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Insertion of Cp*GeCl into a Tungsten−Chlorine Bond and Crystal Structures of the Germylenes Cp*GeCl, $[Cp^*GeBr]_2$, and $[Cp^*Ge][BF_4]$ (Cp* = Pentamethylcyclopentadienyl)

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Insertion of the chlorogermylene Cp*GeCl (**2**) (Cp* = pentamethylcyclopentadienyl) into the W−Cl bond of $CpW(CO)_3Cl$ (**1**) (Cp = cyclopentadienyl) affords the germyl complex $CpW(CO)_3GeCl_2Cp^*$ (**3**). Treatment of $GeCp^*_2$ with 1 equiv of HBr gives the bromogermylene $[Cp^*GeBr]_2$ (**5**). The crystal structures of the halogermylenes **2** and **5** are described. **2** is monomeric in the solid-state, whereas **5** has a dimeric structure, which is characterized by two germylene units associated through asymmetric bromo bridges. In both compounds the pentamethylcyclopentadienyl group is bonded to the germanium atom in an asymmetric η^2 fashion. In comparison, the crystal structure of $[Cp^*Ge][BF_4]$ (**6**) reveals the presence of BF_4 anions and Cp*Ge cations, in which the Cp* ligand is η^5 bonded to the germanium atom.

Introduction

Germylenes, the germanium analogues of carbenes, have been the subject of numerous studies in the last 25 years.[1] Most of these compounds are not stable under normal conditions aggregating rapidly to form oligomeric or polymeric products. Stabilization of germylenes can be achieved by n-donor[2] or π-donor substituents,[3] which reduce the electrophilicity of the germanium atom donating electrons into its vacant p-orbital, and by bulky substituents to prevent dimerization or oligomerization.[4] Among the groups, which proved to be very useful for the electronic stabilization of germylenes are cyclopentadienyl ligands. These allowed the isolation of several germanocenes, $GeCp'_2$ (Cp′ = substituted cyclopentadienyl)[1e,h,5] and neutral or ionic half-sandwich compounds of the type Cp*GeR (R = Cl, CF_3SO_3, amino, aryl, alkyl) and $[Cp^*Ge]^+[X]^-$ (X = BF_4, $GeCl_3$, $C_5(CO_2Me)_5$, $AlCl_4$).[1e,5c,g,6]

We are interested in the insertion chemistry of germylenes[1a−c,i] as a possible approach to transition-metal germyl complexes and thereof derived compounds

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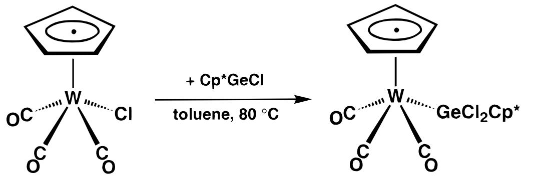
with a metal−germanium multiple bond.[7] In this context we have recently shown that $GeCl_2$ insertion into Mo−Cl, W−Cl, and Mo−H bonds provides a valuable route to trichlorogermyl and dichlorogermyl complexes of the type $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(L)_nGeCl_{3-m}H_m$ (R = H, Me; M = Mo, W; n, m = 0, 1; L = PMe_3, EtNC).[8] Continuing our work in this field, we report on the insertion reaction of the chlorogermylene Cp*GeCl (**2**) into the W−Cl bond of $CpW(CO)_3Cl$ (**1**), the synthesis of the bromogermylene $[Cp^*GeBr]_2$ (**5**), and the crystal structures of **2**, **5**, and $[Cp^*Ge][BF_4]$ (**6**).

Results and Discussion

Treatment of $CpW(CO)_3Cl$ (**1**) with a slight excess of Cp*GeCl (**2**) in toluene at 80 °C afforded the germyl complex $CpW(CO)_3GeCl_2Cp^*$ (**3**) after insertion of the chlorogermylene into the W−Cl bond of **1** (eq 1). IR monitoring of the reaction revealed the formation of a byproduct, which was identified as the trichlorogermyl complex $CpW(CO)_3GeCl_3$ (**4**). However, complex **3** could be easily separated from **4** and isolated as a yellow, microcrystalline solid in 88% yield (see Experimental Section).



1 **3** (1)

In comparison, no reaction of **1** with **2** was observed in CH_2Cl_2 at ambient temperature or even 40 °C, indicating that Cp*GeCl (**2**) reacts considerably slower with **1** than $GeCl_2$(1,4-dioxane).[8a] The lower reactivity of Cp*GeCl can be attributed to the reduced electrophilicity and the increased steric shielding of the germanium center.[9]

Complex **3** is a slightly air-sensitive solid, which decomposes upon heating at 220 °C. It has a higher solubility in all common organic solvents than **4** and is very soluble in CH_2Cl_2, THF, toluene, and Et_2O and sparingly soluble in pentane. However, solutions of **3** in CH_2Cl_2, THF, and Et_2O, which were kept under exclusion of air for several days at room temperature, showed a slight decomposition of **3** to give **4** and some insoluble material. The origin and course of this decomposition is currently unknown.

