

Introduction of Bulky Substituents at the Bridgehead Position of a 9-Silatriptycene: Pentacoordinate Hydridoorganosilicates as Intermediates

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The reaction of 10-phenyl-10-germa-9-silatriptycene (**1b**) with phenyllithium in THF/HMPA produced 9,10-diphenyl-10-germa-9-silatriptycene (**1a**), which had hitherto not been accessible. The reaction proceeds by attack of the phenyl anion on **1b** via the intermediate silicate anion **7**, which was identified by ²⁹Si NMR spectroscopy. The structure of **1a** was confirmed by X-ray crystallography. As a model reaction, the attack of phenyllithium on triphenylsilane (**8**) and diphenylsilane (**14**) was investigated by ²⁹Si NMR spectroscopy, revealing the formation of a number of novel hydridosilicates analogous to **7**.

Introduction

We recently reported a novel one-pot synthesis of 9,10-dimetallatriptycenes of group 14 (**1**) by reaction of (*o*-phenylene)magnesium (**2**) with organometal trihalides RMCl₃ (**3**) (Scheme 1).¹ Evidence was obtained that the process occurred in two stages: reaction of 3 molar equiv of C₆H₄Mg (**2**, which is the tetramer (C₆H₄Mg)₄)² with 1 molar equiv of **3** furnished selectively the intermediate tri-Grignard species **4**; in the second stage, **4** reacted with a second equivalent of **3** to give triptycenes which are symmetrical (**1**; RM = R'M'), while with a different trihalide R'M'Cl₃ (**3'**), unsymmetrical triptycenes (**1**, RM ≠ R'M') were obtained.

Surprisingly, there was strong dependence of the yield of **1** on the size of both the metal M and the substituent R; reasonable yields were obtained only if R was small and/or M was large.¹ In all cases, the intermediate **4** had been formed nearly quantitatively, as demonstrated by deuteriolysis after the first stage, which furnished **5** in high yield. Therefore, it seemed reasonable to assume that the combination of a large R and a small M leads to derailment in the second stage: reaction of **4** with the first chlorine of the second equivalent of **3** obviously will give rise to the formation of an intermediate such as **6**, which undergoes the desired intramolecular double ring closure leading to **1** only in the absence of steric

hindrance; otherwise, **6** reacts *intermolecularly* to form polymeric products.

In view of the fact that a number of triptycenes are known in the parent series with the smaller carbon at the bridging positions carrying bulky substituents,³ it was unlikely that analogous derivatives of **1** such as 9,10-diphenyl-10-germa-9-silatriptycene (**1a**) were not capable of existence; rather, one had to devise a different approach for their synthesis.

Results and Discussion

Synthesis and Crystal Structure of 1a. An additional reason for choosing **1a** as the synthetic goal was the availability of 10-phenyl-10-germa-9-silatriptycene (**1b**)^{1b} as a precursor; its Si–H functionality was expected to serve as a starting point for transformation to the desired Si–Ph group. Indeed, the reaction of **1b** with an excess of phenyllithium in diethyl ether at room temperature did furnish **1a**; after 1 min, the reaction was complete, and on workup **1a** was isolated in 70% yield (Scheme 2).

The structure of **1a** was confirmed by an X-ray crystal structure determination (*R* = 0.0685; Figure 1). Unfortunately, due to disorder, a differentiation between the Ge and Si atoms in the molecule could not be made; only average bond lengths and angles were obtained (see legend to Figure 1). These structural parameters generally agree with those of related 9,10-diheterotriptycenes, in particular with those of **1b**.^{1b} It should, however, be pointed out that an unusual and rather unfavorable eclipsing of one phenyl substituent (Figure 1: C(23)–

