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# (Tris(trimethylsilyl)methyl)- and (2,4,6-Tri-*tert*-butylphenyl)(pentamethylcyclopentadienyl)germylene: Synthesis and Structure

P. Jutzi,* A. Becker, C. Leue, H. G. Stammler, and B. Neumann

*Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld 1, Germany*

M. B. Hursthouse and A. Karaulov

*Department of Chemistry, Queen Mary College, University of London, London E1 4NS, U.K.*

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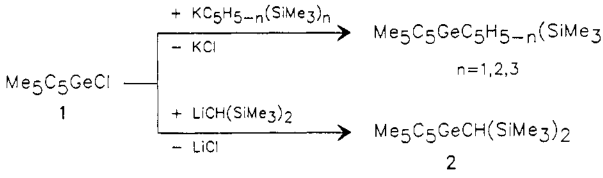
(Pentamethylcyclopentadienyl)germanium chloride (1) reacts with (tris(trimethylsilyl)methyl)lithium to give (pentamethylcyclopentadienyl)(tris(trimethylsilyl)methyl)germylene (3) and with (2,4,6-tri-*tert*-butylphenyl)lithium to yield (pentamethylcyclopentadienyl)(2,4,6-tri-*tert*-butylphenyl)germylene (4). Both germylenes (3 and 4) are monomeric with a fluxional $\eta^2$ bonding between the germanium center and the $Me_5C_5$ ring. Compound 3 crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a$ = 9.954 (1) Å, $b$ = 8.759 (2), Å, $c$ = 29.416 (6) Å, $\beta$ = 95.05 (2)°, and $Z$ = 4. Complex 4 crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a$ = 10.404 (5) Å, $b$ = 13.519 (6) Å, $c$ = 19.203 (10) Å, $\beta$ = 103.62 (4)°, and $Z$ = 4.

## Introduction

The chemistry of diorganogermanium(II) compounds (germylenes) has been extensively studied during the past 15 years, but the number of stable monomeric species is still quite small.[1] Generally, inorganic and organic germylenes can be stabilized kinetically by bulky ligands and thermodynamically by intramolecular electron donation from the ligands.[2,3] A common feature of most of these compounds is the fact that the two ligands are the same.[3,4] There were only a few exceptions until the introduction of the pentamethylcyclopentadienyl ligand (Cp*) into germylene chemistry.[5,6]

In 1986 we reported the synthesis and characterization of mixed germylenes by a two-step alkylation of $GeCl_2$·diox (diox = dioxane) with different nucleophiles.[7] The first step is the preparation of (pentamethylcyclopentadienyl)germanium chloride (1) by reaction with (pentamethylcyclopentadienyl)lithium.[8] In a subsequent step 1 is treated with various nucleophiles. Thus, reaction of 1 with substituted cyclopentadienides yields mixed germanocenes, and reaction with (bis(trimethylsilyl)methyl)lithium leads to (bis(trimethylsilyl)methyl)(pentamethylcyclopentadienyl)germylene (2) (eq 1). The crystal structure of 2 shows the monomeric character of this compound in the solid state and the $\eta^2$ bonding between the $Me_5C_5$ ring and the germanium atom. Comparison of the structure of 2 with that of its pentacarbonyltungsten complex $Me_5C_5[(Me_3Si)_2CH]_2Ge{\rightarrow}W(CO)_5$ shows no significant differences in the geometry around the germanium atom.[9]

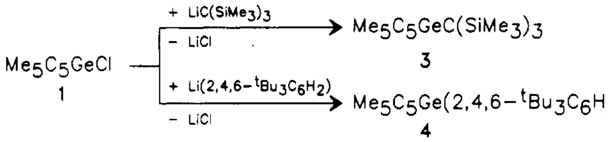


$$\underset{1}{Me_5C_5GeCl} \xrightarrow[-\ KCl]{+\ KC_5H_{5-n}(SiMe_3)_n} Me_5C_5GeC_5H_{5-n}(SiMe_3)_n \quad n=1,2,3 \qquad (1)$$
$$\underset{1}{Me_5C_5GeCl} \xrightarrow[-\ LiCl]{+\ LiCH(SiMe_3)_2} \underset{2}{Me_5C_5GeCH(SiMe_3)_2}$$

Meanwhile, it is well-known that the Cp* ligand can be used experimentally as a leaving group.[6] In this context we are interested to examine Cp*-functionalized germylenes in substitution reactions. Therefore, it was of particular interest to investigate the influence of other bulky alkyl or aryl ligands at the Ge center on the stability and the structure of the corresponding germylenes. Here we report the synthesis and structure of (pentamethylcyclopentadienyl)(tris(trimethylsilyl)methyl)germylene (3) and of (pentamethylcyclopentadienyl)(2,4,6-tri-*tert*-butylphenyl)germylene (4).

## Results and Discussion

The synthesis of the compounds 3 and 4 was performed by reaction of $Me_5C_5GeCl$ (1) with $(Me_3Si)_3CLi$·2THF and (2,4,6-tri-*tert*-butylphenyl)lithium, respectively (eq 2).



$$\underset{1}{Me_5C_5GeCl} \xrightarrow[-\ LiCl]{+\ LiC(SiMe_3)_3} \underset{3}{Me_5C_5GeC(SiMe_3)_3} \qquad (2)$$
$$\underset{1}{Me_5C_5GeCl} \xrightarrow[-\ LiCl]{+\ Li(2,4,6\text{-}{}^tBu_3C_6H_2)} \underset{4}{Me_5C_5Ge(2,4,6\text{-}{}^tBu_3C_6H_2)}$$

Subsequent workup leads to orange-yellow products, which are soluble in all common organic solvents; they can be crystallized from hexane solution.

