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Reaction of Decamethylsilicocene with Group 13 Element Halides: Insertions, Rearrangements, and Eliminations

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In the reaction of decamethylsilicocene (**1**; $(Me_5C_5)_2Si$) with halides or organohalides of trivalent boron, aluminum, gallium, and indium, quite different and sometimes very complex pathways are observed which include adduct formation, 1,2-halide or -alkyl shifts, 1,2-dyotropic rearrangements, and reductive elimination and oxidative addition reactions. Cp^*BCl_2 (Cp* = pentamethylcyclopentadienyl), BCl_3, and BBr_3 reacted with **1** to form the pentacarba-*nido*-hexaboronium salts $[Cp^*SiCl_2BCp^*]^+[Cp^*BCl_3]^-$ (**3a**) and $[Cp^*SiX_2BCp^*]^+[BX_4]^-$ (**3b**, X = Cl; **4**, X = Br). A second product (**5b**) of composition $Cp^*_3Si_2Br_4B$ with an *arachno*-cluster framework was isolated from the reaction with BBr_3. With $AlCl_3$ and $AlBr_3$ metathesis reactions gave the ionic compounds $[Cp^*_2Al]^+[AlX_4]^-$ (**6a,b**, X = Cl, Br), respectively. The formation of **6a,b** is the result of a Lewis-base-catalyzed dismutation of Cp^*AlX_2 in which **1** is the base, as proved by separate experiments. The compound $Cp^*Al(Me)Cl$ (**7**) was formed in the reaction of **1** with Me_2AlCl. Silicocene **1** functioned as a dehalogenating agent in its reactions with $GaCl_3$, $GaBr_3$, Cp^*GaBr_2, $InCl_3$, and $InBr_3$, giving the corresponding monovalent, metastable (“GaCl”, “GaBr”) or stable (Cp*Ga, InCl, InBr) species. All new compounds were characterized by NMR (^1H, ^{13}C, ^{11}B, ^{29}Si) and mass spectrometry. The solid-state structures of **3a** and **5b** were determined by X-ray diffraction analysis.

Introduction

In 1986 we synthesized decamethylsilicocene (**1**), the first stable monomeric compound with silicon in the formal oxidation state +2.[1] In this species the central silicon atom is π-bound to two pentamethylcyclopentadienyl (Cp*) ligands. The bonding is best described as an interaction of the Cp* π-orbitals of appropriate symmetry with empty p orbitals on silicon. As a consequence, the lone electron pair on silicon has nearly exclusive s-character. The reactivity of **1** can best be described as that of a nucleophilic silylene.[2] In conjunction with the synthesis of **1** and with the preparation of 1,3-di-*tert*-butyl-1,3,2-diazasilol-2-ylidene (**2**), the first stable two-coordinate silylene, in 1994 by Denk et al.[3] there has been increased interest in the reactions of nucleophilic silylenes.[4]

After earlier preliminary investigations[5] we recently have concentrated on the reactivity of **1** toward compounds of group 13 elements, where a variety of reduction, insertion, and rearrangement processes has been observed. Only very few reactions of carbene analogue species of silicon, germanium, and tin with compounds of group 13 elements have been described. In 1996 Denk and Metzler reported on the reaction of **2** with tris(pentafluorophenyl)borane in which a Lewis-acid−Lewis-base complex was formed which rearranged by insertion of the silylene into a B−C bond.[6] Very recently, Belzner et al. reported the insertion of a diarylsilylene into an Al−C bond of trimethylaluminum.[7] In 1992 Nöth and co-workers described the reaction of the transient dimethylgermylene with chloro- and hydridoboranes,[8] earlier on Zuckerman and Harrison discussed the reaction of stannocene with boron trifluoride,[9] and recently the

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(1) (a) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem.* **1986**, *98*, 163. (b) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, R.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629.

(2) See for example: Jutzi, P.; Eikenberg, D.; Bunte, E.-A.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 1930 and references therein.

(3) (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) Haaf, M.; Scmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714.

(4) See for example: (a) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599. (c) Denk, M. K.; Hatano, K.; Lough, A. J. *Eur. J. Inorg. Chem.* **1998**, 1067. (d) Boesfeld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1999**, 755. (e) Schäfer, A.; Saak, W.; Weidenbruch, M.; Marsmann, H.; Henkel, G. *Chem. Ber./Recl.* **1997**, *130*, 1733. (f) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211. (g) Denk, M.; West, R. *Pure Appl. Chem.* **1996**, *68*(4), 785. (h) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813. (i) Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1997**, 1845.

(5) Jutzi, P. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1991.

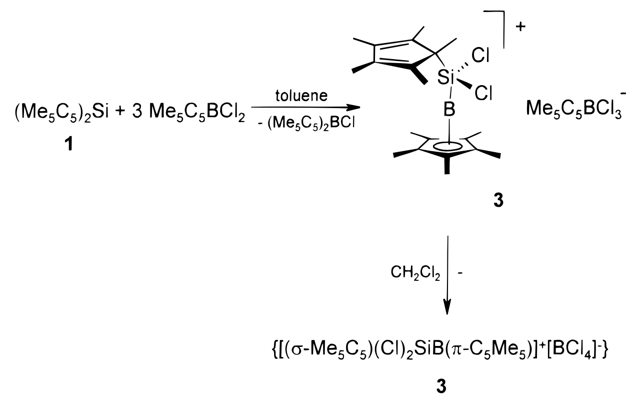
(6) Denk, M.; Metzler, N. *Chem. Commun.* **1996**, 2657−2658.

(7) Belzner, J.; Ronneberger, V.; Schär, D.; Brönnecke, C.; Herbst-Irmer, R.; Noltemeyer, M. *J. Organomet. Chem.* **1999**, *577*, 330−336.

(8) Mayer, E. P.; Nöth, H.; Rattay, W.; Wietelmann, U. *Chem. Ber.* **1992**, *125*, 401−405.

10.1021/om9906114 CCC: $18.00

Scheme 1



group of Lappert reported the characterization of borane (BH_3) adducts of a germylene and of a stannylene.[10]

Here we report the reactions of decamethylsilicocene (**1**) with trihalides of boron, aluminum, gallium, and indium and with some organo-substituted derivatives of these elements.

Results and Discussion

The reaction of decamethylsilicocene (**1**) with Cp*BCl_2, BX_3, AlX_3, Cp*$AlCl_2$, Me_2AlCl, GaX_3, Cp*$GaBr_2$, and InX_3 (X = Cl, Br) proceeded cleanly under mild conditions. In all cases the reaction pathway can be described as a sequence of adduct formation followed by subsequent rearrangement steps.

