Interpretation of shifts of signals closer to the metal center is even more complex.[22] No doubt, because of this complexity, we know of no successful extensive correlations of the types described here in other organometallic systems. Clearly, more work is needed particularly in view of the initial success in correlating shifts of ^{1}H, ^{31}P, and ^{13}C shifts of alkylcobalamins with changes in their structure and thermodynamic properties.[19,22]

In conclusion, we have shown that, particularly with regard to ^{13}C NMR shifts, the effects of substituent Y on the α-C of an alkyl group appear to have an additive effect. The substituent effects can be quantitated and the analysis gives a substituent constant, ΔY. With these constants, a second constant (EP) for the entire ligand can be calculated. The EP values can be extended with ^{13}C NMR data to acido ligands.

Acknowledgment. This work was supported by NIH Grant 29225 (L.G.M.) and by a grant (to L.R.) from MPI, Rome, Italy. The purchase of the 360-MHz spectrometer was supported in part by an NSF departmental instrument grant.

Registry No. I, 103751-75-3; II, 28136-56-3; (py)Co(DH)$_2$CH(CN)CH$_2$CN, 14783-94-9; (py)Co(DH)$_2$CH(Me)CN, 28136-55-2; (4-CNpy)Co(DH)$_2$CH(CN)CH$_2$CN, 103751-60-6; (4-CNpy)Co(DH)$_2$CH(Me)CN, 103881-18-1; P(OMe)$_3$Co(DH$_2$)CH(CN)CH$_2$CN, 103751-61-7; P(OMe)$_3$Co(DH)$_2$CH(Me)CN, 103751-62-8; P(OMe)$_3$Co(DH)$_2$CH(CN)Cl, 103751-63-9; PhNH$_2$Co(DH)$_2$Cl, 23575-27-1; (py)Co(DH)$_2$Cl, 23295-32-1; PhNH$_2$Co(DH)$_2$CH(CN)Cl, 103751-64-0; (4-CNpy)Co(DH)$_2$CH(CN)Cl, 103751-65-1; (4-CNpy)Co(DH)$_2$CH$_2$CN, 103751-66-2; (4-CNpy)Co(DH)$_2$CH$_2$CH$_2$CN, 103751-67-3; (4-*t*-Bupy)Co(DH)$_2$CH(CN)CH$_2$CN, 103751-68-4; (4-*t*-Bupy)Co(DH)$_2$CH$_2$NO$_2$, 103751-69-5; (4-*t*-Bupy)Co(DH)$_2$CHBr$_2$, 55886-72-1; (4-*t*-Bupy)Co(DH)[2CH$_2$CF$_3$, 103751-70-8; (4-*t*-Bupy)Co(DH)$_2$CH$_2$CO$_2$Me, 103751-71-9; (4-*t*-Bupy)Co(DH)$_2$CH$_2$Br, 55886-76-5; (4-*t*-Bupy)Co(DH)$_2$DDT, 103751-72-0; (4-*t*-Bupy)Co(DH)$_2$CH=CH$_2$, 103751-73-1; (4-*t*-Bupy)Co(DH)$_2$Me, 51194-36-6; (4-*t*-Bupy)Co(DH)$_2$CH$_2$Ph, 55886-75-4; (4-*t*-Bupy)Co(DH)$_2$CH$_2$SiMe$_3$, 55886-77-6; (4-*t*-Bupy)Co(DH)$_2$Et, 55886-79-8; (4-*t*-Bupy)Co(DH)$_2$CH$_2$CMe$_3$, 103751-74-2; (4-*t*-Bupy)Co(DH)$_2$Pr-*i*, 55886-80-1; (py)Co(DH)$_2$CH(CN)Br, 81853-27-2; (py)Co(DH)$_2$CH$_2$C(Me)(CO$_2$Et)$_2$, 57620-61-8; (py)Co(DH)$_2$CH$_2$NO$_2$, 73202-88-7; (py)Co(DH)$_2$CH$_2$CN, 56498-36-3; (py)Co(DH$_2$CH$_2$CF$_3$, 41659-66-9; (py)Co(DH)$_2$CH$_2$CO$_2$Me, 27902-04-1; (py)Co(DH)$_2$CH$_2$Br, 35654-77-4; (py)Co(DH)$_2$CH$_2$I, 35654-78-5; (py)Co(DH)$_2$Pr-*i*, 30974-90-4; (py)Co(DH)$_2$DDT, 103751-76-4; (py)Co(DH)$_2$CH=CH$_2$, 56710-86-2; PhNH$_2$Co(DH)$_2$CH(CN)CH$_2$CN, 103751-59-3; PhNH$_2$Co(DH)$_2$CH(Me)CN, 14637-49-1; (py)Co(DH)$_2$Me, 23642-14-0; (py)Co(DH)$_2$CH$_2$SiMe$_3$, 42934-31-6; (py)Co(DH)$_2$Et, 25360-57-0; (py)Co(DH)$_2$CH$_2$-*i*-Pr, 29131-79-1; (py)Co(DH)$_2$CH$_2$CMe$_3$, 54631-04-8; (py)Co(DH)$_2$CH$_2$OMe, 35654-83-2; (py)Co(DH)$_2$CH(Me)Et, 54712-55-9; (py)Co(DH)$_2$Cl$_6$H$_{11}$-c, 28206-03-3; (py)Co(DH)$_2$CHEt$_2$, 103751-77-5; (py)Co(DH)$_2$CH(Me)(*i*-Pr), 103751-78-6; (py)Co(DH)$_2$R (R = adamantyl), 65466-85-5; (4-N(H)=C(OMe)py)Co(DH)$_2$Et, 103881-19-2; (4-CNPy)Co(DH)$_2$CH$_2$CF$_3$, 86942-05-4; (4-Me$_2$Npy)Co(DH)$_2$R (R = adamantyl), 103751-79-7; fumaronitrile, 764-42-1; acrylonitrile, 107-13-1; 2-chloropropionitrile, 1617-17-0.

