The Si−Ge Bond: Rearrangements, Migrations, and Cleavages

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1-Chloropentamethyl-1-silylgermane, $ClSiMe_2GeMe_3$ (**1**), and 1-chloromethylpentamethyl-1-silylgermane, $ClCH_2SiMe_2GeMe_3$ (**2**), undergo Lewis acid-catalyzed rearrangements to $ClGeMe_2SiMe_3$ (**3**) and $ClSiMe_2CH_2GeMe_3$ (**4**), respectively. Under similar conditions the isomeric $ClGeMe_2SiMe_3$ (**3**) undergoes a fragmentation reaction involving the formation of Me_3SiCl and Me_2GeCl_2, and $ClCH_2GeMe_2SiMe_3$ (**5**) rearranges to $ClMe_2GeCH_2SiMe_3$ (**6**). Methyllithium treatment of $Ph_3SiGeMe_3$ and $Me_3SiGePh_3$ and [1,1′]-tetramethylsilylgermylferrocenophane $[(1,1'\text{-}Me_2SiMe_2Ge((\eta^5\text{-}C_5H_4)_2Fe]$ results in methylation of the silicon atom and formation of the corresponding germyl anion. When the silicon−germanium-bonded fragment is incorporated into a bimetallic transition metal complex, i.e., $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}SiMe_2GeMe_2Fe(\eta^5\text{-}C_5H_5)(CO)_2$ (**7**), base treatment with 1 equiv of lithium diisopropylamide (LDA) leads to predominance of silyl group migration to the cyclopentadienyl ring over germyl migration (9:1). Treatment of **7** with a 2.5 molar excess of LDA, followed by quenching with Me_3SnCl, results in migration of both the silyl and germyl ends of the bridging group to form $(\eta^5\text{-}\{Me_3Sn(CO)_2Fe(\eta^5\text{-}C_5H_4GeMe_2SiMe_2C_5H_4\})Fe(CO)_2SnMe_3$ (**8**).

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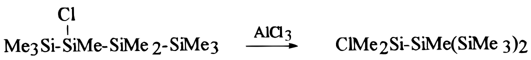
Introduction

The chemistry of the silicon−silicon bond is a mature area of investigation;[1,2] however, until very recently the related chemistry of the silicon−germanium bond has been undeveloped.[3−9] We have studied the structural,[6] physical,[7] and chemical[8−10] properties of such bonds and report here some interesting new chemistry of the Si−Ge bond.

During $AlCl_3$-catalyzed chlorinations (using HCl) of $HSiMe_2GeMe_2Ph$ to form $ClSiMe_2GeMe_2Cl$, monitored by ^{29}Si NMR, we observed unexplained intermediate signals that suggested some interesting rearrangements were occurring. We therefore initiated a study on $AlCl_3$-catalyzed reactions of simple halo- and halomethylsilylgermanes and their isomeric halo- and halomethylgermylsilanes and now report our results. Early studies by Kumada et al.[11] which showed that aluminum chloride treatment of (chloromethyl)pentamethyldisilane resulted in a molecular rearrangement to 1-chloro-1-(trimethylsilylmethyl)dimethylsilane, eq 1, are pertinent. The Kumada group also studied $AlCl_3$-catalyzed rearrangements of both permethylated and chlorooligosilanes and observed rearrangements of the type illustrated in eqs 2.[1]

$$Me_3Si\text{-}Si\text{-}CH_2Cl \xrightarrow[70\,^{\circ}C]{AlCl_3} Me_3Si\text{-}CH_2\text{-}SiMe_2Cl \quad (1)$$

$$ClMe_2Si\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_3 \xrightarrow{AlCl_3} ClMe_2Si\text{-}SiMe(SiMe_3)_2 \quad (2a)$$



$$Me_3Si\text{-}\overset{Cl}{\overset{|}{Si}}Me\text{-}SiMe_2\text{-}SiMe_3 \xrightarrow{AlCl_3} ClMe_2Si\text{-}SiMe(SiMe_3)_2 \quad (2b)$$

After these pioneering studies, Blinka and West observed that the $AlCl_3$-catalyzed rearrangements and alkyl redistributions of permethylated cyclosilanes did not occur in the absence of iron chloride mixed with the $AlCl_3$ catalyst.[12]

Also of interest in our studies have been the alkyllithium-promoted cleavage of the Si−Ge bond, and the base-induced migrations of a bimetallic Si−Ge-bonded complex $FpSiMe_2GeMe_2Fp$, which demonstrate sharp distinctions in the reactivity of the Si and Ge atom.

[†] Dr. Sneh Sharma died May 24, 1999, in El Paso, Texas. Her great talent for chemical research and mentoring undergraduate students set an example for all of us, as did her modesty and professionalism. She is survived by her husband, Dr. Hemant K. Sharma, and son, Ankit. Sneh was much loved.

