Aromatic Benzannulated Germole Dianions. The Dilithio and Disodio Salts of a Germaindenyl Dianion

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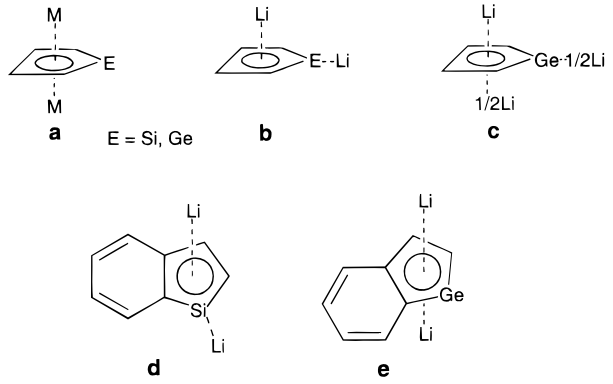
*Summary: Conversion of the neutral 1,1-dichloro-DPGI (**1**) (DPGI = 2,3-diphenyl-1-germaindene) to the lithium dianion (**2a**) or sodium dianion (**2b**) leads to the highly unusual phenomenon of aromatization of the GeC_4 portion of 1-germaindene at the expense of the aromatic annulated C_6 ring. Treatment of **2a** with trimethylchlorosilane gave the 1,1-bis(trimethylsilyl)-DPGI derivative (**3**) in high yield. The structure of **2a** was determined by X-ray crystallography and found to possess two η^5-coordinated lithium ions. The five-membered ring of the germaindenyl system undergoes significant carbon−carbon bond equalization upon formation of the dianion, while the remaining four carbon atoms become diene-like, exhibiting two short bonds separated by a long bond.*

Introduction

The structural characterization of the dianionic siloles and germoles by West,[1] Tilley,[2] and our group[3,4] provide strong support for our initial postulation, based on NMR data,[5] that these species were aromatic. All the spectroscopic data and the typical structures **a** and **b** in $R_4E^{2-}\cdot 2M^+$ (E = Si, Ge; M = Li, Na, and K) have also been supported by calculations.[6]

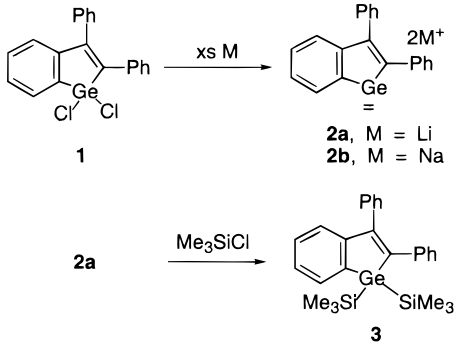


Recently we have reported the unique bonding structure **c** providing the strong possibility for the interconversion between the structures **a** and **b** in solution.[3] Moreover, we were also able to directly compare the aromaticity between the silole dianion and benzene in silaindenyl dianion molecule **d**, which indicates that the significant aromaticity in the silicon-containing ring is responsible for changing the fused benzene ring in the precursor to a cyclohexadiene moiety in the dianionic silaindene.[4]

Herein we report the synthesis and characterization of the first benzannulated germole dianions, dilithium DPGI (**2a**) (DPGI = 2,3-diphenyl-1-germaindene) and disodium DPGI (**2b**). To our surprise, we find that, upon formation of the dianion, the germanium-containing ring becomes aromatic, apparently at the expense of the fused benzene ring, which takes on the features of a conjugated diene (**e**).

Result and Discussion

Stirring of 1,1-dichloro-DPGI (**1**)[7] with excess lithium in THF produced a dark red solution. After removal of unreacted lithium, treatment of this solution with an excess of trimethylchlorosilane gave 1,1-bis(trimethylsilyl)-DPGI (**3**) in high yields (eq 1).



(1)

For comparative purposes, the molecular structure of 1,1-bis(trimethylsilyl)-DPGI (**3**) was determined. The X-ray structure of 1,1-bis(trimethylsilyl)-DPGI (**3**) is shown in Figure 1. The crystallographic data are in Table 1. Selected bond lengths and bond angles are listed in Table 2. The GeC_4 ring has inequivalent C−C distances, indicating isolated single (1.485 Å) and double

(1) (a) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608. (b) West, R.; Sohn, H.; Bankwitz, U.; Powell, D. R.; Mueller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002.

