IS-T 1693

The Crystal and Molecular Structure of Azatranes: Azavanadatran (Z=t-Bu), Monoazasilatrane (Z=H), Azalithatrane (Z=ClO₄*), Azaphosphatrane (Z=Me), Azagermatrane (Z=t-Bu) and Azaalumatran (Z=nothing)

by

Wang, Tieli

MS Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: April 23, 1996

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

This dissertation is dedicated to my parents and my teachers

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vii
ACKNOWLEDGMENT	viii
ABSTRACT	ix
INTRODUCTION	1
EXPERIMENTAL	2
(<i>t</i> -Bu)NV(MeNCH ₂ CH ₂) ₃ N(1)	
Crystal Data	3
Collection and Reduction of X-Ray Intensity Data	4
Structure Solution and refinement	4
HSi(OCH ₂ CH ₂) ₂ (HNCH ₂ CH ₂)N(2)	
Crystal Data	9
Collection and Reduction of X-Ray Intensity Data	10
Structure Solution and refinement	11
O ₄ CLi(HNCH ₂ CH ₂) ₃ N(3)	
Crystal Data	13
Collection and Reduction of X-Ray Intensity Data	14
Structure Solution and Refinement	14
MeP(Me ₃ NCH ₂ CH ₂) ₃ N(4)	
Crystal Data	18
Collection and Reduction of X-Ray Intensity Data	19
Structure Solution and Refinement	19
<i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	
Crystal Data	22
Collection and Reduction of X-Ray Intensity Data	23
Structure Solution and Refinement	23
Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	
Crystal Data	26

Collection and Reduction of X-Ray Intensity Data	27
Structure Solution and Refinement	27
DESCRIPTION OF THE STRUCTURES AND DISCUSSION	31
CONCLUSION	55
REFERENCE	58

LIST OF TABLES

Table 1. Positional parameters and B(eq) for (<i>t</i> -BuN)V(MeNCH ₂ CH ₂) ₃ N (1)	7
Table 2. Thermal Parameters for (<i>t</i> -BuN)V(MeNCH ₂ CH ₂) ₃ N (1)	8
Table 3. Positional parameters and B(eq) for HSi(OCH ₂ CH ₂) ₂ (HNCH ₂ CH ₂)N(2)	11
Table 4. Thermal Parameters for HSi(OCH ₂ CH ₂) ₂ (HNCH ₂ CH ₂)N(2)	12
Table 5. Positional parameters and B(eq) O ₄ ClLi(HNCH ₂ CH ₂) ₃ N(3)	16
Table 6. Thermal Parameters for O ₄ ClLi(HNCH ₂ CH ₂) ₃ N(3)	17
Table 7. Positional parameters and B(eq) for MeP(MeNCH ₂ CH ₂) ₃ Ni(4)	21
Table 8. Thermal Parameters for MeP(MeNCH ₂ CH ₂) ₃ Ni(4)	21
Table 9. Positional parameters and B(eq) <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	25
Table 10 Thermal Parameters for <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	25
Table 11 Positional parameters and B(eq) Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	29
Table 12 Thermal Parameters for Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	30
Table 13. Selected Bond Distances for (<i>t</i> -BuN)V(MeNCH ₂ CH ₂) ₃ N (1)	42
Table 14. Selected Bond Angles for (<i>t</i> -BuN)V(MeNCH ₂ CH ₂) ₃ N(1)	43
Table 15. Selected Bond Distances for HSi(OCH ₂ CH ₂) ₂ (HNCH ₂ CH ₂)N(2)	44
Table 16. Selected Bond Angles for HSi(OCH ₂ CH ₂) ₂ (HNCH ₂ CH ₂)N(2)	45
Table 17. Selected Bond Distances for O ₄ ClLi(HNCH ₂ CH ₂) ₃ N(3)	46
Table 18. Selected Bond Angles for O ₄ ClLi(HNCH ₂ CH ₂) ₃ N(3)	47
Table 19. Selected Bond Distances for MeP(MeNCH ₂ CH ₂) ₃ Ni(4)	48
Table 20. Selected Bond Angles for MeP(MeNCH ₂ CH ₂) ₃ Ni(4)	49

Table 21. Selected Bond Distances for <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	50
Table 22. Selected Bond Angles for <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	51
Table 23. Selected Bond Distances for Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	52
Table 24. Selected Bond Angles for Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	53
Table 25. Comparison of Some of Parameters among Six Compounds	54

LIST OF FIGURES

Figure 1. ORTEP Structure for $(t\text{-BuN})\text{V}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(1)$	36
Figure 2. ORTEP Structure for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}(2)$	37
Figure 3. ORTEP Structure for $\text{O}_4\text{ClLi}(\text{HNCH}_2\text{CH}_2)_3\text{N}(3)$	38
Figure 4. ORTEP Structure for $\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{Ni}(4)$	39
Figure 5. ORTEP Structure for $t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}(5)$	40
Figure 6. ORTEP Structure for $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(6)$	41

Table 21. Selected Bond Distances for <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	50
Table 22. Selected Bond Angles for <i>t</i> -BuGe(HNCH ₂ CH ₂) ₃ N(5)	51
Table 23. Selected Bond Distances for Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	52
Table 24. Selected Bond Angles for Al(Me ₃ SiNCH ₂ CH ₂) ₃ N(6)	53
Table 25. Comparison of Some of Parameters among Six Compounds	54

LIST OF FIGURES

Figure 1. ORTEP Structure for $(t\text{-BuN})\text{V}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(\mathbf{1})$	36
Figure 2. ORTEP Structure for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}(\mathbf{2})$	37
Figure 3. ORTEP Structure for $\text{O}_4\text{CLi}(\text{HNCH}_2\text{CH}_2)_3\text{N}(\mathbf{3})$	38
Figure 4. ORTEP Structure for $\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{NI}(\mathbf{4})$	39
Figure 5. ORTEP Structure for $t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}(\mathbf{5})$	40
Figure 6. ORTEP Structure for $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(\mathbf{6})$	41

ACKNOWLEDGMENT

I would like to give my special thanks to my advisor, Dr. Robert A. Jacobson, for his supervision and encouragement throughout this work. I am very grateful to him for his support of my research and career. I was extremely impressed by his scientific expertise, personality, and help which will continue to inspire me in my future science career.

I would like to thank Dr. John Verkade for his collaboration and I appreciate the support of my committee members Dr. Augustin Kintanar and Dr. Jacob W. Petrich.

It has been a nice experience to work with members of Dr. Jacobson's laboratory. I would also like to thank Dr. Yingzhong Su, Dr. Cathy Day and Ms. Sharon Ringrose for their help in the cooperation while conducting my experiments.

I have been fortunate to have met many wonderful people during my stay in the Department of Chemistry. I would like to thank all my friends, especially Jingyuan Wang, Jianhua Lin, Jianshen Tang, Jingtai Zhao, Jibing Lin, Yanjian Van, Xue Li, Gang Zhao, Chenming Zhang and Weiliang Ding for helping me to get through the most difficult time in my life.

Finally to Ms. Brenda Smith for her assistance, not the least of which was fast typing.

ABSTRACT

The crystal and molecular structures of azatranes have been extensively studied for a variety of M atoms. The crystal and molecular structures of six similar cage compounds: $(t\text{-Bu})\text{NV}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$, $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}$, $\text{O}_4\text{CLi}(\text{HNCH}_2\text{CH}_2)_3\text{N}$, $\text{MeP}(\text{Me}_3\text{NCH}_2\text{CH}_2)_3\text{N}$, $t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}$, and $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$ were determined by the use of three-dimensional, single crystal x-ray diffraction.