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Table 1. Spectroscopic and Analytical Data for New Compounds: Yield; bp (mp); Anal. C, H, Calcd (Found)

	PhGeMe$_2$CH$_2$SiMe$_3$
	35.2%; 95−98 °C/20 mmHg; C, 53.98 (54.42); H, 8.30 (8.06)
^{1}H	−0.004 (CH$_2$), 0.02 (SiMe$_3$), 0.40 (GeMe$_2$), 7.47, 7.44 (Ph)
^{13}C	−0.67 (GeMe$_2$), 1.24 (SiMe$_3$), 2.32 (CH$_2$), 128.9, 133.2, 134.0, 143.2 (Ph)
^{29}Si	1.62
	ClGeMe$_2$CH$_2$SiMe$_3$, **6**
	53.5%; 88−90 °C/48 mmHg; C, 31.98 (31.83); H, 7.60 (7.64)
^{1}H	0.026 (SiMe$_3$); 0.17 (CH$_2$); 0.52 (GeMe$_2$)
^{13}C	0.92 (SiMe$_3$); 6.31 (GeMe$_2$); 9.37 (CH$_2$)
^{29}Si	0.76
	ClSiMe$_2$CH$_2$GeMe$_3$, **4**
	70%; 86−88 °C/48 mmHg; C, 31.98 (31.66); H, 7.60 (7.38)
^{1}H	0.00 (CH$_2$); 0.13 (GeMe$_3$); 0.30 (SiMe$_2$)
^{13}C	0.49 (GeMe$_3$); 4.44 (SiMe$_2$); 6.32 (CH$_2$)
^{29}Si	31.20
	ClGeMe$_2$SiMe$_3$, **3**
	49.8%; 87−89 °C/50 mmHg; C, 28.41 (28.27); H, 7.10 (7.05)
^{1}H	0.56 (GeMe$_2$); 0.09 (SiMe$_3$)
^{13}C	3.1 (GeMe$_2$); −2.2 (SiMe$_3$)
^{29}Si	−6.0
	1,1′-GeMe$_2$SiMe$_2$(η^5-C$_5$H$_4$)$_2$Fe, **9**
	57%; 128−129 °C; C, 48.76 (49.09); H, 5.85 (6.13)
^{1}H	0.33 (GeMe$_2$), 0.46 (SiMe$_2$), 4.13, 4.15, 4.45, 4.47 (Fc)
^{13}C	−2.49 (GeMe$_2$), −1.59 (SiMe$_2$), 70.03, 70.52, 71.03, 71.51, 73.13, 73.79 (Fc)
^{29}Si	0.12
	(η^5-{Me$_3$Sn(CO)$_2$Fe(η^5-C$_5$H$_4$GeMe$_2$SiMe$_2$C$_5$H$_4$})Fe(CO)$_2$SnMe$_3$, **8**
	58%, C, 34.30 (34.20); H, 4.55 (4.52)
^{1}H	0.35 (SiMe$_2$), 0.42 (GeMe$_2$), 0.49, 0.51 (SnMe$_3$), 4.19, 4.21 (C$_5$H$_4$)
^{13}C	δ −4.4 (SnMe$_3$), −2.91 (GeMe$_2$), −2.30 (SiMe$_2$), 83.16, 83.81, 86.63, 87.20 (C$_5$H$_4$), 215.65, 216.0 (CO)
^{29}Si	−15.8
^{119}Sn	−140.9, −141.9
ν(CO)	1986.3, 1938.5 cm^{-1}
	(η^5-FpGeMe$_2$SiMe$_2$C$_5$H$_4$)Fe(CO)$_2$SnMe$_3$ and (η^5-FpSiMe$_2$GeMe$_2$C$_5$H$_4$)Fe(CO)$_2$SnMe$_3$
^{1}H	0.42 (SiMe$_2$), 0.53 (GeMe$_2$), 0.70 (SnMe$_3$), 4.08 (C$_5$H$_5$), 4.19, 4.26 (C$_5$H$_4$)
^{13}C	−3.7 (SnMe$_3$), −1.53 (GeMe$_2$), 2.03 (SiMe$_2$), 82.49 (C$_5$H$_5$), 83.54, 87.15 (C$_5$H$_4$)
^{29}Si	−9.73 FpGeMe$_2$SiMe$_2$(η^5-C$_5$H$_4$)Fe(CO)$_2$SnMe$_3$; 26.79 FpSiMe$_2$GeMe$_2$(η^5-C$_5$H$_4$)Fe(CO)$_2$SnMe$_3$
	(η^5-C$_5$H$_4$GeMe$_2$GePh$_3$)Fe(η^5-C$_5$H$_4$SiMe$_3$)
	66%, C, 59.7 (59.37); H, 5.77 (5.89)
^{1}H	δ 0.20 (SiMe$_2$), 0.70 (GeMe$_2$), 3,97, 4.15 (Fc), 7.16, 7.57, 7.5 (Ph)
^{13}C	δ −1.40 (GeMe$_2$), −0.28 (SiMe$_2$), 77.50, 76.99, 76.49 (Fc), 128.09, 128.40, 135.26, 137.96 (Ph)
^{29}Si	−3.23