Silicocene **1** reacted slowly with Cp*BCl_2 in benzene or toluene at room temperature. Three equivalents of the boron compound was needed for complete consumption of **1** (Scheme 1), and **3a** was formed as a colorless solid that is sparingly soluble in aliphatic or nonpolar, aromatic solvents. **3a** is thermally stable at room temperature but very reactive toward air and moisture.[11] Besides **3a**, 1 equiv of the known Cp*$_2$BCl[12] was formed, which was unambiguously identified by means of ^{1}H and ^{11}B NMR spectroscopic examination of the reaction mixture or of the mother liquor after crystallization of **3a**.

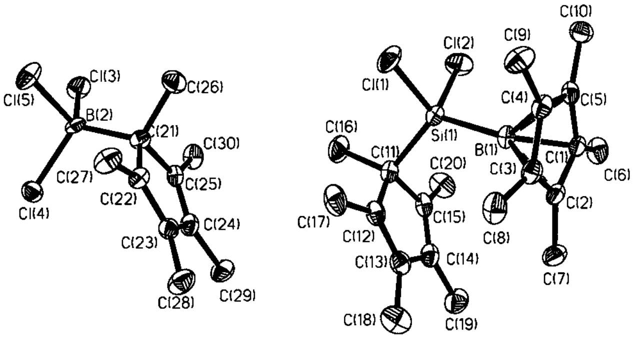


Figure 1. ORTEP plot of **3a**. Thermal ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3a

Bond Lengths			
B(1)−C(1)	1.738(6)	B(1)−X_{Cp}	1.262
B(1)−C(2)	1.747(6)	B(1)−Si(1)	1.973(5)
B(1)−C(3)	1.749(6)	Si(1)−C(11)	1.865(4)
B(1)−C(4)	1.762(6)	Si(1)−Cl(1)	2.0666(16)
B(1)−C(5)	1.768(6)	Si(1)−Cl(2)	2.0671(16)
Bond Angles			
Cl(1)−Si(1)−Cl(1)	102.50(8)	C(3)−B(1)−Si(1)	139.9(3)
C(11)−Si(1)−B(1)	118.4(2)	C(4)−B(1)−Si(1)	127.7(3)
C(1)−B(1)−Si(1)	136.0(3)	C(5)−B(1)−Si(1)	130.0(3)
C(2)−B(1)−Si(1)	144.6(3)	X_{Cp}−B(1)−Si(1)	170.8

Due to the low solubility of **3a** it was not possible to obtain NMR spectra in solvents other than CD_2Cl_2 or $CDCl_3$. Under these conditions the Cp*BCl_3^- anion decomposes with formation of Cp*H and BCl_4^-. Accordingly, **3b** was formed in these solutions (Scheme 1). Similar behavior has been observed in the case of base adducts of Cp*BCl_2.[13] The spectroscopic data of the cation in **3a** are not affected by the change in anion. In the ^{1}H NMR spectrum, one sharp resonance, in accordance with a π-bound Cp* ring, was found as well as broadened signals due to another Cp* ring that is σ-bound and undergoes relatively slow sigmatropic shifts. No signal in the ^{29}Si NMR spectrum could be detected, probably due to fast relaxation processes caused by the quadrupole moment of the neighboring $^{11/10}$B nucleus. The ^{13}C NMR resonances were consistent with the interpretation of one slowly rearranging σ-bound and one π-bound Cp* ring. In the ^{11}B NMR spectrum, signals were observed at 6.1 and −54.6 ppm. The latter value is in a range characteristic for pentacarba-*nido*-hexaborane cations;[14] the former corresponds to the tetrachloroborate anion.

Crystals of **3a** suitable for an X-ray structure analysis were obtained by recrystallization from hot benzene or toluene. An ORTEP plot of the molecular structure of **3a** is shown in Figure 1. Selected bond lengths and angles are given in Table 1, and crystallographic data are collected in Table 2.

In the cation of **3a** one Cp* ring is bound in an η^1-fashion to the silicon atom, while the other one is η^5-bound to the boron atom with an average B−C bond length of 1.75 Å. This compares to 1.68 Å in [Cp*BBr]$^+$-[$AlBr_4$]$^-$,[15] to 1.70 Å in 2,3,4,5-tetracarba-*nido*-hexaborane ($C_4B_2H_6$),[16] and to 1.81 Å in [(Cp*B)Fe(CO)$_4$].[17] The angle Si−B−X_{Cp} (where X_{Cp} is the in-plane center of the Cp* ring) is 171°; the deviation from the expected linear arrangement can be explained by crystal-packing effects. As predicted by theoretical calculations,[18] the methyl groups of the η^5-Cp* ring are bent toward the boron center with an average deviation from the ring

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[9] (a) Harrison, P. G.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 2577. (b) Dory, T. S.; Zuckerman, J. J.; Barnes, C. L. *J. Organomet. Chem.* **1985**, *281*, C1.

[10] Drost, C.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1998**, *17*, 3838 and literature cited therein.

[11] No satisfactory microanalytical data could be obtained for compounds **3**−**5**. This is most probably due to (a) the high reactivity of the compounds toward even trace amounts of air or moisture and (b) partial formation of B_4C_3 on combustion.

[12] Jutzi, P.; Krato, B.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1987**, *120*, 565.

[13] Jutzi, P.; Krato, B. Unpublished results.

[14] (a) Jutzi, P.; Seufert, A. *Angew. Chem.* **1977**, *89*, 339. (b) Jutzi, P.; Seufert, A.; Buchner, W. *Chem. Ber.* **1979**, *112*, 2488. (c) Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1978**, *161*, C5.

[15] Dohmeier, C.; Köppe, R.; Robl, C.; Schnöckel, H. *J. Organomet. Chem.* **1995**, *487*, 127.

[16] Pasinski, J. P.; Beaudet, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 928.

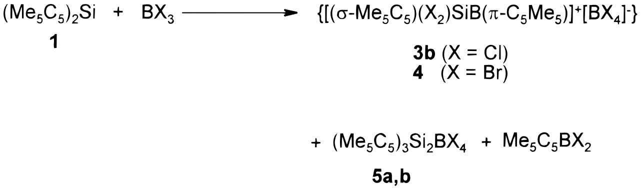
[17] Cowley, A. H.; Lomelf, V.; Voigt, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401.