Complex **3** was fully characterized. Thus, the IR spectrum of **3** in pentane shows two ν(CO) absorption bands at 2027 and 1948 cm^{-1}. According to group theory this compound should have three infrared-active CO stretching fundamentals, the two symmetric A′ modes, and the antisymmetric A″ mode, if a local C_s symmetry is assumed for the $M(CO)_3$ fragment.[10] The observation of only two ν(CO) absorptions in the solution IR spectra of **3** suggests an accidental degeneracy of the lower frequency A′ mode with the A″ mode. Both ν(CO) bands of **3** appear at lower wavenumbers [ν(CO) in toluene: 2021 s, 1941 vs cm^{-1}] than those of the trichlorogermyl complex $CpW(CO)_3GeCl_3$ (**4**) [ν(CO) in toluene: 2042 s, 1972 m, 1954 vs cm^{-1}] indicating a stronger metal(dπ)−CO(π^*) back-bonding in **3** than in **4**. This shows that the $GeCl_2Cp^*$ group is a stronger electron-donating ligand than the $GeCl_3$ group.[11]

Complex **3** is fluxional like other pentamethylcyclopentadienyl compounds of tetravalent germanium. Thus, the ^1H NMR spectrum of **3**, recorded on a 300 MHz instrument, shows in $CDCl_3$ at 298 K one broad signal for the methyl protons of the Cp* group at δ 1.83 and a sharp singlet for the cyclopentadienyl ring protons at δ 5.59. Upon cooling of the sample, the signal of the Cp ring protons remained sharp, whereas the resonance of the methyl protons of **3** split into three signals of the relative intensity 3:6:6, which appeared in the low exchange limit spectrum (230 K) at δ 1.60, 1.78, and 1.92, respectively. These changes were entirely reversible on warming the $CDCl_3$ solution of **3**. The fluxionality of **3** was also evident in the variable-temperature ^{13}C NMR spectra. Only one broad signal at δ 12.2 was observed for the methyl carbon atoms of **3** at 298 K, and the corresponding resonance of the Cp* ring carbon atoms was not observed at all. In comparison, the ^{13}C NMR spectrum of **3** showed at the low-exchange limit (230 K) three methyl carbon resonances at δ 11.6, 12.0, and 12.1 and three resonances for the Cp* ring carbon atoms at δ 71.7, 133.7, and 139.6. By contrast, the signals of the $CpW(CO)_3$ group of **3** remained sharp in the temperature range of 230−298 K and appeared at

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(9) Several features of the $GeCl_2$ insertion reaction into the M−Cl bonds of the complexes $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(L)_nCl$ (R = H, Me; M = Mo, W; n = 1, 2; L = PMe_3, EtNC) such as the observed high stereoselectivity, the rate increase, when the metal complex becomes more "electron-rich" and the ligand sphere less crowded, or when the reaction is carried out in poor coordinating solvents, as well as the lack of evidence for the formation of escape products, exclude a radical abstraction−recombination pathway or a mechanism involving ionic intermediates. They instead support a pathway via a donor−acceptor complex intermediate, which is formed from the transition metal complex acting as the Lewis base and $GeCl_2$ acting as the Lewis acid.[1i] The lower reactivity of Cp*GeCl is also consistent with such a mechanism.

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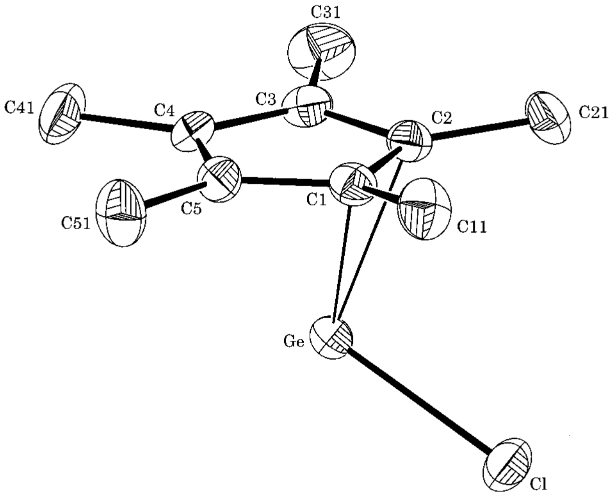

Figure 1. ZORTEP plot of the molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

298 K at δ 91.9 (Cp ligand) and 214.3 and 218.7 (CO ligands). The temperature-dependent ^{1}H NMR and ^{13}C NMR spectra of **3** are very similar to those of Cp*$GeCl_3$ and let us suggest that the same sigmatropic process occurs in **3** involving a 1,2 shift of the germanium fragment $GeCl_2[W(CO)_3Cp]$.[12]

Germylenes of the type RGeX, in which a germanium atom is covalently bonded to an organic group and a halogen atom, are usually very reactive species, which are not stable under normal conditions. It is therefore not surprising that only five halogermylenes have been isolated so far, i.e., Cp*GeCl,[6a] $(C_5Me_4CH_2CH_2NMe_2)$-GeCl,[13] Mes*GeCl (Mes* = 2,4,6-tri-*tert*-butylphenyl),[4f] $(Me_3Si)_3CGeCl\cdot LiCl\cdot 3THF$,[14] and $[(C_6H_3\text{-}2,6\text{-}Mes_2)GeCl]_2$ (Mes = 2,4,6-trimethylphenyl).[4i] Consequently structural studies on halogermylenes are also rare and include a gas phase electron diffraction study of Cp*GeCl[15] and the single-crystal X-ray diffraction studies of $(C_5Me_4CH_2CH_2NMe_2)GeCl$[13] and $[(C_6H_3\text{-}2,6\text{-}Mes_2)\text{-}GeCl]_2$.[4i] This has prompted us to determine the crystal structures of the halogermylenes Cp*GeX (*X* = halogen) and compare the bonding parameters of these compounds with those of the ionic derivative [Cp*Ge][BF_4]. Suitable single crystals of Cp*GeCl (**2**) were obtained upon slow evaporation of a pentane solution of **2** at ambient temperature in a glovebox. Compound **2** crystallizes in the space group $P2_1/n$. A ZORTEP plot of a single molecule with the atom-labeling scheme adopted is shown in Figure 1. Selected bond lengths and angles are listed in Table 1.

