or trimethylgermyl groups in their ^{1}H NMR spectra and retention times of GLC[17] and also by the coupling constant ($^3J_{C,H}$) between the olefinic proton and the nitrile carbon in ^{13}C NMR.[18] The relations are as follows. ^{1}H NMR ($CDCl_3$): δ olefinic proton, $E < Z$; Me_3Si or Me_3Ge, $E < Z$ (except for **15e** and **20e**). GLC (silicone SE-30, DC-550, or XE-60): retention time, $E < Z$ (except for **15e** and **20e**). ^{13}C NMR ($CDCl_3$): $^3J_{C,H}$, E (17–19 Hz) > Z (9–11 Hz). The results are summarized in Table III.

Isomers of 2-(trimethylsilyl)- [or 2-(trimethylgermyl)-] cinnamonitrile (**15e**-*E*,*Z* or **20e**-*E*,*Z*) showed a reverse relation for the aliphatic analogues (**15a–d**, **20a–d**) in the chemical shift of Me_3Si or Me_3Ge ($E > Z$) (presumably anisotropic effect of a benzene ring) and the retention time ($E \geq Z$) of GLC. Their stereochemistry were confirmed by hydrolysis to cinnamonitrile. Thus, a solution of **20**-*E* (or *Z*) (246 mg, 1 mmol), n-Bu_4NF (834 mg, 3 mmol), and $KF{\cdot}2H_2O$ (385 mg, 3 mmol) in acetonitrile (5 mL)[19] was stirred for 1 h at 60 °C. After the addition of H_2O, the mixture was extracted with hexane. The organic leyer was washed with water, dried ($MgSO_4$), evaporated, and then chromatographed on a silica gel column (hexane/AcOEt, 10:1) to give (*Z*)-cinnamonitrile (117 mg, 91%) from **20e**-*E* and (*E*)-cinnamonitrile (124 mg, 96%) from **20e**-*Z*.

Reaction of Lithiobis(trimethylsilyl)acetonitrile (11) with Benzaldehyde (12e). According to the general procedure described for **15** or **20**, **3** (185 mg, 1 mmol), n-BuLi (0.64 mL, 1 mmol), and **12e** (127 mg, 1.2 mmol) was reacted. Four reaction products were detected on a silica gel TLC, and they were chromatographed on a silica gel column (hexane/diethyl ether, 20:1) and eluted in the following order: **15e**-*E*, 66 mg (33%); (*E*)-2-cyano-1,3-diphenyl-3-[(trimethylsilyl)oxy]-1-propane (**17**-*E*), 43 mg (14%); **15e**-*Z*, 14 mg (7%), and (*Z*)-2-cyano-1,3-diphenyl-3-[(trimethylsilyl)oxy]-1-propane (**17**-*Z*), 55 mg (18%). The characteristic data of **15e**-*E*,*Z* are summarized in Table III.

17-*E*: mp 74.0–75.0 °C (from hexane); IR (Nujol) 2220 (CN), 1063 cm^{-1} (SiOC); NMR ($CDCl_3$) δ 0.15 (9 H, s, $SiMe_3$), 5.44 (1 H, s, CHOSi), 7.19–8.01 (11 H, m, Ph and =CH). Anal. Calcd for $C_{19}H_{21}NOSi$: C, 74.22; H, 6.88; N, 4.56. Found: C, 74.02; H, 6.71; N, 4.54.

17-*Z*: bp 140 °C (3 mmHg, oven temperature of Kugelrohr distillation apparatus); IR (film) 2220 (CN), 1065 cm^{-1} (SiOC); NMR ($CDCl_3$) δ 0.03 (9 H, s, $SiMe_3$), 5.77 (1 H, s, CHOSi), 7.22–7.30 (11 H, m, Ph and =CH). Anal. Calcd for $C_{19}H_{21}NOSi$: C, 74.22; H, 6.88; N, 4.56. Found: C, 73.87; H, 6.85; N, 4.56.

