

Multiple Silyl Exchange Reactions: A Way to Spirooligosilanes

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Tetrakis(dimethylphenylsilyl)silane can be obtained in a one-pot reaction by treating tris-(trimethylsilyl)silylpotassium with excess dimethylphenylfluorosilane. This silyl exchange process works also with pentamethylfluorodisilane to give tetrakis(pentamethyldisilanyl)silane. The use of 1,4-difluorooctamethyltetrasilane produces cyclic compounds such as 1,1-bis(trimethylsilyl)octamethylcyclopentasilane or even spirocyclic ones such as hexadecamethylspiro[4.4]nonasilane.

Introduction

Salt elimination reactions of negatively charged species with electrophiles are among the workhorses of organic and inorganic synthesis. They are especially important in branches of organoelement chemistry where multiple bonds and thus the associated addition chemistry are not readily accessible. This is particularly true for the field of organosilicon chemistry, where salt elimination reactions of oligosilylpotassium compounds with silicon and numerous other element halides have helped us tremendously to expand the field of polysilane chemistry.¹

Compounds with multiple electrophilic functionalities are very common. Silanes with one, two, three, or four leaving groups (e.g., halide substituents) at the same atom are quite abundant. From a synthetic point of view, such reagents are regarded as bearing one, two, three, or four formal positive charges, as they can participate in as many salt elimination reactions. Contrasting this, compounds with several formal negative charges at one atom are not very common. A few examples of 1,1-dilithiosilanes, which can be considered as reagents with two formal negative charges, were reported

over the past few years.^{2,3} These compounds are highly reactive and require bulky substituents at the silicon atom for stabilization. In addition, their preparation frequently requires starting materials that are difficult to obtain. Nonetheless, 1,1-dilithiosilanes serve as fascinating synthetic building blocks and have been used to obtain a number of novel compounds with highly interesting bonding situations.⁴ They are, for example, perfectly suitable to generate double bonds of silicon to other atoms in salt elimination reactions with 1,1-dihalides. In addition, they can be reacted either with two electrophiles or with chains containing leaving groups in the terminal positions, to obtain chains or silacyclic compounds. The use of tetralithiosilane as the synthetic equivalent of a 4-fold negatively charged silicon reagent has been reported but for some reason never adopted for synthetic purposes.⁵

One way to circumvent the concurrent existence of several negative charges on a silicon atom is the use of the Wurtztype coupling protocol. The consecutive reduction of halide substituents to negative charges allows for the synthesis of high molecular weight polysilanes.6 In this regard, the reaction of SiCl₄ with 4 equiv of Me₃SiCl in the presence of lithium corresponds to the hypothetical reaction of SiLi₄ with 4 equiv of Me₃SiCl.⁷ However, this protocol is not very tolerant of functional groups, and even phenyl groups are frequently reduced under the conditions of the Wurtz

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Scheme 1. Tris(trimethylsilyl)silylpotassium Exchange Reaction of All Trimethylsilyl against Dimethylphenylsilyl Groups Terminated by Potassium Fluoride Elimination



coupling reaction.⁸ Its use for the synthesis of oligosilanes of slightly higher structural complexity is therefore usually associated with very disappointing yields.⁹ Imitating the Wurtz-type coupling in more controlled ways, we have developed stepwise strategies that make use of trimethylsilyl groups as masked negative charges that are successively released at the same silicon atom.^{1,10}

Results and Discussion

A recent observation suggested a way to avoid the mentioned stepwise procedure. We found that the reaction of trimethylsilyl-substituted silylpotassium compounds with an excess of dimethylphenylfluorosilane (Scheme 1) yielded tetrakis(dimethylphenylsilyl)silane (1) in almost quantitative yield. The alternative synthetic access to this compound via Wurtz-type coupling of dimethylphenylchlorosilane with SiCl₄ and lithium is much less clean due to side reactions associated with reductive silylation of the phenyl groups.¹¹

The use of oligosilylpotassium compounds other than tris-(trimethylsilyl)silylpotassium provided some insight into the nature of this process. Reaction of bis(trimethylsilyl)methylsilylpotassium with excess dimethylphenylfluorosilane shut down the multiple exchange and resulted in exclusive salt elimination, yielding bis(trimethylsilyl)(dimethylphenylsilyl)methylsilane (2). Introducing a phenyl or phenylethynyl group to the charge-bearing silicon atom showed the exchange mechanism to be operational, and phenyltris(dimethylphenylsilyl)silane (3) and phenylethynyltris(dimethylphenylsilyl)silane (4) were obtained (Scheme 2).

