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Reduction of Terphenyltrifluorosilanes: C−C Insertion Products and Possible Formation of a Disilyne

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The new terphenyl trifluorosilanes $Mes_2C_6H_3SiF_3$ (**1**) and $Tip_2C_6H_3SiF_3$ (**2**) have been synthesized, and their reduction behavior has been investigated in detail. Reduction with sodium in both cases results in insertion of the silicon center into C−C bonds of the substituent. The reactive intermediates giving rise to the C−C insertion most likely involve fluorosilylene or disilyne species. The final product is a bis-silafluorenyl (**3**) in the case of **1** and a silafluorenyl anion in the case of **2**. The anion can be protonated to give a stable silafluorene. The reduction of **1** and **2** with potassium gives a completely different result, and radical species are formed instead. The different reaction pathway is probably caused by the existence of a poorly soluble intermediate [$2Mes_2C_6H_3SiF_3{\cdot}3KF$] (**10**) that lowers the concentration of the starting material and therefore influences the reaction kinetics. Crystal structures are presented for **1**, **2**, the insertion product **3**, and the intermediate adduct **10**.

Introduction

In general, compounds of the heavier main group elements containing sterically hindered substituents are promising precursors for the formation of multiply bonded or otherwise unsaturated systems. Recently, terphenyl ligands in particular have been very useful in this respect.[1] Several examples with tin and germanium illustrate the ability of bulky terphenyl ligands to stabilize systems with interesting bonding,[2,3] while for silicon this ligand system has been rather unexploited so far.[4] Therefore, we were interested in synthesizing suitable terphenyl silanes and investigating their reduction behavior regarding the formation of unsaturated silicon compounds.

Results and Discussion

Although terphenyltrichlorosilanes had already been described,[4] we chose the so far unknown corresponding trifluorosilanes $Mes_2C_6H_3SiF_3$ (**1**) and $Tip_2C_6H_3SiF_3$ (**2**) (Mes = 2,4,6-trimethylphenyl; Tip = 2,4,6-triisopropylphenyl) as starting points of our synthetic route. Reasons for this choice included the lower tendency of fluorine for homolytic bond cleavage and lower steric interaction between the ligand and halogen. Moreover, we considered the NMR activity of the ^{19}F nucleus a valuable tool to follow any reaction progress.

In analogy with known procedures[5] trifluorosilanes **1** and **2** can be readily synthesized from $Mes_2C_6H_3Li$ or $Tip_2C_6H_3Li$ and silicon tetrafluoride in excellent yields. In contrast with the corresponding chloro derivatives,[4] the trifluorosilanes **1** and **2** are air-stable solids, perhaps because of the higher dissociation energy of the Si−F compared to the Si−Cl bond. While their ^{29}Si NMR shifts are in the normal range for such compounds ($\delta(^{29}Si)$: −73.6 ppm, $^1J_{SiF} = 270$ Hz (**1**); −72.8 ppm, $^1J_{SiF} = 271$ Hz (**2**)), the ^{19}F NMR shifts for the two compounds differ quite markedly ($\delta(^{19}F)$: −135.6 ppm (**1**); −64.6 ppm (**2**)). However, according to X-ray diffraction experiments, there is no marked difference between the geometrical parameters of **1** and **2** in the solid state. In both **1** and **2** the planes of the trialkylphenyl rings are almost perpendicular to the plane of the central phenyl rings. The $Si-C_{aryl}$ distance in **1** is slightly shortened compared to the corresponding chloro derivatives[4] and roughly 6 pm (∼3%) shorter than in **2**. On the other hand, the Si−F bond lengths in **1** are more than 3 pm (∼2%) longer than in **2**. Both observations indicate a weaker aryl−Si interaction concomitant with a stronger Si−F interaction in **2**, probably due to the larger steric repulsion of the bigger terphenyl ligand. It should noted

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[1] Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1.

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10.1021/om990924z CCC: $19.00

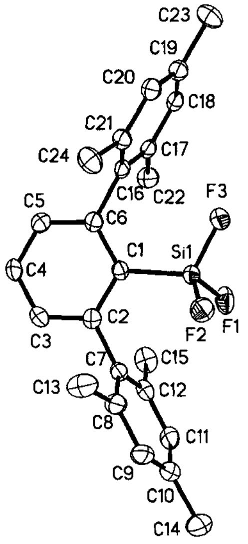


Figure 1. Crystal structure of **1**. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms were omitted for clarity.

