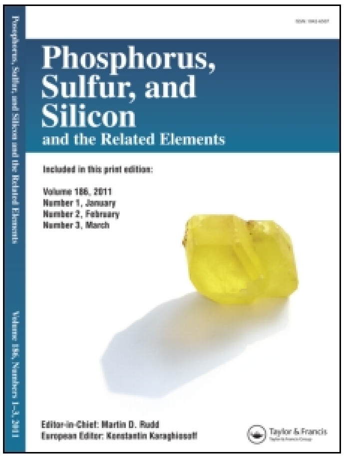


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REVERSIBLE SKELETAL SUBSTITUTION REACTIONS INVOLVING GROUP 13 HETEROPHOSPHAZENES

Eric Rivard[a]; Andrew R. McWilliams[a]; Alan J. Lough[a]; Ian Manners[a]
[a] University of Toronto, Toronto, Ontario, Canada

To cite this Article Rivard, Eric , McWilliams, Andrew R. , Lough, Alan J. and Manners, Ian(2004) 'REVERSIBLE SKELETAL SUBSTITUTION REACTIONS INVOLVING GROUP 13 HETEROPHOSPHAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 845 — 847

To link to this Article: DOI: 10.1080/10426500490427312

URL: http://dx.doi.org/10.1080/10426500490427312

Phosphorus, Sulfur, and Silicon, 179:845–847, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427312

REVERSIBLE SKELETAL SUBSTITUTION REACTIONS INVOLVING GROUP 13 HETEROPHOSPHAZENES

Eric Rivard, Andrew R. McWilliams, Alan J. Lough, and Ian Manners
University of Toronto, Toronto, Ontario, Canada

(Received August 17, 2003; accepted October 3, 2003)

An unusual, reversible skeletal substitution reaction involving boron- and aluminum-based heterophosphazenes is described.

Keywords: Aluminatocyclophosphazenes; boratocyclophosphazenes

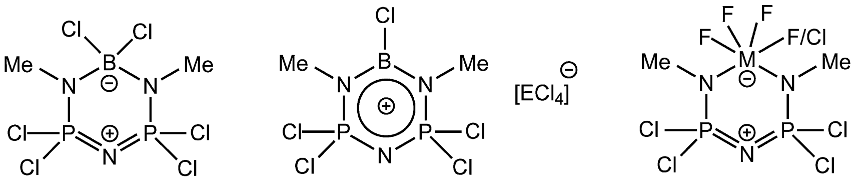
Cyclic heterophosphazenes have received considerable attention in our group as a result of their interesting structural features[1] and due to their use as precursors to novel inorganic polymers via ring-opening polymerization (ROP).[2] In this regard, the polymerization of a number of main group carbon, sulfur (IV), and sulfur (VI) heterophosphazenes have been described.[3]

CHEMISTRY OF BORATOPHOSPHAZENES

We began our investigation concerning the ROP of boron-nitrogen-phosphorus rings by exploring the chemistry of the zwitterionic boratophosphazene **1**. Although this species did not undergo successful ROP, treatment of **1** with group 13 halide acceptors (ECl_3, E = B, Al, and Ga) afforded the first examples of the planar borazine-phosphazine hybrid cations $[\mathbf{2}]^+$. Surprisingly, an attempt to form $[\mathbf{2}]^+$ via the reaction of **1** with the silver salts $Ag[MF_6]$ (M = As and Sb)

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for support.

Address correspondence to Ian Manners, Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6, Canada. E-mail: imanners@chem.utoronto.ca



1

[2]⁺

E = B, Al And Ga

M = As **3**

M = Sb **4**

SCHEME 1

led to the formation of the hithero unknown arsenic and antimony heterophosphazenes **3** and **4**.[4]

REVERSIBLE SKELETAL SUBSTITUTION REACTIONS

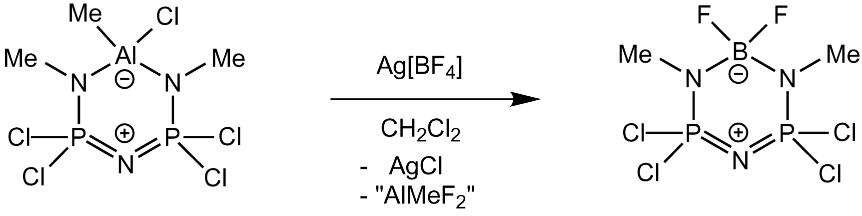
Due to the unusual (and possibly useful) nature of the skeletal substitution chemistry of **1**, we decided to further explore the reactivity of this species. It was found that treatment of **1** with $AlMe_3$ in toluene afforded the methylated aluminatophosphazenes **5** and **6** when two and four equivalents of $AlMe_3$ was added. Both isolated products did not exhibit any ^{11}B NMR resonance and the substitution of B for Al was further confirmed by a single crystal x-ray diffraction study involving **5** (aluminatophosphazene **6** is an oil).[5] In both cases, the only boron-containing species that could be observed in solution was BMe_3, thus indicating complete exchange between the B-Cl and Al-Me groups had transpired.

5

6

SCHEME 2

When we attempted to abstract a halide from the aluminum center in **5** using $Ag[BF_4]$, a surprising reaction was observed. Instead of isolating the target alumazine-phosphazene cation $[N(PCl_2NMe)_2AlMe]^+$ [**7**]$^+$, quantitative formation of the previously characterized fluorinated boratophosphazene **8** had occurred (as determined by comparison of the ^1H, ^{11}B, ^{19}F, and ^{31}P NMR of the isolated product with an authentic sample of **8**).



5 **8**

SCHEME 3

No intermediates (including possibly transient [**7**]$^+$) could be detected during the course of the reaction. The above mentioned replacement of B for Al, coupled with the initial synthesis of **5**, represents a unique, formally reversible, skeletal substitution process involving main group elements.

REFERENCES

[1] Y. Ni, A. J. Lough, A. L. Rheingold, and I. Manners, *Angew. Chem. Int. Ed. Engl.*, **34,** 998 (1995).

[2] I. Manners, *Angew. Chem. Int. Ed. Engl.*, **35,** 1602 (1996).

[3] D. P. Gates and I. Manners, *J. Chem. Soc. Dalton Trans.*, 2525 (1997).

[4] D. P. Gates, A. R. McWilliams, R. Ziembinski, L. M. Liable-Sands, G. P. A. Yap, A. L. Rhiengold, and I. Manners, *Chem. Eur. J.*, 1489 (1998).

[5] A. R. McWilliams, E. Rivard, A. J. Lough, and I. Manners, *Chem. Commun.*, 1102 (2002).