The unit cell is composed of discrete Cp*GeCl molecules as shown by the closest Ge−Ge′ and Ge−Cl′ contacts between neighboring molecules, which are 3.466 and 4.153 Å, respectively. Therefore, the crystal structure of **2** differs from that of the related tin compounds CpSnCl[16] and Cp*SnCl,[17] in which two additional weak Sn−Cl interactions to neighboring molecules exist to produce a ladder structure.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for 2

Ge−C(1)	2.214(3)	C(2)−C(3)	1.439(4)
Ge−C(2)	2.221(2)	C(3)−C(4)	1.397(4)
Ge−C(3)	2.487(3)	C(4)−C(5)	1.402(4)
Ge−C(4)	2.599(3)	C(1)−C(5)	1.427(4)
Ge−C(5)	2.437(3)	Ge−C_g[a]	2.070
Ge−Cl	2.3841(8)	Ge−C_f[a]	2.024
C(1)−C(2)	1.435(4)	Ge−C_m[a]	2.098
C_g−Ge−Cl	126.3	C_m−Ge−Cl	99.2
C_f−Ge−Cl	111.3		

[a] C_g, C_f, and C_m denote the center of the Cp* ring, the foot of the germanium-to-ring normal, and the center of the C(1)−C(2) bond, respectively.

2 has a bent structure as shown by the angle between the germanium-to-ring normal and the Ge−Cl bond axis of 111.3°. This angle has a similar value to that found for **2** in the gas-phase [110(2)°] and indicates the presence of a stereochemically active lone pair. The Cp* ligand is bonded to the germanium atom in an asymmetric η^2 fashion as revealed by a comparison of the Ge−C_{ring} distances. Thus, the Ge−C(1) and Ge−C(2) bonds are with 2.214(3) and 2.221(2) Å considerably shorter than the distances of the germanium atom to the other ring carbon atoms [Ge−C(3) = 2.487(3) Å; Ge−C(4) = 2.599(3) Å; Ge−C(5) = 2.437(3) Å] and are similar in length to the Ge−C_{ring} bonds in the cation [Cp*Ge]$^+$ [average Ge−C = 2.255(2) Å], in which the Cp* ligand is pentahapto coordinated to the germanium center (see crystal structure of **6**). In addition, only the methyl groups at the carbon atoms C(1) and C(2) are appreciably bent out of the Cp* ring plane in a direction opposite to the germanium atom, as evidenced by the dihedral angle of 8.8° between the least-squares planes defined by the atoms C(1)−C(2)−C(3)−C(5) and C(11)−C(1)−C(2)−C(21), respectively. All these parameters support an η^2 coordination of the Cp* ligand in **2**. Consequently, the germanium atom does not reside above the Cp* ring center but is displaced laterally by 0.434 Å toward the carbon atoms C(1) and C(2), and the distance of the germanium atom from the Cp* ring plane [Ge−C_f = 2.024 Å] is shorter than that from the Cp* ring center [Ge−C_g = 2.070 Å] (Table 1). This displacement occurs in such a way as to place the chlorine atom beyond the periphery of the Cp* ring and the lone pair in the electron void above the ring center. Ab initio molecular orbital calculations on CpGeCl have shown this conformation to be energetically preferred.[18] The germanium−ring distance in **2** (2.024 Å) is shorter than that found for **2** in the gas phase [2.11(2) Å][15] and compares well with Ge−C(sp^2) single bond lengths, e.g. $GeMes^*_2$ [average Ge−C = 2.047(4) Å],[4h] $[(C_6H_3\text{-}2,6\text{-}Mes_2)GeCl]_2$ [Ge−C = 2.000(6) Å],[4i] $Ge(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ [Ge−C = 2.033(4) Å],[4i] $Ge[C_6H_2\text{-}2,4,6\text{-}(CF_3)_3]_2$ [average Ge−C = 2.077(3) Å],[4j] and Cp*GeMes* [Ge−C(Mes*) = 2.087(7) Å].[6e] The asymmetrical π-bonding of the Cp*

