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Bis(dimethylgermyl)alkane–Iron Tetracarbonyls: Synthesis, Photolysis, and Reactivity

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This work concerns the synthesis, spectroscopic analysis, and reactivity of tetracarbonyliron bis(dimethylgermyl)alkanes $Me_2\underline{Ge(CH_2)_nGe(Me_2)Fe}(CO)_4$ (n = 1, 2). These heterocycles are obtained by cyclization of bis(dimethylgermyl)alkanes $Me_2HGe(CH_2)_nGeHMe_2$ (n = 1, 2) with $Fe(CO)_5$ under UV irradiation. They are stable at room temperature, but the heterocycle with n = 1 decomposes under prolonged UV irradiation with formation of the heterocycle with n = 2, perhydrotetragermin, and $(CO)_3Fe(\mu\text{-}GeMe_2)_3Fe(CO)_3$. Various CO substitution reactions with phosphines and cleavage reactions with organic and organometallic halides are described; they provide a convenient procedure for the generation of germanium or tin–carbonyl iron clusters. Reactions of tetracarbonyliron bis(dimethylgermyl)methane with sulfur and with oxygen presumably lead first to the dithia- (or dioxa-) digermolane $Me_2\underline{GeCH_2Ge(Me_2)Y\text{-}Y}$ (Y = S or O) and after, by sulfur (or oxygen) loss, to thia- (or oxa-) digermetane $Me_2\underline{GeCH_2GeMe_2Y}$ (Y = S or O), which are unstable, giving products suggestive of Me_2GeY (Y = O or S) and $Me_2Ge{=}CH_2$ intermediates.

Introduction

Species having M_{14}–M' catenation in polynuclear derivatives are now well-known[1-18] (M' = transition metal). The group of M_{14}–Fe compounds is one of the most studied, and derivatives having one, two, or more iron atoms that are linear or cyclic or involving the M_{14} atom in the form of an R_2M group have been reported.[18,19] However, to our knowledge no four- or five-ring heterocycles having C–Fe–Ge linkages have been described. Since one of the main routes to M_{14}–Fe bonds is through the use of M_{14}–Hg reagents, we thought of using the previously reported germamercurocane[20] precursors and have thereby been able to develop routes to bis(dimethylgermyl)methane–iron tetracarbonyl, $Me_2\underline{GeCH_2Ge(Me_2)Fe}(CO)_4$ (1), and 1,2-bis(dimethylgermyl)ethane–iron tetracarbonyl, $Me_2\underline{GeCH_2CH_2Ge(Me_2)Fe}(CO)_4$ (2).

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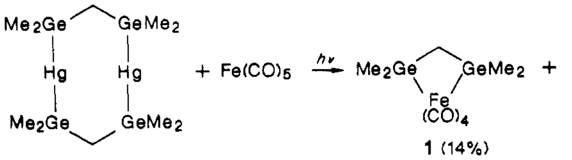
Table I

compds	IR[a] ν_{CO}	^1H NMR[b] CH$_2$	^1H NMR[b] CH$_3$	^{13}C NMR[b] CO$_{ax}$	^{13}C NMR[b] CO$_{eq}$	^{13}C NMR[b] CH$_2$	^{13}C NMR[b] CH$_3$
1	1995 (10), 2035 (9.1), 2060 (5.9) 2080 (5)	0.4	0.7	208.65	208.45	23.96	5.98
2	1980 (9.1), 2000 (10), 2050 (1.1) 2060 (5)	1.15	0.65	209.44	208.99	20.58	4.33

[a] C_6D_6; ν, cm^{-1}; intensity in parentheses. [b] C_6D_6 (δ, ppm)

Results and Discussion

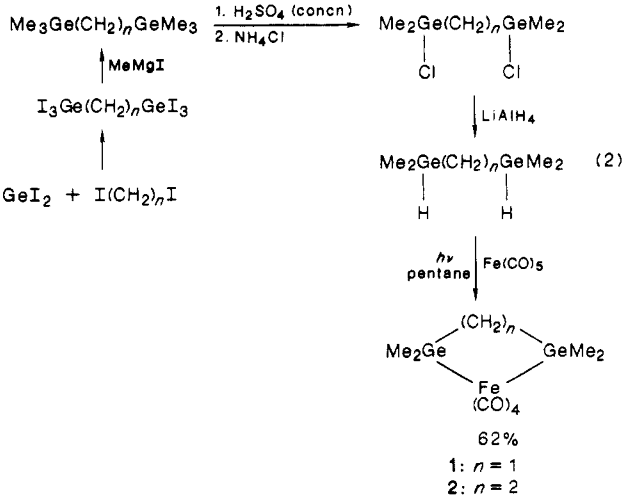
(1) $Me_2Ge(CH_2)_nGe(Me_2)Fe(CO)_4$ (n = 1, 1; n = 2, 2). The bis(dimethylgermyl)methane–iron tetracarbonyl was first obtained by a mercury route involving the elimination of Hg during the UV irradiation of a mixture of the tetragermadimercurocane $Me_2GeHgGe(Me_2)CH_2Ge(Me_2)HgGe(Me_2)CH_2$ and iron pentacarbonyl according to eq 1.



2Hg + CO + unidentified compounds (1)

The low yield obtained in this reaction, the formation of byproducts that were difficult to separate, and, by contrast, the high yields in reactions starting from germanium hydrides and $Fe(CO)_5$[18] encouraged us to use the latter method with bis(dimethylgermyl)alkanes, $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ (n = 1 or 2). These hydrides were obtained by the lithium aluminium hydride reduction of bis(chlorodimethylgermyl)alkanes, $Me_2(Cl)Ge(CH_2)_nGe(Cl)Me_2$ (n = 1 or 2).[21]

The cyclization reaction is practically over after several hours of UV irradiation, and the resulting compounds can be distilled (eq 2).



Compounds 1 and 2 were characterized by MS, IR, and NMR (^1H and ^{13}C) spectroscopy (Table I). The appearance of four CO bands with the usual intensity pattern for $(R_3M)_2Fe(CO)_4$ species[18d] in the IR and of sharp ^1H NMR singlets for methyl and methylenic or ethylenic protons of the germyl ligand are characteristic of C_{2v} local symmetry at iron in the compounds (Figure 1). Their ^{13}C NMR spectra show high stereochemical rigidity because even at 150 °C coalescence of signals due to axial–equatorial exchange of CO is not observed.

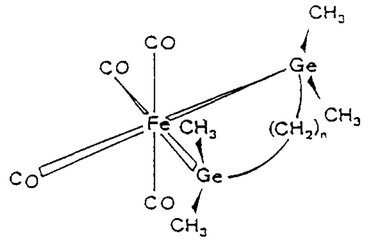
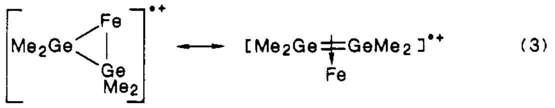
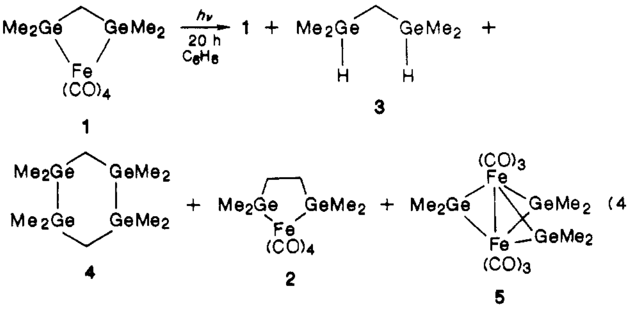


Figure 1.

All mass spectra have peaks corresponding to molecular ions M$^+$ (of weak relative intensity in the case of 1) and to fragmentations characteristic of such heterocyclic structures (loss of carbonyl groups and substituents on the germanium atoms). For the five-membered ring compound 2, the most intense peak corresponds to [M − 140]$^+$, due to loss of all CO groups and C_2H_4, which suggests the formation of a germanium species of the type shown in eq 3. By comparison, in the case of the four-membered ring compound 1, the peak that corresponds to the loss of all carbonyls and :CH$_2$ is much less intense. The most intense peak in this case is [M − 4CO]$^+$, corresponding to usual behavior.



(2) Photochemical Decomposition. Compound 2 is stable photochemically, whereas UV irradiation of 1 in benzene solution produces a complex mixture of germanium derivatives besides $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Analyses by NMR and MS confirm the formation of bis(dimethylgermyl)methane (3), perhydro-1,2,4,5-tetragermin (4),[20] 2, and $(CO)_3Fe(\mu\text{-}GeMe_2)_3Fe(CO)_3$ (5)[22] as represented by eq 4.