A mixture of **17**-*E* (62 mg) and 1% HCl–MeOH (5 mL) was stirred for 1 h at room temperature. After the addition of 50 mL of ether, the mixture was washed with saturated NaCl, the solvent was removed, and then the residue was purified on a preparative TLC (silica gel; $CHCl_3/Et_2O$, 10:1) to give 49 mg (96%) of (*E*)-2-cyano-1,3-diphenyl-3-hydroxy-1-propene, which was identical with an authentic sample.[9]

Registry No. **1**, 18293-53-3; **3**, 18881-60-2; **4**, 101652-74-8; **5**, 101652-75-9; **6**, 101652-76-0; **7**, 101652-77-1; **8**, 101652-78-2; **9**, 101652-79-3; **10**, 101652-80-6; **12a**, 124-13-0; **12b**, 123-05-7; **12c**, 2043-61-0; **12d**, 630-19-3; **12e**, 100-52-7; **12f**, 98-01-1; (*E*)-**15a**, 86536-63-2; (*Z*)-**15a**, 101652-87-3; (*E*)-**15b**, 82125-00-6; (*Z*)-**15b**, 101652-89-5; (*E*)-**15c**, 82124-99-0; (*Z*)-**15c**, 85520-60-1; (*E*)-**15d**, 95085-49-7; (*Z*)-**15d**, 101652-92-0; (*E*)-**15e**, 82125-02-8; (*Z*)-**15e**, 96475-95-5; (*E*)-**20a**, 101652-81-7; (*Z*)-**20a**, 101652-88-4; (*E*)-**20b**, 101652-82-8; (*Z*)-**20b**, 101652-90-8; (*E*)-**20c**, 101652-83-9; (*Z*)-**20c**, 101652-91-9; (*E*)-**20d**, 101652-84-0; (*Z*)-**20d**, 101652-93-1; (*E*)-**20e**, 101652-85-1; (*Z*)-**20e**, 101652-94-2; (*E*)-**20f**, 101652-86-2; (*Z*)-**20f**, 101652-95-3; Me_3GeBr, 1066-37-1; $Me_3GeC_4H_9$, 1000-46-0; $(Me_3Ge)_2$, 993-52-2; chloroacetonitrile, 107-14-2.

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(20) 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 eliminated 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.)

Preparation of Tin and Germanium Metallocenes from Tetravalent Precursors

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A selective reduction of appropriate tetravalent compounds provides an alternative synthetic approach to tin and germanium metallocenes. The preparation of decamethylstannocene (**1**) was carried out by treating bis(pentamethylcyclopentadienyl)tin dihalides with lithium metal, lithium naphthalenide, and dilithium cyclooctatetraenide. For the reduction of bis(pentamethylcyclopentadienyl)dichlorogermane to decamethylgermanocene (**4**), dipotassium cyclooctatetraenide was found to be the appropriate reagent.

Introduction

Since the work of Löwig[1] and Frankland[2] in the middle of the last century, it is known that the reduction of diorganotin dihalides with electropositive metals such as sodium and zinc leads to diorganotin(II) compounds. Modern analytical methods revealed these to be oligomeric or even polymeric. The degree of polymerization among cyclic $[R_2Sn]_n$ and acyclic $R_{2n+2}Sn_n$ polystannanes (R = alkyl, aryl, halogen) was shown to vary markedly.[3] Several well-defined cyclic compounds such as $(Me_2Sn)_6$ or $(Ph_2Sn)_6$ can be prepared by treating diorganotin dihalides with sodium metal or sodium naphthalenide. During the last 2 years Masamune[4] and Neumann[5] reported the first cyclotristannanes, formed upon reduction of diorganotin

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(1) Löwig, C. *Justus Liebigs Ann. Chem.* **1852**, *84*, 308.

(2) Frankland, A. *Justus Liebigs Ann. Chem.* **1853**, *85*, 329.

(3) Review: Neumann, W. P. *The Organic Chemistry of Tin*; Wiley-Interscience: London and New York, 1970.

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dichlorides with lithium naphthalenide. Thus, the only monomeric species that had been obtained was bis[bis(trimethylsilyl)methyl]tin(II), prepared from the corresponding diorganotin dichloride with dilithium cyclooctatetraenide by Lappert.[6] In germanium chemistry the reduction of dihalogermanes with lithium metal and sodium naphthalenide was used to prepare pentameric and hexameric diphenylcyclogermanes $(Ph_2Ge)_n$[7] and recently also trimeric species.[8,9] A reduction leading to monomeric germylene species has not been reported as yet.

In this paper we describe new syntheses of bis(pentamethylcyclopentadienyl)dihalides of germanium and tin and the first reductive approach to group 4B (14[18]) metallocenes.