Complex 3 is rather stable against air and moisture, whereas 4 is more sensitive. In solution, 4 decomposes at temperatures above 60 °C; this decomposition does not lead to an insertion of the germanium atom into one of the C–H bonds of the *tert*-butyl groups of the phenyl ligand, as observed in the case of bis(2,4,6-tri-*tert*-butylphenyl)germylene.[10]

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**Table I. Crystallographic Data for 3 and 4**

| | 3 | 4 |
|---|---|---|
| emp formula | $C_{20}H_{42}Si_3Ge$ | $C_{28}H_{44}Ge$ |
| fw | 439.4 | 453.2 |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ |
| $Z$ | 4 | 4 |
| cell consts | | |
| $a$, Å | 9.954 (1) | 10.404 (5) |
| $b$, Å | 8.759 (2) | 13.519 (6) |
| $c$, Å | 29.416 (6) | 19.203 (10) |
| $\beta$, deg | 95.05 (2) | 103.62 (4) |
| $V$, Å$^3$ | 2555.13 | 2625 (2) |
| $\mu$, cm$^{-1}$ | | 11.60 |
| $D_{calc}$, g cm$^{-3}$ | 1.103 | 1.147 |
| $F$(000) | 884 | 976 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.71069) | Mo K$\alpha$ (0.71069) |
| 2$\theta$ range, deg | 3.0–42.0 | 3.0–50.0 |
| temp, K | 295 ± 2 | 170 |
| scan type | $\omega$ | $\omega$ |
| *hkl* collcd | ±9,+8,+28 | +12,+16,±22 |
| no. of reflcns collcd | 3037 | 5082 |
| no. of independent reflcns | 2733 | 4590 |
| no. of obsd reflcns | 1730 | 2413 |
| significant test | $F_o > 3\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ |
| abs corr | semiempirical | |
| no. of params refined | 325 | 262 |
| data:param ratio | 5.32:1 | 9.2:1 |
| $R$ | 0.0635 | 0.0613 |
| $R_w$ | 0.0492 | 0.0425 |
| weighting scheme | $w^{-1} = \sigma^2F_o + 2.3642F_o^2$ | $w^{-1} = \sigma^2F_o$ |

**Table II. Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ × 10$^3$) of 3**

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ge | 1599 (1) | 6766 (1) | 1315 (1) | 420 (4) |
| Si(1) | 3928 (3) | 7489 (4) | 685 (1) | 538 (13) |
| Si(2) | 4327 (3) | 7564 (4) | 1758 (1) | 549 (12) |
| Si(3) | 3257 (3) | 10415 (4) | 1218 (1) | 583 (14) |
| C(1) | −378 (10) | 7924 (13) | 1400 (4) | 503 (38) |
| C(2) | −474 (10) | 7318 (13) | 948 (4) | 507 (36) |
| C(3) | −792 (10) | 5744 (13) | 996 (4) | 537 (38) |
| C(4) | −902 (10) | 5393 (15) | 1446 (4) | 562 (39) |
| C(5) | −635 (10) | 6716 (16) | 1697 (4) | 543 (40) |
| C(6) | 3255 (9) | 8250 (12) | 1224 (3) | 399 (34) |
| C(01) | −415 (14) | 9617 (14) | 1503 (6) | 1044 (45) |
| C(02) | −569 (12) | 8225 (20) | 512 (5) | 1163 (42) |
| C(03) | −969 (15) | 4703 (19) | 599 (6) | 1090 (50) |
| C(04) | −1046 (12) | 3751 (16) | 1636 (7) | 1030 (46) |
| C(05) | −578 (13) | 6740 (20) | 2217 (4) | 1069 (43) |
| C(11) | 5859 (15) | 7483 (18) | 698 (7) | 970 (46) |
| C(12) | 3244 (14) | 8549 (17) | 171 (4) | 791 (42) |
| C(13) | 3317 (14) | 5435 (14) | 570 (4) | 867 (42) |
| C(21) | 5889 (13) | 8632 (17) | 1915 (4) | 917 (44) |
| C(22) | 4929 (14) | 5538 (13) | 1723 (5) | 814 (45) |
| C(23) | 3282 (13) | 7686 (17) | 2265 (4) | 787 (42) |
| C(31) | 4867 (15) | 11217 (15) | 1068 (6) | 903 (40) |
| C(32) | 1892 (12) | 11290 (12) | 805 (5) | 784 (41) |
| C(33) | 2991 (14) | 11190 (13) | 1805 (5) | 903 (42) |

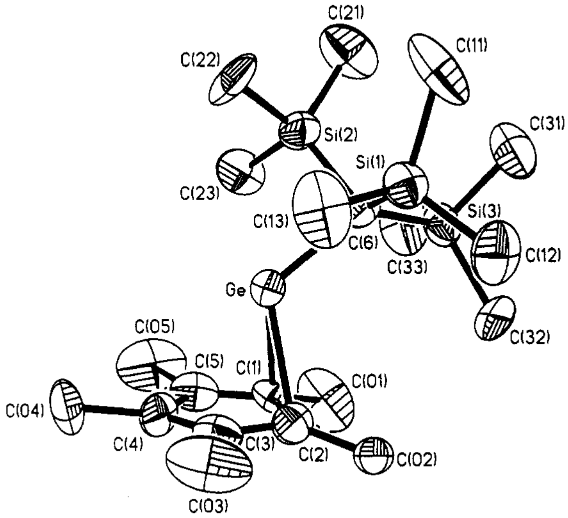

Figure 1. X-ray structure of $Me_5C_5GeC(SiMe_3)_3$ (**3**).