This reaction can be explained by an initial loss of CO, under photochemical activation, and formation of the intermediate 1′ which can lead to 3 or 4 by reductive elimination (Scheme I, path A$_1$) and to 2 or 5 by retro [2 + 2] cleavage (Scheme I, path A$_2$). This last cycloreversion could involve formation and symmetrization of an intermediate germaethylene–germylene complex of iron that strongly resembles a key step in the olefin metathesis reaction catalyzed by transition-metal complexes.[23] But we cannot exclude the intervention of radical processes involving homolytic scission (i) of Ge–Fe bonds (Scheme

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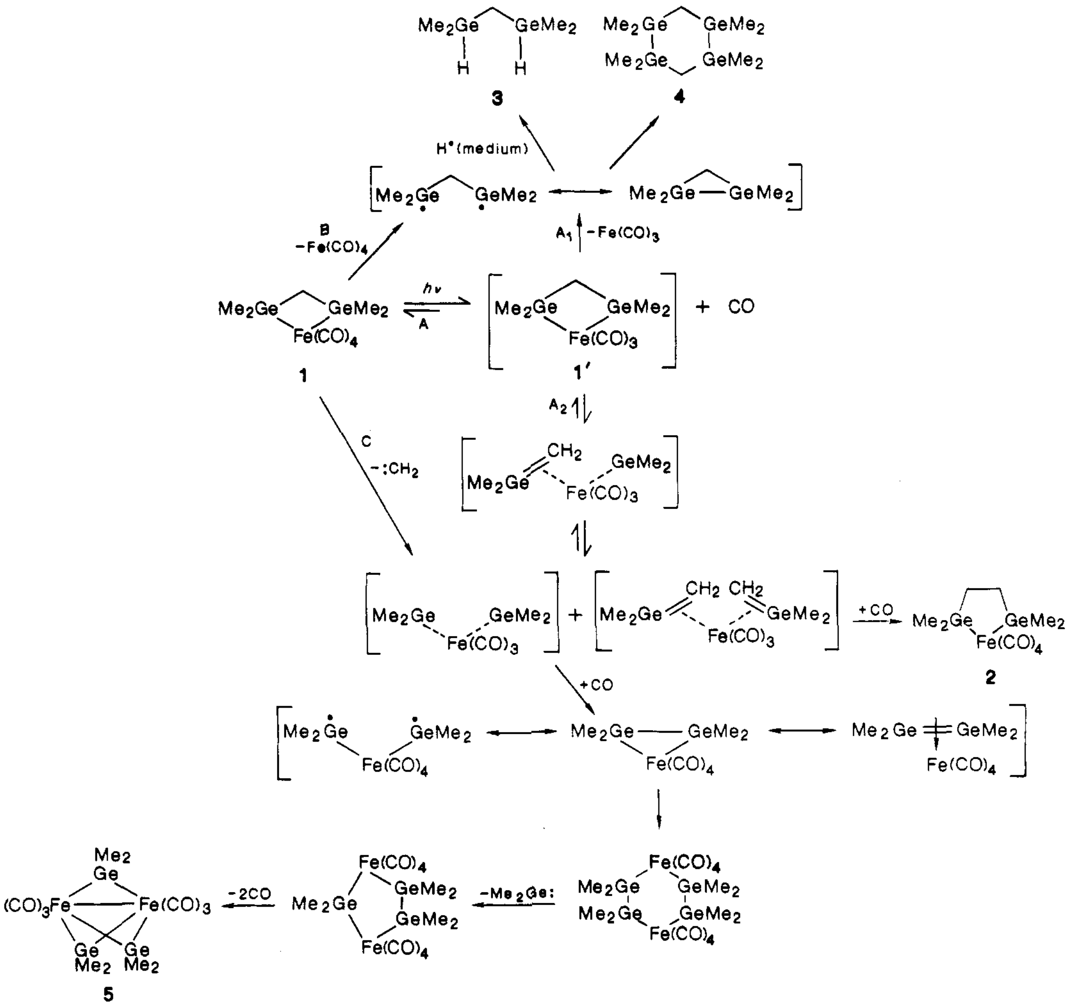
(22) Triplett, K.; Curtis, M. D. *Inorg. Chem.* **1975**, *14*, 2284. Brooks, E. H.; Elder, M.; Graham, W. A. G.; Hall, D. *J. Am. Chem. Soc.* **1968**, *90*, 3587.

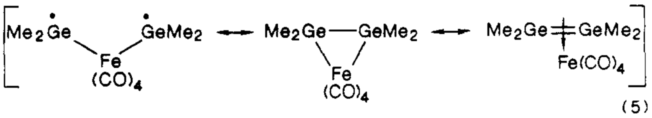
(23) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

Scheme I



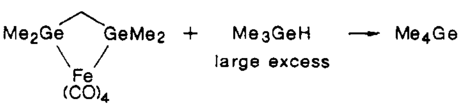
I, path B), probably leading directly to the digermyl biradical

and (ii) of Ge–C bonds (Scheme I, path C), resulting in the formation of carbene, :CH_2 (which can react with **1** or with an intermediate derived from **1** to give **2**), and in the direct formation of the biradical shown in eq 5 which by dimerization, loss of germylene, loss of CO, and rearrangement of Ge–Ge bonds leads to **5** as proposed in ref 22.



(5)

The formation of carbene, :CH_2, during the course of this photolysis finds support in the photolysis of compound **1** in the presence of trimethylgermane (eq 6). Even though



(6)

the yield of Me_4Ge is low (~12%), it is necessary to point out that we observed a parallel decrease in the formation of **2** in the mass balance of this photolysis.

To provide some evidence for methylene intervention in this photolysis, we tried to carry out the photolysis of **1** with CH_2N_2 as precursor of :CH_2. The heterocycle **1** is very sensitive to CH_2N_2 and reacts with it at low temperature, so the formal ring expansion pathway to **2** has not been observed under these experimental conditions. Indeed, hydrolysis of the reaction mixture with deoxygenated water leads to a mixture of iron products and oxides: **12** (major product derived from hydrolysis of **1**) and traces of $(Me_3GeCH_2GeMe_2)_2O$, the production of which suggests the formation of the adduct $\underline{Me_2GeCH_2Ge(Me_2)CH_2Fe}(CO)_4$.

We again found such a decomposition involving formal carbene addition during the attempted synthesis of $\underline{Me_2SiCH_2Si(Me_2)Fe}(CO)_4$, the silicon analogue of **1**, from bis(dimethylsilyl)methane and iron pentacarbonyl, in which distillation of the reaction mixture gave only the adduct bis(dimethylsilyl)ethane–iron tetracarbonyl (**6**).[24] Chromatography on a silica column of the same reaction mixture allowed the isolation only of bis(dimethylsilyl)methane–diiron octacarbonyl (**7**), as has already been observed,[25] according to eq 7. It seems that **6** and **7** are both directly formed during this reaction as **6** is stable on the chromatography column.

(3) Reactions with Phosphines. Since ligands having a lone electron pair are able to substitute one or more CO groups of metal carbonyls, triphenylphosphine complexes of **1** and **2** were easily prepared. Triphenylphosphine reacts with compounds **1** and **2** only under UV irradiation, or on heating. In addition to the expected substitution products **8** and **9**, we observed substantial formation of

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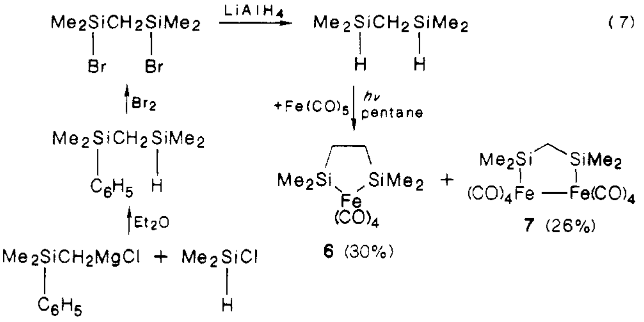
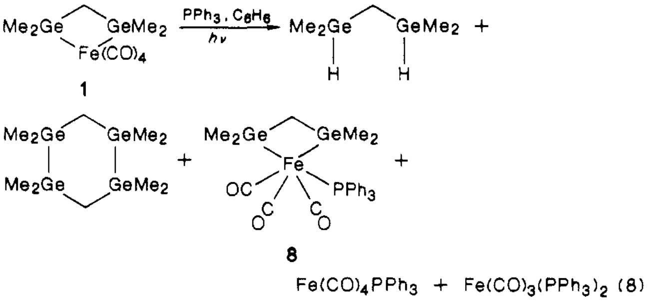
[24] Vancea, L.; Graham, W. A. G. *Inorg. Chem.* **1974**, *13*, 511.

