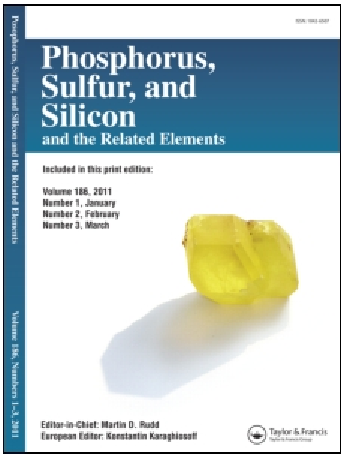


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Aluminum and Gallium Atrane Structures and Reactivities

J. Pinkas[a]; J. G. Verkade[a]
[a] Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa

To cite this Article Pinkas, J. and Verkade, J. G.(1994) 'Novel Aluminum and Gallium Atrane Structures and Reactivities', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 333 — 337
To link to this Article: DOI: 10.1080/10426509408021848
URL: http://dx.doi.org/10.1080/10426509408021848

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 333–337
Reprints available directly from the publisher
Photocopying permitted by license only

NOVEL ALUMINUM AND GALLIUM ATRANE STRUCTURES AND REACTIVITIES

J. PINKAS AND J. G. VERKADE*
Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011

Abstract New monomeric azaaluminatranes and gallatranes of the type

$M(RNCH_2CH_2)_3N$ (M = Al, R = Me_3Si (**8**) or *tert*-$BuMe_2Si$ (**9**); M = Ga, R = Me_3Si (**10**) or *tert*-$BuMe_2Si$ (**11**)) have been prepared, with characterization including a molecular structure determination in the case of **8**. Three dimeric

azaalumatranes, namely, $[Al(MeNCH_2CH_2)_3N]_2$ (**12**) and

$[Al(Me_3SiNCH_2CH_2)_2(HNCH_2CH_2)N]_2$ (**13**) and $[Ga(MeNCH_2CH_2)_3N]_2$ (**14**) have also been structurally characterized and all three compounds feature a central $(M\text{-}N)_2$ four-membered ring with a *cis* configuration of the nitrogen substituents. Some of the reaction chemistry of these systems is outlined and ^{27}Al NMR trends as a function of coordination number and geometry are discussed.

INTRODUCTION

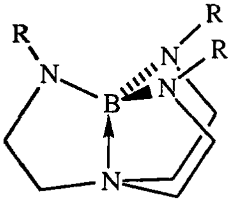
Owing to efforts to improve the preparation of nitride ceramic materials and semiconductors[1-6], reactivity and structural studies of compounds of group 13 elements bonded to nitrogen is a research area of considerable current activity. While there is a vast literature concerning such compounds with multidentate amine ligands, few of these amines are highly symmetrical ones[7].

SYNTHESES AND REACTIONS

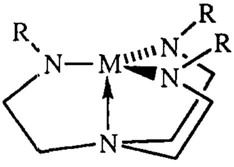
During the last few years we have focused our attention on utilizing symmetrical tripodal tetramine ligands such as **1-5** in the synthesis of volatile azatranes as potential nitride film

R = H (**1**), Me (**2**), *iso*-Pr (**3**), Me_3Si (**4**), *tert*-$BuMe_2Si$ (**5**)

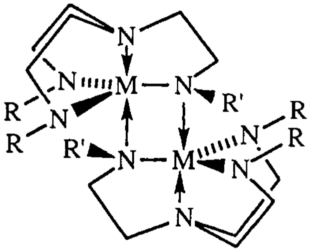
precursors.



	R
6	Me
7	$SiMe_3$



	M	R
8	Al	$SiMe_3$
9	Al	$SiMe_2$-*tert*-Bu
10	Ga	$SiMe_3$
11	Ga	$SiMe_2$-*tert*-Bu



	M	R	R'
12	Al	Me	Me
13	Al	$SiMe_3$	H
14	Ga	Me	Me

The preparation of monomeric **6**-**11** and dimeric **12** and **14** occurs by transamination reactions involving the corresponding reactants $(RHNCH_2CH_2)_3N$ and $M(NMe_2)_3$ in which Me_2NH is evolved[8-10]. Compounds **6** and **14** were also formed by a transmetallation reaction involving the dimeric azaaluminatrane **12**:

$$B(OMe)_3 + \mathbf{12} \longrightarrow \mathbf{6} + [Al(OMe)_3]_x \tag{1}$$

$$Ga(acac)_3 + \mathbf{12} \longrightarrow \mathbf{14} + Al(acac)_3 \tag{2}$$

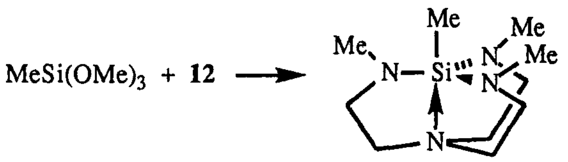
Similarly, **11** forms in the reaction of monomeric **9** with $Ga(acac)_3$:

$$Ga(acac)_3 + \mathbf{9} \longrightarrow \mathbf{11} + Al(acac)_3 \tag{3}$$

Although the source of the elements of water remain obscure so far, dimeric **13** arises in attempts to recrystallize **8**[10]:

$$\mathbf{8} \xrightarrow{H_2O} \mathbf{13} \tag{4}$$

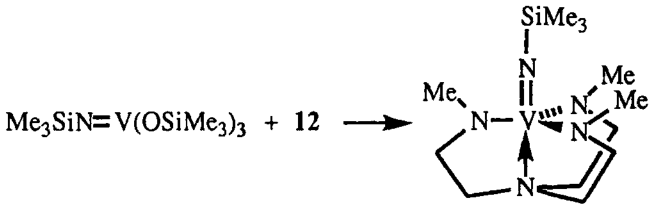
There are two major influences in promoting the transmetallation reactions 1-3. The higher strength of Al-O relative to B-O, Ga-O and Al-N bonds is responsible for an enthalpic advantage, while the conversion of dimeric **12** to monomeric **6** is favored entropically. Another factor in the case of azatrane systems is the stabilization effect of the transannular bond. Thus while $MeSi(OMe)_3$ reacts easily with dimeric azaalumatrane **12** in reaction 5, the analogous reaction of $MeC(OMe)_3$ failed. The transition metal



15

(5)

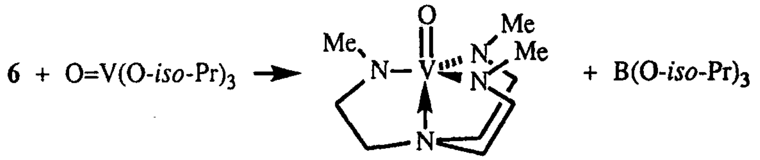
compound **16** can also be made from **12**[8]:



16

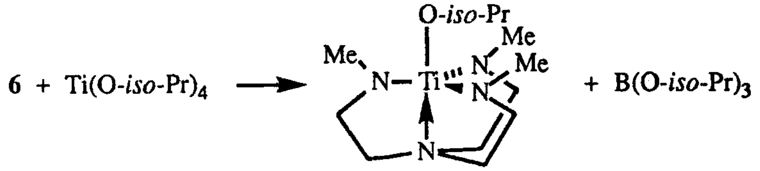
(6)

In a similar way, monomeric **6** and **8** can be used to construct transition metal azatranes[8].



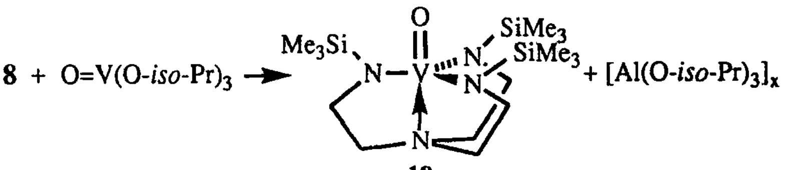
17

(7)



18

(8)



19

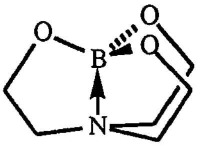
(9)

We have also found it possible to replace an entire tripodal ligand by another in the case of **12** and **8**[11], and also for **6** and **15**[10]:

$$\mathbf{12} + (HOCH_2CH_2)_3N \rightarrow \underset{\mathbf{20}}{[Al(OCH_2CH_2)_3N]_4} + (MeHNCH_2CH_2)_3N \quad (9)$$

$$\mathbf{8} + (HOCH_2CH_2)_3N \rightarrow \mathbf{20} + (Me_3SiHNCH_2CH_2)_3N \quad (10)$$

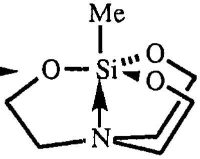
$\mathbf{6} + (HOCH_2CH_2)N \longrightarrow$



$+ (MeHNCH_2CH_2)_3N$ (11)

21

$\mathbf{15} + (HOCH_2CH_2)_3N \rightarrow$



$+ (MeHNCH_2CH_2)_3N$ (12)

22

STRUCTURAL CONSIDERATIONS

Dimers **12**[10], **13**[9] and **14**[10] each feature a cis configuration of the substituents on the central four-membered $(M\text{-}N)_2$ ring. This isomer was also observed to be the only species in solution as judged by ^1H and ^{13}C NMR spectroscopies. Heating **12** or **14** for 60 h at 120 °C in sealed NMR tubes resulted in no observation of trans isomers at room temperature. Moreover, their spectra remained unchanged up to 100 °C, thus indicating that fluxionality caused by racemization between the two enantiomers of the cis species is slow on the NMR time scale.