Supplementary Material Available: Tables of elemental analyses, bond lengths and angles, and hydrogen atom coordinates (9 pages); a listing of structure factors (20 pages). Ordering information is given on any current masthead page.

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Mixed Germylenes from (Pentamethylcyclopentadienyl)germanium Chloride and (Pentamethylcyclopentadienyl)germanium Tetrafluoroborate

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(Pentamethylcyclopentadienyl)germanium chloride, Me$_5$C$_5$GeCl (**1**), undergoes replacement of chlorine by various nucleophiles. Nucleophiles also react with the (pentamethylcyclopentadienyl)germanium cation of Me$_5$C$_5$Ge$^+$BF$_4^-$ (**2**) to give new germylene compounds. Reactions with silyl-substituted cyclopentadienides yield unsymmetrical germanocenes Me$_5$C$_5$GeC$_5$H$_{5-n}$(SiMe$_3$)$_n$ (**3**, $n = 1$; **4**, $n = 2$; **5**, $n = 3$), which show no ligand symmetrization reactivity. The germylenes **1** and **2** react with lithium bis(trimethylsilyl)amide, lithium 2,2,6,6-tetramethylpiperidide, and [bis(trimethylsilyl)methyl]lithium to produce substituted germylenes Me$_5$C$_5$GeN(SiMe$_3$)$_2$ (**6**), Me$_5$C$_5$GeNC$_9$H$_{18}$ (**7**), and Me$_5$C$_5$GeCH(SiMe$_3$)$_2$ (**8**). Although they can be considered as redistribution products of decamethylgermanocene with other well-known diorganogermylenes, these unsymmetrically substituted germylenes show no tendency to rearrange into the symmetrical compounds. X-ray structural investigations on **8** show a monomeric species in which the electron deficiency at the Ge center is adjusted by η^2-bonding of the cyclopentadienyl ring. Crystals of **8** are monoclinic, space group $P2_1/a$, with $a = 8.844$ (5) Å, $b = 15.530$ (6) Å, $c = 15.916$ (6) Å, $\beta = 102.37$ (4)°, $V = 2135.3$ Å^3, and $Z = 4$. Refinement using 2485 observed diffractometer data converged at $R = 0.052$ and $R_w = 0.046$.

Introduction

Carbene-analogous, and therefore electron-deficient, compounds of the heavier group 4B (14[30]) elements can be stabilized either kinetically, by using the steric hindrance of bulky ligands, or thermodynamically, by means of additional intramolecular electron donation by the ligands. Of the few stable monomeric diorganogermanium(II) compounds known, most belong to one or another of two groups. The first comprises those species with the germanium linked to highly substituted nitrogen, oxygen, and

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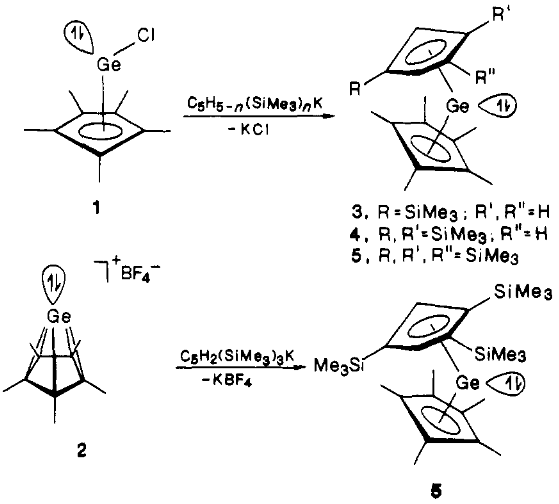
carbon ligands such as bis[bis(trimethylsilyl)amino]germylene,[1] bis[*tert*-butyl(trimethylsilyl)amino]germylene,[1] bis(2,2,6,6-tetramethylpiperidino)germylene,[2-4] bis(2,6-di-*tert*-butyl-4-methylphenoxy)germylene,[4,5] bis(tri-*tert*-butylmethoxy)germylene,[6] and bis[bis(trimethylsilyl)methyl]germylene.[7] The second consists of dicyclopentadienylgermanium[8] and substituted germanocenes such as 1,1′-dimethylgermanocene,[9] 1,1′-bis(trimethylsilyl)-1,1′,3,3′-tetrakis(trimethylsilyl)-, and 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)germanocene,[10] and decamethylgermanocene.[11] One common feature of both groups of compounds, however, is the fact that in most cases the two ligands are the same. Exceptions to this are some mixed germanium(II) compounds with amino, alkoxy, or halogen ligands that have been described recently[4] and several germanium(II) species that contain a second, mainly inorganic, unit. Besides (pentamethylcyclopentadienyl)germanium chloride, Me_5C_5GeCl (1),[12] this group of semi-inorganic species includes (pentamethylcyclopentadienyl)germanium trifluoromethanesulfonate[13] and also those species where the bonding of the inorganic unit is reduced to an electrostatic interaction, as in the case of (pentamethylcyclopentadienyl)germanium tetrafluoroborate,[11] trichlorogermanate(II),[12] pentakis(methoxycarbonyl)cyclopentadienide,[14] and tetrachloroaluminate.[15] We were interested in preparing further examples of mixed germylenes and considered as possible routes the nucleophilic substitution of chlorine in (pentamethylcyclopentadienyl)germanium chloride or the addition of suitable nucleophiles to the (pentamethylcyclopentadienyl)germanium cation itself.

