

### Chemistry of the Aromatic 9-Germafluorenyl Dianion and Some Related Silicon and Carbon Species

Yuxia Liu,<sup>†,§</sup> David Ballweg,<sup>†</sup> Thomas Müller,<sup>‡</sup> Ilia A. Guzei,<sup>†</sup> Robert W. Clark,<sup>†</sup> and Robert West<sup>\*,†</sup>

Contribution from the Organosilicon Research Center, Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706, and Institut für Anorganische Chemie der Goethe Universität Frankfurt, Frankfurt am Main, D-60439, Federal Republic of Germany

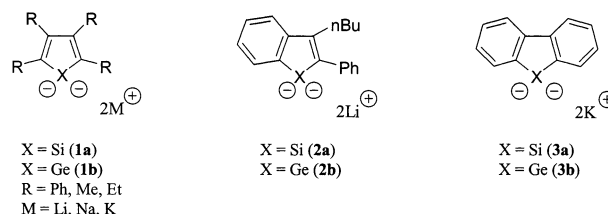
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**Abstract:** Dipotassio-9-germafluorenyl dianion (**3b**) was synthesized by reduction of 9,9-dichloro-9-germafluorene (**4b**) with sodium/potassium alloy in tetrahydrofuran. The X-ray crystal structure of **3b**, like that for the analogous silicon compound **3a**, shows C—C bond length equalization in the five-membered metallole rings and C—C bond length alternation in the six-membered benzenoid rings, indicating aromatic delocalization of electrons into the germole ring of **3b**. Calculated nucleus independent chemical shift (NICS) values indicate that the five-membered ring is more aromatic than the six-membered rings in **3a** and **3b**. Derivatization of **3b** with Me<sub>3</sub>SiCl gave 9,9-bis(trimethylsilyl)-9-germafluorene (**5**). Controlled oxidation of **3b** yielded dipotassio-9,9'-digerma-9,9'-bifluorenyl dianion (**6**). Reaction of **6** with MeOH yielded 9,9'-digerma-9,9'-bifluorene (**7**). The X-ray structure of **6** indicates C—C bond length alternation in the five-membered rings. Thus dianion **6**, like its silicon analogue **8**, has the negative charges localized at metal atoms and no aromatic character. Dipotassio-9,9'-bifluorenyl dianion (**9**), the carbon analogue of **6**, exhibits aromaticity with its X-ray crystal structure showing the C—C bond length equalization in both the five- and six-membered rings. Derivatization of **9** with MeI gave 9,9'-dimethyl-9,9'-bifluorene (**10**). The structure of **10** shows that the two fluorenyl rings are cis to each other with a torsional angle of 59° and a long C—C single bond (1.60 Å) connecting them.

#### Introduction

Since the discovery of the tetraphenylsilole dianion (**1a**, R = Ph, M = Na),<sup>1</sup> several dianionic derivatives of siloles and germoles have been synthesized and structurally characterized (**1a** and **1b**, Chart 1).<sup>2–10</sup> All these compounds exhibited similar aromaticity with delocalization of (4n + 2) π electrons and C—C bond length equalization in the five-membered silole rings. Boudjouk and co-workers recently reported the synthesis and characterization of silaindenyl and germaindenyl dianions (**2a** and **2b**, Chart 1).<sup>11,12</sup> The structures of both dianions

Chart 1



showed C—C bond length equalization in the five-membered ring and C—C bond length alternation in the six-membered rings, indicating aromatic electron delocalization in the five-membered rings and loss of aromaticity in the six-membered rings.

Recently, we have reported the synthesis and characterization of 9-silafluorenyl dianion (**3a**) by potassium reduction of 9,9-dichloro-9-silafluorene (**4a**) in refluxing tetrahydrofuran (THF; Scheme 1).<sup>13,14</sup> Both X-ray crystal structure and NMR spectroscopy of **3a** indicated considerable electron delocalization in the five-membered ring, and thus we proposed that dianion **3a** had aromatic character.

\* To whom correspondence should be addressed. E-mail: west@chem.wisc.edu.

<sup>†</sup> University of Wisconsin—Madison.

<sup>‡</sup> Institut für Anorganische Chemie der Goethe Universität Frankfurt.

<sup>§</sup> Current address: National Starch and Chemical Company, 10 Funderne Avenue, Bridgewater, NJ 08807.

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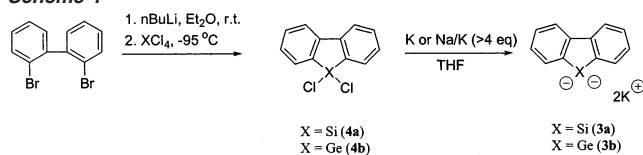
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## Scheme 1



We now report the synthesis, X-ray structure, aromaticity and chemistry of 9-germafluorenyl dianion (**3b**). Quantum mechanical calculations were carried out to obtain geometric and magnetic criteria to investigate the aromaticity of both the five-membered and six-membered rings of **3b** and its silicon analogue **3a**. Related to this work, we will also discuss the synthesis and structural studies of 9,9'-bifluorenyl dianions (**6**, **8**, **9**) for three group 14 elements: carbon, silicon, and germanium.

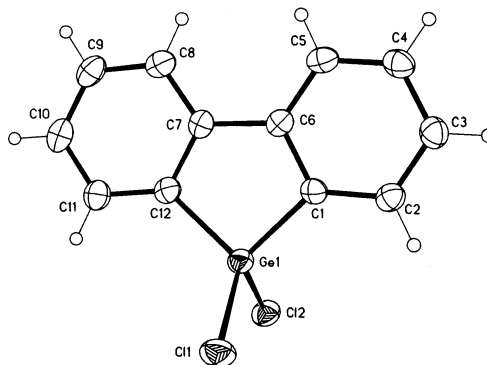
## Results and Discussion

Synthesis of 9,9-dichloro-9-germafluorene (**4b**), the precursor for dianion **3b**, has been described in the literature.<sup>15,16</sup> However, we found that **4b** could be prepared in much higher yield (74%) than reported earlier by reaction of 2,2'-dibromobiphenyl with *n*-butyllithium and germanium tetrachloride (Scheme 1). A thermal ellipsoid diagram and crystal parameters for **4b** are shown in Figure 1 and Table 1. The two benzenoid six-membered rings have equal C–C bond lengths (1.40 Å), while the five-membered germole ring is cyclopentadiene-like with a C–C bond length of 1.51 Å and a C=C bond length of 1.42 Å.