Experimental Details

All solvents were dry and oxygen-free; ClSiMe$_2$GeMe$_3$ (**1**), ClGeMe$_2$SiMe$_3$ (**3**), and their chloromethyl derivatives (**2** and **4**) were prepared by literature procedures,[8a,9] as were Ph$_3$GeSiMe$_3$, Ph$_3$SiGeMe$_3$, and FpSiMe$_2$GeMe$_2$Fp.[6a,8b] Anhydrous aluminum chloride was purchased from Sigma; silica gel (Mallinckrodt) and alumina (Fisher) 70−200 mesh were used for column chromatography. Mass spectral analysis was obtained using a Hewlett-Packard 5890/5971 GC/mass spectrometer with 70 eV ionizing energy. NMR spectra were obtained from a Bruker NR 200, 250, or 300 MHz instrument. LDA was freshly prepared from diisopropylamine and *n*-BuLi. Typical syntheses of the new compounds are illustrated below, and the spectroscopic and analytical data are given in Table 1.

AlCl$_3$ Treatment of ClCH$_2$GeMe$_2$SiMe$_3$. Into a 50 mL Schlenk flask was placed 1.00 g of ClCH$_2$GeMe$_2$SiMe$_3$ (4.43 mmol) in 15 mL of dry benzene, 0.090 g (0.674 mmol) of AlCl$_3$ was added, and the mixture was stirred at room temperature for 24 h. ^{29}Si NMR (0.70 ppm) at this time showed that the compound ClCH$_2$GeMe$_2$SiMe$_3$ had rearranged to ClGeMe$_2$CH$_2$SiMe$_3$. Hexane (20 mL) was added to precipitate AlCl$_3$. After filtering the solution, solvents were distilled and the crude rearranged product ClGeMe$_2$CH$_2$SiMe$_3$ (0.50 g, 2.21 mmol, 50%) was obtained. To confirm the rearrangement, the crude ClGeMe$_2$CH$_2$SiMe$_3$ was treated with Fp$^-$Na$^+$ in THF at 0 °C, and the mixture was brought to room temperature and stirred overnight. After the removal of THF, the red oil was extracted with 50 mL of hexane and the salts were filtered. The filtrate was concentrated to 5 mL and passed through a silica gel column, and a yellow band was developed with hexane and collected. After removing solvents, 0.3 g of FpGeMe$_2$CH$_2$SiMe$_3$ (37%) was obtained. The NMR data of the compound were in total accord with published data.[9]

The rearranged compound, ClGeMe$_2$CH$_2$SiMe$_3$, was also synthesized by the aluminum chloride-catalyzed chlorination of PhGeMe$_2$CH$_2$SiMe$_3$.

Synthesis of PhGeMe$_2$CH$_2$SiMe$_3$. PhMe$_2$GeLi, obtained from 7.3 g (33.9 mmol) of PhMe$_2$GeCl and 0.95 g (0.14 g-atom) of Li in 60 mL of THF, was added dropwise to 4.15 g (33.9 mmol) of ClCH$_2$SiMe$_3$ in 30 mL of THF at −25 °C. The reaction mixture was brought to room temperature and stirred for 24 h. THF was removed under vacuum, and the mixture was extracted with 60 mL of hexane and filtered. After the removal of solvents under vacuum, the product, PhGeMe$_2$CH$_2$SiMe$_3$, was distilled at 95−98 °C/20 mmHg. Yield: 3.2 g (11.9 mmol, 35.2%).

Synthesis of ClGeMe$_2$CH$_2$SiMe$_3$. In a 50 mL Schlenk flask, equipped with a gas inlet tube and stirrer, was placed 2.0 g (7.46 mmol) of PhGeMe$_2$CH$_2$SiMe$_3$ in 15 mL of dry C$_6$H$_6$ and 0.06 g (0.45 mmol) of AlCl$_3$. Dry hydrogen chloride gas was bubbled through the mixture with stirring at room temperature; a slightly exothermic reaction took place. The reaction was monitored by ^{29}Si NMR spectroscopy. After about 20 min the ^{29}Si NMR resonance of the starting material at 1.6 ppm had disappeared, and a new ^{29}Si NMR resonance

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appeared at 1.1 ppm. At this point bubbling of hydrogen chloride was discontinued, and 2 mL of acetone was added to deactivate the $AlCl_3$ catalyst. Removal of the solvents, followed by the distillation (bp 88−90 °C/48 mmHg) of the residue, gave 0.9 g (3.98 mmol, 53.5% yield) of $ClGeMe_2CH_2SiMe_3$.

Synthesis of $ClSiMe_2CH_2GeMe_3$. The Grignard reagent Me_3GeCH_2MgCl was synthesized from 2.51 g (15.0 mmol) of Me_3GeCH_2Cl and 0.36 g (0.015 g-atom) of Mg in 30 mL of dry diethyl ether. The Grignard reagent was added dropwise to 1.93 g (15.0 mmol) of Me_2SiCl_2 in 20 mL of diethyl ether at 0 °C. The reaction mixture was stirred at this temperature for about 3 h and then brought to room temperature slowly and stirred for 18 h. Diethyl ether was distilled, and salts were precipitated with 50 mL of hexane. After filtration and removal of solvents, the colorless liquid product, $ClSiMe_2CH_2GeMe_3$, was distilled at 86−88 °C/48 mmHg. Yield: 0.5 g (2.21 mmol, 14.7%).