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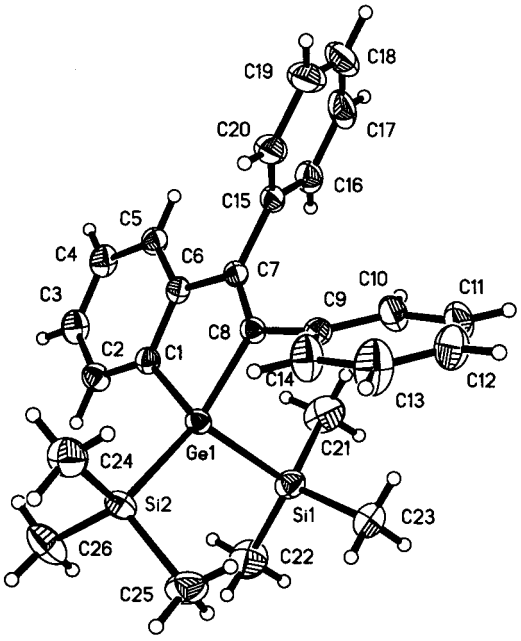

Figure 1. ORTEP drawing of **3** showing 30% probability ellipsoids.

Table 1. Crystal Data and Structure Refinement for 2a·LiCl·3TMEDA and 3

	2a·LiCl·3TMEDA	**3**
empirical formula	$C_{38}H_{62}ClGeLi_3N_6$	$C_{26}H_{32}GeSi_2$
fw	731.80	473.29
temp, K	298(2)	295(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a, Å	11.1629(10)	7.6855(11)
b, Å	11.1858(10)	26.523(4)
c, Å	17.4193(16)	12.7667(18)
α, deg	97.964(2)	90
β, deg	93.703(2)	94.531(2)
γ, deg	96.514(2)	90
volume (Å^3), Z	2133.1(3), 2	2594.3(6), 4
density(calcd), Mg/m^3	1.139	1.212
abs coeff, mm^{-1}	0.812	1.283
F(000)	780	992
cryst size, mm	0.3 × 0.4 × 0.3	0.6 × 0.6 × 0.8
θ range, deg	1.84−25.00	1.54−28.30
index ranges	$-13 \le h \le 13$	$-10 \le h \le 7$
	$-13 \le k \le 13$	$-35 \le k \le 35$
	$-15 \le l \le 20$	$-16 \le l \le 16$
no. of reflns collected	11 018	15 675
no. of ind reflns	7368 [R(int) = 0.0142]	5947 [R(int) = 0.0638]
no. of data/restraints/params	7368/0/442	5947/0/262
goodness-of-fit on F^2	0.946	0.994
final R indices [$I > 2\sigma(I)$]	R1 = 0.0428	R1 = 0.0339
	wR2 = 0.1040	wR2 = 0.0817
largest diff peak and hole, e Å^{-3}	0.682 and −0.623	0.416 and −0.555

(1.356, 1.410 Å) bonds. Meanwhile the fused six-membered carbon ring has the equalized C−C bond distances of benzene.

Compound **2a**, while extremely air sensitive, is thermally stable under argon. X-ray quality crystals of **2a** were grown from a concentrated ether solution in the presence of TMEDA (tetramethylethylenediamine) at room temperature. The X-ray structure of **2a** is shown in Figure 2. The crystallographic data are in Table 1. Selected bond lengths and bond angles are listed in Table 3. Unlike the silaindenyl dianion, which has η^1- and η^5-lithium coordination with polymeric crystal

