SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF SILYLBIGUANIDES

By

SAMPRIYA N.

Submitted

in fulfillment of the requirements of the degree of

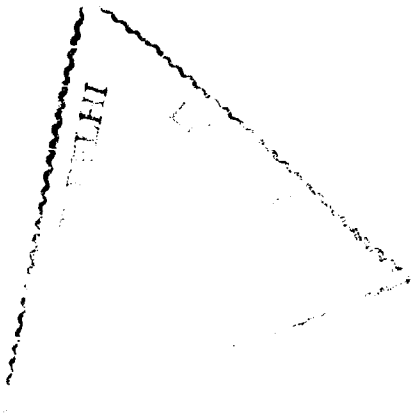
DOCTOR OF PHILOSOPHY

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

January 2003

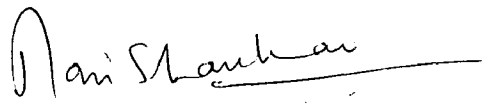


To My Achchan & Amma To Whom I Shall Remain Indebted For Setting The Foundation

CERTIFICATE

This is to certify that the thesis entitled, "Synthesis, Characterization and Reactivity of Silylbiguanides", being submitted by Ms. Sampriya N. to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy is a bonafide research work carried out by her. Ms. Sampriya N. has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in this thesis have not been submitted, in part or in full to other University or Institute for the award of any degree or diploma.



(Ravi Shankar)

Associate Professor
Department of Chemistry
Indian Institute of Technology
New Delhi-110016
INDIA

ACKNOWLEDGEMENTS

Over the past few years of doing Ph.D I have accumulated many debts. To fully do justice to them would require more than mere acknowledgement of the gratitude that I have felt. However since that is the only recourse left to me I hope that it will partly serve the purpose.

I begin by thanking my constant companion, GOD for being there for me and guiding my footsteps.

I wish to express my deep sense of gratitude to my research supervisor Dr. Ravi Shankar, Associate Professor, Department of Chemistry, Indian Institute of Technology, Delhi, for his untiring guidance, keen interest, valuable suggestions and constant encouragement, which made this work possible. The discussions with him have enriched me in many ways.

I take this opportunity to thank profusely Professor A. S. Brar for his constant encouragement and moral support. I also extend my gratitude to the present and erstwhile Heads of the Department of Chemistry, Prof. H. M. Chawla, and Prof. M. N. Gupta for providing the essential facilities for carrying out my research.

My sincere thanks to Prof. G. N. Rao, Dr. J. D. Singh, Dr. N. D. Kurur, Dr. A. Ramanan, Dr. A. K. Ganguli and Dr. N. G. Ramesh for their encouragement. I would like to thank the people at NMR lab Mr. Munna Lal and Mr. Keshav Dev, whose dedication and flexibility went a long way in the completion of thesis work. Thanks are due to Mr. A. K. Agarwal, Mr. R. K. Singh and Mrs. Shanta for assiting me during my research work. I thank RSIC, Lucknow and RSIC, Panjab University, Chandhigarh, for FAB/EI mass spectral data.

My friends deserve a special mention. How can I ever forget the constant love, support and affection that I received from Ruchi and Sadia who were always ready to help me whenever I was in need! Preeti has been there always cheerfully and willingly to lend a helping

hand. I thank Sonal, Muthu and Kadal for their goodness of heart and unselfish help. Gayathri would always be remembered for her ways of cheering me up. Pankaj bhaiya is thanked for boosting my enthusiasm and Thirumal for those encouragements and practical advices.

Subba, Anu, Lallitha and Kirupa deserve a special mention for brightening my life with the spark of their friendship.

I wish to express my appreciation and warm feelings to all my lab colleagues in particular to Mukesh, Pooja, Anubhav and Aarti.

It has been memorable experience to come across people like Gunjan, Marilyn, Arunima, Sanjeev, Rashmi Chauhan, Rashmi Bagai, Shweta, Pooja Purang, Arti Agarwal, Balamurugan, Sooriya, Ayyappan, Durai, Parvesh, Dr. Achintya Das and Rajesh Grover. They would be fondly remembered for their well wishes and help during the tenure of my research.

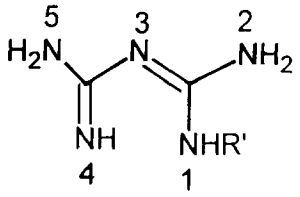
Finally, I thank my family for their love, affection and unstinted support: my parents who have always sacrificed so much for me and for making me the person I am today, for never asking me anything in return. I thank my brothers Sangeeth and Santhosh for their support and eternal love... they never let me feel lonely. I am grateful to Sooru attan for his willingness to help always. Both my ammama deserve a special mention for their unconditional love, affection and constant motivation at each and every stage of my life.

Sampriya. N

(**SAMPRIYA N.**)

ABSTRACT

During the past decades, chemistry of Si-N bonded derivatives has expanded rapidly as new applications of these compounds continue to emerge in the domain of material research. While majority of the known Si-N bonded compounds are derived from ammonia or amines, analogous compounds with polyaza ligands have not received adequate attention. The work embodied in the present thesis is aimed at the synthesis of hitherto unknown Si-N bonded compounds incorporating biguanide ligands in the structural framework.



(R' = H, alkyl, aryl)

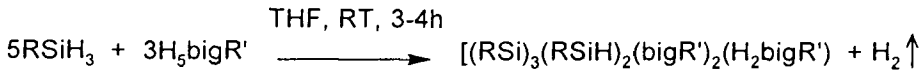
Biguanide

The choice of these ligands stem from their unique structural feature such as the presence of both amino and imine functional groups as well as selective ability of the imine functions to bind transition metal ions in their normal or unusual oxidation states. These ligands are also of current interest owing to their medicinal properties such as hypoglycemic, antimalarial activity and therapeutic treatment of pain, anxiety and memory disorders.

The Si-N bonded derivatives incorporating biguanide ligands are accessible by the synthetic method which involves SiH/NH hetero-

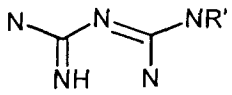
dehydrocoupling between various organosilanes/carbosilanes and the reactive NH_2 sites of the biguanide. For the clarity of discussion, biguanide/1-cyclohexylbiguanide is abbreviated hereafter as H_5bigR' (R' = H or Cy). In addition, reaction chemistry of a few silylbiguanide derivatives obtained above towards titanium(IV) chloride has been explored. The results obtained from these studies are discussed in chapters III-V

Chapter III is devoted to a comprehensive study of the reactions of primary/secondary organosilanes with biguanide/1-cyclohexyl biguanide ligands. Phenylsilane/p-tolylsilane as well as diphenylsilane/ methylphenylsilane are employed as the precursors. Although these reactions are found to proceed via SiH/NH dehydrocoupling pathway, significant difference in the reaction rates are discernable depending upon the nature of the organosilanes used. SiH/NH dehydrocoupling reactions of primary organosilanes with biguanide ligands are extremely facile (RT, 4h) even at room temperature. Thus, addition of two equivalents of phenylsilane/ p-tolylsilane to either a suspension of biguanide or to a clear solution of 1-cyclohexylbiguanide in THF results in brisk effervescence in each case that apparently slows down with time. Subsequent work-up of the reaction mixture yields a white solid in each case. The compounds **1 – 4**, thus obtained have a similar empirical composition and can be represented as shown in equation 1.



-----1

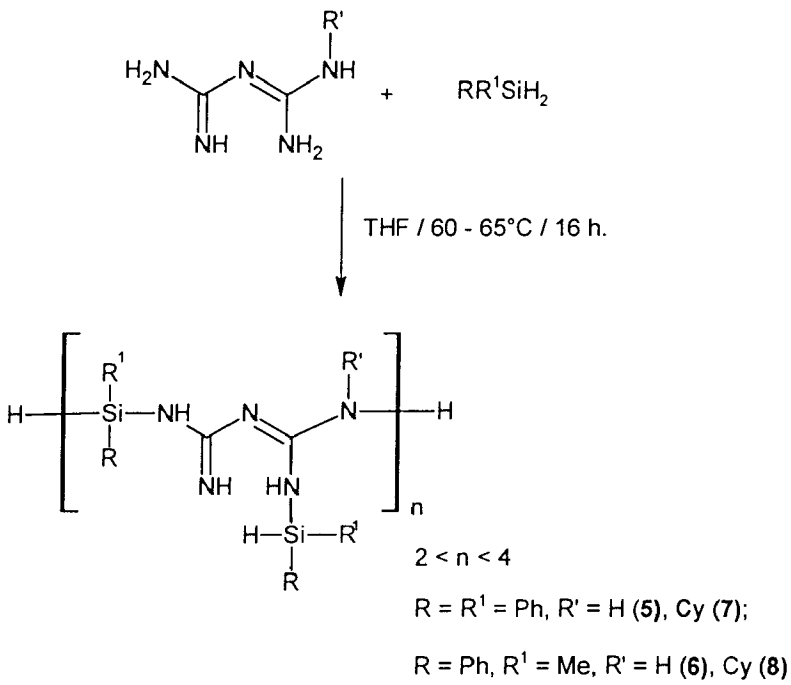
Compound	R	R'
1	Ph	H
2	p-tol	H
3	Ph	Cy
4	p-tol	Cy

R'big = 

These compounds have been characterized by elemental analysis, FAB mass spectrometry as well as IR and multinuclear NMR studies. The FAB mass spectra reveal the presence of M^+ ion at m/z 817 and 887 corresponding to the molecular formula $C_{36}H_{35}N_{15}Si_5$ (for **1**) and $C_{41}H_{45}N_{15}Si_5$ (for **2**) respectively. These results are in conformity with the idealized representation as shown in equation 1. Although the FAB mass spectra of **3** and **4** do not show M^+ ion, important fragment ion such as m/z 1015 $[M - 3NH_2]^+$ (for **3**) and 1101 $[M - 2NH_2]^+$ (for **4**) are discernable. IR spectra of these compounds are devoid of absorptions due to νNH_2 (3420 cm^{-1}) and δSiH_2 (930 cm^{-1}) modes and provide a qualitative evidence in favor of SiH/NH dehydrocoupling. Nevertheless, the identity of SiH, NH, C=N and NCN functional groups is established by their characteristic absorptions at 2150, 3385 - 3200, 1646 – 1624 and 1558 –1540 cm^{-1} respectively. The ^1H NMR spectra of the compounds **3** and **4** provide a fair estimate of the composition, as evident from the integral intensities of Ph/p-tol (δ 7.56, 7.34/7.48, 7.13, 2.35) and NCy (δ 3.35, 1.64, 1.18) groups. However, the resonance

due to NH protons is invariably observed as a broad signal spanning the range of δ 3.8 – 6.5 and impedes the unequivocal detection of SiH protons. The organic functionalities such as Ph/p-tol, C=N and N-Cy (for **3, 4**) are detected by their characteristic resonances in the ^{13}C NMR (quantitative) spectra. The integral intensities of these signals are in conformity with the empirical composition as given in equation 1. The ^{29}Si $\{^1H\}$ NMR spectra of **1 - 4** are quite similar and reveal two prominent resonances in the chemical shift region between δ -127.3 to -127.8 and -131.7 to -132.1. The DEPT-135 pulse sequence confirms the signals to arise from $RSiHN_2$ and quartenary $RSiN_3$ species respectively. An intriguing feature is the marked upfield ^{29}Si chemical shift values relative to those normally observed for related tetra-coordinated compounds such as silylcarbodiimides, $-[RHSi(NCN)_2]_n-$ (δ -50 to -60). A plausible explanation to this effect has been put forth on the basis of hyper-coordinated silicon moieties in these compounds resulting from the coordinative association of imine/amino groups. Based on the above results, it may be concluded that biguanide ligands provide multiple NH_2 sites to undergo hetero-dehydrocoupling with the primary SiH_3 groups under extremely mild conditions. The similarities in the analytical and spectroscopic data suggest similar structural organization for **1 - 4**. Accordingly, the formation of cyclic structure comprising of $RSiHN_2$ and $RSiN_3$ moieties is suggested.

A detailed study on the reactivity behavior of secondary organosilanes RR^1SiH_2 (R = R^1 = Ph; R = Ph, R^1 = Me) towards biguanide/1-cyclohexylbiguanide reveals that the SiH/NH dehydrocoupling proceed at a much slower rate (64 - 65°C, 16h) than the analogous reactions of primary organosilanes (RT, 4h) discussed above. These reactions afford the corresponding 1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanides (**7, 8**) as white hygroscopic solids (Scheme 2).



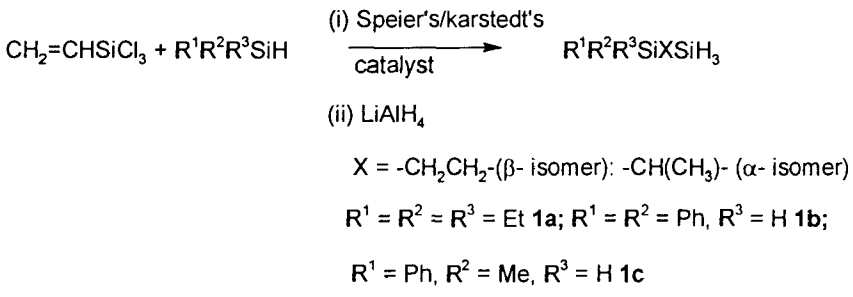
Scheme 2

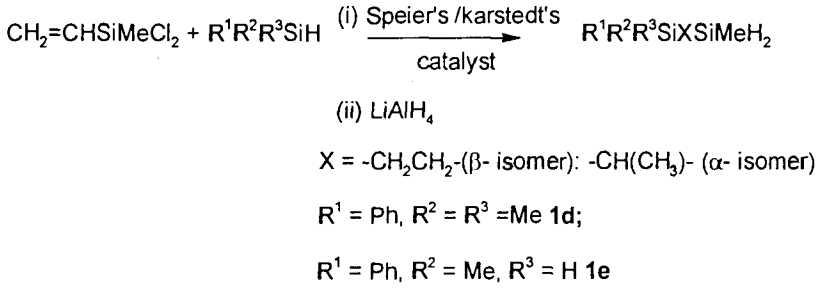
These are characterized by analytical and spectroscopic techniques such as FAB mass, UV, IR, multinuclear (^1H, ^{13}C, ^{29}Si) NMR, GPC and TGA studies. FAB mass spectra of 1,4-bis(diphenylsilyl)biguanide (**5**) and 1-cyclohexyl-2,5-bis(diphenylsilyl)

biguanide (**7**) show the highest ions at m/z 929 $[M+H]^+$ and 1094 $[M+2H]^+$ respectively corresponding to the dimeric structures. Tetrameric structures are suggested for 1,4-bis(methylphenylsilyl) biguanide (**6**) and 1-cyclohexyl-2,5-bis(methylphenylsilyl)biguanide (**8**) on the basis of structurally important fragment ions observed in the FAB mass spectra. The GPC data (polystyrene standard) also support the formation of oligomeric structures (M_w = 1380 - 1710) with a narrow polydispersity (1.06 - 1.15). Notable feature of the IR spectra (KBr pellets/ CH_2Cl_2 solution) is the presence of two medium intensity absorptions at ~2200 and 2130 cm^{-1} due to νSiH mode. The spectral pattern suggests the presence of conformational mixtures in these compounds. ^1H and ^{13}C NMR data are in conformity with the idealized structure as shown in scheme 2. An unequivocal assignments of the observed $^{29}Si\ \{^1H\}$ NMR signals (- 42.6, -46.0 (for **5, 6**), -30.1, -30.4, -32.7, -33.6 (for **7, 8**)) are made on the basis of ^{29}Si (DEPT-135) NMR spectra. Accordingly, the former $\delta\ ^{29}Si$ values are attributed to C_2HSiN (^1J(Si-H) = 190 - 196 Hz) and the later to C_2SiN_2 moieties. The $^{29}Si\ \{^1H\}$ chemical shift values of **5 - 8** are found to be comparable with those of analogous silylcarbodiimides, $-[R_2SiNCN]_n-$ known in literature.

Chapter IV is divided into two sections. Section A, deals with the synthesis and characterization of a few carbosilanes bearing terminal SiH, SiH_2 and/or SiH_3 groups. Section B describes the reactivity of these carbosilanes towards biguanide/1-cyclohexylbiguanide ligands.

The synthesis of carbosilanes **1a - 1e** (Scheme 3) involves hydrosilylation reaction between appropriate hydrosilane and trichlorovinylsilane/ dichloromethylvinylsilane and subsequent treatment of the resulting chlorocarbosilanes with lithium aluminium hydride.





Scheme 3

The compounds **1a - 1e** are colorless, distillable liquids and are obtained as a mixture of α and β- isomers. IR and multinuclear NMR studies have been employed to characterize these compounds. ^{1}H NMR spectra of **1c** and **1e** exhibit doublet of doublet due to CCH_3 and SiMe protons arising from α-isomer and suggest the presence of diastereomers by virtue of adjacent chirality at Si and C centers. In accord with the ^{1}H NMR data, ^{13}C $\{^{1}H\}$ NMR spectra reveal two signals each for CH and CH_3 carbons associated with diastereotopic α-

isomers. ^{29}Si $\{^1H\}$ NMR spectra of these carbosilanes reveal three distinct signals each in the region of δ -7.3 to -11.2 and -53.0 to -54.2 (for **1c**)/-28.0 to -29.7 (for **1e**). The former values are ascribed to PhMeHSi moiety while the later to SiH_3/SiH_2 group.

The carbosilanes, **1a - 1c** are alkyl analogs of primary organosilanes and thus provide useful models to study the SiH/NH dehydrocoupling reactions with biguanide/1-cyclohexylbiguanide. In addition, choice of carbosilanes such as **1b** and **1c** also provide an insight into the reactivity behavior of tertiary SiH group which is present in these compounds. A detailed study however reveals that these carbosilanes undergo SiH/NH dehydrocoupling at a much slower rate (20–24h, 60-65°C) as compared to analogous reactions with arylsilanes, $RSiH_3$ (R = Ph or p-tol), discussed in chapter III (section A). This has led to the isolation of the silylbiguanides, **9 - 14** which possess an idealized composition $[RSiH)_2(HbigR')]_n$ (equation 3). The identity of the proposed structural unit for the compounds **9 - 14** has been validated by EI/FAB mass spectral data. For example, the FAB mass spectrum of **14** shows the presence of M^+ ion at m/z 535 corresponding to the suggested empirical formula while structurally significant fragment ions are seen in the EI/FAB mass spectra of other silylbiguanide derivatives {m/z 395 $[M- 2CH_3 -2H]^+$ for **9**, 346 $[M- 3Ph]^+$ for **10**, 626 $[2M- 3C_6H_6-3CH_3]^+$ for **11**, 460 $[M - 2C_2H_6 -3H]^+$ for **12**}.

$$RSiH_3 + H_5bigR' \xrightarrow[60 - 65°C]{THF} [(RSiH)_2(HbigR')]_n + H_2\uparrow \quad \text{----- 3}$$

Compound	R	R'
9	Et_3SiX	H
10	Ph_2HSiX	H
11	PhMeHSiX	H
12	Et_3SiX	Cy
13	Ph_2HSiX	Cy
14	PhMeHSiX	Cy

where X = $-CH_2CH_2-$ or $-CH(CH_3)$

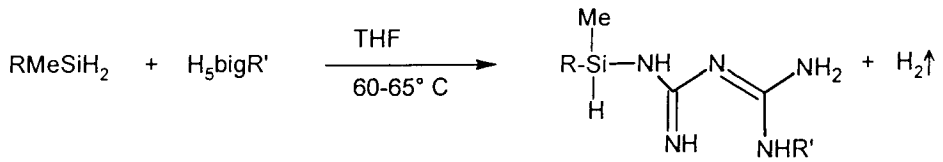
The ^1H NMR spectra of **12 - 14** show characteristic resonances due to RSi (R = Et_3SiX, Ph_2HSiX or PhMeHSiX) and NCy moieties. These groups integrate in a definite stoichiometry of 2 : 1, irrespective of the nature of carbosilane used. $^{29}Si\{^1H\}$ NMR spectra of these compounds reveal the signals associated with the corresponding pendant carbosilyl groups, at δ 8.1 - 8.2 (for Et_3Si (**9, 12**)), -10.9 to –11.2 (for Ph_2HSi (**11, 13**)), -9.2 to –10.6 (for PhMeHSi (**12, 14**)) similar to those found in the corresponding precursor carbosilanes. The results are particularly significant in order to illustrate the inert nature of Ph_2SiH (for **10, 13**) and PhMeSiH (for **11, 14**) groups towards dehydrocoupling. In addition a new signal at δ -117 to -121 is assigned to $CSiHN_2$ moiety. These results find an analogy with those obtained in case of silybiguanides derived from organosilanes (chapter III, section A). It is thus proposed that the silicon atoms associated with $CSiHN_2$ moiety are hyper-coordinated by virtue of the coordinative association of imine groups.

An idealized structure comprising of cyclic dimer (n = 2) is proposed for these compounds.

The carbosilanes **1d** and **1e** represent the alkyl analogs of secondary organosilanes. The reactions of these carbosilanes with biguanide/1-cyclohexylbiguanide also proceed via SiH/NH dehydrocoupling pathway. However the rate of hetero-dehydrocoupling is found to be extremely slow (60-65°C, 72h) in comparison to similar reactions involving secondary organosilanes (discussed earlier). This has led to the isolation of 1-(carbosilyl) biguanide (**15, 16**) and 1-cyclohexyl-5-(carbosilyl)biguanide (**17, 18**) as molecular entities (scheme 4).

The IR spectra of **15 - 18** exhibit two medium intensity absorptions (2190 – 2099 cm^{-1}) due to νSiH mode. This observation is analogous to that found for silylbiguanides (**5 – 8**) obtained from secondary organosilanes (chapter III, Section B). Such spectral behavior is thought to arise due to the presence of conformers. ^{1}H NMR spectral data reveal the presence of $PhMe_2SiX$/PhMeHSiX as well as NCy groups (wherever applicable) at their usual chemical shift values. A definite 1 : 1 stoichiometry of RSi : R'N groups in **17** and **18** is clearly evident from the integral ratio. The ^{29}Si $\{^{1}H\}$ NMR spectra show the signals associated with the pendant carbosilyl groups at δ -0.9, –1.2 (for $PhMe_2SiX$) and -9.3, –10.1 (for PhMeHSiX). These chemical shift values are similar to those found in the corresponding precursor

carbosilanes. In addition, the spectrum of each compound exhibits a resonance at δ -9.6 to -11.5 due to RMeHSiN moiety.

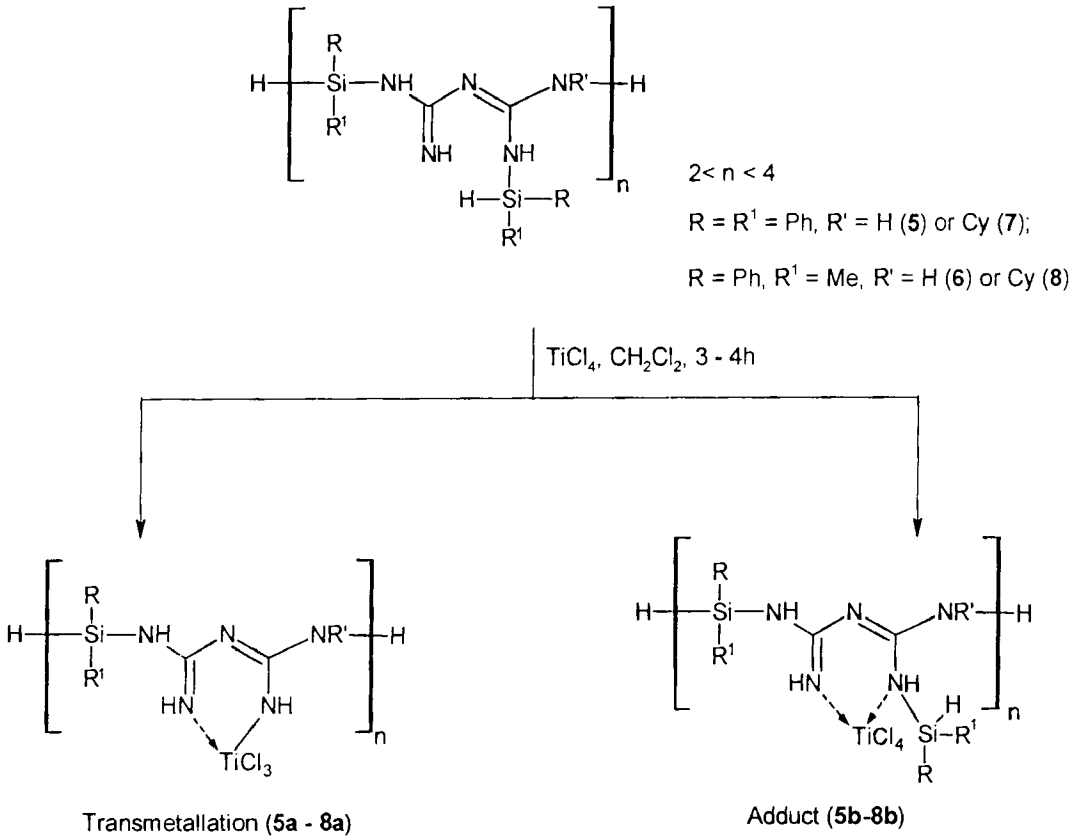


Compound	R	R'
15	$PhMe_2SiX$	H
16	PhMeHSiX	H
17	$PhMe_2SiX$	Cy
18	PhMeHSiX	Cy

where X = $-CH_2CH_2-$ or $-CH(CH_3)$

Scheme 4

In chapter V, preliminary studies have been made to understand the reaction chemistry of 1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanides (**7, 8**) towards titanium(IV) chloride. In these reactions, transmetallation competes with coordinative association leading to the isolation of compounds, **5a - 8a** and **5b - 8b** as shown in scheme 5. However, effective separation of these compounds as analytically pure products is possible due to the preferential solubility of **5b - 8b** in CH_2Cl_2 while **5a - 8a** remain practically insoluble.



Scheme 5

Conductivity measurements of 1 mmol solution of these compounds in DMSO show specific conductance κ in the range of 98 - 100 μScm^{-1}. This suggests that these compounds are predominantly non-electrolytes. A comparison of the IR spectra of these compounds with those of the precursor silylbiguanides reveal a lowering of νNH frequencies (3252 –3200 cm^{-1}) by ~ 80 - 120 cm^{-1}. A positive spectral shift (40 - 60 cm^{-1}) for νCN + νNCN modes in the region between 1700 - 1600 cm^{-1} is also observed. The ^1H NMR spectrum of each compound exhibits three distinct resonances between δ 8.62 – 9.48 due to NH protons. A significant downfield shift of these signals relative to those

observed in the parent silylbiguanides (δ 3.64 - 5.45) suggest the coordinative association of the NH group. The ^{29}Si $\{^1H\}$ NMR spectra (DMSO-d_6) show multiple pattern in a narrow chemical shift range δ -20 to -22 (for **5a, 7a**) and -14 to -17 (for **6b, 8b**). These values show a downfield shift of 15 - 20 ppm relative to those observed for the parent silylbiguanides (**5 - 8**). It is likely that the coordinative association of C=N/NH groups to the titanium(IV) centers bring about this phenomenal change in these compounds.

CONTENTS

List of figures

LIST OF TABLES

Glossary of Symbols and Abbreviations

%	percent
δ	chemical shift
μ	micro
Å	Angstrom
°C	degree centigrade
b.p.	boiling point
br	broad signal
Bu	butyl
Cat.	catalytic
cm	centimeter
Conc.	concentrated
Cy	cyclohexyl
d	doublet
dd	doublet of a doublet
DEPT	distortionless enhancement by polarisation transfer
DMF	N,N-dimethylofmamide
DMSO	dimethylsulphoxide
e.g.	for example
EI	electron ionisation
Et	ethyl
FAB	fast atom bombardment
i.e.	that is
g	gram
GPC	gel permeation chromatography
h	hour
Hz	Hertz
IR	infrared
J	coupling constant
m	multiplet (in NMR)

m/z	mass/charge
MHz	Mega Hertz
M^+	molecular ion
Me	methyl
Mes	mesityl
min.	minutes
mg	milligram
mmol	millimol
mol	mole
MOCVD	metal organic chemical vapor deposition
mL	millilitre
mm	millimeter
N	normality
nm	nanometer
NMR	nuclear magnetic resonance
Oct	octyl
Ph	phenyl
ppm	parts per million
py	pyridine
Pr	propyl
ROP	ring opening polymerisation
RT	room temperature
s	singlet
S	Siemen (conductance measurement)
t	triplet
tol	tolyl
THF	tetrahydrofuran
TMS	tetra methyl silane
UV	ultra violet

CHAPTER I

INTRODUCTION

Though silica and silicates form the major components of the earth's crust, sources of organosilicon compounds in nature are scarce. Thus the origin of organometallic chemistry of silicon is treated as purely a product of laboratory research. Earlier work in this field centered on attempts to demonstrate similarities in the chemistry of analogous silicon and carbon compounds. Kipping and coworkers,[1] after an extensive series of investigations concluded that the chemistry of silicon compounds did not match that of carbon compounds. The fundamental properties that distinguish silicon from carbon are summarized as follows.

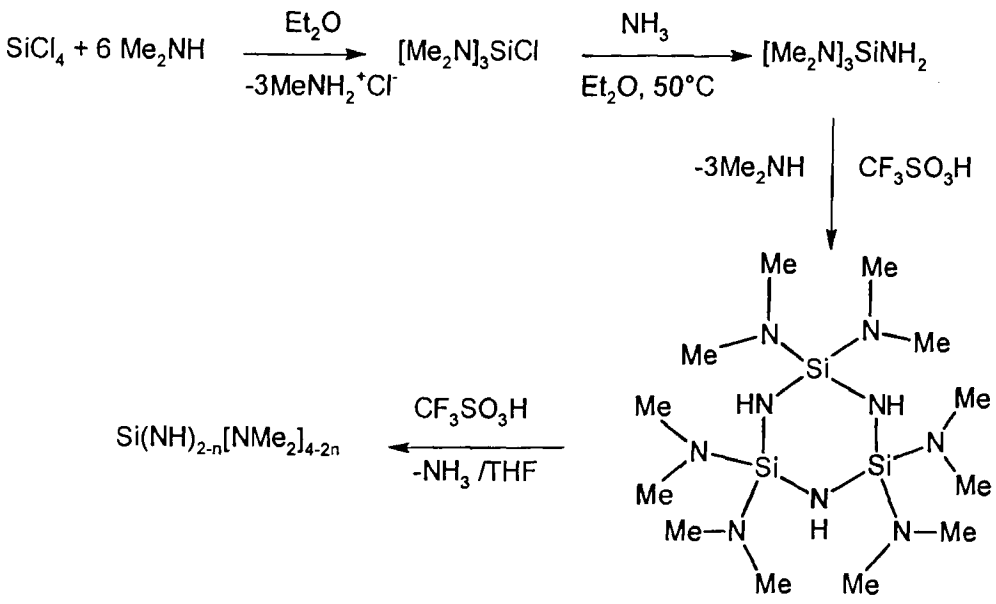
Silicon atom is about 50% larger than carbon (Si = 1.77Å, C = 0.77Å). This increased size has several ramifications including lower barrier of silicon-element bond rotation and also less propensity to form stable π bonds. The smaller electronegativity of silicon in comparison to carbon (χ ; C = 2.5, Si = 1.8 Pauling scale) results in polar SiC bond and thus provides driving force in many reactions. Silicon differs from carbon in forming stable derivatives with coordination number higher than four due to the participation of d-orbitals.

Real progress in synthetic organosilicon chemistry has followed closely with the commercial availability of methylchlorosilanes (Rochow's process)[2] and has moved ahead in well defined areas leading to the synthesis of a large number of compounds containing silicon as the central atom. An important offshoot to the development of

organosilicon chemistry is the study of compounds containing silicon-nitrogen bond. In spite of a long history,[3] Si-N bonded derivatives have witnessed an unseeming proliferation in recent years, as new applications of these compounds continue to emerge in the domain of materials research. In this regard, oligomeric/polymeric silazanes $-[R_2SiNH]_n-$ (R = H or alkyl) have been extensively studied as precursors for pyrolytic conversion to silicon-nitride.[4-8] The chemistry of silylcarbodiimide is well known and their application in non-hydrolytic sol-gel process has been reported recently.[9-11] The reaction of trichloromethylsilane with bis(trimethylsilyl)carbodiimide in presence of pyridine as catalyst is found to produce a transparent, three dimensional stable gel.

$$n\ MeSiCl_3 + 1.5n\ Me_3Si\text{-}N{=}C{=}N\text{-}SiMe_3 \xrightarrow{\text{Pyridine}} \underset{\text{gel}}{[MeSi(NCN)_{1.5}]_n} + 3nMe_3SiCl$$

Bradley *et al.*[12] have studied acid catalyzed ammonolysis of tris-(dimethylamino)silylamine $(Me_2N)_3SiNH_2$. The method provides a sol-gel route to porous, carbon free, silicon diimide gel containing terminal NH_2 groups. Such studies are of potential interest in the synthesis of non-oxide ceramics and nitridosilicates.[13, 14]



The scope of molecular Si-N bonded compounds has also expanded manifold due to their compatibility in MOCVD process.[15-17] Earlier work on the synthesis and structural aspects of Si-N bonded compounds have been the subject of a few review articles.[18,19] In the following section, a brief survey of literature highlighting recent advances in the synthesis, structure and bonding aspects of Si-N bonded compounds is presented. The primary focus is on the linear/cyclic aminosilane and silazane derivatives.

1. 1 Synthetic routes to Si-N bonded derivatives

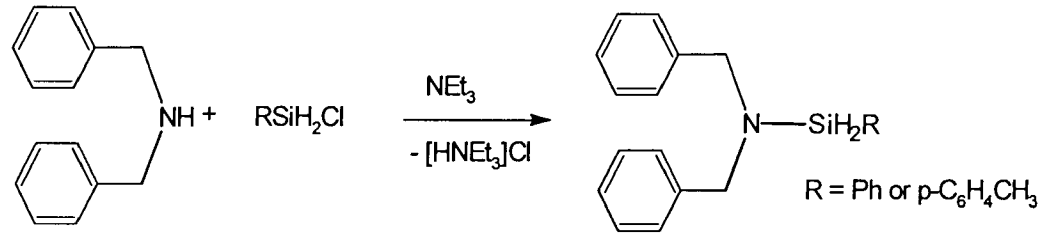
With the advanced applications of Si-N bonded compounds, there has been renewed interest in the development of new synthetic methodologies which afford otherwise inaccessible derivatives.

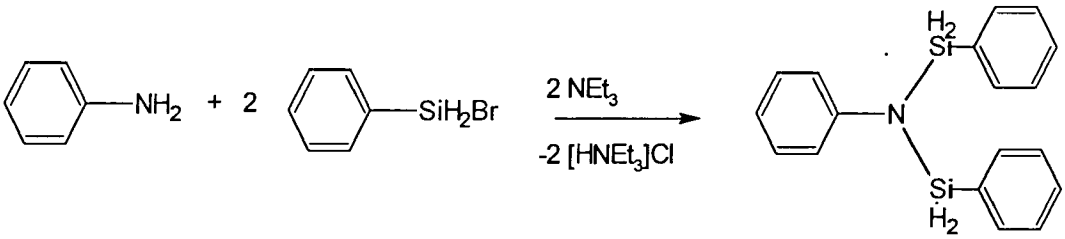
Significant among these are the methods involving aminolysis/ammonolysis of halosilanes, silyltriflates as intermediates, transition metal/base catalyzed SiH/NH dehydrocoupling, nucleophilic activation of SiH bond by F^- ion and anionic/cationic ring opening polymerization. Using these routes, diverse structural varieties of Si-N bonded compounds ranging from molecular entities to cage-like, polymeric and dendritic structures have been reported during the past two decades.

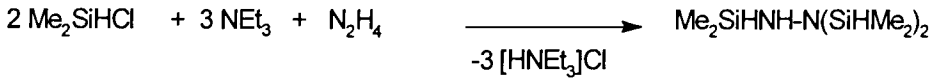
1.1.1 Ammonolysis/aminolysis reactions

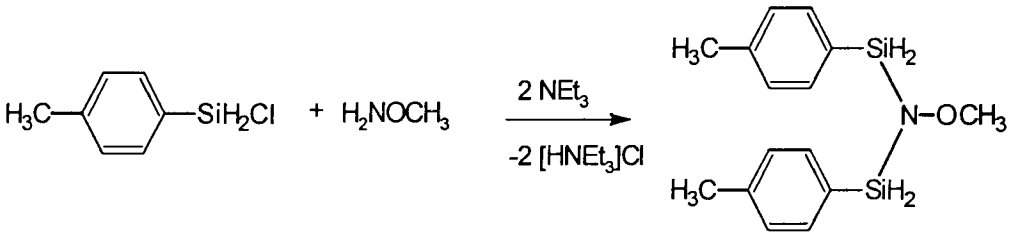
Ammonolysis/aminolysis of halosilanes is one of the earliest development in the synthetic chemistry of Si-N bonded compounds.[20] This method is quite versatile for the synthesis of molecular, oligomeric as well as cyclic derivatives.

Using this approach, Schmidbaur et al.[21-24] have reported the synthesis of a number of molecular compounds containing Si-N bonds with varying substituents at silicon and nitrogen atoms. Majority of these compounds have been structurally characterized by X-ray crystallography. The structure of methyl-N,N-bis(p-tolylsilyl)hydroxyl amine, $(p\text{-}CH_3C_6H_4SiH_2)_2NOMe$ has been shown to possess pyramidal geometry for Si_2NO group.[24]

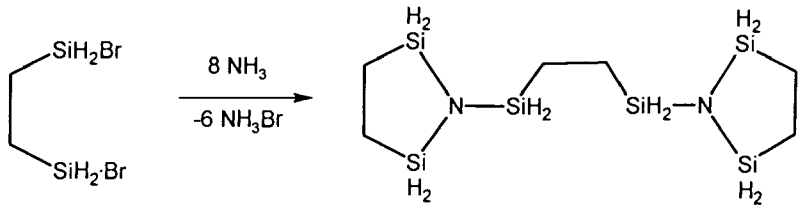


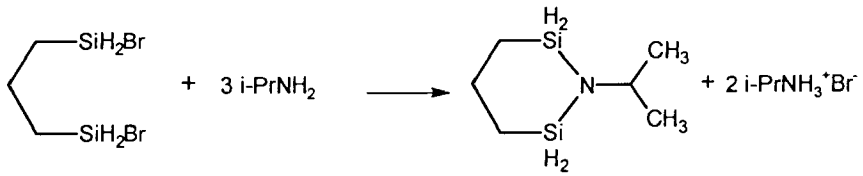




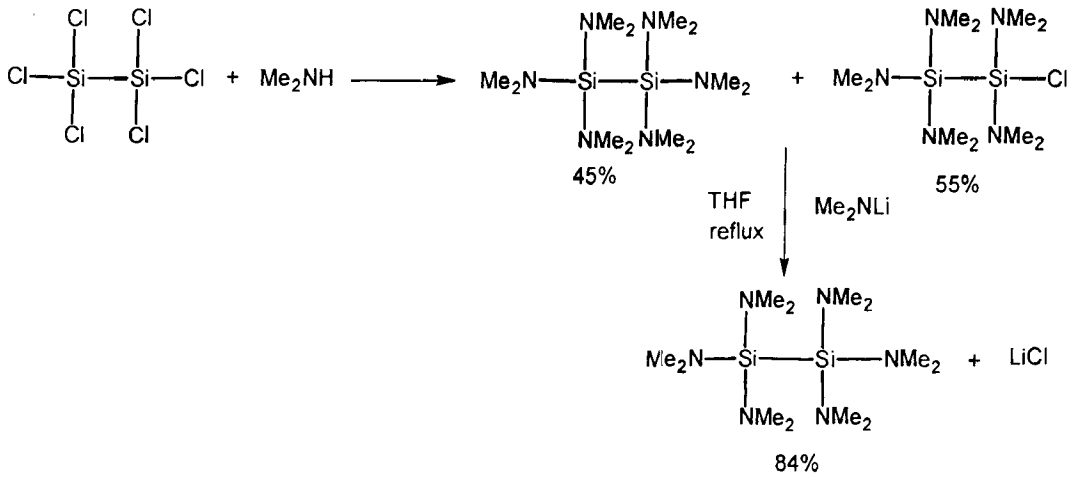


Synthesis of cyclic silylamines, rich in SiH contents has been achieved from the reaction of α,ω-bis(bromosilyl)alkanes $BrH_2Si(CH_2)_nSiH_2Br$ (n = 2 or 3) with ammonia.[25]

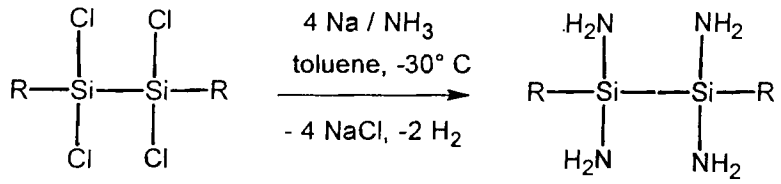




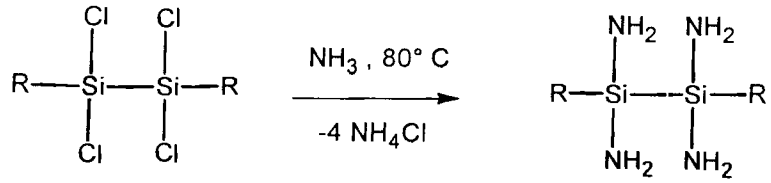
Verkade *et al.*[26] have reported that the reaction of Si_2Cl_6 with large excess of Me_2NH invariably affords a mixture of $(Me_2N)_3SiSi(NMe_2)_2Cl$ and $Si(NMe_2)_6$. However hexakis-(dimethylamino)disilane is accessible in greater than 84% yield by treating the mixture with Me_2NLi in THF.



Using bulky substituents on the silicon atom, Roesky *et al.*[27] have synthesized a number of tetraaminodiorganodisilanes by ammonolysis of halogenodisilanes.

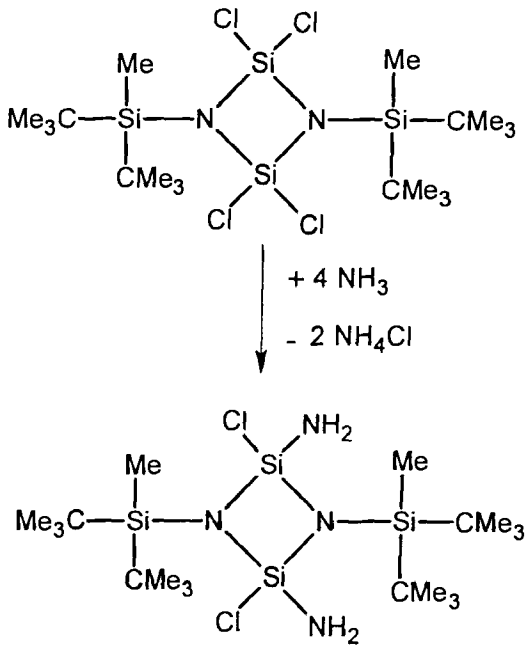


where R = Cp* or $(Me_3Si)_2CH$



where R = $(Me_3Si)_3C$

Klingebiel *et al.*[28] have studied the ammonolysis of tetrachloro-cyclodisilazane $[Cl_2SiNSiMe(CMe_3)_2]_2$. Under the reaction conditions employed, substitution of only one chlorine at each silicon atom by NH_2 groups was observed.



Ammonolysis/aminolysis of dihalosilanes is extremely sensitive to the steric factors of the substituents on silicon as well as nitrogen atom. With less bulky substituents, these reactions generally afford linear/cyclic oligomers. Arai *et al.*[29] have shown that complexation of dichloromethylsilane with pyridine and subsequent reaction with ammonia afford higher molecular weight oligosilazanes in comparison to the one obtained by direct ammonolysis.

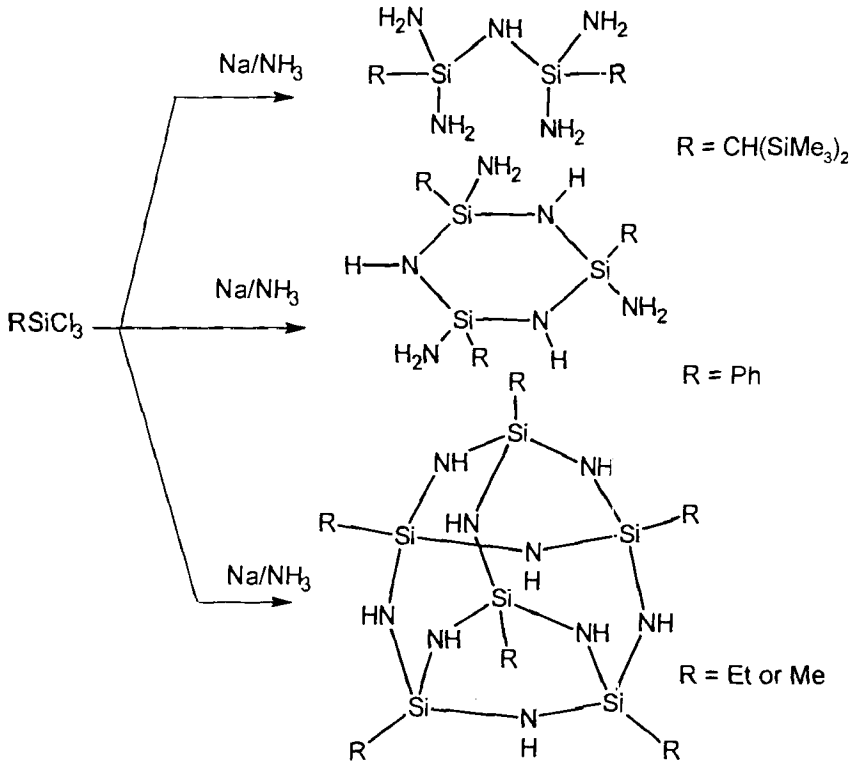
$$MeHSiCl_2 + 2py \longrightarrow MeHSiCl_2.2py$$

$$MeHSiCl_2.2py + NH_3 \longrightarrow -[MeHSiNH]_n- + NH_4Cl \text{ (or pyHCl)}$$

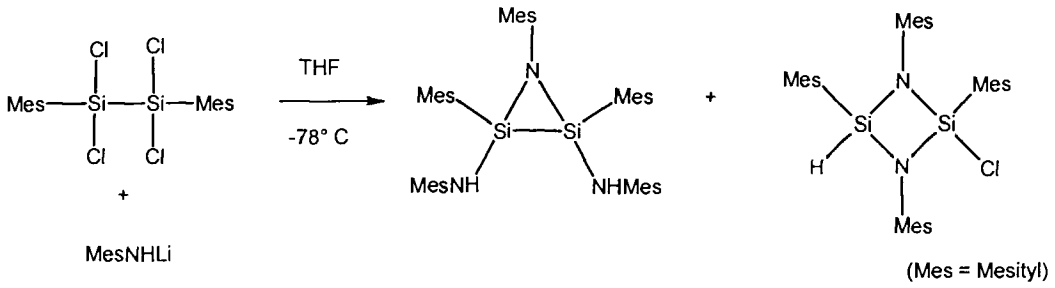
A major drawback in ammonolysis/aminolysis of chlorosilanes is the undesirable formation of ammonium chloride as the by-product that is difficult to remove and often acts as a catalyst in cleavage of Si-N bonds. An alternate approach involving the SiCl/SiN metathesis reaction between hexamethyldisilazane and dichloroorganosilanes has been reported.[30] These reactions afford Si-N bonded oligomers with volatile chlorotrimethylsilane as the by-product.

$$R_2SiCl_2 + Me_3SiNHSiMe_3 \longrightarrow -[SiR_2\text{-}NH]\text{-}_n + Me_3SiCl$$

Roesky *et al.*[31,32] have shown that the use of sodium in ammonolysis reactions of halosilanes is advantageous since NaCl can be easily removed from the reaction mixture. These reactions are found to be susceptible to the steric effect of the substituents at silicon and lead to SiN bonded derivatives with interesting structural motifs.