Results and Discussion

To prepare decamethylstannocene (**1**)[10] from tetravalent tin compounds, appropriate precursors appear to be bis(pentamethylcyclopentadienyl)tin chloride (**2a**), dibromide (**2b**), and diiodide (**2c**), which have already been described.[10] The dichloro compound was obtained from tin tetrachloride with 2 equiv of lithium pentamethylcyclopentadienide, while the other compounds were prepared from the metallocene 1 via oxidative addition of halogen.[10] However, both substances could be prepared from tin tetrahalides (eq 1). The diorganotin dihalides obtained

$$SnX_4 + 2Me_5C_5Li \rightarrow \underset{\substack{\mathbf{2a},\ X = Cl\\ \mathbf{2b},\ X = Br\\ \mathbf{2c},\ X = I}}{(\eta^1\text{-}Me_5C_5)_2SnX_2} \qquad (1)$$

were moderately thermally labile compounds, melting with decomposition. We investigated such a decomposition in detail for the bromo compound **2b**. The basic reaction was found to be a reductive elimination, leading to bi[1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl][10] and the corresponding tin dihalide (eq 2). In the presence of

$$\underset{\mathbf{2b}}{(\eta^1\text{-}Me_5C_5)_2SnBr_2} \xrightarrow{\Delta} (Me_5C_5)_2 + SnBr_2 \qquad (2)$$

$$\underset{\mathbf{2b}}{(\eta^1\text{-}Me_5C_5)_2SnBr_2} + \underset{\mathbf{1}}{(\eta^5\text{-}Me_5C_5)_2Sn} \xrightarrow{\Delta} (Me_5C_5)_2 + 2\underset{\mathbf{3}}{(\eta^5\text{-}Me_5C_5)SnBr} \qquad (3)$$

decamethylstannocene (**1**), the formation of the dihalide is followed by a redistribution reaction, yielding (pentamethylcyclopentadienyl)tin bromide (**3**) (eq 3). As bis(η^1-pentamethylcyclopentadienyl)tin diiodide undergoes thermal decomposition at room temperature within a few minutes, the chloride **2a** and the bromide **2b** as the more stable compounds were preferred for investigations on reductive metallocene syntheses.

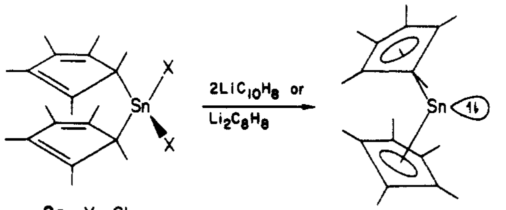
The reduction of bis(η^1-pentamethylcyclopentadienyl)tin dihalides does not stop at the metallocene stage but continues on to yield metallic tin on treatment with an excess of the reducing agent or in the heterogeneous system with alkali metals as reducing agents. The reaction of decamethylstannocene (1) with sodium and potassium in tetrahydrofuran or 1,2-dimethoxyethane in fact yielded metallic tin and alkali-metal pentamethylcyclopentadienide after a short reaction time (eq 4); only in the case of lithium a much slower reaction was observed; within 7 days about 63% of 1 remain unchanged. As a consequence of these observations, bis(η^1-pentamethylcyclopentadienyl)tin dibromide (**2**) was treated with lithium dispersion in tetrahydrofuran. Upon stirring the mixture at room temperature, the reaction was complete within 3 days to give decamethylstannocene (1), which was isolated in 56% yield (eq 5).

$$\underset{\mathbf{1}}{(\eta^5\text{-}Me_5C_5)_2Sn} + 2M \rightarrow 2Me_5C_5M + Sn \qquad (4)$$

$$M = (Li),\ Na,\ K$$

$$\underset{\mathbf{2b}}{(\eta^1\text{-}Me_5C_5)_2SnBr_2} + 2Li \rightarrow \underset{\mathbf{1}}{(\eta^5\text{-}Me_5C_5)_2Sn} + 2LiBr \qquad (5)$$

The use of naphthalenides or cyclooctatetraenides instead of the pure alkali metals is assumed to lead to a kinetic activation and a reduced reduction power (thermodynamic deactivation). It was hoped that these systems might favor the first reduction step to the metallocene. In fact, the reduction of the bis(η^1-pentamethylcyclopentadienyl)tin dihalides **2a,b** with lithium naphthalenide (eq 6) in tetrahydrofuran at −60 °C went to completion immediately to give decamethylstannocene (1) quantitatively as determined spectroscopically, but the separation of 1 from naphthalene proved to be difficult,[11] and the preparation of the analytically pure compound involves loss of large amounts of the product. As cyclooctatetraene is more volatile, it is easier to isolate a pure product. Treatment of bis(η^1-pentamethylcyclopentadienyl)tin dihalides **2a,b** with dilithium cyclooctatetraenide (eq 6) in diethyl ether/tetrahydrofuran at −80 °C yielded pure decamethylstannocene (1) in about 70% yield. Further reduction to tin metal was observed only to a small extent



