$[Cp^*Ru(PR_3)Cl_2]$.[5] Now we have found that treatment of these phosphine adducts with excess NaSPh in MeOH gives monomeric thiolate complexes $[Cp^*Ru(PR_3)(SPh)_2]$ (R = Me, Ph) in 39 and 74% yields, respectively. Solutions of these complexes are EPR-active, and both show broad singlet resonances at $g = 2.08$. In the cyclic voltammograms of these complexes appear two reversible waves corresponding to reversible one-electron oxidation and reduction processes (R = Me, +0.14, −0.82 V; R = Ph, +0.50, −0.73 V). Especially in the case of the PMe_3 adduct the complex is susceptible to oxidation at a less positive potential of +0.14 V due to the strong electron-donating ability of the phosphine ligand.

Further investigations of the reactions of complex 2 and its phosphine adducts with a variety of sulfur compounds are in progress to prepare highly aggregated ruthenium–sulfur clusters.

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen coordinates (2 pages); a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Reaction of Chloro(chloromethyl)dimethylsilane and -germane with Group 14 Element Nucleophiles

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Reaction of chloro(chloromethyl)dimethylsilane (**1**) or -germane (**2**) with group 14 element nucleophiles, $R_3M'Li$ (**3**, M′ = Si, Ge, and Sn), was examined to prepare $R_3M'–MMe_2–CH_2–Cl$ compounds (**4**, M = Si; **5**, M = Ge). However, disubstituted compounds $R_3M'–MMe_2–CH_2–M'R_3$ (**6** or **7**) were mainly produced because the carbon–chlorine bonds in **4** or **5** are activated by the β-effect of the R_3M' groups.

There are few reports on the syntheses of hexaorganodigermanes containing functional group(s) on the alkyl substituents. Although (chloromethyl)pentaalkyldigermane is a key compound for the preparation of such compounds, no appropriate preparation method has been reported.[1]

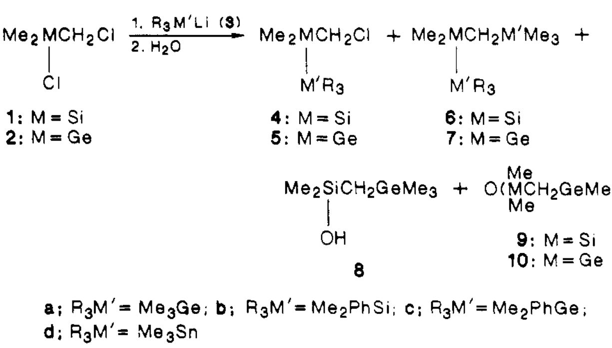
Organo(chloromethyl)dimethylsilane or -germane is easily prepared by treatment of chloro(chloromethyl)dimethylsilane (**1**) or -germane (**2**)[2] with organolithium compounds[3] or Grignard reagents[4] because the Si–Cl or Ge–Cl bond is more reactive than the respective C–Cl bond toward ordinary carbon nucleophiles.

We examined the reaction of **1** and **2** with group 14 element nucleophiles such as R_3Si^-, R_3Ge^-, and R_3Sn^- (**3**) in order to prepare periodic group 14 element–element bonded compounds containing a chloromethyl substituent.

Results and Discussion

When a solution of **1** in tetrahydrofuran (THF) was treated at −78 °C with (trimethylgermyl)lithium (**3a**), prepared from chlorotrimethylgermane and lithium in hexamethylphosphoric triamide (HMPA),[5] the product was not 1-chloro-2,2,3,3-tetramethyl-2-sila-3-germabutane (**4a**) as expected but was a mixture of 2,2,3,3,5,5-hexamethyl-3-sila-2,5-digermahexane (**6a**), 2,4,4-trimethyl-2-sila-4-germa-2-pentanol (**8**), and 1,1,3,3-tetramethyl-1,3-bis[(trimethylgermyl)methyl]disiloxane (**9**) (entry 1 in Table I). A similar result was obtained even at −100 °C (entry 2). This result indicates that the C–Cl bond is attacked more quickly than the Si–Cl bond by **3a**. However, the formation of **8** and **9** was not suppressed by the use of **3a** in excess (entries 3 and 4).