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 3

Ge(1)−C(1)	1.9477(18)	Ge(1)−C(8)	1.9615(18)
Ge(1)−Si(1)	2.3849(7)	Ge(1)−Si(2)	2.3838(6)
C(1)−C(2)	1.388(3)	C(1)−C(6)	1.410(3)
C(2)−C(3)	1.391(3)	C(3)−C(4)	1.378(3)
C(4)−C(5)	1.386(3)	C(5)−C(6)	1.396(3)
C(6)−C(7)	1.485(2)	C(7)−C(8)	1.356(2)
C(7)−C(15)	1.498(2)	C(8)−C(9)	1.481(2)
C(1)−Ge(1)−C(8)	88.23(7)	C(1)−Ge(1)−Si(1)	105.12(6)
C(8)−Ge(1)−Si(1)	101.73(6)	C(1)−Ge(1)−Si(2)	117.95(6)
C(8)−Ge(1)−Si(2)	125.06(5)	Si(1)−Ge(1)−Si(2)	114.46(2)
C(2)−C(1)−C(6)	119.66(17)	C(2)−C(1)−Ge(1)	131.84(15)
C(6)−C(1)−Ge(1)	108.42(12)	C(1)−C(2)−C(3)	120.1(2)
C(2)−C(3)−C(4)	120.33(18)	C(5)−C(4)−C(3)	120.38(19)
C(4)−C(5)−C(6)	120.18(19)	C(1)−C(6)−C(5)	119.32(17)
C(1)−C(6)−C(7)	116.38(15)	C(5)−C(6)−C(7)	124.30(17)
C(8)−C(7)−C(6)	116.63(15)	C(8)−C(7)−C(15)	123.63(16)
C(6)−C(7)−C(15)	119.73(15)	C(7)−C(8)−C(9)	126.83(16)
C(7)−C(8)−Ge(1)	109.79(12)	C(9)−C(8)−Ge(1)	122.10(13)

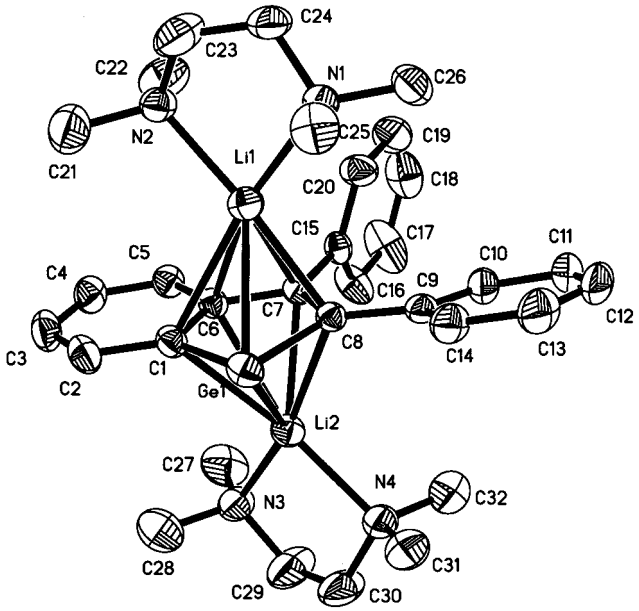

Figure 2. Thermal ellipsoid diagram (30% probability) of structure **2a**·2TMEDA. LiCl·TMEDA and all hydrogens are omitted for clarity.

linkage, the analysis of the X-ray data for **2a** shows two η^5-coordinated lithium ions with monomeric crystal packing. Most notable among the structural differences between the **2a** and **3** are those in the carbon−carbon bond lengths in both the germole ring and the six-membered carbon ring (Figure 3).

Significant shortening of the C6−C7 bond to 1.438 Å from 1.485 Å in **3** and lengthening of the C1−C6 and C7−C8 bonds to 1.443 and 1.483 Å, respectively, (1.410 and 1.356 Å in **3**) are observed in the germole ring of **2a**. In contrast, the three nearly equal (1.391, 1.378, 1.386 Å) carbon−carbon bonds linking C2, C3, C4, and C5 in **3**, consistent with a high degree of aromaticity in the six-membered ring, undergo bond length alternation (1.350, 1.412, 1.359 Å) in that portion of **2a** (Figure 3, a and b). The germanium carbon bonds in germoles appear to be relatively insensitive to the nature of the substituents on germanium (germanium−carbon bond distances: 1.949, 1.987 Å in **2a**; 1.948, 1.962 Å in **3**). This is similar to that observed in the analogous silaindene system. For example, the Si−C bond distances are 1.836 and 1.856 Å in 1,1-dichloro-3-*n*-butyl-

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 2a·LiCl·3TMEDA[a]