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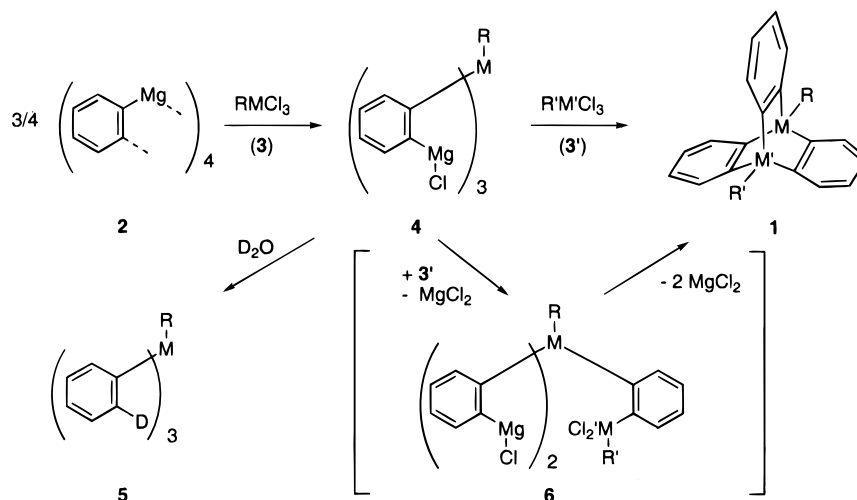
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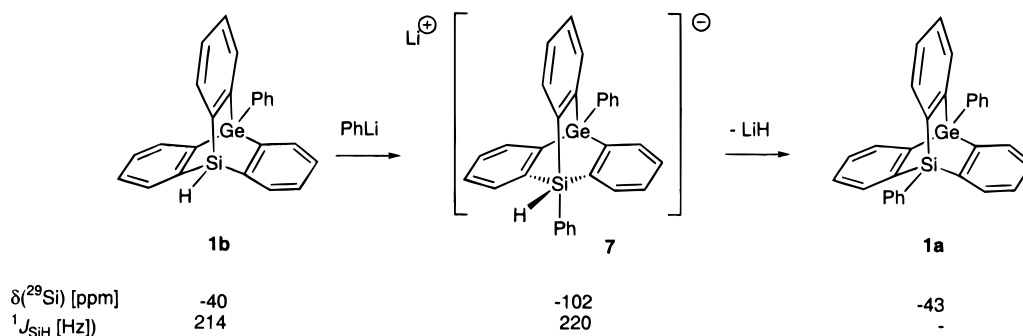
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Scheme 1



Scheme 2



C(28)) with one of the *o*-phenylene units (C(11)–C(16)) occurs; we have at present no explanation for this remarkable phenomenon.

Ate Intermediates during the Nucleophilic Substitution of Si–H Bonds. Besides achieving our primary goal to obtain a 9,10-dimetallatriptycene with

two bulky substituents at the bridgehead positions, interesting information was obtained about details of the process of substitution at a silicon bridgehead and on the occurrence of pentacoordinate silicate anions carrying *exclusively* carbon and hydrogen as substituents at silicon.

The transformation of 1b to 1a involves nucleophilic substitution of an Si–H function, and it occurs at a bridgehead position; both types of reactions are well-established.⁴ Fascinated by the ease of the transformation in the present case, we investigated the interaction of 1b with phenyllithium (1.5 equiv) in a mixture of THF and HMPA (20:1) at -80°C by means of ^{29}Si NMR spectroscopy in search for intermediates. The signal of 1b (doublet at $\delta -40$ ppm, $^1J_{\text{SiH}} = 215$ Hz) had completely disappeared, but in addition to the singlet of the final product 1a ($\delta -43$ ppm), a new doublet at $\delta -102$ ppm ($^1J_{\text{SiH}} = 220$ Hz) was observed (ratio about 1:1); it was assigned to the pentacoordinate silicate intermediate 7 (Scheme 2). The signal of 7 was still present after warming to room temperature, but it disappeared on standing overnight. Afterward, depending on the conditions (see Experimental Section), several signals were observed in the silane region ($\delta(^{29}\text{Si})$ -19 , -21 , -23 , -44 ppm); they might in part be due to products formed by ring opening of the strained triptycene skeleton, but on workup, well-defined products could not be isolated.

Two aspects of 7 drew our attention. First, while many examples of pentacoordinate silicates are known, they generally carry one or more electronegative ligands

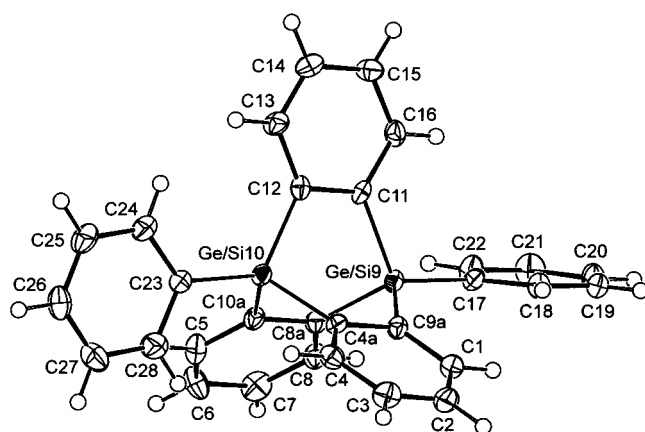


Table 1. Ratio of Products Formed in the Reaction of **8 and PhLi (1.5 equiv) in THF (HMPA) (Determined by $^{29}\text{Si}\{^1\text{H}\}$ NMR Spectroscopy)^a**

