The hydride complex thus formed reacts with H_3O^+ to evolve H_2 with regenerating $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, while the reaction of $[Ru(bpy)_2(CO)H]^+$ with H_2O may participate into the production of H_2 to some extent. These reaction-pathways are strongly supported by the isolation or characterization of all the intermediates.

Acknowledgment. We thank Prof. R. B. King, University of Georgia, for helpful discussions.

Registry No. $[Ru(bpy)_2(CO)Cl](PF_6)$, 86389-99-3; $[Ru(bpy)_2(CO)_2](PF_6)_2$, 75550-97-9; $[Ru(bpy)_2(CO)(H_2O)][B(C_6H_5)_4]_2$, 100190-77-0; $[Ru(bpy)_2(CO)(OH)](PF_6)$, 100190-79-2; $[Ru(bpy)_2(CO)C(O)OH](PF_6)$, 86536-99-4; $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6)$, 100190-81-6; $Ru(bpy)_2Cl_2$, 15746-57-3; $Ru(bpy)_2O_2MoO_2$, 100190-82-7; $[Ru(bpy)_2(CO)H](PF_6)$, 82414-89-9; Na_2MoO_4, 7631-95-0.

Electrophilic Attack at Pentamethylcyclopentadienyl-Substituted Germylenes

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Received July 1, 1985

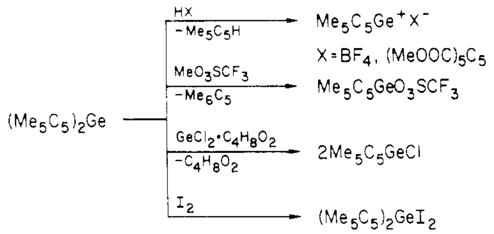
The pentamethylcyclopentadienyl-substituted germylenes $Me_5C_5GeCH(SiMe_3)_2$ (1) and Me_5C_5GeCl (2) exhibit nucleophilic reactivity at the π-system of the Me_5C_5 ligand, at the chlorine atom, and at the Ge–C σ-bond of the Ge–$CH(SiMe_3)_2$ group. Furthermore, oxidative addition reactions with alkylating and acylating agents may be rationalized in terms of electrophilic attack at the germanium center and thus suggest nucleophilic activity also of the lone pair of electrons.

Introduction

The analogous carbene species of germanium and tin possess a nonbonding pair of electrons as well as an empty p_z orbital. In the cyclopentadienyl-substituted species the π-bonded ligand partly saturates the electron deficiency at the 4B (14^{24}) element. Nucleophilic attack, however, still can take place at the metal center.[1] For an electrophilic attack the molecule provides as objectives the π-system of the cyclopentadienyl ligand, a center of electron density at the second ligand, or its σ-bond to the 4B (14) element (with the $R_5C_5El^+$ cation[2-4] acting as a leaving group) and the lone pair of electrons of the 4B (14) element.

Electrophilic attack at the π-system of the cyclopentadienyl ligand has been demonstrated upon protonation[3,5] and alkylation[6] of bis(pentamethylcyclopentadienyl)germanium, as well as in its reaction with germanium dichloride–dioxane,[7] which acts as a Lewis acid. The reactions of bis(pentamethylcyclopentadienyl)germanium with electrophiles are shown in Scheme I.

Scheme I



The existence of a nucleophilic center at the 4B(14) element to date has not clearly been demonstrated. Although analogous carbene complexes of the type $R_2Ge \rightarrow M(CO)_5$ (R = $(Me_3Si)_2CH$, $(Me_3Si)_2N$; M = Cr, W) are available by irradiation of hexacarbonylchromium and -tungsten[8,9] in the presence of the free germylene, the complexation of cyclopentadienyl-substituted species failed.[10] The identity of adducts from $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ with transition-metal Lewis acids[11] as well as with boron and aluminum trihalides,[12] reported in the literature, is uncertain. A detailed scrutiny of the product of the reaction from stannocene with boron trifluoride has been reported recently.[13] Experimental evidence for the activity of the lone pair at the 4B(14) element was given first by the synthesis of the complexes $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$[10] and $Me_5C_5((Me_3Si)_2CH)Ge \rightarrow W(CO)_5$[14] whose structures have been confirmed by X-ray crystallography. Unfortunately, these adducts are only accessible by a synthetic detour, based on an already established 4B(14)

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(1) Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J., in preparation.

