

National Library of Canada

Bibliothèque nationale du Canada

Direction des acquisitions et

des services bibliographiques

Acquisitions and Bibliographic Services Branch

395 Weilington Street Ottawa, Ontario K1A 0N4 395, rue Wellington Ottawa (Ontario) K1A 0N4

Non-time Systemethyles in

#### Our life - Note reference

### NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments. La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

AVIS

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

2.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

# Canada

# SILYLHYDRAZINES: CHEMISTRY AND PYROLYTIC CONVERSION TO SI-N-C CERAMIC MATERIALS

by

JILIANG HE

Department of Chemistry McGill University Montreal May 1995

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Copyright © Jiliang He, 1995



National Library of Canada

Accuisitions and

Bibliothèque nationale du Canada

Direction des acquisitions et des services bibliographiques Bibliographic Services Branch

395 Wellington Street Ottawa, Ontario K1A 0N4

395, rue Wellington Ottawa (Ontario) K1A 0N4

Your time Votre reference

Our line - Notre reference

The author has granted an irrevocable non-exclusive licence allowing the National Library of reproduce, loan, Canada to distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive à la Bibliothèque permettant nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-08112-5



### SILYLHYDRAZINES: CHEMISTRY AND PYROLYTIC CONVERSION TO SI-N-C CERAMIC MATERIALS

Ph.D.

Jiliang He

Chemistry

#### Abstract

A new synthetic route to silvlhydrazine molecules and polymers has been developed by the heterodehydrocoupling of organosilanes with hydrazines. A dimethyltitanocene catalyst has been employed to facilitate the dehydrocoupling reaction. The dehydrocoupling was shown to proceed by stepwise replacement of Si-H with hydrazino groups. The controlled hydrolysis of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> formed a hydrazinodisiloxane. Cyclizations of  $Ph_2Si(NHNHMe)_2$  to form cyclic silver silver a chieved by the reaction with *n*-BuLi/Ph2SiCl2, or MeI (or HCl or Ph2SiCl2), or thermolysis. Crystal structures of  $Ph_2Si(NHNR)(NRNH)SiPh_2$  (R = H, Me) reveal chair (R = H) and twist-boat (R = Me) conformations of the Si<sub>2</sub>N<sub>4</sub> ring, respectively. Planar and pyramidal nitrogen geometries were found to coexist in a hydrazino unit. A preceramic polymer, synthesized by the polymerization of MeHSiCl<sub>2</sub> with hydrazine in an appropriate ratio, was pyrolyzed to  $Si_3N_4/SiC_xN_y$  in 67-80% ceramic yields. It is proposed that the structural unit of this polymer is a tetraazadisilacyclohexane bridged by MeHSi groups. This assignment is based on <sup>1</sup>H and <sup>29</sup>Si NMR measurements, as well as by comparison with the well-defined reaction product of Me<sub>2</sub>Si[NHNH]<sub>2</sub>SiMe<sub>2</sub> with MeHSiCl<sub>2</sub>. The pyrolysis was carried out from room temperature to 1500 °C under argon and studied by using thermogravimetric analysis, solid-state <sup>29</sup>Si NMR spectroscopy, infrared spectroscopy, X-ray powder diffraction, and elemental analysis. Serial structural changes were characterized in the pyrolyzed solid products. The ceramic product of this polymer at 1100 °C was found to possess a quasi-metallic electrical conductivity ( $\sigma = 10^3 (\Omega \text{cm})^{-1}$ ), and was evaluated as an electrode material.

## Silylhydrazines: Chimie et Conversion à des Matériaux Céramiques Si-N-C par Pyrolyse

Ph.D.

Jiliang He

Chimie

### Résumé

Le couplage hétérodéshydrogénatif d'organosilanes avec des hydrazines a conduit à une nouvelle méthode de synthèse de molécules et de polymères de silylhydrazine. La réaction est favorisée par l'utilisation du diméthyltitanocène comme catalyseur. Il a été démontré que le couplage déshydrogénatif procède par un remplacement en étapes des groupes Si-H par des groupes hydrazinés. L'hydrolyse contrôlée du Ph2Si(NHNHMe)2 a produit un hydrazinosilane. Les réactions de cyclisation du Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> pour produire des silylhydrazines cycliques ont été effectuées par la réaction du composé avec le n-BuLi/Ph2SiCl2, ou le MeI (ou le HCl ou le Ph2SiCl2), ou par thermolyse. Les structures déterminées par la diffraction de rayons-X de  $Ph_2Si(NHNR)(NRNH)SiPh_2$  (R = H, Me) ont révélé soit une conformation chaise (R = H) ou une conformation twist-boat (R = Me)du cycle Si<sub>2</sub>N<sub>4</sub>. Les atomes d'azote dans le fragment hydraziné ont une géométrie soit plane ou pyramidale. La pyrolyse du polymère préparé par la réaction du MeHSiCl2 et de l'hydrazine a produit des matériaux céramiques Si<sub>3</sub>N<sub>4</sub>/SiC<sub>x</sub>N<sub>y</sub> dans des rendements de 67 à 80%. On propose comme unité structurale du polymère le tétraazadisilacyclohexane pontée par des groupes MeHSi. Cette attribution est basée sur des analyses par résonance magnétique nucléaire (RMN) (<sup>1</sup>H et <sup>29</sup>Si), et par la comparaison avec le produit bien défini de la réaction du Me<sub>2</sub>Si[NHNH]<sub>2</sub>SiMe<sub>2</sub> avec le MeHSiCl<sub>2</sub>. Entre la température ambiante et 1500° C, la pyrolyse a été effectuée sous argon et a été suivie par l'analyse thermogravimétrique, la RMN <sup>29</sup>Si à l'état solide, la spectroscopie infrarouge, la diffraction de poudres par rayons-X, et l'analyse élémentaire. Les changements de structure des

produits solides qui se produisent lors de la pyrolyse ont ainsi été déterminés. Le produit céramique de la pyrolyse du polymère à 1100° C a des propriétés de conductivité électrique à caractère quasi-métallique ( $\sigma = 10^3 (\Omega \text{ cm})^{-1}$ ), ce qui a mené à son évaluation comme matériau d'électrode.

### ACKNOWLEDGMENTS

Over the past three and half years at McGill, I have had the good fortune of working alongside one fine group of people. I wish to acknowledge their constant support and friendship, without which the work presented in this thesis would not be possible. Among them are:

Prof. John F. Harrod, my research supervisor for total support and his neverending enthusiasm in the quest for knowledge;

Dr. Jesse Ng, for his excellent proofreading, helpful discussions, and for translating the abstract;

Dr. Rosemary Hynes, for X-ray crystallography measurements;

Dr. Anne-Marie Lebuis, for ORTEP plottings, excellent proofreading and corrections of Chapter IV and résumé;

Dr. Fred Morin, for measuring solid-state <sup>29</sup>Si MAS NMR spectra;

Dr. Wen-Bing Zhang, for measuring cyclic voltammograms;

All in laboratory 435, Hélène Boily, Vladimir Dioumaev, Mohammad El-Khateeb, David Hall, Yin Mu, Mihai Scarlete, Maurus Spescha, Larry Tarazano, Darlene Trojansek, Lei Wang, Hee-Gwon Woo, and especially Shixuan Xin, for their friendship, the enjoyable working environment and the wonderful summer softball games.

I would like to express my sincere gratitude to professors in the Inorganic Division: Alan Shaver, Ian S. Butler, Ashok Kakkar, Mark Andrews, and Jim Hogan, for their stimulating discussions.

I would also like to acknowledge all members of the support staff in the Department of Chemistry, in particular Ms. Renée Charron for her considerable help in dealing with the bureaucratic red tape during the past years. To my parents and my wife, for their love and support throughout all these years

# TABLE OF CONTENTS

	Page
ABSTRAC	Ti
RÉSUMÉ	ii
ACKNOW	LEDGEMENTSiv
TABLE OF	CONTENTS
LIST OF TA	ABLESix
LIST OF FI	GURESxi
LIST OF A	ABBREVIATIONSxiii
CHAPTER	I. GENERAL INTRODUCTION 1
I.1	Silylhydrazines2
I.1.1	History2
I.1.2	Synthesis 4
I.1.3	Properties and Applications
I.2	Polymeric Precursors to Si <sub>3</sub> N <sub>4</sub> /SiN <sub>x</sub> C <sub>y</sub>
I.2.1	Synthesis of Preceramic Polysilazanes
I.2.2	Pyrolysis
I.3	Catalytic Dehydrocoupling of Si-H with N-H Bonds20
I.3.1	Alkali Metal Catalysed Dehydrocoupling
1.3.2	Transition Metal Catalysed Dehydrocoupling21
I.4	Scope of the Thesis23
CHAPTER	II. DEHYDROCOUPLING REACTIONS OF ORGANOSILANES WITH HYDRAZINES24

<b>II.</b> 1	Introduction24	•
П.2	Results and Discussion25	ł

II.2.1	Uncatalysed Reactions of PhSiH <sub>3</sub> and MeSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub>	25
11.2.2	Catalysed Reactions of PhSiH3 with H2NNH2, MeHNNH2, Me2NNH2 andMeHNNHMe	31
II.2.3	Catalysed Reactions of Ph2SiH2 with H2NNH2, MeHNNH2, Me2NNH2 and MeHNNHMe	37
II.2.4	Synthesis of Me <sub>2</sub> Si(NHNH) <sub>2</sub> SiMe <sub>2</sub>	45
II.3	Summary	47
II.4	Experimental Section	47
П.4.1	General Procedures	47
П.4.2	Chemicals	49
П.4.3	Dehydrocoupling Reactions	50

### CHAPTER III. REACTIVITY AND CYCLIZATION OF Ph2Si(NHNHMe)2

	$Ph_2Si(NHNHMe)_2$
III.1	Introduction57
III.2	Results and Discussion58
III.2.1	Controlled Hydrolysis of Ph2Si(NHNHMe)2: Synthesis of [Ph2Si(NHNHMe)]2O
III.2.2	Cyclization of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub> by Reaction with <i>n</i> -BuLi/Ph <sub>2</sub> SiCl <sub>2</sub> and Ring Isomerization
III.2.3	Cyclization of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub> by Reaction with MeI, HCl, or Ph <sub>2</sub> SiCl <sub>2</sub> 67
III.2.4	Cyclization of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub> by Thermolysis70
III.3	Summary74
Ш.4	Experimental Section
<b>III.4.1</b>	Controlled Hydrolysis of Ph2Si(NHNHMe)2: Synthesis of [Ph2Si(NHNHMe)]2O
III.4.2	Reaction of Ph2Si(NHNHMe)2 with n-BuLi/Ph2SiCl275
III.4.3	Ring Isomerization of triazadisilacyclopentane to tetraazadisilacyclohexane
III.4.4	Reactions of Ph2Si(NHNHMe)2 with MeI, HCl, or Ph2SiCl277

III.4.5	Thermolysis of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub>
CHAPTER	IV. STRUCTURE OF SILYLHYDRAZINES: PLANARITY VS PYRAMIDICITY AT NITROGEN
IV.1	Introduction — Is the geometry at nitrogen certain in Si-N compounds?
IV.2	Results and Discussion
IV.2.1	Chair and Twist-boat Conformations in Tetraazadisilacyclohexanes
IV.2.2	Planarity vs Pyramidicity at Nitrogen in Silylhydrazines
IV.3	Summary97
IV.4	Experimental Section
CHAPTER	V. SYNTHESIS OF POLY(METHYLSILDIAZANE) AND ITS PYROLYTIC TRANSFORMATION TO Si-N-C CERAMICS
V.1	Introduction98
V.2	Results and Discussion 100
<b>V.2.</b> 1	Synthesis and Characterization of Poly(methylsildiazane) 100
V.2.2	Pyrolytic Conversion of Poly(methylsildiazane) to $Si_3N_4/Si_NxC_y$
V.2.3	Pyrolysis Chemistry of Poly(methylsildiazane) 117
V.2.4	Poly(methylsildiazane)-derived Quasimetallic Conducting SiN <sub>x</sub> C <sub>y</sub>
V.3	Summary 124
V.4	Experimental Section 125
V.4.1	Synthesis of Polymers 126
V.4.3	Bulk Pyrolysis 127
V.4.3	Characterization127

CHAPTER	VI.	CONCLUDING REMARKS	129
VI.1	From	m Fundamental Chemistry to Advanced Materials	129
VI.2	Con	tributions to Original Knowledge	131
VI.3	Sug	gestions for Further Work	132
REFERENC	CES.		134
APPENDIX	Ι	X-RAY CRYSTAL STRUCTURE ANALYSIS OF Ph2Si(NHNH)2SiPh2	145
APPENDIX	Π	X-RAY CRYSTAL STRUCTURE ANALYSIS OF Ph2Si(NHNMe)(NMeNH)SiPh2	150
APPENDIX	ш	X-RAY CRYSTAL STRUCTURE ANALYSIS OF Ph2Si(NHNHMe)2	155
APPENDIX	IV	X-RAY CRYSTAL STRUCTURE ANALYSIS OF [Ph2Si(NHNHMe)]2O	160

### LIST OF TABLES

<u>Table</u>	Page
П.1	Some data for uncatalyzed reactions of phenylsilane with hydrazine
II.2	Dehydrocoupling reactions between diphenylsilane and hydrazines
<b>III</b> .1	Comparison of NMR data for Compounds 21 and 14 59
III.2	Reactions of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub> with MeI, HCl, and Ph <sub>2</sub> SiCl <sub>2</sub> , and the product distribution
IV.1	Selected bond distances(Å) and bond angles (degrees) for the molecule shown in Figure IV.2 (compound 9)
IV.2	Selected bond distances(Å) and bond angles (degrees) for compound 23 86
IV.3	Selected bond distances(Å) and bond angles (degrees) for compound 14 89
<b>IV.4</b>	Selected bond lengths (Å) and angles (degrees) of 21
IV.5	Comparison of Si-N and N-N bond lengths and sum of angles about nitrogen in some silylhydrazine compounds
V.1	Elemental analysis data and morphology of the isolated solids by heating PMSDZ to selected temperatures
V.2	Assignment of IR absorption bands for the initial polymer and its pyrolysis product
AI.1	Crystal data and data collection parameters for 9145
AI.2	Atomic coordinates and isotropic thermal parameters for 9146
AI.3	Anisotropic thermal parameters [u(i,j)x100] for 9147
AI.4	Selected bond distances (Å) and bond angles (degrees) for 9148
AI.5	Hydrogen atom parameters for 9149
АП.1	Crystal data and data collection parameters for 23150
АП.2	Atomic coordinates and isotropic thermal parameters for 23
AII.3	Anisotropic thermal parameters [u(i,j)x100] for 23152
AII.4	Selected bond distances (Å) and bond angles (degrees) for 23153
AII.5	Hydrogen atom parameters for 23154
AIII.1	Crystal data and data collection parameters for 14155

AIII.2	Atomic coordinates and isotropic thermal parameters for 14	156
AIII.3	Anisotropic thermal parameters [u(i,j)x100] for 14	157
AIII.4	Selected bond distances (Å) and bond angles (degrees) for 14	158
AIII.5	Hydrogen atom parameters for 14	159
AIV.1	Crystal data and data collection parameters for 21	
AIV.2	Atomic coordinates and isotropic thermal parameters for 21	<b>16</b> 1
AIV.3	Anisotropic thermal parameters [u(i,j)x100] for 21	162
AIV.4	Selected bond distances (Å) and bond angles (degrees) for 21	163
AIV.5	Hydrogen atom parameters for 21	164

### LIST OF FIGURES

Figure		Page
I.1	Proposed structures of polysilazanes	17
II.1	<sup>1</sup> H NMR spectrum of the polymer formed by the reaction of PhSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub>	27
II.2	Solid-state <sup>29</sup> Si CPMAS NMR spectra of the polymer formed by the reaction of PhSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub> (5.5:8.2), using variable contact time	28
II.3	Solid-state <sup>29</sup> Si CPMAS NMR spectra of the polymer formed by the reaction of PhSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub> (6.0:6.0), using variable contact time	29
П.4	FT-IR spectrum of the polymeric material formed by the reaction of $MeSiH_3$ with $H_2NNH_2$	32
11.5	Solid-state <sup>29</sup> Si spectrum of the polymeric material formed by the reaction of MeSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub>	33
П.6	Thermogravimetric analysis of the polymeric material formed by the reaction of MeSiH <sub>3</sub> with H <sub>2</sub> NNH <sub>2</sub>	33
II.7	DEPT <sup>29</sup> Si NMR spectra of the polymeric product formed by DMT- catalysed reaction of PhSiH <sub>3</sub> with MeHNNH <sub>2</sub>	35
II.8	Multi-nuclei NMR spectra of compound 9. (a) <sup>1</sup> H, (b) <sup>29</sup> Si, and (c) $^{15}N$	39
II.9	The course of the dehydrocoupling of diphenylsilane with methylhydrazine.	42
II.10	<sup>1</sup> H NMR spectrum of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub>	43
II.11	2D <sup>15</sup> N- <sup>1</sup> H HMQC NMR spectrum of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub>	44
III.1	<sup>1</sup> H NMR spectra of the isomerization of 22 to 23 and 24 in the presence of $0.1\%$ <i>n</i> -BuLi at 30 °C	62
Ш.2	<sup>29</sup> Si NMR spectra of (a) 22, (b) 24, and (c) 23	64
Ш.3	The course of the isomerization of 22 to 23 and 24 in the presence of $2.5\%$ <i>n</i> -BuLi at 50 °C.	65
III.4	Thermogravimetric analysis of Ph2Si(NHNHMe)2	70
Ш.5	<sup>1</sup> H NMR spectra for the thermolysis of Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub>	73
IV.1	Packing diagram for 9	82

IV.2	ORTEP view of 9
IV.3	ORTEP view of 23
IV.4	ORTEP view of 14
IV.5	ORTEP view of 21
IV.6	Stabilizing interaction of pyramidal nonbonding electron pair (n) with the adjacent E-N bonds
IV.7	Conformations of H <sub>2</sub> NNH <sub>2</sub> projected along the N-N bond
IV.8	ORTEP fragments of compounds (a) 21, (b) 9, and (c) 23, projected along the N-N bonds to show the conformational relationship between the planar and pyramidal nitrogens
V.1	Solution NMR spectra of PMSDZ (a) <sup>1</sup> H and (b) <sup>29</sup> Si NMR101
V.2	Solution <sup>29</sup> Si NMR spectrum of the ladder polymer 32102
V.3	TGA for polymers. (a) PMSDZ, (b) PMSDZ cured by 1% Cp <sub>2</sub> TiMe <sub>2</sub> catalyst, and (c) PMSDZ cured at 150 °C without catalyst104
V.4	Plots of the loss of (a) carbon, (b) hydrogen, and (c) nitrogen in heating PMSDZ from room temperature to 1100 °C106
V.5	Solid-state <sup>29</sup> Si MAS NMR spectra of (a) PMSDZ, and the solid pyrolysis products at selected temperatures
V.6	DTA for polymers. (a) PMSDZ, (b) PMSDZ cured by 1% Cp <sub>2</sub> TiMe <sub>2</sub> catalyst, and (c) PMSDZ cured at 150 °C without catalyst109
V.7	EPR spectra of the solid residues formed by the pyrolysis of PMSDZ at selected temperatures
V.8	FT-IR spectra of (a) PMSDZ, and the solid pyrolysis products at selected temperatures
V.9	FT-IR spectra of PMSDZ in air, showing the degree of hydrolysis with the exposure time
V.10	X-ray powder diffraction patterns of the solid pyrolysis products (a) at 1100 °C and (b) at 1500 °C117
<b>V.</b> 11	Cyclic voltammograms of 1.0 mM K4Fe(CN)6/0.1 M KCl at silicon carbonitride and glassy carbon electrodes, respectively, using Ag/AgCl as reference electrode

### LIST OF ABBREVIATIONS

Å	angstrom $(1 \text{\AA} = 10^{-10} \text{ m})$
b.p.	boiling point
n-Bu	normal-butyl
i-Bu	iso-butyl
t-Bu	tert-butyl
CI-MS	chemical ionization mass spectrometry
Ср	$\eta^{5}$ -cyclopentadienyl ( $\eta^{5}$ -C <sub>5</sub> H <sub>5</sub> )
CP MAS	cross polarization magic angle spinning
D	Dalton (1 $D = 1$ atomic mass unit)
DEPT	distortionless enhancement by polarization transfer
DMT	dimethyltitanocene
DPn	number average degree of polymerization
DTA	differential thermal analysis
EI-MS	electron impact mass spectrometry
EPR	electron paramagnetic resonance
Et	ethyl
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HMQC	heteronuclear multiple quantum coherence
INEPT	insensitive nuclei enhancement by polarization transfer
Me	methyl
M <sub>n</sub>	number-average molecular weight
m.p.	melting point
MS	mass spectrometry
M <sub>w</sub>	weight-average molecular weight

.

- NMR nuclear magnetic resonance
- NOE nuclear Overhauser effect
- ORTEP Oak Ridge Thermal Ellipsoid Plot
- Ph phenyl
- PMSDZ poly(methylsildiazane)
- ppm parts per million
- Tf triflate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>)
- THF tetrahydrofuran
- TGA thermogravimetric analysis
- TMS tetramethylsilane (Si(CH<sub>3</sub>)<sub>4</sub>)
- XRD X-ray diffraction
- UV ultraviolet

### Abbreviations used to describe NMR peaks

br	broad
d	doublet
dd	doublet of doublets
q	quartet
qd	quartet of doublets
S	singlet
sept	septet
t	triplet
	Abbreviations used to describe IR bands
br	broad
S	strong
m	medium

Chapter I

### **GENERAL INTRODUCTION**

"If one would surrender to geological phantasies, one could imagine that during the formation of our planet, when elements combined to the compounds making up its crust and mountain ranges, silicon reacted with nitrogen, and the still red-hot nitrogen-silicon, on contact with water, may have decomposed to silicic acid and ammonia. Thus, ammonia may have been formed originally and nitrogen thereby introduced into the forming organic compounds when living nature first started to appear."

H. Sainte-Claire Deville and F. Wöhler: "Ueber die Directe Bildung des Stickstoffsiliciums", Ann. Chem. Pharm. 1859, 34, 248.

Although in 1859 Sainte-Claire Deville and Wöhler had speculated on silicon nitride as a possible raw material for the synthesis of ammonia, the "red-hot nitrogen-silicon" chemistry was never attempted until organosilicon chemists tried to synthesize organosilicon-dinitrogen compounds. Exactly 100 years later, the first reports of silylhydrazine compounds made this "red-hot nitrogen-silicon" chemistry accessible.

#### I.1 Silylhydrazines

#### I.1.1 History

The first synthesized silvlhydrazine compound was tetrasilvlhydrazine (SiH<sub>3</sub>)<sub>4</sub>N<sub>2</sub>, prepared from the reaction of iodosilane with hydrazine by Aylett in 1956.<sup>1</sup> Following this work, Wannagat and coworkers prepared a large number of acyclic and cyclic silvlhydrazine compounds by using the reaction of halosilanes with hydrazines.<sup>2-7</sup> However, some synthetic challenges remained for this classical method. It was shown that primary silvlhydrazines,  $R_3$ SiNHNH<sub>2</sub> (R = Me, Et, or Pr) cannot be isolated, as they immediately undergo further disproportionation to 1,2-bis(silyl)hydrazines with the elimination of hydrazines, and only Ph3SiNHNH2 was isolated.<sup>2,4</sup> Steric hindrance makes it impossible to synthesize silul-substituted hydrazines of the type (R<sub>3</sub>Si)<sub>2</sub>NN(SiR<sub>3</sub>)<sub>2</sub> directly from the reaction of halosilane with hydrazine, except for (H<sub>3</sub>Si)<sub>2</sub>NN(SiH<sub>3</sub>)<sub>2</sub>. The major research efforts on silvlhydrazines during this period were directed toward synthetic techniques with little emphasis on the study of their chemical properties. The synthetic methods developed for silvlhydrazines were essentially the same as those for silylamines, e.g. (i) the reactions of hydrazines with halosilanes by the elimination of hydrohalides, (ii) reactions of metallated hydrazines with halosilanes, and (iii) the exchange of hydrazines with silylamines. Silylhydrazine chemistry has not been previously reviewed as a topic but has been covered in early review articles on silicon-nitrogen compounds.89

The horizon of silylhydrazine chemistry was expanded by the discovery of anionic rearrangement reactions, in which silyl groups migrate from one nitrogen atom to another in silylhydrazines under basic conditions.<sup>10-11</sup> West and coworkers reported that the rate of migration of silyl groups in the rearrangement is at least 10<sup>12</sup> more rapid than for phenyl or methyl groups.<sup>12</sup>

Like their amine derivatives, silylhydrazines have also recently been developed as reagents in organic and organometallic synthesis. Examples include the synthesis of hydrazones from the reaction of silylhydrazines with aldehydes or ketones,<sup>13</sup> the generation of silylaminyl radicals by the photolysis of silylhydrazines,<sup>14,15</sup> and the synthesis of dinitrogen-containing organometallic complexes through the metallation of silylhydrazines.<sup>16-19</sup> Silylhydrazine polymers, or polysildiazanes, have also been used as potential ceramic precursors to silicon nitride and silicon carbonitride.<sup>20,21</sup>

Recent advances in silvlhydrazine chemistry have also been brought about by improved, or new, synthetic methods, which provide more efficient and/or accessible routes to known and unknown silvlhydrazine compounds. Klingebiel and coworkers have reported that primary and fluoro-functional silvlhydrazines can be stabilized kinetically by the use of bulky t-butyl groups on silicon.<sup>22,23</sup> Lithium derivatives of these silvlhydrazines allow a stepwise synthesis of cyclic silylhydrazines, e.g. three-, four-, five- and sixmembered silvlhydrazine ring systems, via LiF elimination.<sup>22-26</sup> Multisilylated hydrazines, especially (Me<sub>3</sub>Si)<sub>2</sub>NN(SiMe<sub>3</sub>)<sub>2</sub>, can be synthesized in extremely high yields by the reaction of disilanes with hydrazines under basic conditions.<sup>13</sup> The disilane, such as Me<sub>3</sub>SiSiMe<sub>3</sub>, functions as a counterattack reagent in this reaction (see I.2.4). The heterodehydrocoupling reaction of organosilanes with hydrazines represents an interesting and clean route to silvlhydrazines and polysildiazanes. Reactions of di- and some monoorganosilanes with hydrazines are not spontaneous, but can be facilitated by catalysts to give mixtures of ring and chain silvlhydrazines, in ratios depending on the reactants and the reaction conditions.<sup>27</sup> It has been observed that both phenylsilane and methylsilane react spontaneously with hydrazine to give polysildiazanes.<sup>27,28</sup>

Very little work has been done on the structures of silylhydrazines, compared to silylamine derivatives. Before 1990, only three silylhydrazine structures had been reported, <sup>25,29,30</sup> among which was (H<sub>3</sub>Si)<sub>2</sub>NN(SiH<sub>3</sub>)<sub>2</sub> whose structure was first determined in the gas-phase by electron diffraction.<sup>29</sup> Recently, several crystal structures of cyclic and acyclic silylhydrazines have been determined.<sup>26,27,31-33</sup> The reported structural data have shown that planar nitrogen geometry exists in Si<sub>2</sub>NNSi<sub>2</sub>

fragments,<sup>29,31,32</sup> while both planar and pyramidal nitrogen geometies co-exist in SiNN fragments.<sup>26,27,33</sup> This variable nitrogen geometry will stimulate further fundamental interest in the factors determining nitrogen geometry in silicon-nitrogen compounds.

### I.1.2 Synthesis

(i) Reactions of Halosilanes with Hydrazines. Reactions of halosilanes with hydrazines occur exothermally in inert organic solvents or in the gas phase. Excess of the hydrazine or an auxiliary base (e.g., Et<sub>3</sub>N) is required to remove the hydrohalide (HX) generated in the reaction. The product of the silylation is determined by the steric hindrance of substituents on both silicon and hydrazine.

$$= Si - X + H - N - N \leq - - = Si - N - N \leq + HX \quad (I.1)$$

Complete silylation of hydrazine to prepare tetrakis(silyl)hydrazine, (H<sub>2</sub>RSi)<sub>2</sub>NN(SiRH<sub>2</sub>)<sub>2</sub>, has only been achieved with these monohalosilanes, H<sub>2</sub>RSi-X, where R = H, X = I;<sup>1</sup> R = Me, X = Br;<sup>32a</sup> R = Ph, X = CL<sup>32a</sup> Me<sub>2</sub>HSi-Br and Me<sub>3</sub>Si-Cl to give tris(dimethylsilyl)hydrazine<sup>32a</sup> and 1,2-bis(trimethylsilyl)hydrazine,<sup>2,4</sup> respectively. Generally, 1,2-disubstitution of hydrazine is preferred to 1,1-disubstitution when trialkylor triaryl-substituted halosilanes are used. The monosilylhydrazines may be prepared by increasing the steric hindrance of the silyl group, or the ratio of hydrazine to chlorosilane. Thermally stable monosilylhydrazines which have been reported are Ph<sub>3</sub>SiNHNH<sub>2</sub>,<sup>4</sup> R'<sub>2</sub>RSiNHNH<sub>2</sub> (R = F, R' = CMe<sub>3</sub> or N(CHMe<sub>2</sub>)<sub>2</sub>; R = Me, CMe<sub>3</sub>).<sup>26</sup>

In the reaction of a chlorosilane with a substituted hydrazine, the silyl group shows a preference for the unsubstituted nitrogen of the hydrazine (reaction I.2). Some monosilylhydrazines, such as 1-methyl-2-(trimethylsilyl)hydrazine, undergo disproportionation to form 1,2-disubstituted hydrazines with the release of free hydrazines (reaction I.3).<sup>5</sup>

$$Me_3SiCl + 2 NH_2NHR - Me_3SiNHNHR + RNHNH_2HCl (1.2)$$
(R = Me, Ph)

2 Me<sub>3</sub>SiNHNHMe  $\longrightarrow$  (Me<sub>3</sub>Si)MeNNHSiMe<sub>3</sub> + MeHNNH<sub>2</sub> (1.3)

When dichlorosilanes react with hydrazines, either polymers or six-membered rings or bis(hydrazino)silanes are formed, depending on the reactants. Dimethyldichlorosilane and hydrazine form a polymer of molecular weight ca. 3500, with a proposed structural unit -[-Me<sub>2</sub>SiNHNH-]-.<sup>2</sup> Diphenyldichlorosilane and substituted hydrazines (H<sub>2</sub>NNR'R") yield bis(2-substituted hydrazino)silanes.<sup>3</sup>

$$Ph_2SiCl_2 + 4 NH_2NR'R^* - Ph_2Si(NHNR'R^*)_2 + 2 R'R^*NH_2HCI (1.4)$$
  
(R' = Me, R'' = Me; R' = H, R'' = Ph)

However, Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> cannot be prepared by this method, probably because it will further react with the HCl generated in the reaction to form cyclic compounds.<sup>34</sup>

(ii) Reaction of Metallated Hydrazines with Halosilanes. The following reaction:



also leads to silvl substitution on N atoms already carrying a silvl or phenyl group. This method is especially useful for the preparation of fully silvlated hydrazines, such as reaction (I.6).<sup>35</sup> As when halosilanes are reacted with hydrazines, complete silvlation is very difficult.

$$(Me_3Si)_2NNH(SiMe_3) \xrightarrow{PhLi} (Me_3Si)_2NN(Li)SiMe_3 \xrightarrow{Me_3SiCl} (Me_3Si)_2NN(SiMe_3)_2 (I.6)$$

Alkyl lithiums and aryl lithiums are particularly suitable as metallating agents for hydrazine derivatives; but NaNH<sub>2</sub> in benzene, which is effective for metallating silylamines, causes cleavage of the N-N bond.<sup>9</sup> In some cases, a mixture of isomeric products may be obtained in the reaction of a lithium derivative of silylhydrazine with chlorosilanes. This has been attributed to the anionic rearrangement of lithiated silylhydrazides (see I.1.3).<sup>36</sup>

$$t\text{-BuMe}_{2}\text{SiNHNHMe} \xrightarrow{1. n\text{-BuLi}} (t\text{-BuMe}_{2}\text{Si})(\text{Me}_{3}\text{Si})\text{NNHMe} (32\%)$$

$$2. \text{ Me}_{3}\text{SiCl} + t\text{-BuMe}_{2}\text{SiNHN}(\text{Me})\text{SiMe}_{3} + \text{Me}_{3}\text{SiNHN}(\text{Me})\text{Si} \cdot t\text{-BuMe}_{2} (1.7)$$

$$(\text{total 68\%})$$

Unlike other halosilanes, fluorosilanes do not react directly with hydrazines to give silylhydrazines via HF elimination. However, the reaction of fluorosilanes with lithiated hydrazines, which occurs readily to form silylhydrazines via LiF elimination, provides an improved, controlled pathway to the synthesis of cyclic silylhydrazines, as shown in Schemes  $1^{24}$  and  $2^{26}$  below.



Recently, the first lithium derivative of (t-Bu)<sub>2</sub>MeSiNHNH<sub>2</sub> was crystallized as a hexamer with Li<sup>+</sup> ions bound side-on and end-on to the N-N moiety.<sup>23</sup> The crystal structure of this compound exhibits two tautomeric silylhydrazide units III and IV. This phenomenon accounts for the isomerizations that occur during secondary substitutions<sup>11</sup> and the formation of the five-membered ring in Scheme 2.





(iii) Reaction of Hydrazines with Silylamines. This reaction (eq. I.8) occurs in satisfactory yield only in the presence of small quantities of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>Cl as a catalyst. Since (Me<sub>3</sub>Si)<sub>2</sub>NH must be prepared from Me<sub>3</sub>SiCl, the reaction using this method is more tedious and expensive than the direct method (i). It has been employed previously,<sup>37</sup> however, with advantage for valuable hydrazines, since the loss due to the formation of the hydrazine hydrochloride is prevented. Silylation with (Me<sub>3</sub>Si)<sub>2</sub>NH or Me<sub>3</sub>SiNHMe has also been carried out with varying success for (PhO)<sub>2</sub>PO(NHNH<sub>2</sub>) and NH<sub>2</sub>CONHNH<sub>2</sub>.<sup>37c,d</sup>

$$2 \text{ RNHNH}_2 + (\text{Me}_3\text{Si})_2\text{NH} \longrightarrow 2 \text{ RNHNHSiMe}_3 + \text{NH}_3 \quad (I.8)$$
$$(\text{R} = \text{H}, \text{Ph})$$

(iv) Synthesis of Multisilylated Hydrazines by Using Disilanes as Counterattack Reagents<sup>13</sup>. This method employs disilane as a "counterattack reagent". Such a reagent generally contains a leaving group that reattacks a stable intermediate generated *in situ*. Scheme 3 illustrates a one-pot preparation of tetrakis(trimethylsilyl)hydrazine via a "triple-counterattack" pathway.



Under basic conditions, hydrazine is first converted into a hydrazide anion, which attacks Me<sub>3</sub>SiSiMe<sub>3</sub> to generate a (trimethylsilyl)hydrazine and a trimethylsilyl anion. This trimethylsilyl anion should counterattack (trimethylsilyl)hydrazine to produce silyl hydrazide as the major intermediate. The disilane plays a dual role in this reaction: silylating agent and source of base. In the overall process, silylation alternates with proton abstraction. This alternation repeated four times would convert H<sub>2</sub>NNH<sub>2</sub> to (Me<sub>3</sub>Si)<sub>2</sub>NN(SiMe<sub>3</sub>)<sub>2</sub> without isolation of any intermediate. Thus, only a catalytic amount of base (KH) is required. The counterattack method shown in Scheme 3 is much more efficient than the classic procedure through the combination of methods (i) and (ii) (8%).<sup>35</sup>

(v) Silylation of Diazo Compounds. This method has been used to a limited extent for lack of appropriate diazo compounds. The following reactions (I.9), (I.10) and (I.11) have been reported.<sup>38</sup>

$$\begin{array}{rcl} PhN=NPh & \begin{array}{rcl} Ph_{3}SiH \\ \hline PhN=NPh & \begin{array}{rcl} Ph_{3}SiH \\ \hline f\cdot Bu_{2}O_{2} \end{array} & \begin{array}{rcl} Ph_{3}SiN(Ph)NHPh & (I.9) \\ \hline Me_{3}SiN=NSiMe_{3} & \begin{array}{rcl} Me_{3}SiH \\ \hline Me_{3}SiN=NSiMe_{3} \end{array} & \begin{array}{rcl} (Me_{3}Si)NNHSiMe_{3} & (I.10) \\ \hline Mes_{2}Si=SiMes_{2} \end{array} & \begin{array}{rcl} Ph \\ \hline N \\ \hline Mes_{2}Si=SiMes_{2} \end{array} & \begin{array}{rcl} PhN=NPh & \begin{array}{rcl} hv \\ \hline N \\ \hline Mes_{2}Si=SiMes_{2} \end{array} & \begin{array}{rcl} SiMes_{2} \end{array} & \begin{array}{rcl} (I.11) \\ \hline Mes_{2}Si=SiMes_{2} \end{array} & \begin{array}{rcl} PhN=NPh \\ \hline Mes_{2}Si=SiMes_{2} \end{array} & \begin{array}{rcl} I.10 \\ \hline Mes_{2}SiMes_{2} \end{array} & \begin{array}{rcl} I.10 \\ \hline \\ & \begin{array}{rcl} I.10 \\ \hline \\ & \begin{array}{rcl} I.10 \\ \end{array} & \begin{array}{rcl} I.10 \\ \hline \\ & \begin{array}{rcl} I.10 \\ \end{array} & \begin{array}{rcl} I.10 \\ \hline \\ \end{array} & \begin{array}{rcl} I.10 \\ \hline \\ \end{array} & \begin{array}{rcl} I.10 \\ \end{array} &$$

### I.1.3 Properties and Applications

The majority of the known silyl hydrazines are colorless mobile liquids or white solids, which sometimes smell like camphor or the silyl-free hydrazine. They may be distilled or sublimed under vacuum as they are not sensitive to heat. Silylation as a rule changes the boiling point by very little [b.p./12 mmHg of PhNHNH2, 120°; of PhNHNHSiMe3, 117°; of Ph(Me3Si)N-NHSiMe3, 123°];<sup>9</sup> there is clearly a balance between the increase in the mass of the molecule and the decrease in the tendency to hydrogen bonding.

Most silylhydrazines of the type RR'N-NRR' (R, R' can be any combination of H, alkyl, aryl, silyl substituents) are readily soluble in the usual organic solvents and are not particularly sensitive to moisture. They are, however, readily cleaved solvolytically by acids in ether. Hydrazinosilanes  $R_2Si(NR'NR'R'')_2$ , and polysildiazanes -(-RR'Si-NHNH-)<sub>n</sub>- are particularly sensitive to protolysis. Even traces of water will transform them into siloxanes.<sup>39</sup>

Silylhydrazines have reducing properties. They react violently with concentrated HNO<sub>3</sub> or with furning HNO<sub>3</sub>. When a Si-H bond is present, as in RSiH(NHNR<sub>2</sub>)<sub>2</sub>, they will convert Cu<sup>2+</sup> to Cu,  $[Ag(NH_3)_2]^+$  to Ag, and Hg<sup>2+</sup> to Hg<sub>2</sub><sup>2+</sup> and Hg.<sup>9</sup> On exposure to air (H<sub>3</sub>Si)<sub>2</sub>NN(SiH<sub>3</sub>)<sub>2</sub> explodes.