| entry | <i>T</i> (°C) | solvent ^b | ratio (%) | | | | | |
|-----------------|------------------|----------------------|-----------|----------|-----------|-----------|-----------|----------------------------|
| | | | 8 | 9 | 10 | 11 | 12 | [13] ^c |
| 1 ^d | −80 | A | 5 | 20 | 28 | 36 | | |
| 2 ^d | −80 ^e | A | 6 | 13 | 32 | 39 | | |
| 3 ^d | −80 ^f | A | 6 | 11 | 35 | 35 | | |
| 4 ^d | −93 | A | 5 | 8 | 36 | 38 | | |
| 5 ^d | −65 | A | 4 | 6 | 34 | 32 | | |
| 6 ^d | −50 | A | | | 10 | 18 | 24 | 4 |
| 7 ^d | −6 | A | | | 19 | | 23 | 9 |
| 8 ^d | −50 | A | | | 34 | | 22 | 4 |
| 9 ^g | −80 | B | 56 | | 38 | | 6 | |
| 10 ^g | −100 | B | 40 | | 52 | | 8 | |
| 11 ^g | −80 | A | | 3 | 30 | 35 | 29 | 3 |
| 12 ^g | room temp | A | | 3 | 25 | 27 | 39 | 6 |

^a Relative yields based on the integrals of the decoupled singlets (corrected for the number of scans). ^b Legend: A, in THF/HMPA (7:1); B, in THF. ^c Unidentified product at δ −15 ppm. ^d Experiment 1. ^e After 24 min. ^f After 42 min. ^g Experiment 2.

at silicon.⁴ Only very recently, the first silicate complexes with five carbon-bonded ligands have been observed by NMR spectroscopy;⁵ apart from gas-phase species,^{6a,b} only one silicate has so far been identified in solution with silicon bonded to carbons and hydrogens only.^{6c} The second interesting aspect of **7** is the coupling constant $^1J_{\text{SiH}} = 220$ Hz, which is rather large for a hydridosilicate (vide infra).

Therefore, we studied triphenylsilane (**8**) as an acyclic model for **1b**. Depending on the temperature (Table 1, entries 1–8), a solution of **8** and phenyllithium (1.5 equiv) in THF/HMPA (7:1) showed four ^{29}Si signals, which on the basis of their chemical shift and SiH

coupling were assigned to **9**–**12**, as shown in Scheme 3. As in the case of **1b**, the starting material **8** was completely converted. Besides tetraphenylsilane (**10**), the straightforward phenyl substitution product corresponding to **1a**, three ate adducts were identified by their strongly shielded ^{29}Si chemical shifts: **9** (doublet at $\delta(^{29}\text{Si})$ −94 ppm, $^1J_{\text{SiH}} = 140$ Hz), the phenyl adduct of **8**, **11** ($\delta(^{29}\text{Si})$ −103 ppm, no $^1J_{\text{SiH}}$ coupling), the known phenyl adduct of **10**,^{5a} and, at first surprisingly, **12** (triplet at $\delta(^{29}\text{Si})$ −70 ppm, $^1J_{\text{SiH}} = 130$ Hz), the formal lithium hydride adduct of **8**.

At low temperatures, the composition of the reaction mixture changed little with time (Table 1, entries 1–4). While the sum of **10** and **11** was constant, **11** increased at the expense of **10**; this may be due to a slow reaction of **10** with the excess of phenyllithium still present at that time. When the temperature was raised to −6 °C, the silicates **9** and **11** disappeared (entries 5–8); only **10** and **12** remained. At $T \geq -50$ °C, the unidentified silane **13** ($\delta(^{29}\text{Si})$ −15 ppm) was formed in low yield (Table 1, entries 6–8).

In a second experiment (Table 1, entries 9–12), the reaction was initially performed in THF in the absence of HMPA. Under these conditions, the conversion was much slower, as indicated by a large amount of unreacted **8**. Only the substitution product **10** and minor amounts of **12** were observed, but no **9** and **11** (entries 9 and 10). This illustrates that the formation of silicate anions depends on effective solvation of the lithium counterion.^{4–7} Indeed, after addition of HMPA to this reaction mixture at −80 °C, the reaction went to completion (entry 11); under these conditions some **9** and **11** survived after warming to room temperature for about 14 h (entry 12).