Changing the fluorosilane component from dimethylphenylfluorosilane to pentamethylfluorodisilane allowed the convenient synthesis of the star-type oligosilane tetrakis(pentamethyldisilanyl)silane (5) (Scheme 3), so far only accessible by photolysis of the tris(pentamethyldisilanyl)silyl radical.¹²

The corresponding tris(pentamethyldisilanyl)silyl anion **6**, which was prepared previously from the respective

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Scheme 2. Substituent Exchange Reaction of Phenyl- and Phenylethynylbis(trimethylsilyl)silylpotassium







Scheme 4. Generation of Tris(pentamethyldisilanyl)silylpotassium (6)



Scheme 5. Access to Tetrakis(dimethylphenylsilyl)germane (7) and -stannane (8)



tris(pentamethyldisilanyl)silylmercury compounds,¹³ could be obtained conveniently by treatment of tetrakis(pentamethyldisilanyl)silane (**5**) with potassium *tert*-butoxide (Scheme 4).¹⁴

Also the question whether the exchange reaction is limited to silyl anions was addressed. Reactions of dimethylphenylfluorosilane with the analogous tris(trimethylsilyl)germylpotassium¹⁵ and -stannylpotassium¹⁶ compounds led to essentially the same results, but proceeded more sluggishly compared to the silyl case (Scheme 5). The formation of tetrakis(dimethylphenylsilyl)stannane (8) required additional portions of potassium *tert*-butoxide to proceed to completion.

When 1,4-difluorooctamethyltetrasilane was used instead of dimethylphenylfluorosilane, 1 equiv of the fluorosilane reacted with tris(trimethylsilyl)silylpotassium to give the known 1,1-bis(trimethylsilyl)octamethylcyclopentasilane¹⁷ (9) (Scheme 6).

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Scheme 7. Synthesis of Hexadecamethylspiro[4.4]nonasilane (11)



Scheme 8. One-Pot Synthesis of Hexadecamethylspiro[4.4]nonasilane (11) Starting from Tris(trimethylsilyl)silylpotassium



Certain oligosilanes are difficult to prepare in a stepwise manner. An occasion where the availability of a 1,1-dianionic silicon atom would be particularly useful is the synthesis of spirocyclic oligosilanes.¹⁸ Preliminary synthetic attempts to obtain compounds containing the spiro[4.4]nonasilane skeleton with two cyclopentasilane units were based on reactions of 1,4-dianionic tetrasilanes with SiCl₄.¹⁹ However, likely for steric reasons, only two or three of the required four bonds were formed during the salt elimination reactions. When 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (9) was converted to the corresponding silylpotassium compound **10** by reaction with potassium *tert*-butoxide¹⁴ and then treated with 1 equiv of 1,4-difluorooctamethyltetrasilane, the synthesis of hexadecamethylspiro[4.4]nonasilane (11) was achieved (Scheme 7).

As we have observed multiple exchange reactions with monofluorosilanes, it could be expected that the spirosilane **11** would form directly from tris(trimethylsilyl)silylpotassium by reacting with 2 equiv of 1,4-difluorooctamethyltetrasilane. This was indeed the case (Scheme 8), but the reaction was not as clean and the yield was substantially lower compared to the stepwise protocol.

Attempts to extend this strategy to the synthesis of spirosilanes of other ring sizes and substitution pattern were met with different success. The reaction of 1,4,4-tris(trimethylsilyl)octamethylcyclohexasilanylpotassium did not lead to the formation of the expected spiro[5.4]decasilane. NMR spectroscopic evidence hints to dodecamethylcyclohexasilane as the major product. When, however, one of the trimethylsilyl groups in

Scheme 9. Synthesis of Spiro[5.4]decasilane 13



the 4-position was replaced by methyl (12), the reaction gave the expected spirosilane 13 (Scheme 9).

