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In Search Of An Alternative Route To Germasilenes: The Synthesis And Chemistry Of (halosilyl)germanes

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IN SEARCH OF AN ALTERNATIVE ROUTE TO GERMASILENES: THE SYNTHESIS AND CHEMISTRY OF (HALOSILYL)GERMANES

by

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Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
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ABSTRACT

This thesis describes attempts to prepare a germasilene, a compound containing a germanium-silicon double bond, by either a ß-elimination reaction or a reductive elimination reaction.

The precursor, $Mes_2HGeSiClMes_2$, 1, (Mes = 2,4,6-trimethylphenyl) was prepared by the addition of Mes_2HGeLi to Mes_2SiCl_2 in THF in excellent yield. We examined the effect of changing the nature of the solvent, leaving group, base and ligands on the reaction between 1 and base.

$Mes_2ClGeSiClMes_2$, 29, and $Mes_2BrGeSiClMes_2$, 30, prepared by the chlorination and bromination of 1 respectively, were treated with lithium naphthalenide (LiNp) in an attempt to prepare $Mes_2Ge=SiMes_2$ by a reductive elimination reaction. Although a stable germasilene was not isolated from the reaction between 29 or 30 and LiNp, the intermediate formation of a germasilene cannot be ruled out.

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To my parents, Urmila and Ramji

TABLE OF CONTENTS

LIST OF FIGURES

APPENDIX - SELECTED NMR SPECTRA

ABBREVIATIONS

Bu = 1 Butyl

BuLi = Butyllithium

DME = Dimethoxyethane

Et_3N = Triethylamine

epr = Electron paramagnetic resonannce

Et_2O = Diethyl ether

GC = Gas chromatography

h = Hour

HMPA = Hexamethylphosphoramide

IR = Infrared

Is = Isityl

LDA = Lithium diisopropylamide

LiNp = Lithium naphthalenide

LiOMe = Lithium methoxide

Me = Methyl

MeI = Iodomethane

MeOH = Methanol

Mes = Mesityl

Me_3Si = Trimethylsilyl

Me_3SiCl = Trimethylsilyl chloride

mp = Melting point

MS = Mass spectrum

NaOMe = Sodium methoxide

NMR = Nuclear magnetic resonance

OMe = Methoxy

Ph = Phenyl

$PhCH_2$ = Benzyl

$PhCH_2Br$ = Benzyl bromide

PhLi = Phenyllithium

^{i}Pr = Isopropyl

^{i}PrLi = Isopropyllithium

$^iPr_2NH$ = Diisopropylamine

rt = Room temperature

tert-BuLi = *tert*-Butyllithium

THF = Tetrahydrofuran

CHAPTER 1-INTRODUCTION

1.1 INTRODUCTION

The carbon-carbon double bond is an important functional group in organic chemistry that has been extensively studied and well-documented in the literature. Compounds containing a carbon-carbon double bond can be prepared by a variety of methods and can easily be converted into many other classes of compounds. One of the most important classes of compounds derived from alkenes are polymers. Synthetic polymers have a variety of applications such as in coatings (e.g. Teflon), paints, coffee cups, food wrapping (e.g. Saran Wrap), electrical insulation, automotive moldings, medical devices (e.g. artificial heart valves), carpet fibres, adhesives and so on. Although the above list is incomplete, it can be seen that these polymers have a great effect on our lives in that they are used in the manufacturing of simple objects such as coffee cups and also in the manufacturing of highly technical objects such as automobile parts and medical devices.

The study of the heavier congeners of alkenes[1a-i], on the other hand, has not been as extensive; mainly because of the belief (prior to 1967) that doubly bonded silicon, germanium, and tin compounds were too unstable to exist because of weak $p\pi$-$p\pi$ bonding (Classical Double Bond Rule[2]). This resulted in the rather late development of this area of chemistry compared to that of alkenes. However, in 1967, Gusel'nikov and Flowers[3] provided the first indirect evidence for the formation of a silene, a compound containing a silicon-carbon double bond, from the thermolysis of 1,1-dimethyl-1-silacyclobutane. This event sparked intense activity in the preparation of other doubly bonded species involving the heavier group 14 elements. Although several transient doubly bonded compounds involving heavy group 14 elements were postulated[1c,f], it was only in 1981 that the first solid, stable compounds containing a doubly bonded silicon atom, namely tetramesityldisilene and 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silene, were isolated by R. West and co-workers[4], and A.G. Brook and co-workers[5], respectively, and fully characterized. Since then many other doubly bonded group 14 compounds have been isolated and their chemistry studied; included in this list are, for example, silicon-carbon[1c,g,i], silicon-silicon[1,4], silicon-phosphorus[6,7], germanium-carbon[1e,i,8], germanium-nitrogen[1e], germanium-germanium[1e], germanium-phosphorus[1e,9,10], tin-carbon[11,12,13], and tin-phosphorus[14] double bonds. Absent from the above list are heteronuclear dimetallenes between group 14 elements of row 3 and below. From these studies, it is now evident that bulky ligands such as 2,6-di- or 2,4,6-trialkylphenyl, adamantyl, bis(trimethylsilyl)-methyl, or fluorenylidene groups are needed to kinetically stabilize the doubly bonded compounds towards dimerization and/or polymerization reactions. However, small molecules still react readily with these species.

In contrast to their carbon analogues, which have a wide range of applications and have been extensively studied, silicon-based polymers, formally derived from doubly bonded silicon compounds, have not been as extensively studied and as a result, their use is not as widespread. However, recently much interest has been generated by the unusual electronic behaviour of polysilanes, polymers with a silicon backbone. These polymers have been found not only to absorb strongly in the near uv region (suggesting significant electron delocalization within the σ-bonded framework),[15] but also are highly light sensitive[15,16], with scission being the only observed process for alkyl-substituted polymers, and both scission and crosslinking processes occuring for phenyl-substituted polymers. Because of these properties, these polymers have found use as photoinitiators for olefin polymerizations[15,16] and as photoresists[15,16]. Polysilanes are usually prepared by a Wurtz-type coupling of dichlorosilanes with sodium, potassium or sodium-potassium alloys, although Sakurai and co-workers[17] have found that the anionic polymerization of masked disilenes also looks promising.

Trefonas and West[16] have found that polygermanes as well as poly(organogermane-organosilane)s, synthesized by a Wurtz-type coupling of dichlorosilanes and -germanes, have similar properties to polysilanes and have suggested their possible use as photoresists. Additionally, Takeda and co-workers[18] have indicated that silicon-germanium ordered co-polymers should correspond to a one dimensional superlattice structure rather than an amorphous structure that is seen in random silicon-germanium co-polymers. This led Isaka and co-workers[19] to synthesize ordered silicon-germanium co-polymers (i.e. a polymer with the following structure $(\text{-}R_2SiR_2SiR'_2Ge\text{-})_n$) by polymerizing $ClMe_2SiBu_2GeSiMe_2Cl$. Another pathway envisioned to prepare these mixed co-polymers is the polymerization of a compound containing a silicon-germanium double bond or a masked derivative thereof. In order to polymerize a doubly bonded silicon-germanium compound (also known as a germasilene), not only would routes to such compounds need to be investigated, but also the nature of such a bond needs to be explored. This project focussed on exploring various synthetic routes to a dimetallene involving silicon and germanium.

A survey of the literature indicated that stable, isolable dimetallenes can be prepared by one of four general methods:

1) dimerization of photogenerated metallylenes($R_2M:$) from bis(trimethylsilyl)metallanes, a method developed by R. West and co-workers (figure 1-1).[1d,h]

2) photolysis of a homonuclear 3-membered ring. This method was developed by S. Masamune and co-workers (figure 1-2).[1h]

3) reductive coupling or elimination reactions using metals or lithium

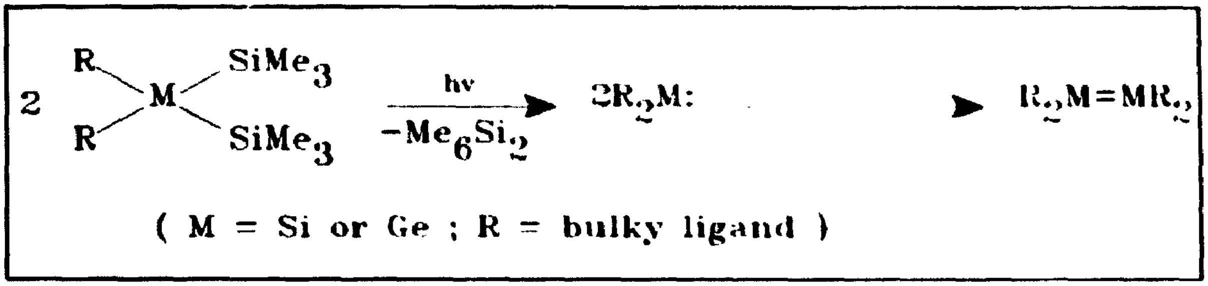


Figure 1-1: Preparation of dimetallenes by photolysis of bis(trimethylsilyl)-metallanes

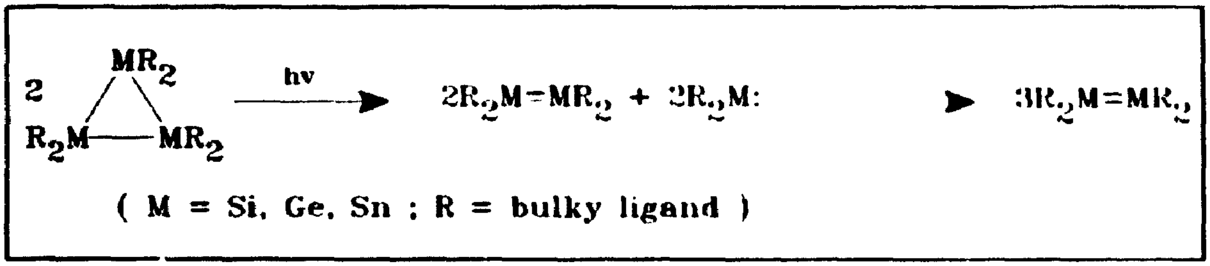


Figure 1-2: Preparation of dimetallenes from cyclotrimetallanes

naphthalenide. This method has been used in the preparation of disilenes and digermenes (figure 1-3).[1h,20a,b,c]

The above three methods were used primarily to synthesize homonuclear dimetallenes.

4) Heteronuclear dimetallenes, on the other hand, have been prepared by a 1,2-salt elimination (figure 1-4). This method has been used successfully by Wiberg[1i,21,22] to synthesize silenes, germenes, stannenes and silaphosphenes, and by Satgé[1e] to prepare germenes, germaphosphenes, germanimines, and stannaphosphenes.

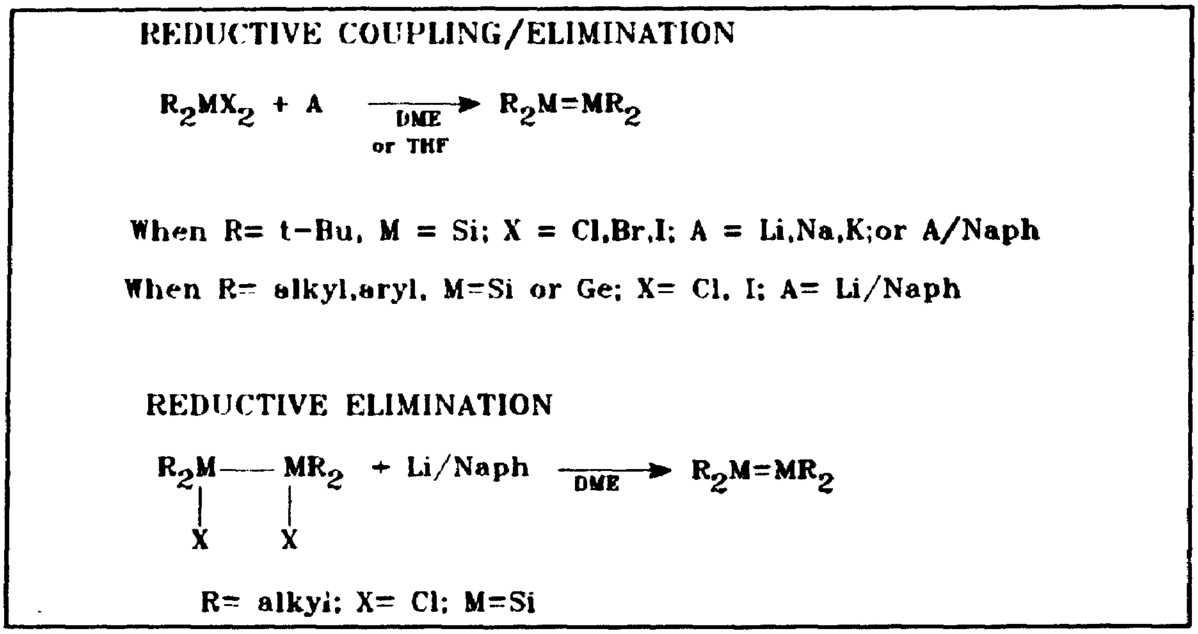


Figure 1-3: Preparation of dimetallenes by reductive coupling/elimination reactions

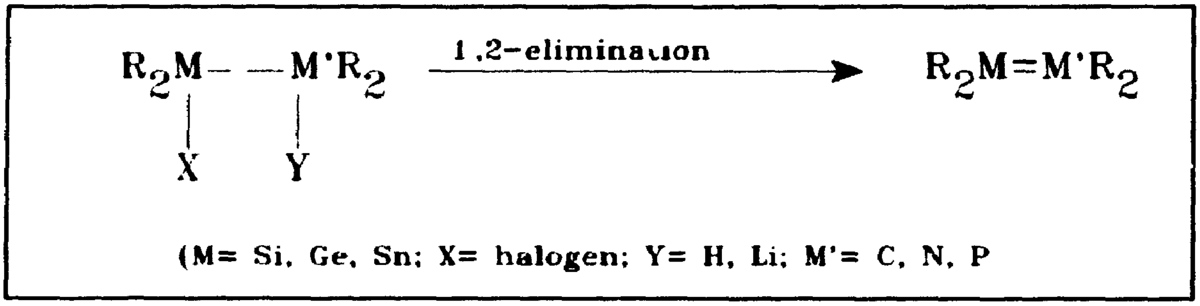


Figure 1-4: Preparation of dimetallenes by a 1,2-salt elimination reaction

West and Shepherd[23] attempted unsuccessfully to prepare a germasilene by method 1. The products obtained on co-photolysis of $Ar_2Ge(SiMe_3)_2$ and $Ar_2Si(SiMe_3)_2$ were disilenes and digermenes. In 1991, K.M. Baines and J.A. Cooke[24,25] reported the synthesis of the first germasilene, namely $Mes_2Ge=SiMes_2$ (Mes = mesityl = 2,4,6-trimethylphenyl). This germasilene was prepared by the photolysis of a siladigermirane, a three-membered ring compound containing one silicon and two germanium atoms. However, this route has a major drawback; the reaction also produces one equivalent of the reactive germylene, R_2Ge: (R = 2,4,6-trimethylphenyl) (figure 1-5). This germylene has to be accounted for in any subsequent reactions. A second drawback is that the starting siladigermirane is contaminated with hexamesitylcyclotrigermane, $(Mes_2Ge)_3$, which cannot be removed by conventional means. Thus, an alternative method is needed to synthesize a germasilene cleanly, free from products derived from the germylene and any products arising from the cyclotrigermane. The method chosen was the 1,2-elimination reaction used successfully by Wiberg[11,21,22] and Satgé[16] to synthesize heteronuclear dimetallenes. We decided to focus our attention on a β-elimination reaction from a silylgermane using a strong base. A possible precursor for the elimination has a proton on germanium and a halogen on silicon (compound A, figure 1-6); the other possible precursor

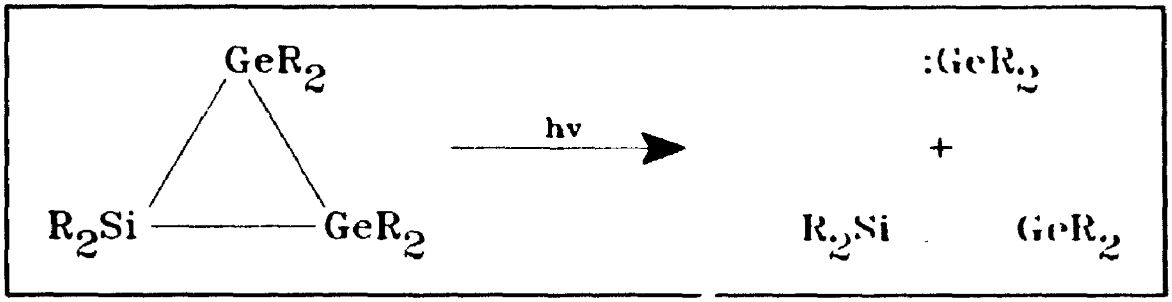
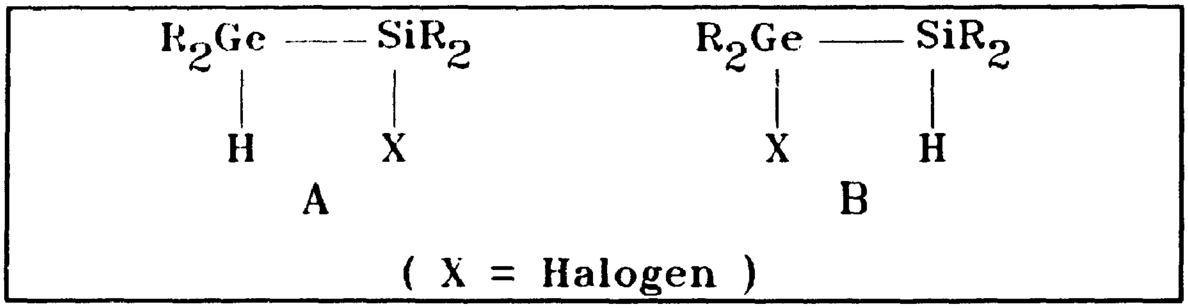


Figure 1-5: Preparation of a germasilene from hexamesitylsiladigermirane

has the functionalities reversed (i.e. proton on silicon and halogen on germanium, compound B, figure 1-6). However, a study of the literature reveals that whereas the metallation, at low temperature, of germanium-hydrogen bonds is facile,[26] the metallation of silicon-hydrogen bonds does not take place so readily: the only known example of metallation of a silicon-hydrogen bond involves reacting triorganosilyl hyrides with potassium hydride in either DME or HMPA.[27] Efforts in our lab to produce silyl anions from silanes by a metallation reaction were also unsuccessful. For example, the products obtained on reaction of $Ph_2HSiSiHPh_2$ with *tert*-BuLi and quenching with $PhCH_2Br$ were Ph_2HSi(*tert*-Bu) and $Ph_2HSi(CH_2Ph)$ (see figure 1-7).[28] This result indicates that cleavage of the central silicon-silicon bond is favoured rather than abstraction of the proton by the base. For this reason, A was chosen as the most appropriate precursor. The ready access to 2,4,6-trimethylphenyl (or mesityl) and phenyl containing compounds made the choice of ligand to be used straightforward. Thus, the compounds



$R_2Ge(H)-SiR_2(X)$ A

$R_2Ge(X)-SiR_2(H)$ B

Figure 1-6: Possible germasilene precursors

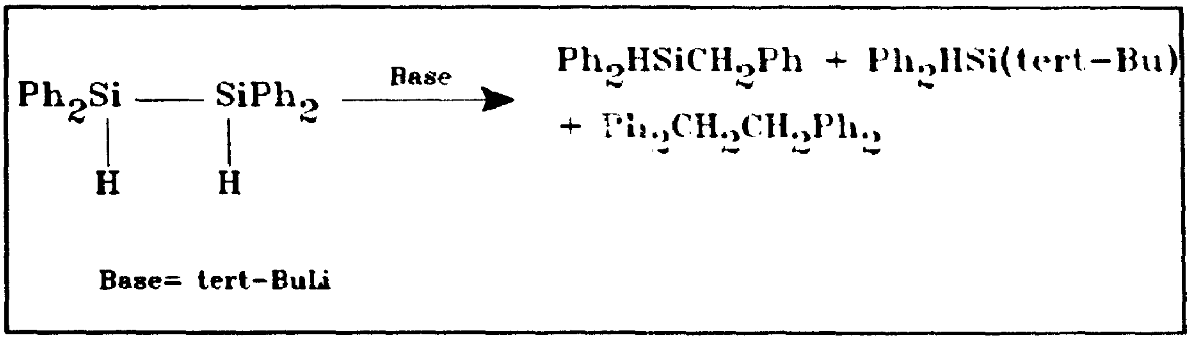
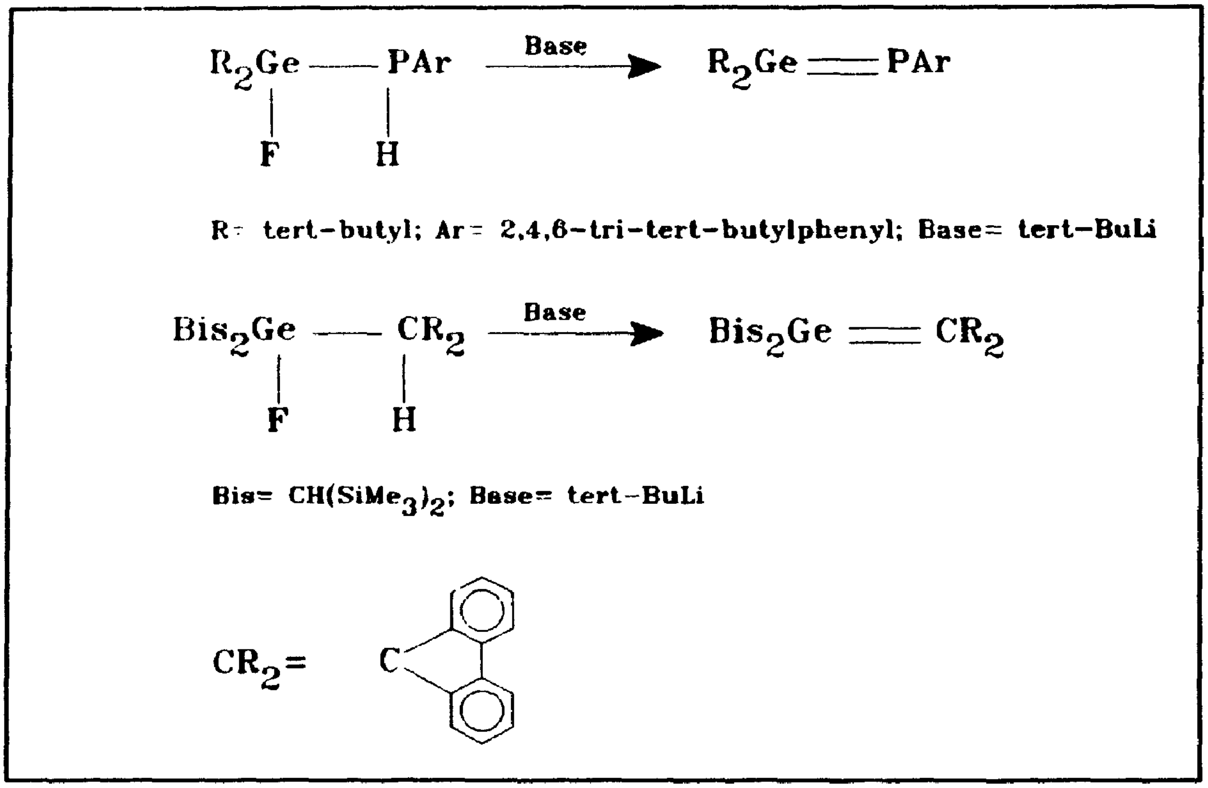


Figure 1-7: Reaction between tetraphenyldisilane and *tert*-BuLi

selected as the germasilene precursors were (halodimesitylsilyl)diarylgermanes (i.e compound A, figure 1-6 with R= mesityl or phenyl). The halide selected initially was chloride; this was also due to the ready access to the appropriate starting material. Therefore, the most promising germasilene precursors appeared to be $Mes_2HGeSiClMes_2$, 1 and $Ph_2HGeSiClMes_2$, 22. It should be noted that J. Satgé and co-workers[1e] used fluorine as the halogen in the synthesis of germenes and germaphosphenes by a 1,2-salt elimination reaction (figure 1-8). The syntheses of compounds 1 and 22 parallel the method used by J. Satgé for the synthesis of asymmetrical digermanes (figure 1-9)[10] and is outlined in figure 1-10. Attempts to synthesize a germasilene by a *β*-elimination reaction from these precursors as well as attempts to synthesize the fluorinated analogs will be discussed.

The preparation of a germasilene by reductive elimination using (halodiarylsilyl)halodiarylgermanes and lithium naphthalenide (LiNp) was also attempted and will be discussed. As mentioned previously, this



R= tert-butyl; Ar= 2,4,6-tri-tert-butylphenyl; Base= tert-BuLi

Bis= CH(SiMe$_3$)$_2$; Base= tert-BuLi

Figure 1-8: Preparation of doubly bonded germanium compounds

$$R_2GeHLi + Et_3GeCl \longrightarrow R_2HGeGeEt_3$$

R= phenyl or 2,4,6-trimethylphenyl

Figure 1-9: Preparation of asymmetrical digermanes

method has been used successfully to prepare digermenes and disilenes (figure 1-3).

$$\mathrm{R_2GeHLi + R_2SiCl_2 \longrightarrow \underset{1}{R_2HGeSiClR_2}}$$

R= 2,4,6-trimethylphenyl

$$\mathrm{R_2GeHLi + R'_2SiCl_2 \longrightarrow \underset{22}{R_2HGeSiClR'_2}}$$

R= phenyl
R'= 2,4,6-trimethylphenyl

Figure 1-10: Preparation of 1 and 22

1.2 REFERENCES

1) a) Ge=M: Satgé, J. *Adv. Organomet. Chem.* **1982**, 21, 241-247.

b) P=P, Si=M, Ge=M, Sn=M: Cowley, A.H.; Norman, N.C. *Prog. Inorg. Chem.* **1986**, 34, 1-63.

c) Si=C: Brook, A.G.; Baines, K.M. *Adv. Organomet. Chem.* **1986**, 25, 1-44.

d) Si=Si: West, R. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 1201-1211.

e) Ge=M: Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, 90, 283-319.

f) Si=M: Gusel'nikov, L.E.; Nametkin, N.S. *Chem. Rev.* **1979**, 79, 529-577.

g) Si=M: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, 85, 419-509.

h) Si=Si, Ge=Ge, Sn=Sn: Tsumuraya, T.; Batcheller, S.A.; Masamune, S. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 902-930.

i) Si=M, Ge=M: Wiberg, N. *J. Organomet. Chem.* **1984**, 273, 141-177.

2) a) Jutzi, P. *Angew. Chem. Int. Ed. Engl.* **1975** 14, 232-245.

b) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, 70, 2140-2145.

c) Mullikin, R. S. *J. Am. Chem. Soc.* **1950**, 72, 4493-4503.

3) Gusel'nikov, L.E.; Flowers, M.C. *J. Chem. Soc. Chem. Comm.* **1967**,

864-865.

4) West, R.; Fink, M.J.; Michl, J. *Science (Washington D.C.)* **1981**, 214, 1343-1344.

5) Brook, A.G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R.K. *J. Chem. Soc., Chem. Comm.* **1981**, 191-192.

6) Smith, C.N.; Lock, F.M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, 25, 3011-3014.

7) Smith, C.N.; Bickelhaupt, F. *Organometallics* **1987**, 6, 1156-1163.

8) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, 109, 4411-4412.

9) Escudié, J.;Couret, C.; Satgé, J.; Andrianarison, M.; Andrianizaka, J.D. *J. Am. Chem. Soc.* **1985**, 107, 3378-3379.

10) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J., Dräger, M. *New. J. Chem.* **1989**, 13, 389-398.

11) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure. & Appl. Chem.* **1987**, 59, 1011-1014.

12) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 546-549.

13) Anselme, G.; Couret, C.; Escudié, J.; Richelme, S.; Satgé, J. *J. Organomet. Chem.* **1991**, 418, 321-328.

14) Couret, C.; Escudié, J.; Satgé, J.; Raharimrina, A.; Andriamizaka, J.D. *J. Am. Chem. Soc.* **1985**, 107, 8280-8281.

15) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, 89, 1359-1410.

16) Trefonas, P.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, 23, 2099-2106.

17) a) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, 23, 4494-4496.

b) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, 111, 7641-7643.

18) Takeda, K.; Shiraishi, K.; Matsumoto, N. *J. Am. Chem. Soc.* **1990**, 112, 5043-5053.

19) Isaka, H.; Fujiki, M.; Fujino, M.; Matsumoto, N. *Macromolecules* **1991**, 24, 2647-2648.

20) a) Weidenbruch, M.; Schäfer, A.; Thom, K.L. *Z. Naturforsch.* **1983**, 38b, 1695-1696.

b) Weidenbruch, M.; Kramer, K.; Peters, K.; von Schnering, H. G. *Z. Naturforsch.* **1985**, 40b, 601-606.

c) Weidenbruch, M.; Kramer, K.; Schäfer, A.; Blum, J. K. *Chem. Ber.* **1985**, 118, 107- 115.

21) Wiberg, N.; Vasisht, S. K. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 93-95.

22) Wiberg, N.; Schuster, H. *Chem. Ber.* **1991**, 124, 93-95.

23) Shepherd, B.; West. R. *Private Communication.*

24) Baines, K.M.; Cooke, J.A. *Organometallics* **1991**, 10, 3419-3421.

25) Baines, K.M.; Cooke, J.A. *Organometallics* **1992**, 11, 3487-3488.

26) Lesbre, M.; Mazerolles, P.; Satgé, P. *The Organic Compounds Of Germanium* **1971**, J. Wiley and Sons, Toronto, p274.

27) Colvin, E. W. *Silicon in Organic Synthesis*; Robert E. Krieger Publishing Company: Malabar, Florida, **1985**, p135.

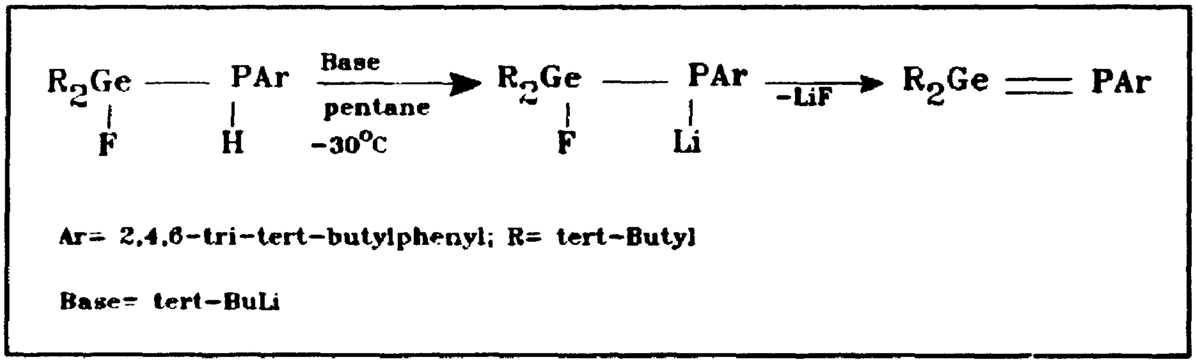
28) Mehta, R.; Parshotam, U. R. *unpublished studies*.

CHAPTER 2-ATTEMPTED SYNTHESIS OF A GERMASILENE BY A β-ELIMINATION REACTION

2.1 PREVIOUS STUDIES

2.1.1 R. Groh; Chemistry Honors Thesis

The synthesis of the starting material $Mes_2HGeSiClMes_2$, 1, and initial reactions involving 1 were carried out by R. Groh.[1] The compound was prepared, as stated previously, by reacting Mes_2HGeLi[2] with Mes_2SiCl_2[3] in THF. Trituration of the crude product with MeOH yielded 1 in 60% yield. This was followed by the attempted synthesis of a germasilene by a β-elimination reaction, similar to the method used by Satgé[4] for the synthesis of a stable germaphosphene (figure 2-1).