2a, X = Cl
2b, X = Br

1

(6)

Bis(η^1-pentamethylcyclopentadienyl)dihalogermanes, the possible precursors to decamethylgermanocene (**4**),[12] have not yet been reported. The direct synthesis of the dichloro compound **5** from germanium tetrachloride and lithium pentamethylcyclopentadienide (eq 7) proved to be difficult, because the formation of byproducts (including bi[1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl][10]) dominates the introduction of a second pentamethylcyclopentadienyl ring at the germanium; thus the yield of **5** did not exceed 34%.

$$GeCl_4 + 2Me_5C_5Li \xrightarrow[-2LiCl]{} \underset{\mathbf{5}}{(\eta^1\text{-}Me_5C_5)_2GeCl_2} \qquad (7)$$

An alternative synthetic route to the decamethylgermanocene precursor **5** is the introduction of an incompletely substituted second cyclopentadienyl ligand followed by completion of its substitution. Treatment of (η^1-pentamethylcyclopentadienyl)trichlorogermane[13] with

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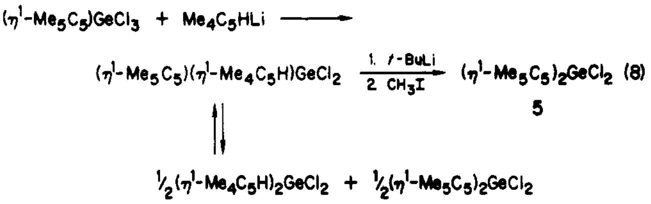
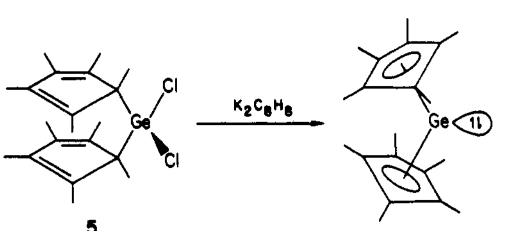
(tetramethylcyclopentadienyl)lithium yielded a mixture of tetramethyl- and pentamethylcyclopentadienyl-substituted dichlorogermanes. Permethylation was then effected by reaction with *tert*-butyllithium at low temperatures followed by addition of iodomethane[14] (eq 8).



$$(\eta^1\text{-Me}_5\text{C}_5)\text{GeCl}_3 + \text{Me}_4\text{C}_5\text{HLi} \longrightarrow (\eta^1\text{-Me}_5\text{C}_5)(\eta^1\text{-Me}_4\text{C}_5\text{H})\text{GeCl}_2 \xrightarrow[2.\ \text{CH}_3\text{I}]{1.\ t\text{-BuLi}} \underset{\mathbf{5}}{(\eta^1\text{-Me}_5\text{C}_5)_2\text{GeCl}_2} \quad (8)$$

$$(\eta^1\text{-Me}_5\text{C}_5)(\eta^1\text{-Me}_4\text{C}_5\text{H})\text{GeCl}_2 \rightleftharpoons \tfrac{1}{2}(\eta^1\text{-Me}_4\text{C}_5\text{H})_2\text{GeCl}_2 + \tfrac{1}{2}(\eta^1\text{-Me}_5\text{C}_5)_2\text{GeCl}_2$$

Decamethylgermanocene (4) was found to react with the alkali metals to give elemental germanium (in analogy to eq 4). To avoid the problem of purifying a naphthalene-containing product, the reduction of **5** was attempted with alkali cyclooctatetraenides. The lithium and sodium species do not react with **5** to produce the desired germanocene **4**. However, a useful route to **4** is provided by the reaction with dipotassium cyclooctatetraenide (eq 9),



(9)

5 **4**

which occurs without considerable reduction of the metallocene to elemental germanium. Germanocene **4** was obtained in about 54% yield. The structures of **2a**, **2b**, and **5**, as shown in eqs 6 and 9, are assumed to be analogous to those of the corresponding silicon compounds, which had been investigated by x-ray crystallography.[14]

In summary, we have shown that the preparation of group 4B (14) metallocenes from tetravalent precursors provides a useful synthetic alternative. However, specific conditions must be chosen for the desired metallocene syntheses, because the reaction products from a first reduction step can easily be reduced further to the 4B (14) metal by the alkali metals as well as by some alkali-metal naphthalenides and cyclooctatetraenides.