**Table III. Bond Lengths (Å) of 3**

| | | | |
|---|---|---|---|
| C(1)–Ge | 2.246 (18) | C(2)–Ge | 2.294 (18) |
| C(3)–Ge | 2.637 (19) | C(5)–Ge | 2.579 (18) |
| C(6)–Ge | 2.135 (17) | C(1)–C(2) | 1.426 (22) |
| C(1)–C(01) | 1.515 (25) | C(2)–C(3) | 1.424 (23) |
| C(2)–C(02) | 1.505 (25) | C(3)–C(4) | 1.374 (22) |
| C(3)–C(03) | 1.479 (26) | C(4)–C(5) | 1.387 (23) |
| C(4)–C(04) | 1.554 (28) | C(5)–C(1) | 1.411 (22) |
| C(5)–C(10) | 1.526 (24) | C(6)–Si(1) | 1.895 (16) |
| Si(1)–C(11) | 1.920 (24) | Si(1)–C(12) | 1.853 (23) |
| Si(1)–C(13) | 1.919 (22) | C(6)–Si(2) | 1.917 (16) |
| Si(2)–C(21) | 1.838 (21) | Si(2)–C(22) | 1.879 (20) |
| Si(2)–C(23) | 1.894 (23) | C(6)–Si(3) | 1.897 (19) |
| Si(3)–C(31) | 1.838 (23) | Si(3)–C(32) | 1.902 (20) |
| Si(3)–C(33) | 1.896 (24) | | |

**Table IV. Bond Angles (deg) of 3**

| | | | |
|---|---|---|---|
| C(2)–Ge–C(1) | 36.6 (5) | C(3)–Ge–C(2) | 32.6 (5) |
| C(5)–Ge–C(1) | 33.1 (5) | C(5)–Ge–C(3) | 50.5 (6) |
| C(3)–Ge–C(1) | 54.6 (7) | C(5)–Ge–C(2) | 55.6 (7) |
| C(6)–Ge–C(2) | 119.1 (7) | C(6)–Ge–C(1) | 115.7 (7) |
| C(6)–Ge–C(3) | 147.7 (6) | C(5)–Ge–C(6) | 140.4 (6) |
| C(12)–Si(1)–C(6) | 112.0 (9) | C(13)–Si(1)–C(6) | 110.3 (9) |
| C(13)–Si(1)–C(12) | 103.8 (11) | C(11)–Si(1)–C(6) | 114.3 (10) |
| C(11)–Si(1)–C(12) | 108.2 (12) | C(11)–Si(1)–C(13) | 107.6 (11) |
| C(21)–Si(2)–C(6) | 116.3 (10) | C(23)–Si(2)–C(6) | 108.9 (8) |
| C(23)–Si(2)–C(21) | 106.6 (10) | C(22)–Si(2)–C(6) | 114.1 (10) |
| C(22)–Si(2)–C(21) | 103.1 (11) | C(22)–Si(2)–C(23) | 107.2 (12) |
| C(33)–Si(3)–C(6) | 110.4 (9) | C(32)–Si(3)–C(6) | 114.1 (9) |
| C(31)–Si(3)–C(6) | 112.7 (9) | C(32)–Si(3)–C(33) | 106.7 (11) |
| C(31)–Si(3)–C(33) | 106.0 (12) | C(31)–Si(3)–C(32) | 106.4 (11) |
| C(2)–C(1)–Ge | 73.5 (11) | C(5)–C(1)–Ge | 86.5 (11) |
| C(5)–C(1)–C(2) | 107.3 (16) | C(01)–C(1)–Ge | 120.1 (13) |
| C(01)–C(1)–C(2) | 123.4 (20) | C(01)–C(1)–C(5) | 126.9 (20) |
| C(1)–C(2)–Ge | 69.9 (11) | C(3)–C(2)–Ge | 87.0 (12) |
| C(3)–C(2)–C(1) | 105.4 (17) | C(02)–C(2)–Ge | 119.9 (13) |
| C(02)–C(2)–C(1) | 126.3 (20) | C(02)–C(2)–C(3) | 126.6 (21) |
| C(2)–C(3)–Ge | 60.3 (10) | C(4)–C(3)–Ge | 83.0 (12) |
| C(4)–C(3)–C(2) | 110.4 (18) | C(03)–C(3)–Ge | 122.1 (14) |
| C(03)–C(3)–C(2) | 122.1 (22) | C(03)–C(3)–C(4) | 127.5 (22) |
| C(6)–C(4)–C(3) | 107.4 (18) | C(04)–C(4)–C(3) | 124.9 (22) |
| C(04)–C(4)–C(5) | 126.9 (20) | Si(1)–C(6)–Ge | 103.0 (8) |
| Si(2)–C(6)–Ge | 95.0 (7) | Si(2)–C(6)–Si(1) | 111.3 (8) |
| Si(3)–C(6)–Ge | 127.7 (8) | Si(3)–C(6)–Si(1) | 110.1 (9) |
| Si(3)–C(6)–Si(2) | 108.7 (9) | C(1)–C(5)–Ge | 60.4 (10) |
| C(4)–C(5)–Ge | 85.1 (11) | C(4)–C(5)–C(1) | 109.5 (15) |
| C(05)–C(5)–Ge | 118.7 (12) | C(05)–C(5)–C(1) | 128.2 (22) |
| C(05)–C(5)–C(4) | 122.2 (21) | | |