Reduction of **4b** with excess sodium/potassium alloy ( $\geq 4$  equiv of K) in THF at room temperature or with potassium metal in refluxing THF gave a dark green solution containing the potassium salt of 9-germafluorenyl dianion, **3b**. Deep green crystals of **3b** were isolated from THF/hexane solution in the presence of 18-crown-6 and Na/K. The structures and crystal parameters for **3b** are shown in Figures 2 and 3 and Table 1. There are two types of structures for **3b** in each unit cell. In the first type, designated **3b'**, both K atoms are  $\eta^5$ -bonded to the Ge-containing ring (Figure 2). The second type, which we designate **3b''**, contains one K atom  $\eta^5$ -bonded to the germole ring, and the other coordinated mainly to several carbon atoms of the germafluorene ring, as shown in Figure 3. Each of the K atoms is also coordinated by a crown ether molecule.

The five-membered rings in both kinds of **3b** dianions contain nearly equalized C–C bond lengths, indicating considerable delocalization of electrons in the five-membered rings (Figure 4). Alternation of bond lengths, indicating some localization of electron density, is found in the six-membered benzene rings. Thus, aromatic delocalization into the germole rings of **3b** appears to take precedence over benzenoid delocalization, as was found earlier for **3a**.<sup>13,14</sup> In **3b'**, the bond lengths are distributed almost symmetrically about the two halves of the anion, but in the less symmetrical form **3b''** there is more variation, consistent with the greater polarization in this anion.

Table 2 shows a comparison of <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of 9-germafluorenyl dianion **3b** and corresponding di-



**Figure 1.** Thermal ellipsoid diagram of structure **4b**. Selected bond lengths (Å) and angles (deg): Ge(1)–C(1) 1.926(3), Ge(1)–Cl(1) 2.1660(9), C(1)–C(2) 1.404(4), C(1)–C(6) 1.422(4), C(2)–C(3) 1.400(5), C(3)–C(4) 1.398(5), C(4)–C(5) 1.399(5), C(5)–C(6) 1.401(4), C(6)–C(7) 1.507(4), C(1)–Ge(1)–C(12) 92.86(13), C(1)–Ge(1)–Cl(1) 116.39(9), Cl(1)–Ge(1)–Cl(2) 103.40(4), C(6)–C(1)–Ge(1) 106.9(2), C(1)–C(6)–C(7) 116.4(3).

chloride **4b** with their silicon analogues **3a** and **4a**. The resonance peaks of the dianions, **3a** and **3b**, in both <sup>1</sup>H and <sup>13</sup>C NMR spectra, are spread out over wide ranges: from 8.42 to 6.36 ppm ( $\Delta\delta = 2.06$ ) for **3a** and from 8.42 to 6.31 ( $\Delta\delta = 2.11$ ) for **3b** in <sup>1</sup>H NMR; from 167.86 to 110.53 ppm ( $\Delta\delta = 57.33$ ) for **3a** and from 178.85 to 111.40 ppm ( $\Delta\delta = 67.45$ ) for **3b** in <sup>13</sup>C NMR. In comparison, the peak ranges are 7.87–7.31 ppm ( $\Delta\delta = 0.56$ ) for precursor dichloride **4a** and 8.03–7.47 ppm ( $\Delta\delta = 0.56$ ) for dichloride **4b** in <sup>1</sup>H NMR, and 146.75–122.08 ppm ( $\Delta\delta = 24.67$ ) for **4a** and 143.13–123.10 ppm ( $\Delta\delta = 20.03$ ) for **4b** in <sup>13</sup>C NMR. These chemical shift variations in both dianions, **3a** and **3b**, are consistent with electron localization and loss of aromaticity in the benzene rings.

Quantum mechanical calculations<sup>17</sup> at the hybrid density functional B3LYP/6-31+G(d) level<sup>18,19</sup> were carried out to evaluate the aromaticity of the dianions, **3a,b**, in comparison to their protonated analogues **3a(H<sub>2</sub>)** and **3b(H<sub>2</sub>)** and to a set of standard compounds. The obtained molecular structures for the dianions **3a,b** (see Table 3) agree well with the experimental structures found for the potassium salts. In agreement with the structural analysis of the experimental geometries, the calculated structures of the dianions **3a,b** reveal a bond length equalization for the central five-membered rings and increased bond length alternation for annelated benzene when compared to their saturated analogues **3a(H<sub>2</sub>)** and **3b(H<sub>2</sub>)**. A quantitative measure of aromaticity based on bond length equalization was suggested by Julg using the parameter *A*,<sup>20</sup> which is widely used as a structural measure for aromaticity.<sup>21,22</sup> Julg's parameter *A* is defined by the difference between the individual CC bond length  $r_i$  and the average CC bond length

(17) All calculations were performed with Gaussian 94, Revisions C2-E2, and Gaussian 98 Revisions A3-A7, Gaussian, Inc., Pittsburgh, PA, 1995 and 1999.

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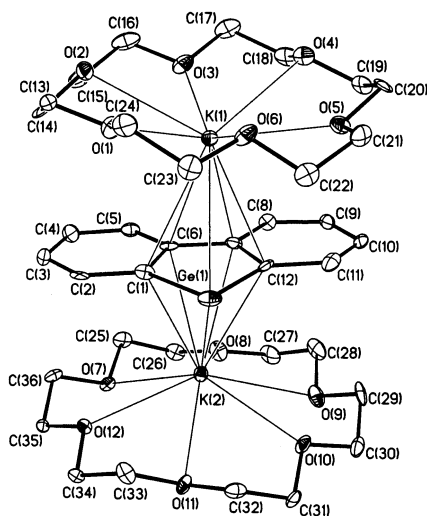
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**Table 1.** Crystallographic Data<sup>a</sup> for Compounds **3b**, **4**, **6**, **8**, **9**, and **10**

	4·3b·2THF·7(18-c-6)	4	6·4DME	8·4DME	9·1.613Et <sub>2</sub> O·0.387THF <sup>d</sup>	10
formula	C <sub>140</sub> H <sub>216</sub> Ge <sub>4</sub> K <sub>8</sub> O <sub>44</sub>	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub> Ge	C <sub>40</sub> H <sub>56</sub> K <sub>2</sub> O <sub>8</sub> Ge <sub>2</sub>	C <sub>40</sub> H <sub>56</sub> K <sub>2</sub> O <sub>8</sub> Si <sub>2</sub>	C <sub>34</sub> H <sub>35.23</sub> K <sub>2</sub> O <sub>2</sub>	C <sub>28</sub> H <sub>22</sub>
fw	3206.29	295.67	888.23	799.23	554.05	358.46
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> <b>1</b>	<i>P</i> <b>1</b>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> <b>1</b>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Z	1	2	2	2	2	4
T, °C	−100	−140	−140	−140	−140	−100
a, Å	10.502 (2)	7.3066 (11)	12.6292 (7)	12.6822 (15)	10.022 (8)	12.7914 (14)
b, Å	16.601 (3)	9.1777 (14)	12.8673 (7)	12.7774 (11)	12.251 (8)	11.9120 (12)
c, Å	23.357 (4)	9.5212 (15)	13.3347 (7)	13.2890 (15)	12.755 (10)	12.8235 (14)
α, deg	99.846 (3)	66.887 (2)	90	90	89.70 (2)	90
β, deg	102.058 (3)	89.616 (2)	93.776 (2)	94.019 (2)	89.962 (12)	102.873 (2)
γ, deg	94.103 (3)	86.590 (2)	90	90	67.56 (2)	90
V, Å <sup>3</sup>	3899.2 (13)	586.09 (16)	2162.2 (2)	2148.1 (4)	1447.4 (19)	1904.8 (4)
d <sub>calc</sub> , g cm <sup>−3</sup>	1.365	1.675	1.364	1.236	1.271	1.250
μ, mm <sup>−1</sup>	1.054	3.030	1.629	0.324	0.356	0.071
θ range, deg	0.91–21.00	2.33–28.31	2.15–28.27	2.15–25.00	2.20–25.00	2.03–28.36
GOF (F <sup>2</sup> )	1.141	1.113	0.971	1.012	0.989	1.040
R <sub>1</sub> <sup>b</sup> (wR <sub>2</sub> <sup>c</sup> ), %	14.6 (30.4)	3.50 (10.0)	5.84 (14.4)	5.09 (11.1)	8.19 (22.6)	4.37 (10.9)