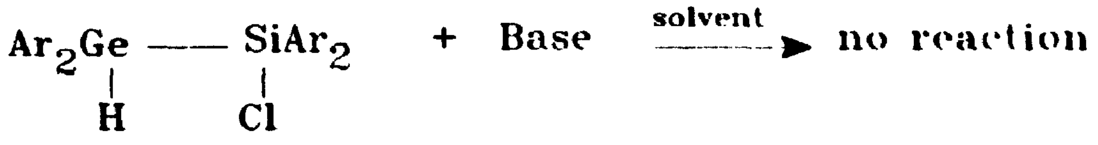
$$\underset{F}{R_2Ge}-\underset{H}{PAr}\xrightarrow[\text{pentane, }-30^{o}C]{\text{Base}}\underset{F}{R_2Ge}-\underset{Li}{PAr}\xrightarrow{-LiF}R_2Ge=PAr$$

Ar= 2,4,6-tri-tert-butylphenyl; R= tert-Butyl

Base= tert-BuLi

Figure 2-1: Preparation of a germaphosphene

No reaction was observed to occur upon addition of strong bases (such as *tert*-BuLi, PhLi and KH) to 1 in hydrocarbon solvents, even under reflux conditions (figure 2-2). However, upon changing to an ethereal



$$Ar_2\underset{H}{\overset{|}{Ge}}-\underset{Cl}{\overset{|}{Si}}Ar_2 + \text{Base} \xrightarrow{\text{solvent}} \text{no reaction}$$

1

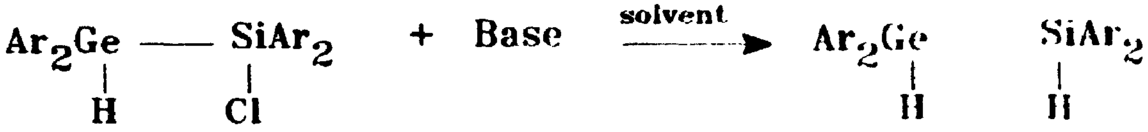
Ar= 2,4,6-trimethylphenyl

Base= tert-BuLi, PhLi, KH

solvent= pentane, cyclohexane

Figure 2-2: Reaction between 1 and base in hydrocarbon solvents

solvent, THF, treatment of 1 with *tert*-BuLi (at temperatures greater than -23°C) resulted in the formation of $Mes_2HGeSiHMes_2$, 2 (figure 2-3). It was found that no reaction occurred below -23°C.



$$Ar_2\underset{H}{\overset{|}{Ge}}-\underset{Cl}{\overset{|}{Si}}Ar_2 + \text{Base} \xrightarrow{\text{solvent}} Ar_2\underset{H}{\overset{|}{Ge}}-\underset{H}{\overset{|}{Si}}Ar_2$$

1 2

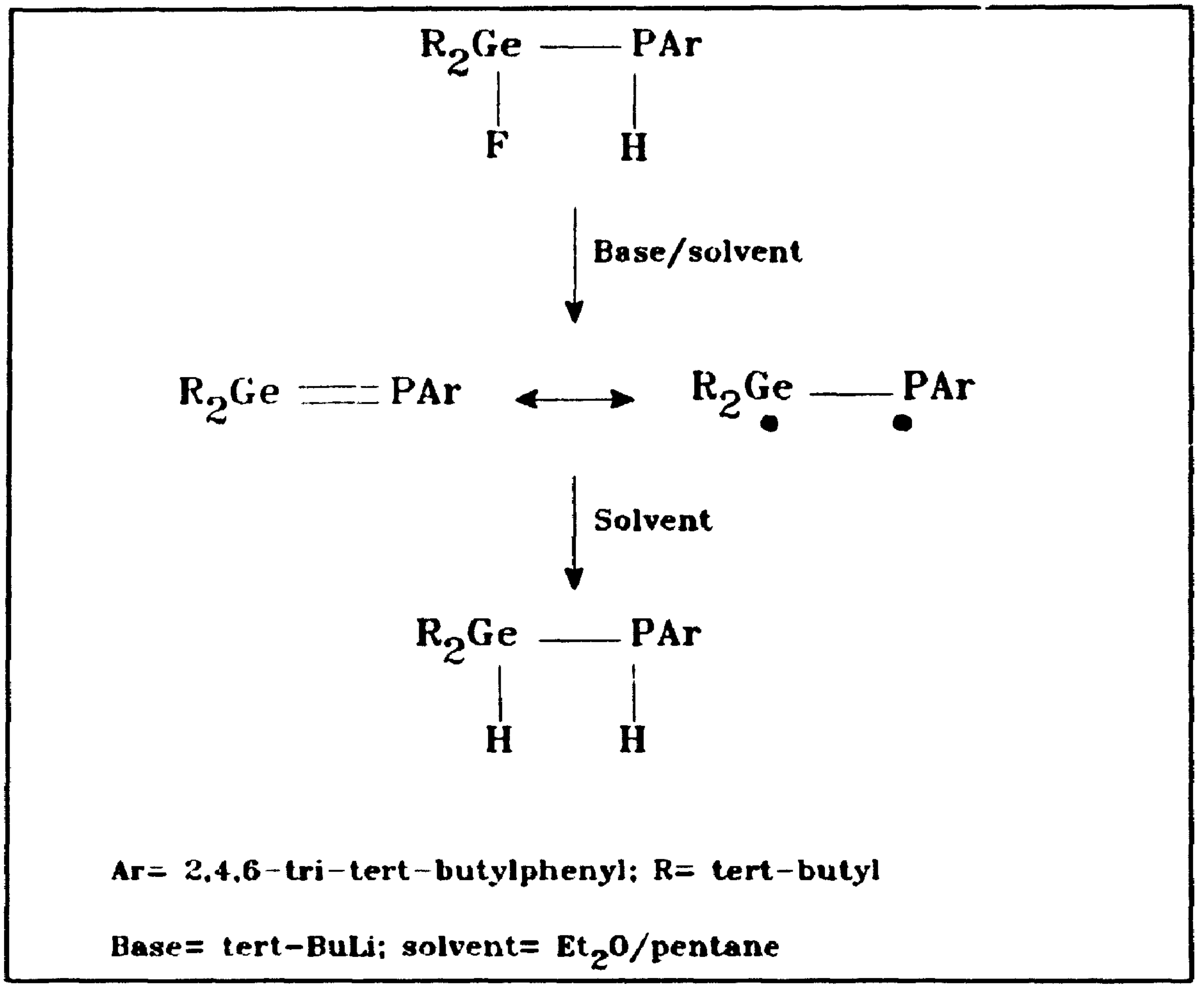
Ar= 2,4,6-trimethylphenyl

Base= tert-BuLi

solvent= THF

Figure 2-3: Reaction between 1 and base in THF

It is likely that compound 2 is formed by one of the following mechanisms. The first mechanism is similar to that suggested by Satgé[4] to account for the reduction of (*tert*-Bu)$_2$Ge=PAr to (*tert*-Bu)$_2$HGePHAr (Ar= 2,4,6-tri-*tert*-butylphenyl) (figure 2-4); the reaction between 1 and *tert*-BuLi yields a germasilene, which exhibits some diradical character. This diradical-like species could then abstract hydrogens from the solvent to give the reduced product (figure 2-5).



Ar= 2,4,6-tri-tert-butylphenyl; R= tert-butyl

Base= tert-BuLi; solvent= Et$_2$O/pentane

Figure 2-4: Preparation of a germaphosphine from a fluorogermaphosphine

The second mechanism involves the trapping by MeOH of a silyl anion, formed by a lithium-chlorine exchange reaction (figure 2-6).

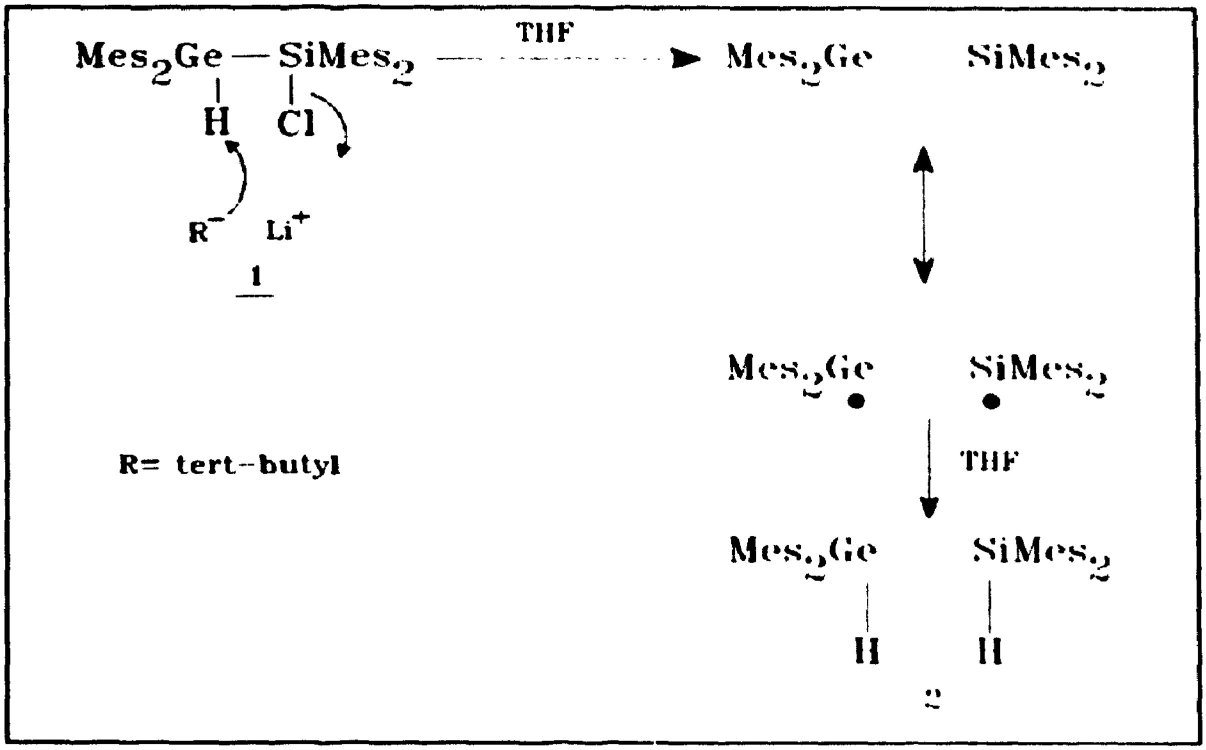


Figure 2-5: Possible mechanism for formation of 2 from 1

The following experiments were done to probe the reaction mechanism:

i) The reaction was carried out in THF-d_8 yielding 2, but no deuterium incorporated compound. The mechanism proposed by Satgé,[4] if the correct one, would yield a deuterated product, namely $Mes_2DGeSiDMes_2$.

ii) When the reaction was quenched with MeOH-d_4, the two products obtained were identified as $Mes_2HGeSiHMes_2$, 2 and a deuterium containing derivative. It was not known, at the time, whether the deuterium was attached to the

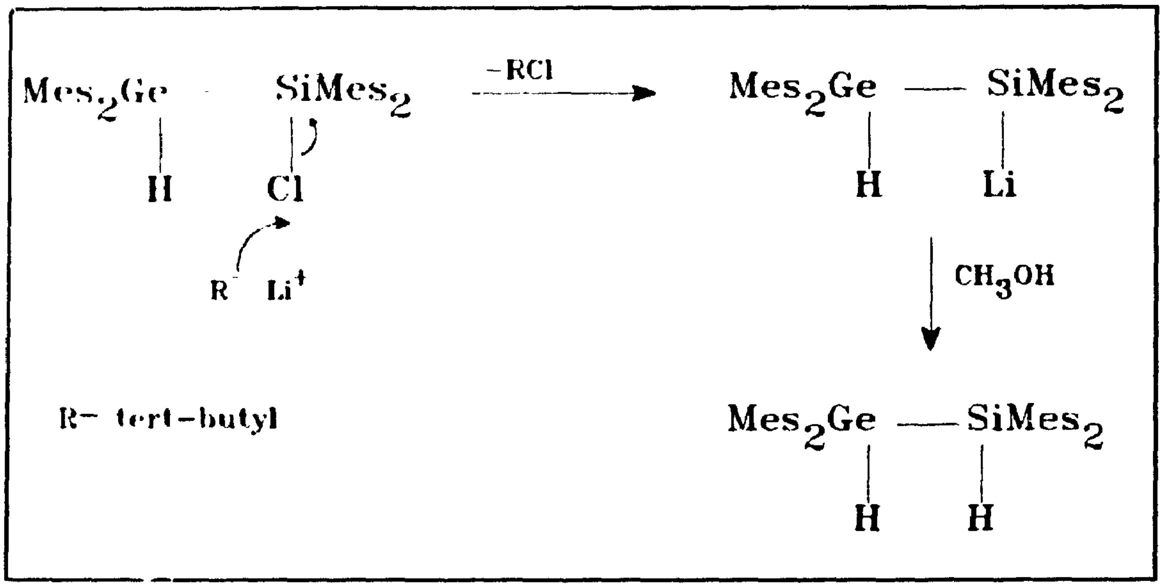


Figure 2-6: Possible mechanism for the formation of 2 from 1

germanium or silicon atom.

From the above results, it can be concluded that since no deuterium incorporation occurred when THF-d_8 was used as the solvent, the mechanism similar to the one suggested by Satgé[4] cannot be correct (figure 2-5). However, the above results do not rule out the mechanism involving the trapping of a silyl anion by MeOH.

2.1.2 B. Joseph; M.Sc. Thesis

B. Joseph[5] obtained similar results as those mentioned above with $Is_2HGeSiClMes_2$, 3 (Is = isityl = 2,4,6-triisopropylphenyl). The synthesis of the starting material was similar to that of 1 (i.e. the appropriate germyllithium, Is_2GeHLi, was added to Mes_2SiCl_2 in THF). It was also noted that 3 did not react with *tert*-BuLi, MeLi, BuLi or PhLi in hydrocarbon solvents or Et_2O. However, when 3 was refluxed with *tert*-BuLi in cyclohexane, the product obtained was 1-(diisitylgermyl)-1-mesityl-4,6-dimethyl-1-siladihydrobenzocyclobutene, 4. It is believed that *tert*-BuLi abstracts a proton from one of the o-methyl groups of the mesityl substituent to give a carbanion which then undergoes an intramolecular substitution with the silyl chloride to form 4 (figure 2-7).

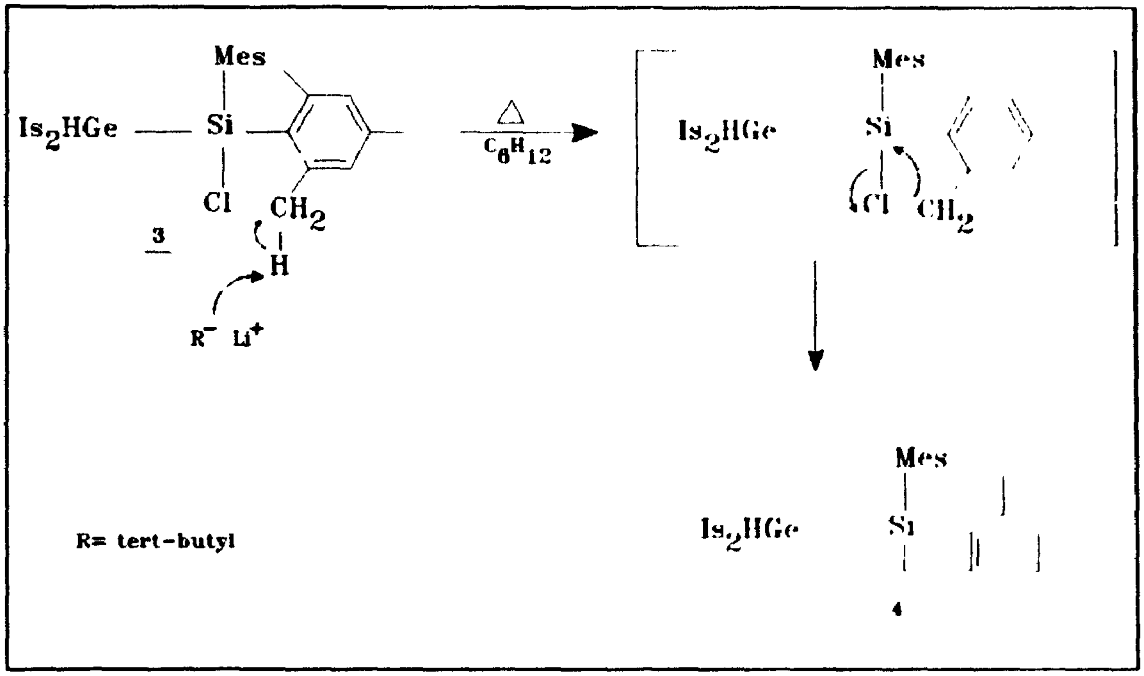
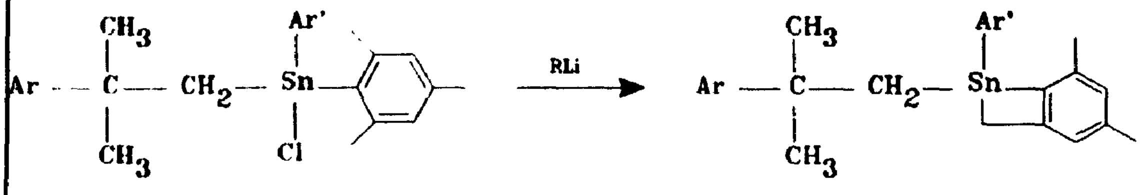


Figure 2-7: Possible mechanism for the formation of 4 from 3

This mechanism is supported by deuterium labelling studies. A similar mechanism has been proposed by M. Weidenbruch[6] for the formation of a stannacyclobutene, when the chlorostannane $RR'ClSnCH_2CMe_2R''$ (R = 2,4,6-trimethylphenyl, R' = 2,4,6-tri-*tert*-butylphenyl, R" = 3,5-di-*tert*-

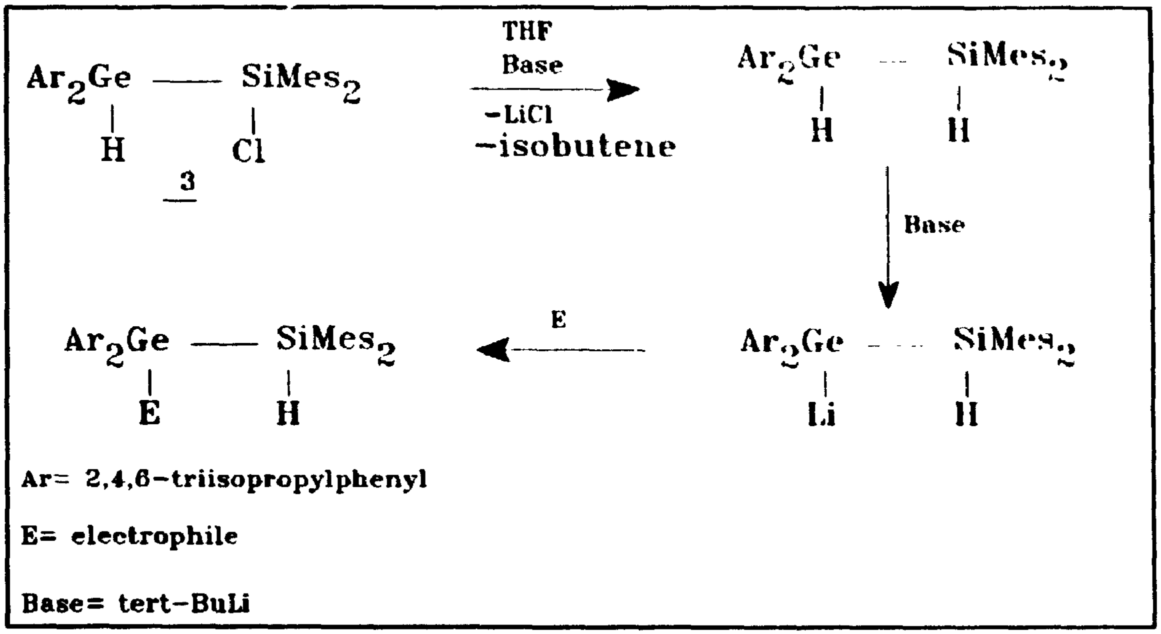
butylphenyl), dissolved in petroleum ether, was treated with *tert*-BuLi (figure 2-8).



Ar= 3,5-tert-butylphenyl; Ar'= 2,4 6-tri-tert-butylphenyl; R= tert-butyl

Figure 2-8: Preparation of a stannacyclobutene from a chlorostannane

Similar to compound 1, 3 reacts with *tert*-BuLi in THF to give the dihydro product $Is_2HGeSiHMes_2$, 5, upon quenching with MeOH. The methylated product, $Is_2(Me)GeSiHMes_2$, 6, was isolated when MeI was used as the quenching agent. The mechanism proposed for the reaction between 3 and *tert*-BuLi is shown in figure 2-9. This mechanism will be discussed in greater detail below.



Ar= 2,4,6-triisopropylphenyl

E= electrophile

Base= tert-BuLi

Figure 2-9: Possible mechanism for the reaction between 3 and base

2.2 SYNTHESIS AND REACTIONS OF $Mes_2HGeSiClMes_2$, 1

As noted above, $Mes_2HGeSiClMes_2$, 1, was prepared in an unoptimized yield of 60%; this was increased to over 90% by the addition of a more accurately determined amount of base in the preparation of Mes_2HGeLi from Mes_2GeH_2 and *tert*-BuLi.[a] It was found that the isolated yield of 2 could also be improved (to 33%) by addition of the base (approximately 4 equivalents) at dry ice/CCl_4 temperatures, followed immediately by removal of the bath and then stirring for an hour before

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[a] The concentration of the base used by R. Groh was not known at the time and, as a result, 1 was prepared in a lower yield.

quenching with MeOH.[b] When the reaction was quenched by MeOH-d_4, in addition to $Mes_2HGeSiHMes_2$, a compound that had a deuterium incorporated was also isolated, but it was not known whether the deuterium was bonded to the germanium or silicon atom. Of these two possibilities, the product was identified as $Mes_2DGeSiHMes_2$, 7, and not $Mes_2HGeSiDMes_2$, 8, by ^{29}Si, ^{2}H and two dimensional ^{29}Si-^{1}H heteronuclear correlation NMR spectroscopy. If a proton was attached to silicon, a $^{1}J_{Si\text{-}H}$ coupling constant of approximately 200 Hz is expected; if not (i.e. a deuterium is attached to Si) a smaller $^{1}J_{Si\text{-}D}$ coupling constant (32 Hz based on the following equation[7]: $J_{B\text{-}X} = (J_{A\text{-}X}(\gamma_B/\gamma_A)$ where $A = H$, $B = D$, $X = Si$, $\gamma =$ gyromagnetic ratio) is expected. The ^{1}H-coupled ^{29}Si NMR signal obtained from the product when MeOH-d_4 was used as a quenching agent has a coupling constant of 191 Hz. This confirmed that a proton is attached to silicon while the deuterium is attached to germanium and thus, the species most likely trapped by MeOH-d_4 was $Mes_2LiGeSiHMes_2$, 9. In addition, the ^{2}H NMR of the product spectrum has only one signal, in the 5-6 ppm region, which corresponded to Ge-H signal in the ^{1}H NMR spectrum (the Si-H signal was assigned by two dimensional ^{29}Si-^{1}H heteronuclear correlation NMR spectroscopy).

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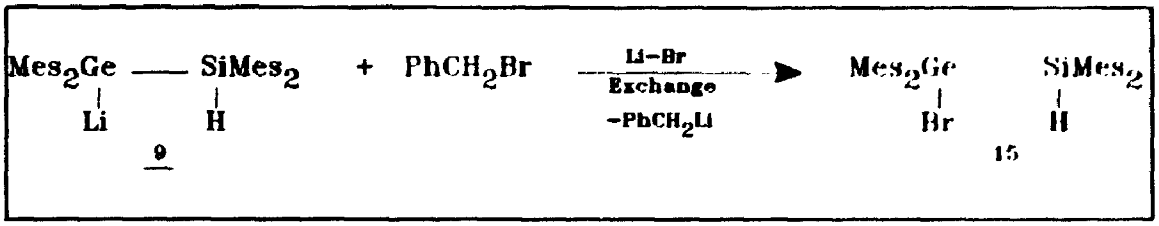
[b] The use of excess base has the advantage of decreasing the time needed for reaction to occur between 1 and *tert*-BuLi, but has the disadvantage of increasing the amount of cleavage product (i.e. Mes_2GeH_2) obtained.

To provide further evidence that the immediate precursor to compounds 2 and 7 was the germyl anion 9, trapping experiments with various electrophiles were carried out. When the trapping agent used was MeI, $Mes_2(Me)GeSiHMes_2$, 10, was isolated. (In addition to 10, the dihydro compound, 2, was also obtained. This product could not be separated from the methyl-analog). With Me_3SiCl as the electrophile, the product obtained was $Mes_2(Me_3Si)GeSiHMes_2$, 12, in 39% isolated yield. (The product, again, was contaminated with 2). With $PhCH_2Br$, the expected benzyl derivative, $Mes_2(PhCH_2)GeSiHMes_2$, 14, was not obtained. The product isolated was identified as the bromo derivative, $Mes_2BrGeSiHMes_2$, 15, (15 was obtained in 28% isolated yield). The isolated product did not contain 2. Bibenzyl was also formed in the reaction, but was not isolated. A possible route for the formation of 15 is by a lithium-bromine exchange reaction between 5 and $PhCH_2Br$ (figure 2-10).



$$\underset{\textbf{9}}{\underset{Li}{Mes_2Ge}-\underset{H}{SiMes_2}} + PhCH_2Br \xrightarrow[\text{Exchange}\ -PhCH_2Li]{Li-Br} \underset{\textbf{15}}{\underset{Br}{Mes_2Ge}-\underset{H}{SiMes_2}}$$

Figure 2-10: Possible route for formation of 15

This reaction could occur by the reversible formation of an ate complex, similar to a mechanism postulated by Wittig and Schöllkopf[8b] in their studies on the reaction between either $PhCH_2Br$ or bromotrypticene (9,10-o-benzeno-9-bromo-10H-anthracene) and BuLi (figure 2-11), or by an electron transfer reaction as has been suggested by Tokitoh

$$R{-}Li \;+\; R'{-}X \;\rightleftharpoons\; \underset{\text{"ate complex"}}{\left[R{-}\overset{-}{X}{-}R'\ Li^{+}\right]} \;\rightleftharpoons\; R{-}X \;+\; R'{-}Li$$

Figure 2-11: Lithium-halogen exchange by a nucleophilic mechanism

and co-workers to account for the formation of TbBr from the reaction between TbLi and $PhCH_2Br$ (Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl; figure 2-12).[9]

In addition to compounds derived from the trapping of 9 (i.e. compounds 10, 12 and 15), compounds derived from the cleavage of the silicon-germanium bond were also obtained (i.e. Mes_2HGeMe, 11, $Mes_2HGe(SiMe_3)$, 13, and $Mes_2HGe(CH_2Ph)$, 16, when the quenching agents were MeI, Me_3SiCl and $PhCH_2Br$, respectively). The cleavage products derived from the silicon part of 1 were not isolated. The isolation of 11, 13 and 16 not only suggested that the anion trapped by the electrophiles was Mes_2HGeLi, but that the cleavage of the central silicon-germanium bond by *tert*-BuLi is regioselective.

Attempts to improve yields of 10, 12 and 15 by longer reaction times were unsuccessful. It should be noted that the purification of the

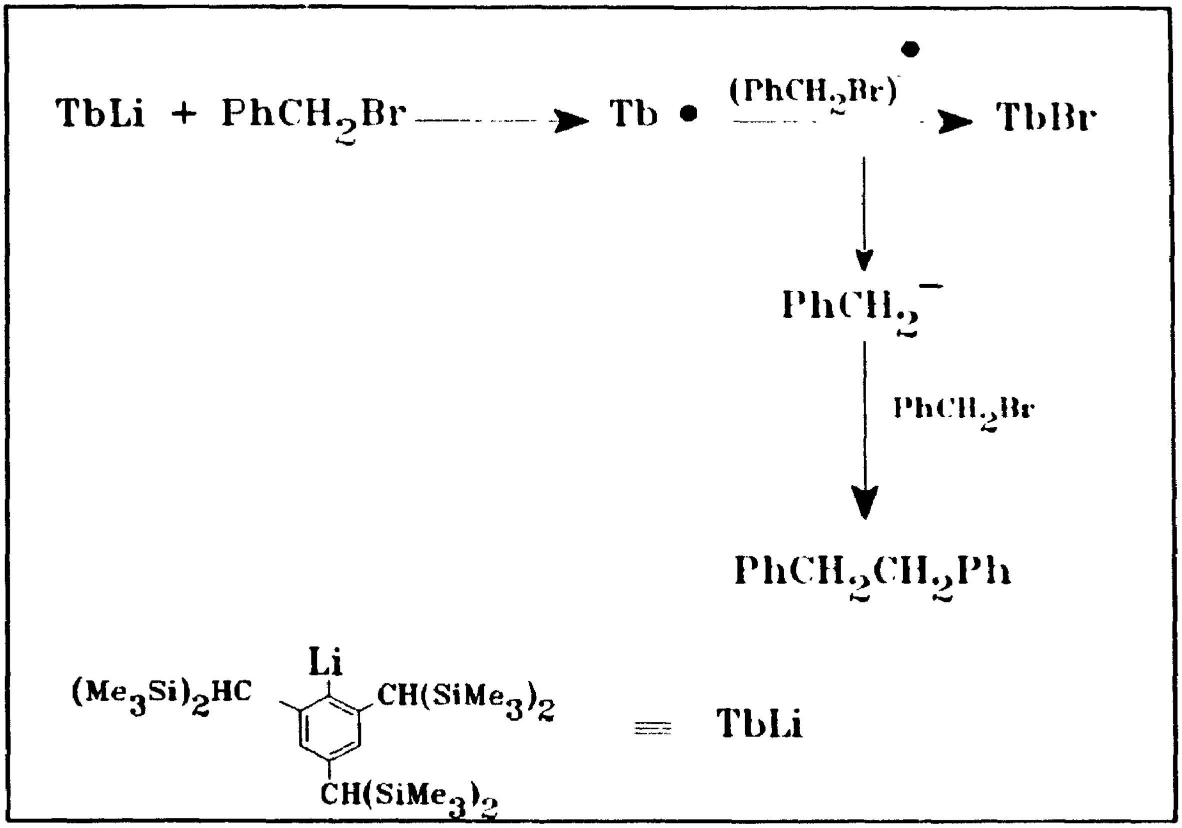
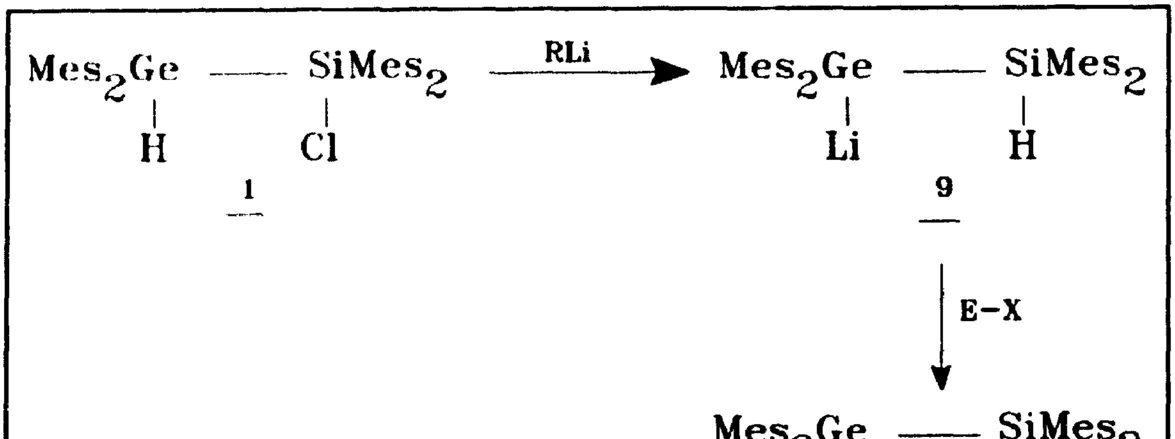


Figure 2-12: Lithium-halogen exchange by an electron transfer mechanism

reaction mixtures is a problem in that although the NMR spectra of the crude mixtures are clean, the isolated yields of the purified products are low.