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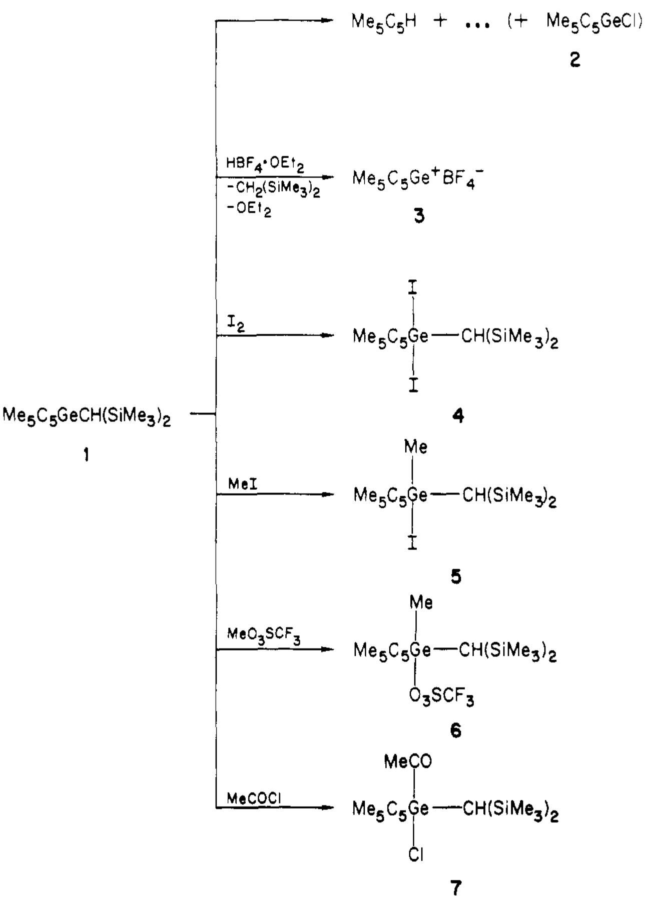
0276-7333/86/2305-0730$01.50/0

Scheme II



element–transition-metal bond.

The only examples of involvement of the lone pair of electrons in cyclopentadienyl-substituted germylenes and stannylenes are oxidative addition reactions with halogens[15-18] (addition of iodine[19] in Scheme I). These reactions, however, were described as analogous carbene insertion reactions[15] and therefore claimed to follow a nonpolar, synchronous mechanism. For methyl iodide the mechanism was suggested to be the same, in spite of the polar nature of the carbon–halogen bond and the alkylating action of the agent.[15]

Results

The reactions of [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (**1**) with various electrophiles are listed in Scheme II.

Protonation with hydrogen chloride mainly yields pentamethylcyclopentadiene, but small amounts of (pentamethylcyclopentadienyl)germanium chloride (**2**) were detected spectroscopically (NMR). Upon protonation of **1** with ethereal tetrafluoroboric acid, formation of the well-known ionic species $Me_5C_5Ge^+BF_4^-$ (**3**)[3] takes place.

The course of the reactions with the other electrophiles in Scheme II looks quite uniform, as far as halogenation, alkylation, and acylation reactions always result in addition of the agent to give a Ge(IV) product.

The oxidative addition of iodine occurred as expected to give [bis(trimethylsilyl)methyl]diiodo(pentamethylcyclopentadienyl)germane (**4**). The formation of germane **5** from **1** on reaction with methyl iodide proceeds very slowly, while the reaction of the more reactive methyl trifluoromethanesulfonate immediately leads to the corresponding germane **6**. As products **5** and **6** possess centers of chirality at the germanium atom, NMR spectra show a duplication of the Me_3Si signal and, at low temperatures where the fluxionality of the Me_5C_5–germanium bond is impeded all together, five different Me–C units for the Me_5C_5 ligand (see Experimental Section).

A chiral product also is formed upon treatment of **1** with acetyl chloride. The addition of this reagent results in immediate formation of acetyl[bis(trimethylsilyl)methyl]chloro(pentamethylcyclopentadienyl)germane (**7**). This reaction is a novel route to ketogermanes.[20]

The reactions of (pentamethylcyclopentadienyl)germanium chloride (**2**) with various electrophiles are given in Scheme III.

Protonation of **2** with equimolar amounts of hydrogen chloride yields pentamethylcyclopentadiene and (pentamethylcyclopentadienyl)germanium trichlorogermanate (**8**) which crystallized from the reaction mixture. As this product has been found to react only very slowly with (remaining) hydrogen chloride, it has been isolated in 27% yield. In contrast, to this, protonation of **2** with ethereal tetrafluoroboric acid causes loss of chloride leading to the ionic species $Me_5C_5Ge^+BF_4^-$ (**3**). The displacement of chloride is not unexpected in that it is a useful leaving group in the synthesis of mixed germylenes[1] such as **1**.

The chlorine as an objective of electrophilic attack had become obvious from the formation of (pentamethylcyclopentadienyl)germanium trichlorogermanate (**8**) upon reaction of bis(pentamethylcyclopentadienyl)germanium with an excess of $GeCl_2 \cdot C_4H_8O_2$.[7] The reaction of equimolar amounts gave (pentamethylcyclopentadienyl)germanium trichlorogermanate (**8**) in 92% yield. A similar reaction occurs upon treatment of **2** with aluminum trichloride to give (pentamethylcyclopentadienyl)germanium tetrachloroaluminate (**9**).

Upon iodination of **2** the addition of iodine takes place to form initially the corresponding mixed-halogen(IV) compound. However, chlorodiiodo(pentamethylcyclopentadienyl)germanium (**10**) undergoes halogen exchange; NMR spectra and mass spectra of the product obtained reveal it to consist of the three trihalo(pentamethylcyclopentadienyl)germanes **10**, **11**, and **12**. Upon repeated recrystallization the pure triiodo compound **12** was obtained.