The $^1$H and $^{13}$C NMR spectra of **3** and **4** show equivalent methyl groups and ring carbon atoms for the Cp* ligand indicating either a fast 1,5-sigmatropic rearrangement of a $\sigma$-bonded Cp* ligand or a higher degree of hapticity between a fluxional Cp* ring and the germanium center. The $Me_3Si$ groups in **3** are equivalent and give rise to sharp singlets. The *tert*-butyl groups of the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ ligand in **4** appear as two singlets in a 2:1 ratio.

The solid-state structures of **3** and **4** have been investigated by X-ray crystallography. A diagram of the molecular structure of **3** is shown in Figure 1. The crystallographic data of **3** are summarized in Table I, the atomic coordinates are in Table II, and bond lengths and angles are given in Tables III and IV. The molecular structure corresponds qualitatively to that found for **2** with an $\eta^2$-bonded $Me_5C_5$ ligand and a $\sigma$-bonded alkyl ligand, but in

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(11) Also other reactions of **3** with electrophiles and nucleophiles are kinetically hindered: Becker, A. Dissertation, Universität Bielefeld, 1990.

**Table V. Ge–C σ-Bond Lengths and RGeR Angles in Germanium Compounds**

| compd | Ge–C, Å | R–Ge–R, deg |
|---|---|---|
| $Me_5C_5GeC(SiMe_3)_3$ (**3**) | 2.14 | 118.9 |
| $Me_5C_5Ge(2,4,6\text{-}^tBu_3C_6H_2)$ (**4**) | 2.09 | 100.8 |
| $Me_5C_5GeCH(SiMe_3)_2$ (**2**)[7] | 2.04 | 106.9 |
| $Me_5C_5GeCH(SiMe_3)_2{\cdot}W(CO)_5$[9] | 1.99 | 102 |
| $Me_5C_5GeCl{\cdot}W(CO)_5$[18] |  | 101 |
| $[(Me_3Si)_2CH]_2Ge(s)$[2] | 1.98, 2.04 | 112.5 |
| $[(Me_3Si)_2CH]_2Ge(g)$[19] | 2.04 | 107.2 |
| $[(Me_3Si)_2CH]_2Ge{\cdot}Cr(CO)_5$[20] | 1.98 | 102.8 |
| $(Me_3Si)_2CHGeC(SiMe_3)_3$[21] | 2.01, 2.06 | 111.3 |
| $[(Me_3Si)_2N]_2Ge$[22] |  | 101 (g), 111 (s) |
| $(C_9H_{18}N)_2Ge$[23] |  | 111.4 |
| $[(2,6\text{-}Et_2C_6H_3)_2Ge]_2$[24] | 1.96 | 115.4 |
| $GeMe_4$[25] | 1.95 |  |
| $^tBu_8Ge_8Br_2$[26] | 2.01 |  |

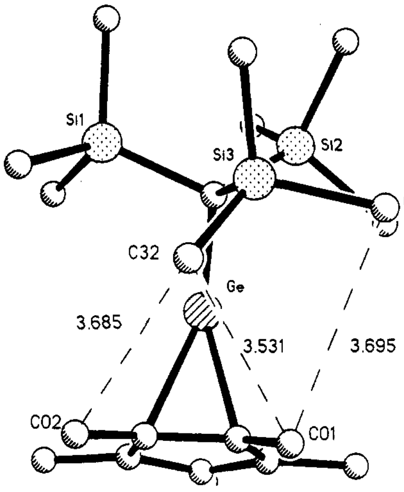

**Figure 2.** Shortest nonbonding distances between the Cp* ligand and the $(Me_3Si)_3C$ ligand in **3**.

detail the present structure shows some differences due to the additional $Me_3Si$ group within the alkyl ligand. Thus, the angle between the C(6)–Ge bond and the vector from the germanium atom to the midpoint of the C(1)–C(2) bond is 118.9°. This angle is much larger than that in **2** (Table V) and the consequence of an increased steric repulsion between the alkyl ligand and the methyl groups on C(1) and C(2), caused by the additional $Me_3Si$ group. The shortest nonbonding distances between the methyl groups of the Cp* ring and the $(Me_3Si)_3C$ ligand are in the range of the sum of the van der Waals radii of two methyl groups (Figure 2). As a further consequence of steric repulsion, the Ge–C(6)–Si(3) angle [127.7 (8)°] is larger than the Ge–C(6)–Si(1) angle [103.08°] and the Ge–C(6)–Si(2) angle [95.0 (7)°]. The angle of 118.9° found at the Ge(II) center in **3** presumably is the smallest angle possible for this molecule. As a further indication of steric crowding, the bond length of the Ge–C(6) bond is about 2.14 Å. This is one of the longest Ge–C σ bonds known so far (Table V). The observed geometry at the germanium atom in **3** indicates the existence of a stereochemically active lone pair at the Ge(II) center. On the other hand, the Ge center seems to be highly shielded against nucleophilic or electrophilic attack, as demonstrated by the stability of **3** against air and moisture.[11]