In summary the novel germyl anion, $Mes_2LiGeSiHMes_2$, 9, is most likely formed in the reaction between $Mes_2HGeSiClMes_2$ and *tert*-BuLi, and this anion can easily be trapped by various electrophiles (figure 2-13).

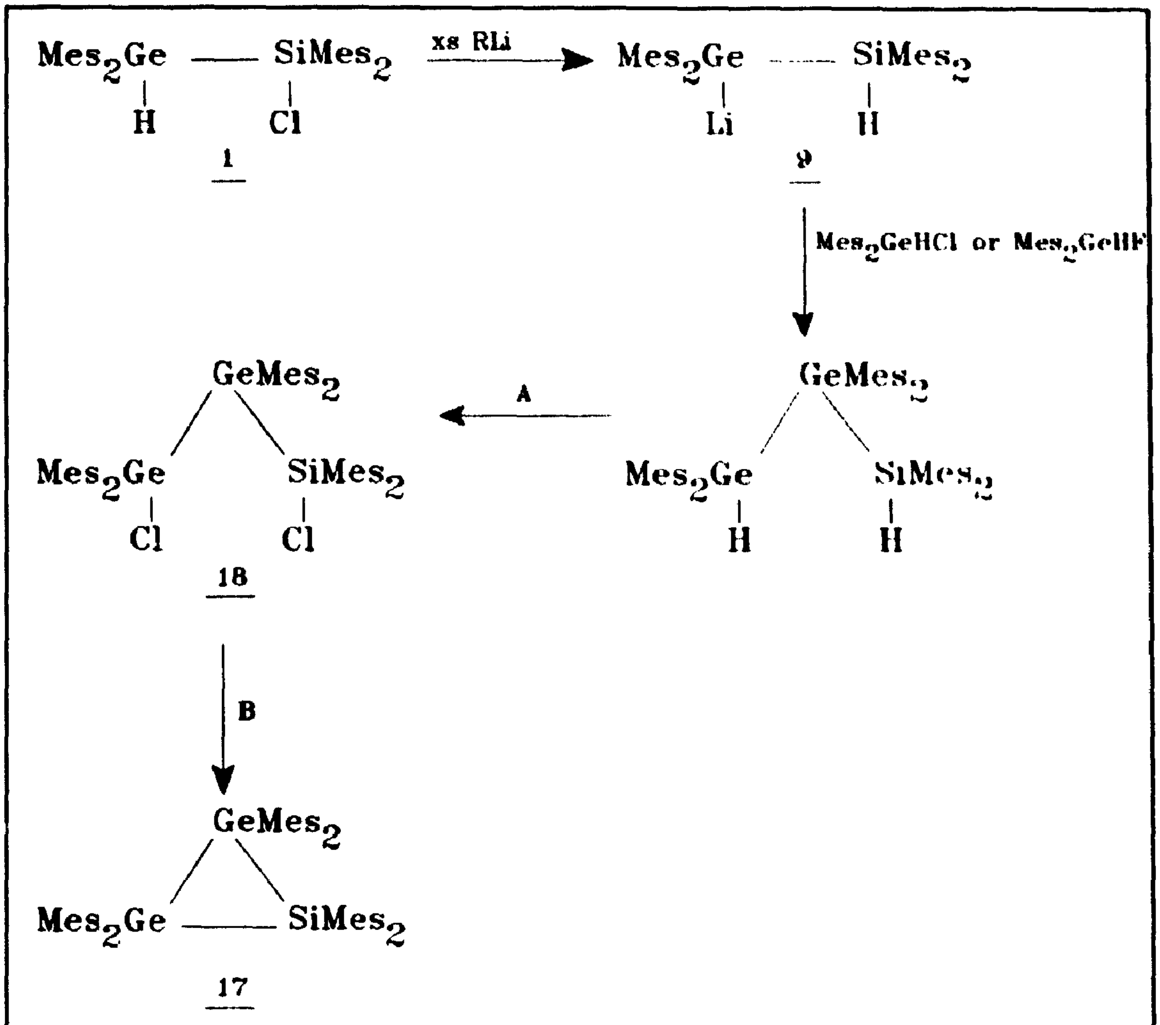
Germyl anion 9, which is formed by the treatment of 1 with *tert*-BuLi, has the potential to be used in the preparation of other mixed silicon-germanium compounds. For example, hexamesitylsiladigermirane,



R= tert-butyl
E−X= MeI, Me_3SiCl, $PhCH_2Br$
E= Me, Me_3Si, Br

Figure 2-13: Quenching of the reaction between 1 and base with different electrophiles

17, which is the only known germasilene precursor[10], may be prepared from the cyclization of $Mes_2ClGeMes_2GeSiClMes_2$, 18; the key step in the synthesis being the coupling of germyl anion 9 to a halodimesitylgermane to prepare $Mes_2HGeMes_2GeSiHMes_2$, the immediate precursor to $Mes_2ClGeMes_2GeSiClMes_2$, 18 (figure 2-14). The currently used method of synthesizing 17, the reductive cyclization of Mes_2SiCl_2 and $Mes_2ClGeGeClMes_2$ using lithium naphthalenide, has the disadvantage of producing significant amounts (up to 20%) of hexamesitylcyclotrigermane, $(Mes_2Ge)_3$ as well.[11] This cyclotrigermane cannot be separated from 17 by conventional means and, as a result, the



A= Chlorinating agent; B= Li/naphthalene; R= tert-butyl

Figure 2-14: A synthetic route to 17

germasilene obtained from the photolysis of 17 is contaminated with products derived from $(Mes_2Ge)_3$. Thus, an alternative synthetic pathway to 17 is needed. The route suggested in figure 2-14 should produce 17 without the cyclotrigermane by-product.

After providing some evidence for the formation of 9 from the reaction between 1 and *tert*-BuLi and demonstrating the usefulness of this germyl anion in the preparation of new mixed silicon-germanium compounds, a piece of the puzzle that remained a mystery was the mechanism for the formation of 9.

The most probable mechanism involves the reduction of 1 by *tert*-BuLi, followed by proton abstraction from germanium to give 9, which can be trapped by various electrophiles (figure 2-15). Support for this

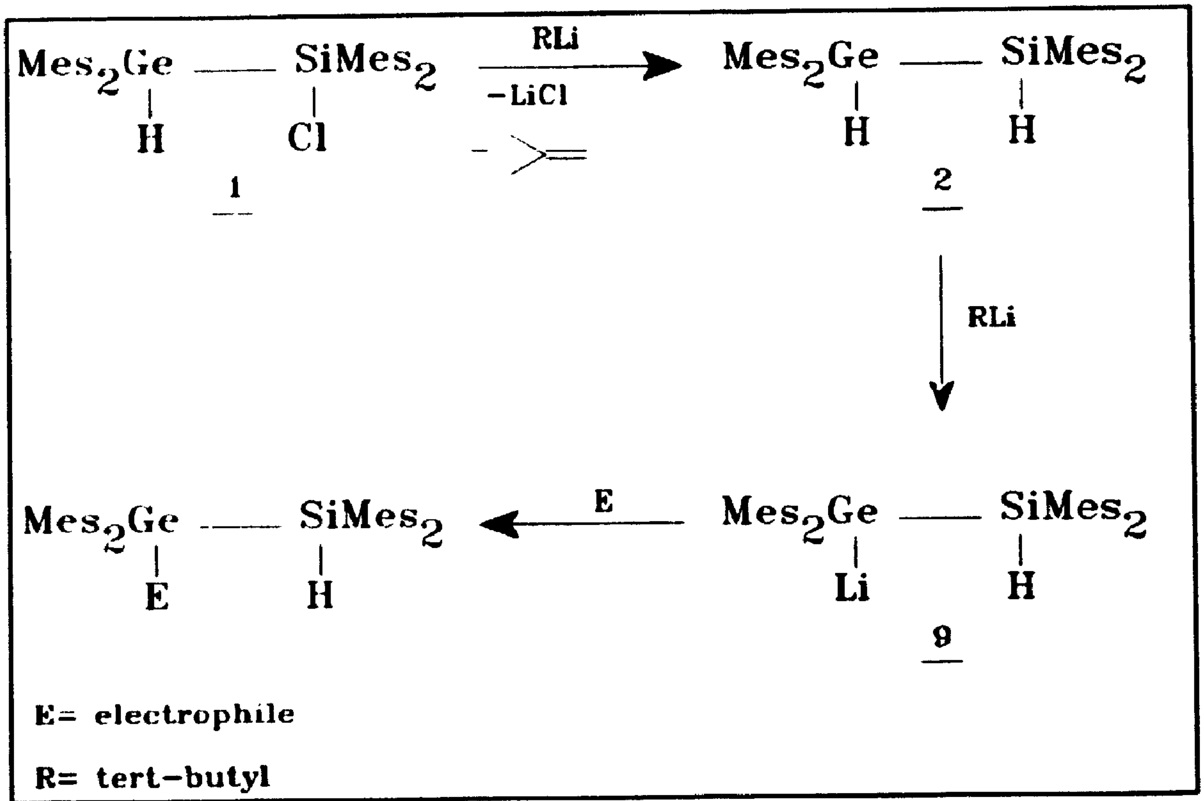


Figure 2-15: Possible mechanism for the reaction between 1 and base

mechanism is as follows:

i) It was found that the reaction requires two equivalents of *tert*-BuLi to go to completion.

ii) The reduction of silyl chlorides by alkyllithium compounds is known.

It is known that bases (such as Grignard reagents and alkyllithiums) with ß-hydrogens can act as hydride donors. For example, M. Weidenbruch^{12} has found that ^{i}PrLi acts as a hydride donor in the reduction of ^{i}Pr$_2$HSiSiCl^{i}Pr$_2$ to ^{i}Pr$_2$HSiSiH^{i}Pr$_2$ (figure 2-16). A.G. Brook and co-workers^{13} have also proposed that Grignard reagents with a ß-hydrogen can act as a hydride donor as evidenced by the reduction of an acylsilane by ethylmagnesium bromide to an alcohol (after acid work up). A similar reduction is proposed in the reaction between 1 and *tert*-BuLi (figure 2-15, step 1).

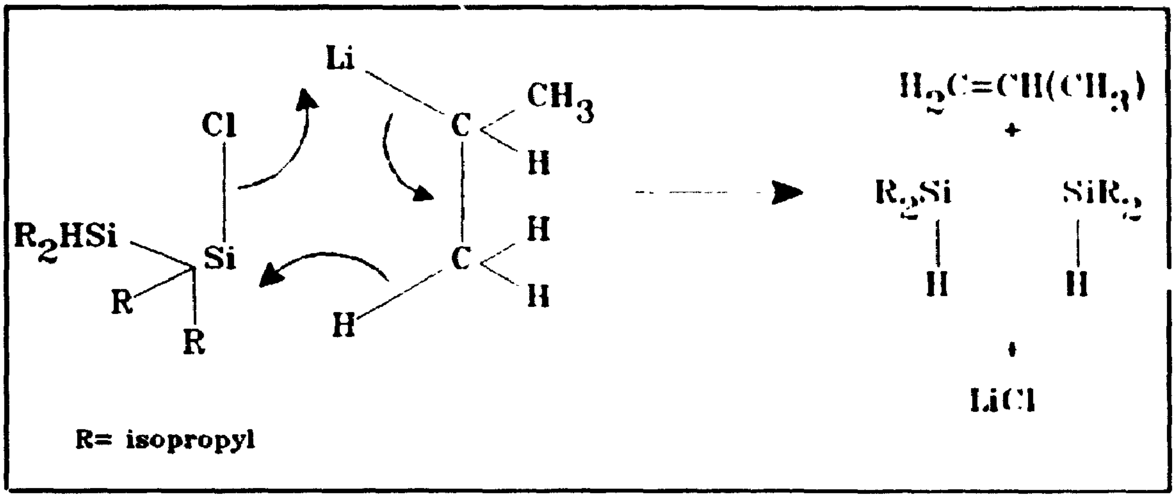


Figure 2-16: Reduction of a chlorosilane by an alkyllithium reagent

iii) By monitoring (using ^{1}H NMR spectroscopy) the reaction between Mes$_2$DGeSiClMes$_2$, 1a, and *tert*-BuLi, it was determined that reduction of 1a by the base to form Mes$_2$DGeSiHMes$_2$, 7, is followed by deprotonation by a second equivalent of base to form $Mes_2HGeSiHMes_2$, 2, upon quenching with H_2O.

iv) Compound 2, synthesized independently, does react with *tert*-BuLi to form the germyl anion which was trapped by MeI to give $Mes_2MeGeSiHMes_2$, 10, in a 60% isolated yield. No compound from the abstraction of a proton by base from the silicon centre was obtained. The lack of product arising from deprotonation at the silicon centre was expected, as metallation of silicon-hydrogen bonds does not take place readily.[14]

A second possible mechanism involves a lithium-chlorine exchange between *tert*-BuLi and 1 to yield the silyl anion 19 which can then rearrange (inter or intramolecularly) to 9 (figure 2-17). This mechanism seemed to be supported by the fact that minor amounts of 8, $Mes_2HGeSiDMes_2$, were trapped when the reaction between 1 and *tert*-BuLi is quenched with D_2O or MeOH-d_4 in under an hour. However, this mechanism is not supported by the following observations:

i) the silyl anion could not be trapped with MeI under conditions similar to those used in the trapping reactions with MeOH-d_4 or D_2O. The product obtained was $Mes_2(Me)GeSiHMes_2$, 10,

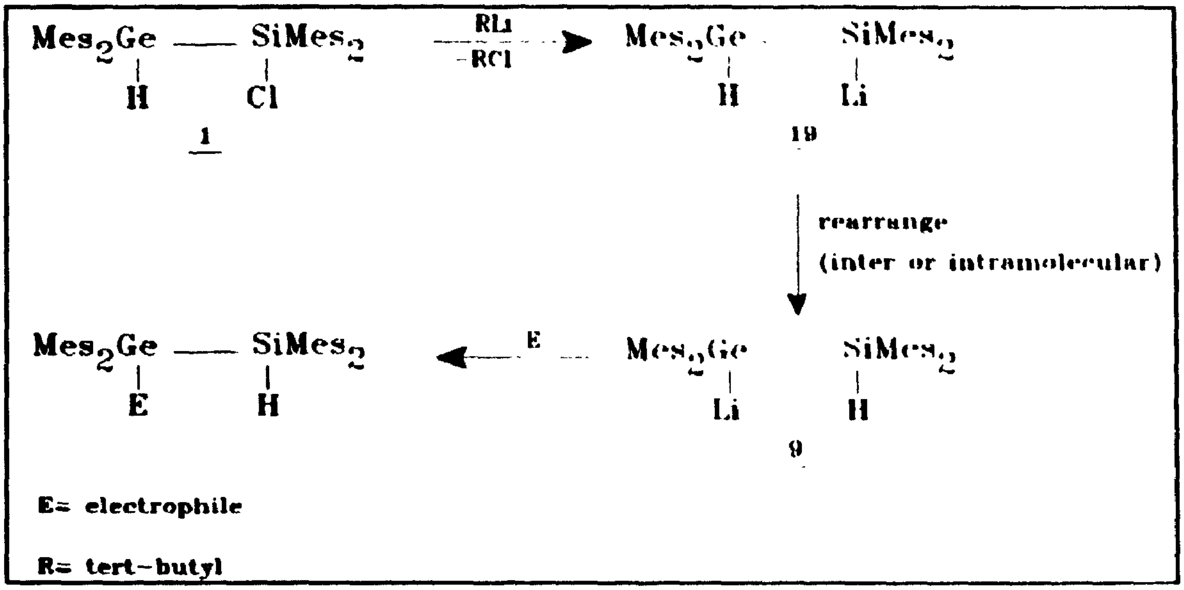


Figure 2-17: Possible mechanism for the reaction between 1 and base

ii) when the reaction between *tert*-BuLi and $Mes_2DGeSiClMes_2$, 1a, was quenched with MeI, the product obtained was 10; no deuterium containing product was obtained, i.e. $Mes_2MeGeSiDMes_2$,

and,

iii) lithium-halogen exchanges between alkyllithiums and chlorosilanes are not common

The mechanism for the formation of minor amounts of compound $Mes_2HGeSiDMes_2$, 8, is not known at this time. It does not seem likely that:

i) Compound 8 is formed by the trapping of $Mes_2HGeSiLiMes_2$, 19, as this anion was not trapped by MeI.

and,

ii) Compound 8 is formed by a radical/radical anion pathway as no signal, which disappeared over time, was observed in an epr spectrum of the reaction between 1 and *tert*-BuLi.

A final mechanism, similar to that proposed by Satgé[15,16] for the formation of Bis_2HMCHR_2 from Bis_2FMCHR_2 (M = Sn or Ge, CR_2 = fluorenylidene, Bis = $(Me_3Si)_2HC$; figure 2-18), involving the formation of a germasilene by dehydrochlorination, followed by a single electron transfer from one equivalent of base, and finally, abstraction of a hydrogen from solvent, has been eliminated since no deuterium incorporation was observed when the reaction was carried out in THF-d_8.[17]

In summary, the addition of *tert*-BuLi to 1 in THF in the cold (-23°C) followed by warming to room temperature yields a red-brown solution, which upon treatment with MeOH, D_2O (or MeOH-d_4), MeI, Me_3SiCl and $PhCH_2Br$ gave $Mes_2HGeSiHMes_2$, 2, $Mes_2DGeSiHMes_2$, 7, $Mes_2MeGeSiHMes_2$, 10, $Mes_2(SiMe_3)GeSiHMes_2$, 12, or $Mes_2BrGeSiHMes_2$, 15 respectively. A probable route to the intermediate germyl anion $Mes_2LiGeSiHMes_2$, 9 is by reduction of 1 with one equivalent of *tert*-BuLi to form $Mes_2HGeSiHMes_2$, 2, followed by deprotonation by a second equivalent base to form the germyl anion 9. Also obtained from the treatment of 1 and base were Mes_2HGeMe, 11,

$Mes_2HGe(SiMe_3)$, 13, and $Mes_2HGe(CH_2Ph)$, 16, which are derived from the cleavage of the central silicon-germanium bond. From the above discussion, it is apparent that the desired reaction (i.e. metallation at the germanium centre followed by elimination of lithium chloride) had not occurred. Thus, alternative approaches to the elimination reaction were investigated. This investigation included the systematic study of the following variables on the reaction between 1 and base:

i) influence of the solvent,

ii) nature of the leaving group,

iii) nature of the base,

iv) influence of the size of the ligands at the germanium centre.

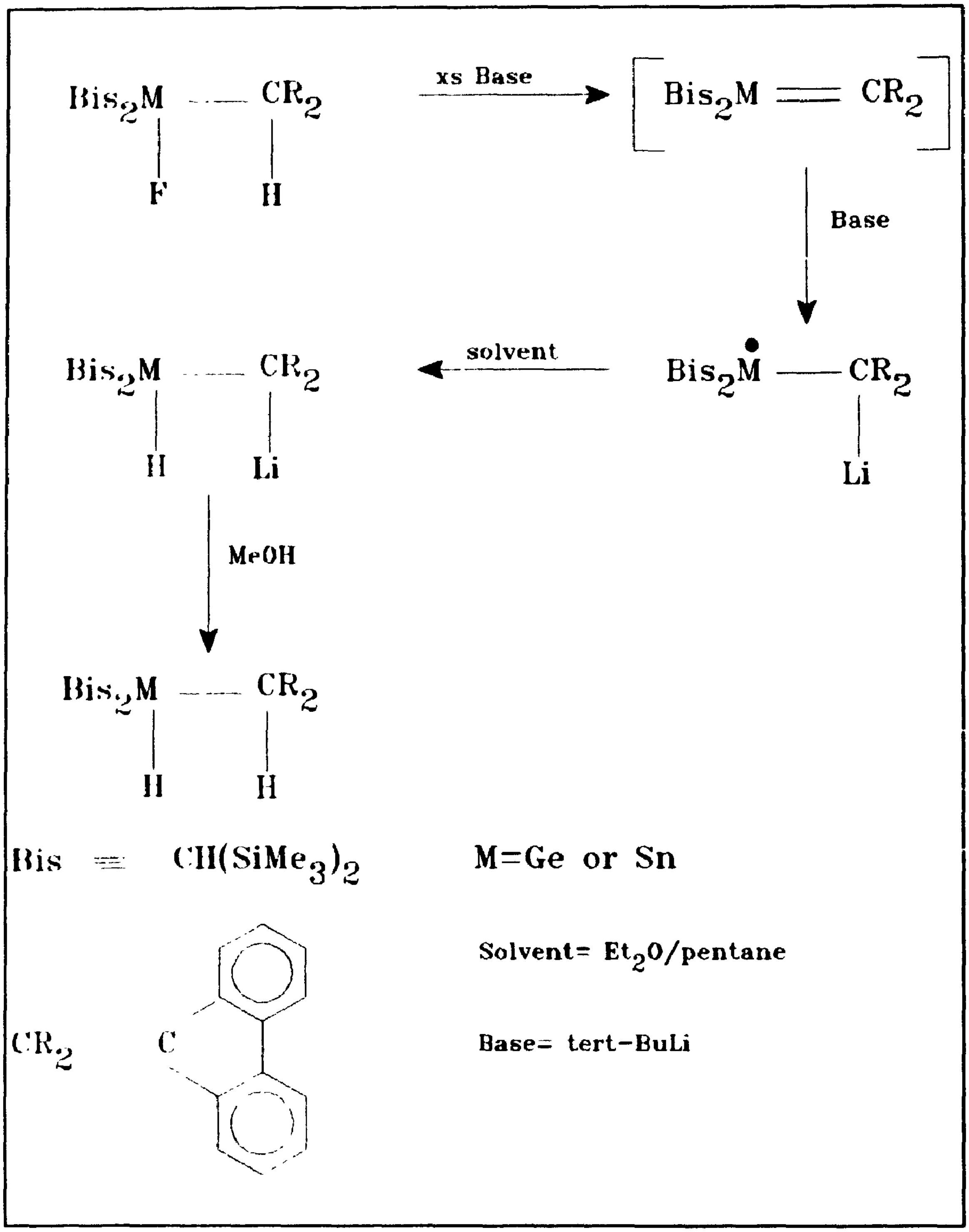
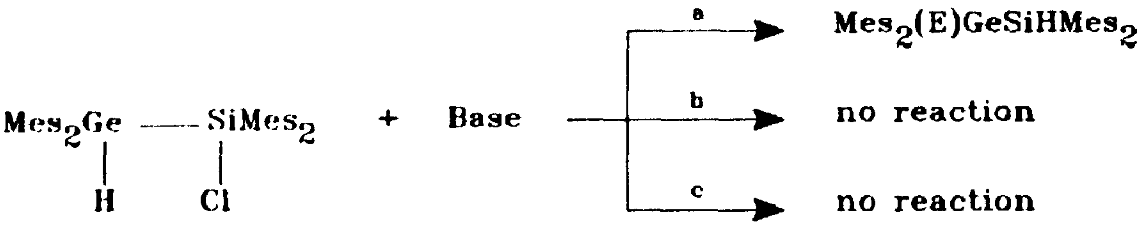


Figure 2-18: Preparation of metallanes from halometallanes

2.3 EFFECT OF SOLVENT ON THE REACTION BETWEEN $Mes_2HGeSiClMes_2$, 1, AND *tert*-BuLi

Changes in solvent can produce changes in the reactivity of organometallic reagents; for example, the reactivity of alkyllithium reagents is known to decrease when there is a change in solvent from a coordinating to a non-coordinating one.[18] Also, J. Satgé and co-workers[4,15,19,21] have found that the use of hydrocarbon solvents increases the yields of germaphosphenes, germenes, etc. obtained by ß-elimination reactions. The observations listed above suggest that a ß-elimination of HX from 1 may be possible using hydrocarbon solvents. However, when *tert*-BuLi was added to 1 in pentane/Et_2O, the starting material was recovered in good yield. As noted in section 2.1.2., when $Is_2HGeSiClMes_2$, 3, was reacted with *tert*-BuLi in refluxing cyclohexane, 1-(diisitylgermyl)-1-mesityl-4,6-dimethyl-1-siladihydrobenzocyclobutene, 4 (isityl = 2,4,6-triisopropylphenyl) was the product obtained. Under similar conditions, however, the addition of base to 1 did not yield such a product; the starting material was recovered in moderate yield (57%). When the solvent was changed from THF to the less basic Et_2O, no reaction was observed when *tert*-BuLi was added to 1 (figure 2-19). The results obtained from changing the solvent suggest that for any reaction to occur between 1 and *tert*-BuLi, THF needs to be employed as solvent. However, the desired reaction does not occur and a change in the solvent



a= 1)THF 2)Electrophile

b= Diethyl ether

c= Cyclohexane or diethyl ether/pentane

E= electrophile

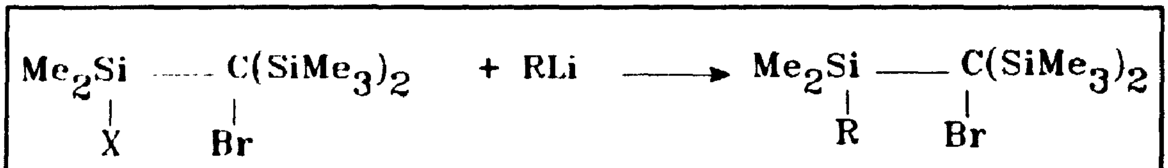
Base= tert-BuLi

Figure 2-19: Reaction between 1 and base in various solvents

does not appear to change the course of the reaction; rather it stops any reaction.

2.4 ATTEMPTED SYNTHESIS OF $Mes_2HGeSiFMes_2$, 20

The reaction of 1 and *tert*-BuLi in THF resulted in the reduction of 1 to 2 after work up. This is believed to occur by first, reduction of the silyl chloride to a silane followed by proton abstraction from germanium to give the germyl anion 9 which could be subsequently trapped with a proton source. In order for an elimination to occur, metallation at the germanium centre must occur first, followed by the β-elimination. A change in the solvent failed to bring about the desired abstraction reaction; in fact, no reaction occurred when the solvent was changed to either a hydrocarbon or Et_2O. An alternative approach to the germasilene involved changing the leaving group on silicon such that lithiation at germanium occurs first. Thus, we examined the possibility of changing the leaving group on 1. J. Satgé[4,19] has suggested that the use of fluorine as opposed to other halogens in reactions to form doubly bonded compounds involving group 14 elements eliminates side reactions such as lithium-halogen exchanges and direct alkylation (when the base used is *tert*-BuLi). J. Satgé[20,21] also observed that the yield of $Mes_2Ge=PAr$ is better when $Mes_2FGePHAr$ (Ar = 2,4,6-tri-*tert*-butylphenyl) is used as the precursor as compared to the chloro derivative. However, it must be noted that the bases used in the reactions with the chloro derivatives were trimethylmethylenephosphorane ($Me_3P=CH_2$) or 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) and not *tert*-BuLi which was used in the reaction with the fluorinated derivative. Similar observations have been made by Wiberg and co-workers:[22,23] alkylation of $Me_2XSiCBr(SiMe_3)_2$ (X = I,Br,Cl) by PhLi or BuLi is eliminated on going from the iodo-, bromo-, or chloro- to the fluoro derivative (figure 2-20). In addition to the above reasons, use of the smaller fluorine as compared with the larger chlorine as the leaving group should decrease the steric hindrance towards attack of the base at the Ge-H. Therefore, our attention was turned to the synthesis of $Mes_2HGeSiFMes_2$, 20.



$$\mathrm{Me_2Si(X){-}C(SiMe_3)_2Br} + \mathrm{RLi} \longrightarrow \mathrm{Me_2Si(R){-}C(SiMe_3)_2Br}$$

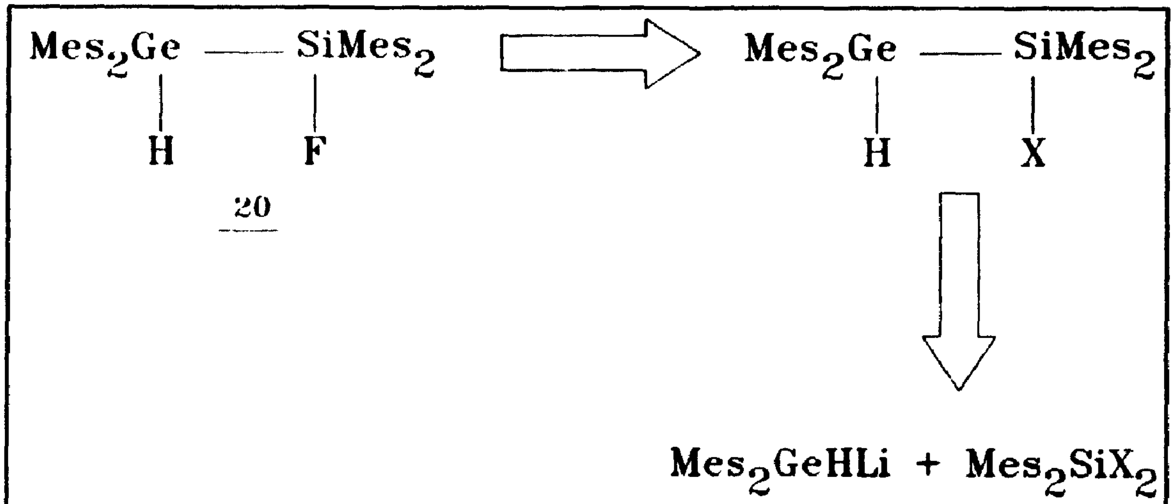
R-Li=PhLi or BuLi; X=I,Br,Cl

When X=F, no alkylation

Figure 2-20: Alkylation of halosilanes

There were two synthetic pathways envisioned for the preparation of compound 20:

Pathway 1) coupling of the appropriate silicon and germanium moieties (figure 2-21),



20

$$\mathrm{Mes_2Ge(H){-}SiMes_2F} \Longrightarrow \mathrm{Mes_2Ge(H){-}SiMes_2X} \Longleftarrow \mathrm{Mes_2GeHLi} + \mathrm{Mes_2SiX_2}$$

X= leaving group other than fluorine

Figure 2-21: A synthetic route to 20

or,

Pathway 2) by fluorination of 1 (figure 2-22).