The molecular structure determination of **8** reveals the first example of a trigonal monopyramidal coordination geometry for aluminum, which is rare for main group elements in general. The propeller-like conformation of **8** implies the presence of Λ and Δ enantiomers in the solid state. An estimation of $\Delta S^\ddagger$ of racemization was precluded, however, by the observation that **8** and also **9** (which has even bulkier substituents) are freely fluxional down to -95 °C on the NMR time scale. Reasons for facile inversion of the rings in these compounds include a large aluminum atom and long $Al\text{-}N_{eq}$ and $Al\text{-}N_{ax}$ bonds compared with the tetrahedral boron analogue **7** for which a $\Delta S^\ddagger$ value could be estimated[8].

Our syntheses of the trigonal monopyramidal aluminum compounds **8** and **9** and the trigonal bipyramidal examples **12** and **13** in combination with trigonal planar[12], tetrahedral[13] and octahedral[14] aluminum structures found in the literature allowed us to examine the ^{27}Al NMR chemical shift for a variety of aluminum coordination numbers and geometries in which the metal atom is surrounded only by nitrogen ligands. The trend in δ^{27}Al is toward high field in the order trigonal planar, trigonal monopyramidal, tetrahedral, trigonal bipyramidal, octahedral, thus reflecting in an unusually detailed manner the trend typically seen for NMR-active nonmetallic elements.

ACKNOWLEDGMENT

The authors thank the National Science Foundation and the Iowa State Center for Advanced Technology Development for grants supporting this work, and the Hampshire Chemical Company for research samples of $(H_2NCH_2CH_2)_3N$.

REFERENCES

1. R. T. Paine and C. K. Narula, Chem. Rev., 90, 73 (1990).
2. T. Wade, J. Park, E. G. Garza, C. B. Ross, D. M. Smith and R. M. Crooks, J. Am. Chem. Soc., 114, 9457 (1992).
3. C. Jones, G. A. Loutsantonis and C. L. Raston, Polyhedron, 12, 1829 (1993).
4. (a) M. J. Almond, C. E. Jenkins, D. A. Rice and K. Hagen, J. Organomet. Chem., 439, 251 (1992). (b) M. J. Almond, C. E. Jenkins and D. A. Rice, ibid, 443, 137 (1993).
5. A. H. Cowley and R. A. Jones, Angew. Chem., Int. Ed. Engl., 28, 1208 (1989).
6. R. Riedel, S. Schaible, V. Klingebiel, M. Noltemeyer and E. Werner, Zeitschr. Anorg. Allg. Chem., 603, 119 (1991).
7. (a) F. Moise, W. T. Pennington and G. H. Robinson, J. Coord. Chem., 24, 93 (1991). (b) D. A. Atwood, V. O. Atwood, A. H. Cowley, J. L. Atwood and E. Roman, Inorg. Chem., 31, 3871 (1992). (c) J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, Inorg. Chem., 30, 4868 (1991). (d) A. Coutsolelos, R. Guilard, A. Boukhirs and C. Lecomte, J. Chem. Soc. Dalton Trans., 1779 (1986).
8. J. Pinkas, B. Gaul and J. G. Verkade, J. Am. Chem. Soc., 115, 3925 (1993).
9. J. Pinkas, T. Wang, R. A. Jacobson and J. G. Verkade, *Inorg. Chem.*, in press.
10. J. Pinkas, T. Wang, R. A. Jacobson and J. G. Verkade, *Inorg. Chem.*, in press.
11. J. Pinkas and J. G. Verkade, *Inorg. Chem.*, **32**, 2711 (1993).
12. (a) M. A. Petrie, K. Ruhlandt-Senge and P. P. Power, Inorg. Chem., 32, 1135 (1993). (b) J. K. Ruff, J. Am. Chem. Soc., 83, 2835 (1961). (c) M. F. Lappert, A. R. Sanger, R. C. Srivastava and P. P. Power, Metal and Metalloid Amides (Ellis-Horwood. Chichester, U.K., 1980).
13. K. M. Waggoner, M. M. Olmstead and P. P. Power, Polyhedron, 9, 257 (1990).
14. (a) A. H. Cowley, C. J. Carrano, R. L. Geerts, R. A. Jones and C. M. Nunn, Angew. Chem., Int. Ed. Engl., 27, 277 (1988). (b) J. T. Leman, A. R. Barron, J. W. Ziller and R. M. Kren, Polyhedron, 8, 1909 (1989). (c) J. T. Lehman, J. Braddock-Wilking, A. J. Coolong and A. R. Barron, Inorg. Chem., 32, 4324 (1993). (d) Z. Jiang, L. V. Interrante, D. Kwon, F. S. Tham and R. Kullnig, Inorg. Chem., 31, 4815 (1992).