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ligand in **2** has been observed also in other compounds of main-group elements, in which isolobal fragments to the :Ge−Cl unit, such as ER_2 (E = Al, Ga, In) or $:ER^+$ (E = P, As) groups, are bonded to a cyclopentadienyl group.[1e] This bonding mode causes only a slight variation of the C−C bonds within the Cp* ring, the bonds between the carbon atoms closest to germanium [C(1)−C(2) = 1.435(4) Å; C(1)−C(5) = 1.427(4) Å; C(2)−C(3) = 1.439(4) Å] being slightly longer than those between the more distant carbon atoms [C(3)−C(4) = 1.397(4) Å; C(4)−C(5) = 1.402(4) Å] (Table 1). Furthermore, the Cp* ring is almost planar, which indicates extensive π-electron delocalization. This is evidenced by the maximum deviation of only 0.01 Å of two of the ring carbon atoms [C(1) and C(5)] from the least squares plane and by the small angle (0.4°) between the planes defined by the atoms C(1), C(2), C(3), C(5) and C(3), C(4), C(5), respectively. Compound **2** differs thereby from most transition metal cyclopentadienyl compounds, in which asymmetrical π-bonding of the Cp ligand causes a folding of the five-membered ring.[19] **2** also differs from the base-stabilized germanium(II) compounds ($C_5Me_4CH_2CH_2NMe_2$)GeCl[13] and ($C_5H_4CH_2CH_2NMe_2$)GeCl.[20] An η^1 coordination of the functionalized cyclopentadienyl ligand to the germanium atom has been observed in these compounds resulting in a slight folding of the five-membered ring and in short−long alternating C−C bonds between the ring carbon atoms, which are not bonded to the germanium atom.

The angle between the Ge−Cl bond and the axis connecting the germanium atom with the center of the C(1)−C(2) bond is with 99.2° smaller than that expected for an sp^2-hybridized atom and indicates as in other germylenes a rehybridization of the bonding orbitals of the Ge^{II} center in order to decrease the energy of the lone pair orbital. This angle is more acute than that of Cp*GeCH($SiMe_3$)$_2$ (106.9°),[5g] Cp*GeC($SiMe_3$)$_3$ (118.9°),[6e] and Cp*GeMes* (101.0°)[6e] probably due to a decreased steric repulsion between the substituents in **2**. Furthermore, the Ge−C(1) and Ge−C(2) bonds of **2** are shorter than the corresponding Ge−C_{ring} bonds in the germanium(II) pentamethylcyclopentadienyl compounds Cp*GeCH($SiMe_3$)$_2$ [average Ge−C = 2.246(8) Å],[5g] Cp*GeC($SiMe_3$)$_3$ [average Ge−C = 2.27(2) Å],[6e] and Cp*GeMes* [average Ge−C = 2.314(8) Å],[6e] suggesting a tighter Ge−Cp* bond in **2**.

The Ge−Cl bond of **2** is with 2.3841(8) Å remarkably long. Thus, this bond is longer than that found for **2** in the gas-phase [Ge−Cl = 2.26(1) Å] and also longer than the Ge−Cl bonds of other germanium(II) chlorides, such as $GeCl_2$(g) [Ge−Cl = 2.186(4) Å],[21] $GeCl_2$(1,4-dioxane) (average Ge−Cl = 2.265 Å),[2b] [(C_6H_3-2,6-Mes_2)GeCl]$_2$ [Ge−Cl = 2.120(2) Å],[4i] $RbGeCl_3$ [average Ge−Cl = 2.313(4) Å],[22] [NMe_4][$GeCl_3$] [average Ge−Cl = 2.294(7) Å],[23] and [$HPMe_3$][$GeCl_3$] [average Ge−Cl = 2.3071(9) Å].[24] The Ge−Cl bond of **2** compares well only with that of the germanium(II) compounds ($C_5Me_4CH_2CH_2NMe_2$)GeCl [Ge−Cl = 2.369(1) Å][13] and ($C_5H_4CH_2CH_2NMe_2$)GeCl [Ge−Cl = 2.381(1) Å],[20] for which intramolecular coordination of the amino functionality in the side chain of the cyclopentadienyl ligand to the germanium atom has been shown to weaken drastically the Ge−Cl bond. This structure parameter and the observed nucleophilic reactivity of **2** toward the acids $GeCl_2$(1,4-dioxane), HBF_4, and $AlCl_3$ to afford the ionic compounds [Cp*Ge][X] (X = $GeCl_3$, BF_4, $AlCl_4$)[6d] let us suggest a strong polarization of the Ge−Cl bond in **2**.

To study the effect of the halogen atom on the structure of the compounds Cp*GeX, the bromo derivative **5** was prepared upon treatment of decamethylgermanocene with 1 equiv of HBr in Et_2O and isolated as a white to pale-yellow, thermostable, and air-sensitive solid in 95% yield (eq 2). Electrophilic cleavage of one of the Cp* groups of decamethylgermanocene has been shown by Jutzi et al. to be a valuable route to half-sandwich compounds of germanium(II).[5c,6b,c]

$$2\ GeCp^*_2 \xrightarrow[Et_2O,\ 20\ ^\circ C]{+2\ HBr,\ -2\ Cp^*H} \underset{\mathbf{5}}{[Cp^*GeBr]_2} \quad (2)$$

Compound **5** melts at 94 °C and is soluble in all common aprotic polar and nonpolar solvents. Its solubility in pentane is slightly lower than that of the chloro derivative **2**. The colorless pentane solutions of **5** turn rapidly brown, when they are exposed to air. The ^1H NMR spectrum of **5** in C_6D_6 at 298 K displays a singlet resonance for the methyl protons at δ 1.66, and the $^{13}C\{^1H\}$ NMR spectrum shows two resonances for the methyl and the ring carbon nuclei at δ 9.6 and 119.9, respectively. The chemical shift of the methyl protons is nearly identical to that of **2** [δ_{Me} = 1.67 (C_6D_6, 298 K)] and shows the same solvent dependence [e.g.: **5**, δ_{Me} = 2.00 (CD_2Cl_2, 298 K); **2**, δ_{Me} = 2.02 (CD_2Cl_2, 298 K)]. These spectroscopic data indicate that compound **5** is as **2** and other germanium(II) pentamethylcyclopentadienyl compounds highly fluxional. In fact, the static structure of **5** could not be frozen out in CD_2Cl_2 even at −80 °C (300 MHz spectrometer). The electron impact mass spectrum of **5** does not show the ions corresponding to the dimeric or monomeric bromogermylene but only fragment ions such as [Cp*Ge]$^+$.