The surprising thermal stability of the dihydrido-triphenylsilicate **12** might be ascribed to its two small apical hydride ligands, which reduce steric hindrance. Its identity and unusual stability was confirmed by independent synthesis from diphenylsilane (**14**) and phenyllithium (Scheme 4), yielding **12** as the exclusive product when phenyllithium was used in (slight) excess, and only traces of **9**, **10**, or **11** were sometimes observed by ^{29}Si NMR spectroscopy. With an excess of **14**, interesting exchange reactions occurred. These phenomena, and the mechanism of ligand exchange^{4k,l,o,p,8} which leads to the products formed from **8** shown in Scheme 3, are currently under investigation.

Stereochemistry of Hydridosilicates. All new pentacoordinate silicate anions are characterized by strongly shielded ^{29}Si signals which are typical for such species;^{4q,5–8} this supports their general structural assignment. However, the matter of their stereochemical arrangement is more difficult for several reasons.

There is general agreement that, in the absence of special factors, the trigonal bipyramid (TBP) is the preferred geometry of pentacoordinated phosphoranes and silicates; minor distortions of the TBP toward the square pyramid (SP) along the Berry exchange coordinate⁹ are frequently observed.⁴ In the absence of ex-

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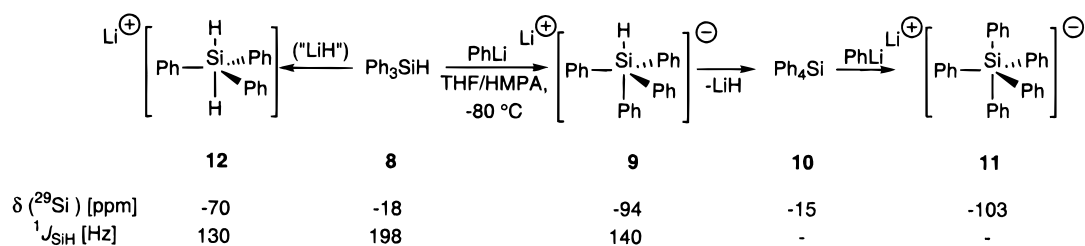
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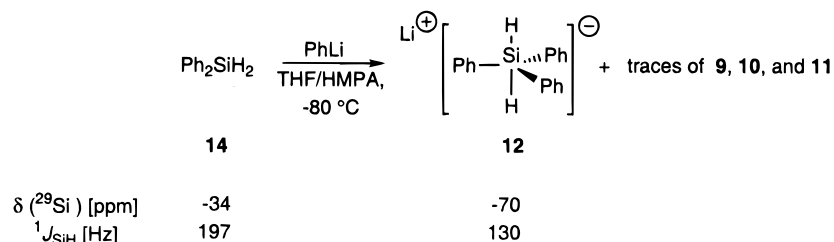
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Scheme 3



Scheme 4

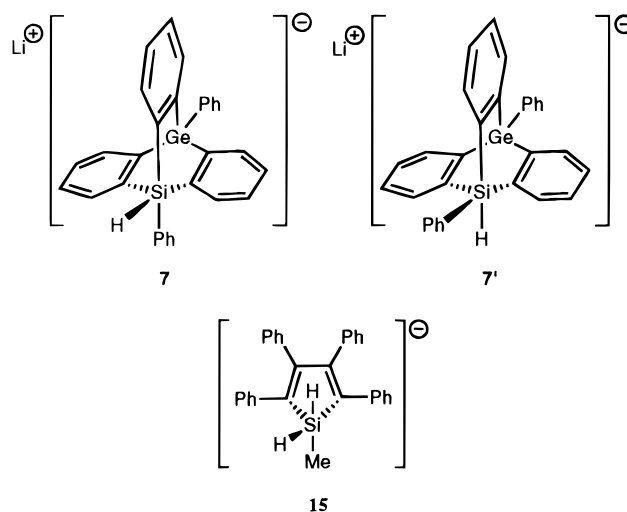


perimental data, one can only speculate about the structures of the silicates **9**, **11**, and **12**, but very likely, they are close to a TBP, as there are no distorting forces imposed by unusual ligands or small rings. This assumption is supported by the NMR data. Hydrogen is usually more apicophilic than the phenyl group and is therefore expected to occupy an apical position in a hydrosilicate of the kind discussed here. Because the apical bonds are longer and weaker, one expects the apical ^{29}Si –H coupling of a silicate to be smaller than that of a related tetracoordinate silane, and indeed, it decreases from the silanes **8** ($^1J_{\text{SiH}} = 198$ Hz) and **14** ($^1J_{\text{SiH}} = 197$ Hz) to the silicates **9** ($^1J_{\text{SiH}} = 140$ Hz) and **12** ($^1J_{\text{SiH}} = 130$ Hz).