Mechanistic Considerations

The described silvl exchange reactions are certainly based on equilibration processes. The fact that trimethylfluorosilane, which is rather volatile, is formed facilitates the process. We assume that the reaction proceeds via a pentacoordinate transition state. In cases where the incoming nucleophile is stabilized, either by three silvl groups or by two silvl and one additional phenyl or phenylethynyl group, it seems likely that the leaving fluoride attacks a silvl group in β -position, similar to the Peterson olefination²⁰ reaction (Scheme 10). A fluorosilane is thus released and the negative charge remains at the same silicon atom. The alternative salt elimination process leading to the formation of potassium fluoride seems to be less favorable. Nevertheless, once the salt elimination reaction takes place, it terminates the exchange process. To rule out the involvement of external fluoride attack, the hypothetical reaction of tetrakis(trimethylsilyl)silane with excess dimethylphenylfluorosilane was carried out in the presence of variable amounts of potassium fluoride, with and without crown ether present. No conversion was observed in any case.

Crystal Structure Analyses

Compounds 5, 6, 7, and 11 could be subjected to crystal structure analysis. Nonasilane 5 (Figure 1) crystallizes in the monoclinic space group P2(1)/c. The quality of the crystals was unfortunately not very good. Nevertheless, a basic description of the structure is possible. The geometry around the central silicon atom is distorted tetrahedral with bond angles ranging from 104.8° to 116.3°. The Si–Si bond distance connecting the pentamethyldisilanyl unit with the widest bond angles is consequently the shortest (2.352 Å). The other distances to the central atom are 2.367, 2.370, and 2.385 Å. The sterically less encumbered bonds to the peripheral trimethylsilyl groups are all in the range between 2.35 and 2.36 Å.

Compound **6** (Figure 2) is interesting, as it allows a direct comparison to the respective silyllithium compound (Me₃-SiMe₂Si)₃SiLi, which has been described to show an unusual umbrella effect.¹³ This effect was associated with torsional angles of about 35.7° for the segment $Li-Si-SiMe_2-SiMe_3$. The analogous angles for $K-Si-SiMe_2-SiMe_3$ of **6** were found to be between 66° and 70°. The reason for the less pronounced back-bending seems to be the larger spatial demand of the crown ether. In (Me₃SiMe₂Si)₃SiLi, lithium and the negatively charged silicon atoms are both tetracoordinate. Thus, a staggered conformation around the Si-Li bond allows the trimethylsilyl groups to reach over into

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Scheme 10. Supposed Reaction Mechanism of the Silyl Exchange Process

C(5A)

C(7A)

C(15)

C(12)

C(6A)

C(13)

C(14)



Figure 1. Molecular structure and numbering of 5. Selected bond lengths [Å] and bond angles [deg] with SDs: Si(1)-C(1) 1.877(7), Si(1)-Si(2) 2.360(3), Si(2)-Si(3) 2.367(3), Si(3)-Si(6) 2.352(2), Si(3)-Si(8) 2.370(3), Si(3)-Si(4) 2.385(3), Si(6)-Si(3)-Si(2) 116.31(10), Si(6)-Si(3)-Si(8) 113.04(10), Si(2)-Si(3)-Si(8) 108.66(10), Si(6)-Si(3)-Si(4) 106.51(10), Si(2)-Si(3)-Si(4) 104.82(10), Si(8)-Si(3)-Si(4) 106.73(10).