Suitable single crystals of **5** for an X-ray diffraction study were obtained upon slow evaporation of a hexane solution in a glovebox. Compound **5** crystallizes in the space group *C*2/*c*. A ZORTEP plot of a single molecule with the atom-labeling scheme adopted is given in Figure 2. Selected bond lengths and angles are collected in Table 2.

Compound **5** crystallizes as a C_2 symmetric dimer in which two Cp*GeBr units are associated through bridging bromine atoms. The resulting Ge_2Br_2 quadrangle is folded as shown by the angle of 23.7° between the planes defined by the atoms Ge, Br, Br#1 and Ge#1, Br and Br#1, respectively. The Cp* groups are *cis* arranged. The asymmetry of the bromo bridges, as evidenced by the Ge−Br distances of 2.706(1) and 3.133(1) Å, suggests that there may be a strong tendency

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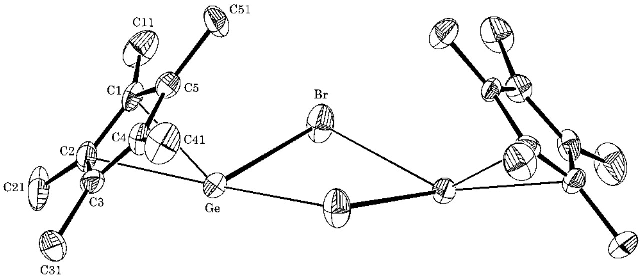

Figure 2. ZORTEP plot of the molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for 5

Ge−C(1)	2.201(5)	C(2)−C(3)	1.403(8)
Ge−C(2)	2.292(5)	C(3)−C(4)	1.424(9)
Ge−C(3)	2.484(5)	C(4)−C(5)	1.387(8)
Ge−C(4)	2.535(5)	C(1)−C(5)	1.441(8)
Ge−C(5)	2.389(5)	Ge−C$_g$[a]	2.055
Ge−Br	2.706(1)	Ge−C$_f$[a]	2.025
Ge−Br#1	3.133(1)	Ge−C$_m$[a]	2.129
C(1)−C(2)	1.440(7)		
C$_g$−Ge−Br	123.8	Br−Ge−Br#1[b]	83.55(4)
C$_m$−Ge−Br	97.0		

[a] See Table 1 for the notation of C$_g$, C$_f$, and C$_m$. [b] Symmetry operations used to generate equivalent atoms: #1, $-x + 1, y, -z + 1/2$.

Table 3. Selected Bond Lengths (Å) with Estimated Standard Deviations for the Cation in 6

Ge−C(1)	2.258(3)	C(2)−C(3)	1.435(4)
Ge−C(2)	2.251(2)	C(3)−C(4)	1.436(3)
Ge−C(3)	2.246(2)	C(4)−C(5)	1.429(4)
Ge−C(4)	2.258(2)	C(1)−C(5)	1.431(3)
Ge−C(5)	2.261(2)	Ge−C$_g$[a]	1.897
C(1)−C(2)	1.431(3)	Ge−C$_f$[a]	1.897

[a] See Table 1 for the notation of C$_g$ and C$_f$.

of **5** to dissociate to monomers in solution. The Ge⋯Ge#1 distance is with 4.272 Å considerably longer than that calculated for a Ge−Ge single bond (2.40 Å)[25] and longer than twice the van der Waals radius of germanium estimated by Bondi [r_W(Ge) = 1.95 Å].[26] Each germanium atom is bonded to a Cp* group [Ge−C$_g$ = 2.055 Å] and a bromine atom [Ge−Br = 2.706(1) Å] and forms a weaker 2c−2e bond to a second bromine atom [Ge−Br#1 = 3.133(1) Å] (Table 2). The distance of the germanium atom from the Cp* ring [Ge−C$_f$ = 2.025 Å] is nearly identical to that in **2** (Tables 1 and 2) but considerably longer than that in the ion [Cp*Ge]$^+$ [**6**: Ge−C$_f$ = 1.897 Å] (Table 3), indicating that the Ge−Cp* bond of the halogermylenes **2** and **5** is weaker than that of the [Cp*Ge]$^+$ ion. These findings support the results of ab initio molecular orbital calculations on the species CpGeCl and [CpGe]$^+$, which have shown the lone pair at the germanium atom of CpGeCl to occupy an orbital that is antibonding to the Ge−Cp bond.[18a] The Ge−Br bonds of **5** are considerably longer than those of GeBr$_2$(g) (Ge−Br = 2.337 Å)[27] and of Ge^{IV} compounds, e.g. GeBr$_4$ [Ge−Br = 2.272(1) Å],[28] MeGeBr$_3$ [Ge−Br = 2.276(2) Å],[29] Me$_2$GeBr$_2$ [Ge−Br = 2.303(2) Å],[29] and Mes$_2$GeBr$_2$ [Ge−Br = 2.3264(7) Å],[20] suggesting as for **2** a strong polarization of the germanium−halogen bonds. The additional 2c−2e Ge−Br bond in **5** results in some small but remarkable changes in the bonding features of the Cp* group, if compared with **2**. For example, the germanium atom is shifted in **5** in a position closer to one of the two bonded ring carbon atoms [Ge−C(1) = 2.201(5) Å; Ge−C(2) = 2.292(5) Å] indicating a change of the hapticity of the Cp* group from η^2 toward η^1. Furthermore, the C−C bonds within the ring show a larger variation in **5** than in **2**. Finally, the folding of the Cp* ring in **5** is smaller than that of (C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$)GeCl[13] or (C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)GeCl,[20] containing an η^1-coordinated functionalized cyclopentadienyl group. This is shown by the angle between the planes defined by the atoms C(2), C(3), C(4), C(5) and C(1), C(2), C(5), which is 1.4° in **5**, 3.5° in (C$_5$Me$_4$CH$_2$CH$_2$NMe$_2$)GeCl, and 4.3° in (C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)GeCl.