<sup>a</sup> Obtained with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). <sup>b</sup> R<sub>1</sub> = Σ||F<sub>o</sub>| − |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>c</sup> wR<sub>2</sub> = [Σw(F<sub>o</sub><sup>2</sup> − F<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>. <sup>d</sup> One solvent site appeared to be occupied by both diethyl ether and tetrahydrofuran. The refined occupancies for this site are 0.613(6) for diethyl ether, O(1B)–C(30B), and 0.387(6) for THF, O(1′)–C(30′).

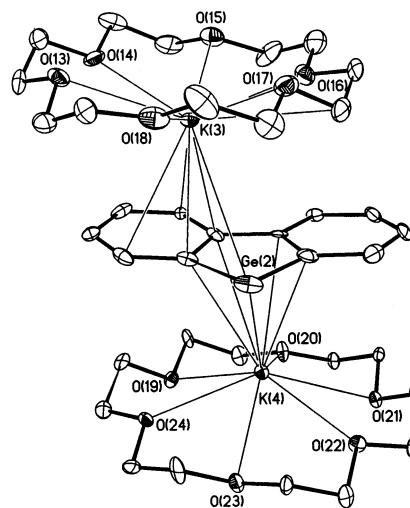


**Figure 2.** Thermal ellipsoid diagram of **3b'**. Selected bond lengths (Å) and angles (deg): Ge(1)–C(1) 1.974(18), Ge(1)–K(2) 3.327(4), Ge(1)–K(1) 3.530(4), Ge(2)–C(13) 1.935(18), Ge(2)–K(4) 3.357(4), Ge(2)–K(3) 3.532(4), K(1)–C(6) 3.132(19), K(1)–C(7) 3.196(18), K(1)–C(1) 3.211(18), K(1)–C(12) 3.341(16), K(3)–C(19) 3.073(19), K(3)–C(13) 3.202(19), K(3)–C(24) 3.292(19), C(1)–C(6) 1.41(3), C(1)–C(2) 1.43(3), C(2)–C(3) 1.35(3), C(3)–C(4) 1.38(3), C(4)–C(5) 1.40(3), C(5)–C(6) 1.39(3), C(6)–C(7) 1.47(2), C(13)–C(18) 1.44(2), C(13)–C(14) 1.45(3), C(14)–C(15) 1.35(3), C(15)–C(16) 1.40(3), C(16)–C(17) 1.38(2), C(17)–C(18) 1.40(2), C(18)–C(19) 1.48(3), C(12)–Ge(1)–C(1) 82.4(7), C(1)–Ge(1)–K(2) 126.5(5), C(1)–Ge(1)–K(1) 64.3(5), K(2)–Ge(1)–K(1) 143.40(11), C(13)–Ge(2)–C(24) 84.7(8), C(13)–Ge(2)–K(3) 64.1(5), K(4)–Ge(2)–K(3) 119.43(11), C(6)–C(1)–Ge(1) 115.5(13), C(1)–C(6)–C(7) 113.0(16), C(18)–C(13)–Ge(2) 115.0(13), C(13)–C(18)–C(19) 114.4(15).

*r* of the *n* bonds in cyclic molecules (eq 1).

$$A = 1 - (225/n) \sum (1 - r_i/r)^2 \quad (1)$$

For benzene, *A* = 1 and the scaling factor 225 in eq 1 is used to set *A* = 0 for Kekulé benzene (*r*(C–C) = 1.520 and *r*(C=C) = 1.330).<sup>20</sup> In both dianions the parameter *A* for the five-membered ring is larger than that in the neutral compounds (*A* = 0.99 (**3a**), *A* = 0.88 (**3a**(H<sub>2</sub>)), *A* = 1.0 (**3b**), *A* = 0.87 (**3b**(H<sub>2</sub>))), and for the annelated benzene rings the reverse trend is computed: *A* decreases comparing the dihydrido species with



**Figure 3.** Thermal ellipsoid diagram of **3b''**. Selected bond lengths and angles: Ge(2)–K(3) 3.8715(19), Ge(2)–K(4) 3.4341(18), K(3)–C(37) 3.055(8), K(3)–C(41) 3.324(7), K(3)–C(38) 3.342(8), K(4)–C(37) 3.361(8), K(4)–C(42) 3.305(8), K(4)–C(43) 3.184(7), K(4)–C(48) 3.178(9), C(37)–Ge(2)–C(48) 84.7(3), C(37)–Ge(2)–K(4) 71.2(2), C(48)–Ge(2)–K(4) 77.1(2), C(48)–Ge(2)–K(4) 65.8(2), K(4)–Ge(2)–K(3) 113.24(4).

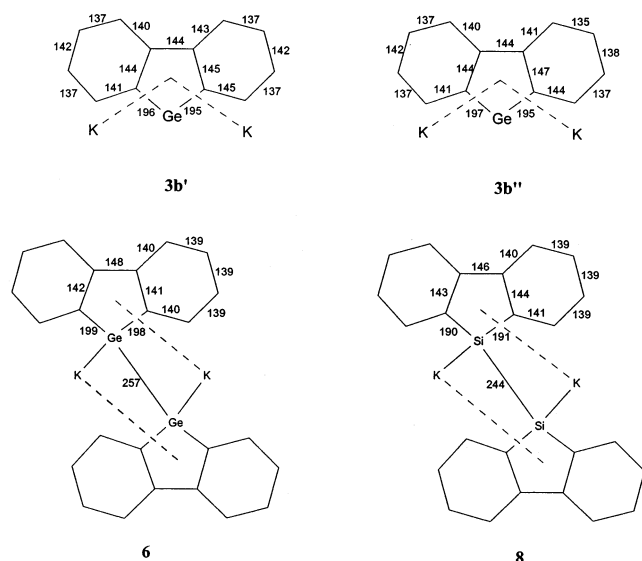
the dianions (*A* = 0.99 (**3a**(H<sub>2</sub>)), *A* = 0.94 (**3a**), *A* = 0.99 (**3b**(H<sub>2</sub>)), *A* = 0.94 (**3b**)).