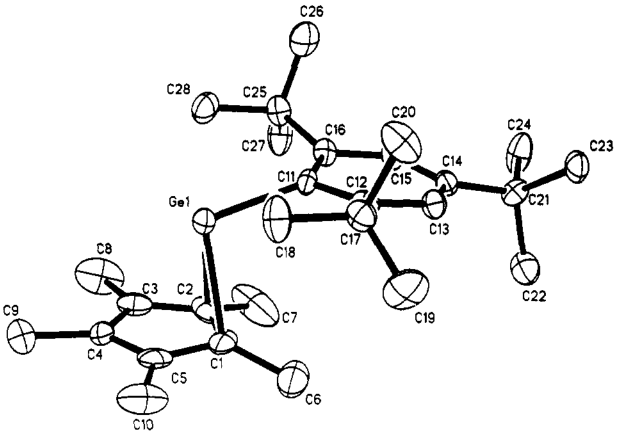

**Figure 3.** X-ray structure of $Me_5C_5Ge(2,4,6\text{-}^tBu_3C_6H_2)$ (**4**).

**Table VI. Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ × $10^3$) of 4**

|  | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Ge(1) | −125 (1) | 1276 (1) | 4581 (1) | 24 (1) |
| C(2) | 734 (7) | 2379 (6) | 3880 (5) | 41 (3) |
| C(3) | 1710 (7) | 1654 (5) | 3841 (4) | 34 (3) |
| C(4) | 2586 (7) | 1595 (5) | 4509 (4) | 28 (3) |
| C(5) | 2189 (8) | 2245 (5) | 4988 (4) | 32 (3) |
| C(1) | 1025 (8) | 2738 (5) | 4605 (5) | 37 (3) |
| C(7) | −154 (8) | 2900 (7) | 3258 (5) | 95 (5) |
| C(8) | 1803 (8) | 1068 (6) | 3190 (4) | 63 (4) |
| C(9) | 3739 (7) | 893 (5) | 4724 (4) | 53 (4) |
| C(10) | 2864 (8) | 2412 (6) | 5763 (4) | 53 (4) |
| C(6) | 510 (8) | 3705 (6) | 4826 (5) | 82 (5) |
| C(11) | −2061 (6) | 1802 (5) | 4403 (3) | 21 (2) |
| C(12) | −2453 (6) | 2448 (5) | 4904 (3) | 22 (3) |
| C(13) | −3465 (6) | 3116 (5) | 4668 (3) | 25 (3) |
| C(14) | −4222 (7) | 3157 (5) | 3961 (4) | 25 (3) |
| C(15) | −3952 (6) | 2428 (5) | 3509 (3) | 24 (3) |
| C(16) | −2925 (6) | 1732 (5) | 3712 (3) | 23 (3) |
| C(17) | −1923 (7) | 2382 (5) | 5732 (4) | 28 (3) |
| C(18) | −725 (6) | 1693 (5) | 5983 (3) | 37 (3) |
| C(19) | −1574 (8) | 3382 (5) | 6102 (4) | 52 (3) |
| C(20) | −3045 (7) | 1933 (6) | 6034 (3) | 42 (3) |
| C(21) | −5245 (7) | 3962 (5) | 3728 (3) | 25 (3) |
| C(22) | −4524 (7) | 4936 (5) | 3660 (4) | 40 (3) |
| C(23) | −6126 (6) | 4093 (5) | 4261 (3) | 33 (3) |
| C(24) | −6181 (7) | 3739 (6) | 2993 (3) | 45 (3) |
| C(25) | −2951 (7) | 877 (5) | 3178 (3) | 28 (3) |
| C(26) | −4254 (7) | 293 (5) | 3130 (4) | 41 (3) |
| C(27) | −2960 (7) | 1244 (6) | 2415 (3) | 46 (3) |
| C(28) | −1823 (7) | 131 (5) | 3384 (4) | 39 (3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table VII. Bond Lengths (Å) of 4**

|  |  |  |  |
|---|---|---|---|
| Ge(1)–C(2) | 2.325 (9) | Ge(1)–C(1) | 2.304 (7) |
| Ge(1)–C(11) | 2.087 (7) | C(2)–C(3) | 1.427 (11) |
| C(2)–C(1) | 1.438 (12) | C(2)–C(7) | 1.501 (11) |
| C(3)–C(4) | 1.390 (9) | C(3)–C(8) | 1.502 (11) |
| C(4)–C(5) | 1.402 (11) | C(4)–C(9) | 1.509 (9) |
| C(5)–C(1) | 1.426 (10) | C(5)–C(10) | 1.506 (10) |
| C(10)–C(6) | 1.511 (11) | C(11)–C(12) | 1.428 (10) |
| C(11)–C(16) | 1.420 (8) | C(12)–C(13) | 1.380 (9) |
| C(12)–C(17) | 1.560 (9) | C(13)–C(14) | 1.401 (9) |
| C(14)–C(15) | 1.386 (10) | C(14)–C(21) | 1.514 (9) |
| C(15)–C(16) | 1.408 (9) | C(16)–C(25) | 1.541 (10) |
| C(17)–C(18) | 1.540 (10) | C(17)–C(19) | 1.530 (10) |
| C(17)–C(20) | 1.545 (11) | C(21)–C(22) | 1.535 (10) |
| C(21)–C(23) | 1.537 (10) | C(21)–C(24) | 1.544 (8) |
| C(25)–C(26) | 1.553 (10) | C(25)–C(27) | 1.544 (10) |
| C(25)–C(28) | 1.527 (10) |  |  |