Scheme I



Scheme II

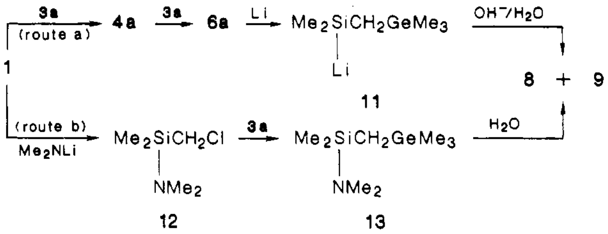


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Table I. Reaction of Chloro(chloromethyl)dimethylsilane (1) and -germane (2) with Group 14 Element Nucleophiles (3a–d)

entry	compd	nucleophile (equiv)[a]	method[b]	reactn conditns		products (%)[c]		
				solvent	temp, °C			
1	1	**3a** (1.2)	A	THF/HMPA	-78		**6a** (29)[d]	**8** + **9** (31 + 16)[d]
2	1	**3a** (1.2)	A	THF/HMPA	-100		**6a** (31)[d]	**8** + **9** (40 + 14)[d]
3	1	**3a** (3.0)	A	THF/HMPA	-78		**6a** (56)[d]	**8** + **9** (19 + 24)[d]
4	1	**3a** (5.0)	A	THF/HMPA	-78		**6a** (48)[d]	**8** + **9** (32 + 20)[d]
5	1	**3a** (1.2)	B	THF/HMPA	-78		**6a** (15)[d]	**8** + **9** (62 + 14[d])
6	1	**3a** (3.0)	B	THF/HMPA	-78		**6a** (0)	**8** (84)
7	1	**3a**[e] (3.0)	B	THF/HMPA	-78		**6a** (52)[d]	**8** + **9** (19 + 18[d])
8	1	**3a** (3.0)	C	hexane/THF/HMPA	-78	**4a** (28)	**6a** (34)	
9	1	**3b** (0.7)	D	THF	-78	**4b** (10)[f]	**6b** (74)[f]	
10	1	**3b** (1.2)	D	THF	-78	**4b** (9)	**6b** (36)	
11	1	**3b** (2.4)	D	THF	-78		**6b** (81)	
12	1	**3b** (1.2)	D	THF/HMPA	-78		**6b** (44)	
13	1	**3b** (1.2)	D	hexane/THF	-78	**4b** (26)	**6b** (31)	
14	1	**3b** (1.2)	D	hexane/THF	-95	**4b** (34)	**6b** (35)	
15	1	**3b** (1.2)	D	pentane/THF	-125	**4b** (29)	**6b** (40)	
16	1	**3c** (1.2)	D	hexane/THF	-95	**4c** (27)	**6c** (41)	
17	1	**3d** (1.2)	D	hexane/THF	-95	**4d** (8)	**6d** (44)	
18	2	**3a** (1.2)	A	THF/HMPA	-78		**7a** (44)[g]	
19	2	**3a** (1.2)	B	THF/HMPA	-78		**7a** (10)	**10** (30)
20	2	**3a** (3.0)	C	hexane/THF/HMPA	-78	**5a** (37)	**7a** (41)	
21	2	**3b** (1.2)	D	THF	-78	**5b** (19)	**7b** (22)	
22	2	**3b** (2.4)	D	THF	-78		**7b** (55)	
23	2	**3b** (1.2)	D	hexane/THF	-95	**5b** (44)	**7b** (15)	
24	2	**3c** (1.2)	D	hexane/THF	-95	**5c** (57)	**7c** (19)	

[a] Amount of **3a–d** corresponds to that of chlorotrimethylgermane, chlorodimethylphenylsilane, 1,1,2,2-tetramethyl-1,2-diphenyldisilane, 1,1,2,2-tetramethyl-1,2-diphenyldigermane, or chlorotrimethyltin treated with 2.5–5 times excess of lithium. [b] A: prepared according to Wickham's report.[5] B: prepared under ultrasonic irradiation. C: magnesium dibromide was added to **3a**. D: prepared in THF. [c] Isolated yield. [d] GLC yield. [e] Stoichiometric amount of lithium was used. [f] Based on $Me_2PhSiCl$ used. [g] Based on Me_3GeCl used.

When the preparation of **3a** in HMPA using lithium in excess was carried out under ultrasonic irradiation, the yield of **8** was nearly doubled and **6a** decreased (entries 5 and 6). However, no effect of ultrasonic irradiation was observed when a stoichiometric amount of lithium was used (compare entries 3 and 7). These results suggest that the Si–Ge bond in **6a** is cleaved by lithium dissolved in HMPA to give [dimethyl((trimethylgermyl)methyl)silyl]lithium (**11**). Then **11** is converted to **8** and **9** during aqueous workup via 2,2,4-trimethyl-4-sila-2-germapentane which is unstable in alkaline medium (route a in Scheme II).[6] Indeed, this cleavage was proved experimentally.