C(13)



Figure 2. Molecular structure and numbering of 6. Selected bond lengths [Å] and bond angles [deg] with SDs: K(1)-O(1) 2.885(5), K(1)-Si(1) 3.673(3), O(1)-C(12) 1.431(10), Si(1)-Si(4) 2.382(3), Si(1)-Si(6) 2.390(3), Si(1)-Si(2) 2.398(3), Si(2)-C (13) 1.935(8), Si(4)-Si(1)-Si(6) 100.61(10), Si(4)-Si(1)-Si(2) 100.14(11), Si(6)-Si(1)-Si(2) 99.70(11), Si(4)-Si(1)-K(1) 118.22(9), Si(6)-Si(1)-K(1) 115.70(9), Si(2)-Si(1)-K(1) 119.11(9).



the areas between the THF molecules. For the case of **6** the potassium atom is surrounded by the crown ether. Conformational changes would not open space for the trimethylsilyl groups. Consequently, these groups avoid approaching the vicinity of the potassium atom. Even if the Si-K bond is approximately 0.9 Å longer than the Si-Li distance, the trimethylsilyl groups of **6** have to be accommodated in an approximate C_3 symmetric arrangement closer to the neighboring wing. This causes a substantial elongation of the involved Si-Si bonds. While for $(Me_3SiMe_2Si)_3SiLi$ rather common values of ca. 2.36 Å for the LiSi-SiMe₂ bond and 2.35 Å for the Me₂Si-SiMe₃ units were found, these values increase to 2.40 and 2.39 Å, respectively, in **6**.

As expected, the structure of the tetrasilylated germane 7 (Figure 3) is isomorphous to the corresponding $(Me_2PhSi)_4$ -Si.^{11b} Both crystallize in the space group C2/c with the cell parameters of 7 being slightly enhanced. The Si–Si bond lengths of $(Me_2PhSi)_4$ Si were found to be 2.37 Å, and also the Si–Ge bond distances of 2.394 and 2.400 Å for 7 are common for this type of compounds.²¹

The structure of the spirocyclic nonasilane **11** (Figure 4) does not appear to be very strained. Bond distances between silicon atoms range from 2.33 to 2.36 Å, which is quite typical and indicative of not much steric interaction. The two five-membered rings are both exhibiting envelope conformation. They share a silicon atom, which is part of the envelope's fold. The two envelope planes are at an angle of about 70°. As both flaps open to the same side in angles of 41° and 43°, a *transoid* aligned pentasilane

⁽²¹⁾ A search for the structural unit Si₃Ge in the Cambridge Crystallographic Database using Conquest Version 1.10 provided an average value of 2.377 Å and a median value of 2.398 Å for the Si–Ge distance.



Figure 4. Molecular structure and numbering of 11. Selected bond lengths [Å] and bond angles [deg] with SDs: Si(1)–Si(2) 2.3456(15), Si(1)–Si(6) 2.3504(14), Si(1)–Si(5) 2.3612(15), Si(2)–C(1) 1.871(4), Si(2)–Si(3) 2.3299(16), Si(2)–Si(1)–Si(6) 112.65(6), Si(2)–Si(1)–Si(9) 114.87(6), Si(6)–Si(1)–Si(6) 101.22(6), Si(2)–Si(1)–Si(5) 100.57(6), Si(6)–Si(1)–Si(5) 114.47(6), Si(9)–Si(1)–Si(5) 113.71(7).