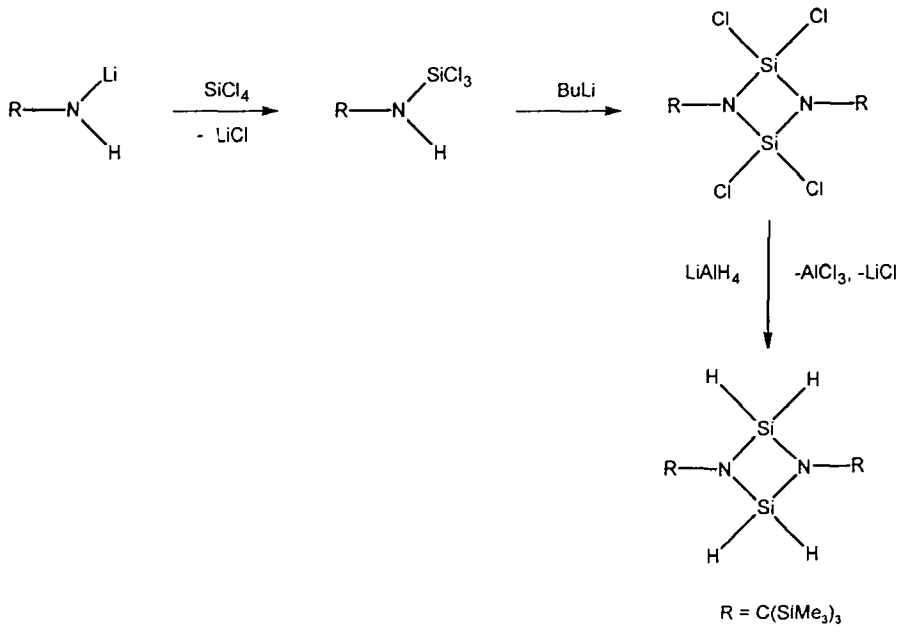


The reaction between appropriate halosilane/halodisilane with lithium amide is found to be useful in generation of novel Si-N bonded strained cyclic structures.[33-35] For example, N-Lithio-2,4,6-trimethylaniline was found to react with 1,1,2,2-tetrachloro-1,2-dimesityldisilane to afford the unexpected cyclic products such as cyclodisilazanes and azadisilacyclopropane.[33]



(Mes = Mesityl)

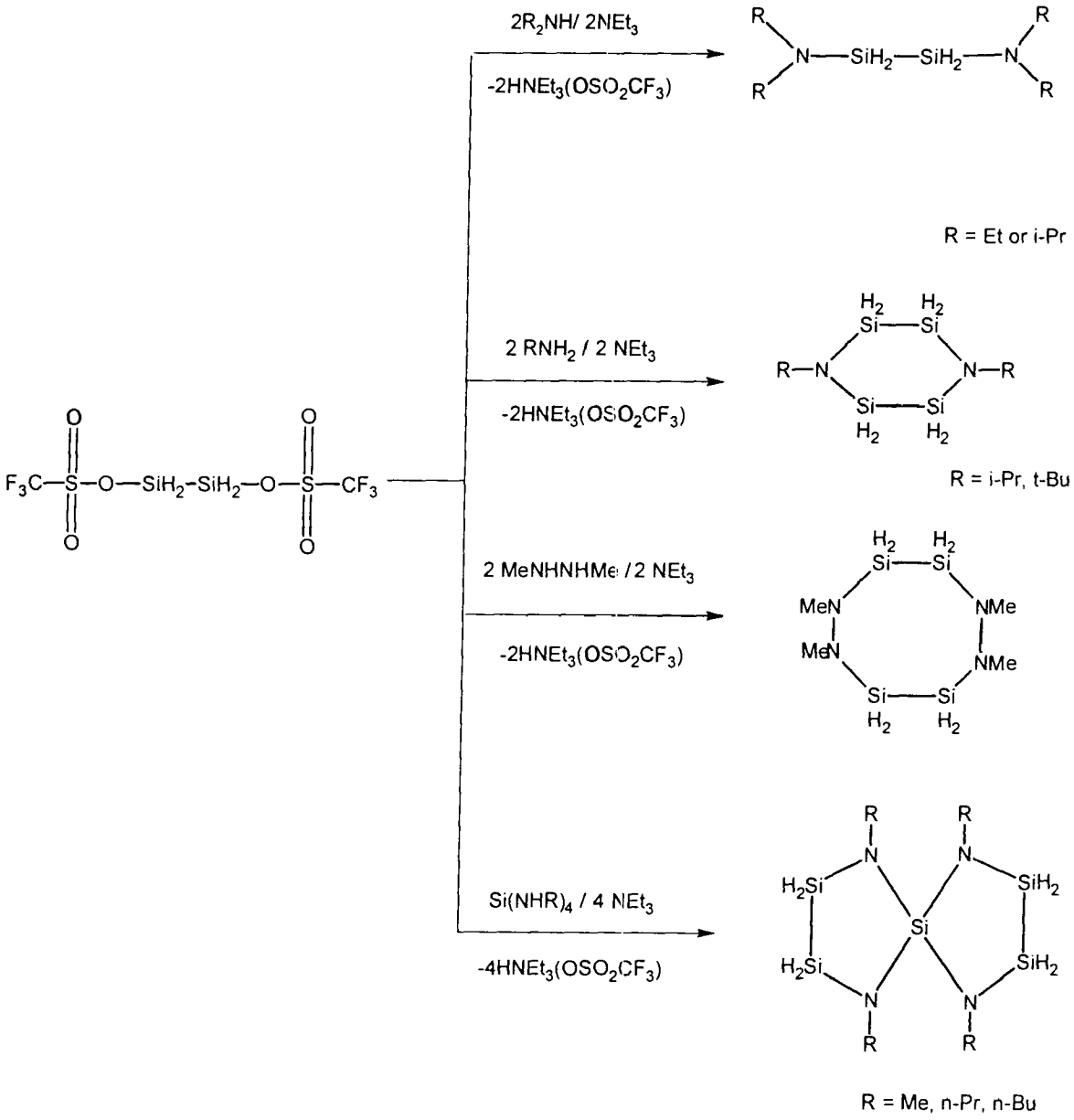
Klingebiel *et al.*[35] have reported the synthesis of cyclodisilazane that bears hydrogen atoms at the silicon and silyl groups at the nitrogen atom.



R = $C(SiMe_3)_3$

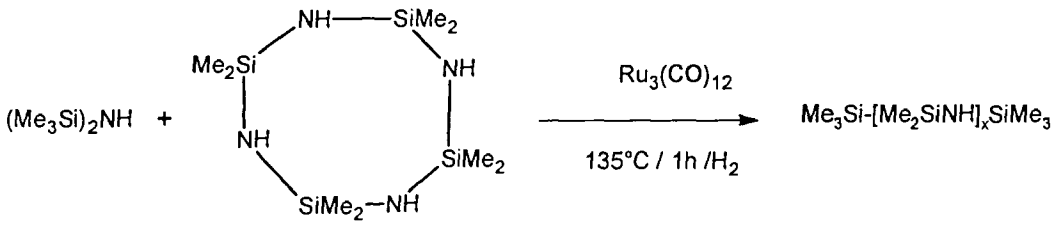
1.1.2 Silyltriflate route

Schmidbaur *et al.*[36-38] have reported that 1,2 disilanediyl-bistriflate is a useful intermediate for the preparation of linear/cyclic Si-N bonded derivatives which are rich in silicon and hydrogen contents. These compounds serve as potential single source precursors for the vapor deposition of silicon nitride.

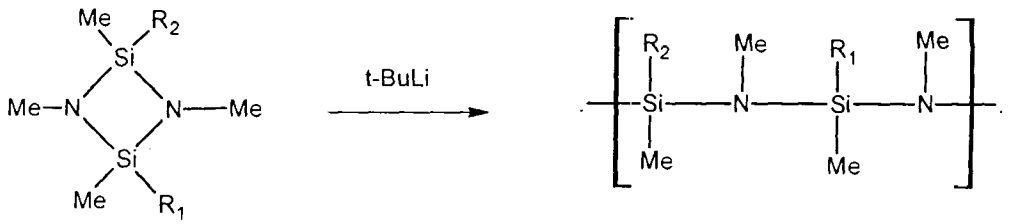


1.1.3 Ring opening polymerization

The search for silicon containing polymers that serve as precursors for the pyrolytic generation of silicon nitride-based ceramics has led to the development of new synthetic routes. In this respect,ring opening polymerization of various cyclosilazanes induced by transition-metal catalyst or anionic/cationic initiators have received adequate attention. Laine and Blum have reported the use of a number of homogeneous as well as heterogeneous transition metal-based catalysts for the ring opening polymerization of octamethylcyclotetrasilazane.[39, 40]



It has been observed that the ring opening polymerization induced by anionic (RLi where R = Bu or Me) or cationic (CF_3SO_3Me) initiators depend on the size of the ring and on the nature of substituents at both nitrogen as well as silicon atoms.[41,42] By appropriate choice of the substituents, the cyclodisilazanes can afford high molar mass polysilazanes.



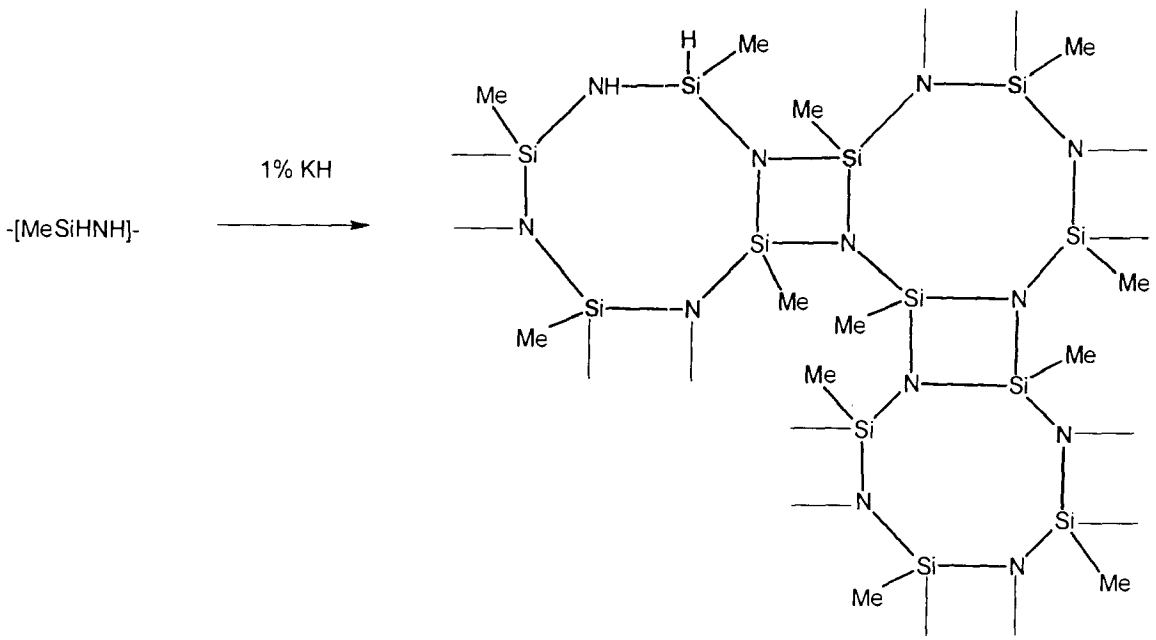
R_1 = Vinyl; R_2 = Me

$R_1 = R_2$ = Vinyl

M_n = 45,000-1,00,000

1.1.4 SiH/NH dehydrocoupling reaction

Following the work of Fink,[43] Seyferth and Wisemann have shown that cyclomers and oligomers of the type $-[MeSiHNH]_x-$ produced by ammonolysis of $MeSiHCl_2$, react with KH to undergo "dehydrocyclization" reaction. The resultant product is a soluble, tractable, sheet-like polymer (only an idealized structure) that can be spun into fibers and gives extremely high ceramic yields upon pyrolysis.[44, 45]



Dehydrocoupling of SiH/NH bonds in the presence of nucleophilic catalyst like F^- ion was reported by Corriu and co-workers.[46] The reactivity of silanes towards dehydrocoupling follows the sequence $OctSiH_3$> $PhMeSiH_2$ > Ph_2SiH_2 > $PhMe_2SiH$.

Prior reports of metal catalyzed dehydrogenative coupling include the work of Sommer and Citron.[47] Recent efforts for the synthesis of oligosilazanes have focused on catalytic dehydrogenative coupling of organosilanes and amines with other transition-metal complexes.

$$Et_3SiH + R'NH_2 \xrightarrow{Pd/C} Et_3Si\text{-}NHR' + H_2$$

Laine and co-workers have investigated the use of various homogenous and heterogeneous catalysts including $Ru_3(CO)_{12}$ and Pd/C.[48,49] Barton and co-workers have examined dehydrogenative coupling between Et_2SiH_2 and $BuMeNH_2$ using $PdCl_2$ as the catalyst.[50] Wang and Eisenberg have shown that dehydrogenative coupling of SiH and NH bonds is promoted by several binuclear rhodium complexes and afford oligosilazanes.[51] The steric effect of substituents plays a pivotal role in determining the efficacy of these reactions, with the degree of coupling decreasing as the silane and amine become more bulky. For example, the reaction of $PhSiH_3$ with t-$BuNH_2$ results in the formation of linear silazanes, while similar reactions with ammonia/methylamine yield branched silazanes. Liu and Harrod have studied the use of CuCl and CuH as catalysts for silane/amine

coupling.[52] More recently, these authors have investigated the dehydrocoupling of silanes and ammonia in presence of dimethyltitanocene (DMT).[53] The reactions of methyldiphenylsilane and methylphenylsilane with ammonia are effectively catalyzed by DMT to afford Si-N bonded derivatives.

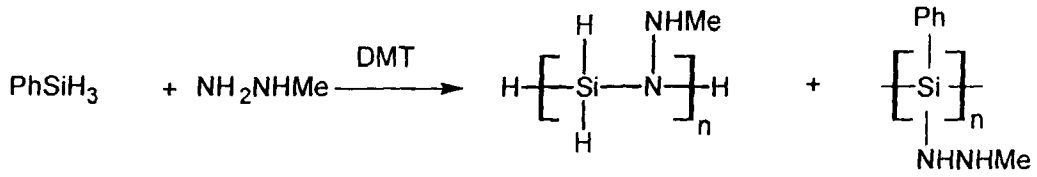
$$Ph_2MeSiH + NH_3 \xrightarrow{DMT} Ph_2MeSiNHSiMePh_2$$

The reactions of primary silanes with ammonia in the presence of DMT are unexpectedly slower than those of tertiary and secondary silanes. In these reactions, homo-dehydrocoupling competes effectively with amination reaction and results in poly(aminosilanes).

$$PhSiH_3 + NH_3 \xrightarrow{DMT} \left[\begin{array}{c} Ph \\ | \\ Si \\ | \\ NH_2 \end{array} \right]_x$$

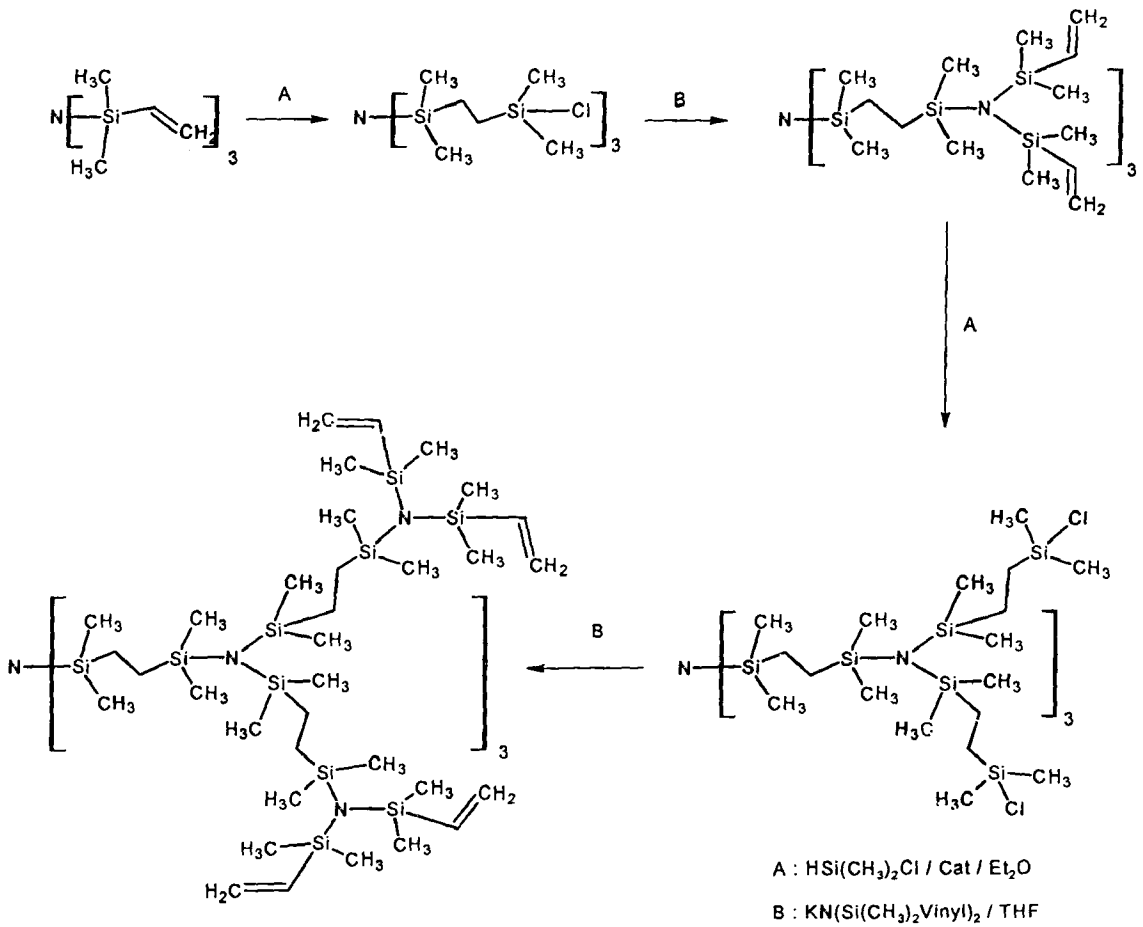
Similar reactions of phenylsilane or diphenylsilane with hydrazine/methyl substituted hydrazines have also been studied.[54] In the reaction of phenylsilane with 1-methylhydrazine, homocoupling competes with SiH/NH hetero dehydrocoupling reactions as shown in equation below.

$$Ph_2SiH_2 + NH_2NH_2 \xrightarrow{DMT} Ph_2Si(NHNH)_2SiPh_2$$



1.1.5 SiN bonded dendrimers

A few studies related to the synthesis of organosilicon dendrimers containing $N(Si(CH_3)_2)_3$ core units that are connected by $-CH_2CH_2-$ chains are reported.[55,56] These are obtained by the divergent approach as shown in the scheme.



1.2 Structural features of Si-N bonded compounds

One unique feature of Si-N bonded derivatives that differs from the carbon analog is the planarity at nitrogen center. This was first discovered for trisilylamine, $(H_3Si)_3N$ in gas phase electron diffraction study by Hedberg[3] and later confirmed for the crystalline phase by Barrow and Ebsworth.[57] Since then, structural features of Si-N bonded compounds have been studied extensively with particular emphasis on aminosilanes and organosilylamines. A large variety of substituents with different steric and electronic effects at the silicon and nitrogen atoms have been investigated till date. While most of these compounds are found to be planar,[58,59] only a few monosilylated amines with pyramidal geometry have been observed.[60-63]

For a long time, it was argued that the planarity of Si-N bonded compounds results from the $p\pi$-$d\pi$ interaction.[64-68] However more sophisticated theoretical treatments have shown that the effect arising from negative hyperconjugation[68-71] or electrostatic interaction[72-75] can also be employed for the rationalization of geometry around nitrogen atom in these derivatives. Recently, Gao *et al.*[76] have used block-localised wave function to examine the stereoelectronic effect on the origin of the structural difference between trisilylamine and trimethylamine. It has been concluded that the pyramidal geometry of trimethylamine is consistent with the traditional VSEPR (valence shell electron-pair repulsion) model for σ bonding and the electron

delocalisation is entirely due to the $n_N \rightarrow \sigma_{CH}^*$ negative conjugation. On the other hand, in trisilylamine theoretical examination was conducted to distinguish the significant contribution due to $p\pi$-$d\pi$ bonding, $n_N \rightarrow \sigma_{CH}^*$ negative hyperconjugation and stereoelectronic interaction. Due to low electronegativity of silicon, the Si-N bond is much more polar than the C-N bond. It is suggested that the polar σ effect, rather than the $p\pi$-$d\pi$ donation and negative hyperconjugation makes the predominant contribution in determining the observed planar geometry at trisilylamine due to significant long-range electrostatic repulsion between silyl groups. Thus only the most electronegative substituents such as F and OH at the nitrogen center result in a pyramidal geometry in silylamines. The electrostatic model mentioned above is in accord with the crystal structures of silylhydroxylamines[24] such as $CH_3N(OCH_3)SiH_3$, $(p\text{-}CH_3C_6H_4SiH_2)_2NOMe$ and $(H_3Si)_2NOMe$. In all these compounds, a pyramidal geometry at the nitrogen center has been observed as evidenced by the deviation of the sum of the angles at the nitrogen from 360°.

1.3 Characterization by ^{29}Si NMR studies

As early as 1962, the promise of ^{29}Si NMR as a structural probe in organosilanes and siloxanes was demonstrated in Lauterbur's review.[77] ^{29}Si is the only naturally occurring isotope of silicon with non-zero spin ($I = ½$). Its low natural abundance (4.7%) and low NMR sensitivity (7.84×10^{-3}) at constant field relative to ^1H places it with ^{13}C

in the group of "rare" spin nuclei. Fortunately, the recent use of FT NMR spectrometers eliminates the problem of low sensitivity.[78,79] Since the magnetogyric ratio (γ) of ^{29}Si is negative, the nuclear overhauser effect (NOE) under proton decoupling condition does not allow the signal enhancement. These factors taken together result in greatly reduced signal intensity, signals nulled into the baseline or negative peaks. Further complication is the relatively higher spin-lattice relaxation time (T_1) for most ^{29}Si nuclei, which makes time averaged experiments very time-consuming.[80] Substantial sensitivity improvements have been achieved by utilizing nonselective polarization transfer pulse sequence (insensitive nuclei enhanced by polarization transfer – INEPT).[81-83] Kupce and Lukevics reported that routine measurement of $^{1}J(^{29}Si\text{-}^{15}N)$ is possible in ^{29}Si NMR spectra using polarization transfer method (INEPT, DEPT etc.) for a series of aminosilane derivatives.[84] The values of $^{29}Si\text{-}^{15}N$ coupling constant ranged from +6 to +47.6 Hz. It is observed that ^{1}J ($^{29}Si\text{-}^{15}N$) values show marked dependence on the nature of Si-N bonds, specifically on the extent of (p-d)π bonding, nitrogen hybridization, electronegativity of the group attached to silicon and Si-N bond lengths and polarity. Also the ^{29}Si chemical shift tends to vary in parallel with $^{1}J(^{29}Si\text{-}^{15}N)$ variation. An empirical correlation suggesting a linear relationship between δ ^{29}Si and ^{1}J ($^{29}Si\text{-}^{15}N$) has been reported.

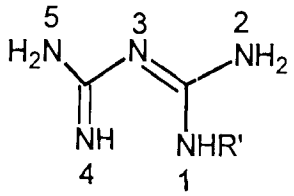
$$^{1}J(^{29}Si\text{-}^{15}N) = 15.7 - 0.384\ \delta\ ^{29}Si$$

Schmidbaur et al. have found that the $^{1}J(^{29}Si\text{-}^{15}N)$ coupling constant show a linear correlation with the Si-N bond lengths for a series of aminosilanes.[21,23]Another noteworthy information obtained from the ^{1}J ($^{29}Si\text{-}^{15}N$) coupling constant is the geometry around the nitrogen atom. It is observed that ^{1}J ($^{29}Si\text{-}^{15}N$) value decreases with the pyramidal nature of the aminosilanes as compared to those found in planar compounds.

SCOPE AND AIM

As discussed earlier in this chapter, recent interest in silicon-nitrogen bonded compounds stems from their potential application in the preparation of ceramic materials of technological importance. While majority of these compounds are derived from ammonia or amines as N-ligands, analogous compounds with polyaza ligands are rare.

Biguanide and its derivatives, $RC_2H_6N_5$ (R = H, alkyl or aryl) belong to a class of polyaza, π-electron rich ligands comprising of both amino and imine functional groups in the structural framework.[85, 86]



Biguanide

Literature is abound in reports on the use of these ligands in coordination chemistry of transition metal complexes.[87-90] These compounds are also of current interest owing to their medicinal properties such as hypoglycemic, antimalarial activity and therapeutic treatment of pain, anxiety and memory disorders.[91-95] A perusal of the literature reveals that potential use of these compounds in the domain of main group chemistry has not been exploited so far. It is envisioned that incorporation of these ligands in the Si-N bonded structural framework is accessible by virtue of the availability of reactive $-NH_2$

sites. In this pretext, synthetic strategy involving SiH/NH dehydrocoupling between various organosilanes and biguanide ligands has been explored. The reactivity behavior of a number of primary/secondary/tertiary organosilanes R_4SiH_{4-n} (n = 1 - 3) as well as carbosilanes towards biguanide and 1-cyclohexylbiguanide has been examined in order to delineate various factors influencing SiH/NH dehydrocoupling pathway. In addition, the silylbiguanide derivatives isolated from the above studies have been examined for their reactivity towards titanium(IV) chloride. The results obtained from these studies are discussed in chapters III to V of the dissertation. The contents are presented in the following order.

Chapter II - Materials and Methods

Chapter III - Reactions of primary/secondary organosilanes with biguanide/1-cyclohexylbiguanide.

Section A - Reactivity of primary organosilanes towards biguanide/1-cyclohexylbiguanide

Section B - Reactivity of secondary organosilanes with biguanide/1-cyclohexylbiguanide.

Chapter IV - Reactions of carbosilanes with biguanide/ 1-cyclohexylbiguanide.

Section A - Synthesis of carbosilanes bearing SiH_3/SiH_2 group

Section B - Reactivity of the primary/secondary carbosilanes towards biguanide/1-cyclohexylbiguanide.

Chapter V – Reactions of silyl-biguanides towards titanium(IV) chloride.

CHAPTER II

MATERIALS AND METHODS

2.1 PURIFICATION OF SOLVENTS AND REAGENTS.

2.1.1 Solvents

Purification of solvents such as diethyl ether, n-hexane, chloroform, dichloromethane, methanol, tetrahydrofuran etc. was carried out by method known in literature.[96, 97]

Diethyl ether

Diethyl ether (Merck) was gently refluxed over sodium wire with a pinch of benzophenone. The appearance of a blue color (benzophenone ketyl) ensures moisture and oxygen free solvent. The solvent was distilled (b.p.34 - 35°C) freshly prior to use.

n-Hexane

Hexane (Merck) was distilled over P_2O_5 and the fraction boiling at 69 -70°C was stored in well-stoppered bottles containing sodium wire.

Dichloromethane

Dichloromethane (Merck) was refluxed over P_2O_5 and distilled. The fraction boiling at 38 - 39°C was stored in well-stoppered bottles containing molecular sieves.

Methanol

75 mL of methanol (Merck) was refluxed on magnesium turning (~5g) with a pinch of iodine till magnesium cake was formed. Methanol

(~1.0 L) was added into the flask and refluxed for 5 - 6 h. It was then distilled at 64 - 65°C and stored in well-stoppered bottles.

Tetrahydrofuran

Tetrahydrofuran (s.d. fine chem.) was kept over NaOH for 2-4 h. The decant was distilled and middle fraction was kept over freshly drawn sodium wire in a round-bottomed flask. Benzophenone was added and the flask transferred to a reflux-cum-distillation unit. The solvent was refluxed till blue color was attained. Dry and oxygen free THF was distilled as and when required (b. p. 65-67°C)

Dimethyl sulfoxide

Dimethyl sulfoxide was kept overnight on activated alumina. The decant was refluxed over calcium oxide and distilled solvent was kept over anhydrous copper sulfate. The distillate was refluxed over CaH_2 and finally distilled under vacuum (120°C/5mm Hg).

2.1.2 Reagents

Organosilanes

Trichlorovinylsilane, trichlorophenylsilane, dichloromethylvinyl silane, dichloromethylphenylsilane, dichlorodiphenylsilane, silicon tetrachloride (Aldrich) were distilled over magnesium turnings prior to use. Triethylsilane and dimethylphenylsilane (Aldrich) were used as procured.

Magnesium Turnings

Magnesium turnings were washed with diethyl ether twice and then placed in an oven at 120°C for 4 - 5 h before use.

Cyclohexylamine

Cyclohexylamine was refluxed over potassium hydroxide beads for 4 - 5 h and then distilled at 134°C prior to use.

Other reagents

Speier's catalyst (hexachloroplatinic acid), Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylene), lithium aluminium hydride, p-bromotoluene (Aldrich) were used as procured.

2.2 PHYSICAL MEASUREMENTS

NMR spectra

The NMR experiments were performed on a Bruker – DPX 300 MHz NMR spectrometer. The chemical shifts for ^{1}H, ^{13}C and ^{29}Si nuclei are reported with respect to tetramethylsilane (TMS) as an internal standard.

^{13}C $\{^{1}H\}$ NMR spectra were accumulated with a relaxation delay of 2s containing 16k data points. The quantitative ^{13}C $\{^{1}H\}$ NMR experiments were carried out using the inverse-gated decoupling pulse program with 10s delay time.

^{29}Si {^{1}H} NMR spectra were accumulated with a relaxation delay of 10s or 30s containing 16k data points. ^{13}C and ^{29}Si NMR measurements in the DEPT mode were carried out using the standard pulse sequence with a J modulation time of 3.7ms (^{1}J(C-H) = 135 Hz) for carbon and 2.5ms (^{1}J(Si-H) = 200 Hz, ^{3}J(Si-H) = 7.2 Hz) for silicon. The 90° pulse was calibrated for each sample which was used for DEPT-135 experiments.

Infrared spectra

IR spectra were recorded on Nicolet FT-IR 460 (Protégé) spectrophotometer in the range 4000 – 400cm^{-1}. The spectra of liquid samples were taken as neat on sodium chloride/potassium bromide optics, while those of solid samples were recorded either as KBr pellets or nujol mull on sodium chloride/potassium bromide optics.

UV spectra - Diffused reflectance

The diffused reflectance were measured on a 50 mm integrating sphere Perkin-Elmer (Lambda Bio 20) spectrophotometer using $BaSO_4$ as matrix.

Mass spectra

The FAB mass spectra in 3-nitrobenzyl alcohol (NBA) matrix were recorded at room temperature on a JEOL SX 102/DA-6000 Mass spectrometer/data system using Argon/Xenon (6kV, 10mA) as the FAB gas. The accelerating voltage was 10kV. EI (70 eV) mass spectra of

the samples were carried out on VG Analytical (Model 70-s) mass spectrometer.

Thermogravimetric analysis

Thermogravimetric analysis was carried out in the temperature range of 30 - 900°C (heating rate 10°C/min, N_2 atmosphere) using a Perkin-Elmer 7 Series Thermal Analysis System.

Molecular weight determination

Gel permeation chromatography (GPC) of the new compounds were carried out in THF solution on a Water associated liquid chromatogram comprising of ultragel permeation columns, a Waters 1525 HPLC solvent delivery system and R-400 refractive index detector. Polystyrene standards were used for calibration.

Elemental analysis (C, H, N)

C, H and N analyses were carried out on a Perkin-Elmer Series II CHNS/O 2400 analyzer. Silicon, titanium and chlorine were estimated by gravimetric methods.[98]

2.3 PREPARATIVE METHODS

All the reactions were carried out under dry nitrogen using Schlenk technique. The glasswares were thoroughly dried in an oven at 110-120°C and flame dried under a stream of dry nitrogen prior to use. Nitrogen gas was passed through long columns filled with potassium hydroxide (pellets), anhydrous calcium chloride and

phosphorous pentaoxide to remove the traces of moisture. Heating of reaction mixture, refluxing and distillation were done under controlled temperature using electrically heated oil bath with relay controlled contact thermometer (IKA - RCT basic). Low temperature reactions were carried out using cryo-cool (Julabo FT 9090).

2.3.1 Preparation of Biguanide

Biguanide base was prepared by following the procedure known in the literature.[99] Dicyanodiamide (25.2 g, 0.03 mol) was mixed thoroughly with ammonium chloride (40.1 g, 0.75 mol). The mixture was heated with constant stirring until a liquid melt was obtained. This melt was held at 160 - 165°C for 10 min with constant stirring. On cooling, the solid obtained was crushed into small lumps and dissolved in 150 mL of hot water. The filtrate was treated with a slight excess of ammonical copper (II) sulfate solution when rose-red precipitate of copper-biguanide sulfate was obtained. It was filtered, washed with water and dissolved in 35 mL hot 10% sulfuric acid. Upon cooling, crude crystals of biguanide sulfate-hydrate appeared which was dissolved in hot water and again cooled in ice. The resulting colorless crystals were filtered, washed and dried. Anhydrous biguanide sulfate was obtained by heating the crystals at 120°C for 24h.

Biguanide sulfate (4.0 g, 0.02 mol) was added to a methanolic solution of sodium hydroxide (3.6 g, 0.09 mol). The mixture was stirred for two hours at room temperature and then for 45 min at reflux

temperature (60 - 65°C). The hot solution was filtered and sodium sulfate cake was washed with hot methanol. The filtrate was concentrated under reduced pressure until a heavy crop of crystals separated. Precipitation was completed by addition of dry ether. The white fluffy solid thus obtained was filtered, dried and stored. [m.p 120-125°C, Analysis. found (calculated): for $C_2H_7N_5$: C, 23.6 (23.7); H, 6.9 (6.9); N, 69.2 (69.3). IR (KBr, cm^{-1}) 3418 (νNH_2), 3360, 3217 (νNH), 1632 (νCN), 1541 (νNCN), 1457 (δNH_2)].

2.3.2 Preparation of 1-cyclohexylbiguanide

1-cyclohexylbiguanide was prepared in two steps by the following procedure as described in literature.[100]

1-Cyclohexylbiguanide sulfate: Crude rose-violet copper cyclohexylbiguanide sulfate complex was obtained by refluxing a mixture of copper sulfate, dicyanodiimide and 1-cyclohexylamine in molecular proportion 1 : 2 : 3 ratio on a water bath with occasional stirring. The crude complex was dissolved in 18 N H_2SO_4 and the rose-violet copper complex was precipitated with dilute ammonia. The product, thus purified, was dissolved in 9 N H_2SO_4 and H_2S was passed into the solution and copper(II) sulfide was precipitated. The filtrate was concentrated to 100 mL over conc. H_2SO_4. The concentrated solution was treated with alcohol or acetone, when snow-white crystalline 1-cyclohexylbiguanide sulfate separated out.

1- Cyclohexylbiguanide: 1-Cyclohexylbiguanide sulfate (2.0 g, 7.12 mmol) was added to a methanolic solution of sodium hydroxide (1.14 g, 28.5 mmol). The mixture was stirred for two hours at room temperature and then at reflux temperature for 45 min. The hot methanol solution was filtered and the sodium sulfate cake was washed with hot methanol. The filtrate was concentrated under vacuum until a heavy crop of solid was obtained. Complete precipitation of 1-cyclohexylbiguanide was obtained by the addition of dry diethyl ether. The white fluffy solid was then filtered. Recrystallization of the solid from dry dichloromethane gave analytically pure 1-cyclohexyl biguanide. Analysis. found (calculated): For $C_8H_{17}N_5$, C, 52.4 (52.5); H, 9.3 (9.3); N, 38.2 (38.3). IR (KBr, cm^{-1}): 3480 (νNH_2), 3369, 3217 (νNH), 1635 (νCN), 1539 (νNCN), 1488 (δNH_2). ^1H NMR (DMSO-d_6, δ (ppm)) 5.73 (br, 6H, NH), 3.26 (m, 1H, NCH), 1.63 (m, 4H, CH_2), 1.18 (m, 6H, CH_2). ^{13}C {^1H} NMR (DMSO-d_6, δ (ppm)): 161.8, 159.3 (C=N), 48.9 (C1), 33.2 (C2,2'), 25.4 (C3,3'), 24.5 (C4).

2.3.3 Preparation of organosilanes

Following the known procedures,[101] diphenylsilane, methylphenylsilane and phenylsilane were prepared from reaction of the corresponding chlorosilane (1.0 mmol) with lithium aluminium hydride (1.10 or 1.56 mmol) in dry diethyl ether. The salt formed was hydrolyzed with 1 N HCl. The ether layer was dried over sodium sulfate and distilled [b.p. 95 – 97°C/ 5mm Hg (for Ph_2SiH_2); 138 - 140°C (for

$MePhSiH_2$); 112 - 115°C (for $PhSiH_3$)]. The identity of each compound was confirmed by IR and ^1H NMR spectra.

Preparation of p-tolylsilane

To a stirred suspension of magnesium (6.0 g, 0.25 mol) in diethyl ether (~200 mL), p-bromotoluene (42.6 g, 30.8 mL, 0.25 mol) was added dropwise in 4 - 5 h. The reaction mixture was stirred for 10 - 12h to get the desired Grignard reagent.

The Grignard reagent was added drop wise to silicon tetrachloride (42.5 g, 0.25 mol) in diethyl ether at 0°C. A curdy white solid was formed during the addition. The resulting reaction mixture was refluxed at 30 - 35°C for nearly 5-6h and then filtered. The solvent was distilled from the filtrate and n-hexane (~50 mL) was added. The solution was left overnight to allow complete precipitation of the salt, which was eliminated by filtration. The filtrate was distilled under vacuum, (98-100°C/5mm Hg) to yield trichloro-p-tolylsilane. Treatment of the chlorosilane (22.6 g, 0.1 mmol) with lithium aluminium hydride (4.29 g, 0.11 mmol) in diethyl ether and subsequent work-up of the reaction mixture gave p-tolylsilane as colorless, distillable liquid (b.p. 140-142°C). The compound was characterized by IR, ^1H NMR spectra.

2.3.4 Preparation of carbosilanes (1a - 1e)

(a) Preparation of $Et_3SiXSiH_3$ (1a) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

To a stirred solution of trichlorovinylsilane (8.76 g, 6.9 mL, 56.85 mmol) containing catalytic amount of Karstedt's catalyst (10^{-5} mole of Pt/mole of silane used), triethylsilane (4.2 g, 5.8 mL, 36.2 mmol) was added dropwise over a period of 2h. A strong induction period was observed after 10 - 15 min resulting in an exothermic reaction. The temperature was maintained below 60°C during this period. The contents were heated at 78°C for 10h and distilled (b. p. 85-88°C/5mm Hg). The distillate (9.2 g, 33.1 mmol) was treated with $LiAlH_4$ (2.0 g, 52.9 mmol) in diethyl ether. After gentle refluxing of the reaction mixture for 5-6h, the salt formed was hydrolyzed with 1.0 N HCl. The ether layer was dried over sodium sulphate and fractionally distilled. **1a** was obtained as a colorless liquid (b. p. 50 - 52°C/5mm Hg).

(b) Preparation of $Ph_2HSiXSiH_3$ (1b) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

To a stirred solution of trichlorovinylsilane (4.80 g, 3.8mL, 29.7 mmol) containing catalytic amount of H_2PtCl_6 (solution in 2-propanol, 10^{-7} mole of Pt/mole of silane used), diphenylsilane (4.97 g, 5mL, 27.0 mmol) was added dropwise. The contents were heated at 80°C for 12h and distilled (b. p. 138-142°C/5mm Hg). The chlorocarbosilane (8.20 g, 23.7 mmol) thus obtained was reacted with $LiAlH_4$ (1.44 g, 38.0 mmol) in a similar manner as discussed above for **1a** to afford the product **1b** as a colorless liquid (b. p. 115-120°C/5mm Hg).

(c) Preparation of $PhMeHSi(X)SiH_3$ (1c) [X = CH_2CH_2, -$CH(CH_3)$]

The reaction was carried out in a manner similar to that described for **1b** using trichlorovinylsilane (6.22 g, 4.9 mL, 38.5 mmol) and methylphenylsilane (4.27 g, 4.8 mL, 33.5 mmol). An induction period was observed after a few mL of the silane was added. The reaction mixture was heated at 70°C for 10h. The crude mixture was fractionally distilled (b. p. 90-95°C/5mm Hg). The resulting chlorocarbosilane (8.43g, 29.7 mmol) in diethyl ether was added drop wise to a dispersion of $LiAlH_4$ (1.81 g, 47.6 mmol) in ether at 0°C. Usual work up of the reaction mixture yielded **1c** as a colorless liquid (b. p. 40-42°C/ 5mm Hg).

(d) Preparation of $PhMe_2SiXSiMeH_2$ (1d) [X = -CH_2CH_2-, $CH(CH_3)$]

The reaction was carried out in a manner similar to that described for **1a** using dimethylphenylsilane (7.10 g, 8.0 mL, 52.1 mmol) and dichloromethylvinylsilane (11.1 g, 10.3 mL, 78.5 mmol). The contents were heated at 80°C for 10h and distilled (b. p. 95-97°C/5mm Hg). The chlorocarbosilane (11.67 g, 42.1 mmol) thus obtained was treated with $LiAlH_4$ (1.76 g, 46.3 mmol) and subsequent work up of the reaction mixture gave **1d** as a colorless liquid (b. p. 130 -135°C).

(e) Preparation of $PhMeHSi(X)SiMeH_2$ (1e) [X = -CH_2CH_2-, -$CH(CH_3)$]

To a stirred solution of dichloromethylvinylsilane (5.43 g, 5.0 mL, 38.5 mmol) containing catalytic amount of H_2PtCl_6 (solution in 2-propanol, 10^{-7} mole of Pt/mole of silane used), methylphenylsilane

(4.27 g, 4.8 mL, 35.0 mmol) was added drop wise. Induction period was observed after a few mL of the silane was added. The reaction mixture was heated at 70°C for 10h. The crude mixture was fractionally distilled (b. p. 90-95°C/5 mm Hg). The resulting chlorocarbosilane (8.76g, 30.0 mmol) in diethyl ether was added drop wise to a dispersion of $LiAlH_4$ (1.15 g, 33.0 mmol) in ether at 0°C. The contents were gently refluxed for 12h and then hydrolyzed with 1N HCl. Ether layer was extracted and dried over anhydrous sodium sulfate. Thereafter, the solvent was removed and the contents were distilled under vacuum to yield **1e** as a colorless liquid (b. p. 40-42°C/ 5mm Hg).

2.3.5 Preparation of silylbiguanides

Reaction of phenylsilane/p-tolylsilane with biguanide – preparation of $[(RSi)_3(RSiH)_2(Hbig)_2(H_3big)]$ (R = Ph (1), p-tol (2))

To a stirred suspension of biguanide (0.40 g, 4.0 mmol) in dry THF (~60mL), phenylsilane (0.87g, 1.0 mL, 8.0 mmol) or p-tolylsilane (1.0 g, 1.0 mL, 8.0 mmol) was added with the help of hypodermic syringe. A brisk effervescence was observed in each case immediately upon mixing the reactants. The reaction mixture was allowed to stir for 4-5 h at room temperature. A curdy white solid thus formed was filtered, washed with n-hexane and dried under vacuum. [Analysis. found (calculated): For **1**, $C_{36}H_{35}N_{15}Si_5$: C, 52.8 (52.9); H, 4.3 (4.3); N,

25.7 (25.6); Si, 17.4 (17.1). For **2**, $C_{41}H_{45}N_{15}Si_5$; C, 55.5 (55.6); H, 5.1 (5.1); N, 23.9 (23.7); Si, 15.9 (15.8)].

Reaction of phenylsilane/p-tolylsilane with 1-cyclohexylbiguanide – preparation of $[(RSi)_3(RSiH)_2(bigCy)_2(H_2bigCy)]$ (R = Ph (3), p-tol (4))

To a clear solution of 1-cyclohexylbiguanide (0.73 g, 4.0 mmol) in dry THF (60 mL), phenylsilane (0.87 g, 1.0 mL, 8.0 mmol)/ p-tolylsilane (1.0 g, 1.0 mL, 8.0 mmol) was added with the help of hypodermic syringe. A brisk effervescence was observed upon mixing the reactants. The reaction mixture was allowed to stir for 4-5 h at room temperature. Thereafter the solution was concentrated under vacuum and n-hexane was added to it. A curdy white solid was obtained in each case which was filtered, washed with n-hexane and dried under vacuum. [Analysis. found (calculated) for **3**, $C_{54}H_{65}N_{15}Si_5$: C, 60.8 (60.9); H, 6.3 (6.1); N, 19.5 (19.8), Si, 13.5 (13.2). For **4**, $C_{46}H_{75}N_{15}Si_5$: C, 62.8 (62.5); H, 6.5 (6.6); N, 18.3 (18.5), Si, 12.2 (12.4)].

Reaction of diphenylsilane/ methylphenylsilane with biguanide – preparation of 1,4-bis(silyl)biguanides (5, 6)

To a stirred suspension of biguanide (0.32 g, 3.14 mmol) in dry THF (~60 mL), diphenylsilane (1.16 g, 1.2 mL, 6.28 mmol) or methylphenylsilane (0.77 g, 0.9 mL, 6.28 mmol) was added with the help of hypodermic syringe. A brisk effervescence was observed immediately upon mixing the reactants. Slow dissolution of the solid occurs upon heating (60–62°C) for 3-4h. The reaction mixture was

refluxed at 60-62°C for 16h. The solvent was stripped off under vacuum to reduce the volume to ~10 mL and n-hexane was added. A solid was obtained in each case, which was filtered and dried under vacuum. [Analysis. found (calculated) For **5**, $C_{26}H_{25}N_5Si_2$: C, 67.1 (67.4); H, 5.6 (5.4); N, 15.0 (15.1), Si, 12.0 (12.1). For **6**, $C_{16}H_{21}N_5Si_2$: C, 56.3 (56.6); H, 6.0 (6.2); N, 20.5 (20.6), Si, 15.7 (16.5)].

Reaction of diphenylsilane/methylphenylsilane with 1-cyclohexyl biguanide – preparation of 1-cyclohexyl-2,5-bis(silyl)biguanides (7, 8)

The reaction between 1-cyclohexylbiguanide (0.57 g, 3.14 mmol) and diphenylsilane (1.16 g, 1.2 mL, 6.28 mmol)/ methylphenylsilane (0.77 g, 0.9 mL, 6.28 mmol) was performed under similar conditions as described above for (**5**) and (**6**). The clear reaction mixture was concentrated to ~ 10 mL and n-hexane was added. The corresponding silylbiguanides (**7**) and (**8**) were obtained as white solids. [Analysis. found (calculated) For **7**, $C_{32}H_{35}N_5Si_2$: C, 70.1 (70.3); H, 6.8 (6.6); N, 12.4 (12.8); Si, 10.5, (10.3). For **8**, $C_{22}H_{31}N_5Si_2$: C, 62.8 (62.6); H, 7.8 (7.6); N, 16.4 (16.6), Si, 13.5 (13.3)].

Reaction of $Et_3SiXSiH_3$ (1a) with biguanide - preparation of $[(Et_3SiXSiH)_2(H_2big)]_n$ (9) [X = $-CH_2CH_2-$/ $-CH(CH_3)$]

To a stirred suspension of biguanide (0.20 g, 2.0 mmol) in dry THF (30mL), the carbosilane **1a** (0.69 g, 0.7 mL, 4.0 mmol) was added with the help of hypodermic syringe. Slow dissolution of the solid

occurs upon heating the contents at 60 - 62°C for 6 - 7h. The reaction mixture was refluxed for 18h at the same temperature and cooled. The resulting solution was concentrated to ~10mL under vacuum and n-hexane was added. A curdy white solid appeared which was filtered, washed with n-hexane and dried under vacuum. [Analysis. found (calculated) for **9**, $C_{18}H_{43}N_5Si_4$: C, 48.6 (49.0); H, 9.7 (9.5); N, 15.4 (15.9); Si, 25.7 (25.5)].

Reaction of $Ph_2HSiXSiH_3$ (1b) with biguanide - preparation of $[(Ph_2HSiXSiH)_2(H_2big)]_n$ (10) [X = $-CH_2CH_2-$ /$-CH(CH_3)$]

The reaction between the carbosilane **1b** (0.97 g, 1.0 mL, 4.0 mmol) and biguanide (0.20 g, 2.0 mmol) in dry THF was performed under similar conditions as described for **9**. A white solid was obtained which was filtered, washed with n-hexane and dried under vacuum. [Analysis. found (calculated) for **10**, $C_{30}H_{35}N_5Si_4$: C, 62.7 (62.4); H, 6.0 (6.1); N, 11.8 (12.1); Si, 19.3 (19.4)].

Reaction of $PhMeHSiXSiH_3$ (1c) with biguanide - preparation of $[(PhMeHSiXSiH)_2(H_2big)]_n$ (11) [X = $-CH_2CH_2-$/ $-CH(CH_3)$]

To a suspension of biguanide (0.20 g, 2. 0 mmol) in dry THF (~30mL), the carbosilane **1c** (0.72 g, 0.8 mL, 4.0 mmol) was added with the help of hypodermic syringe. The reaction conditions were kept similar to that described for **9**. The silylbiguanide **11** was isolated as a white solid. [Analysis. found (calculated) for **11**, $C_{20}H_{31}N_5Si_4$: C, 52.7 (52.9); H, 13.3 (13.0); N, 15.1 (15.5); Si, 24.9 (24.7)].

Reaction of $Et_3SiXSiH_3$ (1a) with 1-cyclohexylbiguanide - preparation of $[(Et_3SiXSiH)_2(HbigCy)]_n$ (12) [X = $-CH_2CH_2-$ /- $CH(CH_3)$]

The carbosilane **1a** (0.69 g, 0.7 mL, 4.0 mmol) was added to a clear solution of 1-cyclohexylbiguanide (0.37g, 2.0 mmol) in THF (~30 mL) with the help of hypodermic syringe. The contents were heated at 60-65°C for ~24 h and subsequent work up with n-hexane gave the desired product as white solid. [Analysis. found (calculated) for **12**, $C_{24}H_{53}N_5Si_4$: C, 54.2 (54.4); H, 11.4 (11.1); N, 12.9 (13.2); Si, 20.9 (21.1)].

Reaction of $Ph_2HSiXSiH_3$ (1b) with 1-cyclohexylbiguanide - preparation of $[(Ph_2HSiXSiH)_2(HbigCy)]_n$ (13) [X = $-CH_2CH_2-$ /- $CH(CH_3)$]

The carbosilane **1b** (0.97 g, 1.0 mL, 4.0 mmol) was added to a clear solution of 1-cyclohexylbiguanide (0.37g, 2.0 mmol) in dry THF (~30mL), The reaction was carried out in a manner similar to that described for **9**. A white solid thus obtained was isolated and characterized as the silylbiguanide (**13**). [Analysis. found (calculated) for **13**, $C_{36}H_{45}N_5Si_4$: C, 65.8 (65.6); H, 6.5 (6.8); N, 10.4 (10.6); Si, 16.7 (16.9)].

Reaction of $PhMeHSiXSiH_3$ (1c) with 1-cyclohexylbiguanide - preparation of $[(PhMeHSiXSiH)_2(HbigCy)]_n$ (14) [X = $-CH_2CH_2-$ /- $CH(CH_3)$]

The carbosilane **1c** (0.72 g, 0.8 mL, 4.0 mmol) was added to a clear solution of 1-cyclohexylbiguanide (0.37 g, 2.0 mmol) in dry THF (~30mL). The reaction was carried out in a manner similar to that described for **9**. A white solid was obtained upon addition of n-hexane in the reaction mixture. It was isolated and dried under vacuum [Analysis. found (calculated) for **14**, $C_{26}H_{41}N_5Si_4$: C, 58.5 (58.3); H, 7.8 (7.6); N, 12.8 (13.1); Si, 20.7 (20.9)].

Reaction of $PhMe_2SiXSiMeH_2$ (1d) with biguanide – preparation of 1-(carbosilyl)biguanide (15) [X = $-CH_2CH_2-/-CH(CH_3)$]

The titled carbosilane **1d** (0.83 g, 0.9 mL, 4.0 mmol) was added to a suspension of biguanide (0.20 g, 2.0 mmol) in dry THF (~20 mL). Slow dissolution of the solid occurs with time upon heating the contents at 62 - 65°C. The reaction mixture was refluxed at the same temperature for ~ 72 h. The solution was then concentrated under vacuum and n-hexane was added. A curdy white precipitate was obtained. It was filtered off, washed with n-hexane and dried under vacuum. [Analysis. found (calculated) for **15**, $C_{13}H_{25}N_5Si_2$: C, 51.1 (50.8); H, 7.9 (8.1); N, 22.5 (22.8); Si, 18.0 (18.2)].