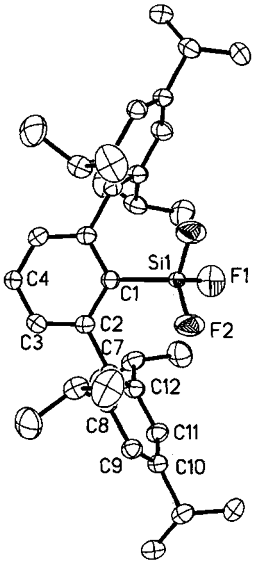


Figure 2. Crystal structure of **2**. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms were omitted for clarity.

that the fluorine atoms in **2** are disordered and that the molecule contains a mirror plane perpendicular to the central phenyl ring.

Various conditions were used to bring about defluorination of **1** and **2**, but definitive results were obtained only for **1** with sodium metal. Reaction of **1** with 3 equiv of sodium in THF led to a product **3** with a high-resolution mass spectrum indicating the formal constitution $(Mes_2C_6H_3Si)_2$. The ^1H and ^{13}C NMR data show that the symmetry of the organic ligand has been lowered and the signals of the mesityl groups are no longer equivalent. On the basis of the NMR spectra a structure can be deduced in which both silicon atoms insert into one of the CH_3-C_{aryl} bonds on the ligand. This structure is confirmed by the X-ray crystal structure of the compound (Figure 3). Although the *R* value for this structure is rather high due to poor crystal quality, the structure clearly reveals that both silicon atoms have the same absolute configuration, which is also the arrangement with the least steric repulsion of the substituents.

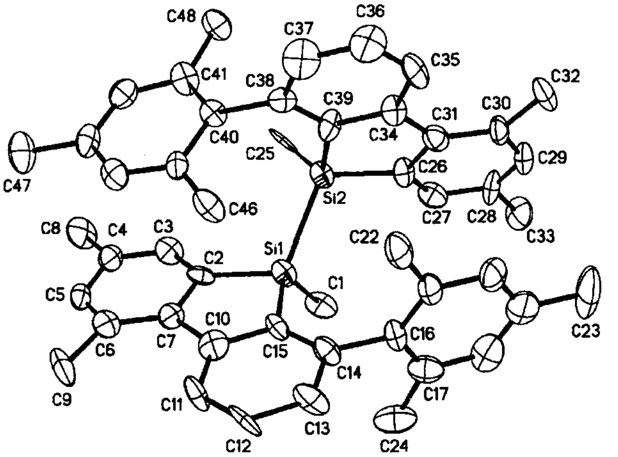
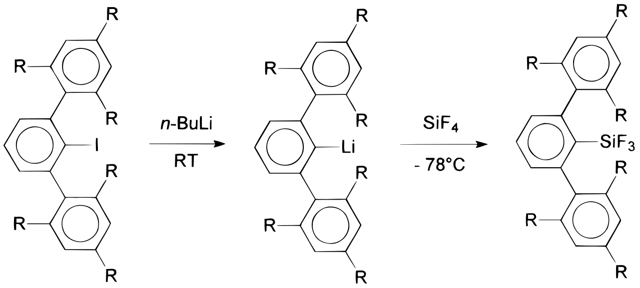


Figure 3. Crystal structure of **3**. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms were omitted for clarity.

Scheme 1. Synthesis of 1 (R =Methyl) and 2 (R = Isopropyl)



(1, 2)

The reaction product **3** suggests the formation of a highly reactive intermediate, capable of inserting into a C−C bond. One possible intermediate would be an isomer of **3**, the disilyne **4** (Scheme 2). An alternative suggestion could be the fluoro-substituted silylene **5**. We are aware that without any direct evidence both alternatives are highly speculative; however these intermediates would explain the formation of the obtained product **3**.

Quantum chemical calculations predict a *trans*-bent structure for a disilyne with a formulation more as a bis-silylene (**4b**) rather than a classical triple bond (**4a**).[6] This bis-silylene structure could be prone to give a double insertion product, as we observed experimentally. On the other hand, calculations on fluoro-substituted silylenes rule out a dimerization with Si−Si bonds and favor a double fluorine-bridged structure to fill the vacant orbital of the silylene.[7] In addition, assuming the silylene **5** was formed, the resulting insertion product **6** would represent a highly hindered fluorosilane. Reductive coupling of **6** to form **3** does not then seem very likely.