Comparable properties were found for the compound formed upon addition of methyl iodide. The initial product **13** undergoes halogen redistribution reactions leading to the germanes **14** and **15**. Mass spectroscopic investigations show the presence of all three dihalomethyl(pentamethylcyclopentadienyl)germanes, while continued recrystallization leads to pure dichloromethyl(pentamethylcyclopentadienyl)germane (**14**).

An oxidative addition also takes place when **2** is treated with acetyl chloride; the similar reaction of the germylene **1** suggests this to be a useful, general route to ketogermanes.

While the action of methyl iodide on **2** was found to proceed very slowly, the reaction of methyl trifluoromethanesulfonate again occurs immediately. But in contrast to its addition to [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germanium (**1**), a substitution of chlorine was found in the case of the germylene **2**. Replacement of methyl trifluoromethanesulfonate by the

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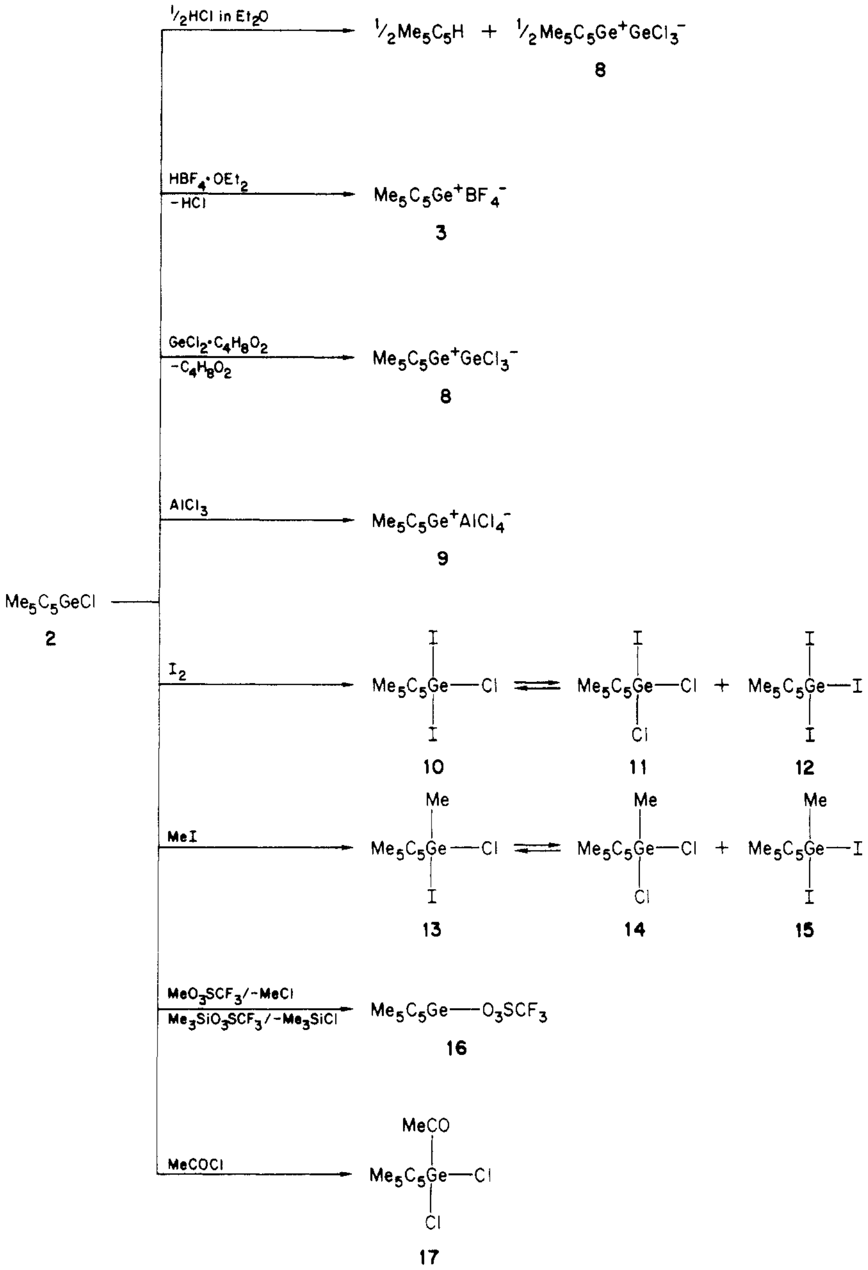
Scheme III



corresponding trimethylsilyl ester also yielded the substituted compound **16**.

Except for the halogen exchange products **10**, **11**, **13**, and **15**, which were spectroscopically detected, all the compounds reported were obtained as crystalline products. Composition and identity were confirmed by elemental analyses and spectroscopic data (see Experimental Section).

Discussion

Cyclopentadienyl-substituted germylenes provide four objectives for an electrophilic attack: the π-system of the cyclopentadienyl ligand, lone pairs of electrons at the second ligand as well as its bonding electrons, and finally the lone pair of electrons at the germanium center (see Figure 1).