Silylhydrazines with H atoms still linked to N react with phenyl isocyanate and as a rule only one PhNCO is added per N atom. The resulting silyl-substituted product is readily hydrolyzed. This may allow a differentiation, for example, between the 1,1 and 1,2 isomers Ph(R<sub>3</sub>Si)N-NH<sub>2</sub> and (R<sub>3</sub>Si)HN-NHPh. The first will give PhNHNHCONHPh by PhNCO addition and hydrolysis and the second HN(CONHPh)-NPh(CONHPh). This method has been used to elucidate the position of Ph or R<sub>3</sub>Si on N or N in a series of bis(silyl) or phenylsilyl hydrazines.<sup>37a,d</sup> However, this chemical method is not entirely reliable because the phenyl isocyanate may cleave Si-N bonds to give a 1,2-disubstituted product in its reaction with the 1,1 isomer. An alternative method to distinguish between 1,1 and 1,2 isomers by using IR spectroscopy has been suggested,<sup>40</sup> based on the difference in the N-H stretching region (3500-3200 cm<sup>-1</sup>). In the 1,1 isomer, the two N-H modes should interact strongly to give in-phase and out-of-phase stretching bands of markedly different frequencies. In the 1,2 isomer, coupling between the two N-H stretching modes should be weak, and the splitting should be small or nonexistent.

In the presence of catalytic amounts of strong base (alkyllithium), silylhydrazines with H atoms on N readily undergo rearrangements to give a mixture of isomeric silyl-substituted hydrazines.<sup>11</sup> This is thought to result from hydrazide equilibration via a pentacoordinate silicon transition state, and so is not subject to the orbital symmetry restriction of organic 1,2-anionic rearrangements. Therefore, the silyl migrations in the rearrangements are fully intramolecular, and at least 10<sup>12</sup> times faster than those of phenyl or methyl groups.<sup>12</sup> The equilibration reaction follows first-order kinetics in which the protonation-deprotonation steps, rather than the actual anionic rearrangement, are rate-limiting. A typical example is illustrated in Scheme 4.<sup>36</sup> The rearrangement of 1-phenyl-1-trimethylsilyl-2-*t*-butyldimethylsilylhydrazine (V) gives the double-rearrangement product VII more rapidly than VI in the early stages of the reaction, but the latter dominates under thermodynamic control. This result shows that protonation must be the rate-determining step in the rearrangement, and further, protonation of VIIa must be more rapid than that of



VIa, since the phenyl ring electronically stabilizes the anionic charge on nitrogen and retards the rapid protonation.

The N-N bond of  $(R_3Si)_2NN(SiR_3)_2$  (R = Me, Et) is readily cleaved by u.v. photolysis (ca. 260-340 nm) to generate  $(R_3Si)_2N$  radicals.<sup>14</sup> The resulting radical is much more reactive than a dialkylaminyl radical. It abstracts hydrogen from aliphatic C-H groups, adds to ethylene, *t*-butyl isocyanide, and trialkyl phosphites.<sup>15</sup> Differences between  $(R_3Si)_2N$  and  $(R_3C)_2N$  have been attributed to the  $\sigma$ -donor- $\pi$ -acceptor substituent effect of the trialkylsilyl ligand.<sup>15</sup> The reactivity of  $(R_3Si)_2N$  is generally similar to that of *t*-BuO, although the steric congestion at the radical center in the former results in a preference for attack at less hindered sites.

Structures of silylhydrazines show that the average Si-N bond length is in the range 1.70-1.76 Å, which is also the range for most neutral aminosilanes. The average N-N bond length fits well in the range for most hydrazines (1.43-1.50 Å). It seems that the steric crowding of the substituents only affect these bond lengths very slightly. Silylhydrazines containing Si<sub>2</sub>NNSi<sub>2</sub> fragments possess two Si<sub>2</sub>N planes in orthogonal or nearly orthogonal position, and two N atoms in a trigonal planar geometry.<sup>30-32</sup> However, both planar and pyramidal N atoms are found in the compounds containing a SiNN fragments.<sup>26,27,33</sup> The rotational barrier of the N-N bond is in the range of ca. 15-18 kcal/mol for compounds (XMe<sub>2</sub>Si)MeNNMe(SiMe<sub>2</sub>X) (X = Ph, Cl, Br)<sup>41</sup> and (Me<sub>2</sub>HSi)(PhH<sub>2</sub>Si)NN(SiHMe<sub>2</sub>)2,<sup>32a</sup> reflecting the energy maximum of the repulsion of

the nitrogen lone pairs (in parallel orientation). The energy barrier in silylhydrazines is generally influenced by electronic rather than steric effects. Downfield shifts are observed in the <sup>29</sup>Si NMR spectra of silylhydrazines relative to their amine derivatives. Like most silicon-containing small ring compounds, the diazasilacyclopropane II (see Scheme 1) shows a significant upfield shift of the <sup>29</sup>Si NMR signal of endo-silicon.<sup>24</sup>

Silylhydrazines are weaker bases than hydrazines, and the silyl substituents are, in general, good leaving groups. Reaction of an aldehyde or a ketone with about one equivalent of 1,1-bis(silyl)hydrazines in the presence a catalyst (Me<sub>3</sub>SiOTf) produces the corresponding hydrazone in very good yield.<sup>13</sup> The reaction of CpTiCl<sub>3</sub> with a variety of trimethylsilylhydrazines, Me<sub>3</sub>SiN(R)NR'<sub>2</sub>, produces organohydrazide derivatives.<sup>17</sup> In the case of Me<sub>3</sub>SiNHNHPh the product was CpTiCl<sub>2</sub>( $\eta^2$ -NPhNH<sub>2</sub>) resulting from a 1,2-hydrogen shift.<sup>18</sup>

CpTiCl<sub>3</sub> + Me<sub>3</sub>SiN(R)NR'<sub>2</sub>  $\longrightarrow$  CpTiCl<sub>2</sub>(NRNR'<sub>2</sub>) + Me<sub>3</sub>SiCl (I.12) However, CpTiCl<sub>3</sub> reacted with Me<sub>3</sub>SiNHNHSiMe<sub>3</sub> in a 2:1 ratio to release N<sub>2</sub> and NH<sub>3</sub> through reductive disproportionation of bound NHNH<sup>2-</sup> and (NHNHSiMe<sub>3</sub>)<sup>-</sup>.<sup>19</sup> The stoichiometric reaction of (Me<sub>3</sub>Si)<sub>2</sub>NN(SiMe<sub>3</sub>)<sub>2</sub> with NbCl<sub>5</sub> in the presence of THF gives high yields (ca. 80%) of [{NbCl<sub>3</sub>(THF)<sub>2</sub>}<sub>2</sub>N<sub>2</sub>].<sup>16</sup> By contrast (Me<sub>3</sub>Si)<sub>2</sub>NN(SiMe<sub>3</sub>)<sub>2</sub> reduces [MoCl<sub>4</sub>L<sub>2</sub>] (L = MeCN or THF) complexes at the metal to produce [MoCl<sub>3</sub>L<sub>3</sub>] together with dinitrogen and Me<sub>3</sub>SiCl.<sup>16</sup>

Silylhydrazine polymers, polysildiazanes, have been used as silicon nitride and/or silicon carbonitride ceramic precursors. These polymers containing a Si-N-N backbone are nitrogen-rich polysilazane type ceramic precursors and may incorporate more nitrogen content in the ceramic product by pyrolysis. A series of polysildiazanes, synthesized from the reactions of SiCl<sub>4</sub> or RMeSiCl<sub>2</sub> (R = H, Me, C<sup>-</sup><sub>2</sub>-CH<sub>2</sub>) with H<sub>2</sub>NNH<sub>2</sub>, has been pyrolysed to silicon-containing ceramics under an inert atmosphere.<sup>20,21</sup> The precursor from MeHSiCl<sub>2</sub> and H<sub>2</sub>NNH<sub>2</sub> gave 72% of a Si-N-C ceramic (the highest yield among these polymers) at 1000 °C under N<sub>2</sub>.<sup>20b</sup>

÷

### I.2 Polymeric Precursors to Silicon Nitride/Silicon Carbonitride

Silicon nitride and silicon carbide are important structural materials based on their resistance to corrosion under severe thermal and chemical environments, high hardness, low density, good thermal shock resistance, and retention of mechanical strength at elevated temperatures.<sup>42</sup> Some applications derived from these attributes include high-speed cutting tools, heat exchangers, abrasives, engine components, oxidation-resistant coatings, furnace fixtures and heating elements.

The use of powders as precursors for either reaction-bonded or hot-pressed silicon nitride limits the possible size and configuration of the ceramic articles attainable. Preceramic polymers offer certain processing advantages over traditional powder processing methods due to their rheology, solubility, low decomposition temperatures, and the ability to tailor the microstructure of the ceramic product. Particularly, polymers offer promise for specific forms such as fibers<sup>43</sup> and coatings<sup>44</sup> which are essentially unattainable by conventional methods.

The concept of generating non-oxide ceramic fibers from preceramic polymers was first proposed in the early 1960s, almost simultaneously, by Aylett<sup>45</sup> and Chantrell and Popper<sup>46</sup>. The polymeric approach to ceramics was promoted by the early work of Verbeek<sup>47</sup> and Yajima<sup>48</sup> on polysilazanes for Si<sub>3</sub>N<sub>4</sub>/SiC and polycarbosilanes for SiC in the 1970s. Thereafter, investigations on preceramic polymers synthesis, pyrolysis and fabrication of ceramic articles have led to numerous patents and publications, which have been reviewed by several authors.<sup>49-54</sup> In the case of silicon nitride, two main routes to ceramic products involving the pyrolysis of organosilicon polymeric precursors have been employed. One of these involves the direct pyrolysis, *in vacuo* or in an inert atmosphere, of polysilazanes. The other approach involves the pyrolysis of organosilicon polymeric precursors in ammonia, leading to pure Si<sub>3</sub>N<sub>4</sub> ceramic product. The precursors utilized in this approach can be polysilazanes, polysilanes, or polycarbosilanes. In the following sections, polysilazane precursors will be discussed in relation to the work reported in this thesis.

#### I.2.1 Synthesis of Preceramic Polysilazanes

From a practical point of view, the design of preceramic polysilazanes requires: (1) a high ceramic yield upon pyrolysis; (2) close stoichiometric fit to Si<sub>3</sub>N<sub>4</sub>; (3) processability (soluble or meltable). Therefore, only small substituents (CH<sub>3</sub>, H) on the polymer Si-N backbone are desirable. In the following sections, a few synthetic approaches to preceramic polysilazanes, of some historical importance, which use only a single monomer will be described. However, a considerable body of work has been carried out using two or three monomers to prepare polymers with optimized properties.

(i) Polymerization by Ammonolysis and Aminolysis. The simplicity of the ammonolysis or aminolysis of tri- or di-halosilanes made them the method of choice for the synthesis of preceramic polysilazanes. Reaction of MeSiCl<sub>3</sub> with NH<sub>3</sub> gives a methylsilazane resin, which generates a mixture of Si<sub>3</sub>N<sub>4</sub> and SiC by pyrolysis under N<sub>2</sub>, shown in process (I.13).

$$4 \text{ MeSiCl}_3 + 9 \text{ NH}_3 \xrightarrow{\text{CH}_2\text{Cl}_2/40 \circ \text{C}}_{-\text{NH}_4\text{Cl}} 4 \xrightarrow{\text{Si}}_{-\text{Si}}^{-(\text{NH})_{1.5}} \frac{1000 - 1450 \circ \text{C}}{1} \text{Si}_3\text{N}_4/\text{SiC} \quad (I.13)$$
  
Methylsilazane resin

This process was first studied by Winter and Verbeek<sup>47b</sup> and reinvestigated by other researchers later.<sup>49</sup> The precursor, methylsilazane resin, was isolated as a white brittle solid which is soluble in organic solvents and softens at 45-70 °C. Its structure was proposed to contain acyclic, cyclic and cage units.<sup>49</sup> Pyrolysis of this precursor gave 72% ceramic yield.

In the cases of dihalosilanes, only  $H_2SiCl_2$  is useful in the preparation of preceramic polysilazane by direct ammonolysis, and a carbon-free precursor can been obtained. The ammonolysis of other dihalosilanes gives only cyclomers or oligomers. Seyferth *et al.* reported that an oily oligosilazane based on the [H<sub>2</sub>SiNH] unit was obtained from the reaction of H<sub>2</sub>SiCl<sub>2</sub> with NH<sub>3</sub>.<sup>55</sup> This oligomer underwent cross-linking at room temperature and gave Si-rich product in 70% ceramic yield on pyrolysis to 1150 °C *in vacuo* and under argon. In independent studies, a novel approach to ammonolysis has been devised wherein H<sub>2</sub>SiCl<sub>2</sub> is modified by complexation to pyridine prior to ammonolysis.<sup>56</sup> The polysilazane formed via this approach gives higher molecular weight (M<sub>w</sub> = 1300 D) than obtainable by direct ammonolysis. The polymer is not stable and cross-links to form an intractable product in a short time in the absence of solvent. Pyrolysis of this material gives an 80% ceramic yield of silicon nitride mixed with silicon. The proposed structure of the polysilazane is shown in Figure I.1a.<sup>56a</sup> The presence of SiH<sub>3</sub>, measured by IR and NMR spectroscopies, must arise as a consequence of a redistribution process.

(ii) Ring Opening Polymerization. Ring opening polymerization represents an alternative to direct ammonolysis even though the cyclomer precursors are normally made by ammonolysis or aminolysis. Early work showed that heating cyclotri- and cyclotetrasilazanes with ammonium halide catalysts results in high molecular weight ( $M_n = 10 \text{ KD}$ ) polysilazanes.<sup>57</sup> Analytical results suggest that these polysilazanes consist of rings linked by silyl bridges. Base catalyzed polymerization of cyclosilazanes has also been examined.<sup>58</sup> It was found that the reactions proceed with evolution of NH<sub>3</sub>, hydrocarbons and the formation of intractable, crosslinked, brittle products even at temperatures below 300 °C. Although this early work was not directed towards the synthesis of preceramic polymers, and hence the high temperature pyrolysis of the resulting polymers was not studied, recent study of the polymerization of octamethylcyclotetrasilazane using KOCH<sub>3</sub>

as a catalyst has confirmed the previous observations, and the resulting polysilazane seems to be a good precursor to  $Si_3N_4/SiC.^{59}$ 

Ring opening polymerization can also be catalyzed by transition metals as shown in reaction (I.14).<sup>60</sup> The value of x in the product varies depending on the relative proportions of the capping agent, (Me<sub>3</sub>Si)<sub>2</sub>NH, to the tetracyclomer. If the reaction is carried out under H<sub>2</sub> in the absence of capping agent then polymers with  $M_n \approx 2000$  D can be isolated. The product polymers are suggested to contain both condensed ring systems and hydrogen capped linear oligomers via Si-N bond cleavage and reformation.

$$(Me_3Si)_2NH + [Me_2SiNH]_4 \xrightarrow{Ru_3(CO)_{12}/H_2/135^{\circ}C} Me_3Si-[Me_2SiNH]_x-SiMe_3 (I.14)$$

(iii) Transamination/Condensation Polymerizations. Reaction (I.15) was the first reaction successfully used to synthesize preceramic polysilazanes. Verbeek *et al.*<sup>47</sup> found that fusible polysilazane resins could be produced by pyrolysis of bis- or trisalkylaminosilanes (or mixtures):

$$R_{2}Si(NHMe)_{2} \xrightarrow{200-800 \circ C} polymer + MeNH_{2} + [R_{2}SiNMe]_{3} (l.15)$$

$$RSi(NHMe)_{3} \xrightarrow{520 \circ C} polymer + MeNH_{2} (l.16)$$

The polymer produced in (I.15) has a softening point of 190 °C and a C:Si ratio of 1:1.18. Filaments 5-18  $\mu$ m in diameter can be spun at 315 °C. The precursor fiber is then rendered infusible by exposure to air and transformed into a ceramic fiber by heating to 1200 °C under N<sub>2</sub>. The ceramic yield is of the order of 54%, although the composition of the resulting amorphous product was not reported.

Reaction (I.16) has recently been studied in greater detail.<sup>61</sup> The structure of the polymer (R = Me) has been proposed to have trisilacyclohexanes bridged by amino groups, as shown in Figure I.1b.<sup>61c</sup> This polysilazane has weight-average molecular weights ranging from 1500 to 4000 D and it can be hand-drawn to give 10 - 20 µm preceramic fibers. Pyrolysis of the fibers cured in humid air gives fibers with the same ceramic yield,

55%, as found earlier.<sup>47</sup> The ceramic products are mainly amorphous  $Si_3N_4/SiC/SiO_2$  (a consequence of the humidity treatments).



Figure I.1. Proposed Structures of the Mentioned Polysilazanes

#### (iv) Si-Cl/Si-N Redistribution Polymerizations<sup>62,63</sup>.

In the past several years, researchers at Dow Corning have made a concentrated effort to explore and develop the use of Si-Cl/Si-N redistributions as a means of preparing tractable polysilazane precursors to Si<sub>3</sub>N<sub>4</sub>. The redistribution reaction (I.17) yields a hydridopolysilazane with  $M_n \approx 3500 \text{ D}$  ( $M_w \approx 15000 \text{ D}$ ).<sup>63</sup>

 $HN(SiMe_3)_2 + HSiCl_3 \longrightarrow Me_3SiCl + -[HSi(NH)_{1,5}]_x[HSiNH(NHSiMe_3)]_y - (I.17)$ 

The sequence of redistribution reactions leading to the polymer is illustrated in Scheme 5.



The resulting polymer can be spun to give  $15 - 20 \,\mu\text{m}$  fibers. Gas-phase curing of the polymer fibers with HSiCl<sub>3</sub> followed by pyrolysis gave high-nitrogen, low-carbon, silicon-nitride-type fibers, and the overall ceramic yield was approximately 45 - 55%.

(v) Dehydrocyclodimerization Reactions. Cyclomers and oligomers of the type  $-[MeHSiNH]_{x}$ , produced by ammonolysis of MeHSiCl<sub>2</sub>, can react with a strong base, e.g., KH, to undergo dehydrocyclodimerization, exemplified by reaction (I.18). The resulting products are soluble and meltable polymers that can be spun into fibers and give Si<sub>3</sub>N<sub>4</sub>/SiC in extremely high (80-85%) ceramic yields upon pyrolysis.<sup>64</sup> Obviously, the reaction could occur on all sides of the rings, and rings of different sizes could be fused. Polymerization leads to the likely formation of a combination of both ladder, sheet, cage, and linear type structures. A detailed discussion of dehydrocoupling reactions will be given in Section I.3.



### I.2.2 Pyrolysis

Polymeric precursors are solidified by pyrolysis, rather than by the sintering process normally employed in conventional ceramic powder technology. The key questions in this regard are the ceramic yield and the composition of ceramic product. A variety of analytical techniques have been employed to study the pyrolytic chemistry, such as coupled TGA-MS to measure the ceramic yield and to detect the volatile products evolved from precursors at the same time,<sup>65</sup> IR spectroscopy to detect the gaseous and solid products,<sup>66</sup> solid-state
<sup>29</sup>Si NMR spectroscopy to analyse pyrolysis residues,<sup>67</sup> and XRD to measure the crystallinity of the product.<sup>68</sup>

In general, highly cross-linked polysilazanes with low carbon content give higher ceramic yields. Decomposition, polymerization, and split-off of volatile products occurs primarily in the temperature range 200 °C to 600 °C. In the case of chlorinated polymers, chlorine-containing volatile species are observed at lower temperature between 200 and 400 °C. Although pyrolysis mechanisms vary with polymer precursors, the following reactions may occur in most precursors during pyrolysis.<sup>51</sup>

(i) Dehydrocoupling reaction (I.19): leads to cross-linking and further polymerization.



(ii) Thermolytic retroversion reaction (I.20): gives loss of volatile silazanes.



(iii) Transamination reaction (I.21): leads to the loss of amines or silanes and increases cross-linking.

(iv) Nucleophilic substitution reaction (I.22): gives loss of hydrocarbon (methane).

At higher temperature radical reactions may take place.

# I.3 Catalytic Dehydrocoupling of Si-H and N-H bonds

# I.3.1 Alkali Metal Catalysed Dehydrocoupling

The classical synthetic routes to the Si-N bond involve the aminolysis or ammonolysis of halosilanes. A clean approach to the formation of Si-N bonds is the heterodehydrocoupling of Si-H and N-H bonds. Alkali metal catalysed dehydrocoupling, as shown in reaction (I.23), was pioneered by Fink<sup>69</sup> and later studied by Andrianov and coworkers<sup>70</sup>. Although Fink described the synthesis of the first polysilazane (reaction (I.23)) by using the diamine H<sub>2</sub>NRNH<sub>2</sub>,<sup>69d</sup> this route to oligo- and polysilazanes remained unexplored until the work of Seyferth and Wiseman twenty years later.<sup>64</sup>

$$R_2SiH_2 + R'NH_2 \xrightarrow{KH} 1/2 'RN NR' + 2H_2$$
 (l.23)

The mechanism of the dehydrocyclization reaction is not completely understood. Two alternatives have been proposed,<sup>71</sup> one which proceeds via a silaimine mechanism such as the reaction (I.24), and one wherein ring closure occurs by the displacement of hydrogen shown in the reaction (I.25).

$$2 R_{2}Si(H) - NR'(Li) \xrightarrow{-LiH} 2 [R_{2}Si = NR'] \xrightarrow{-RN} RN \xrightarrow{R_{2}} NR' \quad (I.24)$$

$$2 R_{2}Si(H) - NR'(Li) \xrightarrow{-LiH} [R_{2}HSi - NR' - SiR_{2} - NR'(Li)] \xrightarrow{-LiH} 'RN \xrightarrow{R_{2}} NR' \quad (I.25)$$

Modelling studies where R = R' = Me provide evidence in favor of a silaimine intermediate; however, efforts to trap the silaimine species were unsuccessful. Thus, the support for a specific ring closure mechanism remains inconclusive.

### I.3.2 Transition Metal Catalysed Dehydrocoupling

Transition metal catalysed heterodehydrocoupling offers an alternative to the alkali metal catalysed dehydrocoupling process. Sommer and Citron first reported the synthesis of silylamines by the heterodehydrocoupling of R<sub>3</sub>SiH with R'NH<sub>2</sub>, reaction (I.26) using Pd/C as catalyst.<sup>72</sup> Later, Andrianov *et al.* attempted to catalyse reactions such as (I.26) by using a variety of transition metal catalysts but with limited success.<sup>73</sup>

$$R_3SiH + R'NH_2 \xrightarrow{\text{catalyst}} H_2 + R_3SiNHR' \qquad (I.26)$$

Recent work has shown that the heterodehydrocoupling of R<sub>2</sub>SiH<sub>2</sub> with R'NH<sub>2</sub> to prepare silazane cyclomers and oligomers can be efficiently catalysed by late transition metals or their complexes, such as Fe,<sup>74</sup> Ru<sub>3</sub>(CO)<sub>12</sub>,<sup>75</sup> PdCl<sub>2</sub>,<sup>76</sup> Rh<sub>2</sub>H(CO)<sub>2</sub>(dppm)<sub>2</sub> (dppm = bis(diphenylphosphino)methane),<sup>77</sup> CuCl and CuH<sup>78</sup>. Notable in this regard is the work of Laine and coworkers,<sup>60,75</sup> who have investigated a variety of heterodehydrocoupling reactions including organosilanes or simple hydridosilazanes with ammonia or amines, by using Ru<sub>3</sub>(CO)<sub>12</sub> as a catalyst. They also explored the synthesis of preceramic polysilazanes through cross-linking silazane oligomers by dehydrocoupling Si-H with N-H bonds in the same precursor.<sup>75b</sup> Kinetic studies of the ruthenium-catalyzed reaction of Et<sub>3</sub>SiH with RNH<sub>2</sub> (R = *n*-Pr, *n*-Bu, *i*-Bu, and *t*-Bu) showed that the dehydrocoupling sie dependent on the steric requirements of the amine and fragmentation of the starting Ru<sub>3</sub>(CO)<sub>12</sub> cluster.

The heterodehydrocoupling can also be catalyzed by early transition metal complexes. The most interesting results were obtained with the Cp<sub>2</sub>TiMe<sub>2</sub> (DMT) catalyzed

reactions of ammonia with silanes.<sup>79</sup> It has been observed that DMT is a very effective catalyst for the coupling of tertiary and secondary alkyl- and arylalkylsilanes with ammonia, according to reaction (I.27):

$$2 \text{ RR'R"SiH} + \text{NH}_3 \xrightarrow{\text{DMT}} \text{RR'R"SiNHSiRR'R"} + 2 \text{H}_2 \quad (1.27)$$
90°C/1 h/1 atm

As expected, the secondary silanes react much faster than the tertiary ones. However, the reactions of primary silanes were unexpectedly much slower than those of secondary and tertiary silanes. In addition, the nature of the products was quite different, as shown in reaction (I.28).

RSiH<sub>3</sub> + NH<sub>3</sub> 
$$\frac{DMT}{100^{\circ}C/24 \text{ h/2 atm}} - \left(\begin{array}{c} R \\ I \\ Si \\ I \\ NH_2 \end{array}\right) + 2 H_2 \quad (I.28)$$

The key to this difference in behavior is the much greater activity of primary silanes towards homo-dehydrocoupling, relative to that of more heavily substituted tertiary and secondary silanes. Thus, silane oligomers and polymers were formed first and then ammoniated to yield poly(aminosilane) in reaction (I.28). There is a complementary inhibition of both the homo- and heterodehydrocouplings by the two reactants. Both the homo- and heterodehydrocoupling rates are thus much slower than they would be in the absence of the other reactant. A possible catalytic cycle is shown in Scheme 5.



### I.4 Scope of the Thesis

This thesis includes the synthesis, structural characterization, reactivities and pyrolysis of some silylhydrazines. In Chapter II the heterodehydrocoupling reaction of some organosilanes (PhSiH<sub>3</sub>, MeSiH<sub>3</sub> and Ph<sub>2</sub>SiH<sub>2</sub>) with hydrazines (H<sub>2</sub>NNH<sub>2</sub>, MeHNNH<sub>2</sub>, Me<sub>2</sub>NNH<sub>2</sub> and MeHNNHMe) is studied. The dehydrocoupling methodology is also applied to the synthesis of cyclic Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub>. In Chapter III the reactivities of a hydrazinosilane, Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>, are investigated. Examples include the controlled hydrolysis to give bis(hydrazino)disiloxane, and cyclizations to give triazadisilacyclopentane and tetraazadisilacyclohexanes. Structural studies are focused on the conformations of tetraazadisilacyclohexanes and nitrogen geometries in silylhydrazine molecules, and the results are presented in Chapter IV. In the last part of this thesis, Chapter V, the synthesis and structural characterization of poly(methylsildiazane) and its pyrolysis to silicon nitride and silicon carbonitride are described. The electrical conductivity of the ceramic product is also examined.

### Chapter II

# DEHYDROCOUPLING REACTIONS OF ORGANOSILANES WITH HYDRAZINES

### **II.1 Introduction**

Dehydrocoupling of covalent hydrides represents an interesting route to the formation of element-element bonds for a number of reasons. Most important, this chemistry has provided routes to hitherto unknown compounds, but it is also environmentally attractive in that it does not produce side products that are difficult and costly to dispose of.<sup>80</sup> The group 4 metallocene catalyzed dehydrocoupling of silanes, and germanes, to give either simple oligomers, or relatively long chains, has been extensively investigated by several groups.<sup>81-86</sup> Catalyzed heterodehydrocoupling has also been reported for SiH/NH<sup>69-79</sup>, SiH/CH<sup>87</sup> and SiH/OH<sup>88</sup>, as well as BH/NH reactions.<sup>89</sup>

Poly(organosilazanes) have recently attracted interest as potential polymer precursors to silicon nitride (Si<sub>3</sub>N<sub>4</sub>). Our laboratory has studied the catalyzed reactions of organosilanes with primary amines, and with ammonia with a view to synthesizing poly(organosilazanes).<sup>78,79</sup> A problem with the simple polysilazanes as precursors for Si<sub>3</sub>N<sub>4</sub> is that the polymer is nitrogen-deficient with respect to the Si/N stoichiometry of the product. A possible way of redressing this nitrogen deficiency would be to incorporate some -NH-NH- units into the polysilazane.<sup>90</sup> A study was therefore undertaken to investigate the dehydrocoupling chemistry of organosilanes with hydrazines.

Silylhydrazine chemistry has been well developed since the 1950's and a few synthetic methods have been applied for the preparation of silylhydrazines, as mentioned in

Chapter I. However, there is only one previous preliminary report on the heterodehydrocoupling reaction of phenylsilane with hydrazine.<sup>90</sup> In this chapter, an exploration of the heterodehydrocoupling of silanes with hydrazines will be described. This work was undertaken with the aim of developing a new and clean route to silylhydrazines as simple molecules and polymers. The dehydrocoupling reactivity is illustrated by the reactions of primary silanes (*e.g.*, phenylsilane and methylsilane) and secondary silanes (*e.g.*, diphenylsilane) with hydrazine and 1-methyl-, 1,1- and 1,2-dimethyl- hydrazines, respectively. Dimethyltitanocene (Cp<sub>2</sub>TiMe<sub>2</sub>) has been employed to facilitate these reactions. This dehydrocoupling methodology has been successfully applied to achieve the first synthesis of 1,2,4,5-terraaza-3,3,6,6-terramethyl-3,6-disilacyclohexane.

### **II.2 Results and Discussion**

# II.2.1 Uncatalyzed Reactions of Phenylsilane and Methylsilane with Hydrazine

(i) Phenylsilane. Phenylsilane reacts slowly with hydrazine at room temperature. When equimolar amounts of the reactants are used, a third of the silane is consumed within 15 h of reaction. At elevated temperatures the rates are much faster and some results are summarized in Table II.1.

reaction	PhSiH <sub>3</sub> [M]	$H_2NNH_2[M]$	T (°C)	t (min)	conv (mol%)[a]	Mw <sup>[b]</sup>
1	4.3	12.9	90	100	100	840
2	5.5	8.2	90	120	94	910
3	6.0	6.0	100	90	83	780
4	6.0	6.0	25	4320	75	

Table II.1 Some data for uncatalyzed reactions of phenylsilane with hydrazine.

[a] Based on silane consumption.

[b]  $M_w/M_n$  ca. 1.1-1.2; monomodal distribution.

N.B. Calibration of GPC vs polystyrene.

The product of the reaction, a glassy white solid, is soluble in benzene, toluene and THF but is insoluble in hexane. Further, the molecular weight of the product seems to be more or less independent of the reaction conditions. The low molecular weight and the narrow polydispersity ( $M_w/M_n \sim 1.1-1.2$ ) point towards the product as being a relatively simple molecular species. On the other hand, the amorphous nature of the solid and the very broad resonances in the NMR spectra are more typical of a mixture of polymeric materials.

A striking feature of reaction 2 in Table II.1 is the essentially complete disappearance of Si-H, monitored by both IR ( $V_{Si-H}$ : 2140 cm<sup>-1</sup>) and <sup>1</sup>H NMR ( $\delta_{Si-H}$ : 4.2 ppm for PhSiH<sub>3</sub>; 5.2 - 5.4 ppm for Si(H)N) (Figure II.1). In the course of the reaction, a group of three proton resonances at 5.23, 5.26 and 5.28 ppm, whose total integral never exceeds 6 per cent of the phenyl proton integral, are assigned to intermediates containing the Si(H)-N function. In addition, the hydrazine proton resonance at 2.5 ppm broadens considerably and diminishes in intensity to about half its original integral relative to the phenyl protons, while the peak maximum shifts to 3.05 ppm. An INEPT <sup>15</sup>N NMR spectrum of the product revealed a single broad resonance of the NH functionality at -338.0 ppm (relative to MeNO<sub>2</sub>).<sup>27</sup> The <sup>15</sup>N chemical shift of Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub>, 9, described below, was measured to be -337.2 ppm. This evidence shows that the nitrogen is most likely present in the form of rings analogous to 9.

Figures II.2 and II.3 show the solid-state <sup>29</sup>Si CP MAS NMR spectra of the products from the reactions 2 and 4, respectively. In this cross-polarization (CP) NMR spectroscopic study, different contact times of 200, 500 and 2000  $\mu$ s were used to investigate the presence of protonated and nonprotonated Si atoms. Si atoms with directly attached protons will cross-polarize faster than Si with no directly attached protons; thus a short contact time will show more contribution from protonated Si atoms whereas a longer contact time will enhance the contribution from nonprotonated Si atoms. Obviously, the resonance at -25 ppm can be attributed to the resonance of Si-H<sub>n</sub> (most likely n = 1)







Figure II.2 Solid-state <sup>29</sup>Si CP MAS NMR spectra of the polymer formed by the reaction of PhSiH<sub>3</sub> with H<sub>2</sub>NNH<sub>2</sub> (5.5:8.2), using variable contact time. (a) 200  $\mu$ s, (b) 500  $\mu$ s, and (c) 2000  $\mu$ s.



Figure II.3 Solid-state <sup>29</sup>Si CP MAS NMR spectra of the polymer formed by the reaction of PhSiH<sub>3</sub> with H<sub>2</sub>NNH<sub>2</sub> (6.0:6.0) at 100 °C, using variable contact time. (a) 200  $\mu$ s, (b) 500  $\mu$ s, and (c) 2000  $\mu$ s.

species, whereas the resonance at -31.7 ppm is due to the nonprotonated Si atoms, namely those fragments with three coordinated nitrogen atoms. The essentially single resonance at -31.7 ppm in Figure II.2 suggests that the majority of Si atoms are probably in the same local environment. The small broad resonance at -100 ppm in Figure II.2 is assigned to siloxane species, probably due to the hydrolysis of the polymer, and the small resonance at -59 ppm in Figure II.3 remains unidentified.

An earlier study of the copolymerization of phenylsilane with hydrazine suggested that the following reaction occurs:

$$3 \text{ PhSiH}_3 + 4 \text{ H}_2 \text{NH}_2 \longrightarrow - \left[ \text{PhSi}_{N-N} \right] \text{SiPh} + N \text{HNHSi}(\text{Ph}) \text{NHNH}_2 + 8 \text{ H}_2$$

It was assumed that a polymeric material was obtained from the above reaction by coupling of the unsaturated valencies at N and Si, but the exact structure of the polymer was not determined. The fact that all three hydrogens of PhSiH<sub>3</sub> react with hydrazine, and that only traces of an intermediate PhSiH<sub>n</sub>(NHNH<sub>2</sub>)<sub>3-n</sub> species are observed during the reaction, strongly suggests that replacement of Si-H by Si-N results in activation of the remaining Si-H bonds. Therefore, a trifunctional phenyl- or methylsilane and a multifunctional hydrazine may lead to the reaction product as having the structure shown below:



(Ph or Me groups on Si atoms are omitted for clarity)

(ii) Methylsilane. The reaction of methylsilane with hydrazine proceeds at room temperature without a catalyst. When methylsilane gas was introduced into the reactor, a milky substance was produced immediately accompanied by the evolution of hydrogen gas. Attempts to isolate this substance, however, were unsuccessful, as it underwent crosslinking at room temperature to give an insoluble polymeric product. After 24 h, the gas bubbling almost stopped and a white glassy solid was precipitated. The IR spectrum of that product shows bands that could be assigned to  $v_{C-H}$  of the CH<sub>3</sub> group (2956 and 2899 cm<sup>-1</sup>),  $v_{N-H}$  (3165 to 3317 cm<sup>-1</sup>),  $v_{NH2}$  (1589 cm<sup>-1</sup>),  $\delta_{CH3}$  (1409 cm<sup>-1</sup>),  $v_{Si-C}$  (1253 cm<sup>-1</sup>),  $v_{N-N}$  (1113 cm<sup>-1</sup>),  $v_{Si-N}$  (1028 cm<sup>-1</sup>) and  $\delta_{Si-C}$  (921 cm<sup>-1</sup>). The absence of Si-H bands in the IR spectrum (Figure II.4) should be noted. A solid-state <sup>29</sup>Si MAS NMR spectrum (Figure II.5) showed a single broad resonance centered at - 21.33 ppm, suggesting that the majority of silicon atoms have the same coordination environment and most probably coordinate with three nitrogen atoms. Hence, the structure of this polymeric product probably is similar to structure 1.

The pyrolysis of this polymer was studied. TGA shows that about 61 wt% of ceramic residue was obtained at 1000 °C. Gradual weight loss occurs from 50 to 700 °C under a flow of nitrogen (Figure II.6). Although the ceramic yield is good, the fact that this polymer is insoluble in most solvents and does not melt make it unsuitable for coatings and fiber drawing. Nevertheless, the spontaneous dehydrocoupling of N-H with Si-H is probably responsible for the curing, or thermoset, step in the low temperature pyrolysis of poly(methylsildiazane), as described in Chapter V.

II.2.2 Catalyzed Reactions of phenylsilane with hydrazines.

(i) Phenylsilane with hydrazine. Dimethyltitanocene (DMT) has been previously shown to be an efficient catalyst in the heterodehydrocoupling reactions of silanes with amines and ammonia.<sup>79</sup> The reaction of phenylsilane with hydrazine is greatly accelerated at room temperature by catalytic amounts of DMT. The reaction is quite violent and leads to a complex mixture of products which were not charaterized further. The product quickly gels to a three dimensional network. This may be due to the steric requirements of the



Figure II.4 FT-IR spectrum of the polymeric material formed by the reaction of MeSiH<sub>3</sub> with H<sub>2</sub>NNH<sub>2</sub>.



Figure II.5 Solid-state <sup>29</sup>Si spectrum of the polymeric material formed by the reaction of MeSiH<sub>3</sub> with H<sub>2</sub>NNH<sub>2</sub>.



Figure II.6 Thermogravimetric analysis of the polymeric material formed by the reaction of MeSiH<sub>3</sub> with H<sub>2</sub>NNH<sub>2</sub>.

catalyst-containing transition state which disfavors the closure of the six membered ring, relative to the spontaneous reaction, and hence leading to an increase in cross-linking.

(ii) Phenylsilane with 1-methylhydrazine. The rate of reaction of phenylsilane with methylhydrazine is very slow under ambient conditions. The presence of 1 mol % of DMT greatly accelerates the rate of reaction. With equimolar amounts of reactants, about 90% of phenylsilane was converted into silylhydrazine oligomer at ambient temperature in 44 h. At 75 °C, 94% conversion was achieved in 12 h. The molecular weight of the product of this reaction, measured by GPC, was  $M_n = 550 \text{ D} (M_w = 614 \text{ D})$ . The formation of the oligomer was monitored by <sup>1</sup>H NMR. Coupling between the proton and the methyl groups in the moleties -NHMe was observed by <sup>1</sup>H NMR throughout the course of the reaction, indicating the presence of SiNNHMe groups in the product. This means that further dehydrocoupling of Si-H with N-H of the -NHMe groups may not take place, or only happens to a minor extent. The <sup>29</sup>Si NMR spectrum of the product showed a broad resonance from - 19.0 to - 36.0 ppm. A DEPT <sup>29</sup>Si NMR experiment (Figure II.7) showed that the product contains Si-H and Si-H<sub>2</sub> species. Based on the above results, molecules having structure 2 may exist in the product. However, the integral ratios of (Ph-Si) : (H-SiN) : (Me-N + H-N) were observed to be about 8: 1 : 7 in the <sup>1</sup>H NMR spectrum of the product. This means that the product may contain another structure, such as 3. The formation of 3 is likely since a poly(aminosilane) analog has been reported in the DMTcatalyzed ammonolysis of primary silanes, and it has a very close  $\delta$  (<sup>29</sup>Si) chemical shift to that of the corresponding polysilazane.<sup>79</sup> Due to the presence of some very sharp single resonances in the DEPT <sup>29</sup>Si NMR spectrum, simple compounds ( $n \ge 1$ ) are also present.

$$H = \begin{pmatrix} H & NHMe \\ I & I \\ H = \begin{pmatrix} Si & N \end{pmatrix} H \\ Ph & H = \begin{pmatrix} Si & NHNHMe \\ I & I \\ Ph & Ph \\ 2 & 3 \end{pmatrix}$$



Figure II.7 DEPT <sup>29</sup>Si NMR spectra of the polymeric product formed by DMT-catalysed reaction of PhSiH<sub>3</sub> with MeHNNH<sub>2</sub> (1:1): (a) all-Si, (b) Si-H, (c) SiH<sub>2</sub>, and (d) SiH<sub>3</sub>.