Fable 1. Crystallographic Data for Compounds 5. 6. 7. and 1	
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	5	6	7	11		
empirical formula	Si ₉ C ₂₀ H ₆₀	KO ₆ Si ₇ C ₂₇ H ₆₉	GeSi ₄ C ₃₂ H ₄₄	Si ₉ C ₁₆ H ₄₈		
M_{w}	553.49	725.55	613.62	493.35		
temperature [K]	100(2)	100(2)	100(2)	100(2)		
size [mm]	$0.33 \times 0.20 \times 0.14$	$0.44 \times 0.34 \times 0.30$	$0.40 \times 0.32 \times 0.22$	$0.28 \times 0.23 \times 0.20$		
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic		
space group	P2(1)/c	P2(1)/n	C2/c	P2(1)/n		
a [Å]	11.329(2)	12.684(3)	16.389(3)	10.447(2)		
b [Å]	13.412(3)	18.764(4)	9.6252(2)	18.580(4)		
c [Å]	23.939(5)	19.958(4)	22.329(5)	16.570(3)		
a [deg]	90	90	90	90		
β [deg]	93.40(3)	97.66(3)	111.02(3)	101.64(3)		
γ [deg]	90	90	90	90		
$V[Å^3]$	3631.1(2)	4708(2)	3287.9(2)	3150(2)		
Z	4	4	4	4		
$\rho_{\rm calc} [\rm g \ cm^{-3}]$	1.012	1.024	1.240	1.040		
absorp coeff [mm ⁻¹]	0.337	0.320	1.097	0.381		
F(000)	1224	1584	1296	1080		
θ range [deg]	$1.70 < \theta < 24.00$	$1.50 < \theta < 26.41$	$1.95 < \theta < 26.35$	$1.67 < \theta < 26.38$		
reflns collected/unique	23 620/5688	35049/9578	12483/3340	24 901/6427		
completeness to θ [%]	99.8	99.0	99.7	99.8		
data/restraints/params	5688/0/282	9578/0/387	3340/0/172	6427/0/242		
goodness of fit on F^2	1.18	0.93	1.13	1.04		
final R indices $[I > 2\sigma(I)]$	R1 = 0.099, wR2 = 0.167	R1 = 0.091, wR2 = 0.216	R1 = 0.036, wR2 = 0.082	R1 = 0.068, wR2 = 0.163		
<i>R</i> indices (all data)	R1 = 0.140, wR2 = 0.184	R1 = 0.195, wR2 = 0.269	R1 = 0.039, wR2 = 0.084	R1 = 0.098, wR2 = 0.180		
largest diff peak/hole $[e^-/Å^3]$	0.58/-0.57	0.04/-0.02	0.84/-0.25	1.38/-0.33		

segment, which includes the joint silicon, the two flaps, and the other fold atoms, is observed with torsional angles of 164° and 167°.

Conclusion

The attempted salt elimination reaction of tris(trimethylsilyl)silylpotassium with excess dimethylphenylfluorosilane was unexpectedly accompanied by the exchange of all trimethylsilyl for dimethylphenylsilyl groups. The thus obtained tetrakis(dimethylphenylsilyl)silane is not easily prepared by Wurtz-type coupling. The silyl exchange reaction was found to be dependent on the presence of chargestabilizing substituents on the silylpotassium species. Reaction of methylbis(trimethylsilyl)silylpotassium with excess dimethylphenylfluorosilane gave the salt elimination product methyl(dimethylphenylsilyl)bis(trimethylsilyl)silane, exclusively. Tris(trimethylsilyl)silylpotassium could be reacted with excess pentamethylsilylfluorodisilane to give tetrakis-(pentamethyldisilanyl)silane.

The use of 1,4-difluorooctamethyltetrasilane provided a unique opportunity to utilize this exchange reaction to obtain spirocyclic oligosilanes, first examples of which have been obtained this way.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of nitrogen or argon using either Schlenk techniques or a glovebox. Solvents were dried using a column solvent purification system.²² Potassium *tert*-butanolate was purchased from Merck.

¹H (300 MHz), ¹³C (75.4 MHz), ²⁹Si (59.3 MHz), and ¹¹⁹Sn (111.8 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise, samples for NMR spectra were dissolved in deuterated benzene. In the case of reaction control by means of ²⁹Si NMR spectroscopy aliquots were measured with a D₂O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ²⁹Si, the INEPT pulse sequence was used for the amplification of the signal.²³

Elemental analysis was carried out using a Heraeus Vario Elementar instrument (in cases of bad carbon values WO₃ was added to facilitate complete combustion and to suppress silicon carbide formation).