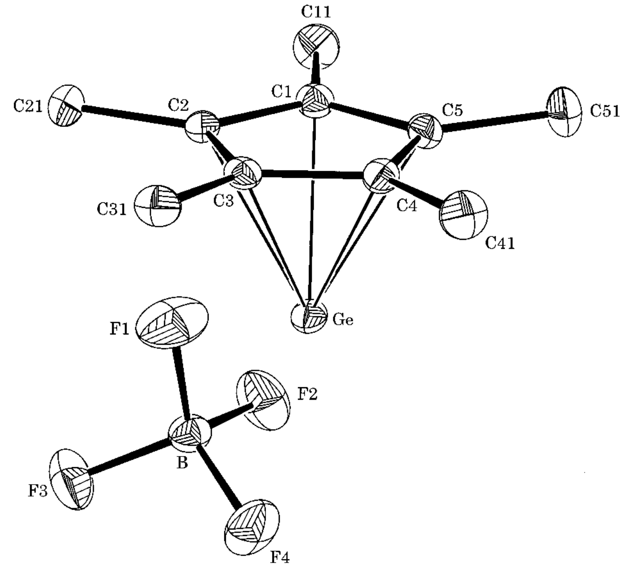

Figure 3. ZORTEP plot of **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Finally, we have also determined the crystal structure of [Cp*Ge][BF$_4$] (**6**). Suitable single crystals of **6** were obtained upon diffusion of a Et$_2$O/pentane mixture into a solution of **6** in CH$_2$Cl$_2$ at ambient temperature. A ZORTEP plot of **6** is shown in Figure 3, and selected bond lengths are summarized in Table 3.

The crystal lattice is composed of pentagonal-pyramidal [Cp*Ge] cations and tetrahedral BF$_4$ anions. The Cp* group is pentahapto coordinated to the germanium atom as shown by the Ge−C$_{ring}$ bond lengths, which range from 2.246(2) to 2.261(2) Å and have an average value of 2.255(2) Å. The Cp* ring is planar, and the methyl groups are bent out of the ring plane away from the germanium atom. This is evident from the angles between the ring plane and the least-squares planes defined by two adjacent ring carbon atoms and the attached methyl carbon atoms, which have an average

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value of 2.3°. The Ge−C_g distance is with 1.897 Å shorter than that of the analogous tin cation in [Cp*Sn][BF_4] [Sn−C_g = 2.157 Å].[17] The difference of the average M−C_{ring} bond lengths of the cations $[Cp^*Sn]^{+}$ [5c] and $[Cp^*Ge]^{+}$ is 0.21 Å and corresponds well to the difference of the covalent radii of tin and germanium (r_{Sn} = 1.40 Å; r_{Ge} = 1.20 Å).[25] Finally, the C_{ring}−C_{ring} bond lengths are nearly identical averaging 1.432(3) Å.

Conclusion

The reported insertion reaction of Cp*GeCl into the W−Cl bond of $CpW(CO)_3Cl$ demonstrates the possibility to extend the insertion chemistry of $GeCl_2$ to other halogermylenes and provides an easy access to functionalized metallagermanes. The difference of the crystal structures of Cp*GeCl and $[Cp^*GeBr]_2$ underlines the structural variety of halogermylenes stimulating further studies on related compounds.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane and hexane over CaH_2, diethyl ether, dibutyl ether, and toluene over Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy), distilled under argon, and stored over 4 Å molecular sieves prior to use.

Elemental analyses were obtained from the Zentrale Analytische Gruppe des Instituts für Chemie der Humboldt-Universität zu Berlin. IR spectra were recorded in solution on a Bruker IFS-55 spectrometer using a CaF_2 cell. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated benzene-d_6, toluene-d_8, chloroform-d_1, or methylene-d_2 chloride. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were calibrated against the internal residual proton or the natural abundance ^{13}C resonances of the deuterated solvent (benzene-d_6, δ_H 7.15 and δ_C 128.0 ppm; toluene-d_8, δ_{Me} 2.09 and δ_{Me} 20.4 ppm; chloroform-d_1, δ_H 7.24 and δ_C 77.0 ppm; methylene-d_2 chloride, δ_H 5.32 and δ_C 53.8 ppm). Mass spectra were obtained with a Hewlett Packard 5995A spectrometer; *m/z* values are given relative to the ^{184}W, ^{79}Br, ^{74}Ge, and ^{35}Cl isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed under argon in capillary tubes and heated with a rate of 1 K/min. IR and/or ^{1}H NMR spectra of the heated samples were recorded and compared with those of authentic samples to determine whether the compounds had decomposed.