Reaction of $PhMeSiHXSiMeH_2$ (1e) with biguanide – preparation of 1-(carbosilyl)biguanide (16) [X = $-CH_2CH_2-/-CH(CH_3)$]

Preparation of the silylbiguanide **16** was achieved from the reaction of the carbosilane **1e** (0.78 g, 0.8 mL, 4.0 mmol) with biguanide (0.20 g, 2.0 mmol) under conditions similar to that described above for **15**. The compound **16** was obtained as a white solid. [Analysis. found (calculated) for **16**, $C_{12}H_{23}N_5Si_2$: C, 49.7 (49.3); H, 7.4 (7.5); N, 23.7 (23.9); Si, 18.9 (19.2)].

Reaction of $PhMe_2SiXSiMeH_2$ (1d) with 1-cyclohexylbiguanide – preparation of 1-cyclohexyl-5-(carbosilyl)biguanide (17) [X = $-CH_2CH_2-/-CH(CH_3)$]

To a clear solution of 1-cyclohexylbiguanide (0.37 g, 2.0 mmol) in dry THF (~20 mL), the carbosilane **1d** (0.83 g, 0.9 mL, 4.0 mmol) was added with the help of hypodermic syringe. The reaction mixture was refluxed at 62 - 65°C for 72h. The clear solution was then concentrated under vacuum and n-hexane was added. A curdy white precipitate was obtained. It was filtered off, washed with n-hexane and dried under vacuum. [Analysis. found (calculated) for **17**, $C_{19}H_{35}N_5Si_2$: C, 58.9 (58.6); H, 8.7 (8.9); N, 17.8 (17.9); Si, 14.7 (14.5)].

Reaction of $PhMeSiHXSiMeH_2$ (1e) with 1-cyclohexylbiguanide – preparation of 1-cyclohexyl-5-(carbosilyl)biguanide (18) [X = $-CH_2CH_2-/-CH(CH_3)$]

The reaction between the carbosilane **1e** (0.78 g, 0.8 mL, 4.0 mmol) and 1-cyclohexylbiguanide (0.37 g, 2.0 mmol) in dry THF (~20 mL) was performed under the similar condition as described above for **17**. The solid compound obtained was filtered off, washed with n-hexane and dried over vacuum. [Analysis. found (calculated) for **18**, $C_{18}H_{33}N_5Si_2$: C, 58.1 (57.8); H, 8.8 (8.6); N, 18.5 (18.7), Si, 14.6 (14.9)].

2.3.6 Reactions of 1,4-bis(silyl)biguanides and 1-cyclohexyl-2,5-bis(silyl)biguanides with titanium(IV) chloride

2.3.6.1 Reaction of 1,4-bis(diphenylsilyl)biguanide (5)/ 1,4-bis(methylphenylsilyl)biguanide (6) with titanium(IV) chloride

The silylbiguanide (**5** or **6**) (0.93 g/0.68 g, 2.0 mmol) in dry dichloromethane (~50 mL) was cooled to – 50°C and titanium(IV) chloride (0.38 g, 0.22 mL, 2.0 mmol) in the same solvent was added with the help of hypodermic syringe. The reaction mixture was stirred for 3h at – 50°C and subsequently allowed to attain room temperature. An orange solid, obtained in each case was filtered, washed with dichloromethane and dried under vacuum. These compounds were identified as the transmetallated products, **5a** and **6a**. The orange-red filtrates obtained from the above reactions were concentrated and n-hexane was added. An orange solid appeared upon stirring the

contents at room temperature for 2 - 3 h. The compounds thus obtained were identified as the adducts **5b** and **6b**. [Analysis. found (calculated): For **5a**, $C_{14}H_{24}N_5SiTiCl_3$: Si, 7.3 (7.5); Ti, 12.7 (12.9); Cl, 28.3 (28.5). For **6a**, $C_9H_{12}N_5SiTiCl_3$: Si, 12.2 (12.1); Ti, 6.1 (6.4); Cl, 24.3 (24.5). For **5b**, $C_{26}H_{25}N_5Si_2TiCl_4$: Si, 10.3 (10.6); Ti, 9.0 (9.1); Cl, 26.8 (26.8). For **6b**, $C_{16}H_{21}N_5Si_2TiCl_4$: Si, 8.4 (8.6); Ti, 7.2 (7.3); Cl, 21.6 (21.7)].

2.3.6.2 Reactions of 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide (7)/ 1-cyclohexyl-2,5-bis(methylphenylsilyl)biguanide (8) with titanium(IV) chloride

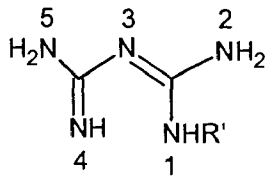
The titled reactions between 1-cyclohexyl-2,5-bis(silyl)biguanide (**7** or **8**) (1.09 g/ 0.84 g, 2.0 mmol) in dry dichloromethane (~50 mL) and titanium(IV) chloride (0.38 g, 0.22 mL, 2.0 mmol) were carried out under identical conditions as described above in 2.3.6.1. An orange-red solid was isolated in each case and identified as the transmetallated products **7a** and **8a.** The deep red filtrate in each case was concentrated in vacuum and n-hexane was added. This gave another crop of solid compounds which were identified as the adducts, **7b** and **8b.** [Analysis. found (calculated): For **7a**, $C_{20}H_{24}N_5SiTiCl_3$: Si, 6.0 (6.1); Ti, 10.7 (10.5); Cl, 23.3 (23.4). For **8a**, $C_{15}H_{22}N_5SiTiCl_3$: Si, 5.5 (5.4); Ti, 9.2 (9.3); Cl, 20.5 (20.5). For **7b**, $C_{32}H_{35}N_5Si_2TiCl_4$: Si, 9.3 (9.2); Ti, 7.9 (7.8); Cl, 23.1 (23.2). For **8b**, $C_{22}H_{31}N_5Si_2TiCl_4$: Si, 7.4 (7.6); Ti, 6.2 (6.5); Cl, 19.3 (19.2)].

CHAPTER III

REACTIONS OF PRIMARY/SECONDARY ORGANOSILANES WITH BIGUANIDE/ 1-CYCLOHEXYLBIGUANIDE

The contents of this chapter are divided into two sections. Section A deals with the reactivity of primary organosilanes, $RSiH_3$ (R = Ph or p-tol) with biguanide and 1-cyclohexylbiguanide. In section B, analogous reactions of secondary organosilanes, $RR'SiH_2$ (R = Ph, R' = Me; R = R' = Ph) with the biguanide ligands are described. For the clarity of discussion being presented in this and subsequent chapters, it is imperative to summarize a brief account of important features of biguanide.

The synthetic method for biguanide and 1-substituted biguanide has been known for a long time.[99,100] These are known to be one of the strongest bases with pK_a = 10 - 13.[102] In earlier reports, IR and UV spectral studies have been extensively discussed in order to elucidate their structural features.[91] Strong evidence in favor of unsymmetrical structure as shown in figure 1 comes from the X-ray crystal structure of biguanide,[85] as well as the ^{15}N NMR studies of biguanide derivatives in solution.[86] Structural representation and also the numbering scheme as recommended in IUPAC nomenclature are shown in figure 1.[103]



H_5bigR'

Figure 1

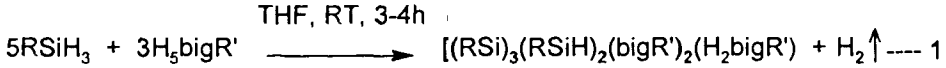
The synthesis of biguanide and 1-cyclohexylbiguanide being under investigation is achieved by following the procedure known in literature.[99,100] Elemental analysis, IR and UV spectral data of these ligands are in conformity with those reported earlier. In view of the paucity of NMR data of these ligands and its relevance to the present studies, ^{1}H and ^{13}C NMR spectra of these compounds have been recorded and results are summarized in the experimental section (chapter II). Notable feature in the ^{1}H NMR studies is the broad resonance in the region of δ 4.5 - 5.0 due to NH protons which show concentration dependent chemical shifts. Phenylsilane, p-tolylsilane, diphenylsilane and methylphenylsilane have been prepared by reduction of the corresponding chlorosilanes with $LiAlH_4$ as reported in literature.[101]

3.1 Section A- Reactivity of primary organosilanes towards biguanide/ 1-cyclohexylbiguanide

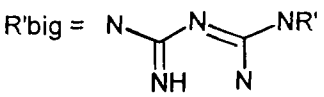
SiH/NH dehydrocoupling reaction between various primary/secondary organosilanes and ammonia/hydrazine is known to be a simple and straightforward route to Si-N bond formation.[47-54] Studies reported so far reveal that these reactions can proceed under uncatalyzed as well as transition metal catalyzed conditions to yield Si-N bonded compounds of varying composition. This synthetic strategy is advantageous due to the formation of hydrogen gas as the only by-product. In the titled reactions too, a facile SiH/NH dehydrocoupling

between the organosilanes and biguanide or 1-cyclohexylbiguanide takes place under extremely mild conditions to yield new family of Si-N-C-N-C-N based structures.

Addition of two equivalents of phenylsilane/p-tolylsilane to either a suspension of biguanide or to a clear solution of 1-cyclohexylbiguanide in dry THF results in brisk effervescence in each case which apparently slows down within 3-4h. Subsequent work up of the concentrated reaction mixture with n-hexane affords the corresponding Si-N bonded silylbiguanides, **1 – 4** (equation 1). These compounds possess a robust composition with silane : biguanide ratio as 5 : 3. A general representation depicting the empirical formulation of the products can be described as shown in equation 1, wherein biguanide ligands are abbreviated as H_5bigR' (R' = H or Cy).



Compound	R	R'
1	Ph	H
2	p-tol	H
3	Ph	Cy
4	p-tol	Cy



Carrying out these reactions with excess (3 equivalents) of organosilanes do not alter the product composition and the unreacted silane can be recovered. These reactions when carried out for prolonged period (RT, 18h) or under reflux temperature (60-65°C, 12h)

afford the corresponding products, which possess identical analytical and spectroscopic data as those of **1 - 4**. This implies that a facile SiH/NH dehydrocoupling takes place in the initial stages of these reactions and form robust assemblies **1 - 4** whose composition remain unaltered.

3.2 Characterization of silylbiguanides (1 -- 4)

The compounds **1 - 4** are moisture sensitive solids. While **3** and **4** are soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, THF and DMSO, the compounds **1** and **2** are only soluble in DMSO. These have been characterized by a combination of analytical and spectroscopic techniques including elemental analysis, FAB mass, IR, multinuclear (^1H, ^{13}C, ^{29}Si) NMR spectroscopy and thermogravimetric analysis. Elemental analyses (chapter II) conform to the idealized composition of these compounds as shown in equation 1.

3.2.1 FAB mass spectral analysis

In the absence of X-ray structure analysis, FAB mass spectroscopy has been successfully employed for the characterization of these compounds. The relevant FAB mass data in 3-nitrobenzyl alcohol matrix are summarized in tables 3.1 and 3.2. The spectra of silylbiguanides **1** and **2** reveal the M^+ ion at m/z 817 and 887 respectively (Figure 3.1), corresponding to molecular formula $C_{36}H_{35}N_{15}Si_5$ (for **1**) and $C_{41}H_{45}N_{15}Si_5$ (for **2**). These results are in

Table 3.1 FAB mass data (commonly observed fragment ions) for $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R' = H, R = Ph (1); R' = Cy, R = Ph (3))

m/z	**1** (M = 817)	**3** (M = 1063)
817	$[M]^+$	$[M- 3C_6H_{10}]^+$
757	$[M-4NH]^+$	$[M-3C_6H_{10}-4NH]^+$
697	$[M-PhSi-NH]^+$	$[M-3C_6H_{10}-PhSi-NH]^+$
637	$[M-PhSi-C_6H_3]^+$	$[M-3C_6H_{10}-PhSi- C_6H_3]^+$
577	$[M-3C_6H_3-NH]^+$	$[M-3C_6H_{10}-3C_6H_3-NH]^+$

Ions observed corresponding to the ligands

For **1**, m/z 103 $[C_2H_9 N_5]^+$; For **3**, 185 $[C_8H_{19} N_5]^+$

Table 3.2 FAB mass data (commonly observed fragment ions) for $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R' = H, R p-tol (2); R' = Cy, R = p-tol (4))

m/z	**2** (M = 887)	**4** (M = 1133)
887	$[M]^+$	$[M\text{-}3C_6H_{10}]^+$
812	$[M\text{-}5CH_3]^+$	$[M\text{-}3C_6H_{10}\text{-}5CH_3]^+$
633	$[M\text{-}2\ CH_3C_6H_4Si\ \text{–}NH_2]^+$	$[M\text{-}3C_6H_{10}\text{-}2CH_3C_6H_4Si\text{-}\ NH_2]^+$
559	$[M\text{-}2\ CH_3C_6H_4Si\text{-}\ CH_3C_6H_3]^+$	$[M\text{-}3C_6H_{10}\text{-}2CH_3C_6H_4Si\text{-}\ CH_3C_6H_3]^+$

Other significant ions observed: for **2**, m/z 103 $[C_2H_9N_5]^+$. For **4**, 184 $[C_8H_{18}N_5]^+$

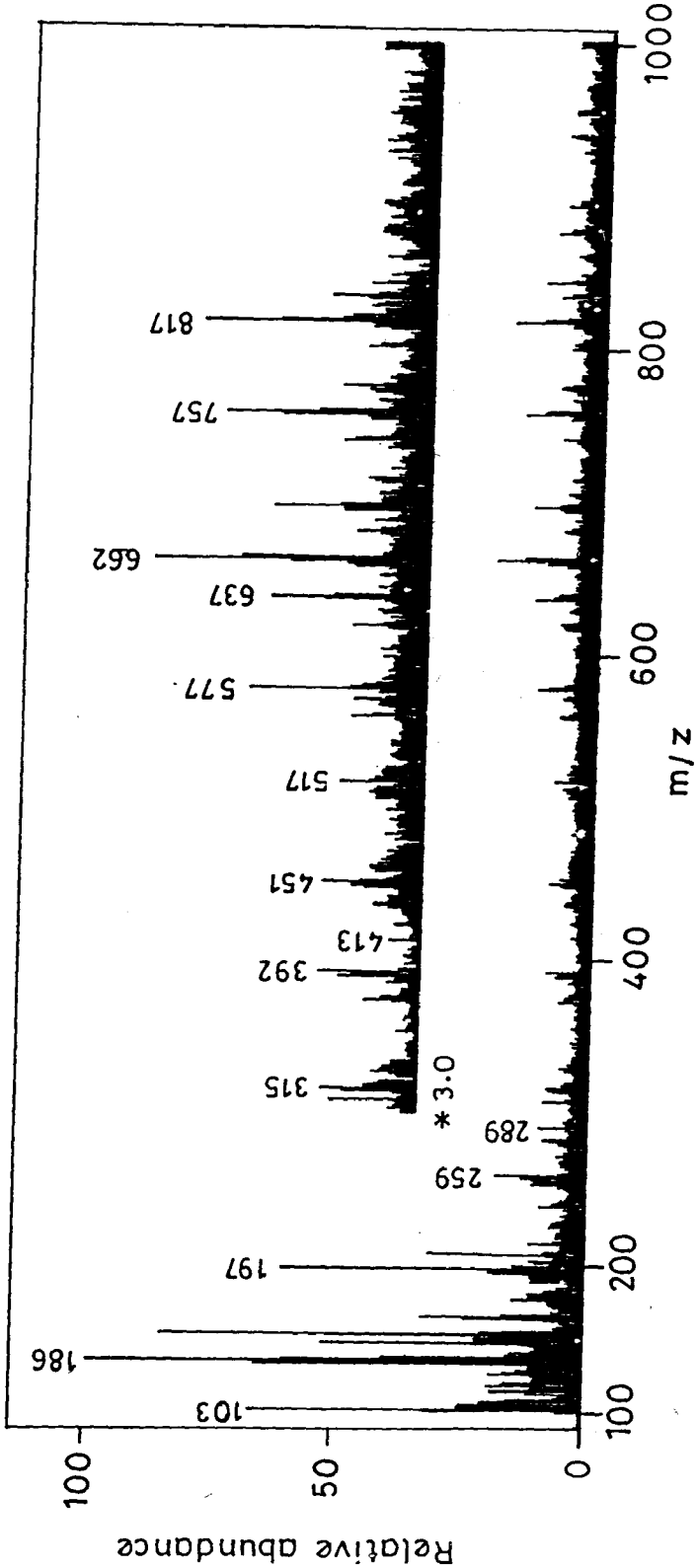


Figure 3.1 FAB mass spectrum of $[(PhSi)_3(PhSiH)_2(Hbig)_2(H_3big)]$ (1)

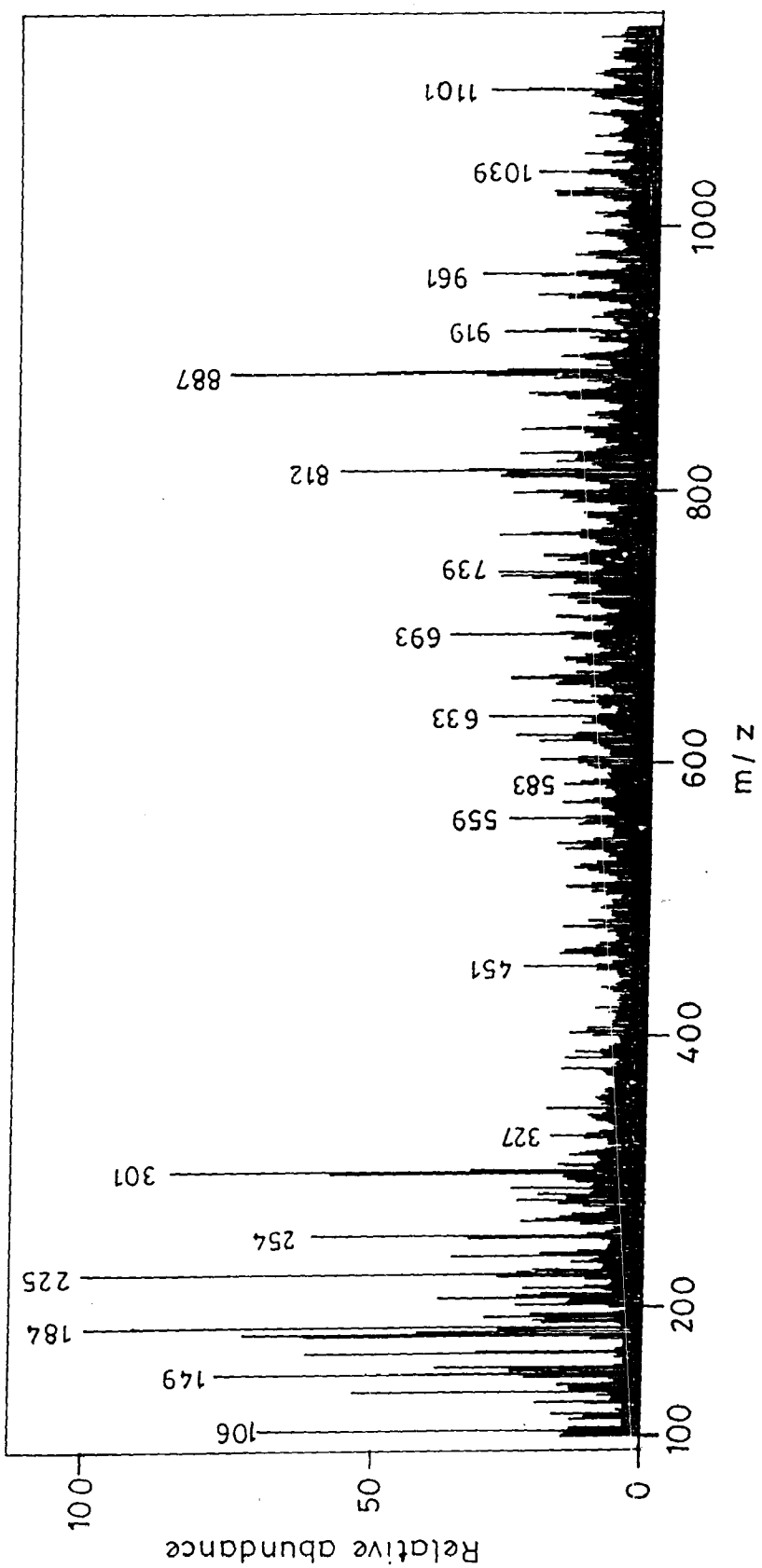


Figure 3.2 FAB mass spectrum of [(p-tolSi)$_3$(p-tolSiH)$_2$(bigCy)(H$_2$bigCy)] (4)

conformity with the idealized representation $[(RSi)_3(RSiH)_2(Hbig)_2(H_3big)]$ [R = Ph (**1**), p-tol (**2**)] as shown in equation 1. Although the FAB mass spectra of **3** and **4** do not show M^+ ion peak, important fragment ions such as m/z 1015 $[M - 3NH_2]^+$ for **3** and 1101 $[M - 2NH_2]^+$ for **4** provide strong evidence in favor of the composition $[(RSi)_3(RSiH)_2(bigCy)_2(H_2bigCy)]$ [R = Ph (**3**), p-tol (**4**)] (Figure 3.2). A detailed analysis of the spectra reveals a number of commonly observed fragment ions primarily arising from the loss of Ph/p-tol, PhSi/p-tolSi, Cy, NH and NH_2 ions. The FAB mass data also point towards the structural similarities of these compounds.

3.2.2 Infrared Spectra

Pertinent IR absorptions of silylbiguanides **1 - 4** along with their assignments are given in table 3.3. The distinct absorptions at 3381-3207 cm^{-1} in the spectrum of each compound are attributed to the νNH mode. A notable feature is the complete absence of νNH_2 absorption at ~3420 cm^{-1} which is quite prominent in the parent biguanide/ 1-cyclohexylbiguanide. This suggests the absence of primary NH_2 functionalities in these compounds. While a weak absorption at 2161-2157 cm^{-1} due to νSiH mode is observed, the spectra are devoid of δSiH_2 absorption at 945 cm^{-1} (Figure 3.3). These spectral features can be considered as qualitative evidence in favor of SiH/NH dehydrocoupling involving organosilane and the $-NH_2$ sites of biguanide/1-cyclohexylbiguanide. In addition, IR spectra also exhibit

Table 3.3 IR (KBr, cm^{-1}) spectral data of $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R' = H, R = Ph (1) or p-tol (2); R' = Cy, R = Ph (3) or p-tol (4))

Compound	νNH	νCH (aromatic)	νCH (aliphatic)	νSiH	νCN	νNCN	νSiPh
1	3381 3207	3068 3050	-	2161	1634	1541	1124
2	3353 3209	3061 3055	2957 2871	2157	1624	1540	1119
3	3337 3210	3068 3051	2957 2853	2158	1620	1557	1125
4	3381 3221	3066 3050	2907 2865	2158	1646	1558	1120

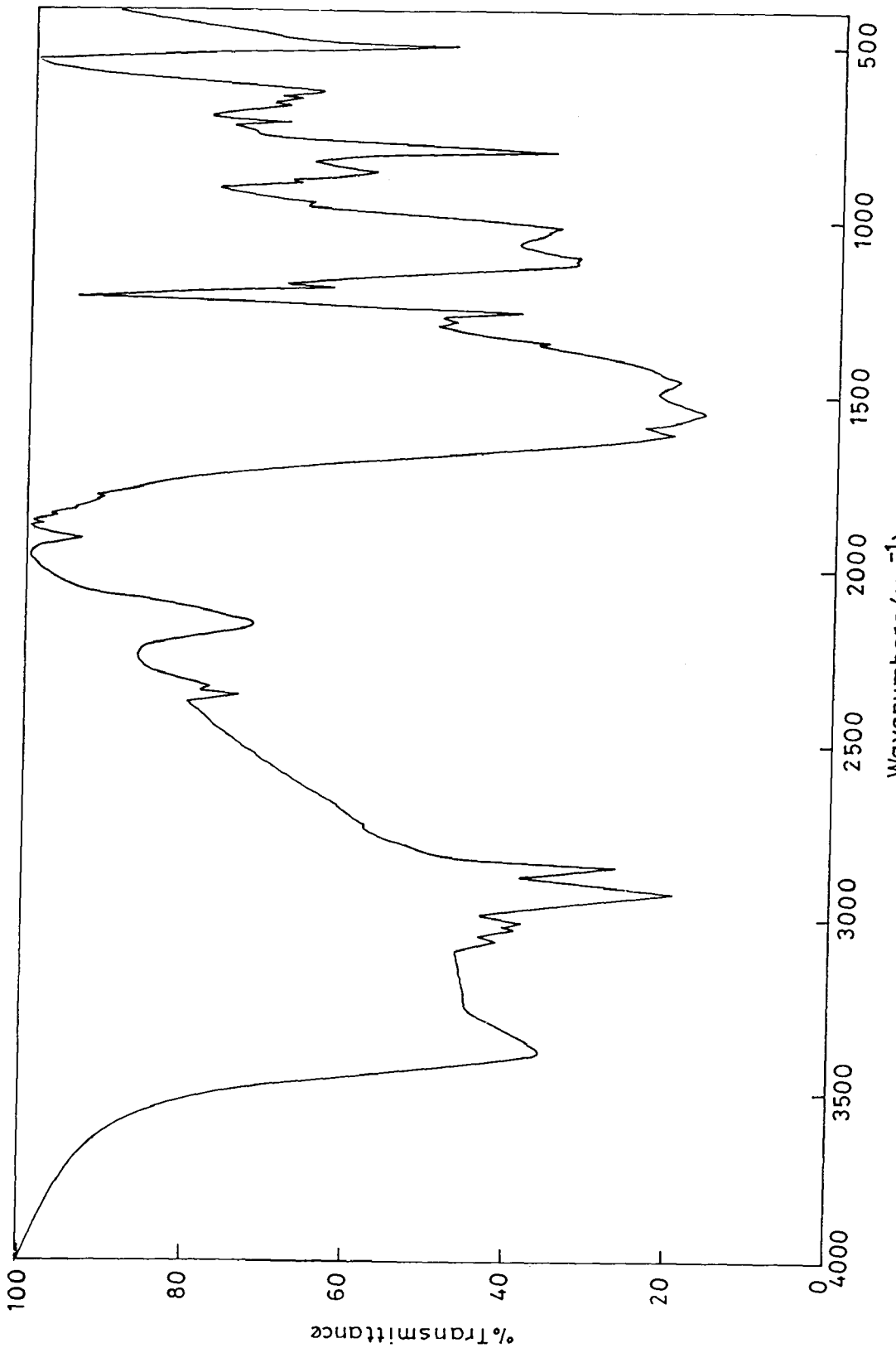


Figure 3.3 IR spectrum of [(PhSi)$_3$(PhSiH)$_2$(bigCy)(H$_2$bigCy)] (3)

routine absorptions due to the other functional groups; e. g., the bands at 1646 - 1620 and 1558 - 1540 cm^{-1} are ascribed to νCN and νNCN (skeletal modes) respectively. These absorptions remain practically unaltered in comparison to those observed in the parent ligands. The characteristic absorption due to PhSi group appears at 1119 - 1125 cm^{-1}. νCH (aliphatic) and νCH (aromatic) modes appear at the routine positions in the spectra of these compounds.

3.2.3 NMR spectral studies

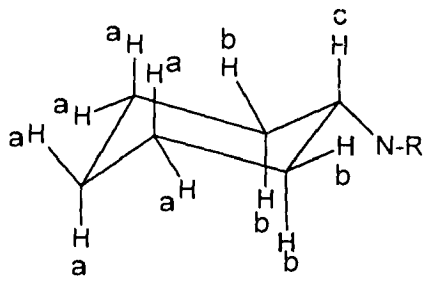
^{1}H NMR spectra

^{1}H NMR spectra of the silylbiguanides, $[(RSi)_3(RSiH)_2(Hbig)_2(H_3big)]$ (R = Ph (**1**), p-tol (**2**)) derived from biguanide ligand exhibit two multiplets at δ 7.56-7.47 and 7.34-7.13 due to meta and ortho/para (where ever applicable) aromatic protons[104] (Table 3.4). For the compound **2**, a singlet at δ 2.33 is ascribed to the p-tol-CH_3 group. ^{1}H NMR spectrum of each compound shows a singlet at δ 4.60 - 4.62, which is reminiscent of SiH protons. The NH protons appear as a broad signal spanning the region δ 3.4 - 6.5 and show concentration dependent chemical shifts due to fast exchange of NH protons with traces of moisture or solvent protons.[105] Similar phenomenon is also observed in biguanide ligand. It is also imperative to mention that a large uncertainty in the integral of SiH and NH signals is observed due to the broadening of NH signals. Thus a definite

Table 3.4 ^{1}H NMR spectral data δ (ppm) of $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R' = H, R = Ph (1) or p-tol (2); R' = Cy, R = Ph (3) or p-tol (4))

Compound	$C_6H_5/C_6H_4CH_3$	NH	SiH	$CH_3C_6H_4$	NCy
1	7.56 (m, meta) 7.34 (m, ortho/para)	5.33 (br)	4.61	-	-
2	7.47 (m,2H, meta) 7.26 (m, 2H, ortho)	5.43 (br)	4.60	2.33 (s, 3H)	-
3	7.56 (m, 10H, meta) 7.34 (m, 15 H, ortho/para)	5.38 (br)	4.62	-	3.35 (br,3H, CH^c) 1.64 (m, 12H, CH_2^b) 1.18 (m, 18H,CH_2^c)
4	7.48 (m,10H, meta) 7.13 (m, 10H, ortho)	5.35 (br)	4.60	2.35 (s,15H)	3.36 (br,3H, CH^c) 1.64 (m, 12H, CH_2^b) 1.18 (m, 18H,CH_2^c)

* The assignments follow the structure as



compositional assignment of these compounds has been precluded based on the ^{1}H NMR data alone.

On the other hand, ^{1}H NMR spectra of the compounds $[(RSi)_3(RSiH)_2(bigCy)_2(H_2bigCy)]$ (R = Ph (**3**), p-tol (**4**)) derived from 1-cyclohexylbiguanide are quite informative (Figure 3.4). The spectrum of each compound shows characteristic signals due to Ph/p-tol groups in their usual chemical shift values (Table 3.4). The NCH proton associated with cyclohexyl group appears as a broad singlet at δ 3.35-3.36 while CH_2 protons are observed as two multiplets at δ 1.18 and 1.64. The relative integration ratio of RSi and NCy groups is found to be 5 : 3 and conform to the proposed formulation. The spectral region between δ 3.4 - 6.5 is dominated by a broad signal due to NH protons. In addition, a sharp singlet at δ 4.60-4.62 is attributed to SiH group. However, a quantitative estimation of the SiH and NH protons present in these compounds could not be made.

^{13}C {^{1}H} NMR spectra

Since ^{1}H NMR studies of the silylbiguanides $[(RSi)_3(RSiH)_2(Hbig)_2(H_3big)]$ (R = Ph (**1**), p-tol (**2**)) do not provide enough information regarding their empirical composition, it was of interest to gauge an estimate of the RSi and biguanide moieties present in these compounds by quantitative ^{13}C {^{1}H} NMR spectroscopy. Pertinent ^{13}C NMR data are given in table 3.5. For **1**, the ^{13}C NMR signals arising from PhSi (δ 138.3, 133.5, 130.2, 127.3) and

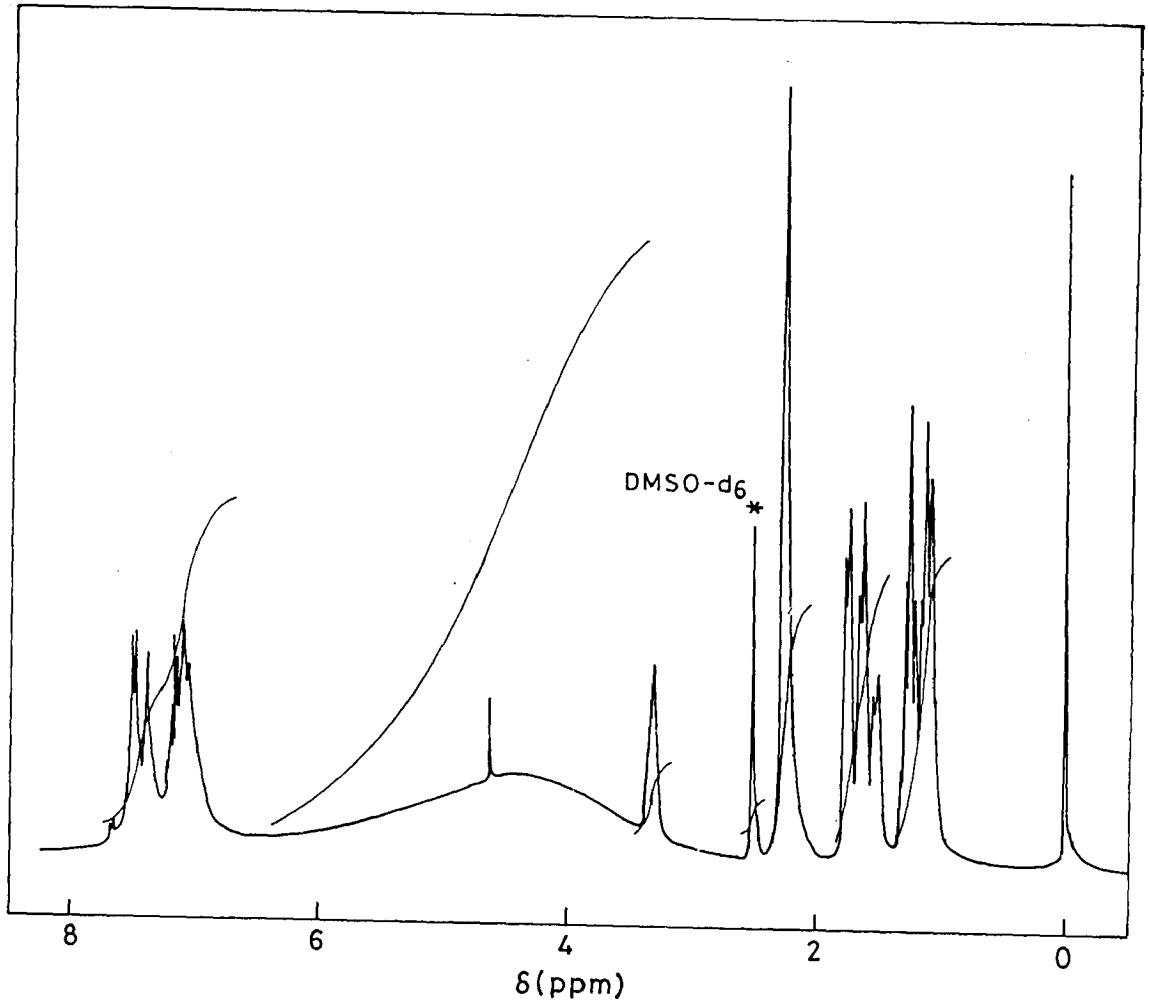


Figure 3.4 ^{1}H NMR spectrum of [(p-tolSi)$_3$(p-tolSiH)$_2$(bigCy)(H$_2$bigCy)] (4)

Table 3.5 ^{13}C $\{^{1}H\}$ spectral data δ (ppm) of $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R' = H, R = Ph (1) or p-tol (2); R' = Cy, R = Ph (3) or p-tol (4))

Compound	C=N	C_6H_5/C_6H_4	CH_3	Cy
1	162.7	i = 138.3, o = 133.5, p = 130.2, m = 127.3	-	-
2	162.7	i = 139.5, m= 131.6, o/p = 128.2	21.1	-
3	161.7, 159.2	i = 138.2, o = 133.5, p = 130.1, m = 127.3	-	49.0 (C1) 33.2 (C2, C2') 25.2 (C3,C3') 24.5 (C4)
4	161.8, 159.3	i = 139.8, m = 131.5, o/p = 127.3	21.1	49.0 (C1) 33.2 (C2, C2') 25.5(C3,C3') 24.4(C4)

C=N (δ 162.7) moiety of the biguanide group are found to integrate in a definite ratio of 5 : 3. Similarly for **2**, stoichiometry of p-tolSi and C=N groups as 5: 3 has been deduced from ^{13}C {^{1}H} NMR signals at δ 139.5, 131.6, 128.2 and 21.1 as well as 162.7 (C=N). These results provide fair evidence to the empirical composition as suggested. For the silylbiguanides [$(RSi)_3(RSiH)_2(bigCy)_2(H_2bigCy)$] (R = Ph (**3**), p-tol (**4**)) quantitative ^{13}C {^{1}H} NMR spectra reveal distinct resonances (wherever applicable) due to PhSi (138.2, 133.5, 130.1, 127.3), p-tolSi (δ 139.8, 131.5, 127.3, 21.1) and C=N (δ 161.8, 159.3) groups. The signals due to N-cyclohexyl group (Figure 3.5) appear at δ 49.0 (C1, NCH) and 33.2 (C2, 2', CH_2), 25.2 (C3, 3', CH_2), 24.5 (C4, CH_2). The relative integration of RSi and NCy/C=N groups is found to be 5 : 3, irrespective of the nature of R and R' group. These results are in conformity with those obtained from ^{1}H NMR spectra of these compounds.

^{29}Si {^{1}H} NMR spectra

^{29}Si {^{1}H} NMR spectra of **1 - 4** in DMSO-d_6 offer important structural information. The spectrum of each compound shows two distinct resonances in the chemical shift region of δ -127.3 to –132.1. In order to confirm the nature of silicon species, spectral studies in ^{29}Si {^{1}H} DEPT–135 mode have been carried out (Figure 3.6). Interestingly, the spectrum of each compound reveals the disappearance of the

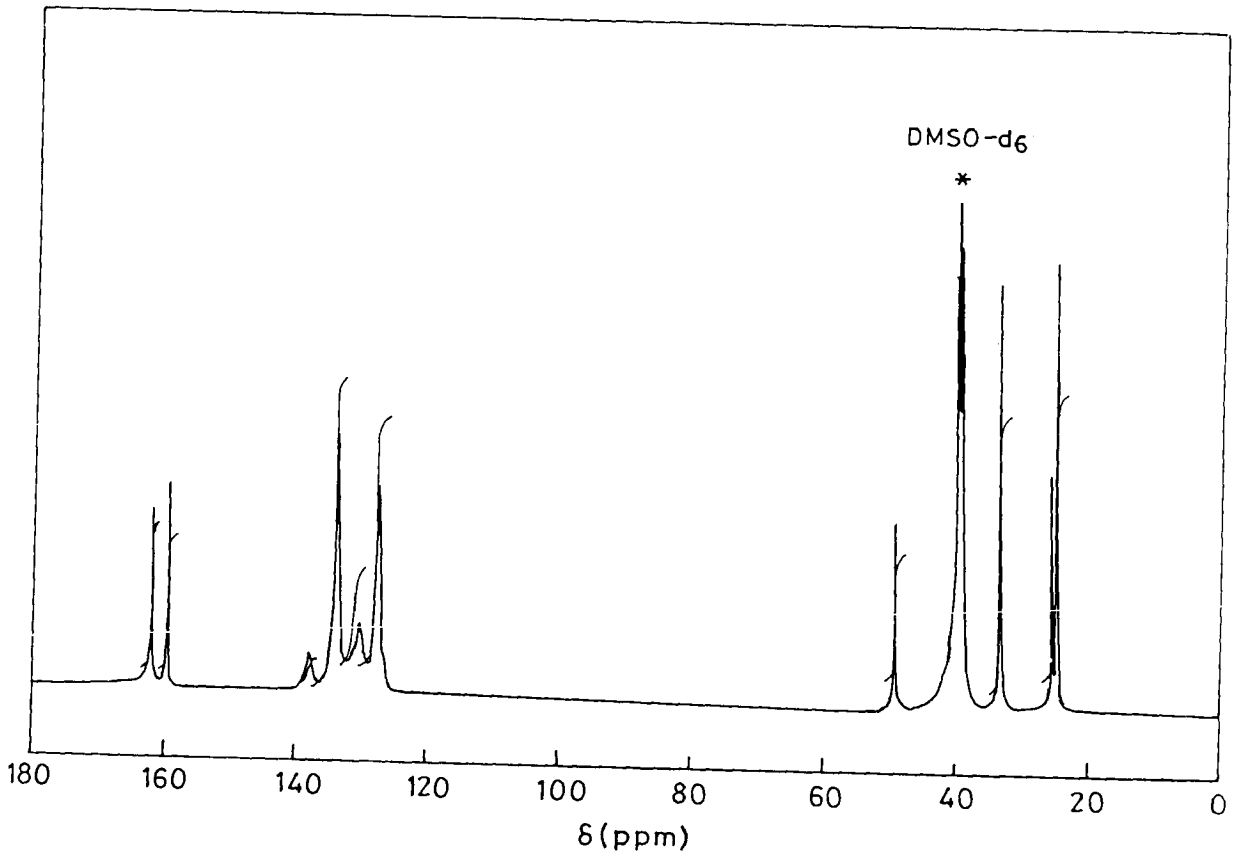


Figure 3.5 ^{13}C {^{1}H} NMR spectrum of [$(PhSi)_3(PhSiH)_2(bigCy)_2(H_2bigCy)$] (3)

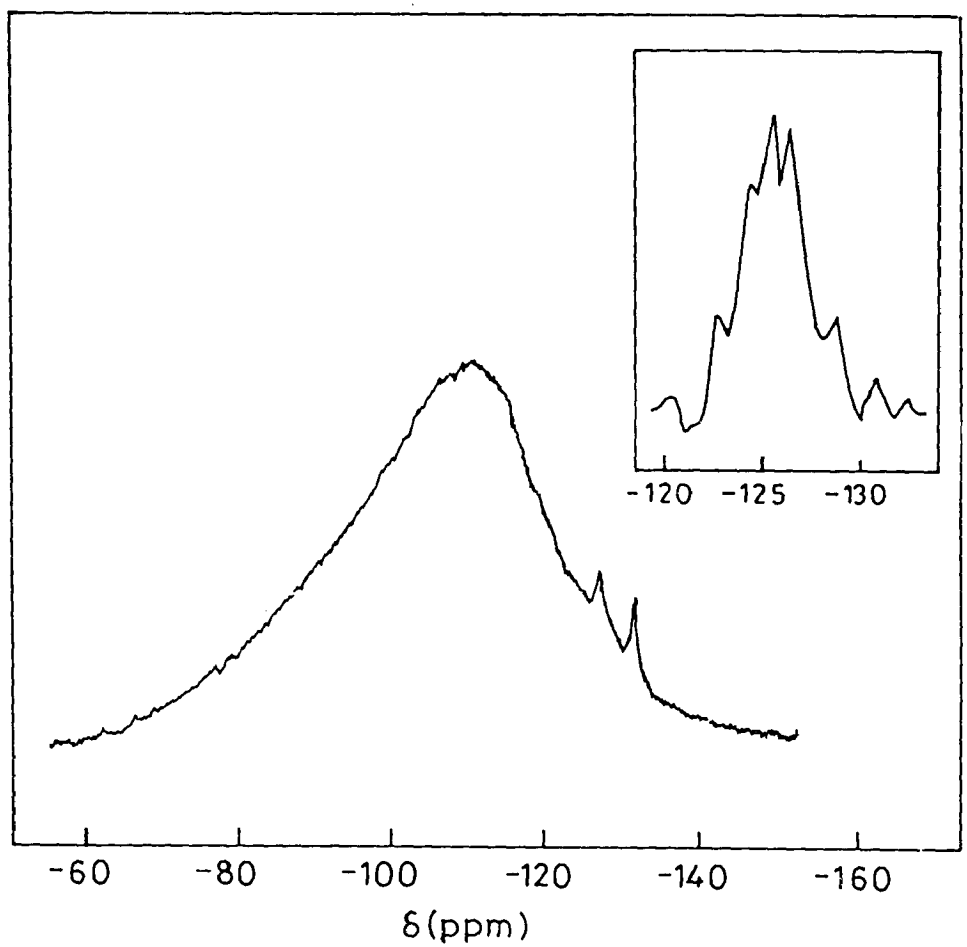


Figure 3.6 $^{29}Si\{^{1}H\}$ NMR spectrum of $[(PhSi)_3(PhSiH)_2(Hbig)_2(H_3big)]$ (1)
(inset picture shows its DEPT-135 Spectrum)

signal at δ -131.7 to –132.1 and is reminiscent of quaternary silicon species. Consequently, the origin of this resonance is conceived to arise from $RSiN_3$ moieties, which are present in the structural framework. The signal at δ -127.3 to -127.8 appears as a quintet in the DEPT–135 mode. The splitting pattern is reminiscent of ^{29}Si-^{14}N coupling with $^1J(^{29}Si$-$^{14}N)$ = 46.2 – 47.1 Hz, and suggests the presence of $RSiHN_2$ moieties in the structural framework. The ^1J(Si-N) coupling information in the DEPT mode as observed in these compounds is not unusual since the application of DEPT ^{29}Si NMR in extracting similar information has been reported earlier for a number of organosilylamines.[84] A close resemblance of δ ^{29}Si NMR data for **1 - 4** is suggestive of their structural similarities. A striking feature is the marked upfield ^{29}Si chemical shift values in comparison to those normally observed for tetracoordinated Si-N bonded compounds (δ -20 to –30).[53] The values of $^1J(^{29}Si$-$^{14}N)$ obtained herein are also much higher than expected for classical tetra coordinated silicon-nitrogen compounds.

Using an empirical relationship (equation 2) Kupce and Lukevics have observed that a linear correlation between δ ^{29}Si and $^1J(^{29}Si$-$^{15}N)$ data exists in the family of silylamines.[84] For the silylamines, $R_3SiNR'_2$ it was observed that ^1J(Si-N) values increases with electronegative substituents at silicon atom in the following series R = Me < Ph < NR_2 < OR. In order to validate the spectral data in **1 - 4**, the relation between

the observed δ ^{29}Si and $^{1}J(^{29}Si\text{-}^{14}N)$ data has been examined in terms of the empirical relationship (equation 2) as suggested by Kupce and Lukevics.[32] The values of $^{1}J(^{29}Si\text{-}^{15}N)$ have been deduced from the established correlation, $^{1}J(^{29}Si\text{-}^{14}N) = 0.7129\ ^{1}J(^{29}Si\text{-}^{15}N)$ and ^{29}Si chemical shifts of **1 - 4** have been calculated.

$$^{1}J(^{29}Si\text{-}^{15}N) = 15.7 - 0.384\ \delta\ ^{29}Si \qquad \text{----2}$$

The relevant data are summarized in table 3.6. A good agreement between the observed and calculated ^{29}Si chemical shifts has been observed. Since spectral data for the compounds **1 - 4** is validated, an explanation to the unusually upfield ^{29}Si chemical shifts as well as high $^{1}J(^{29}Si\text{-}^{14}N)$ value has been sought. Based on the group-electronegativity concept, the δ ^{29}Si data of **1 - 4** are compared with those of closely related compounds such as poly(silylcarbodiimides) $[RSi(NCN)_{1.5}]_n$.[10] ^{29}Si chemical shifts of these polymers are known to lie in the range of δ –60 to –70. It thus appears that electronegativity effect of the biguanide group(s) alone does not provide a satisfactory explanation for the observed upfield ^{29}Si NMR chemical shifts for the silylbiguanides **1 - 4**. It is likely that these compounds possess hypercoordinated silicon atoms by virtue of the presence of potential donor sites such as imine and amine groups associated with the biguanide ligand. Bassindale et al. have reported a similar analogy in the δ ^{29}Si NMR data of tetra coordinated silyl-triflates,

Table 3.6 ^{29}Si NMR spectral data δ (ppm) of $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$
(R' = H, R = Ph (1) or p-tol (2); R' = Cy, R = Ph (3) or p-tol (4))

Compound	Moiety	δ ^{29}Si (observed)	$^1J(^{29}Si-^{14}N)$ (Hz)	$^1J(^{29}Si-^{15}N)$*(Hz)	δ ^{29}Si (calculated)*
1	$PhSiHN_2$, $PhSiN_3$	-127.3, -131.7	47.1	66.1	-131.2
2	p-tolSiHN$_2$, p-tolSiN$_3$	-127.8, -132.1	-	-	-
3	$PhSiHN_2$, $PhSiN_3$	-127.4, -131.9	46.4	65.0	-128.4
4	p-tolSiHN$_2$, p-tolSiN$_3$	-127.5, -131.8	46.2	64.8	-127.9

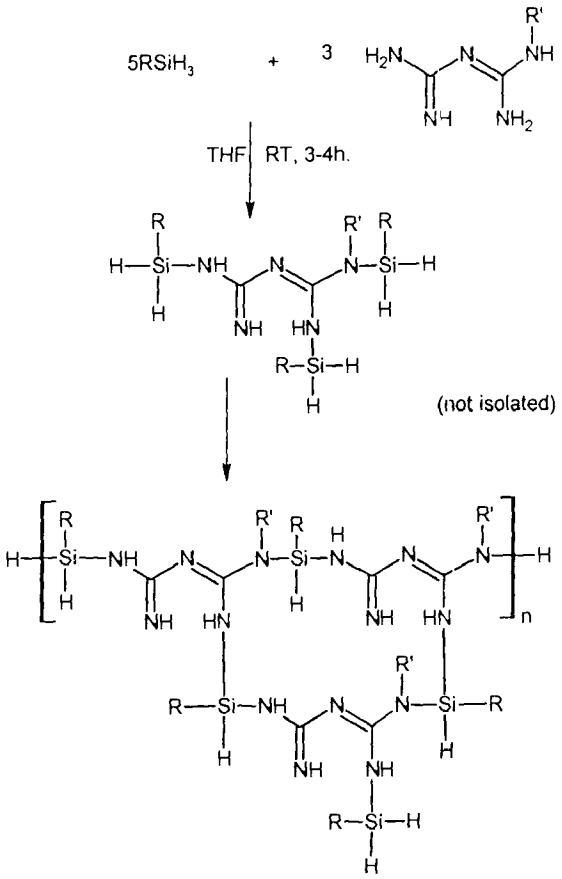
$RHSi(OTf)_2$ and their pentacoordinated analogs $RHSi(OTf)_2L$ (where L = donor ligands).[106]

3.2.4 UV/Visible spectral studies

The reflectance spectra of the compounds **1 - 4** reveal a band near 233-238 nm in each case. The apparent similarities of the spectral data with those of the parent biguanide/1-cyclohexylbiguanide (230-233 nm) suggest that the underlying electronic environment associated with π delocalized framework remain unperturbed in the silylbiguanide derivatives.