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(6) (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489. (c) Yamaguchi, Y.; DeLeeuw, B. L.; Richards Jr., C. A.; Schaefer, H. F., III; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 11922. (d) DeLeeuw, B. J.; Grev, R. S.; Schaefer, H. F., III. *J. Chem. Educ.* **1992**, *69* (6), 441.

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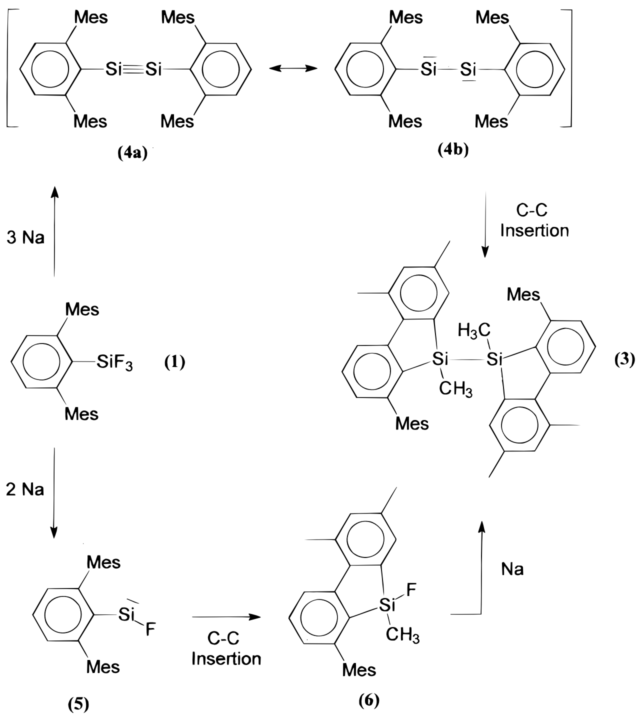
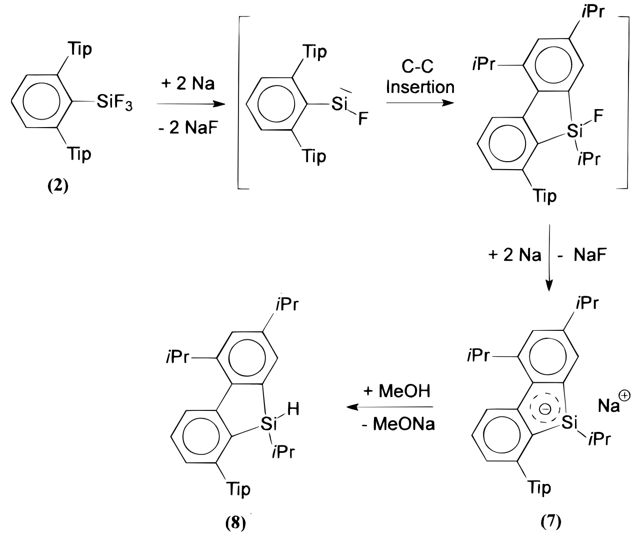
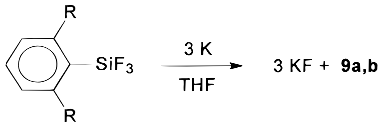
Scheme 2. Possible Intermediates in the Formation of 3



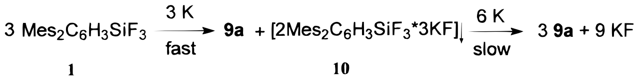
Scheme 3. Proposed Mechanism for the Formation of 7 and 8



Scheme 4. Synthesis of 9a (R = 2,4,6-Trimethylphenyl) and 9b (R = 2,4,6-Triisopropylphenyl)