Recently, Schleyer and co-workers have proposed the use of the negative of the magnetic shieldings computed at the ring center, or nucleus independent chemical shift (NICS), as a simple gauge for aromaticity.<sup>23</sup> As an indicator of aromaticity, NICS agrees well with the energetic, geometric, and magnetic criteria in five-membered heterocycles, and also has the advantage of being less dependent on ring size and not requiring an increment system. Moreover, NICS is an effective probe of the individual rings in polycyclic systems.<sup>23–25</sup> We have carried out NICS calculations on the fluorenyl dianion **3a,b** and similar analogues with the ghost atom located 2.0 Å above the ring

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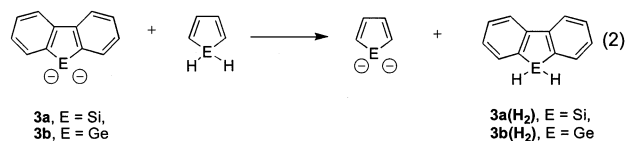
**Figure 4.** Comparison of selected bond lengths (pm) in the two forms of dipotassio-9-germafluorenyl dianion, **3b'** and **3b''**, dipotassio-9,9'-digerma-9,9'-bifluorenyl dianion (**6**), and dipotassio-9,9'-disila-9,9'-bifluorenyl dianion (**8**). To facilitate comparison, values are given only to three significant figures.

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  Chemical Shifts for Dipotassio-9-silafluorenyl Dianion, **3a**,<sup>16</sup> Dipotassio-9-germafluorenyl Dianion, **3b**, 9,9-Dichloro-9-silafluorene, **4a**,<sup>16</sup> and 9,9-Dichloro-9-germafluorene, **4b**

<b>3a</b> (THF- <i>d</i> <sub>6</sub> )	<b>4a</b> (THF- <i>d</i> <sub>6</sub> )	<b>3b</b> (THF- <i>d</i> <sub>6</sub> )	<b>4b</b> (THF- <i>d</i> <sub>6</sub> )
$^1\text{H}$ (ppm)			
8.42 (br, 2H)	7.87 (d, 2H)	8.42 (br, 2H)	8.03 (d, 2H)
7.83 (br, 2H)	7.66 (d, 2H)	7.92 (br, 2H)	7.82 (d, 2H)
6.55 (br, 2H)	7.49 (t, 2H)	6.41 (br, 2H)	7.61 (t, 2H)
6.36 (br, 2H)	7.31 (t, 2H)	6.31 (br, 2H)	7.47 (t, 2H)
$^{13}\text{C}$ (ppm)			
167.86 (C)	146.75 (C)	178.85 (C)	143.13 (C)
134.41 (CH)	133.49 (CH)	136.38 (CH)	133.98 (CH)
131.58 (C)	133.19 (CH)	132.82 (C)	132.84 (CH)
121.14 (CH)	131.39 (C)	121.89 (CH)	132.04 (C)
115.55 (CH)	129.44 (CH)	113.89 (CH)	130.67 (CH)
110.53 (CH)	122.08 (CH)	111.40 (CH)	123.10 (CH)

centroid [NICS(2.0)] in order to minimize local contributions of  $\sigma$  bonds<sup>26,27</sup> and to minimize the in-plane deshielding influence from the annelated benzene rings in the central five-membered ring.<sup>24,28</sup> The results are summarized in Table 3 and Scheme 2. The five-membered rings in both dianions **3a,b** have more negative NICS values than the six-membered benzenoid rings, indicating greater aromatic character for the five-membered ring, in contrast to the neutral fluorenes **3a**(H<sub>2</sub>) and **3b**(H<sub>2</sub>), for which NICS calculations suggest nonaromaticity of the five-membered ring (−1.1 (**3a**(H<sub>2</sub>)), −1.3 (**3b**(H<sub>2</sub>))) and aromaticity for the benzenoid ring. This trend, increase of the magnitude of the NICS value of the five-membered ring at the expense of the NICS value of the annelated benzene, is found also for fluorenyl monoanion and fluorene, although to a smaller extent (Scheme 2).<sup>24</sup> Interestingly, the dianions **3a,b** appear by the NICS measure to be not only more aromatic than their

monocyclic counterparts, the dianions of silole and germole,<sup>8,9,22,29</sup> but also more aromatic than most of the common monocyclic aromatic molecules (Scheme 2). In qualitative agreement, dianions **3a,b** are also thermodynamically more stable than their monocyclic analogues. Thus, according to the isodesmic eq 2 **3a** is 18.1 kcal mol<sup>−1</sup> more stable than the silole



dianion, and similarly **3b** is 17.2 kcal mol<sup>−1</sup> more stable than the germole dianion (B3LYP/6-31+G(d)). Thus, structural and magnetic criteria uniformly suggest that in dianions **3a,b** the central heterocyclic ring is more aromatic than the annelated benzene rings.

Dianion **3b** is extremely reactive toward electrophiles and oxidants. Nucleophilic reaction of **3b** with trimethylchlorosilane yielded 94% 9,9-bis(trimethylsilyl)-9-germafluorene (**5**, Scheme 3). In the absence of NaK, dianion **3b** easily underwent oxidation in THF solution by trace amounts of oxygen. The major oxidized product is a dimerized dianion, dipotassio-9,9'-digerma-9,9'-bifluorenyl dianion (**6**). Reaction of **6** with MeOH gave 9,9'-digerma-9,9'-bifluorene (**7**).

The X-ray crystal structure and parameters of **6** are shown in Figure 5 and Table 1. Unlike dianion **3b**, the lone pairs of electrons are largely localized at Ge atoms. C–C bond length alternation is observed for the five-membered germole ring, while the aromaticity of the benzenoid rings remains unchanged, with C–C bond lengths between 1.39 and 1.40 Å (Figure 4). Figure 4 also shows selected bond lengths of the silicon analogue of **6**, dipotassio-9,9'-disila-9,9'-bifluorenyl dianion (**8**). We have previously reported the synthesis and the X-ray crystal structure of **8** from a crystal solvated by THF.<sup>14</sup> In order to compare it with the structure of **6**, we obtained a crystal of **8** in DME/hexane solution and its structure is shown in Figure 6. The crystal structures from two different solvent systems are similar except that coordination numbers between the solvent molecules and K cations are different, with each K coordinating to two oxygen atoms in THF complexation and to four oxygen atoms in DME complexation. The structure of dianion **8** shows, in both crystals, similar C–C bond length alternation in the five-membered rings and bond equalization in the six-membered rings.