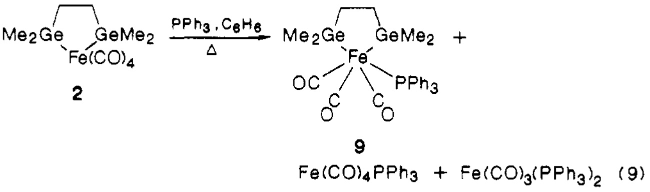
[25] Greene, J.; Curtis, M. D. *Inorg. Chem.* **1978**, *17*, 2324.

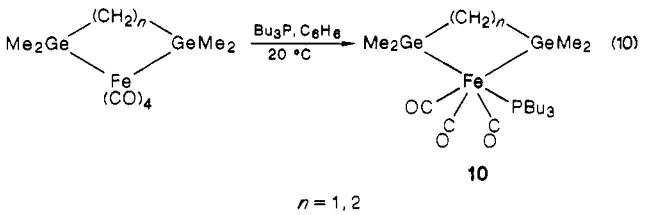


6, isolated by distillation; 7, isolated by column chromatography

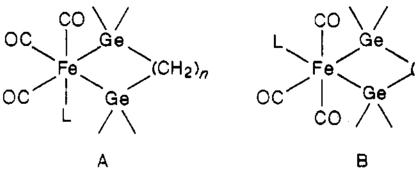
$Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. Since compound **2** is stable to UV irradiation, it seems that in the two cases entry of the phosphine into the coordination sphere of iron causes Ge ligand displacement (eq 8 and 9). In contrast, tributylphosphine reacts nearly quantitatively at ambient temperature without irradiation (eq 10).







Compounds **8**, **9**, and **10** were characterized by NMR, IR, and MS. Two isomers are possible (A, B), each with three infrared-active carbonyl stretching modes. Three

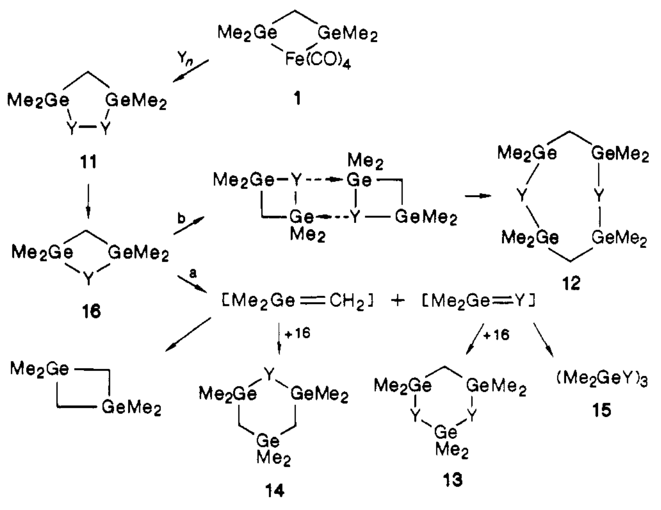


A B

bands are seen in the IR spectra of the compounds reported. Intensity considerations[26] lead us to expect in the spectrum of isomer B a weak A′ mode at the highest frequency, a very strong A″ mode for the mutually trans arrangement of two carbonyls, and a strong A′ mode for the third carbonyl. The observed intensities certainly favor B but do not make an unambiguous choice possible.

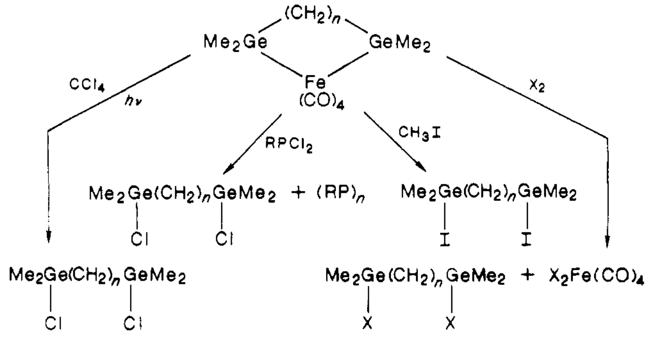
(4) Oxidations by O_2 and S_8. Compounds **1** and **2** are very sensitive to oxygen and sulfur. The behavior of bis(dimethylgermyl)methane–iron tetracarbonyl (**1**) with respect to O_2 and S_8 implies the formation of unstable

Scheme II



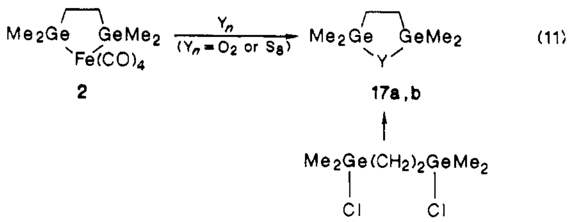
$Y_n = O_2$ or S_8

Scheme III



X = Br or I

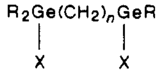
1,5-dioxa- and 1,5-dithia-2,4-digermolanes, the decompositions of which probably involve the tricoordinated species $Me_2Ge{=}CH_2$ and $Me_2Ge{=}Y$ (Y = O, S), as this has been observed in analogous reactions of tetragermadimercurocane[20] and can be summarized by the same reaction sequence (Scheme II). In contrast, reactions of 1,2-bis(dimethylgermyl)ethane–iron tetracarbonyl (**2**) with O_2 and S_8 lead to formation of the corresponding stable oxa- and thiadigermolanes. These are also accessible from the dichloride $Me_2ClGe(CH_2)_2GeClMe_2$ (eq 11).



Y = O, hydrolysis in OH^- medium, **17a**; Y = S, reaction with Na_2S **17b**

(5) Reactions with Halogens and Halides. Like all metal carbonyls, compounds **1** and **2** are very reactive toward halogens and organic and organometallic halides. Halogens and organic halides form dihalo derivatives of the type $Me_2(X)Ge(CH_2)_nGe(X)Me_2$ (n = 1 or 2) (Scheme III). Reactions with bromine are more rapid than with iodine (especially in the case of compound **2**).

The reactions of M_{14} organometallic halides with compounds **1** and **2** are more interesting because they lead to dihalides



$$\underset{X}{R_2Ge}(CH_2)_n\underset{X}{GeR_2}$$

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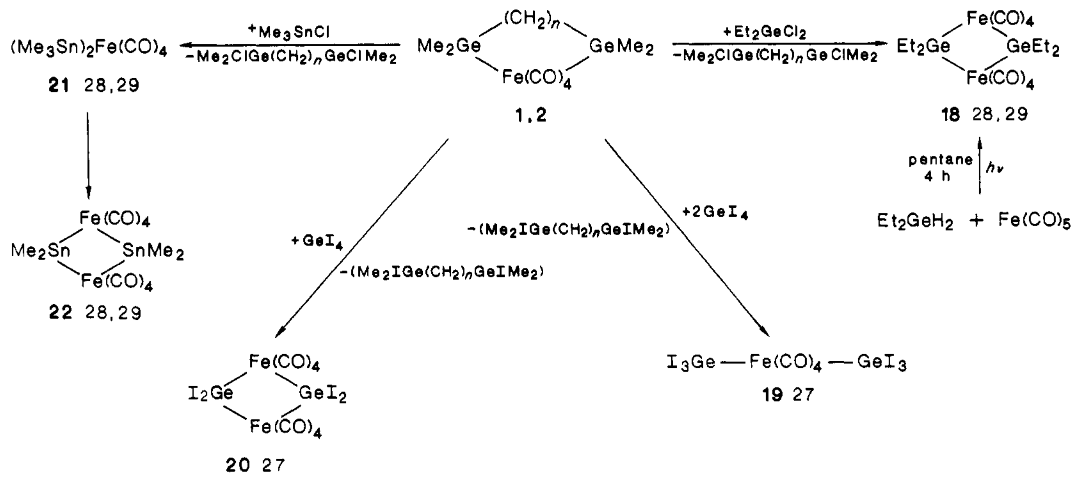
(26) Taylor, R. C.; Horrocks, W. D., Jr. *Inorg. Chem.* **1964**, *3*, 584.

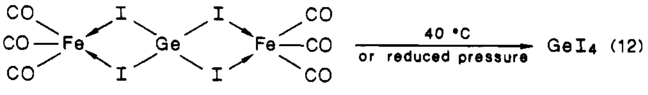
Scheme IV



and to M$_{14}$–iron carbonyl compounds, as summarized by (Scheme IV).