X-ray Structure Determination. For X-ray structure analyses crystals were mounted onto the tip of glass fibers, and data

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collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Ka radiation (0.71073 Å). Data were reduced to F_0^2 and corrected for absorption effects with SAINT²⁴ and SADABS,²⁵ respectively. Structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).²⁶ All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All ORTEP plots (Figures 1-4) were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-666916 (5), 666914 (6), 666915 (7), and 695767 (11). Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

The following compounds were synthesized according to the reported procedures: dimethylphenylfluorosilane,²⁷ methylbis-(trimethylsilyl)silylpotassium,²⁸ phenylbis(trimethylsilyl)silylpotassium,²⁸ pentamethylfluorosilane,²⁹ tris(trimethylsilyl)silylpotassium,¹⁴ 1,4-difluorooctamethyltetrasilane,³⁰ 1,1-bis(trimethylsilyl)octamethylcyclopentasilane,^{17c} tris(trimethylsilyl)germylpotassium,¹⁵ tris-(trimethylsilyl)stannylpotassium,¹⁶ and 1,1,4-tris(trimethylsilyl)nonamethylcyclohexasilane.¹⁰

Tetrakis(dimethylphenylsilyl)silane (1). To a solution of dimethylphenylfluorosilane (4.499 g, 29.16 mmol) in toluene (50 mL) was added tris(trimethylsilyl)silylpotassium [generated *in situ* from tetrakis(trimethylsilyl)silane (1.127 g, 3.514 mmol) and KO^{*t*}Bu (394 mg, 3.51 mmol)] in THF (10 mL) over a period of 10 min. The resulting yellow solution was stirred for 5 days until complete conversion was detected. All volatile components (solvents and silylfluorides) were removed under vacuum. The residue was dissolved in diethyl ether and washed with dilute sulfuric acid. After drying over Na₂SO₄ the product crystallized from the ethereal solution, which was allowed to slowly evaporate. Compound **1** was obtained as a colorless crystalline material (1.88 g, 93%) with spectroscopic properties in accordance with published values.^{11b}

Methylbis(trimethylsily)dimethylphenylsilylsilane (2). To a solution of dimethylphenylfluorosilane (983 mg, 6.37 mmol) in toluene (10 mL) was added methylbis(trimethylsilyl)silylpotassium (1.40 mmol) in THF (3 mL) over a period of 10 min. After stirring for 24 h the precipitate was removed by filtration, and after removal of all volatiles **2** (443 mg, 98%) was obtained as a colorless oil. ¹H NMR: δ 7.46 (m, 2H), 7.18 (m, 3H), 0.44 (s, 6H), 0.11 (s, 18H). ¹³C NMR: δ 134.0, 133.9, 128.6, 128.0, 0.3, -1.3, -12.8. ²⁹Si NMR: δ -12.6, -16.1, -87.5. Anal. Calcd for C₁₅H₃₂Si₄ (324.76): C 55.48, H 9.93. Found: C 54.91, H 9.99.

Phenyltris(dimethylphenylsilyl)silane (3). The reaction was carried out according to the procedure described for **1** using dimethylphenylfluorosilane (794 mg, 5.15 mmol) in toluene (10 mL) and phenylbis(trimethylsilyl)silylpotassium (1.40 mmol) in THF (5 mL). Compound **3** (497 mg, 90%) was obtained as a colorless oil. ¹H NMR: δ 7.60 (m, 2H), 7.36 (m, 9H), 7.13 (m, 9H), 0.37 (s, 18H). ¹³C NMR: δ 140.2, 137.4, 134.5, 129.0, 128.1, 128.0, 128.0, -0.4.

²⁹Si NMR: δ –16.2, –76.2.³¹ Anal. Calcd for C₃₀H₃₈Si₄ (510.96): C 70.52, H 7.50. Found: C 70.59, H 7.62.

Tris(dimethylphenylsilyl)phenylethynylsilane (4). The reaction was carried out as described above for the synthesis of **1** with dimethylphenylfluorosilane (265 mg, 1.72 mmol) in toluene (30 mL) and phenylethynylbis(trimethylsilyl)silylpotassium (0.29 mmol) in THF (8 mL). Compound **4** (95 mg, 61%) was obtained as a slightly brown oil. ¹H NMR: δ 7.17 (m, 15H), 7.01 (m, 5H), 0.37 (s, 18H). ²⁹Si NMR: δ –15.7, –99.9. Anal. Calcd for C₃₂H₃₈Si₄ (534.99): C 71.84, H 7.16. Found: C 70.91, H 7.12.