It is against this background that the Si–H coupling for **7** ($^1J_{\text{SiH}} = 220$ Hz) is highly unusual, as it is even slightly larger than that of the parent silane **1b** ($^1J_{\text{SiH}} = 215$ Hz). This means that the s character in the Si–H bond increases from **1b** to **7**, which, in a TBP structure, would indicate that hydrogen is in an equatorial position in spite of the presence of four aryl ligands which normally are less apicophilic! As far as we are aware, there is only one report on two neutral compounds, i.e., *o*-Me₂NCH₂C₆H₄SiHMePh and *o*-Me₂NCH₂C₆H₄SiH₂Ph, with pentacoordinate silicon arising from intramolecular coordination of a tertiary amine to a tetracoordinate silicon center, both of which have the hydrogens in equatorial positions and the phenyl group in an axial position.¹⁰

Of course, in the case of **7**, the situation is more complicated because the three phenylene groups of the triptycene skeleton are restricted in adopting ideal positions both in the TBP and in the SP. For reasons of angle strain, the triptycene ipso carbons in a TBP can only be arranged in an approximately apical-diequatorial fashion, while in an SP, an apical-dibasal arrangement would be preferred. Presumably, the actual configuration is somewhere between these extremes, but as pointed out above, the increase of s character of the

Chart 1



Si–H bond from **1b** to **7** is more in line with a quasi-equatorial position of the hydrogen in a (slightly distorted) TBP. This configuration is the one initially formed when the phenyl anion approaches the silicon of **1b** from an apical direction.^{4p,10} Apparently **7** is stuck in this unusual configuration instead of relaxing to the normally more stable stereoisomer **7'** with an apical hydrogen (Chart 1). Possibly, steric effects^{7b,11} are responsible; a TBP model of **7** showed that the free phenyl group in the (usually preferred) equatorial position as in **7'** would experience considerable steric hindrance from the three ortho hydrogens of the triptycene unit. For the formation of **1a**, however, the hydrogen has to be transferred from the equatorial to the apical position by a pseudorotation from **7** to **7'** before it can act as a leaving group.^{4p}

The proposed structural assignment of **7** is supported by $^1J_{\text{SiH}}$ values of other hydrosilicates. Couplings for equatorial Si–H bonds have been assigned in $[\text{HSi}(\text{OR})_4]^-$ ($J_{\text{eq}} = 209\text{--}296$ Hz),^{4j} $[\text{H}_2\text{Si}(\text{OR})_3]^{2-}$ ($J_{\text{eq}} = 222$ Hz, $J_{\text{ap}} = 194$ Hz),^{4k} and **15** (Chart 1; $J_{\text{eq}} = 192.5$ Hz, $J_{\text{ap}} = 179.6$ Hz).^{6c} In these compounds, the expected trend of

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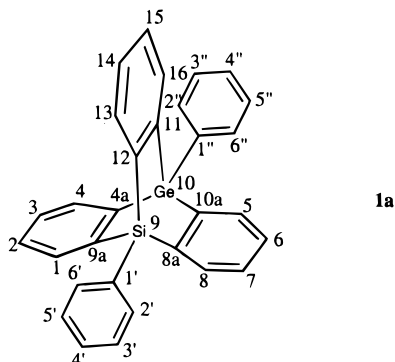


Figure 2. Numbering system of **1a**.

$J_{\text{eq}} > J_{\text{ap}}$ is realized. The same order has been reported for $^1J_{\text{PF}}$ couplings in pentacoordinate fluorophosphoranes.¹² However, the opposite order $J_{\text{ap}} > J_{\text{ex}}$ has been assigned for $^1J_{\text{SiF}}$ in fluorosilicates^{7,13} and, by analogy, for $^1J_{\text{SiC}}$ in a pentaorganosilicate.^{5b} The reason for this discrepancy is not clear at the moment.