$AlCl_3$ Treatment of $ClSiMe_2GeMe_3$. A 100 mL sidearm flask was fitted with a magnetic stirring bar and a Claisen adapter with a nitrogen inlet at the top. To a solution of 4 g (18.8 mmol) of **1** in 30 mL of benzene was added 1.14 g (8.5 mmol) of anhydrous aluminum chloride. The mixture was stirred at room temperature for 48 h and monitored by ^{29}Si NMR for that period. The disappearance of the ^{29}Si NMR signal at 28 ppm indicated the reaction was complete. The reaction mixture was then flash-distilled under vacuum to separate the product from the aluminum chloride catalyst. Fractional distillation of this catalyst-free distillate gave 2 g (9.4 mmol, 50%) of the isomer $ClGeMe_2SiMe_3$.

$AlCl_3$ Treatment of $ClGeMe_2SiMe_3$. The procedure was the same as above except that 1 g (4.7 mmol) of compound **3** was allowed to react with 0.28 g (2.1 mmol) of anhydrous aluminum chloride. No rearrangement of this compound occurred, and instead fragmentation of the compound was observed. The main fragmentation involved cleavage of the Si−Ge bond and produced trimethylchlorosilane, as evidenced by NMR spectral data.

$AlCl_3$ Treatment of $ClCH_2SiMe_2GeMe_3$. A 100 mL sidearm flask was fitted in the same fashion as above. To the flask was added a solution of 3 g (13.3 mmol) of **2** in 35 mL of benzene and then 0.8 g (5.9 mmol) of anhydrous aluminum chloride. The mixture was stirred at room temperature for 10 h and monitored by ^{29}Si NMR; $ClCH_2SiMe_2GeMe_3$ (^{29}Si NMR (δC_6D_6): −7.2 ppm) rearranged smoothly to produce 2.09 g (9.3 mmol, 70%) of the isomer $ClSiMe_2CH_2GeMe_3$ (**4**) (^{29}Si NMR (δC_6D_6): 31 ppm).

Reaction of MeLi with $Ph_3SiGeMe_3$. To 0.25 g (0.66 mmol) of $Ph_3SiGeMe_3$ in 5 mL of THF in a 50 mL round-bottomed Schlenk flask was added 0.45 mL of MeLi (1.4 M solution in ether) at room temperature and stirred for 1 h. The color of the solution turned light brown, and 0.18 g of Ph_3GeCl (0.66 mmol) dissolved in 5 mL of THF was added. The color of the solution disappeared immediately. The solvent was removed, and the residual white solid was dissolved in 10 mL of hexane and filtered. GC/MS analysis of the filtrate showed it to be a mixture of Ph_3SiMe and $Ph_3GeGeMe_3$. After recrystallization from hexane 0.22 g of $Ph_3GeGeMe_3$ (0.52 mmol, 78%) was obtained as a first crop. The mother liquor was decanted into another flask and concentrated to give 0.14 g (0.51 mmol, 77%) of Ph_3SiMe. Both materials were identified by spectroscopic analysis and comparison with authentic materials.

Synthesis of 1,1′-$GeMe_2SiMe_2(\eta^5\text{-}C_5H_4)_2Fe$. To 2.8 g (15.0 mmol) of ferrocene, dissolved in 150 mL of hexanes in a 250 mL Schlenk flask, was added 5.5 mL (37 mmol) of TMEDA followed by 23 mL (37 mmol) of an *n*-BuLi solution (1.6 M) in hexane. The mixture was stirred overnight at room temperature. During this time an orange precipitate formed and the solution was red in color. The solution was transferred via cannula to another flask, and the orange precipitate was washed with hexanes three times. To the precipitate was added 50 mL of hexanes, the flask was cooled to −78 °C, and then 3.5 g (15.0 mmol) of $ClSiMe_2GeMe_2Cl$ (dissolved in 20 mL of hexanes) was added dropwise and the reaction mixture was brought to room temperature slowly and stirred overnight. The solution was filtered through Celite and, after removing the solvent, yielded a yellow solid. The yellow solid was recrystallized from hexanes to yield **9**, 2.1 g (6.1 mmol, 57%), mp 128−129 °C.

Reaction of MeLi with 1,1′-$GeMe_2SiMe_2(\eta^5\text{-}C_5H_4)_2Fe$. To 0.100 g (0.29 mmol) of 1,1′-$GeMe_2SiMe_2(\eta^5\text{-}C_5H_4)_2Fe$ in 10 mL of THF in a 100 mL Schlenk flask was added 0.20 mL of MeLi at room temperature. Immediately, the color of the solution turned dark orange, and the solution was stirred for 1 h. A solution of Ph_3GeCl (0.098 g, 0.29 mmol dissolved in 10 mL of THF) was added to the dark orange-colored solution. The solution was stirred for 30 min, and then the THF was removed. An orange waxy material was extracted in 20 mL of hexane. The solution was filtered, concentrated to 5 mL, and chromatographed on a 2 × 25 cm silica gel column. The orange band was extracted with hexane. Hexane was removed, and 0.120 g (0.19 mmol, 66%) of $(\eta^5\text{-}C_5H_4GeMe_2GePh_3)Fe(\eta^5\text{-}C_5H_4\text{-}SiMe_3)$ was obtained as an orange solid (mp 73−75 °C).