[18] Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

Table 2. Crystallographic Data

	3a	5b
empirical formula	$C_{30}H_{45}B_2Cl_5Si$	$C_{30}H_{45}BBr_4Si_2$
cryst size, mm^3	1 × 0.4 × 0.2	0.5 × 0.4 × 0.3
fw	632.62	792.3
cryst syst	monoclinic	triclinic
space group	*Cc*	*P*1
lattice params		
a, Å	8.757(3)	8.386(4)
b, Å	15.192(5)	8.530(5)
c, Å	25.281(7)	13.970(6)
α, deg	90	104.97(4)
β, deg	98.85(3)	92.23(4)
γ, deg	90	117.36(4)
V, Å^3	3323.3(18)	842.8(7)
Z	4	1
d_{calcd}, g/cm^3	1.264	1.561
diffractometer	Siemens R3	Siemens P2(1)
F(000)	1336	398
μ(Mo Kα), Å	0.710 73	0.710 73
temp, °C	−100	−100
$2\theta_{max}$, deg	57	54
no. of data collected	4634	3931
no. of params refined	358	195
no. of obsd data ($F > 4\sigma(F)$)	3976	3275
residuals: R_F, $R_{wF}{}^2$ for obsd data	0.0457, 0.1101	0.0526, 0.1267
largest peak in final diff map, e/Å^3	0.397	1.243
program used in refinement	SHELX97	SHELX97
abs cor	empirical	empirical

Scheme 2



plane of 4.2°. This behavior is documented in the literature thus far only for $[Cp^*BBr]^+[AlBr_4]^-$ (3.9°).[15] In addition to the η^5-Cp* moiety, the boron center bears a Cp^*SiBr_2 substituent. The boron−silicon distance of 1.973(5) Å is comparable to that of 1.976(4) Å in *t*-Bu−N═B−Si(SiMe$_3$)$_3$[19] and is well in the range of the sum of the covalent radii of boron (0.81 Å) and silicon (1.17 Å).[20] In the $Cp^*BCl_3^-$ anion of **3a**, the Cl−B−Cl angles are slightly smaller than expected for ideal tetrahedral symmetry (∼106°), while the angles between the chlorine atoms and the Cp* carbon atom are slightly widened (∼113°). This is most probably due to the steric bulk of the Cp* ligand.

The reaction of **1** with boron trihalides is more complex. At least three different types of products are formed, and the product ratio was found to depend on the chosen solvent (Scheme 2). On reaction of **1** with boron trichloride or tribromide in toluene at low temperature, a deep red reaction mixture was obtained initially. The red color vanished nearly immediately to yield a yellow solution, from which **3b** or **4** precipitated during the reaction. The compounds were isolated in moderate yield as a colorless powder and a crystalline solid, respectively. Both are very sensitive toward air and moisture. Both compounds are sparingly soluble in benzene or aliphatic hydrocarbons, with **4** being slightly more soluble in benzene than **3b,** but they dissolve readily in dichloromethane or chloroform. The NMR spectroscopic examination of the reaction mixtures showed that **5a**,**b** and Cp^*BX_2 were formed as byproducts (vide infra).

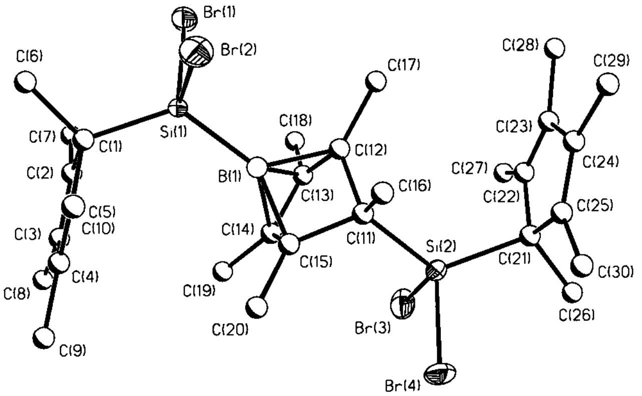


Figure 2. ORTEP plot of **5b**. Thermal ellipsoids are shown at the 50% probability level.

Compounds **3b** and **4** were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy.[11] The spectra of **3b** were identical with those described above. The ^1H and ^{13}C NMR spectra of **4** show resonances that were assigned to two different Cp* rings. In the ^{11}B NMR spectrum signals at −3.8 ppm for BBr_4^- and at −55.1 ppm for the boron center in the cluster cation were detected.

As pointed out above, the product ratio depends strongly on the polarity of the solvent. In the reaction with BBr_3 in dichloromethane/hexane (2/1) **5b** was isolated as the main product, although in moderate yield. After storage for 2 weeks at −30 °C, colorless crystals of **5b** had precipitated from the yellow solution. In the mother liquor, **4** and Cp^*BBr_2 were identified by NMR spectroscopy.[14b]

The ^1H and ^{13}C NMR spectra of **5b** are consistent with the presence of three different σ-Cp* moieties. The ^{13}C NMR data show that one Cp* ring additionally engages in some kind of π-coordination. The ^{11}B NMR spectrum shows one resonance at − 39.2 ppm; in the ^{29}Si NMR spectrum one signal at 20.0 ppm is observed.

The quality of the crystalline material of **5b** was sufficient to prove the connectivity by an X-ray structure analysis. Figure 2 shows an ORTEP plot of the molecular structure of **5b**. The boron center is η^4-bonded to a pentamethylcyclopentadiene unit. One Cp^*SiBr_2 group is σ-bonded to the boron atom, while another one is σ-bonded at an allylic position of the π-bonded pentamethylcyclopentadiene. Difficulties occurred in the X-ray diffraction experiment. The collected data did not allow us to surely distinguish between a displacement of the molecule at a center of inversion or a racemic twinning of the crystal. The plot shows the results of a calculation assuming a twinned crystal (space group *P*1) with a domain distribution of 57:43. Therefore, no detailed discussion of the structural data is possible. Crystallographic data are collected in Table 2.

Compound **3a** is best described as a pentacarba-*nido*-hexaboronium salt. Figure 3 shows the two possible descriptions of the central unit in the cation, as a π-complex of a borylene fragment or as a *nido* cluster according to the rules established by Wade and Min-

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(19) Haase, M.; Klingebiel, U.; Boese, R.; Polk, M. *Chem. Ber.* **1986**, *119*, 1117.

(20) Holleman-Wiberg. *Textbook of Inorganic Chemistry*, 91−100th ed.;, Walter de Gruyter: Berlin/New York, 1985.

