthesis of the first example of a well-characterized borazine–phosphazene hybrid, **2**, via halide abstraction with GaCl₃ from the boratophosphazene **1**.[7,8] In our recent studies of the reactivity of the cation we have found that **2** reacts with tertiary amines such as NEt₃ to reform boratophosphazene **1** together with Et₃N·GaCl₃, rather than the expected adduct at boron.[9] This observed reactivity pattern prompted us to explore the possibility of preparing analogues of **2** with alternative, less reactive fluorinated counterions. In
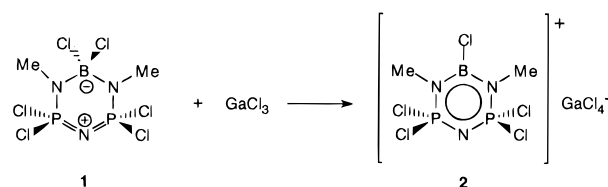
this paper we report the unexpected reactions of **1** with the silver salts Ag[AsF₆] and Ag[SbF₆].

When a solution of **1** was added to Ag[AsF₆] in CH₂Cl₂, the immediate formation of a fine white precipitate of AgCl was observed. After 12 h a pressure buildup was detected. The solution was then decanted, and the solvent removed to yield a white crystalline solid. The product was analyzed by ³¹P NMR in CDCl₃, which showed the presence of a dominant singlet at 30.6 ppm.[10] This resonance was not consistent with the formation of the analogue of **2** with AsF₆⁻ as counterion [for **2**, $\delta(^{31}P, CDCl_3) = 35.0$ ppm]. Remarkably, no nonvolatile boron-containing species were detected by ¹¹B NMR. Colorless crystals were obtained by slow evaporation of solvent from a solution of the product in dichloromethane/hexanes (1:1). A crystal was analyzed by X-ray diffraction, which surprisingly showed the product of the reaction to be the arsenic(V) heterophosphazene **3**.[11–13]
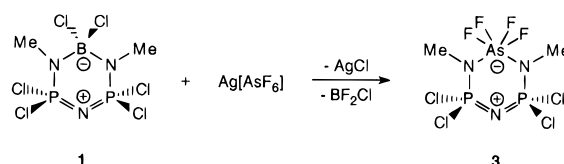
Compound **3** (Figure 1) adopts a boat conformation with As and N(1) removed substantially from the plane of the other four ring atoms. Unlike **1** where one B–Cl bond is highly elongated,[6] all As–F bonds in **3** are equal (1.724(2)–1.735(3) Å) and longer than the As(V)–F bonds in AsF₆⁻ (1.68 Å).[14] The P–N bonds flanking N(1) are shorter (av 1.558(6) Å), than those involving the methyl-substituted nitrogen atoms N(2) and N(3) (av 1.592(5) Å), reflecting a greater degree of π bonding

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(1) See for example: Chivers, T.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **1995**, *117*, 2359. Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144. Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421. Qiao, S.; Hoic, D. A.; Fu, G. *J. Am. Chem. Soc.* **1996**, *118*, 6329. Hasselbring, R.; Roesky, H. W.; Heine, A.; Stalke, D.; Sheldrick, G. M. *Z. Naturforsch.* **1993**, *48b*, 43. Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 6880. Agocs, L.; Burford, N.; Cameron, T. S.; Curtis, J. M.; Richardson, J. F.; Robertson, K. N.; Yhard, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 3225. Beswick, M. A.; Davies, M. K.; Paver, M. A.; Raithby, P. R.; Steiner, A.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1508. Paetzold, P.; von Plotho, C.; Niecke, E.; Rüger, R. *Chem. Ber.* **1983**, *116*, 1678.

(2) See for example: Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106. Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. Sauls, F. C.; Interrante, L. V. *Coord. Chem. Rev.* **1993**, *128*, 193. Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 806. Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Paine, R. T.; Sneddon, L. G. In *Inorganic and Organometallic Polymers II*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds. *ACS Symp. Ser.* **1994**, *572*, 358.

(3) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1602. Manners, I. *Adv. Mater.* **1994**, *6*, 68. Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. Ni, Y.; Lough, A. J.; Rheingold, A. L. Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998.

(4) Maringgele, W. In *The Chemistry of Inorganic Homo and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 1, Chapter 2.
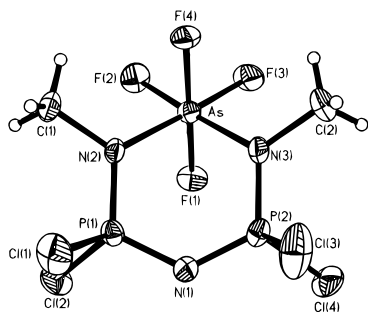
(5) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972; Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.