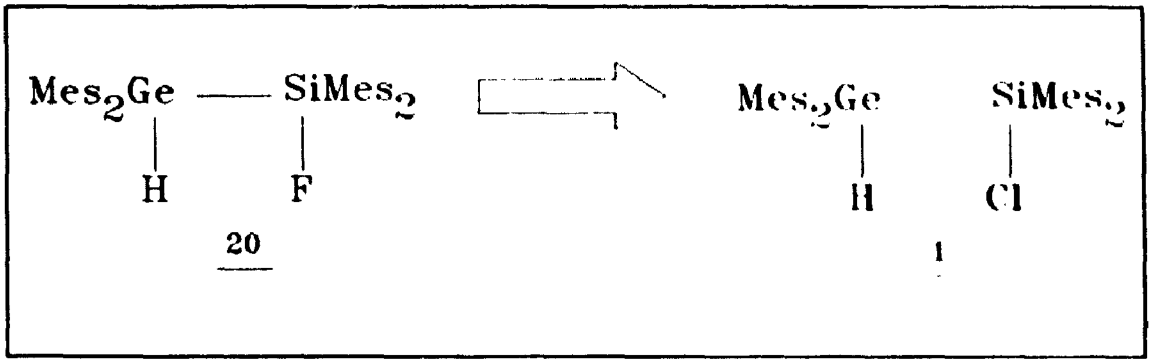


Figure 2-22: A synthetic route to 20

2.4.1. Coupling Of Mes_2HGeLi and Mes_2SiX_2

All attempts to couple Mes_2HGeLi and Mes_2SiF_2[24] were unsuccessful. When the solvent used was THF, the products isolated included Mes_2GeH_2, Mes_2FSi(*tert*-Bu) and $(Mes_2FSi)_2O$ (figure 2-23). Mes_2GeH_2 is most likely formed by the quenching of unreacted Mes_2HGeLi by acid during work up, or to a lesser extent, originates from unreacted starting material. Mes_2SiF(*tert*-Bu) could be formed by a nucleophilic attack of excess *tert*-BuLi on Mes_2SiF_2. The disiloxane, $(Mes_2FSi)_2O$, is likely to be formed by the reaction of Mes_2SiF_2 with water during work up to form Mes_2FSiOH and then condensation of the silanol to form the disiloxane.[25] From the products obtained, two things were obvious: no coupling had occurred between Mes_2HGeLi and Mes_2SiF_2 and secondly, the excess *tert*-BuLi used in the preparation of Mes_2HGeLi readily reacted with Mes_2SiF_2. In an attempt to reduce the reactivity of the *tert*-BuLi

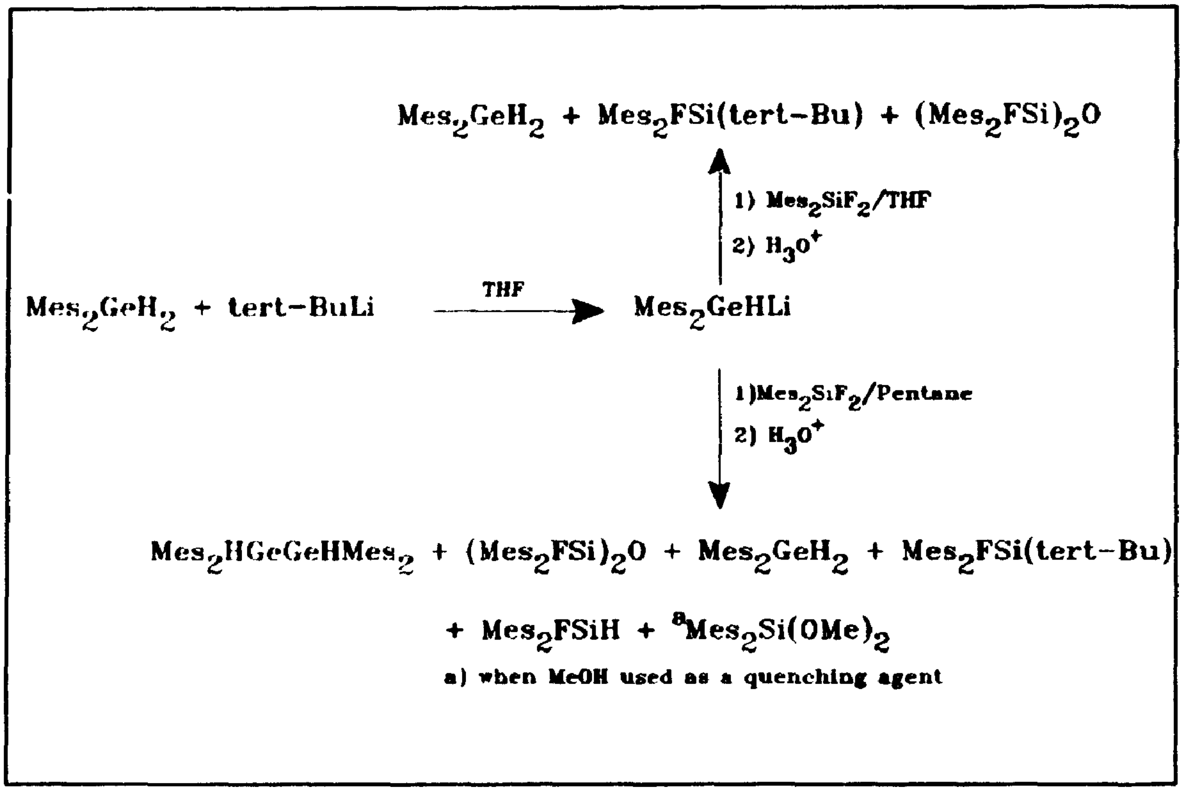


Figure 2-23: Attempted coupling of Mes_2GeHLi and Mes_2SiF_2

(towards Mes_2SiF_2) the solvent was changed from THF to a hydrocarbon; Mes_2HGeLi was added to Mes_2SiF_2 in pentane. Again, coupling to give $Mes_2HGeSiFMes_2$, 20, did not occur, but rather the following compounds were isolated: Mes_2GeH_2, Mes_2FSi(*tert*-Bu), Mes_2SiHF, $Mes_2HGeGeHMes_2$, $(Mes_2FSi)_2O$, and $Mes_2Si(OMe)_2$ when MeOH was used as a quenching agent (figure 2-23). The formation of Mes_2GeH_2, Mes_2FSi(*tert*-Bu), and $(Mes_2FSi)_2O$ has been discussed above. Mes_2SiHF may be formed by the reaction between *tert*-BuLi and Mes_2SiF_2 with the base acting as a hydride donor, forming isobutene, LiF, and Mes_2SiHF (figure 2-24). The reduction of a silicon-fluorine bond, by a base with

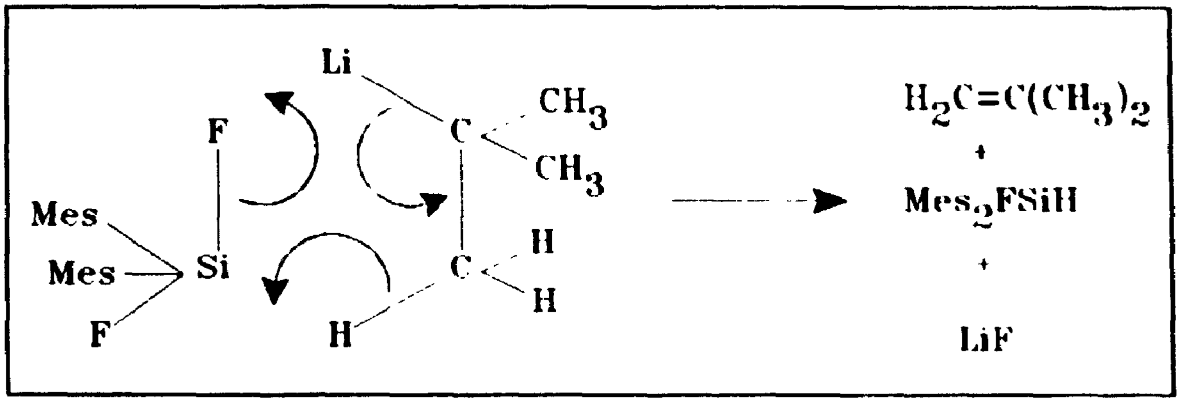


Figure 2-24: Reduction of a fluorosilane by an alkyllithium reagent

β-hydrogens, though not as common as the reduction of silicon-chlorine bonds, has been postulated in the reaction between SiF_4 and excess *tert*-BuLi.[26] The product from the reaction was $(tert\text{-}Bu)_3SiH$. $Mes_2Si(OMe)_2$ is most probably formed as a result of nucleophilic attack by MeOH (or methoxide) on Mes_2SiF_2. The digermane, $Mes_2HGeGeHMes_2$, is most likely formed in the first step of the reaction by the coupling of Mes_2HGeLi and Mes_2GeH_2. Cross and Glockling[27] have suggested that digermanes can be formed by the reaction between germyllithiums and germanes: they have proposed that the reaction between Ph_2HGeLi and Ph_2GeH_2 results in the formation of $Ph_2HGeGeHPh_2$.

The failure of Mes_2HGeLi to couple to Mes_2SiF_2 required an alternative pathway for the synthesis of <u>20</u> was necessary. The route selected is shown in figure 2-25.

Silicon-oxygen bonds can easily be transformed into halosilanes by reacting alkoxysilanes (or even silanols) with hydrohalic acids (figure

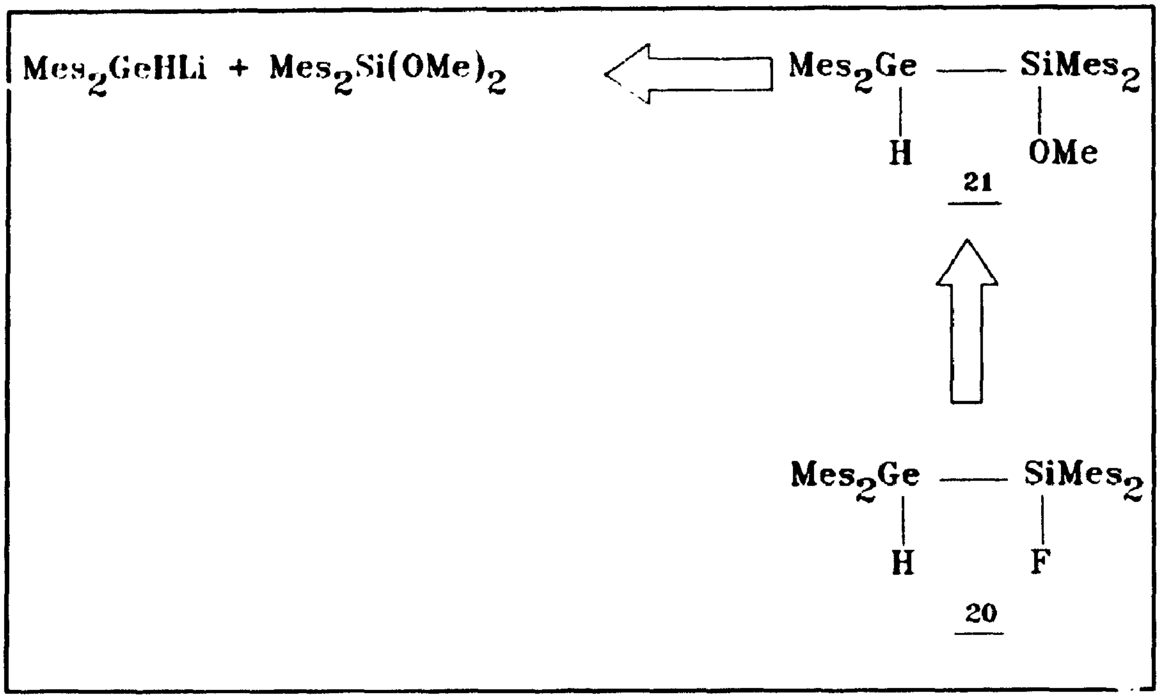


Figure 2-25: Pathway for the synthesis of 20

2-26).[78] Fluorosilanes are made by reacting organosilicon alkoxides with aqueous or aqueous-alcoholic hydrogen fluoride. The alkoxysilyl

$$Me_3SiOR + HCl \longrightarrow Me_3SiCl + ROH\ (or\ RCl)$$

$$^iPr_2Si(OEt)_2 + 2HF \longrightarrow {}^iPr_2SiF_2$$

$$Ph_3Si(OEt) + HF \longrightarrow Ph_3SiF$$

$R=$ Bu, $PhCH_2CH_2$, $PhCH_2CH_2CH_2$

Figure 2-26: Preparation of halosilanes from organosilicon alkoxides compounds are prepared quite easily by the reaction between chlorosilanes and either alcohols or sodium alkoxides. When alcohols are used to prepare organosilicon alkoxides, bases such as pyridine or dimethylaniline are frequently added to the reaction mixtures to remove the hydrogen chloride that is formed. Alternatively, the hydrogen chloride can be removed by heating in a high-boiling hydrocarbon solvent if a base is not present in the reaction mixture. If the hydrogen chloride is not removed, it can react with

i) the alcohol to give the alkyl chloride and H_2O, and the latter may then hydrolyze the organosilicon alkoxide or chloride,

or,

ii) the alkoxysilyl compound to give back the alcohol and a silyl chloride.

$Mes_2Si(OMe)_2$ can be prepared by two methods:

i) refluxing Mes_2SiCl_2 in a mixture of MeOH, Et_3N and benzene, (This is not the preferred method because the yield of $Mes_2Si(OMe)_2$ varies greatly),

or by,

ii) refluxing $Mes_2ClSiOMe$, which is prepared by refluxing Mes_2SiCl_2 in MeOH and Et_3N, with NaOMe.

However, no reaction occurred between Mes_2HGeLi and $Mes_2Si(OMe)_2$, even when the reaction mixture was warmed to 40°C. Since Mes_2HGeLi can be coupled to a chlorosilane (namely Mes_2SiCl_2), we explored the possibility of synthesizing the methoxy derivative of 1, $Mes_2HGeSi(OMe)Mes_2$, 21, by the coupling of Mes_2HGeLi and $Mes_2ClSiOMe$; however, this reaction did not proceed as expected. Mes_2GeH_2 and $Mes_2HGeGeHMes_2$ were the only products isolated from the reaction mixture indicating that no coupling occurred between the germyllithium and the chlorosilane.

The above results indicated that coupling did not occur between Mes_2GeH_2 and a difunctional silane, Mes_2SiXY (where X = F when Y = F, or X = OMe or Cl when Y = OMe). This coupling was necessary to form 20 by pathway 1. Therefore, the second pathway (i.e. converting 1 directly into 20) to synthesize $Mes_2HGeSiFMes_2$ was investigated (figure 2-22).

2.4.2. Attempted Fluorination Of $Mes_2HGeSiClMes_2$, 1

There are several reagents available for the conversion of a chlorosilane into a fluorosilane.[29] Ammonium hexafluorosilicate,which has been used by R. Damrauer and co-workers[24] to convert bulky chlorosilanes into fluorosilanes, was used in an attempt to fluorinate 1. However, no reaction was observed between 1 and $(NH_4)_2SiF_6$, even upon refluxing or sonication.

Silver tetrafluoroborate is a reagent that has also been used to convert bulky halosilanes into their fluorinated analogs. C. Eaborn and co-workers have used this reagent to convert TsiSiMeHI[30] (Tsi = $(Me_3Si)_3C$) and $(Me_3Si)_2C(GeMe_3)(SiMe_2Br)$[31] into their fluoro derivatives. Attempts to synthesize 20 using this reagent were unsuccessful. When Et_2O was used as the solvent, no reaction occurred between 1 and the reagent; on changing the solvent to CH_2Cl_2 two compounds were isolated: recovered starting material and Mes_2SiF_2 (figure 2-27). The formation of the difluorosilane indicated that the reaction conditions were too harsh resulting in the regioselective cleavage of the silicon-germanium bond; the product derived from the germanium part of the molecule was not detected.

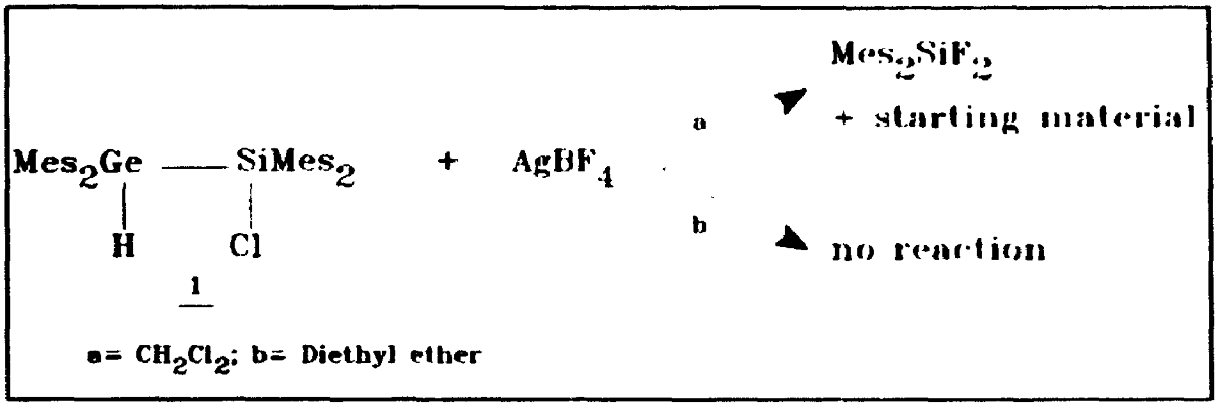


Figure 2-27: Reaction between 1 and $AgBF_4$

Cesium fluoride is another reagent that was used in the attempted fluorination of 1. R. West and co-workers[32] converted $RClSi(SiMe_3)_2$ (R = 2,4,6-triisopropylphenyl) into the fluoro analog using this reagent (figure 2-28). When the reaction between CsF and 1 was carried out in

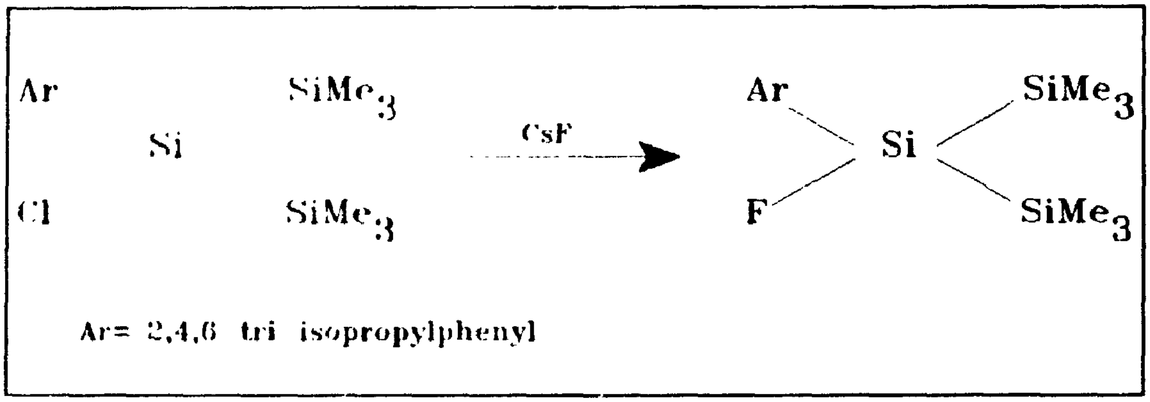


Figure 2-28: Reaction between a chlorosilane and CsF

refluxing THF, the compounds obtained after work up were Mes_2GeH_2 and Mes_2HSiF (again indicating regioselective cleavage of the central silicon-germanium bond of 1); at room temperature, no reaction occurred.

One final attempt to form 20 paralleled the method described in section 2.4.1., to transform chlorosilanes first into a methoxysilane using $Et_3N/MeOH$ followed by conversion into the fluorosilane using HF/H_2O. However, refluxing 1 in $Et_3N/MeOH$ did not yield $Mes_2HGeSi(OMe)Mes_2$, 21.

In summary, the preparation of 20 by various methods were all unsuccessful (figure 2-29). When Mes_2GeHLi was added to Mes_2SiF_2, no evidence for any coupling product was obtained. A similar coupling reaction, attempted by B. Joseph[5], between Is_2GeHLi, and Mes_2SiF_2 resulted in the isolation of Is_2GeH_2, Mes_2SiF(*tert*-Bu) and Mes_2SiF_2. No coupling was observed when Mes_2HGeLi was added to either

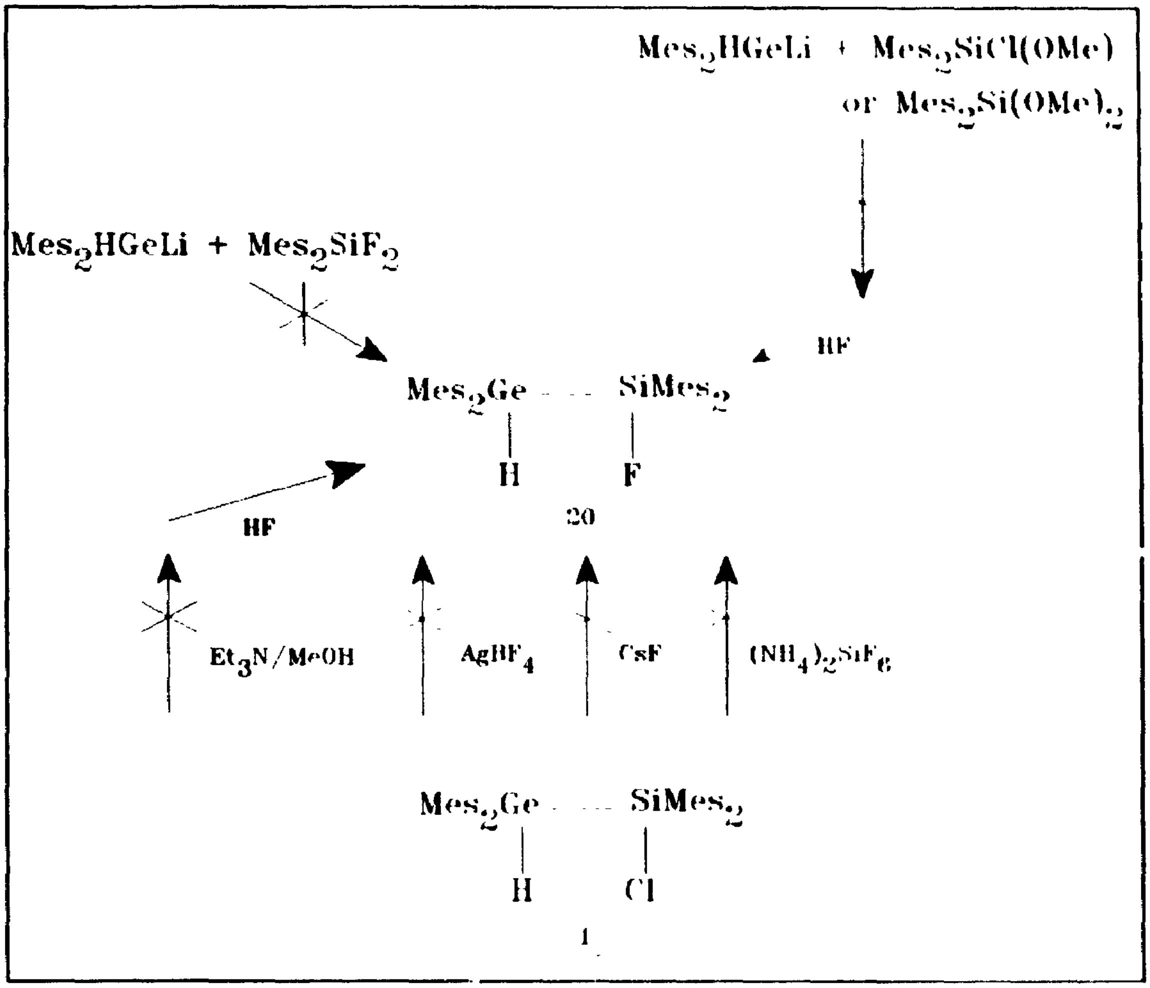


Figure 2-29: A summary of the attempts to prepare 20

$Mes_2Si(OMe)_2$ or $Mes_2ClSiOMe$. Also, attempts to convert 1 into 20 using $(NH_4)_2SiF_6$ or $AgBF_4$ (in Et_2O) failed. When 1 was stirred with $AgBF_4$ in CH_2Cl_2, cleavage of the central silicon-germanium bond to form Mes_2GeH_2 and Mes_2HSiF was observed. A similar observation was made when the fluorinating agent was CsF.

The steps required for the preparation of a germasilene by ß-elimination are metallation of the germanium-hydrogen bond followed by elimination of a lithium salt. This has not been the case in the reaction of 1 and *tert*-BuLi in THF: metallation at the germanium centre occurs after reduction of the silicon-chlorine bond. Changing the solvent to a hydrocarbon or diethyl ether resulted in no reaction occurring between 1 and the base. Attempts to study the effect of leaving group on metallation was not possible as the appropriate substrate could not be synthesized. Another variable that could influence the first step of the elimination is the nature of the base. *Tert*-BuLi not only can act as a base, but also as a reducing agent as has been observed. In order to overcome the latter mode of reactivity, a base that has no tendency to act as a hydride donor should be employed. Thus, 1 was treated with different bases in an attempt to synthesize a stable germasilene by dehydrochlorination.

2.5. EFFECT OF BASE

The types of base that were used in an attempt to prepare a germasilene by a β-elimination reaction were alkyllithiums (i.e. BuLi, PhLi, *tert*-BuLi), nitrogen bases (i.e. LDA) as well as hydride bases (i.e. KH).

2.5.1. Alkyllithium Bases

On treating 1 with *tert*-BuLi the novel germyl anion 9 (p.32), was formed. This anion could be trapped by various electrophiles. Similar results were obtained when the substrate was $Is_2HGeSiClMes_2$, 3. In an attempt to use a more reactive base,[33] a complexing agent, TMEDA, was added to BuLi. However, the conditions were too harsh resulting in the regioselective cleavage of the central silicon-germanium bond to give, upon work up, Mes_2GeH_2, Mes_2HSiBu and $Mes_2ClSiBu$. As noted previously (section 2.2), organometallic reagents with ß-hydrogens can act as hydride donors, and thus to overcome this, a base with no ß-hydrogens, PhLi, was used; however, no reaction occurred between this base and 1 in THF.

2.5.2. Hydride Bases

Corriu and Guerin[34] have found that germanium-hydrogen bonds can be cleaved by alkali metal hydrides. Thus, potassium hydride was used as the base in an attempted reaction with 1. No reaction was observed between 1 and KH in cyclohexane; the starting material was recovered in good yield. The lack of reaction between the base and 1 is most probably the result of the heterogeneous nature of the reaction mixture; under these conditions, 1 would have to be adsorbed onto the solid surface before any reaction with the base could occur. Because of the steric bulk of 1, it is not surprising that no reaction occurred between these two compounds.

2.5.3. Nitrogen Bases

If a base is to react with 1, it should have the following properties:

i) strong enough to remove a proton from germanium,

ii) bulky (this is necessary to prevent any nucleophilic substitution reactions),

and,

iii) should not have a tendency to act as a hydride donor.

A family of bases which has such characteristics is amides, LDA being the most commonly used in this family of bases.

Surprisingly, the addition of LDA to 1 in THF, followed by quenching with MeI resulted in the formation of $Mes_2(Me)GeSiHMes_2$, 10. When Me_3SiCl was used as the quenching agent, the products isolated (in minor amounts) were $Mes_2HGe(SiMe_3)$,13, and $Mes_2(Me_3Si)GeSiHMes_2$, 12. The isolation of 10 and 12 implied that the reaction between 1 and LDA in THF is similar to the reaction between 1 and *tert*-BuLi in THF (i.e. reduction at the silicon centre was followed by proton abstraction at the germanium centre. See figure 2-13). A search of the literature revealed that LDA has indeed been found to be able to act as a hydride donor; it can reduce both aldehydes[35] and ketones[36,37,38] to the corresponding alcohols.

From the above results (figure 2-30), it can be concluded that bases such as LDA and *tert*-BuLi are not only strong enough to remove a

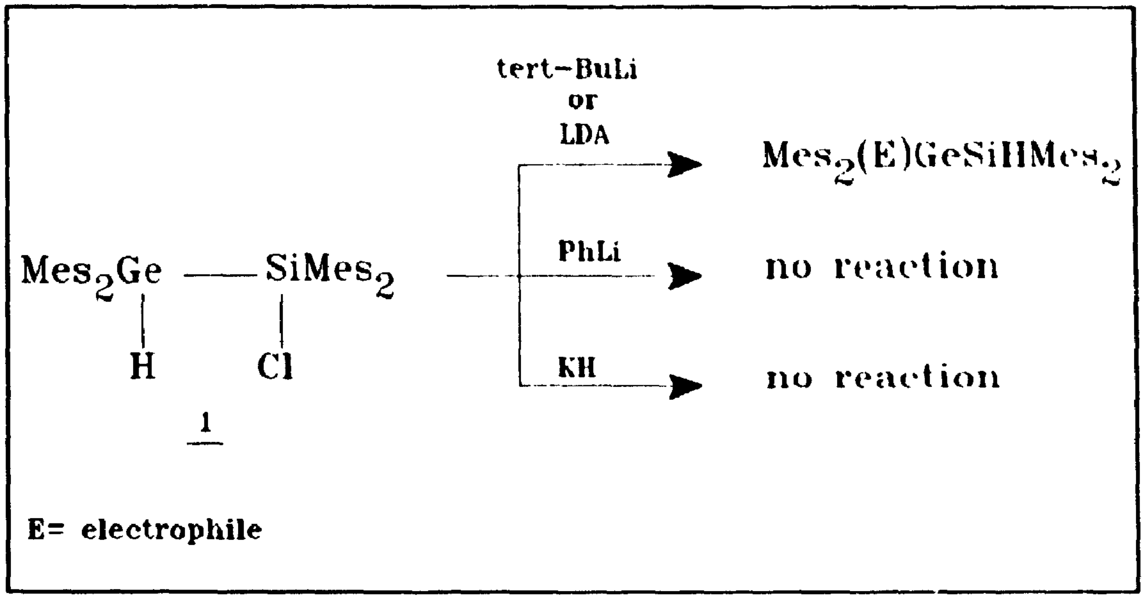


Figure 2-30: Reaction between 1 and various bases

proton from germanium, they have the disadvantage of acting also as reducing agents. Thus, the goal of first metallating the germanium centre of 1 was not achieved with a change in base.

2.6 SYNTHESIS AND REACTIONS OF $Ph_2HGeSiClMes_2$, 22

Attempts to prepare a stable germasilene by the elimination of hydrogen halide from 1 were unsuccessful. The reaction between 1 and *tert*-BuLi in THF resulted in the formation of a germyl anion, $Mes_2LiGeSiHMes_2$, 9, which could be trapped by various electrophiles. No reaction occurred when the solvent was changed to Et_2O or hydrocarbons. However, when the base was changed to LDA, the germyl anion 9, $Mes_2LiGeSiHMes_2$, was also formed. In hydrocarbon solvents, no reaction was observed to occur between starting material and a variety of bases. Attempts to change the leaving group on 1 to fluorine were not successful, and thus, the effect of changing the nature of the leaving group on the reaction between *tert*-BuLi and 1 was not explored. When the ligands on germanium were changed to the larger 2,4,6-triisopropylphenyl (isityl) group, a germyl anion similar to 9 was trapped.[5] From the results obtained so far, it can be concluded that changing the base or solvent in the reaction between 1 and base did not result in the isolation of a germasilene. The lack of success in the preparation of a germasilene may be due to the following:

i) the silicon-chlorine bond is easily reduced by *tert*-BuLi to a silicon-hydrogen bond,

and,

ii) the large groups on germanium may prevent the base from removing the proton at this centre.

Attempts to remedy the first problem were not successful as the appropriate germasilene precursor, $Mes_2HGeSiFMes_2$, 20, could not be synthesized. A possible solution to the second problem is to decrease the size of the ligands on germanium allowing easier access by the base to the germane hydrogen. Thus, the aryl groups on germanium were changed from mesityl to phenyl.

The synthesis of $Ph_2HGeSiClMes_2$, 22, paralleled that of

$Mes_2HGeSiClMes_2$, 1: Ph_2GeH_2, which is prepared by the reaction of PhMgBr and $GeCl_4$ followed by lithium aluminum hydride reduction (figure 2-31), was treated with *tert*-BuLi to give Ph_2HGeLi.[2] Addition of the

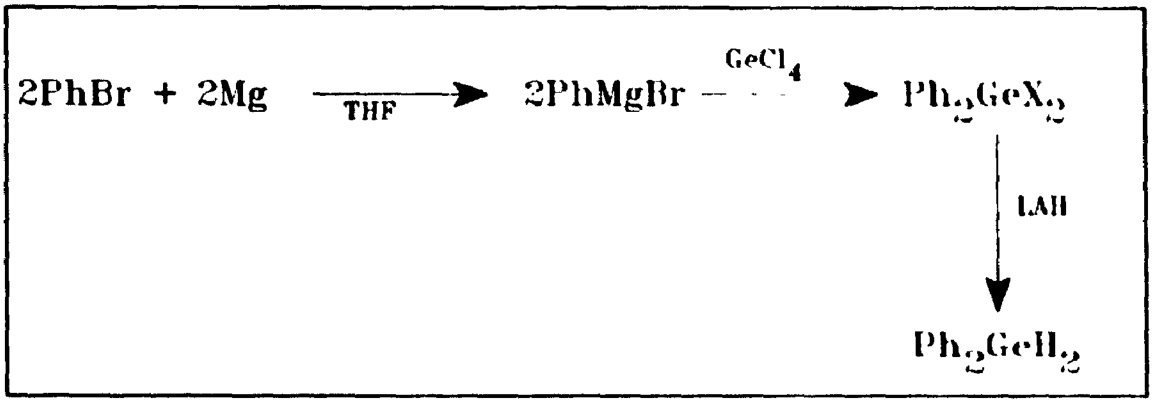


Figure 2-31: Preparation of Ph_2GeH_2

germyllithium reagent to a solution of Mes_2SiCl_2 in THF yielded $Ph_2HGeSiClMes_2$, 22, $(Ph_2HGe)_2SiMes_2$, 23, and unreacted starting materials (figure 2-32). Purification of the crude reaction mixture was very difficult; not only was there a significant loss of material (presumably by hydrolysis) during chromatographic separation of the products, cleavage of the mesityl groups was also observed. The latter was overcome by using alumina rather than silica gel as the adsorbent. However, the use of alumina did not prevent the loss of material. In addition, 22 could not be separated from all the by-products. Thus, in some cases, the crude product was used as the substrate in reactions where 22 was required.