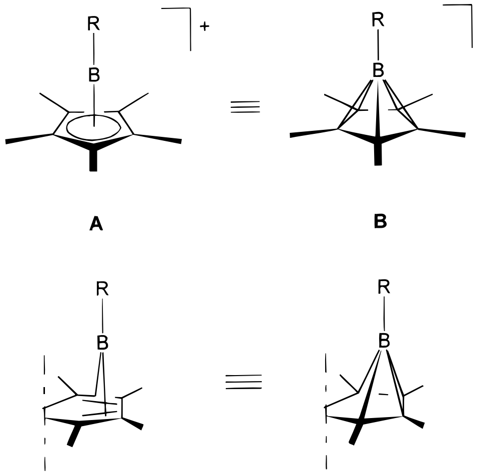


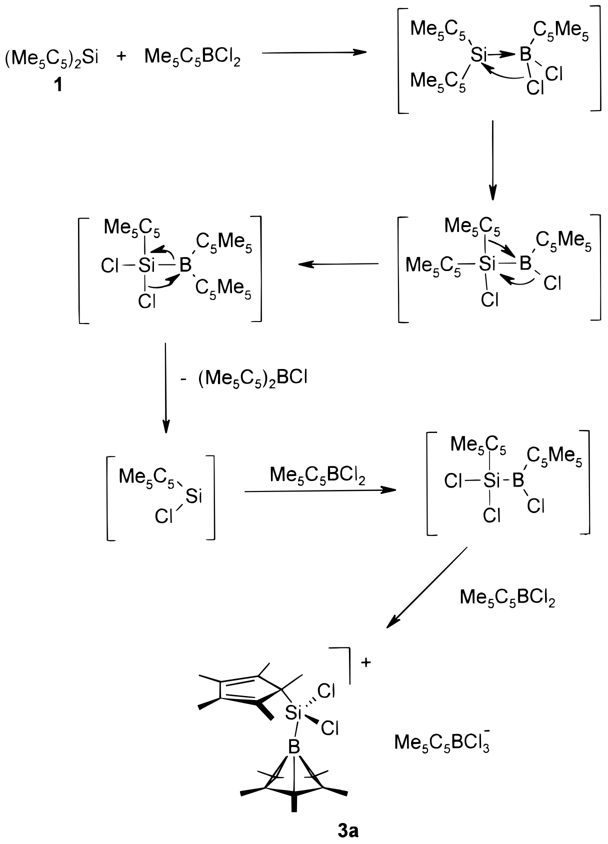
Figure 3.

gos.[21] In analogy to the considerations concerning the structure of **3a**, the structure of the central fragment in **5b** can be described as a π complex or as an *arachno*-carborane derived from pentaborane(11), as shown in Figure 3. To our knowledge **5b** is the first example of a tetracarba-*arachno*-pentaborane that is stable at ambient temperature.

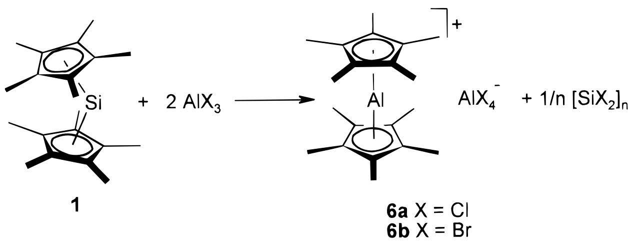
The *arachno* structure of **5b** can be formally constructed by attaching an anionic Cp*SiBr$_2^-$ fragment to the π-bonded Cp* ring in the cation of **4**. Presumably **4** is an intermediate in the formation of **5b.** This suggestion was supported by NMR monitoring experiments. The ^{11}B NMR spectra showed that, when the starting materials were combined, at first only the signal due to **4** at −55 ppm was present in the reaction mixture. After a short period of time a signal at −39 ppm for **5b** became apparent.

Although we have not as yet carried out detailed mechanistic studies, we wish to propose possible pathways for the reactions described above as summarized in Scheme 3. In the reaction of **1** with Cp*BCl$_2$, the first step is a nucleophilic attack of **1** on the Lewis-acidic boron center. The adduct formation is followed by a halide shift from boron to silicon. This process corresponds to a formal insertion of a silylene into a boron−halogen bond. The insertion product is a reactive intermediate and rearranges by exchange of a Cp* ligand from silicon to boron and of a halide ligand from boron to silicon. This double migration corresponds to a [1,2]^2-dyotropic rearrangement,[22,23] a concerted mechanism anticipated. The intermediate reacts further by reductive elimination of Cp*SiCl and formation of Cp*$_2$BCl. This kind of metathesis reaction has also been observed for **1** in reactions with aluminum compounds (see below). The silylene formed can be assumed to be stable enough against rapid polymerization[24] to allow its insertion into a B−Cl bond of a Cp*BCl$_2$ molecule. Abstraction of a chloro ligand by attack of a further Cp*BCl$_2$ molecule leads to the final product. This proposed mechanism is in accordance with the fact that

Scheme 3



Scheme 4



3 equiv of the boron compound is needed for complete consumption of **1,** and it explains the formation of 1 equiv of Cp*$_2$BCl as a byproduct.

The situation is obviously more complicated for the reaction of **1** with boron trihalides. At least three different products are found (**3b**/**4**, **5a**,**b**, Cp*BX$_2$) in different amounts, depending on the solvent. The mechanisms leading to the final products are not fully understood, but it is reasonable to assume pathways which are in part comparable to those described in Scheme 3.

The reaction of **1** with AlCl$_3$ or AlBr$_3$ in 1:1 stoichiometry led to a mixture of unidentified products. When **1** was reacted with 2 equiv of the aluminum trihalides, the known decamethylaluminocenium salts **6a**,**b**[25] were formed in high yield (Scheme 4). These were isolated as colorless, crystalline materials which are very sensitive toward air and moisture and virtually insoluble in nonpolar solvents but easily soluble in dichloromethane. **6a**,**b** were identified by ^{27}Al NMR spectroscopy. As a

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(21) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29.

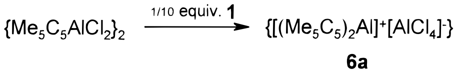
(22) This designation of the rearrangement as [1,2]^2 was introduced by Paetzold in: Paetzold, P. I.; Grundke, H. *Synthesis* **1973**, 635.

(23) Reetz, M. T. *Adv. Organomet. Chem.* **1976**, *16*, 33.

(24) Apeloig, Y.; Maxka, J. *J. Chem. Soc., Chem. Commun.* **1990**, 737.

(25) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem.* **1993**, *105*, 1714.

Scheme 5



$$\{Me_5C_5AlCl_2\}_2 \xrightarrow{1/10\ \text{equiv.}\ \mathbf{1}} \{[(Me_5C_5)_2Al]^+[AlCl_4]^-\}$$

6a

further reaction product, small amounts of the known corresponding (pentamethylcyclopentadienyl)aluminum dihalide[26] were found. It was not possible to characterize a silicon-containing product in the reaction mixture.