Some diphenyldisilane (less than 4%) has also been identified in the product, as determined by <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy.

(iii) Phenylsilane with 1,1-dimethylhydrazine. The rate of reaction of 1,1dimethylhydrazine with phenylsilane is very slow in the absence of catalyst. In the presence of 1 mol % of DMT about 90% of PhSiH<sub>3</sub> was consumed in 20 h at 70 °C. However, homocoupling of phenylsilane to oligophenylsilanes competes effectively with the hydrazine reaction, to give 1,2-diphenyldisilane and 1,2,3-triphenyltrisilane in about the same amount as oligomeric silylhydrazines. The composition of the silylhydrazine products was deduced from <sup>1</sup>H NMR to be a mixture of poly[phenylsil-N-(dimethylamino)azane], 4, and poly[phenyl(dimethylhydrazino)silane], 5, the analogs of 2 and 3.



From the relative sharpness of the NMR resonances, the degree of polymerization does not appear to be very high. The combination of overall low activity, homopolymerization of silane and aminolysis of backbone Si-H groups is reminiscent of the reactions of ammonia with primary silanes.<sup>79</sup>

(iv) Phenylsilane with 1,2-dimethylhydrazine. The rate of the DMT-catalyzed reaction of 1,2-dimethylhydrazine with phenylsilane is faster than that of 1,1-dimethylhydrazine, and there is no competition from the homocoupling reaction of the silane. In this case the products are simple silylhydrazines, PhSiH<sub>2</sub>(NMeNHMe), 6, and PhSiH(NMeNHMe)<sub>2</sub>, 7, resulting from the stepwise replacement of the Si-H groups of the phenylsilane by hydrazino groups.

The difference in behavior between the 1,1- and the 1,2-dimethylhydrazines may be sought in the differing properties of the two intermediates PhSiH<sub>2</sub>NHNMe<sub>2</sub>, 8, and

in ege

PhSiH<sub>2</sub>NMeNHMe, 6, initially formed during the reaction in the two cases. The presence of the methyl group on the  $\alpha$ -nitrogen of 6 increases the steric encumbrance of the transition states for both homo- and heterodehydrocoupling. This results in essentially complete suppression of the former, but does not prevent the substitution of a second Si-H by heterodehydrocoupling to give PhSiH(NMeNMeH)<sub>2</sub>, 7. This is attributed in part to the fact that the increased Si-H reactivity, induced by Si-N formation, partly overrides the negative effect of steric encumbrance. Compound 6 does not, however, react significantly via the  $\beta$ -NH to give the 1,2-bis(phenylsilyl) derivative because the reactivity of the  $\beta$ -NH is reduced by the electronic effect of the first silyl group as well as by the presence of the methyl group. Substitution of the third Si-H group is extremely slow due to the excessive steric encumbrance of the two  $\alpha$ -NMe substituents.

Compound 8 can further undergo another heterodehydrocoupling step to produce a second Si-N bond, on the way to giving the oligosilazane structure 4, or homodehydrocoupling of Si-H to give the hydrazino substituted poly(phenylsilane) 5 ( $n \ge$ 1). This pattern of behavior follows that previously observed for the DMT-catalyzed dehydrocoupling of primary silanes with ammonia.<sup>79</sup>

# II.2.3 Catalysed Reactions of Diphenylsilane with Hydrazines

(i) Diphenylsilane with hydrazine. Diphenylsilane does not react spontaneously with hydrazine at temperatures up to 120 °C. In the presence of 1 mole per cent of DMT, an equimolar mixture of diphenylsilane and hydrazine reacts slowly at room temperature and quite rapidly at 80 °C and above. The results of the two reactions are summarized in Table 2 (p 41). In both cases the NH region of the <sup>1</sup>H NMR spectra contained many peaks between 2.2 and 3.4 ppm. However, the resonances of compounds 9 to 13 were easily identified and their integrals were measurable. In both the low temperature and high temperature reactions these small molecules accounted for about 65 - 70 per cent of the

NMR measurable NH species. The remainder is assumed to be due to higher molecular weight oligomers.

Compound Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub>, 9, was successfully crystallized from the product mixture and its structure was determined by single crystal X-ray diffraction (see Chapter IV), and characterized by <sup>1</sup>H, <sup>29</sup>Si and <sup>15</sup>N NMR spectroscopies. The spectra are shown in Figure II.8. Although the crystal structure reveals two different N atoms (*i.e.*, planar and pyramidal) coexisting in the NHNH moiety, both <sup>1</sup>H (for NH) and <sup>15</sup>N NMR spectra of solutions exhibit only one peak for the corresponding resonance, even at a temperature as low as - 70 °C. The structures of 10, 11 and 12 were deduced from their NMR spectra and CI-MS data, and 13 was identified by comparison of its properties to those of an authentic sample.

According to the product distribution, the DMT-catalysed reaction of diphenylsilane with hydrazine proceeds in a stepwise manner, with each of the Si-H bonds reacting in sequence with a similar reactivity, but with only one of the NH bonds of each nitrogen reacting. Scheme 6 shows the reaction pattern. The formation of large amounts of 9 shows that once the species Ph<sub>2</sub>Si(NHNH<sub>2</sub>)(NHNHSiHPh<sub>2</sub>) is formed, ease of ring closure by intramolecular dehydrocoupling is greater than that of further extension of the chain by intermolecular coupling. This behavior parallels the reaction of dichlorodiphenylsilane with hydrazine.<sup>4</sup>



Figure II.8 Multi-nuclear NMR spectra of compound 9. (a)  $^{1}$ H, (b)  $^{29}$ Si, and (c)  $^{15}$ N.



(ii) Diphenylsilane with 1-methylhydrazine. Methylhydrazine does not react spontaneously with diphenylsilane. No reaction was detected after 4 h at 80 °C. In the presence of 1 mole per cent of DMT, about 99 per cent of the silane had reacted under these conditions. The products of two reactions are listed in Table II.2. Two simple hydrazinosilane compounds, *i.e.* Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>, 14, and Ph<sub>2</sub>SiH(NHNHMe), 15, were formed as the major products in the reactions. Their structures were determined from <sup>1</sup>H NMR and EI-MS data. The course of the reaction was followed by <sup>1</sup>H NMR and the results of one such reaction are summarized in Figure II.9. The phenylsilane was first converted to 15 which further reacted with H<sub>2</sub>NNHMe to give 14. In the first 3 h of reaction about 95% of the Ph<sub>2</sub>SiH<sub>2</sub> was consumed and the percentage of 15 reached a maximum (about 50%). As the reaction went on, the concentration of 15 decreased while the concentration of 14 increased. It is clear that the reactivities of the two Si-H functions are very similar and that the reaction proceeds in a stepwise manner.

The reaction of diphenylsilane with methylhydrazine is similar to that with hydrazine, except that the NHMe group is essentially unreactive towards further dehydrocoupling. This is reflected in the accumulation of high yields of 14 and essentially no cyclic products, even under forcing conditions. The overall lower reactivity of the methylhydrazine also results in the appearance of some tetraphenyldisilane, 16, since the rate of homodehydrocoupling is competitive with that of heterodehydrocoupling.

reaction	T (°C)	t	conv (%) <sup>b</sup>	products
$Ph_2SiH_2 + H_2N-NH_2$	25	5 days	75	Ph2Si(NHNH)2SiPh2 (9) (15%)
(1:1 mole)				Ph2Si(H)NHNH2 (10) (20%)
(neat)				Ph <sub>2</sub> Si(NHNH <sub>2)2</sub> (11) (25%)
				and higher oligomers
11	120	24 h	100	<b>9</b> (40%)
(1:1 mole)				Ph2Si[NHNHSiPh2H]2
(in 65 vol. % toluene)				(12) (15%)
				[Ph2SiNH]3 (12) (10%)
				10(5%)
				11(5%)
				and higher oligomers
Ph2SiH2 + 2 H2N-NHMe	25	2 days	70	Ph2Si(NHNHMe)2 (14) (25%)
(1:2 mole)				Ph2Si(H)NHNHMe (15) (35%)
(neat)				HPh2SiSiPh2H (16)(5%)
				and higher oligomers
	80	20 h	100	14 (70%)
				15 (15%)
				16 (< 5%)
				and higher oligomers
Ph2SiH2 + H2N-NMe2	70	20 h	36	<b>16</b> (16%)
(1:1)				Ph2SiH(NHNMe2) (17) (13%)
(in 40 vol % hexane)				(Ph2SiH)2NNMe2 (18) (7%)

Table 2 Dehydrocoupling reactions between diphenylsilane and hydrazines<sup>a</sup>

a. Catalyst: 1 mol % DMT; b. Based on diphenylsilane consumption as measured by <sup>1</sup>H NMR.



Figure II.9 The course of the dehydrocoupling of diphenylsilane with methylhydrazine. (Ph<sub>2</sub>SiH<sub>2</sub>: 4.00 mL; MeHNNH<sub>2</sub>: 2.24 mL; DMT: 93 mg.)

Compound 14 can be synthesized in a yield as high as 80%, and is easily isolated by crystallization. Its structure was determined by X-ray crystallography (see Chapter IV). A <sup>1</sup>H NMR study of 14 shows the proton coupling in the NHMe moiety, as being a quartet (N-H) and a doublet (C-H) with a coupling constant <sup>3</sup>J<sub>HNCH</sub> of 6 Hz (Figure II.10). Although the hydrogen atoms on nitrogen atoms were not located in the crystal structure, the connectivity between the H and N atoms was confirmed by 2D <sup>1</sup>H NMR using a HMQC (Heteronuclear Multiple Quantum Coherence) pulse sequence through <sup>1</sup>J<sub>N-H</sub> (90 Hz) coupling, as shown in Figure II.11.







(iii) Diphenylsilane with 1,1-dimethylhydrazine. The reaction of diphenylsilane with 1,1-dimethylhydrazine took place slowly in the presence of DMT at 70 °C. The results are listed in Table II.2. The product distribution shows that competition of homocoupling and heterodehydrocoupling occurs during this reaction, in a manner similar to the results described above for phenylsilane.

(iv) Diphenylsilane with 1,2-dimethylhydrazine. The strong inhibiting effect of methyl substitution, as reflected in the preceeding result, was also evident in the complete failure of 1,2-dimethylhydrazine to react under any conditions with diphenylsilane.

### II.2.4 Synthesis of Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub>

Tetraazadisilacyclohexanes are important Si-N ring systems. They exhibit interesting structural features in the solid state (see Chapter IV). The synthesis of RR'Si(NHNH)<sub>2</sub>SiRR' (R, R' = H, Me) was prompted by the modelling study of the structure of poly(methylsildiazane), described in Chapter V. The conventional synthetic method for the preparation of tetraazadisilacyclohexanes is the intermolecular reaction of a hydrazine with a dihalosilane, with the elimination of hydrogen halide. However, attempts by Wannagat to react Me<sub>2</sub>SiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> yielded only a polymeric product and no simple tetraazadisilacyclohexane was isolated.<sup>2</sup> The reaction of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> gives a polymeric product, even at lower temperature, as described in Chapter V. Further, the direct dehydrocoupling of MeHSiH<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub>, described above, also yields a polymeric product.

Attempts to synthesize  $Me_2Si(NHNH)_2SiMe_2$ , 19, through the reaction of  $Me_2SiH_2$  and  $H_2NNH_2$  were unsuccessful. Spontaneous dehydrocoupling of  $Me_2SiH_2$  with  $H_2NNH_2$  occurs slowly to give a polymeric product with no 19 formed. However, this ring compound can be synthesized by the dehydrocoupling reaction of 1,2-

bis(dimethylsilyl)hydrazine, 20, with hydrazine. Scheme 7 shows the synthetic route starting with Me<sub>2</sub>HSiCl and H<sub>2</sub>NNH<sub>2</sub>.



Reaction of Me<sub>2</sub>HSiCl with H<sub>2</sub>NNH<sub>2</sub> in 2:1 molar ratio affords a mixture of 20 and (Me<sub>2</sub>HSi)<sub>2</sub>NNH(SiHMe<sub>2</sub>). Triethylamine (Et<sub>3</sub>N) was used as an auxiliary base to capture HCl generated in the reaction. Fractional distillation of the product mixture at 105 °C gives ca. 60% of 20. In the absence of solvent, the dehydrocoupling reaction of 20 with hydrazine took place spontaneously to form 19 in 78% yield. An attempt to synthesize 19 by the reaction of Me<sub>2</sub>SiHCl with excess hydrazine in an one-pot reaction was unsucessful. This is probably because complexation of hydrazine to dimethylchlorosilane occurs, as no precipitation of Et<sub>3</sub>NHCl was observed. Complexation of amine (or ammonia to halosilanes to form adducts is well-known.<sup>8</sup>

Compound 19 was characterized by <sup>1</sup>H and <sup>29</sup>Si NMR. In the <sup>1</sup>H NMR spectrum, two resonances at 2.35 ppm and 0.19 ppm in a 1:3 ratio are assigned to N-H and Si-CH<sub>3</sub>, respectively. The <sup>29</sup>Si NMR spectrum exibits a single resonance at -3.71 ppm. The identification of 19 was further confirmed by CI-MS (molecular ion: m/e = 176). 19 is a crystalline solid at ambient temperature. It can be purified by sublimation at 65 °C under vacuum (0.01 mmHg).

#### **II.3** Summary

Dehydrocoupling of organosilanes with hydrazines provides a new and clean route to silylhydrazines as simple molecules or polymers. Phenylsilane and methylsilane spontaneously react with hydrazine to give polymeric products. The replacement of Si-H by Si-N activates the remaining Si-H bonds, whereas the substitution of N-H by either Si or C strongly suppresses reaction of the second N-H. Dimethyltitanocene is an efficient catalyst for the dehydrocoupling of phenylsilane and diphenylsilane with hydrazines. The catalyzed dehydrocoupling reactions proceeds in a stepwise manner.

# **II.4 Experimental Section**

### **II.4.1 General Procedures**

All manipulations were performed under a dry nitrogen or argon atmosphere, using Schlenk techniques. All glassware was dried at 115 °C and cooled under vacuum. Solvents were freshly distilled and degassed before use. Degassing was generally accomplished by the use of three freeze-pump-thaw cycles. Flasks and Schlenk tubes were evacuated and filled with argon three times before or after reagents were charged. Solvents and liquid reagents were transferred by cannula or syringe. All of the dehydrocoupling reactions of organosilanes with hydrazines (noncatalyzed or catalyzed by titanocene) were carried out at room or higher temperature in flasks or Schlenk tubes. Typically, the flasks or tubes were charged with degassed solvent, the appropriate organosilane and hydrazine, and catalyst precursor if it was a catalytic reaction. The reaction mixture was periodically sampled and the course of the reaction was monitored by IR, <sup>1</sup>H- and <sup>29</sup>Si NMR spectroscopies.

<sup>1</sup>H NMR spectra were recorded on a Varian XL-200 FT-NMR (200 MHz), or a Varian XL-300 FT-NMR (300 MHz) spectrometer at 20 °C. Benzene-d<sub>6</sub> was used as solvent and the chemical shift of the residual protons was set as the reference ( $\delta$  7.15 ppm). <sup>29</sup>Si and <sup>15</sup>N NMR spectra were measured on a Varian XL-300 FT-NMR spectrometer operating at 59.6 and 30.4 MHz, respectively, in C<sub>6</sub>D<sub>6</sub> at 20 °C. The spectra were referenced externally with respect to TMS (<sup>29</sup>Si) or MeNO<sub>2</sub> (<sup>15</sup>N) at 0.00 ppm. Solid-state <sup>29</sup>Si MAS NMR spectra were acquired on a Chemagnetics CMX-300 spectrometer at 59.52 MHz. Single-pulse excitation (60° pulse) with proton decoupling during data aquisition and magic angle spinning at 3.5 kHz, using cylindrical rotors, was employed. Typically, 256 transients ( 30.03 kHz spectral width) were taken at 15s intervals. A cross-polarization (CP) pulse sequence at different contact times was used to differentiate protonated and nonprotonated Si atoms.The chemical shift values were referenced to external tetramethylsilane (0.00 ppm).

IR spectra were recorded, under dry air purge, on a Bruker IFS-88 FT spectrometer at a resolution of  $4 \text{ cm}^{-1}$  and using a mercury cadmium telluride (MCT) detector. Samples were prepared as a thin film on KBr plates.

The molecular weights of polymers were measured on a Varian 5000 gel permeation chromatograph, equipped with a Waters Ultrastyragel 1000 Å column, or 500 Å and 100 Å columns in tandem at 35 °C, and with THF as solvent. Polystyrene standards were used for calibration.

Thermogravimetric analyses (TGA) were performed on a Seiko 220 TG/DTA instrument. A flow of N<sub>2</sub> (~80 mL/min) was maintained during the TGA runs. The samples (ca. 5 - 10 mg) were heated in an alumina ceramic pan at a rate of 5 °C/min from 50 to 750 °C and then at 15°C/min from 750 to 1000 °C.

Low resolution mass spectra were obtained on a DuPont 21-492b spectrometer with an ion source temperature of 25 °C and an ionizing energy of 70 eV.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, USA.

### **II.4.2** Chemicals

Toluene, hexanes, tetrahydrofuran (THF) and diethylether were refluxed over sodium/benzophenone and collected by distillation under nitrogen. Subsequent freeze-thaw degassing was performed under argon. Benzene- $d_6$  and toluene- $d_8$  were purchased from Merck Sharp and Dohme, and were generally used as received after degassing and purging with argon.

Organosilanes were prepared from the corresponding chlorosilanes (Aldrich) by reduction with LiAlH<sub>4</sub> (Aldrich).<sup>91,92</sup> Cp<sub>2</sub>TiMe<sub>2</sub> was prepared according to literature procedures,<sup>93</sup> and was stored in the mother liquor at -20 °C in the dark.

Hydrazine (anhydrous, 97%, Anachemia Canada) was purified by double distillation from crushed BaO.<sup>94</sup> The sample to be purified was refluxed *in vacuo* with five times its weight of BaO at 70 °C and distilled. The process was repeated with one-half the original amount of BaO.

Methylhydrazine (Eastman Kodak Company) was purified by fractional distillation from CaH<sub>2</sub> after refluxing for 3 h under 1 atm of N<sub>2</sub>. The distillate was collected over the range 88.0 - 88.1 °C.

1,1-Dimethylhydrazine (anhydrous, 98%, Anachemia Canada Inc.), was refluxed under vacuum at 50 - 60 °C for 1 h with five times its weight of crushed BaO and then distilled.

1,2-Dimethylhydrazinedihydrochloride (Aldrich) was treated with crushed reagent grade NaOH pellets *in vacuo* to obtain free MeNHNHMe. The material so obtained was dried over NaOH pellets and distilled three times. Finally, CaH<sub>2</sub> was added to remove the last traces of moisture, and the material was fractionally distilled at atmospheric pressure. The fraction to be used was collected over the range 81.0 - 82.0 °C.

### **II.4.3 Dehydrocoupling Reactions**

(i) Dehydrocoupling of Phenylsilane with Hydrazine. Noncatalytic reactions were carried out under argon in Schlenk flasks equipped with a reflux condenser. After the flask was evacuated, it was charged with 10 mL of toluene, followed by 1.7 mL of PhSiH<sub>3</sub> (0.014 mol) and 0.66 mL of hydrazine (0.021 mol). This mixture was stirred and the dehydrocoupling reaction took place with the evolution of hydrogen gas at ambient temperature. The solution became gradually more viscous as the reaction progressed. The course of reaction was followed by <sup>1</sup>H NMR. After 2 h at 90 °C, the consumption of phenylsilane was 94%. The solvent was then removed under reduced pressure. A white, amorphous polymeric product was isolated in ca. 85 % yield. <sup>1</sup>H NMR :  $\delta$  2.2-3.7 (br, 1 H, NH), 6.5-8.2 (br, 2.8 H, Ph). GPC: M<sub>n</sub> = 910, M<sub>w</sub>/M<sub>n</sub> = 1.1. Solid-state <sup>29</sup>Si CPMAS NMR: -25.3 ppm (br, Si-H<sub>n</sub>); -31.7 ppm (br, PhSi(N)<sub>3</sub>).

For the catalytic reaction, 1.0 mol% of DMT (58 mg) was added into the above mixture. Reaction was vigorous and produced a gelled material in 5 h at ambient temperature.

The results of other experiments under a variety of conditions are summarized in Table II.1.

(ii) Dehydrocoupling of Methylsilane with Hydrazine. The polymerization of methylsilane with hydrazine proceeds at room temperature without a catalyst. A typical experiment is as follows. Hydrazine (0.88 mL, 0.0281 mol) was mixed with toluene (15 mL) in a thick walled 120-mL Schlenk tube equipped with a magnetic stirrer and a Rotaflow valve. Methylsilane gas (105 mL, 100 psi, 0.0281 mol) was introduced into the reaction vessel and the mixture was stirred at room temperature. The mixture turned milky along with the evolution of hydrogen gas. After 24 h, the gas bubbling almost stopped and a white glassy solid was precipitated. The reaction was continued for another 5 h. The white glassy solid was separated from the solution and dried under reduced pressure.

Yield: 0.503 g (51.5 wt%). IR (neat, cm<sup>-1</sup>): 3165 to 3317 cm<sup>-1</sup> ( $V_{N-H}$ ), 2956, 2899 cm<sup>-1</sup> ( $V_{C-H3}$ ), 1589 cm<sup>-1</sup> ( $V_{NH2}$ ), 1409 cm<sup>-1</sup> ( $\delta_{CH3}$ ), 1253 cm<sup>-1</sup> ( $V_{Si-C}$ ), 1113 cm<sup>-1</sup> ( $V_{N-N}$ ), 1028 cm<sup>-1</sup> ( $V_{Si-N}$ ) and 921 cm<sup>-1</sup> ( $\delta_{Si-C}$ ). Solid-state <sup>29</sup>Si MAS NMR: -21.3 ppm. TGA: black ceramic product in 61% yield after pyrolysis at 1000 °C.

(iii) Catalytic dehydrocoupling of phenylsilane with methylhydrazine. A typical experiment is as follows. Phenylsilane (2.50 mL, 0.020 mol), methylhydrazine (1.07 mL, 0.020 mol), toluene (8 mL) and DMT (82 mg, 1 mol%) were charged into a Schlenk flask (25 mL), equipped with a condenser. The mixture was stirred at ambient temperature. The course of reaction was monitored by following the disappearance of the Si-H resonance of PhSiH<sub>3</sub> by <sup>1</sup>H NMR. After 44 h, 90% of the phenylsilane was consumed. A similar reaction at 75 °C for 12 h gave 94% conversion. A polymeric product was obtained after the removal of toluene. GPC:  $M_n = 550$  D,  $M_w/M_n = 1.1$ . <sup>1</sup>H NMR:  $\delta$  2.10 - 3.30 (br, 7H, NH + NMe), 5.00 - 5.40 (br, 1H, NSiH), 7.00 - 8.30 (br, 8H, Ph). <sup>29</sup>Si NMR (DEPT) :  $\delta$  = 19.0 to - 32.0 (br, SiH), - 31.0 to - 36.0 (br, SiH<sub>2</sub>).

(iv) Catalytic dehydrocoupling of Phenylsilane with 1,1-dimethylhydrazine. A typical experimental procedure is as follows: Phenylsilane (1.7 mL, 0.014 mol), 1,1dimethylhydrazine (1.06 mL, 0.014 mol), hexane (8 mL) and DMT (58 mg, 1 mol%) were charged into a Schlenk flask (25 mL), equipped with a condenser. The reaction mixture was stirred while heated to 70 °C. The course of the reaction was monitored by following the disappearance of the Si-H resonance of PhSiH<sub>3</sub> by <sup>1</sup>H NMR. After 20 h, the reaction was stopped and the mixture was cooled to ambient temperature and the solvent was removed under reduced pressure. The consumption of phenylsilane (37%) and the oligomeric product 4 and 5 (46%). <sup>1</sup>H NMR: 1,2-diphenyldislane  $\delta$  4.48 (s, 4H, SiH), 6.95 - 7.90 (m, 10H, Ph); 1,2,3-triphenyltrisilane  $\delta$  4.60 (br, 5H, SiH), 6.95 - 7.90 (m, 15H, Ph); 4 and 5  $\delta$  2.15 - 2.60 (m, NH + NMe), 5.03 - 5.40 (m, NSiH), 6.95 - 7.90 (m, Ph). (v) Catalytic dehydrocoupling of Phenylsilane with 1,2-dimethylhydrazine. A typical procedure using DMT as catalyst is as follows: phenylsilane (1.7 mL, 0.014 mol), 1,2-dimethylhydrazine (1.02 mL, 0.014 mol), hexane (8 mL) and DMT (58 mg, 1 mol%) were charged into a Schlenk flask (25 mL), and the mixture was stirred at ambient temperature. The course of reaction was followed by <sup>1</sup>H NMR. After 20 h, phenylsilane was completely consumed. <sup>1</sup>H NMR analysis showed the product to contain about 65% of PhSiH<sub>2</sub>(NMeNHMe) and 18% of PhSiH(NMeNHMe)<sub>2</sub>. <sup>1</sup>H NMR: PhSiH<sub>2</sub>(NMeNHMe),  $\delta$  2.25, 2.23 (d, 3H,  $\beta$ -NCH), 2.37 (m, 1H,  $\beta$ -NH), 2.48 (s, 3H,  $\alpha$ -NCH), 5.16 (s, 2H, SiH), 7.20, 7.62 (m, 5H, Ph); CI-MS (m/e): 166. PhSiH(NMeNHMe)<sub>2</sub>,  $\delta$  2.33, 2.31(d, 6H,  $\beta$ -NCH), 2.44 (m, 2H,  $\beta$ -NH), 2.56 (s, 6H, SiNCH<sub>3</sub>), 5.14 (s, 1H, SiH), 7.20, 7.80 (m, 5H, Ph); CI-MS (m/e): 224. When a mixture with a 1: 2 molar ratio of phenylsilane and 1,2-dimethylhydrazine was heated for 15 h at 70 °C, 72% of PhSiH(NMeNHMe)<sub>2</sub> and 14% of PhSiH<sub>2</sub>(NMeNHMe) were obtained. The remaining product was a viscous oligomer. Pure PhSiH(NMeNHMe)<sub>2</sub> can be obtained by fractional distillation at 65 °C (0.25 mm Hg).

(vi) Catalytic dehydrocoupling of diphenylsilane with hydrazine. A Schlenk flask was charged with Ph<sub>2</sub>SiH<sub>2</sub> (5.0 mL, 27 mmol), N<sub>2</sub>H<sub>4</sub> (0.85 mL, 27 mmol) and toluene (12 mL), then DMT (98 mg, 0.47 mmol) was added. The solution changed from orange to dark brown within 10 minutes . The mixture was refluxed at 120°C and periodically sampled and analyzed by <sup>1</sup>H NMR. Gas(es) evolved vigorously in the first 2 hours and no further gas was observed after 12 hours. The solution became gradually viscous as the reaction proceeded. Stirring was continued for 24 hours. The yields of the several products formed in the reaction were roughly measured from their <sup>1</sup>H NMR spectra. Ph<sub>2</sub>SiH(NHNH<sub>2</sub>) (ca.5% yield): <sup>1</sup>H NMR:  $\delta$  2.43(br, 2H,  $\beta$ -NH), 2.87(br, 1H,  $\alpha$ -NH), 5.545 (d, <sup>3</sup>J<sub>HSiNH</sub> = 2 Hz, 1H, HSi), 7.0-8.2(m, 10H, Ph). Ph<sub>2</sub>Si(NHNH<sub>2</sub>)2 (ca.5%): <sup>1</sup>H NMR:  $\delta$  2.77(br, 4H,  $\beta$ -NH), 3.16(br, 2H,  $\alpha$ -NH), 7.0-8.2(m, 10H, Ph). Ph<sub>2</sub>Si(NHNH<sub>2</sub>)H<sub>2</sub> (ca.15%): <sup>1</sup>H NMR :  $\delta$  2.94(s, 4H, NH), 5.63(s, 2H, SiH),

7.0-8.2(m, 30H, Ph). [Ph<sub>2</sub>SiNH]<sub>3</sub> (ca.10%): <sup>1</sup>H NMR: δ 2.63(s, 3H, NH), 7.0-8.2(m, 30H, Ph). Ph<sub>2</sub>Si[NHNH]<sub>2</sub>SiPh<sub>2</sub> (2.3 g, 40% yield) was crystallized out by the addition of a minimum amount of hexane to the reaction mixture in toluene; <sup>1</sup>H NMR: δ 3.31(s, 4H, NH), 7.20, 7.65(m, 20H, Ph); <sup>29</sup>Si: δ -19.89 (ppm). <sup>15</sup>N: δ -337.22 (ppm). IR (neat, cm<sup>-1</sup>): 428(m), 462(s), 488(vs), 529(w), 552(vs), 610(w), 621(m), 697(vs), 717(vs), 737(s), 800(vs), 922(w), 997(m, N-Si), 1029(w), 1066(s,), 1113(vs, Ph-Si), 1122(vs), 1185(w), 1263(m), 1305(w), 1346(w), 1376(m), 1427(vs, Ph-Si), 1482(m), 1586, 2915(w, C=C), 2998(m, Ar-H), 3026(m, Ar-H), 3051(w, Ar-H), 3065(m, Ar-H), 3342(s, N-H): EI-MS (m/e, abundance, fragmentation): 424(100) [M\*+], 393(6) [M\*+ - NHNH<sub>2</sub>], 378(20) [M\*+ - HNNH<sub>2</sub> -NH], 364(5) [M\*+ - 2 NHNH], 317(33) [M\*+- Ph - NHNH], 285(4) [M\*+ - Ph - 2 NHNH<sub>2</sub>], 158(24) [M\*+ - 3 PhH - H<sub>2</sub>NNH<sub>2</sub>]; m.p.: 162.5-164.5 °C (uncorrected). Analysis: Calcd: C, 67.88%; H, 5.69%; N, 13.19%.

(vii) Catalytic dehydrocoupling of diphenylsilane with methylhydrazine. The experimental procedure for the catalytic reaction of diphenylsilane with methylhydrazine was similar to the previous reaction. Ph<sub>2</sub>SiH<sub>2</sub> (4.0 mL, 22.4 mmol), MeHNNH<sub>2</sub> (2.24 mL, 44.8 mmol) and DMT (93 mg, 0.44 mmol) were charged into 50mL Schlenk flask, equipped with a condenser. Reaction took place immediately after the mixture was stirred, but gas evolution was slower than in the case of hydrazine. The mixture was heated to 80 °C and periodically sampled and analysed by <sup>1</sup>H NMR. After 20 h, the solution was allowed to cool to ambient temperature and Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> crystallized out (3.8g; 65%). It was purified by recrystallization from toluene/hexane (5:2). The residual brown oil was distilled *in vacuo*. The distillate collected over the range of 80-90 °C (0.25 mm Hg) was found to be Ph<sub>2</sub>Si(H)NHNHMe, a colorless oil (0.87g, 15%). Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>: <sup>1</sup>H NMR:  $\delta$  2.32, 2.35(d, <sup>3</sup>J<sub>HNCH</sub> = 6 Hz, 6H,  $\beta$ -NCH), 2.55, 2.58, 2.61, 2.64(q, <sup>3</sup>J<sub>HNCH</sub> = 6 Hz, 2H,  $\beta$ -NH), 2.91(br, 2H,  $\alpha$ -NH), 7.25- 7.85(m, 10H, Ph); <sup>29</sup>Si:  $\delta$  -29.51 (ppm); <sup>15</sup>N (HMQC):  $\delta$  - 305.43 (SiNH), - 327.35 (NHMe). IR (neat, cm<sup>-1</sup>): 499(s), 552(s), 701(vs), 742(s), 838(w), 870(m), 996(m, br, N-Si), 1014(w), 1101(w), 1120(vs), 1187(m), 1260(w), 1363(w), 1427(s, Ph-Si), 1478(m, C-N), 1590; 2783(m, br), 2837(w), 2858(w), 2931(s, C-H); 2976(m, C-H), 3016(w, C-H), 3049(m, Ar-H), 3066(s, Ar-H); 3273(w, N-H), 3282(s, N-H), 3327(m, N-H); EI-MS (m/e, abundance, fragmentation): 272(71) [M<sup>\*+</sup>], 226(73) [M<sup>\*+</sup> - H<sub>2</sub>NNHMe], 198(93) [M<sup>\*+</sup> - H<sub>2</sub>NNHMe - N<sub>2</sub>], 183(55) [M<sup>\*+</sup> - H<sub>2</sub>NNHMe - N<sub>2</sub> - CH<sub>3</sub>], 149(100) [M<sup>\*+</sup> - Ph -H<sub>2</sub>NNHMe]; m.p.: 95 °C. Analysis: Calcd: C, 61.72%; H, 7.39%; N, 20.56%. Found: C, 61.36%; H, 7.47%; N, 20.96%. Ph<sub>2</sub>Si(H)NHNHMe: <sup>1</sup>H NMR: δ 2.23, 2.26(d, 3H, β-NCH), 2.55-2.70(br, 2H, SiNHNHC), 5.61, 5.62(d, <sup>3</sup>J<sub>HSiNH</sub>=1.5 Hz, 1H, SiH), 7.0-8.2(m, 10H, Ph); EI-MS (m/e, abundance, fragmentation): 228(21) [M<sup>\*+</sup>], 198(49) [ M<sup>\*+</sup> -NHMe], 183(71) [M<sup>\*+</sup> - NHNHMe], 150(19) [M<sup>\*+</sup> - PhH], 120(100) [M<sup>\*+</sup> - NHMe -Ph], 105(69) [M<sup>\*+</sup> - NHNHMe - PhH].

(viii) Catalytic dehydrocoupling of diphenylsilane with 1,1dimethylhydrazine. The above procedure was followed. Ph<sub>2</sub>SiH<sub>2</sub> (2.5 mL, 14 mmol), Me<sub>2</sub>NNH<sub>2</sub> (1.06 mL, 14 mmol), hexane(8.0 mL) and DMT (58 mg, 0.28 mmol) were charged into a 25-mL Schlenk flask. The dehydrocoupling of diphenylsilane with 1,1dimethylhydrazine did not occur at ambient temperature, but the dimerization of diphenylsilane took place very slowly with 10% consumption of diphenylsilane after 3 days. When the mixture was refluxed at 70 °C for 20 h, 36% of diphenylsilane was converted to H(Ph<sub>2</sub>Si)<sub>2</sub>H (16%), Ph<sub>2</sub>SiH(NHNMe<sub>2</sub>) (13%) and (Ph<sub>2</sub>SiH)<sub>2</sub>NNMe<sub>2</sub> (7%). <sup>1</sup>H NMR: H(Ph<sub>2</sub>Si)<sub>2</sub>H,  $\delta$  5.49 (s, 2H, SiH), 7.0-7.6 (m, 20H, Ph); Ph<sub>2</sub>SiH(NHNMe<sub>2</sub>),  $\delta$  2.22 (s, 6H, NMe), 5.62 (s, 1H, SiH), 7.2-8.0 (m, 10H, Ph); CI-MS (m/e): 242. (Ph<sub>2</sub>SiH)<sub>2</sub>NNMe<sub>2</sub>,  $\delta$  2.53 (s, 6H, NMe), 5.63 (s, 2H, SiH), 7.2-8.0 (m, 20H, Ph); CI-MS (m/e): 424.

(ix) Catalytic dehydrocoupling of diphenylsilane with 1,2dimethylhydrazine. The above procedure was followed. Ph<sub>2</sub>SiH<sub>2</sub> (2.5 mL, 14 mmol), Me<sub>2</sub>NNH<sub>2</sub> (1.06 mL, 14 mmol), hexane (8.0 mL) and DMT (58 mg, 0.28 mmol) were
charged into a 25-mL Schlenk flask. The heterodehydrocoupling of diphenylsilane with 1,2-dimethylhydrazine did not occur either at ambient temperature or at 70 °C, but the dimerization of diphenylsilane took place slowly at 70 °C with about 20% conversion of diphenylsilane after 20 h.

(x) Synthesis of Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub> (19). Me<sub>2</sub>HSiNHNHSiHMe<sub>2</sub> (20) (3.0 mL, 0.0174 mol) was charged into a 20-mL Schlenk tube containing 0.68 mL of H<sub>2</sub>NNH<sub>2</sub> (0.019 mol) and a stirrer. After the mixture was stirred, the reaction took place immediately at ambient temperature with the evolution of hydrogen gas. The reaction mixture was stirred for 20 h, and a viscous product was obtained. Sublimation of this viscous material at 65 °C under 0.01 mmHg vacuum gave a crystalline product 19 in 78% yield. <sup>1</sup>H NMR:  $\delta$  2.35 (s, 4H, NH), 0.19 (s, 12H, CH). <sup>29</sup>Si NMR:  $\delta$  -3.73 ppm. Cl-MS: 176. m.p.: 32.5 °C.

The starting material, Me<sub>2</sub>HSiNHNHSiHMe<sub>2</sub>, was prepared by the reaction of Me<sub>2</sub>HSiCl with H<sub>2</sub>NNH<sub>2</sub>. A typical procedure is as follows. A 250-mL three-neck flask equipped with a magnetic stirrer, an addition funnel, and a condenser with N<sub>2</sub> inlet was charged with diethylether (30 mL), triethylamine (15.0 mL, 0.109 mol), and hydrazine (3.6 mL, 0.1098 mol). Dimethylchlorosilane (12.0 mL, 0.1098 mol) was syringed into the addition funnel together with diethylether (10 mL). The dimethylchlorosilane solution was added dropwise to the mixture in the flask at ambient temperature while it was stirred over 30 min. After the mixture had been stirred for 5 h at ambient temperature, the supernatant was separated from the solid triethylammonium chloride precipitate using a fritted glass filter. Fractional distillation of the solution gave 3.87 g (ca. 60%) of 20 and 5.4 g (ca. 40%) of (Me<sub>2</sub>HSi)<sub>2</sub>NNH(SiHMe<sub>2</sub>). Physical data for 20: <sup>1</sup>H NMR:  $\delta = 0.13$  [d, <sup>3</sup>J<sub>HCSH</sub> = 3.1 Hz, 12H, (H<sub>3</sub>C)<sub>2</sub>Si], 2.47 (s, 2H, NH), 4.60 (sept, <sup>3</sup>J<sub>HSiCH</sub> = 3.1 Hz, 2H, HSi). <sup>29</sup>Si NMR:  $\delta = -8.90$  (SiNH). MS (CI): 146. b.p.: 105 °C (756 mmHg). Physical data for (Me<sub>2</sub>HSi)<sub>2</sub>NNH(SiHMe<sub>2</sub>): <sup>1</sup>H NMR:  $\delta = 0.10$  [d, <sup>3</sup>J(HCSiH) = 3.1 Hz, 6H, (H<sub>3</sub>C)<sub>2</sub>SiNH], 0.17 [d, <sup>3</sup>J(HCSiH) = 3.1 Hz, 12H, (H<sub>3</sub>C)<sub>2</sub>Si)<sub>2</sub>N], 2.16 (s, 3H, HN),

4.67 [sept, <sup>3</sup>J(HSiCH) = 3.1 Hz, 2H, (HSi)<sub>2</sub>N], 4.76 [sept, <sup>3</sup>J(HSiCH) = 3.1 Hz, 1H, HSiNH]; <sup>29</sup>Si NMR:  $\delta$  - 7.77 (Si<sub>2</sub>N), - 7.36 (SiNH). MS (CI): 206.