Treatment of a solution of 22 in THF with *tert*-BuLi yielded

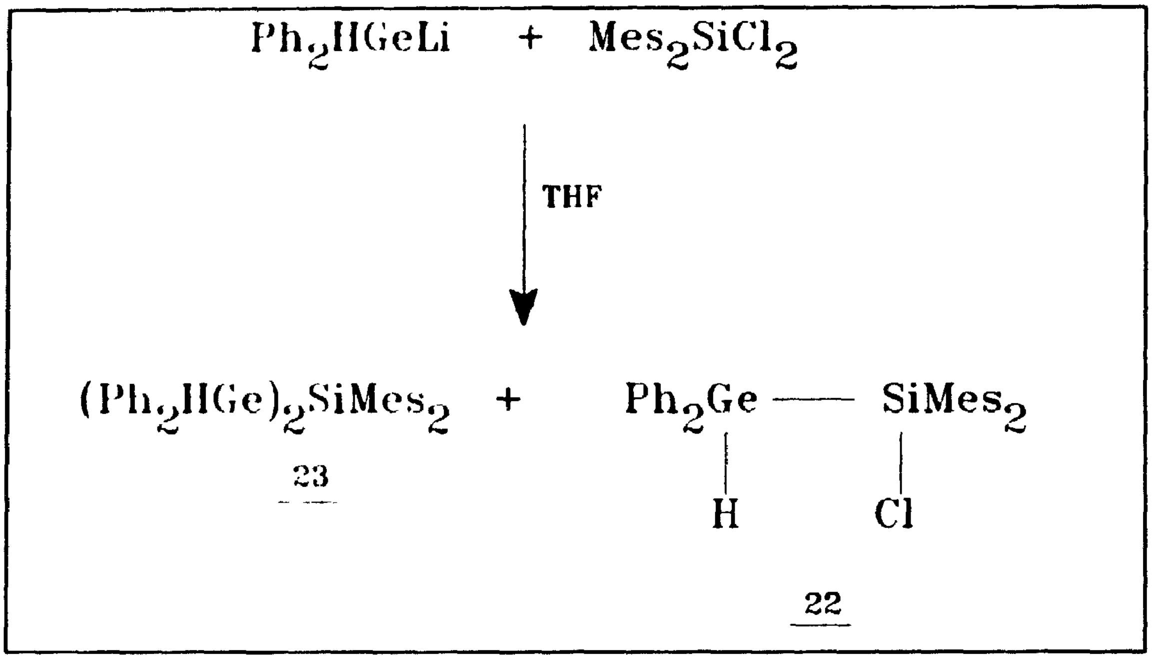
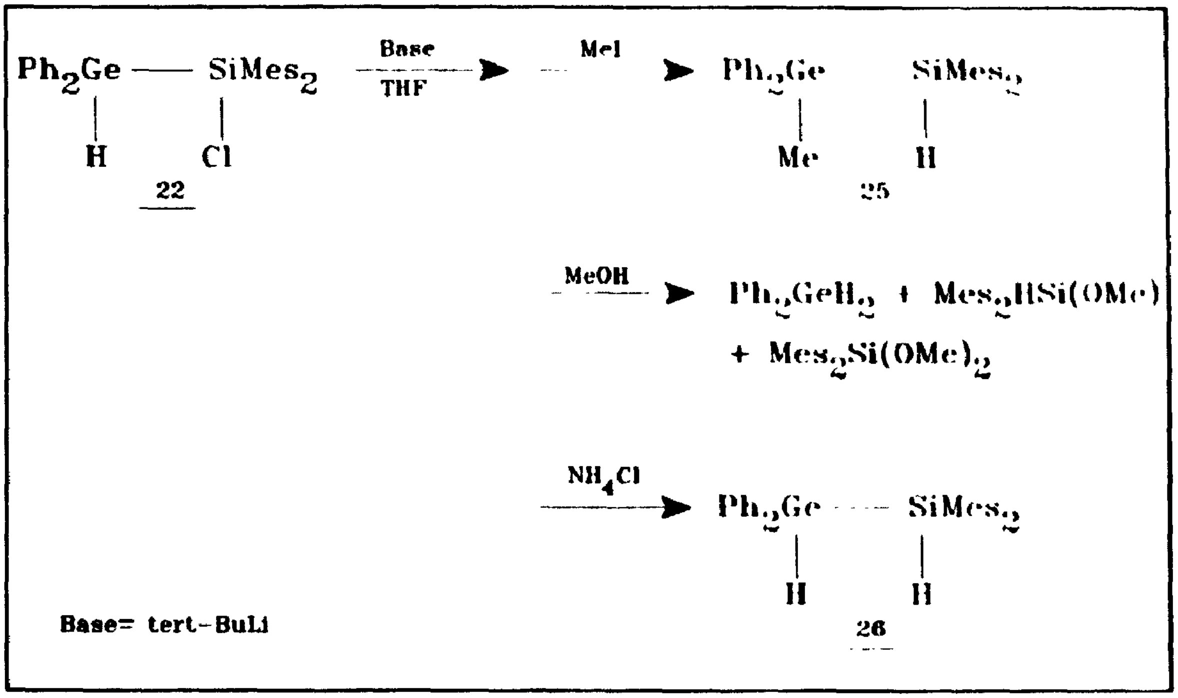


Figure 2-32: Preparation of 22 and 23

$Ph_2(Me)GeSiHMes_2$, 20, upon quenching with MeI (figure 2-33). When MeOH was used as the quenching agent, however, the products isolated were Ph_2GeH_2, $Mes_2HSiOMe$ and a trace amount of $Mes_2Si(OMe)_2$ (figure 2-33). Ph_2GeH_2 and $Mes_2HSiOMe$ most likely arise from the cleavage of $Ph_2HGeSiHMes_2$, 26, by LiOMe. Again, cleavage of the central germanium-silicon bond appears to be regioselective. $Ph_2HGeSiHMes_2$ is formed most likely by the trapping of the germyl lithium, $Ph_2LiGeSiHMes_2$, 24, by MeOH (figure 2-34). $Mes_2Si(OMe)_2$ is formed most likely via a nucleophilic attack by methoxide ion on $Mes_2HSiOMe$. The possible sources of LiOMe are:

i) the reaction between excess *tert*-BuLi and MeOH. This



Base= tert-BuLi

Figure 2-33: Quenching the reaction between 1 and base with different electrophiles

source of LiOMe could be reduced by using less base; however, this was not easily done because in some cases impure 22 was used. This made it difficult to determine the exact amount of base required for the reaction with 22,

ii) the reaction between 24 and MeOH (figure 2-34, step 1), and,

iii) the reaction between Mes_2HGeLi and MeOH (figure 2 34, step 3).

The result obtained when MeOH is used to quench the reaction between 22 and *tert*-BuLi is different from compound 1: the quenching of the

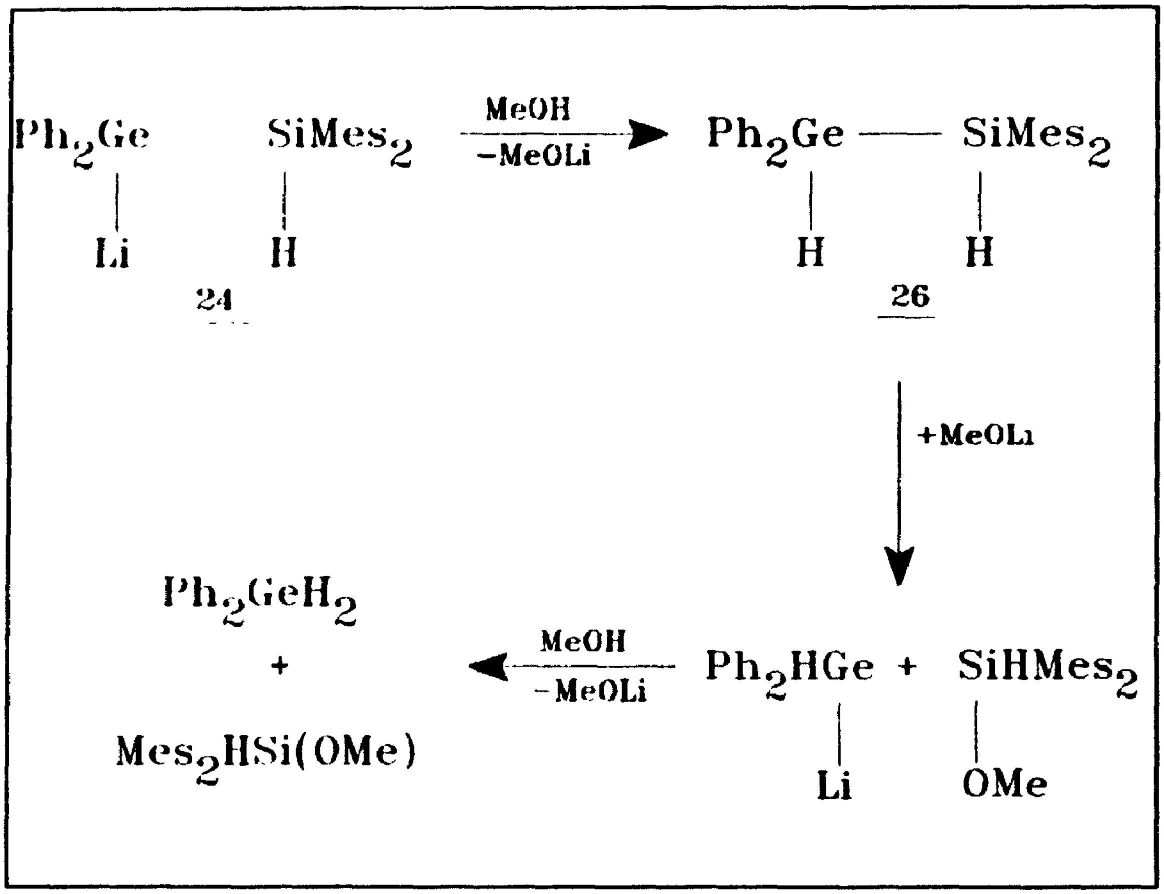


Figure 2-34: Reaction between 24 and MeOH

reaction between 1 and *tert*-BuLi with MeOH yields $\mathrm{Mes_2HGeSiHMes_2}$, 2. The difference is most likely due to the ligands used: in 1 the larger mesityl groups on germanium prevent nucleophilic attack of methoxide ion at silicon, whereas in 26 the smaller phenyl groups on germanium makes it easier for such an attack to occur. Thus, a proton source with a less nucleophilic conjugate base was needed to prepare 26. When the reaction between 22 and *tert*-BuLi was quenched with saturated $\mathrm{NH_4Cl}$ solution, the product obtained was $\mathrm{Ph_2HGeSiHMes_2}$, 26 (figure 2-33).

The above results suggest that the immediate precursor to compounds 25 and 26 was the germyl anion $Ph_2LiGeSiHMes_2$, 24. The mechanism envisaged for the formation of 24 is analogous to that proposed for the reaction between 1 and *tert*-BuLi; 22 is first reduced by the base to form the dihydro compound 26. A second equivalent of base may then abstract a proton from the germanium atom to give the germyllithium compound 24 (figure 2-35).

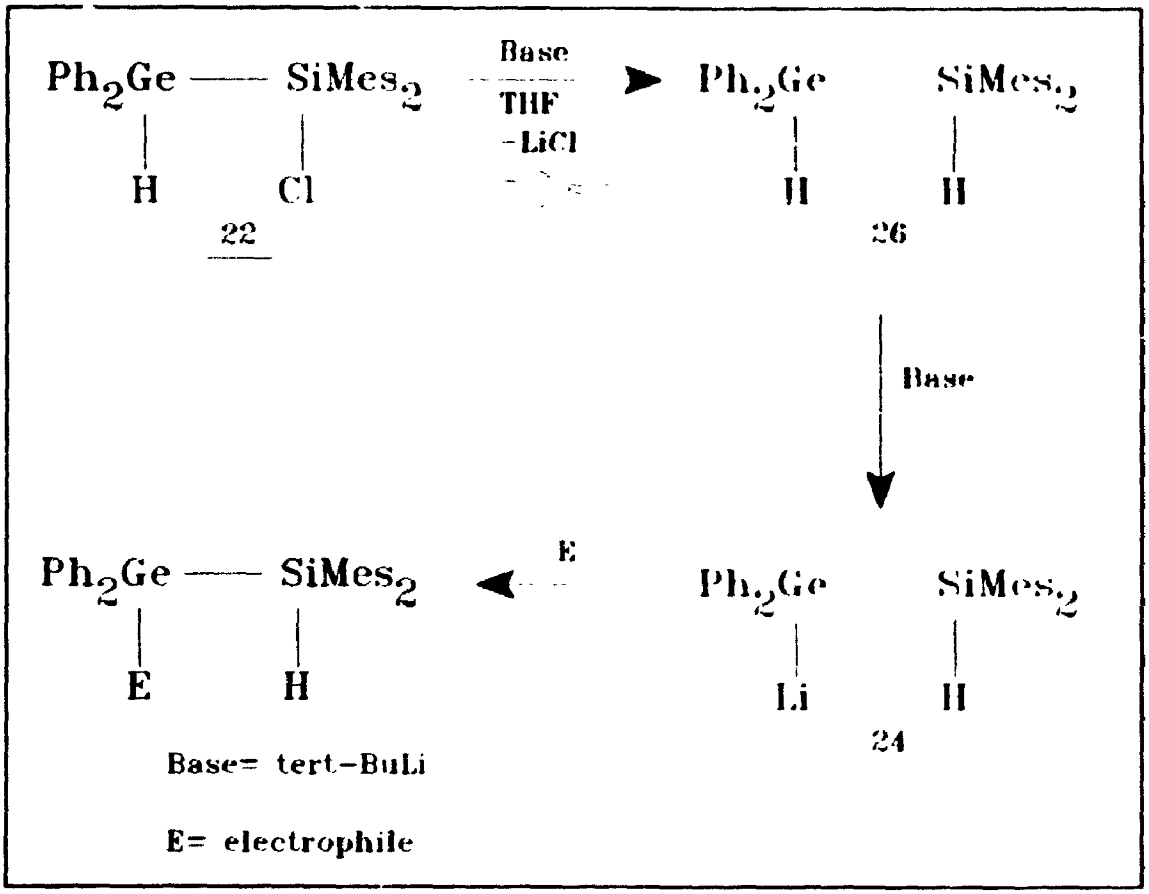


Figure 2-35: Possible mechanism for the reaction between 22 and base

When the solvent was changed to cyclohexane or pentane, the reaction between 22 and *tert*-BuLi, followed by quenching with MeI gave 25. Quenching the same reaction with MeOH gave Ph_2GeH_2, $Mes_2Si(OMe)_2$ and $Ph_2HGeSi(OMe)Mes_2$, 27. Considering that the product formed by the addition of MeOH to $Mes_2Ge=SiMes_2$ is $Mes_2HGeSi(OMe)Mes_2$,[11] the isolation of 27 suggested that a germasilene had been formed in the reaction between 22 and base in a hydrocarbon solvent. However, quenching the reaction with MeOH-d_4 gave $Ph_2HGeSi(OCD_3)Mes_2$ rather than $Ph_2DGeSi(OCD_3)Mes_2$. This suggests that compound 27 results from the reaction of MeOH or methoxide with unreacted 22 (i.e. substitution of chloride by OMe) rather than by addition of MeOH across the double bond of a germasilene. Compound 1 did not react with *tert*-BuLi in hydrocarbon solvents.

It is evident that there are similarities as well as differences in the reaction between *tert*-BuLi and either 1 or 22. Both compounds react with the base in THF to give germyl anions, $Mes_2LiGeSiHMes_2$, 9 and $Ph_2LiGeSiHMes_2$, 24. Both these anions can be trapped by electrophiles; however, with MeOH, 1 gives the dihydro compound 2 whereas in compound 22 cleavage of the central silicon-germanium bond is observed. Also compound 1 does not react with base in hydrocarbons; the opposite is true for 22. In hydrocarbons, the treatment of 22 with *tert*-BuLi does not yield a germasilene, but rather the same products that are obtained when THF is used as solvent. The germyl anions 9 and 24 are most likely formed by the same mechanism: reduction of the silicon-chlorine bond is followed by proton abstraction from the germanium atom.

2.7 ATTEMPTS TO PREPARE $Ph_2HGeSiFMes_2$, 28

As seen in section 2.6, reducing the steric bulk at germanium did not yield a stable germasilene, rather a germyl anion, 24, was obtained from the reaction between *tert*-BuLi and 22 in THF or hydrocarbons. This result also suggested that the silicon-chlorine bond is easily reduced. It was hoped that this could be overcome by changing the halogen from chlorine to fluorine. Although attempts to prepare fluorinated analogs of 1 and 3 were unsuccessful, it was hoped that 22 being less crowded at the silicon atom would be easier to fluorinate.

All attempts to prepare $Ph_2HGeSiFMes_2$, 28, were unsuccessful (figure 2-36). The coupling reaction between Ph_2HGeLi and Mes_2SiF_2 in THF was attempted and was found to be unsuccessful. The products obtained were Ph_2GeH_2, Mes_2SiF_2 and Mes_2FSi(*tert*-Bu).

An attempt to fluorinate 27 using aqueous hydrofluoric acid was not possible because $Ph_2HGeSi(OMe)Mes_2$, 27, could not be prepared by the coupling of Ph_2GeH_2 and $Mes_2Si(OMe)Cl$. Although compound 27 was prepared previously (section 2.6), the yield was very low and therefore, this was not a viable source of this compound.

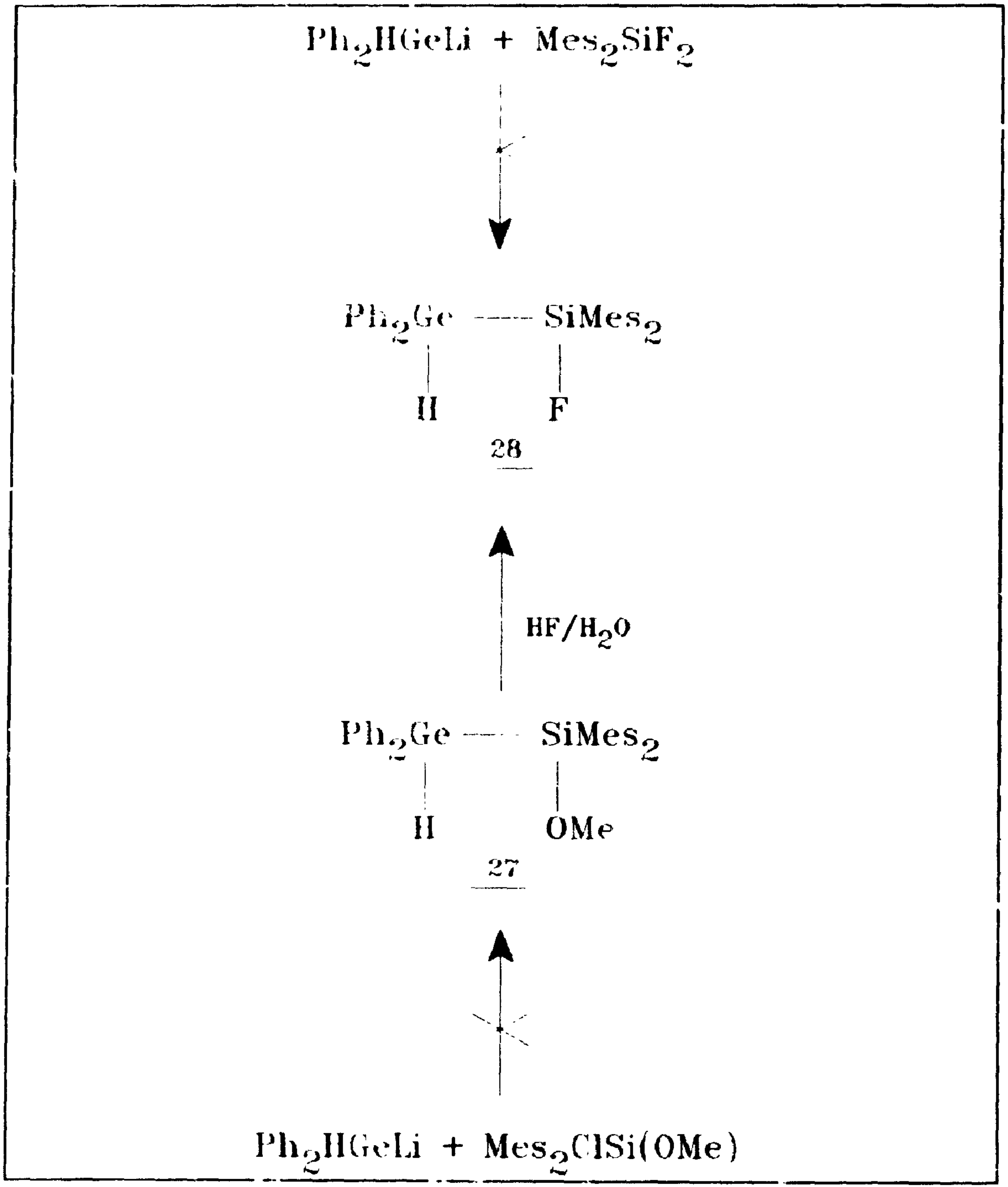


Figure 2-36: A summary of the results to prepare <u>28</u>

2.8 PRODUCTS OBTAINED FROM THE CLEAVAGE OF THE GERMANIUM-SILICON BOND

It is evident from the results obtained so far that cleavage of the central germanium-silicon bond appears to be regioselective; attack by the nucleophile (i.e. F^-, *tert*-Bu^-, Bu and MeO) at the silicon centre results in the formation of a silane and a germyl anion. This germyl anion has, in some cases, been trapped by electrophiles such as MeI, Me_3SiCl and $PhCH_2Br$. The regioselectivity of the cleavage reactions may be a result of the following:

i) germanium, being lower in the periodic table, forms a more stable anion than silicon,

and,

ii) silicon, being more electropositive than germanium, is more susceptible to attack by the nucleophile.

2.9 REFERENCES

1) Groh, R. *Chemistry 490 Thesis*, University of Western Ontario, **1990**.

2) Castel, A.; Riviere, P.; Satgé, J.; Ko, H. Y. *Organometallics* **1990**, 9, 205-210.

3) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, 3, 793-800.

4) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M. *New J. Chem.* **1989**, 13, 389-398.

5) Joseph, B. *M. Sc. Thesis*, University of Western Ontario, **1992**.

6) Weidenbruch, M.; Schäfers, K. S.; Schaefke, J.; Peters, K.; Schnering, H. G. *J. Organomet. Chem.* **1991**, 415, 343-348.

7) Becker, E.D. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed, Academic Press, Toronto, **1980**, 94.

8) a)Bailey, W. F.; Patricia, J. J.; *J. Organomet. Chem.* **1988**, 352, 1-46.

b)Wittig, G.; Schöllkopf, U. *Tetrahedron* **1958**, 3, 91-93.

9) Tokitoh, N.; Matsumoto, T.; Suzuki, H.; Okazaki, R. *Tetrahedron Lett.* **1991**, 32, 2049-2052.

10) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, 11, 3487-3488.

11) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, 10, 3419-3421.

12) Weidenbruch, M.; Peter, W. *J. Organomet. Chem.* **1975**, 84, 151-163.

13) Brook A.G.; Chiu P.; McClenaghan J.; Lough A.J. *Organometallics* **1991**, 10, 3292-3301.

14) a) Lesbre, M.; Mazerolles, P.; Satgé, J. The Organic Compounds of Germanium J. Wiley and Sons, **1971**, Toronto, 274.

b) Colvin, E. W. Silicon in Organic Synthesis Robert E. Krieger Publishing Company: Malabar, Florida, **1985**, p135.

15) Lazaraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Soufiaoui, M. *Polyhedron* **1991**, 10, 1153-1161.

16) Anselme, G.; Couret, C.; Escudié, J.; Richelme, S.; Satgé, J. *J. Organomet. Chem.* **1991**, 418, 321-328.

17) Baines, K. M.; Groh, R. J.; Joseph, B.; Parshotam, U. R. *Organometallics* **1992**, 11, 2176-2180.

18) a) McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H. R. *J. Am. Chem. Soc.* **1985**, 107, 1810-1815.

b) Petrosyan, V. S.; Reutov, O. A. *J. Organomet. Chem.* **1973**, 52, 307-314.

c) Coates, G. E.; Green, M. L. H.; Wade, K. Organometallic Compounds, vol. 1, London, **1967**, 14-20.

19) Anselme, G.; Couret, C.; Escudié, J.; Richelme, S.; Satgé, J. *J. Organomet. Chem.*, **1991**, 403, 93-100.

20) Escudié, J.; Couret, C.; Satgé, J.; Andrianarison, M.; Andriamizaka, J.D. *J. Am. Chem. Soc.*, **1985**, 107, 3378-3379.

21) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev*, **1990**, 90, 283-319.

22) Wiberg, N.; Preiner, G.; Scheida, O. *Chem. Ber.* **1981**, 114, 2087-2103.

23) Wiberg, N. *J. Organomet. Chem.* **1984**, 273, 141-177.

24) Damrauer R.; Simon R.A.; Kanner B.; *Organometallics* **1988**, 7, 1161-1164.

25) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, 111, 3250-3258.

26) Armitage, D. A. in *Comprehensive Organometallic Chemistry: The Synthesis and Structure of Organometallic Compounds* Eds. Sir G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, Toronto, **1982**, Vol. 2, Chapter 1, p12.

27) Cross R.J.; Glockling F. *J. Organomet. Chem.* **1965**, 3, 146-155.

28) Eaborn, C. *Organosilicon Compounds* Butterworths Scientific Publications, London, **1960**, p 171, 288, 304.

29) Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*, Elsevier Publishing Company, New York, **1967**, p 58-61.

30) Eaborn C.; Reed D.E. *J. Chem. Soc. Perkin Trans II* **1985**, 1687-1693.

31) Eaborn C.; Saxena A.K. *J. Chem. Soc. Perkin Trans II* **1987**, 779-782.

32) Archibald, R. S.; van den Winkel, Y.; Millevolte, A.J.; Despar, M.; West, R. *Organometallics*, **1992**, 11, 3276-3281.

33) Wakefield, B. J. *Organolithium Methods* Academic Press: Toronto, **1988**, p4.

34) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, 197, C19-C21.

35) Majewski, M. *Tetrahedron Lett.* **1988**, 29, 4057-4060.

36) Kowalski, C.; Creary, X.; Rollin, A. J.; Birk, M. C. *J. Org. Chem.* **1978**, 43, 2601-2608.

37) Newcomb, M.; Burchill, M. J. *J. Am. Chem. Soc.* **1984**, 106, 2450-2451.

38) Newcomb, M.; Burchill, M. J. *J. Am. Chem. Soc.* **1984**, 106, 8276-8287.

CHAPTER 3-ATTEMPTED PREPARATION OF A GERMASILENE BY A REDUCTIVE ELIMINATION REACTION

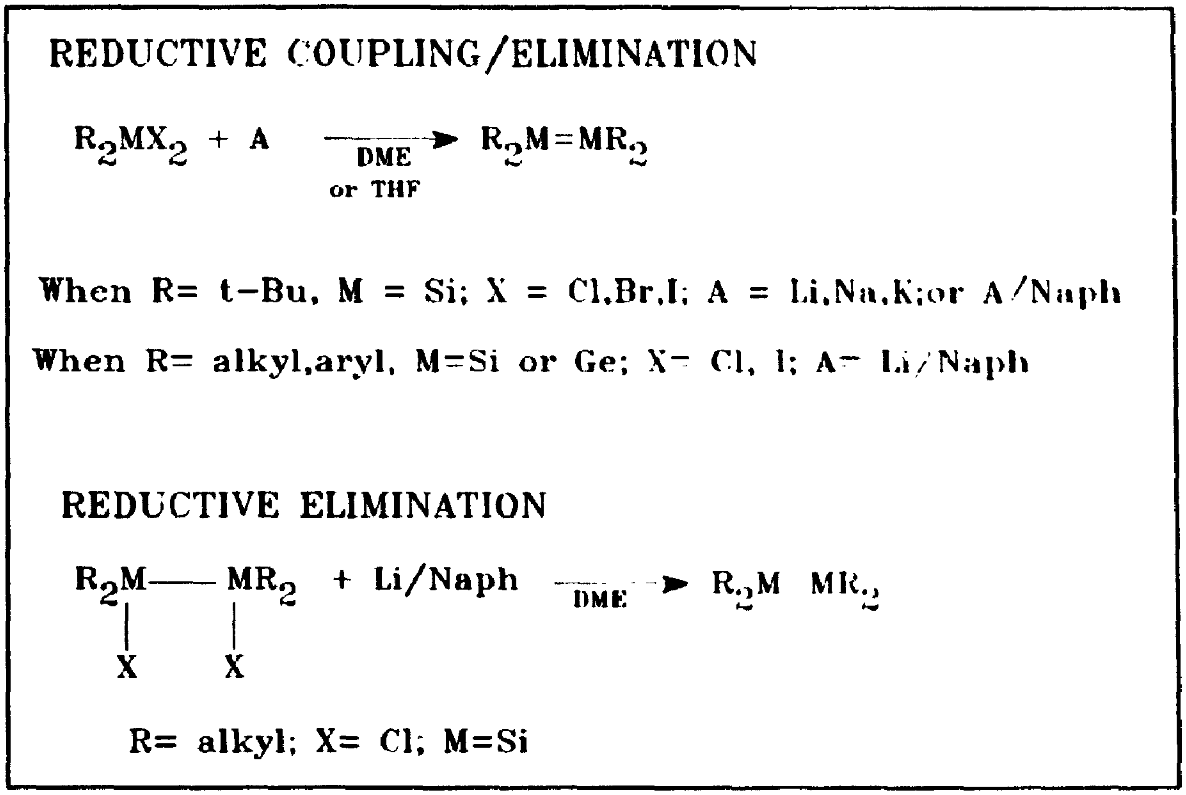
3.1 INTRODUCTION

Attempts to prepare a germasilene by the elimination of HX from $Mes_2HGeSiClMes_2$, 1, using strong bases have so far been unsuccessful. The treatment of 1 with *tert*-BuLi in THF resulted in the formation of the germyl anion $Mes_2LiGeSiHMes_2$, 9, which could be trapped by various electrophiles. A change in solvent to Et_2O or hydrocarbon, or a change in the bulk of the R groups did not result in the isolation of a compound containing the desired silicon-germanium double bond.

In addition to the above method, another possible route to a germasilene is reductive elimination using metals or lithium naphthalenide, LiNp, (method 3, chapter 1, figure 3-1). Although this method has been used to synthesize group 14 dimetallenes (for example, disilenes and digermenes), this method has not been utilized in cases involving heteronuclear systems.