$(t\text{-BuN})\text{V}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(1)$ crystallizes in the monoclinic space group $\text{P2}_1/\text{n}$ with $a = 9.423(2)\text{\AA}$, $b = 10.155(3)\text{\AA}$, $c = 18.000(5)\text{\AA}$ and $\beta = 100.96(1)^\circ$. $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)(2)$ crystallizes in the monoclinic space group $\text{P2}_1/\text{a}$ with $a = 13.093(2)\text{\AA}$, $b = 10.098(2)\text{\AA}$, $c = 6.589(2)\text{\AA}$ and $\beta = 92.97(2)^\circ$. $\text{ClO}_4\text{Li}(\text{HNCH}_2\text{CH}_2)_3\text{N}(3)$ crystallizes in the monoclinic space group $\text{P2}_1/\text{m}$ with $a = 7.076(1)\text{\AA}$, $\beta = 8.459(2)^\circ$, $c = 10.337(2)\text{\AA}$ and $b = 102.91(1)^\circ$. $\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(4)$ crystallizes in the trigonal space group P31c with $a = 8.107(1)\text{\AA}$, $c = 13.1193(8)\text{\AA}$. $\text{Ge-}t\text{-Bu}(\text{HNCH}_2\text{CH}_2)_3\text{N}(5)$ crystallizes in the rhombohedral(hexagonal axes) space group R3(h) with $a = 10.370(3)\text{\AA}$, $c = 21.416(2)\text{\AA}$. $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(6)$ crystallizes in the monoclinic space group $\text{P2}_1/\text{c}$ with $a = 3.503(5)\text{\AA}$, $b = 10.621(4)\text{\AA}$, $c = 17.840(6)\text{\AA}$, $\beta = 93.29(3)^\circ$. All the structures were refined by a block-matrix/full matrix procedure to final conventional residual indices of $R=0.058, 0.063, 0.063, 0.024, 0.042$ and 0.052 , respectively. All were shown to be cage compounds with a trigonal bipyramidal vanadium, silicon, lithium, phosphorus and germanium centers and a trigonal monopyramidal aluminium center. The V-N_{ax} , Si-N_{ax} , Li-N_{ax} , P-N_{ax} , Ge-N_{ax} and

Al-N_{ax} bond distances are 2.233(5)Å, 2.114(4)Å, 2.15(1)Å, 2.778(5)Å, 2.361(6)Å and 1.983(6)Å respectively. The sum of the bond angles for the three V-N_{eq}, Si-N_{eq}, Li-N_{eq}, P-N_{eq}, Ge-N_{eq} and Al-N_{eq} linkages are 349.4(2)°, 356.3(2)°, 354.8(6)°, 339.5(1)°, 347.67(7)° and 359.7(3)°. A nearly right angle relationship of the N_{ax}-M bond with the N_{eq}-M linkages was found. The sum of bond angles of the three C-N_{eq} linkages for the center of V, Si, Li, P, Ge and Al atoms are 337.8(7)°, 338.7(5)°, 336(2)°, 357.2(1)°, 342.1(2)° and 341.7(7)°.

INTRODUCTION

Atranes have been extensively studied for a variety of M atoms and Z substituents and have been known for a long time,

particularly for the group 14 elements¹. By contrast, few azatranes were known (except for a few examples with $M=Si^2$) until interest in such compounds was aroused by their use as MOCVD agents for metal and non-metal nitrides. Thus Dr. Verkade and his co-workers have recently expanded this class of compounds to include a broad variety of azatranes compounds. We present here the crystal and molecular structures of the six azatranes: azavanadatrane ($Z= Nt\text{-}Bu$), monoazasilatrane ($Z = H$), Azalithatrane ($Z = ClO_4$), azaphosphatrane ($Z=Me$), azagermatrane ($Z= t\text{-}Bu$) and azaalumatrane ($Z = \text{nothing}$). The structure determinations for these six products from the synthesis reactions were carried out to determine their stereochemistries and to help better elucidate the reactions involved. Samples of all compounds

were kindly supplied by the students Yanjian Van, Jiri Pinkas, Thyragajan Mohan from Dr. John Verkade's group.

EXPERIMENTAL

All reactions were carried under argon with strict exclusion of moisture using Schlenk or dry box techniques³. All compounds are air sensitive and each was mounted carefully in the capillary in a nitrogen box in Dr. Miller's group or in the nitrogen bag. Data for first two compounds (*t*-BuN)V(MeNCH₂CH₂)₃N, HSi(OCH₂CH₂)₂(HNCH₂CH₂)N were collected on a Hilger Watts diffractometer. The rest of them ClO₄Li(HNCH₂CH₂)₃N, MeP(MeNCH₂CH₂)₃N, *t*-BuGe(HNCH₂CH₂)₃N, Al(Me₃SiNCH₂CH₂)₃N were collected on a Rigaku diffractometer. In each case, from 12 to 25 reflections were found by random search techniques and used to determine lattice constants and probable lattice types. A Laue check and a cell determination using high angle reflection were also done on a Rigaku diffractometer before data collection. All structures were solved by direct methods except the third one, ClO₄Li(HNCH₂CH₂)₃N, which was solved by direct methods and Patterson superposition methods,⁴ and refined by full-matrix least-squares refinement. More complete experimental details for each of the structure determinations follows.

(*t*-BuN)V(MeNCH₂CH₂)₃N (1)

Crystal data.

(*t*-BuN)V(MeNCH₂CH₂)₃N, M.W. = 307.36 g mole⁻¹, monoclinic P2₁/n, *a* = 9.423(2) Å, *b* = 10.155(3) Å, *c* = 18.000(5) Å, β = 100.96 (1)°, *V* = 1691 (1) Å³, *d*_{calc} = 5.432 g/cm³, *Z* = 4, μ = 25.38 cm⁻¹ (MoKα, λ = 0.71069 Å).

A yellow almost spherical crystal of (*t*-BuN)V(MeNCH₂CH₂)₃N having approximate dimensions 0.24 X 0.18 X 0.20 mm was mounted in a glass capillary. All measurements were made on a Hilger Watts diffractometer with graphite monochromated MoKα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 12 carefully centered reflections in the range 22.45° < 2Θ < 27.22°, corresponded to a monoclinic cell.

Based on the systematic absences of:

$$h0l: h+l \neq 2n$$

$$0k0: k \neq 2n$$

and the successful solution and refinement of the structure, the space group was determined to be:

$$P2_1/n \text{ (\#14)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω scan technique to a maximum 2Θ value of 50.2° . Omega scans of width $(1.84 + 0.30 \tan\Theta)^\circ$ were made at a variable scan speed. The background measurements were made at the beginning and end of each scan for 20% of the scan time. The diameter of the incident beam collimator was 0.7mm and the crystal to detector distance was 21cm.

Data reduction

Of the 6961 reflections which were collected, 4350 were unique; equivalent reflections were merged ($R_{\text{int}} = .078$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for Mo $K\alpha$ is 25.4 cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.82 to 1.00. The data were also corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 1423 observed reflections ($I > 4.00\sigma(I)$) and 172 variable parameters and converged (largest

parameter shift was 1.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.065$$

$$R_w = [(\sum \omega (|F_o| - |F_c|)^2 / \sum \omega F_o^2)]^{1/2} = 0.077$$

The standard deviation of an observation of unit weight⁷ was 6.58. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum \omega (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \Theta / \lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.62 and -0.76 $e^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from those of Cromer and Waber⁸. Anomalous dispersion effects were included in F_{calc} ⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, $B(eq)$, bond distance and angles for the compound **1** are listed in table 1 and table 2.

Table 1. Positional parameters and B(eq) for the atoms of (*t*-BuN)V(MeNCH₂CH₂)₃N (1)

atom	X	Y	Z	B(eq)
V	0.9337(1) ^b	0.8697(1)	0.1552(1)	2.7(1)
N1	1.0564(5)	0.7533(5)	0.1533(3)	3.0(3)
N2	0.7669(6)	0.7906(6)	0.0935(3)	3.6(3)
N3	1.0186(6)	1.0120(5)	0.1112(3)	3.3(3)
N4	0.7662(6)	1.0245(6)	0.1567(3)	3.6(3)
N5	0.9378(6)	0.8857(5)	0.2606(3)	3.1(3)
C6	1.0290(1)	0.8174(9)	0.3225(5)	4.0(4)
C7	1.1590(8)	0.6480(7)	0.1521(4)	3.5(4)
C8	1.3030(1)	0.6850(1)	0.2027(6)	4.9(5)
C9	0.6290(9)	0.8580(9)	0.0793(5)	4.6(4)
C10	1.1850(1)	0.6280(1)	0.0720(6)	5.4(5)
C11	0.9440(1)	1.1388(8)	0.0987(5)	4.2(5)
C12	0.7940(1)	1.0836(9)	0.2329(5)	5.5(5)
C13	1.1599(9)	1.0200(1)	0.0917(5)	4.0(5)
C14	0.7640(1)	0.6773(8)	0.0443(5)	4.3(4)
C15	1.1030(1)	0.5260(1)	0.1826(7)	5.9(5)
C16	0.8440(1)	0.9760(1)	0.2904(5)	4.2(4)
C17	0.7830(1)	1.1170(1)	0.0960(6)	5.8(5)
C18	0.6250(1)	0.9550(1)	0.1400(6)	5.8(5)

^bIn all tables in parentheses indicate standard deviations in the least significant figures.

$$B(\text{eq}) = 8\pi^2/3 \sum_i \sum_j U_{ij} \bullet a_i^* \bullet a_j^* \bullet (a_i \bullet a_j)$$

Table 2. Thermal Parameters for (*t*-BuN)V(MeNCH₂CH₂)₃N (1)