Results

For the preparation of unsymmetrical metallocenes of the group 4B (14) elements there are various methods available, such as subsequent modification of a cyclopentadienyl ligand in a metallocene[16] or replacement of one cyclopentadienyl ring using the protonation equilibria between cyclopentadienes of different acidity.[14] Another synthetic approach, consisting of a two-step alkylation at the 4B (14) halide with different lithium cyclopentadienides, has been mentioned in connection with the syntheses of phenylated and acylated stannocenes.[17,18] Treatment of the semi-inorganic (pentamethylcyclopentadienyl)germanium chloride (1) with potassium mono-, bis-, and tris(trimethylsilyl)cyclopentadienide yielded the corresponding silylated 1,2,3,4,5-pentamethylgermanocenes 3, 4, and 5. The action of potassium 1,2,4-tris(trimethylsilyl)cyclopentadienide on (pentamethylcyclopentadienyl)germanium tetrafluoroborate (2) also gave 1,2,3,4,5-pentamethyl-1′,2′,4′-tris(trimethylsilyl)germanocene (5). Attempts to prepare 1,2,3,4,5-pentamethylgermanocene from the reaction of 1 or 2 with (unsubstituted) potassium cyclopentadienide failed.[19]



1

2

3, R = SiMe$_3$; R′, R″ = H
4, R, R′ = SiMe$_3$; R″ = H
5, R, R′, R″ = SiMe$_3$

5

The unsymmetrical germanocenes 3, 4, and 5 were obtained as colorless crystals from hexane; in general their properties are analogous to those of decamethylgermanocene,[11] but for a considerably higher solubility. The identity of the compounds was confirmed by analytical and spectroscopic data (see Experimental Section). As NMR spectra of mixtures of 3, 4, or 5 with decamethylgermanocene show individual peaks for the Me_5C_5 ligands of the single compounds and as the spectra of pure 3, 4, and 5 show no additional peaks after standing for a long period of time, redistribution of the cyclopentadienyl ligands, and thus formation of a mixture of the well known parent germanocenes,[10,11] can be ruled out.

The bis(trimethylsilyl)amino ligand and also the 2,2,6,6-tetramethylpiperidino ligand have already been shown to stabilize subvalent 4B (14) species.[1-4] Reaction of (pentamethylcyclopentadienyl)germanium chloride (1) with lithium bis(trimethylsilyl)amide and lithium 2,2,6,6-tetramethylpiperidide gave the amino(pentamethylcyclopentadienyl)germylenes 6 and 7[20] as extremely air-sensitive yellow-to-orange crystals (from hexane), which show high solubility in nonpolar solvents. The identity of the compounds was confirmed by analytical and spectroscopic data (see Experimental Section). Although the compounds can be considered as cross-breedings between decamethylgermanocene[11] and Lappert's diaminogermylenes, they normally do not redistribute into the "parent" germanocene and diaminogermylene; as in the case of the germanocenes 3, 4, or 5, the NMR spectra of mixtures of 6 with decamethylgermanocene show individual peaks for

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(18) Dory, T. S.; Zuckerman, J. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *281*, C8.

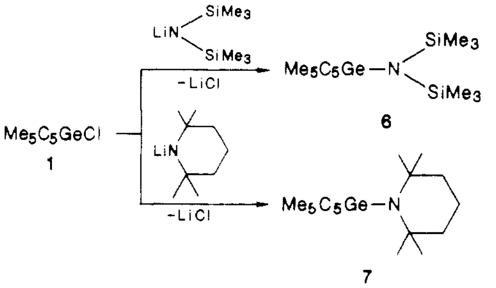
(19) The reaction yielded a colorless crystalline material; elemental analysis, however, gave reproducible low values for carbon, and ^1H NMR spectra gave no correct integral.

(20) *tert*-Butyl(trimethylsilyl)amino(pentamethylcyclopentadienyl)germylene, formed upon reaction of 1 with the corresponding lithium amide was not obtained in analytical purity.

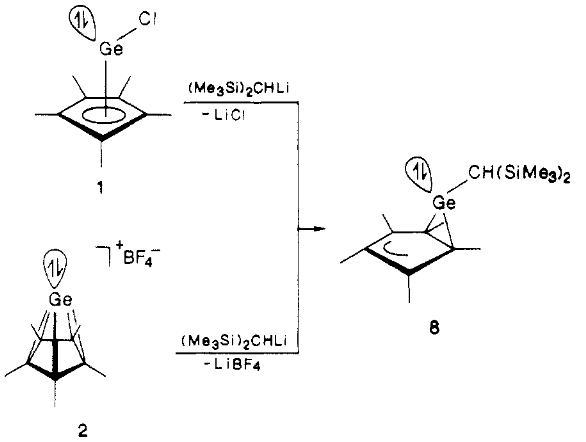
Table I. Bond Lengths (Å) for (Me$_5$C$_5$)Ge(CH(SiMe$_3$)$_2$)