3.2.5 Proposed structure

The paucity of X- ray crystallographic data has eluded a definite structural assignment of these compounds. Nevertheless, the identity of the structural unit such as $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ in each compound has been firmly established from the spectroscopic data. Based on this, possible propositions of an idealized structure can be put forth. Due to the presence of multiple reactive sites in primary silanes and biguanide/1-cyclohexylbiguanide, SiH/NH dehydrocoupling can be considered to proceed in various pathways. A plausible reaction pathway may be implicated via the initial formation of a trisilylated biguanide species $[(RSiH_2)_3H_2bigR^1]$ (scheme 1). It is likely that the residual $-SiH_2$ groups in these intermediates undergo further SiH/NH dehydrocoupling and subsequent cyclization via intramolecular SiH/NH group affords the robust compounds **1 - 4** (structure A).



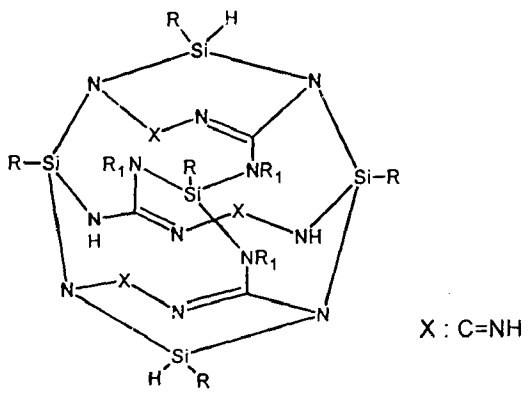
Scheme 1

Structure A

Although the structural motif conforms to RSi : R'N ratio as 5: 3, as expected, IR, ^{29}Si NMR data as well as FAB mass spectra are not consistent with this structural proposition. For example, (i) the results obtained from ^{29}Si NMR studies reveal the presence of $RSiN_3$ and $RSiHN_2$ groups as distinct entities in the structural framework, which is not substantiated in the proposed structure. (ii) The IR spectra provide no evidence for the presence of SiH_2 functions in these compounds.

(iii) The observed M^+ ion in the FAB mass spectra is not in conformity with this proposed structure.

An alternate structural possibility for the compounds **1 - 4** can be viewed by considering the high reactivity of arylsilanes towards SiH/NH dehydrocoupling. The definite stoichiometry of 5 : 3 (silane : biguanide) as well as the presence of $RSiN_3$ and $RSiHN_2$ moieties as evident from the spectroscopic data can be best described by considering a cage like structure. A possible representation of such a structure is shown in structure B and may be thought to arise by virtue of SiH/NH dehydrocoupling between the trifunctional silane and the NH_2/NHR' sites of the biguanide/1-cyclohexylbiguanide ligands leading to the formation of macrocyclic structure possessing $RSiN_3$ moieties. The residual NH protons undergo heterodehydrocoupling with the primary silane precursors to yield $RSiHN_2$ moieties in these compounds. The constraints imposed by the cyclic structure offer the possibility of hyper-coordinated silicon by virtue of strong coordinative association with imine/amino functionalities.



Structure B

3.2.8 Thermogravimetric analysis

The TGA profiles for all the compounds **1 - 4** are similar. As evident from figure 3.7, the onset of thermal decomposition begins at ~200°C and occurs predominantly in two stages. In the first step, approximately 20-40% weight loss was observed at 200-300°C followed by a loss of ~20-40% at 500-600°C. Depending on the nature of the R and R^1 groups, the residual yield varies between 20-50%. For example, maximum yield of 50% was observed when R = p-tol and R^1 = Cy. Another noteworthy observation is appearance of plateau between 300-500°C suggesting the formation of stable intermediate products under thermally induced condition. A detailed study of thermal transformation in these silylbiguanides derivatives is warranted.

3.3 Section B - Reactivity of secondary organosilanes towards biguanide/ 1-cyclohexylbiguanide.

As described in section A of this chapter, the reactions between primary arylsilanes, $RSiH_3$ (R = Ph or p-tol) and biguanide/1-cyclohexylbiguanide proceed via a facile SiH/NH dehydrocoupling pathway under extremely mild conditions (RT, 3h). The availability of NH_2/NHR^1 groups in biguanide/1-cyclohexylbiguanide provide multicentered reactive sites to undergo SiH/NH dehydrocoupling with the primary silanes. This has led to the isolation of a new family of Si-N bonded derivatives comprising of –[SiNCNCN]- based structural

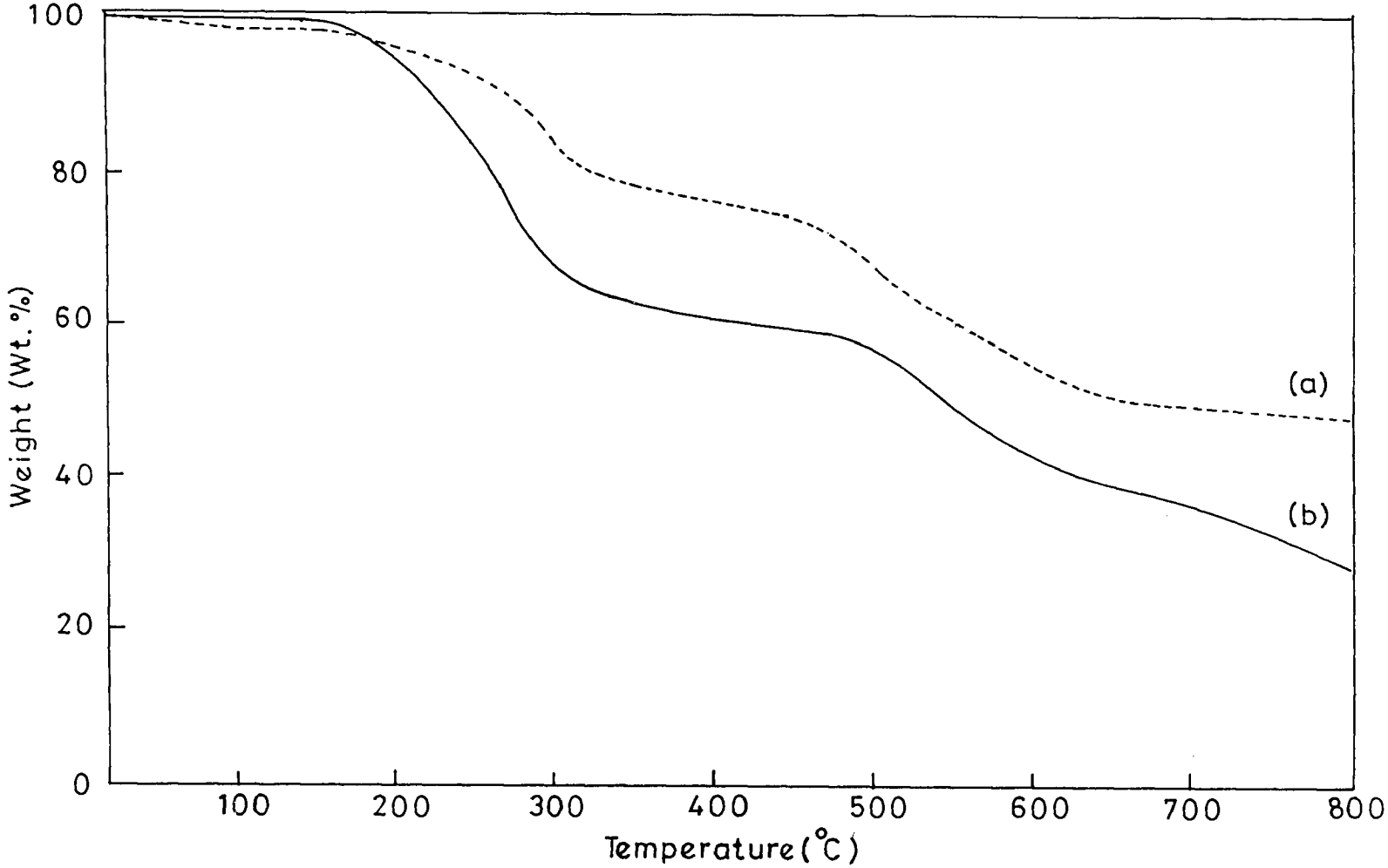


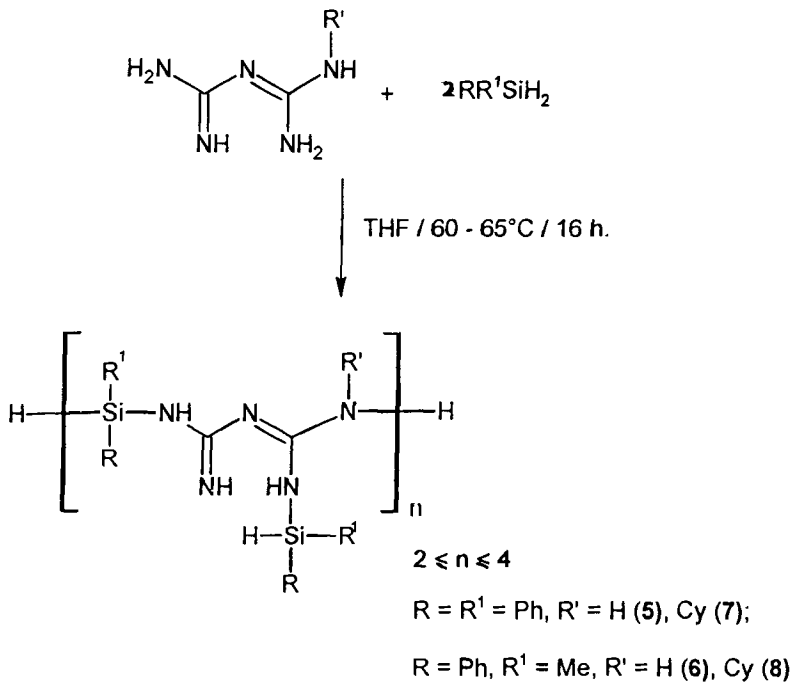
Figure 3.7 TGA of (a) $[(p\text{-tolSi})_3(p\text{-tolSiH})_2(bigCy)_2(H_2bigCy)]$ (4) and

(b) $[(p\text{-tolSi})_3(p\text{-tolSiH})_2(Hbig)_2(H_3big)]$ (2)

framework. Spectroscopic data of these compounds provide evidence of a complex structural motif. It is well known in literature that primary arylsilanes are more reactive towards dehydrocoupling as compared to secondary and tertiary silanes under uncatalyzed /transition metal catalyzed conditions. Notable in this regard are the studies on the reactivity of organosilanes towards ammonia and hydrazines by Harrod *et al.*[54, 55]

In this section, the reactions between diphenylsilane/ methylphenylsilane towards biguanide or 1-cyclohexylbiguanide have been investigated in detail. This has led to the isolation of oligomeric 1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanides (**7, 8**) (Scheme 2). These new siylbiguanide derivatives have been characterized by elemental analysis, IR, multinuclear NMR as well as FAB mass spectral data.

Addition of two equivalent of diphenylsilane or methylphenylsilane to either a suspension of biguanide or to a clear solution of 1-cyclohexylbiguanide in THF medium results in a brisk effervescence in each case that apparently slows down with time. It is imperative to carry out these reactions at higher temperature for a prolonged period (60-70°C/15-16h) in order to obtain analytically pure solid products, identified as the corresponding oligo-1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanide (**7, 8**).



Scheme 2

The overall reactions can be presented as shown in scheme 2. Carrying out the reaction with an excess (3 equivalent) of the diorganosilane does not alter the product composition of **5 - 8** and the unreacted silane can be recovered.

3.4 Characterization of the silylbiguanides (5 – 8)

All the compounds obtained above are white, moderately air sensitive solids and are soluble in solvents such as CH_2Cl_2, $CHCl_3$, THF, DMF, DMSO etc. These have been characterized by a combination of analytical and spectroscopic techniques including elemental analyses, GPC, FAB mass, IR, multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectroscopy and thermogravimetric analyses. The analytical data (C, H, N, Si) for these compounds are given in the experimental section (Chapter II)

3.4.1 FAB mass spectra

Evidence in support of the oligomeric nature of these compounds comes from the FAB mass spectra. Under FAB mass conditions, 1,4-bis(diphenylsilyl)biguanide (**5**) and 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide (**7**) display the highest ion at m/z 929 $[M+H]^+$ and 1094 $[M+2H]^+$ respectively, which are attributed to arise from dimeric entities (Figure 3.8). For 1,4-bis(methylphenylsilyl) biguanide (**6**) and 1-cyclcohexyl-2,5-bis(methylphenylsilyl)biguanide (**8**), the highest ion at m/z 1204 $[M-2Ph]^+$ and 1429 $[M-Cy-Ph-CH_3]^+$ respectively are assigned based on a tetrameric structural unit $[M]^+$. The data reveal a number of commonly observed fragment ions that are associated primarily with the skeletal backbone units (Table 3.7, 3.8). These fragment ions primarily arise from the loss of Ph, CH_3, NH, NH_2, Ph_2Si/PhMeSiH and Cy ions.

3.4.2 GPC analysis

GPC analysis of these oligomers reveal weight average molecular weights (M_w) ranging between 1380 and 1690 with polydispersity of 1.06-1.15. For silylbiguanides **5** and **7**, the M_w values (1386 for **5**; 1513 for **7**) are found to be much higher (≈ 38-49%) than the proposed dimeric structure obtained from FAB mass data. However there is a fortuitous close proximity of the M_w values for **6** (1536) and **8** (1710) corresponding to the tetrameric units. The simple FAB mass

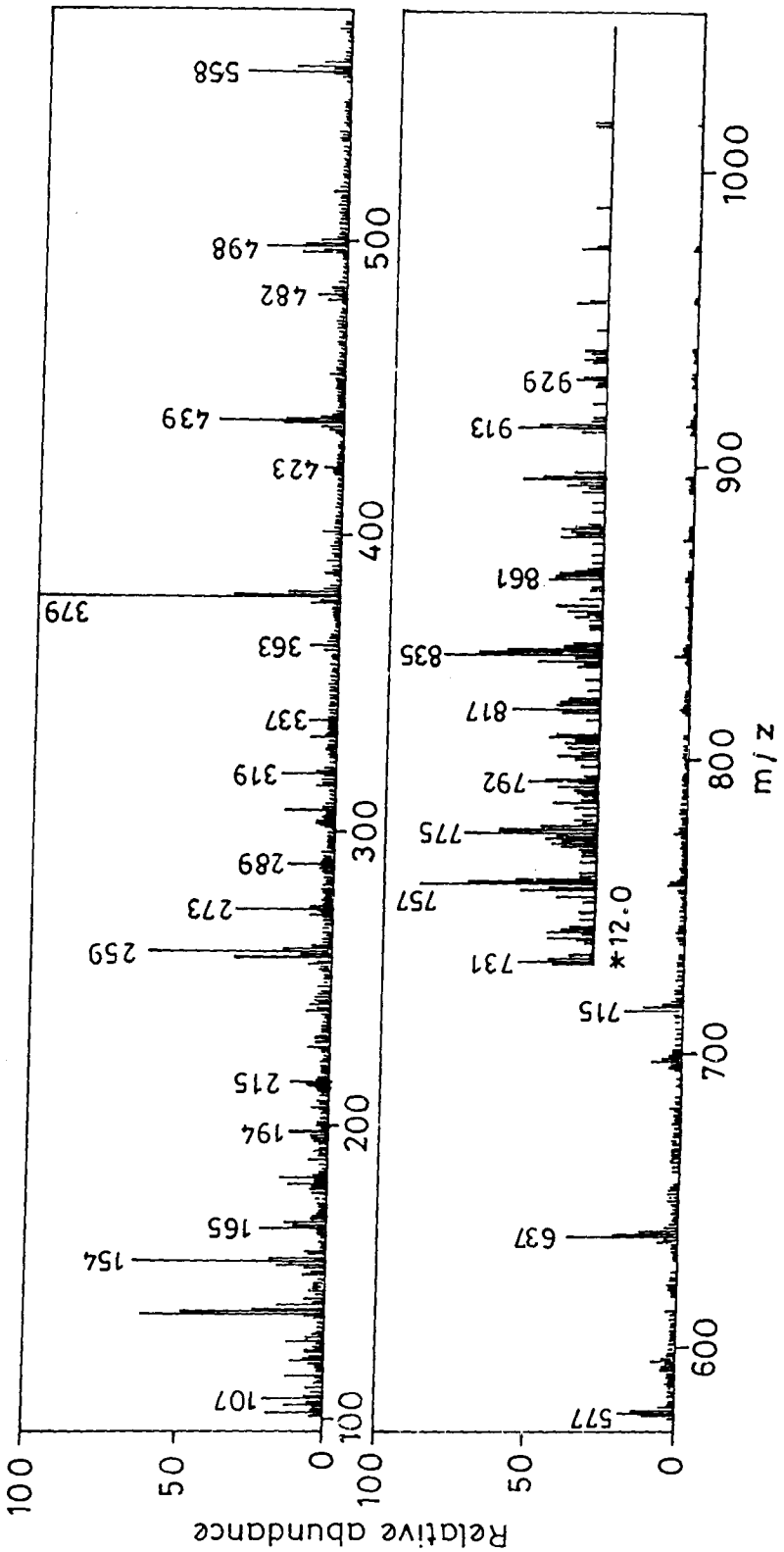


Figure 3.8 FAB mass spectrum of 1,4-bis(diphenylsilyl)biguanide (5)

Table 3.7 FAB mass data (commonly observed fragment ions) of oligo-1,4-bis(diphenylsilyl)biguanide (5) and 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide (7)

m/z	**5** (M = 928)	**7** (M = 1092)
895	$[M\text{-}NH_3\text{-}NH_2]^+$	$[M\text{- }NHCy\text{-}NH_2Cy\ ]^+$
835	$[M\text{-}Ph\text{-}NH_2]^+$	$[M\text{- }Ph\text{ - }NCy\text{-}Cy]^+$
757	$[M\text{-}2Ph\text{-}NH_3]^+$	$[M\text{-}2Ph\text{-}NHCy\text{-}Cy]^+$
697	$[M\text{-}3Ph]^+$	$[M\text{-}2C_6H_4\text{- }Ph\text{ - }2Cy]^+$
637	$[M\text{-}Ph_2SiH(NH)\text{ -}Ph\text{ -}NH_2]^+$	$[M\text{- }Ph_2SiH(NH)\text{-}NH_2\text{-}Ph\text{-}2C_6H_{10}]^+$
259	$[M\text{-}2Ph_2Si\text{-}3C_6H_4\text{-}Ph]^+$	$[M\text{-}2Ph_2Si\text{-}4C_6H_4\text{-}C_6H_{10}\text{- }Cy]^+$

Other significant ions observed
For **5**, m/z 929 $[M+H]^+$, 775 $[M\text{-}Ph\text{-}C_6H_4]^+$
For **7**, m/z 1094, $[M+ 2H]^+$, 1075 $[M\text{-}NH_3]^+$, 981$[M\text{-}Ph\text{-}2NH_3]^+$

Table 3.8 FAB mass data (commonly observed fragment ions) of oligo-1,4-bis(methylphenylsilyl)biguanide (6) and 1-cyclohexyl-2,5-bis(methylphenylsilyl)biguanide (8)

M/z	**6** (M = 1358)	**8** (M = 1604)
1167	$[M\text{-}2Ph\text{-}NH_3\text{-}H]^+$	$[M\text{-}Ph\text{–}C_6H_4\text{-}2NH_3\text{-}4Cy]^+$
1045	$[M\text{-}4C_6H_6\text{-}H]^+$	$[M\text{-}4Ph\text{-}H\text{-}4Cy]^+$
908	$[M\text{-}5C_6H_6\text{-}4CH_3]^+$	$[M\text{-}C_6H_6\text{–}4Ph\text{–}4CH_3\text{–}4Cy]^+$
893	$[M\text{-}5C_6H_6\text{-}5CH_3]^+$	$[M\text{-}C_6H_6\text{–}4Ph\text{-}5CH_3\text{-}4Cy]^+$
603	$[M\text{-}2PhMeSiH\text{-}6C_6H_6\text{-}3CH_3]^+$	$[M\text{-}2PhMeSiH\text{-}2C_6H_6\text{-}4Ph\text{-}3CH_3\text{-}4Cy]^+$

Other significant ions observed
For **6**, m/z 1204 $[M\text{-}2Ph]^+$, 1774 $[M\text{-}2Ph\text{-}2CH_3]^+$
For **8**, m/z 1429 $[M\text{-}Cy - Ph\text{-}CH_3]^+$,1401 $[M\text{-}C_6H_{12}\text{-}C_6H_6\text{-}3CH_3]^+$

behavior coupled with the low molecular weight and narrow polydispersity (M_w/M_n) in the GPC point towards the products being simple oligomeric species.

3.4.3 Infrared spectra

Pertinent IR absorptions of the silylbiguanides **5 - 8** along with their tentative assignments are given in table 3.9. The IR spectra of the oligomers obtained as KBr pellets reveal a few distinct features in the region of 3450 - 3000, 2200 - 2000 and 1000 - 900 cm^{-1}. While the absorptions characteristic of νNH mode appear at 3371 - 3208 cm^{-1}, the band at 3420 cm^{-1} due to νNH_2 mode is appreciably reduced in comparison to those of the parent biguanides. In addition, the characteristic absorption at 930 – 920 cm^{-1} due to δSiH_2 (deformation mode) is completely absent in the spectra of all the compounds. These observations can be considered as qualitative evidence in favor of SiH/NH dehydrocoupling involving organosilanes and NH_2 sites of the biguanide ligands. A noteworthy feature in the spectra is the appearance of two medium intensity absorptions at 2197 - 2104 cm^{-1} due to νSiH mode (Figure 3.9). These absorptions also persist in CH_2Cl_2 solution, though the intensity of the bands varies with time. Such spectral behavior is thought to arise due to the existence of two (or more) conformers, which undergo slow interconversion in the solution state. Similar spectral behavior has been reported earlier for

Table 3.9 IR (KBr, cm^{-1}) spectral data of oligo-1,4-bis(silyl)biguanides (5, 6) and 1-cyclohexyl-2,5-bis(silyl)biguanides (7, 8)

Compound	νNH_2	νNH	νCH (aromatic)	νCH (aliphatic)	νSiH	νCN	νNCN	νSiPh	νSiMe
5	3417	3347 3268	3068 3051	–	2194 2104	1635	1540	1117	-
6	3420	3337 3208	3067 3052	2957 2955	2189 2112	1635	1558	1124	1250
7	3450	3365 3250	3066 3053	2957 2875	2197 2108	1613	1552	1117	-
8	3447	3371 3247	3067 3055	2956 2843	2181 2107	1646	1558	1121	1251

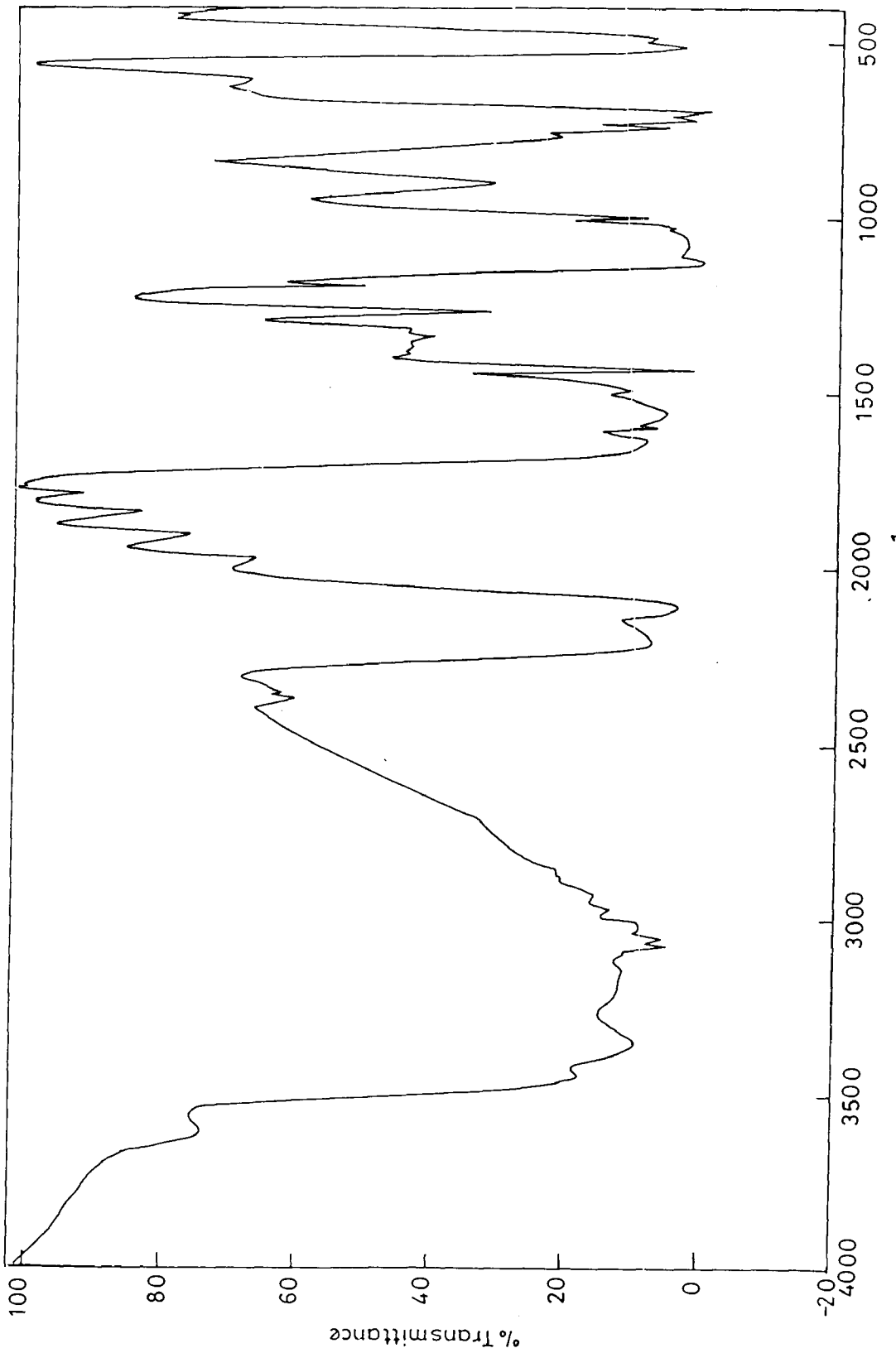


Figure 3.9 IR spectrum of 1,4-bis(diphenylsilyl)biguanide (5)

conformational mixtures in unsymmetrically substituted aminosilanes[107] as well as disilanes.[108,109]

In addition, the IR spectra exhibit routine absorptions due to other functional groups. For example, the bands at 1646 - 1613 and 1558 – 1540 cm^{-1} are ascribed to νC=N as well as νNCN (skeletal mode) respectively. These absorptions remain practically unaltered in comparison to those observed for the free ligands. The characteristic absorptions due to SiMe and SiPh groups appear at 1251 - 1250 and 1124 - 1117 cm^{-1} respectively. νCH (aliphatic) and νCH (aromatic) modes (wherever applicable) appear at the routine positions.

3.4.4 NMR spectra

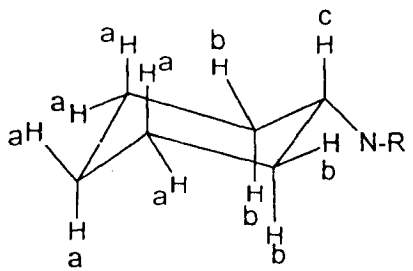
^{1}H NMR spectra

^{1}H NMR spectral data of the silylbiguanides **5 - 8** are summarized in table 3.10. ^{1}H NMR spectra of 1,4-bis(diphenylsilyl) biguanide **(5)** and 1,4-bis(methylphenylsilyl)biguanide **(6)** reveal two multiplets at δ 7.57 – 7.55 and 7.35 – 7.31 due to meta and ortho/para aromatic protons respectively. For **6**, the CH_3Si protons appear as a complex pattern of signals at δ 0.38 - 0.12 (Figure 3.10). On close examination, the presence of three doublets centered at δ 0.40 (^{3}J(H-H) = 7.5 Hz), 0.32 (^{3}J(H-H) = 6.6 Hz), 0.11 (^{3}J(H-H) = 7.8 Hz) as well as singlets at δ 0.29, 0.22, 0.17 are discernable. These are believed to arise from the methyl protons associated with Ph(Me)HSiN and $PhMeSiN_2$ groups respectively. The spectral region between δ 4.8 - 6.5

Table 3.10 ^{1}H NMR Spectral data δ (ppm) for oligo-1,4-bis(silyl)biguanides (5, 6) and 1-cyclohexyl-2,5-bis(silyl)biguanides (7, 8)

Compound	C_6H_5	NH	SiH	NCy	CH_3
5	7.57 (m, meta) 7.31(m, ortho/para)	5.99 (br)	4.62	-	-
6	7.55 (m, 2H, meta) 7.35 (m, 3H, ortho/para)	5.85 (br)	4.61	-	0.38-0.12 (m, 3H)
7	7.42(m, 8H, meta) 7.18 (m, 12H,ortho/para)	5.77 (br)	4.62	3.31(m, 1H, CH^c) 1.58 (m, 4H, CH_2^b) 1.17 (m, 6H, CH_2^a)	-
8	7.41(m, 4H, meta) 7.20 (m, 6H, ortho/para)	5.35 (br)	4.63	3.36 (m, 1H, CH^c) 1.56 (m, 4H, CH_2^b) 1.16 (m, 6H, CH_2^a)	0.39-0.12 (m, 6H)

* The assignments follow the structure as



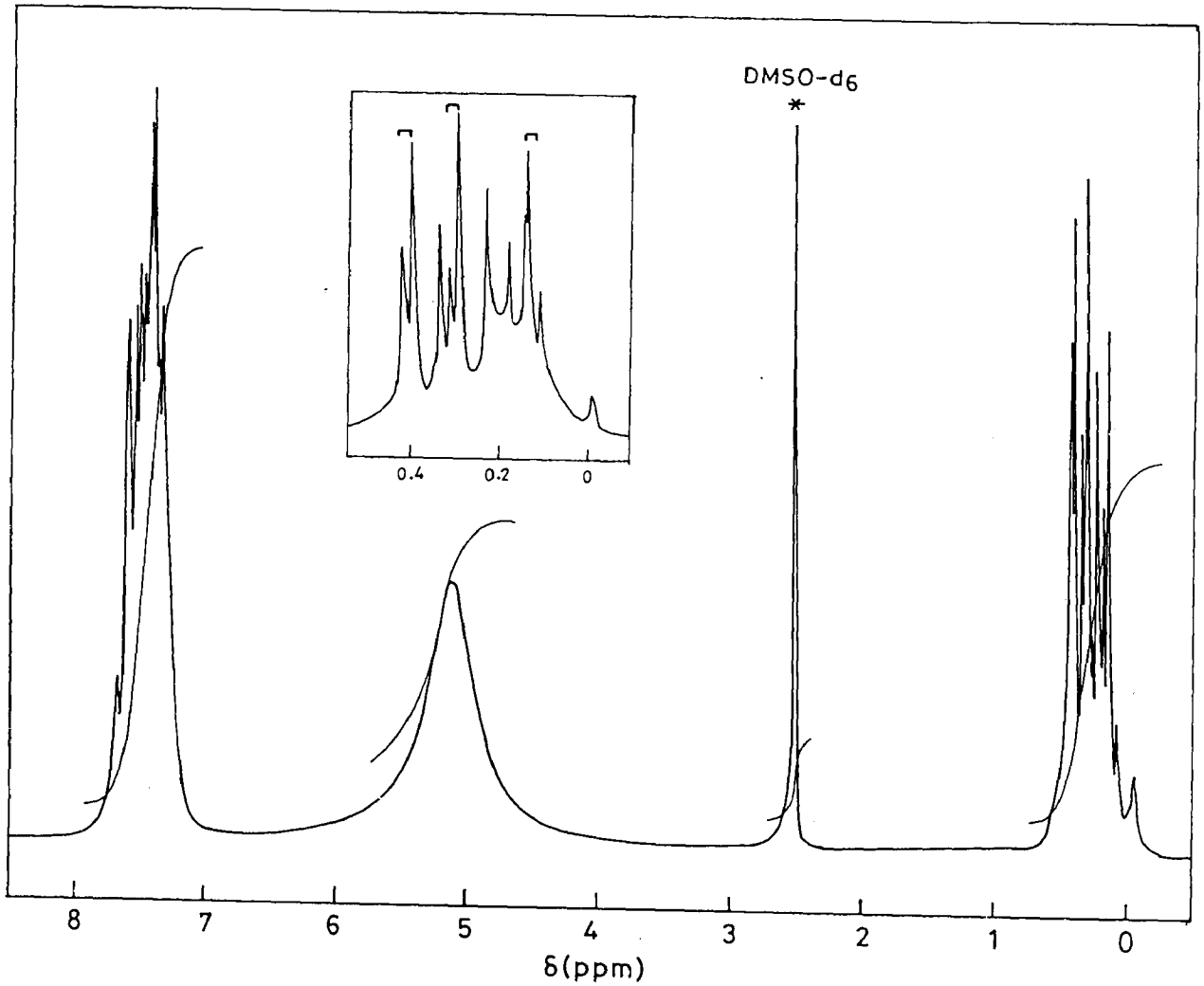


Figure 3.10 ^{1}H NMR spectrum of 1,4-bis(methylphenylsilyl)biguanide (6)

(inset methyl region showing ^{3}J(H-H) = 6-7 Hz)

is dominated by a broad signal due to the NH protons and show concentration dependent chemical shifts. This spectral behavior finds an analogy with that observed for the compounds **1 - 4** discussed in section A. It is considered that the fast exchange of NH protons with traces of moisture or solvent protons results in extensive broadening of the signals. The identity of SiH protons could be established from a singlet at δ 4.61 – 4.62. Nevertheless, a large uncertainty in the integral of SiH and NH signals is observed, thus eluding a definite estimation of the SiH protons in these compounds.

On the other hand, ^{1}H NMR spectra of 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide **(7)** and 1-cyclohexyl-2,5-bis(methylphenylsilyl) biguanide **(8)** provide a fair evidence with regard to their composition (Figure 3.11). The spectrum of each compound shows characteristic signals due to PhSi protons in their usual chemical shift values. For **8**, the spectral region at δ 0.38 - 0.12 is quite complex and reveals doublets at δ 0.39 (^{3}J(H-H) = 6.8 Hz), 0.31(^{3}J(H-H) = 7.8 Hz), 0.12 (^{3}J(H-H) = 7.6 Hz) and singlets at δ 0.28, 0.21, and 0.16. This behavior has also been previously observed for **6** and is ascribed to the methyl groups arising from the PhMeHSiN and $PhMeSiN_2$ moieties. The protons associated with N-bonded cyclohexyl groups appear at δ 3.36 (NCH) while two multiplets at δ 1.58 - 1.56 and 1.17 - 1.16 are assigned to the CH_2 groups. The Ph_2Si/PhMeSi and NCy groups in the

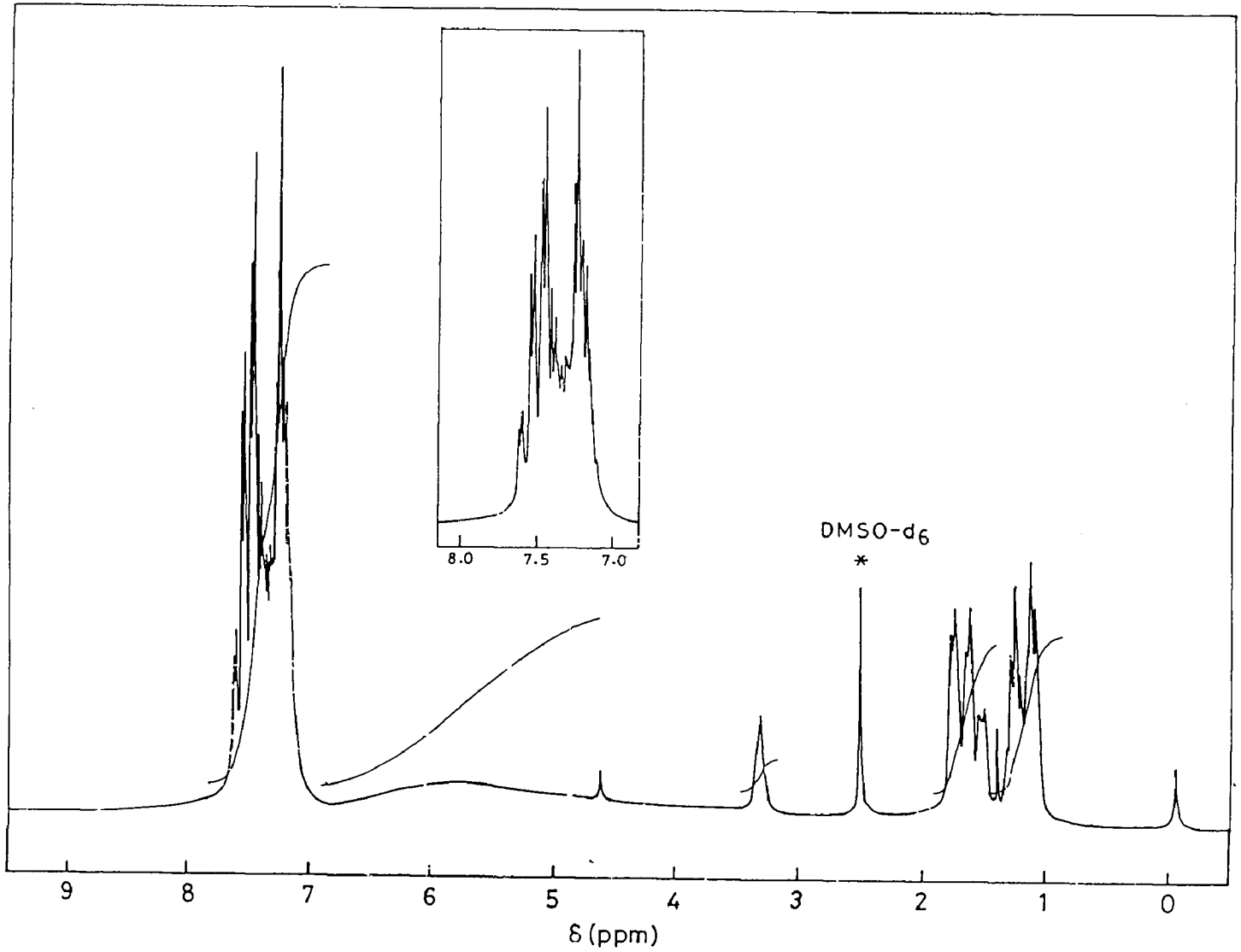


Figure 3.11 ^{1}H NMR spectrum of 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide (7)

(inset phenyl region showing fine coupling)

spectra integrate in a 2 : 1 ratio and are consistent with structural composition as shown in scheme 2. As expected, a broad signal due to NH protons appears between δ 3.8 - 6.5. Since the SiH protons are also routinely observed in this spectral region, unequivocal chemical shift assignments of SiH protons present in these compounds could not be made. This impairs the quantitative estimation of SiH and NH protons present in these compounds too.

^{13}C {^{1}H} NMR spectra

The ^{13}C NMR spectra for 1,4-bis(diphenylsilyl)biguanide **(5)** and 1,4-bis(methylphenylsilyl)biguanide **(6)** have been studied in quantitative mode in order to gauze an estimation of the various groups. For **5**, the signals arising from PhSi (δ 138.3 - 127.1) and C=N (δ 159.6, 158.7) groups are found to integrate in a definite ratio of 2 : 1. ^{13}C {^{1}H} NMR spectrum of **6** also shows similar results with regard to its composition [δ 138.0 - 127.0 (PhSi), 0.5 to –1.0 (MeSi) and 162.4, 161.4 (C=N)] (Figure 3.12). These results are in conformity with those obtained from elemental analysis and support the empirical composition, as suggested in scheme 2. The ^{13}C {^{1}H} NMR spectral assignment for 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide **(7)** and 1-cyclohexyl-2,5-bis(methylphenylsilyl) biguanide **(8)** have been similarly made and the results are summarized in table 3.11. A common feature in the ^{13}C NMR spectra of **5 - 8** is the presence of two resonances for

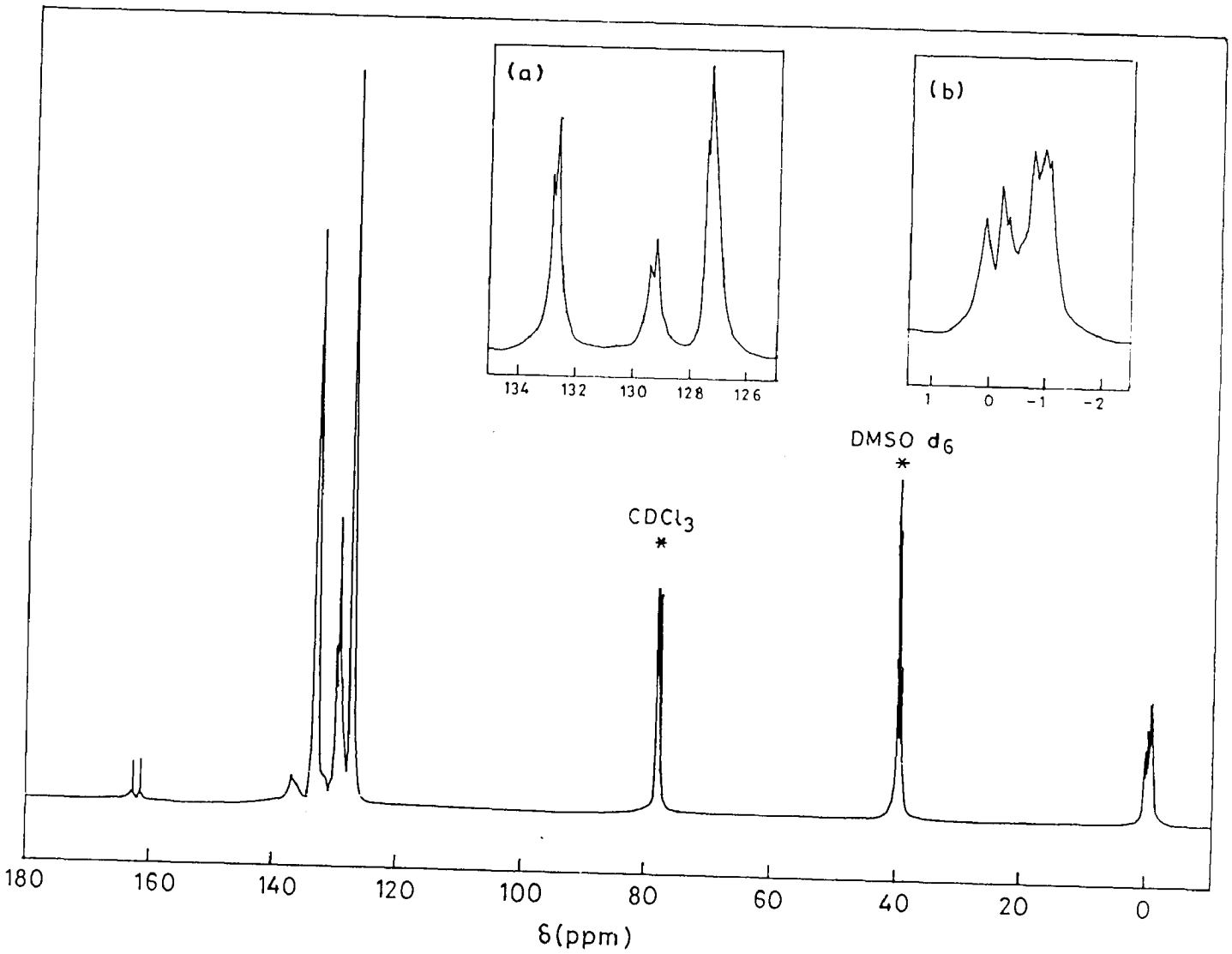


Figure 3.12 $^{13}C\{^1H\}$ NMR spectrum of 1,4-bis(methylphenylsilyl)biguanide (6)

(inset showing (a) aromatic region (b) methyl region)

Table 3.11 ^{13}C {^{1}H} spectral data δ (ppm) for oligo-1,4-bis(silyl)biguanides (5, 6) and 1-cyclohexyl-2,5-bis(silyl)biguanides (7, 8)

Compound	C=N	C_6H_5	Cy	CH_3
5	159.6 158.7	i = 138.3,138.1 o =133.5,133.3 p =129.7,129.4 m =127.4,127.1	-	-
6	162.4 161.4	i = 138.0,137.8 o = 132.7,132.6 p = 129.7,129.5 m = 127.2,127.0	-	0.5 to -1.0
7	160.5 159.9	i = 139.0, 136.6 o = 134.4,134.3 p = 129.9,129.7 m = 127.5, 127.3	49.9 (C1) 33.0 (C2, 2') 25.2 (C3, 3') 24.7 (C4)	-
8	160.3 159.7	i = 138.1,137.9 o = 133.6, 133.3 p = 129.8,129.7 m = 127.8, 127.5	49.7(C1) 33.2 (C2, 2') 25.5 (C3, 3') 24.4 (C4)	0.4 to -1.1

each aromatic carbon (Figures 3.12, 3.13). The methyl carbons for **6, 8** also appear as multiple signals. Such a spectral pattern may be thought to arise due to the presence of conformers in these compounds and compliments the IR and ^{1}H NMR spectral data.

^{29}Si {^{1}H} NMR spectra

^{29}Si NMR spectral studies of the compounds **5 - 8** have been carried out in the normal and DEPT mode. A detailed ^{29}Si NMR spectral study is helpful to bring about the nature of silicon containing species in these compounds. The relevant data are given in table 3.12. In addition, fundamental issues given below have also been addressed.

(a) As described in section A of this chapter, the ^{29}Si NMR spectral features in the DEPT-135 mode provides important information regarding the ^{29}Si-^{14}N coupling. It is imperative to examine the DEPT-135 ^{29}Si NMR of **5 - 8** in the light of these results.

(b) For the compounds **1 – 4**, unusually high ^{29}Si chemical shifts have been observed. A comparison of group electronegativity of the biguanide groups with silylcarbodiimides has been conceived to be one of the factors to explain this phenomenon. It is desired to rationalize this proposition in the present compounds too.