The composition of the various compounds thus obtained were determined by NMR, by elemental analyses, and by comparisons with authentic samples previously prepared by methods described in the literature.[27-30]

Interestingly, note that during the course of our various syntheses of **20** UV irradiation for 4 h of a mixture of GeI_4 and $Fe(CO)_5$ in a 1:4 mole ratio gave an extremely volatile dark red crystalline compound whose analysis corresponds to the composition $GeI_4Fe_2(CO)_6$ (**23**). This compound, which like its silicon analogue, shows four CO stretching vibrations (two resulting from splitting of the largest wave bond in its IR spectrum), certainly has an identical structure with cis configuration for both iron atoms, assuming coupling of the CO vibration via GeI_4 can be ruled out in these compounds[31] (eq 12). The $Fe(CO)_3$ group



23

probably prevents iodine–germanium intermolecular interactions (which occur in crystalline GeI_4), thereby accounting for the high volatility of **23**. Only peaks characteristic of GeI_4 are detected in the mass spectrum of **23**. Compound **23** decomposes rapidly above 40 °C to give GeI_4.

Experimental Section

Compounds **1** and **2** that have germanium–transition-metal bonds are extremely sensitive to hydrolysis and oxidation. They must be manipulated in an argon-filled vacuum manifold. Solvents were rigorously dried and degassed. The relative amounts of various components in a mixture were determined by measuring chromatographic peak areas and by comparison with those of a standard mixture as well as from integrations of NMR peaks.

Gas chromatographic analyses were done on a Varian 1400 (column S.E. 30) apparatus.

Infrared spectra were measured on a Perkin-Elmer 457 instrument. Proton NMR spectra were recorded on Varian T 60 and Varian EM 360 A spectrometers and ^{13}C spectra on a Beckman WP 60 spectrometer. Chemical shifts are given relative to TMS as the internal reference. Melting points were measured on a Reichert apparatus.

Mass spectra were recorded on a Ribermag R 1010 or a Varian Mat 311 A spectrometer operating in the electron-impact mode at 70 eV and samples contained in glass capillaries under argon. In all cases the complex envelope of peaks obtained for polygermanes agreed with the isotopic distribution characteristic of germanium.[32]

Ultraviolet irradiations were done with the aid of a quartz photochemical reaction equipped with a mercury lamp (λ = 254 nm).

Reaction of Iron Pentacarbonyl with Tetragermadimercurocane. A solution of $Me_2GeHgGe(Me_2)CH_2Ge(Me_2)HgGe(Me_2)CH_2$[20] (1.12 g, 1.33 mmol) and $Fe(CO)_5$ (0.26 g, 1.33 mmol) in 4 mL of pentane was irradiated for 5 h at ambient temperatures in a quartz tube by using an Hg lamp (λ = 254 nm). Argon was bubbled through the solution to purge the CO that had been formed. The course of the reaction was followed by GC (disappearance of $Fe(CO)_5$ and formation of $Me_2GeCH_2Ge(Me_2)Fe(CO)_4$). A deposit of Hg formed at the bottom of the photochemical tube. After filtration under argon and concentration of the solvent, distillation gave $Me_2GeCH_2Ge(Me_2)Fe(CO)_4$ (**1**): 0.14 g, 14% yield; bp 62 °C (0.6 mmHg); ^1H NMR (C_6H_6) δ 0.70 (s, 12 H, CH_3), 0.40 (s, 2 H, CH_2); ^{13}C NMR (C_6D_6) δ 5.98 (CH_3), 23.96 (CH_2), 208.49 (CO_{eq}), 208.65 (CO_{ax}); IR (C_6H_6, cm^{-1}) ν_{CO} 2080 m, 2060 m, 2035 s, 1995 s; UV λ_{max} 252 nm (log ϵ 3000); mass spectrum (EI, 70 eV), m/e 388 (M^+), 360 ($(M - CO)^+$), 332 ($(M - 2CO)^+$), 304 ($(M - 3CO)^+$), 276 ($(M - 4CO)^+$), 262 ($(M - 4CO - CH_2)^+$). Anal. Calcd for $C_9H_{14}O_4FeGe_2$: C, 27.89; H, 3.62. Found: C, 27.98; H, 3.76.

1,2-Bis(trimethylgermyl)ethane, $Me_3GeCH_2CH_2GeMe_3$. A mixture of GeI_2 (108.4 g, 0.332 mol) and $BrCH_2CH_2Br$ (28.38 g, 0.151 mmol) was heated at 140 °C in a sealed tube for 48 h. The reaction mixture was dissolved in diethyl ether (300 mL), and CH_3MgI (1 mol dissolved in 1 L of Et_2O) was added drop by drop under magnetic stirring. The mixture was heated at reflux for 2 h. After hydrolysis, the aqueous phase was washed twice with Et_2O (200 mL), and the organic phase was dried with Na_2SO_4. Fractional distillation of the organic mixture gave the known compound $Me_3GeCH_2CH_2GeMe_3$[33] (35 g, 89% yield): bp 90 °C (10 mmHg); ^1H NMR (C_6H_6) δ 0.20 (s, 18 H, CH_3), 0.70 (s, 4 H, CH_2).

1,2-Bis(chlorodimethylgermyl)ethane, $Me_2(Cl)GeCH_2CH_2Ge(Cl)Me_2$. A mixture of bis(trimethylgermyl)ethane (32.3 g, 0.123 mmol) and concentrated H_2SO_4 (126 g) was agitated for 30 h and then treated with NH_4Cl (20.23 g, 0.38 mmol). After

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extraction into petroleum ether and concentration of the organic phase, the known $Me_2(Cl)GeCH_2CH_2Ge(Cl)Me_2$[34] (31 g, 83% yield) was obtained in the form of white crystals: mp 82 °C; ^1H NMR (C_6H_6) δ 0.40 (s, 12 H, CH_3), 1.05 (s, 4 H, CH_2).

1,2-Bis(dimethylgermyl)ethane, $Me_2(H)GeCH_2CH_2Ge(H)Me_2$. 1,2-Bis(chlorodimethylgermyl)ethane (15 g, 49 mmol) dissolved in Et_2O (100 mL) was added drop by drop to a suspension of $LiAlH_4$ (1.90 g, 50 mmol) in Et_2O (50 mL). After hydrolysis (HCl, aqueous solution 10%), extraction, and concentration, distillation of the organic phase (dried over Na_2SO_4) gave 1,2-bis(dimethylgermyl)ethane (10.4 g, 90% yield): bp 145 °C (760 mmHg); ^1H NMR (C_6H_6) δ 0.15 (d, J = 4 Hz, 12 H, CH_3), 0.80 (t, J = 4 Hz, 4 H, CH_2), 4.05 (m, 2 H, Ge–H); IR (C_6H_6, cm^{-1}) ν_{Ge-H} 2020. Anal. Calcd for $C_6H_{18}Ge_2$: C, 30.61; H, 7.65. Found: C, 30.47; H, 7.57.

Bis(dimethylgermyl)methane–Iron Tetracarbonyl, $Me_2GeCH_2Ge(Me_2)Fe(CO)_4$ (1). A solution of bis(dimethylgermyl)methane[22] (2 g, 9.04 mmol) and $Fe(CO)_5$ (1.77 g, 9.04 mmol) in pentane (5 mL) was irradiated for 4 h at room tempereature using a Hg lamp (254 nm). Argon was bubbled through the solution to purge the CO which had formed. The progress of the reaction was followed by GC (disappearance of bis(dimethylgermyl)methane and formation of 1) and ^1H NMR. After concentration of the solvent under reduced pressure (10 mmHg) distillation gave 1 (2.17 g, 62% yield).

1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl, $Me_2GeCH_2CH_2Ge(Me_2)Fe(CO)_4$ (2). Under the same operating conditions as in the preceding preparation, a mixture of $Fe(CO)_5$ (1.25 g, 6.38 mmol) and 1,2-bis(dimethylgermyl)ethane (1.5 g, 6.38 mmol) in pentane (5 mL) was irradiated. Distillation of the reaction mixture gave $Me_2GeCH_2CH_2Ge(Me_2)Fe(CO)_4$ (1.58 g, 62% yield): bp 75 °C (0.5 mmHg); ^1H NMR (C_6H_6) δ 0.65 (s, 12 H, CH_3), 1.15 (s, 4 H, CH_2); ^{13}C NMR (C_6D_6) δ 4.33 (CH_3), 20.58 (CH_2), 208.99 (CO_{eq}), 209.44 (CO_{ax}); IR (C_6D_6, cm^{-1}) ν_{CO} 2060 m, 2050 w, 2000 s, 1980 s; UV λ_{max} 252 nm (log ϵ 2840); mass spectrum, *m/e* 402 (M^+), 374 ($(M - CO)^+$), 346 ($(M - 2CO)^+$), 318 ($(M - 3CO)^+$), 290 ($(M - 4CO)^+$), 262 ($(M - 4CO - C_2H_4)^+$). Anal. Calcd for $C_{10}H_{16}O_4FeGe_2$: C, 29.91; H, 3.99. Found: C, 30.13; H, 4.11.