Atoms	U11	U22	U33	U12	U13	U23
V	0.0329(9)	0.0310(9)	0.0368(9)	0.0037(6)	0.0034(6)	-0.0012(6)
N1	0.035(3)	0.033(4)	0.044(4)	0.013(3)	-0.001(3)	0.000(3)
N2	0.041(4)	0.040(4)	0.051(4)	0.000(3)	-0.000(3)	-0.010(3)
N3	0.036(4)	0.044(4)	0.044(4)	0.003(3)	0.005(3)	0.004(3)
N4	0.039(4)	0.047(4)	0.048(4)	0.011(3)	0.005(3)	-0.003(4)
N5	0.038(3)	0.040(3)	0.039(4)	0.008(3)	0.006(3)	0.004(3)
C6	0.053(6)	0.042(5)	0.055(6)	-0.008(4)	0.002(5)	0.008(5)
C7	0.049(5)	0.035(5)	0.047(5)	0.005(4)	0.004(4)	0.001(4)
C8	0.043(6)	0.062(7)	0.075(6)	0.022(5)	-0.002(5)	0.003(5)
C9	0.037(6)	0.064(6)	0.068(6)	-0.001(5)	-0.007(5)	-0.023(6)
C10	0.062(7)	0.069(7)	0.071(8)	0.029(6)	0.007(5)	-0.023(6)
C11	0.061(7)	0.043(6)	0.055(7)	0.036(6)	0.017(5)	-0.006(6)
C12	0.086(7)	0.069(7)	0.071(8)	0.029(6)	0.007(5)	-0.014(6)
C13	0.046(6)	0.058(6)	0.049(6)	-0.004(4)	0.011(5)	-0.003(5)
C14	0.058(6)	0.035(5)	0.066(6)	-0.008(4)	0.001(5)	-0.011(5)
C15	0.072(7)	0.048(6)	0.110(1)	0.015(6)	0.025(6)	0.004(6)
C16	0.047(5)	0.070(6)	0.046(6)	0.003(5)	0.015(5)	0.003(5)
C17	0.070(7)	0.058(6)	0.096(8)	0.022(5)	0.021(6)	0.011(6)
C18	0.042(6)	0.079(7)	0.093(8)	0.011(5)	-0.006(5)	-0.021(6)

Crystal Data

$\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}$, M.W. = 480.23, Monoclinic $P2_1/a$, $a = 13.093(2)\text{\AA}$, $b = 10.098(2)\text{\AA}$, $c = 6.589(2)\text{\AA}$, $\beta = 92.97(2)^\circ$, $V = 872.7(6)\text{\AA}^3$, $d_{\text{calc}} = 1.457\text{ g/cm}^3$, $Z = 4$, $\mu = 39.95\text{ cm}^{-1}$, ($\text{MoK}\alpha$, $\lambda = 0.71069\text{ \AA}$).

A clear almost spherical crystal of approximate dimensions of $0.34 \times 0.28 \times 0.20\text{ mm}$ was mounted in a glass capillary. All measurements were made on a Hilger Watts diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 12 carefully centered reflections in the range $20.00^\circ < 2\Theta < 28.00^\circ$, corresponded to a monoclinic cell.

Based on the systematic absences of:

$$h0l: h \neq 2n$$

$$0k0: k \neq 2n$$

the space group was determined to be:

$$P2_1/a \text{ (#14)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω scan technique to a maximum 2Θ value of 50.2° . Omega scans of width $(1.84 + 0.30 \tan\Theta)^\circ$ were made at a

variable scan speed from 2° to 30° /min . The background measurements were made at the beginning and end of each scan for 20% of the scan time. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21cm.

Data reduction

Of the 3742 reflections which were collected, 2027 were unique; equivalent reflections were merged ($R_{\text{int}} = .094$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for Mo $K\alpha$ is 36.9cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.83 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵. The non-hydrogen atoms and the one hydrogen atom which connects with silica atom were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 1033 observed reflections ($I > 4.00\sigma(I)$) and 100 variable parameters and converged (largest parameter shift was 0.29 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.063$$

$$R_w = [(\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)]^{1/2} = 0.079$$

The standard deviation of an observation of unit weight⁷ was 2.47. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma \omega (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \Theta / \lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.29 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from those of Cromer and Waber⁸. Anomalous dispersion effects were included in Fcalc⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, B(eq), bond distance and angles for the compound **2** are listed in table 3 and table 4.

Table 3. Positional Parameters and B(eq) for the atoms of HSi(OCH₂CH₂)₂(HNCH₂CH₂)NN(**2**)

Atom	X	Y	Z	B(eq)
Si	0.8618(1)	0.2433(1)	0.04951(2)	2.8(1)
O1	0.9717(3)	0.1998(4)	0.06121(6)	4.2(2)
O2	0.7982(3)	0.1212(3)	0.3753(5)	3.8(2)
N1	0.8395(4)	0.4054(4)	0.4289(7)	4.0(2)
N2	0.9481(3)	0.2483(4)	0.2329(6)	3.2(2)
C2	0.9125(6)	0.3643(6)	0.1120(1)	5.2(3)
C3	0.9254(6)	0.1233(6)	0.1269(9)	5.2(3)
C4	1.0544(5)	0.2625(7)	0.3090(1)	5.6(3)
C5	0.8171(5)	0.0902(6)	0.1740(1)	4.9(3)
C6	1.0619(4)	0.1826(6)	0.509(1)	5.0(3)
H14	0.802(4)	0.246(5)	0.670(6)	6(3)

Table 4. Thermal Parameters for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}(2)$

Atom	U11	U22	U33	U12	U13	U23
Si	0.0317(7)	0.0423(8)	0.0340(7)	0.0001(6)	0.0034(5)	0.0015(6)
O1	0.043(2)	0.062(3)	0.052(2)	0.004(2)	-0.002(2)	0.006(2)
O2	0.044(2)	0.046(2)	0.053(2)	-0.014(2)	0.003(2)	-0.001(2)
N1	0.054(3)	0.040(2)	0.058(3)	0.007(2)	0.010(2)	-0.005(2)
C1	0.079(4)	0.028(3)	0.061(4)	0.007(2)	-0.007(3)	0.005(2)
N2	0.052(3)	0.029(2)	0.040(2)	-0.001(2)	0.011(2)	0.001(2)
C2	0.103(6)	0.043(3)	0.053(4)	-0.006(3)	0.012(4)	-0.002(3)
C3	0.091(5)	0.064(4)	0.047(4)	-0.017(3)	0.022(3)	-0.020(3)
C4	0.047(4)	0.080(4)	0.087(5)	-0.009(3)	0.0259(4)	-0.010(4)
C5	0.073(4)	0.047(3)	0.063(4)	-0.016(3)	-0.007(3)	-0.009(3)
C6	0.039(3)	0.058(4)	0.094(5)	0.005(3)	-0.004(3)	0.012(3)
H14	0.06(3)	0.12(4)	0.03(3)	0.05(3)	0.06(3)	0.03(3)

Crystal Data

$\text{O}_4\text{CILi}(\text{HNCH}_2\text{CH}_2)_3\text{N}$, M.W. = 249.58, Monoclinic $P2_1/m$, $a = 7.076(1)\text{\AA}$, $b = 8.459(2)\text{\AA}$, $c = 10.337(2)\text{\AA}$, $\beta = 102.91(1)^\circ$, $V = 603.1(2)\text{\AA}^3$, $d_{\text{calc}} = 1.393\text{ g/cm}^3$, $Z = 2$, $\mu = 3.182\text{ cm}^{-1}$, (MoK α , $\lambda = 0.71069\text{ \AA}$).

A transparent monoclinic crystal of $\text{O}_4\text{CILi}(\text{HNCH}_2\text{CH}_2)_3\text{N}$ having approximate dimensions of 0.34 X 0.28 X 0.20 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $37.42^\circ < 2\Theta < 39.94^\circ$, corresponded to a monoclinic cell.

Based on the systematic absences of:

$$0k0: k \neq 2n$$

and a statistical test indicating a center of symmetry, the space group was determined to be:

$$P2_1/m (\#11)$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω - 2Θ scan technique to a maximum 2Θ value of 50.1° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.41° using a take-off angle of 6.0° . Scans of

width $(1.57 + 0.30 \tan \Theta)^\circ$ were made at a speed of $16^\circ/\text{min}$ (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data reduction

Of the 1250 reflections which were collected, 1154 were unique; equivalent reflections were merged ($R_{\text{int}} = .049$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for Mo $K\alpha$ is 3.182cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.95 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵ combined with Patterson superposition methods. Although statistical test indicated $P2_1/m$ rather than $P2_1$, the structure determination indicated that the mirror symmetry may only be approximate; however the structure was close

enough to the higher symmetry to prevent satisfactory refinement. It is presented here for completeness for these series compounds. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 1033 observed reflections ($I > 3.00\sigma(I)$) and 144 variable parameters and converged (largest parameter shift was still 0.29 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.063$$

$$R_w = [(\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)]^{1/2} = 0.078$$

The standard deviation of an observation of unit weight⁷ was 2.79. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma \langle \omega (|F_o| - |F_c|)^2 \rangle$ versus $|F_o|$, reflection order in data collection, $\sin\Theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.31 and -0.34 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from those Cromer and Waber⁸. Anomalous dispersion effects were included in F_{calc} ⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, $B(eq)$, bond distance and angles for the compound **3** are listed in table 5 and table 6.