The reaction of a catalytic amount of MeLi with [1,1′]-tetramethylsilylgermylferrocenophane resulted in the formation of a small amount of ferrocenylene polymer (<5%).

Treatment of $FpSiMe_2GeMe_2Fp$ with 1 equiv of LDA. To a 50 mL THF solution of $FpSiMe_2GeMe_2Fp$ (0.60 g, 1.16 mmol) was added 2.0 mL of a 0.56 M solution of freshly prepared LDA in THF at −25 °C. There was an immediate color change from yellow to red-orange, and after the solution had been stirred for 1 h, IR monitoring showed the formation of the anion by the appearance of ν(CO) bands at 1868.1, 1812.3, 1779.5, and 1753.9 cm^{-1}. This solution was treated with Me_3SnCl (0.230 g, 1.15 mmol) and slowly brought to room temperature. The solvent was removed, and the resulting reddish-brown waxy material was extracted with 30 mL of hexane and filtered. The solution was concentrated to 5 mL and placed on a 2.5 × 10 cm alumina column. The resulting yellow band was eluted with hexane. Removal of the solvent yielded a mixture of starting material (40%), $(\eta^5\text{-}FpGeMe_2\text{-}SiMe_2C_5H_4)Fe(CO)_2SnMe_3$ (50%), and $(\eta^5\text{-}FpSiMe_2GeMe_2C_5\text{-}H_4)Fe(CO)_2SnMe_3$ (10%). The migrated product was contaminated with a small amount of starting material even after repeated crystallization (mp 132−134 °C).

Treatment of $FpSiMe_2GeMe_2Fp$ with 2 equiv of LDA. To a THF solution (50 mL) of $FpSiMe_2GeMe_2Fp$ (0.40 g, 0.77 mmol) in a 100 mL Schlenk flask was added 4.00 mL (1.80 mmol) of a LDA solution at −25 °C. The solution turned deep orange, and the solution was stirred for 2 h. IR monitoring of the reaction at this time indicated the presence of ν(CO) bands at 2005.6, 1989.5, 1944.2, 1916.0 1867.1, 1809.8, 1773.5, and 1751.2 cm^{-1}. A solution of Me_3SnCl (0.310 g) in 10 mL of THF was added at −25 °C, and after 1 h IR analysis showed only two bands at 1978.7 and 1927.6 cm^{-1}. The solvent was removed, and the resulting brown waxy material was extracted with a 90:10 hexane/methylene chloride mixture. This solution was placed on a 2.5 × 10 cm alumina chromatography column. The resulting yellow band was eluted with a 90:10 hexane/methylene chloride mixture. Removal of the solvent and recrystallization from hexane yielded 0.38 g (0.45 mmol, 58%) of yellow $(\eta^5\text{-}\{Me_3SnFe(CO)_2(\eta^5\text{-}C_5H_4SiMe_2GeMe_2C_5H_4)\}Fe(CO)_2\text{-}SnMe_3)$ (mp 135−137 °C).

Results and Discussion

Aluminum Chloride Interactions with Halo- and Halomethylsilyl(germyl)germane(silane). The reactions of the silicon−germanium-bonded compounds **1**, **2**, **3**, and **5** with $AlCl_3$ led to products that involved molecular rearrangements (**1** → **3**, **2** → **4**, and **5** → **6**) or

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Table 2. Relevant Bond Energies

bond	*D* (kJ/mol)	refs
C−Cl	−; 327; 327	18−21
Si−Cl	391; 391; 381; **427;** 490	18−22
Ge−Cl	340; 342; 350; **385**	18−21
Si−C	301; 301; 318; **356;** 394	18−22
Ge−C	237; 270; 213; **314**	18−21
Si−Si	226; 297; 222; **297;** 332	18−22
Ge−Ge	163; 260; 188; **264**	18−21
Si−Ge[a]	195; 278; 205; **280**	18−21

[a] Estimated from the averages of the Si−Si and Ge−Ge bond energies. Values in **bold** represent the average of various high-level calculations (MP2, PMP2, MP3, MP4) from ref 21.

cleavage of the Si−Ge bond in the case of **3**, eqs 3−6.

$$\mathrm{ClSiMe_2GeMe_3}\ (\mathbf{1}) \xrightarrow{\mathrm{AlCl_3}} \mathrm{ClGeMe_2SiMe_3}\ (\mathbf{3}) \quad (3)$$