Ge(1)−C(1)	1.949(3)	Ge(1)−C(8)	1.987(2)
Ge(1)−Li(2)	2.694(4)	Ge(1)−Li(1)	2.716(4)
N(1)−Li(1)	2.227(5)	Li(1)−N(2)	2.115(5)
Li(1)−C(8)	2.295(5)	Li(1)−C(7)	2.330(5)
Li(1)−C(6)	2.496(5)	Li(1)−C(1)	2.604(5)
C(1)−C(2)	1.425(4)	C(1)−C(6)	1.443(4)
C(1)−Li(2)	2.566(5)	Li(2)−N(3)	2.120(5)
Li(2)−N(4)	2.143(5)	Li(2)−C(8)	2.340(5)
Li(2)−C(7)	2.350(5)	Li(2)−C(6)	2.471(5)
C(2)−C(3)	1.350(4)	C(3)−C(4)	1.412(5)
C(4)−C(5)	1.359(4)	C(5)−C(6)	1.420(4)
C(6)−C(7)	1.438(4)	C(7)−C(8)	1.438(3)
C(7)−C(15)	1.500(3)	C(8)−C(9)	1.483(4)
C(1)−Ge(1)−C(8)	83.28(11)	C(1)−Ge(1)−Li(2)	64.79(13)
C(8)−Ge(1)−Li(2)	57.65(12)	C(1)−Ge(1)−Li(1)	65.48(13)
C(8)−Ge(1)−Li(1)	55.85(12)	Li(2)−Ge(1)−Li(1)	98.13(14)
C(2)−C(1)−C(6)	116.8(3)	C(2)−C(1)−Ge(1)	128.7(2)
C(6)−C(1)−Ge(1)	114.54(19)	Li(2)−C(1)−Li(1)	104.46(17)
C(3)−C(2)−C(1)	122.7(3)	C(2)−C(3)−C(4)	120.0(3)
C(5)−C(4)−C(3)	120.3(3)	C(4)−C(5)−C(6)	121.3(3)
C(5)−C(6)−C(7)	126.5(2)	C(5)−C(6)−C(1)	118.9(2)
C(7)−C(6)−C(1)	114.5(2)	C(8)−C(7)−C(6)	113.7(2)
C(8)−C(7)−C(15)	128.5(2)	C(6)−C(7)−C(15)	117.5(2)
C(7)−C(8)−C(9)	124.8(2)	C(7)−C(8)−Ge(1)	113.93(18)
C(9)−C(8)−Ge(1)	121.26(18)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+1$.

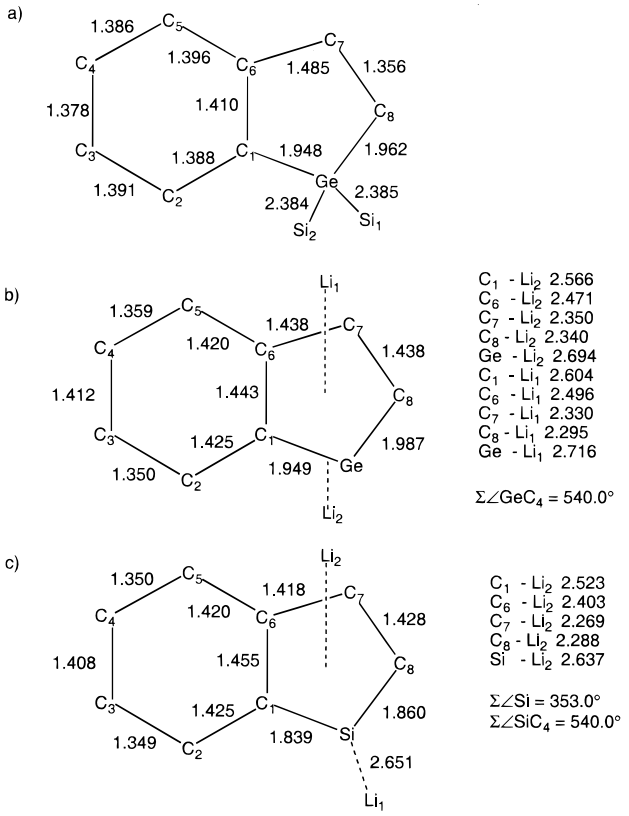

Figure 3. (a) Selected bond lengths (Å) of 1,1-bis(trimethylsilyl-1-germaindene (**3**). (b) Selected bond lengths (Å) and angles (deg) of 1,1-dilithio-1-germaindene (**2a**). (c) Selected bond lengths (Å) and angles (deg) of 1,1-dilithio-1-silaindene.[4]

2-phenyl-1-silaindene and 1.839 and 1.860 Å in 1,1-dilithio-3-*n*-butyl-2-phenyl-1-silaindene.[4]

We attribute these differences to a fundamental alteration in the bonding of the germaindenyl system upon formation of the dianion; that is, the GeC_4 ring becomes aromatic like other germole dianions and the six-membered ring takes on the properties of a cyclohexadiene. Consistent with this proposal is the planar geometry of the GeC_4 ring ($\sum_{ring}\angle = 540.0°$) in **2a**. It is noteworthy that the carbon−carbon bond distances in **2a** and in 1,1-dilithio-3-*n*-butyl-2-phenyl-1-silaindene are very similar despite different heteroatoms and different substituents at the C7 position (Figure 3, b and c).