Table 5. Positional Parameters and B(eq) for the atoms of $\text{O}_4\text{C}(\text{Li}(\text{HNCH}_2\text{CH}_2)_3\text{N})(3)$

Atom	X	Y	Z	B(eq)
Cl	0.2400(2)	0.2071(2)	0.6430(2)	3.33(7)
O1	0.3973(8)	0.201(2)	0.5777(5)	5.9(3)
O2	0.310(1)	0.197(2)	0.7758(6)	10.5(6)
O3	0.122(2)	0.079(2)	0.592(1)	8.4(6)
O4	0.130(2)	0.343(2)	0.617(2)	12(1)
N1	0.3724(7)	0.201(2)	0.1525(5)	3.0(2)
N2	0.260(2)	-0.022(2)	0.320(1)	5.0(6)
N3	0.258(2)	0.427(2)	0.320(1)	4.2(6)
N4	0.6919(8)	0.206(3)	0.3730(6)	5.3(4)
C1	0.196(2)	-0.037(2)	0.170(2)	5.5(7)
C2	0.297(5)	0.066(3)	0.097(2)	9(1)
C3	0.228(3)	0.460(2)	0.190(2)	6.5(8)
C4	0.247(4)	0.340(3)	0.102(1)	11(1)
C5	0.720(1)	0.210(4)	0.243(1)	7.0(6)
C6	0.568(1)	0.210(5)	0.1375(9)	10(1)
Li	0.390(2)	0.204(4)	0.362(1)	3.9(5)

Table 6. Thermal Parameters for $\text{O}_4\text{CILi}(\text{HNCH}_2\text{CH}_2)_3\text{N}(\mathbf{3})$

Atom	U11	U22	U33	U12	U13	U23
Cl	0.0382(9)	0.049(1)	0.042(1)	-0.004(3)	0.0145(7)	0.007(3)
O1	0.051(3)	0.012(6)	0.056(3)	0.050(7)	0.020(3)	0.006(7)
O2	0.135(7)	0.23(1)	0.040(4)	0.08(1)	0.024(4)	0.05(1)
O3	0.077(7)	0.17(1)	0.085(6)	-0.070(8)	0.050(6)	-0.058(7)
O4	0.14(1)	0.052(7)	0.29(2)	0.048(8)	0.10(1)	0.03(1)
N1	0.040(3)	0.042(3)	0.034(3)	-0.004(8)	0.017(2)	-0.015(8)
N2	0.055(7)	0.058(8)	0.08(1)	0.012(6)	0.021(8)	0.026(8)
N3	0.058(9)	0.07(1)	0.040(8)	0.019(7)	0.024(7)	0.003(6)
N4	0.043(3)	0.098(7)	0.060(4)	-0.02(1)	0.007(3)	-0.04(1)
C1	0.062(8)	0.10(1)	0.044(7)	-0.029(8)	0.011(6)	-0.038(8)
C2	0.22(2)	0.10(2)	0.07(1)	-0.08(2)	0.09(1)	-0.04(1)
C3	0.10(1)	0.035(8)	0.10(1)	0.031(7)	0.01(1)	-0.011(8)
C4	0.24(2)	0.14(2)	0.012(6)	0.14(2)	-0.01(1)	-0.001(7)
C5	0.046(4)	0.15(1)	0.084(6)	-0.05(1)	0.035(4)	-0.04(1)
C6	0.057(6)	0.29(3)	0.049(5)	-0.03(2)	0.032(5)	0.01(2)
Li	0.050(6)	0.066(9)	0.037(6)	0.03(2)	0.020(5)	0.03(1)

Crystal Data

$\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{NI}$, M.W. = 406.25, trigonal P31c, $a = 8.107(1)\text{\AA}$, $c = 13.1193(8)\text{\AA}$, $V = 746.7(2)\text{\AA}^3$, $d_{\text{calc}} = 1.807\text{ g/cm}^3$, $Z = 2$, $\mu = 22.22\text{ cm}^{-1}$, (MoK α , $\lambda = 0.71069\text{ \AA}$).

A light yellow irregularly shaped crystal of $\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{NI}$ having approximate dimensions of 0.20 X 0.40 X 0.20 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $39.45^\circ < 2\Theta < 39.80^\circ$ corresponded to a trigonal cell.

Based on the systematic absences of:

$$hh2hl: l \neq 2n$$

the space group was determined to be:

P31c (#159)

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω - 2Θ scan technique to a maximum 2Θ value of 60.0° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.36° with a take-off angle of 6.0° . Scans of width $(1.57 + 0.30 \tan\Theta)^\circ$ were made at a speed from $16^\circ/\text{min}$ (in omega). The weak

reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0mm.

Data reduction

Of the 2686 reflections which were collected, 969 were unique; equivalent reflections were merged ($R_{\text{int}} = .032$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for Mo $K\alpha$ radiation is 22.22cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 1033 observed reflections ($I > 3.00\sigma(I)$) and 48 variable parameters and converged (largest

parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.024$$

$$R_w = [(\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)]^{1/2} = 0.028$$

The standard deviation of an observation of unit weight⁷ was 1.26. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma \omega (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \Theta / \lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.61 and -0.25 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from those of Cromer and Waber⁸. Anomalous dispersion effects were included in Fcalc⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, $B(\text{eq})$, bond distance and angles for the compound 4 are listed in table 7 and table 8.

Table 7. Positional Parameters and B(eq) for the atoms of MeMeNCH₂CH₂)₃Ni(4)

Atoms	X	Y	Z	B(eq)
I1	1.0000	0.0003	0.4640	3.88(1)
P2	0.6667	0.3332	0.2301(2)	2.94(4)
N2	0.6657	0.3341	0.0188(6)	3.5(2)
C1	0.6671	0.3330	0.3681(7)	4.5(2)
N1	0.5837(5)	0.1114(5)	0.1969(3)	3.4(1)
C2	0.4646(7)	0.0366(6)	0.1049(4)	3.8(2)
C3	0.5742(7)	0.1296(7)	0.0081(3)	3.8(1)
C4	0.675(1)	0.0056(6)	0.2325(4)	4.8(2)

Table 8. Thermal Parameters for MeP(MeNCH₂CH₂)₃Ni(4)

Atom	U11	U22	U33	U12	U13	U23
I1	0.0490(2)	0.0490	0.0495(2)	0.0245	0	0
P2	0.0355(4)	0.0355	0.041(1)	0.018	0	0
N2	0.042(2)	0.042	0.049(4)	0.021	0	0
C1	0.064(4)	0.064	0.042(4)	0.032	0	0
N1	0.040(2)	0.035(2)	0.054(2)	0.019(1)	-0.002(2)	0.004(1)
C2	0.045(2)	0.035(2)	0.056(2)	0.014(2)	-0.003(2)	-0.001(2)
C3	0.053(3)	0.045(2)	0.046(2)	0.026(2)	-0.009(2)	-0.009(2)
C4	0.079(4)	0.058(3)	0.056(2)	0.042(3)	-0.004(3)	0.006(2)

Crystal Data

$t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}$, M.W. = 269.89, trigonal R3(h), $a = 10.370(4)\text{\AA}$, $c = 21.416(2)\text{\AA}$, $V = 1994(1)\text{\AA}^3$, $d_{\text{calc}} = 1.349\text{ g/cm}^3$, $Z = 6$, $\mu = 22.52\text{ cm}^{-1}$, (MoK α , $\lambda = 0.71069\text{ \AA}$).

A transparent monoclinic crystal of $t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}$ having approximate dimensions of 0.40 X 0.60 X 0.20 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer using graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $30.95^\circ < 2\Theta < 38.32^\circ$, corresponded to a rhombohedral (hexagonal axes) cell.

Based on the systematic absences of:

$$hkl: -h+k+l \neq 3n$$

and packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$R3(h) (\#148)$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω - 2Θ scan technique to a maximum 2Θ value of 60.1° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.35° with a take-off angle of 6.0° . Scans of

width $(1.52 + 0.30 \tan \Theta)^\circ$ were made at a speed of $16^\circ/\text{min}$ (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data reduction

Of the 2761 reflections which were collected, 1303 were unique; equivalent reflections were merged ($R_{\text{int}} = .058$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for $\text{MoK}\alpha$ is 22.52cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.84 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 872 observed reflections ($I > 3.00\sigma(I)$) and 46 variable parameters and converged (largest

parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.042$$

$$R_w = [(\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)]^{1/2} = 0.051$$

The standard deviation of an observation of unit weight⁷ was 1.57. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma \omega (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\Theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.56 and -0.55 $e^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from those of Cromer and Waber⁸. Anomalous dispersion effects were included in F_{calc} ⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, $B(eq)$, bond distance and angles for the compound **5** are listed in table 9 and table 10.