The reagent most commonly used in reductive elimination reactions is LiNp. This reagent is easily prepared by ultrasound irradiation of a solution of lithium and naphthalene in either THF or DME.[1]

In heavy group 14 chemistry, LiNp has also been used in reductive cyclization reactions. For example, LiNp has been used as a reagent in



REDUCTIVE COUPLING/ELIMINATION

$$R_2MX_2 + A \xrightarrow[\text{or THF}]{\text{DME}} R_2M{=}MR_2$$

When R= t–Bu, M = Si; X = Cl,Br,I; A = Li,Na,K;or A/Naph

When R= alkyl,aryl, M=Si or Ge; X= Cl, I; A= Li/Naph

REDUCTIVE ELIMINATION

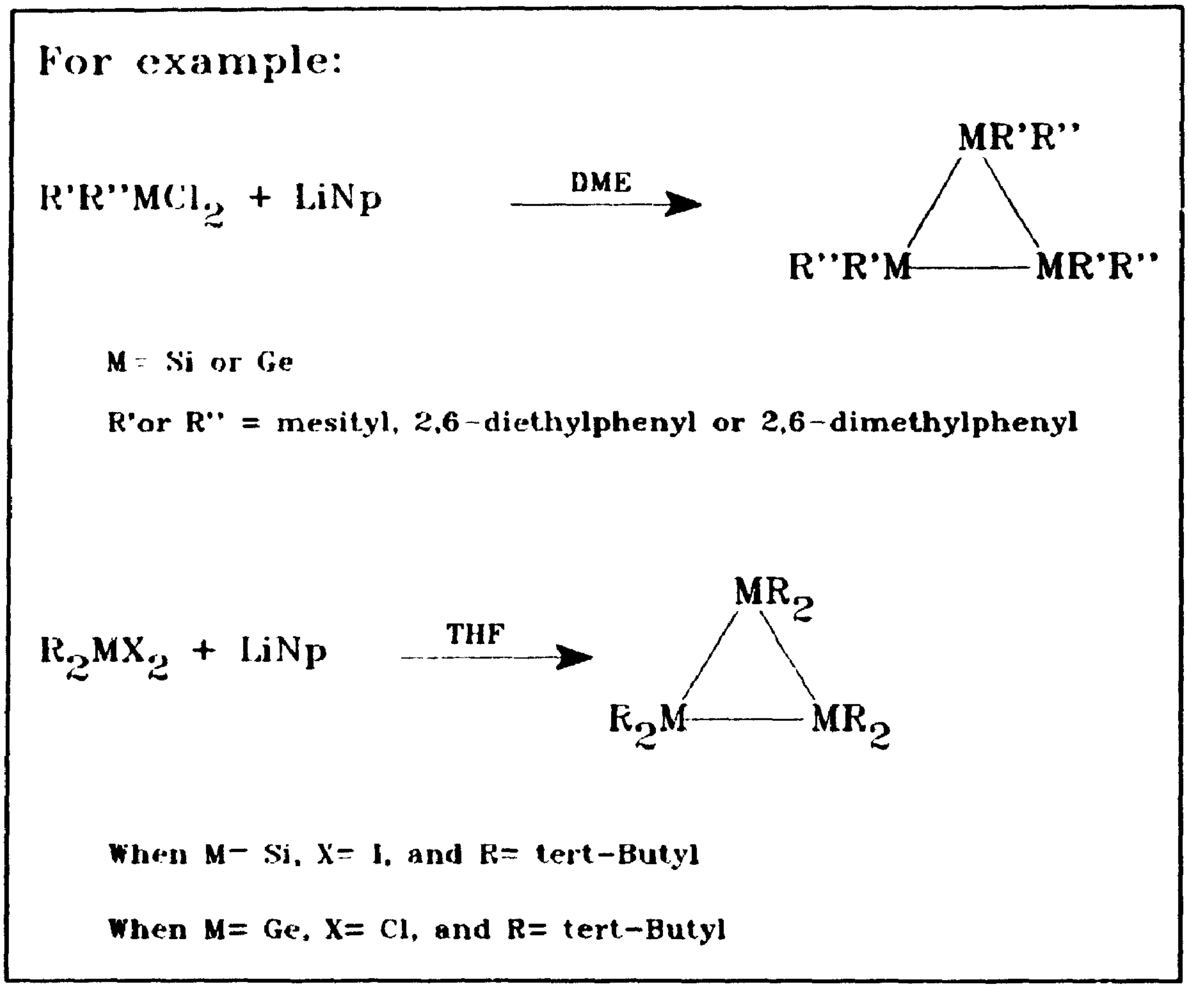
$$\underset{X}{R_2M}\text{—}\underset{X}{MR_2} + \text{Li/Naph} \xrightarrow{\text{DME}} R_2M\ \ MR_2$$

R= alkyl; X= Cl; M=Si

Figure 3-1: Preparation of dimetalienes by reductive coupling/elimination reactions

the preparation of cyclotrimetallanes from dihalometallanes (figure 3-2).[7] The reagent has also been utilized, as stated earlier, in the preparation of dimetallenes from either dihalodimetallanes or dihalometallanes (figure 3-1).[2] It has been suggested by Masamune and co-workers[3] that the steric bulk of the ligands on silicon or germanium determines whether one obtains a cyclometallane (pathway A, figure 3-3) or a dimetallene (pathway B, figure 3-3) on treatment of dihalosilanes or -germanes with LiNp.

The ligands that have been used in the preparations of either



M= Si or Ge

R'or R'' = mesityl, 2,6-diethylphenyl or 2,6-dimethylphenyl

When M= Si, X= I, and R= tert-Butyl

When M= Ge, X= Cl, and R= tert-Butyl

Figure 3-2: Preparation of cyclotrimetallanes

cyclotrimetallanes or dimetallenes include 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl, *tert*-butyl and even bis(trimethylsilyl)methyl; the use of these bulky ligands is necessary to kinetically stabilize the doubly bonded compounds towards dimerization and/or polymerization. The solvent used was either DME or THF. The halogen most commonly used in the reductive coupling and elimination reactions involving LiNp is chlorine; however, in some cases iodine has been used as the halogen. For

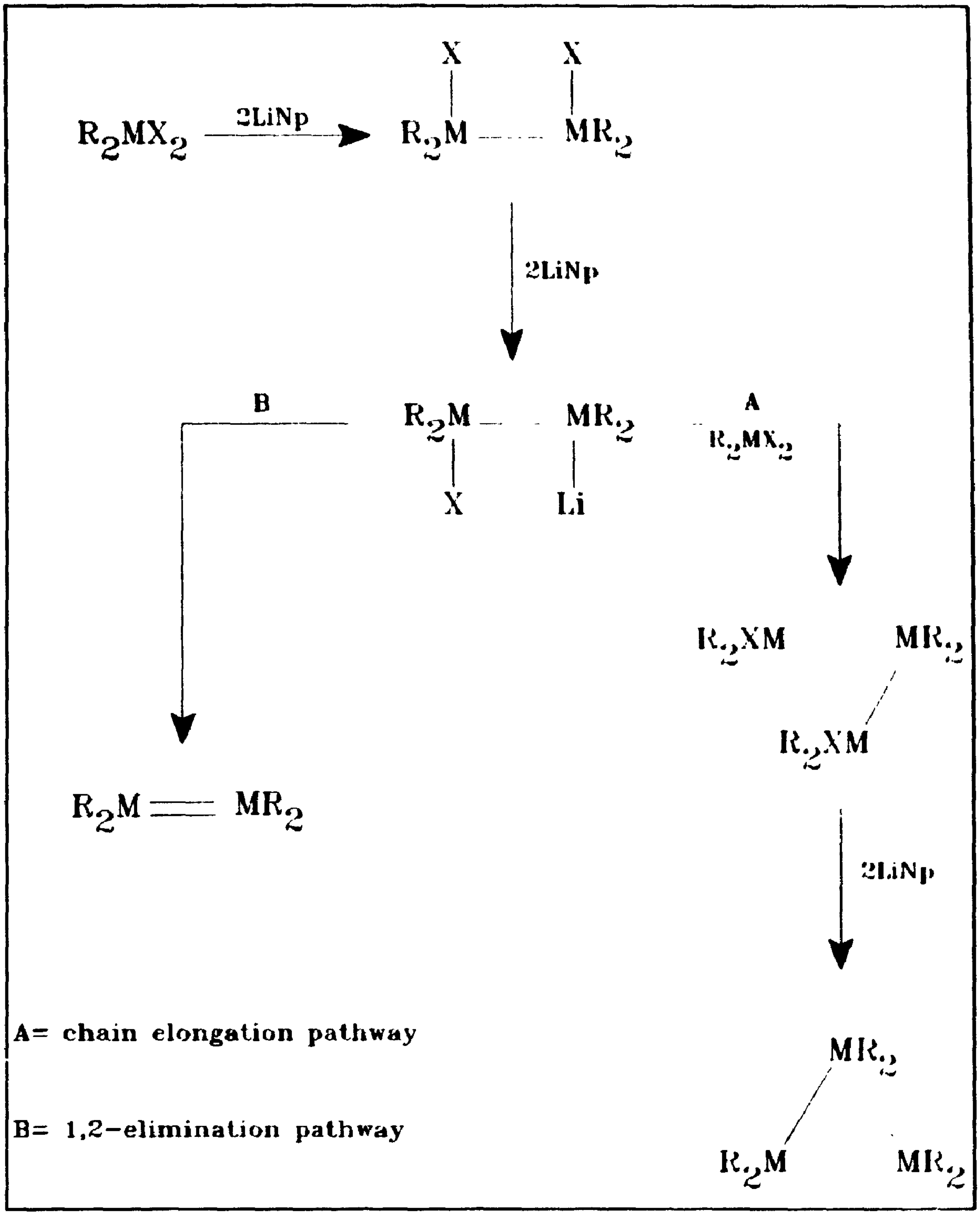
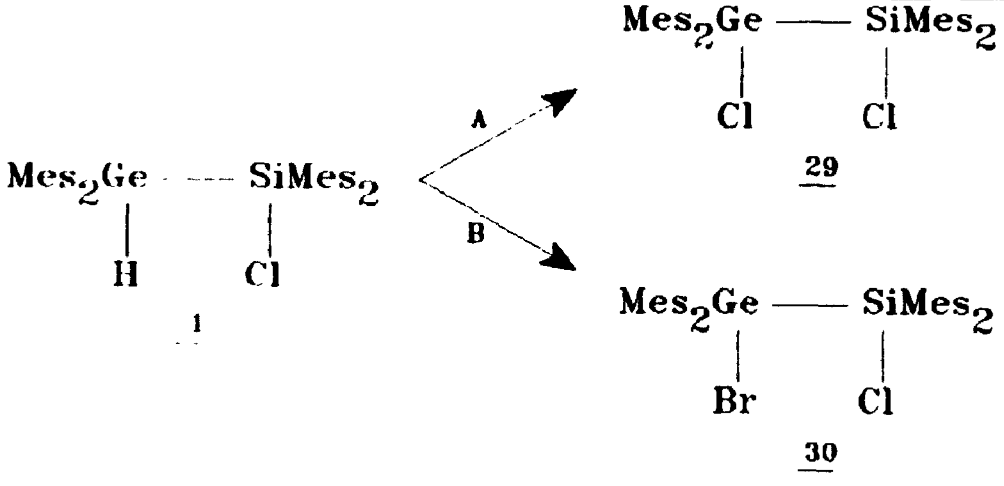


Figure 3-3: Reductive coupling of dihalometallanes

example, S. Masamune and co-workers[2] isolated the first stable tetraalkyldisilene, namely $Bis_2Si=SiBis_2$ (Bis = $(Me_3Si)_2HC$), by the reaction between LiNp and Bis_2SiI_2 in THF. Based on the above criteria, and the ready access to mesityl containing silicon and germanium compounds, the systems which were to be used in the reductive elimination reactions were $Mes_2ClGeSiClMes_2$, 29, and $Mes_2BrGeSiClMes_2$, 30. These systems had the added advantage of not only being prepared from a common precursor, namely $Mes_2HGeSiClMes_2$, 1, but this precursor had already been synthesized in excellent yield (figure 3-4).

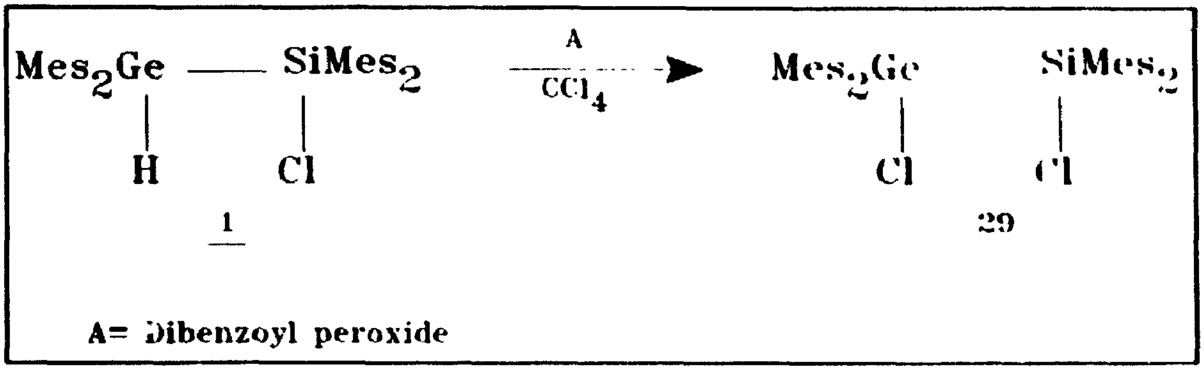


A= chlorinating agent; B= brominating agent

Figure 3-4: Synthetic pathways for the preparation of 29 and 30

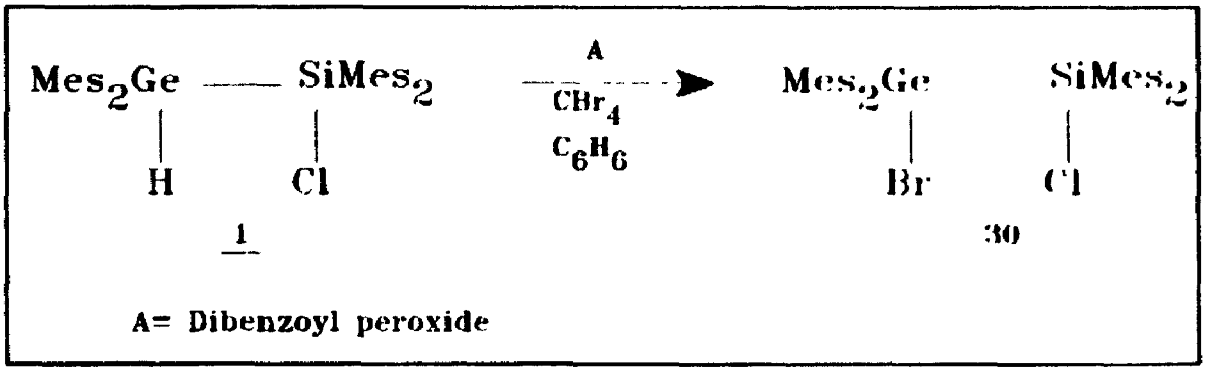
3.2 REACTION BETWEEN 29 OR 30 AND LITHIUM NAPHTHALENIDE

Compound 29 was prepared by chlorination of 1 using dibenzoyl peroxide and carbon tetrachloride (figure 3-5).[4] Compound 30 was prepared by a similar method using dibenzoyl peroxide and carbon tetrabromide with benzene as a solvent (figure 3-6).



A= Dibenzoyl peroxide

Figure 3-5: Preparation of 29



A= Dibenzoyl peroxide

Figure 3-6: Preparation of 30

Compounds 29 and 30 exhibited some hindered rotation about both the Ge-Mes and Si-Mes bonds as seen in the ^{1}H NMR spectrum of each compound at room temperature; the *m*-H and *o*-Me hydrogen atoms of the mesityl groups in compound 29 were two broad peaks at room temperature (rt).[4] At 60°C, the downfield signal sharpens to two singlets assigned to the *m*-H's of the two different mesityl groups (6.65, 6.67 ppm) and at 100°C the broad signal at 2.4 ppm appears as two sharp singlets (2.40, 2.37 ppm) corresponding to the *o*-Me groups of the two mesityl groups (see appendix, spectra 1 and 2). A similar trend is observed in the ^{1}H variable temperature NMR spectrum of compound 30. The broad signal observed at 6.7 ppm at rt, which has been assigned to the *m*-H protons of the mesityl groups, sharpens to two singlets at 60°C; whereas the *o*-Me signals sharpen at 100°C (see appendix, spectra 3 and 4).

On reacting 29 with LiNp (10 molar equivalents), the following products were obtained: a mixture of Mes_2SiH_2 and Mes_2GeH_2 in a ratio of 15:85, $Mes_2HGeSiHMes_2$, 2, and unidentified products (figure 3-7). Using

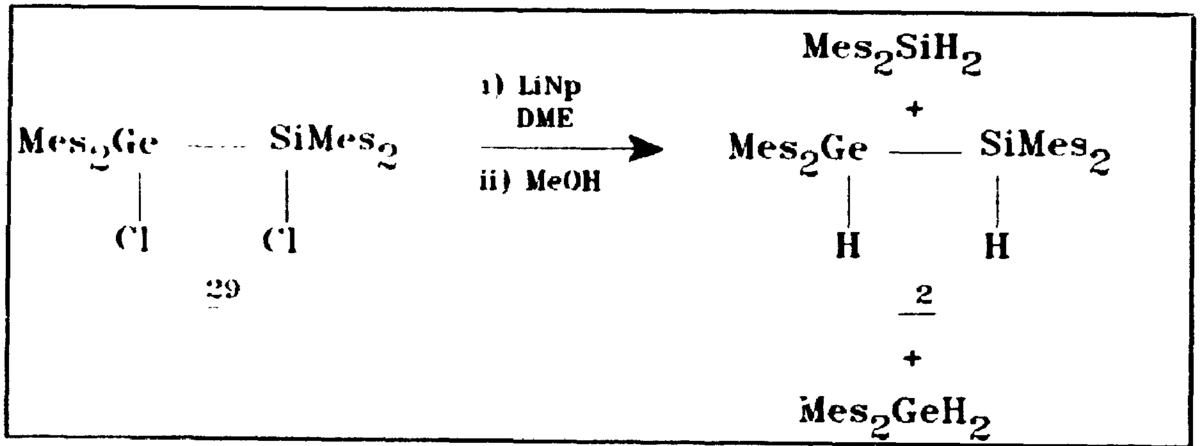


Figure 3-7: Reaction between 29 and excess lithium naphthalenide

two molar equivalents of LiNp, $Mes_2HGeSiClMes_2$, 1, apparently from the selective reduction of the germanium-chlorine bond, was obtained in addition to the above products. The ratio of cleavage products (i.e. Mes_2SiH_2 and Mes_2GeH_2) to 2 to 1 was 5:35:60. The reaction between 29 and LiNp, followed by quenching with D_2O yielded $Mes_2DGeSiHMes_2$, 7, $Mes_2HGeSiDMes_2$, 8 , Mes_2SiHD and Mes_2GeHD but no $Mes_2HGeSiHMes_2$, 2. From the integration of the Ge-H/Si-H and mesityl methyl region of the ^{1}H NMR spectrum, it was apparent that little or no $Mes_2DGeSiDMes_2$ is formed in the above reaction. This result suggests that the products that are trapped are most likely anionic (i.e. $Mes_2LiGeSiHMes_2$, 9, $Mes_2HGeSiLiMes_2$, 19, Mes_2HSiLi and Mes_2HGeLi). A possible mechanism to account for the products obtained on treating 29 with LiNp is as follows (figure 3-8): 29 reacts with one equivalent of LiNp to form a germanium centred radical which could abstract a proton from DME (the solvent) to yield $Mes_2HGeSiClMes_2$, 1, or react with a second equivalent of LiNp to give a germyl anion, $Mes_2LiGeSiClMes_2$. This germyl anion could then eliminate LiCl to form $Mes_2Ge=SiMes_2$, which reacts with another equivalent of LiNp to form a radical anion. The abstraction of hydrogen by the radical anion from the solvent would yield compounds $Mes_2LiGeSiHMes_2$, 9 and $Mes_2HGeSiLiMes_2$, 19. 9 and 19 are then trapped by D_2O. The origin of the cleaved products is uncertain at this time; it may arise from the cleavage of the radical anion or 9 or 19. From the results obtained so far, it appears that the amount of LiNp used determines whether 1 or products derived from the trapping of 9 or 19 is obtained. With two equivalents LiNp, 1 is obtained in the greater yield, whereas with ten equivalents LiNp, 2 is obtained in the larger amount on quenching the reaction mixture with MeOH. In support of this mechanism are the following observations. Weidenbruch and co-workers[5] have found that the reduction of dihalodisilanes, $R_2XSiSiXR_2$ ($R =$ mesityl; $X = Cl$ or Br), with alkali metals gives an epr signal assigned to the radical anion $[R_2Si=SiR_2]^-$. Weidenbruch and co-workers[5] have also indicated that the unpaired electron is delocalized over both silicon atoms. In addition, S. Masamune and co-workers[3] have shown that digermenes can also be reduced by excess LiNp to yield, upon addition of MeOH, diarylgermane (7%), tetraaryldigermane (14%) and unidentifiable polymers (40%) (figure 3-9).

Compound 30 also reacted with LiNp (2.5 molar equivalents) to give a mixture of Mes_2SiH_2 and Mes_2GeH_2 (20:80), $Mes_2HGeSiHMes_2$, 2, and unidentified products (figure 3-10). Using only two molar equivalents of LiNp also resulted in the isolation of 1 and starting material.

From the above results, it can be concluded that

i) the reaction between 29 or 30 and LiNp does not appear to be a promising route to stable germasilenes; although intermediate formation of a germasilene cannot be ruled out at this point.

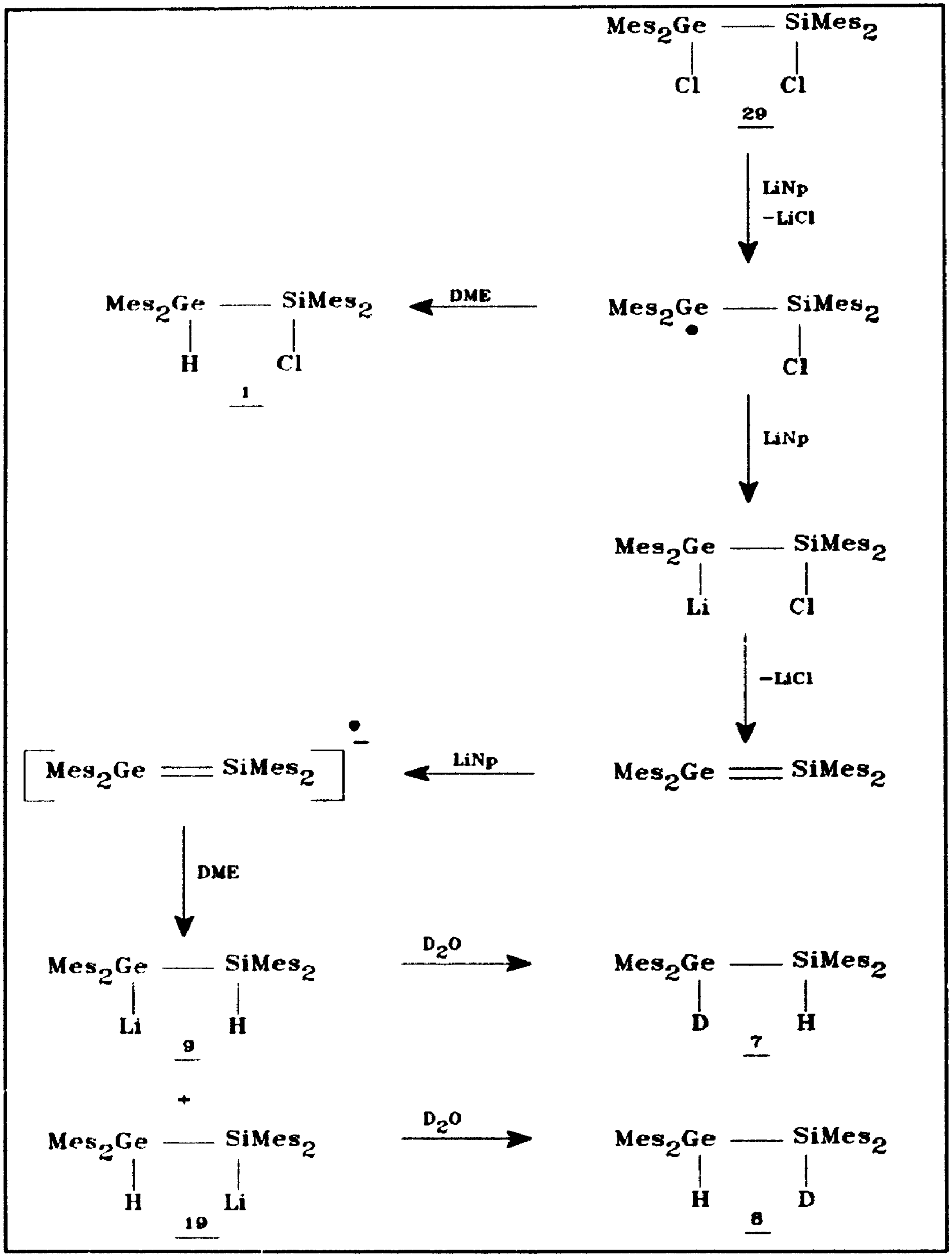


Figure 3-8: Possible mechanism for the reaction between 29 and lithium naphthalenide

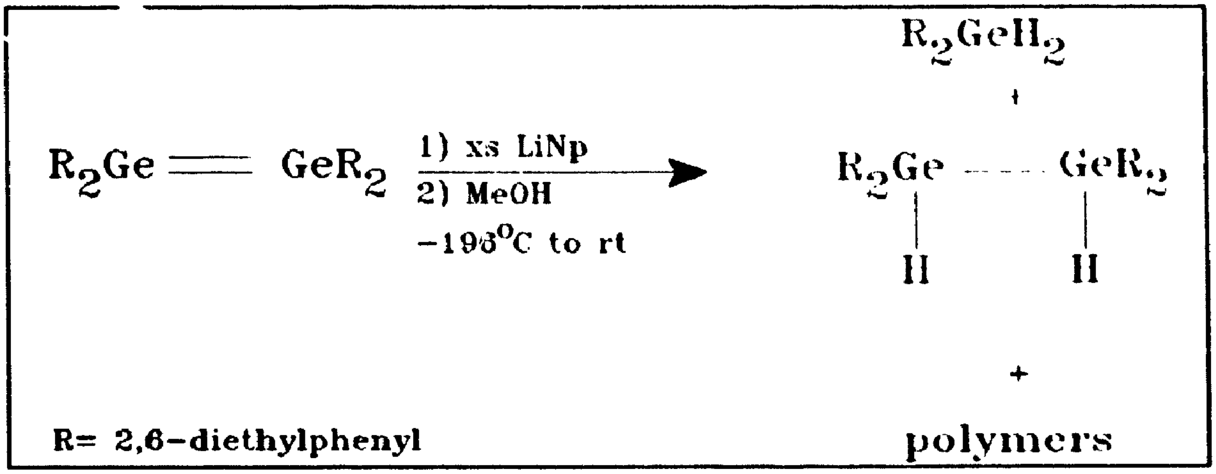


Figure 3-9: Reaction between a digermene and excess lithium naphthalenide

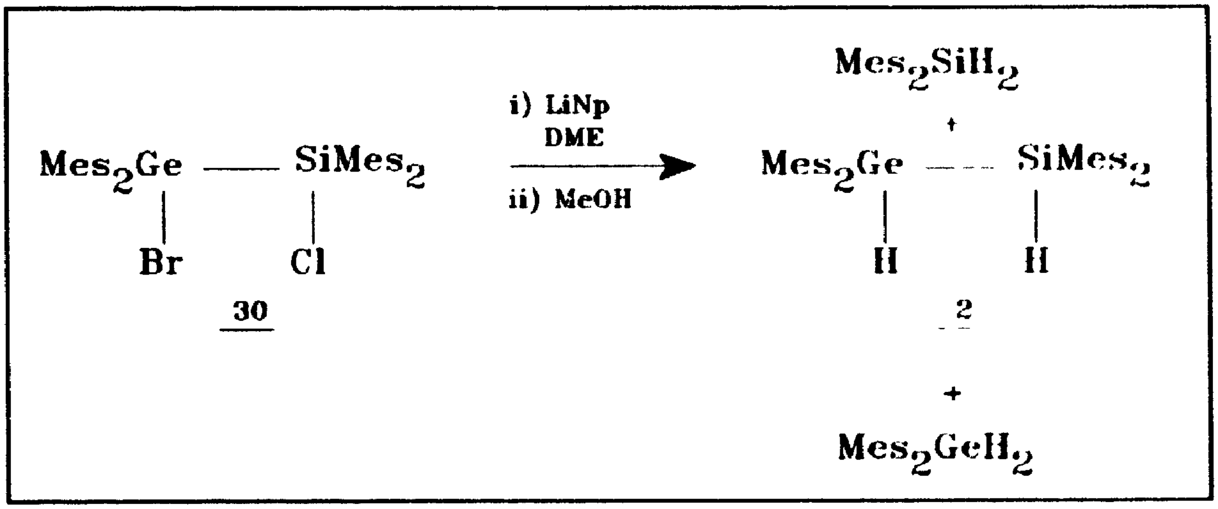


Figure 3-10: Reaction between 30 and excess lithium naphthalenide

ii) reduction of the germanium-halogen bond occurs prior to that of the silicon-chlorine bond.

iii) cleavage of the central silicon-germanium bond is also observed.

iv) the reaction between LiNp and either 29 or 30 results in the formation of anionic species which can be trapped with D_2O.

3.3 REFERENCES

1) Azuma, T.; Yanagida, S.; Sakurai, H.; Sasa, S.; Yoshino, K. *Syn. Comm.* **1982**, 12, 137-140.

2) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 902-930.

3) Park, J.; Batcheller, S. A.; Masamune, S. *J. Organomet. Chem.* **1989**, 367, 39-45.

4) Groh, R. *Chemistry 490 Thesis*, The University of Western Ontario, **1990**.

5) a) Weidenbruch, M.; Kramer, K.; Schäfer, A.; Blum, J. K. *Chem. Ber.* **1985**, 118, 107-115.

b) Weidenbruch, M.; Kramer, K.; Peters, K.; von Schnering, H. G. *Z. Naturforsch.* **1985**, 40b, 601-606.

CHAPTER 4-CONCLUSIONS

The preparation of $Mes_2HGeSiClMes_2$, 1, has been accomplished in excellent yield. Dehydrochlorination of 1 has been attempted in both hydrocarbon and ethereal solvents using different bases. In hydrocarbon solvents or Et_2O, no reaction occurred between 1 and *tert*-BuLi. When the solvent was changed to THF, treatment of 1 with *tert*-BuLi yielded a germyl anion, $Mes_2LiGeSiHMes_2$, 9, which can be trapped by various electrophiles to give a variety of substituted silylgermanes. Also obtained were products derived from the regioselective cleavage of the central germanium-silicon bond. Germyl anion 9 is believed to be formed in the following manner: in the first step, *tert*-BuLi acts as a reducing reagent, converting 1 to the corresponding dihydro analog 2. A second equivalent of base then abstracts the proton from the germanium atom to give 9. Germyl anion 9 is also formed, albeit in lower yield, when 1 was treated with LDA. A change in the base to BuLi/TMEDA, PhLi or KH did not yield a germasilene.

The preparation of $Ph_2HGeSiClMes_2$, 22, has been accomplished in moderate yield. The reaction between 22 and *tert*-BuLi in THF yielded a germyl anion similar to 9; this germyl anion, $Ph_2LiGeSiHMes_2$, 24, can also be trapped by various electrophiles. Compound 22, unlike 1, does react with *tert*-BuLi in hydrocarbon solvents in a manner similar to what occurs in THF (i.e. products derived from the trapping of 24 are obtained).

Attempts to synthesize fluorinated derivatives of 1 and 22 were unsuccessful.