Distillation of the reaction mixture of **1** with **3a** (prepared under ultrasonic irradiation) without aqueous workup gave a 45% yield of *N*,*N*-dimethyl-1,1,3,3-tetramethyl-1-sila-3-germabutanamine (**13**) which was quickly hydrolyzed to **8** in the presence of water. Bulten et al. reported that lithium dimethylamide was produced as a byproduct when (triethylgermyl)lithium was prepared from chlorotriethylgermane and lithium in HMPA.[7] Compound **13** may be formed by amination followed by germylation via route b in Scheme II. Thus, considerable amounts of **8** and **9** may be formed via route b and the others via route a in Scheme II.

Reaction of chloro(chloromethyl)dimethylgermane (**2**) with **3a** also gave a mixture of 2,2,3,3,5,5-hexamethyl-2,3,5-trigermahexane (**7a**) and 1,1,3,3-tetramethyl-1,3-bis[(trimethylgermyl)methyl]digermoxane (**10**) (entries 18 and 19).

Preparation of **3a** from chlorotrimethylgermane or hexamethyldigermane with lithium requires the presence of HMPA which causes undesired side reactions. (Dimethylphenylsilyl)lithium (**3b**)[8] and (dimethylphenylgermyl)lithium (**3c**) are obtainable from chlorodimethylphenylsilane[8a] or 1,1,2,2-tetramethyl-1,2-diphenyldisilane[8b,9] and 1,1,2,2-tetramethyl-1,2-diphenyldigermane[10] in THF, respectively, in which dissolution of lithium and the formation of lithium dimethylamide do not occur.

Reaction of **1** with **3b** in THF gave a mixture of 1-chloro-2,2,3-trimethyl-3-phenyl-2,3-disilabutane (**4b**) and 2,3,3,5-tetramethyl-2,5-diphenyl-2,3,5-trisilahexane (**6b**) without the corresponding silanol (entry 10 in Table I). The yield of **4b** based on **3b** was not improved by the use of **3b** in less than an equivalent amount (entry 9). The use of **3b** in excess or addition of HMPA as a cosolvent brought about the formation of **6b** only (entries 11 and 12). The best result was obtained when the reaction was carried out in a mixture of hexane (or pentane) and THF at -95 °C (compare entries 13, 14, and 15).

The reaction of **1** or **2** with (dimethylphenylgermyl)lithium (**3c**) similarly gave a moderate yield of 1-chloro-2,2,3-trimethyl-3-phenyl-2-sila-3-germabutane (**4c**) or 1-chloro-2,2,3-trimethyl-3-phenyl-2,3-digermabutane (**5c**) accompanied by 2,3,3,5-tetramethyl-2,5-diphenyl-3-sila-2,5-digermahexane (**6c**) or 2,3,3,5-tetramethyl-2,5-diphenyl-2,3,5-trigermahexane (**7c**) (entries 16 and 24). Employment of (trimethylstannyl)lithium (**3d**),[11] however, resulted in a low yield of 1-chloro-2,2,3,3-tetramethyl-2-sila-3-stannabutane (**4d**) (entry 17).

Thus, the stepwise substitution reaction using the silyl- (**3b**), germyl- (**3a** and **3c**), and stannyllithium (**3d**) for **1** and **2** was difficult, unlike the carbon analogue,[3] though a decrease in polarities of the solvents improves the yields of **4** and **5**.

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Table II. Characteristic Data of the Products 4, 5, 6, and 7