#### Chapter III

#### REACTIVITIES AND CYCLIZATIONS OF Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>

#### **III.1 Introduction**

Hydrazinosilanes,  $R_nSi(NR'NR''R''')_{4-n}$ , represent an important class of silicon-hydrazine compounds. The synthesis of this class of compounds is generally possible through the reaction of halosilanes with hydrazines, as for example the syntheses of Ph<sub>2</sub>Si(NHNMe<sub>2</sub>)<sub>2</sub> and Ph<sub>2</sub>Si(NHNHPh)<sub>2</sub> from reactions of Ph<sub>2</sub>SiCl<sub>2</sub> with H<sub>2</sub>NNMe<sub>2</sub> and H<sub>2</sub>NNHPh, respectively.<sup>3</sup> However, the compound Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>, 14, is inaccessible through this route, and has only been synthesized by the dehydrocoupling reaction of Ph<sub>2</sub>SiH<sub>2</sub> with H<sub>2</sub>NNHMe, as described in Chapter II. This molecule possesses several interesting functionalities, including a labile Si-N bond and two different NH groups. We have therefore employed 14 as a model compound to explore the reactivity of hydrazinosilanes.

Relatively little research has been carried out on the chemical behavior of hydrazinosilanes. It has been reported that hydrazinosilanes readily undergo hydrolysis, and (hydrazino)disiloxanes can be synthesized by the controlled hydrolysis of bis(hydrazino)silanes.<sup>39</sup> It is also known that in the presence of strong base silylhydrazines (and hydrazinosilanes) undergo anionic rearrangement to give a mixture of isomers.<sup>36,11</sup> In the following sections, these reactions will be examined with a view to synthesizing new silylhydrazine compounds. Thermolysis of 14 and its reactions with iodomethane, HCl, and Ph<sub>2</sub>SiCl<sub>2</sub> will also be discussed. Cyclization of 14 takes place during these reactions through a process which represents a new reaction of hydrazinosilanes.

### III.2.1 Controlled Hydrolysis of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>: Synthesis of [Ph<sub>2</sub>Si(NHNHMe)]<sub>2</sub>O

The compound 14 is extremely moisture sensistive, and undergoes hydrolysis with complete loss of hydrazino substituents and the formation of cyclic siloxanes or poly(siloxanes). However, partial loss of hydrazino substituents can be achieved by controlled hydrolysis. In reaction (III.1), a stoichiometric amount of H<sub>2</sub>O dissolved in toluene/THF was added very slowly into a toluene/THF solution containing 14 at ambient temperature. The resulting product [Ph<sub>2</sub>Si(NHNHMe)]<sub>2</sub>O, 21, was isolated in 62% yield.

$$\frac{\text{toluene/THF}}{14} = \frac{1/2 \text{ H}_2 \text{O}}{14} + \frac{1/2 \text{ H}_2 \text{O}}{14} + \frac{1/2 \text{ O}[\text{SiPh}_2(\text{NHNHMe})]_2}{21}$$
(III.1)

Although analogs of 21, O[SiPh<sub>2</sub>(NHNMe<sub>2</sub>)]<sub>2</sub> and O[SiPh<sub>2</sub>(NHNHPh)]<sub>2</sub> have been prepared by Wannagat and Niederprüm,<sup>39</sup> the molecular structures of these compounds were not determined. Crystals of 21 were obtained from toluene/hexane solution (1:1), and analyzed by X-ray crystallography. The crystal structure reveals a linear Si-O-Si arrangement, and both planar N(1) and pyramidal N(2) atoms in the hydrazino substituents (see Chapter IV for detailed discussion). In order to obtain more information about the nature of the Si-O bond, NMR data for 21 and 14 are compared in Table III.1.

The <sup>15</sup>N NMR spectra show that the N(1) resonance shifts downfield (5.7 ppm) in 21 relative to 14, while the N(2) resonance in both compounds is the same. This suggests a lower electron density at N(1) in 21 than in 14. This fact is also evident in the <sup>1</sup>H NMR data which show a downfield shift (0.17 ppm) of the proton at N(1) in 21 when compared to that in 14. A significant shielding (6.7 ppm) of <sup>29</sup>Si in 21 relative to 14 may be attributed to the delocalization of the lone pairs on oxygen into unoccupied orbitals on

silicon.<sup>95</sup> There may also be a contribution from the fact that the  $\equiv$ Si-O group is less electron-withdrawing than the MeNHNH group.

Compound	<sup>1</sup> H(δ) <sup>[a]</sup>	<sup>29</sup> Si(δ)	<sup>15</sup> N(δ)
$O[SiPh_2(N^1HN^2HMe)]_2$ 21	2.24 (CH <sub>3</sub> ), 2.62 (N <sup>2</sup> H),	- 36.21	- 299.7 (N <sup>1</sup> ), - 327.8 (N <sup>2</sup> )
Ph2Si(N <sup>1</sup> HN <sup>2</sup> HMe) <sub>2</sub> 14	2.34 (CH <sub>3</sub> ),	- 29.51	- 305.4 (N <sup>1</sup> ),
	2.59 (N <sup>2</sup> H), 2.91 (N <sup>1</sup> H)		- 327.3 (N <sup>2</sup> )

Table III.1 Comparison of NMR data for Compounds 21 and 14.

[a]. Phenyl group resonances in both compounds show multiple peaks in the region 7.20-7.80 ppm.

#### III.2.2 Cyclization of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> by Reaction with *n*-BuLi/Ph<sub>2</sub>SiCl<sub>2</sub>

(i) Formation of 1,2,4-triaza-1-methyl-4-methylamino-3,3,5,5-tetraphenyl-3,5-disilacyclopentane. Reaction of 14 with *n*-BuLi in THF/hexane yielded a pale yellow solution, which was then added into Ph<sub>2</sub>SiCl<sub>2</sub> to afford 1,2,4-triaza-1-methyl-4methylamino-3,3,5,5-tetraphenyl-3,5-disilacyclopentane (22) in 64% yield (by <sup>1</sup>H NMR), as shown in reaction (III.2). In addition to the major product 22, two tetraazadisilacyclohexane isomers, namely, 1,2,4,5-tetraaza-1,4-dimethyl-3,3,6,6tetraphenyl-3,6-disilacyclohexane, 23 (22%), and 1,2,4,5-tetraaza-1,5-dimethyl-3,3,6,6tetraphenyl-3,6-disilacyclohexane, 24 (14%) were also generated in the reaction.



The identification of 22 is based on <sup>1</sup>H, <sup>29</sup>Si and <sup>15</sup>N NMR, EI-MS and elemental analysis. In the <sup>1</sup>H NMR spectrum, in addition to the phenyl resonances, there are 4 resonances in the range 2.40 to 3.50 ppm. The endocyclic N<sup>2</sup>-H and N<sup>1</sup>-Me resonances are shifted downfield relative to the exocyclic N<sup>4</sup>-H and N<sup>4</sup>-Me resonance. The exocyclic N<sup>4</sup>HMe moiety exhibits coupling between the proton and the methyl group, as shown in Figure III.1a. The integral ratios of the various peaks correspond to the H, Me and phenyl groups in the proposed structure. The connectivity between H and N atoms was confirmed by 2D <sup>1</sup>H NMR using a HMQC (Heteronuclear Multiple Quantum Coherence) pulse sequence through <sup>1</sup>J<sub>N-H</sub> coupling. The <sup>29</sup>Si NMR spectrum (Figure III.2a) showed two resonances, with one resonance (-16.38 ppm, Si(NH)) having a stronger NOE than the other (-17.55 ppm, Si(NMe)). Mass spectroscopy showed a parent molecular ion (*m*/*e* = 452) corresponding to 22. These data unambiguously confirm the structure of 22.

Compound 22 was isolated in 54% yield (96% isomeric purity) from the mixture in a toluene-hexane solution by controlled crystallization. Significant solubility differences allow the efficient separation of compounds 22, 23 and 24. These three compounds are all soluble in toluene, whereas 22 is insoluble in hexane. Compound 23 is soluble in warm hexane, but has low solubility in hexane at ambient temperature and is insoluble in pentane. 24 is soluble in hexane and pentane at ambient temperature. These compounds are colorless crystalline solids. Although they are mildly moisture sensitive, they can be handled in air for a short period of time.

Inverse addition, *i.e.*, the addition of diphenyldichlorosilane to the preformed lithiohydrazide from 14 results in an increase of 23 and 24 at the expense of 22. This is due to the rearrangement of 22 to 23 and 24 under basic conditions. A study of the base-catalysed rearrangement of 22 was therefore undertaken and is described below.

A tentative pathway for the formation of 22 is illustrated in Scheme 8. The first step is the reaction of one of the N<sub> $\beta$ </sub>H in 14 with one equivalent of BuLi, leading to the formation of 25. The fact that reaction of 14 with *n*-BuLi and Ph<sub>2</sub>SiCl<sub>2</sub> in 1:1:1 ratio

affords 24 as a dominant product<sup>\*</sup> indicates that the reaction of  $N_{\alpha}H$  with the first equivalent of *n*-BuLi does not take place and 25 is a plausible product from the reaction of 14 with one equivalent of *n*-BuLi. In the complexes 25 and 26 the lithium atoms are coordinated by two N atoms and the remaining hydrogen atoms may be attached to either N atom individually or, more likely, hydrogen bonded between two nitrogens.Therefore, in Scheme 8 the exact locations of the charges and the position of the hydrogen atoms are uncertain. Addition of a second mole of *n*-BuLi yields 26. This is attributed to the tight hydrogen bonding and low acidity of the second N<sub>β</sub>H, which is therefore less likely to react with *n*-BuLi than the proton of the N<sub>α</sub>H moiety. When Ph<sub>2</sub>SiCl<sub>2</sub> is added to 26, 22 is formed by the elimination of 2 moles of LiCL.



<sup>\*</sup> The product consisted of 23 (36%), 24 (47%) and probably Ph<sub>2</sub>Si(NHNMeSiPh<sub>2</sub>Cl)<sub>2</sub> (17%) when 14 reacted with one equivalent of n-BuLi followed by the addition of one equivalent of Ph<sub>2</sub>SiCl<sub>2</sub>. The formation of 24 is probably due to the reaction of 14 with HCl formed during the reaction.



Figure III.1 <sup>1</sup>H NMR spectra of the isomerization of 22 to 23 and 24 in the presence 0.1% *n*-BuLi at 30 °C. (a) before the addition of *n*-BuLi; (b) 2 h, (c) 10 h, (d) 18 h, and (e) 32 h after the addition of *n*-BuLi.

(ii) Ring isomerization of triazadisilacyclopentane to tetraazadisilacyclohexanes. The isomerization of 22 into 23 and 24 occurred in the presence of catalytic amounts of n-BuLi and finally reached an equilibrium among these three isomers (Reaction III.3).



Compound 23 was isolated by crystallization from a hexane solution. Its <sup>1</sup>H NMR spectrum shows endocyclic NH (3.44 ppm) and NMe (2.89 ppm) resonances, in a 1:3 ratio. It also exhibits a single <sup>29</sup>Si resonance at -19.92 ppm (Figure III.2c), very close to -19.89 ppm for the known analogue, 1,2,4,5-tetraaza-3,3,6,6-tetraphenyl-3,6-disilacyclohexane (9). The connectivity between H and N atoms was also confirmed by 2D <sup>1</sup>H NMR using a HMQC pulse sequence. Compound 24 was recrystallized from a concentrated pentane solution and identified by its <sup>1</sup>H and <sup>29</sup>Si NMR spectra. In the <sup>1</sup>H NMR spectrum of 24, both N-H and N-CH resonances are shifted upfield about 0.05 ppm relative to the corresponding peaks of 23. The <sup>29</sup>Si NMR spectrum of 24 shows two resonances at -18.52 and -18.73 ppm (Figure III.2b). The resonance at -18.52 ppm has almost twice the intensity of the resonance at -18.73 ppm. This effect is due to a stronger NOE in the SiNH moiety than in the SiNCH moiety. A comparison of the <sup>29</sup>Si resonances of 22, 23 and 24 reveals a deshielding effect on <sup>29</sup>Si chemical shifts associated with ring strain. This trend is in agreement with that found in most cyclic silane compounds.<sup>96</sup>

The isomerization rate increased with increasing *n*-BuLi concentration, but no measurable effect on the proportion of isomers was observed at equilibrium by varying the amount of *n*-BuLi catalyst. However, the ratio of 23 to 24 was influenced by temperature, while the amount of 22 remained roughly constant (approximately 10%) at equilibrium.

1

0 -2 -4 -6 -0 -10 -12 -14 -16 -2 -2 -28 -29 -20 -22 -28 -38 -38 -20 -20 -22 -28 -28 -28 -28 -28 

Figure III.2 <sup>29</sup>Si NMik spectra of (a) 22, (b) 24, and (c) 23.

A lower temperature favors the formation of 23. This is evident from the results shown in Figures III.1 and III.3, in which 69% of 23 and 18% of 24 were formed at 30 °C and 54% of 23 and 36% of 24 at 50 °C. In both cases, 23 is the dominant product.



Figure III.3 Course of the isomerization of 22 to 23 and 24 in the presence of 2.5% *n*-BuLi at 50 °C.

The base-catalysed rearrangement of open-chain silylhydrazines was thoroughly investigated by West and co-workers.<sup>11</sup> A mechanism was proposed involving the deprotonation of the silylhydrazine substrate by base, anionic rearrangement of the

resulting silylhydrazide, and reprotonation of the rearranged silylhydrazide by substrate, as depicted in Scheme 4 in Chapter I. A pentacoordinate transition state is thought to occur in the rearrangement,<sup>12a</sup> and protonation-deprotonation are the rate-limiting steps.<sup>36</sup> This mechanism can also be applied to the present cyclic system, and is illustrated in Scheme 9. Both steric and electronic effects of the adjacent NMe group disfavor the 24a transition state. This accounts for 23 as the dominant product.



# III.2.3 Cyclization of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> by Reactions with MeI, HCl, or Ph<sub>2</sub>SiCl<sub>2</sub>

The reaction of 14 with MeI unexpectedly gave the two cyclic isomers, 23 and 24. The use of MeI in this reaction was to test the reactivity of N-H groups in 14 towards this reagent. The fact that a non-stoichiometric amount of MeI can lead to complete cyclization of 14 led to speculation about a possible mechanism for the reaction. HCl and Ph<sub>2</sub>SiCl<sub>2</sub> were also found as useful reagents for the cyclization.

The reaction of 14 with an equimolar amount of iodomethane in toluene yielded a mixture of 23 and 24 with no other detectable silylhydrazine, as shown in reaction III.4.



In a typical experiment, compounds 23 and 24 accounted for 56% and 44% of the product, respectively, as measured by <sup>1</sup>H NMR spectroscopy. The separation of 23 from the mixture was accomplished as described in section III.2.2. The isolated yields of 23 and 24 were 45% and 40%, respectively. The product 24 isolated in this way was contaminated with about 15% of 23. It was obtained in higher purity by recrystallization from pentane. <sup>1</sup>H and <sup>29</sup>Si NMR and EI-MS spectra were consistent with the assigned structures for both compounds.

In order to understand the origin of the product distribution, the reaction was followed by <sup>1</sup>H NMR spectroscopy. In the early stages of the reaction, 23 was the dominant product. The proportion of 24 in the product increased gradually as the reaction proceeded and finally accounted for 46% of the product. With 0.6 to 1.0 mole equivalent of MeI to 14, approximately the same product distribution was obtained. The results are summarized in Table III.2.

These experiments indicate that HI produced in the reaction can play the same role as MeI before the hydrazonium iodide salt is completely precipitated. This was confirmed by the reaction of 14 with anhydrous HCl (in diethyl ether). A similar result to that with MeI was obtained, except for a small amount of a new unidentified compound (18%) in the product. For most silylhydrazines, the Si-N bond is readily cleaved by acids, and in particular by anhydrous hydrogen halides in solution, as shown in equation (III.5):

$$\frac{1}{3} \sin \frac{N}{N} + 2 \operatorname{HCl} \longrightarrow \frac{1}{3} \sin \frac{N}{N} + \left[ N - \frac{N}{N} - \frac{N}{N} - \frac{1}{N} \right] \operatorname{HCl} \quad (\text{III.5})$$

Table III.2 Reactions of  $Ph_2Si(NHNHMe)_2$  with MeI, HCl, and  $Ph_2SiCl_2$ , and the product distribution.

Reaction	Molar Ratio	Time (h)	Product Distribution (%) <sup>[a]</sup>	
	<u> </u>		23	24
Ph2Si(NHNHMe)2	1:1	3	47	10
+ MeI		10	56	44
	1:0.8	12	55	45
	1 : 0.6	12	58	42
Ph2Si(NHNHMe)2 + HCl <sup>[b]</sup>	1:1	24	58	24
Ph <sub>2</sub> Si(NHNHMe) <sub>2</sub> + Ph <sub>2</sub> SiCl <sub>2</sub> <sup>[c]</sup>	1:1	16	45	29

[a]: based on <sup>1</sup>H NMR measurement.

[b]: The product also consists of 18% of unidentified compound(s).

[c]: The product also consists of 26% of 29.

A possible pathway which accounts for the formation of 23 and 24 is shown in Scheme 10. The first step is the formation of an iodosilyl-substituted methylhydrazine, 27, through the attack of MeI on 14, with the elimination of MeHNNHMe. Compound 27 is apparently a reactive intermediate since it is not observed and such a compound has not been synthesized, although fluorosilyl-substituted hydrazines have recently been prepared and isolated by Klingebiel.<sup>22</sup> This compound can either undergo an autocondensation reaction to yield 23 by the elimination of two molecules of HI, or it can be further attacked by MeI to form diiododiphenylsilane, 28, which can react with 14, with ring closure, to give 24 after elimination of HI. In addition to precipitation as methylhydrazonium iodides, the HI formed in the reaction can also form 27, or 28 by displacement of one or two moles of H<sub>2</sub>NNHMe.



Compounds 23 and 24 are also the products of the reaction of  $Ph_2SiCl_2$  with 14. In addition to 23 (45%) and 24 (29%), a third product, 29, is also produced. In the early stages of reaction, compounds 24 and 29 predominate, but the amount of 23 increases gradually with the passage of time. Compound 29 was not isolated in a pure state, but it was tentatively assigned as  $Ph_2Si(NHNMeSiPh_2Cl)_2$  based on its <sup>1</sup>H and <sup>29</sup>Si NMR spectra. This compound is one of the expected products of the reaction of  $Ph_2SiCl_2$  with 14. As the reaction proceeds,  $Ph_2SiCl_2$  is depleted and the formation of 24 and 29 is slowed dowr. The reaction of 14 with HCl generated in the reaction begins to compete and the relative rate of formation of 23 increases.

#### III.2.4 Cyclization of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> by Thermolysis

A thermogravimetric analysis of 14 was performed from 25 to 600 °C. Figure III.4 shows the total weight loss which starts at ~200 °C and ends at ~450 °C. Within this temperature range, the weight loss at 265 and 332 °C, respectively, occurs dramatically (as indicated by the DTG curve), while the DTA curve shows a slight exotherm at ~300°C. This fact suggests that a major decomposition (or structural change) occurs around 300°C.



Figure III.4 Thermogravimetric analysis of  $Ph_2Si(NHNHMe)_2$  at a heating rate of 10 °C/min under a flow of  $N_2$  (120 mL/min).

In order to understand this thermal behavior, an NMR study of the thermal decomposition products at 250, 300 and 350 °C was carried out. Figure III.5 shows the <sup>1</sup>H NMR spectra of the products at these temperatures. The results indicate that 52% of 14

is converted into 22 (31%), 23 (14%) and 24 (7%) at 250 °C under the same heating conditions as that in Figure III.5. The remainder of the product was a mixture of unreacted 14 and an unidentified compound. The unknown compound is probably  $Ph_2(MeHNHN)SiNHNMeSi(NHNHMe)Ph_2$ , 30. However, its structure could not be assigned unequivocally on the basis of NMR data. At 300 °C, 14 was completely converted to a mixture of 22 (16%), 23 (21%) and 24 (17%), and about 46% of uncharacterised oligomers.

A proposed mechanism for the formation of 22, 23 and 24 is shown in Scheme 11. In this scheme two molecules of 14 undergo self-condensation to form intermediate 30. Under the same conditions, intramolecular condensation of 30 takes place to yield compounds 22, 23 and 24 by the pathways 1, 2 and 3, in which three different nitrogen atoms serve as the species which can attack the two silicon atoms.



By comparison of the products at 250 °C and 300 °C, it is evident that the formation of 22 (5-membered ring) is more favorable at 250 °C. Indeed, when pure compound 22 was heated to 300 °C under the same conditions, 23 and 24 were obtained.<sup>\*\*</sup> In accordance with the mechanism in Scheme 11, the formation of 23 is favored over that of 24 (in which two NMe groups are on the same Si atom) due to the unfavorable steric effect. The weight loss (ca. 50%) at 300 °C in the TGA does not correlate with that (17%) depicted in Scheme 11. This difference is probably due to the loss of 14, or small ring compounds by sublimation or evaporation at high temperature under the flow of N<sub>2</sub>.

The product distribution at 350 °C is more complicated. The <sup>1</sup>H NMR spectrum shows that the composition of the residue is dominated by phenyl groups. Decomposition and cleavage of N-N bonds could be the main thermal process at this temperature, as a gaseous product was observed to evolve from the residue during heating. This thermal behavior is also observed during the pyrolysis of poly(methylsildiazane), described in Chapter V.

<sup>\*\*.</sup> When compound 22 was heated at 300 °C under the same conditions as that of 14, the pyrolysis residue consisted of 23 (27%), 24 (23%), oligometric product (33%) and 17% of 22 remained, as measured by <sup>1</sup>H NMR.



Figure III.5 <sup>1</sup>H NMR spectra for the thermolysis of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>. (a) before heating; (b) at 250 °C; (c) at 300 °C; and (d) at 350 °C.

#### **III.3 Summary**

Reactivity studies using  $Ph_2Si(NHNHMe)_2$  as a model compound have revealed an interesting aspect of the chemistry of hydrazinosilanes. Controlled hydrolysis of this compound leads to partial loss of hydrazino groups to form bis(hydrazino)bis(diphenyl)disiloxane. The hydrazino substituent, NHNHMe, provides two N-H groups of different acidity, which show a preference in the sequential reaction with *n*-BuLi. The two nitrogen atoms in the hydrazino substituent also have different basicities which may be responsible for the production of two isomeric tetraazadisilacyclohexanes and one amino-triazadisilacyclopentane during the thermolysis of  $Ph_2Si(NHNHMe)_2$ . The reactions of  $Ph_2Si(NHNHMe)_2$  with iodomethane, HCl, and  $Ph_2SiCl_2$ , gave two isomeric tetraazadisilacyclohexanes, a rather unusual result for hydrazinosilanes.

#### **III.4 Experimental Section**

The general procedures follow those described in Chapter II. Anhydrous HCl (1.0 M in diethyl ether) and *n*-BuLi (2.5 M in hexane) were purchased from Aldrich, and used as received. Other chemicals including  $Ph_2Si(NHNHMe)_2$  and solvents were obtained in the same manner as described in Chapter II.

# III.4.1 Controlled Hydrolysis of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>: Synthesis of [(MeNHNH)Ph<sub>2</sub>Si]<sub>2</sub>O

The reaction was carried out at ambient tomperature in a 25-mL Schlenk flask, equipped with a stirring bar and a rubber septum. After it was purged with argon, the flask was charged with 0.40 g (1.47 mmol) of 14 and 5 mL of toluene. A solution of H<sub>2</sub>O (0.0126 mL) in toluene/THF (10:1) (8 mL) was added dropwise to the above solution through a reduced pressure. The crude residue was redissolved in toluene/hexane (1:1) and the solution cooled at 4 °C. After 2 weeks, crystals of 21 were recovered (0.42 g, 62%). The structure of 21 was determined by X-ray crystallography. Analytical data for [(MeNHNH)Ph<sub>2</sub>Si]<sub>2</sub>O: <sup>1</sup>H NMR (200 MHz):  $\delta$  2.24 (s, 3H, N<sup>2</sup>CH), 2.62 (br, 1H, N<sup>2</sup>H), 3.07 (s, 1H, N<sup>1</sup>H), 7.20 (m, 6H, Ph<sub>2</sub>Si), 8.00 (m, 4H, Ph<sub>2</sub>Si). <sup>29</sup>Si NMR (59.6 MHz):  $\delta$  -36.21 . <sup>15</sup>N{<sup>1</sup>H} NMR (HMQC, 499.84 MHz):  $\delta$  -299.72 (N<sup>1</sup>), -327.81 (N<sup>2</sup>). *EI-MS* (m/e, abundance, fragmentation): 424(100) [M<sup>++</sup> - H<sub>2</sub>NNHMe], 379(6) [M<sup>++</sup> - H<sub>2</sub>NNHMe - HNNHMe], 347(7) [M<sup>++</sup> - H<sub>2</sub>NNHMe - Ph], 318(11) [M<sup>++</sup> - H<sub>2</sub>NNHMe - PhH - Si], 303(13) [M<sup>++</sup> - H<sub>2</sub>NNHMe - PhH- Si - Me]. *IR*: 3337 s, 3302 s (v<sub>N-H</sub>); 1098s, (v<sub>Si-O-Si</sub>); 996 s, 974 s (v<sub>Si-N</sub>). mp: 130-132 °C.

Anal. C<sub>26</sub>H<sub>30</sub>Si<sub>2</sub>N<sub>4</sub>O (21): Calcd, C 66.34%; H 6.42%; N 11.90%. Found, C 66.61%, H 6.41%, N 11.95%.

#### III.4.2 Reactions of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> with *n*-BuLi and Ph<sub>2</sub>SiCl<sub>2</sub>.

A solution of 1.12 g (4.12 mmol) of 14 in 20.0 mL of THF/hexane (5:1) under dry argon was cooled to - 30 °C, and 3.2 mL (8.24 mmol) of *n*-BuLi (2.5 M in hexane) were added dropwise while the mixture was stirred. The pale yellow solution was allowed to warm to room temperature and stirred for 20 min. It was then added dropwise into a solution containing 0.86 mL (4.12 mmol) of Ph<sub>2</sub>SiCl<sub>2</sub> in 4 mL of THF/hexane (5:1) through a cannula. After the mixture was stirred for 1 h, the solvents were removed under reduced pressure and the residue was redissolved in toluene/hexane (10/1) to precipitate LiCl, which was removed by filtration through Celite. The product isolated from the filtrate was found to be 22 (64%), 23 (22%) and 24 (14% ) by <sup>1</sup>H NMR. Compound 22 was isolated in 54% yield by crystallization from the mixture in toluene/hexane (1/2) at ambient temperature. Further separation of 23 from 24 in the residue was not performed. Analytical data for 22: <sup>1</sup>H NMR (200 MHz):  $\delta$  2.42 (d, <sup>3</sup>J<sub>HNCH</sub> = 4.2 Hz, 3H, N<sup>4</sup>CH<sub>3</sub>), 2.79 (s, 3H, N<sup>1</sup>CH<sub>3</sub>), 2.89 (q, <sup>3</sup>J<sub>HNCH</sub> = 4.2 Hz, 1H, N<sup>4</sup>H), 3.23 (s, 1H, N<sup>2</sup>H), 7.20 (m, 12H, Ph<sub>2</sub>Si), 7.86 (m, 8H, Ph<sub>2</sub>Si). <sup>29</sup>Si NMR (59.6 MHz):  $\delta$  -16.38 (SiNH), -17.55 (SiNCH<sub>3</sub>). <sup>15</sup>N{<sup>1</sup>H} NMR (HMQC, 499.84 MHz, <sup>1</sup>J<sub>N-H</sub> = 90 Hz):  $\delta$  -307.02 (N<sup>2</sup>{H}), -326.68 (N<sup>4</sup>{H}). *EI-MS* (m/e, abundance, fragmentation): 452(100) [M\*+], 407(5) [M\*+ - HNNHMe], 378(27) [M\*+- HNNHMe - NMe], 331(38) [M\*+ - SiPh - MeH], 302(27) [M\*+- HNNHMe - SiPh], 226(12) [M\*+- HNNMe - SiPh<sub>2</sub>]. IR (neat, cm<sup>-1</sup>): 3433(br), 3315(br), (V<sub>N-H</sub>); 994s, 934s (V<sub>Si-N</sub>). mp: 146-148 °C (uncorrected).

Anal. C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>Si<sub>2</sub> (22): Calcd: C 68.98%; H 6.23%; N 12.37%. Found: C 68.53%; H 6.28%; N 12.23%.

When the same reaction was carried out with "inverse" addition of  $Ph_2SiCl_2$  to the lithium hydrazide, the product was shown by NMR to be 48% 22, 30% 23 and 22% 24.

### III.4.3 Ring Isomerization of triazadisilacyclopentane to tetraazadisilacyclohexare.

*n*-Butyllithium solution (0.5 mL, 2.5x10<sup>-3</sup> M in C<sub>6</sub>D<sub>6</sub>, diluted from the commercial 2.5 M in hexane) was added to 0.565 g (1.25 mmol) of 22 in toluene at 30 °C. The mixture was stirred for 60 h. After work up, the product was found to be 69% 23, 18% 24 and 13% 22. After removal of 22, 23 was isolated in 56% yield from the mixture by crystallization in hexane solution at 4 °C. Crystals of 23 suitable for X-ray crystallography were obtained when a warm hexane solution of the mixture was cooled slowly to ambient temperature. Analytical data for 23: <sup>1</sup>H NMR (200 MHz):  $\delta$  2.89 (s, 6H, NCH), 3.44 (s, 2H, NH), 7.20 (m, 12H, Ph), 7.70 (m, 8H, Ph). <sup>29</sup>Si NMR (56.9 MHz): -19.92. <sup>15</sup>N{<sup>1</sup>H} NMR (HMQC, 499.84 MHz):  $\delta$  -311.82 (N{H}). *EI-MS* (m/e, abundance, fragmentation): 452(100) [M<sup>++</sup>], 407(4) [M<sup>++</sup> - HNNHMe], 378(19) [M<sup>++</sup>-HNNHMe - NMe], 331(26) [M<sup>++</sup> - SiPh - MeH], 302(22) [M<sup>++-</sup> HNNHMe - SiPh], 226(12) [M<sup>++</sup> - HNNMe - SiPh\_2]. IR (neat, cm<sup>-1</sup>): 3331s, 3302s (v<sub>N-H</sub>); 1018vs, 994s (v<sub>Si-N</sub>). *mp*: 149 - 150 °C.

Anal. C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>Si<sub>2</sub> (3): Calcd: C 68.98%; H 6.23%. Found: C 68.58%; H 6.32%.

When the base catalysed rearrangement of 22 was carried out with 2.5% of *n*butyllithium at 50 °C, the product was found to be 10% 22, 54% 23 and 36% 24. After the separation of 22 and 23 from 24, 15% of 24 was isolated by recrystallization from a concentrated pentane solution of the product mixture at 4 °C. Analytical data for 24:  ${}^{1}H$ *NMR* (200 MHz):  $\delta$  2.83 (s, 6H, NCH), 3.39 (s, 2H, NH), 7.20 (m, 12H, Ph), 7.82 (m, 8H, Ph).  ${}^{29}Si$  *NMR* (56.9 MHz): -18.52 (SiNH), -18.73 (SiNCH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 3373s, 3321s (V<sub>N-H</sub>); 1022s, 998s (V<sub>Si-N</sub>). *mp*: 102 - 104 °C.

The progress of the rearrangement was monitored by NMR. A typical experiment is as follows. A sample of 22 (0.0119 g; 0.0263 mmol) was placed in a clean, dry sample tube, and dissolved in C<sub>6</sub>D<sub>6</sub> (0.4 ml). *n*-Butyllithium (0.26 ml;  $2.5 \times 10^{-3}$  M in C<sub>6</sub>D<sub>6</sub>) was injected into the solution. After the reagents were mixed, the sample tube was sealed and then placed in an oil bath at the required temperature.

#### III.4.4 Reactions of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> with MeI, HCl, and Ph<sub>2</sub>SiCl<sub>2</sub>

(i) Reaction of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> with MeI. The reaction was carried out in a 50 mL Schlenk flask at ambient temperature under dry argon. 14 (1.28 g, 4.72 mmol) was dissolved in 20.0 mL of toluene-hexane (10:1), into which MeI (0.29 mL, 4.72 mmol) was added dropwise while the mixture was stirred. Precipitation took place immediately in the solution upon the addition of MeI. Stirring was periodically stopped so that the supernatant could be sampled for <sup>1</sup>H NMR measurements. Compound 23 was the major product (ca. 80%) in the first 3 h. After 10 h, the reaction was complete, and the start was filtered under an argon atmosphere. All the solvents were removed under reduced pressure. The final yields were 56% for 23 and 44% for 24, as measured by <sup>1</sup>H NMR. Various stoichiometric ratios of MeI with 14 were tried and the results are listed in Table 3.2.

The residue was redissolved in hot *n*-hexane (20 mL), and the solution was cooled to ambient temperature to give 23 in an isolated yield of 0.48 g (45%). After isolation of 23, the solvent was evaporated, the residue was redissolved in 10 mL of hexane, and the solution was cooled to 4  $^{\circ}$ C to remove residual 23. The mother liquor was then evaporated to yield 24 in 85% isomeric purity (0.43g, 40%). 24 was further purified by recrystallization from pentane at 4  $^{\circ}$ C. The experiment was attempted with different amounts of MeI, and the results are listed in Table III.2.

Analytical data for 23 and 24 are the same as those described above.

(ii) Reaction of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> with HCl. The general procedure was the same as in the previous experiment. 14 (1.36 g, 5.00 mmol) was dissolved in 20.0 mL of toluene-hexane (10:1), into which 5.0 mL of anhydrous HCl (5.00 mmol, 1.0 M in diethyl ether) was added dropwise with the mixture being stirred. Fumes were observed and precipitation took place immediately as HCl came in contact with the solution. The mixture was periodically sampled for <sup>1</sup>H NMR measurements. The reaction was complete in 24 h. After work up, the final product was 23 (58%), 24 (24%) and 18% of an unidentified product, by <sup>1</sup>H NMR.

(iii) Reaction of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> with Ph<sub>2</sub>SiCl<sub>2</sub>. The procedure described above was followed. 14 (1.42 g, 5.20 mmol) was dissolved in 15.0 mL of toluene/hexane (10:1), into which 0.55 mL of Ph<sub>2</sub>SiCl<sub>2</sub> (2.60 mmol) was added dropwise with the mixture being stirred. Precipitation took place immediately in the solution upon the addition of Ph<sub>2</sub>SiCl<sub>2</sub>. The mixture was periodically sampled for <sup>1</sup>H NMR measurements. Compound 24 was formed mainly in the early stages of the reaction, and the proportion of compound 23 increased gradually as the reaction progressed. The formation of compound 29 occurred continuously throughout the reaction, which was complete in 16 h. After work up, the final product gave 23 (45%), 24 (29%) and 29 (26%), as measured by <sup>1</sup>H NMR. Analytical data for 29: <sup>1</sup>H NMR (200 MHz):  $\delta$  2.79 (s, 6H), 3.21 (s, 2H), 7.15 (m, 18H, Ph), 7.50 (m, 12H, Ph). <sup>29</sup>Si NMR (56.9 MHz): -4.56 (SiCl), -8.75 (SiN<sub>2</sub>).

#### III.4.5 Thermolysis of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>

Thermogravimetric analysis (TGA) was performed on a Seiko 220 TG/DTA instrument. A flow of N<sub>2</sub> (~120 mL/min) was maintained during the TGA runs. The sample (8.80 mg) was heated in an aluminium pan at a rate of 10 °C/min from 25 to 600°C. The result is shown in Figure III.4. The weight loss (5%) at 90 - 170°C was attributed to the presence of solvent (toluene) in the sample.

General procedure for the preparation of NMR samples. About 80 mg of  $Ph_2Si(NHNHMe)_2$  was placed in an NMR tube, which was heated in a furnace at ca. 10 °C/min up to a given temperature (250, 300 and 350 °C, respectively) under argon atmosphere, and held at that temperature for 5 minutes. The tube was then cooled to ambient temperature. The liquid formed during heating was removed under reduced pressure. 0.5 mL of  $C_6D_6$  was then added into the tube to redissolve the residue and the sample was analyzed by <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy.

In order to trap and identify the liquid formed on heating, a larger amount of 14 (ca. 1.00 g) was placed in a 10-mL Schlenk tube (1.5 cm in diameter) which was connected to a trap immersed in liquid nitrogen. The sample was heated to 300 °C and the volatile product was collected under vacuum in the trap. This product was found to be H<sub>2</sub>NNHMe. <sup>1</sup>H NMR :  $\delta$  2.32 (s, 3H, NCH), 3.05 (br, 3H, NH).

At 250 °C, the residue was composed of 22 (31%), 23 (14%), 24 (7%), 14 and some unidentified compound(s) (total 48%). At 300 °C,  $Ph_2Si(NHNHMe)_2$  was completely converted to 22 (16%), 23 (21%), 24 (17%) and an oligomeric product (46%). At 350 °C, a gaseous product was observed to evolve from the residue during heating. The pyrolysis residue consisted of 23 and 24 (total, 10%) and an uncharacterized oligomeric product.

#### Chapter IV

### STRUCTURE OF SILYLHYDRAZINES: PLANARITY VS PYRAMIDICITY AT NITROGEN

## IV.1 Introduction — Is the geometry at nitrogen certain in Si-N compounds?

Structural investigations of compounds containing Si-N and Si-O bonds have been the subject of long and continuing interest due to the anomalous geometries at nitrogen or at oxygen when compared with their carbon analogues.<sup>95, 97-99</sup> Striking features for these compounds are the shortness of the Si-N and Si-O bonds in comparison to the Schomaker-Stevenson corrected sum of the covalent radii<sup>\*</sup>, the planarity at nitrogen and the widening bond angle about oxygen (140-180°). The most frequently used rationalization for these observations is  $(p-d)\pi$  bonding with the donation of lone pair of electrons from nitrogen and oxygen into the vacant 3*d* orbitals of silicon.<sup>100</sup> Over the years this bonding model has been questioned, particularly from a theoretical point of view. Extensive semi-empirical and *ab initio* calculations have shown that the role of  $(p-d)\pi$  bonding is either very small or nonexistent, and if present, it is not enough to have much structural significance.<sup>101,102</sup> Several other interpretations for these structural features have also been proposed in terms of  $\sigma/\pi$  hyperconjugative effects<sup>102</sup>, steric and electrostatic effects<sup>103</sup>, and second-order

<sup>\*</sup> Schomaker, V.; Stevenson, D.P. J. Am. Chem. Soc. 1941, 63, 37. The Schomaker-Stevenson equation ( $R_{xy} = R_x + R_y - 0.09 |\chi_x - \chi_y|$ ) corrects the bond length for ionic contributions by using the electronegativities of X and Y atoms, *i.e.*,  $\chi_x$  and  $\chi_y$ . Si-O and Si-N bond lengths are calculated to be 1.76 and 1.80 Å, respectively. The experimental Si-O and Si-N bond lengths are always ca. 0.05 - 0.15 Å shorter.