The nucleophilicity of the π-system of the cyclopentadienyl ligand has been demonstrated previously. It may be noted, however, that it was mainly in the chemistry of the bis(pentamethylcyclopentadienyl) compound where an electrophilic attack at the cyclopentadienyl ligand has been detected.[3,5-7] In the case of the mixed germylenes $Me_5C_5GeCH(SiMe_3)_2$ (**1**) and Me_5C_5GeCl (**2**), an electrophilic attack at the cyclopentadienyl ligand was observed only upon protonation with ethereal hydrogen chloride. The nucleophilicity of chlorine, allowing for the formation of more or less stable chlorogermylenes,[21] might be responsible for this.

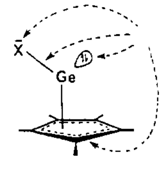


Figure 1. Sites for an electrophilic attack at cyclopentadienyl-substituted germylenes.

In contrast to hydrogen chloride, ethereal tetrafluoroboric acid attacks the germylene Me_5C_5GeCl (**2**) under displacement of the chlorine ligand to yield the well-known $Me_5C_5Ge^+$ cluster cation.[3] The existence of a nucleophilic center at the chlorine also becomes obvious from reactions

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[21] Meller, A. Gräbe, C.-P. *Chem. Ber.* **1985**, *118*, 2020.

with main-group acceptors such as $GeCl_2{\cdot}C_4H_8O_2$ and $AlCl_3$. Protonation of **1** with ethereal HBF_4 also yielded the $Me_5C_5Ge^+$ cation, thus indicating an electrophilic attack at the germanium–carbon σ-bond, resulting in cleavage of the $(Me_3Si)_2CH$ group.

Various electrophiles such as MeCOCl, MeI, and I_2 were found to react with the mixed germylenes **1** and **2** to yield germanium(IV) compounds, indicating the electrophilic attack to occur at the germanium center. We suggest these reactions to proceed via a polar two-step mechanism involving the lone pair of electrons in the initial step. A one-step addition, characterized as analogous carbene insertion reaction,[15] or a two-step free radical process[22] we consider to be unlikely. The reactions of germylenes **1** and **2** with a strong alkylating agent, methyl trifluoromethanesulfonate, were of interest. While treatment of [bis(trimethylsilyl)methyl](pentylmethylcyclopentadienyl)germylene (**1**) yielded the corresponding germanium(IV) compound, the alkylation of (pentamethylcyclopentadienyl)germanium chloride (**2**) gave the divalent germanium compound $Me_5C_5Ge–O_3SCF_3$ (**16**), indicating an electrophilic attack at the chlorine. In a control experiment, trimethylsilyl trifluoromethanesulfonate was shown to give the same reaction. Regarding the stability of the products **5**, **13**, **14**, and **15**, where no elimination reactions were observed, the origin of **16** from an addition–elimination path, as had been suggested for $(C_5H_5)_2Pb$,[23] can be ruled out.

Summarizing, it should be noted that an electrophilic attack at cyclopentadienylsubstituted germylenes can take place at different sites of the molecule in question. While mild agents prefer to attack the central germanium atom to give oxidative addition reactions, strong electrophiles already react at the periphery of the molecule.

Experimental Section

All reactions were performed in an atmosphere of dried, oxygen-free argon using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified.

Melting points: Büchi 510 capillary melting point apparatus. ^1H NMR spectra: Varian EM 360 L (60-MHz) and Bruker AM 300 (300-MHz) spectrometers. ^{13}C NMR spectra: Bruker AM 300 (75-MHz) spectrometer, ^1H decoupled; NMR spectra were recorded at room temperature except if otherwise stated. IR spectra: Perkin-Elmer 598 infrared spectrometer. Mass spectra: Varian 311 A (70 eV, 300-μA emission) spectrometer; only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen) or the analytical laboratory of the Universität Bielefeld.

[Bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (1)[1] **and (pentamethylcyclopentadienyl)germanium chloride (2)**[7] were prepared as previously described.

Protonation of 1 with Hydrogen Chloride. A solution of hydrogen chloride in diethyl ether (0.49 mL of 1.38 M, 0.68 mmol) was slowly added to a solution of 0.25 g of **1** (0.68 mmol) cooled to −80 °C. After the mixture was allowed to warm to room temperature and the solvent evaporated in vacuo, a yellow oil was obtained. The ^1H NMR spectrum (in $CDCl_3$) showed it to consist mainly of pentamethylcyclopentadiene δ 1.80 (br s) and 1.05 (d, $^3J_{H-H}$ = 7.6 Hz); also small amounts of (pentamethylcyclopentadienyl)germanium chloride (**2**) were observed (δ 2.03).

(Pentamethylcyclopentadienyl)germanium Tetrafluoroborate (3)[3] **via Protonation of 1 with Ethereal Tetrafluoroboric Acid.** A solution of tetrafluoroboric acid in diethyl ether (0.14 mL of 9.51 M, 1.33 mmol) was added to a solution of 0.50 g of **1** (1.35 mmol) in 20 mL of diethyl ether at −80 °C. After the mixture was allowed to warm to room temperature, a colorless material precipitated, which was filtered, washed with diethyl ether, and dried in vacuo to yield 0.20 g (54%) of a white, microcrystalline solid: mp 156–158 °C; ^1H NMR ($CDCl_3$) δ 2.15 (s); ^{13}C NMR ($CDCl_3$) δ 8.77 (*Me_5C_5*), 121.56 (Me_5*C_5*). Anal. Calcd for $C_{10}H_{15}BF_4Ge$ (294.62): C, 40.77; H, 5.13. Found: C, 40.39; H, 5.12.