Scheme 5. Formation of Intermediate 10



Similarly, the reduction of **2** with sodium can also be accomplished, even though the reaction takes much longer. In this case again insertion into a C−C bond occurs, resulting in the formation of a silafluorenyl system. However, no Si−Si bond is present in the product **7**, suggesting a reaction mechanism via a fluorosubstituted silylene (Figure 3) or else reductive cleavage of an intermediate comparable to **3**. The anion **7** can be detected spectroscopically and gives rise to a broad absorption in the ^{29}Si spectra ($\delta = -3.6$ ppm, $\nu_{1/2} = 50$ Hz). The ^{29}Si resonance of this silafluorenyl anion is between that of the unsubstituted 1-methyl-1-silafluorenyl anion ($\delta = -22.1$ ppm), which is considered to be localized, and that of a delocalized silole anion ($\delta = 25.1$ ppm), indicating at least partial delocalization.[8] With methanol **7** can be converted into the stable silafluorenyl derivative **8**. The $^{1}J_{\mathrm{SiH}}$ coupling constant for **8** is rather small, 198 Hz, perhaps indicating low s-character of the Si−H bond. This may be due to the strained arrangement caused by the repulsive interaction of the other substituents at the silicon center.

The reactions presented above appear to be the first examples of silicon inserting into C−C bonds. Such insertion behavior is not completely unprecedented for terphenyl ligands, however. For instance comparable C−C insertion has been reported for the reduction of a terphenyl borane involving an intermediate boranediyl and a related terphenyl phosphane.[9]

Both **1** and **2** are reduced by potassium at room temperature in THF, but the products are completely different from those with sodium. The final resulting products are in both cases radicals **9a**,**b** that show a characteristic deep red color (broad absorption at $\lambda_{\max}$ 500 nm). Even over a long period (1 year) radicals **9a** and **9b** do not dimerize or decompose. However, their solutions are extremely air sensitive, decolorizing instantaneously when exposed to aerobic conditions. EPR experiments confirmed the radical nature of the products but gave no unambiguous proof for their actual structures. No coupling is resolved in the EPR spectrum of **9a**, while **9b** shows a doublet with a hyperfine splitting of 3.2 G and additional satellites (33 G). Reasonable assumptions for the identity of **9a**,**b** could include a silafluorenyl structure as well as the sila analogues of compounds that were isolated in similar reactions with tin and germanium.[2,3] Our attempts to derivatize radicals **9a** and **9b** indicate that they are the predominant species in solution, but rearrangements involved in these processes make it difficult to draw conclusions on their actual structure. So far, we have no unambiguous evidence for the identity of **9a**,**b**; a detailed discussion of the experimental facts exceeds the scope of this paper and will be reported elsewhere. Reduction of **1** or **2** with sodium/naphthalene, or with KC_8, produced the same radical species. No reaction was observed with lithium or magnesium.

Not surprisingly, the course of the heterogeneous reaction of **1** or **2** with potassium is rather complex and involves various intermediates. The onset of the reaction can be easily monitored visually, since on immersion of

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(8) Hong, J. H.; Boudjouk, P.; Stoenescu, I. *Organometallics* **1997**, *15*, 22179.

(9) (a) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981. (b) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357. Moreover, C−H insertion to give a silafluorene has been observed in the reduction of 2,4,6-triphenylphenyl-substituted trichlorosilane: Millevolte, A. J.; van den Winkel, Y.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5375.