The preparation of $Mes_2BrGeSiClMes_2$, 30, has been accomplished in moderate yield. Attempts to prepare a stable germasilene from $Mes_2ClGeSiClMes_2$, 29, and 30 using LiNp were unsuccessful. From the identity of the products obtained, at this point, an intermediate germasilene cannot be ruled out.

Although the synthesis of a relatively stable germasilene was not achieved by either a ß-salt elimination or a reductive elimination reaction, much has been learned about the chemistry of mixed germanium-silicon compounds. From the results obtained, the following conclusions can be made:

i) hindered silylgermyl anions can be prepared by the treatment of (halosilyl)germanes with bases such as *tert*-BuLi or LDA in THF,

and,

ii) the cleavage of germanium-silicon bonds by nucleophiles appears regioselective.

CHAPTER 5-EXPERIMENTAL SECTION

5.1 EXPERIMENTAL

All reactions were carried out in oven-dried glassware under an atmosphere of argon. THF and Et_2O were distilled from the sodium ketyl of benzophenone, pentane and cyclohexane were distilled from $LiAlH_4$, CH_2Cl_2 was distilled from CaH_2 and MeOH was distilled from magnesium methoxide prior to use. BuLi, PhLi, and *tert*-BuLi were obtained from the Aldrich Chemical Co., and their concentrations were periodically checked using the Gilman double titration method.[1] $GeCl_4$ was used as received from the Toronto Research Co.. Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research) or conventional preparative plates, or by flash column chromatography.[2] Acidic work up refers to the slow addition of 1N or 6N HCl to the reaction mixture, followed by separation of the two layers and extraction of the organic phase with water and brine, and drying over anhydrous $MgSO_4$. Aqueous work up is similar to an acidic work up, except that water rather than acid is used.

NMR spectra were recorded on a Gemini 200, Varian XL-200 (200.1 MHz for ^1H and 50.3 MHz for ^{13}C), or an XL-300 or Gemini 300 (299.9 MHz for ^1H, 75.4 MHz for ^{13}C and 59.6 MHz for ^{29}Si) spectrometer using deuterated benzene as a solvent unless otherwise noted. The standards used were as follows: residual C_6D_5H, 7.15 ppm for ^1H NMR spectra; C_6D_6 central transition, 128.00 ppm for ^{13}C NMR spectra; Me_4Si as an external standard, 0.00 ppm for ^{29}Si NMR spectra. The ^{13}C NMR signal assignments were supported using the DEPT[3] pulse sequence. IR spectra were recorded on a Bruker FT infrared spectrometer controlled by an IBM System 9000 computer or a Perkin Elmer System 2000 FT-IR, a Finnegan MAT model 8230 was used with an ionizing voltage of 70 eV to obtain electron impact mass spectra (reported in mass-to-charge units, *m/z*, with intensities of peaks relative to the base peak and ion identity in parentheses). Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

5.2 Synthesis of $Mes_2HGeSiClMes_2$ and Reaction with *tert*-BuLi.

5.2.1 Synthesis of $Mes_2HGeSiClMes_2$, 1.

A solution of Mes_2GeHLi (from *tert*-BuLi, 7.75 mmol, and Mes_2GeH_2, 1.50 g, 4.79 mmol, in anhydrous THF) was added to Mes_2SiCl_2 (1.62 g, 4.82 mmol) in THF (10 mL) at -23°C (dry ice-CCl_4). The solution was allowed to warm to 20°C and stirred for 21 h before work up under acidic conditions (1 M HCl). The crude product was triturated with MeOH yielding a white solid (2.79 g, 94%).

mp 200°C (dec).

IR (KBr pellet, cm^{-1}) 2046 (s, Ge-H).

^{1}H NMR (ppm) 6.72, 6.63 (each s, total 8H, Mes-H), 5.86 (s, 1H, Ge-H), 2.37 (bs, 12H, *o*-Me), 2.36 (s, 12H, *o*-Me), 2.09, 2.03 (each s, total 12H, *p*-Me).

^{13}C NMR (ppm, 60°C) 144.62, 144.28, 139.88, 138.30, 135.20, 132.62 (Mes-C), 130.23, 129.17 (Mes-CH), 24.85, 24.57, 20.93, 20.86 (Me).

^{29}Si NMR ($CDCl_3$, ppm) 4.58 (d, J = 19 Hz).

MS *m/z* (%) 613 (6, M^+-1), 579 (32), 495 (16), 312 (100), 301 (64), 265 (16), 192 (24), 119 (10).

High Resolution MS: calcd for *m/z* $C_{36}H_{45}{}^{35}Cl^{74}Ge^{28}Si$ 614.2191, found 614.2196.

Analysis calcd for $C_{36}H_{45}ClGeSi$ %C, 70.44, %H, 7.39; Found %C, 69.28, %H, 7.15.

$\underline{Mes_2DGeSiClMes_2,\ 1a.}$

Mes_2GeD_2 was prepared by reduction of Mes_2GeX_2 with $LiAlD_4$. Mes_2GeD_2 was then substituted for Mes_2GeH_2 in the preparation of $\underline{1}$ to give $\underline{1a}$.

IR (thin film, cm^{-1}) no Ge-H.

^{2}H NMR (C_6H_6, ppm) 5.89 (Ge-D).

5.2.2 Reaction Between $Mes_2HGeSiClMes_2$ and *tert*-BuLi in THF. E = MeOH; $Mes_2HGeSiHMes_2$, 2.

Addition of *tert*-BuLi (3.2 mL, 5.0 mmol, 1.55 M in pentane) to $\underline{1}$

(0.50 g, 0.82 mmol) in THF (15 mL) at -23°C (dry ice-CCl_4) followed by warming to 20°C and stirring for 6 h yielded a red-brown solution. Addition of MeOH to the reaction mixture resulted in immediate decolorization (to pale yellow). After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give **2** (0.15 g, 33%) and Mes_2GeH_2 (0.02 g, 8%).

Characterization for **2**:

mp 183°C (dec.).

IR (KBr pellet, cm^{-1}) 2133, 2023 (SiH/GeH).

Raman (solid, cm^{-1}) 578, 563, 553, 528, 434, 149.

^1H NMR (ppm) 6.69, 6.65 (each s, total 8H, Mes-H), 6.01 (d, 1H, J = 11 Hz, Si-H; assigned by ^{29}Si-^1H correlation spectroscopy), 5.75 (d, 1H, J = 11 Hz, Ge-H), 2.37, 2.34 (each s, total 24H, *o*-Me), 2.08, 2.05 (each s, total 12H, *p*-Me).

^1H NMR ($CDCl_3$, ppm) 6.68 (bs), 5.60 (d), 5.33 (d), 2.20 (s), 2.19 (s), 2.15 (s), 2.09 (s).

^{13}C NMR (ppm) 145.17, 144.05, 139.11, 135.96, 135.07, 130.05 (Mes-C), 129.22, 128.96 (Mes-CH), 24.30, 23.91, 21.05, 21.00 (Me).

^{29}Si NMR (ppm) -47.96 (d of m, J = 194 Hz).

MS *m/z* (%) 579 (4, M^+-1), 312 (50), 267 (40), 207 (100), 192 (46), 119 (32).

High Resolution MS: calcd for *m/z* $C_{36}H_{45}{}^{74}Ge^{28}Si$ (M^+-1) 579.2508, found

579.2493.

Analysis calcd for $C_{36}H_{46}GeSi$ %C, 74.62, %H, 8.00; Found %C, 74.06, %H, 7.72.

E = MeOH-*d_4*; $Mes_2DGeSiHMes_2$, 7.

Characterization for 7 containing approximately 40% of 2:

^1H NMR (ppm) 6.01 (bs, Si-H).

^2H NMR ($CHCl_3$, ppm) 5.27 (bs).

^2H NMR (C_6H_6, ppm) 5.75 (bs).

^{29}Si NMR ($CDCl_3$, ppm) -48.71 (d of m, J=191 Hz).

E = H_2O; Reaction Between 1a and *tert*-BuLi

Addition of *tert*-BuLi (1 mL, 1.7 mmol, 1.7 M in pentane) to 1a (0.19 g, 0.32 mmol) in THF (15 mL) at -23°C (dry ice-CCl_4) followed by warming to 20°C. Aliquots (1 mL) were taken at 5, 10, 15, 30, 60, 120 and 240 minutes and were quenched with H_2O. After work up, an ^1H NMR spectrum was obtained of the resulting solid. The results obtained from this experiment is shown below.

TIME/ minutes	Ratio of 2	Ratio of 7
5	61	39
10	63	37
15	60	40
30	67	33
60	75	25

120	79	21
240	79	21

E= MeI; $Mes_2(Me)GeSiHMes_2$, 10.

To a solution of 1 (98.7 mg, 0.161 mmol) dissolved in $LiAlH_4$-dried THF (5 mL) was added *tert*-BuLi (0.3 mL, 0.4 mmol, 1.55 M in pentanes) at -23°C (dry ice-CCl_4). The cold bath was removed and the reaction mixture was stirred for 4.3 h. MeI (0.5 mL) was then added. After aqueous work up, the products were separated by chromatography (silica gel; hexanes, CH_2Cl_2 to give 52.5 mg of a white solid which consisted of a mixture of compounds 10 and 2 in a ratio of 80:20, respectively (by ^1H NMR spectroscopy). Characterization for 10 containing approximately 10% of 2:

IR (thin film, cm^{-1}) 2141, 2029.

^1H NMR (ppm) 6.69, 6.68 (each s, total 8H,Mes-H), 5.96 (s, Si-H), 2.29, 2.23 (each s, total 24H, *o*-Me), 2.10, 2.08 (each s, total 12H, *p*-Me), 1.26 (s, 3H, Ge-Me).

^{13}C NMR (ppm) 145.00, 143.83, 138.83, 137.64, 131.30 (Mes-C), 129.47, 129.25 (Mes-CH), 24.72, 24.29, 21.06, 20.91, 7.12 (all Me).

^{29}Si NMR (ppm) -48.41 (d, J = 189 Hz).

MS *m/z* (%) 594 (0.6, M^+), 578 (0.8, M^+-Me-1), 475 (2, M^+-Mes), 327 (100, Mes_2GeHMe), 311 (10), 281 (11), 267 (24, Mes_2SiH), 235 (7, MesSiGeMe), 147 (4, MesSi), 119 (3, Mes).

High Resolution MS: calcd for *m/z* $C_{37}H_{47}{}^{74}Ge^{28}Si$ (M^+-1) 593.2659; found 593.2634.

E = Me_3SiCl; $Mes_2(SiMe_3)GeSiHMes_2$, 12.

To a solution of 1 (79.4 mg, 0.13 mmol) dissolved in THF (5 mL) was added *tert*-BuLi (1.5 mL, 2.3 mmol, 1.55 M in pentanes) at -23°C (dry ice-CCl_4). The cold bath was removed and the reaction mixture was stirred for 3.5 h. Me_3SiCl (0.4 mL, distilled from $CaCl_2$ prior to use) was then added. After aqueous work up, the products were separated by chromatography (silica gel; hexanes, CH_2Cl_2 to give 12 (33.1 mg) and $Mes_2HGe(SiMe_3)$, 13 (9.6 mg, 19.3%). Characterization for 12 containing approximately 25% of 2:

IR (thin film, cm^{-1}) 2137, 2029.

^1H NMR (ppm) 6.70, 6.67 (each s, total 8H, Mes-H), 6.16 (s, 1H, Si-H), 2.36, 2.23 (each s, total 24H, *o*-Me), 2.10, 2.08 (each s, total 12H, *p*-Me), 0.34 (s, 9H, $SiMe_3$).

^{13}C NMR (ppm) 144.85, 143.83, 139.10, 138.46, 137.04, 132.06 (Mes-C), 129.07, 128.96 (Mes-CH), 25.95, 24.99, 21.05, 20.89, 3.63 (all Me).

^{29}Si NMR (ppm) -2.93 (m, J=6 Hz), -48.50 (d, J=186 Hz).

MS *m/z* CI, isobutane (%) 652 (6, M^+), 651 (10, M^+-1), 637 (2, M^+-Me), 579 (5, M^+-$SiMe_3$), 460 (38, M^+-$SiMe_3$-Mes), 385 (100, $Mes_2GeSiMe_3$), 312 (56, Mes_2Ge), 294 (33, $MesGe(SiMe_3)Si$), 267 (85, Mes_2SiH), 266 (23, Mes_2Si), 221 (56, MesGeSi), 193 (40, MesGe), 147 (41), 119 (42, Mes), 73 (77, $SiMe_3$).

High Resolution MS: calcd for *m/z* $C_{39}H_{53}{}^{74}Ge^{28}Si$ (M^+-1) 651.2898, found 651.2930.

Characterization for $Mes_2GeH(SiMe_3)$, <u>13</u>:

^1H NMR 6.77 (s, 4H, Mes-H), 5.18 (s, 1H, Ge-H), 2.40 (s, 12H, *o*-Me), 2.12 (s, 6H, *p*-Me), 0.25 (s, 9H, $SiMe_3$).

^{13}C NMR (ppm) 143.34, 137.49, 135.17, 128.22, 24.56, 20.98, 0.33.

MS *m/z* CI, isobutane (%) 386 (18, M^+), 385 (40), 371 (5, M^+-Me), 313 (8, M^+-$SiMe_3$), 267 (28, M^+-Mes), 221 (20), 193 (25, MesGe), 147 (28, MesSi), 119 (20, Mes), 73 (100, $SiMe_3$).

<u>E = $PhCH_2Br$; $Mes_2BrGeSiHMes_2$, 15.</u>

To a solution of <u>1</u> (97.7 mg, 0.158 mmol) dissolved in THF (5 mL) was added *tert*-BuLi (1.5 mL, 2.6 mmol, 1.7 M in pentanes) at -23°C (dry ice-CCl_4). The reaction mixture was then stirred at room temperature for 5 h before the addition of $PhCH_2Br$ (0.3 mL). After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give <u>15</u>* (29.1 mg; 28%) and $Mes_2HGe(CH_2Ph)$, <u>16</u> (5.4 mg; 6%).

IR (KBr, cm^{-1}) 2151 (SiH).

Raman (solid, cm^{-1}) 580, 564, 553, 530, 426, 264, 184, 176, 155.

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* the crude reaction mixture can be washed with pentane to yield <u>15</u>.

^{1}H NMR (ppm) 6.67, 6.64 (each s, total 8H, Mes-H), 6.18 (s, 1H, Si-H), 2.45, 2.38 (each s, total 24H, *o*-Me), 2.06, 2.05 (each s, total 12H, *p*-Me).

^{13}C NMR ($CDCl_3$, ppm) 145.26, 142.96, 139.44, 138.79 (Mes-C), 129.40, 128.80 (Mes-CH), 128.51 (Mes-C), 24.42, 21.08, 20.90 (Me).

^{29}Si NMR (ppm) -44.56 (d, J=187 Hz).

MS *m/z* CI, isobutane (%) 660, 658 (0.4, 0.6, M^+), 579 (4, M^+-Br), 391 (12, MesGeBr), 312 (100, Mes_2Ge), 267 (98, Mes_2Si), 193 (18).

High Resolution MS: calcd for *m/z* $C_{38}H_{45}{}^{79}Br^{74}Ge^{28}Si$ 658.1686, found 658.1691.

Characterization for $Mes_2HGe(CH_2Ph)$, <u>16</u>:

^{1}H NMR (ppm, 6.85-6.99 (m, 5H, Ph-H), 6.69 (s, 4H, Mes-H), 5.45 (d, J=4.4 Hz, 1H, Ge-H), 2.82 (t, J=4.5 Hz, 2H, CH_2), 2.18 (each s, 12H, *o*-Me), 2.09 (s, 6H, *p*-Me).

^{13}C NMR ($CDCl_3$, ppm) 143.35, 138.26, 133.61, 128.48, 128.30, 128.05, 124.47, 27.33, 23.53, 21.04.

MS *m/z* CI, isobutane (%) 404 (4, M^+), 403 (5, M^+-1), 314 (12, Mes_2GeH_2), 313 (32, Mes_2HGe), 312 (42, Mes_2Ge), 193 (12, MesGe), 119 (14, Mes), 91 (100, $PhCH_2$).

5.3 Attempted Synthesis of $Mes_2HGeSiFMes_2$, 20.

Two different routes were tried for the synthesis of

$Mes_2HGeSiFMes_2$, 20

5.3.1 Attempted conversion of 1 to 20 using different fluorinating agents.

The preparation of $Mes_2HGeSi(OMe)Mes_2$, 21, was also attempted by reacting 1 with a mixture of MeOH and Et_3N. Once prepared, it was hoped that this derivative could be fluorinated using aqueous HF.

5.3.1.1 Using ammonium hexafluorosilicate.

A mixture of 1 (0.1302 g, 0.21 mmol), $(NH_4)_2SiF_6$ (0.2894 g, 1.62 mmol) and DME (25 mL) was refluxed for 8.5 h. The reaction mixture was cooled and then added to a saturated solution of NH_4Cl. This mixture was extracted with Et_2O and the ether extracts were combined and dried over $MgSO_4$. After removal of the solvents no products were detected, by ^1H NMR spectroscopy, in the residue. The starting material was recovered in significant amount.

5.3.1.2 Using silver tetrafluoroborate.

i) A mixture of 1 (85.3 mg, 0.14 mmol), $AgBF_4$ (57.5 mg, 0.30 mmol), and Et_2O (5 mL) was stirred at rt for 4 h. The solvent was removed yielding only starting material.

ii) A mixture of 1 (105.9 mg, 0.17 mmol), $AgBF_4$ (41.2 mg, 0.22 mmol), and anhydrous CH_2Cl_2 (4 mL) was stirred at rt for 10 h. The reaction mixture was then filtered through Celite. The solvent was evaporated yielding Mes_2SiF_2 and mesitylene in addition to unreacted starting material. A shorter reaction time (4 h) yielded mesitylene and 1.

5.3.1.3 Using cesium fluoride.

A mixture of 1 (0.1061 g, 0.17 mmol) and cesium fluoride (0.2798 g, 1.84 mmol) dissolved in THF (30 mL) was refluxed for 3.5 h. The reaction mixture was allowed to cool and then filtered through Celite. The solvent was then removed. Purification of the crude white solid by chromatography (silica gel; hexanes, CH_2Cl_2) yielded starting material, Mes_2GeH_2 and Mes_2HSiF.

5.3.1.4 Using methanol/triethylamine.

A mixture of 1 (100 mg, 0.16 mmol), benzene (15 mL), MeOH (4 mL), and Et_3N (4 mL) was refluxed for 4 h before allowing the mixture to cool to rt. The solvent was then evaporated. No products were detected by ^1H NMR spectroscopy in the residue. The starting material was recovered in good yield.

5.3.2 Attempted coupling between Mes_2GeHLi and Mes_2SiXY (X=Y=F; X=Y=OMe; X=Cl, Y=OMe).

5.3.2.1 Preparation of $Mes_2Si(OMe)_2$ and $Mes_2ClSiOMe$.

A solution of Mes_2SiCl_2 (2.75 g, 8.2 mmol) in benzene (6 mL), MeOH (20 mL), and Et_3N (20 mL) was refluxed for 7.5 h. The solvent was removed yielding a white solid. After washing the residue with hexanes, the solid was separated by gravity filtration. The product obtained after solvent removal was identified as $Mes_2ClSiOMe$. To this yellow solid was added NaOMe, and the solution was then refluxed for 7 h before quenching the reaction mixture with water. The reaction mixture was extracted with ether, the ether extracts were combined, dried over $MgSO_4$, and all solvents were removed. Purification by chromatography (silica gel; hexanes, CH_2Cl_2) yielded 1.40 g (52%) $Mes_2Si(OMe)_2$.

Characterization for $Mes_2ClSiOMe$:

^1H NMR (ppm) 6.79 (s, 4H, MesH), 3.45 (s, 3H, OMe), 2.63 (s, 12H, *o*-Me), 2.10 (s, 6H, *p*-Me).

Characterization for $Mes_2Si(OMe)_2$:

^1H NMR (ppm): 6.74 (s, 4H, MesH), 3.35 (s, 6H, OMe), 2.53 (s, 12H, *o*-Me), 2.10 (s, 6H, *p*-Me).

^{13}C NMR (ppm): 145.08, 139.48, 129.63, 129.45, 49.33, 23.61, 21.10.

^{29}Si NMR (ppm): -22.06.

MS *m/z* (%) 328 (6.7, M^+), 313 (0.6, M^+-Me), 297 (2.2, M^+-OMe), 282 (0.6, M^+-OMe), 266 (0.5, Mes_2Si), 208 (100), 178 (10, MesSiOMe), 147 (8, MesSi), 59 (38, SiOMe).

5.3.2.2 Attempted coupling between Mes_2GeHLi and $Mes_2Si(OMe)_2$.

A solution of Mes_2GeHLi (made from Mes_2GeH_2 (0.1252 g, 0.4 mmol) and *tert*-BuLi (0.94 mmol) in anhydrous THF) was added dropwise to $Mes_2Si(OMe)_2$ (0.0997 g, 0.30 mmol) in THF (5 mL) at -23°C. After removing the dry ice-CCl_4 bath, the reaction mixture was heated at 40°C for 22 h. Acidic work-up followed by purification (silica gel; hexanes,

CH_2Cl_2) by chromatography yielded Mes_2GeH_2 (5.8 mg, 5%), $Mes_2Si(OMe)_2$ and $Mes_2HGeGeHMes_2$ (46.7 mg; in ratio of 13:87).

5.3.2.3 Attempted coupling between Mes_2GeHLi and $Mes_2ClSiOMe$.

A solution of Mes_2GeHLi (made from Mes_2GeH_2 (0.1239 g, 0.40 mmol) and *tert*-BuLi (1.25 mmol) in THF) was added dropwise to $Mes_2ClSiOMe$ (0.1137 g, 0.34 mmol) in THF (5 mL) at -23°C. After removing the dry ice bath, the reaction mixture was stirred at rt for 24 h. Acidic work-up followed by purification by chromatography (silica gel; hexanes, CH_2Cl_2) yielded Mes_2GeH_2 (51.7 mg, 42%) and $Mes_2HGeGeHMes_2$ (16.5 mg, 6.5%).

Characterization for $Mes_2HGeGeHMes_2$:

^1H NMR (ppm) 6.68 (s, 8H, Mes-H), 5.92 (s, 2H, GeH), 2.36 (s, 24H, *o*-Me), 2.07 (s, 12H, *p*-Me).

Lit.[4] ^1H NMR (ppm) 6.68 (s, 8H, Mes-H), 5.92 (s, 2H, GeH), 2.35 (s, 24H, *o*-Me), 2.07 (s, 12H, *p*-Me).

5.3.2.4 Attempted coupling between Mes_2GeHLi and Mes_2SiF_2.

i) A solution of Mes_2GeHLi (made from Mes_2GeH_2 (0.8255 g, 2.64 mmol) and *tert*-BuLi (3.74 mmol) in anhydrous THF) was added dropwise to Mes_2SiF_2 (0.8032 g, 2.65 mmol) in THF (20 mL) at -23°C. The reaction mixture was allowed to warm to rt and stirred for 21 h before work-up under acidic conditions. The reaction mixture was extracted with ether, the ether extracts were combined, dried over $MgSO_4$, and all solvents were removed. The crude product was purified by chromatography (silica gel; hexanes, CH_2Cl_2). In addition to starting materials, the following compounds were isolated: Mes_2FSi(*tert*-Bu), Mes_2SiHF, and $Mes_2HGeGeHMes_2$.

Characterization for Mes_2FSi(*tert*-Bu):

^{1}H NMR (ppm) 6.71 (s, 4H, MesH), 2.55 (d, J = 2.02 Hz, 12H, *o*-Me), 2.07 (s, 6H, *p*-Me), 1.25 (s, 9H, *t*-Bu).

Characterization for Mes_2SiHF:

^{1}H NMR (ppm) 6.68 (s, 4H, MesH), 5.61 (d, J = 29.4 Hz, SiH), 2.37 (d, J = 2 Hz, 12H, *o*-Me), 2.07 (s, 6H, *p*-Me).

ii) A solution of Mes_2GeHLi (made from Mes_2GeH_2 (0.0572 g, 0.18 mmol) and *tert*-BuLi (0.47 mmol) in anhydrous THF) was added dropwise to Mes_2SiF_2 (0.1441 g, 0.47 mmol) in pentane (20 mL) at 23°C. The reaction mixture was allowed to warm to rt and stirred for 23 h before work-up under acidic conditions (6M H_2SO_4). The reaction mixture was extracted with ether, the ether extracts were combined and dried over $MgSO_4$. All solvents were removed. The crude mixture was purified by chromatography (silica gel; hexanes, CH_2Cl_2). In addition to starting materials, the following compounds were separated and identified: Mes_2FSi(*tert*-Bu), Mes_2SiHF, $Mes_2HGeGeHMes_2$ (total weight 50.6 mg), and $(Mes_2FSi)_2O$ (34.3 mg, 12%).

Characterization for $(Mes_2FSi)_2O$:

^{1}H NMR (ppm) 6.61 (s, 8H, MesH), 2.45 (d, J = 2.1 Hz, 24H, *o*-Me), 2.03 (s, 12H, *p*-Me).

^{1}H NMR ($CDCl_3$, ppm) 6.84 (s, 8H, MesH), 2.41 (d, J = 2.2 Hz, 24H, *o*-Me), 2.29 (s, 12H, *p*-Me).

^{19}F NMR ($CDCl_3$, ppm) -119.9 (d, J_{SiF} = 289 Hz)

^{29}Si NMR ($CDCl_3$, ppm) -22.7 (d, J_{SiF} = 289 Hz)

MS *m/z* CI, isobutane (%) 586(0.25, M^+), 468(0.5), 467(34, M^+-Mes), 303(100), 302(44, Mes_2FSiOH), 285(8, Mes_2SiF), 283(20, Mes_2SiOH).

Lit.[5] ^{1}H NMR ($CDCl_3$, ppm): 6.69 (s, 8H, *m*-H, aromatic ring), 2.50 (s, 24H, *o*-Me), 2.22 (s, 12H, *p*-Me).

^{19}F NMR ($CDCl_3$, ppm) -120.9 (d, J_{SiF} = 287 Hz)

^{29}Si NMR ($CDCl_3$, ppm) -31.53 (d, J_{SiF} = 287 Hz)

5.4 Reaction between 1 and LDA

5.4.1 E= MeI.

To a solution of 1 (0.12 g, 0.20 mmol) in THF (10 mL) was added LDA[6] (1 mL of a solution made from $^iPr_2NH$ (5 mL, 35.7 mmol), BuLi (16.5 mL, 44.1 mmol, 2.67 M in hexanes) and hexanes (20 mL)) at -23°C (dry ice-CCl_4). The bath was removed and the solution was stirred for 6 h before quenching with MeI. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give $Mes_2(Me)GeSiHMes_2$,10, (2.5 mg, 2%) and some unidentified products.

5.4.2 E= Me_3SiCl.

To a solution of 1 (0.11 g, 0.19 mmol) in THF (10 mL) was added LDA[6] (1 mL of a solution made from $^iPr_2NH$ (5 mL, 35.7 mmol), BuLi (16.5 mL, 44.1 mmol, 2.67 M in hexanes) and hexanes (20 mL)) at -23°C (dry ice-CCl_4). The bath was removed and the solution was stirred for 6 h before quenching with Me_3SiCl. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give $Mes_2HGe(SiMe_3)$ (13.5 mg), 16, $Mes_2(Me_3Si)GeSiHMes_2$ (5.4 mg), 12 and unidentified products. Both $Mes_2HGe(SiMe_3)$ and $Mes_2(Me_3Si)GeSiHMes_2$ contained unidentified products.

5.5 Synthesis and Reaction of $Ph_2HGeSiClMes_2$ with *tert*-BuLi.

5.5.1 Synthesis of Ph_2GeH_2

Phenylmagnesium bromide was prepared by the addition of a solution of bromobenzene (10 mL, 14.9 g, 95 mmol) dissolved in Et_2O (100 mL) into a flask containing Mg (4.8 g, 197 mmol) in Et_2O (50 mL), over 1.5 h. The mixture was stirred well during the addition and then refluxed for 3 h. The concentration of the Grignard reagent was determined by back-titration. To a vigorously stirred solution of $GeCl_4$ (4.6 mL, 40.3 mmol) dissolved in Et_2O (75 mL) was added at 0°C the Grignard reagent (138 mL, 0.58 M, 79.3 mmol) over 1.25 h. The mixture was then stirred for 3 h at 0°C, hydrolyzed using 1 N HCl, and extracted with Et_2O, and the combined extracts were dried over $MgSO_4$. All the solvents were removed to yield a yellow liquid. To the crude product was added dry Et_2O (115 mL). To this solution was added $LiAlH_4$ (2.2g, 58 mmol). The mixture was refluxed for 3.5 h. Excess $LiAlH_4$ was destroyed by the slow addition of saturated NH_4Cl solution. The reaction mixturewas extracted with Et_2O. The combined organic layers were washed with brine and then dried over $MgSO_4$ and filtered. Removal of the solvent yielded a yellow liquid. The crude product was purified by a vacuum distillation (64°C, 0.04 mm Hg) to yield Ph_2GeH_2 (5.17g, 57%).

IR (thin film, cm^{-1}) 2051 (Ge-H)

^1H NMR (ppm) 7.07-7.63 (m, 10H, Ph-H), 5.15 (s, 1H, Ge-H).

^{13}C NMR (ppm) 135.48 (Ar-CH), 134.19 (Ar-C), 129.29, 128.65 (Ar-CH).

MS m/z (%) 230 (30, M^+), 153 (30, M^+-Ph), 152 (100, M^+-Ph-1), 151 (92, PhGe).

5.5.2 Synthesis of $Ph_2HGeSiClMes_2$, 22.

To a solution of Ph_2GeH_2 (0.72 g, 3.12 mmol) dissolved in THF (20 mL) at -23°C (dry ice-CCl_4) was added *tert*-BuLi (3 mL, 3.63 mmol, 1.21 M in pentane) in one shot. The reaction mixture was stirred well for 6 h at -23°C (dry ice-CCl_4). The yellow germyllithium solution was then added dropwise to a solution of Mes_2SiCl_2 (1.32 g, 3.9 mmol) dissolved in THF (40 mL) at -23°C (dry ice-CCl_4). The resulting solution was warmed to rt and stirred overnight. After removing the solvent, the crude product was washed with pentane to remove the lithium salts.

Purification[b] by chromatography (neutral alumina; 5% CH_2Cl_2 in hexane) yielded $Ph_2HGeSiClMes_2$,22 (548 mg, 33%) and $(Ph_2HGe)_2SiMes_2$ (214 mg, 19%), 23.

Characterization for $Ph_2HGeSiClMes_2$, 22:

IR (thin film, cm^{-1}) 2039 (Ge-H)

^1H NMR (ppm) 7.08-7.63 (m, 10H, Ph-H), 6.60 (s, 4H, Mes-H), 5.54 (s, 1H, Ge-H), 2.35 (s, 12H, *o*-Me), 2.04 (s, 6H, *p*-Me).

^{13}C NMR (ppm) 143.56, 139.98, 136.51 (Ar-C), 136.11 (Ar-CH), 131.57 (Ar-C), 130.03, 128.96, 128.42 (Ar-CH), 24.41, 20.99 (Me).

^{29}Si NMR 2.14 (d, J = 18 Hz).

MS m/z (%) 530 (3, M^+), 495 (0.4, M^+-Cl), 410 (1.1), 347 (6), 301 (100, Mes_2SiCl), 267 (60), 193 (6, MesGeSi), 181 (12, MesSiCl-1), 151 (12, PhGe), 147 (14, MesSi), 119 (21, Mes).

High resolution MS: calcd for *m/z* $C_{30}H_{33}{}^{35}Cl^{74}Ge^{28}Si$ 530.1252, found 530.1255.

Characterization for $(Ph_2HGe)_2SiMes_2$, 23:

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[b] Purification of the crude reaction mixtures was tricky: the use of silica gel resulted in the loss of product. The loss was reduced when alumina was used as solid absorbent during column chromatography. However, the fractions collected from chromatography contained (in some cases) impurities (Ph_2GeH_2, Mes_2SiCl_2 and/or $(Ph_2HGe)_2SiMes_2$) which could not be separated from $Ph_2HGeSiClMes_2$. Thus, in reactions between $Ph_2HGeSiClMes_2$ and *tert*-BuLi, the crude or partially purified $Ph_2HGeSiClMes_2$ was used.