Photolytic Decomposition of 1. Compound 1 (1.2 g, 3.09 mmol) in C_6H_6 (4 mL) was irradiated with a Hg lamp (λ = 254 nm) in a quartz tube. After 20 h the color had changed from yellow to dark brown and an insoluble material had appeared. The supernatant liquid was removed with a syringe and analyzed by GC and ^1H NMR. GC analysis (including coinjection with authentic samples) showed **2**, **3**,[20] and **4**,[20] to be present in relative amounts of 44%, 12%, and 15%, respectively, in this solution. The ^1H NMR spectrum of this solution revealed the formation of **5**[22] in 27% yield. MS and IR spectra indicated $Fe_3(CO)_{12}$ (2048 (s), 2028 (sh) cm^{-1}) to be the major iron-containing product in the solid material filtered.

CH_2 Transfer from Compound 1. A solution of 1 (0.72 g, 1.86 mmol) and Me_3GeH (0.88 g, 7.44 mmol) in C_6H_6 (3 mL) was irradiated in a quartz tube with a Hg lamp (λ = 254 nm) for 20 h. ^1H NMR and GC MS analyses of the supernatant solution revealed the formation of Me_4Ge (12% yield) and derivatives **2**, **3**, **4**, and **5** (characterised by ^1H NMR only) in yields of 27%, 7%, 10%, and 38%, respectively.

Reaction of 1 with Diazomethane. A benzene solution of 1 (0.4 mmol) was transferred to an ethereal solution of diazomethane (4 mmol, dried over KOH and degassed) under argon at −78 °C. After the addition was completed, the resulting mixture was warmed to room temperature. During the reaction, dinitrogen was evolved and the solution became pale brown. After hydrolysis with deoxygenated water and filtration of iron products, GC–MS analysis showed formation of two products, A and B (in 95% and 5% yields, respectively). A = **12**[20] (MS 457 [$M^+ - 15$]); B (MS 471 attributed to $(Me_3GeCH_2GeMe_2)_2O$ [$M^+ - 15$]).

Synthesis of $Me_2(C_6H_5)SiCH_2Cl$. C_6H_5MgBr (63.42 g, 0.35 mmol, prepared from 8.51 g of Mg and 54.9 g of C_6H_5Br in 300 mL of Et_2O) was added drop by drop with agitation to $Me_2Si(Cl)CH_2Cl$ (50 g, 0.35 mmol). The reaction mixture was heated at reflux for 2 h. After hydrolysis with 10% HCl and extraction into ether, the organic phase was dried over $CaCl_2$. Fractional distillation gave the known compound $Me_2(C_6H_5)SiCH_2Cl$[35] (55 g, 85% yield): bp 90 °C (5 mmHg); ^1H NMR (C_6D_6) δ 7.1–7.6 (m, 5 H, C_6H_5), 2.6 (s, 2 H, CH_2), 0.25 (s, 6 H, CH_3).

Synthesis of $Me_2(C_6H_5)SiCH_2Si(H)Me_2$. Dimethylchlorosilane (16 g, 0.169 mmol) in Et_2O (100 mL) was added drop by drop with magnetic stirring to $Me_2(C_6H_5)SiCH_2MgCl$ (35.30 g, 0.169 mmol), obtained from Mg (4.11 g) and $Me_2(C_6H_5)SiCH_2Cl$ (31.19 g) in Et_2O (200 mL). After the addition was completed, the mixture was heated at reflux for 3 h and then it was hydrolyzed, extracted, and concentrated. Distillation of the organic phase gave $Me_2(C_6H_5)SiCH_2Si(H)Me_2$ (25 g, 71% yield): bp 120 °C (10 mmHg); ^1H NMR (C_6H_6) δ 7.15–7.65 (m, 5 H, C_6H_5), 0.40 (s, 6 H, $CH_3Si{-}C_6H_5$), 0.25 (d, 6 H, J = 4 Hz, CH_3SiH), 0.06 (d, 2 H, J = 4 Hz, CH_2), 4.30 (m, 1 H, SiH). Anal. Calcd for $C_{11}H_{20}Si_2$: C, 63.46; H, 9.65. Found: C, 63.53; H, 9.57.

Bis(bromodimethylsilyl)methane, $Me_2(Br)SiCH_2Si(Br)Me_2$. A solution of bromine (18.4 g, 115.1 mmol) in EtBr (50 mL) was added to $Me_2(C_6H_5)SiCH_2Si(H)Me_2$ (12 g, 57.6 mmol) in EtBr (50 mL). The reaction was very exothermic. The mixture was kept at room temperature and stirred for 8 h. After concentration of the solvent at reduced pressure (10 mmHg), distillation of the remainder gave $Me_2(Br)SiCH_2Si(Br)Me_2$ (11 g, 66% yield): bp 140 °C (10 mmHg); ^1H NMR (C_6H_6) δ 0.43 (s, 12 H, CH_3), 0.50 (s, 2 H, CH_2). Anal. Calcd for $C_5H_{14}Br_2Si_2$: C, 20.69; H, 4.83; Br, 55.17. Found: C, 20.91; H, 4.99; Br, 55.38.

Bis(dimethylsilyl)methane, $Me_2(H)SiCH_2Si(H)Me_2$. Bis(bromodimethylsilyl)methane (8.5 g, 29 mmol) in Et_2O (50 mL) was added drop by drop to a suspension of $LiAlH_4$ (2.20 g, 58 mmol) in Et_2O (50 mL). After workup with NH_4Cl (aqueous saturated) and extraction with Et_2O (50 mL), the organic phase was dried over Na_2SO_4. Distillation gave the known bis(dimethylsilyl)methane[24] (3.5 g, 26.5 mmol): 91% yield; bp 92 °C (760 mmHg); ^1H NMR (C_6H_6) δ 0.20 (d, 3 H, J = 4 Hz, CH_3), −0.25 (t, 2 H, J = 4 Hz, CH_2), 4.25 (m, 2 H, SiH).

1,2-Bis(dimethylsilyl)ethane–Iron Tetracarbonyl, $Me_2SiCH_2CH_2Si(Me_2)Fe(CO)_4$ (6). A mixture of bis(dimethylsilyl)methane (1.2 g, 9.09 mmol) in pentane (5 mL) and $Fe(CO)_5$ (1.78 g, 9.09 mmol) in pentane (5 mL) and $Fe(CO)_5$ (1.78 g, 9.09 mmol) in a quartz tube was irradiated with a Hg lamp (λ = 254 nm) for 2 h. The reaction was followed by GC (disappearance of bis(dimethylsilyl)methane and $Fe(CO)_5$ and appearance of 6) and ^1H NMR. Distillation of the product mixture gave **6** (0.85 g, 30% yield): bp 44 °C (1.6 mmHg); ^1H NMR ($CDCl_3$) δ 0.56 (s, 12 H, CH_3), 1.0 (s, 4 H, CH_2); ^{13}C NMR (toluene) δ 8.37 (CH_3), 17.54 (CH_2), 207.86 (CO_{eq}), 208.89 (CO_{ax}); IR (heptane, cm^{-1}) ν_{CO} 2068 m, 2003 m, 2000 w, 1978 s; mass spectrum, *m/e* 312 (M^+), 284 ($(M - CO)^+$), 256 ($(M - 2CO)^+$), 228 ($(M - 3CO)^+$), 200 ($(M - 4CO)^+$), 172 ($M - 4CO - C_2H_4)^+$). Anal. Calcd for $C_{10}H_{16}O_4FeSi_2$: C, 38.46; H, 5.13. Found: C, 38.69; H, 5.25.

Bis(dimethylsilyl)methane–Diiron Octacarbonyl, $Me_2SiCH_2Si(Me)_2Fe(CO)_4Fe(CO)_4$ (7). An identical reaction mixture was evaporated at reduced pressure, and the residue was dissolved in a minimum quantity of ligroin. The mixture was then chromatographed over a Florisil column with deoxygenated petroleum ether as eluent. The major yellow band gave, after concentration at 10 mmHg, **7** (1.06 g, 2.3 mmol, 24% yield); yellow crystals; mp 78 °C; ^1H NMR (C_6H_6) δ 0.35 (s, 12 H, CH_3), 0.45 (s, 2 H, CH_2); IR (hexane, cm^{-1}) ν_{CO} 2080 w, 2040 m, 2020 m, 1980 w, 1960 m, 1950 s, 1940 w. Anal. Calcd for $C_{13}H_{14}O_8Fe_2Si_2$: C, 33.48; H, 3.00. Found: C, 33.65; H, 3.17.