Tetrakis(pentamethyldisilyl)silane (5). The reaction was carried out according to the synthesis of 1 with pentamethylfluorodisilane (416 mg, 2.77 mmol) in toluene (3 mL) and tris-(trimethylsilyl)silylpotassium (0.461 mmol) in THF (3 mL). Complete conversion was reached after 16 h. After recrystallization of the white residue from 2-propanol at -30 °C compound 5 (130 mg, 51%) was obtained as colorless crystals. Mp: 54– 55 °C. ¹H NMR: δ 0.38 (s, 24H), 0.22 (s, 36H). ¹³C NMR: δ 0.4; -0.2. ²⁹Si NMR: δ -14.0; -38.4; -110.9. UV-vis (pentane, $\lambda_{max}(\varepsilon)$): 211 nm (4.0 × 10⁴), 222 nm (2.8 × 10⁴). Anal. Calcd for C₂₀H₆₀Si₉ (553.46): C 43.40, H 10.93. Found: C 43.17; H 10.86.

Tris(pentamethyldisilanyl)silylpotassium · 18-crown-6 (6). Compound **5** (169 mg, 0.305 mmol), KO'Bu (34 mg, 0.30 mmol), and 18-crown-6 (81 mg, 0.31 mmol) were dissolved in benzene (3 mL) and stirred overnight at rt. Removal of benzene under vacuum was followed by dissolving the residue in toluene (3 mL) and pentane (0.3 mL). Compound **6** (201 mg, 92%) was obtained as red crystals after cooling to -35 °C. ¹H NMR: δ 3.17 (s, 24H, 18-crown-6), 0.68 (s, 18H), 0.45 (s, 27H). ¹³C NMR: δ 69.8 (18-crown-6), 4.4, 0.3. ²⁹Si NMR: δ –16.1, –33.8, –181.2.

Tetrakis(dimethylphenylsilyl)germane (7). The reaction was carried out according to the synthesis of **1** with dimethylphenyl-fluorosilane (533 mg, 3.45 mmol) and tris(trimethylsilyl)germylpotassium (0.42 mmol). After 48 h some additional KO'Bu (23 mg, 0.21 mmol) was added. Complete conversion was reached after another 48 h. Compound **7** (75 mg, 29%) was obtained after recrystallization from ether at 0 °C as colorless crystals. Mp: 107–112 °C. ¹H NMR: δ 7.25 (m, 20H), 0.41 (s, 24H). ¹³C NMR: δ 141.4, 134.4, 128.7, 128.0, 1.9. ²⁹Si NMR: δ -8.2. Anal. Calcd for C₃₂H₄₄GeSi₄ (613.64): C 62.63, H 7.23. Found: C 62.35, H 7.37.

Tetrakis(dimethylphenylsilyl)stannane (8). To a solution of dimethylphenylfluorosilane (648 mg, 4.20 mmol) in THF/diethyl ether (ca. 1:1, 5 mL) was added tris(trimethylsilyl)stannylpotassium [generated *in situ* from tetrakis(trimethylsilyl)stannane (173 mg, 0.420 mmol) and KO'Bu (49 mg, 0.44 mmol)] in THF (4 mL over a period of 2 min. After 24 h additional KO'Bu (49 mg, 0.44 mmol) was added. Another 24 h later, the formation of **8** as the only tin-containing species was unambiguously verified by multinuclear NMR spectroscopy, alongside formation of tetramethyl-1,3-diphenyldisiloxane and *tert*-butyl (dimethylphenylsilyl) ether. ¹H NMR (C₆D₆): δ 7.25 (m, 20H), 0.44 (s, 24H, ³J_{1H-117/119Sn} = 20.9/21.5 Hz). ¹³C NMR (C₆D₆): δ 140.6, 133.6, 128.6, 128.0, 2.0 (²J_{13C-117/119Sn} = 39/41 Hz). ²⁹Si NMR (C₆D₆): δ -634.5 (¹J_{29Si-117/119Sn} = 323/339 Hz). ¹¹⁹Sn NMR (C₆D₆): δ -634.5 (¹J_{29Si-119Sn} = 339 Hz, ²J_{13C-119Sn} = 41 Hz).