Table 9. Positional Parameters and B(eq) for the atoms of *t*-BuGe(HNCH₂CH₂)₃N(5)

Atom	X	Y	Z	B(eq)
Ge	0	0	0.2749(1)	2.7(1)
N1	0.1920(4)	0.0483(5)	0.02926(2)	5.1(2)
C1	0.1114(7)	0.1544(6)	0.1571(2)	6.4(2)
C2	0.2485(5)	0.0639(5)	0.3547(2)	4.6(2)
C3	-0.036(1)	0.109(1)	0.4014(3)	13.4(5)
C4	0.0018	0.0085	0.1820(3)	3.7(2)

Table10. Thermal Parameters for *t*-BuGe(HNCH₂CH₂)₃N(5)

Atom	U11	U22	U33	U12	U13	U23
Ge	0.0344(3)	0.0344	0.0337(3)	0.0172	0	0
N1	0.043(2)	0.108(3)	0.046(2)	0.038(2)	-0.002(2)	-0.008(2)
N2	0.051(2)	0.051	0.037(3)	0.026	0	0
C1	0.099(4)	0.079(4)	0.051(3)	0.051(3)	0.034(3)	0.013(3)
C2	0.052(2)	0.071(3)	0.057(3)	0.034(2)	-0.011(2)	-0.004(2)
C3	0.38(1)	0.24(1)	0.0044(3)	0.27(1)	0.012(6)	-0.007(5)
C4	0.050(2)	0.050	0.039(4)	0.025	0	0

Crystal data

$\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$, M.W. = 377.67, monoclinic $P2_1/c$, $a = 13.503(5)\text{\AA}$, $b = 10.621(2)\text{\AA}$, $c = 17.840(6)\text{\AA}$, $\beta = 93.29(3)^\circ$, $V = 2554(2)\text{\AA}^3$, $d_{\text{calc}} = 0.982\text{ g/cm}^3$, $Z = 4$, $\mu = 2.18\text{ cm}^{-1}$, (MoK α , $\lambda = 0.71069\text{ \AA}$).

A transparent irregularly-shaped crystal of $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$ having approximate dimensions of 0.24 X 0.40 X 0.50 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for datacollection, obtained from a least-squares refinement using the setting angles of 17 carefully centered reflections in the range $12.68^\circ < 2\Theta < 15.30^\circ$, corresponded to a monoclinic cell.

Based on the systematic absences of:

$$h0l: l \neq 2n$$

$$0k0: k \neq 2n$$

and the successful solution and refinement of the structure, the space group was determined to be:

$$P2_1/c \text{ (\#14)}$$

The data were collected at a temperature of $-20 \pm 1^\circ$ using the ω - 2Θ scan technique to a maximum 2Θ value of 55.1° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.40° with a take-off angle of 6.0° . Scans of width $(1.05 + 0.30 \tan\Theta)^\circ$ were made at a speed of $16^\circ/\text{min}$ (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data reduction

Of the 9762 reflections which were collected, 4923 were unique; equivalent reflections were merged ($R_{\text{int}} = .118$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability; no decay correction was applied.

The linear absorption coefficient for $\text{MoK}\alpha$ is 2.2cm^{-1} . Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods⁵. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement⁶ was based on 1528 observed reflections ($I > 3.00\sigma(I)$) and 208 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.052$$

$$R_w = [(\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)]^{1/2} = 0.058$$

The standard deviation of an observation of unit weight⁷ was 1.82. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma \omega (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\Theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.22 and -0.19 $e/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from those of Cromer and Waber⁸. Anomalous dispersion effects were included in F_{calc} ⁹; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer¹⁰. All calculations were performed using the TEXSAN¹¹ crystallographic software package of Molecular Structure Corporation. The positional parameters, $B(eq)$, bond distance and angles for the compound **6** are listed in table 11 and table 12.

Table 11. Positonal Parameters and B(eq) for the atoms of Al(Me₃SiNCH₂CH₂)₃N(6)

Atom	X	Y	Z	B(eq)
Si1	0.9837(2)	0.2606(2)	0.1380(1)	5.7(1)
Si2	0.7178(2)	-0.1045(2)	0.1057(1)	5.5(1)
Si3	0.6058(2)	0.3446(2)	0.1622(1)	7.1(1)
Al	0.7634(2)	0.1872(2)	0.0712(1)	4.2(1)
N1	0.7483(5)	0.2257(60)	-0.0376(3)	5.3(3)
N2	0.7109(4)	0.0320(5)	0.0576(3)	4.8(3)
N3	0.8967(4)	0.2075(5)	0.0730(3)	5.5(3)
N4	0.6849(4)	0.3183(5)	0.0939(3)	5.2(3)
C1	0.7098(6)	0.1076(8)	-0.0726(4)	6.2(4)
C2	0.6526(6)	0.0365(7)	-0.0726(4)	6.2(4)
C3	0.8499(7)	0.2557(9)	-0.0588(4)	7.8(6)
C4	0.9236(6)	0.189(1)	-0.0049(5)	8.2(6)
C5	0.6778(7)	0.3321(8)	-0.0432(4)	7.2(5)
C6	0.6886(7)	0.4062(7)	0.0300(5)	7.6(5)
C11	0.9250(6)	0.2776(8)	0.2277(4)	7.6(5)
C12	1.0894(6)	0.1505(9)	0.1507(5)	9.5(6)
C13	1/0360(7)	0.4139(8)	0.1104(5)	9.5(6)
C21	0.7702(7)	-0.2350(8)	0.0522(6)	10.7(7)
C22	0.5954(6)	-0.1570(8)	0.1333(6)	9.9(6)
C23	0.7973(7)	-0.0778(8)	0.1920(6)	10.7(7)
C31	0.638(1)	0.4933(8)	0.2145(5)	12.3(7)
C32	0.6166(6)	0.2149(7)	0.2297(4)	7.0(5)
C33	0.4766(8)	0.357(2)	0.1257(7)	19(1)

Table 12. Thermal Parameters for $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(6)$

Atom	U11	U22	U33	U12	U13	U23
Si1	0.070(2)	0.080(2)	0.065(1)	-0.020(1)	0.004(1)	-0.010(1)
Si2	0.057(1)	0.056(1)	0.095(2)	0.001(1)	0.005(1)	0.017(1)
Si3	0.102(2)	0.093(2)	0.076(2)	0.036(2)	0.014(1)	-0.004(2)
Al	0.061(2)	0.054(1)	0.047(1)	-0.010(1)	0.004(1)	0.003(1)
N1	0.094(5)	0.070(5)	0.036(4)	-0.019(4)	0.006(3)	-0.005(3)
N2	0.060(4)	0.055(4)	0.066(5)	-0.013(3)	-0.014(3)	0.011(3)
N3	0.068(4)	0.096(5)	0.047(4)	-0.022(4)	0.015(3)	-0.018(3)
N4	0.095(5)	0.052(4)	0.049(4)	0.013(4)	0.005(3)	0.006(5)
C1	0.092(6)	0.087(6)	0.056(5)	-0.012(5)	-0.017(6)	-0.006(5)
C2	0.090(6)	0.061(5)	0.084(7)	-0.021(5)	-0.016(6)	0.009(5)
C3	0.112(8)	0.133(9)	0.055(5)	-0.055(7)	0.028(5)	-0.017(6)
C4	0.068(6)	0.16(1)	0.081(7)	-0.041(6)	0.011(5)	-0.039(7)
C5	0.158(9)	0.056(6)	0.0600(6)	0.002(6)	0.011(6)	0.020(5)
C6	0.150(8)	0.065(6)	0.075(7)	0.012(6)	-0.001(6)	0.010(5)
C11	0.089(6)	0.135(8)	0.062(5)	-0.032(6)	-0.007(5)	-0.019(5)
C12	0.098(7)	0.132(8)	0.062(5)	-0.032(6)	-0.007(5)	-0.019(5)
C13	0.133(8)	0.115(8)	0.111(8)	-0.061(7)	-0.013(6)	0.015(6)
C21	0.147(9)	0.077(7)	0.19(1)	0.016(6)	0.061(8)	0.000(7)
C22	0.087(7)	0.098(7)	0.19(1)	-0.002(6)	0.046(7)	0.055(7)
C23	0.136(8)	0.105(8)	0.16(1)	0.006(7)	-0.052(7)	0.062(7)
C31	0.29(1)	0.079(7)	0.097(8)	0.042(8)	0.052(9)	-0.006(6)
C32	0.113(7)	0.080(6)	0.075(6)	0.004(5)	0.044(5)	-0.007(5)
C33	0.13(1)	0.44(2)	0.13(1)	0.15(1)	-0.020(8)	0.01(1)

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

Three of six structures crystallize in the monoclinic space group $P2_1/c$ (6) (or its equivalent $P2_1/n$ (1) or $P2_1/a$ (2)) with four molecules per unit cell, and one of them in the monoclinic space group $P2_1/m$ (3) with two molecules per unit cell. The fourth one crystallizes in the trigonal space group $P31c$ (4) with two molecules per unit cell and the fifth crystallizes in the trigonal space group with hexagonal axis $R3(h)$ (5) with six molecules per unit cell. All of them have similar cages around center atom as is shown in ORTEP drawings which are presented in Figure 1 to 6; selected bond lengths and angles are given in Tables 13-24 for compound 1 through 6, respectively.