			^{1}H NMR ($CDCl_3$), δ			elemental anal. found (calcd)	
compd	bp, °C (mmHg)[a]	IR (film), cm^{-1}	CH_2	Me_2M	R_3M'	C	H
4a	90 (25)	1250, 1050, 830, 810, 595, 565	2.89	0.22	0.22	32.30 (31.98)	7.50 (7.60)
4b	130 (27)	1430, 1250, 1110, 835, 805, 735, 700, 650	2.82	0.16	0.42 (Me) 7.20–7.56 (Ph)	54.15 (54.39)	7.82 (7.88)
4c	140 (13)	1430, 1250, 1090, 835, 795, 730, 700	2.86	0.22	0.46 (Me) 7.11–7.43 (Ph)	45.99 (45.97)	6.53 (6.66)
4d	75 (9)	1245, 840, 800, 765, 520	2.98	0.32	0.12	26.78 (26.55)	6.34 (6.31)
5a	90 (10)	1230, 825, 800, 600, 555	3.08	0.32	0.29	26.99 (26.71)	6.36 (6.35)
5b	155 (26)	1430, 1250, 1105, 835, 800, 735, 700, 650, 600	2.96	0.24	0.46 (Me) 7.16–7.56 (Ph)	46.23 (45.97)	6.61 (6.66)
5c	155 (10)	1440, 1240, 1100, 840, 800, 740, 705, 605, 470	3.03	0.34	0.55 (Me) 7.18–7.50 (Ph)	40.22 (39.81)	5.77 (5.77)
6a	80 (6)	1250, 1050, 825, 800, 600, 590, 565	−0.09	0.13	0.13, 0.18	35.13 (35.15)	8.40 (8.52)
6b	150 (0.9)	1430, 1250, 1120, 1050, 830, 800, 730, 700	0.00	0.01	0.25, 0.30 (Me) 7.30–7.47 (Ph)	66.97 (66.59)	8.80 (8.82)
6c	150 (0.25)	1435, 1250, 1100, 1045, 840, 790, 735, 700	0.18	0.10	0.39 (Me) 7.15–7.45 (Ph)	53.14 (52.86)	6.94 (7.00)
6d	135 (25)	1245, 1000, 840, 765, 520	−0.03	0.23	0.04, 0.12	26.85 (27.04)	6.47 (6.56)
7a	110 (24)	1235, 1040, 820, 785, 595, 560	0.03	0.23	0.15, 0.21	30.87 (30.70)	7.35 (7.44)
7b	155 (0.8)	1425, 1245, 1115, 1040, 830, 780, 730, 700, 645	0.07	0.11	0.23, 0.36 (Me) 7.30–7.47 (Ph)	58.52 (58.94)	7.85 (7.81)
7c	130 (0.15)	1430, 1235, 1095, 1040, 785, 730, 700, 600, 460	0.29	0.21	0.37, 0.45 (Me) 7.16–7.64 (Ph)	47.94 (47.92)	6.34 (6.35)

[a] Oven temperature of Kugelrohr distillation apparatus.

Effect of the counterion of the triorganosilyl or -germyl anion was also examined for these substitution reactions. When **3a** was added to a solution of magnesium dibromide in THF and the mixture was then treated with **1** or **2**, the yield of **4a** or 1-chloro-2,2,3,3-tetramethyl-2,3-digermabutane (**5a**) was increased without formation of **8**, **9**, or **10** (entries 8 and 20). Thus, the metal exchange from lithium to magnesium suppressed the cleavage of the Si–Ge bond (route a in Scheme II) and the nucleophilic attack of amide anion (route b). However, the use of a large excess of **3a** was required because a considerable amount of hexamethyldigermane was formed from **3a** by the addition of magnesium bromide. Reaction of **1** with $Me_2PhSiAlEt_2$[12] gave only **6b** in a 59% yield. Employment of $Me_2PhSiMgMe$,[12] $Me_2PhSiZnEt_2Li/CuCN$,[13] $(Me_2PhSi)_2CuLi{\cdot}LiCN$,[14] or $Me_2PhSiNBu_4$[15] brought no fruitful results.

(β-Haloalkyl)silanes $R_3SiCH_2CH_2X$ (X = halogen) are generally much more reactive than the α- or γ-substituted compounds (β-effect of silicon). The C–Cl bonds in **4** and **5** may be more reactive than those of (chloromethyl)triorganosilane or -germane because the chlorine atoms link with the β-position carbon from the silicon or germanium atom introduced.

We compared the relative reaction rate between M–M–C–Cl and M–C–Cl (M = Si or Ge) bond compounds in the reaction with **3b**. Mixtures of **4b** and (chloromethyl)trimethylsilane (**14**) or (chloromethyl)dimethylphenylsilane (**16**) and of **5c** and (chlromethyl)trimethylgermane (**18**) in a 1:1 mole ratio were treated at −95 °C with **3b**, respectively, and the yields of the products were determined after aqueous workup. The yields of M–M–C–Si bond compounds **6b** and 2,3,3,5-tetramethyl-2,5-diphenyl-5-sila-2,3-digermahexane (**19**) were 2–4 times greater than those of the corresponding M–C–Si bond compounds 2,4,4-trimethyl-2-phenyl-2,4-disilapentane (**15**),[16] 2,4-dimethyl-2,4-diphenyl-2,4-disilapentane (**17**),[17] and 2,4,4-trimethyl-2-phenyl-2-sila-4-germapentane (**20**) (see Scheme III). These results indicate that the C–Cl bonds in **4** and **5** are activated by the β-effect of the silyl or germyl group introduced at the first step of the reaction and the second step of the reaction is accelerated to give **6** and **7**.