1,1-Bis(trimethylsilyl)octamethylcyclopentasilane (9). To a solution of 1,4-difluorooctamethyltetrasilane (140 mg, 0.516 mmol) in toluene (2 mL) was slowly added tris(trimethylsilyl)silylpotassium (0.491 mmol) in THF (2 mL). After stirring for 14 h the reaction mixture was poured onto 0.5 M H_2SO_4 /water/ice and extracted several times with ether. The combined organic layers were dried with Na_2SO_4 and the solvent was removed under vacuum. NMR analysis revealed the formation of 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (NMR data in accordance with published

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values: refs 17b,c) as the main product along with some tris (trimethylsilyl)(4'-fluorooctamethyltetrasilanyl)silane.

Trimethylsilyloctamethylcyclopentasilylpotassium (10). A mixture of 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (900 mg, 2.21 mmol) and KO'Bu (261 mg, 2.32 mmol) was dissolved in THF (15 mL). The yellow solution was stirred for 3 h until complete anion formation was detected. ²⁹Si NMR data were in close agreement with the previously prepared crown ether adduct of $10:^{32}-3.4, -23.6, -23.6, -184.9$.

Hexadecamethylspiro[4.4]nonasilane (11). To a solution of 1,4-difluorooctamethyltetrasilane (616 mg, 2.28 mmol) in toluene (50 mL) was slowly added compound 10 (2.21 mmol) in THF (15 mL). After stirring for 14 h the reaction mixture was poured onto 0.5 M H₂SO₄/water/ice and extracted several times with ether. The combined organic layers were dried with Na₂SO₄ and the solvent was removed under vacuum. After recrystallization from 2-propanol/heptane/DME 11 was obtained as colorless crystals (985 mg, 90%). Mp: 88–91 °C. UV–vis (pentane, λ_{max} (ε)): 190 nm (5.0 × 10⁴), 237(s) nm (1.5 × 10⁴), 282(s) nm (3.8 × 10³). ¹H NMR δ (CDCl₃): 0.31 (s, 24H), 0.19 (s, 24H). ¹³C NMR δ (CDCl₃): -1.2, -6.2. ²⁹Si NMR δ (C₆D₆): -28.3, -41.6, -130.2. Anal. Calcd for C₁₆H₄₈Si₉ (493.32): C 38.95, H 9.81. Found: C 38.37, H 9.64.

8-Trimethylsilylheptadecamethylspiro[5.4]decasilane (13). To a solution of 1,4-difluorooctamethyltetrasilane (35 mg, 0.13 mmol) in toluene (5 mL) was added slowly 1,4-bis(trimethylsilyl)nonamethylcyclohexasilan-1-ylpotassium (12) [prepared from 1,1,4tris(trimethylsilyl)heptamethylcyclohexasilane (65 mg, 0.13 mmol) and KO'Bu (15 mg, 0.13 mmol) in THF (2 mL); ^{29}Si NMR δ (D₂Ocapillary): -2.0, -10.0, -27.7, -39.9, -81.1, -188.5]. After stirring for 14 h the reaction mixture was poured onto 0.5 M H₂SO₄/water/ ice and extracted several times with ether. The combined organic layers were dried with Na2SO4 and the solvent was removed under vacuum. 13 was obtained as a highly viscous oil (36 mg, 48%). ¹H NMR δ (C₆D₆): 0.37 (s, 6H), 0.35 (s, 6H), 0.32 (s, 6H), 0.29 (s, 6H), 0.28 (s, 6H), 0.24 (s, 6H), 0.21 (s, 9H), 0.20 (s, 3H), 0.19 (s, 6H), 0.19 (s, 6H). ²⁹Si NMR δ (C₆D₆): -9.5, -26.0, -30.2, -32.4 (2 signals), -38.9 (2 signals), -41.2, -42.1, -82.3, -127.5. Anal. Calcd for C₂₀H₆₀Si₁₁ (609.63): C 39.40, H 9.92. Found: C 38.92, H 9.97.

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Supporting Information Available: X-ray crystallographic information in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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