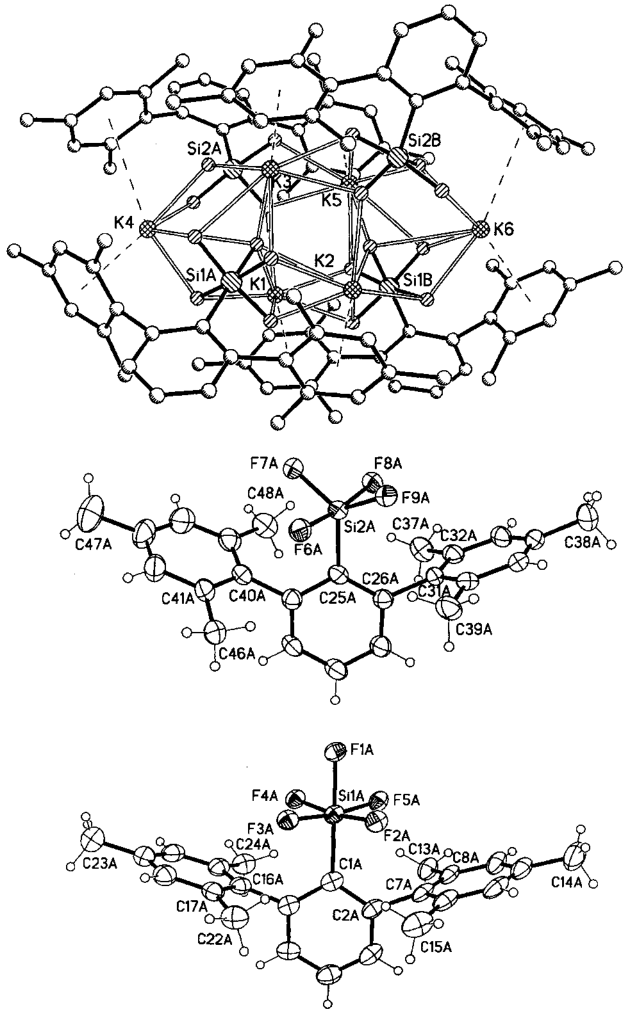

Figure 4. Crystal structure of **10**. Overview of the aggregate and detailed views of the penta- and hexafluorosilicate subunits (displacement ellipsoids are drawn at the 50% probability level).

the potassium in a clear solution of **1** the metal surface turns immediately red-violet even at −78° C. After some time a white voluminous precipitate is formed, which later redissolves, forming a clear dark red solution. We have been able to isolate and characterize the white intermediate **10** in the reduction of **1**, and its crystal structure is depicted in Figure 4.

The intermediate is a novel adduct that is represented by the general formula [$2Mes_2C_6H_3SiF_3 \cdot 3KF$]. Roughly it can be described as a fluorosilicate network embedded in a shell of organic ligands. Each of these aggregates contains two pentacoordinate and two hexacoordinate silicate centers per unit, bridged by potassium cations. The bond lengths of the axial positions of the hexacoordinate subunits are 177.1(2) pm (Si−F) and 196.9(3) pm (Si−C), unusually long compared to other known structures.[10] Another interesting detail of the structure is the coordination environment of the potassium cations. For instance K(4) and K(6) are coordinated to five fluorine atoms on one hemisphere, while the other side is oriented toward the phenyl rings. The situation is comparable for the other cations K(1,2,3,5) and some K−C distances appear rather short (310−320 pm), possibly indicating attractive interactions.

As a consequence of the formation of this complex, the concentration of the starting trifluorosilane cannot be raised; once the reaction starts, the KF formed limits the trifluorosilane concentration by formation of the insoluble complex **10**. The low concentration of **1** during the reduction might be an explanation for the completely different result for the reduction with K compared to Na. An alternative explanation could involve the reportedly higher reactivity of pentacoordinate fluorosilanes toward substitution reactions.[11]

Experimental Section

All reactions were performed under an atmosphere of dry oxygen-free argon with solvents freshly distilled from the appropriate drying agent. Mes_2PhI was prepared according to ref 5b. NMR spectra were recorded on Bruker AC+ 300 (^1H, ^{13}C, ^{19}F) and Varian Unity 500 (^{29}Si) spectrometers at room temperature and referenced vs TMS or $CFCl_3$. EPR spectra were recorded on a Bruker ESP 300 E.

Synthesis of $Mes_2C_6H_3SiF_3$ (1). To a suspension of $Mes_2C_6H_3I^{5b}$ (4.12 g, 9.36 mmol) in 60 mL of hexanes is added n-BuLi (6.44 mL, 10.3 mmol), and the mixture is stirred for 12 h. The solvent is removed in a vacuum and the residue redissolved in 100 mL of ether. After cooling to −78 °C, a continuous flow of SiF_4 is passed over the solution for 30 min. The solution is slowly warmed to room temperature, while stirring for another 12 h. The solvent is removed in a vacuum and the residue extracted twice with 50 mL of hexanes. After removal of insoluble material the solution is concentrated and the precipitating product collected. Recrystallization from hexanes (20 mL) yields **1** (3.09 g, 83%) as colorless crystals (mp: 190 °C). Anal. Calcd for $C_{24}H_{25}F_3Si$ (398.5): C, 72.33; H, 6.32. Found: C, 72.37; H, 6.55. ^1H NMR ($CDCl_3$): 7.7 (t, ^3J(H, H) = 7.5 Hz, 1H; CH), 7.2 (d, ^3J(H, H) = 7.5 Hz, 2H; CH), 6.9 (s, 4H; CH), 2.0 (s, 12H; CH_3), 2.3 (s, 6H; CH_3). ^{13}C NMR ($CDCl_3$): 150.2 (C_q), 137.8 (C_q), 137.5 (C_q), 136.0 (C_q), 128.5 (CH), 128.0 (CH), 124.0 (C_q), 21.1 (CH_3), 20.3 (CH_3). ^{29}Si NMR ($CDCl_3$): −73.6 (q, ^1J(Si, F) = 270.3 Hz). ^{19}F NMR ($CDCl_3$): −135.6 (s). MS (EI): m/z(%): 398.1678, calc 398.1678, (100) [M^+]; 383.1 (14) [$M - CH_3^+$]; 313.2 (19) [$M - SiF_3^+$].