Reaction of Triphenylphosphine. (a) With Bis(dimethylgermyl)methane–Iron Tetracarbonyl. To 1 (1.00 g, 2.58 mmol) in C_6H_6 (2 mL) was added $(C_6H_5)_3P$ (0.676 g, 2.58 mmol), and the solution was irradiated (λ = 254 nm) in quartz

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tube for 4 h at ambient temperature. Yellow crystals of $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$[38] were recovered by filtration. Distillation of the filtrate at 100 mmHg provided a liquid fraction containing bis(dimethylgermyl)methane (**3**) (16% yield in NMR), compound **4** (22% yield in NMR), and a residual thick orange oil formulated as the complex $Me_2GeCH_2Ge(Me_2)Fe(CO)_3PPh_3$ (**8**) (62% yield): ^1H NMR (C_6D_6) δ 0.95 (s, 12 H, CH_3), 0.35 (s, 2 H, CH_2), 7.10–6.65 (m, 15 H, C_6H_5); ^{31}P NMR (C_6D_6) δ 62.26, IR (C_6D_6, cm^{-1}) ν_{CO} 2040 w, 2035 m, 2000 s; mass spectrum, *m/e* 622 (M^+), 594 ($(M - CO)^+$), 566 ($(M - 2CO)^+$), 538 ($(M - 3CO)^+$). ^1H and ^{31}P NMR or GC indicated that impurities (less than 10%) are present (germylated oxides and $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$).

(b) With 1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl. A C_6H_6 (10 mL) solution of **2** (1.25 g, 3.11 mmol) was treated with Ph_3P (0.815 g, 3.11 mmol), and the mixture was heated in a sealed tube at 140 °C for 20 h under argon. A yellow oil was obtained in a manner identical with that reported for **8**. ^1H and ^{31}P NMR, IR, and MS confirmed the formation of $Me_2GeCH_2CH_2Ge(Me_2)Fe(CO)_3PPh_3$ (**9**) in 65% yield: ^1H NMR (C_6D_6) δ 0.30 (s, 12 H, CH_3), 0.90 (s, 4 H, CH_2), 8.0–6.9 (m, 15 H, C_6H_5); ^{31}P NMR (C_6D_6) δ 60.65; IR (C_6D_6, cm^{-1}) ν_{CO} 2020 w, 2010 m, 1990 s; mass spectrum, *m/e* 636 (M^+), 608 ($(M - CO)^+$), 580 ($M - 2Ceo)^+$), 552 ($M - 3CO)^+$), 524 ($M - 3CO - C_2H_4)^+$).

Reaction of Tri-*n*-butylphosphine. (a) With Bis(dimethylgermyl)methane–Iron Tetracarbonyl. Tri-*n*-butylphosphine (0.5 g, 2.47 mmol) was added drop by drop to **1** (0.960 g, 2.47 mmol) dissolved in C_6H_6 (3 mL), giving a slightly exothermic reaction with rapid evolution of CO. The solvent was removed to give a yellow oil from which neither component could be induced to crystallize. ^1H and ^{31}P NMR and MS showed that $Me_2GeCH_2Ge(Me_2)Fe(CO)_3PBu_3$ (**10a**) had been formed in 82% yield: ^1H NMR (C_6H_6) δ 1.70–1.35 (m, 27 H, *n*-Bu), 1.05 (s, 12 H, CH_3), 0.5 (s, 2 H, CH_2); ^{31}P NMR (C_6D_6) δ 41.36; IR (C_6H_6, cm^{-1}) ν_{CO} 2020, w, 1965 m, 1950 m; mass spectrum, *m/e* 562 (M^+), 534 ($(M - CO)^+$), 506 ($(M - 2CO)^+$), 478 ($(M - 3CO)^+$).

(b) With 1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl. Using the same operating conditions as in the preceding preparation, **2** (0.95 g, 2.37 mmol) and $(n\text{-}Bu)_3P$ (0.48 g, 2.37 mmol) gave $Me_2GeCH_2CH_2Ge(Me_2)Fe(CO)_3PBu_3$ (**10b**) in 93% yield: ^1H NMR (C_6H_6) δ 1.8–0.9 (m, 31 H, CH_2; n-Bu_3), 0.70 (s, 12 H, CH_3); ^{31}P NMR (C_6D_6) δ 35.2; IR (C_6D_6, cm^{-1}) ν_{CO} 1980 m, 1945 w, 1910 m; mass spectrum, *m/e* 576 (M^+), 548 ($(M - CO)^+$), 520 ($(M - 2CO)^+$), 492 ($M - 3CO)^+$), 464 ($M - 3CO - C_2H_4)^+$).

Reaction of Dioxygen. (a) With Bis(dimethylgermyl)methane–Iron Tetracarbonyl. A solution of **1** (0.700 g, 1.80 mmol) in dry and degassed C_6H_6 (10 mL) was oxidized in a Schlenk tube by bubbling a mixture of dinitrogen and dioxygen through it for 15 min. The reaction was exothermic, and the solution immediately became black. ^1H NMR and GC–MS of the supernatant solution revealed that **11**, **12**, **13**, and **14** had been formed in relative amounts of 14%, 42%, 30%, and 11%, respectively, in addition to traces of **16**, $(Me_2GeO)_3$, and $Me_2GeCH_2GeCH_2Me_2$. All these compounds were identified by GC and (or) GC–MS comparison with authentic samples described in ref 20.

(b) With Bis(dimethylgermyl)ethane–Iron Tetracarbonyl. Dioxygen was bubbled through a C_6H_6 solution of **2** (1.00 g, 2.49 mmol). GC and ^1H NMR analyses of the product mixture showed the presence of $Me_2GeCH_2CH_2Ge(Me_2)O$ (**17a**), which was then recovered by distillation (0.55 g, 88% yield). **17a** was identified by GC and NMR comparisons with an authentic sample synthesized in the next reaction.

Synthesis of $Me_2GeCH_2CH_2Ge(Me_2)O$. A solution of 1,2-bis(dimethylgermyl)ethane (2.30 g, 7.56 mmol) in Et_2O (20 mL) was treated with 20% aqueous ammonia (10 mL). After extraction with petroleum ether, the solution was dried over $CaCl_2$. By distillation of the organic phase, $Me_2GeCH_2CH_2Ge(Me_2)O$ (**17a**) (1.40 g, 74% yield) was isolated: bp 54 °C (0.8 mmHg); ^1H NMR (C_6H_6) δ 0.35 (s, 12 H, CH_3), 0.95 (s, 4 H, CH_2); mass spectrum, *m/e* 235 ($(M - CH_3)^+$). Anal. Calcd for $C_6H_{16}OGe_2$: C, 28.89; H, 6.42. Found: C, 28.95; H, 6.57.

Reaction of Sulfur, S_8. (a) With Bis(dimethylgermyl)methane–Iron Tetracarbonyl. To a C_6H_6 (5 mL) solution of **1** (0.8 g, 2.06 mmol) was added S_8 (0.529 g, 2.06 mmol), and the mixture was stirred at 20 °C for 8 h. ^1H NMR, GC, and GC–MS analyses of the supernatant solution showed the presence of **11**, **12**, **13**, **14**, and $(Me_2GeS)_3$ in relative amounts of 58%, 16%, 11%, 5%, and 8%, respectively, and trace quantities of **16** and $Me_2GeCH_2GeCH_2Me_2$. All these compounds were identified by GC and (or) GC–MS (comparison with authentic samples described in ref 20 and 21).

(b) With 1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl. A mixture of S_8 (0.44 g, 1.74 mmol) and **2** (0.7 g, 1.74 mmol) in C_6H_6 (8 mL) was heated in a sealed tube at 140 °C for 18 h. ^1H NMR and GC analyses of the liquid phase confirmed that $Me_2GeCH_2CH_2Ge(Me)_2S$ (**17b**) had been formed almost exclusively (91% yield). **17b** was identified by GC comparison with an authentic sample synthesized in the next reaction.

Synthesis of $Me_2GeCH_2CH_2Ge(Me)_2S$. 1,2-Bis(chlorodimethylgermyl)ethane (3.4 g, 11.1 mmol) in THF (50 mL) was treated with Na_2S (1.29 g, 16.5 mmol). After filtration of the mixture, distillation of the filtrate gave $Me_2GeCH_2CH_2Ge(Me_2)S$ (**17b**): 1.80 g, 61% yield; bp 114 °C (10 mmHg); ^1H NMR (C_6H_6) δ 0.45 (s, 12 H, CH_3), 1.05 (s, 4 H, CH_2): mass spectrum, *m/e* 266 (M^+). Anal. Calcd for $C_6H_{16}SGe_2$: C, 27.15; H, 6.03. Found: C, 26.97; H, 6.05.