A diagram of the molecular structure of **4** is shown in Figure 3. The crystallographic data are summarized in Table I, the atomic coordinates are in Table VI, and bond lengths and angles are given in Tables VII and VIII. The molecular structure is similar to that found for **2** and **3** and shows an $\eta^2$-$Me_5C_5$ ligand and a σ-bonded $2,4,6\text{-}^tBu_3C_6H_2$ group. The angle between the Ge–C(11) bond and the vector from Ge to the midpoint of the C(1)–C(2) bond is about 101.0°. Compared with the other $Me_5C_5$-substituted germylenes, it is the smallest value so far observed (Table V). This small bond angle in **4** is only possible because

**Table VIII. Bond Angles (deg) of 4**

| | | | |
|---|---|---|---|
| C(2)–Ge(1)–C(1) | 36.2 (3) | C(2)–Ge(1)–C(11) | 100.0 (3) |
| C(1)–Ge(1)–C(11) | 100.8 (3) | Ge(1)–C(2)–C(3) | 88.0 (5) |
| Ge(1)–C(2)–C(1) | 71.1 (5) | C(3)–C(2)–C(1) | 107.0 (6) |
| Ge(1)–C(2)–C(7) | 120.9 (5) | C(3)–C(2)–C(7) | 126.4 (8) |
| C(1)–C(2)–C(7) | 124.2 (7) | C(2)–C(3)–C(4) | 108.1 (7) |
| C(2)–C(3)–C(8) | 126.3 (6) | C(4)–C(3)–C(8) | 125.6 (7) |
| C(3)–C(4)–C(5) | 109.8 (6) | C(3)–C(4)–C(9) | 126.4 (7) |
| C(5)–C(4)–C(9) | 123.6 (6) | C(4)–C(5)–C(1) | 107.5 (6) |
| C(4)–C(5)–C(10) | 127.0 (7) | C(1)–C(5)–C(10) | 125.5 (7) |
| Ge(1)–C(1)–C(2) | 72.7 (4) | Ge(1)–C(1)–C(5) | 89.0 (5) |
| C(2)–C(1)–C(5) | 107.5 (7) | Ge(1)–C(1)–C(6) | 122.1 (6) |
| C(2)–C(1)–C(6) | 123.7 (7) | C(5)–C(1)–C(6) | 125.1 (7) |
| Ge(1)–C(11)–C(12) | 121.0 (4) | Ge(1)–C(11)–C(16) | 120.4 (5) |
| C(12)–C(11)–C(16) | 116.8 (6) | C(11)–C(12)–C(13) | 119.8 (6) |
| C(11)–C(12)–C(17) | 124.4 (6) | C(13)–C(12)–C(17) | 115.5 (6) |
| C(12)–C(13)–C(14) | 123.7 (6) | C(13)–C(14)–C(15) | 115.4 (6) |
| C(13)–C(14)–C(21) | 120.6 (6) | C(15)–C(14)–C(21) | 123.9 (6) |
| C(14)–C(15)–C(16) | 123.7 (6) | C(11)–C(16)–C(15) | 119.1 (6) |
| C(11)–C(16)–C(25) | 125.4 (6) | C(15)–C(16)–C(25) | 115.1 (5) |
| C(12)–C(17)–C(18) | 114.8 (6) | C(12)–C(17)–C(19) | 114.3 (6) |
| C(18)–C(17)–C(19) | 107.7 (5) | C(12)–C(17)–C(20) | 106.8 (5) |
| C(18)–C(17)–C(20) | 105.8 (6) | C(19)–C(17)–C(20) | 107.0 (6) |
| C(14)–C(21)–C(22) | 108.6 (5) | C(14)–C(21)–C(23) | 111.9 (5) |
| C(22)–C(21)–C(23) | 109.7 (5) | C(14)–C(21)–C(24) | 112.2 (5) |
| C(22)–C(21)–C(24) | 107.8 (5) | C(23)–C(21)–C(24) | 106.5 (5) |
| C(16)–C(25)–C(26) | 107.4 (6) | C(16)–C(25)–C(27) | 112.7 (6) |
| C(26)–C(25)–C(27) | 107.3 (5) | C(16)–C(25)–C(28) | 115.5 (5) |
| C(26)–C(25)–C(28) | 106.6 (6) | C(27)–C(25)–C(28) | 106.9 (6) |

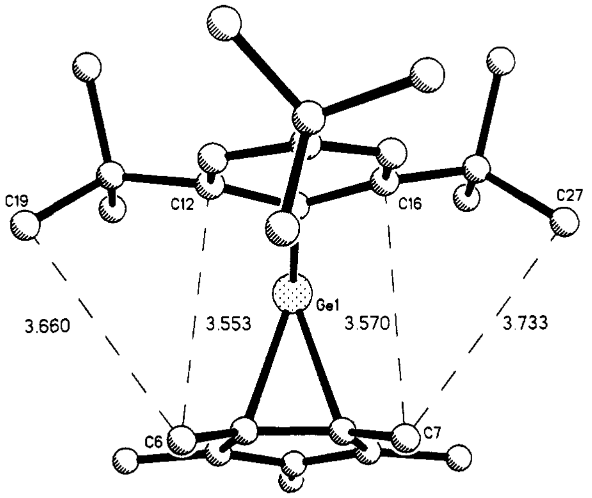

**Figure 4.** Shortest nonbonding distances between the Cp* ligand and the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ system in 4.

