This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Online publication date: 12 August 2010



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

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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 boronand aluminum-based heterophosphazenes is described.

Keywords: Aluminatocyclophosphazenes; boratocyclophosphazenes

Cyclic heterophosphazenes have received considerable attention in our group as a result of their interesting structural features¹ 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-nitrogenphosphorus 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 (ECl₃, E = B, Al, and Ga) afforded the first examples of the planar borazinephosphazine hybrid cations $[2]^+$. Surprisingly, an attempt to form $[2]^+$ 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

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 AlMe₃ in toluene afforded the methylated aluminatophosphazenes **5** and **6** when two and four equivalents of AlMe₃ was added. Both isolated products did not exhibit any ¹¹B 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 boroncontaining species that could be observed in solution was BMe₃, thus indicating complete exchange between the B-Cl and Al-Me groups had transpired.

SCHEME 2

When we attempted to abstract a halide from the aluminum center in **5** using Ag[BF₄], 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).

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

REFERENCES

main group elements.

- 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).