Synthesis of $Tip_2C_6H_3SiF_3$ (2). To a suspension of $Tip_2C_6H_3I^{5c}$ (1.87 g, 3.1 mmol) in a mixture of 10 mL of ether and 20 mL of hexanes is added n-BuLi (2.13 mL, 3.41 mmol) at −78 °C. The mixture is slowly warmed to room temperature over a period of 12 h. The solvent is removed in a vacuum and the residue redissolved in 50 mL of ether. After cooling to −78 °C, a continuous flow of SiF_4 is passed over the solution for 30 min. The solution is slowly warmed to room temperature, while stirring for another 12 h. The solvent is removed in a vacuum and the residue extracted twice with 25 mL of hexanes. After removal of insoluble material the solution is concentrated and the precipitated product collected. Recrystallization from hexanes (15 mL) yields **2** (1.24 g, 71%) as colorless crystals (mp: 227 °C). ^1H NMR (C_6D_6): 7.2 (s, 4H; CH), 7.1 (s, 3H), 2.5 (m, 6H), 1.2 (d, ^3J(H, H) = 7.0 Hz, 12H, CH_3), 1.0 (d, ^3J(H, H) = 6.6 Hz, 24H, CH_3). ^{13}C NMR (C_6D_6): 150.0 (C_q), 149.5 (C_q), 147.5 (CH), 136.5 (C_q), 132.0 (C_q), 130.0 (CH), 121.3 (C_q), 121.0 (CH), 35.0 (CH), 31.5 (CH), 25.5 (CH_3), 24.5 (CH_3). ^{29}Si NMR (C_6D_6): −72.8 (q, ^1J(Si, F) = 271 Hz). ^{19}F NMR (C_6D_6): −64.6 (s). MS (EI): 566.3535, calc 566.3555, (4) [M^+]; 482.4 (100) [$MH - SiF_3^+$]; 439.3 (10) [$M - C_3H_5SiF_3^+$].

Synthesis of 3. Sodium metal (0.07 g, 3 mmol) is added to a solution of **1** (0.398 g, 1 mmol) in THF (10 mL). The mixture initially is heated to reflux and then stirred for 21 h. The solvent is removed in a vacuum and the resulting white

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(11) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17.