Jahn-Teller effects<sup>104</sup>. In any case, simple explanations do not account for all the structural and chemical features of Si-N and Si-O compounds. Recently, an alternative explanation that considers the details of frontier orbital interactions involving only p and s orbitals satisfactorily accounts for the structural and chemical observations in a comprehensive manner.<sup>95</sup>

Planar coordination of nitrogen was first observed in the N(SiH3)3 molecule in a gas-phase electron diffraction study by Hedberg in 1951.<sup>105</sup> This discovery led to an explosion in the number of structural investigations of Si-N compounds. All doubly and triply silvlated amines whose structures have been determined have planar geometry at nitrogen.<sup>97,106</sup> Calculations have also pointed to a planar geometry at nitrogen, and have indicated that the energy necessary for nitrogen inversion in silvlamines is small, i.e. only a few kJ/mol.<sup>107</sup> Pyramidal coordination at nitrogen in silvlamines has been assigned in the monosilylated amines,  $NMe_2(SiH_nMe_{3-n})$  (n = 1-3) by a gas-phase electron diffraction study.<sup>108</sup> This assignment was later questioned as to whether the average structure is truly pyramidal at nitrogen or is in fact planar with a large amplitude out of plane vibration.<sup>110</sup> It was also suspected that these molecules could have phase-dependent structures. Unfortunately, neither NMe2(SiH2Me) nor NMe2(SiHMe2) could be obtained as crystals as they form glasses when cooled. Crystals of NMe2(SiH3) were successfully studied and they revealed a cyclic pentameric structure with tetrahedral coordination at nitrogen and trigonal bipyramidal coordination at silicon.<sup>109</sup> However, structural studies on NMe<sub>2</sub>SiMe<sub>3</sub> indicated a planar geometry in the gas phase and close to planar geometry at nitrogen (sum of angles at N ca. 358°) in the solid state.<sup>110</sup> Recently, pyramidal nitrogen coordination has been found in crystals of some aminosilanes of the type  $R_n Si(NH_2)_{4-n}$  (n = 1-3).<sup>99</sup> Thus, uncertainty exists when the geometry at nitrogen is considered in Si-N compounds.

Analysis of a few cyclic and acyclic silylhydrazine compounds containing Si<sub>2</sub>-N-N-Si<sub>2</sub> fragments have revealed planar nitrogen coordination in the structures.<sup>29-32</sup> In attempts to elucidate more silylhydrazine structures and to contribute to the discussion with more experimental data, several silvlhydrazines have been synthesized and characterized in the solid state by X-ray crystallography in the present study. The structures described in the following sections will show that both pyramidal and planar nitrogen coordinations coexist in compounds containing Si-N-N fragments in the solid state.

#### **IV.2 Results and Discussion**

IV.2.1 Chair and Twist-boat Conformations in Tetraazadisilacyclohexanes

### (i) 1,2,4,5-Tetraaza-3,3,6,6-tetraphenyl-3,6-disilacyclohexane, chair conformation

Crystals of 1,2,4,5-tetraaza-3,3,6,6-tetraphenyl-3,6-disilacyclohexane (9) are monoclinic and belong to the space group A2/a with 12 molecules in the unit cell. It crystallizes with two independent molecules in the unit cell, one at a general position and the other with the Si<sub>2</sub>N<sub>4</sub> ring centered about an inversion center in the packing unit, as shown in Figure IV.1.



Figure IV.1 Packing diagram for 9, showing two crystallographically independent molecules.

Both molecules possess an  $Si_2N_4$  ring arranged in a chair conformation. The ORTEP plot (Figure IV.2) shows only the molecule at the general position. Table IV.1 lists selected bond lengths and bond angles for 9.



Figure IV.2 ORTEP view of 9, showing the atom numbering scheme.

Atoms Si2, N4, Si3, and N6 are coplanar, whereas the atoms N3 and N5 are 0.633(6) and 0.563(6) Å above and below this plane, respectively. The average Si-N bond length for both molecules is 1.731(4) Å, which is well within the range of 1.70 - 1.75 Å found in most neutral silylamines. The average N-N bond length is 1.455(6) Å, close to the expected value (1.45 Å) based on the sum of the covalent radii of N.<sup>100a</sup> The tetrahedral Si coordination and the average Si-C bond length are comparable to those found in other

organosilicon compounds. However, the most remarkable features of the structure are the geometries about the N atoms. A planar geometry is found at both N4 and N6 (angle sums: 360.0(4) at N4, 359.1(4) at N6), and pyramidal at both N3 and N5 ( angle sums: 336.0(3) at N3, 344.8(3) at N5).

Table IV.1 Selected bond distances(Å) and bond angles (degrees) for the molecule shown in Figure IV.2 (compound 9).

Si2-N3 1.739(5)	Si3-N5 1.742(5)	
Si2-N4 1.718(5)	Si3-N6 1.716(5)	
Si2-C31 1.875(4)	Si3-C51 1.884(3)	
Si2-C41 1.886(3)	Si3-C61 1.878(4)	
N3-N6 1.463(6)	N4-N5 1.452(6)	
N3-Si2-N4 110.67(24)	Si2-N3-N6 111.3(3)	
N3-Si2-C31 107.34(20)	Si2-N3-H 114.7	
N3-Si2-C41 107.77(21)	N6-N3-H 110.0	
N4-Si2-C31 109.50(21)	Si2-N4-N5 116.8(3)	
N4-Si2-C41 109.11(21)	Si2-N4-H 131.9	
C31-Si2-C41 112.42(18)	N5-N4-H 111.3	
N5-Si3-N6 111.19(23)	Si3-N5-N4 112.9(3)	
N5-Si3-C51 107.26(20)	Si3-N5-H 114.6	
N5-Si3-C61 106.22(20)	N4-N5-H 117.3	
N6-Si3-C51 109.75(21)	Si3-N6-N3 118.2(3)	
N6-Si3-C61 109.37(21)	Si3-N6-H 135.0	
C51-Si3-C61 113.00(17)	N3-N6-H 105.9	

### (ii) 1,2,4,5-Tetraaza-1,4-dimethyl-3,3,6,6-tetraphenyl-3,6disilacyclohexane, twist-boat conformation

Crystals of 1,2,4,5-tetraaza-1,4-dimethyl-3,3,6,6-tetraphenyl-3,6-disilacyclohexane (23) are monoclinic and belong to space group  $P2_1/n$  with 4 molecules in the unit cell. An ORTEP plot is shown in Figure IV.3. Selected bond lengths and bond angles are given in Table IV.2.



Figure IV.3 ORTEP view of 23, showing the atomic numbering scheme.

The average bond lengths of Si-N (1.719(4) Å) and N-N (1.436(6) Å) are comparable to those of the analogous tetraazadisilacyclohexane, 9, as described above. Two geometries at the nitrogen atoms are also found in the -N(Me)-N(H)- units, *i.e.*, planar at NMe (sum of angles: N1: 359.9 and N3: 360.0°, respectively), and pyramidal at NH (sum of angles: N2: 350.0 and N4: 353.5°, respectively). However, the conformation differs dramatically between 23 and 9. While 9 adopts a conformation close to an ideal chair, 23 adopts a twist-boat conformation. Neither of the crystal structures of 9 and 23 shows any evidence for either intermolecular, or intramolecular, hydrogen bonding or N...Si interaction. It seems that the replacement of the H on the planar N of 9 by a Me group leads to the flattening of the adjacent pyramidal N of 23, accompanied by ring flipping from the chair in 9 to the twist-boat in 23.

Si1-N1 1.725(4)	Si2-N3 1.722(4)	
Si1-N2 1.714(4)	Si2-N4 1.721(4)	
Si1-C3 1.861(5)	Si2-C15 1.854(5)	
Si1-C9 1.867(5)	Si2-C21 1.869(5)	
N1-N4 1.428(7)	N2-N3 1.443(5)	
N1-C1 1.449(6)	N3-C2 1.443(6)	
N1-Si1-N2 105.98(21)	Si1-N1-N4 118.2(3)	
N1-Si1-C3 106.75(21)	Si1-N1-C1 127.3(4)	
N1-Si1-C9 115.40(21)	N4-N1-C1 114.4(4)	
N2-Si1-C3 114.11(22)	Si1-N2-N3 115.2(3)	
N2-Si1-C9 105.40(21)	Si1-N2-H 122.6	
C3-Si1-C9 109.39(23)	N3-N2-H 112.7	
N3-Si2-N4 105.28(21)	Si2-N3-N2 117.8(3)	
N3-Si2-C15 115.52(21)	Si2-N3-C2 127.0(3)	
N3-Si2-C21 105.37(19)	N2-N3-C2 114.1(3)	
N4-Si2-C15 104.98(22)	Si2-N4-N1 117.7(3)	
N4-Si2-C21 113.37(23)	Si2-N4-H 124.4	
C15-Si2-C21 112.32(25)	N1-N4-H 111.4	

Table IV.2 Selected bond distances(Å) and bond angles (degrees) for compound 23

The structures of two other tetraazadisilacyclohexane analogs, *i.e.* 1,2,4,5-tetraaza-3,3,6,6-tetra(*t*-butyl)-1,4-bis(*t*-butyldimethylsilyl)-3,6-disilacyclohexane,<sup>26</sup> **31**, and 1,2,4,5-tetraaza-3,3,6,6-tetrafluoro-1,2,4,5-tetrakis(*t*-butyldimethylsilyl)-3,6disilacyclohexane,<sup>31</sup> **32**, have recently been determined by Klingebiel (for the chemical structures of **31** and **32** see Table IV.5). Interestingly, **31** adopts a chair conformation while 32 shows a twist-boat conformation. The nitrogen coordinations of the >N-N< fragment in 31 are both pyramidal (NH moiety) and planar, whereas in 32 all four nitrogens are close to planar (sum of angles:  $357.6^{\circ}$ ). A theoretical calculation for the conformation of a tetraazadisilacyclohexane has previously been made on Me<sub>2</sub>Si(NMeNMe)<sub>2</sub>SiMe<sub>2</sub>.<sup>111</sup> The results showed that the chair conformation is energetically more favorable for this molecule and the methyl substituents on the nitrogen atoms are located in alternating equatorial and axial positions. However, this study was based on the assumption that all four nitrogen atoms were pyramidal, which is quite unlikely according to the experimental data on the four tetraazadisilacyclohexanes 9, 23, 31, and 32. Obviously, the change of nitrogen geometry will trigger a change of conformation. The driving force for the conformational preference is likely influenced by intramolecular steric and electronic effects, and intermolecular lattice forces. It is premature to attempt a detailed discussion of this question before theoretical calculations based on the structural parameters for 9, 23, 31 and 32 are provided.

#### IV.2.2 Planarity and Pyramidicity at Nitrogen in Silylhydrazines

As mentioned above, the structures of 9 and 23 reveal the coexistence of both planar and pyramidal geometries at nitrogen. This is very rare since in most known structures of Si-N compounds, planar geometry at nitrogen predominates. In order to discuss the trends in nitrogen coordination in silylhydrazines, the structures of bis(2-methylhydrazino)diphenylsilane and bis(2-methylhydrazino)bis(diphenyl)disiloxane were studied.

#### (i) Bis(2-methylhydrazino)diphenylsilane

The structure of bis(2-methylhydrazino)diphenylsilane (14) is the first reported for a hydrazinosilane compound. Crystals of 14 are monoclinic and belong to the space group

P2<sub>1</sub>/c with 4 molecules in the unit cell. Figure IV.4 shows the ORTEP plot. Selected bond lengths and angles are listed in Table IV.3. The average Si-N bond length of 1.695(4) Å in 14 is the shortest reported distance found in a silylhydrazine compound, and it is 0.036(4) Å shorter than that in 9. The average N-N bond length in 14 is 0.025(5) Å shorter than that in 9. This is attributed to more steric crowding of phenyl groups in 9 than in 14.



Figure IV.4 ORTEP view of 14, showing the atomic numbering scheme.

Si-N1	1.710(4)		421(5)
Si-N2	1.690(4)	N2-N4 1.4	139(5)
Si-C11	1.874(5)	N3-C1 1.4	154(6)
Si-C21	1.874(4)	N4-C2 1.4	39(6)
}			
N1-Si-N2	114.18(18)	C11-Si-C21	111.02(19)
NI-Si-CII	110.89(19)	Si-N1-N3	119.3(3)
N1-Si-C21	103.17(18)	Si-N2-N4	117.3(3)
N2-Si-C11	104.78(19)	N1-N3-C1	110.2(3)
N2-Si-C21	112.98(18)	N2-N4-C2	111.6(3)

Table IV.3 Selected bond distances(Å) and bond angles (degrees) for compound 14

The hydrogens on the nitrogen atoms were not located in this structure. However, the values of  $\angle$ Si-N1-N3 117.3° and  $\angle$ Si-N2-N4 119.3° are so close to 120° as to suggest a planar geometry at N1 and N2, whereas the values of  $\angle$ N1-N3-C1 and  $\angle$ N2-N4-C2 are close to 109°, indicative of pyramidal geometry at N3 and N4. This conclusion is supported by the observation of planar geometry at N1 and pyramidal geometry at N2 in bis(2methylhydrazino)bis(diphenyl)disiloxane, as described below.

#### (ii) bis(2-methylhydrazino)bis(diphenyl)disiloxane

Crystals of bis(2-methylhydrazino)bis(diphenyl)disiloxane (21) are monoclinic and belong to the space group  $P2_1/n$  with 2 molecules in the unit cell. An ORTEP plot showing the structure of 21 is presented in Figure 4.5. Selected bond lengths and bond angles for 21 are given in Table IV.4.

The structure is centrosymmetric, with the bridging O atom at the center of symmetry and a strictly linear SiOSi skeleton. A linear SiOSi geometry has previously been found in the disiloxanes  $O(SiPh_3)_2^{112}$ ,  $O[Si(CH_2Ph)_3]_2^{113}$ ,  $O[Si(CH=CH_2)_3]_2^{114}$  and  $O[SiFCH_3FeCp(CO)_2]_2^{95b}$ . The Si-O distance 1.6131(13) Å in 21 is the same, within experimental uncertainty, as that in these four compounds. The Si-C distances, mean value

1.870(5) Å, lie very close to those of  $O(SiPh_3)_2$  1.866(2)<sup>112</sup>, and Ph<sub>4</sub>Si 1.872(7)<sup>115</sup>. The bond angles about the silicon atoms are all close to tetrahedral. The Si-N distance, 1.695(4) Å, and the N-N distance, 1.430(5) Å, are identical to those in compound 14. In this molecule, the hydrogen atoms on both N1 and N2 were located. The sums of angles about N1 and N2 are 360.0 and 330.7°, respectively. This reveals a planar geometry at N1 and a pyramidal geometry at N2.



Figure IV.5 ORTEP view of 21, showing the atomic numbering scheme.
Si-O 1.6131(13)	O-Sia 1.6131(13)
Si-N(1) 1.695(4)	N(1)-N(2) 1.430(5)
Si-C(2) 1.876(5)	N(2)-C(1) 1.432(7)
O-Si-N1 113.02(15)	Si-N1-N2 114.3(3)
O-Si-C2 109.54(15)	Si-N1-H 127.0(3)
O-Si-C8 107.93(16)	N2-N1-H 118.7(3)
N1-Si-C2 106.75(20)	N1-N2-C1 111.7(4)
N1-Si-C8 110.37(19)	N1-N2-H 107.1(3)
C2-Si-C8 109.18(19)	C1-N2-H 111.9(4)
Si-O-Sia 180.0	$\Sigma < N1: 360.0; N2: 330.7^{[a]}$

Table IV.4 Selected bond lengths (Å) and angles (degree) of 21

[a] Sum of angles at N atoms.

Table IV.5 lists the structural parameters for some silylhydrazines whose structures have been determined. The longer Si-N and N-N distances in the silylhydrazines **31-36** can be explained in terms of steric repulsion due to the presence of bulky substituents on both nitrogen atoms. It is interesting to note that the Si-N bond lengths in all silylhydrazines lie in the range 1.70-1.76 Å which is also the range for most neutral aminosilanes.<sup>97</sup> It seems that the Si-N distances are not significantly affected by the formal oxidation state of the nitrogen atoms.<sup>32</sup>

Further scrutiny of Table IV.5 leads to the conclusion that the geometry about nitrogen in silylhydrazines falls into two categories. The first is characterized by one nitrogen which is planar and another which is pyramidal, such as is found in the compounds containing a -(Si)NN< fragment (9, 14, 21, 23, and 31). In the second, both nitrogens are planar, as in the compounds containing a Si<sub>2</sub>NNSi<sub>2</sub> fragment (32, 33, 34, 35, and 3 6). It is unlikely that planarity or both pyramidicity and planarity at the nitrogen atoms in silylhydrazines are induced exclusively by extrinsic forces such as packing effects, since each geometry is observed in several different molecules.

Compound <sup>[c]</sup>	Si-N(Å)	N-N(Å)	$\sum < N^{[a]}$	Ref.
Bis(2-methylhydrazino)diphenylsilane 14	1.695(4)	1.430(5)	[b]	this work
Bis(2-methylhydrazinodiphenyl)- disiloxane 21	1.695(4)	1.430(5)	360.0 N(1), 330.7 N(2)	this work
1,2,4,5-Tetraaza-3,3,6,6-tetraphenyl-3,6- disilacyclohexane 9	1.731(4)	1.455(6)	360.0 N(1), 344.8 N(2), 359.1 N(4), 336.0 N(5)	this work
1,2,4,5-Tetraaza-1,4-dimethyl-3,3,6,6- tetraphenyl-3,6-disilacyclohexane 23 <sup>[d]</sup>	1.719(4)	1.436(6)	360.0 N(1), 353.5 N(2), 359.9 N(4), 350.5 N(5)	this work
1,2,4,5-tetraaza-3,3,6,6-tetra(t-butyl)-1,4- bis(-butyldimethylsilyl)-3,6- disilacyclohexane <b>31</b>	1.747(2)	1.480(2)	359.8 N(1), 359.8 N(4), 349.9 N(2), 349.9 N(5)	26
1,2,4,5-Tetraaza-3,3,6,6-tetrafluoro- 1,2,4,5-tetrakis(t-butyldimethylsilyl)-3,6,- disilacyclohexane <b>32</b>	1.748(4)	1,491(8)	357.8	31
Tetrasilylhydrazine 33	1.731(4)	1.457(16)	360	29
Tetrakis(phenylsilyl)hydrazine 34	1.728(2)	1.482(3)	360	32a
1,6-Diaza-2,5,7,10- tetrasila[4.4.0]bicyclodecane 35	1.722(2)	1.497(2)	360	33b
Bis(1-aza-2,6-disila-1-cyclohexyl) 36	1.730(2)	1.474(3)	360	33ь

Table IV.5 Comparison of Si-N and N-N bond lengths and sum of angles about nitrogen in some silylhydrazine compounds.

[a] Sum of angles at N.

[b] Hydrogens on nitrogens were not located; however, the angle value of Si-N1-N2 119.3(3) is suggestive of planar geometry at N1, whereas that of N1-N2-C 110.2(3) indicates a pyramidal geometry at N2.

[c] Chemical structures of compounds 31-36.



[d] One of the examiners in the defence committee pointed out that the nitrogen geometry is very difficult to be decided in this case as the standard deviation of the angles  $\angle$ H-N-Si and  $\angle$ N-N-H are big. The auther agrees this comment.

A more likely explanation is the inductive silicon effect, because the attachment of silicon to nitrogen decreases the pyramidal inversion barrier of the nitrogen, and at the same time the nitrogen nonbonding electron pair (n) is stabilized through the interaction of n with the adjacent E-N (E = Si, C, or H) bonds, resulting in the stabilization of the hydrazine conformation. This stabilizing interaction can be treated in the same manner as that established in H<sub>2</sub>NNH<sub>2</sub> molecule, *i.e.* hyperconjugative interaction or its molecular orbital counterparts  $n-\sigma^*$  and  $n-\pi^*$  interactions, as shown in Figure IV.6.



Figure IV.6 Stabilizing interaction of pyramidal nonbonding electron pair (n) with the adjacent E-N bonds.

It has been established experimentally and theoretically that the ground-state conformation of N<sub>2</sub>H<sub>4</sub> is gauche, with a dihedral angle,  $\theta$ , close to 90° (Figure IV.7a).<sup>116</sup> Pyramidal inversion of a nitrogen in N<sub>2</sub>H<sub>4</sub>, with a barrier of 6.1 kcal/mol, leads to a "bisected" conformation (Figure IV.7b), which was shown to be a transition state.<sup>116</sup> A "crossed" conformation (Figure IV.7c) can be brought about if the second nitrogen also inverts, but this double inversion requires at least twice the energy of the "bisected" conformation, and hence it is less likely to happen.



Figure IV.7 Conformations of H<sub>2</sub>N-NH<sub>2</sub> projected along N-N.

The silicon effect on nitrogen inversion may be illustrated by noting that the inversion barrier in NH<sub>3</sub> is 5.8-6.0 kcal/mol whereas in H<sub>3</sub>SiNH<sub>2</sub> it is calculated to be barely 1 kcal/mol.<sup>107</sup> If it is accepted that the introduction of a single silyl group in hydrazine

reduces the inversion barrier by *a*/bout 5 kcal/mol, it is reasonable to expect the observations of the "bisected" conformation in -(Si)NN< or Si<sub>2</sub>NN<, and "crossed" conformation in Si<sub>2</sub>NNSi<sub>2</sub> fragments. The conformations for the fragments -(Si)NN(Si)- and Si<sub>2</sub>NN(Si)- can be either "bisected" or "crossed" or in between, depending on the intramolecular interactions, *e.g.*, steric effects.

Projections of ORTEP models for fragments of 9, 21, and 23 along the N-N bond are shown in Figure IV.8. These conformations exhibit a "bisected" (Figure IV.8a) or nearly "bisected" (Figures IV.8b and IV.8c) geometry. It should be noted that the pyramidal nitrogen lone pair and the adjacent N-Si bond are periplanar (IV.8a) or nearly antiperiplanar (IV.8b and IV.8c), which maximizes the hyperconjugative interaction between the lone pair with the polar N-Si bond. Therefore the "bisected" conformation is stabilized.

It has been shown that the silylhydrazines containing Si<sub>2</sub>NNSi<sub>2</sub> fragments, such as compounds **32-36**, have two Si<sub>2</sub>N planes which are orthogonal or nearly orthogonal to each other. As noted above, the nitrogen atoms in these molecules are all planar. Projection of the Si<sub>2</sub>NNSi<sub>2</sub> fragment along N-N bond should give a "crossed" conformation. Similarly, stabilization of this conformation is also brought about by the maximized "hyperconjugative interaction" of the planar nitrogen lone pairs with the adjacent N-Si bonds.



Figure IV.8 ORTEP fragments of compounds (a) 21, (b) 9, and (c) 23, projected along the N-N bonds to show the conformational relationship between the planar and pyramidal nitrogens.

#### **IV.3** Summary

One of the most intriguing structural features of Si-N compounds is the geometry about nitrogen. Planarity at nitrogen is found in most silylamines, whereas pyramidicity at nitrogen is only found in a few selected monosilylated amines. In silylhydrazine compounds, pyramidicity *vs* planarity at nitrogen has been observed in the fragments such as -(Si)NN<, -(Si)NN(Si)- and -(Si)NNSi<sub>2</sub>, and planarity at nitrogen in the fragment Si<sub>2</sub>NNSi<sub>2</sub>. These observations can be qualitatively explained in term of an inductive silicon effect, which decreases the inversion barrier at nitrogen and stabilizes the nitrogen conformation. Theoretical calculations are needed so that the energy levels of the various nitrogen conformations can be studied quantitatively. Likewise, this will also be helpful for the understanding of the chair and twist-boat conformations in tetraazadisilacyclohexanes.

### **IV.4 Experimental Section**

Single crystals of 9, 14 and 21 were obtained from toluene/hexane, and 23 from hexane. They were sealed in glass capillaries under argon and mounted on a Rigaku diffractometer. Data were collected using the  $\omega/2\theta$  scan mode and Mo-K<sub> $\alpha$ </sub> radiation. The measured reflections were corrected for decay and extinction effects. The structures were solved by direct methods (SHELXS)<sup>117</sup> and completed by difference Fourier syntheses. Phenyl rings were refined as rigid groups and the hydrogens on the rings were included in calculated positions. Hydrogen atoms on nitrogen atoms in compounds 9, 21 and 23 were located in d-maps and then constrained to an idealized H-N bond length of 1.08 Å without refinement except for those in 23. All non-hydrogen atoms were refined with anisotropic displacement parameters. The function minimized was  $\sum w(|F_0| - |F_c|)^2$ ,  $w = 1/[\sigma^2(F_0) + k(F_0)^2]$ . All computations were performed using the NRCVAX system<sup>118</sup> of crystallographic software. The structural analysis data for 9, 14, 21 and 23 are compiled in Appendices I, III, IV and II

#### Chapter V

# SYNTHESIS OF POLY(METHYLSILDIAZANE) AND ITS PYROLYTIC TRANSFORMATION TO SI-N-C CERAMICS

## V.1 Introduction

The development of inorganic and organometallic polymers as ceramic precursors for the manufacture of high performance ceramics, such as silicon carbide, silicon nitride, silicon oxynitride (Si<sub>2</sub>N<sub>2</sub>O) and boron nitride, has received considerable attention.<sup>50-54,119</sup> Polymeric precursors afford unique processing advantages, (such as solubility, fusibility, spinnability and relatively low transformation temperatures) over more conventional powder metallurgical processes. They have promising applications as binders,<sup>120-122</sup> and as precursors to ceramic objects of low dimensionality, *e.g.* fibers<sup>43</sup> and coatings,<sup>44</sup> which are often difficult to make, or unattainable, by conventional routes.

In the context of the continuing search for improved polymeric precursors to  $Si_3N_4$ , a number of polysilazanes of general formula -[-SiRR<sup>1</sup>-NR<sup>2</sup>-]<sub>n</sub>- (R, R<sup>1</sup> and R<sup>2</sup> can be any combination of H, alkyl and aryl groups) have been prepared and pyrolyzed to ceramics in the past several years.<sup>65a,75b,123,124</sup> Seyferth and co-workers have reported the use of poly(methylsilazane) (synthesized by the reaction of methyldichlorosilane with ammonia, with subsequent cross-dehydrocoupling of Si-H with N-H using a KH catalyst) as siliconderived-ceramic precursors.<sup>64,66,67</sup> A silicon nitride/silicon carbide mixture was obtained by heating this precursor to 1400 °C under N<sub>2</sub>, and pure silicon nitride was obtained when the pyrolysis was carried out under a reactive ammonia atmosphere.<sup>66</sup> To minimize, or completely eliminate, excess carbon in the ceramic product from the pyrolysis under inert atmosphere, two methods have been employed to optimize the precursors. On one hand, carbon-free polysilazane, -[-SiH<sub>2</sub>NH-]<sub>n</sub>-, synthesized from the reaction of dichlorosilane (H<sub>2</sub>SiCl<sub>2</sub>) with NH<sub>3</sub>, has been used. However, several groups have shown that this polymer is rather unstable and when the pyrolysis is carried out in an inert atmosphere (N<sub>2</sub> or Ar)<sup>55,56b,68</sup> the resulting silicon nitride product is contaminated with excess silicon. On the other hand, nitrogen-rich precursors have been employed, *e.g.* polymers from thermal condensation of tetrasilazanes of the type Si(NRR')<sub>4</sub>, in which silicon is bonded only to nitrogen.<sup>125,126</sup> Interrante and co-workers have reported a pyrolysis study of the precursor produced by the thermal condensation of Si(NHEt)<sub>4</sub>. In this case a substantial excess of carbon was found in the final Si<sub>3</sub>N<sub>4</sub>/SiC ceramic product.<sup>126</sup>

A simple alternative way to achieve nitrogen-rich precursors is to use a polymeric precursor with a -[Si-N-N]<sub>n</sub>- backbone. Relatively little work has been done on this type of precursor. Colombier has shown that the polymer from the reaction of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> gives about 70% ceramic yield at 1000 °C.<sup>20</sup> Although the gaseous pyrolysis products were studied by using mass spectrometry, structural characterization of the polymer and the solid pyrolysis products was apparently not investigated. In addition to their potential as a novel class of nitrogen-rich polymeric precursors for Si<sub>3</sub>N<sub>4</sub>, the following aspects are also of interest: (1) the pyrolysis chemistry of polymers with an Si-N-N backbone, poly(sildiazanes), may have some relevance to the thermal nitridation of silicon powder (Si + N<sub>2</sub>), a conventional process for the preparation of Si<sub>3</sub>N<sub>4</sub>;<sup>127</sup> (2) the polymer may generate silylaminyl radicals upon ultraviolet irradiation, since sildiazanes such as (Me<sub>3</sub>Si)<sub>2</sub>NNH(SiMe<sub>3</sub>) and (Me<sub>3</sub>Si)<sub>2</sub>NN(SiMe<sub>3</sub>)<sub>2</sub>, have been commonly used to prepare silylaminyl radicals.<sup>15</sup> This chemistry may be used to design a UV curable polysildiazane, as a precursor to a highly cross-linked polysilazane.

The heterodehydrocoupling of MeSiH<sub>3</sub> with  $H_2NNH_2$  gave a polymeric product which is insoluble and contains essentially no Si-H bond, as shown in Chapter II. These properties result is the difficulty for further processing the polymer. Therefore, the polymerization of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> with the elimination of HCl was employed to synthesize soluble poly(methylsildiazane) containing Si-H bonds. In the following sections, the characterization of the resulting polymer, its pyrolysis products and the pyrolysis chemistry will also be described.

# V.2 Results and Discussion

#### V.2.1 Synthesis and Characterization of Poly(methylsildiazane)

The reaction of MeHSiCl<sub>2</sub> with  $H_2NNH_2$  in the presence of triethylamine produced a polymer in 83% yield. The reaction and anticipated formula for the polymer are represented in reaction (V.1).

The polymer is soluble in toluene, benzene and THF, and barely soluble in hexane. It softens at about 75 °C. The number average molecular weight ( $M_n$ ) was measured to be ca. 2600 Daltons by GPC calibrated with polystyrene. This value is viewed as approximate, since polystyrene may not be a good standard for polymethylsildiazane. The solution <sup>1</sup>H NMR spectrum of the polymer, shown in Figure V.1a, shows three broad resonances at 5.4 - 4.7 ppm (SiH), 3.3 - 2.1 ppm (NH) and 0.8 - 0 ppm (SiCH<sub>3</sub>). Their relative integrals are 18.8, 13.5 and 57.1, respectively, which is close to the ratio of 3 : 2.2 : 9, indicating a lower N-H content than that required for the product indicated in reaction (V.1). The <sup>29</sup>Si NMR spectrum of the polymer (Figure V.1b) shows two broad resonances centered at - 14.0 ppm and - 17.5 ppm, with an integral ratio of roughly 2:1. Both resonances can be reasonably attributed to <u>Si(NN)</u>2MeH moities, as the reaction took place by the elimination of HCl and the MeHSi group remained intact. Based on the well known fact that <sup>29</sup>Si resonances are usually at lower field in ring compounds than in open chain compounds,<sup>96</sup> the peak at low-field (- 14.0 ppm) can be assigned to <u>Si(NN)</u>2MeH in

a ring while the peak at high-field (- 17.5 ppm) is assigned to <u>Si(NN)</u><sub>2</sub>MeH in an open chain. This suggests that the product may have the structure shown in **31**.





Figure V.1 Solution NMR spectra of PMSDZ (a) <sup>1</sup>H and (b) <sup>29</sup>Si NMR

The assignment of the <sup>29</sup>Si resonance of the  $\underline{Si(NN)}_2$ MeH moieties in the tetraazadisilacyclohexane ring was supported by the well-defined reaction of Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub> with MeHSiCl<sub>2</sub> in a 1:2 molar ratio, in which a ladder polymer 32 is formed (reaction V.2) and the MeHSi moieties in the ring show a <sup>29</sup>Si resonance centred at -14.5 ppm (Figure V.2).



Figure V.2 Solution <sup>29</sup>Si NMR spectrum of the ladder polymer 32.

Converting elemental analysis data (Table V.1) for this polymer into an empirical formula,  $(CH_3SiH)_3(NNH)_{1.97}C_{0.54}H_{0.38}$ , indicates that there are approximately two NNH groups for every three MeSiH groups. This is in agreement with the proposed structure **31**. The discrepancy for the excess of  $C_{0.53}H_{0.38}$  is probably due to residual solvent (toluene) used in the synthesis, since traces of toluene are very difficult to remove from the polymer sample at ambient temperature. The <sup>1</sup>H NMR spectrum in Figure V.1a

and the TG analysis also indicated the presence of toluene. The polymer is essentially free of Cl contamination since the elemental analysis showed less than 0.005 wt% of chlorine. The IR spectrum of the polymer (Figure V.8a) shows a band at 1579 cm<sup>-1</sup>, assigned to a vibration of the >NNH<sub>2</sub> moiety (see below). This is because the molar ratio of H<sub>2</sub>NNH<sub>2</sub> to MeHSiCl<sub>2</sub> in the reaction mixture was 1.4:1, and the presence of >NNH<sub>2</sub> end groups in the polymer is expected.

The analytical results outlined above lead to the conclusion that the poly(methylsildiazane) consists primarily of chains of tetraazadisilacyclohexane units bridged by MeHSi groups. It seems likely, therefore, that the reaction of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> forms tetraazadisilacyclohexane ring species first, in the same way as Ph<sub>2</sub>SiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub>.<sup>3</sup> One of the N-H bonds in each NHNH group on this ring species then reacts with MeHSiCl<sub>2</sub> with the elimination of HCl, building up the polymer chain. In this process the hydrazine behaves as a trifunctional monomer toward the difunctional MeHSiCl<sub>2</sub>. It has been reported that the reaction of diorganodichlorosilanes with hydrazine yields simple tetraazadisilacyclohexanes if the organo-substituent on the silane is relatively bulky.<sup>9</sup> With small organo-substituents, or H, as in MeHSiCl<sub>2</sub>, polymerization readily occurs. Since hydrazine is also a base and can compete with triethylamine to capture the HCl generated in the reaction, excess hydrazine relative to MeHSiCl<sub>2</sub> is necessary to effect complete reaction of MeHSiCl<sub>2</sub> and remove all of the chlorine from the polymer. The use of excess hydrazine results in >NNH<sub>2</sub> end-groups on the polymer chain.

# V.2.2 Pyrolytic Conversion of Poly(methylsildiazane) to Si<sub>3</sub>N<sub>4</sub>/SiC<sub>x</sub>N<sub>y</sub>

(i) Weight Loss. Figure V.3 shows the TGA curves for the polymers, including noncured (Figure V.3a), DMT-cured (Figure V.3b) and thermally cured (Figure V.3c), heated from 50 to 1000 °C under N<sub>2</sub>. Up to 150 °C, both non-cured and DMT-cured polymers lose about 5% of their initial weight, which can be partially attributed to the loss of solvent. A significant loss (16%) is observed in the uncured sample from 150 to 300 °C, whereas only a small loss (5%) is seen for both cured samples in the same temperature range. The substantial weight loss in the non-cured polymer indicates that the distillation of low molecular weight species occurred during the pyrolysis in this temperature range. Between 350 to 1000 °C, the decomposition behaviour of the three polymers is essentially the same. They all show a very small weight loss (ca. 2%) from 350 to 500 °C and then about 9% loss between 500 and 700 °C, followed by a plateau up to 1000 °C. Ultimately, ceramic yields of 67%, 76% and 81% were obtained for the non-cured, DMT-cured and thermally cured polymers, respectively.



Figure V.3 TGA for polymers. (a) PMSDZ, (b) PMSDZ cured by 1% Cp<sub>2</sub>TiMe<sub>2</sub> catalyst, and (c) PMSDZ cured at 150 °C without catalyst.

(ii) Composition of the Pyrolysis Products. The changes in composition of the solid residues obtained at temperatures of 150, 300, 500, 700, and 1100 °C were monitored by elemental analysis. In Table V.1, the data have been converted to an empirical formula normalized to the respective silicon values. The normalized C, H and N values with the change of temperature are represented graphically in Figure V.4. The atomic ratio of carbon to silicon stays close to 1 from 150 to 300 °C, indicative of little or no cleavage of Si-C bonds up to 300 °C. On the other hand, the data clearly reveal a decrease in the ratio of hydrogen to silicon over this temperature range, suggesting that a loss of hydrogen is taking place, either in the form of H<sub>2</sub> or N<sub>x</sub>H<sub>y</sub> (x = 1 or 2, y = 3 or 4), or both, but not as CH<sub>4</sub>. On heating the polymer up to 700 °C, a steady loss of carbon and hydrogen is evident from the analyses. Above 700 °C, very little further C and H losses occur. This fact suggests that the organic/inorganic transition has largely taken place by about 700 °C.

Table V.1 Elemental analysis data and morphology of the isolated solids by heating PMSDZ to selected temperatures.

temp	% Si	% N	% C	% H	% UA <sup>[a]</sup>	emp formula [b]	Morphology
r.t.	41.61	27.17	20.92	7.59	2.71	SiN1.31C1.17H5.13	white glassy solid
150 °C	43.30	23.51	19.47	7.17	6.55	SiN1.08C1.05H4.63	white glassy solid
300 °C	44.21	21.90	18.31	6.29	9.29	SiN0.99C0.97H4.01	white glassy solid
500 °C	49.25	28.63	14.98	3.50	3.64	SiN1.17C0.71H2.00	yellow glassy solid
700 °C	54.91	30.54	12.86	0.93	0.76	SiN1.11C0.55H0.47	brown glassy solid
1100 °C	56.32	30.43	12.43	0.59	0.23	SiN1,08C0.52H0.29	black glassy solid

[a]. Unaccounted residue, which may be due to either oxygen from the hydrolysis of samples occurring prior to or during analysis, or incomplete combustion of samples in analysis.[b]. The formula does not include unaccounted content.

The somewhat high values of unaccounted residues in samples at 150 and 300 °C may signal higher nitrogen contents for these samples than are shown by the measured percent nitrogen values. Both the loss of  $N_xH_y$  and the unaccounted residues probably

contribute to the sharp drop in N analysis at 150 and 300 °C. The decrease of the N/Si ratio on heating the polymer from 500 to 1100 °C is small compared to the decreases in the C/Si and H/Si ratios, showing that the loss of nitrogen is small at temperatures above 500 °C.



Figure V.4 Plots of the loss of (a) carbon, (b) hydrogen, and (c) nitrogen in heating PMSDZ from room temperature to 1100 °C.

These results from solid pyrolysis residues are consistent with the earlier analyses of the gaseous pyrolysis products from the same type of polymer, reported by Colombier.<sup>20b</sup> In that work the major species detected were hydrazine (below 300 °C), NH<sub>3</sub> (250 - 500 °C), CH<sub>4</sub> (400 - 1000 °C), and H<sub>2</sub> (maximum at 800 °C).

(iii) Solid-State <sup>29</sup>Si MAS NMR Spectroscopy. Solid residues from pyrolyses at temperatures of 150, 300, 500, 700, 1100, and 1500 °C were also studied using solidstate <sup>29</sup>Si MAS NMR spectroscopy. The spectra of these materials are illustrated in Figure V.5. The structural changes occurring at the various reaction temperatures in the pyrolysis products are evident in the <sup>29</sup>Si NMR spectra. The peak at -17.5 ppm diminishes in intensity and is shifted to -14.0 ppm when the polymer is heated at 150 °C. This is indicative of the conversion of the bridged SiHMe mojeties to cyclic SiHMe mojeties. This conversion is even more obvious when the temperature is raised to 200 °C. At 300 °C, the pyrolysis product exhibits a single, broadened resonance at - 22.45 ppm. This resonance is virtually identical to that of a Seyferth/Wiseman-type methylhydropolysilazane<sup>67</sup> and can be assigned to SiHMe(N)2 and SiMe(N)3 coordinations about Si. This result suggests that the N-N bonds in the precursor have been cleaved at this temperature, and agrees with the result, reported by Colombier,<sup>20b</sup> that NH<sub>3</sub> is the most important gaseous product during the pyrolysis of polymethylsildiazane from 250 to 500 °C. The cleavage of N-N bonds to form Si-N and N-H bonds is acccompanied by a large exotherm in the DTA profile for this polymer at about 300 °C (Figure V.6).