C(01)–Ge(1)	2.243 (8)	C(02)–Ge(1)	2.250 (9)
C(05)–Ge(1)	2.626 (9)	C(1)–Ge(1)	2.044 (7)
C(011)–C(01)	1.513 (10)	C(02)–C(01)	1.434 (9)
C(05)–C(01)	1.417 (9)	C(021)–C(02)	1.519 (11)
C(03)–C(02)	1.399 (9)	C(031)–C(03)	1.508 (12)
C(04)–C(03)	1.403 (10)	C(041)–C(04)	1.496 (10)
C(05)–C(04)	1.379 (9)	C(051)–C(05)	1.509 (11)
Si(1)–C(1)	1.870 (8)	Si(2)–C(1)	1.858 (8)
C(11)–Si(1)	1.865 (10)	C(12)–Si(1)	1.879 (9)
C(13)–Si(1)	1.874 (10)	C(21)–Si(2)	1.833 (11)
C(22)–Si(2)	1.868 (10)	C(23)–Si(2)	1.889 (12)

the Me$_5$C$_5$ ligands of the single compounds. Redistribution products were only detected in the mass spectrum of **7**.[21]



The bis(trimethylsilyl)methyl ligand was shown to form the only pure diorganogermylene species in the sense that the metal center is bound to carbon atoms possessing also a sextet of electrons, at least in the gas phase.[22] As the compound dimerizes in the solid state,[23] it was of particular interest to attach this ligand to the (pentamethylcyclopentadienyl)germanium unit. In the case of the complex-stabilized pentacarbonyltungsten adduct of **1**[24] nucleophilic substitution with [bis(trimethylsilyl)methyl]lithium yielded the complex Me$_5$C$_5$((Me$_3$Si)$_2$CH)Ge→W(CO)$_5$, which was found to be a monomer.[25] Treatment of uncomplexed **1** with an equimolar amount of [bis(trimethylsilyl)methyl]lithium in diethyl ether at −80 °C gave [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (**8**), which was also synthesized from the ionic species **2**.



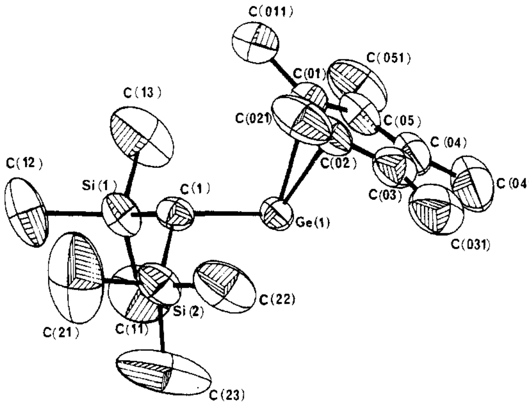


Figure 1. Molecular structure of compound **8**.

Table II. Bond Angles (deg) for (Me$_5$C$_5$)Ge(CH(SiMe$_3$)$_2$)

C(02)–Ge(1)–C(01)	37.2 (2)	C(05)–Ge(1)–C(01)	32.6 (2)
C(05)–Ge(1)–C(02)	55.2 (3)	C(1)–Ge(1)–C(01)	104.3 (3)
C(1)–Ge(1)–C(02)	106.5 (3)	C(1)–Ge(1)–C(05)	132.5 (2)
C(011)–C(01)–Ge(1)	120.5 (5)	C(02)–C(01)–Ge(1)	71.6 (4)
C(02)–C(01)–C(011)	123.9 (6)	C(05)–C(01)–Ge(1)	88.7 (5)
C(05)–C(01)–C(011)	126.8 (7)	C(05)–C(01)–C(02)	106.5 (5)
C(01)–C(02)–Ge(1)	71.1 (5)	C(021)–C(02)–Ge(1)	119.3 (6)
C(021)–C(02)–C(01)	123.7 (6)	C(03)–C(02)–Ge(1)	90.3 (5)
C(03)–C(02)–C(01)	107.2 (6)	C(03)–C(02)–C(021)	126.4 (7)
C(031)–C(03)–C(02)	124.8 (7)	C(04)–C(03)–C(02)	109.0 (6)
C(04)–C(03)–C(031)	126.2 (6)	C(041)–C(04)–C(03)	126.6 (6)
C(05)–C(04)–C(03)	108.0 (6)	C(05)–C(04)–C(041)	125.0 (7)
C(01)–C(05)–Ge(1)	58.6 (4)	C(04)–C(05)–Ge(1)	85.3 (5)
C(04)–C(05)–C(01)	109.2 (6)	C(051)–C(05)–Ge(1)	122.0 (6)
C(051)–C(05)–C(01)	124.3 (6)	C(051)–C(05)–C(04)	126.5 (6)
Si(1)–C(1)–Ge(1)	107.8 (4)	Si(2)–C(1)–Ge(1)	110.3 (4)
Si(2)–C(1)–Si(1)	117.0 (4)	C(11)–Si(1)–C(1)	110.8 (4)
C(12)–Si(1)–C(1)	114.1 (4)	C(12)–Si(1)–C(11)	107.8 (5)
C(13)–Si(1)–C(1)	110.7 (4)	C(13)–Si(1)–C(11)	106.5 (5)
C(13)–Si(1)–C(12)	106.6 (5)	C(21)–Si(2)–C(1)	113.3 (5)
C(22)–Si(2)–C(1)	112.8 (4)	C(22)–Si(2)–C(21)	106.1 (5)
C(23)–Si(2)–C(1)	110.5 (5)	C(23)–Si(2)–C(21)	110.0 (7)
C(23)–Si(2)–C(22)	103.7 (5)		

The orange crystals of **8** (from hexane) show high solubility in all common solvents: in comparison to the amino-substituted compounds **6** and **7**, the product is less air-sensitive and decomposes rather slowly. The identity of **8** was initially confirmed by analytical and spectroscopic data (see Experimental Section). The NMR spectra show equivalent methyl groups and ring carbon atoms for the pentamethylcyclopentadienyl ring in **6**, **7**, and **8** even at −60 °C, which indicates a higher degree of hapticity or a highly fluxional behavior of the element 4B (14) fragment toward the cyclopentadienyl system.