of the flat structure of the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ ligand. In Figure 4 it is shown that the shortest nonbonding distances between the methyl groups of the Cp* ligand [C(6) and C(7)] and the methyl groups C(19) and C(27) within the *tert*-butyl ligands fixed at the ring carbon atoms C(12) and C(16) are in the range of the sum of the van der Waals radii of two methyl groups. As a consequence of this steric crowding, a distortion of the aryl ring into a "boat conformation" can be observed.

Figure 5 shows a diagram of the Ge(2,4,6-$^t$Bu$_3$C$_6$H$_2$) unit in 4 displaying some interesting deformation parameters. The *tert*-butyl groups in the 2- and 6-positions are distorted above an optimized plane[12] within the aryl system [C(17) about 12.5°; C(25) about 11.9°], and the germanium-bonded carbon atom C(11) is distorted about 11.3° under this optimized plane. In addition, a deviation ($\alpha$ = 13°) from a linear arrangement at the C(11) center is observed for the Ge–C(11) bond. Similar deformations were first described by Yoshifuji in the compound P(O)(2,4,6-$^t$Bu$_3$C$_6$H$_2$)$_2$Cl;[13] they have later been found also in other 2,4,6-$^t$Bu$_3$C$_6$H$_2$-substituted species and attest to the crowding within those molecules.[14] The crowding in 4 is also demonstrated by the Ge–C(11) distance (2.087 Å), which is quite long compared with the Ge–aryl distance (1.962 Å) in [(2,6-Et$_2$C$_6$H$_3$)$_2$Ge]$_2$[23] (Table V). The overall shielding of the Ge center in 4 is not as effective as in compound 3, as shown by the higher reactivity of 4 with air and moisture.

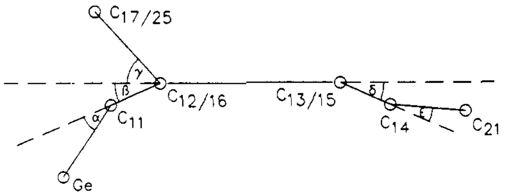

**Figure 5.** Deformation parameters of the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ system of 4 defined by the bond angle vectors: $\alpha$ = 13°; $\beta$ = 11.3°; $\nu$ = 11.9° (C(25)), 12.5° (C(17)); $\delta$ = 3.8°; $\epsilon$ = 0.6°.

It is difficult to decide whether a stereochemically active lone pair also influences the geometry around the germanium atom in 4. The small bonding angle at the Ge center and the distortion of the aryl ligand might be a consequence of nonattractive forces between the stereochemically active lone pair and the $\pi$-electron system of the aryl ring.

The structural investigation of the germylenes 2, 3, and 4 shows that the $\eta^2$ bonding between the Me$_5$C$_5$ ring and the germanium atom depends only marginally upon the nature of the alkyl or aryl ligand. In cyclopentadienyl chemistry, this kind of bonding is a common feature of element fragments isolobal and isoelectronic to the RGe: unit.[6] Theoretical calculations supporting the $\eta^2$ bonding have been published.[15]

The stability of Ge(II) compounds is increased drastically by the introduction of a $\pi$-bonded Cp* ligand. Furthermore, the Cp* ligand is known to act as a leaving group,[6] so that Cp*-substituted alkylgermylenes can be regarded as synthons for highly reactive cationic RGe$^+$ or neutral RGe$^\bullet$ fragments. Thus, pentamethylcyclo-

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[12] The plane is generated between C(12), C(13), C(15), and C(16).

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pentadienyl-substituted organogermylenes represent a promising class of compounds in the chemistry of low-valent germanium.

## Experimental Section

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

Melting points were determined with a Büchi 510 capillary melting point apparatus. $^1H$ NMR spectra were recorded on a Bruker AM 300 (300-MHz) spectrometer; $^{13}C$ NMR spectra (75-MHz, $^1H$-decoupled) were also recorded on the Bruker AM 300 spectrometer. Mass spectra were obtained from a Varian 311 A spectrometer (70 eV, 300-$\mu$A emission); only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen, Germany). (Pentamethylcyclopentadienyl)germanium chloride (1),[7] (tris(trimethylsilyl)methyl)lithium,[16] and (2,4,6-tri-*tert*-butylphenyl)lithium[17] were prepared as previously described.

**(Pentamethylcyclopentadienyl)(tris(trimethylsilyl)methyl)germylene (3).** A solution of (tris(trimethylsilyl)methyl)lithium–2-tetrahydrofuran (54.3 mL, 10.25 mmol) in diethyl ether was added to a solution of $Me_5C_5GeCl$ (1) (2.50 g, 10.25 mmol) in 75 mL of toluene at –80 °C. The solution, which turned immediately orange-red, was allowed to warm up to room temperature within 5 h. After evaporation of the solvent in vacuo, the red residue was extracted with hexane. Concentrating the solution and cooling to –55 °C yielded 2.79 g (62%) of red-orange crystals: mp 87 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 1.95 (s, 15 H), 0.36 (s, 27 H); $^{13}C$ NMR ($C_6D_6$) $\delta$ 120, 43 ($\mathrm{Me}_5\mathit{C}_5$), 10.97 ($\mathit{Me}_5\mathrm{C}_5$), 6.31 ($\mathit{Me}_5\mathrm{Si}$); MS (*m/z* (relative intensity)) 305 ($[Me_3Si]_3CGe^+$, 4), 209 ($Me_5C_5Ge^+$, 100), 73 ($Me_3Si^+$, 33). Anal. Calcd for $C_{20}H_{42}Si_3Ge$ (*Mn* = 439.40): C, 54.67; H, 9.64. Found: C, 55.60; H, 9.79.