In addition to the main resonance at - 24.76 ppm (SiHMeN<sub>2</sub>/SiMeN<sub>3</sub>), the <sup>29</sup>Si NMR spectrum of the product produced at 500 °C also has two smaller peaks at - 10.89 and - 45.30 ppm. These features could be due to the formation of <u>SiMe(CH<sub>2</sub>)N<sub>2</sub> and <u>SiN<sub>4</sub></u>, respectively. The former species could be formed by methylene insertion into the polysilazane chain (see below). All of the samples from room temperature to 500 °C show strong cross-polarization from <sup>1</sup>H to <sup>29</sup>Si nuclei, contrary to the samples produced above 700 °C.</u>



Figure V.5 Solid-state 29Si MAS NMR spectra of (a) PMSDZ, and the solid pyrolysis products at (b) 150 °C, (c) 200 °C, (d) 300 °C, (e) 500 °C, (f) 700 °C, (g) 800 °C, (h) 1000 °C, (i) 1100 °C, and (j) 1500 °C.

This is presumably due to the persistence of a fairly high concentration of protons in the samples. As a result, better signal/noise performance is obtained with the cross-polarization pulse sequence.



Figure V.6 DTA for polymers. (a) PMSDZ, (b) PMSDZ cured by 1% Cp<sub>2</sub>TiMe<sub>2</sub> catalyst, and (c) PMSDZ cured at 150 °C without catalyst.

No peaks could be seen in any spectrum of the products at 700 and 800 °C. This seems to be due to the generation of a significant number of persistent free radicals (or unpaired spins) which relax the <sup>29</sup>Si nuclei so rapidly as to broaden the signal into the baseline. This phenomenon, suggested by very weak or no resonances in <sup>29</sup>Si MAS NMR spectra, was also reported for the pyrolysis products of some polysilazanes at temperatures

between 700 and 1000 °C,<sup>51,128</sup> but is not observed in the pyrolysis of polymethylsilane to SiC.<sup>129</sup> The presence of radicals in the pyrolysis products at 700 and 1100 °C has been qualitatively confirmed by EPR measurements (Figure V.7). The spectra consist only of a broad featureless signal, with no evident hyperfine coupling. The intensity of the signal indicates that a much higher proportion of unpaired spins exists in the residue of 700 °C than in that of 1100 °C. The NMR spectra at 1000 - 1500 °C show the return of the <sup>29</sup>Si resonances and a corresponding decrease in free radicals. At 1000 °C the <sup>29</sup>Si NMR spectrum shows a broad resonance covering the entire range characteristic of Si-to-C and Si-to-N bonds and indicative of an amorphous silicon carbonitride (SiC<sub>x</sub>N<sub>y</sub>) material. In the spectrum at 1100 °C, this resonance has evolved into a distinct peak at - 49.69 ppm and a broad shoulder at - 33.00 ppm. The former peak is characteristic of SiN4 in amorphous  $Si_3N_4$ ,<sup>130</sup> and the latter is assigned to the formation of <u>SiCxNy</u> local environments. The spectrum of the pyrolysis product at 1500 °C exhibits similar, but better resolved resonances. It is evident from these spectra that  $Si_3N_4$  is the major component in the residue over these two temperatures. A longer recycle delay of 30 minutes was employed in the NMR acquisition to identify crystalline Si<sub>3</sub>N<sub>4</sub> in the 1500 °C sample, however, only small quantities of crystalline product were observed, most of the sample still being amorphous.



Figure V.7 EPR spectra of the solid residues formed by the pyrolysis of PMSDZ at (a) 700  $^{\circ}$ C and (b) 1100  $^{\circ}$ C.

(iv) Infrared Spectroscopy. The FT-IR spectrum (Figure V.8a) of the initial polymer exhibits bands indicative of N-H (3358 cm<sup>-1</sup>), C-H (2800-3000 cm<sup>-1</sup>) and Si-H (2132 cm<sup>-1</sup>) functionalities. The band at 1579 cm<sup>-1</sup> is attributed to the NH<sub>2</sub> deformation mode, by analogy to a similar band in methylhydrazine (NH<sub>2</sub> 1587 cm<sup>-1</sup>).<sup>131</sup> The bands at 1250 and 1400 cm<sup>-1</sup> have the normal positions and intensities characteristic of the symmetric and antisymmetric deformations, respectively, of Si-CH<sub>3</sub>. The band at 1348 cm<sup>-1</sup> could be due to a mode of the Si-N-N moiety, since the hydrolysis of the polymer leads to the disappearance of this band simultaneously with the development of V<sub>Si-O</sub> (1108 cm<sup>-1</sup>), as shown in Figure V.9. A similar band was also found in the spectra of Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub> and (Ph<sub>2</sub>SiNHNHMe)<sub>2</sub>O. The Si-N-Si vibration is evident at 995 cm<sup>-1</sup>. The assignments of the major absorptions in the spectra (Figure V.8) are compiled in Table V.2.

frequency[cm <sup>-1</sup> ]	assignment
3358	vN-H
3358sh	vN-H
2960	vasCH
2903	ν <sub>s</sub> CH
2128	vSi-H
1579	$\delta_{ip}NH_2$ (hydrazino functionality)
1543	$\delta NH_2$ (amino functionality)
1400	δ <sub>as</sub> Si-CH <sub>3</sub>
1348	v <sub>as</sub> Si-N-N
1356	wSi-CH2-Si
1250	δ <sub>s</sub> Si-CH <sub>3</sub>
1170	δNH
995	v <sub>as</sub> Si-N-Si
840	v <sub>as</sub> Si-N-Si (cyclic)
836	v <sub>as</sub> Si-N
761	δSi-H

Table V.2 Assignment of IR absorption bands for initial polymer and its pyrolysis product.



Figure V.8 FT-IR spectra of (a) PMSDZ, and the solid pyrolysis products at (b) 150 °C, (c) 300 °C, (d) 500 °C, (e) 700 °C and (f) 1100 °C.



Figure V.9 FT-IR spectra of PMSDZ in air, showing the degree of hydrolysis with the exposure time. (a) PMSDZ, (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min.

The spectrum of the sample at 150  $^{\circ}$ C (V.8b) exhibits essentially the same bands and intensities as those in the initial polymer (V.8a), except for the reduced intensity of the NH<sub>2</sub> band (1579 cm<sup>-1</sup>) and the increased intensity of the band at 840 cm<sup>-1</sup>. The absorption around 840 cm<sup>-1</sup> is also characteristic of the presence of Si-N-Si. Bands in this region have been previously assigned to modes of endocyclic Si-N bonds in cyclodisilazane rings.<sup>126,132</sup> Consistent with the <sup>29</sup>Si NMR results, this band is assigned to the formation of tetraazadisilacyclohexane rings. The NMR results show dramatic structural changes occurring when the temperature is increased from 150 to 300 °C. These changes are also evident from the following changes in the IR spectra: (1) the contour of the sym/antisym N-H stretching modes shows a broad shoulder at higher wavenumber than the main band, rather than the small shoulder at lower wavenumber than the main bands seen in the spectra of the initial polymer and of product at 150 °C. These features are typical of the N-H stretching mode of a silazane, or an aminosilane; (2) the band at 1348 cm<sup>-1</sup>, assigned to the Si-N-N group, totally disappears; (3) the band at 1579 cm<sup>-1</sup>, assigned to a polysiladiazane-type NH2 bending mode, vanishes and a very weak -NH2 absorption band, typical of a silazane, appears at 1543 cm<sup>-1</sup>. These facts all accord with the cleavage of N-N bonds to form silazane species, as previously indicated by the results of DTA and <sup>29</sup>Si NMR measurements.

Other changes in the IR spectra, not related directly to the loss of the N-N groups, were observed. The intensity of the  $V_{Si-H}$  band of samples produced at 300 - 500 °C is decreased relative to that of  $V_{C-H}$  band. This change is indicative of a loss of Si-H groups. The appearance of a weak absorption band at 1356 cm<sup>-1</sup> in the pyrolysis residue at 500 °C should also be noted. A band in this region has been assigned to  $\omega_{Si-CH2-Si}$  by Seyferth and coworkers in their study of the pyrolysis of poly(methylsilazane).<sup>66</sup> The existence of an Si-CH<sub>2</sub>-Si moiety conforms with the observation of MeSi(CH<sub>2</sub>)N<sub>2</sub> species by <sup>29</sup>Si NMR. With increasing temperature, the intensity of the V<sub>C-H</sub> band undergoes a substantial decrease and at 700 °C it is significantly diminished and broadened, signalling that the organic/inorganic transformation takes place at about 700 °C. It is observed that loss of hydrogen occurs more rapidly from C-H bonds than from Si-H bonds above 500 °C, contrary to what one might expect on the basis of bond strength,<sup>133</sup> but commonly observed in most polysilazane pyrolysis.

Decreased resolution of individual bands is observed in the fingerprint region (1200-600 cm<sup>-1</sup>) as the pyrolysis temperature increases from 150 to 1100 °C. The IR spectrum of sample at 1100 °C exihibits an intense, broad absorption centered at 836 cm<sup>-1</sup>, the typical stretching mode for Si-N in silicon carbonitride  $(SiC_xN_y)$ .<sup>126,134a</sup> The asymmetry in the band centered at 840 cm<sup>-1</sup> in the spectrum of amorphous Si<sub>3</sub>N<sub>4</sub> is not uncommon. Usually, four different states of the Si-N stretching mode, located at 800, 835, 950 and 1015 cm<sup>-1</sup>, combine and the proportion of each of the four states determines the shape of the final spectrum.<sup>134b</sup> The assignment of an absorption for silicon carbide in this spectrum is difficult due to the intense absorption of silicon nitride in this region. The Si-N band centered at 836 cm<sup>-1</sup> has a broad shoulder around 1170 cm<sup>-1</sup>. This feature can be assigned to the N-H bending mode at 1170 cm<sup>-1</sup>. The N-H streching band (3200 - 3400 cm<sup>-1</sup>), while extremely broad, is still evident in the 1100 °C sample, indicating that at least part of the residual hydrogen is attached to nitrogen.

(v) Crystallinity of the Ceramic Products. XRD data were acquired on products pyrolysed to 1100 and 1500 °C. The results are shown in Figure V.10. The product at 1100 °C is entirely amorphous by the diffraction criterion, but crystallization is evident in the sample which was heated to 1500 °C. The diffraction pattern corresponds to that of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.<sup>136a</sup> As seen in Figure V.10b, a large quantity of amorphous material is also still present in the sample at 1500 °C. These observations are in agreement with the results of the <sup>29</sup>Si NMR study.



Figure V.10 X-ray powder diffraction patterns of the solid pyrolysis products (a) at 1100 °C and (b) at 1500 °C.

# V.2.3 Pyrolysis Chemistry of Poly(methylsildiazane)

The presence of Si-H and N-H functionalities in the polymer affords the means to crosslink the polymer chains through catalytic or thermal curing processes, thus allowing achievement of higher ceramic yields. Catalytic curing was achieved by the use of 1 mol% of Cp<sub>2</sub>TiMe<sub>2</sub> catalyst. Cp<sub>2</sub>TiMe<sub>2</sub> is an efficient catalyst for the heterodehydrocoupling of Si-H with N-H to form Si-N bonds<sup>27,79</sup> and dehydrocoupling Si-H bonds to form Si-Si bonds<sup>81c,92</sup>. The dehydrocoupling reactions may take place between or within the polymer chains, leading to a highly cross-linked network polymer. The resulting precursors gave relatively high ceramic yields when pyrolysed in N<sub>2</sub>, since the depolymerization reaction was significantly suppressed by the cross-linking. This effect accounts for the relatively small weight loss over the 150 - 500 °C temperature range in the TGA curve (Figure V.3b), Thermal curing at 150 °C transformed the bridging, acyclic MeHSi moieties into the fully cyclic structures. The ring closure could proceed via the following mechanism:



Both heterodehydrocoupling of Si-H with N-H and transamination between N-Si and N-H can occur between two chains of poly(methylsildiazane), leading to the formation of a fused tricyclic ring unit. The transamination reaction may account for the formation of volatile fragments, which would be distilled out under the conditions of the pyrolysis. The decreased intensity of the IR band due to >NNH<sub>2</sub> (Figure V.8b) indicates that the end-group (>NNH<sub>2</sub>) is involved in the thermolysis at 150 °C. On one hand, a condensation reaction could take place between two >NNH<sub>2</sub> end-groups, with elimination of a hydrazine molecule. As shown in Chapter III, the acyclic hydrazinosilane Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> readily undergoes ring closure through a thermal condensation reaction. On the other hand, a transamination reaction, with the involvement of >NNH<sub>2</sub>, along with dehydrocoupling between Si-H and N-H, could also occur in a similar fashion to reaction (V.2). This will result in the formation of a fused bicyclic ring unit, as illustrated in reaction (V.3).



Obviously, ring fusion could also take place through the exclusive heterodehydrocoupling of Si-H with N-H. A reasonable structure for the thermally cured precursor would consist of monocyclic, bicyclic and tricyclic fused rings, which form a sheet-like network.

Further heating of poly(methylsildiazane) to 300 °C results in the cleavage of N-N bonds and the formation of a polysilazane-type material. This transformation is clearly evident in the <sup>29</sup>Si NMR and FT-IR spectra. Thermally induced cleavage of N-N bonds is a well-known method for the preparation of aminyl radicals.<sup>135</sup> It has been reported that silylaminyl radicals such as (R<sub>3</sub>Si)<sub>2</sub>N, generated by the photolysis of tetrakis(trialkylsilyl)hydrazine, are much more reactive towards hydrogen abstraction than dialkylaminyl radicals.<sup>15</sup> Pyrolysis of poly(methylsildiazane) at 300 °C would produce silylaminyl radicals, as shown in reaction (V.4). The radicals formed would then abstract hydrogens from Si-H (the weakest X-H bonds in the system) to form -Si-NH-Si- (reaction V.5). Since the N-H bond (ca. 100 kcal/mol) is considerably stronger than the Si-H bond (ca. 90 kcal/mol),<sup>136a</sup> this hydrogen abstraction is expected to be highly exothermic, which explains the large exotherm observed in the DTA measurements. Abstraction of H from a methyl group would not compete significantly with this reaction due to the greater strength of the C-H bond. Reactions V.5a and 5b are responsible for the formation of MeHSi(N)2 fragments in the pyrolysis residue by the successive cleavage of N-N bonds, followed by abstraction of hydrogen.





The recombination of radicals (reaction V.6) accounts for the formation of MeSi(N)<sub>3</sub> fragments in the residue. Si-NH<sub>2</sub> groups generated in reaction (V.5b) will further condense to give ammonia (reaction V.7), which was observed by GC-MS at about 300  $^{\circ}C.^{20b}$ 



Solid-state <sup>29</sup>Si NMR (Figure V.6e) and FT-IR (Figure V.3d) spectra suggest that MeSi(CH<sub>2</sub>)N<sub>2</sub> fragments are formed through a methylene insertion reaction at 500 °C. The radical combination of silyl radicals to form Si-Si bonds and subsequent methylene insertion, shown in reactions V.8a and 8b, could account for the formation of MeSi(CH<sub>2</sub>)N<sub>2</sub>. Step b (in reaction V.8) is the well-known Kumada rearrangement, which is usually observed in polymethylsilane at 250-300 °C.<sup>137</sup>

In addition, the possibility for the abstraction of hydrogen attached to carbon as in reaction V.9 may also be high at that temperature. The combination of  $\equiv$ Si· with  $\equiv$ C· (reaction V.10) could lead to the formation of MeSi(CH<sub>2</sub>)N<sub>2</sub>.

$$R \cdot + H_3 C \cdot S_1^{i} \longrightarrow RH + H_2 \dot{C} \cdot S_1^{i}$$
(V.9)

(where R<sup>•</sup> = silyl and silylaminyl radicals)

According to the elemental analysis, the loss of carbon and hydrogen in the pyrolysis residue is quite significant as the temperature is increased from 300 to 500 °C. Methane was detected as one of the gaseous products during pyrolysis at about 500 °C.<sup>20b</sup> Both methylene insertion and evolution of methane can possibly be explained in the reaction (V.11), which has been proposed previously by Seyferth.<sup>66</sup> Furthermore, reaction (V.12) could also lead to the evolution of methane and the simultaneous production of Si(N)<sub>4</sub> fragments in the residue.

The onset of the organic/inorganic transformation occurs above 500 °C and approaches completion at 700 °C. This transformation is indicated by the significant loss of carbon and hydrogen from the pyrolysis residues, manifest in the elemental analyses

$$2 - Si - CH_3 - - - Si - C - - Si - + CH_4 \qquad (V.11)$$

$$- \underset{l}{\overset{l}{\text{Si-CH}_3}} + HN(\underset{l}{\overset{l}{\text{Si-f}_2}} \longrightarrow N(\underset{l}{\overset{l}{\text{Si-f}_3}} + CH_4 \qquad (V.12)$$

and FT-IR spectra. Methane and hydrogen are the major gaseous pyrolysis products at about 700 °C.<sup>20b</sup> This gas evolution is due to the cleavage of a large proportion of the Si-H, Si-Me, C-H and N-H bonds to yield progressively an inorganic residue. In addition to reactions such as (V.11) and (V.12), free radical mechanisms involving the homolytic cleavage of these bonds as well as the recombination of radicals could account for the evolution of both methane and hydrogen. Such processes have been commonly proposed for the pyrolysis of other polysilane, polycarbosilane and polysilazane systems.<sup>65b,138,139</sup>

The existence of high concentrations of persistent free radicals in the residue from pyrolysis at 700 °C was confirmed by EPR measurements (Figure V.8). In a related study, Schmidt and coworkers have observed a high concentration of free radicals in the residue from the pyrolysis of vinylic polysilane at 650 °C, which are suppressed under ammonia.<sup>139</sup> The nature of the free radicals, or paramagnetic centers, is not presently understood. Amorphous silicon carbonitride  $(SiC_xN_y)$  is formed during the organic/inorganic transformation. Fixation of carbon in the residue is likely due to methylene insertion reactions such as (V.8), (V.10) and (V.11), since loss of methane from carbosilane units is less likely than loss from Si-Me units. As the pyrolysis temperature increases to 1100 °C, microdomains of silicon nitride are developed but the residue is still amorphous. Although the overall chemical composition of this residue can be tentatively expressed as a formal ceramic composition of 76 % Si<sub>3</sub>N<sub>4</sub>, 15 % SiC, 1 % C and 8 % (CH)<sub>x</sub> (on a weight percent basis), none of the analytical methods used in the present study provides any evidence for the existence of segregated SiC, C or (CH)<sub>x</sub> phases. Based on the FT-IR spectrum (Figure V.3f), much of the remaining hydrogen is in the form of N-H. The presence of hydrogen has been commonly observed in the products of the pyrolysis of silazanes at about 1100 °C, but its bonding mode (Si-H, C-H, N-H) is uncertain.<sup>67,134</sup> However, the residual hydrogen appears to play a role in suppressing crystallization of the ceramic product.

# V.2.4 Poly(methylsildiazane)-derived Quasimetallic Conducting Silicon Carbonitride.

Thin layers of silicon carbonitride on various substrates (such as quartz plate, single-crystal silicon wafer and polycrystalline alumina plate) were prepared by coating poly(methylsildiazane) precursor on the substrates. The thin films were then pyrolysed at 1100 °C under a flow of N<sub>2</sub>. Four-point probe measurements on the ceramic layers have

shown that this silicon carbonitride material possesses electrical conductivity in the order of  $\sim 10^3 \ (\Omega \ cm)^{-1}$ , which is close to the conductivity of glassy carbon. This is in sharp contrast to the N-doped SiC material with composition of about SiCN<sub>0.1</sub>, prepared by the nitridation of poly(methylsilane) and poly(methylcarbosilane), where conductivities of *ca* 10 to 30 ( $\Omega \ cm$ )<sup>-1</sup> were observed.<sup>28</sup>

The reason for the quasimetallic conductivity remains unknown. However, this conducting property of silicon carbonitride suggests a number of applications in electronic devices. The low resistivity of silicon carbonitride thin layers could permit their use as contacts and interconnects in microelectronic devices and as active layers in sensors, such as what has already been done with metal silicides. The ease of coating poly(methylsildiazane) on silicon wafers to prepare thin ceramic layers could facilitate the fabrication of devices. Another interesting exploitation of the thermal and chemical stability of the conducting silicon carbonitride is as a high-temperature electrode material. Preliminary results have shown that this silicon carbonitride behaves in a manner similar to glassy carbon. Figure V.11 shows the cyclic voltammograms of 1.0 mM K4Fe(CN)6/0.1 M KCl at both silicon carbonitride and glassy carbon electrodes. The silicon carbonitride electrodes were prepared as thin layers on a polycrystalline alumina plate. The electrode surface was relatively rough and was not further polished, in constrast to that of glassy carbon. The silicon carbonitride electrode seemed to be hydrophobic as its surface was not wetted well by the solution. Therefore, it exibited relatively smaller electroactive surface area in aqueous solution.



Figure V.11. Cyclic voltammograms of 1.0 mM K<sub>4</sub>Fe(CN)<sub>6</sub>/0.1 M KCl at silicon carbonitride (—) and glassy carbon (----) electrodes, respectively, using Ag/AgCl as reference electrode. Scan rate: 100 mV/S.

# V.3 Summary

The structure of poly(methylsildiazane), PMSDZ, synthesized by the copolymerization of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> in a 1:1.4 molar ratio consists of tetraazadisilacyclohexane rings bridged by MeHSi groups. This polymer decomposes to a mixture of silicon nitride and silicon carbonitride when heated above 1100 °C under N<sub>2</sub> atmosphere. High ceramic yields have been achieved by cross-linking poly(methylsildiazane) with a dimethyltitanocene catalyst, or by thermal curing at 150 °C.

The pyrolytic conversion of PMSDZ to ceramic products has been studied by characterizing the solid residues by using FT-IR and solid-state <sup>29</sup>Si MAS NMR

spectroscopies, elemental analysis and X-ray powder diffraction. Thermal curing of PMSDZ at 150 °C results mostly in the cyclization of the bridged MeHSi moieties, forming a sheet-like network precursor which consists of monocyclic, bicyclic and tricyclic fused rings. At 300 °C N-N bond cleavage occurs rapidly with the formation of a polysilazane-type structure built up mainly of MeHSi(N)<sub>2</sub> and MeSi(N)<sub>3</sub> fragments.

A mechanism involving the formation and reaction of silylaminyl radicals accounts for all of the changes occurring as a result of the polysildiazane to polysilazane transformation. This interesting reaction could be used in the design of an ultravioletcurable polysilazane precursor by photolytic conversion of polysildiazane to polysilazane.

At 500°C methylene insertion occurs, to form MeSi(CH<sub>2</sub>)(N)<sub>2</sub> units. This step is critical for the incorporation of carbon into the ceramic product. At the same time Si(N)<sub>4</sub> fragments are also generated. At around 700 °C the organic/inorganic transition takes place and a high concentration of persistent free radicals is formed. Amorphous silicon carbonitride (SiNC<sub>0.5</sub>H<sub>0.3</sub>) was produced at 1100 °C, and finally a small amount of crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> is observed at 1500 °C.

The PMSDZ-derived silicon carbonitride possesses a remarkable electrical conductivity ( $\sigma = \sim 10^3 (\Omega \text{ cm})^{-1}$ ). This quasimetallic conducting property could make this material suitable for some applications in electronic devices.

## **V.4 Experimental Section**

All syntheses and manipulations were carried out in oven-dried glassware under  $N_2$  using standard Schlenk and glovebox techniques. Hydrazine (anhydrous, 97%, Anachemia Canada Inc.) was purified by double distillation from crushed BaO. Methyldichlorosilane (Aldrich Chemical Co, Inc.) was distilled under  $N_2$  and collected at 37 °C. Other reagents used were prepared in the same way as described in Chapter II. V.4.1 Polymer Synthesis.

(i) Poly(methylsildiazane) A 1000-mL three-neck flask equipped with a magnetic stirrer, an addition funnel, and a condenser with Ar inlet was charged with toluene (500 mL), triethylamine (42.8 mL, 0.290 mol), and hydrazine (6.4 mL, 0.203 mol). Methyldichlorosilane (15.0 mL, 0.145 mol) was syringed into the addition funnel together with toluene (80 mL). The methyldichlorosilane solution was added dropwise to the other reactants in the flask at ambient temperature with stirring over 1 h. After the mixture had been stirred overnight at ambient temperature, the supernatant solution was removed from the solid triethylammonium chloride salt using a fritted glass filter. Evaporation of the solvent under reduced pressure gave 14.8 g of polymer (83% yield based on MeHSiCl<sub>2</sub>), as a white solid. The polymer was stored in a Schlenk flask under argon for further use.

(ii) Cured poly(methylsildiazane). The poly(methylsiladiazane) was further cured either through a dimethyltitanocene catalysed dehydrocoupling or through a thermal reaction at 150°C. The catalytically cured polymer was prepared by the addition of 5.60 g (0.0022 mol) of poly(methylsildiazane) to 0.0046 g ( $2.2x10^{-5}$  mol) of Cp<sub>2</sub>TiMe<sub>2</sub> in toluene at ambient temperature. The resulting mixture was heated in an oil bath at 60 °C for 3 h and then cooled to ambient temperature. The solvent was removed under reduced pressure to yield a brown solid, which was no longer soluble in toluene, THF, or hexane. Thermally cured polymer was prepared by heating the polymer at 150 °C for 1 h (see bulk pyrolysis below).

(iii) Ladder polymer. Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub> (1.524 g,  $8.66\times10^{-3}$  mol) was dissolved in a mixture of 30 mL of toluene and 5 mL of Et<sub>3</sub>N in a 250 mL flask. MeHSiCl<sub>2</sub> (1.80 mL,  $1.73\times10^{-2}$  mol) was added dropwise into this solution. The mixture was stirred for 6 h at ambient temperature. After the removal of the precipitate (Et<sub>3</sub>NHCl) and solvents, a white waxy solid was obtained. Yield: 2.07 g (72%).
V.4.2 Bulk Pyrolysis.

Samples (ca. 1 g) were placed in alumina combusion boats (Fisher Scientific) and transferred to a microprocessor-controlled horizontal tube furnace (Lindberg) under argon. They were heated at about 1 °C/min to 150 °C, held at 150°C for 1 h, heated at 1.5 °C/min to various temperatures (300, 500, 700, 800, 1000 and 1100 °C) and held for 1 h at the temperature in a constant flow (approximately 80 mL/min) of N<sub>2</sub>. The 1100 °C product was further heated to 1500 °C over 1.5 h in a high-temperature furnace and held for 1 h. At the end of each heat treatment, samples were collected in the glovebox and packaged under argon for solid-state NMR, FT-IR, and elemental analysis. X-ray powder diffraction was performed on the products obtained at 1100 and 1500 °C.

#### V.4.3 Characterization.

Thermogravimetric analyses (TGA) were performed on a Seiko 220 TG/DTA instrument. A flow of N<sub>2</sub> ( ~80 mL/min) was maintained during the TGA runs. The samples (ca. 5 - 10 mg) were heated in an alumina ceramic pan at a rate of 5 °C/min from 50 to 750 °C and then at 15°C/min from 750 to 1000 °C.

Solution <sup>1</sup>H NMR spectra were recorded on a Varian XL-200 FT-NMR (200 MHz) or a Varian XL-300 FT-NMR (300 MHz) spectrometer at 20 °C. Benzene- $d_6$  was used as solvent and the chemical shift of the residual protons in the solvent were used as the reference ( $\delta$  7.15 ppm). Solution <sup>29</sup>Si NMR spectra were measured on a Varian XL-300 FT-NMR spectrometer operating at 59.6 MHz in C<sub>6</sub>D<sub>6</sub> at 20 °C. An external standard of TMS ( $\delta$  0.00 ppm) was used. Solid-state <sup>29</sup>Si MAS NMR spectra were acquired on a Chemagnetics CMX-300 spectrometer at 59.52 MHz. Single-pulse excitation (60° pulse) with proton decoupling during data aquisition and magic angle spinning at 3.5 kHz, using cylindrical rotors, was employed. Typically, 256 transients ( 30.03 kHz spectral width) were taken at 15s intervals. The presence of a fairly high concentration of protons in the samples from room temperature to 500 °C allowed the aquisition of spectra with superior signal/noise by the use of cross-polarization (CP). For those samples above 500 °C, the spectra were obtained without CP, since there were not enough protons in these samples.

EPR spectra were recorded on a Bruker ESP 300E spectrometer equipped with an BVT 2000 variable-temperature unit. The magnetic field was calibrated with a Bruker BNM 12 gaussmeter. The microwave frequency was measured with a Systron Donner frequency counter.

Infrared spectra were recorded on a Bruker IFS-88 FT spectrometer equipped with a Deltech dry air purge assembly using a liquid N<sub>2</sub> cooled mercury cadmium telluride detector. Samples for FT-IR analysis were prepared by finely grinding the solid samples with potassium bromide (KBr) in a boron carbide mortar and pestle, and pressing them into pellets for transmission studies.

The molecular weights of polymers were measured on a Varian 5000 gel permeation chromatograph (GPC), equipped with Waters Ultrastyragel 1000 Å, 500 Å and 100 Å columns in tandem at 35 °C, and with THF as solvent. Polystyrene standards were used for calibration.

XRD patterns of the 1100 and 1500 °C samples were collected on a Siemens D-500 powder diffractometer using a scan rate of  $2^{\circ}/min$  from  $10^{\circ}$  to  $60^{\circ}$  for Cu K<sub> $\alpha$ </sub> radiation.

Cyclic voltammograms of 1.0 mM K<sub>4</sub>Fe(CN)<sub>6</sub>/0.1 M KCl using silicon carbonitride and glassy carbon electrodes were carried out on an EG&G PAR Model 273 Potentiostat/Galvanostat instrument.

Elemental analyses of Si, N, C and H were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA.

#### Chapter VI

## CONCLUDING REMARKS

#### VI.1 From Fundamental Chemistry to Advanced Materials

Silylhydrazine chemistry was once viewed as an unproductive field of silicon-nitrogen chemistry; even the pioneer Ulrich Wannagat called it a field of "sin" (Si-N). This can also be perceived by the scrutiny of the literature in this field over the past four decades. In this thesis, the study of silylhydrazines was carried out on syntheses, reactivities, structures and their use as ceramic precursors.

A new route to silvlhydrazines as simple molecules and polymers has been developed by the dehydrocoupling of organosilanes with hydrazines, in which hydrogen gas is the only by-product. Depending on the reactants, the dehydrocoupling reactions either took place spontaneously or were promoted by dimethyltitanocene catalyst. This method affords good yields of the new compounds Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> and Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub>.

The ease of isolation and characterization of the end-products allowed a thorough investigation of the cyclization of Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>. Its thermolysis provided insight into the understanding of the ring closure of poly(methylsildiazane) during pyrolysis. Structural study of the silylhydrazines Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub>, Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>, Ph<sub>2</sub>Si(NHNMe)(NMeNH)SiPh<sub>2</sub> and the derivatives [Ph<sub>2</sub>Si(NHNHMe)]<sub>2</sub>O revealed interesting features, such as the coexistence of pyramidal and planar nitrogen atoms in a hydrazino group. Our initial interest in silylhydrazine polymers, polysildiazanes, was to utilize their nitrogen-rich nature to obtain a higher nitrogen content when pyrolyzed to give a final ceramic product. The pyrolysis chemistry showed that the poly(methylsildiazane) precursor was converted to a Seyferth/Wiseman poly(methylsilazane) precursor at about 300 °C. Obviously the final ceramic composition would be no different in either the polysildiazane or the polysilazane precursor. However, in the present case the Seyferth/Wiseman poly(methylsilazane) product formed from the dehydrocyclodimerization of cyclic silazanes. This dehydrocyclodimerization transforms some of the MeHSi(N)<sub>2</sub> groups in the cyclic silazanes into MeSi(N)<sub>3</sub> fragments in the polysilazane precursor. In this manner, the nitrogen incorporation is increased in the precursor and possible methylene insertion reactions are reduced during pyrolysis. Therefore, the original goal has been achieved.

The determination of the structure of poly(methylsildiazane), synthesized by the polymerization of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub>, was mainly based on its <sup>1</sup>H and <sup>29</sup>Si NMR spectra and by a comparison with the well-defined product of the reaction of Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub> with MeHSiCl<sub>2</sub>. Pyrolysis chemistry of the polymer-to-ceramic conversion was focused on the structural changes of the pyrolysis products isolated at various pyrolysis temperatures. Solid-state <sup>29</sup>Si MAS NMR spectroscopy proved to be a valuable tool in that silicon coordinations in the pyrolysis products gave important clues to the assignments of their structures. The fundamental study of the dehydrocoupling reaction provided an effective way to increase the ceramic yield of poly(methylsildiazane) by using a Cp<sub>2</sub>TiMe<sub>2</sub> catalyst or thermolysis to cross-link the precursor.

Finally, the remarkable quasi-metallic conductivity of silicon carbonitride derived from poly(methylsildiazane) was evaluated with respect to its use as an electrode. The utilization of this property for advanced applications will present a fascinating challenge to ceramic chemists.

## VI.2 Contributions to Original Knowledge

1. Heterodehydrocoupling reactions of organosilanes with hydrazines were studied and led to the development of a new route to silylhydrazines. Phenylsilane and methylsilane spontaneously react with hydrazine to give polymeric products. Dimethyltitanocene was employed as a catalyst to facilitate the dehydrocoupling of phenylsilane and diphenylsilane with hydrazines.

2. Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub> and a new compound Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> were synthesized from the Cp<sub>2</sub>TiMe<sub>2</sub>-catalysed dehydrocouplings of Ph<sub>2</sub>SiH<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> and MeHNNH<sub>2</sub>, respectively. The dehydrocoupling reaction was shown to proceed by stepwise replacement of Si-H with hydrazino groups. The dehydrocoupling methodology was also applied to the synthesis of a new compound Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub>.

3. Reactivities of  $Ph_2Si(NHNHMe)_2$  were studied.  $[Ph_2Si(NHNHMe)]_2O$  was synthesized by the controlled hydrolysis of  $Ph_2Si(NHNHMe)_2$ . The reaction of  $Ph_2Si(NHNHMe)_2$  with *n*-BuLi/Ph\_2SiCl\_2 gave three structural isomers, namely, the 5membered ring (1,2,4-triaza-1-methyl-4-methylamino-3,3,5,5-tetraphenyl-3,5disilacyclopentane) and the two 6-membered rings (1,2,4,5-tetraaza-1,4-dimethyl-3,3,6,6tetraphenyl-3,6-disilacyclohexane and 1,2,4,5-tetraaza-1,5-dimethyl-3,3,6,6-tetraphenyl-3,6-disilacyclohexane). These two 6-membered ring isomers were also synthesized by the cyclization of  $Ph_2Si(NHNHMe)_2$  with MeI, or HCI or  $Ph_2SiCl_2$  as reagents. Thermolysis of  $Ph_2Si(NHNHMe)_2$  also gave these three structural isomers. Mechanisms for the formation of these isomers in each reaction above were proposed.

4. The isomerization of the 5-membered ring to the two six membered rings with catalytic amounts of *n*-BuLi was studied. A mechanism for this isomerization was proposed.

5. Crystal structures of Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub>, Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub>, [Ph<sub>2</sub>Si(NHNHMe)]<sub>2</sub>O and Ph<sub>2</sub>Si(NHNMe)(NMeNH)SiPh<sub>2</sub> were determined. An inductive silicon effect was proposed to explain the unusual coexistence of pyramidal and planar nitrogen atoms in the hydrazino groups.

6. A preceramic polymer, poly(methylsildiazane), was synthesized by the polymerization of MeHSiCl<sub>2</sub> with H<sub>2</sub>NNH<sub>2</sub> in 1:1.4 ratio. The thermally cured poly(methylsildiazane) was pyrolysed to give an excellent yield (81%) of  $Si_3N_4/SiC_xN_y$  ceramics. The polymer-to-ceramic conversion was monitored by a study of the silicon coordinations in the isolated pyrolysis residues. A series of mechanisms for this conversion was proposed.

7. The poly(methylsildiazane)-derived ceramic product at 1100 °C was found to possess a quasi-metallic electrical conductivity ( $\sigma = \sim 10^3 (\Omega \text{ cm})^{-1}$ ). Its application as a potential electrode material was evaluated.

## **VI.3 Suggestions for Further Work**

1. The crystal structure of Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub> shows a chair conformation, while Ph<sub>2</sub>Si(NHNMe)(NMeNH)SiPh<sub>2</sub> possesses a twist-boat conformation. The driving force for the conformational difference is still not clear. It would be interesting to determine the structures of Me<sub>2</sub>Si(NHNH)<sub>2</sub>SiMe<sub>2</sub> and Ph<sub>2</sub>Si(NHNMe)<sub>2</sub>SiPh<sub>2</sub>. The comparison of their conformations might give insight into the driving force.

2. In silvlhydrazine compounds, different nitrogen geometries, such as both pyramidal and planar or only planar geometries, are observed. An inductive silicon effect was proposed to qualitatively account for this feature. It would be interesting to know the energy level of the nitrogen atoms with different geometries by theoretical calculations. These calculations may also allow a better understanding of the driving force for the variable conformations in tetraazadisilacyclohexanes.

3. Photolytic conversion of polysildiazane to highly crosslinked polysilazane by UV irradiation has been proposed in Chapter V. This proposal deserves further work, because of the important technical advantages of using this methodology.

4. Several possibilities could account for the conductivity of silicon carbonitride derived from poly(methylsildiazane). These include excess unpaired electrons in the bulk ceramic and nanocarbon wires (or particles) which lead to the high electrical conductivity. Clarification of these speculations would be interesting and necessary because the application of this conducting property in electronics requires the knowledge of the conducting cause.

5. Preliminary electrochemical study of the conducting silicon carbonitride electrode showed that it behaved in a similar manner to glassy carbon electrode. It would be worthwhile to compare their behaviours in different redox solutions (aqueous and organic) and in different temperature ranges.

6. A preliminary coating study, not described in the thesis, showed that thin ceramic films can be easily obtained through vapor deposition from pyrolyzed poly(methylsildiazane) at high temperature. This work deserves further study.

### REFERENCES

- 1. Ayent, B.J. J. Inorg. Nucl. Chem. 1956, 2, 325.
- 2. Wannagat, U.; Liehr, W. Angew. Chem. 1957, 69, 783.
- 3. Wannagat, U.; Niederprum, H. Angew. Chem. 1958, 70, 745.
- 4. Wannagat, U.; Liehr, W. Z. Anorg. Allg. Chem. 1958, 297, 129-136.
- 5. Wannagat, U.; Liehr, W. Z. Anorg. Allg. Chem. 1959, 299, 341.
- Wannagat, U.; Brandmair, F.; Liehr, W.; Niederprum, H. Z. Anorg. Allg. Chem. 1959, 302, 185.
- 7. Wannagat, U.; Niederprum, H. Angew. Chem. 1959, 71, 574.
- 8. Fessenden, R.; Fessenden, J.S. Chem. Rev. 1961, 61, 378.
- 9. Wannagat, U. Adv. Inorg. Chem. Radiochem. 1964, 6, 243.
- 10. Bailey, R.E.; West, R. J. Am. Chem. Soc. 1964, 86, 5369.
- 11. West, R. Advan. Organomet. Chem., 1977, 16, 1, and references therein.
- (a) West, R.; Ishikawa, M. J. Am. Chem. Soc. 1967, 89, 4072. (b) West, R.;
   Bichlmeir, B. J. Am. Chem. Soc. 1972, 94, 1649.
- 13. Hwu, J.R.; Wang, N. Tetrahedron 1988, 44(13), 4181.
- 14. Brand, J.C.; Cook, M.D.; Price, A.J.; Roberts, B.P. J. Chem. Soc. Chem. Commun. 1982, 151.
- 15. Brand, J.C.; Roberts, B.P.; Winter, J.N. J. Chem. Soc. Perkin Trans. II 1983, 261.
- Dilworth, J.R.; Harrison, S.J.; Henderson, R.A.; Walton, D.R.M. J. Chem. Soc. Chem. Commun. 1984, 176.
- 17. Dilworth, J.R.; Latham, I.A.; Leigh, G.J.; Hunttner, G.; Jibril, I. J. Chem. Soc. Chem. Commun. 1983, 1368.
- Latham, I.A.; Leigh, G.J.; Hunttner, G.; Jibril, I. J. Chem. Soc. Dalton. Trans. 1986, 385.