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 were obtained with Büchi 510 capillary melting point apparatus. Instruments used in data collection: ^{1}H NMR spectra, Varian EM 360 L (60 MHz) and Bruker AM 300 (300 MHz); ^{13}C NMR spectra, Bruker AM 300 (75 MHz), ^{1}H-decoupled; ^{119}Sn NMR spectra, Bruker AM 300 (112 MHz), ^{1}H-decoupled; mass spectra, Varian 311 A (70 eV, 300 μA emission); only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen) or the analytical laboratory of the Universität Bielefeld.

Bis(pentamethylcyclopentadienyl)tin Dibromide (2b). Molten tin(IV) bromide (33.4 g, 76.2 mmol) was added during 30 min to an ice-cooled suspension of lithium pentamethylcyclopentadienide, prepared from 20.7 g (152 mmol) of pentamethylcyclopentadiene[15] and 100 mL of a 1.52 M solution of *n*-butyllithium in hexane (152 mmol) in about 300 mL of petroleum ether. Upon stirring for 1 h the suspension turned orange. After the insoluble material was filtered, the solution was concentrated in vacuo and cooled to −30 °C to yield 32.3 g (77%) of orange scales: mp 88 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.78 (s, $^3J_{\text{SnH}} = 41.3$ Hz); ^{13}C NMR (CDCl$_3$) δ 123.8 (Me$_5$*C*$_5$), 12.4 (*Me*$_5$C$_5$); ^{119}Sn NMR (CDCl$_3$, external Me$_4$Sn) δ −59. Anal. Calcd for $C_{20}H_{30}Br_2Sn$ (548.97): C, 43.76; H, 5.51. Found: C, 44.06; H, 5.63.

Bis(pentamethylcyclopentadienyl)tin Diiodide (2c). Tin(IV) iodide (25.04 g, 40.0 mmol) was added during 30 min at −20 °C to a suspension of lithium pentamethylcyclopentadienide, prepared from 10.88 g of pentamethylcyclopentadiene (79.9 mmol) in ether (400 mL) and 50 mL of a 1.60 M solution of *n*-butyllithium in hexane (80.0 mmol). Stirring at −20 °C was continued for about 1 h to give a clear red-orange solution. Removal of the solvent and extraction of the residue with petroleum ether (250 mL) were carried out at low temperatures. Concentration of the extracts yielded 15.5 g (60%) of red-orange scales: mp 69 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.77 (s, $^3J_{\text{SnH}} = 41.7$ Hz); ^{13}C NMR (CDCl$_3$) δ 124.0 (Me$_5$*C*$_5$), 12.8 (*Me*$_5$C$_5$); ^{119}Sn NMR (CDCl$_3$, external Me$_4$Sn) δ −68. Anal. Calcd for $C_{20}H_{30}SnI_2$ (642.96): C, 37.36; H, 4.70. Found: C, 36.96; H, 4.51.

(Pentamethylcyclopentadienyl)tin(II) Bromide (3) from Thermal Decomposition of Bis(pentamethylcyclopentadienyl)tin Dibromide (2b) in the Presence of Decamethylstannocene (1). A mixture of crystals of **2** (4.12 g, 7.51 mmol) and of decamethylstannocene[10,12] (**1**) (2.90 g, 7.45 mmol) was fused and heated to 90 °C, where the orange liquid solidified. The mixture was washed with cold petroleum ether (50 mL) (see below), and the residue was dissolved in dichloromethane (15 mL). The solution was concentrated to about 5 mL, carefully layered with petroleum ether (30 mL), and stored at −30 °C to yield 1.76 g (70%) of colorless needles: mp 178 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.06 (s); ^{13}C NMR (CDCl$_3$) δ 118.2 (Me$_5$*C*$_5$), 10.1 (*Me*$_5$C$_5$); ^{119}Sn NMR (CDCl$_3$, external Me$_4$Sn) δ −1630;[16] MS, *m/e* (relative intensity) 334 (M$^+$, 12.7), 255 (Me$_5$C$_5$Sn$^+$, 100), 199 (SnBr$^+$, 13.8), 135 (Me$_5$C$_5$$^+$, 26.2). Anal. Calcd for $C_{10}H_{15}BrSn$ (333.83); C, 35.98; H, 4.53. Found: C, 35.80; H, 4.51. Evaporation of the solvent from the petroleum ether phase yielded bi[1,2,3,4,5-pentamethylcyclopentadienyl][10] as a light yellow oil which cyrstallized upon cooling; the crude product was identified spectroscopically without further purification: ^{1}H NMR (CDCl$_3$) δ 1.60, 1.63 (2s, sp^2 C–Me), 1.03 (s, sp^3 C–Me); ^{13}C NMR (CDCl$_3$) δ 137.7, 134.1 (sp^2 C), 51.5 (sp^3 C), 14.0 (sp^3 C–*Me*), 11.5, 11.0 (sp^2 C–*Me*); MS, *m/e* (relative intensity) 270 (M$^+$, 7.0), 135 (C$_5$Me$_5$$^+$, 100).