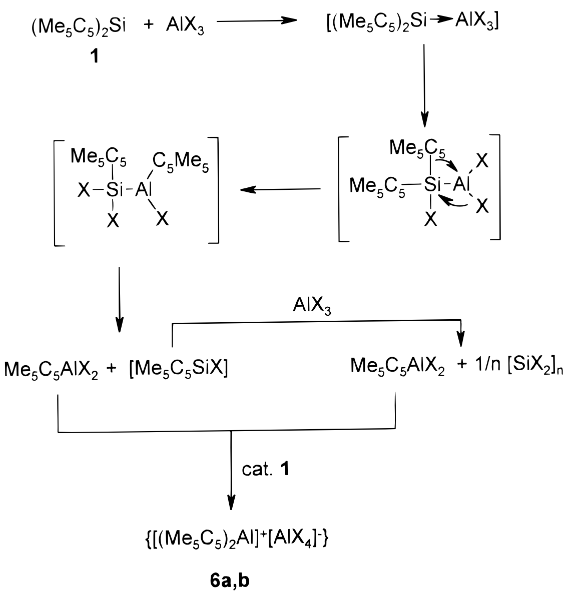
It was surprising that the reaction proceeded under 2-fold Cp* transfer from a silicon to an aluminum center. A better understanding of the process described in Scheme 4 could be achieved after investigating the reaction of **1** with Cp*$AlCl_2$. When **1** was added to an equimolar amount of Cp*$AlCl_2$ in toluene, a colorless solid precipitated within a short period of time. The product was unambiguously identified as the aluminocenium salt **6a**.[25] Even with a 10-fold excess of Cp*$AlCl_2$, complete conversion to the aluminocenium salt was observed without any consumption of **1** (Scheme 5).

Since no stoichiometric relationship between the two components was found and **1** could be recovered quantitatively from the reaction mixture, the process is best described as a decamethylsilicocene-catalyzed dismutation of the aluminum compound (the dimeric Cp*$AlCl_2$ and the aluminocenium salt **6a** are structural isomers with the molecular formula Cp*$_2Al_2Cl_4$). Base-induced dismutation reactions of cyclopentadienylaluminum alkyls have been reported, but not for Cp*-substituted compounds and not as quantitative processes.[27] The fact that **6a** precipitates from solution is probably the driving force for the quantitative conversion. This is the first time that the function of **1** as a mere Lewis-base catalyst has been observed.

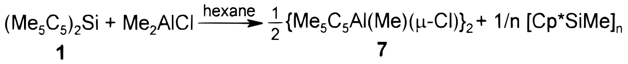
Considering these results, we suggest that the aluminocenium salts obtained from the reaction of **1** with aluminum trihalides are formed via the corresponding (pentamethylcyclopentadienyl)aluminum dihalides (Cp*AlX_2). The proposed reaction pattern is shown in Scheme 6. Nucleophilic attack of **1** on the aluminum center and formation of a Lewis-acid−Lewis-base complex is followed by halide transfer from aluminum to silicon. The formed Si(IV) species rearranges by Cp* transfer to aluminum and halide transfer to silicon. Subsequently Cp*SiX is formed by reductive elimination. As pointed out above, this silylene can be considered stable enough against polymerization to allow further reaction with AlX_3 to form another 1 equiv of Cp*AlX_2 and SiX_2. Since **1** is present in the solution, it enforces the dismutation of Cp*AlX_2 to **6a**,**b**. At a certain point **1** has been completely consumed in the metathesis step. Afterward no further dismutation occurs, and a small amount of Cp*AlX_2 is left in the reaction mixture.

In the reaction described in Schemes 4 and 6, a silicon atom which is introduced in the form of **1** leaves the reaction sequence as the dihalo compound SiX_2, which is a highly reactive species that can be assumed to form a complex mixture of oligomers. This assumption is in accordance with the fact that no defined silicon-containing product was detected. The reaction pathway described is also in accordance with the observation of Cp*AlX_2 as a "byproduct".

Scheme 6



Scheme 7



$$(Me_5C_5)_2Si + Me_2AlCl \xrightarrow{\text{hexane}} \tfrac{1}{2}\{Me_5C_5Al(Me)(\mu\text{-}Cl)\}_2 + 1/n\ [Cp^*SiMe]_n$$

1 **7**

As the reactions of **1** with aluminum trihalides show, halide ligands on aluminum are very easily substituted by Cp* ligands. Use of dimethylaluminum chloride should allow the substitution of only one halide ligand and stop the reaction at an earlier state. Therefore, we studied the reaction of **1** with Me_2AlCl. Surprisingly, the aluminum compound Cp*Al(Me)Cl[28] (**7**) was formed in good yield (Scheme 7). The product was identified by ^1H and ^{27}Al NMR and mass spectrometry. All attempts to isolate or to trap the extruded [Cp*SiMe] have been unsuccessful to date. It is remarkable that in this reaction metathesis occurs with transfer of a methyl rather than a chloro ligand. This surprising result has initiated further exchange experiments with homoleptic group 13 element alkyls.[29]

On going from the aluminum trihalides to the trihalides of the heavier homologues gallium and indium, an interesting change in reactivity was observed. Instead of reacting by Cp* transfer, **1** now served as a reducing agent. In the reaction of **1** with equimolar amounts of $GaCl_3$ or $GaBr_3$ in toluene as solvent, at low temperature (−80 °C), an orange solution was obtained. On warming to room temperature, the color changed to yellow; the quantitative conversion of **1** to the corresponding dihalosilane Cp*$_2SiX_2$[30] was proved by NMR spectroscopy. Within 3 to 5 days at room temperature, gallium metal precipitated as a gray powder; Cp*$_2SiCl_2$

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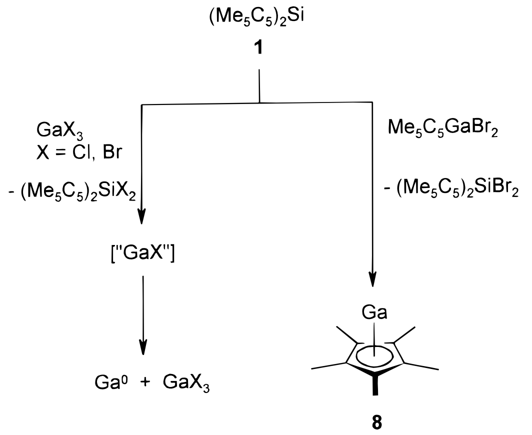
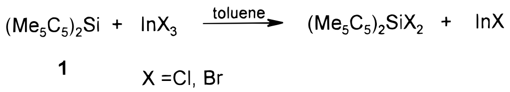
Scheme 8

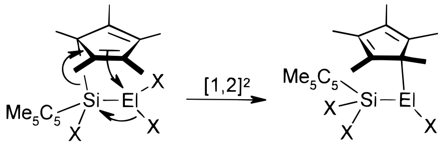


Scheme 9



$$\underset{\mathbf{1}}{(Me_5C_5)_2Si} + \underset{X = Cl,\ Br}{InX_3} \xrightarrow{toluene} (Me_5C_5)_2SiX_2 + InX$$

Scheme 10



and Cp*$_2$SiBr$_2$, respectively, as well as the corresponding gallium trihalide could be isolated from solution. The silicon compounds were identified by NMR spectroscopy;[30] the gallium trihalides were identified in form of their pyridine adducts. In these reactions, **1** obviously serves as a dehalogenating agent, and not yet characterized species of the composition “GaX” are formed, which slowly disproportionate to yield GaX$_3$ and Ga^0 (Scheme 8). This behavior is similar to that of metastable solutions of Ga(I) halides as described by Schnöckel and co-workers.[31] The compounds described here disproportionate at comparably higher temperatures; thus, a different structure (perhaps comparable to “GaI” as described by Green et al.[32]) and/or a stabilization by Cp*$_2$SiX$_2$ molecules has to be taken into account. When the yellow solutions were not allowed to stand for a few days, and when all volatiles were removed immediately after warming to room temperature, a yellow residue was obtained, consisting of “GaX” and Cp*$_2$SiX$_2$. In the solid state as well as in C$_6$D$_6$ solution the residue decomposed with precipitation of gallium metal within a few days.