Table 1. Crystallographic Data and Summary of Data Collection and Refinement

	1	2	3	4
formula	$C_{24}H_{25}F_3Si$	$C_{36}H_{49}F_3Si$	$C_{48}H_{50}Si_2$	$C_{54}H_{56}F_9K_3Si_2$
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
space group	*Pbca*	*Pbcm*	$P\bar{1}$	*P*2(1)/*c*
cryst dimens, mm	0.20 × 0.20 × 0.20	0.40 × 0.30 × 0.30	0.42 × 0.20 × 0.06	0.35 × 0.30 × 0.20
cryst color	colorless	colorless	white	colorless
unit cell dimens (Å)	$a = 17.7686(3)$	$a = 10.9496(4)$	$a = 8.8406(18)$	$a = 13.7295(10)$
	$b = 7.8881(3)$	$b = 12.0899(5)$	$b = 11.157(2)$	$b = 26.639(2)$
	$c = 30.6968(10)$	$c = 25.4843(9)$	$c = 21.144(4)$	$c = 29.299(2)$
(deg)	$\alpha = 90$	$\alpha = 90$	$\alpha = 88.282(5)$	$\alpha = 90$
	$\beta = 90$	$\beta = 90$	$\beta = 82.740(3)$	$\beta = 97.287(3)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 71{,}166(3)$	$\gamma = 90$
volume, Å^3	4392.5(2)	3373.6(2)	1957.9(6)	10629.3(13)
Z	8	4	2	8
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
temperature	133(2) K	133(2) K	143(2) K	133(2) K
F(000)	1680	1224	732	4368
abs coeff	0.141 mm^{-1}	0.108 mm^{-1}	0.123 mm^{-1}	0.368 mm^{-1}
θ range for data collection	2.65−25.00°	2.45−24.99°	2.45−25.00°	2.45−25.00°
no. of reflns collected	15 563	12 394	17 507	41 016
no. of ind reflns	3784 [*R*(int) = 0.0567]	3039 [*R*(int) = 0.0316]	6737 [*R*(int) = 0.3008]	17 508 [*R*(int) = 0.0595]
no. of data/restraints/params	3784/0/259	3039/85(disorder)/239	6737/0/451	17508/0/1225
$R_w(F^2$all data)	wR2 = 0.1147	wR2 = 0.1481	wR2 = 0.3053	wR2 = 0.1048
R(*F* obsd data)	R1 = 0.0510	R1 = 0.0569	R1 = 0.1186	R1 = 0.0458
Goodness-of-fit on F^2	1.080	1.106	0.897	0.838
observed data [$I > 2\sigma(I)$]	2743	2565	2193	10 538
largest and mean shift/s.u.	0.002 and 0.000	0.029 and 0.001	0.010 and 0.002	0.002 and 0.000
largest diff peak and hole	0.312 and −0.363 e/Å^3	0.679 and −0.405 e/Å^3	0.528 and −0.545 e/Å^3	0.409 and −0.482 e/Å^3

product redissolved in benzene. After removing the solids the solution is concentrated and an equal amount of hexanes is added. **3** is isolated as a colorless crystalline solid (0.25 g, 64%, mp 136 °C, dec). Anal. Calcd for $C_{48}H_{50}Si_2$ (683.1): C, 84.40; H, 7.38. Found: C, 84.49; H, 7.37. ^{1}H NMR (C_6D_6): 8.4 (d, ^3J(H, H) = 6 Hz, 4H; CH), 7.7 (t, ^3J(H, H) = 6 Hz, 2H; CH), 7.3 (m, 2H; CH), 6.9 (m, 2H; CH), 6.3 (m, 4H; CH), 2.6 (s, 12H, CH_3), 2.4 (s, 6H, CH_3), 2.0 (s, 6H, CH_3), 1.5 (s, 6H, CH_3), 0.3 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): 151.7 (C_q), 147.6 (C_q), 143.2 (C_q), 139.3 (C_q), 135.6 (C_q), 135.4 (C_q), 135.3 (C_q), 134.8 (C_q), 134.7 (CH), 133.5 (C_q), 131.4 (CH), 130.2 (CH), 127.5 (CH), 126.7 (CH), 126.6 (CH), 123.6 (C_q), 24.7 (CH_3), 21.1 (CH_3), 20.7 (CH_3), 20.6 (CH_3), −2.9 (CH_3). ^{29}Si NMR (C_6D_6): −16.2 (s). MS (EI): *m*/*z* (%) 682.3507, calc 682.3451 (9) [M$^+$]; 667.3 (8) [M − CH_3^+]; 341.2 (51) [M/2$^+$]; 69.0 (100) [$SiC_3H_4^+$].

Synthesis of 7. To a solution of **2** (0.57 g, 1 mmol) in THF (10 mL) is added sodium metal (0.7 g, 3 mmol) at room temperature. After stirring for 2 days the solvent is removed from the resulting dark clear solution in a vacuum. The residue is partially soluble in benzene and subsequently separated from the insoluble material. After evaporation of the solvent **7** remains as brown solid (0.3 g, 55%). ^{29}Si NMR (C_6D_6): −3.6 ppm (br, $\nu_{1/2} = 50$ Hz).