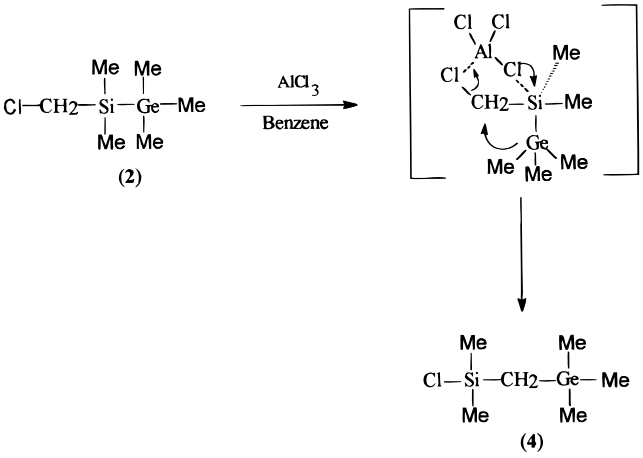
$$\mathrm{ClCH_2SiMe_2GeMe_3}\ (\mathbf{2}) \xrightarrow{\mathrm{AlCl_3}} \mathrm{ClSiMe_2CH_2GeMe_3} \quad (4)$$

$$\mathrm{ClGeMe_2SiMe_3}\ (\mathbf{3}) \xrightarrow{\mathrm{AlCl_3}} \mathrm{ClSiMe_3} + [\mathrm{Me_2GeCl_2}] \quad (5)$$

$$\mathrm{ClCH_2GeMe_2SiMe_3}\ (\mathbf{5}) \xrightarrow{\mathrm{AlCl_3}} \mathrm{ClGeMe_2CH_2SiMe_3} \quad (6)$$

To understand this chemistry, we focus primarily on the thermodynamics involved in the process. The published bond energies associated with the various bonds involved in these rearrangements and cleavages cover a range of values, and a complete set of reliable data does not exist. We have chosen values from several literature sources, both experimental and those derived from various calculations, and such data are collected in Table 2. We found no experimental values for the energetics of the Si−Ge bond and have arbitrarily chosen the average of the published values for the Si−Si and Ge−Ge bonds. A theoretical value of 280 kJ/mol has been published for the compound $\mathrm{SiGeH_6}$. Using the tabulated data, the calculated enthalpies of isomerization for **2** → **4** and **5** → **6** are clearly exothermic, ranging from −136 to −40 kJ/mol. The cleavage of **3**, eq 5, is also strongly exothermic. Thus the rearrangements of **2** → **4** and **5** → **6** ($\mathrm{ClCH_2SiMe_2GeMe_3} \rightarrow \mathrm{ClSiMe_2CH_2GeMe_3}$ and $\mathrm{ClCH_2GeMe_2SiMe_3} \rightarrow \mathrm{ClGeMe_2CH_2SiMe_3}$) involve the transformation of a relatively weaker Cl−C bond to stronger Si−Cl and Ge−Cl bonds. This is further accompanied by rupture of the weak Si−Ge bond with formation of more stable Si−C and Ge−C bonds.

Scheme 1



The transformation **1** → **3** ($\mathrm{ClSiMe_2GeMe_3} \rightarrow \mathrm{ClGeMe_2SiMe_3}$), involving the rupture of the Cl−Si and C−Ge bonds and the formation of the Cl−Ge and C−Si bonds, is less clear. From some published data this seems to be exothermic,[18,20] driven by the lower stability of the Ge−C bond. Using other data,[19] and more recent theoretical bond dissociation energies,[21] the rearrangement appears thermally neutral[21] or even slightly endothermic.[19] However, the cited value for the Ge−C bond energy in ref 19 is noted to be "under revision". Overall the paucity of reliable information prevents a definitive statement at this time.

The mechanism of these rearrangements is presumably similar to that originally suggested by Kumada et al. This involves a transition state containing bridging alkyl, aryl, silyl, and germyl groups with concurrent formation of aluminum halide silyl(germyl) interactions based upon hypervalent geometry at the metalloid atom, e.g., Scheme 1.

It is of interest to note that Fp-substituted silylgermylmethanes and germylsilymethanes, Fp = (η^5-$\mathrm{C_5H_5}$)-$\mathrm{Fe(CO)_2}$), undergo similar rearrangements when treated photochemically, eqs 7.[9]

$$\mathrm{Fp\text{-}CH_2{-}SiMe_2{-}GeMe_3} \rightarrow \mathrm{Fp{-}SiMe_2{-}CH_2{-}GeMe_3} \quad (7a)$$

$$\mathrm{Fp\text{-}CH_2{-}GeMe_2{-}SiMe_3} \rightarrow \mathrm{Fp{-}GeMe_2{-}CH_2{-}SiMe_3} \quad (7b)$$

The mechanism of these rearrangements is very different from that depicted in Scheme 1. For example, the reaction described in eq 7a proceeds via an initial CO expulsion, followed by a β-elimination reaction to form an intermediate complex, (η^5-$\mathrm{C_5H_5}$)Fe(CO)($\mathrm{GeMe_3}$)-($\mathrm{SiMe_2{=}CH_2}$). After rotation about the silene−iron bond, recombination of a CO ligand to the metal atom results in a migratory insertion of the germyl group to the

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silene, thereby forming the isomeric complex.[9] The variation in mechanism is even more complicated since the tungsten analogue, $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3$, undergoes a complete β-elimination of the silene CH_2SiMe_2 with concurrent formation of $(\eta^5\text{-}C_5H_5)W(CO)_3GeMe_3$.[9]