If the proposed formation of “GaX” correctly describes the course of events, then suitable substituents at the gallium center should facilitate the formation of stable Ga(I) compounds. In this context, use of the Cp* substituent occurred to us as particularly promising, since Cp*Ga is a well-known, stable compound.[33] In an NMR experiment, **1** was treated with a stoichiometric amount of Cp*GaBr$_2$. The NMR spectroscopic examination showed ^{1}H, ^{29}Si, and ^{71}Ga resonances that could unambiguously be assigned to Cp*Ga(I) (**8**) and to Cp*$_2$SiBr$_2$ (Scheme 8). The reaction proceeded quantitatively, as no other products were identified.

In contrast to the Ga(I) halides, the monovalent halides of In are stable at room temperature. Thus, we expected a clean redox reaction of indium trihalides with **1**. Indeed, **1** reacted with indium trichloride or tribromide by complete reduction of the In(III) to the In(I) species. In toluene slow dissolution of the indium trihalide was observed on warming from −30 °C to room temperature, followed by precipitation of the corresponding indium(I) halide, which was removed by filtration. From the separated solution, Cp*$_2$SiCl$_2$ and Cp*$_2$SiBr$_2$, respectively, were isolated in nearly quantitative yield (Scheme 9).

Conclusion

The reactions of decamethylsilicocene (**1**) with halides or organohalides of the trivalent group 13 elements boron, aluminum, gallium, and indium can be explained by multistep processes that include insertion reactions of **1**, rearrangements, and reductive-elimination steps. Two different general pathways can be distinguished.

With boron and aluminum compounds, **1** engages in Cp* transfer reactions. Here, the pronounced leaving group character of the Cp* substituent on silicon comes to the fore. In the reactions with boron compounds, the silylboranes **3a**,**b**, **4**, and **5a**,**b** are isolated, while in the reactions with aluminum compounds the Cp*−Al species **6a**,**b** and **7** are formed. In the latter no defined silicon-containing products can be characterized; unstable silylenes are formed which are subject to oligomerization reactions. As shown in Schemes 3 and 6, reaction sequences often include double-migration processes classified as [1,2]^2-dyotropic rearrangements. Generally, the presence of a π-system in one of the migrating groups facilitates such processes due to easy interactions with the involved element center. In this context another advantage of the Cp* ligand comes to the fore, as indicated in Scheme 10. The ligand can easily interact with and migrate to a neighboring element center.

Toward gallium and indium compounds, **1** reacts as a reducing agent. In all cases the corresponding Cp*$_2$SiX$_2$ (X = Cl, Br) is formed in nearly quantitative yield. The low-valent gallium halides that are formed in the reactions with GaX$_3$ so far could only be characterized by their disproportionation products (Ga^0 + GaX$_3$), while in the reaction with Cp*GaBr$_2$ the stable Cp*Ga (**8**) is formed. From the reactions with indium trihalides the stable monohalides can be isolated.

The different results obtained within a series of group 13 element halides once more demonstrate the wide reactivity spectrum of decamethylsilicocene.

Experimental Section

General Considerations. Standard Schlenk techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods and distilled under argon prior to use. Mass spectra were run on a Varian 311 A mass spectrometer (70 eV, 300 μA emission), and NMR spectra were obtained using a Bruker Avance 500 spectrometer (^{1}H, 500.132 MHz; ^{13}C, 125.771 MHz; ^{29}Si, 99.354 MHz; ^{11}B,

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160.462 MHz; ^{27}Al, 130.321 MHz). Proton NMR spectra were referenced to the residual protic impurities of the deuterated solvents, carbon NMR spectra were referenced to the solvent signals, and hetero nuclei (^{29}Si, ^{11}B, ^{27}Al) NMR spectra were referenced to external standards. Melting points (uncorrected) were measured with a Büchi 510 melting point apparatus using sealed capillary tubes. Unfortunately, no satisfactory microanalytical data could be obtained for compounds **3**−**5**, probably due to their distinct sensitivity to even trace amounts of air or moisture and perhaps also due to partial formation of B_4C_3 on combustion. Products that were already known in the literature were identified by comparison of the NMR spectroscopic data.

Reaction of 1 with Cp*BCl$_2$. A solution of 0.52 g of **1** (1.7 mmol) in toluene (12 mL) was added to a solution of 1.12 g (5.2 mmol) of Cp*BCl$_2$ in toluene (17 mL). The resulting yellow reaction mixture was stirred for 24 h and then concentrated to 7 mL. Pentane (7 mL) was added, and the solution was placed in a freezer at −30 °C for 72 h. Afterward the precipitated colorless crystals were filtered at low temperature. The procedure was repeated once more to give a total yield of 997 mg (93%) of **3a** as colorless crystals. The solution was concentrated to yield 600 mg of a yellow residue which was shown by NMR spectroscopy to consist nearly exclusively of Cp*$_2$BCl.[12] Crystals of **3a** which were suitable for X-ray structure analysis were obtained by recrystallization from benzene. Yield: 997 mg (93% with respect to **1**). ^{1}H NMR (CD$_2$Cl$_2$):[37] δ 1.26, 1.93 (br, 15 H, SiCp*), 2.09 (s, 15H, BCp*). ^{13}C NMR (CD$_2$Cl$_2$): δ 9.41 ($\mathrm{B}\mathit{Me}_5\mathrm{C}_5$), 12.48 (br. $\mathrm{Si}\mathit{Me}_5\mathrm{C}_5$), 114.59 ($\mathrm{BMe}_5\mathit{C}_5$), 136.21, 141.71 ($\mathrm{SiMe}_5\mathit{C}_5$). ^{11}B NMR (CD$_2Cl_2$): δ −54.6 (BCp*), 6.1 (BCl_4^-). Mp: 110 °C dec.