The ^1H and ^{13}C NMR spectra for **2a** and **2b** have essentially the same patterns and differ only slightly in chemical shifts for both nuclei. It is noteworthy that the ^1H NMR chemical shifts of the hydrogens on C3 and C4 for **2a** and **2b** (6.38 and 6.03 ppm; 6.34 and 6.00 ppm, respectively) are significantly upfield from that of **1** (7.4 ppm), consistent with π-localization in the six-membered ring.

Experimental Section

General Procedures. All reactions were performed under an inert argon atmosphere using standard Schlenck techniques. Air-sensitive reagents were transferred in an argon-filled glovebox. THF was freshly distilled under nitrogen from sodium/benzophenone ketyl immediately prior to use. Hexane was stirred over sulfuric acid, distilled from calcium hydride, and stored over 4 Å molecular sieves. MS data were obtained on a Hewlett-Packard 5988A GC−MS system equipped with a methyl silicone capillary column. NMR spectra were recorded on a JEOL GSX400 spectrometer at 400 MHz (^1H), 54 MHz (^{29}Si), and 100 MHz (^{13}C).

Synthesis of 1,1-Dichloro-2,3-diphenylgermaindene (1). Refluxing Cp_2ZrPh_2[8] (10 g, 25.3 mmol) and diphenylacetylene (4.8 g, 25.3 mmol) in toluene (150 mL) for 20 h gave an orange solution. Concentration of this solution to 20 mL lead to the precipitation of an orange solid. Filtration and washing with hexane (50 mL × 3) gave 2,3-diphenyl-1-zirconaindene (10 g, yield 71%). ^1H NMR ($CDCl_3$, ref; $CDCl_3$ = 7.24 ppm): 6.60−7.15 (m, 14H), 6.38 (s, 10H). ^{13}C NMR ($CDCl_3$, ref; $CDCl_3$ = 77.23 ppm): 112.8 (Cp), 122.8, 123.6, 125. 1, 125.15, 125.4, 126.4, 127.4, 127.7, 130.4, 136.4, 141.2, 146.0, 146.8, 147.1, 184.9, 194.5.

2,3-Diphenyl-1-zirconaindene (10 g, 21 mmol) was dissolved in THF (200 mL). Then $GeCl_4$ (3.6 mL, 31.5 mmol) was added. The mixture was stirred at 50 °C for 24 h. All of the solvent was removed by vacuum. The residue was washed by 50 mL of hexane and extracted with hexane (approximately 100 mL of hexane can extract 1 g of **1**) (7.2 g, 86% yield). Selected data for **1**: mp 127−130 °C; ^1H NMR ($CDCl_3$, ref; $CDCl_3$ = 7.24 ppm) 7.79 (d, 1H, J = 8 Hz), 7.40−7.46 (m, 5H), 7.19−7.26 (m, 7H), 7.07 (d, 1H, J = 8 Hz); ^{13}C NMR ($CDCl_3$, ref; $CDCl_3$ = 77.23 ppm) 150, 144.3, 138.2, 135.8, 135.1, 134.6, 132.6, 131.2, 129.8, 129.32, 129.27, 129.13, 128.47, 128.43, 127.74, 125.92. Anal. Calcd for $C_{20}H_{14}GeCl_2$: C, 60.38; H, 3.55, Found: C, 59.62; H, 3.60; MS (EI, M^+) 398.

1,1-Dilithio-2,3-diphenylgermaindene (2a). 1 (1.2 g, 3.0 mmol) and lithium metal (0.13 g, 18.0 mmol) were stirred in THF (25 mL) and TMEDA (3 mL) at room temperature for 12 h. All volatiles were removed under reduced pressure, and the residue was extracted with ether (30 mL). Crystallization of the this solution yields dark red X-ray quality crystals of **2a**·LiCl·3TMEDA (0.86 g, yield 50%). The NMR sample was prepared by dissolving the X-ray quality crystals of **2a**·LiCl·3TMEDA in THF-d_8. Selected data: ^1H NMR (THF-d_8, ref; THF-d_8 = 1.72 ppm) 8.02 (d, 1H, J = 8 Hz), 7.71 (d, 1H, J = 8 Hz), 7.25 (d, 2H, J = 8 Hz), 7.21 (d, 2H, J = 8 Hz), 7.07 (t,