Synthesis of 8. To a solution of **7** (0.53 g, 1 mmol) in ether (10 mL) is added dry methanol (0.1 mL) at room temperature. The brown color disappears immediately, and a white solid precipitates from the solution. The solvent is removed in a vacuum, and the remaining residue is extracted with benzene. After separation from the salts, **8** can be obtained by removal of the solvent (0.5 g, 98%). ^{29}Si NMR (C_6D_6): − 12.1 ppm (d, ^1J(Si, H) = 196.7 Hz). ^{1}H NMR (C_6D_6): 7.7 (d, 1H, CH), 7.2 (s, 1H, CH), 7.1 (m, 1H, CH), 7.0 (s, 1H, CH), 6.9 (s, 2H, CH), 6.8 (m, 1H, CH), 4.5 (s, 1H, SiH), 2.8−2.5 (m, 6H, CH), 1.2−0.7 (m, 36H, CH_3). ^{13}C NMR (C_6D_6): 153−129 (C_{arom}), 123−119 ($\mathrm{CH}_{\mathrm{arom}}$), 51.3 (CH), 50.5 (CH), 50.2 (CH), 35.1 (CH), 31.2 (CH), 26−23 (CH_3). MS (EI): *m*/*z* (%) 510.3659, calc 510.3682 (23) [M$^+$]; 509 (24) [M$^+$ − H]; 482 (100) [M$^+$ − Si]; 467 (40) [M$^+$ − C_3H_6].

Synthesis of 9 and 10. To a solution of **1** (0.8 g, 2 mmol) in THF (20 mL) is added freshly peeled potassium (0.2 g, 6 mmol) at room temperature. The mixture is heated until the potassium is molten and then recooled to room temperature. The metal surface shows a deep red color, and after 1−2 h a voluminous white precipitate (**10**) has formed. (By filtration and mechanical separation from the unreacted potassium **10** may be isolated and recrystallized from hot benzene.) If **10** is not separated, it slowly redissolves, forming a deep red solution of **9a** after stirring for an additional 10 h. **9b** can be synthesized accordingly. The different size of the terphenyl ligand in **1** and **2** mainly causes different reaction times for the reduction. While on a millimolar scale **1** is consumed within hours, the reaction of **2** needs several days for completion. We also found a strong solvent dependence of the reaction time. In less polar solvents the reduction is markedly slowed, even though the final product remains the same. For instance the reduction of **1**, which in THF as solvent is normally completed in less than a day, requires several days in ether at the same concentration. Both **9a** and **9b** are extremely sensitive to air and soluble in THF, benzene, and toluene without apparent decomposition. Due to the radical nature of **9a**,**b**, no satisfying NMR spectra could be recorded. EPR spectra show an absorption at $g = 2.00682$ (**9a**) and $g = 2.00599$ (**9b**), the latter showing a hyperfine splitting of 3.2 G. **10**: Anal. Calcd for $C_{48}H_{50}F_9K_3Si_2 \cdot 8C_4H_8O$ (1548.21): C, 62.06; H, 7.42. Found: C, 62.36; H, 7.73. ^{19}F NMR ($CDCl_3$): −115.0 (s, br), −115.8 (s, br). ^{1}H NMR ($CDCl_3$): 7.3−6.6 (14H, CH), 2.3−1.8 (36H, CH_3). No ^{13}C or ^{29}Si NMR data could be obtained due to the poor solubility in common solvents.

X-ray Structure Determination. Intensity data for compounds **1**, **2**, **3**, and **10** were collected using a Siemens SMART ccd area detector[12] mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\alpha = 0.71073$ Å). The detector was operated in 512 × 512 mode and was positioned 5.26 cm from the sample. The data were corrected for absorption by the empirical method.[13] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[14] Hydrogen atom positions were initially determined by geometry and refined by a riding

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(12) (a) Data Collection: *SMART Software Reference Manual*; Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, 1994. (b) Data Reduction: *SAINT Software Reference Manual*; Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, 1995.

(13) Sheldrick, G. M. *SADABS*. Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Germany, 1996

model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Details of the crystallographic data collection are given in Table 1.

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Supporting Information Available: Tables of complete X-ray crystal data, refinement parameters, atomic coordinates, and bond distances and angles for **1**, **2**, **3**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990924Z

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(14) (a) Sheldrick, G. M. *SHELXTL Version 5 Reference Manual*; Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, 1994. (b) *International Tables for Crystallography, Vol C*; Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer: Boston, 1995.