The structure of **8** was investigated by X-ray crystallography. A diagram of the molecule, displaying the monomeric nature of the compound, is shown in Figure 1; bond lengths and angles are given in Tables I and II. The molecular structure corresponds to that found in the pentacarbonyltungsten complex of **8**,[25] having approximate mirror symmetry (through Ge, the bonded carbon C(1) of the silylated ligand and the carbon atom C(04) on the opposite sites of the cyclopentadienyl ring), and with the η^2-Me$_5$C$_5$ ligand oriented so that the unbonded C$_3$ fragment is distal to the alkyl carbon.

The molecular geometry parameters show some small but significant differences from those for its pentacarbonyltungsten complex. Thus, the C(1)–Ge–C(01) and C(1)–Ge–C(02) angles are slightly larger in the present complex (104.4 and 106.5°, respectively, compared with 101.8° × 2 in the tungsten complex), and the alkyl carbon atom in the [(Me$_3$Si)$_2$CH] ligand is more nearly tetrahedral. Additionally, the dihedral angle at the C(01)–C(02) bond, i.e., the angle between the C$_5$ and the GeC$_2$ rings, is smaller here (83.6°) than in the tungsten complex (85.1°). All of these features reflect the reduction in steric crushing by removal of the W(CO)$_5$ fragment, since in the

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(21) The isotopic pattern of the M$^+$ signal is covered by (Me$_5$C$_5$)$_2$Ge$^+$ and Ge(NC$_9$H$_{18}$)$_2$$^+$.

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complex, two of the CO groups are in close steric contact with the unbonded C_3 fragment of the C_5 ring.[25] Nevertheless, it seems likely that steric crowding still exists in this monomer, and the culprit is the lone pair on germanium. First of all, we note that the angle between the C(1)–Ge bond and the vector from Ge to the midpoint of the C(01)–C(02) bond, 106.9°, is much less than the 120° which might be expected on the basis of "sp^2" hybridization at the Ge(II) center. Secondly, we find that from a preliminary examination of the steric energy in this molecule, using our program EENY2,[10] there are significant repulsions (~5–7 kcal/mol) between one methyl group from each Me_3Si fragment and each methyl group on atoms C(01) and C(02) of the Me_5C_5 ligand. These repulsions and the steric energy of the whole molecule can be reduced simply by increasing the C(1)–Ge–C(01) and C(1)–Ge–C(02) angles, and a bending of the Me_5C_5 group about the C(01)–C(02) vector is also sterically possible. A detailed analysis of the steric situation in this molecule and the tungsten complex is in progress and will be reported separately.[26]

Discussion

The $Me_5C_5Ge^+$ unit is known to act as an electrophile[13] so that the nucleophilicity of the counterion X^- determines whether the compound is ionic ($Me_5C_5Ge^+X^-$) or predominantly covalent ($Me_5C_5Ge–X$). The formation of covalent species $Me_5C_5Ge–R$ upon addition of anions R^- from alkali-metal alkyls and amides therefore occurs as expected. But the covalent species $Me_5C_5Ge–Cl$ also exhibits electrophilic character and allows nucleophilic attack at the metal center, which is followed by loss of chloride. The nucleophilic substitution reaction, as well as the addition of a nucleophile at the (pentamethylcyclopentadienyl)germanium cation, provides synthetic approaches to unsymmetrical metallocenes and also to cross products of decamethylgermanocene and Lappert's diorganogermylenes,[1-7] not previously known.

Structural investigations on 8 reveal a η^2-character of the cyclopentadienyl element–4B (14) bond which is more distinct than that of the chloride species 1, investigated by gas electron diffraction.[27] Of particular interest, however, is the comparison of the structure of 8 with its pentacarbonyltungsten complex $Me_5C_5((Me_3Si)_2CH)Ge\rightarrow W(CO)_5$.[25] As there is no significant difference in the geometry around the germanium atom in both structures, the steric activity of the lone pair of electrons at the germanium center in 8 is clearly demonstrated. Furthermore, comparison of the structural data establishes that the interaction with a $W(CO)_5$ fragment is based on a nearly pure n donation of the lone pair of electrons of the germylene, there being no substantial W→Ge π-back-bonding.[24,25] As the formal electron deficiency at the germanium center is already satisfied by additional π-electron donation of the cyclopentadienyl system, there is no necessity for back-bonding in the complex or for intermolecular interactions in the free germylene 8. Therefore, crossing between the monomeric bis(pentamethylcyclopentadienyl)germylene and the dimeric bis[bis(trimethylsilyl)methyl]germylene[23] results in a monomeric product.

In general, it should be noted that the introduction of a pentamethylcyclopentadienyl ligand stabilizes monomeric germylenes by intramolecular adjustment of the electron deficiency of the carbene analogue. The highly fluxional cyclopentadienyl system observed in solution and in the gas phase was found to be frozen in the solid state, presenting a η^2-cyclopentadienyl species.