Conclusions

While 9,10-dimetallatriptycenes with two bulky aryl substituents at the metals have not been accessible by previous approaches, the first representative of this group, 9,10-diphenyl-10-germa-9-sila-9,10[1,2']benzenoanthracene (**1a**), has been prepared by reaction of its 9-H substituted analogue **1b** with phenyllithium. The role of hydridosilicates as intermediates in the substitution of **1b** and of model silanes $\text{Ph}_n\text{H}_{4-n}\text{Si}$ with phenyllithium has been demonstrated by ^{29}Si NMR spectroscopy.

Experimental Section

General Comments. All reactions were carried out under an argon atmosphere. Glassware and syringes were dried in an oven at 120 °C for at least 24 h or flame-dried (glassware) before use. The solvents Et_2O and THF were predried on NaOH and KOH, respectively, distilled from LiAlH_4 , and kept on sodium wire under nitrogen. THF- d_8 and HMPA were dried on molecular sieves and kept under argon. ^1H NMR spectra were measured at 25 °C on a Bruker AC 200 spectrometer and ^2H NMR, ^{13}C NMR, and ^{29}Si NMR spectra on a Bruker MSL 400 spectrometer. Melting points (uncorrected) were measured in a sealed capillary. The chemical shifts and J_{HH} coupling constants were determined by simulation using the gNMR program¹⁴ and from CH correlation spectra. The HRMS measurement of **1a** was performed on a Finnigan MAT 90 mass spectrometer. GC/MS measurements were performed on a HP 5890 II GC/5971 MS combination (70 eV, Chrompack BP 1 (QSGE) 50 m \times 0.25 mm column). Preparative layer chromatography (PLC) was performed on a Merck plate (silica gel 60 F₂₅₄ 20 \times 20 cm, layer thickness 2 mm), using an *n*-hexane/ Et_2O mixture (9:1) as eluent unless stated otherwise. The concentration of phenyllithium was determined by HCl/NaOH titration of the "total" base formed after hydrolysis minus the amount of "rest" base determined after reaction of an aliquot of phenyllithium with 1,2-dibromoethane (dried on molecular sieves). Triptycene **1b** was prepared according to reported procedures.^{1b,c} The numbering system of **1a** is shown in Figure 2.

Synthesis of 9,10-Diphenyl-9,10-dihydro-10-germa-9-sila-9,10[1,2']benzenoanthracene (1a). To a solution of **1b** (0.0558 g, 0.137 mmol) in Et_2O (25 mL) was added phenyllithium in cyclohexane/ Et_2O (0.5 mL, 1.8 M, 0.9 mmol). After 1 min, a saturated aqueous NH_4Cl solution was added to the slightly yellow reaction mixture. After extraction with CHCl_3 , the combined organic layers were filtered and dried by passing through a column of MgSO_4 . The solvent and biphenyl (present in the PhLi solution) were evaporated in vacuo at 110 °C. The resulting yellow solid was washed with a small amount of Et_2O , yielding **1a** as a white powder (0.0463 g, 0.0958 mmol, 70% pure according to ^1H NMR spectroscopy). Crystals for an X-ray crystal structure determination were obtained from C_6D_6 by slow evaporation.