Reduction of Bis(pentamethylcyclopentadienyl)tin Dibromide (2b) with Lithium Dispersion. A solution of **2** (3.48 g, 6.34 mmol) in tetrahydrofuran (30 mL) was added to a suspension of lithium dispersion (88 mg, 12.7 mmol) in tetrahydrofuran (20 mL). Upon stirring for 72 h the orange reaction mixture turned olive in color. Evaporation of the solvent in vacuo followed by extraction of the residue with 50 mL of petroleum ether gave a clear yellow solution. Concentration and cooling to −80 °C yielded 1.37 g (56%) of bright yellow crystals of decamethylstannocene (**1**): ^{1}H NMR (C$_6$H$_6$) δ 2.07 (s, $^3J_{\text{SnH}} = 3.7$ Hz). Anal. Calcd for $C_{20}H_{30}Sn$ (389.15): C, 61.72; H, 7.77. Found: C, 61.23; H, 7.90.

Reduction of 2b with Lithium Naphthalenide. The reducing agent was prepared from lithium dispersion (290 mg, 41.8 mmol) and naphthalene (5.35 g, 41.8 mmol) in tetrahydrofuran (30 mL). The dark green solution of the reagent was added dropwise to a solution of **2b** (11.5 g, 21.4 mmol) in tetrahydrofuran (40 mL) and cooled to −60 °C. The mixture was allowed to warm slowly, and stirring was continued for 48 h. After removal of the solvent in vacuo the residue was extracted with petroleum ether (30 mL). Concentration of the solution and cooling to −20 °C yielded a crude product. Upon recrystallization, 296 mg (4%) of pure decamethylstannocene (**1**) was obtained: ^{1}H NMR (CH$_2$Cl$_2$) δ 2.03 (s, $^3J_{\text{SnH}} = 3.7$ Hz). Anal. Found: C, 61.38; H, 7.57.

Reduction of 2b with Dilithium Cyclooctatetraenide. The reducing agent was prepared from lithium dispersion (172 mg, 24.8 mmol) and cyclooctatetraene (1.40 mL, 12.4 mmol) in diethyl ether (40 mL). The pale brown suspension of the reagent was added dropwise to a solution of **2** (6.80 g, 12.4 mmol) in tetrahydrofuran (40 mL) and cooled to −80 °C. After the mixture was

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Table I. Conditions for the Reduction of 1 and 4

metallocene, amount	alkali metal, amount	reactn time	remaining metallocene	yield of Ge/Sn
$GeC_{20}H_{30}$ (4), 1.00 g, (2.92 mmol)	Li, 42 mg (6.0 mmol)	7 days	not observed	176 mg (83%)
$GeC_{20}H_{30}$ (4), 1.02 g (2.97 mmol)	Na, 0.14 g (5.94 mmol)	46 h	not observed	170 mg (79%)
$GeC_{20}H_{30}$ (4), 1.09 g (3.18 mmol)	K, 0.25 g (6.35 mmol)	24 h	not observed	187 mg (81%)
$SnC_{20}H_{30}$ 1.08 g (2.77 mmol)	Li, 39 mg (5.62 mmol)	7 days	676 mg (63%) isolated	traces
$SnC_{20}H_{30}$ (1), 1.00 g (2.57 mmol)	Na, 0.12 g (5.22 mmol)	25 h	not observed	246 mg (81%)
$SnC_{20}H_{30}$ (1), 1.17 g (3.01 mmol)	K, 0.24 g (6.14 mmol)	$^3/_4$ h	not observed	317 mg (89%)

allowed to warm to room temperature, the solvents were removed in vacuo. Extraction of the residue with pentane (30 mL), concentration of the solution, and cooling to −30 °C yielded 3.36 g (70%) of decamethylstannocene (1): ^{1}H NMR (C_6H_6) δ 2.08 (s, $^3J_{SnH}$ = 3.7 Hz). Anal. Found: C, 61.52; H, 7.64.