Experimental Section

All reactions and preparations were performed in an atmosphere of dried, oxygen-free argon using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified. The following instruments were used: melting points, Büchi 510 capillary melting point apparatus; ^1H NMR spectra, Varian EM 360 L (60-MHz) and Bruker AM 300 (300-MHz) spectrometers; ^{13}C NMR spectra, Bruker AM 300 (75-MHz) spectrometer, ^1H decoupled; ^{29}Si NMR spectra, Bruker AM 300 (60-MHz) spectrometer, ^1H decoupled; mass spectra, Varian 311 A (70 eV, 300-μA emission) spectrometer; only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen) or the analytical laboratory of the Universität Bielefeld.

(Pentamethylcyclopentadienyl)germanium chloride (1) was prepared as previously described.[12] **(Pentamethylcyclopentadienyl)germanium tetrafluoroborate (2)** was prepared according ref 11; without recrystallization the product was obtained in 77% yield.

General Procedure for the Preparation of 3, 4, and 5 from 1. The solution of 1 in benzene (20 mL) was added to a suspension of the silylated potassium cyclopentadienide in benzene (20 mL). After the solution was stirred for 24 h, the solvent was evaporated in vacuo. Extraction of the residue with hexane (20 mL) was followed by concentration of the solution. Upon cooling to −80 °C, a crystalline product separated which was filtered and dried in vacuo.

1,2,3,4,5-Pentamethyl-1′-(trimethylsilyl)germanocene (3). Reaction of 1 (2.07 g, 8.51 mmol) with potassium (trimethylsilyl)cyclopentadienide (1.50 g, 8.50 mmol) yielded 1.73 g (59%) of colorless needles: mp 35 °C; ^1H NMR (C_6D_6) δ 6.14 (m, 4 H, C_5H_4), 1.71 (s, 15 H, Me_5C_5), 0.26 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 125.4 ($\mathit{C}SiMe_3$), 118.50 ($Me_5\mathit{C}_5$), 116.53, 110.33 (CH), 9.45 (Me_5C_5), 0.62 ($SiMe_3$). MS, *m/e* (relative intensity) 345 (M^+ − H, <1), 211 ($(SiMe_3)C_5H_4Ge^+$, 51[28]), 209 ($Me_5C_5Ge^+$, 100[28]). Anal. Calcd for $C_{18}H_{28}GeSi$ (345.15): C, 62.64; H, 8.18. Found: C, 62.16; H, 8.44.

1,2,3,4,5-Pentamethyl-1′,3′-bis(trimethylsilyl)germanocene (4). Reaction of 1 (1.88 g, 7.73 mmol) with potassium 1,3-bis(trimethylsilyl)cyclopentadienide (1.92 g, 7.73 mmol) yielded 1.96 g (61%) of colorless needles: mp 62 °C; ^1H NMR (C_6D_6) δ 6.56 (t, 1 H, C_5H_3, ^4J(HH) = 1.7 Hz), 6.08 (d, 2 H, C_5H_3, ^4J(HH) = 1.7 Hz), 1.74 (s, 15 H, Me_5C_5), 0.29 (s, 18 H, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 128.90, 112.90 (CH), 127.54 ($\mathit{C}SiMe_3$), 118.53 ($Me_5\mathit{C}_5$), 9.61 (Me_5C_5), 0.76 ($SiMe_3$); ^{29}Si NMR ($CDCl_3$) δ −10.5; MS, *m/e* (relative intensity) 283 ($C_5H_3(SiMe_3)_2Ge^+$, 90), 209 ($Me_5C_5Ge^+$, 64), 73 ($SiMe_3^+$, 100). Anal. Calcd for $C_{21}H_{36}GeSi_2$ (417.28): C, 60.45; H, 8.70. Found: C, 59.98; H, 8.82. Molecular weight determination (cryoscopically in C_6H_6): 408.

1,2,3,4,5-Pentamethyl-1′,2′,4′-tris(trimethylsilyl)germanocene (5) from 1. Reaction of 1 (0.97 g, 3.98 mmol) with potassium 1,2,4-tris(trimethylsilyl)cyclopentadienide (1.13 g, 3.98 mmol) yielded 1.30 g (67%) of colorless prisms: mp 61 °C; ^1H NMR ($CDCl_3$) δ 6.22 (s, 2 H), 1.85 (s, 15 H, Me_5C_5), 0.18 (s, 18 H, 2 $SiMe_3$), 0.15 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 130.96, 130.80 ($\mathit{C}SiMe_3$), 128.86 (CH), 118.83 ($Me_5\mathit{C}_5$), 9.66 (Me_5C_5), 2.16 (2 $SiMe_3$), 0.83 ($SiMe_3$); MS, *m/e* (relative intensity) 490 (M^+, 0.2), 355 (M^+ − Me_5C_5, 100), 282 ($(SiMe_3)_2C_5H_2Ge^+$, 11), 209 ($Me_5C_5Ge^+$, 100). Anal. Calcd for $C_{24}H_{44}GeSi_3$ (489.47): C, 58.89; H, 9.06. Found: C, 59.09; H, 9.08.

1,2,3,4,5-Pentamethyl-1′,2′,4′-tris(trimethylsilyl)germanocene (5) from 2. A suspension of potassium 1,2,4-tris(trimethylsilyl)cyclopentadienide (0.38 g, 1.19 mmol) in diethyl ether (40 mL) was added to a suspension of 2 (0.35 g, 1.19 mmol) in diethyl ether (20 mL). After the mixture was stirred for 30 h at room temperature, the solvent was evaporated in vacuo. Extraction of the residue with hexane (5 mL), followed by concentration of the solution and cooling to −80 °C, yielded 0.34 g (58%) of colorless crystals, mp 60 °C, which were filtered and dried in vacuo: ^1H NMR (C_6H_6) δ 6.25 (s, 2 H), 1.88 (s, 15 H,

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[26] Howes, A. J.; Hursthouse, M. B., in preparation.