- 19. Latham, I.A.; Leigh, G.J. J. Chem. Soc. Dalton. Trans. 1986, 399.
- (a) Colombier, C.; Cuer, J.P. Fr. Demande FR 2633301, 1989. (b) Colombier, C. In *Proceedings of the 1st European Ceramic Society Conference*; de With, G., Terpstra, R., Metselaar, R., Eds.; Elsevier Science Publishers: New York, 1989; Vol. 1, pp 143-152.
- (a) Mariam, Y.H.; Pemawansa, K.P.W.; Abrahams, P. Polym. Mater. Sci. Eng. 1987, 56, 73. (b) Mariam, Y.H.; Abrahams, P.; Feng, K. Polym. Mater. Sci. Eng. 1990, 63, 897.
- 22. Drost, C.; Klingebiel, U. Chem. Ber. 1993, 126, 1413.
- 23. Dielkus, S.; Drost, C.; Herbst-Irmer, R.; Klingebiel, U. Angew. Chem. Int. Ed. Engl. 1993, 32, 1625.
- 24. Hluchy, J.; Klingebiel, U. Angew. Chem. Int. Ed. Engl. 1982, 21, 301.
- Clegg, W.; Haase, M.; Hluchy, H.; Klingebiel, U.; Sheldrick, G.M. Chem. Ber. 1983, 116, 290.
- Dielkus, S.; Drost, C.; Herbst-Irmer, R.; Klingebiel, U.; Pauer, F. Organometallics 1994, 13, 3985.
- 27. He, J.; Liu, H.-Q.; Harrod, J.F.; Hynes, R. Organometallics 1994, 13, 336.
- Scarlete, M.; He, J.; Harrod, J.F.; Butler, I.S., in Applications of Organometallic Chemistry in the Synthesis and Processing of Advanced Materials (Eds.: Laine, R.M.; Harrod, J.F.), Kluwer Academic Publishers, Dordrecht, 1995 (in press).
- 29. Clegg, W.; Hluchy, H.; Klingebiel, U.; Sheldrick, G.M. Z. Naturforsch, Teil B 1979, 34, 1260.
- Glidewell, C.; Rankin, D.W.H.; Robiette, A.G.; Sheldrick, G.M. J. Chem. Soc.
   (A) 1970, 318.
- 31. Drost, C.; Klingebiel, U.; Noltemeyer, M. J. Organomet. Chem. 1991, 414, 307.

- 32. (a) Mitzel, N.W.; Bissinger, P.; Schmidbaur, H. Chem. Ber. 1993, 126, 345. (b)
  Mitzel, N.W.; Bissinger, P.; Riede, J.; Dreihaupl, K.H.; Schmidbaur, H.
  Organometallics 1993, 12, 413.
- 33. (a) He, J.; Harrod, J.F.; Hynes, R. Organometallics 1994, 13, 2496. (b) He, J.;
  Harrod, J.F. Heteroatom Chem. 1994, 5, 215.
- 34. He. J.; Harrod, J.F. Can. J. Chem. 1994, 72, 1759.
- 35. (a) Seppelt, K.; Sundermeyer, Chem. Ber. 1969, 102, 1247. (b) Wiberg, N.; Veith,
   M. Chem. Ber. 1971, 104, 3176.
- 36. West, R.; Ishikawa, M. J. Am. Chem. Soc. 1967, 89, 4981.
- 37. (a) Becke-Goehring, M.; Wunsch, G. Chem. Ber. 1960, 93, 326. (b) Fessenden, R.;
  Crowe, D.F. J. Org. Chem. 1961, 26, 4638. (c) Sergeeva, Z.I.; Tszyan-lan, S. Zh.
  Obshch. Khim. 1962, 32, 1987. (d) Wannagat, U.; Kruger, C. Monatsh. Chem.
  1963, 94, 63.
- 38. (a) Linke, K.-H.; Gohausen, H.J. Chem. Ber. 1973, 106, 3438. (b) Gaspar, P.P.;
  Ho, C.-T.; Choo, K.Y. J. Am. Chem. Soc. 1974, 96, 7818. (c) A. Sakakibara, Y.
  Kabe, T. Shimizu and W. Ando, J. Chem. Soc. Chem. Commun. 1991, 43.
- 39. Niederprum, H.; Wannagat, U. Z. Anorg. Allg. Chem. 1961, 311, 270.
- 40. West, R.; Ishikawa, M.; Bailey, R.E. J. Am. Chem. Soc. 1966, 88, 4648.
- 41. Scherer, O.J.; Bültjer, U. Angew. Chem. Int. Ed. Engl. 1971, 10, 343.
- 42. (a) Iseki, T.; Hase, T. In *Fine Ceramics*; Saito, S., Ed.; Elsevier Applied Science Publishers; Essex, England, 1985; p 188. (b) Ziegler, G.; Heinrich, J.; Wotting, G. *J. Mater. Sci.* 1987, 22, 3041.
- 43. (a) G.L. Legrow, T.F. Lim, J. Lipowitz, and R.S. Reaoch, Am. Ceram. Bull.
  1987, 66, 363. (b) Y. Yokoyama, T. Nanba, I. Yasui, H. Kaya, T. Maeshima, and
  T. Isoda, J. Am. Ceram. Soc. 1991, 74, 654. (c) K.J. Thorne, S.E. Johnson, H.
  Zheng, J.D. Mackenzie, and M.F. Hawthorne, Chem. Mater. 1994, 6, 110.

- 44. Mucalo, M.R.; Milestone, N.B.; Vickridge, I.C.; Swain, M.V. J. Mater. Sci., 1994, 29, 4487.
- Aylen, B.J. In Special Ceramics 1964, Popper, E.P., Ed.; Academic Press, London, UK, 1965, p 105.
- Chantrell, P.G.; Popper, E.P. In Special Ceramics 1964, Popper, E.P., Ed.;
   Academic Press, London, UK, 1965, p 87.
- (a) Verbeek, W. US Pat. No. 3853567, 1974. (b) Winter, G.; Verbeek, W.; Mansmann, M. US Pat. No. 3892583, 1975.
- 48. (a) Yajima, S.; Hayashi, J.; Omori, M. Chem. Lett. 1975, 931. (b) Yajima, S.;
  Omori, M.; Hayashi, *ibid*, 1975, 1209. (c) Yajima, S.; Shishido, T.; Kayano, H.
  Nature (London), 1978, 273, 525.
- 49. Wills, R.R.; Markle, R.A.; Mukherjee, S.P. Am. Ceram. Soc. Bull. 1983, 62, 904.
- 50. K.J. Wynne, and R.W. Rice, Annu. Rev. Mater. Sci. 1984, 14, 297.
- 51. M. Peuckert, T. Vaahs, and M. Buck, Adv. Mater. 1990, 2, 398.
- 52. W. Toreki, Polym. News, 1991, 16, 6.
- Atwell, W.H. In Silicon-Based Polymer Science. A Comprehensive Resource; Adv. Chem. Ser. 224; Zeigler, J.M., Fearon, F.W., Eds.; American Chemical Society: Washington, DC, 1990; p 593.
- 54. R.M. Laine and F. Babonneau, Chem. Mater. 1993, 5, 260.
- Seyferth, D.; Wiseman, G.H.; Prudhomme, C.C. J. Am. Ceram. Soc. 1983, 66, C-13.
- (a) Arai, M.; Sakurada, S.; Isoda, T. Tomizawa, T. Am Chem. Soc. Polym. Div. Polym. Prpts. 1987, 27, 407. (b) Funayama, O.; Arai, M.; Tashiro, Y.; Aoki, H.; Suzuki, T.; Tamura, K.; Kaya, H.; Nishii, H.; Isoda, T. J. Ceram. Soc. JPN. 1990, 98, 104.
- (a) Rochow, E.G. Monatsh. Chem. 1964, 76, 650. (b) Kruger, C.R.; Rochow,
   E.G. J. Polym. Sci. A 1964, 2, 3179.

- (a) Andrianov, K.A.; Ismailov, B.A.; Konov, A.M.; Kotrelev, G.V. J. Organomet. Chem. 1965, 3, 129. (b) Andrianov, K.A.; Kotrelev, G.V.; Kamaritski, B.A.; Unitski, I.H.; Sidorova, N.I. J. Organomet. Chem. 1969, 16, 51.
- 59. Sirieix, F.; Goursat, P.; Lecomte, A.; Dauger, A. Comp. Sci. Tech. 1990, 37, 7.
- (a) Zoeckler, M.T.; Laine, R.M. J. Org. Chem. 1983, 48, 2539. (b) Blum, Y.;
   Laine, R.M. Organometallics 1986, 5, 2081.
- (a) Penn, B.G.; Ledbetter III, F.E.; Clemons, J.M.; Daniels, J.G. J. Appl. Polym. Sci. 1982, 27, 3751. (b) Penn, B.G.; Ledbetter III, F.E.; Clemons, J.M. Ind. Eng. Chem. Process. Res. Dev. 1984, 23, 217. (c) Penn, B.G.; Daniels, J.G.; Ledbetter III, F.E.; Clemons, J.M. Polym. Eng. Sci. 1986, 26, 1191.
- 62. (a) Gaul Jr, J.H. US Patent 4340619, 1982. (b) Baney, R.H.; Gaul Jr, J.H. US Patent 4310651, 1982. (c) Gaul Jr, J.H. US Patent 4395460, 1983. (d) Gaul Jr, J.H. US Patent 4312970, 1985. (e) Cannady, J.P. US Patent 4535007, 1985. (e) Bujalski, D.R. Eur. Patent Appl. EP 175382, 1986.
- Legrow, G.E.; Lim, T.F.; Lipowitz, J.; Reaoch, R.S. In Better Ceramics Through Chemistry II, Mater. Res. Symp. Proc. Vol. 73, Brinker, C.J.; Clark, D.E.; Ulrich, D.R. Eds.; 1986, p 553.
- 64. Seyferth D.; Wiseman, G.H. J. Am. Ceram. Soc., 1984, 67, C-132.
- 65. (a) Choong Kwet Yive, N.S.; Corriu, R.J.P.; Leclercq, D.; Mutin, P.H.; Vioux,
  A. Chem. Mater. 1992, 4, 141. (b) Corriu, R.J.P.; Leclercq, D.; Mutin, P.H.;
  Vioux, A. Chem. Mater. 1992, 4, 711.
- 66. Han, H.; Lindquist, D.; Haggery, J.; Seyferth, D. Chem. Mater., 1992, 4, 705.
- 67. Dando, N.R.; Perrotta, A.J.; Strohmann, C.; Stewart, R.M.; Seyferth, D. Chem. Mater. 1993, 5, 1624.
- 68. Blanchard, C.R.; Schwab, S.T. J. Am. Ceram. Soc. 1994, 77, 1729.

- 69. (a) Fink, W. Chem. Ber. 1963, 96, 1071. (b) Fink, W. Helv. Chim. Acta 1964, 47, 498. (c) Fink, W. Helv. Chim. Acta 1964, 49, 1408. (d) Fink, W. Angew. Chem. Int. Ed. Engl. 1966, 5, 760.
- Andrianov, K.A.; Shkol'nik, M.I.; Syrtsova, Zh.S.; Petrov, K.I.; Kopylov, V.M.;
   Zaitseva, M.G.; Koroleva, E.Z. Dokl. Akad. Nauk. SSSR 1975, 223, 347.
- 71. Wiseman, G.H.; Wheeler, D.R.; Seyferth, D. Organometallics 1986, 5, 146.
- 72. Sommer, L.H.; Citron, J.D. J. Org. Chem. 1969, 32, 2470.
- Andrianov, K.A.; Filimonova, M.I.; Sidorov, V.I. J. Organomet. Chem. 1977, 142, 31.
- 74. Kotzsch, H.J.; Vahlensieck, H.J. US Patent 4115427, 1978.
- (a) Biran, C.; Blum, Y.D.; Glaser, R.; Tse, D.S.; Youngdahl, K.A.; Laine, R.M. J. Mol. Catal. 1988, 48, 183. (b) Laine, R.M.; Blum, Y.D.; Tse, D.S.; Glaser, R. In Inorganic and Organometallic Polymers; Zeldin, M., Wynne, K.J., Allcock, H.R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; p 125.
- 76. Kinsley, K.K.; Nielson, T.J.; Barton, T.J. Main Group Met. Chem. 1987, 10, 307.
- 77. Wang, W.D.; Eisenberg, R. Organometallics 1991, 10, 2222.
- 78. Liu, H.Q.; Harrod, J.F. Can. J. Chem. 1990, 68, 1100.
- 79. Liu, H.Q.; Harrod, J.F. Organometallics 1992, 11, 822.
- Harrod, J.F. In Progress in Catalysis, Smith, K.J., Sanford, E.C. Eds.; Elsevier Science Publishers B.V.: Amsterdam, 1992, p 147.
- (a) Aitken, C.; Harrod, J.F.; Samuel, E. J. Organomet. Chem. 1985, 279, C11. (b) Aitken, C.; Harrod, J.F.; Malek, A.; Samuel, E. J. Organomet. Chem. 1988, 349, 285. (c) Aitken, C.; Barry, J.P.; Gauvin, F.; Harrod, J.F.; Malek, A.; Rousseau, D. Organometallics 1989, 8, 1732. (d) Gauvin, F.; Harrod, J.F. Can. J. Chem. 1990, 68, 1638. (e) Mu, Y.; Cote, B.; Aitken, C.A.; Harrod, J.F.; Samuel, E.

Can. J. Chem. 1990, 69, 264. (f) Li, H.; Gauvin, F.; Harrod, J.F. Organometallics 1993, 12, 575.

- 82. (a) Woo, H-G.; Tilley, T.D. J. Am. Chem. Soc. 1989, 111, 8043. (b) Woo, H-G.;
  Tilley, T.D. J. Am. Chem. Soc. 1989, 111, 3757. (c) Tilley, T.D. Comments
  Inorg. Chem., 1990, 10, 37. (d) Woo, H.G.; Walzer, J.F.; Tilley, T.D. J. Am.
  Chem. Soc. 1992, 114, 7047. (e) Tilley, T.D. Acc. Chem. Res. 1993, 26, 22.
- 83. Campbell, W.H.; Hilty, T.K.; Yurga, L. Organometallics 1989, 8, 2615.
- 84. (a) Corey, J.Y.; Chang, L.S.; Corey, E.R. Organometallics 1987, 6, 1596. (b) Chang, L.S.; Corey, J.Y. Organometallics 1989, 8, 1885. (c) Corey, J.Y.; Zhu, X.-H.; Bedard, T.C.; Lange, L.D. Organometallics 1991, 10, 924. (d) Corey, J.Y.; Zhu, X.-H. Organometallics 1992, 11 672.
- 85. Banovetz, J.P.; Stein, R.M.; Waymouth, R.M. Organometallics 1991, 10, 3430.
- Sakakura, T.; Lautenschlager, H.J.; Nakajima, M.; Tanaka, M. Chem. Lett. 1991, 913.
- 87. Procopio, L.J.; Berry, D.H. J. Am. Chem. Soc. 1991, 113, 4039.
- (a) Miller, W.S.; Peake, J.S.; Nebergall, W.H. J. Am. Chem. Soc. 1957, 79, 5604.
  (b) Bedard, T.C.; Corey, J.Y. J. Organomet. Chem. 1992, 428, 315.
- Sneddon, L.G.; Fazen, P.J.; Su, K.; Lynch, A.T.; Bech, J.S.; Remsen, E.E. Abstracts of the 33rd IUPAC Symposium on Macromolecules. Montreal 8-13 July 1990; Session 2.11.3.
- 90. Liu, H.Q.; Harrod, J.F. Polym. Prepr. 1991, 32(3), 563.
- 91. Benkeser, R.A.; Landesman, H.; Foster, D. J. Am. Chem. Soc. 1952, 74, 648.
- Mu,Y.; Harrod, J.F. Inorganic and Organometallic Polymers and Oligomers, Harrod, J.F.; Laine, R.M., Eds.; Kluwer Academic Publishers, Dordrecht, 1991, p 23.
- 93. Claus, K.; Bestian, H. Justus Liebigs Ann. Chem. 1962, 654, 8.
- 94. Hale, C.C.; Shetterly, F.F. J. Am. Chem. Soc. 1911, 33, 1071.

- (a) Shambayati, S.; Blake, J.F.; Wierschke, S.G.; Jorgensen, W.L.; Schreiber,
   S.L. J. Am. Chem. Soc. 1990, 112, 697. (b) Ries, W.; Albright, T.; Silvestre, J.;
   Bernal, I.; Malisch, W.; Burschka, C. Inorg. Chim. Acta 1986, 111, 119.
- Williams, E.A., In The Chemistry of Organic Silicon Compounds, Vol. 1, Eds.;
   Patai, S., Rappoport, Z.; Wiley, New York, 1989, Chapter 8.
- Sheldrick, W.S. In The Chemistry of Organosilicon Compounds, Vol. 1 (Eds.: S. Patai, Z. Rappoport), Wiley: New York, 1989 Chapter 3.
- 98. Janes, N.; Oldfield, E. J. Am. Chem. Soc. 1986, 108, 5743.
- Ruhlandt-Senge, K.; Bartlett, R.A.; Olmstead, M.M.; Power, P.P. Angew. Chem. Int. Ed. Engl. 1993, 32, 425.
- 100. (a) Pauling, L. The Nature of the Chemical Bond, Cornell University Press: Ithaca, New York, 1960. (b) Cradock, S.; Ebsworth, E.A.V.; Savage, W.J.; Whiteford, R.A. J. Chem. Soc. Faraday Trans. 2 1972, 68, 934. (c) Huheey, J.E. Inorganic Chemistry, 4th Ed.; Harper and Row: New York, 1993, pp 866 - 876. (d) Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th Ed.; John Wiley and Sons: New York, 1988, p 269.
- 101. (a) Noodleman, L.; Paddock, N.L. Inorg. Chem. 1979, 18, 354. (b) Livant, P.;
   Mckee, M.L.;. Worley, S.D. Inorg. Chem. 1983, 22, 895.
- 102. (a) Pitt, C.G. J. Organomet. Chem. 1973, 61, 49. (b) Pitt, C.G.; Bursey, M.M.;
  Chatfield, D.A. J. Chem. Soc. Perkin Trans. 2 1976, 434. (c) Albright, T.A.;
  Burdett, J.K.; Whangbo, M.H. Orbital Interactions in Chemistry, Wiley, New York, 1985.
- 103. (a) Sauer, J.; Zurawski, B. Chem. Phys. Lett. 1979, 65, 587. (b) Oberhammer,
  H.; Boggs, J.E. J. Am. Chem. Soc. 1980, 102, 7241. (c) Ernst, C.A.; Allred,
  A.L.; Ratner, M.A.; Gibbs, G.V.; Moskowitz, J.W.; Topiol, S. Chem. Phys. Lett.
  1981, 81, 424. (d) Grigoras, S.; Lane, T.H. J. Comput. Chem. 1986, 9, 25; ibid,
  1987, 8, 84.

- 104. Glidewell, C. Inorg. Chim. Acta 1978, 29, L283; J. Organomet. Chem. 1978, 159, 23.
- Hedberg, K. J. Am. Chem. Soc. 1955, 77, 6491. The structure was further confirmed by electron diffraction, Beagley, B.; Conrad, A.R. Trans. Faraday Soc. 1970, 66, 2740; and by X-ray crystallography, Barrow, M.J.; Ebsworth, E.A.V. J Chem. Soc. Dalton Trans. 1984, 563.
- 106. Burger, H. Angew. Chem. Int. Ed. Engl. 1973, 12, 474.
- 107. Gordon, M.S. Chem. Phys. Lett. 1986, 126, 45.
- 108. (a) Glidewell, C.; Rankin, D.W.H.; Robiette, A.G.; Sheldrick, G.M. J. Mol. Struct.
  1970, 6, 231. (b) Gundersen, G.; Mayo, R.A.; Rankin, D.W.H. Acta Chem.
  Scand. Ser. A, 1984, 38, 579.
- 109. (a) Rudman, R.; Hamilton, W.C.; Novic, S.; Goldfarb, T.D. J. Am. Chem. Soc.
  1967, 89, 5157. (b) Blake, A.J.; Ebsworth, E.A.V.; Welch, A.J. Acta Crystallogr., Sect. C, 1984, 40, 895.
- 110. Blake, A.J.; Ebsworth, E.A.V.; Rankin, D.W.H.; Robertson, H.E.; Smith, D.E.; Welch, A.J. J. Chem. Soc. Dalton Trans. 1986, 91.
- 111. Bock, H.; Kaim, W.; Semkow, A.M.; Noth, H. Angew. Chem. Int. Ed. Engl.
  1978, 17, 286.
- 112. Glidewell, C.; Liles, D.C. Acta Cryst. 1978, B34, 124.
- 113. Glidewell, C.; Liles, D.C. J. Organomet. Chem. 1981, 212, 291.
- Gusev, A.I.; Antipin, M. Yu.; Yufit, D.S.; Struchkov, Yu.T.; Sheludyakov, V.D.;
   Zhun, V.I.; Vlasenko, S.D. Zh. Strukt. Khim. 1983, 24, 178.
- 115. Glidewell, C.; Sheldrick, G.M. J. Chem. Soc. (A) 1971, 3127.
- 116. Cowley, A.H.; Mitchell, D.J.; Whangbo M.-H.; Wolfe, S. J. Am. Chem. Soc. 1979, 101, 5224.
- Sheldrick, G.M. SHELXS 86, Program for Crystal Structure Determination, University of Göttingen, 1986.

- 118. Gabe, E.J.; Le Page, Y.; Charland, J.P.; Lee, F.L.; White, P.S. J. Appl. Cryst. 1989, 22, 384.
- 119. Kimura, Y.; Kubo, Y.; Hyashi, N. Comp. Sci. Tech. 1994, 51, 173.
- 120. Mohr, D.L.; Desai, P.; Star, T.L. Ceram. Eng. Sci. Proc. 1990, 11, 920.
- 121. Schwartz, K.B.; Rowcliffe, D.J.; Blum, Y.D. Adv. Ceram. Mater. 1988, 3, 320.
- 122. Schwab, S.T.; Blanchard-Ardid, C.R. in Better Ceramics Through Chemistry III. Eds. C.J. Brinker, D.E. Clark, and D.R. Ulrich; pp. 345-50, Materials Research Society, Pittsburgh, PA, 1989.
- 123. Seyferth, D.; Wiseman, G.H.; Schwark, J.M.; Yu, Y.-F.; Poutasse, C.A. in Inorganic and Organometallic Polymers; ACS Symp. Ser. 360. Edited by M. Zeldin, K.J. Wynne, and H.R. Allock; pp. 143-55, American Chemical Society, Washington, DC, 1988.
- 124. Arkles, B.; J. Electrochem. Soc. 1986, 133, 233.
- 125. Gordon, R.G.; Hoffman, D.M.; Riaz, U. Chem. Mater. 1990, 2, 480.
- 126. Narsavage, D.N.; Interrante, L.V.; Marchetti, P.S.; Maciel, G.E. Chem. Mater. 1991, 3, 721.
- 127. Lange, H.; WOtting, G.; Winter, G. Angew. Chem. Int. Ed. Engl., 1991, 30, 1579.
- 128. Seyferth, D. in Silicon-Based Polymer Science. A Comprehensive Resource; Adv. Chem. Ser. 224; Eds. J.M. Zeigler, F.W. Fearon; pp. 565-91, American Chemical Society, Washington, DC, 1990.
- 129. Zhang, Z.; Babonneau, F.; Laine, R.M.; Mu, Y.; Harrod, J.F.; Rahn, J. J. Am. Ceram. Soc. 1991, 74, 670.
- 130. Carduner, K.R.; Carter III, R.O.; Milberg, M.E.; Crosbie, G.M. Anal. Chem. 1987, 59, 2794.
- 131. Axford, D.W.E.; Janz, G.J.; Russell, K.E. J. Chem. Phys., 1951, 19, 704.
- 132. Il'in, M.M.; Moskovkin, A.S.; Talanov, V.N.; Miroshnichenko, I.V.; Bochkarev,
  V.N.; Chernyshev, A.E. Zh. Obshch. Khim. 1982, 53, 110.

- 133. Walsh, R. in The Chemistry of Organic Silicon Compounds, Vol.1, Edited by S. Patai and Z. Rappoport. pp. 371-92, Wiley, New York, 1989.
- 134. Bae, Y.W.; Du, H.; Gallois, B.; Gonsalves, K.E.; Wilkens, B.J. Chem. Mater.
  1992, 4, 478. (b) Zhang, B.R.; Yu, Z.; Collins, G.J.; Hwang, T.; Ritchie, W.H. J.
  Vac. Sci. Technol. A 1989, 7, 176.
- 135. Danen, W.C.; Neugebauer, F.A. Angew. Chem. Int. Ed. Engl. 1975, 14, 783.
- 136. (a) Inorganic Powder Diffraction File, Berry, L.G. (Eds), JCPDS card number 9250. Joint Committee on Powder Diffraction Standards: Swarthmore, 1967. (b)
  Handbook of Chemistry and Physics, 61st ed. Kerr, J.A.; Trotman-Dickenson,
  A.S. (Eds.), PF236. CRC Press, Boca Raton, FL, 1980.
- 137. Scarlete, M.; Brienne, S.; Butler, I.S.; Harrod, J.F. Chem. Mater. 1994, 6, 977.
- 138. Bahloul, D.; Pereira, M.; Goursat, P.; Choong Kwet Yive, N.S.; Corriu, R.J.P. J. Am. Ceram. Soc. 1993, 76, 1156.
- 139. Schmidt, W.R.; Marchetti, P.S.; Interrante, L.V.; Hurley, W.J.; Lewis, R.H.; Doremus, R.H.; Maciel, G.E. Chem. Mater. 1992, 4, 937.

## APPENDIX I X-RAY CRYSTAL STRUCTURE ANALYSIS OF Ph<sub>2</sub>Si(NHNH)<sub>2</sub>SiPh<sub>2</sub> (9)

Formula	Si <sub>2</sub> N <sub>4</sub> C <sub>24</sub> H <sub>24</sub>
Fw	424.65
Cryst Size, mm	0.5x0.15x0.10
Cryst System	monoclinic
Space Group	A2/a
a, Å	29.683(5)
b, Å	5.8972(17)
c, Å	39.038(7)
β, deg	105.492(14)
V, Å <sup>3</sup>	6585.2(25)
Z	12
d <sub>calcd</sub> , g cm <sup>-3</sup>	1.285
F(000)	2687.44
temp, °C	20
$\mu$ (Mo-K $\alpha$ ), mm <sup>-1</sup>	0.17
20 <sub>max</sub>	45.0
Scan type	ω/2θ
hkl range	-31/30, 0/6, 0/42
Measured reflets	4422
Unique reflets	4314
Observed reflets (>2.5 $\sigma$ )	2216
Refined parameters	298
R <sub>int</sub>	1.0%
k	0.000100
R	0.054
Rw	0.056
GoF	1.65
$\Delta \rho_{\text{max/min}}, eÅ^{-3}$	0.280/-0.290

Table AI.1 Crystal data and data collection parameters for 9.

\_

$$\begin{split} &R = \sum [|F_0| - |F_c|] / \sum |F_0| \\ &w = 1 / (\sigma^2 |F_0| + \kappa F_0^2) \\ &R_w = [\sum w (|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2} \\ &G_0F = [\sum w (|F_0| - |F_c|)^2 / (n - v)]^{1/2} \end{split}$$

Table AI.2 Atomic coordinates and isotropic thermal parameters for 9

.

	x	У	I	Beq
Si 1	0.05518( 6)	0.4980(3)	0.50389( 5)	2.42(8)
Si 2	0.10983( 6)	0.0471( 3)	0.33099( 5)	2.47 (8)
Si 3	0.22030(6)	0.0156(3)	0.34316( 4)	2.44(8)
NI	0.02266(17)	0.7409(9)	0.50188(13)	2.9 (3)
N 2	0.01906(17)	0.2716(9)	0.48537(12)	2.6 (3)
N 3	0.14668(17)	0.2617(8)	0.35275(12)	2.8 (3)
NANE	0.13955(17) 0.19295(17)	-0.2034(9)	0.33398(13)	2.9 (3)
NG	0.10200(17) 0.10040(17)	-0.2032(9)	0.32341(12) 0.34221(13)	2.7 (3)
CII	0.08387(13)	0.4224(7)	0.54221(13) 0.55152(.8)	2.3(3)
C12	0.08491(14)	0.5850(6)	0.57767(11)	3.4(3)
C13	0.10784(15)	0.5386(7)	0.61308(10)	4.3 (4)
C14	0.12974(14)	0.3297 ( 9)	0.62233 (9)	4.0 (4)
C15	0.12870(14)	0.1671(6)	0.59618(13)	3.8 (4)
C16	0.10576(15)	0.2134 ( 6)	0.56078(11)	3.1 (3)
C21	0.09779(12)	0.5381( 8)	0.47643(10)	2.7 (3)
C22	0.09668(14)	0.7327(7)	0.45589(12)	3.9 (4)
C23	0.12938(17)	0.7612(7)	0.43638(10)	4.4 (4)
C24	0.16320(14)	0.5952(9)	0.43740(10)	4.2 (4)
C25	0.16431(13)	0.4007(8)	0.45794(12)	4.6 (4)
C20	0.13160(15)	0.3/21(6)	0.47745(10) 0.25220(10)	3.7 (4)
C32	0.00147(12) 0.05272(1A)	0.0107( 8)	0.35330(10) 0.37414(11)	2.6(3)
C33	0.03272(14) 0.01652(16)	0.1900(0)	0.39060(10)	3.4 (3)
C34	-0.01092(13)	-0.0158(9)	0.38621(12)	
C35	-0.00216(15)	-0.1940(7)	0.36537(12)	4.7 (4)
C36	0.03403(16)	-0.1767(6)	0.34892(10)	3.8 (4)
C41	0.08769(15)	0.1299(7)	0.28273(8)	2.7 (3)
C42	0.06841(15)	0.3435(6)	0.27282(11)	3.8 (4)
C43	0.04914(15)	0.3943(7)	0.23699(13)	4.7 (4)
C44	0.04915(15)	0.2315(9)	0.21107( 9)	4.7 (4)
C45	0.06843(16)	0.0179(8)	0.22098(10)	4.7 (4)
C46	0.08770(15)	-0.0330(6)	0.25681(11)	3.9 (4)
C51 C52	0.24798(13)	-0.0698(7)	0.39063(8)	2.5 (3)
C52	0.24995(13)	0.0890(6)	0.41748(11)	3.0(3)
C54	0.27290(13) 0.29400(14)	-3.1756(9)	0.45263(10)	
C55	0.29400(14) 0.29203(14)	-0.1736(-0)	0.40033(3)	3 9 (4)
C56	0.25203(14) 0.26902(14)	-0.2815(6)	0 39894 (10)	3.0 (4)
C61	0.26385(13)	0.0472(7)	0.31634(10)	2.6 (3)
C62	0.29637(15)	-0.1258(6)	0.31781(10)	3.9 (4)
C63	0.32844(13)	-0.1108(7)	0.29749(12)	5.1 (4)
C64	0.32798(14)	0.0772(9)	0.27571(11)	5.1 (4)
C65	0.29546(16)	0.2502(7)	0.27425 (10)	4.8 (4)
C66	0.26340(13)	0.2352(6)	0.29456(11)	3.8 (4)

Beq is the mean of the principal axes of the thermal ellipsoid. Phenyl rings were constrained to idealized geometry and refined as rigid groups.

## Table AI.3 Anisotropic thermal parameters [u(i,j)x100] for 9

	<b>ull</b>	ບ22	u33	<b>u12</b>	<b>u13</b>	ບ23
Si 1 Si 2 Si 3 N 1 N 2 N 3 N 4 N 5 Cl1 Cl2 Cl3 Cl4 Cl5 Cl4 Cl5 Cl2 Cl2 Cl2 Cl2 Cl2 Cl2 Cl2 Cl2 Cl2 Cl2	ull 2.74 (11) 3.14 (11) 2.89 (12) 3.1 (3) 3.7 (3) 3.5 (3) 3.5 (3) 3.5 (3) 3.1 (3) 3.1 (3) 2.1 (4) 4.1 (5) 5.4 (5) 4.4 (5) 3.7 (4) 3.8 (4) 2.7 (4) 4.7 (5) 6.3 (5) 5.0 (5) 5.0 (5) 5.3 (5) 3.1 (4) 4.3 (4) 5.1 (5)	$\begin{array}{c} u22\\ 2.91 (11)\\ 2.95 (11)\\ 3.09 (11)\\ 2.9 (3)\\ 3.0 (3)\\ 3.2 (3)\\ 2.6 (3)\\ 3.3 (3)\\ 2.7 (3)\\ 3.3 (3)\\ 2.7 (3)\\ 3.5 (4)\\ 4.9 (5)\\ 6.5 (6)\\ 6.7 (6)\\ 4.4 (5)\\ 3.5 (4)\\ 4.4 (5)\\ 5.6 (5)\\ 6.0 (5)\\ 7.6 (6)\\ 4.4 (5)\\ 5.6 (5)\\ 6.5 (6)\\ 4.7 (5)\\ 3.4 (4)\\ 4.6 (5)\\ 6.5 (5)\\ 6.5 (5)\\ 5.6 (5)\\ 5.6 (5)\\ 6.5 (6)\\ 4.7 (5)\\ 3.4 (4)\\ 4.6 (5)\\ 6.5 (5)\\ 5.5$	u33         3.61       (10)         3.23       (10)         3.28       (10)         5.1       (3)         3.7       (3)         3.8       (3)         5.1       (4)         3.6       (3)         5.1       (4)         3.6       (3)         5.4       (4)         4.0       (4)         4.0       (4)         3.6       (4)         3.6       (4)         3.6       (4)         3.6       (4)         3.6       (4)         3.6       (4)         3.6       (4)         3.7       (4)         4.7       (5)         3.7       (4)         6.4       (5)         5.3       (5)         3.4       (4)         4.2       (4)         4.3       (5)	u12 0.19 (10) 0.18 (10) 0.14 (10) 0.2 (3) 0.2 (3) -0.4 (3) 0.0 (3) -0.1 (3) 0.3 (3) -0.6 (4) -0.7 (5) -0.4 (5) 0.5 (4) 0.3 (4) 0.2 (5) -1.6 (5) 1.4 (5) 0.1 (4) 0.5 (4) -0.2 (5) -0.2 (5)	u13 0.94 (8) 0.78 (9) 0.79 (9) 1.2 (3) 1.7 (3) 0.9 (3) 1.4 (3) 1.1 (3) 1.3 (3) 1.4 (3) 1.4 (3) 1.4 (3) 1.4 (3) 1.4 (3) 1.5 (4) 1.5 (4) 1.5 (4) 1.5 (4) 1.7 (4) 1.7 (4)	u23 0.34 (9) 0.11 (9) 0.33 (9) 0.9 (3) 0.9 (3) 0.2 (3) -0.2 (3) -0.1 (3) -0.6 (3) 0.6 (3) 0.6 (3) 0.4 (3) -0.8 (4) -0.9 (4) 1.1 (4) 1.6 (4) 0.7 (4) -0.1 (3) 2.1 (4) 2.0 (4) 0.2 (5) 0.3 (4) 0.2 (4)
C34 C35 C36 C41	4.6 (5) 5.2 (5) 5.0 (5) 3.0 (4)	9.2 (7) 6.5 (6) 4.7 (5) 4.0 (4)	4.9       (4)         6.7       (5)         5.1       (5)         3.4       (4)	-1.4 (5) -0.7 (4) -0.5 (4)	2.5 (4) 2.5 (4) 1.7 (4) 0.9 (3)	$\begin{array}{c} 0.5 & (3) \\ 0.4 & (5) \\ -0.4 & (4) \\ -0.2 & (3) \end{array}$
C42	5.4 (5)	4.0 (5)	4.3 (4)	0.5 (4)	0.3 (4)	0.1 (4)
C43	6.2 (6)	5.8 (5)	5.1 (5)	-0.3 (5)	0.2 (4)	2.1 (5)
C44	5.6 (5)	8.1 (6)	3.5 (4)	-1.5 (5)	0.0 (4)	1.2 (5)
C45	6.4 ( 6)	7.3 (6)	3.7 (4)	0.5 (5)	0.3 (4)	-1.1 (4)
C46	5.5 ( 5)	4.6 (5)	4.3 (4)	1.0 (4)	0.2 (4)	0.1 (4)
C51	2.6 ( 4)	3.7 (4)	3.2 (4)	0.1 (3)	1.0 (3)	0.2 (4)
C52 C53 C54	3.7 (4) 4.9 (5)	3.9 (4) 6.3 (6) 7.5 (6)	3.6 (4) 3.6 (4) 3.5 (4)	0.3 (4) 0.0 (5) 0.0 (5)	0.6 (3) -0.2 (4) -0.2 (4)	-0.2 (4) -1.5 (4) 0.9 (5)
C55	3.9 (5)	4.5 (5)	5.8 (5)	0.1 (4)	1.0 (4)	1.7 (4)
C56	3.6 (4)	4.1 (5)	4.0 (4)	0.2 (4)	0.9 (3)	0.6 (4)
C61	2.2 (3)	4.1 (4)	5.8 (3)	-0.9 (3)	0.9 (3)	-0.2 (3)
C62	4.9 (4)	5.1 (5)	5.1 (4)	1.6 (4)	1.9 (4)	0.9 (4)
C63	5.8 (5)	7.2 (5)	7.1 (5)	1.1 (5)	3.1 (4)	0.9 (5)
C64	5.2 (5)	9.5 (6)	5.4 (5)	-0.7 (5)	2.2 (4)	0.4 (5)
C65	5.9 (5)	7.7 (6)	5.1 (4)	-0.1 (5)	2.1 (4)	2.2 (4)
C66	5.0 (4)	5.1 (5)	5.0 (4)	-0.3 (4)	2.2 (4)	0.7 (4)

. .

si(1)-N(1)	1.717(	5)	Si(3)-N(5)	1.742	(5)
$S_{1}(1) - N(2)$	1.744 (	5)	Si (3) -N (6)	1.716	(5)
$s_{1}(1) - C(11)$	1 880 (	3)	Si(3)-C(51	) 1.884	(3)
$S_{1}(1) = C(21)$	1 979 (	4)	$S_{1}(3) = C(6)$	1 1 878	(4)
$O_{1}^{2}(1) = O(21)$	1 730()		N(1)-N(2)	1 455	(6)
S1(2) - N(3)	1.733(3	5) 5)	N(2) - N(2) -	1 455	(6)
S1(2) - N(4)	I./IO(:	7) A)	n(2) - n(1) =	1 467	(0)
Si(2) - C(31)	1.875(	4)	N(3)-N(6)	1.403	(0)
Si(2)-C(41)	1.886(	3)	N (4) -N (5)	1.452	(6)
N(1)-Si(1)-N	(2)	110.12(23)	Si(1)-N(1)	-N (2) a	117.5(3)
N(1) = Si(1) = C	(11)	110.10(21)	Si(1)-N(2)	-N(1)a	112.5(3)
$W(1) = S_{2}^{2}(1) = C$	(21)	108 95(21)	Si(2)-N(3)	-N (6)	111.3(3)
$X(2) = e_1(1) = C$	(22)	107 10/201	Si (2) -N (4)	-N (5)	116.8(3)
N(2) = SI(1) = C	(++) /01)		Si (3) -N (5)	-N(4)	112.9(3)
R(2) = 51(1) = 0	(21)	112 AC(17)	Si (3) -N (6)	-N (3)	118.2(3)
		113.40(17)	si(1) - C(1)	1 - C(12)	118 4/31
N(3) - S1(2) - N	(4)	110.0/(24)		1 - C(16)	121 5/31
N(3)-S1(2)-C	(31)	107.34(20)		1 - C(22)	121 0 (3)
N(3)-S1(2)-C	(41)	107.77(21)	$c_{1}(1) = c_{1}(2)$	J = C(22)	110 0/31
N(4)-Si(2)-C	(31)	109.50(21)	51(1)-0(21	) = C(20)	119.0(3)
N(4)-Si(2)-C	(41)	109.11(21)	S1(2) - C(31)	)-0(32)	119.3(3)
C(31)-Si(2)-	C(41)	112.42(18)	Si (2) -C (31	)-C(36)	120.7(3)
N(5)-Si(3)-N	(6)	111.19(23)	Si (2) -C (41	)-C(42)	121.2(3)
N(5)-Si(3)-C	(51)	107.26(20)	Si(2)-C(41	)-C(46)	118.6(3)
N(5)-Si(3)-C	(61)	106.22(20)	si(3)-C(51	)-C(52)	118.6(3)
N(6)-Si(3)-C	(51)	109.75(21)	Si(3)-C(51	)-C(56)	121.2(3)
N(6) - Si(3) - C	(61)	109.37(21)	Si (3) -C (61	)-C(62)	118.5(3)
C(51) = C(2) = C	C (61)	113 00/171	Si (3)-C (61	)-C(66)	121.5(3)
C(21)-21(2)-	C(01)	**2.00/*//			
Atoms flagge	d 'a' :	are symmet:	y equivalents	s.	