The compounds $CpW(CO)_3Cl$ (**1**),[8a] Cp*GeCl (**2**),[6a] $GeCp^*_2$ (**4**),[5c] and [Cp*Ge][BF_4] (**6**)[5c] were prepared according to literature procedures. A 0.9 M solution of HBr in dibutyl ether was obtained by passing HBr gas through the solvent at −78 °C. HBr gas was generated from a concentrated aqueous HBr solution upon treatment with P_4O_{10} and dried by following the procedure described in ref 30.

1. Preparation of $CpW(CO)_3GeCl_2Cp^*$ (3). A 1 g (2.71 mmol) amount of $CpW(CO)_3Cl$ (**1**) and 726 mg (2.98 mmol) of Cp*GeCl (**2**) were weight in a Schlenk tube and dissolved in 100 mL of toluene. The stirring light-red solution was heated to 80 °C. IR monitoring of the reaction revealed a gradual decrease in intensity of the three ν(CO) absorptions of **1** at 2045 (s), 1958 (vs), and 1944 (sh) cm^{-1} and a simultaneous increase in intensity of the two ν(CO) absorptions of **3** at 2021 (s) and 1941 (vs) cm^{-1}. After approximately 9 h the color of the solution had changed to yellow and the ν(CO) absorptions of **1** had been replaced by those of **3**. In addition, three ν(CO) absorptions of low intensity at 2042, 1972, and 1954 cm^{-1} were evident in the IR spectrum of the reaction solution indicating the formation of a small amount of $CpW(CO)_3GeCl_3$ (**4**). The slight cloudy solution was then evaporated to dryness. The residue was washed three times with 15 mL of pentane, and the wash solutions were discarded. The residue was dissolved in 25 mL of toluene, and the solution was filtered from insoluble material. The filtrate was concentrated *in vacuo* to a few milliliters, cooled to −78 °C, and treated with cold pentane (−78 °C). The resulting precipitate was allowed to settle, and the supernatant solution was removed. The precipitate was dried *in vacuo* to give **3** as a yellow solid: yield 1.46 g (88%); mp 220 °C (dec). Anal. Calcd for $C_{18}H_{20}Cl_2GeO_3W$ (611.70): C, 35.34; H, 3.30; Cl, 11.59. Found: C, 35.07; H, 3.37; Cl, 11.96. EI-MS (70 eV), *m/e* (rel intensity): 612 (19) $[M]^{+}$, 577 (2) $[M - Cl]^{+}$, 477 (55) $[M - Cp^*]^{+}$, 449 (9) $[M - Cp^* - CO]^{+}$, 421 (6) $[M - Cp^* - 2CO]^{+}$, 393 (6) $[M - Cp^* - 3CO]^{+}$, 333 (22) $[M - Cp^* - GeCl_2]^{+}$, 305 (4) $[M - Cp^* - GeCl_2 - CO]^{+}$, 284 (9) $[CpWCl]^{+}$, 277 (3) $[M - Cp^* - GeCl_2 - 2CO]^{+}$, 209 (42) $[Cp^*Ge]^{+}$, 135 (53) $[Cp^*]^{+}$, 105 (100). IR (CH_2Cl_2): ν(CO) 2027 (s), 1944 (vs) cm^{-1}. IR (toluene): ν(CO) 2021 (s), 1941 (vs) cm^{-1}. IR (pentane): ν(CO) 2027 (s), 1948 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.83 (broad signal, 15H, C_5Me_5), 5.59 (s, 5H, C_5H_5). ^{1}H NMR (300 MHz, $CDCl_3$, 230 K): δ 1.60 (s, 3H, 1Me, C_5Me_5), 1.78 (s, 6H, 2Me, C_5Me_5), 1.92 (s, 6H, 2Me, C_5Me_5), 5.61 (s, 5H, C_5H_5). ^{1}H NMR (300 MHz, toluene-d_8, 298 K): δ 1.85, 2.15 (broad signals, 15H, C_5Me_5), 4.68 (s, 5H, C_5H_5). ^{1}H NMR (300 MHz, toluene-d_8, 200 K): δ 1.95 (s, 9H, 3Me, C_5Me_5), 2.34 (s, 6H, 2Me, C_5Me_5), 4.21 (s, 5H, C_5H_5). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K): δ 12.2 (broad signal, C_5Me_5), 91.9 (C_5H_5), 214.3 (2CO), 218.7 (1CO) (the signal of the Cp* ring carbon atoms was not observed). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 230 K): δ 11.6 (2C, C_5Me_5), 12.0 (1C, C_5Me_5), 12.1 (2C, C_5Me_5), 71.7 (1C, C_5Me_5), 91.9 (C_5H_5), 133.7 (2C, C_5Me_5), 139.6 (2C, C_5Me_5), 214.5 (2 CO), 218.7 (1 CO).$^{13}C\{^{1}H\}$ NMR (75.5 MHz, toluene-d_8, 298 K): δ 12.5 (broad signal, C_5Me_5), 91.8 (C_5H_5), 215.4 (2CO), 220.4 (1CO) (the signal of the Cp* ring carbon atoms was not observed). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, toluene-d_8, 200 K): δ 11.7 (2C, C_5Me_5), 12.4 (1C, C_5Me_5), 12.6 (2C, C_5Me_5), 71.9 (1C, C_5Me_5), 91.7 (C_5H_5), 134.1 (2C, C_5Me_5), 139.5 (2C, C_5Me_5), 216.3 (2 CO), 221.5 (1 CO).