[27] Fernholt, L.; Haaland, A.; Jutzi, P.; Kohl, F. X.; Seip, R. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 211.

[28] Overlapping isotopic patterns.

Table III. Fractional Atomic Coordinates (×10^4) for $(Me_5C_5)Ge(CH(SiMe_3)_2)$

	x	*y*	*z*
Ge(1)	2788 (1)	5450 (0.5)	8043 (0.5)
C(01)	474 (6)	5851 (4)	8272 (3)
C(011)	−891 (8)	5965 (5)	7524 (4)
C(02)	891 (7)	5047 (4)	8701 (4)
C(021)	35 (9)	4208 (4)	8441 (5)
C(03)	1840 (7)	5234 (4)	9502 (4)
C(031)	2541 (10)	4571 (5)	10164 (5)
C(04)	2043 (7)	6128 (4)	9578 (4)
C(041)	3091 (9)	6599 (5)	10293 (4)
C(05)	1227 (7)	6502 (4)	8831 (4)
C(051)	1105 (9)	7453 (5)	8630 (5)
C(1)	2295 (7)	4897 (3)	6850 (4)
Si(1)	2658 (2)	5720 (1)	6059 (1)
C(11)	4711 (10)	6088 (5)	6326 (6)
C(12)	2223 (11)	5336 (5)	4914 (4)
C(13)	1438 (11)	6700 (5)	6091 (5)
Si(2)	3318 (2)	3851 (1)	6867 (1)
C(21)	2613 (17)	3197 (6)	5904 (6)
C(22)	3136 (10)	3162 (4)	7802 (5)
C(23)	5473 (11)	4027 (6)	7021 (8)

Me_5C_5), 0.45 (s, 18 H, 2 $SiMe_3$), 0.40 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 130.97, 130.85 (*C*$SiMe_3$), 128.86 (CH), 118.86 (Me_5*C*$_5$), 9.67 (*Me*$_5C_5$), 2.18 (2 $SiMe_3$), 0.84 ($SiMe_3$); MS, *m/e* (relative intensity) 355 ($M^+ - Me_5C_5$, 40), 282 ($(SiMe_3)_2C_5H_2Ge^+$, 17), 209 ($Me_5C_5Ge^+$, 38), 73 ($SiMe_3^+$, 100). Anal. Found: C, 58.48; H, 9.10.

General Procedure for the Preparation of 6, 7, and 8 from 1. The solution of **1** in benzene (20 mL) was added to a solution of the alkyllithium reagent, respectively lithium amide in diethyl ether (~30 mL) which was cooled to −80 °C. After the mixture was allowed to warm to room temperature, it was stirred for at least 1 h before the solvent was evaporated in vacuo. Extraction of the residue with hexane (20 mL) was followed by concentration of the solution. Upon cooling to −80 °C, a crystalline product separated which was filtered and dried in vacuo.

[Bis(trimethylsilyl)amino](pentamethylcyclopentadienyl)germylene (6). Reaction of **1** (3.65 g, 15.00 mmol) with lithium bis(trimethylsilyl)amide (2.50 g, 15.00 mmol) yielded 3.96 g (72%) of yellow crystals: mp 59 °C; ^1H NMR (C_6D_6) δ 2.05 (s, 15 H, Me_5C_5), 0.35 (s, 18 H, $SiMe_5$); ^{13}C NMR (C_6D_6) δ 119.75 (Me_5*C*$_5$), 10.71 (*Me*$_5C_5$), 5.15 ($SiMe_3$); MS, *m/e* (relative intensity) 369 (M^+, 0.7), 234 ($M^+ - Me_5C_5$, 7), 209 ($Me_5C_5Ge^+$, 6), 146 ($Si_2Me_6^+$ (?), 100). Anal. Calcd for $C_{16}H_{33}GeNSi_2$ (368.21): C, 52.19; H, 9.03; N, 3.80. Found: C, 51.68; H, 8.83; N, 3.83. Molecular weight determination (cryoscopically in C_6H_6): 377.

(Pentamethylcyclopentadienyl)(2,2,6,6-tetramethylpiperidino)germylene (7). Reaction of **1** (2.64 g, 10.85 mmol) with lithium 2,2,6,6-tetramethylpiperidide (1.60 g, 10.87 mmol) yielded 2.13 g (56%) of lemon chrome crystals: mp 51 °C; ^1H NMR (C_6D_6) δ 2.01 (s, 15 H, Me_5C_5), 1.50 (m, 2 H, NC_5Me_4*H*$_6$), 1.31 (s, 12 H, NC_5*Me*$_4H_6$), 1.20 (m, 4 H, NC_5Me_4*H*$_6$); ^{13}C NMR ($CDCl_3$) δ 118.40 (Me_5C_5), 49.47, 38.57, 18.31 ($NC_5Me_4H_6$), 31.49 (NC_5*Me*$_4H_6$), 9.77 (*Me*$_5C_5$). MS, *m/e* (relative intensity) 349 (M^+, 0.2),[21] 209 ($Me_5C_5Ge^+$, 100), 135 ($Me_5C_5^+$, 25). Anal. Calcd for $C_{19}H_{33}GeN$ (348.07): C, 65.56; H, 9.56; N, 4.02. Found: C, 64.92; H, 9.37; N, 3.62.

[Bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (8) from 1. Reaction of **1** (2.07 g, 8.51 mmol) with a 0.61 M solution of [bis(trimethylsilyl)methyl]lithium (13.95 mL, 8.51 mmol) yielded 2.38 g (76%) of orange crystals: mp 58 °C. ^1H NMR (C_6D_6) δ 1.89 (s, 15 H, Me_5C_5), 1.22 (s, 1 H, *CH*$(SiMe_3)_2$), 0.18 (s, 18 H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 120.14 (Me_5*C*$_5$), 51.29 (*C*$H(SiMe_3)_2$), 10.99 (*Me*$_5C_5$), 3.61 ($SiMe_3$); MS, *m/e* (relative intensity) 233 ($M^+ - Me_5C_5$, 6), 209 ($Me_5C_5Ge^+$, 92), 73 ($SiMe_3^+$, 100); chemical ionization MS, *m/e* (relative intensity) 369 ($M^+ + H$, 18), 209 ($Me_5C_5Ge^+$, 100). Anal. Calcd for $C_{17}H_{34}GeSi_2$ (367.22): C, 55.60; H, 9.33. Found: C, 55.36; H, 9.26. Molecular weight determination (cryoscopically in C_6H_6): 371.

[Bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (8) from 2. A 0.74 M solution of [bis(trimethylsilyl)methyl]lithium in diethyl ether (6.60 mL, 4.88 mmol) was added to a suspension of **2** (1.44 g, 4.89 mmol) in diethyl ether (30 mL) at −80 °C. Allowing the mixture to warm to room temperature gave a deep yellow suspension. Evaporation of the solvent and extraction of the residue with hexane (20 mL) were followed by concentrating the solution. Cooling to −80 °C yielded 1.13 g (63%) of orange crystals, mp 58 °C, which were filtered and dried in vacuo: ^1H NMR (C_6H_6) δ 1.90 (s, 15 H, Me_5C_5), 1.23 (s, 1 H, *CH*$(SiMe_3)_2$), 0.20 (s, 18 H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 120.16 (Me_5*C*$_5$), 51.33 (*C*$H(SiMe_3)_2$), 10.97 (*Me*$_5C_5$), 3.61 ($SiMe_3$); MS, *m/e* (relative intensity) 233 ($M^+ - Me_5C_5$, 2), 209 ($Me_5C_5Ge^+$, 80), 73 (Me_3Si^+, 100). Anal. Found: C, 55.70; H, 9.25.

X-ray Crystallography. A crystal of **8** was sealed under argon in a thin-walled glass capillary for X-ray study. All measurements were made by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature (295 ± 2 K), following previously described procedures.[29] Data were recorded by using an $\omega/2\theta$ scan mode (ω scan width = 0.8 + 0.35 tan θ) for $1.5 \leq \theta \leq 25.0°$, within the *h,k,l* limits 0→10,0→18,−18→18, giving 4174 measured, 3760 unique, and 2485 observed [$I > 1.5\sigma(I)$] reflections. No correction for absorption was made.

Crystal data: $C_{17}H_{34}GeSi_2$, M_r 367.21, monoclinic, space group P_1/a, a = 8.844 (5) Å, b = 15.530 (6) Å, c = 15.916 (6) Å, β = 102.37 (4)°, V = 2135.3 Å^3, Z = 4, D_{calcd} = 1.142 g cm^{-3}, $F(000)$ = 784, μ(Mo Kα) = 15.17 cm^{-1}.

The structure was solved and developed via the heavy-atom method and refined by using full-matrix least squares. All nonhydrogen atoms were refined with anisotropic thermal parameters. The alkyl carbon hydrogens were located in a difference map and included with free isotropic refinement. Although most methyl hydrogens were also located experimentally, they were included in idealized positions (based on the experimental locations, but with regularized geometry) and assigned fixed isotropic thermal parameters equal to 1.2 times the U_{equiv} of the parent carbon.

The function minimized was $\sum\omega|\Delta F|^2$, and weights were calculated as $\omega = 1/(\sigma^2|F_o| + gF_o^2)$, with g = 0.0001 giving acceptable agreement analyses. The final R (= $\sum|\Delta F|/\sum F$) and R_w (= $\sum\omega^{1/2}|\Delta F|/\sum\omega^{1/2}F_o$) values were 0.0519 and 0.0458, respectively, for 317 parameters. Final atomic positional parameters are given in Table III.

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Registry No. **1**, 85085-98-9; **2**, 73274-08-5; **3**, 103731-92-6; **4**, 103731-93-7; **5**, 103731-94-8; **6**, 103731-88-0; **7**, 103731-89-1; **8**, 100333-77-5; $C_5H_4(SiMe_3)K$, 101630-43-7; $C_5H_3(SiMe_3)_2K$, 103731-90-4; $C_5H_2(SiMe_3)_3K$, 103731-91-5; $LiN(SiMe_3)_2$, 4039-32-1; $Li\overline{NC(CH_3)_2(CH_2)_3C}(CH_3)_2$, 38227-87-1; $(Me_3Si)_2CHLi$, 41823-71-6.

Supplementary Material Available: Tables of calculated hydrogen positions and thermal parameters for all atoms (Tables S1 and S2) (2 pages); a listing of F_o/F_c values (Table S3) (15 pages). Ordering information is given on any current masthead page.

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[29] Jones, R. A.; Malik, K. M. A.; Hursthouse, M. B.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128.

[30] 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.)