IR (thin film, cm^{-1}) 2030 (Ge-H)

^{1}H NMR (ppm) 7.00-7.60 (m, 20H, Ph-H), 6.66 (s, 4H, Mes-H), 5.41 (s, 2H, Ge-H), 2.13 (s, 6H, *p*-Me), 2.09 (s, 12H, *o*-Me).

^{13}C NMR (ppm) 144.46, 139.50, 139.06, 136.13 (Ar-C), 135.99, 129.47, 128.70, 128.27 (Ar-CH), 26.47, 21.20 (Me).

^{29}Si NMR -39.14 (t, J = 12 Hz).

MS m/z CI, isobutane (%) 724 (18, M$^+$), 723 (26, M$^+$-1), 722 (24, M$^+$-2), 647 (20, M$^+$-Ph), 646 (M$^+$-Ph-1), 645 (24, M$^+$-Ph-2), 605 (12, M$^+$-Mes), 604 (10, M$^+$-Mes-1), 603 (10, M$^+$-Mes-2), 582 (18), 570 (4, M$^+$-2Ph), 505 (22), 495 (72, Mes$_2$SiGeHPh2), 462 (52), 353 (50), 343 (96, Mes$_2$SiPh), 301 (94), 267 (100, Mes$_2$SiH), 151 (32, PhGe), 147 (12, MesSi), 120 (58, MesH), 119 (46, Mes).

5.5.3 Reaction of Ph$_2$HGeSiClMes$_2$ with *tert*-BuLi in THF.

E = MeI; Ph$_2$MeGeSiHMes$_2$, 25.

Addition of *tert*-BuLi (3.5 mL, 4.24 mmol, 1.21M in pentane) to crude Ph$_2$HGeSiClMes$_2$ (0.27 g) in THF (6 mL) at -23°C (dry ice-CCl$_4$), followed by warming to rt and stirring for 6 h yielded a bright yellow solution. Addition of MeI (3 mL) to the reaction mixture resulted in immediate decolorization. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH$_2$Cl$_2$) to give 25 (83.1 mg) and unidentified products.

IR (thin film, cm^{-1}) 2123 (s, Ge-H)

^{1}H NMR (ppm) 7.10-7.60 (m, 10H, Ph-H), 6.70 (s, 4H, Mes-H), 5.86 (s, 1H, Ge-H), 2.28 (s, 12H, *o*-Me), 2.09 (s, 6H, *p*-Me), 0.88 (s, 3H, Ge-Me).

^{13}C NMR (ppm) 144.86, 140.68, 139.08, 135.93 (Ar-C), 134.96, 129.14, 128.58, 128.38 (Ar-CH), 24.27, 21.09, -2.53 (Me).

^{29}Si NMR -52.92 (d, J=185 Hz).

MS m/z CI, Isobutane (%) 510 (34, M$^+$), 509 (62, M$^+$-1), 495 (16, M$^+$-Me), 433 (46, M$^+$-Ph), 391 (49, M$^+$-Mes), 305 (40), 291 (52), 281 (100), 267 (56, Mes$_2$SiH), 243 (33, Ph$_2$MeGe), 151 (9, PhGe), 147 (22, MesSi), 120 (14, MesH), 119 (22, Mes).

High resolution MS calcd for *m/z* $C_{31}H_{36}{}^{74}Ge^{28}Si$ 510.1798, found 510.1797.

<u>E= NH$_4$Cl; Ph$_2$HGeSiHMes$_2$, 26.</u>

Addition of *tert*-BuLi (3.0 mL, 3.63 mmol, 1.21M in pentane) to Ph$_2$HGeSiClMes$_2$ (0.21 g, 0.40 mmol) in THF (20 mL) at -23°C (dry ice-CCl$_4$), followed by warming to rt and stirring for 6 h yielded a bright yellow solution. Addition of a saturated NH$_4$Cl solution (40 mL) to the reaction mixture resulted in immediate decolorization. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH$_2$Cl$_2$) to give <u>26</u> (85.7 mg, 43.2%).

IR (thin film, cm^{-1}) 2130, 2025 (Si-H/ Ge-H).

^{1}H NMR (ppm) 7.00-7.50 (m, 10H, Ph-H), 6.66 (s, 4H, Mes-H), 5.85 (d, 1H, J=6 Hz), 5.51 (d, 1H, J=6 Hz), 2.31 (s, 12H, *o*-Me), 2.05 (s, 6H, *p*-

Me).

^{13}C NMR (ppm) 144.90, 139.31, 137.48 (Ar-C), 135.78, 129.24 (Ar-CH), 128.87 (Ar-C), 128.76, 128.51 (Ar-CH), 24.30, 21.11 (Me).

^{29}Si NMR -53.05 (dd, J = 185 and 12 Hz).

MS m/z CI, Isobutane (%) 496 (34, M$^+$), 495 (72, M$^+$-1), 377 (44, M$^+$-Mes), 376 (24, M$^+$-Mes-1), 267 (100, Mes_2SiH), 266 (12, Mes_2Si), 229 (7, Ph_2GeH), 228 (5, Ph_2Ge), 151 (5, PhGe), 147 (14, MesSi), 119 (17, Mes).

High resolution MS calcd for *m/z* $C_{30}H_{33}{}^{74}Ge^{28}Si$ (M$^+$-1) 495.1563, found 495.1597.

E = MeOH; $Mes_2HSiOMe$.

Addition of *tert*-BuLi (3.0 mL, 3.63 mmol, 1.21M in pentane) to $Ph_2HGeSiClMes_2$ (0.19 g, 0.37 mmol) in THF (20 mL) at -23°C (dry ice-CCl_4), followed by warming to rt and stirring for 5.5 h yielded a bright yellow solution. Addition of MeOH (2 mL) to the reaction mixture resulted in immediate decolorization. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give Ph_2GeH_2 and unidentified products, $Mes_2HSiOMe$ (77.9 mg, 72%) and unidentified products.

Characterization for $Mes_2HSiOMe$:

IR (thin film, cm^{-1}) 2140 (Si-H).

^{1}H NMR (ppm) 6.71 (s, 4H, Mes-H), 6.06 (s, 1H), 3.38 (s, 3H, OMe), 2 47 (s, 12H, *o*-Me), 2.09 (s, 6H, *p*-Me).

^{1}H NMR (CDCl$_3$, ppm) 6.79 (s, 4H, Mes-H), 5.77 (s, 1H), 3.52 (s, 3H, OMe), 2.35 (s, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me).

^{13}C NMR (ppm) 144.73, 139.74 (Ar-C), 129.37 (Ar-CH), 51.81, 24.30, 21.11 (Me).

^{29}Si NMR -16.47 (d, J=207 Hz).

MS m/z (%) 298 (16, M$^+$), 283 (4, M$^+$-Me), 178 (34, M$^+$-Mes-1), 147 (12, MesSi), 120 (16, MesH), 59 (100, SiOMe).

High resolution MS: calcd for *m/z* $C_{19}H_{26}O^{28}Si$ 298.1753, found 298.1757.

Lit^7 ^{1}H NMR (CCl$_4$, ppm) 6.68 (s, 4H, Mes-H), 5.72 (s, 1H), 3.47 (s, 3H, OMe), 2.32 (s, 12H, *o*-Me), 2.22 (s, 6H, *p*-Me).

5.5.4 Reaction of Ph$_2$HGeSiClMes$_2$ with *tert*-BuLi in a Hydrocarbon Solvent.

5.5.4.1 E= MeI.

Addition of *tert*-BuLi (1.6 mL, 2.7 mmol, 1.7M in pentane) to crude Ph$_2$HGeSiClMes$_2$ (0.36 g) in pentane (10 mL) at -23°C (dry ice-CCl$_4$), followed by warming to rt and stirring for 4.5 h yielded a bright yellow solution. Addition of MeI (2 mL) to the reaction mixture resulted in immediate decolorization. After aqueous work up, the product mixture was separated by chromatography (silica gel; hexanes, CH$_2$Cl$_2$) to give Ph$_2$(Me)GeSiHMes$_2$, 25, (8.0 mg) and unidentified products.

5.5.4.2 E = MeOH.

Addition of *tert*-BuLi (0.5 mL, 0.85 mmol, 1.7M in pentane) to crude $Ph_2HGeSiClMes_2$ (0.17 g) in pentane (10 mL) at -23°C (dry ice-CCl_4), followed by warming to rt and stirring for 4 h yielded a bright yellow solution. Addition of MeOH (3 mL) to the reaction mixture resulted in immediate decolorization. After aqueous work up, the product was purified by chromatography (silica gel; hexanes, CH_2Cl_2) to give Ph_2GeH_2, $Mes_2Si(OMe)_2$ and $Ph_2HGeSi(OMe)Mes_2$, **27**. The latter product results from the reaction between MeOH and unreacted starting material: when MeOH-d_4 was used as the quenching agent, $Ph_2HGeSi(OCD_3)Mes_2$ was isolated from the the reaction mixture.

Characterization for $Ph_2HGeSi(OMe)Mes_2$, **27**:

^1H NMR (ppm) 7.00-7.70 (m, 10H, Ph-H), 6.66 (s, 4H, Mes-H), 5.49 (s, 1H, Ge-H), 3.32 (s, 3H, OMe), 2.35 (s, 12H, *o*-Me), 2.08 (s, 6H, *p*-Me).

^{29}Si NMR (ppm) 2.59 (d, J=4.9 Hz)

MS *m/z* CI, isobutane (%) 526(4, M^+), 525(9, M^+-1), 495(0.5, M^+-OMe), 494(1, M^+-OMe-1), 449(8, M^+-Ph), 448(3, M^+-Ph-1), 407(4, M^+-Mes), 406(2, M^+-Mes-1), 341(10, Mes_2SiGeH), 340(20, Mes_2SiGe), 299(8, PhHGeSiMes), 297(100), 221(53, MesSiGe), 151(1, PhGe), 147(8, MesSi), 120(6, MesH), 119(6, Mes).

5.6 Attempted Synthesis of $Ph_2HGeSiFMes_2$, 28.

5.6.1 Attempted Coupling Between Mes_2SiF_2 and Ph_2GeHLi.

A solution of Ph_2GeHLi (made from Ph_2GeH_2 (1.10 g, 4.81 mmol) and *tert*-BuLi (7mL, 4.81 mmol, 1.21M in pentane) in THF (5 mL)) was added dropwise to Mes_2SiF_2 (1.06 g, 3.49 mmol) in THF (25 mL) at --23°C (dry ice-CCl_4). The solution was allowed to warm to rt and stirred overnight before work up under acidic conditions. Separation and purification by chromatography (silica gel; hexanes, CH_2Cl_2) yielded Ph_2GeH_2, Mes_2FSi(*tert*-Bu) (total weight = 470.7 mg) and Mes_2FSiH (50.1 mg, 4%).

5.6.2 Attempted Coupling Between $Mes_2ClSiOMe$ and Ph_2GeHLi

A solution of Ph_2GeHLi (5 mL of a solution made from Ph_2GeH_2 (0.46 g, 2.01 mmol) and *tert*-BuLi (2.7mL, 3.27 mmol, 1.21M in pentane) was added dropwise to $Mes_2ClSiOMe$ (0.33 g, 1.01 mmol) in THF (20 mL) at -23°C (dry ice-CCl_4). The solution was allowed to warm to rt and stirred overnight before work up under acidic conditions. An ^1H NMR spectrum of the crude reaction mixture indicated that it contained only starting materials.

5.7 Synthesis of $Mes_2XGeSiClMes_2$, (X = Cl or Br), and Reactions with Lithium Naphthalenide.

5.7.1 Synthesis of $Mes_2ClGeSiClMes_2$, 29.

A solution of $Mes_2HGeSiClMes_2$ (1.00 g, 1.63 mmol) and a catalytic amount of dibenzoyl peroxide in CCl_4 was refluxed for 30 h. Removal of the solvent yielded a yellow-white solid, which was purified by chromatography (silica gel; 20% CH_2Cl_2 in hexanes). $Mes_2ClGeSiClMes_2$ was obtained as a white solid (676 mg, 64% yield). Spectroscopic data consistent with literature.[8]

Synthesis of $Mes_2BrGeSiClMes_2$, 30.

A solution of $Mes_2HGeSiClMes_2$ (0.97 g, 1.59 mmol), CBr_4 (1.76 g, 5.32 mmol) and a catalytic amount of dibenzoyl peroxide in benzene (60 mL) was heated at 70°C for 15 h. Removal of the solvent yielded a yellow-brown viscous liquid, which was purified by chromatography (silica gel; 20% CH_2Cl_2 in hexanes). $Mes_2BrGeSiClMes_2$, 30, was obtained as a white solid (266 mg, 24% yield).

^1H NMR (C_7D_8, ppm, 100°C) 6.68, 6.67 (each s, total 8H, Mes H), 2.40 (s, 12H, *o*-Me), 2.37 (s, 12H, *o*-Me), 2.09, 2.07 (each s, 6H, *p*-Me).

^{13}C NMR (ppm, 95°C) 145.33, 143.97 (bs), 140.41, 139.25, 130.47, 130.23, 25.71 (bs), 20.89, 20.81.

^{29}Si NMR (ppm) 0.28.

MS *m/z* (%) 692 (0.2, M^+), 657 (0.1, M^+-Cl), 613 (0.9, M^+-Br), 580 (0.5, M^+-Br-Cl), 391 (10, Mes_2GeBr), 312 (100, Mes_2Ge), 301 (88, Mes_2SiCl), 266 (14, Mes_2Si), 193 (32, MesGe), 192 (50, MesSiCl), 120 (44, MesH), 119 (40, Mes)

5.7.2 Reactions Between 29 or 30 and Lithium Naphthalenide.

5.7.2.1 $Mes_2ClGeSiClMes_2$, 29.

A dark green suspension of LiNp was prepared by sonicating a mixture of Li sand (25% dispersion in oil, 59.2 mg, 2.13 mmol) and naphthalene (197.2 mg, 1.54 mmol) in DME (7 mL) for 0.75 h. A solution of $Mes_2ClGeSiClMes_2$ (0.14 g, 0.22 mmol) in DME (5 mL) was added dropwise at -78°C (dry ice-acetone). The reaction mixture was allowed to stir at -78°C for 2 h and then allowed to warm to rt. After stirring the reaction mixture at rt for 6 h, MeOH (5 mL) was added. Acidic work up was followed by removal of the naphthalene by sublimation. Separation of the crude reaction mixture by chromatography (silica gel; hexanes, CH_2Cl_2) yielded Mes_2GeH_2, Mes_2SiH_2 (5.3 mg, in ratio 95:5), $Mes_2HGeSiHMes_2$ and a trace amount of $Mes_2HGeSiClMes_2$ (40.2 mg, in ratio 93:7).

5.7.2.2 $Mes_2BrGeSiClMes_2$, 30.

A dark green suspension of LiNp was prepared by sonicating a mixture of Li sand (25% dispersion in oil, 3.9 mg, 0.14 mmol) and naphthalene (21.0 mg, 0.16 mmol) in DME (5 mL) for 0.75 h. A solution of $Mes_2BrGeSiClMes_2$ (78 mg, 0.11 mmol) in DME (5 mL) was added dropwise at -78°C (dry ice-acetone). The reaction mixture was allowed to stir at -78°C for 2 h and then allowed to warm to rt. After stirring the reaction mixture at rt for 5 h, MeOH (5 mL) was added. Aqueous work up was followed by separation of the crude product by chromatography (silica gel; hexanes, CH_2Cl_2). The products isolated after purification were Mes_2GeH_2, Mes_2SiH_2 (12.2 mg, in ratio 80:20) and $Mes_2HGeSiHMes_2$ (11.9 mg, 19%).

5.8 REFERENCES:

1) Wakefield, B.J. Organolithium Methods, Academic Press: Toronto, 1988, p18.

2) Harwood, L.M. *Aldrichimica Acta* **1985**, 18, 25.

3) a) Doddrell, D.M.; Pegg, D.T.; Bendall, M.R. *J. Mag. Reson.* **1982**, 48, 323-327.

   b) Doddrell, D.M.; Pegg, D.T. *J. Am. Chem. Soc.* **1980**, 102, 6388-6392.

4) Cooke, J. A. *unpublished studies.*

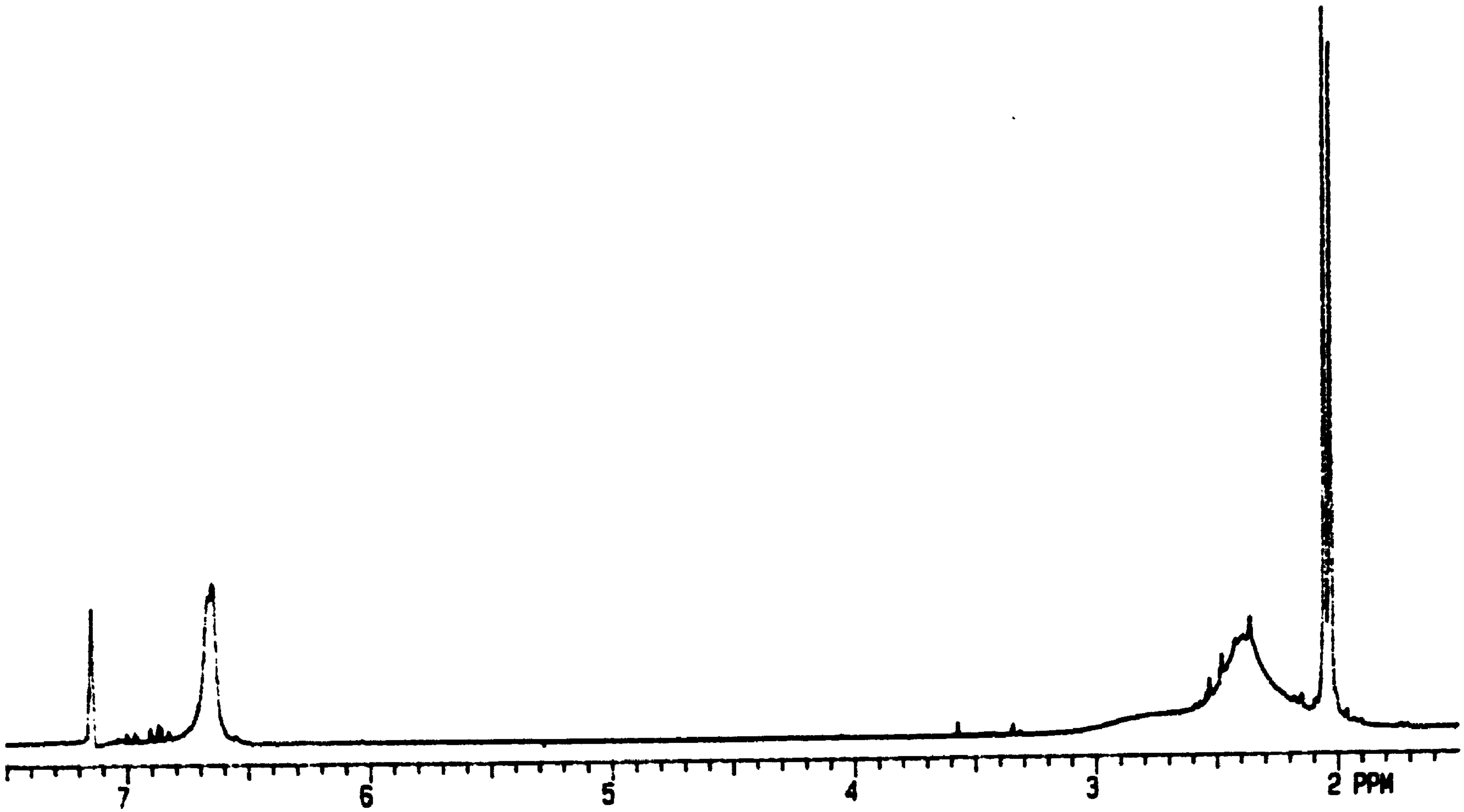
5) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, 111, 3250-3258.

6) House, H. O.; Phillips, W. V.; Sayer J. S. B.; Yau, C. C. *J. Org. Chem.* **1978**, 43, 700-710.

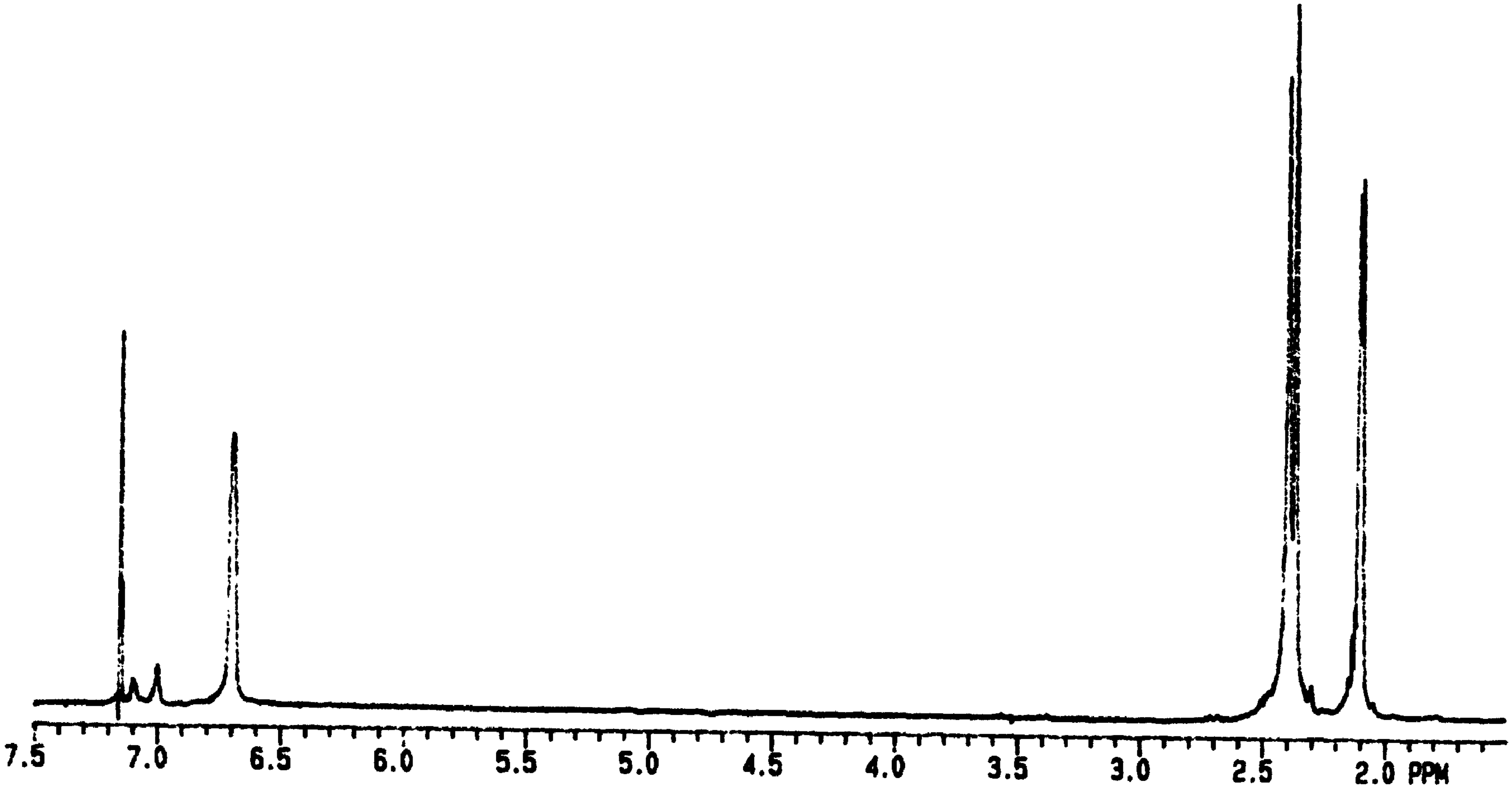
7) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, 194, 147-158.

8) Groh, R. *Honors B.Sc. Thesis*, University of Western Ontario, **1990**.

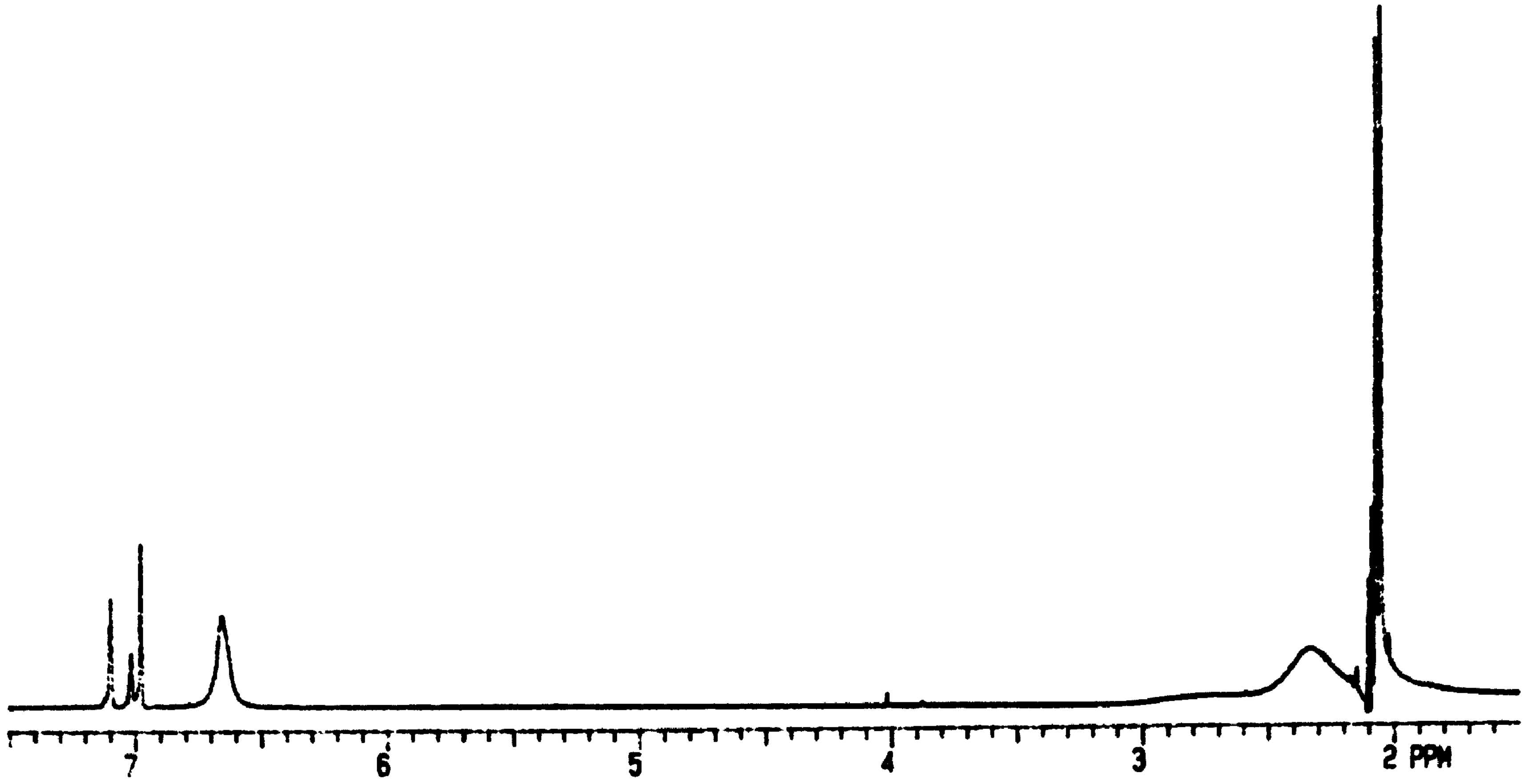
APPENDIX-SELECTED NMR SPECTRA



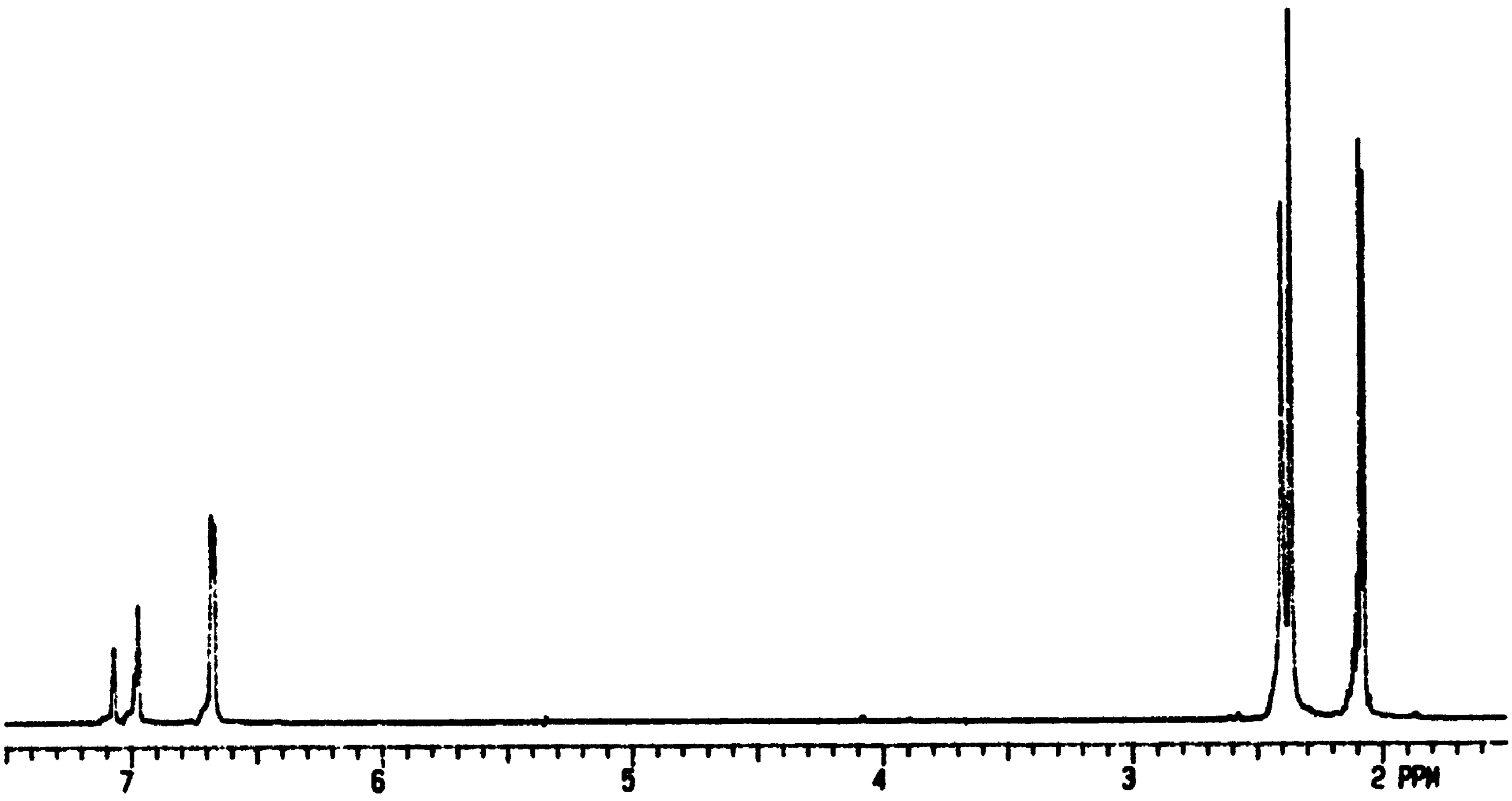
SPECTRUM 1 - ^{1}H NMR Spectrum of 29 at rt



SPECTRUM 2 - ^{1}H NMR Spectrum of 29 at 100°C



SPECTRUM 3 - ^{1}H NMR Spectrum of <u>30</u> at rt



SPECTRUM 4 - ^{1}H NMR Spectrum of <u>30</u> at 100°C