1a: mp 337 °C dec. ^1H NMR (400.1 MHz, CDCl_3): δ 8.35 (m, $J = 7.5$, 1.4, 1.3, 0.6 Hz, 2H; H(2',6')), 8.19 (m, $J = 7.4$, 1.4, 1.4, 0.6 Hz, 2H; H(2'',6'')), 7.81 (m, $J = 7.0$, 1.7, 0.8 Hz, 3H; H(1,8,13)), 7.79 (m, $J = 7.9$, 0.8, 0.7 Hz, 3H; H(4,5,16)), 7.72 (m, $J = 7.5$, 7.4, 1.3, 0.6 Hz, 2H; H(3',5')), 7.72 (m, $J = 7.4$, 1.3 Hz, 1H; H(4')), 7.71 (m, $J = 7.6$, 7.4, 1.3, 0.6 Hz, 2H; H(3'',5'')), 7.68 (m, $J = 7.6$, 1.4 Hz, 1H; H(4'')), 7.23 (m, $J = 7.6$, 7.0, 0.8 Hz, 3H; H(2,7,14)), 7.23 (m, $J = 7.9$, 7.6, 1.7 Hz, 3H; H(3,6,15)). ^1H NMR (400.1 MHz, C_6D_6): δ 8.24 (m, $J = 7.4$, 1.8 Hz, 1.4, 0.7 Hz, 2H; H(2',6')), 8.04 (m, $J = 7.4$, 1.4, 1.3, 0.6 Hz, 2H; H(2'',6'')), 7.88 (m, $J = 7.1$, 1.2, 0.8, 3H; H(1,8,13)), 7.81 (m, $J = 7.6$, 1.0, 0.8 Hz, 3H; H(4,5,16)), 7.40 (m, $J = 7.5$, 1.4 Hz, 1H; H(4')), 7.38 (m, $J = 7.5$, 7.4, 1.6, 0.7 Hz, 2H; H(3',5')), 7.37 (m, $J = 7.6$, 7.4, 1.4, 0.6 Hz, 2H; H(3'',5'')), 7.36 (m, $J = 7.6$, 1.3 Hz, 1H; H(4'')), 7.06 (m, $J = 7.5$, 7.1, 1.0 Hz, 3H; H(2,7,14)), 7.05 (m, $J = 7.6$, 7.5, 1.2 Hz, 3H; H(3,6,15)). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 148.9 (C(4a,10a,11)), 142.6 (C(8a,9a,12)), 137.2 (C(2',6')), 136.6 (C(2'',6'')), 133.9 (C(1,8,13)), 132.2 (C(4,5,16)), 131.0 (C(3')), 130.5 (C(4')), 129.9 (C(1'')), 129.4 (C(3'',5'')), 129.0 (C(3',5')), 128.2 (C(1')), 127.6 (C(2,7,14)), 127.4 (C(3,6,15)). ^{29}Si NMR (79.5 MHz, CDCl_3): δ -43 ($^1J_{\text{SiC}} = 68$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): δ 149.1 (C(4a,10a,11)), 142.9 (C(8a,9a,12)), 137.3 (C(2',6')), 136.7 (C(2'',6'')), 134.1 (C(1,8,13)), 132.4 (C(4,5,16)), 130.8 (C(3')), 130.2 (C(4')), 130.1 (C(1'')), 129.3 (C(3'',5'')), 128.9 (C(3',5')), 128.5 (C(1')), 127.6 (C(2,7,14)), 127.4 (C(3,6,15)). HRMS (EI): calcd for $[\text{C}_{30}\text{H}_{22}\text{Si}^{74}\text{Ge}]^+$, 484.0703; found, 484.0705.

NMR Spectroscopy of Solutions of 1b and Phenyllithium in THF/HMPA. Under argon, THF (2.7 mL), THF- d_8 (0.4 mL), and HMPA (0.15 mL) were added to **1b** (0.0492 g, 0.121 mmol) in an NMR tube of 10 mm diameter. Subsequently, the tube was capped with a septum and cooled (-78 °C). After addition of a solution of phenyllithium in cyclohexane/ Et_2O (0.10 mL, 1.8 M, 0.18 mmol), the dark brown reaction mixture was homogenized on a vortex. ^{29}Si NMR (-80 °C): -19 (?), -43 (**1a**), -102 (**7**, $^1J_{\text{SiH}} = 220$ Hz) in varying ratios due to solubility problems. ^{29}Si NMR spectroscopy at room temperature showed that **1a** and **7** were still present. Upon addition of MeOD (0.25 mL) the brown reaction mixture turned yellow. After the addition of water, the mixture was extracted with CHCl_3 and the combined organic layers were evaporated to dryness in vacuo; a yellow, HMPA-containing oil remained. On addition of water, a white solid precipitated, and the supernatant was removed carefully. The precipitate was washed several times with water and twice with a small amount of EtOH and dried in vacuo. ^1H and ^{13}C NMR spectroscopy showed the white product to be pure **1a** (42.8 mg, 0.089 mmol, 71% yield).

In a second experiment, the reaction was initially performed in THF/THF- d_8 with about 1 equiv of phenyllithium in cyclohexane/ Et_2O (80 μL , 1.8 M, 0.14 mmol). ^{29}Si NMR (-50 °C, -80 °C, -100 °C): -40 (**1b**). Subsequently, HMPA (0.5 mL) and about 1 equiv of phenyllithium in cyclohexane/ Et_2O (40 mL, 1.8 M, 0.07 mmol) were added. ^{29}Si NMR (-40 °C): -43 (**1a**), -102 (**7**), ratio about 1:1. After standing for 14 h at room temperature, three signals at δ -21, -23, -44 (**1a**), ratio

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1:1:1, were observed, but no ate complex. Workup of the reaction mixture as described above, gave a brown sticky powder: ^1H NMR (200.1 MHz, CDCl_3): δ 8.0–6.5 (bm). Attempted separation of the products by PLC was unsuccessful.