The molecular structure of the azavanadatranes ($Z=Nt\text{-}Bu$)(1) shown in Figure 1, features a central vanadium atom in a trigonal bipyramidal (TBP) coordination environment. This compound has a propeller-like geometry, closely, but not exactly possessing three fold symmetry with a C_3 axis through the V and apical N atoms. The two triangular units, VN(2)N(3)N(5) and N(4)C(12)C(17)C(18) are not eclipsed, the average torsional angle being $22.8(6)^\circ$. The three five-membered rings are in an envelope conformation with the "flap" atoms C(12), C(17), C(18) displaced out of the plane of the envelope by $0.51\text{\AA}$, $0.59\text{\AA}$ and $0.57\text{\AA}$ respectively. The equatorial nitrogens are planar, the average of the sum of angles around them being $358.8(2)^\circ$.

The coordination geometry at the vanadium center is not the ideal **TBP** geometry. The angles between nitrogens in the basal triangular face are 118.2° , 116.2° and 115.0° (Table 14), respectively. The vanadium is above the plane of the basal nitrogens by $0.36\text{\AA}$ resulting in N(basal)-V-N(apical) angles of $78.4(2)^\circ$, $79.9(2)^\circ$ and $78.8(2)^\circ$.

The molecular structure of the monoazasilatranes ($Z=\text{H}$) (**2**) is shown in Figure 2. It has somewhat a similar structure to that of **1**, but the silicon atom coordinates with two oxygens and one nitrogen in the basal plane instead of three nitrogens. It possesses unsymmetrical ligands and differently shaped propellers. The average torsion angle between two triangular units, SiN(1)O(1)O(2) and N(2)C(2)C(3)C(4) is $18.5(4)^\circ$. Two of three five-membered rings are in an envelope conformation with the "flap" atoms C(2) and C(4) displaced out of the plane of the envelope by $0.45\text{\AA}$ and $0.51\text{\AA}$; the two atoms C(3) and C(5) in the third ring are displaced out of the plane by $0.38\text{\AA}$ and $0.15\text{\AA}$, respectively but in the opposite direction.

The coordination geometry at the silicon center is not the ideal **TBP** geometry. The angles between oxygens and nitrogen in the basal triangular face are $115.1(2)^\circ$, $120.3(2)^\circ$ and $120.9(2)^\circ$ (Table 17), respectively. The silicon is above the plane of the two basal oxygens and one nitrogen by $0.39\text{\AA}$ resulting in O(basal) or N(basal)-Si-N(apical) angles of $84.1(2)^\circ$, $84.6(2)^\circ$ and $82.0(2)^\circ$.

From Table(16), it's evident that the $\text{N}_{\text{ax}}\text{-C}_3$ geometry is pyramidal (angle sum = $338.7(5)^\circ$). The Si- N_{ax} distance is $2.114(4)\text{\AA}$. This observation along with the upward protrusion of N_{ax} (by $0.40\text{\AA}$ above the plane of the adjacent carbons) suggest the presence of a Si- N_{ax} bond.

The molecular structure of the azalithatranes ($Z=\text{ClO}_4$)(3) shown in Figure 3; the structure is only approximate due to its poor refinement. It also possesses unsymmetrical and differently shaped propellers. The average torsion angle between two triangular units, $\text{LiN}(2)\text{N}(2)\text{N}(3)$ and $\text{N}(1)\text{C}(2)\text{C}(4)\text{C}(6)$ is $18.5(4)^\circ$. One of three five-membered rings is in an envelope conformation with the "flap" atom $\text{C}(4)$ displaced out of the plane of the envelope by $0.11\text{\AA}$; the second ring $\text{LiN}(4)\text{C}(5)\text{C}(6)\text{N}(1)$ is almost planar, and the two atoms $\text{C}(1)$ and $\text{C}(2)$ in the third one $\text{LiN}(2)\text{C}(1)\text{C}(2)\text{N}(1)$ displaced out of the plane by $0.45\text{\AA}$ and $0.19\text{\AA}$ (in the same direction), respectively. Each of the equatorial nitrogens is essentially in the same plane as its three neighbors, the average of the sum of angles around them being 360.0° .

The coordination geometry of the lithium center is not the ideal **TBP** geometry. The angles between nitrogens in the basal triangular face are $127.8(2)^\circ$, $114(2)^\circ$ and $113(2)^\circ$ (Table 18) respectively. The lithium is above the plane of the basal nitrogens by $0.27\text{\AA}$ resulting in $\text{N}(\text{basal})\text{-Li-N}(\text{apical})$ angles which are $83.2(4)^\circ$, $83(1)^\circ$ and $82(1)^\circ$.

The molecular structure of the azaphosphatranes ($Z=\text{Me}$)(4) shown in Figure 4, features a central phosphorus atom in a trigonal bipyramidal (**TBP**) coordination environment. This compound shows a propeller-like geometry, possessing three fold symmetry with a C_3 axis through the P and apical N atoms. Two triangular units, $\text{PN}(1)\text{N}(1\text{A})\text{N}(1\text{B})$ and $\text{N}(2)\text{C}(3)\text{C}(3\text{A})\text{C}(3\text{B})$ shown in Figure 4, are nearly eclipsed with an average torsional angle of only $5.7(5)^\circ$. The five-membered ring is in an envelope conformation with the "flap" two atoms $\text{C}(2), \text{C}(3)$ displaced out of the plane of the envelope by $0.51\text{\AA}$ and $0.72\text{\AA}$, respectively. Each of

the equatorial nitrogens is essentially in the same plane as its three neighbors, the average of the sum of angles around them being $356.7(2)^\circ$.

The coordination geometry at the phosphorus center is not the ideal **TBP** geometry. The angles between nitrogens in the basal triangular face are $113.3(1)^\circ$ (Table 20). The phosphorus is above the plane of the basal nitrogens by $0.48\text{\AA}$ resulting in N(basal)-V-N(apical) angles of $74.6(1)^\circ$. The C(1), P2 and N_{ax} are not exactly colinear with the C₃ axis, the angle being $179.8(1)^\circ$.

The molecular structure of the azagermatranes(Z= *t*-Bu)(5) is shown in Figure 5, and possesses similar structural features to compound 4. Two triangular units, GeN(1)N(1A)N(1B) and N(2)C(3)C(3A)C(3B) are almost eclipsed with an average torsional angle of only $0.7(5)^\circ$. The five-membered rings are in an planar conformation with mean deviation of $0.008\text{\AA}$.

The coordination geometry at the germanium center is again not the ideal **TBP** geometry. The angles between nitrogens in the basal triangular face are $115.88(7)^\circ$ (Table 22). The germanium is above the plane of the basal nitrogens by $0.38\text{\AA}$ resulting in N(basal)-Ge-N(apical) angles of $78.3(1)^\circ$. The C(1),P2 and N_{ax} are not exactly collinear with the C₃ axis, the angle being $176.9(1)^\circ$.

The molecular structure of the monomeric azaalumatrane (Z= nothing)(6) is shown in Figure 6, and features a central aluminum atom in a trigonal monopyramidal (**TMP**) coordination environment. This represents the first example of this geometry for aluminum, and it is rare for the main-group elements in general. This molecule exhibits a propeller-like geometry,

possessing a pseudo three fold symmetry with a pseudo C_3 axis through the Al and apical N atoms. Two triangular units, AlN(2)N(3)N(4) and N(1)C(1)C(3)C(5) shown in Figure 6, are nearly eclipsed with an average torsional angle of only $3.3(6)^\circ$. The five-membered rings are in an envelope conformation with the "flap" atoms C(2),C(4) and C(6) displaced out of the plane of the envelope by $0.59\text{\AA}$. Each of the equatorial nitrogens is essentially in the same plane as its three neighbors, the average of the sum of angles around them being $359.5(5)^\circ$. The coordination geometry of the aluminum center very closely approaches the ideal **TMP** geometry. The angles between nitrogens in the basal triangular face are the same (within 2σ) and their average is $119.9(3)^\circ$ (Table 24). The aluminium is drawn slightly below the plane of the basal nitrogens($0.07\text{\AA}$) resulting in N(basal)-Al-N(apical) angles which lie within 2σ of each other and average $92.1(3)^\circ$.