In general, dianions of germole,<sup>9</sup> germaindene,<sup>12</sup> germafluorene, and the corresponding silicon analogues<sup>5,7,11,13,29</sup> are all aromatic, while the monoanions of these compounds are normally nonaromatic with the lone pair of electrons localized at germanium or silicon atoms.<sup>6,14,30–32</sup> Dimer dianions **6** and **8** are structurally similar to the monoanions, and thus they are also nonaromatic.

For comparison with the Si and Ge compounds, we also synthesized the dipotassium salt of 9,9'-bifluorenyl dianion (**9**)

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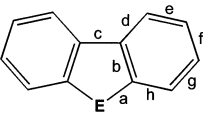
(28) For comparison the NICS values at the ring center are NICS(0): **3a**: −9.8 (five-membered ring), −6.1 (six-membered ring); **3b**: −6.8 (five-membered ring), −6.0 (six-membered ring).

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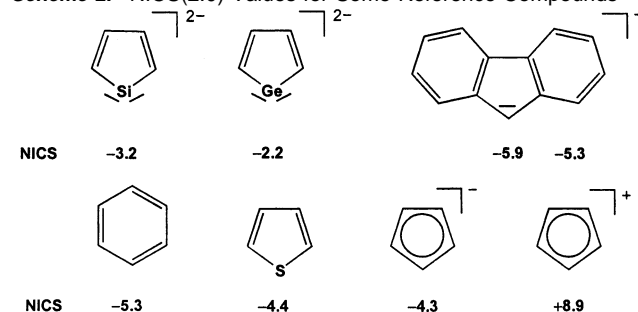
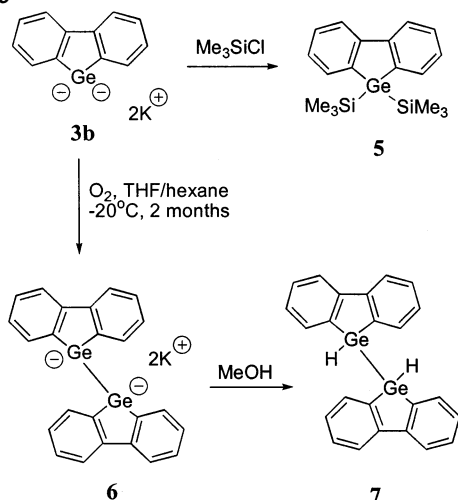
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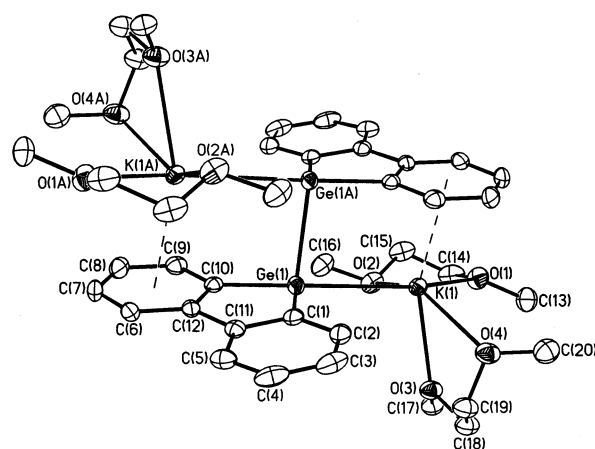
**Table 3.** Calculated Geometries (at B3LYP/6-31+G(d)), Julg Parameters *A*, and NICS Values of Sila- and Germafluorene Dianions and Their Dihydro Analogues


compd	E	a	b	c	d	e	f	g	h	NICS(5)	NICS(6)	<i>A</i> (5)	<i>A</i> (6)
<b>3a</b>	Si <sup>2-</sup>	1.889	1.464	1.442	1.413	1.395	1.427	1.392	1.421	-6.0	-4.0	0.99	0.94
<b>3b</b>	Ge <sup>2-</sup>	1.954	1.456	1.446	1.412	1.395	1.424	1.392	1.416	-5.0	-4.0	1.00	0.94
<b>3a(H<sub>2</sub>)</b>	SiH <sub>2</sub>	1.878	1.420	1.490	1.401	1.397	1.399	1.400	1.398	-1.1	-4.8	0.88	0.99
<b>3b(H<sub>2</sub>)</b>	GeH <sub>2</sub>	1.931	1.416	1.490	1.402	1.397	1.398	1.399	1.394	-1.3	-4.9	0.87	0.99

**Scheme 2.** NICS(2.0) Values for Some Reference Compounds**Scheme 3**

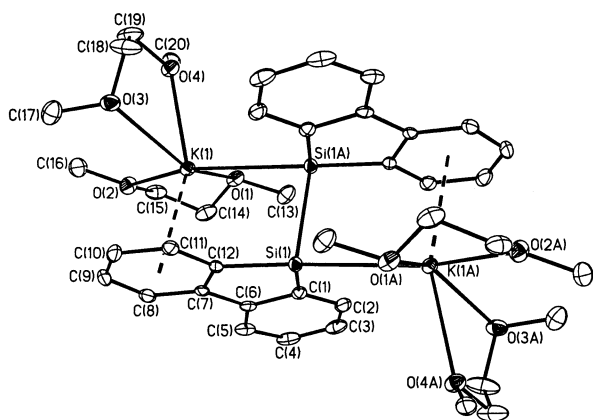
by reacting 9-bromofluorene with *n*-BuLi in Et<sub>2</sub>O followed by K in THF (Scheme 4). The X-ray crystal structure of **9** and its parameters are shown in Figure 7 and Table 1. The two fluorenyl rings of **9** share an in-plane axis but twist with respect to each other by an angle of 46.2(5)°. In comparison, the two fluorenyl rings in either germabifluorenyl dianion **6** or sila-bifluorenyl dianion **8** are parallel but point away from each other. An interesting structural feature of **9** is that, in the same molecule, one fluorenyl group is only η<sup>5</sup>-bonded to a potassium cation at the five-membered ring, while the other fluorenyl group is η<sup>6</sup>-bonded to a potassium cation at the six-membered rings (Figure 8).