Experimental Section

All reactions were carried out under an argon atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl prior to use. Hexane and pentane were distilled from sodium wire. Hexamethylphosphoric triamide (HMPA) was distilled under reduced pressure from sodium. Hexane and pentane were distilled from sodium wire. Hexamethylphosphoric triamide (HMPA) was distilled under reduced pressure from sodium. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX 60, JNM-MH-100, or JNM-GSX-400 spectrometer using Me_4Si as internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by using a JEOL JMS-DX 300 GC-MS system (70 eV, EI; 2-m, 5% Silicone SE-30 column). Gas chromatographic analyses were carried out on a Gasukuro Kogyo Model-370 chromatograph with TCD detector using a 1-m, 20% Silicone SE-30 column. All boiling points are uncorrected.

Reaction of Chloro(chloromethyl)dimethylsilane (1) or -germane (2) with (Trimethylgermyl)lithium (3a). General Procedure. Method A (Entries 1–4 and 18 in Table I). A mixture of chlorotrimethylgermane (551 mg, 3.6 mmol) and finely cut lithium (100 mg, 14.4 mmol) in HMPA (2.5 mL, 14.4 mmol) was stirred for 3 h at room temperature and then was mobilized with THF (7.5 mL) according to Wickham's report.[5] The solution (2.5 times the amount for entry 3 and 4.2 times for entry 4) was filtered from excess metal lithium and added to a solution of **1** (432 mg, 3.0 mmol) or **2** (563 mg, 3.0 mmol) in THF (5 mL) at −78 or −100 °C. After 10 min of stirring, the reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with diethyl ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and

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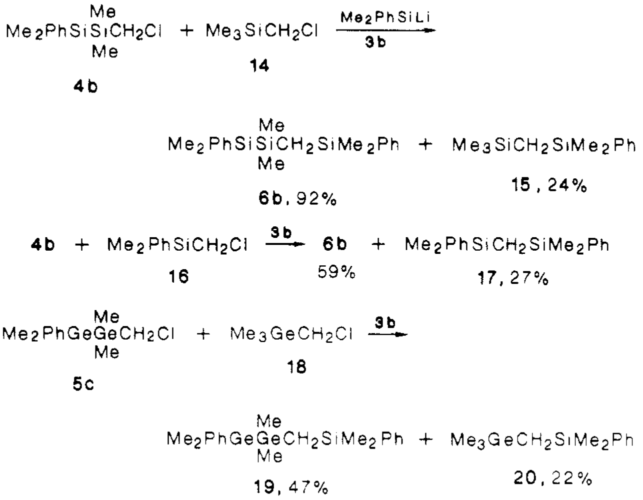
[18] The yields shown in Scheme III are based on the percent yield of each starting chloromethyl compound that was converted to product.

Scheme III[18]



concentrated under reduced pressure.

The residue from 1 was analyzed on a GLC column. The products were identified by comparison of the retention times with authentic samples obtained in the next procedures, and their yields were calculated on the basis of the integrated values of GLC peaks using 1,1,3,3-tetramethyl-1,3-bis(trimethylgermyl)-methyl]disiloxane (**9**) as an internal standard. The yields of 2,2,3,3,5,5-hexamethyl-3-sila-2,5-digermahexane (**6a**), 2,4,4-trimethyl-2-sila-4-germa-2-pentanol (**8**), and **9** are shown in Table I. The characteristic data for **6a** are listed in Table II.

The residue from 2 was chromatographed on a silica gel column (hexane) to give 2,2,3,3,5,5-hexamethyl-2,3,5-trigermahexane (**7a**, 284 mg, 44% based on the chlorotrimethylgermane used). The characteristic data are listed in Table II.

Method B (Entries 5–7 and 19). A mixture of finely cut lithium (100 mg, 14.4 mmol, half the amount for entry 7) in HMPA (2.5 mL, 14.4 mmol) was stirred at 0 °C. After the color changed to blue, a solution of chlorotrimethylgermane (551 mg, 3.6 mmol) in THF (8 mL) was added and the mixture was irradiated with ultrasound for 3 h at room temperature. The solution was treated in a similar manner to that described for method A. The products from 1 were separated on a silica gel column (hexane/AcOEt 10:1) into **8** and a mixture of **6a** and **9**. The yields of **6a** and **9** were determined by GLC analysis.