Table 25 give the comparable angles and distance among these six compounds.

Figure 1. ORTEP structure for $\text{Me}_3\text{VN}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(1)$

Figure 2. ORTEP structure for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}(2)$

Figure 3. ORTEP structure for $\text{O}_4\text{ClLi}(\text{HNCH}_2\text{CH}_2)_3\text{N}(3)$

Figure 4. ORTEP structure for $\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{N}(4)$

Figure 5. ORTEP structure for *t*-BuGe(HCH₂CH₂)₃N(5)

Figure 6. ORTEP structure for $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(6)$

Table 13. Selected Bond Distances for (*t*-BuN)V(MeNCH₂CH₂)₃N (1)

atom	atom	distance	atom	atom	distance
V	N1	1.659(5)	N4	C17	1.47(1)
V	N2	1.920(6)	N4	C18	1.48(1)
V	N3	1.895(6)	N5	C6	1.45(1)
V	N4	2.233(5)	N5	C16	1.443(9)
V	N5	1.898(6)	C7	C8	1.53(1)
N1	C7	1.445(8)	C7	C10	1.52(1)
N2	C9	1.45(1)	C7	C15	1.49(1)
N2	C14	1.45(1)	C9	C18	1.48(1)
N3	C11	1.47(1)	C11	C17	1.52(1)
N3	C13	1.44(1)	C12	C16	1.52(1)
N4	C12	1.47(1)			

Table 14. Selected Bond Angles for (t-BuN)V(MeNCH₂CH₂)₃N (1)

atom	atom	atom	angle	atom	atom	atom	angle
N1	V	N4	179.2(2)	C11	N3	C13	110.7(6)
N2	V	N3	116.2(2)	V	N4	C12	107.3(5)
N2	V	N4	78.4(2)	V	N4	C17	105.1(5)
N2	V	N5	118.2(2)	V	N4	C18	106.0(5)
N3	V	N4	79.9(2)	C12	N4	C17	114.0(7)
N3	V	N5	114.9(2)	C12	N4	C18	112.1(7)
N4	V	N5	78.8(2)	C17	N4	C18	111.7(7)
V	N1	C7	177.7(5)	V	N5	C6	128.6(5)
V	N2	C9	120.8(5)	V	N5	C16	121.9(5)
V	N2	C14	127.3(5)	C6	N5	C16	109.5(6)
C9	N2	C14	110.8(6)	N13	C11	C17	108.8(7)
V	N3	C11	120.3(5)	N4	C12	C16	108.6(7)
V	N3	C13	128.8(5)	N4	C18	C9	108.4(7)

Table 15. Selected Bond Distance for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}(2)$

atom	atom	distance	atom	atom	distance
SI	O1	1.657(4)	N1	C1	1.444(7)
SI	O2	1.663(4)	C1	C2	1.511(9)
SI	N1	1.715(5)	N2	C2	1.479(8)
SI	N2	2.114(4)	N2	C3	1.464(7)
SI	H14	1.40	N2	C4	1.461(7)
O1	C6	1.405(7)	C3	C5	1.504(8)
O2	C5	1.398(7)	C4	C6	1.54(1)

Table 16. Selected Bond Angles for $\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)\text{N}$ (2)

atom	atom	atom	angle	atom	atom	atom	angle
O1	SI	O2	115.1(2)	C1	N1	H13	118.3(1)
O1	SI	N1	120.3(2)	N1	C1	C2	107.2(4)
O1	SI	N2	84.1(2)	C2	N2	C3	112.0(5)
O2	SI	N1	120.9(2)	C2	N2	C4	112.1(5)
O2	SI	N2	84.6(2)	C3	N2	C4	114.6(5)
N1	SI	N2	82.0(2)	C1	C2	N2	106.5(5)
N2	SI	H14	175.4(3)	N2	C3	C5	105.4(4)
SI	O1	C6	122.6(4)	N2	C4	C6	105.1(5)
SI	O2	C5	120.5(3)	O2	C5	C3	111.1(4)
SI	N1	C1	123.7(4)	O1	C6	C4	109.3(5)
SI	N1	H13	118.0(2)				

Table 17. Selected Bond Distances for $\text{ClO}_4\text{Li}(\text{HNCH}_2\text{CH}_2)_2\text{N}$ (3)

atom	atom	distance	atom	atom	distance
N1	C2	1.5(5)	N3	C3	1(1)
N1	C4	1.5(3)	N3	LI	2(4)
N1	C6	1.4(5)	N4	C5	1.5(5)
N1	LI	2.1(9)	N4	LI	2.2(7)
N2	C1	2(1)	C1	C2	1.4(8)
N2	LI	2(4)	C5	C6	1.3(6)

Table 18. Selected Bond Angles for $\text{ClO}_4\text{Li}(\text{HNCH}_2\text{CH}_2)_3\text{N}$ (3)

atom	atom	atom	angle	atom	atom	atom	angle
C2	N1	C4	112(1)	C2	N1	C6	116(2)
C2	N1	Li	112(2)	C4	N1	C6	116(2)
C4	N1	Li	104(1)	C6	N1	Li	105.7(5)
C1	N2	Li	108(1)	C3	N3	Li	111(1)
C5	N4	Li	107.8(6)	N2	C1	N2	114(1)
N1	C2	C1	112(2)	N1	C4	C3	119(1)
N4	C5	C6	121.2(7)	N1	C6	C5	121.9(8)
O1	Li	N1	178(1)	N1	Li	N2	82(1)
N1	Li	N3	83(1)	N1	Li	N4	83.2(4)
N2	Li	N3	127.8(6)	N2	Li	N4	114(2)
N3	Li	N4	113(2)				

Table 19. Selected Bond Distances for MeP(MeNCH₂CH₂)₃N (4)

atom	atom	distance	atom	atom	distance
P2	N2	2.80(1)	C1	N1	2.78(1)
P2	C1	1.85(1)	C1	C4	3.25(1)
P2	N1	1.638(5)	N1	C2	1.45(1)
P2	C2	2.689(7)	N1	C3	2.509(8)
P2	C3	3.276(7)	N1	C4	1.48(1)
P2	C4	2.699(7)	C2	C3	1.57(1)
N2	N1	2.84(1)	C2	C4	2.48(1)
N2	C2	2.449(8)	C3	C4	3.37(1)
N2	C3	1.453(7)			

Table 20. Selected Bond Angles for MeP(MeNCH₂CH₂)₃N (4)

atom	atom	atom	angle	atom	atom	atom	angle
N2	P2	C1	179.871(1)	N1	P2	N1	113.4(1)
N1	P2	N1	113.3(1)	N1	P2	N1	113.3(1)
N2	P2	N1	74.6(2)	C3	N2	C3	118.1(1)
N2	P2	N1	74.5(2)	C3	N2	C3	119.4(2)
N2	P2	N1	74.2(2)	C3	N2	C3	119.4(2)
N2	P2	C1	179.676(2)	P2	N1	C4	120.1(5)
N2	P2	C1	179.941(1)	C2	N1	C4	115.9(5)
N2	P2	C1	179.642(2)				

Table 21. Selected Bond Distances for t-BuGE(HCH₂CH₂)₃N (5)

atom	atom	distance	atom	atom	distance
GE	N1	1.833(3)	N2	C3	1.379(6)
GE	N2	2.361(6)	N2	C3	1.429(6)
GE	C1	2.903(5)	N2	C3	1.387(6)
GE	C2	2.879(4)	C1	C4	1.467(6)
GE	C3	3.028(5)	C1	C4	1.597(6)
GE	C4	1.991(7)	C1	C4	1.528(6)
N1	C2	1.431(5)	C2	C3	1.388(8)

Table 22. Selected Bond Angles for t-BuGe(HCH₂CH₂)₃N (5)

atom	atom	atom	angle	atom	atom	atom	angle
N1	GE	N1	115.88(7)	GE	N2	C3	105.1(3)
N1	GE	N1	115.88(7)	GE	N2	C3	103.3(3)
N1	GE	N2	77.8(1)	GE	N2	C3	104.8(3)
N1	GE	N2	78.9(1)	C3	N2	C3	113.3(2)
N1	GE	N2	77.6(1)	C3	N2	C3	116.0(3)
N1	GE	N1	115.88(7)	C3	N2	C3	112.8(2)
GE	N1	C2	123.3(3)	N1	C2	C3	114.6(4)
GE	N1	C4	42.1(1)	N2	C3	C2	119.4(5)
GE	N1	H1	117.87	N2	C3	C2	119.4(5)
C2	N1	H1	118.78	N2	C3	C2	119.9(4)