Table AI & Selected bond distances	$(\mathbf{A})$ and bond angles	(degrees) for 9
Table AI.4 Selected bond distances	(A) and which angles	

N (2) a	-0.01907	0.72843	0.51463	-x	1-y	1-z
N(1)a	-0.02266	0.25911	0.49812	-x	1-y	1-z

125.8(3)	si2-C41-C46 118.6(3)
116.4(4)	C42-C41-C46 120.0(3)
113.5(3)	C41-C42-H42 120.0(4)
113.2(4)	C43-C42-H42 120.0(4)
114.7(3)	C42-C43-H43 120.0(5)
110.0(4)	C44-C43-H43 120.0(5)
131.9(4)	C43-C44-H44 120.0(5)
111.3(4)	C45-C44-H44 12G.0(5)
114.6(3)	C44-C45-H45 120.0(4)
117.3(4)	C46-C45-H45 120.0(4)
135.0(4)	C41-C46-H46 120.0(4)
105.9(4)	C45-C46-H46 120.0(5)
	125.8(3) 116.4(4) 113.5(3) 113.2(4) 114.7(3) 110.0(4) 131.9(4) 111.3(4) 114.6(3) 117.3(4) 135.0(4) 105.9(4)



	X	У	Ĩ	Beq
HN 1	0.028	0.898	0.489	3.7
HN 2	0.012	0.263	0.457	3.5
HN 3	0.154	0.258	0.381	3.5
HN 4	0.133	-0.371	0.343	3.7
HN 5	0.180	-0.230	0.296	3.5
HN 6	0.192	0.432	0.331	3.7
H12	0.068	0.747	0.571	4.1
H13	0.109	0.664	0.633	4.9
H14	0.147	0.294	0.650	4.8
H15	0.146	0.005	0.603	4.3
H16	0.105	0.088	0.541	4.0
H22	0.071	0.861	0.455	4.7
H23	0.128	0.912	0.420	5.2
H24	0.188	0.617	0.422	5.0
H25	0.190	0.272	0.459	6.0
H26	0.132	0.222	0.493	4.9
H32	0.074	0.348	0.378	4.4
H33	0.010	0.318	0.407	5.1
H34	-0.039	-0.029	0.399	5.6
H35	-0.023	-0.345	0.362	5.5
H36	0.041	-0.314	0.333	4.8
H42	0.068	0.469	0.293	4.5
H43	0.034	0.560	0.229	5.2
H44	0.034	0.271	0.183	5.5
H45	0.068	-0.108	0.201	6.0
H46	0.103	-0.198	0.264	4.6
H52	0.234	0.253	0.411	4.0
H53	0.274	0.159	0.473	4.9
H54	0.312	-0.217	0.488	5.2
H55	0.308	-0.498	0.440	4.4
H56	0.267	-0.404	0.378	4.0
H62	0.297	-0.271	0.335	4.7
H63	0.354	-0.245	0.299	6.2
H64	0.353	0.089	0.260	6.0
H65	0.295	0.396	0.257	5.8
H66	0.238	0.369	0.293	4.8

Phenyl hydrogens were calculated then included as part of the phenyl rigid groups. Other hydrogens were located in a difference map then normalized to a N-H distance of 1.08A and not refined.

## APPENDIX II

Formula	Si <sub>2</sub> N <sub>4</sub> C <sub>26</sub> H <sub>28</sub>
Fw	452.70
Cryst Size, mm	0.40x0.25x0.23
Cryst System	monoclinic
Space Group	P21/n
a, Å	10.691(4)
b, Å	13.178(4)
c, Å	17.812(3)
β, deg	95.11(7)
V, Å <sup>3</sup>	2499.5(13)
Z	4
dcalcd, g cm <sup>-3</sup>	1.203
F(000)	964.22
temp, °C	20
$\mu$ (Mo-K $\alpha$ ), mm <sup>-1</sup>	1.43
20 <sub>max</sub>	110.0
Scan type	ω/2θ
hkl range	-8/8, 0/13, 0/18
Measured reflcts	2924
Unique reflcts	2724
Observed reflcts (>2.5 $\sigma$ )	2024
Refined parameters	298
R <sub>int</sub>	2.9%
k	0.000050
R	0.054
Rw	0.051
GoF	2.66
$\Delta \rho_{\text{max/min}}, eÅ^{-3}$	0.280/-0.310

Table AII.1 Crystal data and data collection parameters for 23.

$$\begin{split} R &= \sum [|F_0| - |F_c|] / \sum |F_0| \\ w &= 1 / (\sigma^2 |F_0| + \kappa F_0^2) \\ R_w &= [\sum w (|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2} \\ G_0F &= [\sum w (|F_0| - |F_c|)^2 / (n - v)]^{1/2} \end{split}$$

Table AII.2 Atomic coordinates and isotropic thermal parameters for 23

	x	У	Z	Beq
Si 1	0.95621(13)	0.97867(10)	0.22405(7)	4.09(7)
Si 2	1.24080(14)	1.08507(9)	0.25600(7)	3.99(6)
N 1	0.9937 (4)	1.1047 (3)	0.21236(21)	4.72 (23)
N 2	1.0965 (4)	0.9158 (3)	0.23958 (23)	4.45 (20)
N 3	1.1923 (4)	0.9688 (3)	0.28650(13)	4.24(19)
N 4	1.1182 (4)	1.1291 (3)	0.19553(25)	4.56(23)
C 1	0.9111 ( 5)	1.1915 (4)	0.2154 (3)	6.0 (3)
C 2	1.2529 (5)	0.9077 (4)	0.3464 (3)	5.7 (3)
С 3	0.8565 ( 5)	0.9728 ( 3)	0.30441(25)	4.2 (3)
C 4	0.9097 ( 5)	0.9773 (4)	0.3783 ( 3)	6.3 (3)
C 5	0.8363 (7)	0.9766 ( 5)	0.4385 ( 3)	7.9 (4)
C 6	0.7083 ( 8)	0.9719 ( 5)	0.4272 ( 4)	7.2 (4)
C 7	0.6520 ( 6)	0.9676 ( 5)	0.3550 ( 4)	7.2 (4)
C 8	0.7273 ( 6)	0.9680 ( 4)	0.2947 ( 3)	6.0 (3)
C 9	0.8725 ( 5)	0.9160 ( 4)	0.1400 ( 3)	4.61(25)
C10	0.8122 ( 5)	0.8229 ( 4)	0.1462 ( 3)	5.7 (3)
C11	0.7490 ( 6)	0.7782 ( 5)	0.0826 ( 4)	8.1 (4)
C12	0.7445 ( 7)	0.8270 ( 8)	0.0125 ( 5)	9.7 (5)
C13	0.8040 ( 7)	0.9170 ( 6)	0.0072 ( 3)	8.6 (4)
C14	0.8685 ( 5)	0.9618 ( 4)	0.0694 (3)	5.9 (3)
C15	1.3778 ( 4)	1.0824 ( 4)	0.19908(24)	4.05(23)
C16	1.4092 ( 5)	0.9926 ( 4)	0.1626 ( 3)	4.8 (3)
C17	1.5044 ( 6)	0.9899 ( 5)	0.1152 ( 3)	5.8 (3)
C18	1.5713 ( 5)	1.0758 ( 5)	0.1019 ( 3)	6.0 (3)
C19	1.5438 ( 5)	1.1656 ( 4)	0.1381 ( 3)	5.6 (3)
C20	1.4489 ( 5)	1.1687 ( 4)	0.1852 ( 3)	4.8 (3)
C21	1.2706 ( 5)	1.1636 ( 3)	0.34312(25)	4.3 (3)
C22	1.1694 ( 5)	1.1986 ( 4)	0.3789 (3)	5.8 (3)
C23	1.1863 ( 7)	1.2529 ( 4)	0.4461 ( 3)	7.3 (4)
C24	1.3050 ( 8)	1.2720 (4)	0.4771 ( 3)	7.2 (4)
C25	1.4087 ( 6)	1.2397 (5)	0.4437 (3)	7.1 (3)
C26	1.3901 ( 6)	1.1857 ( 4)	0.3759(3)	5.8 (3)
HN2	1.130 (5)	0.875 (4)	0.202 (3)	7.3 (15)
HN4	1.122 (5)	1.139 ( 4)	0.146 ( 3)	7.9 (17)

Beq is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For hydrogen atoms, Beq = Biso.

## Table AII.3 Anisotropic thermal parameters [u(i,j)x100] for 23

	<b>ull</b>	u22	u33	<b>u12</b>	<b>u13</b>	u23
Si l	5.51(11)	4.72(9)	5.14(8)	-0.20( 8)	-0.36(7)	-0.07(6)
Si 2	5.47(11)	4.19(8)	5.44(8)	-0.16( 8)	0.25(7)	-0.52( 6)
Nl	5.6 (3)	4.5 (3)	7.8 (3)	0.2 (3)	0.62(25)	0.59(21)
N 2	5.6 (3)	4.46(24)	6.5 (3)	0.08(24)	-1.00(25)	-0.79(21)
N 3	5.8 (3)	4.71(24)	5.38(23)	-0.66(23)	-1.04(22)	0.51(19)
N 4	6.1 (4)	5.4 (3)	5.8 (3)	-0.08(23)	0.6 (3)	0.45(22)
C 1	6.8 (4)	5.4 (3)	10.4 (4)	2.0 (3)	0.2 (3)	0.4(3)
C 2	7.8 (4)	5.8 (3)	7.7 (4)	-0.2(3)	-2.0 (3)	0.8 (3)
С З	5.6 (4)	5.3 (3)	5.0 (3)	-0.4 (3)	-0.2 (3)	-0.10(23)
C 4	7.0 (4)	10.9 ( 5)	6.1 (4)	-0.7 (4)	0.1 (4)	-0.1 (3)
C 5	10.5 ( 6)	12.7 (6)	6.5 (4)	-0.3 (5)	-0.2 (4)	-0.3 (4)
C 6	10.3 ( 6)	9.6 (5)	7.6 (4)	-1.3(5)	2.5 (4)	-0.3 (4)
C 7	6.4 (5)	10.2 (5)	11.0 (5)	-0.8 (4)	1.9 (5)	-0.9 ( 4)
C 8	6.1 (5)	9.0 (4)	7.3 (4)	-0.5 (4)	-0.4 (4)	-0.3 (3)
C 9	5.6 (4)	6.2 (3)	5.5 (3)	0.8 (3)	-0.3 (3)	-0.6 (3)
C10	6.4 (4)	7.6 (4)	7.4 (4)	-0.9 (3)	-0.3 (3)	-1.9(3)
C11	6.9 (5)	10.4 ( 5)	13.2 (6)	-1.0(4)	-0.6 (5)	-6.2 (5)
C12	7.4 (6)	17.5 ( 9)	11.1 (6)	3.9 (6)	-3.5 (5)	-8.4 (7)
C13	11.2 (7)	15.2 (7)	5.6 (4)	6.7 (6)	-2.5 (4)	-2.7 (5)
C14	8.5 (5)	7.6 (4)	6.0 (3)	2.8 (3)	-0.3 (3)	-0.2 (3)
C15	4.7 (4)	5.4 (3)	5.2 (3)	0.1(3)	0.0(3)	-0.4 (3)
C16	5.7 (4)	6.1 (3)	6.5 (3)	0.4(3)	0.2 (3)	-0.7 (3)
C17	7.2 (5)	8.1 (4)	7.0 (4)	2.1(4)	1.2 (3)	-1.0(3)
C18	6.1 (5)	10.2 (5)	6.9 (4)	1.8(4)	1.1 (3)	1.4 ( 4)
C19	5.5 (4)	7.9 (4)	8.0 (4)	0.1(4)	1.2 (3)	1.3 (3)
C20	5.0 (4)	6.2 (4)	6.9 (3)	0.2(3)	-0.2 (3)	0.0 (3)
C21	6.2 (4)	4.7 (3)	5.5 (3)	-0.6(3)	1.0 (3)	-0.24 (24)
C22	8.1 (5)	8.0 (4)	6.0 (3)	1.1 (4)	0.9 (3)	-1.4 (3)
C23	12.4 (6)	8.0 ( 4)	7.5 (4)	1.9 (4)	1.9 (4)	-2.2 (3)
C24	13.9 (7)	6.6 (4)	6.7 (4)	-2.7 (5)	0.3 (5)	-2.2 (3)
C25	10.2 ( 6)	9.7 (5)	6.8 (4)	-4.6 (4)	0.1 (4)	-1.5 (3)
C26	7.2 (5)	8.1 (4)	6.9 (4)	-2.3 (4)	0.8 (3)	-1.1 (3)
				· ·	• • •	/

152

Si (1) -N (1) 1.72 Si (1) -N (2) 1.71 Si (1) -C (3) 1.80 Si (1) -C (9) 1.80 Si (2) -N (3) 1.72 Si (2) -N (4) 1.72 Si (2) -C (15) 1.85 Si (2) -C (21) 1.80 N (1) -N (4) 1.42 N (1) -C (1) 1.44 N (1) -C (1) 1.44 N (2) -N (3) 1.44 N (3) -C (2) 1.44 C (3) -C (2) 1.44 C (3) -C (4) 1.38 C (3) -C (8) 1.37 C (4) -C (5) 1.38 C (5) -C (6) 1.36 C (6) -C (7) 1.37 C (7) -C (8) 1.39	25 (4) 4 (4) 51 (5) 57 (5) 22 (4) 21 (4) 54 (5) 59 (5) 28 (7) 19 (6) 13 (5) 13 (6) 38 (7) 78 (9) 55 (9) 56 (11) 72 (10) 88 (10)	$\begin{array}{c} C(9) - C(10) & 1 \\ C(9) - C(14) & 1 \\ C(10) - C(11) & 1 \\ C(11) - C(12) & 1 \\ C(12) - C(13) & 1 \\ C(12) - C(13) & 1 \\ C(13) - C(14) & 1 \\ C(15) - C(16) & 1 \\ C(15) - C(20) & 1 \\ C(15) - C(20) & 1 \\ C(16) - C(17) & 1 \\ C(17) - C(18) & 1 \\ C(18) - C(19) & 1 \\ C(19) - C(20) & 1 \\ C(21) - C(22) & 1 \\ C(21) - C(22) & 1 \\ C(21) - C(23) & 1 \\ C(23) - C(23) & 1 \\ C(23) - C(25) & 1 \\ C(25) - C(26) & 1 \\ \end{array}$	395 (8) 391 (7) 396 (8) 402 (13) 353 (14) 385 (9) 406 (7) 402 (8) 379 (9) 371 (10) 392 (9) 373 (9) 383 (8) 388 (8) 393 (8) 361 (11) 372 (11) 400 (8)
N(1) -Si(1) -N(2) N(1) -Si(1) -C(3) N(1) -Si(1) -C(3) N(2) -Si(1) -C(9) N(2) -Si(1) -C(9) C(3) -Si(2) -C(3) N(3) -Si(2) -C(15) N(3) -Si(2) -C(21) N(4) -Si(2) -C(21) N(4) -Si(2) -C(21) N(4) -Si(2) -C(21) C(15) -Si(2) -C(21) Si(1) -N(1) -N(4) Si(1) -N(1) -C(1) N(4) -N(1) -C(1) Si(1) -N(1) -C(1) Si(2) -N(3) -C(2) Si(2) -N(3) -C(2) Si(2) -N(3) -C(2) Si(2) -N(3) -C(2) Si(2) -N(3) -C(2) Si(2) -N(3) -C(2) Si(1) -C(3) -C(4) Si(1) -C(3) -C(8) C(4) -C(3) -C(6) C(4) -C(5) -C(6) C(5) -C(6) -C(7)	105.98(21) 106.75(21) 115.40(21) 114.11(22) 105.40(21) 105.28(21) 105.28(21) 105.37(19) 104.98(22) 113.37(23) 112.32(23) 112.32(23) 118.2(3) 127.3(4) 114.4(4) 115.2(3) 127.0(3) 117.7(3) 120.9(4) 122.8(4) 116.3(5) 121.4(5) 121.0(5) 119.3(6)	C(6) - C(7) - C(8) $C(3) - C(8) - C(7)$ $Si(1) - C(9) - C(7)$ $Si(1) - C(9) - C(7)$ $C(10) - C(9) - C(7)$ $C(10) - C(10) - C(7)$ $C(10) - C(10) - C(7)$ $C(10) - C(11) - C$ $C(11) - C(12) - C$ $C(12) - C(13) - C$ $C(12) - C(13) - C$ $C(9) - C(14) - C(7)$ $Si(2) - C(15) - C$ $C(16) - C(17) - C$ $C(16) - C(17) - C$ $C(16) - C(17) - C$ $C(17) - C(18) - C$ $C(15) - C(20) - C$ $Si(2) - C(21) - C$ $Si(2) - C(21) - C$ $C(22) - C(23) - C$ $C(22) - C(23) - C$ $C(24) - C(25) - C$ $C(21) - C(26) - C$	119.1(6) 122.9(5) 10) 121.2(4) 14) 120.4(4) 14) 118.4(4) 11) 120.1(5) (12) 120.3(6) (13) 119.1(6) (14) 121.4(6) 13) 120.8(6) (16) 120.1(4) (20) 123.3(4) (20) 116.5(5) (17) 121.6(5) (19) 119.1(5) (20) 120.4(5) (19) 121.7(5) (20) 120.4(5) (19) 121.7(5) (20) 120.4(5) (19) 121.7(5) (20) 120.4(5) (19) 121.7(5) (20) 121.7(4) (23) 121.3(5) (24) 119.3(6) (25) 121.8(5) (26) 118.2(6) (25) 121.6(5)
Si(1)-N(2)-HN(2) N(1)-N(4)-HN(4) Si(2)-N(4)-HN(4) N(3)-N(2)-HN(2)	122.6(4) 111.4(4) 124.4(4) 112.7(4)		

.

-

## Table AII.4 Selected bond distances (Å) and bond angles (degrees) for 23

x	У	z	Biso
0.945	1.247	0.259	6.9
0.897	1.233	0.162	6.9
0.816	1.168	0.229	6.9
1.184	0.879	0.385	6.4
1.300	0.842	0.326	6.4
1.322	0.951	0.382	6.4
1.016	0.980	0.390	7.3
0.882	0.980	0.497	7.9
0.652	0.973	0.478	7.5
0.545	0.964	0.345	7.8
0.678	0.963	0.236	6.7
0.814	0.782	0.202	6.6
0.697	0.703	0.085	8.6
0.697	0.793	-0.039	9.7
0.801	0.958	-0.049	8.8
0.921	1.035	0.064	6.7
1.355	0.921	0.173	5.6
1.524	0.917	0.086	6.5
1.648	1.073	0.062	6.8
1.600	1.235	0.128	6.8
1.429	1.242	0.213	5.5
1.072	1.182	0.352	6.7
1.102	1.278	0.477	7.7
1.317	1.316	0.528	6.6
1.504	1.257	0.473	7.4
1.475	1.158	0.348	6.3
	x 0.945 0.897 0.616 1.184 1.300 1.322 1.016 0.882 0.652 0.545 0.678 0.678 0.697 0.697 0.697 0.697 0.697 0.801 0.921 1.355 1.524 1.648 1.600 1.429 1.072 1.102 1.317 1.504 1.475	xy0.9451.2470.8971.2330.6161.1681.1840.8791.3000.8421.3220.9511.0160.9800.6820.9800.6520.9730.5450.9640.6780.9630.8140.7820.6970.7030.6970.7930.8010.9580.9211.0351.3550.9211.5240.9171.6481.0731.6001.2351.4291.2421.0721.1821.1021.2781.3171.3161.5041.2571.4751.158	$\mathbf{x}$ $\mathbf{y}$ $\mathbf{z}$ 0.9451.2470.2590.8971.2330.1620.6161.1680.2291.1840.8790.3851.3000.8420.3261.3220.9510.3821.0160.9800.3900.8820.9800.4970.6520.9730.4780.5450.9640.3450.6780.9630.2360.8140.7820.2020.6970.7030.0850.6970.793-0.0390.8010.958-0.0490.9211.0350.0641.3550.9210.1731.5240.9170.0861.6481.0730.0621.6001.2350.1281.4291.2420.2131.0721.1820.3521.1021.2780.4771.3171.3160.5281.5041.2570.4731.4751.1580.348

Hydrogen positions calculated assuming C-H of 1.08A. Biso(H) is from Uiso(H) = Ueq(C) + 0.01.

### APPENDIX III X-RAY CRYSTAL STRUCTURE ANALYSIS OF Ph<sub>2</sub>Si(NHNHMe)<sub>2</sub> (14)

Formula	SiN <sub>4</sub> C <sub>14</sub> H <sub>20</sub>
Fw	272.42
Cryst Size, mm	0.5x0.5x0.45
Cryst System	monoclinic
Space Group	P21/c
a, Å	7.7725(5)
b, Å	9.1289(9)
c, Å	21.2624(17)
β, deg	91.814(7)
V, Å <sup>3</sup>	1507.90(21)
Z	4
d <sub>calcd</sub> , g cm <sup>-3</sup>	1.200
F(000)	584.46
temp, *C	20
μ(Mo-Kα), mm <sup>-l</sup>	0.14
20 <sub>max</sub>	44.9
Scan type	ω/2θ
hkl range	-8/8, 0/9, 0/22
Measured reflcts	2140
Unique reflcts	1971
Observed reflets (>2.5 o)	1469
Refined parameters	173
R <sub>int</sub>	1.4%
κ	0.000050
R	0.054
Rw	0.056
GoF	2.67
Δρ <sub>max/min</sub> , eÅ-3	0.320/-0.450

Table AIII.1 Crystal data and data collection parameters for 14.

$$\begin{split} & R = \sum [iF_0| - |F_c|] / \sum |F_0| \\ & w = 1 / (\sigma^2 |F_0| + \kappa F_0^2) \\ & R_w = [\sum w (|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2} \\ & \text{GoF} = [\sum w (|F_0| - |F_c|)^2 / (n - \nu)]^{1/2} \end{split}$$

	x	У	I	Beq
Si	0.64324(16)	0.35956(14)	0.09176( 6)	3.71(6)
N 1	0.4892 ( 5)	0.2259 (4)	0.09331(16)	4.39(18)
N 2	0.6909 ( 5)	0.4162 (4)	0.01865(16)	4.29(18)
N 3	0.3312(5)	0.2467 (4)	0.05904(18)	4.69(19)
N 4	0.7483 (5)	0.3070 (4)	-0.02473(18)	5.13(21)
C 1	0.2938 (7)	0.1204 (6)	0.01927(24)	6.0(3)
Č 2	0.9020 ( 6)	0.3525 (6)	-0.05528 (23)	6.0 (3)
Č11	0.5699 (5)	0.5290 (5)	0.13286(19)	3.53(21)
C12	0.4325 (6)	0.5202(5)	0.17304 (22)	4.80(24)
C13	0.3728 (7)	0.6426 (7)	0.20412(23)	6.1 (3)
C14	0.4488 (8)	0.7771 ( 6)	0.1963 (3)	5.9 (3)
C15	0.5846 (7)	0.7876 (5)	0.1572 (3)	5.5 (3)
C16	0.6444 (6)	0.6654 (5)	0.12595(22)	4.6 (3)
č21	0.8312 (5)	0.2738 (5)	0.13515(19)	3.65 (20)
C22	0.8894 (6)	0.1338 (5)	0.12161(22)	4.8 (3)
C23	1.0286 (7)	0.0725 (5)	0.1544 (3)	5.9 (3)
C24	1,1141 ( 6)	0.1513 (7)	0.2011 (3)	5.6 (3)
c25	1,0602 ( 6)	0.2897 (6)	0.21605(22)	5.1 (3)
C26	0.9202 ( 6)	0.3503 ( 5)	0.18307(21)	4.46 (22)

Beq is the mean of the principal axes of the thermal ellipsoid.

# Table AIII.3 Anisotropic thermal parameters [u(i,j)x100] for 14

	ull	u22	u33	<b>u12</b>	<b>u13</b>	u23
Si	4.55(8)	4.73(8)	4.81(8)	0.14(7)	0.18( 6)	0.16(7)
N 1	5.22 (25)	4.47(23)	6.9 (3)	-0.66(20)	-1.02(21)	0.90 (20)
N 2	6.4 (3)	4.85(23)	5.05(23)	1.11(21)	0.75 (20)	0.08(19)
N 3	5.3 (3)	4.10(23)	8.3 (3)	0.44(22)	-1.39 (22)	-0.44(21)
N 4	8.1 (3)	4.64 (24)	6.8 (3)	-0.66(24)	1.05(24)	-0.87(22)
c i	7.5 ( 4)	6.9 (4)	8 1 (4)	-0.3 (3)	-1.3 (3)	-0.8 (3)
č 2	5.6 (3)	9.3 (4)	8 0 ( 4)	0.5 (3)	2.0(3)	-1.5 (3)
či i	4.0 (3)	5 0 (3)	4 3 ( 3)	0 32 (24)	0.01(22)	0 30 (23)
c12	6.1 (3)	6 2 (3)	61 (3)	-0.4 (3)	0.9 (3)	-0 4 (3)
CI3	7 1 ( 4)	9 4 ( 4)	6 6 ( 4)	0.6 (4)	1.8 (3)	-1 6 (4)
C14	76(4)		73 (4)	19(4)	-05 (3)	-2 0 ( 3)
C15		5 1 ( 3)	8 8 ( 4)	0 0 ( 3)		-05/3)
C1 6	5 1 ( 3)	5 4 ( 3)	7 1 ( 3)			
C21				-0 47 (25)	0 30 (23)	0 72 ( 22)
C41					0.33(23)	0.12(23)
622 633		4.0 (3)				
C23	7.5 (4)	5.0 (3)	TO O ( 5)	1.3 (3)	0.7(3)	1.5 (3)
C24	5.4 (3)	8.3 (4)	7.7 (4)	0.5 (3)	0.1 (3)	3.0 (3)
C25	5.6 (3)	7.3 (4)	6.2 (3)	-0.2 (3)	-0.6 (3)	1.0 (3)
C76	54(3)	56(3)	59/31		<b>D 3 / 3</b> )	03/31

Si-N(1) 1.710	(4)	C(12) - C(13)	1.385	(8)
Si-N(2) 1.690	(4)	C(13) - C(14)	1.375	(9)
Si-C(11) 1.874	(5)	C(14) - C(15)	1.366	(9)
Si-C(21) 1.874	(4)	C(15) - C(16)	1.387	(7)
N(1) - N(3) = 1.421	(5)	C(21) - C(22)	1.389	(7)
N(2) - N(4) = 1.439	(5)	C(21) - C(26)	1.400	(6)
N(3) - C(1) = 1.454	(6)	c(22) - c(23)	1.387	(7)
N(4) = C(2) 1 439	(6)	C(23) - C(24)	1.380	(9)
C(11) = C(12) + 1 + 391	(7)	C(24) - C(25)	1.372	(8)
C(11) - C(16) = 1 - 382	(7)	C(25) = C(26)	1.390	(7)
C(11) C(10) 1.302	\ * I	0(10) 0(10)	2.020	~ ~ ~
N(1) = Si = N(2)	114.18(18)	C(11) - C(12) -	C (13)	121 4/51
N(1) - Si - C(11)	110 89(19)	C(12) - C(13) - C(13	C(13)	120 7/5
N(1) = Si = C(21)	103 17(18)	C(13) - C(14) -	C(135)	120.7(3)
N(1) = 01 = 0(21) N(2) = 01 = 0(11)	104 78(10)	C(13) = C(14) = C(14		120.0(3)
$N(2) = S_{1} = C(11)$	112 08(18)	C(14) - C(15) - C(15		120.0(3)
R(2) = 31 = C(21)	112.90(10)	C(11) = C(10) = C(2)	0 (TO)	122.7(4)
C(11) - S1 - C(21)	110 3/3/	Si = C(21) = C(2)	2)	122.4(3)
SI = N(I) = N(S)	117 2 (3)	31 - 0(21) - 0(21) = 0		120.6(3)
S1 - N(2) - N(4)	110 2(3)	C(22) = C(21) = C(21) = C(22)		117.0(4)
N(1) = N(3) = C(1)	110.2(3)	C(21) - C(22) - C(22	C(23)	121.4(4)
N(2) = N(4) = C(2)	111.0(3)	C(22) - C(23) - C(23	C(24)	120.1(5)
$S_1-C(11)-C(12)$	113.3(2)	C(23)-C(24)-	C(25)	120.2(5)
$S_1-C(11)-C(16)$	124.0(3)	C(24) -C(25) -	C(26)	119.3(5)
C(12) - C(11) - C(16)	116.7(4) •	C(21)-C(26)-	°C (25)	122.0(4)

	x	У	Z	Biso
HN1	0.510	0.128	0.121	5.2
HN2	0.681	0.530	0.005	5.1
HN3	0.250	0.342	0.060	5.5
HN4	9.684	0.203	-0.033	5.9
H 1A	0.397	0.103	-0.013	6.7
H 1B	0.284	0.023	0.048	6.7
H 1C	0.175	0.133	-0.008	6.7
H 2A	0.877	0.452	-0.082	6.8
H 2B	1.005	0.374	-0.021	6.8
H 2C	0.944	0.271	-0.088	6.8
H12	0.370	0.416	0.180	5.6
H13	0.267	0.632	0.236	6.9
H14	0.400	0.872	0.220	6.7
H15	0.646	0.892	0.151	6.3
H16	0.752	0.676	0.095	5.4
H22	0.826	0.072	6.084	5.6
H23	1.074	-0.936	0.143	6.7
H24	1.222	0.103	0.227	6.4
H25	1.128	0.350	0.253	5.8
H26	0.878	0.460	0.195	5.3

Hydrogen positions calculated assuming C/N-H distance of 1.08A. Biso(H) is from Uiso(H) = Ueq(C/N) + 0.01.

# APPENDIX IV X-RAY CRYSTAL STRUCTURE ANALYSIS OF [Ph<sub>2</sub>Si(NHNHMe)]<sub>2</sub>O (21)

Formula	Si <sub>2</sub> N <sub>4</sub> OC <sub>26</sub> H <sub>30</sub>
Fw	470.72
Cryst Size, mm	0.40x0.25x0.10
Cryst System	monoclinic
Space Group	$P2_{1}/n$
a, Å	10.3200(19)
b, Å	7.3343(20)
c, Å	16.658(3)
β, deg	94.013(15)
V, Å <sup>3</sup>	1257.7(5)
Z	2
d <sub>calcd</sub> , g cm <sup>-3</sup>	1.243
F(000)	500.44
temp, <sup>•</sup> C	20
$\mu$ (Mo-K $\alpha$ ), mm <sup>-1</sup>	0.16
20 <sub>max</sub>	45.0
Scan type	ω/2θ
hkl range	-11/11, 0/7, 0/17
Measured reflcts	1751
Unique reflcts	1646
Observed reflets (>2.5 $\sigma$ )	1017
Refined parameters	152
R <sub>int</sub>	1.2%
κ	0.00005
R	0.047
Rw	0.044
GoF	1.38
Δp <sub>max/min</sub> , eÅ-3	0.210/-0.270

Table AIV.1 Crystal data and data collection parameters for 21.

$$\begin{split} &R = \sum [|F_0| - |F_c|] / \sum |F_0| \\ &w = 1 / (\sigma^2 |F_0| + \kappa F_0^2) \\ &R_w = [\sum w (|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2} \\ &GoF = [\sum w (|F_0| - |F_c|)^2 / (n - \nu)]^{1/2} \end{split}$$

	x	Y	ĩ	Beq
Si	0.65554(12)	0.52349(17)	0.01229( 7)	2.52(5)
0	1/2	1/2	0	3.71 (22)
N 1	0.7327 (4)	0.3293 (5)	0.04342(22)	3.41(19)
N 2	0.7156 (4)	0.1804 (5)	-0.01172(24)	4.06 (22)
C 1	0.8375 ( 6)	0.1104 (7)	-0.0341 (3)	5.7 (3)
C 2	0.6962 (5)	0.7002 ( 6)	0.0915 (3)	2.78 (21)
C 3	0.8246 (5)	0.7381 (7)	0.1162(3)	3.69(24)
C 4	0.8563 (5)	0.8755 (8)	0.1710(3)	4.8 (3)
C 5	0.7605 (6)	0.9767 (8)	0.2023 (3)	4.6 (3)
C 6	0.6325 (6)	0.9412 (7)	0.1789(3)	4.5 (3)
C 7	0.5996(4)	0.8039 ( 6)	0.1239 (3)	3.36(22)
C 8	0.7150(4)	0.6016 ( 6)	-0.0850 (3)	2.72(20)
<b>C</b> 9	0.8477 (5)	0.6013 ( 6)	-0.0953 (3)	3.43(23)
C10	0.8975 (5)	0.6733 (7)	-0.1645 (3)	4.2 (3)
C11	0.8133 ( 6)	0.7491 (8)	-0.2233 (3)	4.8 (3)
C12	0.6836 ( 6)	0.7499 (8)	-0.2141 (3)	4.7 (3)
C13	0.6342 (5)	0.6782 (7)	-0.1452 ( 3)	3.93(24)

Beq is the mean of the principal axes of the thermal ellipsoid.

# Table AIV.3 Anisotropic thermal parameters [u(i,j)x100] for 21

.

.

	<b>u11</b>	u22	<b>u33</b>	<b>u12</b>	<b>u13</b>	u23
si	3.06(7)	2.92(7)	3.63(7)	0.07(7)	0.55(5)	-0 01 ( 7)
0	3.20(25)	4.8 (3)	6.1 ( 3)	-0.3 (3)	0 59 (22)	
N 1	5.2 (3)	3.55 (24)	4.16(23)	0 83 (21)	-0.30(21)	-0.0 (3)
N 2	5 4 ( 3)	3 09 (24)	6 9 ( 3)	0 44 (22)		0.03(20)
<u>c</u> 1	7314	5 1 / 3	0 5 ( 5)		0.09(25)	0.00(22)
čż				1.0 ( 3)	2.4 (4)	-1.2 (3)
		3.3 (3)	3.1 ( 3)	0.1 (3)	0.81(23)	0.13(21)
6.3	4.3 (3)	4.0 (3)	5.0 (3)	-0.2 (3)	0.2 (3)	-1.4 (3)
C 4	5.6 (4)	6.3 (4)	6.1 (4)	-1.0 ( 3)	-0.2 (3)	-0.9 (3)
C 5	8.2 (4)	4.8 (3)	4.3 (3)	-0.8 ( 4)	-0.1(3)	-0.5 (3)
C 6	7.7 (4)	5.4 (4)	4.2 (3)	1.2 (3)	1.5 (3)	-0.9 (3)
C 7	4.2 (3)	4.4 (3)	4.2 (3)	0.6 (3)	0.6 (3)	0.29/251
C 8	4.0 (3)	2.9 (3)	3.5 (3)	0.25 (24)	0.84 (24)	-0 35(22)
C 9	4.6 (3)	3.9 (3)	4.6 (3)	-0.1 (3)	12(3)	0.02(25)
C10	5.6 (4)	5.2 (4)	5.4 ( 3)	-0.7 (3)	25 (3)	
<b>C11</b>	9.0 ( 5)	4.9 ( 3)	AGIA	-0 6 ( 4)		
<b>C12</b>	8014	5 6 / 4				1.1 (3)
<b>C13</b>		5 2 / 2			0.5 (3)	1.7 (3)
<b>673</b>	<b>-</b> , ( )	J.Z ( 3)	2.7 (2)	V.0 (3)	U.6 (3)	0.6 (3)

.-
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	31 (13) 5 (4) 6 (5) 3 (4) 31 (13) 0 (5) 2 (7) 8 (7) 2 (6) 3 (7)	C(4)-C(5) C(5)-C(6) C(6)-C(7) C(8)-C(9) C(8)-C(13) C(9)-C(10) C(10)-C(11) C(11)-C(12) C(12)-C(13)	1.369(8) 1.376(9) 1.388(7) 1.392(7) 1.378(7) 1.397(7) 1.380(8) 1.358(9) 1.391(7)	
O-Si-N(1) O-Si-C(2) O-Si-C(8) N(1)-Si-C(2) N(1)-Si-C(8) C(2)-Si-C(8) Si-O-Sia Si-N(1)-N(2) N(1)-N(2)-C(1) Si-C(2)-C(3) Si-C(2)-C(7) C(3)-C(2)-C(7)	113.02(15) 109.54(15) 107.93(16) 106.75(20) 110.37(19) 109.18(19) 180.0 114.3(3) 111.7(4) 120.6(3) 121.3(4) 118.1(4)	C(3)-C C(4)-C C(5)-C C(2)-C Si-C(8) Si-C(8) C(9)-C C(8)-C C(8)-C C(9)-C C(10)-C C(11)-C C(8)-C	(4) -C (5) (5) -C (6) (6) -C (7) (7) -C (6) ) -C (9) ) -C (13) (8) -C (13) (9) -C (10) (10) -C (11) C (11) -C (12) C (12) -C (13) (13) -C (12)	120.2(5) 119.6(5) 120.6(5) 120.2(4) 119.6(3) 122.6(3) 117.5(4) 121.6(5) 119.2(5) 119.9(5) 120.8(5) 121.1(5)

symmetry	equivalent of	Si				
Sia	0.34446	0.47651	-0.01229	1.000-x	1.000-y	-1

## Table AIV.5 Hydrogen atom parameters for 21

	x	У	Ľ	Beq
HN1	0.790	0.308	0.099	4.3
HN2	0.659	0.078	0.017	5.0
H 1 <b>A</b>	0.889	0.216	-0.064	6.6
H 1B	0.898	0.064	0.017	6.6
H 1C	0.822	-0.001	-0.076	6.6
н З	0.900	0.658	0.092	4.5
н 4	0.957	0.905	0.189	5.5
H 5	0.783	1.084	0.246	5.3
н 6	0.558	1.021	0.205	5.3
H 7	0.498	0.777	0.107	4.2
H 9	0.913	0.545	-0.049	4.2
H10	1.000	0.671	-0.173	5.1
H11	0.853	0.809	-0.276	5.7
H12	0.618	0.802	-0.262	5.6
н13	0.531	0.682	-0.139	4.7

Hydrogen positions calculated assuming C/N-H distance of 1.08A. Biso(H) is from Uiso(H) = 0.01 + Ueq(C/N).