[Bis(trimethylsilyl)methyl]diiodo(pentamethylcyclopentadienyl)germane (4). Upon addition of 0.74 g of iodine (5.83 mmol) in 20 mL of benzene to 1.07 g of **1** (2.91 mmol) in 20 mL of benzene, the iodine solution immediately discolored. After evaporation of the solvent in vacuo, an orange residue was obtained. Extraction with diethyl ether, concentrating the solution, and cooling to −20 °C gave 1.19 g (66%) of orange crystals: mp 177 °C; ^1H NMR ($CDCl_3$) δ 0.19 (s, 18 H, Me_3Si), 1.79 (br s, 15 H, Me_5C_5), further signals not observed; ^{13}C NMR ($CDCl_3$, −58 °C) δ 3.29 (Me_3Si), 5.09 (CH), 11.72, 13.13 and 15.46 (3s, *Me_5C_5*), 65.57, 134.38, and 138.87 (3s, Me_5*C_5*). MS, *m/e* (relative intensity) 622 (M^+, 7), 607 (M^+ − Me, 2), 495 (M^+ − I, 8) 487 (M^+ − Me_5C_5, 66), 463 (M^+ − $(Me_3Si)_2CH$, 3), 361 (M^+ − Me_5C_5 − I, 6), 209 ($Me_5C_5Ge^+$, 13), 201 (GeI^+, 3), 135 ($Me_5C_5^+$, 100). Anal. Calcd for $C_{17}H_{34}GeI_2Si_2$ (621.03): C, 32.88; H, 5.52; I, 40.87. Found: C, 32.73; H, 5.80; I, 37.9.

[Bis(trimethylsilyl)methyl]iodomethyl(pentamethylcyclopentadienyl)germane (5). Methyl iodide (0.27 g, 1.88 mmol) was added to a solution of 0.69 g of **1** (1.88 mmol) in 20 mL of benzene. Within 12 h the deep yellow solution discolored. After evaporation of the solvent, the residue was extracted with hexane. Concentrating the extracts and cooling to −20 °C gave 0.73 g (76%) of colorless prisms: mp 94 °C; ^1H NMR ($CDCl_3$) δ −0.39 (s, 1 H, CH), 0.05 and 0.15 (2s, 18 H, Me_3Si), 1.20 (s, 3 H, MeGe), 1.74 (s, 15 H, Me_5C_5); ^{13}C NMR ($CDCl_3$) δ 3.69 (Me_3Si), 11.56 (MeGe), 12.74 (*Me_5C_5*), further signals not observed; ^{13}C NMR ($CDCl_3$, −58 °C) δ 1.14 (CH), 3.19 and 3.38 (2s, Me_3Si), 11.68 (MeGe), 10.50, 12.30, 13.08, and 15.02 (*Me_5C_5*), 61.31, 133.74, 134.52, and 137.62 (Me_5*C_5*), further signals not observed. MS, *m/e* (relative intensity), 510 (M^+, 5), 495 (M^+ − Me, 2), 383 (M^+ − I, 3), 375 (M^+ − Me_5C_5, 100), 361 (4), 249 (10), 209 ($Me_5C_5Ge^+$, 6), 135 ($Me_5C_5^+$, 44). Anal. Calcd for $C_{18}H_{37}GeISi_2$ (509.16): C, 42.46; H, 7.32; I, 24.92. Found: C, 43.22; H, 7.29; I, 24.7.

[Bis(trimethylsilyl)methyl]methyl(pentamethylcyclopentadienyl)[(trifluoromethanesulfonyl)oxy]germane (6). Methyl trifluoromethanesulfonate (0.32 g, 1.96 mmol) was added to a solution of 0.72 g of **1** (1.95 mmol) in 30 mL of diethyl ether at −80 °C. When the mixture was allowed to warm to room temperature, the light yellow color disappeared. After evaporation of the solvent the residue was extracted with hexane. Concentrating and cooling the extracts to −20 °C gave 0.79 g (76%) of colorless crystals: mp 67 °C; ^1H NMR ($CDCl_3$) δ 0.01 and 0.11 (2s, 18 H, Me_3Si), 1.11 (s, 3 H, MeGe), 1.23 (s, 1 H, CH), 1.78 (s, 15 H, Me_5C_5); ^{13}C NMR ($CDCl_3$) δ 2.98 and 3.12 (2s, Me_3Si), 4.47 (CH), 5.87 (MeGe), 12.08 (*Me_5C_5*), no further signals observed; ^{13}C NMR ($CDCl_3$, −55 °C) δ 2.81 (br s, Me_3Si), 5.63 (s, MeGe), 12.00 (br s, *Me_5C_5*), 64.51, 130.66, and 137.40 (br signals, Me_5*C_5*), 118.15 (q, CF_3, $J_{^{13}C-^{19}F}$ = 327 Hz). MS, *m/e* (relative intensity) 532 (M^+, 7), 517 (M^+ − Me, 5), 397 (M^+ − Me_5C_5, 77), 383 (9), 267 ($(Me_3Si)_2CHGeMeF^+$, 42), 249 (12), 135 ($Me_5C_5^+$, 74), 73 (Me_3Si^+, 100). Anal. Calcd for $C_{19}H_{37}F_3GeO_3SSi_2$ (531.33): C, 42.95; H, 7.02. Found: C, 43.12; H, 7.15.