Table 23. Selected Bond Distances for $\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$ (6)

atom	atom	distance	atom	atom	distance
AL	N1	1.983(6)	N2	C2	1.463(8)
AL	N2	1.805(5)	N3	C4	1.468(9)
AL	N3	1.811(6)	N4	C6	1.476(9)
AL	N4	1.810(6)	C1	C2	1.53(1)
N1	C1	1.482(9)	C3	C4	1.52(1)
N1	C3	1.48(1)	C5	C6	1.52(1)
N1	C5	1.477(9)			

Table 24. Selected Bond Angles for Al(Me₃SiNCH₂CH₂)₃N (6)

atom	atom	atom	angle	atom	atom	atom	angle
N1	AL	N2	92.3(3)	C3	N1	C5	114.9(7)
N1	AL	N3	92.3(3)	AL	N2	C2	106.0(4)
N1	AL	N4	91.8(3)	AL	N3	C4	105.5(4)
N2	AL	N3	119.6(3)	AL	N4	C6	105.6(5)
N2	AL	N4	120.1(3)	N1	C1	C2	107.9(6)
N3	AL	N4	119.9(3)	N2	C2	C1	110.1(6)
AL	N1	C1	104.6(4)	N1	C3	C4	108.9(7)
AL	N1	C3	104.4(5)	N3	C4	C3	110.5(7)
AL	N1	C5	104.7(4)	N1	C5	C6	108.0(6)
C1	N1	C3	112.5(6)	N4	C6	C5	109.2(6)
C1	N1	C5	114.3(6)	SI1	N3	AL	134.4(3)
SI1	N3	C4	119.4(5)	AL	N3	C4	105.4(4)
SI2	N2	AL	135.1(4)	SI2	N2	C2	118.9(5)
AL	N2	C2	105.9(4)	SI3	N4	AL	133.7(3)
SI3	N4	C6	120.2(5)	AL	N4	C6	105.6(5)

Table 25. Selected Bond Distance And Angles of Six Compounds

	1	2	3	4	5	6
Torsion angle between two triangular units	22.8°	18.5°	18.5°	5.7°	0.7°	3.3°
The average of the sum of angles around Neq	358.8°	360.0°	360.0°	356.7°	359.8°	359.5°
The angles between nitrogens in the basal triangular face.	118.2° 116.2° 115.0°	115.1° 120.3° 120.9°	127.8° 114° 113°	113.3°	115.9° 119.6° 120.1°	119.9°
N(Basal)-M-N(apical)	78.4° 79.9° 78.8°	84.1° 84.6° 82.0°	83.2° 83° 82°	74.6°	78.3°	92.1°
The distance of the center atom above the plane of the basal nitrogen	0.36Å	0.39Å	0.27Å	0.48Å	0.38Å	0.07Å
M-N _{ax}	2.335Å	2.114Å	2.15Å	2.778Å	2.361Å	1.983Å

CONCLUSION

The crystal and molecular structures of six azatrane containing vanadium, silicon, lithium, phosphorus, germanium crystallize in either the rhombohedral trigonal crystal system in which a crystallographic three fold axis is utilized or in the monoclinic crystal system. Three of the four which crystallize in the monoclinic system do so with molecules occupying general positions. The only exception is found for the lithium compound and even here, although refinement was carried out using a crystallographic mirror plane, results indicated that the mirror was only approximate.

All these compounds were shown to be cage⁰ compounds with a trigonal bipyramidal structure in the cell of all except the aluminium compound, which adopts a trigonal monopyramidal structure. The metal-N_{ax} bond distances range from 2.778 Å for the phosphorus compound to 1.983 Å for the aluminum compound. The sum of the bond angles for the three metal-N_{eq} bonds range from 339.5° for the phosphorus to 359.7° for the aluminum compound. The N_{basal}-metal-N_{apical} angle range from 74.6° for the phosphorus compound to 92.1° for the aluminum compound.

(*t*-BuN)V(MeNCH₂CH₂)₃N(1) crystallizes in the monoclinic space group P2₁/n. The bond distance of V-N_{ax} is 2.335 Å. The axial nitrogens are quite planar with C-N_{ax}-C angles of approximately but less than 120°, so the axial nitrogen is above the plane of the adjacent carbons by 0.36 Å. The angles of N(Basal)-V-N(apical) are about 78°, and the Vanadium is in a trigonal bipyramidal environment. The whole structure is close to the **TBP**.

$\text{HSi}(\text{OCH}_2\text{CH}_2)_2(\text{HNCH}_2\text{CH}_2)_2$ (2) crystallizes in the monoclinic space group $P2_1/a$. The bond distance of Si-Nax is $2.114\text{\AA}$. The axial nitrogens are quite planar with C-Nax-C angles of approximately 120° and the axial nitrogen is above the plane of the adjacent carbons by $0.39\text{\AA}$. The N-Si-N and N-Si-O bond angles are approximately 84° , which is close to 90° . (The molecular structure of this compound can not be ideal TBP, since two of the three arms contain nitrogen atoms and the other one has an oxygen atom.) $\text{ClO}_4\text{Li}(\text{HNCH}_2\text{CH}_2)_3\text{N}$ (3) crystallizes in the monoclinic space group $P2_1/m$. The bond distance of Li-Nax is $2.15\text{\AA}$. One of the C-Nax-C angles is considerably different than the other two. It is difficult to tell whether the difference is real or due to small distortions from the chosen space group. The axial nitrogen is above the plane of the adjacent carbons by $0.27\text{\AA}$. Each of the N(Basal)-Li-N(apical) bond angles is about 83° . The three arms are not symmetrical and it's not ideal TBP.

$\text{MeP}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$ (4) crystallizes in the trigonal space group $P31c$. The bond distance of P-Nax is $2.778\text{\AA}$. The C-Nax-C angles are approximately 113° . The three arms are approximately symmetrical and the axial nitrogen is above the plane of the adjacent carbons by $0.48\text{\AA}$; this is the largest one in six compounds. The bond angles of N(Basal)-P-N(apical) are 74.6° , which are off 90° a lot more than other five compounds, so the structure has the biggest torsion from TBP.

$t\text{-BuGe}(\text{HNCH}_2\text{CH}_2)_3\text{N}$ (5) crystallizes in the rhombohedral(hexagonal axes) space group $R3(h)$. The bond distance of Ge-Nax is $2.361\text{\AA}$. The C-Nax-C angles are approximately 115.9° . The axial

nitrogen is above the plane of the adjacent carbons by $0.38\text{\AA}$, and the bond angles of N(basal)-Ge-N(apical) are 78.3° . Compared to compound 4, the structure of compound 5 is more trigonal bipyrimidal and the three arms are approximately symmetrical like compound 4.

$\text{Al}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}(\mathbf{6})$ crystallizes in the monoclinic space group $P2_1/c$. The bond distance of Al-Nax is $1.938\text{\AA}$. The axial nitrogens are quite planar with the bond angles of C-Nax-C approximately 120° . The three arms are almost symmetrical. The axial nitrogen is only slightly above the plane of the adjacent carbons by $0.07\text{\AA}$. The bond angles of N(Basal)-Al-N(apical) are 92.1° , which is very close to 90° . All data of this compound show the strong agreement with the trigonal monopyrimidal structure conformation.

REFERENCES

1. Stanislav, N.; Voronkov, M. G.; Alekseev, N.V. *Top. Curr. Chem.* **1986**, *131*, 99 and references therein.
2. Lukevits, E.; Zelchan, E. I.; Solomenikova, I. I.; Liepins, E. E. ; Yanlovskaya, I. S.; Mazheila, I. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*, 98.
3. (a) Korecz, L.; Saghier, A. A.; Burger, K.; Tzschach, A.; Jurkschat, K. *Inorg. Chim. Acta* **1982**, *58*, 243.
(b) Kakimoto, N.; Sato, K.; Mutsui, M.; Takada, T.; Akiba, M. *Heterocycles* **1986**, *24*, 3047.
4. Jacobson, R. A., Patterson superposition method.
5. Structure Solution Methods:
MITHRIL
Gilmore, C.J.; MITHRIL - an integrated direct methods computer program. *J. Appl. Cryst.* *17*, 42- 46, Univ. of Glasgow, Scotland, (1984).
DIRDIF
Beurskens, P.T.; DIRDIF: Direct Methods for Difference Structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1
Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.
6. Least- Squares:

Function minimized: $\sum \omega (|F_o| - |F_c|)^2$

where:

$$\omega = 4|F_o|^2 / \sigma^2(F_o^2)$$

$$\sigma^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2] / Lp^2$$

S = Scan rate

C = Total Integrated Peak Count

R = Ratio of Scan Time to background counting time.

B = Total Background Count

Lp = Lorentz-polarization factor

p = p-factor

7. Standard deviation of an observation of unit weight:

$$[\sum w (|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

8. Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", *Vol. IV*, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
9. Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, *17*, 781 (1964).
10. Cromer, D. T. "International Tables for X-ray Crystallography", *Vol. IV*, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).
11. REXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).