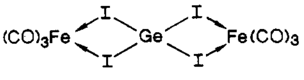
Synthesis of $Et_2GeFe(CO)_4GeEt_2Fe(CO)_4$. A solution of Et_2GeH_2 (2.50 g, 18.8 mmol) and $Fe(CO)_5$ (3.69 g, 18.8 mmol) in pentane (5 mL) was irradiated ($\lambda = 254$ nm) in a quartz tube for 4 h at room temperature. Argon was bubbled through the solution to purge the CO which had formed. The progress of the reaction was followed by GC (disappearance of Et_2GeH_2 and $Fe(CO)_5$). After concentration of the solvent at reduced pressure, distillation gave the known $Et_2GeFe(CO)_4Ge(Et_2)Fe(CO)_4$[28,30] (7.54 g, 67% yield): bp 65 °C (0.4 mmHg); ^1H NMR (C_6H_6) δ 1.3 (q, 8 H, $J = 2$ Hz, CH_2), 1.15 (t, 12 H, $J = 2$ Hz, CH_3); IR (C_6D_6, cm^{-1}) ν_{CO} 2040 w, 2030 w, 2018 s, 1995 s, 1960 s; mass spectrum, *m/e* 598 (M^+), 374 ($(M - 8CO)^+$). IR spectra showed bands of an impurity presumably a hydrido species in addition to the main product.

Reaction of Halogens and Organic and Organometallic Halides. (a) With Bis(dimethylgermyl)methane–Iron Tetracarbonyl. Reactions of **1** with halogens and organic and organometallic halides at 20 °C in C_6H_6 are summarized in Table II.

(b) With 1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl. Mixtures of **2** with halogens and organic and organometallic halides were heated at 140 °C for 8 h in sealed tubes under argon. The results are reported in Table III and the physical properties of the dihalo products are reported in Table IV.

In all cases, after elimination of inorganic iron products by filtration, the dihalo products $Me_2XGe(CH_2)_2GeXMe_2$ were isolated by crystallization from pentane (concentration of the solution under 10 mmHg and addition of a few milliliters of pentane). The other various products were detected directly in the benzene solution by ^1H NMR, IR, or ^{31}P NMR and MS.

Synthesis of $I_4Ge(Fe(CO)_3)_2$. A solution of GeI_4 (2.00 g, 3.44 mmol) and $Fe(CO)_5$ (2.70 g, 13.7 mmol) in C_6H_6 (5 mL) was irradiated in a quartz flask ($\lambda = 254$ nm) for 4 h. After concentration of the solvent at 20 mmHg, the crude residue was dissolved in pentane (20 mL). This solution was left for 12 h at −30 °C. Dark red crystals of



23 (2.48 g, 84% yield)

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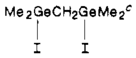
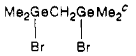
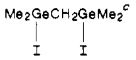
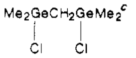
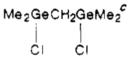
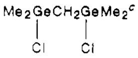
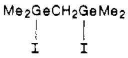
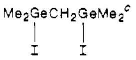
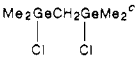
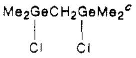
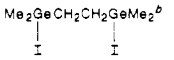
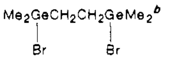
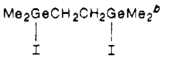
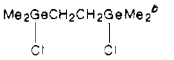
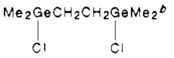
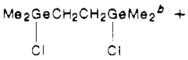
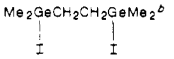
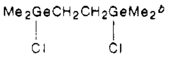
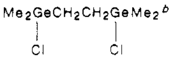
Table II. Reaction of Bis(dimethylgermyl)methane–Iron Tetracarbonyl with Halogens and Organic and Organometallic Halides

reagent			product		
structure	g (mmol)	1, g (mmol)	struct	ref	yield, %
I_2	0.6 (2.36)	0.46 (1.18)	 $\underset{I}{Me_2Ge}CH_2\underset{I}{GeMe_2}^{c}$	20	93
Br_2	0.43 (2.69)	0.52 (1.34)	 $\underset{Br}{Me_2Ge}CH_2\underset{Br}{GeMe_2}^{c}$	20	73
CH_3I	0.37 (2.60)	0.50 (1.30)	 $\underset{I}{Me_2Ge}CH_2\underset{I}{GeMe_2}^{c}$	20	62
CCl_4[a]	0.95 (6.2)	0.6 (1.55)	 $\underset{Cl}{Me_2Ge}CH_2\underset{Cl}{GeMe_2}^{c}$	20	92
t-$BuPCl_2$	0.31 (1.93)	0.75 (1.93)	 $\underset{Cl}{Me_2Ge}CH_2\underset{Cl}{GeMe_2}^{c}$ + $(t\text{-}BuP)_{3}$, Δ^{f}	37	72
$C_6H_5PCl_2$	0.23 (1.29)	0.5 (1.29)	 $\underset{Cl}{Me_2Ge}CH_2\underset{Cl}{GeMe_2}^{c}$ + $(C_6H_5P)_5^{f}$	36	82
GeI_4	0.9 (1.54)	0.3 (0.77)	 $\underset{I}{Me_2Ge}CH_2\underset{I}{GeMe_2}$ + $I_3Ge\text{-}Fe(CO)_4\text{-}GeI_3^{d}$	20 27	91 87
GeI_4	0.67 (1.16)	0.45 (1.16)	 $\underset{I}{Me_2Ge}CH_2\underset{I}{GeMe_2}^{c}$ + $[I_2GeFe(CO)_4]_2^{d}$	20 27	94 89
Et_2GeCl_2[a]	0.78 (3.87)	1.5 (3.87)	 $\underset{Cl}{Me_2Ge}CH_2\underset{Cl}{GeMe_2}^{c}$ + $[Et_2GeFe(CO)_4]_2^{c}$	20	48 24
Me_3SnCl[b]	0.89 (4.44)	0.86 (2.99)	 $\underset{Cl}{Me_2Ge}CH_2\underset{Cl}{GeMe_2}^{c}$ + $(Me_3Sn)_2Fe(CO)_4^{e}$	20 28, 29	67 71

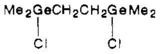
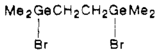
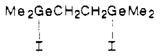
[a] Irradiation by UV (λ = 254 nm)/2 h. [b] 120 °C/2 days. [c] Identified by GC (coinjection with autenthic samples) and ^1H NMR. [d] Identified by IR. [e] Identified by IR and ^1H NMR. [f] Identified by ^{31}P NMR and MS.

Table III. Reaction of 1,2-Bis(dimethylgermyl)ethane–Iron Tetracarbonyl with Halogens and Organic and Organometallic Halides

reagent			product		
structure	g (mmol)	2, g (mmol)	structure	ref	yield, %
I_2	1.5 (5.90)	0.55 (1.37)	 $\underset{I}{Me_2Ge}CH_2CH_2\underset{I}{GeMe_2}^{b}$		81
Br_2	1.3 (8.12)	0.79 (1.97)	 $\underset{Br}{Me_2Ge}CH_2CH_2\underset{Br}{GeMe_2}^{b}$		64
CH_3I	0.70 (4.93)	0.48 (1.20)	 $\underset{I}{Me_2Ge}CH_2CH_2\underset{I}{GeMe_2}^{b}$		72
CCl_4[a]	0.80 (5.18)	0.52 (1.3)	 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}^{b}$		67
t-$BuPCl_2$	0.32 (1.99)	0.80 (1.99)	 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}^{b}$ + $(t\text{-}BuP)_{3,4}^{e}$		74
$C_6H_5PCl_2$	0.45 (2.49)	1 (2.49)	 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}^{b}$ + $(C_6H_5P)_5^{e}$	36	80
GeI_4	1.95 (3.36)	1.35 (3.36)	 $\underset{I}{Me_2Ge}CH_2CH_2\underset{I}{GeMe_2}^{b}$ + $[I_2GeFe(CO)_4]_2^{c}$	 27	94 89
Et_2GeCl_2	0.37 (1.82)	0.73 (1.82)	 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}^{b}$ + $[Et_2GeFe(CO)_4]_2^{b}$		81 12
Me_3SnCl	0.91 (4.6)	0.92 (2.3)	 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}^{b}$ + $(Me_3Sn)_2Fe(CO)_4^{d}$	 28, 29	58 63

[a] Irradiation by UV (λ = 254 nm)/2 h. [b] Identified by GC (coinjection with autenthic samples) and ^1H NMR. [c] Identified by IR. [d] Identified by IR and ^1H NMR. [e] Identified by ^{31}P NMR and MS.