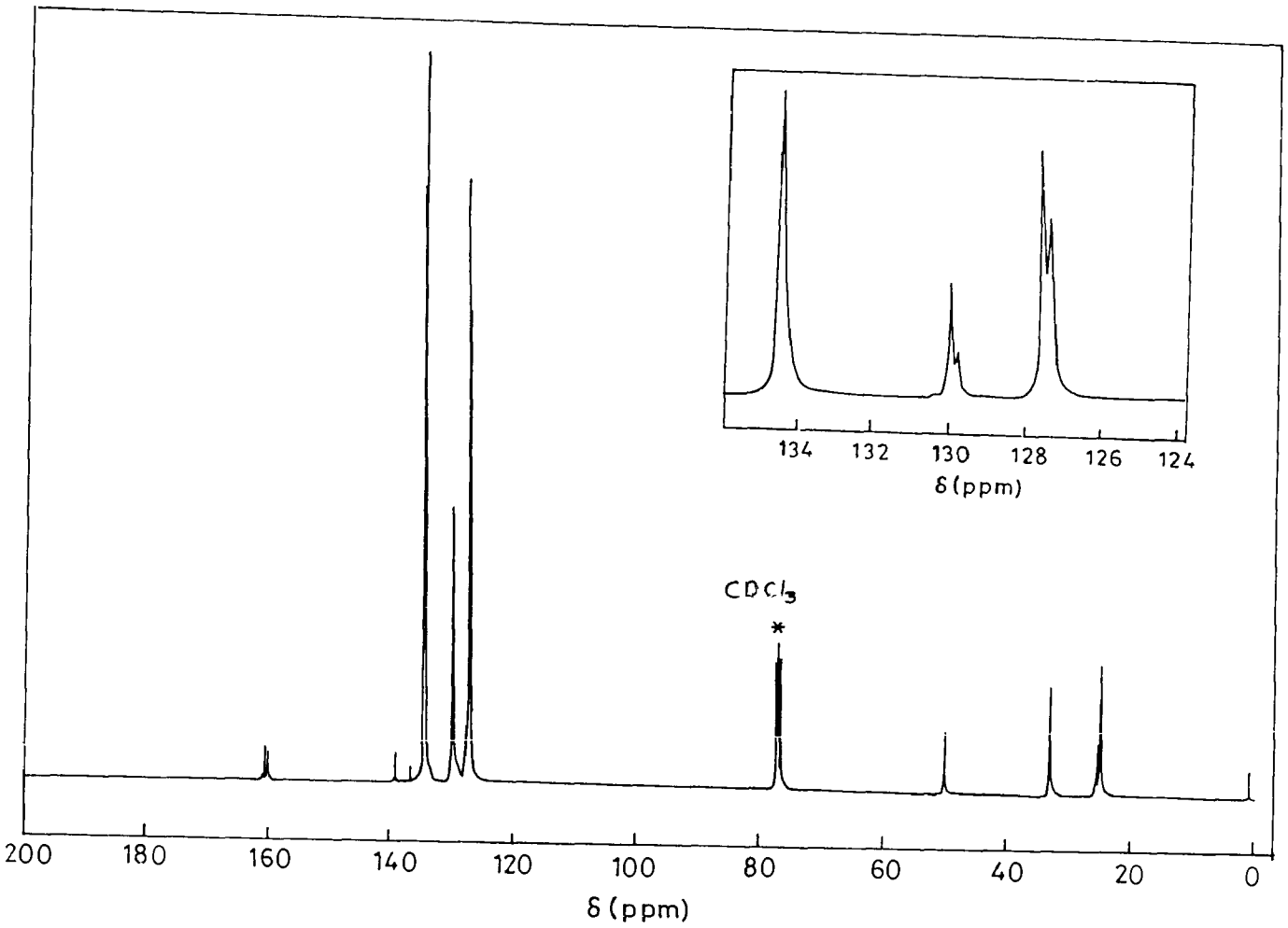


Figure 3.13 $^{13}C\{^{1}H\}$ NMR spectrum of 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide (7)

(inset phenyl region)

Table 3.12 ^{29}Si NMR spectral data δ (ppm) of oligo-1,4-bis(silyl)biguanides (5, 6) and 1-cyclohexyl-2,5-bis(silyl)biguanides (7, 8)

Compound	Moiety	δ ^{29}Si {^{1}H}	δ ^{29}Si {^{1}H} DEPT-135	δ ^{29}Si DEPT-135 $^{1}J(^{29}Si-^{1}H)$ (Hz)
5	Ph_2SiN_2,	-46.2	-	-
	$Ph_2Si(H)N$	-42.6	-42.6	
6	$PhMeSiN_2$,	-32.7,-33.6	-	-
	PhMeSi(H)N	-30.1, -30.4	-	190-196
7	Ph_2SiN_2,	-46.4		
	$Ph_2Si(H)N$	-42.8	-42.8	
8	$PhMeSiN_2$,	-32.5, -33.2	-	
	PhMeSi(H)N	-30.1, -30.4	-30.1, -30.4	

^{29}Si {^{1}H} NMR spectra of oligomeric 1,4-bis(diphenylsilyl)biguanide **(5)** and 1-cyclohexyl-2,5-bis(diphenylsilyl)biguanide **(7)** reveal two distinct signals in each case at δ -42.6, -46.2 and –42.8, -46.4 respectively (Figure 3.14). When the spectra are recorded in DEPT- 135 mode, the signals at δ -42.6 for **5** and –42.8 for **7** persist while the resonance at δ -46.2/-46.4 disappears. Accordingly, the signals are attributed to Ph_2SiN_2 (δ -46.2/-46.4) and Ph_2SiHN (δ -42.6/-42.8) moieties. Interestingly, the DEPT-135 spectra are devoid of ^{29}Si-^{14}N coupling information as observed for the compounds **1 - 4** discussed in Section A. The compounds **5 - 8** under investigation are linear oligomers while **1 - 4** are believed to be cage-like structures with the possibility of hypercoordination at the silicon centers. It is speculated that the observed difference in the DEPT spectra may arise from the different structural motifs. The spectra of 1,4-bis(methylphenylsilyl)biguanide **(6)** and 1-cyclohexyl-2,5-bis(methylphenylsilyl)biguanide **(8)** are apparently similar and exhibit four signals in each case in the chemical shift range of δ ~ -30 to -33 (Figure 3.15). The spectral behavior is thought to arise from the adjacent stereogenic nitrogen and silicon centers. The assignments of these signals come from the ^{29}Si NMR DEPT-135 spectrum (proton coupled) of the representative compound **6**. It is observed that each resonance at δ -30.15 and-30.4 as seen in the normal spectrum is split into a doublet with J(Si-H) = 190-196 Hz, thus providing unequivocal evidence for the presence of R_2SiHN moieties in these compounds. The absence of signals at δ -32.7, -33.6

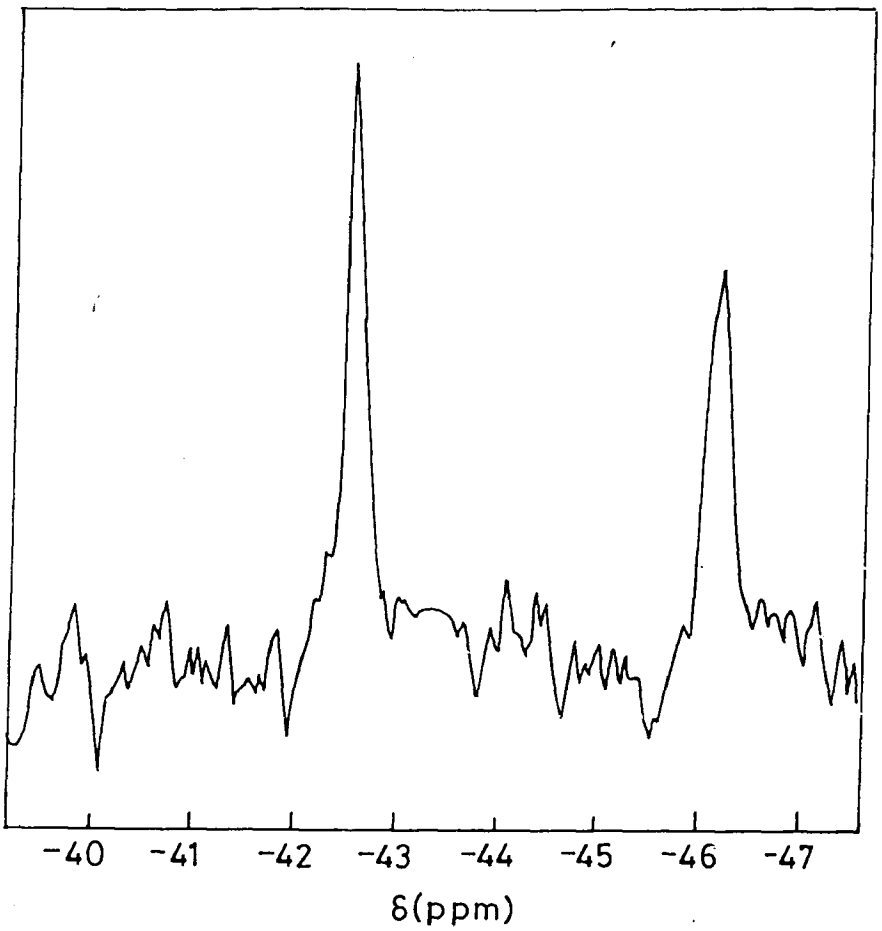


Figure 3.14 ^{29}Si {^{1}H} NMR spectrum of 1,4-bis(diphenylsilyl)biguanide (5)

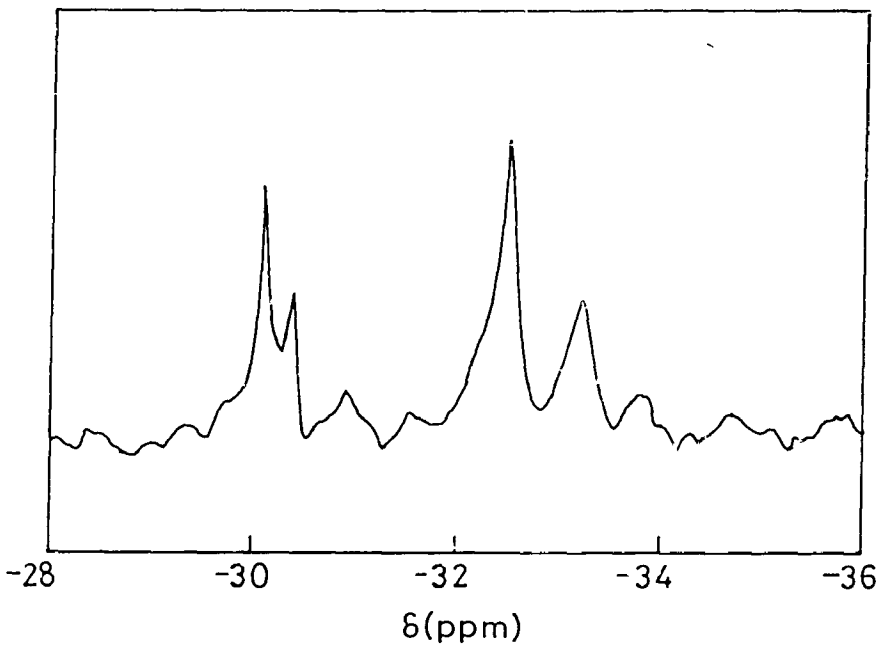


Figure 3.15 ^{29}Si {^{1}H} NMR spectrum of 1-cyclohexyl-2,5-bis(methylphenylsilyl)biguanide (

in the DEPT spectra suggests that the origin of these resonances arises from quaternary silicon centers and are accordingly assigned to $RR'SiN_2$ moieties. The results are in conformity with the idealized structure as shown in scheme 2.

It is imperative to comment on the ^{29}Si chemical shift values for the compounds **5 - 8**. The chemical shift data obtained herein are in close proximity with those of the analogous siloxanes (Ph_2SiO_2 δ -46.1, $PhMeSiO_2$ δ -32.4, -34.9).[110] A similar analogy in δ ^{29}Si values has been reported for poly(silylcarbodimide)s and an argument to this effect has been put forth based on the similarities in the electronegativity of NCN and O_2^- species.[10] It is thus concluded that the group electronegativity of the biguanide ligands is close to the O_2^- or NCN moieties.

3.4.5 Thermogravimetric analysis

The TGA profiles for all the oligomers **5 - 8** are essentially similar (Figure 3.16), showing no significant weight loss until 150 - 160°C. Thermal degradation occurs predominantly in two stages. In the first step, nearly 20% of the weight loss occurs between 150 and 300°C followed by a catastrophic loss of about 70 - 75% between 340 - 550°C. The residual yield in these compounds are much less than that observed for the silylbiguanide **1 – 4** discussed in section A. Apparently, the linear oligomeric structure in **5 - 8** undergo extensive fragmentation under thermally induced conditions.

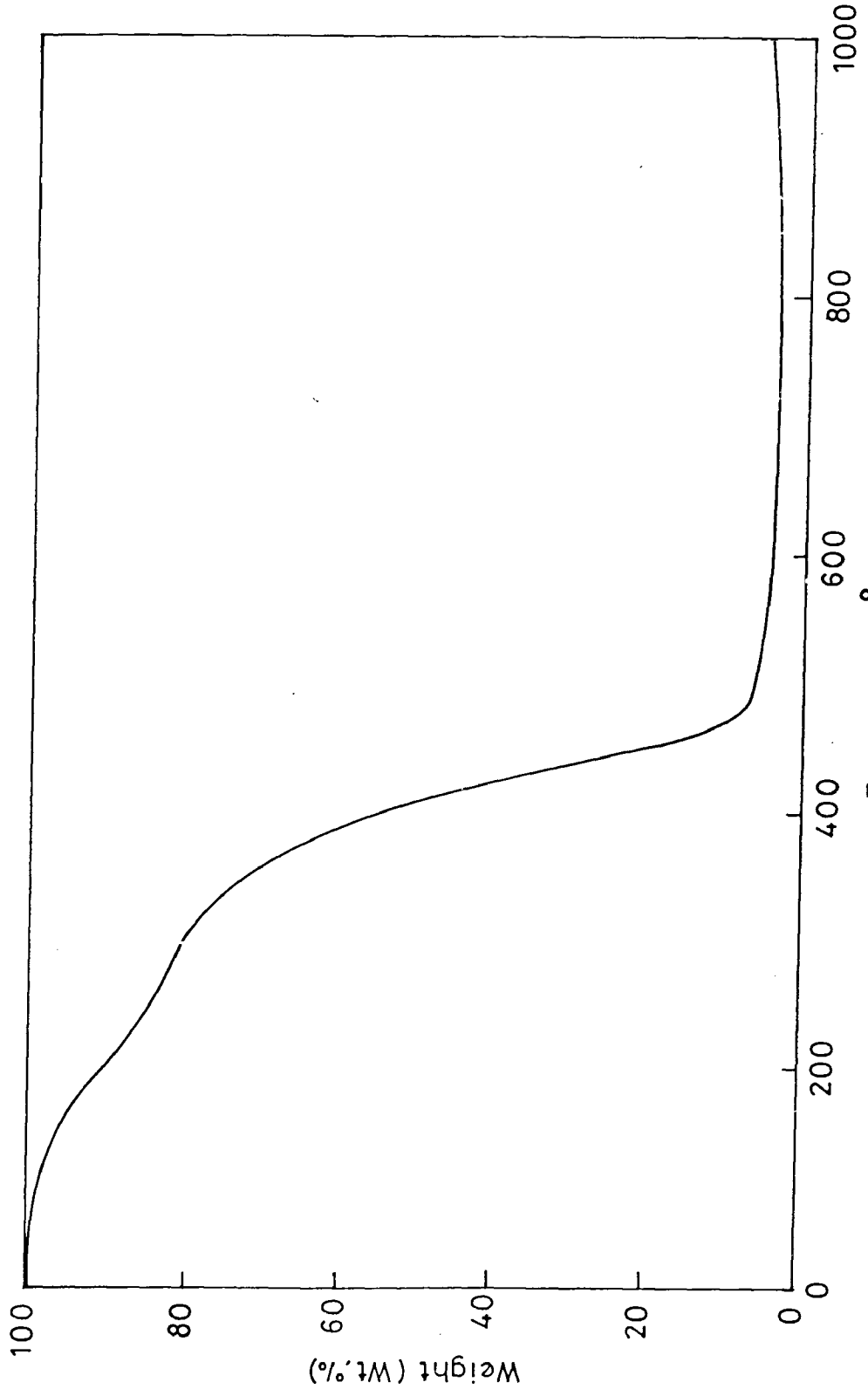


Figure 3.16 TGA of 1,4-bis(diphenylsilyl)biguanide (5)

3.5 Conclusions

Based on the above studies, it is thus concluded that the silylation of biguanide ligands is accessible from the reactions between primary/secondary organosilanes and biguanide/1-cyclohexylbiguanide. The involvement of multiple NH_2 groups as well as SiH_3/SiH_2 groups in the hetero-dehydrocoupling reactions provide different structural motifs, depending upon the nature of the organosilanes used. For example reactions of primary organosilanes $RSiH_3$ (R = Ph or p-tol) with biguanide ligands proceed under extremely mild conditions (RT, 4h) and result in the isolation of robust, cyclic derivatives with an idealized composition as $[(RSi)_3(RSiH)_2(bigR')_2(H_2bigR')]$ (R = Ph, R' = H (**1**) or Cy (**3**); R = p-tol, R' = H (**2**) or Cy (**4**)). The spectroscopic data provide evidence for the presence of hyper-coordinated silicon species in these compounds. On the other hand, analogous reactions of the secondary organosilanes RR^1SiH_2 (R = R^1 = Ph; R = Ph, R^1 = Me) with biguanide/1-cyclohexylbiguanide are relatively slow (64-65° C) and result in linear, oligomeric 1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl) biguanides (**7, 8**). The compounds thus isolated have been characterized by IR, multinuclear NMR and FAB mass spectroscopy as well as TGA studies. IR and NMR spectroscopic data suggest the existence of different conformers in these oligomers.

CHAPTER IV

REACTIONS OF CARBOSILANES WITH BIGUANIDE/1-CYCLOHEXYLBIGUANIDE

Chapter III was devoted to the reactivity studies of primary/ secondary organosilanes such as $RSiH_3$ (R = Ph, p-tol) and $RR'SiH_2$ (R = R' = Ph; R = Ph, R' =Me) with biguanide/1-cyclohexylbiguanide. Spectroscopic data of the compounds isolated from the above studies provide evidence for the SiH/NH dehydrocoupling between the organosilanes and biguanide ligands, the primary silanes being more reactive than the secondary organosilanes.

A perusal of literature reveals that the SiH/NH dehydrocoupling is primarily studied between aryl substituted organosilanes and NH_3/amine.[52,54] On the other hand, related studies on alkylsilanes have not received adequate attention, presumably due to the volatility and/or less reactivity of these silicon compounds. As a logical extension, it was desired to carry out a systematic investigation on the reactivity behavior of a few carbosilanes bearing terminal SiH_3/SiH_2 groups towards the biguanide ligands. The carbosilanes such as $R_3SiCH_2CH_2SiH_3/R_3SiCH_2CH_2SiMeH_2$ as precursors seem advantageous due to the following reasons. These compounds represent alkyl analogs of the primary/secondary organosilanes and are less volatile. In addition, these can be prepared conveniently under laboratory conditions by the hydrosilylation of appropriate silicon reagents.[111] The contents of this chapter are divided into two sections. Section A deals with the preparation and characterization of a few carbosilanes bearing SiH, SiH_2 or SiH_3 groups. In section B, the results

on the reactivity of these carbosilanes towards biguanide/ 1-cyclobiguanide ligands are discussed.

4.1 Section A: Synthesis and characterization of the carbosilanes

The term hydrosilylation is used to describe, an addition reaction of hydrosilanes to unsaturated bonds to afford Si-C derivatives.[112] These reactions are effectively promoted by ultraviolet light, γ-irradiation, electric discharge and catalysts such as peroxides, metal, metal salts or metal complexes. Among the variety of catalysts which promote the addition of hydrosilanes to carbon-carbon multiple bonds, Speier's catalyst (hexachloroplatinic acid) and Karstedt's catalyst have been commonly used.[113-119]

4.2 Synthesis of carbosilanes (1a-1e).

As shown in scheme 3, synthesis of the carbosilanes $R^1R^2R^3SiXSiH_3/R^1R^2R^3SiXSiMeH_2$ [X = $-CH_2CH_2-$ or $-CH(CH_3)$] involves hydrosilylation reactions between the appropriate hydrosilanes and trichlorovinylsilane/dichloromethylvinylsilane in presence of Speier's catalyst or Karstedt's catalyst. Though the resulting chlorocarbosilanes are distillable liquids, no attempts have been made to characterize these compounds due to the presence of reactive SiCl bonds. Instead these chlorocarbosilanes upon treatment with lithium aluminum hydride afford the desired carbosilanes (**1a –1e**).

$CH_2=CHSiCl_3 + R^1R^2R^3SiH \xrightarrow[\text{catalyst}]{\text{(i) Speier's/karstedt's}} R^1R^2R^3SiXSiH_3$

(ii) $LiAlH_4$

X = $-CH_2CH_2-$(β- isomer): $-CH(CH_3)-$ (α- isomer)

$R^1 = R^2 = R^3$ = Et **1a**; $R^1 = R^2$ = Ph, R^3 = H **1b**;

R^1 = Ph, R^2 = Me, R^3 = H **1c**

$CH_2=CHSiMeCl_2 + R^1R^2R^3SiH \xrightarrow[\text{catalyst}]{\text{(i) Speier's /karstedt's}} R^1R^2R^3SiXSiMeH_2$

(ii) $LiAlH_4$

X = $-CH_2CH_2-$(β- isomer): $-CH(CH_3)-$ (α- isomer)

R^1 = Ph, $R^2 = R^3$ =Me **1d**;

R^1 = Ph, R^2 = Me, R^3 = H **1e**

Scheme 3

During the hydrosilylation step, the reaction conditions such as temperature, reaction time and catalytic concentration are optimized to allow formation of the desired carbosilanes. It is also observed that nature of the catalyst also plays an important role. Although, both Speier's and Karstedt's catalysts are not effective in the formation of a single isomer, concentration of the β-isomer increases with the use of Karstedt's catalyst. On the other hand, a major disadvantage of the Karstedt's catalyst is that bis-silylated products such as $RR'Si(CH_2CH_2SiH_3)_2$ (where R = Me or Ph, R' = Ph) are formed, thus appreciably reducing the yield of the desired carbosilanes **1b**, **1c** and **1e**. Thus, these carbosilanes are obtained as a mixture of both α and β

isomers. The varying proportion of these isomers in each carbosilane, as evident from ^{1}H NMR spectra is summarized in table 4.2.

4.3 Characterization of carbosilanes (1a – 1e)

4.3.1 Infrared spectra

Pertinent infrared absorptions of the carbosilanes and their assignments are recorded in table 4.1. For **1a - 1c**, the spectra reveal bands at 2143 - 2148 and 924 - 926 cm^{-1} which are characteristic of symmetric stretching and deformation modes of SiH group respectively. The corresponding absorptions for the carbosilanes **1d – 1e** appear at 2123 - 2126 and 945 - 946 cm^{-1} (Figure 4.1). The absorptions due to MeSi and PhSi groups (wherever applicable) are observed at 1249 - 1254 and 1110 - 1115 cm^{-1} respectively. νCH (aliphatic) and νCH (aromatic) modes appear at their routine positions.

4.3.2 NMR spectra

4.3.2.1 NMR spectral studies of $Et_3SiXSiH_3$, (1a) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

^{1}H NMR spectrum of **1a** reveals two distinct resonances centered at δ 3.53 (t) and 3.56 (d) which are ascribed to SiH_3 protons arising from β and α isomers respectively. On a close scrutiny, ^{1}H NMR spectra of the carbosilane **1a** obtained from Speier's and Karstedt's catalyst reveal that the use of Karstedt's catalyst improves the

Table 4.1 IR (KBr, cm^{-1}) spectral data of carbosilanes (1a - 1e)

Compound		νCH (aromatic)	νCH (aliphatic)	νSiH	νSiMe	νSiPh	δSiH_2
1a	$Et_3SiXSiH_3$	-	2953, 2875	2148	1250	-	924
1b	$Ph_2HSiXSiH_3$	3068, 3050	2950 2870	2145	1254	1114	924
1c	$PhMeHSiXSiH_3$	3061 3052	2990 2865	2143	1252	1110	926
1d	$PhMe_2SiXSiMeH_2$	3069 3050	2956 2909	2126	1249	1113	945
1e	$PhMeHSiXSiMeH_2$	3068 3051	2860 2905	2123	1251	1115	945

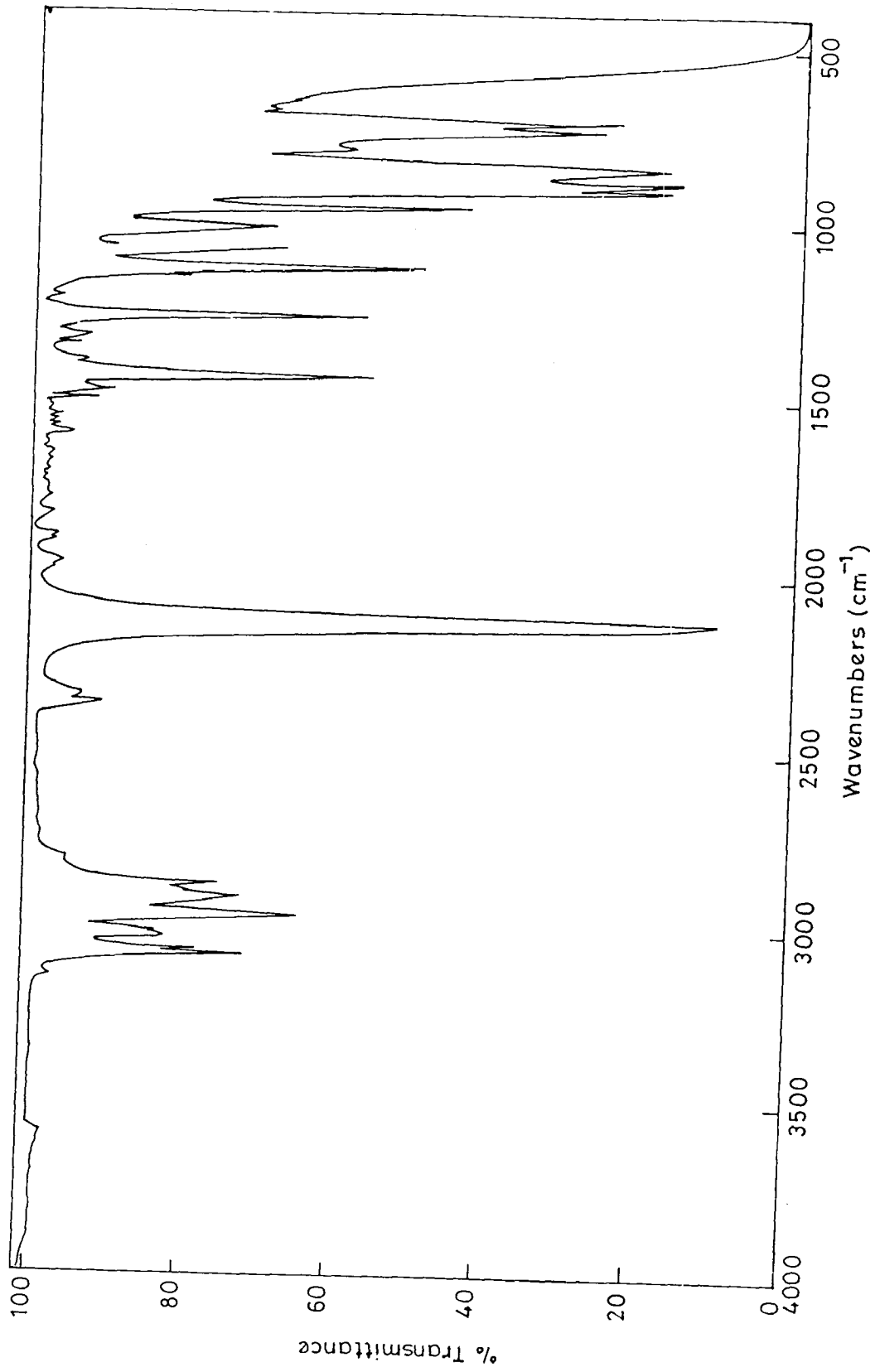


Figure 4.1 IR spectrum of $PhMe_2SiCH_2CH_2SiMeH_2$ (1d)

yield of β addition product. The presence of α isomer is discernable from the appearance of distinct signals at δ 0.25 (m, CH) and 1.13 (d, C-CH_3). The signals arising due to $-CH_2CH_2-$ groups of the β-isomer are found to overlap with CH_2 protons of EtSi at δ 0.59, while CH_3 (Et) protons appear as a triplet at δ 0.94. ^{13}C $\{^1H\}$ DEPT-135 NMR spectrum of **1a** reveals signals at δ 7.4 and 0.7 attributed to CH_3 and CH carbons arising from α addition product, while the CH_2 groups (β-isomer) appear at δ 3.3 and 7.7. The resonance due to ethyl group was found to coincide with the CH_2 carbon of the β isomer at δ 3.3 and CH_3 carbon of the α-isomer at δ 7.4. In the ^{29}Si $\{^1H\}$ NMR spectrum, four distinct ^{29}Si resonances appear at δ 8.1, 8.9 (Et_3Si) and –54.2, -54.3 (SiH_3). The spectral pattern is reminiscent of the presence of both α and β addition products. Unequivocal assignments of the ^{29}Si NMR in the SiH_3 region for the two isomers have been made using ^{29}Si $\{^1H\}$ NMR DEPT-135 experiment with J = 7.2 Hz (Figure 4.2). Accordingly, the signal at δ -54.3 is assigned to the α isomer while the signal at δ -54.2 is attributed to the β isomer. The relevant NMR spectral data is summarized in tables 4.2 - 4.4.

4.3.2.2 NMR studies of $Ph_2HSiXSiH_3$, (1b) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

The relevant NMR spectral data is summarized in tables 4.2 - 4.4. ^1H NMR spectrum of **1b** shows two multiplets centered at δ 7.55 and 7.36 due to meta and ortho/para protons of PhSi groups

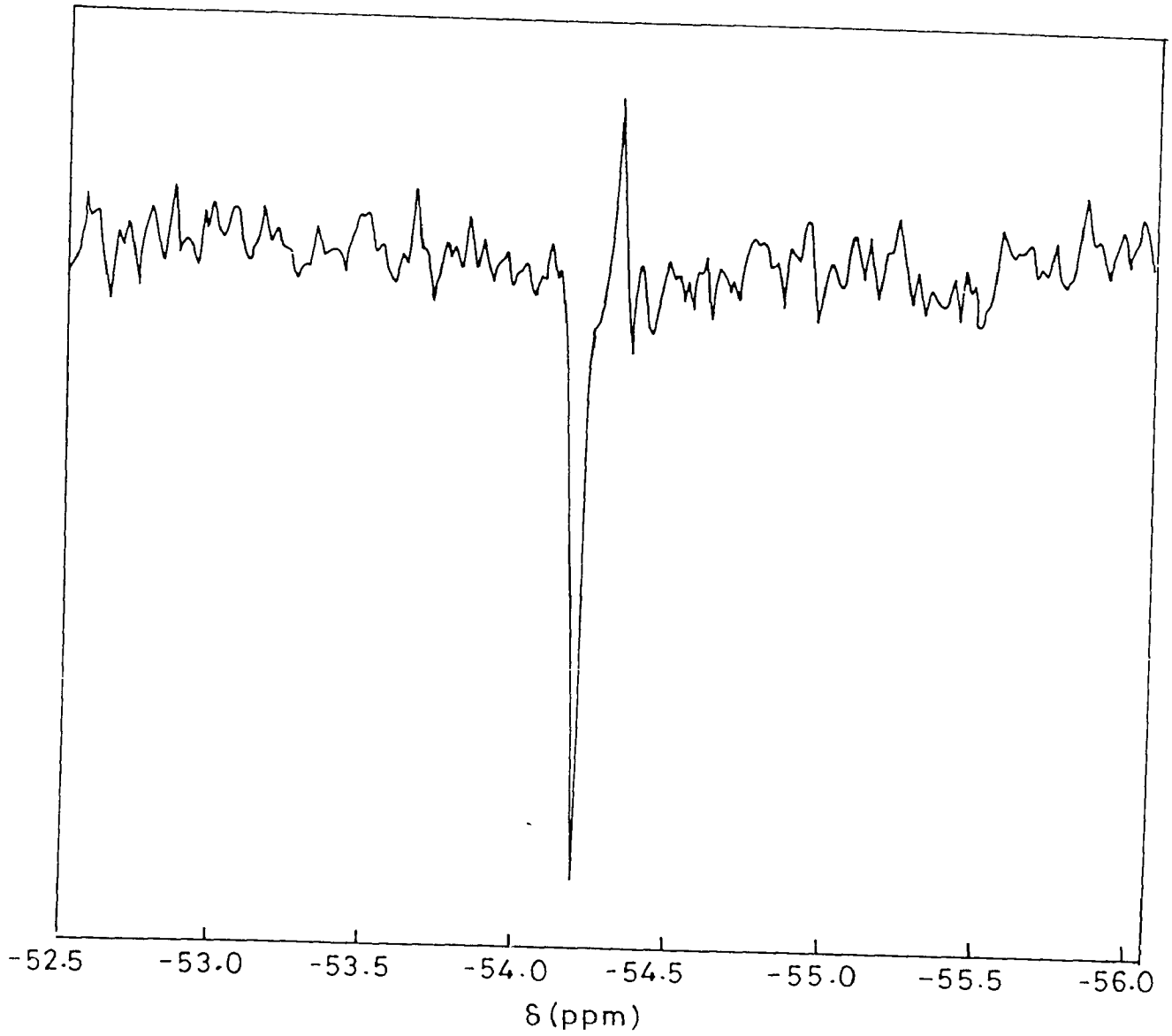


Figure 4.2 ^{29}Si {^{1}H} DEPT-135 NMR spectrum (J = 7.2 Hz) of $Et_3SiXSiH_3$ (1a) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

Table 4.2 ^{1}H NMR δ (ppm) Spectral data of carbosilanes (1a-1e)

	Compound (%) #	Si*Ph*	Si*H*	Si*Me*	Si*CH*$_2$	*CH*	C*CH*$_3$	CH$_3$(Et)
1a	$Et_3SiCH_2^aCH_2^bSiH_3$ (85)		3.53 (t)		0.59(m)^{a,b}			
			3.56 (d)					0.94(t)
	$Et_3SiCH(CH_3)SiH_3$ (15)					0.22(m)	1.13 (d)	
1b	$Ph_2HSiCH_2^aCH_2^bSiH_3$ (55)	7.55(m)	3.52 (t, SiH_3)		0.80(m)^b			
		7.36 (o/p)	4.90 (m, SiH)		1.18(m)^a			
	$Ph_2HSiCH(CH_3)SiH_3$ (45)		3.55 (d, SiH_3)	-		0.62(m)	1.23(d)	
1c	$PhMeHSiCH_2^aCH_2^bSiH_3$ (60)	7.46 (m)	3.56(m, SiH_3)	0.32 (d)	0.74 (m)^b			
		7.36 (o/p)	4.38(m, SiH)	0.38(dd)	0.90 (m)^a			
	$PhMeHSiCH(CH_3)SiH_3$ (40)					0.44 (m)	1.15(dd)	
1d	$PhMe_2SiCH_2^aCH_2^bSiMeH_2$ (86)	7.46 (m)		0.07 (t)	0.56 (m)^b			
		7.33 (o/p)	3.66 (m, SiH_2)	0.24(s)	0.71(m)^a			
	$PhMe_2SiCH(CH_3)SiMeH_2$ (14)			0.01(t)		0.29(m)	1.03(d)	
1e	$PhMeHSiCH_2^aCH_2^bSiMeH_2$ (56)	7.48(m)			0.57 (m)^b			
		7.30(o/p)	3.65 (m, SiH_2)	0.22(d)	0.72 (m)^a			
	$PhMeHSiCH(CH_3)SiMeH_2$ (44)		4.27 (m,SiH)	-0.01(m)		0.32 (m)	1.02(dd)	
				0.26(dd)				

- a and b denote different carbon atoms as specified.

1a and **1d** prepared using Karstedt's catalyst; **1b, 1c, 1e** prepared using Speier's catalyst.

Table 4.3 ^{13}C {^{1}H} DEPT-135 spectral data δ (ppm) of carbosilanes (1a -1e)

	Compounds	C*CH*$_3$	Si*Me*	CH	CH_2	Et	SiPh
1a	$Et_3Si\,CH_2^aCH_2^b\,SiH_3$	-	-	-	3.3 [b]	7.4 (CH_3)	-
					7.7 [a]	3.3 (CH_2)	
	$Et_3SiCH(CH_3)SiH_3$	7.4		0.7			
1b	$Ph_2HSi\,CH_2^aCH_2^b\,SiH_3$	-	-	-	0.1 [b]		128.0(m)
					8.2 [a]		129.6(p)
	$Ph_2HSiCH(CH_3)SiH_3$	12.5	-	-5.1			135.3(o)
1c	$PhMeHSiCH_2^aCH_2^b\,SiH_3$	-	-6.0	-	-0.3 [b]		
					+9.3 [a]		127.5(m)
	$PhMeHSiCH(CH_3)SiH_3$	12.0	-6.0	-4.0	-		129.4(p)
		12.6	-6.9	-4.3			134.5(o)
1d	$PhMe_2^xSiCH_2^aCH_2^b\,SiMe^yH_2$		-0.7^x	2.4	7.3[b]		128.6 (m)
			-2.5^y		9.4[a]		129.7 (p)
	$PhMe_2^xSiCH(CH_3)SiMe^yH_2$	11.6	0.2^x				134.4 (o)
			-2.0^y				
1e	$PhMe^xHSiCH_2^aCH_2^b\,SiMe^yH_2$	-	-6.8^x		3.9[b]	-	127.9(m)
			-8.7^y		7.6[a]		129.4(p)
	$PhMe^xHSiCH(CH_3)SiMe^yH_2$	11.2	-6.0^x	-0.3			134.6(o)
		10.6	-5.7^x	-0.6			
			-8.6^y				

- a, b, x and y denote carbon atoms as specified.

Table 4.4 ^{29}Si {^{1}H} NMR δ (ppm) spectral data ofcarbosilanes (1a – 1e)

	Compound	Et_3Si	$PhMe_2Si$	SiH	SiH_2	SiH_3
1a	$Et_3Si\ CH_2CH_2SiH_3$	8.1	-	-	-	-54.2
	$Et_3SiCH(CH_3)SiH_3$	8.9				-54.3
1b	$Ph_2HSi\ CH_2CH_2\ SiH_3$	-	-	-11.6	-	-53.9
	$Ph_2HSiCH(CH_3)SiH_3$			-9.0		-51.9
1c	$PhMeHSiCH_2CH_2SiH_3$	-	-	-11.1	-	-54.0
	$PhMeHSiCH(CH_3)SiH_3$			-7.2		-53.1
				-8.7		-53.4
1d	$PhMe_2SiCH_2CH_2\ SiMeH_2$	-	0.1	-	-28.5	-
	$PhMe_2SiCH(CH_3)SiMeH_2$		-0.9		-29.4	
1e	$PhMeHSiCH_2CH_2\ SiMeH_2$	-	-	-10.8	-29.1	-
	$PhMeHSiCH(CH_3)SiMeH_2$			-8.4	-28.6	
				-10.1	-29.0	

respectively. The SiH_3 protons appear as a closely placed triplet (δ 3.52) and a doublet (δ 3.55) arising from the β and α isomer respectively whereas SiH protons appear as a multiplet at δ 4.90. The C-CH_3 and CH protons of the α isomer resonate at δ 1.23 and 0.62 respectively while two multiplets at δ 0.80 and 1.18 are suggestive of the $SiCH_2CH_2Si$ fragment of the β isomer. ^{13}C {^1H} DEPT-135 NMR spectrum reveals signals due to aromatic carbons at δ 128.0, 129.6, 135.3. The signals at δ 12.5 and -5.1 are ascribed to the C-CH_3 and CH carbons of the α isomer while the signals at 8.2 and 0.1 ppm are assigned to $SiCH_2CH_2Si$ group of the β isomer (Figure 4.3). ^{29}Si {^1H} DEPT -135 NMR spectrum reveals two sets of signals at δ -11.6, -9.0 and -53.9, -51.9 due to SiH and SiH_3 groups respectively and provide an additional evidence for the presence of β and α isomers.

4.3.2.3 NMR spectral studies of $PhMeHSiXSiH_3$, (1c) [X = -CH_2CH_2-, -$CH(CH_3)$]

^1H NMR spectrum of **1c** allows the detection of α and β isomers by simple inspection. The spectrum reveals two distinct multiplets centered at δ 4.38 and δ 3.56 in 1 : 3 intensity ratio and are attributed to SiH and SiH_3 protons respectively. The chemical shift regime of the SiH and SiH_3 protons associated with α and β isomers is not resolved due to narrow dispersity of their chemical shifts. For the α isomer, the spectrum exhibits doublet of doublet centered at δ 0.38 and 1.15 due to

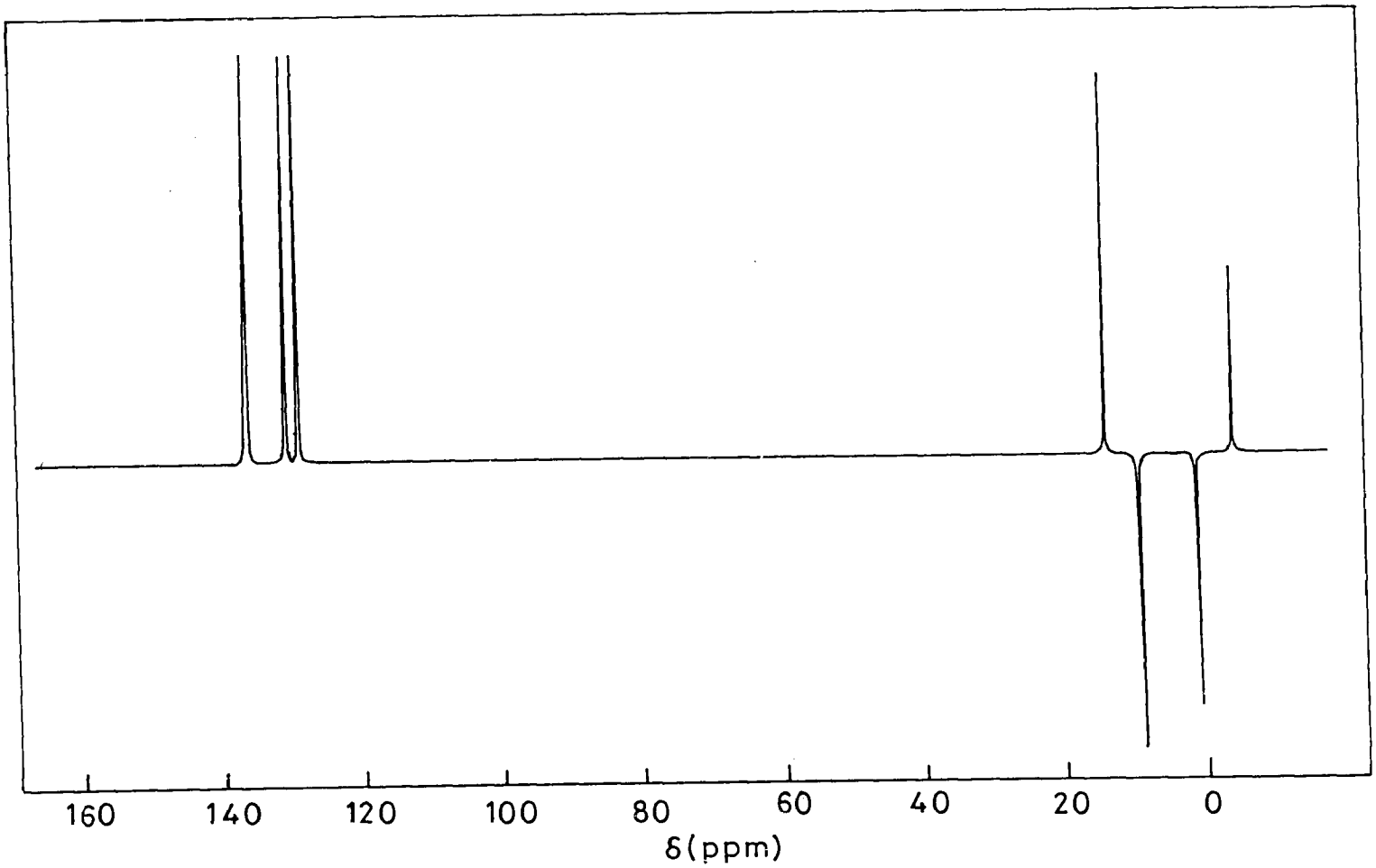


Figure 4.3 ^{13}C {^{1}H} DEPT-135 NMR spectrum of $Ph_2HSiXSiH_3$ (1b) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

MeSi and C-CH_3 protons respectively and suggests the presence of diastereomers by virtue of adjacent chirality at Si and C centers. The CH proton is located at δ 0.44 as a multiplet. The $SiCH_2$ protons of β isomer are seen as two sets of multiplets at δ 0.74 and 0.90. MeSi protons appear as a doublet at δ 0.32. The PhSi protons are observed as two distinct multiplets centered at δ 7.46 and 7.36 due to meta and ortho/para protons respectively.

^{13}C {^1H} DEPT-135 NMR spectrum shows out of phase signals at δ 9.3 and -0.3 due to the CH_2 carbons (β-isomer). Two distinct signals are observed for CCH_3, CH and $SiCH_3$ at δ 12.6/12.0, -4.0/-4.3, -6.0/-6.9 respectively and are attributed to diastereomers arising from α isomers. ^{29}Si {^1H} NMR spectrum of this compound reveal three signals each in the region of δ -53.1 to -54.0 and δ -7.2 to -11.1 and are attributed to the SiH_3 and PhMeHSi fragments respectively (Figure 4.4). Although assignments arising from α and β isomers could not be ascertained unequivocally, the spectral data can be rationalized as arising from the diastereotopic α-isomers and β-isomer. The significant NMR spectral data is summarized in tables 4.2 - 4.4.

4.3.2.4 NMR spectral studies of $PhMe_2SiXSiMeH_2$, (1d) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

From a simple inspection (Figure 4.5), the presence of both β and α isomers can be delineated from the ^1H NMR spectrum. The SiH_2 protons arising from β and α isomers are not well resolved and appear

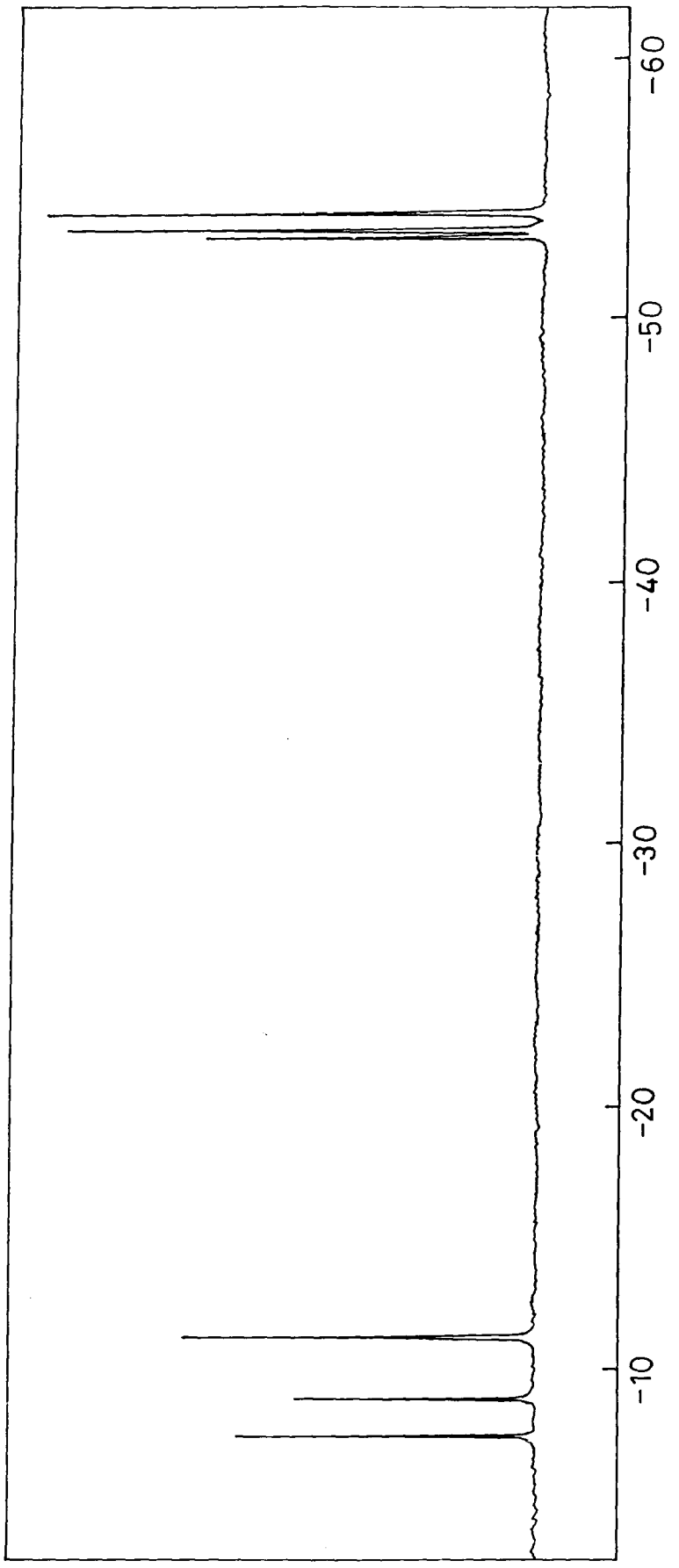


Figure 4.4 ^{29}Si {^{1}H} NMR spectrum of PhMeHSiXSiH$_3$ (1c) [X = -CH_2CH_2-, -$CH(CH_3)$]

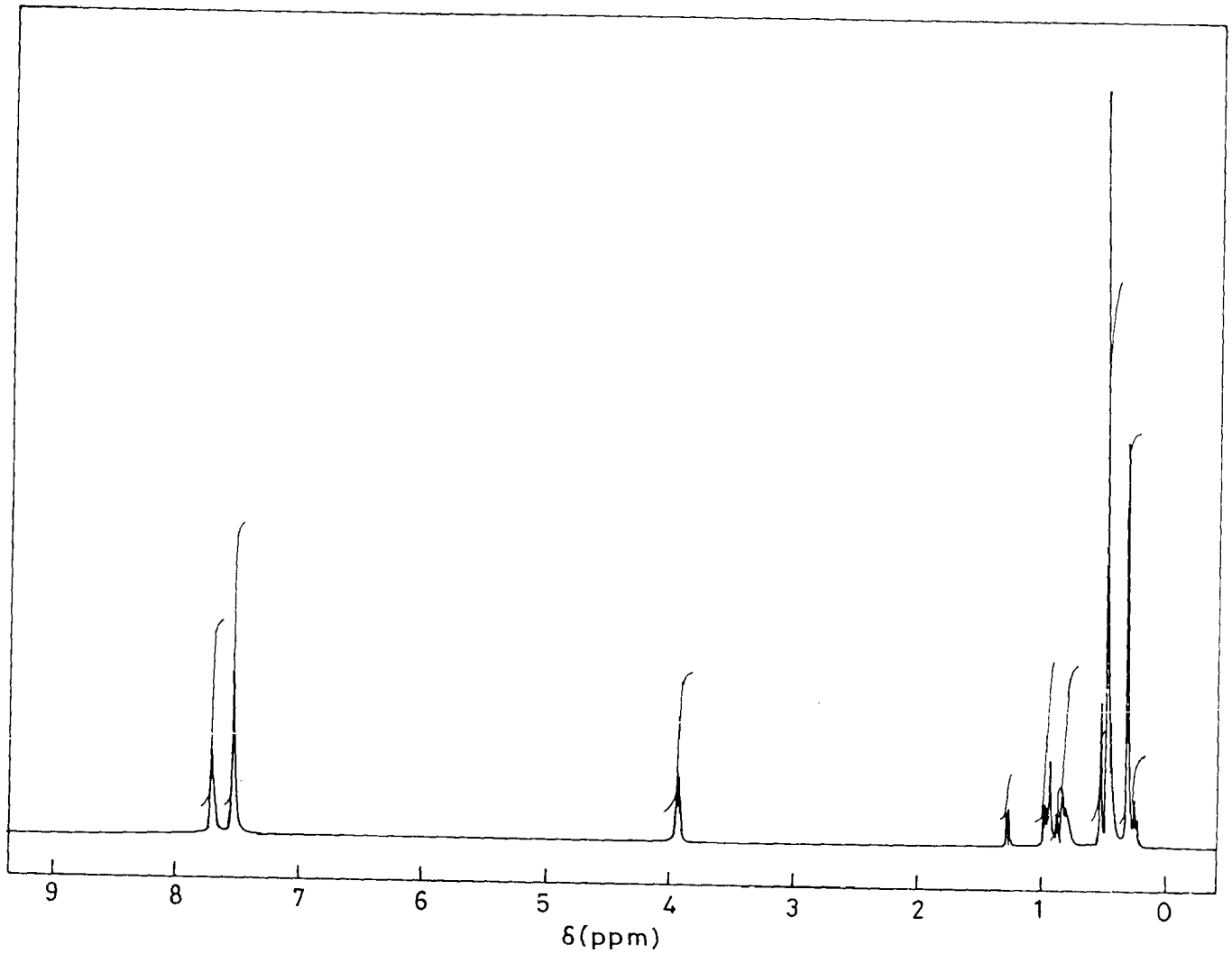


Figure 4.5 ^{1}H NMR spectrum of $PhMe_2SiXSiMeH_2$ (1d) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

as multiplet at δ 3.66. The distinct resonances due to CH, CH_3 protons (α isomer) as well as CH_2 protons (β isomer) can be located at their routine positions and are accordingly assigned (table 4.2). Two distinct triplets at δ 0.01 and 0.07 are assigned to MeSi protons of α and β isomers respectively. ^{13}C $\{^1H\}$ DEPT-135 NMR spectrum reveals signals due to aromatic carbon at δ 134.4, 129.7 and 128.6 (Table 4.3). The signals at δ 9.4 and 7.3 are ascribed to $SiCH_2CH_2Si$ group of β-isomer while the signals at δ 11.6 and 2.4 are assigned to CH_3 and CH carbon of the α-isomer. The signals at –2.0/-2.5 and 0.2/0.7 are assigned to methyl carbons of the $MeSiH_2$ and $PhMe_2Si$ moiety respectively. In the ^{29}Si $\{^1H\}$ NMR spectrum, the signals at 0.1, -0.9 ($PhMe_2Si$) and -28.5, -29.4 (SiH_2) suggest the presence of α and β isomers (Figure 4.6, Table 4.4).