Reaction of 1 with Boron Trichloride. A solution of 0.78 g (2.61 mmol) of **1** in toluene (25 mL) was cooled to −80 °C. On dropwise addition of 11 mL of a 0.23 M solution of BCl$_3$ (2.53 mmol) in toluene a red color appeared, which immediately changed to deep yellow. When the reaction mixture was warmed to room temperature, a colorless solid precipitated. The solvent was removed in vacuo. The yellow residue was recrystallized from methylcyclohexane (80 mL). Yield: 0.46 g (34%) of **3b**. Mp: 151 °C dec. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.26, 1.93 (br, 15 H, SiCp*), 2.09 (s, 15H, BCp*). ^{13}C NMR (CD$_2$Cl$_2$): δ 9.41 ($\mathrm{B}\mathit{Me}_5\mathrm{C}_5$), 12.48 (br, $\mathrm{Si}\mathit{Me}_5\mathrm{C}_5$), 114.59 ($\mathrm{BMe}_5\mathit{C}_5$), 136.21, 141.71 ($\mathrm{SiMe}_5\mathit{C}_5$). ^{11}B NMR (CD$_2Cl_2$): δ −54.6 (BCp*), 6.1 (BCl_4^-). MS (EI): *m*/*z* (%) 414 (3.9), Cp*$_2$SiBCl$_3^+$; 379 (67.5), Cp*$_2$SiBCl$_2^+$; 281 (100), Cp*SiBCl$_3^+$; 181 (75.6), Cp*BCl$^+$; 163 (73.2), Cp*Si$^+$.

Reaction of 1 with Boron Tribromide. To a solution of 2.07 g (6.93 mmol) of **1** in toluene (30 mL) was added dropwise a solution of 1.73 g of BBr$_3$ (6.91 mmol) in toluene (10 mL) while the reaction mixture was cooled to −80 °C. When the mixture was warmed to room temperature, the color changed from red to deep yellow, and a white precipitate was formed. The slurry was concentrated, and pentane (30 mL) was added. The precipitate was filtered, washed with 5 mL of pentane, and recrystallized from dichloromethane. Yield: 2.03 g (37%) of **4**. Mp: >215 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.54 (br s, 15H, SiCp*), 1.65 (s, 15H, Cp*B). ^{13}C NMR (CDCl$_3$): δ 9.7 ($\mathit{Me}_5\mathrm{C}_5\mathrm{B}$), 12.9 ($\mathit{Me}_5\mathrm{C}_5\mathrm{Si}$), 114.5 ($\mathrm{Me}_5\mathit{C}_5\mathrm{B}$), 141.7, 144.1 ($\mathrm{Me}_5\mathit{C}_5\mathrm{Si}$). ^{11}B NMR (CDCl$_3$): δ −55.1 (Cp*B), −23.8 (BBr_4^-). MS (EI): *m*/*z* (%) 469 (42.7), Cp*$_2$SiBBr$_2^+$; 415 (60.2), Cp*SiBBr$_3^+$; 306 (8.5), Cp*SiBBr$_2^+$; 225 (59.4), Cp*BBr$^+$; 163 (100), Cp*Si$^+$.

Reaction of 1 with Boron Tribromide in Dichloromethane/Hexane. A 298 mg portion of **1** (1 mmol) was dissolved in 2 mL of dichloromethane, and the solution was cooled to −80 °C. One milliliter of a 1 M solution of BBr$_3$ in hexane was layered on top, and the mixture was warmed to −30 °C. On addition a dark red color occurred that slowly changed to light yellow. The reaction flask was kept at −30 °C for 2 weeks. From the yellow solution colorless crystals of **5b** did form, which were isolated and dried *in vacuo*. Yield: 198 mg (50% based on **1**) of **5b**. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.98 (s, 6H), 1.05 (s, 3H), 1.21 (s, 3H), 1.24 (br s, 3H), 1.83 (s, 12H), 1.84 (s, 6H), 1.89 (s, 12H). ^{29}Si NMR (CD$_2$Cl$_2$): δ 19.99 ppm. ^{11}B NMR (CD$_2$Cl$_2$): δ −39.2 ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 9.68, 9.89, 10.11, 11.72, 12.03, 13.15, 13.40, 17.08, 18.46 (Cp* *Me*); 51.78, 56.56, 59.01 (Cp* ring/allylic), 109.34, 114.81, 136.96 (+ sh), 139.54, 139.98 (Cp* ring/vinylic). MS (EI): *m*/*z* (%) 792 (<1), M$^+$; 657 (<1), M$^+$ − Cp*; 469 (9.7), M$^+$ − Cp*SiBr$_2$; 415 (39.1), M$^+$ − Cp*SiBr$_2$ − Cp*; 163 (100), Cp*Si$^+$. Mp: >150 °C dec.

Reaction of 1 with Aluminum Trichloride.[38] A slurry of 508 mg (4 mmol) of AlCl$_3$ in toluene (30 mL) was stirred at −80 °C. A solution of 596 mg (2 mmol) of **1** in toluene (10 mL) was added slowly, and the mixture was warmed to room temperature while the color changed from orange to light yellow. The upper solution phase was separated from the resulting oily residue, which was dried in vacuo to yield decamethylaluminocenium tetrachloroaluminate[25] (**6a**) in 80% yield (742 mg). The compound was recrystallized from dichloromethane/pentane. In the upper solution phase trace amounts of (pentamethylcyclopentadienyl)aluminum dichloride[26] were identified by NMR spectroscopy. Yield: 742 mg (80%) of **6a**.[25] ^{1}H NMR (CD$_2$Cl$_2$): δ 2.20 s. ^{13}C NMR (CD$_2$Cl$_2$): δ 9.40 ($\mathit{Me}_5\mathrm{C}_5$), 122.13 ($\mathrm{Me}_5\mathit{C}_5$). ^{27}Al NMR (CD$_2Cl_2$): δ −115 (Cp*$_2Al^+$), 103 ($AlCl_4^-$).

Reaction of 1 with Cp*AlCl$_2$. A solution of 696 mg (3 mmol) of Cp*AlCl$_2$ in 10 mL of toluene was cooled to 0 °C. A solution of 100 mg (330 μmol) of **1** in 1 mL of toluene was added, and the mixture was warmed to room temperature. A colorless precipitate started to form after a few minutes. The solution was separated from the precipitate after 2 h. The colorless solid was identified as decamethylaluminocenium tetrachloroaluminate (**6a**). From the solution **1** could be isolated in 90% yield. Yield: 670 mg (96%) of **6a**.[25] ^{1}H NMR (CD$_2$Cl$_2$): δ 2.20 s. ^{13}C NMR (CD$_2$Cl$_2$): δ 9.40 ($\mathit{Me}_5\mathrm{C}_5$), 122.13 ($\mathrm{Me}_5\mathit{C}_5$). ^{27}Al NMR (CD$_2Cl_2$): δ −115 (Cp*$_2Al^+$), 103 ($AlCl_4^-$).[25]