Acetyl[bis(trimethylsilyl)methyl]chloro(pentamethylcyclopentadienyl)germane (7). Acetyl chloride (0.31 g, 3.89 mmol) was added to a solution of 1.43 g of **1** (3.89 mmol) in 20 mL of diethyl ether at −80 °C. When the mixture was allowed to warm to room temperature the solution discolored. After evaporation of the solvent the yellow oily residue was extracted with 20 mL of hexane. Concentrating the solution and cooling to −80 °C gave 1.35 g (76%) of pale yellow crystals: mp 79 °C; ^1H NMR (C_6D_6) δ −0.48 (s, 1 H, CH), 0.11, 0.30 (2s, 18 H, Me_3Si), 1.74 (s, 15 H, Me_5C_5), 2.31 (s, 3 H, CH_3); ^1H NMR ($CDCl_3$, −60

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[22] Gynane, M. I. S.; Lappert, M. F.; Miles, S. I.; Carty, A. I.; Taylor, N. I. *J. Chem. Soc., Dalton Trans.* **1977**, 2009.

[23] Holliday, A. K.; Makin, P. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 435.

[24] In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminted because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.).

°C) δ −0.73 (s, 1 H, CH), −0.05, 0.10 (2s, 18 H, $\mathrm{Me_3Si}$), 1.50 (br s, 3 H, $\mathrm{Me_5C_5}$), 1.84 (br s, 12 H, $\mathrm{Me_5C_5}$) 2.52 (s, 3 H, MeCO); ^{13}C NMR ($\mathrm{CDCl_3}$, −60 °C) δ −0.73 (CH), 2.71, 3.05 (2s, $\mathrm{SiMe_3}$), 11.14, 11.79, 12.12, 12.74, 13.82 (5s, $\mathit{Me}_5\mathrm{C}_5$), 36.06 (*Me*CO), 63.68, 134.05, 136.04, 136.57, 137.48 (5s, $\mathrm{Me}_5\mathit{C}_5$), 232.16 (Me*C*O); IR (Nujol mull) ν_{CO} 1668 cm^{-1}; MS, *m/e* (relative intensity) 446 (M$^+$, 2), 403 (M$^+$ − MeCO, 39), 269 (55), 253 (16), 209 ($\mathrm{Me_5C_5Ge^+}$, 100), 135 ($\mathrm{Me_5C_5^+}$, 57). Anal. Calcd for $\mathrm{C_{19}H_{37}Cl\,GeOSi_2}$ (445.72): C, 51.20; H, 8.37; Cl, 7.95. Found: C, 51.39; H, 8.39; Cl, 7.7.

(Pentamethylcyclopentadienyl)germanium Trichlorogermanate (8)[7] via Protonation of 2 with Hydrogen Chloride. A solution of hydrogen chloride in diethyl ether (3.87 mL of 1.38 M, 5.34 mmol) was added slowly to a solution of 1.30 g of **2** (5.34 mmol) in 20 mL of diethyl ether at −80 °C. After the mixture was allowed to warm to room temperature, colorless crystals precipitated which were filtered and dried in vacuo: yield 280 mg (27%); mp 135 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.12 (s); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 9.46 (s, $\mathit{Me}_5\mathrm{C}_5$), 121.23 (s, $\mathrm{Me}_5\mathit{C}_5$). Anal. Calcd for $\mathrm{C_{10}H_{15}Cl_3Ge_2}$ (386.77): C, 31.05; H, 3.91. Found: C, 30.77; H, 3.98. After removal of the solvent in vacuo, a light yellow oil was obtained from the mother liquor. The ^{1}H NMR spectrum ($\mathrm{CDCl_3}$) showed it to consist mainly of pentamethylcyclopentadiene (δ 1.80 (br s), 1.05 (d, $^3J_{\mathrm{H-H}}$ = 7.6 Hz)) and **8** (δ 2.12).

(Pentamethylcyclopentadienyl)germanium Tetrafluoroborate (3)[3] via Protonation of 2 with Ethereal Tetrafluoroboric Acid. A solution of tetrafluoroboric acid in diethyl ether (0.59 mL of 9.51 M, 5.59 mmol) was added to a solution of 1.36 g of **2** (5.59 mmol) in 30 mL of diethyl ether at −80 °C. After the mixture was allowed to warm to room temperature, a colorless material precipitated which was filtered, washed with diethyl ether, and dried in vacuo to yield 0.93 g (57%) of a white crystalline solid: mp 156–158 °C. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.15 (s); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 8.90 ($\mathit{Me}_5\mathrm{C}_5$), 121.56 ($\mathrm{Me}_5\mathit{C}_5$); ^{11}B NMR ($\mathrm{CDCl_3}$, external $\mathrm{B(OMe)_3}$) δ −19.60 (s). Anal. Calcd for $\mathrm{C_{10}H_{15}BF_4Ge}$ (294.62): C, 40.77; H, 5.13. Found: C, 40.11; H, 4.99.