4.3.2.5 NMR spectral studies of $PhMeHSiXSiMeH_2$, (1e) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

^1H, ^{13}C, ^{29}Si NMR data for **1e** are given in tables 4.2 - 4.4. ^1H NMR spectrum of the carbosilane shows the presence of β and α isomers in 3:2 ratio. A noteworthy feature of the spectrum is the presence of doublet of doublet centered at δ 1.02 and 0.26 due to $C-CH_3$ and MeSi protons (α-isomer) respectively and suggests the presence of diastereomers by virtue of adjacent chirality at Si and C centers. This is supported by the ^{13}C $\{^1H\}$ NMR spectrum which reveals two distinct resonances each for CCH_3 (δ 11.2/10.6), CH (δ -0.3/-0.6) and Ph*Me*Si

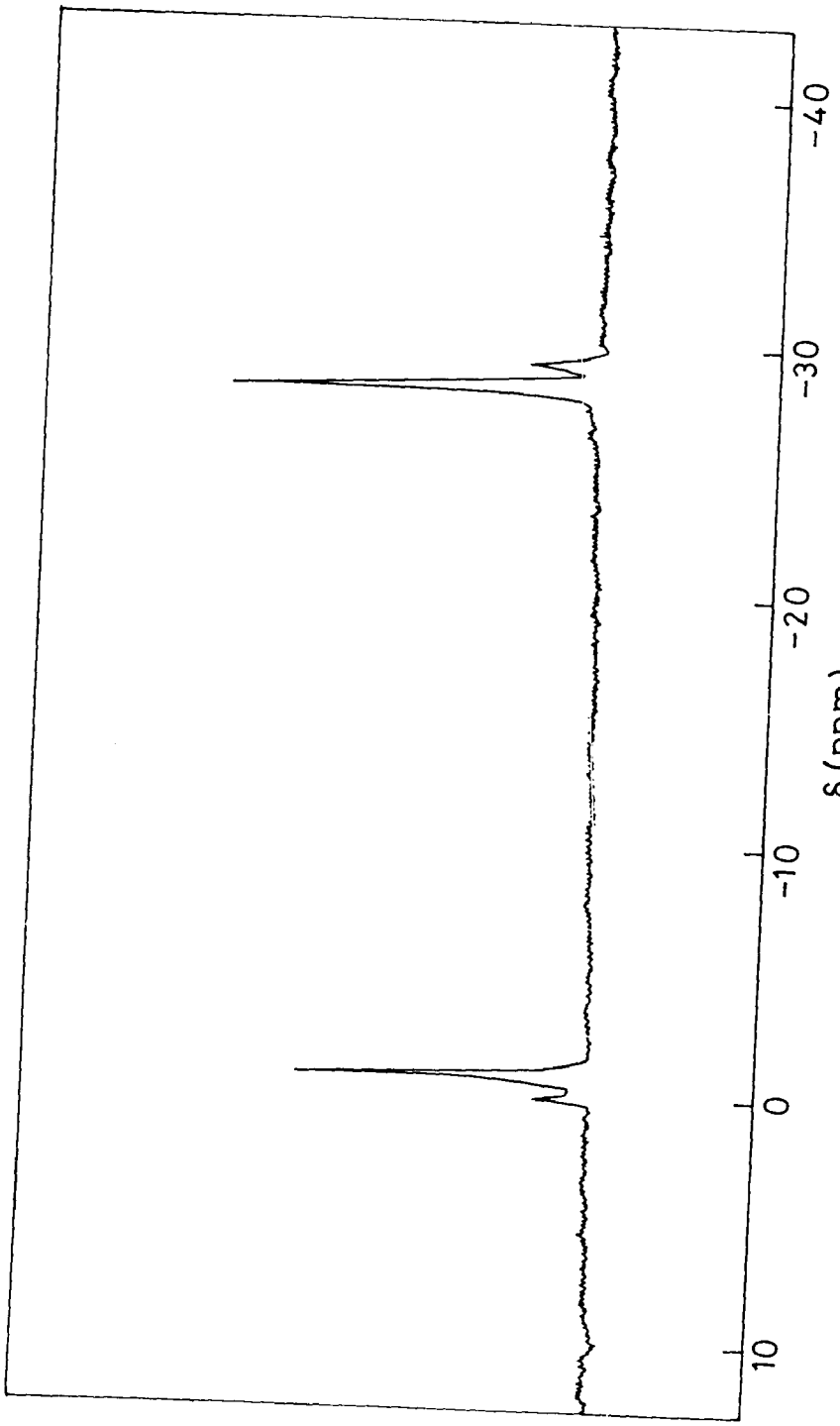


Figure 4.6 ^{29}Si {^{1}H} NMR spectrum of $PhMe_2SiXSiMeH_2$ (1d) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

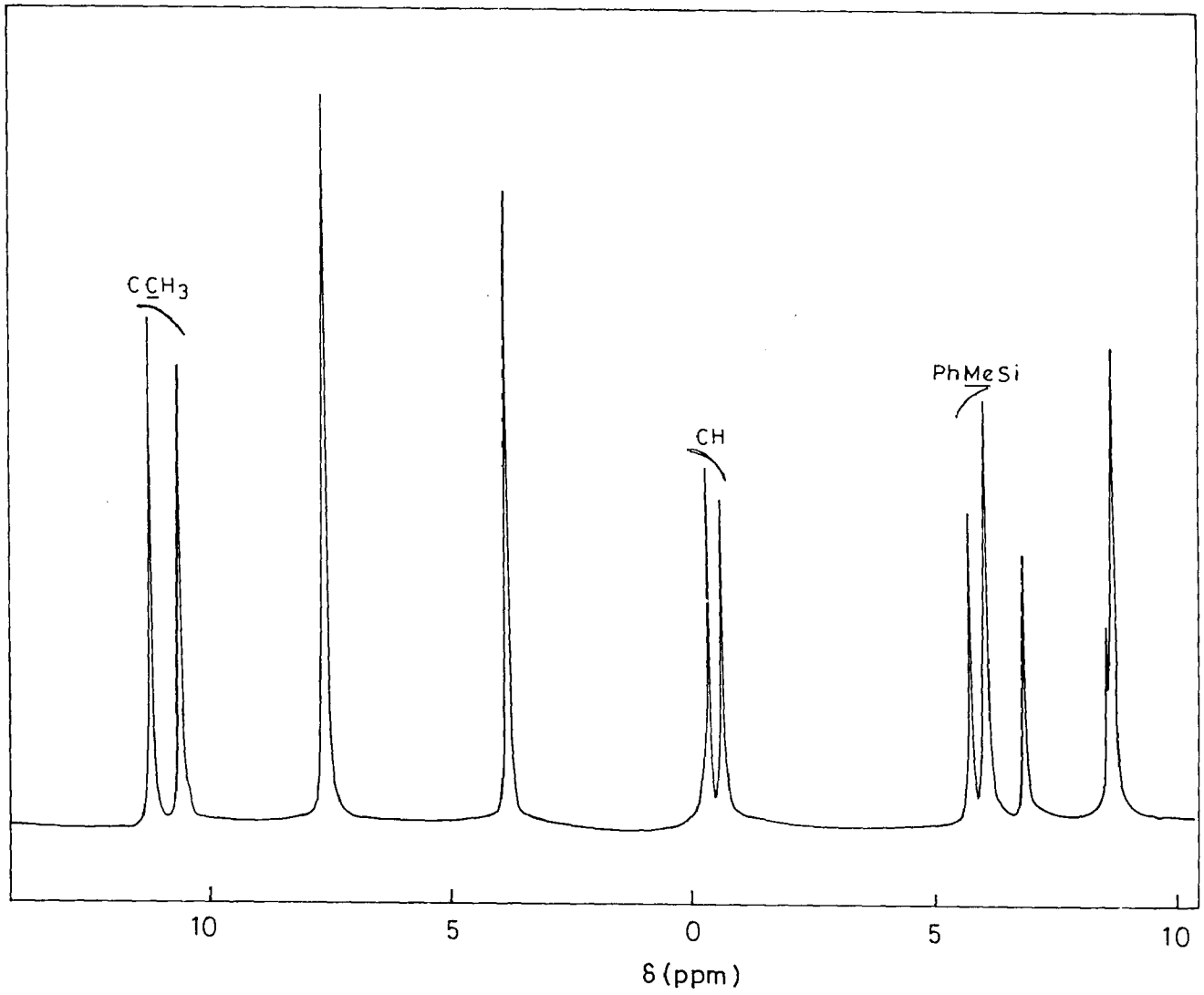


Figure 4.7 ^{13}C {^{1}H} NMR spectrum of $PhMeSiHXSiMeH_2$ (1e) [X = $-CH_2CH_2-$, $-CH(CH_3)$] (aliphatic region only)

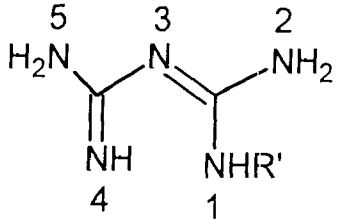
(δ -5.7/-6.0) groups (Figure 4.7). The signals at δ 7.6 and 3.9 are ascribed to $SiCH_2CH_2Si$ group while the signal at –6.8 is attributed to the methyl carbon (PhMeSiH) of the β-isomer. The signals due to $MeSiH_2$ appear at δ –8.6 and –8.7. ^{29}Si $\{^1H\}$ NMR spectrum of this compound reveals three signals each in the region -29.1 to -28.6 and -8.4 to -10.8 and are attributed to SiH_2 and PhMeHSi moieties respectively.

4.3 Section B - Reactivity of the carbosilanes towards biguanide/ 1-cyclohexylbiguanide.

4.4 Reactions of the carbosilanes, $R^1R^2R^3SiXSiH_3$ (1a - 1c) with biguanide/1-cyclohexylbiguanide.

Synthesis and characterization of the carbosilanes $R^1R^2R^3SiXSiH_3$ [$R^1 = R^2 = R^3 = Et$ (**1a**); $R^1 = R^2 = Ph$, $R^3 = H$ (**1b**) and $R^1 = Me$, $R^2 = Ph$, $R^3 = H$ (**1c**), X = $-CH_2CH_2-$ or $CH(CH_3)$] have been discussed in Section A of this chapter. The carbosilane **1a** is obtained as predominantly β-isomer (>85%) while **1b** and **1c** could only be prepared as mixture of α and β-isomers in 2:3 ratio. These carbosilanes are of interest in order to address the phenomena of SiH/NH dehydrocoupling at the primary SiH_3 sites bound to $-CH_2CH_2-$ and/or $-CH(CH_3)$ spacer group. The studies are of significance to delineate the fundamental difference that exists in the reactivity of aryl vs. alkyl substituted primary silanes in relation to SiH/NH dehydrocoupling with biguanide ligands. In addition, choice of the carbosilanes such as **1b** and **1c** also provide an insight into the reactivity behavior of tertiary SiH group which is present in these compounds. It is with this notion that reactions of these carbosilanes with biguanide and 1-cyclohexylbiguanide have been studied in detail. As already mentioned in the chapter III, the general convention of abbreviating the biguanide ligands as H_5bigR' is followed during the course of discussion. This becomes imperative in order to illustrate the

trifunctional NH_2 sites which are susceptible to SiH/NH dehydrocoupling reactions. The results are being discussed below.



H_5bigR'

The SiH/NH dehydrocoupling reactions between the carbosilanes (**1a - 1c**) and biguanide/1-cyclohexylbiguanide are found to be quite sluggish at room temperature (in comparison to the analogous reactions with $PhSiH_3$/p-tolSiH_3, Chapter III). This is evident by monitoring these reactions using ^1H NMR spectra at different time intervals. It is observed that ~ 60% of the primary SiH groups in the parent carbosilanes reacted after 72h. However, the rate of SiH/NH dehydrocoupling is accelerated at elevated temperature. Thus, heating the reaction mixture at 60-65°C for 18 - 20h results in a clear solution. Subsequent addition of n-hexane affords a white solid in each case. Elemental analysis as well as detailed spectral data (IR, ^1H, ^{13}C, ^{29}Si NMR and EI/FAB mass) suggest that these compounds posses the empirical composition $[(RSiH)_2(HbigR')]$ as shown in equation 3.

$$2\ RSiH_3 \quad + \quad H_5bigR' \xrightarrow[60 - 65°C]{THF} [(RSiH)_2(HbigR')]_n \quad + \quad H_2\uparrow \quad \text{----- 3}$$

Compound	R	R'
9	Et_3SiX	H
10	Ph_2HSiX	H
11	PhMeHSiX	H
12	Et_3SiX	Cy
13	Ph_2HSiX	Cy
14	PhMeHSiX	Cy

where X = $-CH_2CH_2-$ or $-CH(CH_3)$

4.5 Characterization of silylbiguanides (9 – 14)

4.5.1 FAB/EI mass spectra

The identity of the proposed structural unit, $[(RSiH)_2(HbigR')]_n$ for the compounds **9 – 14**, has been validated by EI/FAB mass spectral data. For **9 – 11**, the studies are performed in EI (70 eV) mode while the FAB mass spectral data have been collected for **12 – 14**. The illustrative mass spectra for the compounds **9, 11** and **14** are shown in figures 4.8, 4.9, and 4.10. The mass spectra show the presence of highest fragment ions at m/z 395 $[M - 2CH_3 - 2H]^+$ for **9** and 346 $[M - 3Ph]^+$ for **10** which are believed to arise from the fragmentation of the proposed structural unit $[M]^+$. For **11**, the highest ion at m/z 626 is assigned to $[M - 3C_6H_6 - 3CH_3]^+$ based on the dimeric structural entity

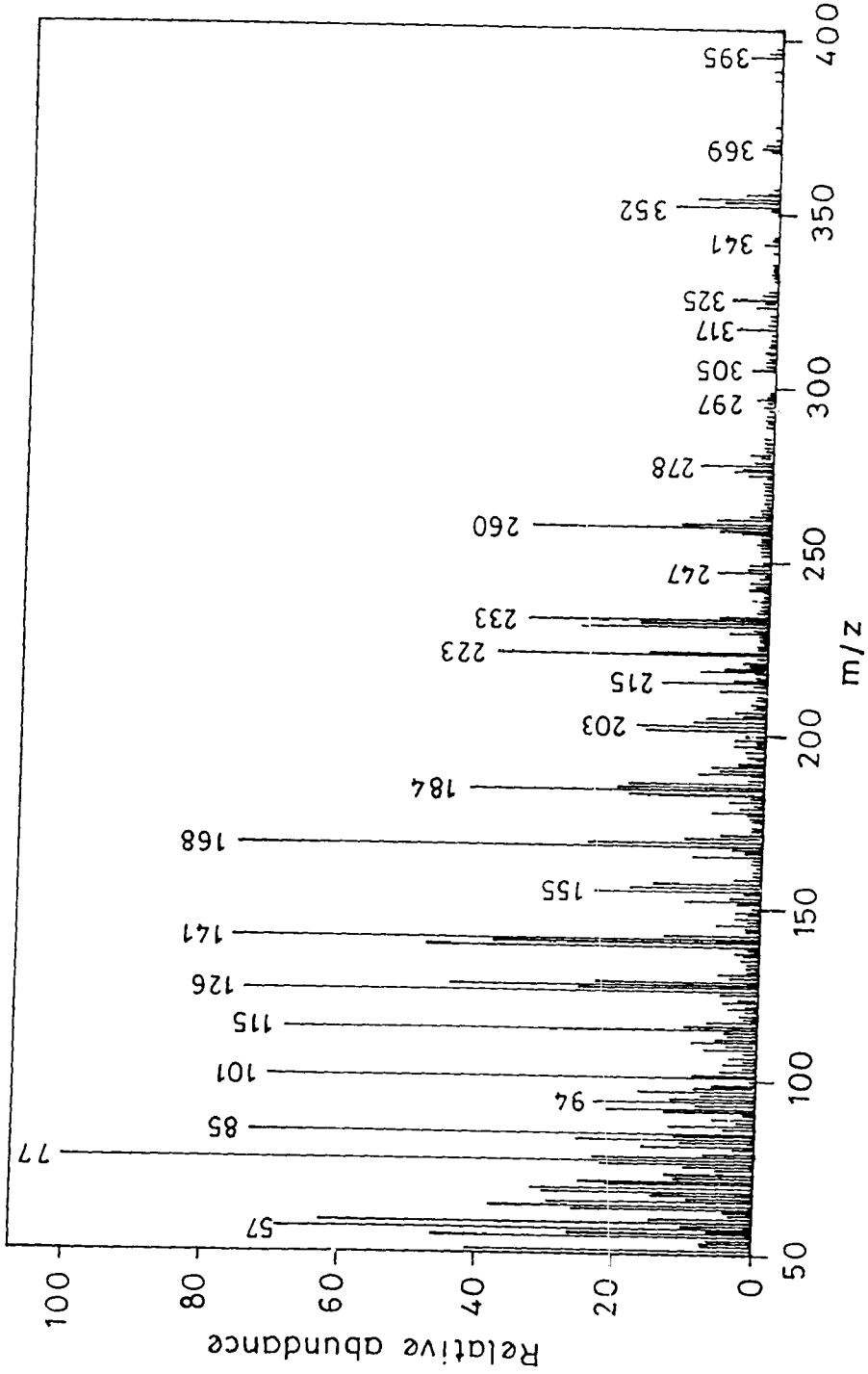


Figure 4.8 EI mass spectrum of $[(Et_3SiXSiH)_2(H_2big)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (9)

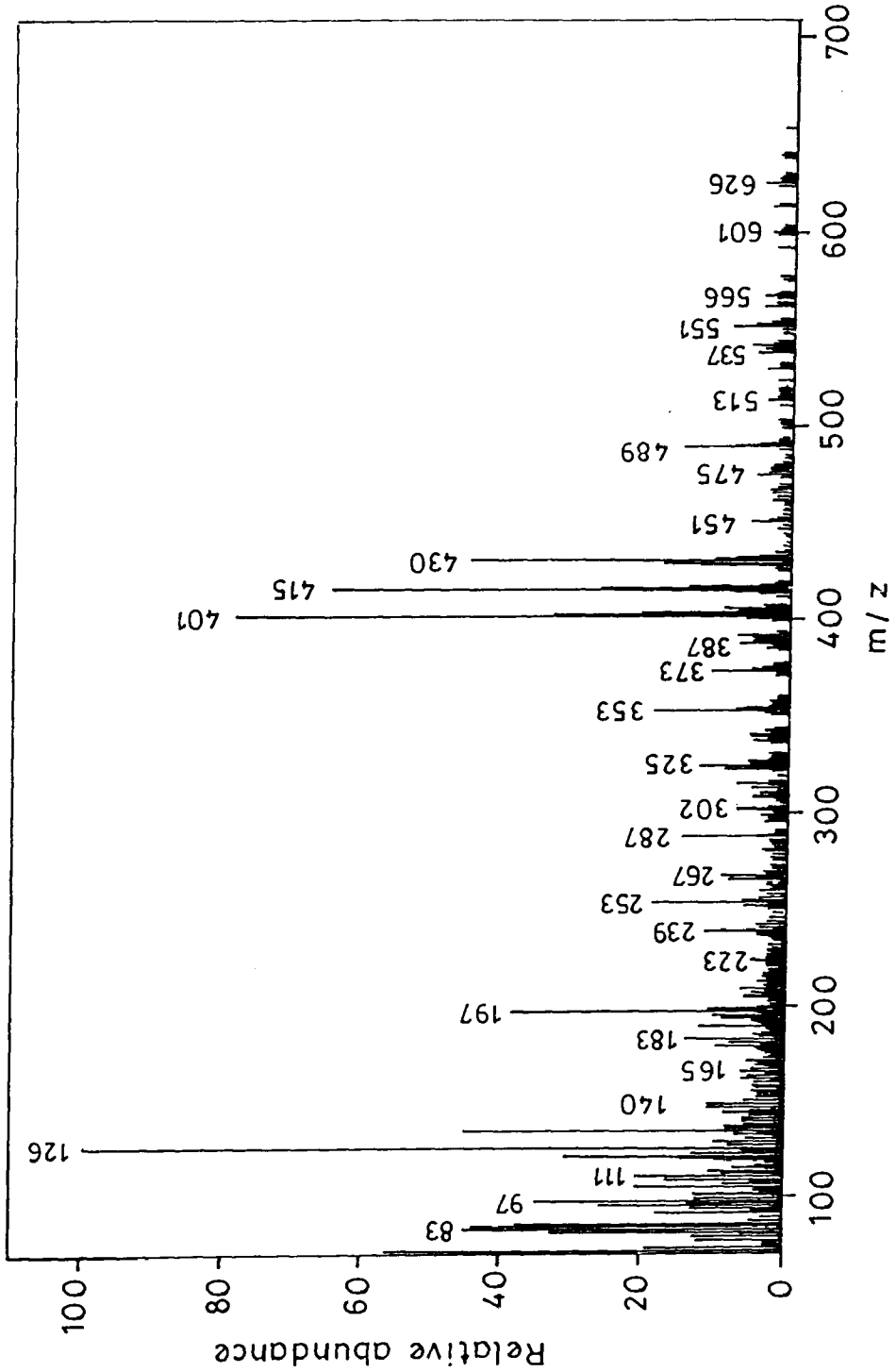


Figure 4.9 EI mass spectrum of $[(PhMeHSiXSiH)_2(H_2big)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (11)

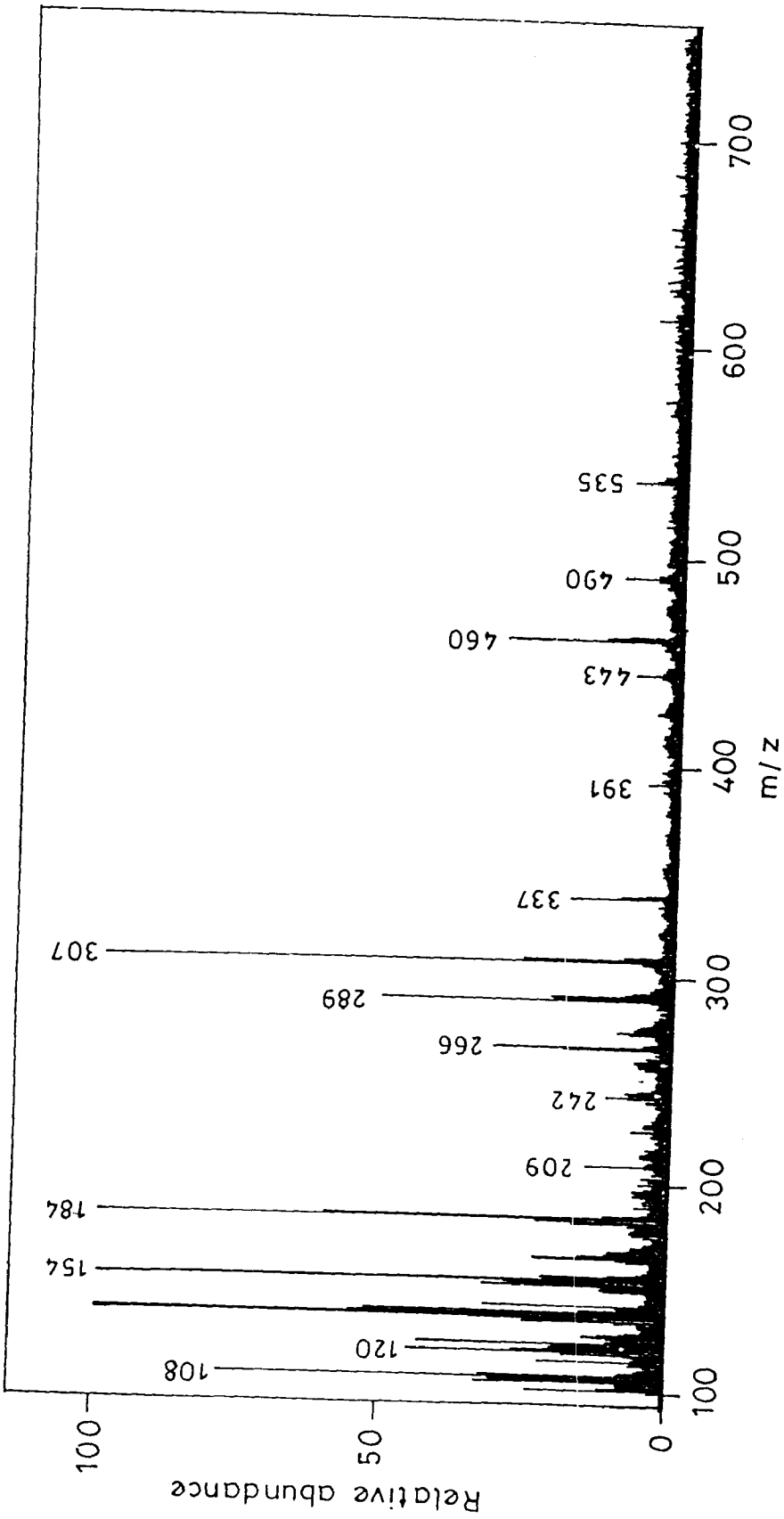


Figure 4.10 FAB mass spectrum of $[(PhMeHSiXSiH)_2(HbigCy)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (14)

$[(PhMeHSiXSiH)_2(H_2big)]_2$. Other significant fragment ions primarily arise from the cleavage of Si-C bond or loss of NH/NH_3. The relevant data is summarized in Table 4.5, 4.6 and 4.7. The FAB mass spectrum of the compound **14** $[(PhMeHSiCH_2CH_2SiH)_2(HbigCy)]$ reveal $[M]^+$ ion at m/z 535. Though the corresponding $[M]^+$ ions for **12** and **13** are not observed in the FAB mass spectra, structurally important fragment ions arising primarily by the Si-C cleavage analogous to those observed for **9 - 11** are discernable. Notable fragment ions and their assignments are summarized in table 4.8 – 4.10.

4.5.2 Infrared spectra

Pertinent IR absorptions of the silylbiguanides **9 - 14** along with their tentative assignments are given in table 4.11. The absence of IR absorptions at ~ 3420 (νNH_2) and 925 - 926 cm^{-1} (δ SiH_2) is a common feature in the spectra of all the compounds and can be considered as a qualitative evidence in favor of SiH/NH dehydrocoupling involving SiH_3 group of the carbosilane and $-NH_2$ sites of biguanide/ 1-cyclohexylbiguanide. The νSiH absorption appears at 2131 - 2109 cm^{-1} and is lowered by 20 - 25 cm^{-1} in comparison to those of the corresponding precursor carbosilanes (2143 - 2148 cm^{-1}). The absorptions due to functional groups such as νNH, νC=N and νNCN (skeletal modes) arising from the biguanide ligands appear at 3358 – 3336, 1636 - 1619, 1558 - 1540 cm^{-1} respectively (Figure 4.11). These absorptions remain practically unaltered in comparison to those

Table 4.5 EI mass data of $[(Et_3SiXSiH)_2(H_2big)]_n$(9) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	M^+ = 442
395	$[M - 2CH_3 - 2H]^+$
352	$[M - 3C_2H_6]^+$
325	$[M - Et_3Si - 2H]^+$
260	$[M - 6C_2H_6 - 2H]^+$
233	$[M - 5C_2H_5 - C_2H_6 - 2NH_3]^+$
184	$[M - Et_3SiCH_2CH_2 - Et_3Si]^+$
168	$[M - Et_3SiCH_2CH_2-Et_3Si - NH_2]^+$

Table 4.6 EI mass spectral data of $[(Ph_2HSiXSiH)_2(H_2big)]_n$(10) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	M^+ = 577
346	$[M - 3Ph]^+$
317	$[M - 2Ph_2SiH - Ph]^+$
240	$[M - 2Ph_2SiH - 2Ph]^+$
225	$[M - 2Ph_2SiH - 2Ph - NH]^+$
155	$[M - 2Ph_2SiHCH_2CH_2]^+$

Table 4.7 EI mass data of $[(PhMeHSiXSiH)_2(H_2big)]_n$ (11) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	M^+ = 906
626	$[2M - 3C_6H_6 - 3CH_3]^+$
551	$[2M - 4C_6H_5 - 2CH_3 - NH_3]^+$
489	$[2M - 2MePhSiH - 2C_6H_6 - NH_3 - 2H]^+$
451	$[M/2 - 2H]^+$
430	$[2M - 2MePhSiCHCH_2 - 2C_6H_5 - 2CH_3]^+$
415	$[2M - 2MePhSiCHCH_2 - 2C_6H_5 - 3CH_3]^+$
401	$[2M - 4MePhSiH - NH_3 - 4H]^+$
373	$[2M - 2MeSiHPhCH_2CH_2 - 2MePhSi]^+$
353	$[2M - 2MeSiHPhCH_2CH_2 - MePhSi - CH_3]^+$
325	$[2M - 3MeSiHPhCH_2CH_2 - MePhSiH - CH_3]^+$

Table 4.8 FAB mass data of $[(Et_3SiXSiH)_2(HbigCy)]_n$ (12) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	$M^+ = 523$
460	$[M - 2C_3H_6 - 3H]^+$
391	$[M - 4C_2H_5 - NH]^+$
337	$[M - Et_3SiCH_2CH_2Si - NH]^+$
307	$[M - Et_3SiCH_2CH_2SiH - 2C_2H_5 - NH]^+$
289	$[M - 2Et_3Si - 4H]^+$

Table 4.9 FAB mass data of $[(Ph_2HSiXSiH)_2(HbigCy)]_n$ (13) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	$M^+ = 659$
428	$[M - 3Ph]^+$
399	$[M - Ph_2SiH - Ph]^+$
346	$[M - 3Ph - Cy]^+$
316	$[M - Ph_2SiH - Ph - Cy]^+$
226	$[M - Ph_2Si - 2Ph - Cy - NH]^+$

Table 4.10 FAB mass spectral data of $[(PhMeHSiXSiH)_2(HbigCy)]_n$ (14) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

m/z	$M^+ = 535$
535	$[M]^+$
490	$[M - 3CH_3]^+$
460	$[M - C_6H_4]^+$
443	$[M - Ph - NH]^+$
391	$[M - C_6H_{10} - 2CH_3 - 2NH]^+$
337	$[M - 2Ph - 2CH_3 - NH]^+$

Table 4.11 IR (KBr, cm^{-1}) spectral data of $[(RSiH)_2(Hbig)]_n$ (R = Et_3SiX, R' = H (9) or Cy (12); R = Ph_2HSiX, R' = H (10) or Cy (13); R = PhMeHSiX, R' = H (11) or Cy (14))

Compound	νNH	νCH (aromatic)	νCH (aliphatic)	νSiH	νCN	νNCN	νSiPh	$\nu SiCH_3$
9	3358		2952 2875	2131	1635	1558		1261
10	3346	3068 3050	2962 2850	2109	1635	1540	1116	1261
11	3353	3067 3051	2956 2868	2117	1635	1540	1115	1259
12	3336		2933 2873	2127	1619	1557		1260
13	3355	3066 3052	2928 2853	2113	1636	1540	1114	1261
14	3348	3067 3053	2929 2854	2111	1635	1558	1113	1259

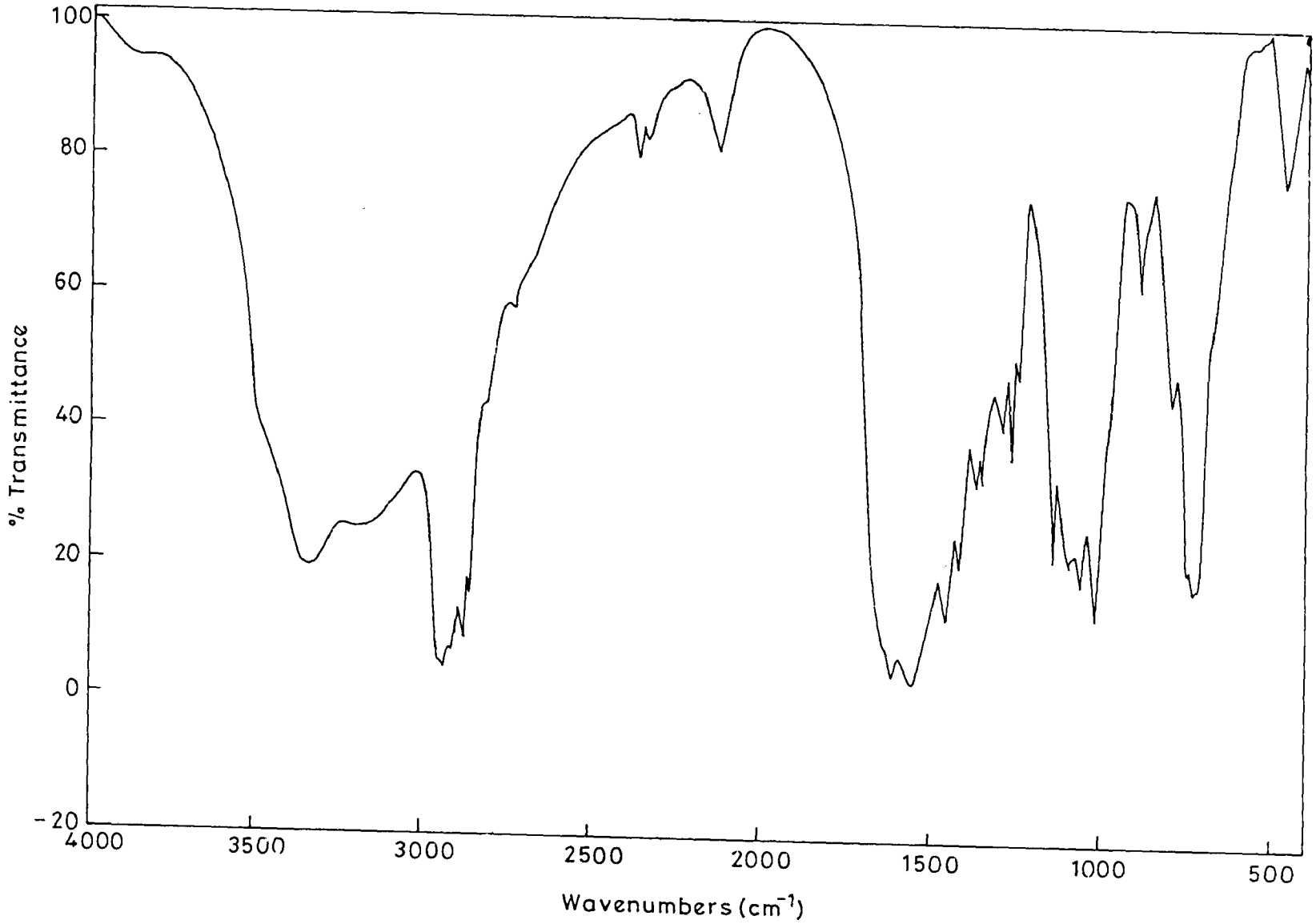


Figure 4.11 IR spectrum of $[(Et_3SiXSiH)_2(HbigCy)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (12)

observed in the parent ligands. The characteristic absorptions due to PhSi and MeSi groups are seen at 1116 - 1113 and 1261 – 1259 cm^{-1} respectively. νCH aromatic (wherever applicable) and νCH aliphatic modes appear at the routine positions.

4.5.3 NMR studies of $[(RSiH)_2(HbigR')]_n$ (9 --14)

^1H NMR spectra

The ^1H NMR spectra (DMSO-d_6) of **9 – 14** reveal that the signals arising from the organic functionalities such as Et_3SiX (for **9, 12**), Ph_2HSiX (for **10, 13**) and PhMeHSiX (for **11, 14**) (where X = $-CH_2CH_2-$, $-CH(CH_3)$) are usually broad and devoid of J coupling information (Figure 4.12). A few important observations that deserve special mention are discussed (Table 4.12). The chemical shifts of SiH protons at δ 4.61 (for **10, 13)** and 4.35 (for **11, 14)** are attributed to the Ph_2HSiX/PhMeHSiX groups respectively and are comparable with those of the parent carbosilanes. These results suggest that the carbosilyl groups bearing tertiary SiH functionalities are tolerant towards the SiH/NH dehydrocoupling. The residual SiH protons in the structural framework are observed at δ 4.62 – 4.25. For the compounds **12 – 14** derived from 1-cyclohexylbiguanide, the protons associated with N-bonded cyclohexyl group are relatively sharp and appear at δ 3.30 - 3.37 (s, NCH), 1.64 – 1.65 (m, CH_2) and 1.17 – 1.19 (m, CH_2) (Table 4.12). The integral ratio of RSi and NCy groups is observed as

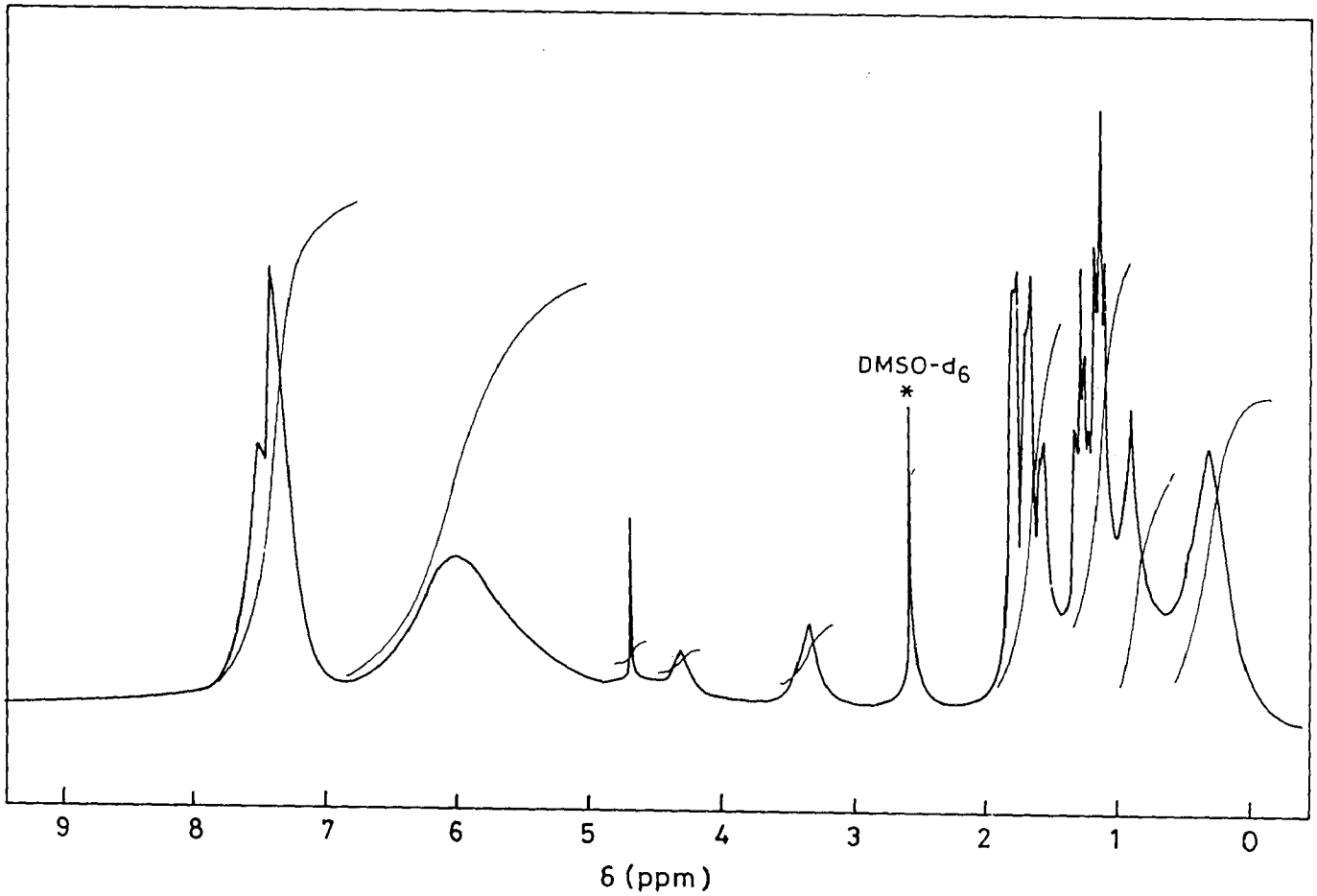
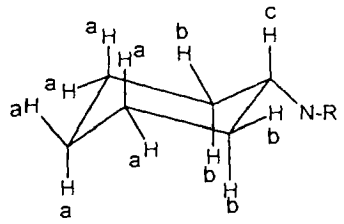


Figure 4.12 ^{1}H NMR spectrum of $[PhMeHSiXSiH)_2(HbigCy)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (14)

Table 4.12 ^{1}H NMR spectral data δ (ppm) of $[(RSiH)_2(HbigR')]_n$ (where R = Et_3SiX, R' = H (9) or Cy (12); R = Ph_2HSiX, R' = H (10) or Cy (13); R = PhMeHSiX, R' = H (11) or Cy (14))

Compound	C_6H_5	NH	SiH	Cy	CH_2	SiMe	CH_3
9	-	5.21 (br)	4.62	-	0.41	-	0.83
10	7.54 (m, meta) 7.26 (m, ortho/para)	4.82 (br)	4.61	-	0.83	-	-
11	7.49 (m, meta) 7.23 (m, ortho/para)	5.49 (br)	4.56 4.35	-	0.77	0.23	-
12	-	5.23 (br)	4.60	3.36 (m, 1H, CH^c) 1.65 (m, 4H, CH_2^b) 1.19 (m, 6H, CH_2^a)	0.42	-	0.83
13	7.41 (m, 8H, meta) 7.25 (m, 12H, ortho/para)	5.04 (br)	4.61 4.25	3.37 (m, 1H, CH^c) 1.64 (m, 4H, CH_2^b) 1.18 (m, 6H, CH_2^a)	0.80	-	-
14	7.41 (m, 4H, meta) 7.29 (m, 6H, ortho/para)	5.97 (br)	4.35 4.25	3.30 (m, 1H, CH^c) 1.64 (m, 4H, CH_2^b) 1.17 (m, 6H, CH_2^a)	0.83	0.25	-

where Cy (a, b, c) is according to the structure



2 : 1 in each case and is in conformity with the empirical composition as proposed. The signal due to NH protons appears at δ 4.82 - 5.97 (br) and show concentration dependent chemical shifts.

^{13}C {^{1}H} NMR spectra

^{13}C {^{1}H} NMR spectra of the compounds **9 - 14** have been studied and the presence of different organic functionalities Et_3SiX (for **9, 12**), Ph_2HSiX (for **10, 13**) and PhMeHSiX (for **11, 14**) (where X = -CH_2CH_2-, -$CH(CH_3)$) have been detected based on their chemical shifts values. The relevant data are given in Table 4.13. The resonances due to $CH_2CH_2/CHCH_3$ are usually broad and are too weak to be assigned unequivocally. Nevertheless, the tentative assignments are made on the basis of ^{13}C {^{1}H} DEPT-135 NMR spectra. The ^{13}C NMR spectrum of **11** is shown in figure 4.13 as an illustration. DEPT spectrum of each compound identifies the out of phase signals arising from the CH_2 carbon of the β isomer while the signals due to CH_3 and CH carbons of the α isomer are assigned by comparing the chemical shift values observed in the parent carbosilanes. For the compounds **12 - 14**, signals due to N-cyclohexyl group appear at δ 48.9 – 49.9 (C1, NCH), 33.0 –33.2 (C2,2', CH_2), 25.2 – 25.3 (C3,3', CH_2) and 24.4 - 24.7 (C4, CH_2).

Table 4.13 ^{13}C {^{1}H} NMR spectral data δ (ppm) of $[(RSiH)_2(HbigR')]_n$ (R = Et_3SiX, R' = H (9) or Cy (12); R = Ph_2HSiX, R' = H (10) or Cy (13); R = PhMeHSiX, R' = H (11) or Cy (14)):

Compound	C=N	C_6H_5	Cy	CH	CCH_3	$SiCH_3$/SiEt	$SiCH_2$
9	162.7	-	-	-	-	7.7 3.0	2.9 7.4
10	162.7	i = 134.3 o = 133.3 p = 128.9 m = 127.1	-	0.3	8.8	-	4.3 3.2
11	162.8	i = 134.5 o = 133.8 p = 129.5 m = 128.1		4.1	10.7	-5.6	8.7 -2.1
12	160.3 159.7	-	49.7 (C1) 33.2 (C2, 2') 25.2 (C3, 3') 24.4 (C4)			7.9 3.2	2.8 7.5
13	160.3 162.1	i = 138.3 o =133.5 p =129.7 m =127.4	49.9(C1) 33.0 (C2, 2') 25.2 (C3, 3') 24.7 (C4)	0.4	8.5		4.5 3.0
14	160.5 162.1	i =135.1 o = 134.2 P = 129.4 M =127.8	48.9 (C1) 33.2 (C2, 2') 25.3 (C3, 3') 24.5 (C4)	5.3	11.2	-6.2	9.1 -2.5

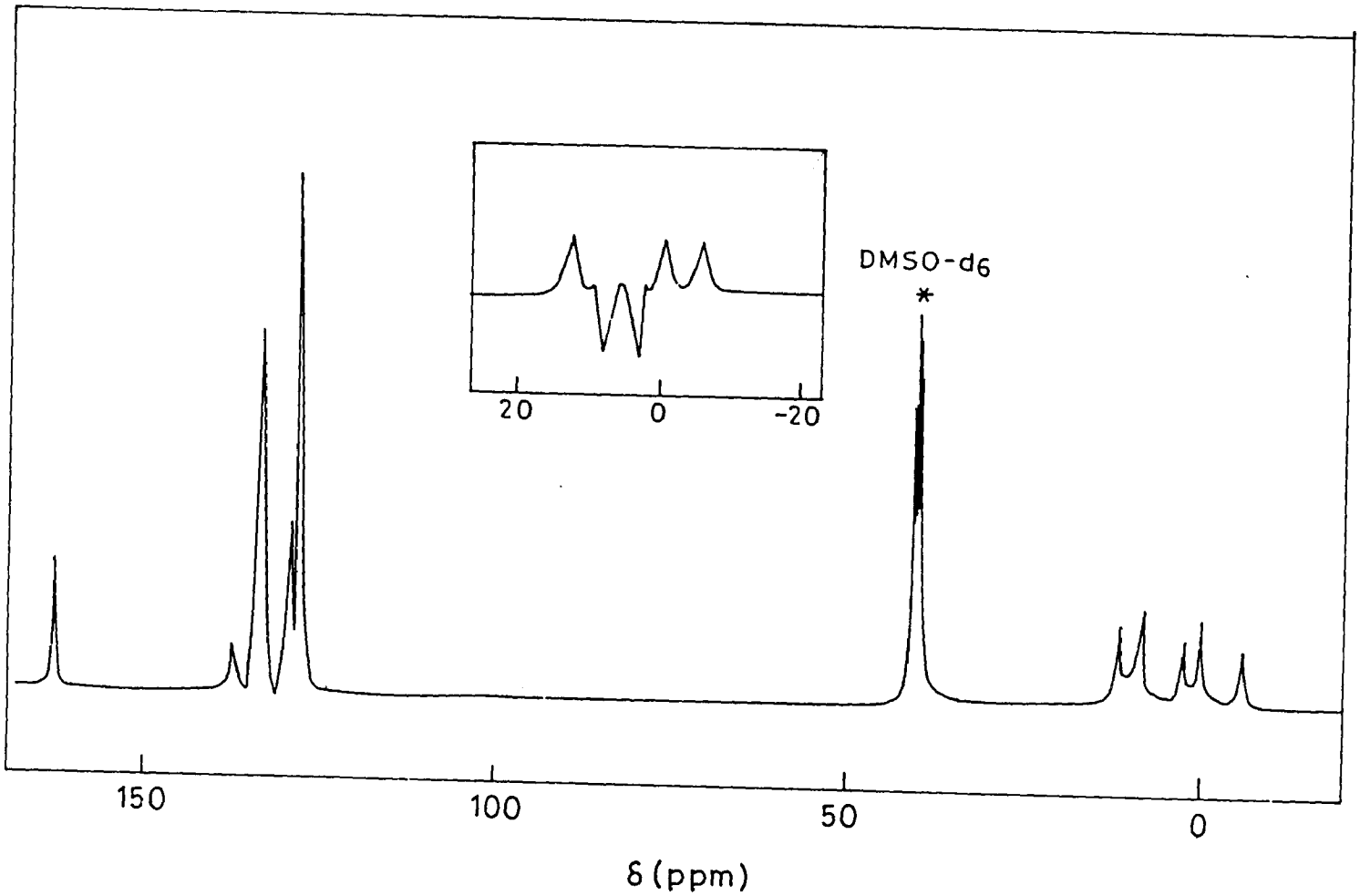


Figure 4.13 ^{13}C {^{1}H} NMR spectrum of $[(PhMeHSiXSiH)_2(H_2big)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (11) (inset picture ^{13}C {^{1}H} DEPT- 135 NMR)

^{29}Si {^{1}H} NMR spectra

^{29}Si {^{1}H} NMR spectrum of each compound reveals that the signals associated with the pendant carbosilyl group i.e. Et_3Si/Ph_2HSi/ PhMeHSi lie in the chemical shift values similar to those found in the corresponding precursor carbosilanes (Table 4.14). The results are particularly significant in order to illustrate the inert nature of Ph_2HSi (for **10, 13**) and PhMeHSi (for **11, 14**) groups towards dehydrocoupling. Interestingly, the spectrum of each compound reveals an additional resonance between δ - 117 to - 121 (Figure 4.14). The spectral studies performed in ^{29}Si {^{1}H} DEPT-135 mode suggest the origin of this signal from the $RSiHN_2$ moiety. The spectral data find an analogy with those of the silylbiguanides **1 - 4** (δ ^{29}Si –127.3 to –132.1) obtained from primary arylsilanes (Chapter III, Section A). It can thus be envisioned that the silicon atom associated with $RSiHN_2$ moiety in the present silylbiguanides are coordinatively associated with the imine/amine donor atoms to yield the formation of hyper-coordinated silicon atoms. In addition, the group electronegativity of biguanide has also been considered as an important factor to explain the unusual upfield ^{29}Si chemical shifts.