NMR Spectroscopy of Solutions of 8 and Phenyllithium in THF(HMPA). Under argon, THF (3 mL), THF- d_8 (0.4 mL) and HMPA (0.5 mL) were added to **8** (0.1049 g, 0.403 mmol) in an NMR tube of 10 mm diameter. Subsequently, the tube was capped with a septum and cooled (-78°C). After addition of a solution of phenyllithium in cyclohexane/ Et_2O (0.33 mL, 1.8 M, 0.6 mmol), the dark brown reaction mixture was homogenized on a vortex. ^{29}Si NMR spectroscopy at low temperature showed several signals, see Table 1 (entries 1–9). After standing for 14 h at room temperature, four signals at δ -12 (19%), -14.6 (60% **10**), -14.8 (11%), and -18 (10%) were observed. After addition of water and extraction with diethyl ether, GC/MS analysis showed the presence of Ph_3SiOH (6%; presumably formed by inadvertent oxidation on workup) and **10** (94%). Ph_3SiOH : MS (EI, m/z (relative intensity)) 276 (M^+ , 57), 199 ($[\text{M} - \text{C}_6\text{H}_5]^+$, 100), 181 (12), 152 (7), 122 ($[\text{M} - 2\text{C}_6\text{H}_5]^+$, 15), 77 (16). **10**: MS (EI, m/z (relative intensity)) 336 (M^+ , 48), 259 ($[\text{M} - \text{C}_6\text{H}_5]^+$, 100), 182 ($[\text{M} - 2\text{C}_6\text{H}_5]^+$, 45), 105 ($[\text{M} - 3\text{C}_6\text{H}_5]^+$, 12), 77 (4).

In a second experiment, the reaction was initially observed in THF/THF- d_8 (Table 2, entries 9 and 10), and at a later stage HMPA (0.15 mL) was added (Table 2, entries 11 and 12, see text); in this experiment, $\delta(^{29}\text{Si})$ -14 was observed for **10**.

NMR Spectroscopy of Solutions of 14 and Phenyllithium in THF(HMPA). Under nitrogen, THF- d_8 (0.523 mL) and HMPA (0.077 mL) were added to **14** (0.062 mmol) in an NMR tube of 5 mm diameter, homogenized, and cooled in liquid nitrogen. After addition of a solution of phenyllithium in cyclohexane/ Et_2O (0.052 mL, 1.8 M, 0.093 mmol), the tube was capped, warmed to -100°C , and then homogenized on a vortex to yield an almost black reaction mixture. ^{29}Si NMR spectroscopy at -80°C showed the practically exclusive formation of **12** ($\delta(^{29}\text{Si})$ -69.9) with occasionally traces of **9** ($\delta(^{29}\text{Si})$ -94) **10** ($\delta(^{29}\text{Si})$ -14), and **11** ($\delta(^{29}\text{Si})$ -103).

Crystal Structure Determination of 1a: $\text{C}_{30}\text{H}_{22}\text{GeSi}$, $M_r = 483.16$, colorless needle, $0.45 \times 0.25 \times 0.20 \text{ mm}^3$, triclinic, $P\bar{1}$, $a = 8.869(2) \text{ \AA}$, $b = 11.176(6) \text{ \AA}$, $c = 12.945(6) \text{ \AA}$, $\alpha = 99.42(3)^\circ$, $\beta = 103.81(2)^\circ$, $\gamma = 110.21(2)^\circ$, $V = 1125.8(8) \text{ \AA}^3$, $Z = 2$, $D = 1.425 \text{ g cm}^{-3}$, 289 parameters, 5442 measured reflections, 5108 unique reflections ($R_{\text{int}} = 0.0584$). R ($I > 2\sigma(I)$): $R1 = 0.0685$, $wR2 = 0.1587$. R (all data): $R1 = 0.1132$, $wR2 = 0.1798$. $S = 1.049$. Intensities were measured on an Enraf-Nonius CAD4T diffractometer with rotating anode (Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$) at a temperature of $150(2) \text{ K}$. The structure was solved with the program SIR97¹⁵ and refined with the program SHELXL97¹⁶ against F^2 values of all reflections up to a resolution of $(\sin \theta)/\lambda_{\text{max}} = 0.65 \text{ \AA}^{-1}$. An absorption correction was not considered necessary. Germanium and silicon atoms were constrained to occupy the same positions in a 1:1 ratio with the same displacement parameters. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The drawing, structure calculations, and checking for higher symmetry was performed with the program PLATON.¹⁷

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Supporting Information Available: Details of the crystal structure analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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