(Pentamethylcyclopentadienyl)germanium Trichlorogermanate (8)[7] via Reaction of 2 with Germanium Dichloride–Dioxane. Germanium dichloride–dioxane (1.02 g, 4.43 mmol) was added to a solution of 1.08 g of **2** (4.42 mmol) in 20 mL of dichloromethane. While the mixture was stirred, the crystalline $\mathrm{GeCl_2{\cdot}C_4H_8O_2}$ dissolved and the light yellow solution discolored within 10 min. Concentrating the solution in vacuo and cooling to −20 °C gave 1.57 g (92%) of colorless crystals: mp 135 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.12 (s); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 9.48 ($\mathit{Me}_5\mathrm{C}_5$), 121.29 ($\mathrm{Me}_5\mathit{C}_5$). Anal. Calcd for $\mathrm{C_{10}H_{15}Cl_3Ge_2}$ (386.77): C, 31.05; H, 3.91. Found: C, 31.32; H, 3.98.

(Pentamethylcyclopentadienyl)germanium Tetrachloroaluminate (9). A solution of 1.78 g of **2** (7.30 mmol) in 50 mL of benzene was added to a suspension of 2.92 g of freshly sublimed aluminum trichloride (21.0 mmol). Within 10 min the reaction mixture deepened to orange and a red oily material separated. After filtration and evaporation of the solvent in vacuo, the red oily residue was dissolved in 5 mL of dichloromethane. After being cooled to 4 °C, the solution was carefully covered with a layer of 20 mL of hexane. Within a few days yellow rhombic crystals separated, which finally were washed with a small quantity of diethyl ether: yield 1.15 g (42%); mp 154 °C dec; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.18 (s); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 9.36 ($\mathit{Me}_5\mathrm{C}_5$), 122.16 ($\mathrm{Me}_5\mathit{C}_5$). Anal. Calcd for $\mathrm{C_{10}H_{15}AlCl_4Ge}$ (376.56): C, 31.90; H, 4.01. Found: C, 31.01; H, 3.76.

Triiodo(pentamethylcyclopentadienyl)germane (12) from 2 with Iodine. Upon addition of 3.17 g of iodine (25.0 mmol) in 60 mL of benzene to 3.04 g of **2** (12.50 mmol) in 20 mL of benzene, the iodine solution immediately discolored. After evaporation of the solvent in vacuo a deep red residue was obtained. Extraction with diethyl ether, concentrating the solution, and cooling to −20 °C gave a red, crystalline solid: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.74, 1.78, and 1.81 (3s, $\mathrm{Me_5C_5GeI_3}$, $\mathrm{Me_5C_5GeI_2Cl}$, $\mathrm{Me_5C_5GeICl_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.34, 11.53, and 11.81 (3s, $\mathit{Me}_5\mathrm{C_5GeICl_2}$, $\mathit{Me}_5\mathrm{C_5GeI_2Cl}$, $\mathit{Me}_5\mathrm{C_5GeI_3}$), 123.88 (br s, $\mathrm{Me}_5\mathit{C}_5$). MS, *m/e* (relative intensity) 589 ($\mathrm{Me_5C_5GeI_3^+}$, 0.6), 497 ($\mathrm{Me_5C_5GeI_2Cl^+}$, 3.3), 406 ($\mathrm{Me_5C_5GeICl_2^+}$, 2.6), 135 ($\mathrm{Me_5C_5^+}$, 100). Repeated recrystallization from diethyl ether yielded 1.60 g of **12** (22%) as crimson crystals: mp 61 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.72 (s, $\mathrm{Me_5C_5}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.85 ($\mathit{Me}_5\mathrm{C}_5$), 123.95 ($\mathrm{Me}_5\mathit{C}_5$). Anal. Calcd for $\mathrm{C_{10}H_{15}GeI_3}$ (588.53): C, 20.41; H, 2.57; I, 64.69. Found: C, 20.38; H, 2.50; I, 64.8.