4.6 Proposed structure

The identity of the structural unit $[(RSiH)_2(HbigR')]_n$ in the silylbiguanides, **9 - 14** has been firmly established from the spectroscopic data such as IR, FAB/EI mass as well as ^{1}H and ^{29}Si

Table 4.14 ^{29}Si {^{1}H} NMR spectral data δ (ppm) of $[(RSiH)_2(HbigR')]_n$ (R = Et_3SiX, R' = H (9) or Cy (12); R = Ph_2HSiX, R' = H (10) or Cy (13); R = PhMeHSiX, R' = H (11) or Cy (14))

Compound	R	$RSiHN_2$
9	8.1	-117.8
10	-10.9,	-121.1
11	-9.2,	-118.2
12	8.2	-117.3
13	-11.2	-121.3
14	-10.6	-119.1

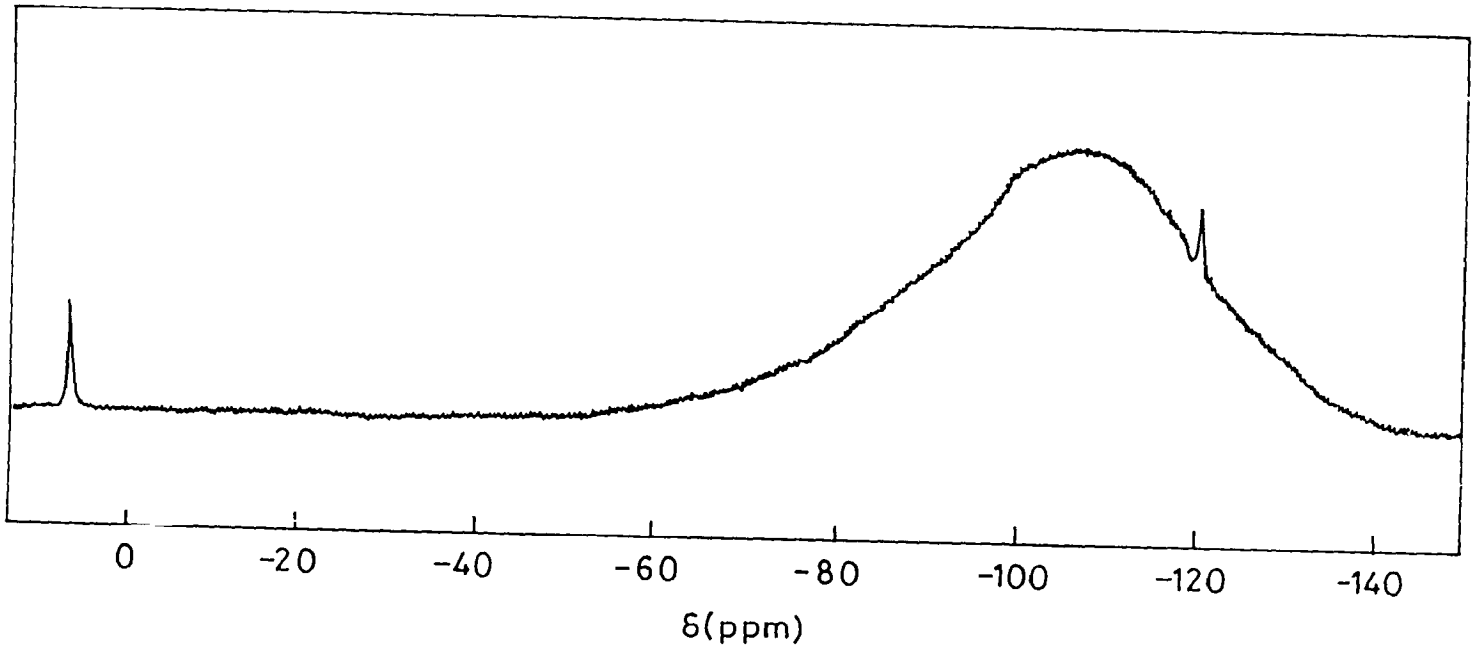


Figure 4.14 ^{29}Si {^{1}H} NMR spectrum of $[(Et_3SiXSiH)_2(H_2big)]_n$ [X = $-CH_2CH_2-$, $-CH(CH_3)$] (9)

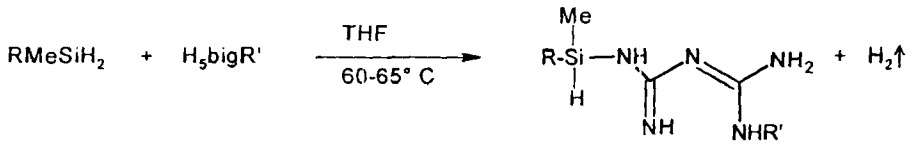
NMR spectra. For structural consideration, formation of the monomeric entity such as bis-silylbiguanide $(RSiH_2)_2H_3bigR'$ can be invoked in the initial stages of the reaction. The secondary SiH_2 groups as well as residual NH/NHR' functionalities present in the monomeric entity bring about further heterodehydrocoupling reactions to afford the cyclic compounds of definite stoichiometry. EI mass spectra of these compounds provide evidence in favor of cyclic dimer of the composition $[(RSiH)_2(HbigR')]_2$ by virtue of the detection of M^+ ion in a few cases. This is further supported by ^{29}Si NMR data which shows the presence of $RSiHN_2$ entity involving hypercoordinated silicon as predominant species in the structural framework. However, unambiguous structural assignments for these compounds can only be delineated from X-ray crystal structure analysis. Due to their extreme sensitive nature, attempts to grow suitable crystals of these compounds have not met with success.

4.7 Reactions of secondary carbosilanes (1d, 1e) with biguanide/ 1-cyclohexylbiguanide

Synthesis of the secondary carbosilanes $R^1R^2R^3SiXSiMeH_2$ [$R^1 = R^2 = Ph$, $R^3 = Me$ **1d**; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$ **1e** (where X = $CH_2CH_2/CHCH_3$)] has been discussed in section A of this chapter. For **1d**, β-isomer is formed in >90% whereas **1e** could only be obtained as a mixture of β : α in a % ratio of 55 : 45. These carbosilanes are the alkyl substituted analogs of secondary silanes and are thought to be

important precursors to address the phenomena of SiH/NH dehydrocoupling with the biguanide ligands. A detailed study on the reactivity behavior of these carbosilanes with biguanide and 1-cyclohexylbiguanide has been undertaken.

Reaction of the carbosilane **1d** or **1e** with biguanide/1-cyclohexylbiguanide in 2 : 1 stoichiometric ratio in THF medium is found to be extremely sluggish in comparison to analogous reactions of secondary organosilanes discussed in chapter III (section B). This is evident by monitoring these reactions at room temperature using ^1H NMR spectroscopy. It is observed that the SiH concentration of the precursor carbosilanes remains practically unaltered even after 48h. The reactions when carried out at 64- 65°C for a prolonged period (72 h), afford the corresponding 1-(carbosilyl)biguanides (**15, 16**) and 1-cyclohexyl-5-(carbosilyl)biguanides (**17, 18**) (scheme 4).



Compound	R	R'
15	$PhMe_2SiX$	H
16	PhMeHSiX	H
17	$PhMe_2SiX$	Cy
18	PhMeHSiX	Cy

where X = $-CH_2CH_2-$ or $-CH(CH_3)$

Scheme 4

4.8 Characterization of the silylbiguanides (15 – 18)

All the compounds mentioned above are white, moderately air sensitive solids and are soluble in solvents such as CH_2Cl_2, $CHCl_3$, THF, DMSO etc. These have been characterized by routine analytical and spectroscopic methods such as elemental analysis, IR and multinuclear ^1H, ^{13}C and ^{29}Si NMR studies.

4.8.1 Infrared Spectra

Pertinent IR absorptions of 1-(carbosilyl)biguanides (**15, 16**) and 1-cyclohexyl-5-(carbosilyl)biguanides (**17, 18**) along with their tentative assignments are given in table 4.15. IR spectra obtained as KBr pellets/nujol mull reveal that the characteristic features of the biguanide/1-cyclohexylbiguanide in the 3354 - 3233 cm^{-1} (NH_2/NH region) are practically retained, except that the band at 3420 cm^{-1} is relatively reduced in intensity. The characteristic absorption due to δSiH_2 at 945 cm^{-1} is completely absent in the spectra of all these compounds. The IR spectra also manifest two medium intensity absorption at 2192 – 2188 and 2111 - 2097 cm^{-1} due to νSiH mode (Figure 4.15). This observation is analogous to that found for silylbiguanides **5 - 8** obtained from secondary organosilanes (Chapter II, Section B). Thus, the presence of conformers in these compounds too is implicated.

In addition, the spectra exhibit routine absorptions due to other functional groups. For example, the bands at 1662 - 1606 and 1593 -

Table 4.15 IR (KBr, cm^{-1}) spectral data for [(RMeSiH)(H_4bigR')] (where R = $PhMe_2SiX$, R' = H (15) or Cy (17); R = PhMeHSiX, R' = H (16) or Cy (18):

Compound	νNH	νCH (aromatic)	νCH (aliphatic)	νSiH	νC=N	νNCN	νSiPh	$\nu SiCH_3$
15	3314 3250	3068 3050	2970 2855	2190 2103	1616	1558	1112	1256
16	3354 3260	3068 3051	2962 2850	2190 2097	1662	1557	1116	1257
17	3330 3233	3067 3050	2931 2855	2192 2099	1620	1593	1114	1254
18	3336 3270	3066 3052	2923 2853	2188 2111	1606	1558	1113	1247

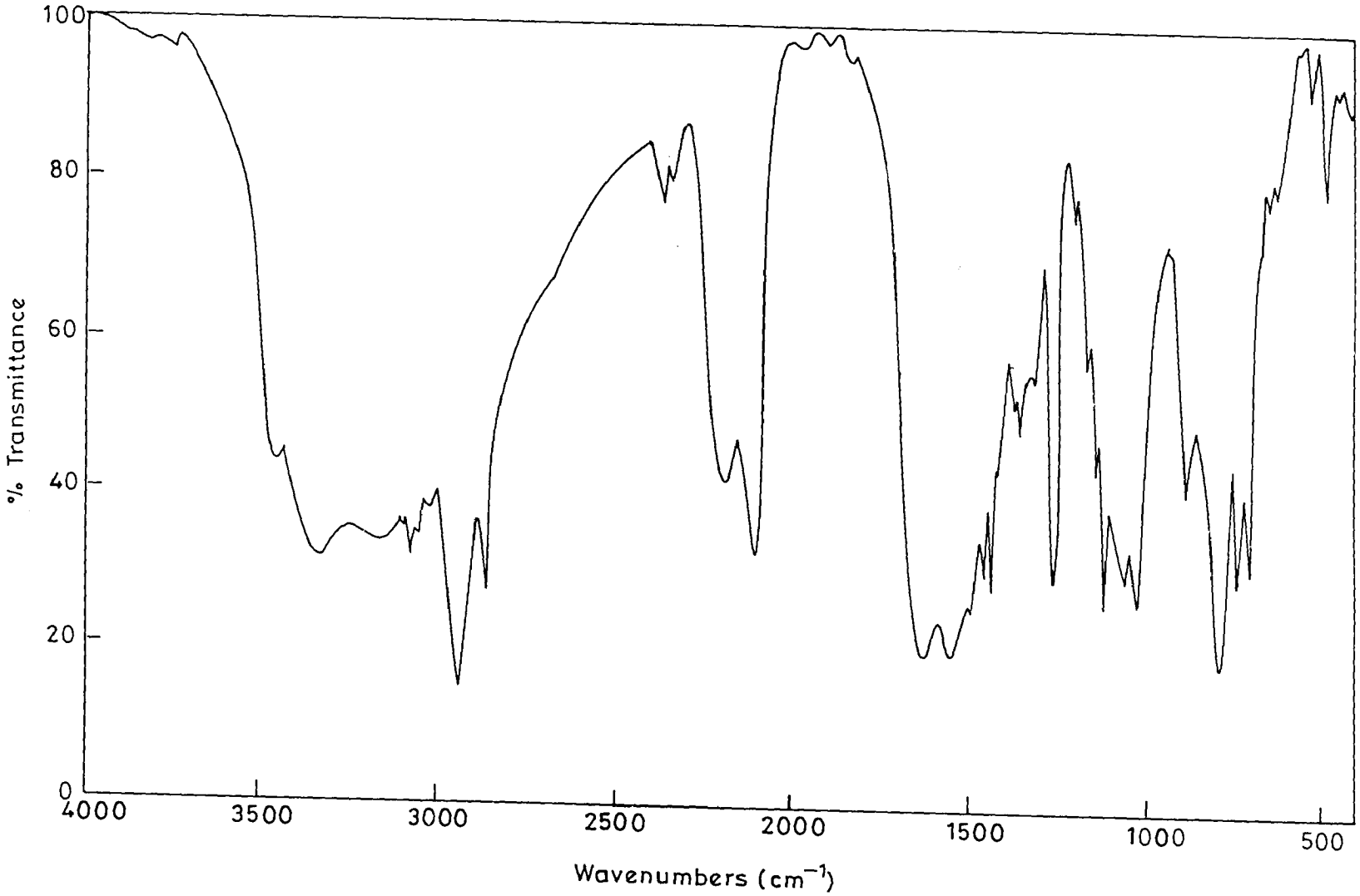


Figure 4.15 IR spectrum of 1-cyclohexyl-5-(carbosilyl)biguanide

$(PhMe_2SiCH_2CH_2SiMeH)(H_3bigCy)]$ (17)

1557 cm^{-1} are assigned to νC=N and νNCN modes respectively. The characteristic absorptions due to PhSi and MeSi groups appear at 1116 -- 1112 and 1257 – 1247 cm^{-1} respectively. νCH aromatic (wherever applicable) as well as νCH aliphatic modes appear at the routine positions in the spectra of these compounds.

4.8.2 NMR spectra

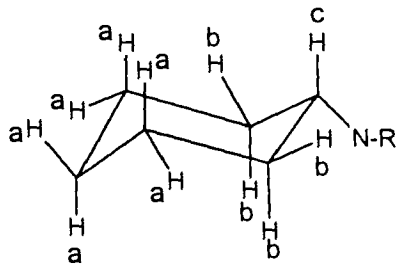
^{1}H NMR spectra

^{1}H NMR spectra of 1-(carbosilyl)biguanides (**15, 16**) and 1-cyclohexyl-5-(carbosilyl)biguanides (**17, 18**) in DMSO-d_6 reveal the presence of different organic functionalities such as $PhMe_2SiX$ (for **15, 17**) and PhMeHSiX (for **16, 18**) (where X = CH_2CH_2, $CHCH_3$) at their usual chemical shift values (Table 4.16). However the signals are invariably broad and do not provide the relevant J coupling information. This intrinsic spectral behavior is also observed for the compounds derived from primary carbosilanes (section 4.5.3) and impair a detailed structural analysis. For the compounds **16** and **18**, the chemical shifts of the SiH protons at δ 4.26 -- 4.28 are comparable with those of parent carbosilanes and are attributed to PhMeHSiX moiety. An additional signal at δ 4.60 - 4.62 is attributed to the residual SiH protons in the structural framework. The NH protons appear as a broad signal in the region δ 3.5 - 5.8 and show concentration dependent chemical shifts. For 1-cyclohexyl-5-(carbosilyl)biguanides **17** and **18**, the NCH protons

Table 4.16 ^{1}H NMR Spectral data δ (ppm) for [(RMeSiH)(H_4bigR')] (where R = $PhMe_2SiX$, R' = H (15) or Cy (17); R = PhMeHSiX, R' = H (16) or Cy (18) [X = -CH_2CH_2-, -$CH(CH_3)$]

Compound	SiPh	NH	SiH	NCy	CH_2	SiMe
15	7.43 (m, meta) 7.34 (m, otho/para)	5.21 (br)	4.62	-	0.88-0.62	0.20 0.05
16	7.47 (m, meta) 7.27 (m, ortho/para)	4.80 (br)	4.61 4.26	-	0.88 – 0.82	0.33 0.20
17	7.42 (m, 2H, meta) 7.35 (m, 3H, ortho/para)	5.49 (br)	4.67	3.29 (br, 1H, CH^c) 1.64 (m, 4H, CH_2^b) 1.18 (m, 6H, CH_2^a)	0.88-0.63	0.21 0.06
18	7.51 (m, 2H, meta) 7.39 (m, 3H, ortho/para)	5.23 (br)	4.60 4.28	3.29 (br, 1H, CH^c) 1.65 (m, 4H, CH_2^b) 1.19 (m, 6H, CH_2^a)	0.88-0.60	0.32 0.18

* The assignments follow the structure as



associated with the cyclohexyl group appear at δ 3.24 while two multiplets around δ 1.64 and 1.18 are assigned to CH_2 protons (Figure 4.16). The integral intensity of signals associated with the carbosilyl group and N-Cy groups are consistent with structural composition as suggested in the scheme 4.

^{13}C {^1H} NMR Spectra

The presence of different organic functionalities such as $PhMe_2SiX$ (for **15, 17**) and PhMeHSiX (for **16, 18**) (where X = $-CH_2CH_2-$, $-CHCH_3$) is evident in the ^{13}C {^1H} NMR spectra (Figure 4.17). The assignments have been made by comparing the chemical shift values with that of the precursor carbosilane and the relevant data are summarized in table 4.17. For the compounds **15** and **17** the resonances associated with α-isomer are very weak, the plausible reason being the low concentration of α-isomer in the precursor carbosilane $PhMe_2SiXSiMeH_2$. The signals due to N-cyclohexyl group appear at δ 48.9 - 49.0 (C1, NCH), 33.0 - 33.2 (C2, 2', CH_2), 25.2- 25.3 (C3, 3', CH_2) and 24.5 - 24.7 (C4, CH_2) for the compounds **17** and **18**.

^{29}Si NMR spectra

^{29}Si {^1H} NMR spectrum of each compound is quite simple and reveals two signals in the region δ -0.9 to –9.3 and –9.6 to –11.5 (table 4.18). The former chemical shift values are similar to those found in the corresponding precursor carbosilanes. Accordingly, these are assigned

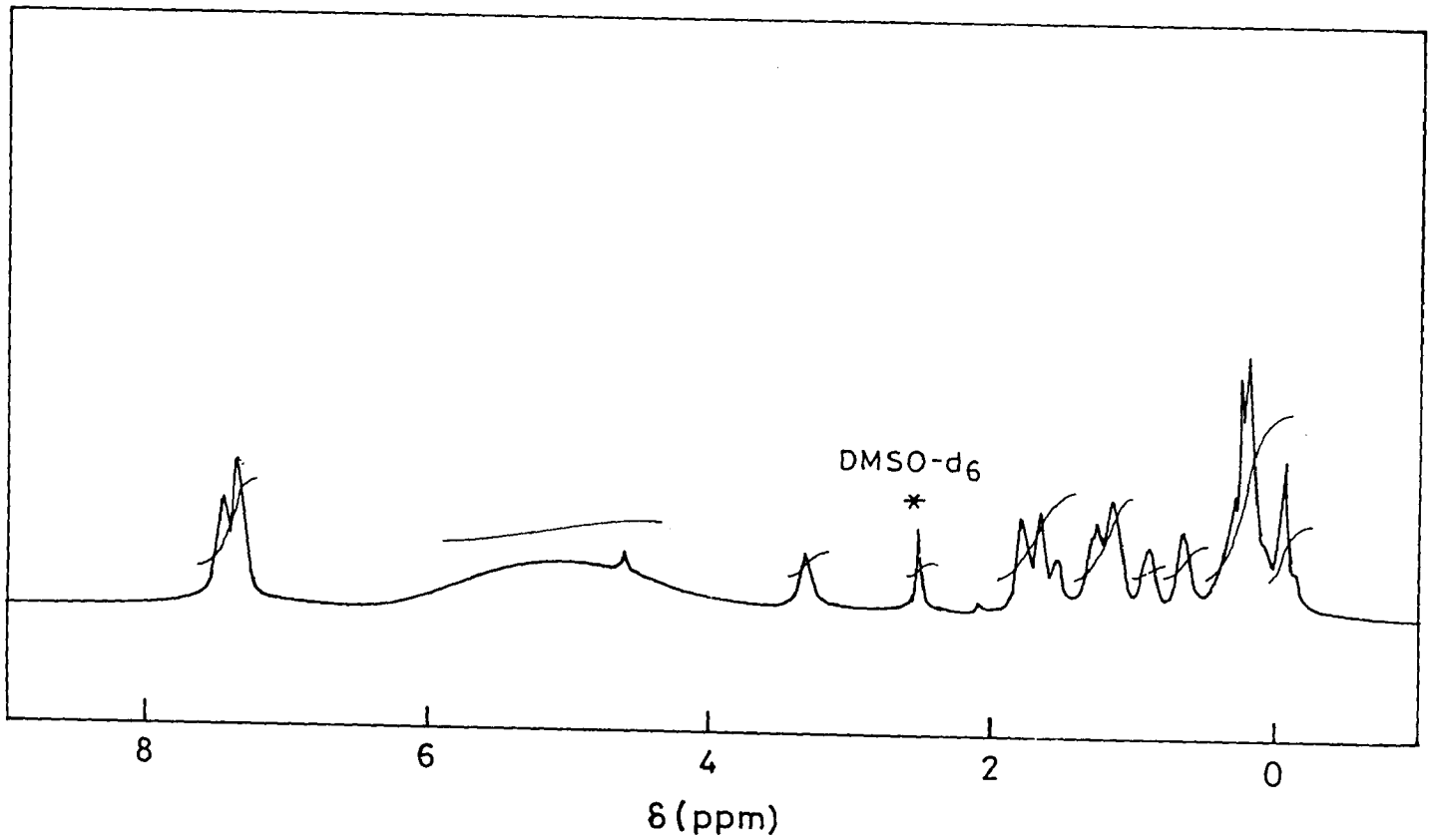


Figure 4.16 ^{1}H NMR spectrum of 1-cyclohexyl-5-(carbosilyl)biguanide

[($PhMe_2SiCH_2CH_2SiMeH$)(H_3bigCy)] (17)

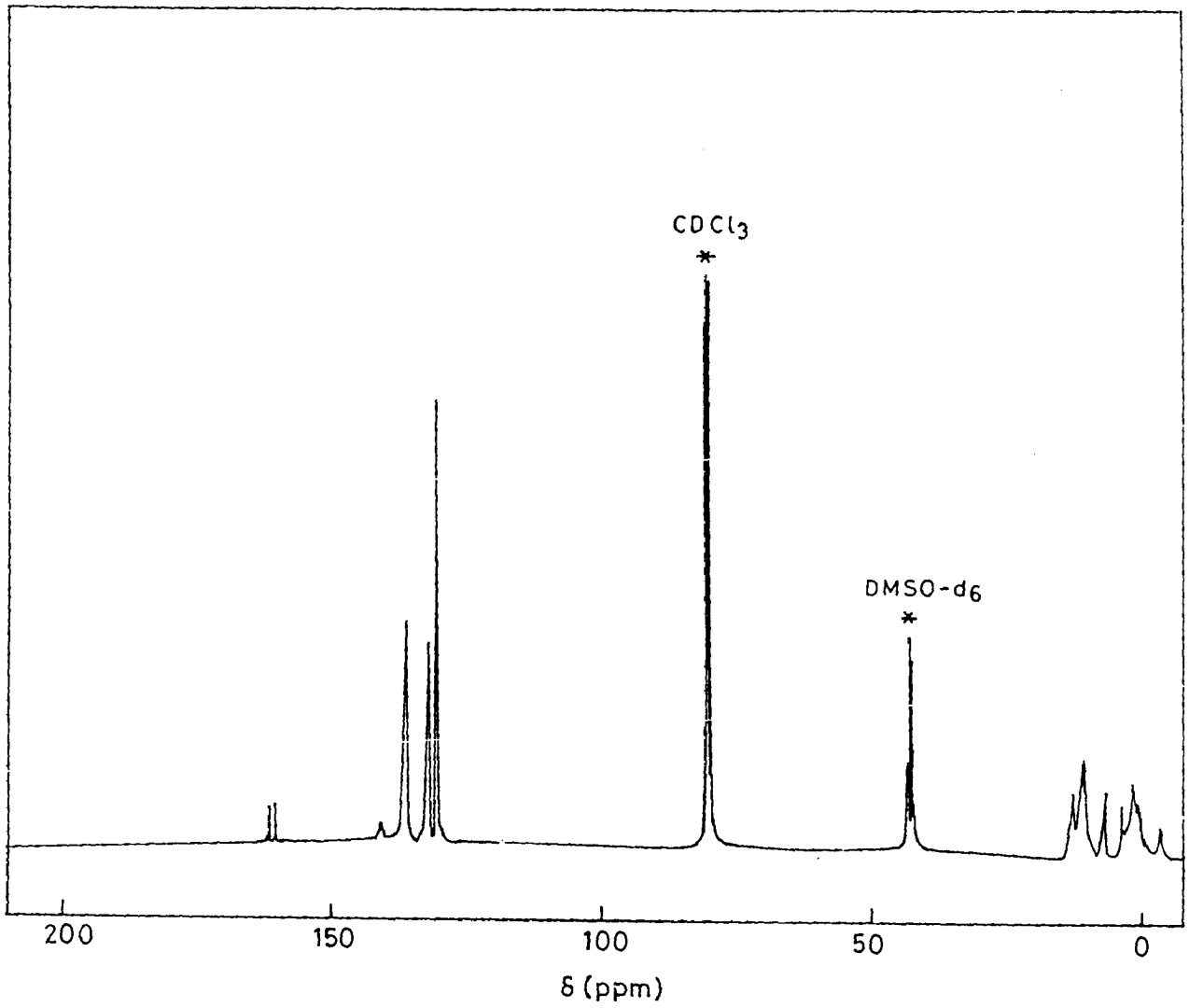


Figure 4.17 ^{13}C {^{1}H} NMR spectrum of 1-(carbosilyl)biguanide

[(PhMeHSiXSiH)(H_4big) [X = -CH_2CH_2-, -$CH(CH_3)$] (16)

Table 4.17 ^{13}C {^{1}H} spectral data δ (ppm) for [(RMeSiH)(H_4bigR')] (where R = $PhMe_2SiX$, R' = H (15) or Cy (17); R = PhMeHSiX, R' = H (16) or Cy (18) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

Compound	C=N	Si-Ph	Cy	SiCH	$CHCH_3$	$SiCH_3$	$SiCH_2$
15	162.4	i = 134.3 o = 133.3 p = 128.9 m = 127.1	-	2.3	11.2	0.52 -1.7	9.3 7.2
16	162.8	i = 133.9 o = 133.3 p = 129.9 m = 128.8		2.7	11.7	0.6 -2.5	9.6 7.2
17	160.3 162.1	i = 138.3 o =133.5 p =129.7 m =127.4	49.0 (C1) 33.0 (C2, 2') 25.2 (C3, 3') 24.7 (C4)	2.0	11.2	0.7 -1.9	9.9 7.3
18	160.5 162.1	i =135.1 o = 134.2 P = 129.4 M =127.8	48.9 (C1) 33.2 (C2, 2') 25.3 (C3, 3') 24.5 (C4)	2.7	11.7	0.6 -2.4	9.7 7.2

Table 4.18 ^{29}Si {^{1}H} NMR data δ (ppm) for silylbiguanides [(RSiMeH)(H_4bigR')] (where R = $PhMe_2SiX$, R' = H (15) or Cy (17); R = PhMeHSiX, R' = H (16) or Cy (18) [X = $-CH_2CH_2-$, $-CH(CH_3)$]

Compound	R	RMeSiHN
15	-0.9	-10.1
16	-10.1	-11.5
17	-1.2	-9.6
18	-9.3	-11.3

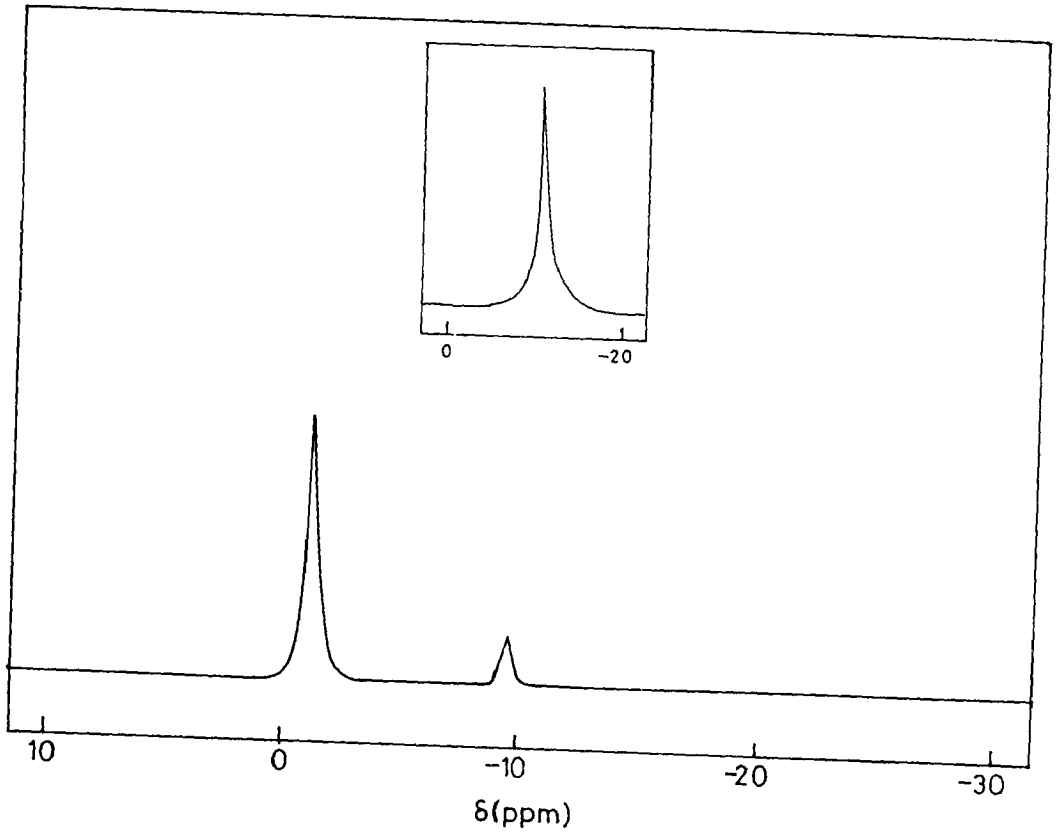


Figure 4.18 ^{29}Si {^{1}H} NMR spectrum of 1-(carbosilyl)biguanide [($PhMe_2SiCH_2CH_2SiMeH$)(H_4big)] (15) (Inset ^{29}Si {^{1}H} DEPT-135 spectrum)

to the silicon atom associated with $PhMe_2Si$/PhMeHSi groups. The resonance between δ -9.6 to –11.5 are assigned to RMeSiHN moiety present in these compounds (Figure 4.18). These assignments have been confirmed by performing ^{29}Si DEPT-135 NMR spectra of **15** and **17**.

4.9 Conclusions

The carbosilanes (**1a - 1e**) represents the alkyl analogs of primary/secondary organosilanes and their reactivity towards biguanide/1-cyclohexylbiguanide have been studied. The carbosilanes were synthesized by hydrosilylation reactions between appropriate hydrosilanes and trichlorovinylsilane/dichloromethylvinylsilane in presence of Speier's or Karstedt's catalyst followed by the reduction of resulting chlorocarbosilanes with lithium aluminium hydride. The reactions between the primary/secondary carbosilanes **1a – 1e** with biguanide/1-cyclohexylbiguanide proceed via SiH/NH dehydrocoupling pathway similar to those of the organosilanes (discussed in chapter III). Nevertheless, these reactions are extremely slow and require a longer heating duration (64 - 65° C, 24 - 72h) in order to yield analytically pure products. In addition, a marked difference in the rate of SiH/NH dehydrocoupling is observed, depending upon the nature of the carbosilanes. The order of reactivity being observed as: primary (SiH_3) > secondary (SiH_2) >> tertiary (SiH). This subtle change in their reactivity pattern is reflected in the empirical composition of the resulting silylbiguanide derivatives. For example, a cyclic dimeric structure of the composition $[(RSiH)_2(HbigR')]_2$ (R = Et_3SiX, R' = H (**9**), Cy (**12**), R =Ph_2HSiX, R' = H (**10**), Cy (**13**); R = PhMeHSiX, R' = H (**11**), Cy (**14**), X = $-CH_2CH_2-$, $-CH(CH_3)$) with the possibility of hyper-coordinated silicon has been suggested for the products obtained from the reaction of primary carbosilanes with biguanide/1-cyclohexyl

biguanide. On the other hand, molecular compounds such as 1-(carbosilyl)biguanides (**15, 16**) and 1-cyclohexyl-5-(carbosilyl) biguanides (**17, 18**) are formed from the analogous reactions with secondary carbosilanes. The identity of these products mentioned above has been delineated by analytical, IR as well as multinuclear NMR studies.

CHAPTER V

REACTIONS OF SILYLBIGUANIDES TOWARDS TITANIUM(IV) CHLORIDE

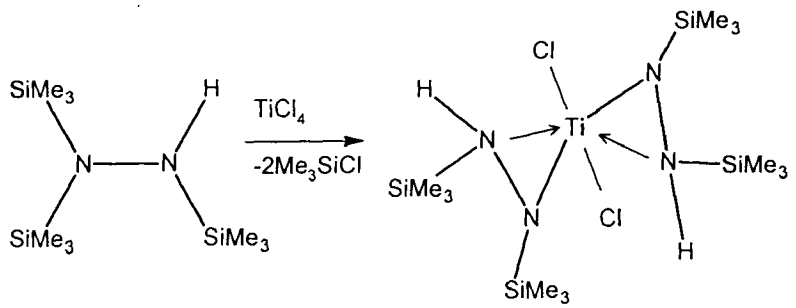
The reaction chemistry of aminosilanes/silazanes with Lewis acids have been known for a long time.[120] Earlier studies centered around attempts to study the basicity of Si-N bonded derivatives by interaction with Lewis acids. Due to the susceptibility of Si-N bond cleavage with electrophilic reagents, transmetallation reactions has also been found to be a useful route for the formation of transition metal amides.[121, 122]

$$4TiCl_4 + 4\,N(SiMe_3)_3 \longrightarrow [Cl_2\,Ti\,N(SiMe_3)]_4$$

Recently Schnick *et al.*[123,124] have investigated the reactions of silazanes/silylhydrazines with various metal chlorides such as $TiCl_4$, $SnCl_4$ and $ZrCl_4$ in search for molecules with nitrido bridges between silicon and transition metals. New structural varieties of metal amides comprising of Si-N-M framework have been isolated.

$$8\,Me_3SiNHSiMe_3 + 8TiCl_4 \longrightarrow (Me_3SiNTiCl_2)_8 + 8Me_3SiCl + 8\,HCl$$

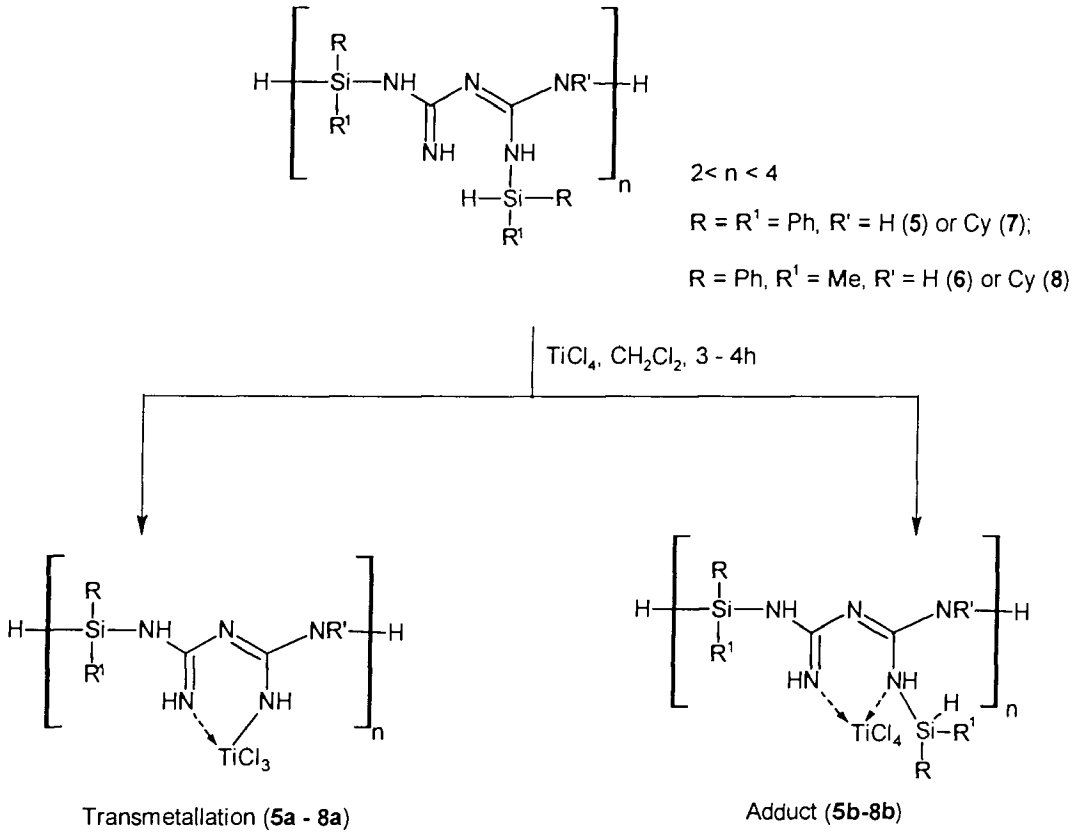
$$4Me_3SiNHSiMe_3 + 4ZrCl_4 \longrightarrow 2Me_3SiCl + [(Me_3Si)_2NH_2]^{2+}\,[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$$



5.1 Reactivity of 1,4-bis(silyl)biguanide and 1-cyclohexyl-2,5-bis(silyl)biguanide with titanium(IV) chloride

In chapter III of the present work, synthesis of linear oligomeric 1,4-bis(silyl)biguanides H-[$RR^1Si(RR^1HSi)H_2big]_n$-H (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanides H-[$RR^1Si(RR^1HSi)HbigCy]_n$-H (**7, 8**) has been described. By analogy with the earlier work on the complexation behavior of biguanides,[87-90] these oligomers can be considered as useful precursors which can act as donor sites to form stable complexes with transition metal ions. More so, transmetallation reactions by cleavage of the Si-N bonds in these oligomers are also accessible. Preliminary results obtained from the reactions of the silylbiguanides **5 - 8** with titanium(IV) chloride reveal that both transmetallation and adduct formation occur in a competitive manner depending upon the reaction conditions.

Dropwise addition of titanium(IV) chloride in dichloromethane to a precooled solution (-10° C) of 1,4-bis(silyl)biguanide (**5, 6**) or 1-cyclohexyl-2,5-bis(silyl)biguanide (**7, 8**) in dichloromethane leads to the immediate formation of an orange-red solid in each case. Their isolation and subsequent characterization reveal them to be transmetallated products of the composition H-[$RR'Si(H_2bigR').TiCl_3]_n$-H (**5a - 8a**) (Scheme 5).



Scheme 5

Interestingly, the formation of these compounds involves the selective Si-N bond cleavage without disturbing the skeletal Si-N bonds. On keeping the filtrate obtained from the above reactions, yet another crop of an orange solid is isolated in each case and identified as the simple Lewis acid adducts H-[$RR^1Si(RR^1HSi)HbigR'.TiCl_4]_n$-H (**5b - 8b**). Thus these reactions proceed in a manner in which transmetallation competes with coordinative association. A similar study when conducted at –78°C follows a similar pathway although adducts **5b - 8b** are formed in higher yield. However, effective separation of these compounds as analytically pure products is possible due to the preferential solubility of adducts (**5b - 8b**) in

dichloromethane while transmetallated products (**5a - 8a**) remain practically insoluble.

5.2 Characterization of H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H (5a-8a) and H-[$RR^1Si(RR^1HSi)H_2bigR'.TiCl_4]_n$-H (5b - 8b)

The compounds **5a - 8a** and **5b - 8b** are agonizingly moisture sensitive solids. Although initially soluble in dichloromethane, the adducts (**5b – 8b**) show a decreasing tendency to solublize in the same solvent upon aging. Conductivity measurements of 1.0 mmol solution of these complexes in DMSO show a specific conductance κ to be 98 - 100 μScm^{-1} and suggest these compounds to be non-electrolytes.[125] These compounds have been characterized by elemental analysis, IR as well as multinuclear (^1H, ^{13}C, ^{29}Si) NMR studies.

5.2.1 Characterization of H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H (5a - 8a)

5.2.1.1 IR spectra

Pertinent IR absorptions of the compounds H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H (**5a - 8a**) derived from transmetallation reaction are given in table 5.1. The notable features that deserve special mention are summarized as follows. The characteristic νNH absorption at 3270 - 3191 cm^{-1} in these compounds appear at a lower frequency (80 - 120 cm^{-1}) as compared to those observed in the parent silylbiguanide (3371 - 3337 cm^{-1}). The absorptions due to νCN and νNCN modes appear at 1700 - 1678 and 1662 - 1600 cm^{-1} respectively

Table 5.1 IR (Nujol, cm^{-1}) spectral data of H-[$RR^1Si(H_2bigR').TiCl_3$]-H (R = R^1 = Ph, R' = H (5a) or Cy (7a); R = Me, R^1 = Ph, R' = H (6a) or Cy (8a))

Compound	νNH	νSiH	νCN	νNCN	νSiPh	νSiMe
5a	3191	2190	1700	1662	1126	-
6a	3253	2190	1678	1646	1121	1263
7a	3270	2196	1678	1600	1122	-
8a	3217	2190	1683	1656	1120	1260

with a positive spectral shift of 40 – 60 cm^{-1} as compared to those observed in the silylbiguanide (1635 – 1540 cm^{-1}). Similar spectral changes have been reported for several coordination complexes of biguanide ligands with transition metal Lewis acids[88,89] and are attributed to arise due to the coordination of imine/amine donor sites to the metal-center. A weak absorption due to νSiH mode appears at 2196 - 2190 cm^{-1} in the spectra of all the compounds (Figure 5.1). The characteristic absorptions due to MeSi (wherever applicable) and PhSi groups appear at 1263 – 1260 and 1126 - 1120 cm^{-1} respectively. νCH aliphatic (wherever applicable) and νCH aromatic appear at the routine position in the spectra of all these compounds.

5.2.1.2 NMR spectra

^{1}H NMR spectra

^{1}H NMR spectra of the compounds H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H **(5a - 8a)** show the presence of three singlets in the range δ 9.49 – 8.62 due to the NH protons (Figure 5.2). These values are appreciably downfield with respect to the precursor silylbiguanides which display a broad resonance in the chemical shift between δ 4.35 - 6.0. For the compounds H-[$RR'Si(H_3big).TiCl_3]_n$-H **(5a, 6a)** the signals at δ 9.40 – 9.45 and 8.87 – 8.82 are of equal intensity and are attributed to the NH attached to the titanium center, while the signal at δ 8.69 – 8.64 is assigned to the skeletal Si-NH protons. For the

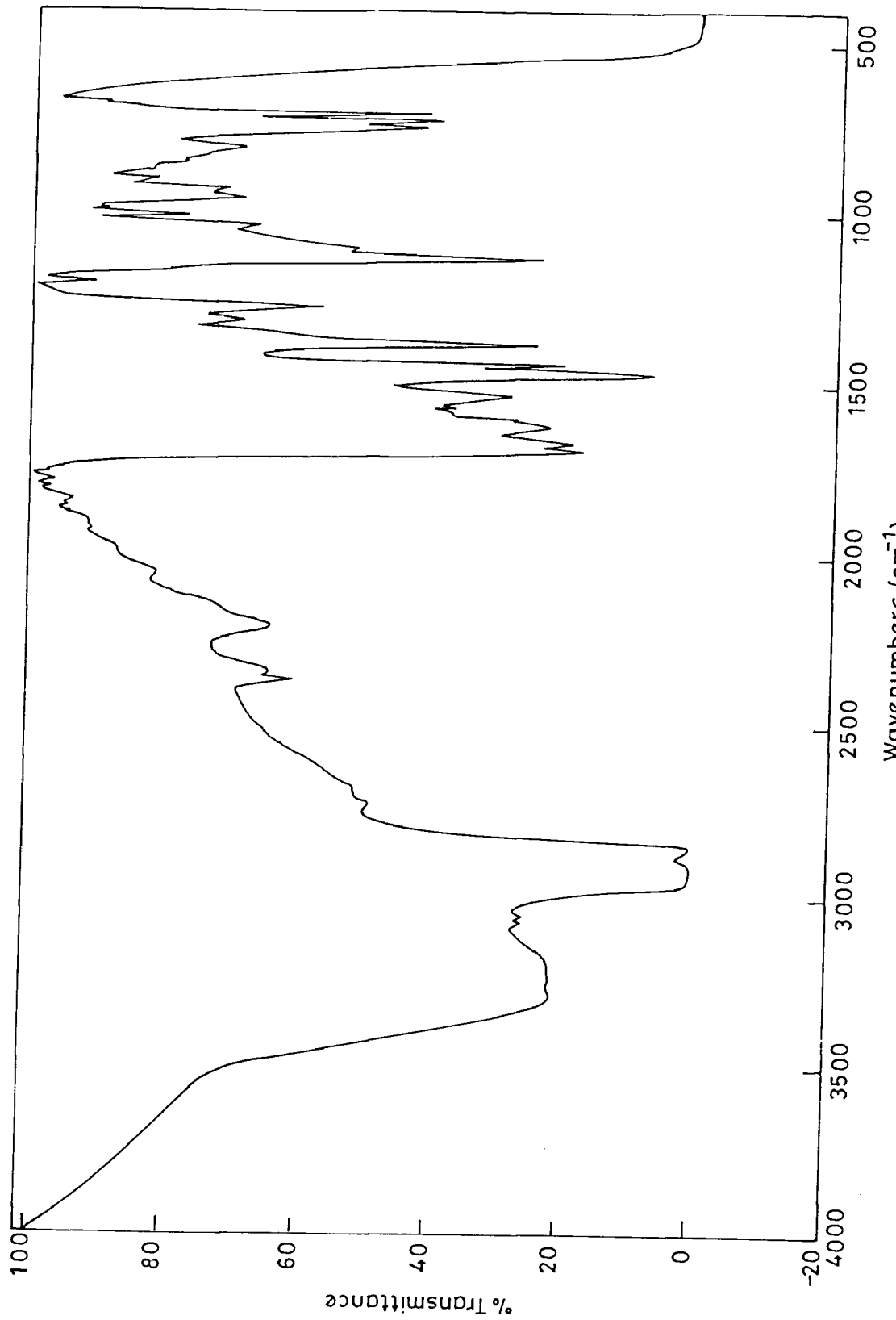


Figure 5.1 IR spectrum of H-[(Ph$_2$Si)(H$_2$bigCy).TiCl$_3$]$_n$-H (7a)

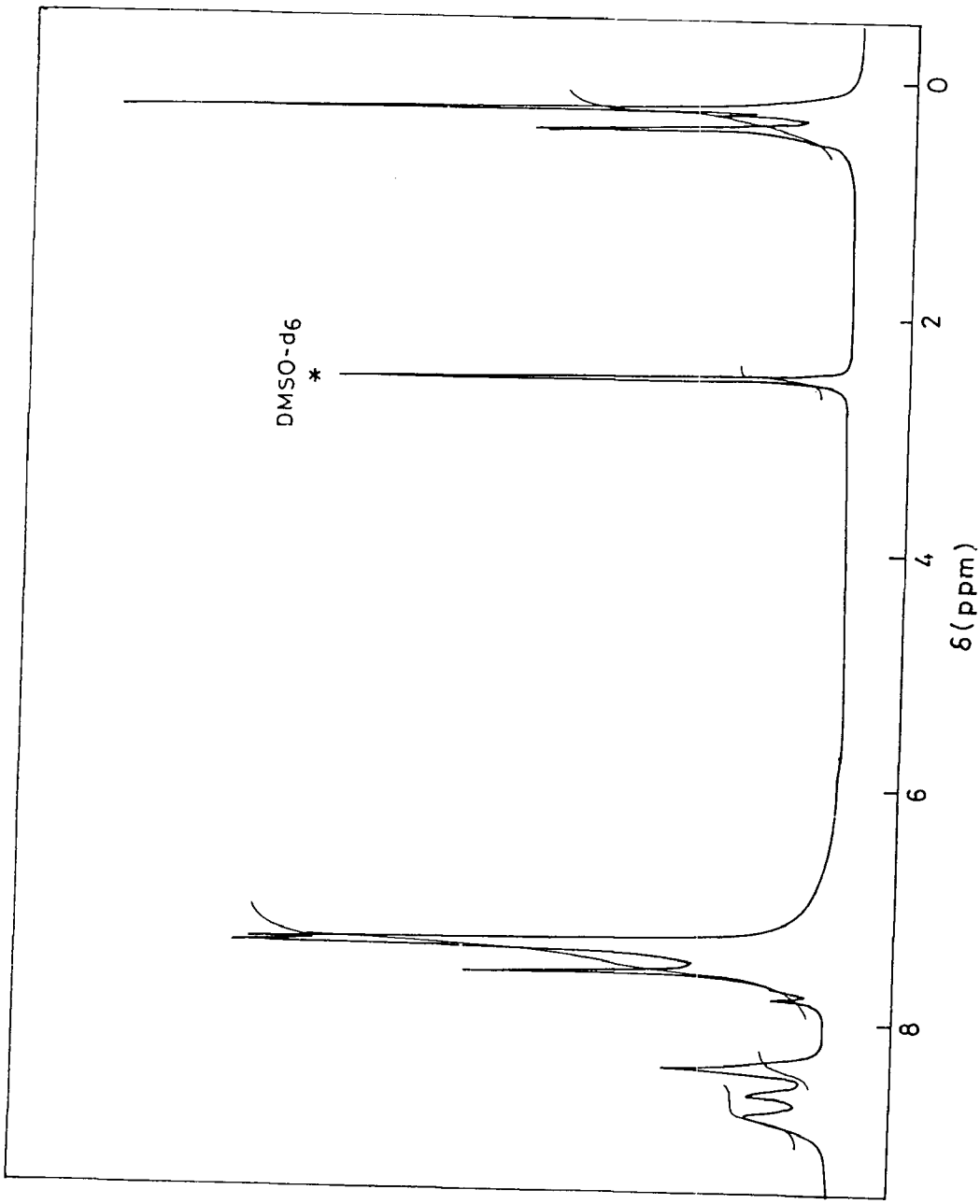


Figure 5.2 ^{1}H NMR spectrum of H-[PhMeSi)(H_3big).$TiCl_3$]$_n$-H (6a)

compounds H-[$RR^1Si(H_2bigCy).TiCl_3]_n$-H (**7a, 8a**), the integral intensities of the NH resonances (δ 9.48, 9.18, 8.62) are similar and their assignments are made by analogy with those of compounds **5a** and **6a**. These spectral observations are in accord with previously reported metal-biguanide complexes of rhenium and technetium.[89] The resonance due to SiH proton is very weak to be quantified in the spectrum of all these compounds. For the compounds **6a** and **8a**, the SiMe protons appear as a doublet at δ 0.38 (^3J = 7.45 Hz) and as a singlet at δ 0.21 arising from the PhMeSiH and $PhMeSiN_2$ groups respectively (Table 5.2). ^1H NMR spectra of the compounds H-[$RR^1Si(H_2bigCy).TiCl_3]_n$-H (**7a, 8a)** display signals associated with cyclohexyl group [δ 3.58 – 3.57 (br, NCH), 1.66 - 1.24 (m, CH_2)]. The ^1H NMR spectral data reveal that integral ratio of Ph_2Si/PhMeSi and NCy/NH groups conforms to 1 : 1 as expected for the proposed composition.