Table IV

product	mp, °C	^1H NMR (C_6H_6), ppm
 $\underset{Cl}{Me_2Ge}CH_2CH_2\underset{Cl}{GeMe_2}$	82	δ_{CH_2} 1.05 (4 H) δ_{CH_3} 0.40 (12 H)
 $\underset{Br}{Me_2Ge}CH_2CH_2\underset{Br}{GeMe_2}$	88	δ_{CH_2} 1.15 (4 H) δ_{CH_3} 0.60 (12 H)
 $\underset{I}{Me_2Ge}CH_2CH_2\underset{I}{GeMe_2}$	94	δ_{CH_2} 1.25 (4 H) δ_{CH_3} 0.80 (12 H)

resulted: mp 42 °C dec; IR (Nujol, cm^{-1}) ν_{CO} 2076 s, 2045 m, 2010 m, 2002 s; mass spectrum, no trace of an iron-containing fragment, GeI_4 is the only species observed, *m/e* 582 (M^+).

Registry No. **1**, 120926-68-3; **2**, 120926-69-4; **3**, 106651-96-1; 4, 106651-97-2; **5**, 20468-10-4; **6**, 43198-13-6; **7**, 66515-94-4; **8**, 120926-70-7;)9, 120926-71-8; **10a**, 120926-72-9; **10b**, 120926-73-0; **11** (Y = O), 106652-05-5; **11** (Y = S), 106652-04-4; **12** (Y = O), 106652-03-3; **12** (Y = S), 98187-54-3; **13** (Y = O), 106652-07-7; **13** (Y = S), 98187-53-2; **14** (Y = O), 106652-08-8; **14** (Y = S), 98187-52-1; **15**, 16090-53-2; **16** (Y = O), 106652-06-6; **16** (Y = S), 98187-51-0; **17a**, 120926-63-8; **17b**, 120926-64-9; **18**, 15708-59-5; **19**, 22033-57-4; **20**, 19601-46-8; **21**, 15376-93-9; **22**, 15418-00-5; **23**, 120926-74-1; $Me_2\overline{GeHgGe(Me_2)CH_2Ge(Me_2)HgGe(Me_2)CH_2}$, 106651-95-0; $Fe(CO)_5$, 13463-40-6; $Me_3Ge(CH_2)_2GeMe_3$, 2097-58-7;

GeI_2, 13573-08-5; $BrCH_2CH_2Br$, 106-93-4; $Me_2Ge(Cl)(CH_2)_2Ge(Cl)Me_2$, 63746-65-6; $Me_2Ge(H)(CH_2)_2Ge(H)Me_2$, 120926-65-0; $Me_2Ge(nH)CH_2Ge(H)Me_2$, 106651-96-1; Me_3GeH, 1449-63-4; Me_4Ge, 865-52-1; $(Me_3GeCH_2GeMe_2)_2O$, 119796-07-5; $Me_2(C_6H_5)SiCH_2Cl$, 1833-51-8; $Me_2Si(Cl)CH_2Cl$, 1719-57-9; $Me_2(C_6H_5)SiCH_2SiCH)Me_2$, 27374-20-5; $Me_2(Br)SiCH_2Si(Br)mE_2$, 999-95-1; $Me_2(H)SiCH_2Si(H)Me_2$, 18163-84-3; Me_2SiHCl, 1066-35-9; $\overline{Me_2GeCH_2GeMe_2CH_2}$, 24329-46-2; Et_2GeH_2, 1631-46-5; GeI_4, 13450-95-8; t-$BuPCl_2$, 25979-07-1; $C_6H_5PCl_2$, 644-97-3; Et_2GeCl_2, 13314-52-8; Me_3SnCl, 1066-45-1; $Me_2Ge(I)CH_2Ge(I)Me_2$, 106652-01-1; $Me_2Ge(Br)CH_2Ge(Br)Me_2$, 106652-02-2; $Me_2Ge(Cl)CH_2Ge(Cl)Me_2$, 98187-50-9; $(t\text{-}BuP)_3$, 61695-12-3; $(C_6H_5P)_5$, 3376-52-1; $Me_2Ge(I)CH_2CH_2Ge(I)Me_2$, 120926-66-1; $Me_2Ge(Br)CH_2CH_2Ge(Br)Me_2$, 120926-67-2; $(t\text{-}BuP)_4$, 5995-07-3.

Synthesis of (Alkoxymethyl)zirconocene Chlorides: Stereochemistry of Carbon–Carbon Bond Formation in a Zirconocene-Wittig Rearrangement

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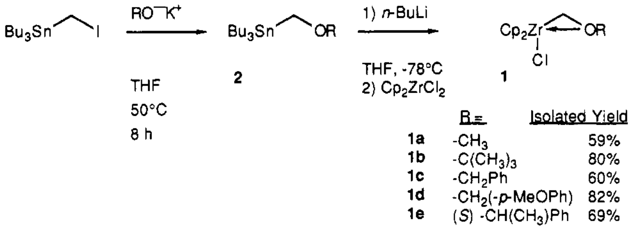
A series of (alkoxymethyl)zirconocene chlorides (1, $Cp_2Zr(Cl)CH_2OR$, Cp = η^5-C_5H_5) has been prepared by treatment of Cp_2ZrCl_2 with (alkoxymethyl)lithium reagents. Compound **1c**, $Cp_2Zr(Cl)CH_2OCH_2C_6H_5$, crystallizes in the orthorhombic space group *Pbca*, with a = 15.417 (9) Å, b = 18.249 (9) Å, c = 11.746 (8) Å, and Z = 8. The X-ray crystal structure shows that the alkoxymethyl ligand is η^2, with a significant Zr–O interaction. Compounds **1** with R = benzyl or substituted benzyl undergo a Wittig rearrangement when heated to give products **3** ($Cp_2Zr(Cl)OCH_2R$). The activation parameters that were determined for the transformation, the effects of substituents on the rate of the reaction, the identity of the reaction's side products, and the retention of configuration at the benzylic carbon are all consistent with the formation of a short-lived radical pair intermediate.

As part of a study directed toward the development of general synthetic routes to transition metal aldehyde complexes, we have synthesized a variety of (alkoxymethyl)zirconocene chlorides (**1**), as shown in Scheme I. Compounds **1** are crystalline, air- and moisture-sensitive solids. They exhibit ^1H NMR, ^{13}C NMR, IR spectra, and combustion analyses or high-resolution mass spectra that are consistent with the structures as shown. They are obtained in good to excellent yield by treatment of zirconocene dichloride with 1 equiv of an (alkoxymethyl)lithium, which is generated by treatment of an (alkoxymethyl)tributylstannane with n-butyllithium.[1] The stannanes **2a–e** are readily prepared by treatment of (iodomethyl)tributylstannane[2] with the appropriate potassium alkoxide or by treatment of (tributylstannyl)lithium[1] with a chloromethyl alkyl ether.

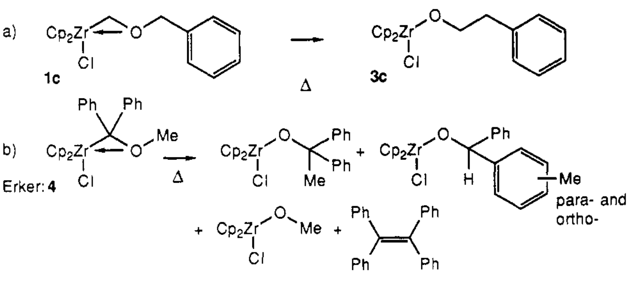
Compounds **1a** and **1b** are unaffected by heating to 110 °C for 8 h, but when the (benzyloxy)methyl compound **1c** is heated, it undergoes a rapid rearrangement to form a mixture of products, in which the (phenethyloxy)zirconocene chloride (**3c**) predominates (ca. 70%, see Scheme II). The identify of **3c** was confirmed by an independent synthesis from Cp_2ZrCl_2 and phenethyl alcohol. Because of our interest in transition-metal-mediated carbon–carbon bond-forming reactions, we decided to further investigate this rearrangement.

Scheme I



	R=	Isolated Yield
1a	$-CH_3$	59%
1b	$-C(CH_3)_3$	80%
1c	$-CH_2Ph$	60%
1d	$-CH_2(-p\text{-}MeOPh)$	82%
1e	(*S*) $-CH(CH_3)Ph$	69%

Scheme II



It should be noted that Erker[3] has reported the preparation of the α-(zirconocenyl)benzhydryl methyl ether **4** shown in Scheme II, and he found that it undergoes a similar rearrangement to give a mixture of products, including the Wittig-rearranged alkoxide. A similar product mixture also resulted from the reaction of the dimeric zirconocene–benzophenone complex with alkyl halides.[3b,c] As our study was being completed, Erker reported[3e] an alternate synthesis and the X-ray crystal structure of the methoxymethyl compound **1a**, and the methoxymethyl ligand was found to be η^2 in the crystal, despite examples of related ligands that are η^1.[4] Several lines of evidence had indicated to us that the alkoxymethyl ligands of **1a–e**

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[4] Young, S. Y.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432.

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