8: bp 90.0–92.0 °C (43 mmHg); IR (film) 3300, 1250, 1045, 860, 820, 795, 600, 580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.03 (2 H, s, CH$_2$), 0.15 (6 H, s, Me$_2$Si), 0.20 (9 H, s, Me$_3$Ge), 1.83 (1 H, s, OH). Anal. Calcd for $C_6H_{18}GeOSi$: C, 34.83; H, 8.77. Found: C, 34.82; H, 8.80.

Fractional distillation of the products from 2 gave **7a** (109 mg, 10%) and 1,1,3,3-tetramethyl-1,3-bis[(trimethylgermyl)-methyl]digermoxane (**10**, 221 mg, 30%): bp 160 °C (21 mmHg, oven temperature of Kugelrohr distillation apparatus); IR (film) 1240, 1035, 855, 820, 780, 680, 620, 600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.18 (18 H, s, Me$_3$Ge), 0.19 (4 H, s, CH$_2$), 0.34 (12 H, s, Me$_2$GeO). Anal. Calcd for $C_{12}H_{34}Ge_4O$: C, 29.73; H, 7.07. Found: C, 30.02; H, 7.02. The characteristic data for **7a** are listed in Table II.

Method C (Entries 8 and 20). A solution of **3a**, prepared from chlorotrimethylgermane (1.38 g, 9 mmol) by method A, was added at 0 °C to a solution of magnesium dibromide prepared from magnesium (243 mg, 10 mmol) and 1,2-dibromoethane (1.70 g, 9.1 mmol) in THF (13 mL). After being stirred for 1 h at room temperature, the mixture was added to a solution of 1 (429 mg, 3.0 mmol) or 2 (563 mg, 3.0 mmol) in hexane (12 mL) at −78 °C. The reaction mixture was worked up after 5 min of stirring in a similar manner as described above. Silica gel column chromatography (hexane) of the products from 1 gave 1-chloro-2,2,3,3-tetramethyl-2-sila-3-germabutane (**4a**, 186 mg, 28%) and **6a** (315 mg, 34%). The products from 2 were similarly separated to 1-chloro-2,2,3,3-tetramethyl-2,3-digermabutane (**5a**, 296 mg, 37%) and **7a** (437 mg, 41%).

Reaction of 1 or 2 with Group 14 Element Anions (3). General Procedure. Method D (Entries 10, 12–17, 21, 23, and 24). (Dimethylphenylsilyl)lithium (**3b**)[8] was prepared from chlorodimethylphenylsilane (615 mg, 3.6 mmol) and lithium (125 mg, 18 mmol) in THF (5 mL) or from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (487 mg, 1.8 mol) and lithium (62 mg, 9 mmol) in THF (3.5 mL). (Dimethylphenylgermyl)lithium (**3c**) was prepared from 1,1,2,2-tetramethyl-1,2-diphenyldigermane[10] (648 mg, 1.8 mmol) and lithium (62 mg, 9 mmol) in THF (3.5 mL). (Trimethylstannyl)lithium (**3d**)[11] was prepared from chlorotrimethyltin (717 mg, 3.6 mmol) and lithium (250 mg, 36 mmol) in THF (3.5 mL).

The solution of **3b–d** was added dropwise to a solution of 1 (429 mg, 3 mmol) or 2 (563 mg, 3 mmol) in 7 mL of THF, THF–HMPA (5:1), hexane, or pentane (see Table I). After 5 min of stirring, the reaction was quenched with saturated aqueous NH$_4$Cl and the mixture was extracted with diethyl ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The residual oils were chromatographed on silica gel columns (hexane), respectively, to give **4b–d**, **5b,c**, **6b–d**, and **7b,c**. The results are summarized in Table I, and the characteristic data are listed in Table II.

1,1,3,3-Tetramethyl-1,3-bis[(trimethylgermyl)methyl]disiloxane (9). A solution of **3a**, prepared from 8 mmol of chlorotrimethylgermane by method A, was added to a solution of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane[19] (694 mg, 3 mmol) in THF (10 mL) at −78 °C. The reaction was quenched with saturated aqueous NH$_4$Cl after 10 min of stirring, and the mixture was extracted with ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous MgSO$_4$, and concentrated. Distillation of the residue under reduced pressure gave **9** (1.05 g, 88%): bp 145 °C (18 mmHg, Kugelrohr); IR (film) 1040, 1250, 850, 820, 800, 600, 580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.10 (4 H, s, CH$_2$), 0.07 (12 H, s, Me$_2$Si), 0.16 (18 H, s, Me$_3$Ge). Anal. Calcd for $C_{12}H_{34}Ge_2OSi_2$: C, 36.42; H, 8.66. Found: C, 36.15; H, 8.57.