(6) Gates, D. P.; Ziembinski, R.; Rheingold, A. L.; Haggerty, B. S.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2277.

(7) Binder, H.; Palmtag, J. *Z. Naturforsch.* **1979**, *34b*, 179.

(8) For early work on boron–nitrogen–phosphorus rings see: Sherif, F. G.; Schmulbach, C. D. *Inorg. Chem.* **1966**, *5*, 322. Becke-Goehring, M.; Müller, H. *Z. Anorg. Allg. Chem.* **1968**, *362*, 51.

(9) Both products were analyzed by X-ray crystallography which confirmed the presence of **1** and Et₃N·GaCl₃. The presence of **1** was also detected by ³¹P NMR. Gates, D. P.; Lough, A. J.; Manners, I. Unpublished results.

(10) A minor impurity with a singlet ³¹P NMR resonance at 16.7 ppm was isolated and found to contain the cation [MeHN(Cl)₂P=N=P-(Cl)₂NHMe]⁺ by comparison of the ³¹P and ¹H NMR spectra with that of [MeHN(Cl)₂P=N=P(Cl)₂NHMe]⁺[BCl₄]⁻ which is an intermediate in the synthesis of **1**.

(11) For both structures, Siemens P4 diffractometer with graphite monochromator, Mo Kα (λ = 0.710 73 Å), colorless crystals mounted in capillaries (**3**, 0.30 × 0.20 × 0.20 mm; **4**, 0.20 × 0.20 × 0.20 mm), semiempirical absorption corrections applied. Solution by direct methods, non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms fixed and idealized.

(12) Crystal data for **3** (yield 51%): $P2_1/c$, $a = 6.424(5)$ Å, $b = 12.531(8)$ Å, $c = 16.129(3)$ Å, $\beta = 95.90(3)°$, $V = 1291(1)$ Å³, $Z = 4$, $\mu = 37.30$ cm⁻¹, $\delta_{calcd} = 2.195$ g cm⁻³, 298(2) K. Of 3191 reflections collected (2.06 ≤ 2θ ≤ 25°) 2265 were independent ($R_{merg} = 0.0393$) and 2265 were observed with $F_o \geq 4\sigma(F_o)$. $R = 0.0335$, $wR2 = 0.0804$, GOF = 1.117, $N_o/N_v = 15.5$, and $\Delta\rho_{max} = 0.446$ eÅ⁻³. Crystal data for **4** (yield 75%): $P2_1/n$, $a = 6.447(2)$ Å, $b = 17.517(5)$ Å, $c = 12.535(3)$ Å, $\beta = 97.09(4)°$, $V = 1404.3(8)$ Å³, $Z = 4$, $\mu = 31.57$ cm⁻¹, $\delta_{calcd} = 2.320$ g cm⁻³, 233(2) K. Of 2419 reflections collected (2.01 ≤ 2θ ≤ 22.5°) 1789 were independent ($R_{merg} = 0.0388$) and 1783 were observed with $F_o \geq 4\sigma(F_o)$. The chlorine on antimony is occupationally disordered as chlorine/fluorine (85:15), modeled as an undersized chlorine atom, and labeled Clf. $R = 0.0340$, $wR2 = 0.0855$, GOF = 1.007, $N_o/N_v = 12.1$, and $\Delta\rho_{max} = 0.870$ eÅ⁻³.

(13) Mass spectrometric analysis of **3** supports the X-ray results with the identification of a molecular ion M⁺ with the expected isotope pattern. See the Supporting Information for details.

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1.

Figure 1. Crystal structure of **3**. Selected bond lengths [Å] and angles [deg]: P(1)−N(1) 1.555(4), P(2)−N(1) 1.562(4), P(1)−N(2) 1.589-(4), P(2)−N(3) 1.595(4), N(2)−As 1.907(3), N(3)−As 1.903(4); P(1)−N(1)−P(2) 124.8(2), N(1)−P(1)−N(2) 114.5(2), N(1)−P(2)−N(3) 114.6 (2), P(1)−N(2)−As 121.3(2), P(2)−N(3)−As 121.5(2), N(2)−As−N(3) 93.3(2).

in the former bonds. The As−N bond lengths (av 1.905(6) Å) are similar to the longest bonds found in the cyclodiars(V)-azane [(CF$_3$)$_2$ClAsNSiMe$_3$]$_2$ [As−N = 1.933(7) Å],[15] and are longer than the As−N multiple bonds in the arsazene [NAsPh$_2$]$_3$ (av 1.758(4) Å).[16]

Skeletal substitution reactions of an atom in an inorganic ring are extremely rare, and to the best of our knowledge, are unprecedented for boron-containing rings.[17,18] Moreover, we assume that the cation of **2** is formed initially in the reaction mixture containing **1** and Ag[AsF$_6$] and the subsequent skeletal replacement of boron in a borazine-like environment would be highly unexpected. It is also noteworthy that AsF$_6^-$ is often used as a "noncoordinating" anion to isolate very reactive cations. Remarkably this anion appears to react readily with the borazine−phosphazene cation in **2**. We believe that the thermodynamic driving force for the observed reaction is the formation of B−F bonds from As−F bonds (B−F, 613 ± 53 kJ/mol; As−F, ca. 406 kJ/mol)[19] and the subsequent elimination of volatile BF$_x$Cl$_{3-x}$.