Dichloromethyl(pentamethylcyclopentadienyl)germane (14) from 2 with Methyl Iodide. Methyl iodide (1.61 g, 11.34 mmol) was added to a solution of 2.76 g of **2** (11.34 mmol) in 40 mL of benzene. Within 3 days the light yellow color of the mixture deepened to orange. After evaporation of the solvent, the residue was extracted with 40 mL of hexane. Concentrating the solution and cooling to −20 °C gave a yellow, crystalline solid: MS, *m/e* (relative intensity) 478 ($\mathrm{Me_5C_5GeMeI_2^+}$, 1.5), 386 ($\mathrm{Me_5C_5GeMeICl^+}$, 1.7), 351 ($\mathrm{Me_5C_5GeMeI^+}$, 4.6), 294 ($\mathrm{Me_5C_5GeMeCl_2}$, 3.9), 259 ($\mathrm{Me_5C_5GeMeCl^+}$, 4.4), 209 ($\mathrm{Me_5C_5Ge^+}$, 3.7), 201 ($\mathrm{GeI^+}$, 2.1), 135 ($\mathrm{Me_5C_5^+}$, 100). Recrystallization from hexane yielded 1.32 g (79%, based on chlorine) of yellow crystals: mp 77 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.52 (s, 3 H, MeGe), 1.81 (s, 15 H, $\mathrm{Me_5C_5}$); ^{13}C NMR ($\mathrm{CDCl_3}$, −50 °C) δ 1.70 (MeGe), 11.50 ($\mathit{Me}_5\mathrm{C}_5$), 65.35, 132.74, and 139.33 (br signals, $\mathrm{Me}_5\mathit{C}_5$). Anal. Calcd for $\mathrm{C_{11}H_{18}Cl_2Ge}$ (293.76): C, 44.98; H, 6.18; Cl, 24.14. Found: C, 44.17; H, 6.07; Cl, 23.9.

(Pentamethylcyclopentadienyl)germanium Trifluoromethanesulfonate (16) via Reaction of 2 with Methyl Trifluoromethanesulfonate. Methyl trifluoromethanesulfonate (1.57 g, 9.53 mmol) was added to a solution of 2.32 g of **2** (9.54 mmol) in 40 mL of diethyl ether at −80 °C. As the reaction mixture was allowed to warm to room temperature, the light yellow color disappeared. After evaporation of the solvents the colorless residue was extracted with 50 mL of toluene. Concentration of the solution in vacuo and cooling to −20 °C yielded 2.47 g (72%) colorless crystals: mp 97 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.13 (s); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 8.94 ($\mathit{Me}_5\mathrm{C}_5$), 120.07 (q, $\mathrm{CF_3}$, $J_{^{13}\mathrm{C}-^{19}\mathrm{F}}$ = 320 Hz), 121.26 ($\mathrm{Me}_5\mathit{C}_5$); MS, *m/e* (relative intensity) 358 (M$^+$, 7), 209 ($\mathrm{Me_5C_5Ge^+}$, 100), 135 ($\mathrm{Me_5C_5^+}$, 36). Anal. Calcd for $\mathrm{C_{11}H_{15}F_3GeO_3S}$ (356.89): C, 37.02; H, 4.24. Found: C, 37,10; H, 4.55.

(Pentamethylcyclopentadienyl)germanium Trifluoromethanesulfonate (16)[6] via Reaction of 2 with Trimethylsilyl trifluoromethanesulfonate. Trimethylsilyl trifluoromethanesulfonate (1.63 g, 7.32 mmol) was added to a solution of 1.78 g of **2** (7.32 mmol) in 30 mL of diethyl ether at −80 °C. Workup as described above gave 1.81 g (69%) of colorless crystals: mp 97 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.14 (s). Anal. Calcd for $\mathrm{C_{11}H_{15}F_3GeO_3S}$ (356.89): C, 37.02; H, 4.24. Found: C, 36.69; H, 4.83.

Acetyldichloro(pentamethylcyclopentadienyl)germane (17). Acetylchloride (0.58 g, 7.44 mmol) was added to a solution of 1.81 g of **2** (7.44 mmol) at −80 °C. As the reaction mixture was allowed to warm to room temperature, the light yellow color deepened to orange. After evaporation of the solvents in vacuo, the residue was extracted with 20 mL of diethyl ether. Concentrating and cooling the solution to −80 °C gave 1.79 g (75%) of colorless crystals: mp 59 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.82 (s, 15 H, $\mathrm{Me_5C_5}$), 2.22 (s, 3 H, MeCO); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 11.39 ($\mathit{Me}_5\mathrm{C}_5$), 35.63 (*Me*CO), 122.78 (br, $\mathrm{Me}_5\mathit{C}_5$), 217.10 (Me*C*O); IR (Nujol mull) ν_{CO} 1704 cm^{-1}; MS, *m/e* (relative intensity) 322 (M$^+$, 9), 244 ($\mathrm{Me_5C_5GeCl^+}$, 14), 209 ($\mathrm{Me_5C_5Ge^+}$, 92), 135 ($\mathrm{Me_5C_5^+}$, 100). Anal. Calcd for $\mathrm{C_{12}H_{18}Cl_2GeO}$ (321.77): C, 44.79; H, 5.64; Cl, 22.04. Found: C, 43.98; H, 5.54; Cl, 22.6.

Acknowledgment. The support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. **1**, 100333-77-5; **2**, 100333-78-6; **3**, 73274-08-5; **4**, 100311-84-0; **5**, 100311-85-1; **6**, 100333-73-1; **7**, 100430-60-2; **8**, 85085-99-0; **9**, 100333-79-7; **10**, 100311-86-2; **11**, 100311-87-3; **12**, 100311-88-4; **13**, 100333-74-2; **14**, 100333-75-3; **15**, 100311-89-5; **16**, 100333-80-0; **17**, 100333-76-4.