Alkali metal salts of 9,9'-bifluorenyl dianion have previously been synthesized from 9,9'-bifluorene<sup>33</sup> or 9,9'-bifluorenylidene<sup>34–36</sup> and studied for their redox reactivity<sup>34</sup> and

**Figure 5.** Thermal ellipsoid diagram of structure **6**. Selected bond lengths (Å) and angles (deg): K(1)–Ge(1) 3.4004(11), Ge(1)–C(1) 1.988(5), Ge(1)–Ge(1)#1 2.5690(10), C(1)–C(2) 1.399(7), C(1)–C(11) 1.420(6), C(2)–C(3) 1.386(7), C(3)–C(4) 1.390(8), C(4)–C(5) 1.366(7), C(10)–Ge(1)–C(1) 84.02(19), C(1)–Ge(1)–Ge(1A) 99.99(12), C(10)–Ge(1)–K(1) 159.80(13), C(1)–Ge(1)–K(1) 114.65(14), Ge(1A)–Ge(1)–K(1) 88.47(3), C(11)–C(1)–Ge(1) 113.2(3), C(7)–C(6)–K(1A) 86.5(3), C(12)–C(6)–K(1A) 69.8(3), C(6)–C(7)–K(1A) 70.4(3), C(8)–C(7)–K(1A) 79.6(3), C(8)–C(9)–K(1A) 85.5(3), C(10)–C(9)–K(1A) 69.7(2), C(9)–C(10)–K(1A) 85.9(3), C(12)–C(10)–K(1A) 75.5(2), Ge(1)–C(10)–K(1) 107.23(16), C(1)–C(11)–C(12) 114.1(4), C(6)–C(12)–K(1A) 85.3(3), C(10)–C(12)–K(1A) 78.6(2), C(11)–C(12)–K(1A) 104.8(3).

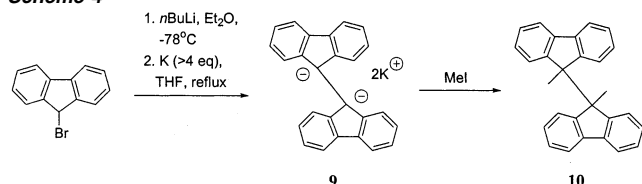
pK<sup>+</sup>s.<sup>37,38</sup> The X-ray crystal structure of a dilithium salt of **9** has been reported, and lithium cations were found to be η<sup>5</sup>-bonded to the five-membered rings.<sup>33</sup> Figure 9 shows a comparison of selected bond lengths for the dilithium salt and dipotassium salt of **9**. In the structure of the lithium salt, C–C bond lengths in the five-membered rings are nearly equal whereas those in the six-membered rings alternate somewhat, indicating aromatic delocalization of the lone pair electrons in the five-membered rings. Theoretical calculations (B3LYP/6-31G(d)\* and MP2/6-31G(d)\*) showed similar bond length equalization in five-membered rings and bond alternation in six-membered rings in both fluorenyl and indenyl monoanions.<sup>24</sup> All monoanions of cyclopentadienyl, indenyl, and fluorenyl rings are apparently aromatic,<sup>24</sup> and the dimer dianion **9** is similar. However, there is one notable difference between the structures of the dipotassium and dilithium salts of **9**. The C–C bond lengths in the structure of dipotassium salt are equalized not only in the five-membered ring but also in the six-membered

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**Figure 6.** Thermal ellipsoid diagram of structure **8**. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.909(3), Si(1)–Si(1)#1 2.4415(16), Si(1)–K(1)#1 3.4565(10), K(1)–Si(1)#1 3.4565(10), C(1)–C(2) 1.410(4), C(1)–C(6) 1.435(4), C(2)–C(3) 1.388(4), C(3)–C(4) 1.390(5), C(4)–C(5) 1.391(4), C(5)–C(6) 1.399(4), C(6)–C(7) 1.464(4), C(12)–Si(1)–C(1) 87.14(13), C(1)–Si(1)–Si(1A) 103.28(9), C(12)–Si(1)–K(1A) 158.06(9), C(1)–Si(1)–K(1A) 112.09(9), Si(1A)–Si(1)–K(1A) 86.41(4), C(12)–K(1)–C(7) 26.26(7), C(12)–K(1)–Si(1A) 60.63(5), C(6)–C(1)–Si(1) 112.3(2), C(1)–C(6)–C(7) 113.5(2), C(8)–C(7)–K(1) 86.19(17), C(12)–C(7)–K(1) 76.34(15), C(6)–C(7)–K(1) 105.24(16), C(9)–C(8)–K(1) 85.70(18), C(7)–C(8)–K(1) 69.16(15), C(8)–C(9)–K(1) 71.46(17), C(10)–C(9)–K(1) 78.25(18), C(11)–C(10)–K(1) 70.66(17), C(9)–C(10)–K(1) 79.02(19), C(10)–C(11)–K(1) 86.30(19), C(12)–C(11)–K(1) 69.61(15), C(7)–C(12)–K(1) 77.39(15), Si(1)–C(12)–K(1) 106.48(10).

#### Scheme 4

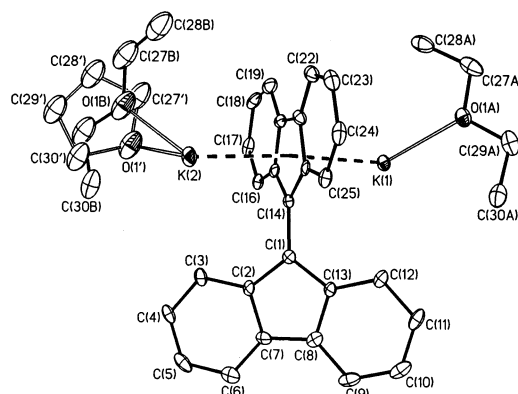


rings, and thus the electron delocalization may be somewhat different in this compound.

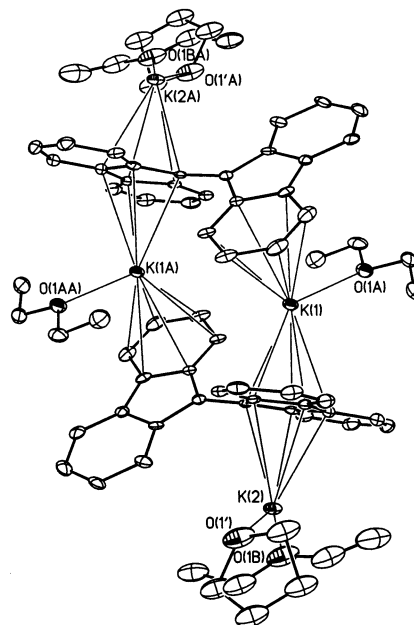
Reaction of **9** with MeI gave 9,9'-dimethyl-9,9'-bifluorene (**10**) as a major product, a known compound (Scheme 4).<sup>39</sup> The crystal structure of **10** is shown in Figure 10. Interestingly, the two fluorenyl rings are *cis* to each other with a torsional angle of 58–59°. A  $\pi$ – $\pi$  interaction between the outer benzoid rings in the fluorenyl moiety may favor such a conformation. The distance of C(1) and C(15) connecting the two fluorenyl rings is 1.5970(18) Å, quite long for a C–C single bond. Steric hindrance between two of the methyl groups, at a distance of 3.126 Å, may account for the lengthening of this C–C bond. This observation confirms the results of the NMR study by Olah et al., that hindered motion exists between the central C–C bond of **10** and its derivatives.<sup>29</sup> Other selected bond lengths of **10** are shown in Figure 9.