Reduction of Bis(pentamethylcyclopentadienyl)tin Dichloride (2a) with Lithium Naphthalenide. Compound **2a** (2.81 g, 6.1 mmol) was treated with the reagent prepared from lithium dispersion (84.8 mg, 12.2 mmol) and naphthalene (1.55 g, 12.2 mmol). The procedure was similar to that used for the corresponding reduction of **2b**. However, extraction with petroleum ether was followed by complete removal of the solvent in vacuo. The product was not purified: ^{1}H NMR (CH_2Cl_2) δ 2.03 (s, 1; $^3J_{SnH}$ = 3.6 Hz), further resonances due to naphthalene; remains of the starting material were not observed.

Reduction of 2a with Dilithium Cyclooctatetraenide. A solution of **2a** (5.51 g, 12.0 mmol) in tetrahydrofuran (30 mL) was treated with the reagent prepared from lithium dispersion (166 mg, 24.0 mmol) and cyclooctatetraene (1.36 mL, 12.0 mmol). The procedure was similar to that used for the corresponding reduction of **2b**. After the reaction mixture was allowed to warm to room temperature, stirring was continued for 6 h before the solvent was removed in vacuo. Extraction of the residue with petroleum ether (30 mL), concentration of the solution, and cooling to −20 °C yielded 3.17 g (67%) of decamethylstannocene (1): ^{1}H NMR (C_6H_6) δ 2.07 (s, $^3J_{SnH}$ = 3.6 Hz). Anal. Found: C, 61.86; H, 7.74.

Bis(pentamethylcyclopentadienyl)dichlorogermane (5) from Germanium(IV) Chloride. Germanium(IV) chloride (8.65 mL, 74.4 mmol) was added during 30 min to an ice-cooled suspension of lithium pentamethylcyclopentadienide (from pentamethylcyclopentadiene (20.3 g, 149 mmol) in petroleum ether (~350 mL) and 100 mL of a 1.49 M solution of *n*-butyllithium in hexane). Refluxing the mixture for 24 h did not lead to completion of the reaction, so the solvent was replaced by tetrahydrofuran (200 mL). Upon refluxing for 1 h, a clear yellow solution was obtained from which the solvent was evaporated in vacuo. Extraction of the residue with petroleum ether (200 mL), concentration of the solution, and cooling to 4 °C yielded 10.5 g (34%) of colorless scales: mp 203–205 °C; ^{1}H NMR (C_6H_6) δ 1.79 (s); ^{13}C NMR (C_6D_6) δ 137.8 ($Me_5\mathit{C}_5$), 11.9 (Me_5C_5); MS, *m/e* (relative intensity) 414 (M^+, 1.9), 270 ($(Me_5C_5)_2^+$, 1.5), 170 ($Me_5C_5Cl^+$, 4.4), 135 ($Me_5C_5^+$, 100). Anal. Calcd for $C_{20}H_{30}Cl_2Ge$ (413.96): C, 58.03; H, 7.31. Found: C, 57.81; H, 7.38.