^{13}C {^1H} NMR spectra

The relevant data are summarized in table 5.3. ^{13}C {^1H} NMR spectra of the complexes H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H **5a - 8a** arising from transmetallation reactions reveal two resonances at δ 156.7 – 155.7, 155.5 – 154.7 due to C=N moiety. These appear upfield in comparison to those observed in the precursor silylbiguanides (162.4, 161.4). The resonances due to aromatic carbons appear at δ 138.9 –

Table 5.2 ^{1}H NMR spectral data δ (ppm) for H-[RR^{1}Si(H_2bigR').$TiCl_3$]$_n$-H

(R = R^1 = Ph, R' = H (5a) or Cy (7a); R = Me, R^1 = Ph, R' = H (6a) or Cy (8a))

Compound	C_6H_5	NH	CH_3Si	NCy
5a	7.53 (4H, meta) 7.30 (6H, ortho/para)	9.40 (1H), 8.87 (1H) 8.69 (2H)		
6a	7.57 (2H, meta) 7.32 (3H, ortho/para)	9.45 (1H), 8.82 (1H) 8.64 (2H)	0.38 (^{3}J = 7.45 Hz) 0.21	-
7a	7.57 (4H, meta) 7.28(6H, ortho/para)	9.48 (1H), 9.19 (1H) 8.63 (1H)	-	3.57 (m, 1H, CH^c) 1.65 (m, 4H, CH_2^b) 1.25 (m, 6H, CH_2^a)
8a	7.56 (2H, meta) 7.33 (3H, ortho/para)	9.49 (1H), 9.18 (1H) 8.62 (1H)	0.37 (^{3}J = 7.56 Hz) 0.22	3.58 (m, 1H, CH^c) 1.66 (m, 4H, CH_2^b) 1.24 (m, 6H, CH_2^a)

* The assignments follow the structure as

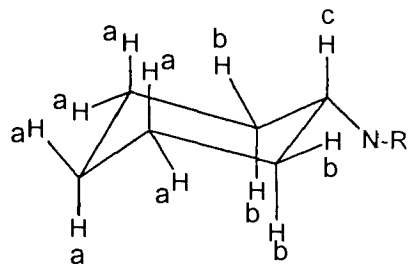


Table 5.3 ^{13}C {^{1}H} NMR spectral data δ (ppm) for H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H

(R = R^1 = Ph, R' = H (5a) or Cy (7a); R = Me, R^1 = Ph, R' = H (6a) or Cy (8a))

Compound	C=N	C_6H_5	NCy	SiMe
5a	155.3 156.7	i = 138.4 o = 133.5 p= 129.7 m =127.4	-	-
6a	156.2 155.5	I = 138.1 o = 132.6 p = 129.6 m = 127.2	-	0.71 - 0.16
7a	155.7 154.9	i = 138.9 o = 134.3 p = 130.2 m = 127.4	49.8 (C1) 33.1 (C2, 2') 25.2 (C3, 3') 24.7 (C4)	-
8a	155.6 154.7	i = 138.0 o = 133.7 p = 129.8 m = 127. 7	49.7 (C1) 33.3 (C2, 2') 25.5 (C3, 3') 24.5(C4)	0.70 – 0.14

127.2. The spectra of **6a** and **8a** reveal three distinct signals at δ 0.72, 0.35 and 0.16 due to SiMe groups (Figure 5.3). For the compounds H-[$RR^1Si(H_2bigCy).TiCl_3]_n$-H (**7a, 8a**), the signals due to N-cyclohexyl group appear at δ 49.7 - 49.8 (C1,NCH), 33.1 - 33.3 (C2,2', CH_2), 25.2 - 25.5 (C3,3', CH_2) and 24.5 - 24.7 (C4, CH_2).

^{29}Si {^{1}H} NMR spectra

^{29}Si {^{1}H} NMR spectra of H-[$Ph_2Si(H_2bigR').TiCl_3]_n$-H (**5a, 7a**) in DMSO-$d_6$ show the presence of multiple signals in the region of δ -20 to –22 (Figure 5.6). In comparison to the chemical shift data of the parent silylbiguanide (δ -42.6 to -46.1), the ^{29}Si values obtained herein undergo an appreciably downfield shift. The spectral change may be attributed to the coordination of the biguanide moiety with titanium in these complexes.

5.2.2 Characterization of H-[$RR^1Si(RR^1SiH)H_2bigR'.TiCl_4]_n$-H (5b - 8b)

5.2.2.1 IR spectra

Significant IR absorptions along with their assignments are given in table 5.4. The prominent features in the IR spectra remain practically similar to those of the transmetallated products **5a – 8a** discussed earlier. The spectra of the titled compounds display νNH absorption at 3252 - 3200 cm^{-1}. This absorption undergoes a shift to

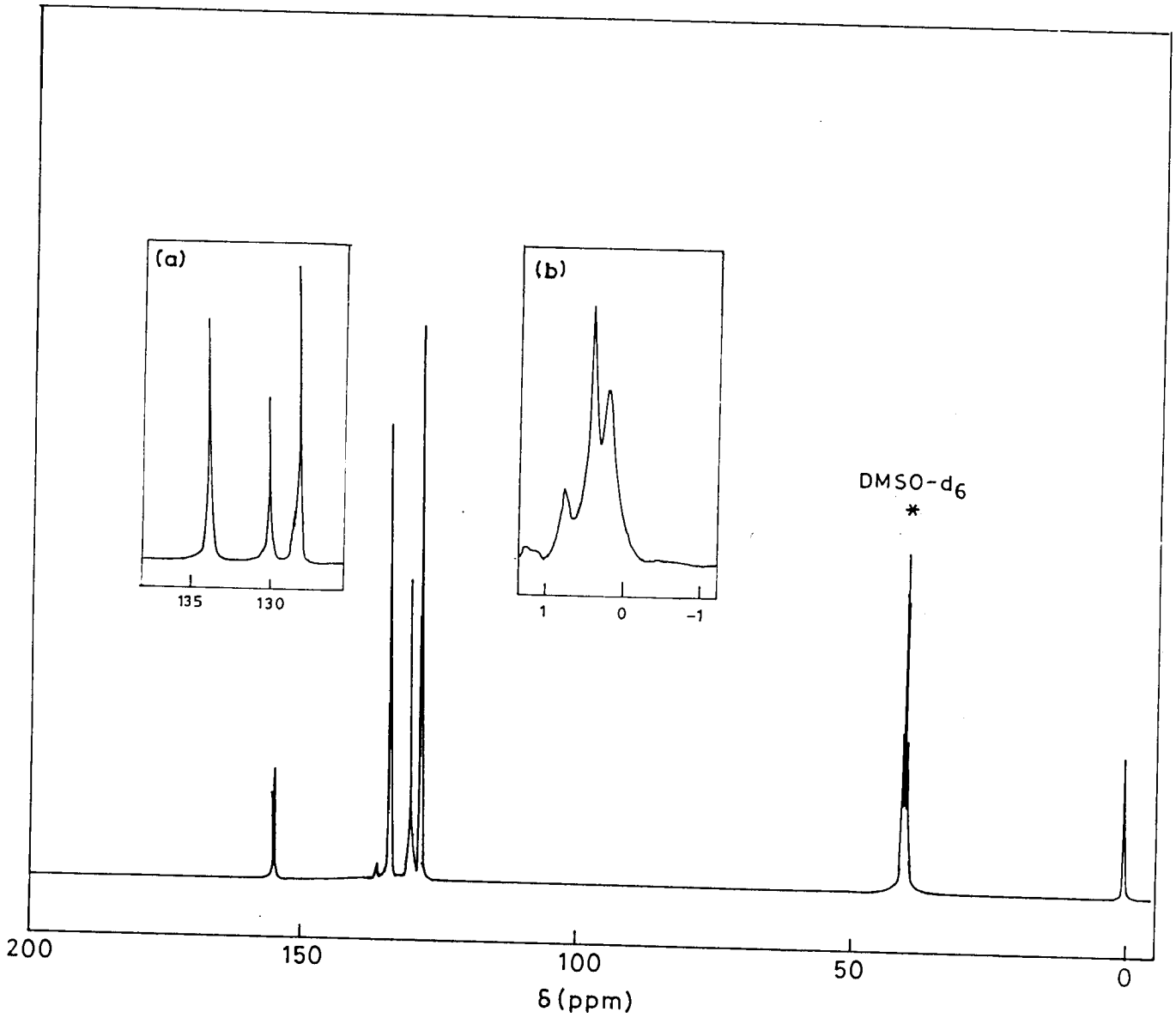


Figure 5.3 ^{13}C {^{1}H} NMR spectrum of H-[PhMeSi)(H_3big).$TiCl_3$]$_\eta$-H (6a)

(inset picture (a) phenyl (b) methyl region)

lower frequency in comparison to those observed for the parent silylbiguanides (3371 – 3337 cm^{-1}). The absorptions due to νCN and νNCN modes appear at 1689 – 1683 and 1662 – 1624 cm^{-1} and are shifted to higher frequency as compared to the parent silylbiguanides (1646 – 1613 and 1558 – 1540 cm^{-1} respectively). These spectral changes in the region of 3300 - 3200 and 1700 - 1500 cm^{-1} are attributed to arise due to the coordination of the biguanide moiety with the titanium center. The SiH stretching mode appears as two distinct absorptions at 2214 – 2103 cm^{-1} in each compound (Figure 5.4) and finds an analogy with those observed for the parent silylbiguanides (**5 - 8**) (Chapter III, Section B). It thus appears that the conformational behavior of the adducts resemble with those of parent silylbiguanides. Other distinctive absorptions due to SiMe, SiPh, CH (aliphatic) and CH (aromatic) groups remain practically unaltered upon complexation and appear at the routine positions.

5.2.2.2 NMR spectra

^{1}H NMR spectra

^{1}H NMR spectra of H-[$RR^1Si(RR^1SiH)(H_2bigR').TiCl_4]_n$-H (R = Ph, R^1 = Me or Ph; R' = H or Cy) **5b – 8b in** DMSO-d_6 reveal characteristic resonances associated with the RR'SiH, N-cyclohexyl and NH protons. The relevant data are summarized in table 5.5. The

Table 5.4 IR (Nujol, cm^{-1}) spectral data of H-[$RR^1Si(RR^1SiH)H_2$bigR'.$TiCl_4$]$_n$-H

(R = R^1 = Ph, R' = H (5b) or Cy (7b); R = Me, R^1 = Ph, R' = H (6b) or Cy (8b))

Compound	νNH	νSiH	νCN	νNCN	νSiPh	νSiMe
5b	3251	2197 2103	1683	1662	1126	-
6b	3252	2191 2110	1680	1640	1121	1263
7b	3247	2208 2107	1689	1624	1125	-
8b	3200	2214 2130	1683	1642	1120	1260

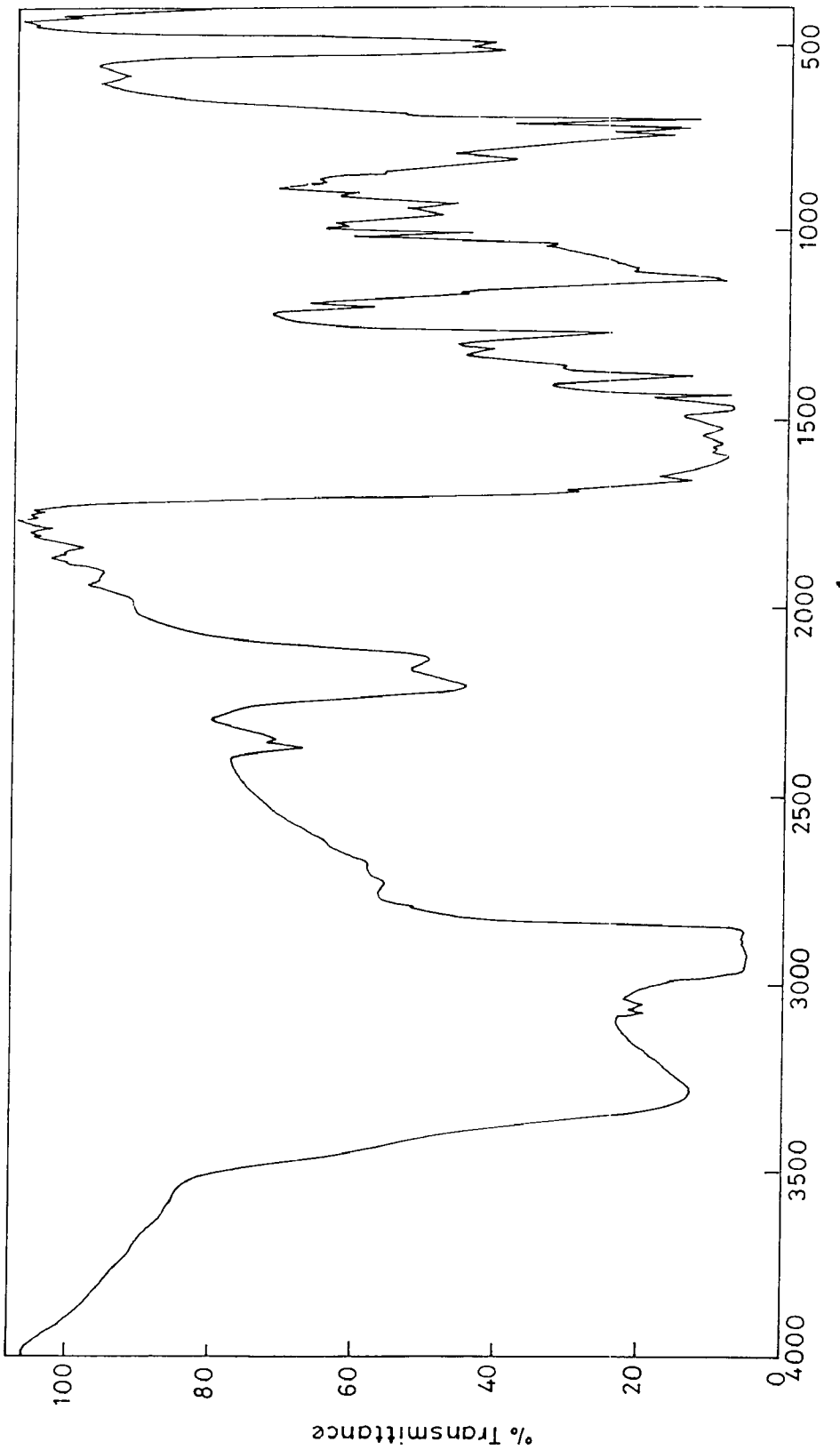


Figure 5.4 IR spectrum of H-[(PhMeSi)(PhMeSiH)(H_2bigCy).$TiCl_4$]$_n$-H (8b)

integral intensities of various signals in each compound suggest that the structural entity of the parent silylbiguanide is retained in these adducts. It is interesting to note that the complex pattern of signals associated with the PhSi/MeSi groups as seen in the parent compounds are retained in these adducts too. This implies that **5b – 8b** exist as conformational mixtures and resembles the parent silylbiguanides in this respect. More so, the NH signals in these compounds are quite sharp and appear as three singlets at δ 8.6 – 9.5 (Figure 5.5). A significant downfield shift of these signals as compared to those observed in parent silylbiguanides suggest a strong coordinative association of NH group(s) to the metal center.

^{13}C {^{1}H} NMR spectra

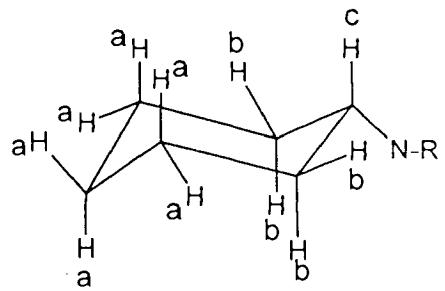
^{13}C {^{1}H} NMR data of the adducts H-[$RR^1Si(RR^1SiH)(H_2bigR').TiCl_4]_n$-H **5b – 8b** are summarized in table 5.6. The spectrum of each compound exhibits two distinct resonance for each phenyl group at δ 127.4 – 138.9. The spectral pattern is believed to arise due to different conformers. The resonance due to C=N group appear as two singlets at δ 156.8 – 156.1 and 155.7 – 154.4. These signals are upfield shifted with respect to the precursor silylbiguanides (δ 162.4, 162.1) and suggest coordinative association of the C=N groups in these adducts. The N-Cy groups in **7b** and **8b** are detected by their characteristic resonances at δ 33.3 – 24.5.

Table 5.5 ^{1}H NMR spectral data δ (ppm) for H-[RR^{1}Si(RR^{1}SiH)H$_2$bigR'.TiCl$_4$]$_n$-H

(R = R^1 = Ph, R' = H (5b) or Cy (7b); R = Me, R^1 = Ph, R' = H (6b) or Cy (8b))

Compound	C_6H_5	NH	CH_3Si	NCy
5b	7.57 (8H, meta) 7.33 (12H, ortho/para)	9.40 (1H), 8.87 (1H) 8.69 (2H)		
6b	7.57 (4H, meta) 7.32 (6H, ortho/para)	9.45 (1H), 8.81 (1H) 8.64 (2H)	0.38 – 0.11	-
7b	7.57 (8H, meta) 7.31 (12H, ortho/para)	9.48 (1H), 9.16 (1H) 8.61 (1H)		3.58 (m, 1H, CH^c) 1.65 (m, 4H, CH_2^b) 1.25 (m, 6H, CH_2^a)
8b	7.55 (4H, meta) 7.33 (6H, ortho/para)	9.45 (1H), 9.20 (1H) 8.64 (1H)	0.39 – 0.10	3.57 (m, 1H, CH^c) 1.66 (m, 4H, CH_2^b) 1.25 (m, 6H, CH_2^a)

* The assignments follow the structure as



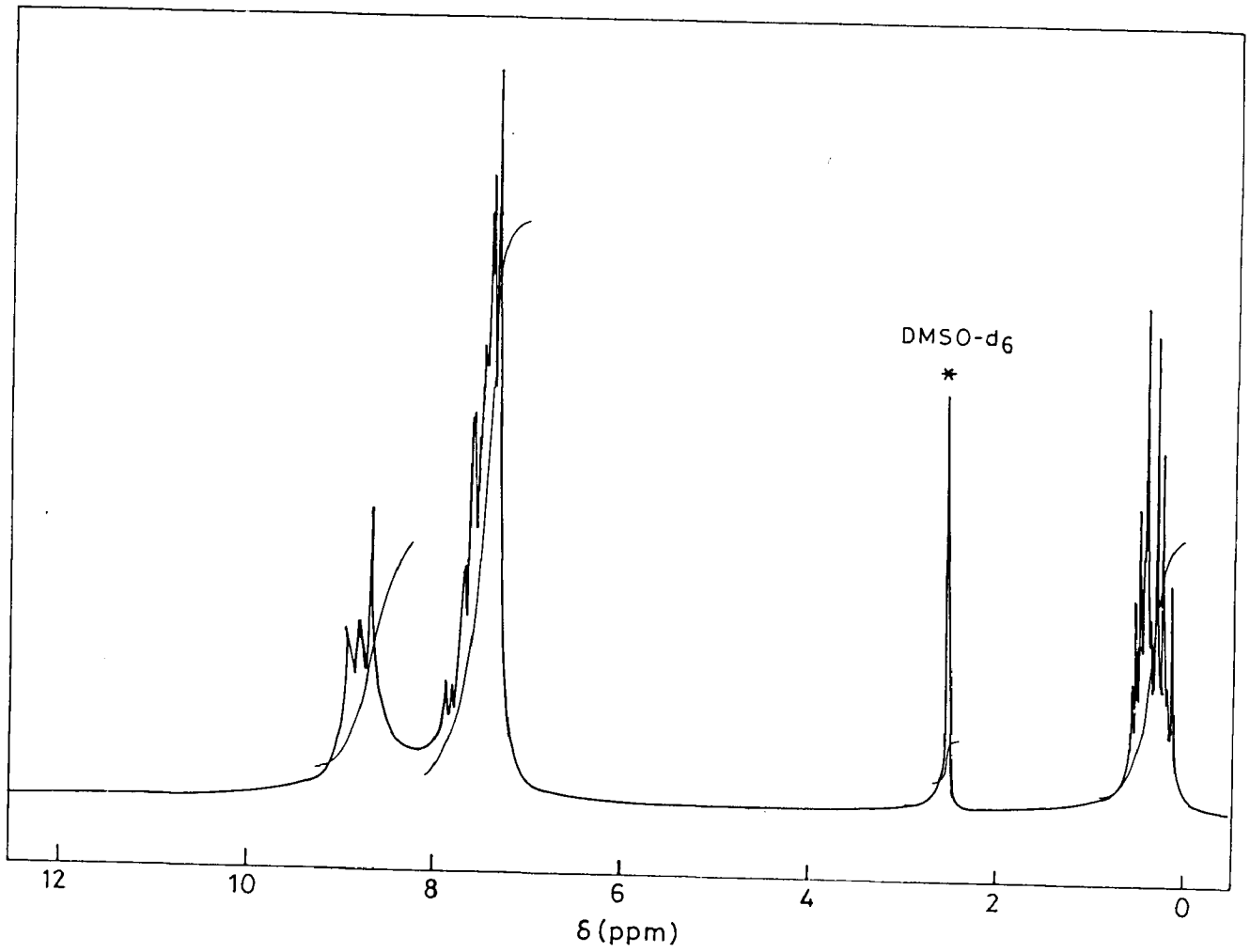


Figure 5.5 ^{1}H NMR spectrum of H-[(PhMeSi)(PhMeSiH)(H_3big).$TiCl_4$]$_n$-H (6b)

Table 5.6 ^{13}C {^{1}H} NMR spectral data δ (ppm) for H-[$RR^1Si(RR^1SiH)H_2$bigR'.$TiCl_4$]$_n$-H

(R = R^1 = Ph, R' = H (5b) or Cy (7b); R = Me, R^1 = Ph, R' = H (6b) or Cy (8b))

Compound	C=N	SiPh	NCy	$SiCH_3$
5b	156.8 155.4	i = 138.4, 138.8 o = 133.5, 133.1 p = 129.7, 129.4 m =127.4, 127.2	-	-
6b	156.1 155.7	i = 138.1, 138.3 o = 132.6, 132.8 p = 129.6, 129.4 m = 127.2,127.4	-	0.58 to - 0.96
7b	155.8 154.5	i = 138.9, 138.7 o = 134.3, 134.0 p = 130.2, 129.9 m = 127.4, 127.6	49.9 (C1) 33.0 (C2, 2') 25.4 (C3, 3') 24.6 (C4)	-
8b	155.7 155.1	i = 138.0, 138.3 o = 133.7, 133.9 p = 129.8, 129.4 m = 127. 7, 127.4	49.7 (C1) 33.3 (C2, 2') 25.2 (C3, 3') 24.5(C4)	0.60 to –0.93

^{29}Si {^{1}H} NMR spectra

^{29}Si {^{1}H} NMR spectra of the adducts H-[$RR^1Si(RR^1SiH)(H_2bigR').TiCl_4]_n$-H (R = Ph, R^1 = Me, R' = H **(6b),** Cy **(8b)**) have been studied as representative examples in order to evaluate the nature of silicon environment in these compounds (Figure 5.7). The spectra reveal the ^{29}Si signals at δ -14.4 (shoulder at δ -14.9), -16.6 and -17.0. Although the spectral features remain practically similar to those observed for the corresponding parent silylbiguanide, a marked downfield shift of the order of (~ 15 ppm) is observed in these compounds. A similar phenomenon in the ^{29}Si NMR is also seen in the case of transmetallated products discussed earlier in section 5.2.1.2. It is likely that the coordinatively association of C=N/NH groups to the titanium(IV) centers bring about this phenomenal change in these compounds.

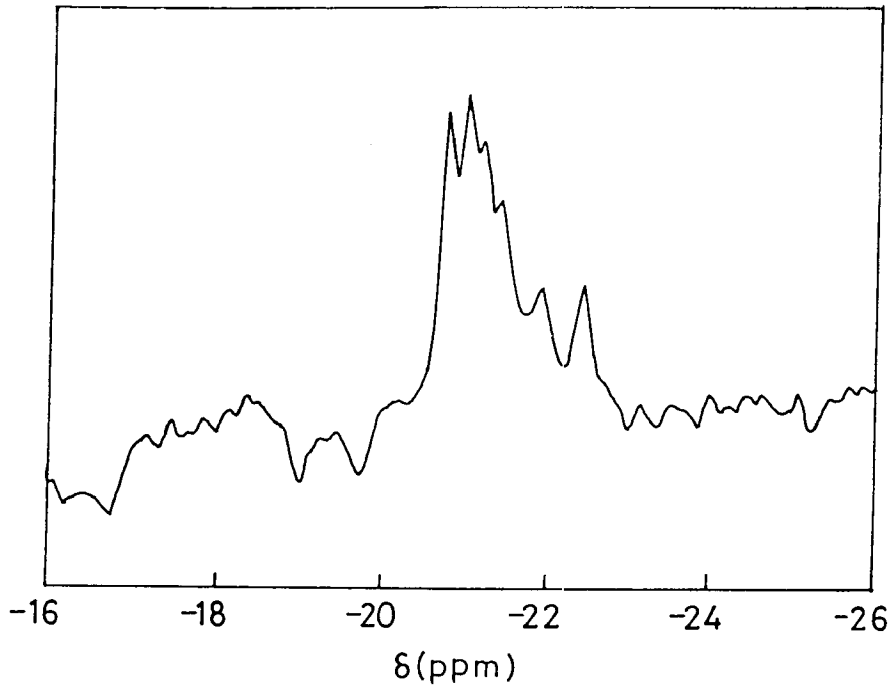


Figure 5.6 ^{29}Si {^{1}H} NMR spectrum of H-[$(Ph_2Si)(H_3big).TiCl_3]_n$-H (5a)

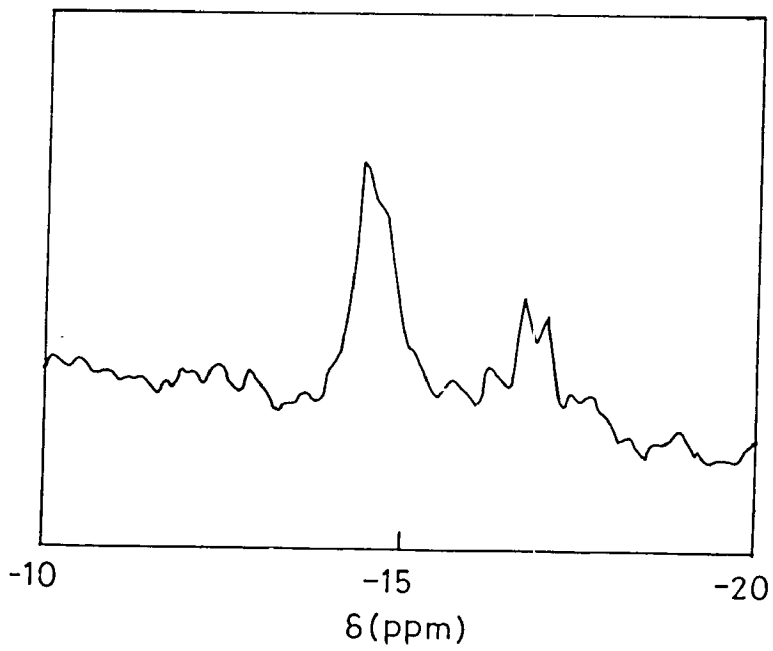


Figure 5.7 ^{29}Si {^{1}H} NMR spectrum of H-[PhMeSi)(PhMeSiH)(H_3big). $TiCl_4]_n$-H (6a)

5.3 Conclusions

The reactions of 1,4-bis(silyl)biguanides (**5, 6**) and 1-cyclohexyl-2,5-bis(silyl)biguanides (**7, 8**) with titanium(IV) chloride proceed in two pathways. The selective cleavage of Si-N bonds in presence of the Lewis acid results in the formation of compounds with general composition H-[$RR^1Si(H_2bigR').TiCl_3]_n$-H (**5a – 8a).** In addition, the formation of simple adducts of the parent silylbiguanide with $TiCl_4$ also occur and afford compounds with the general formula, H-[$RR^1Si(RR^1SiH)(H_2bigR').TiCl_4]_n$-H (**5b – 8b).** All the compounds have been isolated as analytically pure form by virtue of preferential solubility of the adducts (**5b - 8b**) in dichloromethane. Conductance measurements in DMSO reveal them to be non-electrolytes. The coordinative association of the imine groups to titanium(IV) is distinctly evident from lowering of νNH frequency (80 - 100 cm^{-1}) in the IR spectra. ^1H NMR spectra (in DMSO-d_6) also exhibit a downfield shift of resonances due to NH protons (δ 9.48 – 8.61) and support the above proposition ^{29}Si NMR spectra (DMSO-d_6) show multiple pattern in a narrow range of chemical shift, [δ -20 to –22 (for **5a, 7a**) and -14 to -17 (for **6b, 8b**)].

REFERENCES

1. Gilman, H.; Dunn, G. E., *Chem. Rev.*, 1953, **52**, 77.

2. Seyferth, D., *Organometallics,* 2001, **20**, 4978.

3. Hedberg, K., *J. Am. Chem. Soc.*, 1950, **7**, 6491.

4. Blum, Y.; Schwartz, K. B.; Laine, R. M., *J. Mater. Sci.*, 1989, **24**, 1707.

5. Seyferth, D.; Wisemann, G. H.; Schwark, J. M.; Yui, Y.F.; Poutasse, C.A., in Zeldin, M.; Wynne, K.J.; Allcock, H. R. (Eds), "*Inorganic and Organometallics Polymer*", ACS Symposium series 360: American Chemical Society, Washington D.C, 1988, 143.

6. Laine, R.M.; Blum, Y. D.; Tse, D.; Glasser, in Zeldin, M.; Wynne, K.J.; Allcock, H. R. (Eds), "*Inorganic and Organometallics Polymer*", ACS Symposium series 360: American Chemical Society, Washington D.C, 1988, 123.

7. Birot, M.; Pillot, J. P.; Dunogues. J., *Chem. Rev.*, 1995, **95**, 1443.

8. Schubert, U.; Hüsing, N., *"Synthesis of Inorganic Materials",* Wiley-VCH, Weinhein, 2000, 294.

9. Gabriel, A. O.; Riedel, R., *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 384.

10. Riedel, R.; Kroke, E.; Greiner, A.; Gabriel, A. O.; Rutwise, L.; Nicolich, J., *Chem. Mater.*, 1998, **10**, 2964.

11. Schumacher, J.; Weinmann, M.; Bill, J.; Aldinger, F.; Müller, K., *Chem. Mater.*, 1998, **10**, 3913.

12. Rovai, R.; Lehmann, C.W.; Bradley, J. S., *Angew. Chem. Int, Ed. Engl.*, 1999, **38**, 2036.

13. Schnick, W., *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 806.

14. Schnick, W.; Huppertz, H., *Chem. Eur. J*, 1997, **3**, 679.

15. Mitzel, N. W.; Bissinger, P.; Riede, J.; Dreihäupl, K-H.; Schmidbaur, H., *Organometallics*, 1993, **12**, 413.

16. Mitzel, N. W.; Schier, A.; Schmidbaur, H., *Chem. Ber.*, 1992, **125**, 2711.

17. Mitzel, N. W.; Schier, A.; Beruda, H.; Schmidbaur, H., *Chem. Ber.*, 1992, **125**, 1053.

18. Birkofer, L.; Stuhl, O., in Patai. S.; Rappoport. Z., "*The Chemistry of Silicon Compounds*", John Wiley and Sons Ltd., 1989, part 1, 706.

19. Sheldrick, W.S., in Patai. S.; Rappoport, Z., " *The Chemistry of Silicon Compounds*", John Wiley and Sons Ltd., 1989, part 1, 254.

20. Schumb, W. C.; Towle, L. H., *J. Am. Chem. Soc.*, 1953, **75**, 6085.

21. Mitzel, N. W.; Riede, J.; Schier, A.; Paul, M., Schmidbaur, H., *Chem. Ber.*, 1993, **126**, 2027.

22. Mitzel, N. W.; Angermaier, K.; Schmidbaur, H., *Chem. Ber.*, 1994, **127**, 841.

23. Mitzel, N. W.; Bissinger, P.; Schmidbaur, H., *Chem. Ber.*, 1993, **126**, 345.

24. Mitzel, N. W.; Angermaier, K.; Schmidbaur, H., *Organometallics*, 1994, **13**, 1762.

25. Mitzel, N. W.; Schmidbaur, H.; Rankin, D. W. H.; Smart, B. A.; Hofmann, M.; Schleyer, P. V. R., *Inorg. Chem.*, 1997, **36**, 4360.

26. Wan, Y.; Verkade, J. G., *Inorg. Chem.*, 1993, **32**, 341.

27. Ackerhans, C.; Böttcher, P.; Müller, P.; Roesky, H. W.; Usón, I.; Schmidt, H-G.; Noltemeyer, M., *Inorg. Chem.*, 2001, **40**, 3766.

28. Jaschke, B.; Herbst-Irmer, R.; Klingebiel, U.; Pape. T., *J. Chem. Soc., Dalton Trans.*, 2000, 1827.

29. Arai, M.; Sakurada, S.; Isoda, T.; Tomizawa, J.; *Am. Chem. Soc., Polymer Div., Polym. Prepts.*, 1987, **27**, 40.

30. Legrow, G. E.; Lim. T.F.; Lipowitz, I.; Reaoch, R. S.; in Brinker, C. J.; Clark, D. E.; Ulrich, D. R. (Eds), "*Better Ceramic Through Chemistry*", Mat. Res. Symp. Proc., 1986, **73**, 553.

31. Räke, B.; Roesky, H. W.; Usón, I.; Müller, P., *Angew. Chem, Int, Ed.*, 1998, **37**, 1432.

32. Ackerhans, C.; Räke, B.; Krätzner, R.; Müller, R.; Roesky, H. W.; Usón, I., *Eur. J. Inorg. Chem.*, 2000, 827.

33. Shibley, J. L.; West, R.; Tessier, C. A.; Hayashi, R. K., *Organometallics*, 1993, **12**, 3480.

34. Shibley, J. L.; West, R.; Belz, J.; Hayashi, R. K., *Organometallics*, 1994, **13**, 2035.

35. Jaschke, B.; Herbst-Irmer, R.; Klingebiel, U.; Neugebauer, P.; Pape, T., *J. Chem. Soc., Dalton Trans.*, 1998, 2953.

36. Söldner, M.; Schier, A.; Schmidbaur, H., *Inorg. Chem.*, 1997, **70**, 1758.

37. Söldner, M.; Schier, A.; Schmidbaur, H.; *Inorg. Chem.*, 1998, **37**, 510.

38. Söldner, M.; Riede, J.; Schier, A.; Schmidbaur, H., *Inorg. Chem.*, 1998, **37**, 601.

39. Blum, Y. D.; Laine, R. M., *Organometallics,* 1986, **5**, 2081.

40. Zoeckler, M. T.; Laine, R. M., *J. Org. Chem.*, 1983, **48**, 2539.

41. Seyferth, D.; Schwark, M. J.; Stewart, M. R., *Organometallics,* 1989, **8**, 1980.

42. Duguet, E.; Schappacher, M.; Soum. A., *Macromolecules*, 1992, **25**, 4835.

43. Fink, W., *Angew. Chem., Int. Ed.*, 1966, **5**, 760.

44. Wisemann, G.H.; Wheeler, D. R.; Seyferth, D., *Organometallics*, 1986, **5**, 146.

45. Seyferth, D.; Wisemann, G. H.; Prud'homme. C., *J. Am. Ceram. Soc.*, 1983, **66**, C13.

46. Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A., *J. Organomet. Chem.*, 1991, **406**, C1.

47. Sommer, L. H.; Citron, J. D., *J. Org. Chem.*, 1967, **32**, 2470.

48. Blum, Y. D.; Schwartz, K. B.; Laine, R. M., *J. Mater. Sci.*, 1989, **24**, 1707.

49. Biran, C.; Blum, Y. D.; Glaser, R.; Tse, D. S, Youngdahl, K. A.; Laine, R. M., *J. Mol. Catal.*, 1988, **48**, 183.

50. Kinsley, K. K.; Nielson, T. J.; Barton, T., *J. Main. Group. Met. Chem.*, 1987, **10**, 307.

51. Wang, W-D.; Eisenberg, R., *Organometallics*, 1991, **10**, 222.

52. Liu, H. Q.; Harrod, J. F., *Can. J. Chem.*, 1990, **68**, 1100.

53. Liu, H. Q.; Harrod, J. F., *Organometallics*, 1992, **11**, 822.

54. He, J.; Liu, H. Q.; Harrod, J. F.; Hynnes, R., *Organometallics*, 1994, **13**, 336.

55. Hu, J.; Son, D. Y., *Macromolecules*, 1998, **31**, 8644.

56. Veith, M.; Elsässer, R., *Organometallics*, 1999, **18**, 656.

57. Barrow, M. J.; Ebsworth, E. A. V., *J. Chem. Soc., Dalton Trans.*, 1984, 563.

58. Anderson, D. G.; Blake, A. J.; Cradock, S.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E.; Welch, A. J., *J. Chem. Soc., Dalton Trans.*, 1987, 3035.

59. Airey, W.; Glidwell, C; Robiette, A. G.; Sheldrick, G. M.; Freeman, J. M., *J. Mol. Struct.*, 1971, **8**, 423.

60. Blake, A. J.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E.; Smitj. D. E.; Welch, A. J., *J. Chem. Soc., Dalton Trans.*, 1986, 91.

61. Gunderson, G.; Mayo, R. A.; Rankin, D. W. H., *Acta. Chem. Scand. Ser A.*, 1984, **38**, 579.

62. Anderson, D. G.; Blake, A. J.; Cradock, S.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E.; Welch, A. J., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 107.

63. Ruhlandt-Senge, K.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 425.

64. Ebsworth, E. A. V., *Chem. Commun.*, 1966, 531.

65. Nagy, J; Hencsei, P., *J. Organomet. Chem.*, 1972, **38**, 261.

66. Baybutt, P.; Guest, M. F.; Hillier, I. H., *Proc. Roy. Soc., London, Sr A*, 1973, **333**, 225.

67. Shea, K. J.; Gobeille, R.; Bramblett, J.; Thompson, E., *J. Am. Chem. Soc.*, 1978, **100**, 1611.

68. Noodleman, l.; Paddock, N., *Inorg. Chem.*, 1979, **18**, 354.

69. Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M-B.; Apeloig, Y.; Chandrasekhar, Y.; Schleyer, P. V. R., *J. Am. Chem. Soc.*, 1986, **108**, 260.

70. Pitt, C. G., *J. Organomet. Chem.*, 1973, **61**, 49.

71. Fleisher, H.; Brain, P. T.; Rankin, D. W. H.; Robertson, H. E.; Bühl, M.; Thiel, W., *J. Chem. Soc., Daltons Trans.*, 1998, 593.

72. Livant, P.; Mackee, M. L.; Worley. D., *Inorg. Chem.*, 1983, **22**, 895.

73. Mitzel, N. W.; Angermaier, K.; Schmidbaur, H., *Organometallics* 1994, **13**, 176.

74. Mitzel, N. W.; Oberhammer, H., *Inorg. Chem.*, 1998, **37**, 3593.

75. Mitzel, N. W.; Brewing. E.; Blake, A. J.; Robertson, H. E.; Smart, B. A.; Rankin, D. W. H., *J. Am. Chem. Soc.*, 1996, **118**, 2664.

76. Mo, Y.; Zhang, Y.; Gao, J., *J. Am. Chem. Soc.*, 1999, **121**, 5737.

77. Lauterbur, P.C. In "*Determination of Organic Structure by Physical Methods*" Eds Nachod, E. C. Phillips, W. D., Academic press, New York 1962, **2**.

78. Williams, E. A.; Cargiloli, "*Annual reports on NMR spectroscopy*", 1979, **9**, 211.

79. Williams, E. A., "*Annual reports on NMR spectroscopy*", 1983, **15**, 235.

80. Morris, G. A.; Freeman, R., *J. Am. Chem. Soc.*, 1979, **101**, 760.

81. Helmer, B. J.; West, R., *Organometallics*, 1982, **1**, 877.

82. Doddrell, D. M.; Pegg, D. T.; Brooks, W.; Bendall, M. R., *J. Am. Chem. Soc.*, 1981, **103**, 727.

83. Blinka, T. A.; Helmer, B.J.; West, R.; *Adv. Organomet. Chem.*, 1984, **23**, 193.

84. Kupce, E.; Lukevics, E., *J. Magn. Reson.*, 1988, **76**, 63.

85. Ernst, S. R.; Cagle Jr., F.W., *Acta Crystallogr., Sect. B*, 1977, **33**, 235.

86. Clement, B.; Girreser, U., *Magn. Reson. Chem.*, 1999, **37**, 662.

87. Syamal, A., *J. Sci. Ind. Res.*, 1978, **37**, 661.

88. Hart, R. O.C.; Bott, S. G.; Atwood, J. L.; Cooper, S. R., *J. Chem. Soc., Chem. Commun.*, 1992, 894.

89. Marchi, A.; Marvelli, L.; Cattabriga, M.; Rossi, R.; Neves, M.; Bertolasi, V.; Ferretti, V., *J. Chem. Soc., Daltons Trans.*, 1999, 1937.

90. Das, G.; Bharadwaj, P.K.; Ghosh, D.; Chauhari, B.; Banerjee, R., *Chem. Commun.*, 2001, 323.

91. Kurzer, F.; Pitchfork, E. D., *Top. Cur. Chem.*, 1968, **10**, 446.

92. Sirtoi, C. R.; Pasik, C., *Pharmacol. Res.*, 1994, **30**, 187.

93. Gerich, J. E., *N. Engl. J. Med.*, 1989, **321**, 1231.

94. Watkins, W. M.; Chulay, J. D.; Sixsmith, D. G.; Spencer, H. C.; Howells, R. E., *J. Pharm. Pharmacol.*, 1987, **39**, 261.

95. Morain, P.; Abraham. C.; Portevin. B.; Nanteuil De, G., *Mol. Pharmacol.*, 1994, **46**, 732.

96. Riddick, J. A.; Bunger, W. B.; *"Techniques of Chemistry, Organic Solvents"*, 3rd Edn. Wiley Interscience, New York, **2**, 1970.

97. Perrin, D. D.; Armarego, W. L. S.; *"Purification of Laboratory Chemicals"*, 3rd Edn., Pergamon Press. Oxford, 1993.

98. Jeffery, G. H.; Bassett, J; mendham, J.; Denny, R. C.; "*Vogels Textbook of Quantitative Chemical Analysis*", 5th Edn., Bath Press Ltd., London, 1994.

99. Karipides, D.; Fernelius, *Inorg. Synth.*, 1963, **7**, 56.

100. Sen-Gupta, N. R.; *Z. Anorg. Allg. Chem.*, 1962, **315**, 220.

101. Benkeser, R. A.; Landeaman.; Foster, D., *J. Am. Chem. Soc.*, 1952, **74**, 648.

102. Fabbrizzi, L.; Micheloni, M.; Paloletti, P.; Schwarzenbach, G., *J. Am. Chem. Soc.*, 1977, **99**, 5574.

103. *Nomenclature of Organic Chemistry*, Pergamon, Oxford, 1979, Rule C-962.1.

104. Williams, E. A., in Patai. S.; Rappoport, Z., "*The Chemistry of Organic Silicon compounds*" 1989, 516.

105. Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Crooks, R. G., "*Organic Structural Spectroscopy*" Prentice-Hall, New Jersey, 1998, 37.

106. Bassindale, A. R.; Jiang, J., *J. Organomet. Chem.*, 1993, **446**, C3.

107. Fleisher, H.; Mckean, D. C.; Pulham, C. R.; Bühl, M., *J. Chem. Soc., Daltons Trans.*, 1998, 585.

108. Hinchley, S. L.; Smart, A.; Morrison. C. A.; Robertson, H. E.; Rankin, D. W. H.; Zink. R.; Hasssler. K., *J. Chem. Soc., Dalton Trans.*, 1999, 2303

109. Morrison, C. A.; Rankin, D. W. H.; Robertson, H. E.; Lickiss, P. D.; Masangane, P. C., *J. Chem. Soc., Dalton Trans.*, 1999, 2293.

110. Engelhardt, G.; Magi, M.; Lippmaa, E., *J. Organomet. Chem.*, 1973, **54**, 115.

111. Shankar, R.; Saxena, A.; Brar, A. S., *J. Organomet. Chem.*, 2001, **628**, 262.

112. Ojima, I., in Patai, S.; Rappoport, Z. (Eds.), "*The Chemistry of Organic Silicon Compounds*" Wiley, New York, 1989,1479.

113. Speier, J. L., in Stone, F. G. A.; West, R. (Eds.), "*Adv. Organomet. Chem.*", Academic press, New York, 1979, **17**, 407.

114. Ojima, I.; Kogure, T. *Rev. Silicon, Germanium, Tin and Lead Compd.*, 1981, **5**, 7.

115. Capka, M.; Svoboda, P.; Hetflejs, J., *Coll. Czech. Chem. Commun.*, 1973, **38**, 3800.

116. Pang, Y.; Ijadi-Maghsoodi, S.; Barton, J. T., *Macromolecules*, 1993, **26**, 5671.

117. Kunhen, T.; Rufflo.; Straditto, M.; Ulbrich, D.; McGlinchly, M. J.; Brook, M. A., *Organometallics*, 1997, **16**, 5042.

118. Boury, B.; Carpenter, L.; Corriu, R. J. P., *Angew. Chem., Int. Ed. Engl.*, 1990, **102**, 818.

119. Boury, B.; Corriu, R. J. P.; Mutin, P., *Organometallics*, 1991, **10**, 1457.

120. Hughes, J.; Willey. G.R., *J. Am. Chem. Soc.;* 1973, **95**, 8758.

121. Pierce-Butler, M.; Willey, G.R., *J. Organomet. Chem.*, 1973, **54**, C19.

122. Alcock, N. W.; Pierce-Butler, M.; Willey, G.R., *J. Chem. Soc., Chem. Commun.*, 1974, 627.

123. Bettenhausen, R.; Milius, W.; Schnick, W., *Chem. Eur. J.*, 1997, **8**, 1337.

124. Goetze, B.; Knizek, J.; Nöth, H.; Schnick, W., *Eur. J. Inorg. Chem.*, 2000, 1849.

125. Sakamoto, K.; Ikeda.; Akashi, H.; Fukuyama, T.; Orita, A.; Otera, J., *Organometallics*, 2000, **19**, 3242.

BIO-DATA OF THE AUTHOR

SAMPRIYA N.
D/O Mr. E. Narayanan
"Pournami", A. K. G. Road
Perlaseri, P.O.Mundalore
Kannur-670622
Kerala, India.

Personal details

Born	: Kannur, Kerala, India, October/14/1975.
Sex	: Female.
Nationality	: Indian.
Marital status	: Unmarried.
Languages known	: English,Tamil, Malayalam, Hindi and German (Proficiency level).

Academic Qualification

M. Sc. (1996 -1998)	: Applied Chemistry (8.94/10),First Rank, Anna University, Madras, India
B. Sc. (1993 -1996)	: Chemistry (82.95%), First class University of Madras, Madras, India

Academic Awards

- Qualified National Eligibility Test (NET) for lectureship held by Council of Scientific and Industrial Research- University Grants Commission in June 1998
- Qualified Graduate Aptitude Test in Engineering (GATE) in 1998, Subject-Chemistry.
- Recipient of Institute Scholarship, from I. I. T. New Delhi. 1998-till date.
- Awarded certificate for obtaining First Rank in Master of Science (Applied chemistry) by the Vice-Chancellor, Anna University – 1998
- Awarded Certificate of Honor for active participation in college activities.
- Awarded Sri Krishna Bhatkal Memorial Medal for Proficiency in Chemistry (1996) from Shrimati Devkunvar Nanalal Bhatt Vaishnav College for women.
- Awarded proficiency prize (Books) in B. Sc chemistry-1995.
- Awarded Shri Chandrakant M. Tolia Medal in B. Sc Chemistry – 1997 for securing the highest mark in college (1993-1996)

List of Research Publications

1. "Reactions of secondary silanes with biguanide bases – synthesis and characterization of oligomeric 1,4-bis(silyl)biguanides and 1-alkyl-2,5-bis(silyl)biguanides" R. Shankar, Sampriya Narayanan and Pooja Kumar, J. Chem. Soc., Daltons Trans., 2001, 1582.

2. "Reactions of primary silanes with biguanide bases: synthesis and characterization of caged silylbiguanides" R. Shankar, Sampriya Narayanan and Pooja Kumar, (to be communicated)

3. "Functional silazanes and carbosilazanes" R. Shankar, N Sampriya, A. Saxena, and S. Kaur, International Symposium of Silicon Chemistry, held at Sendai, Japan, May 22-28, 1999.

4. "Two-dimensional NMR studies of some chiral carbosilanes" R. Shankar, A. Saxena, and N. Sampriya, International Symposium of Silicon Chemistry, held at Sendai, Japan, May 22-28, 1999.

5. "Titanium catalyzed dehydrocoupling of chiral carbosilanes" R. Shankar, A. Saxena, N Sampriya and A. S. Brar, Moden trends in Inorganic Chemistry XII, IISc Banglore, Jan 18-20, 2000.

6. "Synthesis and characterization of oligomeric silylbiguanides containing hyper coordinated silicon" R. Shankar, Sampriya Narayanan and Pooja Kumar, paper presented in twentieth Annual Conference of the Indian Council of Chemists held at Mysore University, Mysore, December, 2001.