Reaction of 2,2,3,3,5,5-Hexamethyl-3-sila-2,5-digermahexane (6a) with Lithium. A mixture of lithium (40 mg, 5.8 mmol), HMPA (1 mL, 5.8 mmol), and THF (4 mL) was irradiated with ultrasound for 3 h at room temperature and was then added to a solution of **6a** (298 mg, 0.97 mmol) in THF (1 mL) at −78 °C. After 10 min of stirring, the reaction was quenched with saturated aqueous NH$_4$Cl and the mixture was extracted with ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous MgSO$_4$, and concentrated. The residue was chromatographed on a silica gel column (hexane) to give **6a** (107 mg, 36%) and **8** (118 mg, 59%).

***N*,*N*-Dimethyl-1,1,3,3-tetramethyl-1-sila-3-germabutanamine (13).** A solution of **3a**, prepared from 3.6 mmol of chlorotrimethylgermane by method B, was added to a solution of 1 (429 mg, 3.0 mmol) in THF (3 mL) at −78 °C. After being stirred for 0.5 h at the same temperature, the reaction mixture was distilled without aqueous workup to give **13** (315 mg, 45%): bp 90 °C (13 mmHg, Kugelrohr); IR (film) 1280, 1250, 1240, 1180, 1050, 985, 810, 600, 580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ −0.11 (2 H, s, CH$_2$), −0.04 (6 H, s, Me$_2$Si), 0.17 (9 H, s, Me$_3$Ge), 2.43 (6 H, s, Me$_2$N); mass spectrum, *m/z* 235.08192 (M$^+$) (calcd for $C_8H_{23}GeNSi$ 235.08095).

Treatment of a Mixture of 4b and (Chloromethyl)trimethylsilane (14) or (Chloromethyl)dimethylphenylsilane (16) with 3b. To a solution of **4b** (243 mg, 1 mmol) and **14** (123 mg, 1 mmol) or **16** (185 mg, 1 mmol) in hexane (7 mL) was added dropwise at −95 °C a solution of **3b**, prepared from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (162 mg, 0.6 mmol) and lithium (21 mg, 3.0 mmol) in THF (3.5 mL). After completion of the addition, the reaction was quenched immediately with saturated aqueous NH$_4$Cl. The ethereal extract of the reaction mixture was washed with water and saturated aqueous NaCl, dried over MgSO$_4$, and concentrated. Reaction products in the residual oil were identified by comparison of the retention times of GLC with authentic samples of **6b** and **15**[16] or **17**.[17] The yields[18] are shown in Scheme III.

Treatment of a Mixture of 5c and (Chloromethyl)trimethylgermane (18) with 3b. In a manner similar to that described above, a solution of **3b** was allowed to react with a

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[19] *Dictionary of Organometallic Compounds*; Buckingham, J., Ed.; Chapman and Hall: London, 1984; Vol. 2, p 1984.

mixture of **5c** (332 mg, 1 mmol) and **18** (167 mg, 1 mmol) in hexane (7 mL), and the reaction mixture then was worked up. The products were identified as 2,3,3,5-tetramethyl-2,5-diphenyl-5-sila-2,3-digermahexane (**19**, 47%) and 2,4,4-trimethyl-2-phenyl-2-sila-4-germapentane (**20**, 22%).

2,3,3,5-Tetramethyl-2,5-diphenyl-5-sila-2,3-digermahexane (19). To a solution of **5c** (368 mg, 1.1 mmol) in THF (7 mL) was added at −78 °C a solution of **3b** prepared from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (181 mg, 0.67 mmol) and lithium (23 mg, 3.4 mmol) in THF (3 mL). After 0.5 h of stirring at the same temperature, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether. The ethereal extract was chromatographed on a silica gel column (hexane) to give **19** (352 mg, 74%): bp 150 °C (0.35 mmHg, Kugelrohr); IR (film) 1425, 1250, 1115, 820, 785, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (2 H, s, CH_2), 0.20 (6 H, s, Me_2Ge), 0.24 (6 H, s, Me_2Si), 0.44 (6 H, s, Me_2PhGe), 7.28–7.34 (6 H, m, Ph), 7.37–7.40 (2 H, m, Ph), 7.44–7.48 (2 H, m, Ph). Anal. Calcd for $C_{19}H_{30}Ge_2Si$: C, 52.86; H, 7.00. Found: C, 52.78; H, 6.96.