Bis(pentamethylcyclopentadienyl)dichlorogermane (5) from (Pentamethylcyclopentadienyl)trichlorogermane. A solution of (η^1-pentamethylcyclopentadienyl)trichlorogermane[12] (13.4 g, 42.7 mmol) in tetrahydrofuran (30 mL) was added to an ice-cooled suspension of lithium tetramethylcyclopentadienide, prepared from tetramethylcyclopentadiene[17] (5.22 g, 42.2 mmol) in tetrahydrofuran (60 mL) and 30.0 mL of a 1.53 M solution of *n*-butyllithium in hexane (45.9 mmol). Stirring was continued for 15 h and was followed by evaporation of the solvent and extraction of the residue with petroleum ether (100 mL). Upon concentration of the solution and cooling to −30 °C, 15.2 g (90%) of pale yellow scales were obtained: ^{1}H NMR ($CDCl_3$) δ 1.60–2.00 ($(\mathit{Me}_5C_5)_2GeCl_2$, $\mathit{Me}_5C_5(\mathit{Me}_4C_5H)GeCl_2$, $(\mathit{Me}_4C_5H)_2GeCl_2$), signals for $Me_4C_5\mathit{H}$ were not plainly observed; MS, *m/e* (relative intensity) 414 ($(Me_5C_5)_2GeCl_2^+$, 0.7), 400 ($Me_5C_5(Me_4C_5H)GeCl_2^+$, 1.4), 386 ($(Me_4C_5H)_2GeCl_2^+$, 0.6), 270 ($(Me_5C_5)_2^+$, 0.6), 256 ($(Me_5C_5)Me_4C_5H^+$, 1.2), 242 ($(Me_4C_5H)_2^+$, 3.3), 170 ($Me_5C_5Cl^+$, 3.1), 135 ($Me_5C_5^+$, 100), 121 ($Me_4C_5H^+$, 36.7).

The material (8.43 g, ~21.1 mmol) was dissolved in tetrahydrofuran (80 mL) and cooled to −60 °C. Over a period of 30 min 16.8 mL of a 1.25 M solution of *tert*-butyllithium in pentane (21.0 mmol) was added. Stirring at −60 °C was continued for 1 h before methyl iodide (1.75 mL, 28.0 mmol) was added. The reaction mixture was allowed to warm to room temperature, and workup as described above yielded 7.32 g (81%) colorless scales: mp 198 °C; ^{1}H NMR (C_6H_6) δ 1.77 (s); ^{13}C NMR ($CDCl_3$) δ 137.4 ($Me_5\mathit{C}_5$), 11.8 (Me_5C_5). Anal. Found: C, 58.24; H, 7.46.

Reduction of Bis(pentamethylcyclopentadienyl)dichlorogermane (5) with Potassium Cyclooctatetraenide. The reducing agent was prepared by reacting potassium metal (1.22 g, 31.3 mmol) and cyclooctatetraene (1.77 mL, 15.7 mmol) in tetrahydrofuran (30 mL) at 0 °C. The red-brown suspension of the reagent was added dropwise to a solution of 5.48 g of **5** (13.2 mmol) in tetrahydrofuran (50 mL) and cooled to −80 °C. After the mixture was allowed to warm slowly, the solvent was removed in vacuo. Extraction of the residue with petroleum ether (50 mL), concentration of the solution, and cooling to −30 °C yielded 2.45 g (54%) of pale yellow needles of decamethylgermanocene (4): ^{1}H NMR (C_6H_6) δ 2.04 (s); ^{13}C NMR ($CDCl_3$) δ 118.1 ($Me_5\mathit{C}_5$), 9.8 (Me_5C_5). Anal. Calcd for $C_{20}H_{30}Ge$ (343.05): C, 70.02; H, 8.82. Found: 69.95; H, 8.84.

Reduction of the Metallocenes 1 and 4 by Alkali Metals (See Table I). A stoichiometric amount of cut-up alkali metal was added to a solution of the metallocene in tetrahydrofuran. Upon stirring at room temperature the yellow solution turned to a gray-green suspension. Evaporation of the solvent and extraction of the residue with petroleum ether gave a solution which was analyzed for remaining metallocene by ^{1}H NMR. The insoluble material was treated with methanol; elemental germanium/tin was filtered and dried, while the solution was examined for pentamethylcyclopentadiene spectroscopically.

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Registry No. 1, 68757-81-3; **2a**, 69446-40-8; **2b**, 69446-45-3; **2c**, 69446-46-4; **3**, 101834-65-5; **4**, 73274-06-3; **5**, 101481-02-1; $SnBr_4$, 7789-67-5; Me_5C_5Li, 51905-34-1; Me_5C_5H, 41539-64-4; SnI_4, 7790-47-8; $Me_5C_5C_5Me_5$, 69446-48-6; $GeCl_4$, 10038-98-9; $Me_5C_5GeCl_3$, 87795-77-5; Me_4C_5HLi, 87781-76-8; $Me_4C_5H_2$, 79042-55-0; lithium naphthalenide, 7308-67-0; naphthalene, 91-20-3; dilithium cyclooctatetraenide, 34728-91-1; cyclooctatetraene, 629-20-9; potassium cyclooctatetraenide, 101834-66-6.

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[17] Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819.

[18] 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 eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 thorugh 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.)