**(Pentamethylcyclopentadienyl)(2,4,6-tri-*tert*-butylphenyl)germylene (4).** A solution of 1 (7.31 g, 30.10 mmol) in 100 mL of toluene was added to freshly prepared (2,4,6-tri-*tert*-butylphenyl)lithium (7.58 g, 30.10 mmol) in 200 mL of THF/hexane (10:1) within 2 h at –80 °C. The reaction mixture was allowed to warm to room temperature very slowly, giving a orange-red suspension. Evaporation of the solvents and extraction of the residue with hexane (60 mL) were followed by concentrating the solution. Cooling to –25 °C yielded 8.07 g (59%) of orange crystals: mp 103 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.43 (s, 2 H, $C_6\mathit{H}_2{}^tBu_3$), 1.76 (s, 15 H, $\mathit{Me}_5C_5$), 1.50 (s, 18 H, 2,6-$^t$Bu), 1.35 (s, 9 H, 4-$^t$Bu); $^{13}C$ NMR ($CDCl_3$) $\delta$ 164.70, 156.01, 148.35, 120.89, (4 s, $\mathit{C}_6H_2{}^tBu_3$), 120.78 (s, $\mathrm{Me}_5\mathit{C}_5$), 40.38, 34.54 (2 s, $\mathit{C}Me_3$), 34.92, 31.38 (2 s, $C\mathit{Me}_3$), 11.00 (s, $\mathit{Me}_5C_5$); MS (*m/z* (relative intensity)) 319 ($M^+ - Me_5C_5$, 2), 245 ($C_6H_2{}^tBu_3{}^+$, 6), 231 ($C_6H_2{}^tBu_3 - Me^+$, 100), 209 ($Me_5C_5Ge^+$, 24), 57 ($Me_3C^+$, 53). Anal. Calcd for $C_{28}H_{44}Ge$ (*Mr* = 453.25): C, 74.20; H, 9.78. Found: C, 74.13; H, 9.85.

**Registry No.** 1, 85085-98-9; 3, 136630-26-7; 4, 136630-27-8; (tris(trimethylsilyl)methyl)lithium, 28830-22-0; (2,4,6-tri-*tert*-butylphenyl)lithium, 35383-91-6.

**Supplementary Material Available:** Listings of crystal data and structure determination and refinement details, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters for compounds 3 and 4 (9 pages); listings of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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# Bis(acetylide) Complexes of Iron

Leslie D. Field,* Adrian V. George, Elizabeth Y. Malouf, Ingrid H. M. Slip, and
Trevor W. Hambley†

*Department of Organic Chemistry, University of Sydney, Sydney, NSW 2006, Australia*

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The synthesis and spectroscopic characterization of six bis(acetylido)(phosphino)iron(II) complexes is reported. NMR spectroscopy has been used to determine the geometry of the compounds to be trans with respect to the acetylide ligands. The crystal structures of three iron bis(acetylides) are reported. Crystals of $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (**3a**) are tetragonal, space group $P\bar{4}n2$, with $a$ = 9.1599 (5) Å, $c$ = 14.234 (2) Å, $Z$ = 2, and $R$ = 0.040 (877 $F$). Crystals of $Fe(C{\equiv}CPh)_2(DEPE)_2$ (**4b**) are monoclinic, space group $P2_1/c$, with $a$ = 9.783 (2) Å, $b$ = 10.675 (2) Å, $c$ = 17.855 (3) Å, $\beta$ = 94.35 (2)°, $Z$ = 2, and $R$ = 0.040 (2195 $F$). Crystals of $Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (**5a**) are monoclinic, space group $C2/c$, $a$ = 22.017 (5) Å, $b$ = 12.366 (2) Å, $c$ = 16.952 (4) Å, $\beta$ = 135.16 (2)°, $Z$ = 4, and $R$ = 0.034 (2026 $F$).

## Introduction

Transition-metal $\sigma$-acetylide complexes have been formed by a variety of different methods, including displacement of existing ligands by acetylides,[1] by oxidative addition of a coordinatively unsaturated metal center to a terminal acetylene,[2] or by deprotonation of vinylidene species.[3] More recently, successful synthesis of the bond between a metal and an sp-hybridized carbon has been achieved by displacement of a neutral diatomic ligand (dihydrogen or dinitrogen) by an acetylide anion.[4]

Iron(II) dihydrides of the type $FeH_2(PP)_2$ (PP = $R_2PCH_2CH_2PR_2$; R = $CH_3$ (**1a**), $-CH_2CH_3$ (**1b**)) are protonated by weak acids to form a cationic complex containing an $\eta^2$-bound molecule of dihydrogen, $[FeH(H_2)$-

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† Department of Inorganic Chemistry, University of Sydney.

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