(8) (a) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263. (b) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

2H, $J = 8$ Hz), 6.82 (t, 1H, $J = 8$ Hz), 6.72 (t, 2H, $J = 8$ Hz), 6.48 (t, 1H, $J = 8$ Hz), 6.38 (t, 1H, $J = 8$ Hz), 6.03 (t, 1H, $J = 8$ Hz), 2.21 (s, 12H), 2.06 (s, 36H). ^{13}C NMR (THF-d_8, ref; THF-d_8 = 24.45 ppm) 174.87, 167.94, 150.53, 144.95, 137.95, 136.34, 131.31, 128.12, 126.69, 125.77, 122.24, 120.82, 118.86, 117.00, 116.74, 109.92.

1,1-Disodio-2, 3-diphenylgermaindene NMR Reaction. **1** (50 mg, 0.13 mmol) and Na (18 mg, 0.78 mmol) were placed in a 5 mm NMR tube with THF-d_8 (0.75 mL). After sealing the NMR tube under vacuum, sonication of the NMR tube for 12 h gave a dark red solution. Selected data for **2b**: ^{1}H NMR (THF-d_8, ref; THF-d_8 = 1.72 ppm) 8.21 (d, 1H, $J = 8$ Hz), 7.79 (d, 1H, $J = 8$ Hz), 7.31 (d, 2H, $J = 8$ Hz), 7.17 (d, 2H, $J = 8$ Hz), 7.01 (t, 2H, $J = 8$ Hz), 6.69−6.75 (m, 3H), 6.47 (t, 1H, $J = 8$ Hz), 6.34 (t, 1H, $J = 8$ Hz), 6.00(t, 1H, $J = 8$ Hz). ^{13}C NMR (THF-d_8, ref; THF-d_8 = 24.45 ppm) 179.98, 171.02, 152.16, 145.31, 139.41, 137.29, 132.24, 129.35, 127.43, 126.88, 122.05, 120.53, 119.47, 117.79, 117.09, 109.84.

1,1-Bis(trimethylsilyl)-2,3-diphenyl-1-germaindene (3). Stirring of **1** (2.0 g, 5.0 mmol) and lithium (0.20 g, 30.0 mmol) in THF (30 mL) for 3 h gives a dark red solution. Filtration and addition to an excess of trimethylchlorosilane (4.0 mL, 30.0 mmol) with stirring at room temperature produces a pale brown solution immediately. Additional stirring for 3 h gives a colorless solution and a salt. All volatiles are removed under reduced pressure, and the residue is extracted with hexane (yield 92% based on ^{1}H NMR). Crystallization of this solution yields **3** as colorless crystals. Selected data for **1**: mp 97−98 °C. ^{1}H NMR (THF-d_8, ref; THF-d_8 = 1.72 ppm) 7.60 (d, 1H), 7.31 (t, 2H), 7.24 (t, 1H), 7.13−7.17 (m, 4H), 7.03−7.07 (m, 3H), 6.95−6.97 (m, 3H), 0.23 (s, 18H). ^{13}C NMR (THF-d_8, ref; THF-d_8 = 24.45 ppm); 152.53, 150.66, 149.07, 144.37, 142.95, 140.69, 133.32, 131.12, 130.31, 129.16, 128.48, 127.99, 127.54, 126.23, 126.21, 126.06, 0.19. ^{29}Si NMR (THF-d_8, ref: ext. TMS = 0.00) −4.95. MS (EI, M^+), 478.25. Anal. Calcd for $C_{26}H_{32}GeSi_2$: C, 65.98; H, 6.81. Found: C, 65.30; H, 6.86.

X-ray Structure Determination. X-ray quality crystals of **2a** were grown from a concentrated ether solution in the presence of TMEDA at room temperature. X-ray quality crystals of **3** were grown from a concentrated hexane solution of **3**. A single crystal of **2a** or **3** was mounted in a thin-walled glass capillary tube and sealed under nitrogen. Details on machine parameters, crystal data, data collection, and refinement are given in Tables 1, 2, and 3.

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Supporting Information Available: Tables of bond distances and angles, hydrogen atom coordinates, and anisotopic thermal parameters for **2a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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