2,4,4-Trimethyl-2-phenyl-2-sila-4-germapentane (20). To a solution of **18** (502 mg, 3 mmol) in THF (7 mL) was added dropwise at −78 °C a solution of **3b**, prepared from 1,1,2,2-tetramethyl-1,2-diphenyldisilane (487 mg, 1.8 mmol) and lithium (62 mg, 9 mmol) in THF (3.5 mL). After 0.5 h of stirring at the same temperature, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether. The extract was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. Distillation of the residue under reduced pressure gave **20** (734 mg, 92%): bp 150 °C (13 mmHg, Kugelrohr); IR (film) 1430, 1250, 1115, 1025, 810, 730, 695, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (2 H, s, CH_2), 0.10 (9 H, s, Me_3Ge), 0.28 (6 H, s, Me_2Si), 7.30–7.36 (3 H, m, Ph), 7.49–7.54 (2 H, m, Ph). Anal. Calcd for $C_{12}H_{22}GeSi$: C, 53.99; H, 8.31. Found: C, 54.04; H, 8.39.

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Registry No. **1**, 1719-57-9; **2**, 6727-64-6; **3a**, 18489-76-4; **3b**, 3839-31-4; **3c**, 25149-72-8; **3d**, 17946-71-3; **4a**, 119795-94-7; **4b**, 21082-16-6; **4c**, 119795-95-8; **4d**, 119795-96-9; **5a**, 119795-97-0; **5b**, 119795-98-1; **5c**, 119795-99-2; **6a**, 119796-00-8; **6b**, 79180-86-2; **6c**, 119796-01-9; **6d**, 119796-02-0; **7a**, 21458-78-6; **7b**, 119796-03-1; **7c**, 119796-04-2; **8**, 119796-05-3; **9**, 119796-06-4; **10**, 119796-07-5; **13**, 119796-08-6; **14**, 2344-80-1; **15**, 18027-71-9; **16**, 1833-51-8; **17**, 1027-86-7; **18**, 5830-55-7; **19**, 119796-09-7; **20**, 119796-10-0; chlorotrimethylgermane, 1529-47-1; chlorodimethylphenylsilane, 768-33-2; 1,1,2,2-tetramethyl-1,2-diphenyldisilane, 1145-98-8; 1,1,2,2-tetramethyl-1,2-diphenyldigermane, 22702-72-3; chlorotrimethyltin, 1066-45-1; 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane, 2362-10-9.

Stereoselective Intramolecular C–H Bond Activation in a Dinuclear Iridium Complex

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Reaction of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (**1**) with diazomethane affords the methylene bridged dimer $[(\eta\text{-}C_5Me_5)Ir(CO)]_2(\mu\text{-}CH_2)$ (**2**). Compound **2** is formed without fragmentation of the metal–metal double bond in the starting material, as shown by isotopic double-labeling experiments. Compound **2** crystallizes in the monoclinic space group $C2/c$ (No. 15) with a = 11.367 (4) Å, b = 13.994 (3) Å, c = 14.458 (2) Å, β = 97.85°, V = 2271.8 Å^3, and Z = 8. The Ir–Ir distance is 2.689 Å. Protonation of **2** with $HBF_4\cdot Et_2O$ affords a cationic species, **3**. Analytical and spectroscopic data are consistent with the formulation $\{[(\eta\text{-}C_5Me_5Ir(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)\}BF_4$. Monitoring of the protonation reaction by ^1H NMR at low temperatures indicates that the inital protonation is stereoselective to give predominantly the cis isomer of **3** as the kinetic product. A slow isomerization occurs to give ultimately the trans isomer of **3**. Facile site exchange in **3-cis** between the methylene hydrogens and the bridging hydride was detected both by spin saturation transfer and line broadening ($\Delta G^{\ddagger}_{223K}$ = 13 kcal/mol). No such exchange process was detectable in **3-trans**.

Introduction

There is great interest in agostic interactions between transition metals and carbon–hydrogen bonds.[1] An important class of compounds containing such interactions are metal dimers and trimers containing bridging methyl groups. Since the seminal work by Shapley and co-workers[2] which established that $Os_3(CO)_{10}(CH_2)H_2$ is in reversible equilibrium with a methyl tautomer, there has been considerable interest in such equilibria, which may serve as models for the activation of C–H bonds in heterogeneous catalytic processes.[3] One synthetic method that has been widely employed in preparation of bridging methyl species is the addition of protic acids to neutral

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