Reactions of Silicon−Germanium-Bonded Compounds with Organolithium Reagents. The cleavage of silicon−silicon bonds by methyllithium to produce methylsilanes and silyl anions is well-represented in the literature, e.g., eqs 8 and 9.[13]

$$(Me_3Si)_4Si + MeLi \rightarrow [(Me_3Si)_3Si]^-Li^+ + SiMe_4 \quad (8)$$

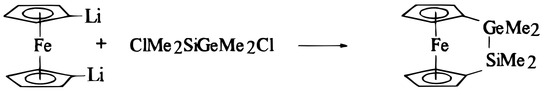
$$(Me_3)_3SiSiMe_2SiMe_2Si(SiMe_3)_3 + MeLi \rightarrow [(Me_3Si)_3SiSiMe_2]^-Li^+ + (Me_3Si)_4Si \quad (9)$$

Similar chemistry should be observable for the reactions of such organolithium reagents with silicon−germanium-bonded compounds. We have chosen to study the isomeric pair of such compounds $Ph_3SiGeMe_3$ and $Me_3SiGePh_3$. Both compounds react smoothly with MeLi to yield only two products, both of which indicate the Si−Ge bond is cleaved to yield the corresponding methylsilane and germyllithium, eqs 10 and 11.

$$Ph_3SiGeMe_3 + MeLi \rightarrow Ph_3SiMe + [Me_3Ge]^-Li^+ \xrightarrow{Ph_3GeCl} Me_3GeGePh_3 \quad (10)$$

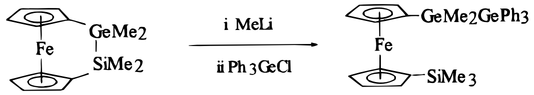
$$Me_3SiGePh_3 + MeLi \rightarrow Me_4Si + [Ph_3Ge]^-Li^+ \xrightarrow{Me_3GeCl} Me_3GeGePh_3 \quad (11)$$

We extended this study to the interesting molecule [1,1′-tetramethylsilylgermyl]ferrocenophane, **9**. This is readily obtained from the reaction of dilithioferrocene and 1,2-dichlorotetramethylsilylgermane, eq 12.



(12)

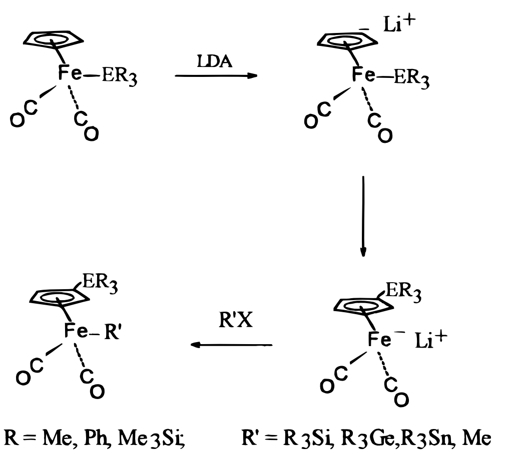
A very smooth and high-yield reaction resulted in the methylation of the silyl group and formation of the germyl anion, which was quenched with Ph_3GeCl, eq 13.



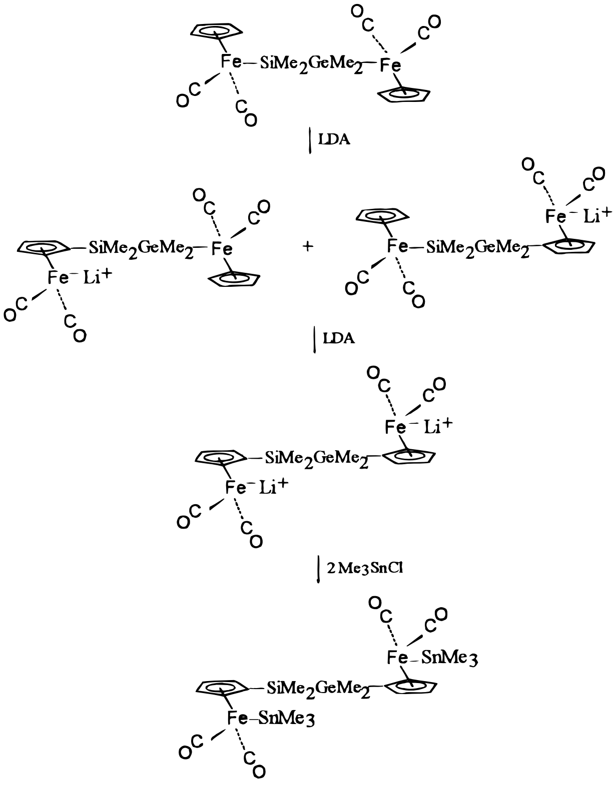
(13)

This result suggested that **9** could be a useful precursor to a series of novel silylene(germylene)ferrocenylene polymers, $[SiMe_2GeMe_2(C_5H_4)Fe(C_5H_4)]_n$, formed by the anionic ring opening as has been observed for the related [1]-silyl-, germyl-, and stannylferrocenophanes.[14] To date we have obtained only trace amounts of polymeric materials from this route, but we are continuing our study of this system.