Reaction of 1 with Dimethylaluminum Chloride. A solution of 596 mg (2 mmol) of **1** in hexane (20 mL) was cooled to − 80 °C. A 2 mL portion of a 1 M solution of dimethylaluminum chloride in hexane was added, and the mixture was warmed to room temperature. The solvent was removed to give a light yellow residue that was washed three times with hexane (10 mL) to yield (pentamethylcyclopentadienyl)methylaluminum chloride (**7**)[28] as a light yellow powder which was recrystallized from toluene or benzene. The pentane extracts were combined and volatiles removed *in vacuo* to give 380 mg of a yellow residue. The ^{29}Si NMR spectroscopic examination allowed no identification of defined products. Yield: 0.28 g (65%) of **7**.[28] ^{1}H NMR (C$_6$D$_6$): δ 1.83 (s, 15H, Cp*Al), −0.61 (s, 3H, MeAl). ^{27}Al NMR (C$_6$D$_6$): δ −3 ppm (br). MS (EI): *m*/*z* (%) 232 (10), Cp*AlCl$_2^+$; 212 (27), Cp*Al(Me)Cl$^+$; 197 (73), Cp*AlCl$^+$; 177 (23), Cp*AlMe$^+$.

Reaction of 1 with Gallium(III) Halides (GaCl$_3$/GaBr$_3$). In a typical experiment 596 mg (2 mmol) of **1** was dissolved in 20 mL of toluene and the solution cooled to −80 °C. An equimolar amount of the gallium halide was dissolved in 10 mL of toluene and added dropwise. On addition the reaction mixture turned orange. After the mixture was warmed to room temperature, the color had changed to light yellow. Within 3−5 days gallium metal precipitated from solution. The gallium metal was separated by filtration. Pyridine was added to the filtrate, and the corresponding gallium trihalide pyridine adduct ($GaX_3 \cdot C_5H_5N$) precipitated, which was also separated by filtration. Volatile components of the filtrate were removed *in vacuo*, and the residue was examined by NMR spectroscopy.

(a) GaCl$_3$: formation of Cp*$_2$SiCl$_2$.[30] ^{1}H NMR (CDCl$_3$): δ 1.15 (br s, 6H), 1.70 (br s, 12H), 1.80 (br s, 12H). ^{13}C NMR (CDCl$_3$): δ 11.47, 12.16, 17.32 ($\mathit{Me}_5\mathrm{C}_5$), 55.10, 136.12, 137.88 ($\mathrm{Me}_5\mathit{C}_5$). ^{29}Si NMR (CDCl$_3$): δ 21.2. Yield: >90% (by ^{1}H NMR and weight); Ga^0:[34] yield 98% (by weight). $GaCl_3 \cdot C_5H_5N$: mp 126 °C (lit.[35]mp 126 °C). ^1H NMR ($CDCl_3$): δ 7.63 (m, 2H), 8.05 (m, 1H), 8.77 (m, 2H), Yield: 87%.

(b) $GaBr_3$: formation of $Cp^*{}_2SiBr_2$.[30] ^1H NMR ($CDCl_3$): δ 1.29 (br s, 6H), 1.59 (br s, 12H), 1.76 (br s, 12H). ^{29}Si NMR ($CDCl_3$): δ 19.3. Yield: >90% (by ^1H NMR and weight). Ga^0: yield 96% (by weight). $GaBr_3 \cdot C_5H_5N$: mp: 126 °C (lit.[35] mp 126 °C). ^1H NMR ($CDCl_3$): δ 7.63 (m, 2H), 8.05 (m, 1H), 8.81 (m, 2H). Yield: 79%.

Reaction of 1 with Cp*GaBr₂. A 49 mg portion of **1** (160 μmol) and 58 mg of Cp^*GaBr_2 (160 μmol) were charged into an NMR tube. A 0.6 mL amount of benzene-d_6 was added to form a yellow solution. $Cp^*{}_2SiBr_2$ and Cp^*Ga (**8**) were detected as the only species present by NMR spectroscopy. ^1H NMR (C_6D_6): δ 1.29 (br s, 6H), 1.59 (br s, 12 H), 1.77 (br s, 12H, Cp*Si), 1.90 (s, 15H, Cp*Ga). ^{29}Si NMR (C_6D_6): δ 19.19 ($Cp^*{}_2SiBr_2$).[30] ^{71}Ga NMR (C_6D_6): δ −639.5 (br, Cp*Ga).[33]

Reaction of 1 with Indium(III) Halides. The indium trihalide was suspended in toluene and cooled to −30 °C. A solution of an equimolar amount of **1** in toluene was added slowly, and the cooling bath was removed. The reaction mixture was then stirred for 12 h. Afterward the precipitated indium(I) halide was filtered. Volatile components of the solution were removed *in vacuo*, and the residue was examined by NMR spectroscopy without further purification.

(a) $InCl_3 \rightarrow InCl$: light yellow powder. Yield: >90% (by weight). Mp: 225 °C (lit.[36] mp 225 °C). $Cp^*{}_2SiCl_2$:[30] ^1H NMR ($CDCl_3$) δ 1.15 (br s, 6H), 1.70 (br s, 12H), 1.80 (br s, 12H); ^{13}C NMR ($CDCl_3$) δ 11.47, 12.16, 17.32 (Me_5C_5), 55.10, 136.12, 137.88 (Me_5C_5); ^{29}Si NMR ($CDCl_3$) δ 21.2; yield: >90% (by ^1H NMR).

(b) $InBr_3 \rightarrow InBr$: orange powder. Yield: >90% (by weight); Mp: 220 °C (lit.[36] mp 220 °C). $Cp^*{}_2SiBr_2$:[30] ^1H NMR ($CDCl_3$) δ 1.29 (br s, 6H), 1.59 (br s, 12H), 1.76 (br s, 12H); ^{29}Si NMR ($CDCl_3$) δ 19.3; yield >90% (by ^1H NMR).

Acknowledgment. This work was generously supported by the *Fonds der chemischen Industrie* and the *Deutsche Forschungsgemeinschaft*.

Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates for **3a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[34] The yields of Ga^0 and the pyridine adducts are given on the basis of the disproportionation process $3\text{“GaX”} \rightarrow 2Ga^0 + GaX_3$. The ^1H NMR spectra of the pyridine adducts correspond to spectra obtained from commercially available gallium trihalides and pyridine.

[35] Greenwood, N. N. *Adv. Inorg. Chem. Radiochem.* **1963**, *5*, 91.

[36] *CRC Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1980.

[37] In C_6D_6 or toluene-d_8 the solubility of **3a** was too low to obtain NMR spectra. In CD_2Cl_2 or $CDCl_3$ the $Cp^*BCl_3^-$ anion decomposes to BCl_4^- (vide supra).

[38] The reaction with aluminum tribromide was carried out in a similar fashion. The product **6b** was also characterized by NMR spectroscopy (^{27}Al NMR ($CDCl_3$): δ −115, 80 ($AlBr_4^-$)).