2. Preparation of $[Cp^*GeBr]_2$ (5). A solution of 583 mg (1.70 mmol) of $GeCp^*_2$ (**4**) in 40 mL of diethyl ether was treated at −78 °C with 1.96 mL (1.76 mmol) of a 0.9 M solution of HBr in dibutyl ether, and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The slight cloudy solution was filtered, and the volatiles were removed *in vacuo*. The residue was washed once with a minimum amount of cold (−78 °C) pentane to afford **5** as a white to pale-yellow, microcrystalline solid: yield 465 mg (95%); mp 94 °C. Anal. Calcd for $C_{20}H_{30}Br_2Ge_2$ (575.46): C, 41.74; H, 5.25; Br, 27.77. Found: C, 40.31; H, 5.04; Br, 26.45. EI-MS (70 eV), *m/e*: 232 $[GeBr_2]^{+}$, 209 $[Cp^*Ge]^{+}$, 194 $[Cp^*Ge - Me]^{+}$, 153 $[GeBr]^{+}$. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.66 (s, 15H, C_5Me_5). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.00 (s, 15H, C_5Me_5). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 9.6 (C_5Me_5), 119.9 (C_5Me_5). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 9.9 (C_5Me_5), 120.1 (C_5Me_5).

3. Crystal Structure Determinations of 2, 5, and 6. A summary of the crystal data, data collection, and refinement for all structures is given in Table 4.

Data collection for the featured structures was performed on a STOE IPDS area detector equipped with a low-temperature device and with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Lattice parameters were refined from 3870−5000 reflections after data collection. Intensity data

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Table 4. Summary of Crystallographic Data for the Complexes 2, 5, and 6

	2	**5**	**6**
empirical formula	$C_{10}H_{15}ClGe$	$C_{20}H_{30}Br_2Ge_2$	$C_{10}H_{15}BF_4Ge$
M_r	243.26	575.48	294.64
temp (K)	200(2)	180(2)	120(2)
cryst color	pale yellow	colorless	colorless
cryst size (mm)	0.57 × 0.57 × 0.38	0.38 × 0.30 × 0.04	0.76 × 0.61 × 0.38
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a (Å)	9.2134(17)	12.793(3)	6.5711(18)
b (Å)	6.9461(8)	10.940(3)	18.632(5)
c (Å)	17.366(3)	17.160(4)	10.035(3)
β (deg)	103.196(19)	111.08(3)	107.42(3)
V (Å^3)	1082.1(3)	2240.9(9)	1172.3(6)
Z	4	4 dimers	4
ρ_{calcd} (g/cm^3)	1.493	1.706	1.669
$\mu_{Mo\ K\alpha}$ (mm^{-1})	3.025	6.145	2.534
$F(000)$	496	1136	592
ϕ movement	rotation	oscillation	rotation
ϕ start/end/increment (deg)	0/200/1.5	0/220/1.5	0/240/1.4
irradiation (min)	2.5	5	2
$2\theta_{min/max}$ (deg)	4.6, 52.4	5, 52	4.4, 52.3
hkl range	−11, 11/−8, 8/−21, 21	−15, 15/−13, 13/−21, 21	−8, 8/−22, 22/−12, 12
tot. data	7963	9489	10723
data unique	2087 [R(int) = 0.1042]	2176 [R(int) = 0.1557]	2295 [R(int) = 0.0693]
min/max density (e Å^{-3})	0.774/−0.995	1.124/−0.775	0.573/−0.483
no. of params refined	110	109	145
extinction coef[a]	0.078(4)		
R_1[b] [$I > 2\sigma(I)$]	0.0365	0.0464	0.0287
wR_2[c]	0.0957	0.0983	0.0788
GOF[d]	1.057	0.909	1.071

[a] $F_c = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [d] GOF $= S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

were integrated and converted into a SHELX *hkl* file with the STOE IPDS software.[31]

The input files for the SHELX programs were prepared with the program UTILITY.[32] Structure solution was performed with the Patterson Method (SHELXS-86, SHELXS-97)[33,34] and subsequent difference-fourier synthesis (SHELXL-97, SHELXL-93).[34,35] Refinement on F^2 was carried out by full-matrix least squares techniques (SHELXL-93, SHELXL-97). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with d(C−H) = 0.98 Å and $U_H = 1.5U_C$. Neutral atom scattering factors were taken from Cromer and Mann.[36] Geometrical calculations and illustrations were performed with PLATON[37] and ZORTEP.[38]

In the final stages of the refinement data for **2** were corrected for secondary extinction effects.

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Supporting Information Available: Further details of the structure determination, including tables of crystal data, atomic coordinates, bond lengths and bond angles, and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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