To explore the generality of this new synthetic procedure, we have also studied the reaction of **1** with Ag[SbF$_6$]. Again,

(15) Roesky, H. W.; Bohra, R.; Sheldrick, W. S. *J. Fluorine Chem.* **1982**, *22*, 199.

(16) Krannich, L. K.; Thewalt, U.; Cook, W. J.; Jain, S. R.; Sisler, H. H. *Inorg. Chem.* **1973**, *12*, 2304.

(17) Binder has considered as a possibility the replacement of a skeletal boron atom by phosphorus in the reaction of **1** with PCl$_5$. However, no convincing structural evidence was provided. See: Binder, H.; Palmtag, J. *Z. Naturforsch.* **1979**, *34b*, 179 (see p 180).

(18) Previous examples of skeletal replacement in inorganic rings include the reactions of titanocene chalcogenide heterocycles with group 16 dihalides to form rings where titanium has been replaced by a chalcogen atom (Steudel, R. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; Vol. 14, p 233), and the use of zirconocene-containing metallacycles to prepare various main-group heterocycles (Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310). In addition, trans-metalation reactions of SnS$_2$N$_2$ rings with Pt complexes to yield PtS$_2$N$_2$ rings have been observed (Jolliffe, J. M.; Kelly, P. F.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2179).

(19) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper-Collins: New York, 1993.
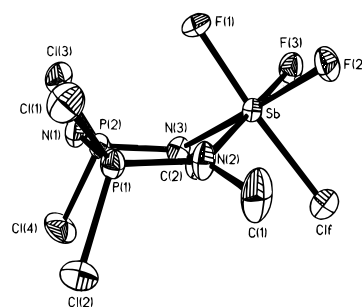
an immediate white precipitate of AgCl formed, and a pressure buildup was detected. After workup, a crystalline solid (**4**) was obtained, and analysis by ^{31}P NMR in CDCl$_3$ revealed two dominant resonances at 28.9 and 27.5 ppm. This is consistent with skeletal replacement of boron but suggests that more than one product is obtained from this reaction. Mass spectral analysis indicated that both **4a** and **4b** were formed, which was confirmed by X-ray crystallographic analysis.[11,12]
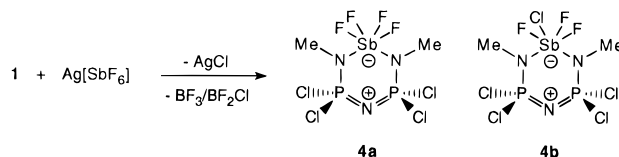
The molecular structure of **4a** and **4b** (Figure 2) confirms the replacement of the skeletal boron atom by antimony(V). Both compounds cocrystallize, and there is occupational disorder of the atom labeled Clf (fractional occupancy Cl:F = 85:15). This structure is similar to that of **3**, where the ring also adopts a boat conformation. It is noteworthy that both **3** and **4** represent rare examples of heterophosphazenes containing high oxidation state group 15 elements beyond the first row.[20]

In summary, we report the unexpected skeletal substitution of boron in a normally highly robust borazine-like environment. Further work is underway aimed at studying the mechanism and exploring the generality of this new class of reaction.

Supporting Information Available: Experimental details and spectroscopic data for **3** and **4** and tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **3** and **4** (12 pages). See any current masthead page for ordering and Internet access instructions.

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(20) For a recent attempt to prepare an antimony(V) heterophosphazene, see: Forster, G. E.; Begley, M. J.; Sowerby, D. B. *Polyhedron* **1996**, *15*, 2151.

Figure 2. Crystal structure of **4**. Selected bond lengths [Å] and angles [deg]: P(1)−N(1) 1.562(6), P(2)−N(1) 1.557(6), P(1)−N(2) 1.581-(6), P(2)−N(3) 1.588(6), N(2)−Sb 2.064(6), N(3)−Sb 2.081(5); P(1)−N(1)−P(2) 128.1(4), N(1)−P(1)−N(2) 113.8(3), N(1)−P(2)−N(3) 114.0 (3), P(1)−N(2)−Sb 122.1(3), P(2)−N(3)−Sb 120.4(3), N(2)−Sb−N(3) 92.2(2).