#### Conclusions

The NaK reduction of 9,9'-dichloro-9-germafluorene **4b** gave dipotassio-9-germafluorenyl dianion **3b** quantitatively. The X-ray structure of **3b** shows C–C bond length equalization in the five-membered ring and C–C bond length alternation in benzenoid rings, indicating aromatic delocalization of electrons



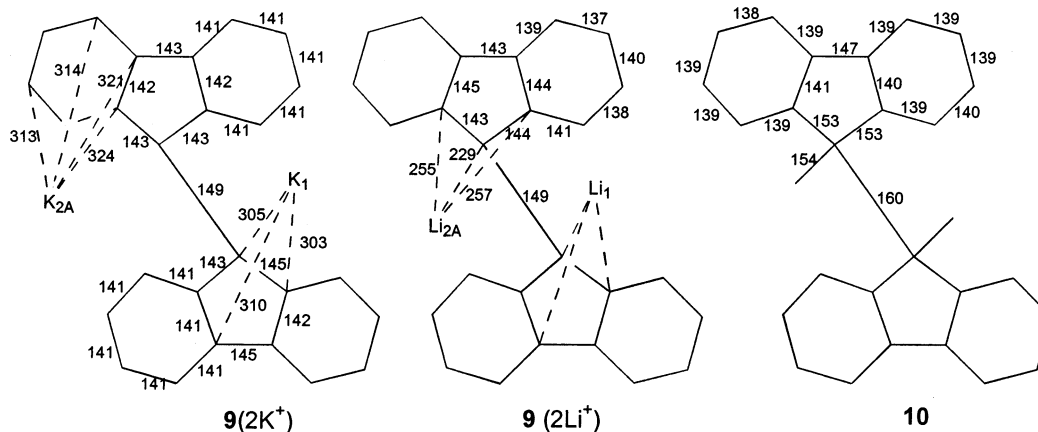
**Figure 7.** Partial thermal ellipsoid diagram of structure **9**. Selected bond lengths (Å) and angles (deg): K(1)–C(15) 3.029(4), K(1)–C(14) 3.052(4), K(1)–C(20) 3.098(5), K(2)–C(26) 3.009(5), K(2)–C(14) 3.022(5), K(2)–C(15) 3.114(4), K(2)–C(20) 3.150(5), C(1)–C(2) 1.427(7), C(1)–C(14) 1.490(8), C(2)–C(3) 1.413(3), C(2)–C(7) 1.415(3), C(3)–C(4) 1.407(3), C(4)–C(5) 1.408(3), C(5)–C(6) 1.407(3), C(6)–C(7) 1.408(3), C(7)–C(8) 1.427(8), C(14)–C(15) 1.431(8), C(14)–C(26) 1.445(8), C(15)–C(16) 1.411(3), C(15)–C(20) 1.414(3), C(16)–C(17) 1.407(3), C(17)–C(18) 1.407(3), C(18)–C(19) 1.405(3), C(19)–C(20) 1.412(3), C(20)–C(21) 1.453(8), C(13)–C(1)–C(2) 106.1(5), C(2)–C(1)–C(14) 126.7(5), C(7)–C(2)–C(1) 109.6(4), C(2)–C(7)–C(8) 107.2(4), C(16)–C(15)–C(20) 119.0(5), C(16)–C(15)–C(14) 131.6(5), C(20)–C(15)–C(14) 109.4(4), K(1)–C(15)–K(2) 133.96(17), C(15)–C(20)–C(21) 107.4(4), K(1)–C(20)–K(2) 129.61(16), K(2)–C(21)–K(1) 130.58(16), K(2)–C(26)–K(1) 135.35(17).



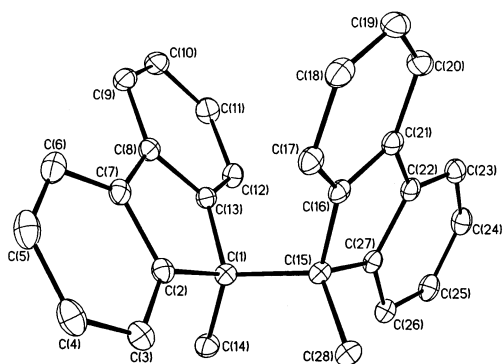
**Figure 8.** Extended structure for **9**.

into the five-membered germole ring of **3b**. By the NICS criterion, the five-membered rings are more aromatic than the six-membered rings in both germafluorenyl and silafluorenyl dianions. Oxidation of **3b** leads to a dimerized dianion **6** which, like its silicon analogue **8**, has C–C bond length alternation in the five-membered rings, and thus the negative charges are localized at the germanium or silicon atoms. On the other hand, the dipotassium salt of 9,9'-bifluorenyl dianion (**9**), the carbon analogue of **6**, has aromatic character, since the X-ray crystal structure of **9** shows C–C bond length equalization in the both five- and six-membered rings.

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**Figure 9.** Comparison of selected bond lengths (pm) in dipotassium salt and dilithium salt<sup>23</sup> of 9,9'-fluorenyl dianion (**9**) and 9,9'-dimethyl-9,9'-bifluorene (**10**).



**Figure 10.** Thermal ellipsoid diagram of structure **10**. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.5297(17), C(1)–C(14) 1.5385(18), C(1)–C(15) 1.5970(18), C(2)–C(3) 1.3907(19), C(2)–C(7) 1.4027(19), C(3)–C(4) 1.3950(19), C(4)–C(5) 1.389(2), C(5)–C(6) 1.385(2), C(6)–C(7) 1.3948(18), C(7)–C(8) 1.4656(19), C(2)–C(1)–C(13) 100.92(10), C(2)–C(1)–C(14) 110.16(11), C(2)–C(1)–C(15) 111.00(10), C(14)–C(1)–C(15) 113.34(10), C(7)–C(2)–C(1) 110.77(11), C(2)–C(7)–C(8) 108.77(11).