Scheme 2



Scheme 3



In the examples noted above, the preference for nucleophilic attack to take place at the silicon atom, regardless of the substituents on silicon and germanium, is striking. Such a result is similar to an early report by Eaborn and Mahmoud, who noted that treatment of $R_3GeSiPh_3$, R = Me, Et, with NaOMe/MeOH resulted in the formation of Ph_3GeH, eq 14.[15]

$$R_3Si{-}GePh_3 + NaOMe/MeOH \rightarrow [R_3SiOMe] + Ph_3GeH \quad (14)$$

The methoxysilane was not observed. It was suggested that this selectivity was due to the greater ease of nucleophilic attack on Si by the methoxide ion and the "*much greater ease of formation of* $[R_3Ge]^-$ *than* $[R_3Si]^-$ *anions from corresponding precursors*". The Baines group have similarly noted methylithium cleavage of a Si−Ge bond in both germasilene[3a] and a cyclic silagermane[16a] with the same type of regiospecificity. Fluoride-induced cleavages of this bond are similarly regiospecific.[16b] We have no precise information concerning the mechanisms of the process of the chemistry

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involving methylithium. A simple and direct nucleophilic attack on silicon is possible, given the greater electronegativity of Ge compared with that of Si using the Allred-Rochow, Mullikan, Allen, and Sanderson scales.[20] However, given the small difference, with group changes about the two atoms this may not always be true. Indeed whereas methyllithium treatment of $(Me_3Si)_4Ge$ yields Me_4Si and $[(Me_3Si)_3Ge]^-Li^+$, similar treatment of $(Me_3Ge)_4Si$ yields Me_4Ge and $[(Me_3Ge)_3Si]^-Li^+$, although these may be special cases.[24] Furthermore, since the outcome is the same regardless of the steric constraints on the two central metalloids for $Ph_3EE'Me_3$, the mechanism may be more complex than a simple S_N2 process. Since nucleophilic attacks are often known to occur via an initial electron-transfer process, such a mechanism cannot be ruled out in the present case.[23] This would involve transient formation of a silylgermyl anion radical which cleaves to form the silyl radical (which recombines with the methyl radical) and germyl anion.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2SiMe_2GeMe_2$ with LDA. If the silicon−germanium bond is transposed into a transition metal environment, changes in the reactivity would be expected. It is now well-established that silicon, germanium, tin, and lead compounds of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2ER_3$, (E = Si, Ge, Sn, Pb) react with bases such as lithium diisopropylamide (LDA) to effect migrations of the metalloid group from the metal center to the cyclopentadienyl ligand, Scheme 2 .[17]

In the case where the ER_3 group in Scheme 2 is an oligosilyl group, clean migrations are obtained. For the corresponding bimetallic complexes, $FpSiMe_2SiMe_2Fp$, both a single and double migration can occur under the appropriate reaction conditions to form $(\eta^5\text{-}FpSiMe_2SiMe_2C_5H_4)Fe(CO)_2R'$ and $[R'(CO)_2Fe]_2(\eta^5\text{-}C_5H_4SiMe_2)]_2$ respectively.[17h] We studied the corresponding Si−Ge bimetallic complex $FpSiMe_2GeMe_2Fp$, and as noted in Scheme 3, two possible outcomes may be expected when this complex is treated with 1 equiv of LDA, and a single outcome when treated with 2 equiv.

As noted in the Experimental Section, we observed a very strong preference for the initial migration of the silyl−iron-bonded portion of the intermetallic bridge. We were unable to separate the two components of the intermediate reaction mixture after addition of 1 equiv of LDA and quenching with Me_3SnCl. However, it was clear from ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy that, of the migrated product involved, >90% proceeded via the silyl migration route to form the ferrate intermediate $[(\eta^5\text{-}FpGeMe_2SiMe_2C_5H_4)Fe(CO)_2]^-Li^+$. ^{29}Si NMR is particularly useful in the analysis of the reaction mixtures since the nonmigrated silicon atom directly bonded to iron exhibits a resonance at ca. 27 ppm, whereas in the migrated product a ^{29}Si resonance is observed at ca. −10 ppm.

Addition of further LDA to this mixture, or treating the starting material with a 2.5-fold excess of LDA, resulted in the formation of the double-migrated salt. Quenching of this ferrate with Me_3SnCl produced $(\eta^5\text{-}\{Me_3Sn(CO)_2Fe(\eta^5\text{-}C_5H_4GeMe_2SiMe_2C_5H_4\ )\})Fe(CO)_2\text{-}SnMe_3$.

These results are similar in outcome to the direct methyllithium treatment of the isomeric compounds $Ph_3SiGeMe_3$ and $Me_3SiGePh_3$ in the sense that nucleophilic substitution occurs at Si rather than Ge when an option exists. It is of interest that we observed no reaction when the bimetallic compound $FpSiMe_2GeMe_2Fp$ was treated with MeLi and found no evidence for Si−Ge bond cleavage reactions.

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