## Experimental Section

**9,9-Dichloro-9-germafluorene (4b).** A solution of 2,2'-dibromobiphenyl (10.0 g, 32.1 mmol) in Et<sub>2</sub>O (150 mL) was cooled to –78 °C under an argon atmosphere, and *n*-BuLi (1.6 M in hexane, 42 mL, 67.2 mmol) was added. The reaction solution was allowed to warm to room temperature and stirred overnight. A cloudy yellow solution was obtained. The resulting solution was cannulated into a solution of GeCl<sub>4</sub> (10 g, 46.6 mmol) in Et<sub>2</sub>O (100 mL) at –95 °C. The reaction mixture was stirred at –95 °C for 4 h and then at room temperature overnight. A yellow solution and a white precipitate were obtained. The white precipitate, mostly LiCl, was removed by filtration under argon, and excess GeCl<sub>4</sub> and solvents were removed by vacuum. The residue was recrystallized from toluene/hexane to give 7.01 g (73.9%) of **4b**. Selected data for **4b**: <sup>1</sup>H NMR (300.133 MHz, THF-*d*<sub>8</sub>): δ = 8.03 (d, 2H), 7.82 (d, 2H), 7.61 (t, 2H), 7.47 (t, 2H); <sup>13</sup>C NMR (125.710 MHz, THF-*d*<sub>8</sub>): δ = 144.13 (C), 133.98 (CH), 132.84 (CH), 132.04 (C), 130.67 (CH), 123.10 (CH); mp 112–114 °C; MS (EI), *m/z* (%): 295.6 (100) (M<sup>+</sup>), 260.4 (61) (M<sup>+</sup> – Cl); high-resolution MS (EI), calcd for [C<sub>12</sub>H<sub>8</sub>GeCl<sub>2</sub>] 291.9246, found 291.9253.

**Dipotassio-9-germafluorenyl Dianion (3b).** A solution of 9,9-dichloro-9-germafluorene, **4b**, (3.01 g, 10.2 mmol) in THF (100 mL) was stirred with sodium/potassium alloy (3.00 g, 76.7 mmol of K; 0.50 g, 21.7 mmol of Na) at room temperature for 6 h under an argon atmosphere. A white precipitate formed rapidly after 10 min of reaction, and the color of the solution changed to a dark red after 1 h. Hexane

(10 mL) and 18-crown-6 (5.00 g, 18.9 mmol) were added and the solution was allowed to precipitate. The supernatant solution was separated and cooled to –20 °C to give red crystals of **3b**. Selected data for **3b**: <sup>1</sup>H NMR (499.895 MHz, THF-*d*<sub>8</sub>): δ = 8.42 (br, 2H), 7.92 (br, 2H), 6.41 (br, 2H), 6.31 (br, 2H); <sup>13</sup>C NMR (125.710 MHz, THF-*d*<sub>8</sub>): δ = 178.85 (C), 136.38 (CH), 132.82 (C), 121.89 (CH), 113.89 (CH), 111.40 (CH).

**9,9-Bis(trimethylsilyl)-9-germafluorene (5).** An excess of Me<sub>3</sub>SiCl was added at 0 °C to a THF (100 mL) solution of **3b**, obtained from a reaction mixture of **4b** (1.00 g, 3.38 mmol) and K (1.00 g, 25.6 mmol) in refluxing THF (50 mL). The volatiles were removed under reduced pressure, and the residue was extracted with toluene (150 mL). The toluene solution was washed with water, dried with MgSO<sub>4</sub>, and filtered. Upon purifying by preparative GPC (toluene elution), white crystals of bis(trimethylsilyl) derivative **5** were obtained (1.18 g, 94.2%). Selected data for **5**: mp 68–68 °C; <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, 2H), 7.53 (d, 2H), 7.30 (t, 2H), 7.16 (t, 2H), 0.10 (s, 18H); <sup>13</sup>C NMR (125.710 MHz, CDCl<sub>3</sub>): δ = 147.52, 143.41, 133.55, 127.49, 126.43, 121.64, 0.02; <sup>29</sup>Si NMR (99.314 MHz, CDCl<sub>3</sub>): δ = –7.379; high-resolution MS (EI), calcd for [C<sub>18</sub>H<sub>26</sub>GeSi<sub>2</sub>] 372.0788, found 372.0802.

**Dipotassio-9,9'-digerma-9,9'-bifluorenyl Dianion (6); 9,9'-Digerma-9,9'-bifluorene (7).** A saturated solution of **3b** in DME (150 mL)/hexane (10 mL) was stored in a Schlenk flask at –20 °C for 2 months. Dark brown crystals of **6** formed in the bottom of the flask. The crystals were treated with MeOH. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (100 mL). After removal of toluene, white solid oligomer **7** was obtained. Selected data for **7**: <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>): δ = 7.91 (d, 4H), 7.62 (d, 4H), 7.44 (t, 4H), 7.28 (t, 4H), 5.33 (s, 2H, GeH); <sup>13</sup>C NMR (75.403 MHz, CDCl<sub>3</sub>): δ = 146.91, 136.62, 134.10, 129.58, 127.60, 121.96; MS (MALDI, anthracene matrix), *m/z*: 451.0 (M<sup>+</sup> – H), isotope pattern matches calcd; *m/z* (%) for (M<sup>+</sup> – H): 445.0 (16), 446.0 (4.4), 447.0 (44), 448.0 (24), 449.0 (92), 450.0 (40), 451.0 (100), 451.9 (48), 453.0 (78), 454.0 (24), 454.9.0 (26). <sup>1</sup>H NMR spectra of **4b**, **5**, and **7** were consistent with purity >97%.

**Dipotassio-9,9'-bifluorenyl Dianion (9).** A solution of 9-bromo-fluorene (5.00 g, 20.4 mmol) in Et<sub>2</sub>O (50 mL) was stirred with *n*-BuLi (1.6 M in hexane, 12.8 mL, 20.5 mmol) at room temperature for 1 h under an argon atmosphere. Potassium (2.00 g, 51.2 mmol) and THF (100 mL) were added, and the mixture was stirred at room temperature overnight. The color of the solution changed to a dark purple. Hexane (10 mL) was added, and the solution was allowed to precipitate. The supernatant solution was taken out and cooled to –20 °C to give orange crystals of **9**. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of **9** are the same as those in the literature.<sup>26</sup>

**9,9'-Dimethyl-9,9'-bifluorene (10).** An excess of MeI was added at 0 °C to a THF solution of **9**. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (150 mL). The toluene solution was washed with distilled water, dried with MgSO<sub>4</sub>, and filtered. After preparative GPC separation (toluene elution), white crystals of **10** were obtained. Selected data for **10**: mp 203–204 °C (lit.<sup>40</sup> 201–203 °C); <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>): δ = 7.40 (d, 4H), 7.17 (t, 4H), 7.01 (t, 4H), 6.79 (d, 4H), 1.89 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (75.403 MHz, CDCl<sub>3</sub>): δ = 149.69, 140.64, 127.00, 125.85, 124.11, 119.05, 55.77, 20.99; MS (EI), *m/z* (%): 358.2 (20) (M<sup>+</sup>), 179.1 (100) (1/2 M<sup>+</sup>); high-resolution MS (EI), calcd for [C<sub>28</sub>H<sub>22</sub>] 358.4883, found 358.4825.

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**Supporting Information Available:** X-ray crystallographic data for structure determination of **3b**, **4b**, **6**, **8**, **9**, and **10**; table with absolute energies for all calculated compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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