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Reviews

Preparation and Reactions of Polysilanyl Anions and Dianions

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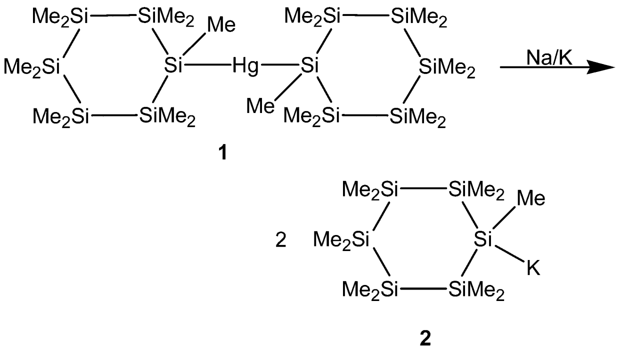
The author's rather accidental discovery of the synthesis of [tris(trimethylsilyl)silyl]potassium by reaction of tetrakis(trimethylsilyl)silane with potassium *tert*-butoxide in 1996 was the starting point for the continuation of some chemistry reported by earlier workers which had been mostly dormant for almost 30 years. The reaction of polysilanes with potassium alkoxides was found to be superior to analogous chemistry using methyllithium. The high selectivity for the cleavage of peripheral trimethylsilyl groups allowed not only the preparation of higher polysilanyl anions but also of dianions. The latter are especially useful for the synthesis of cyclic and also bicyclic polysilanes, including heterocyclic compounds. The incorporation of heteroatoms into the starting materials gave silyl anions with ambiphilic character. (Polysilanyl)potassium compounds were used to prepare a number of transition-metal compounds, including the first example of an early-transition-metal disilene complex. Recent studies have shown that the method of anion formation via the reaction of silylated precursors with potassium *tert*-butoxide works equally well with carbon, germanium, and tin compounds.

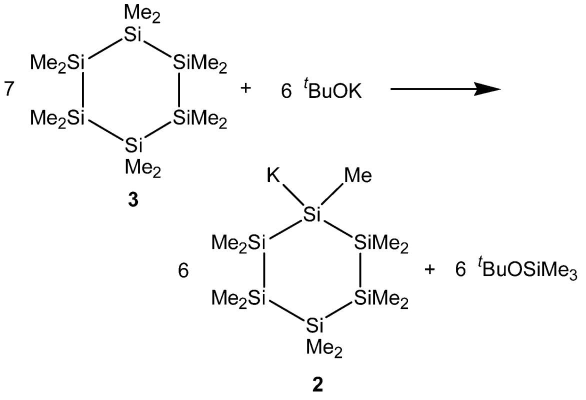
Introduction

In 1994 I returned to the Technical University of Graz in Austria after having spent a marvelous time doing postdoctoral research with Professor Barry Trost at Stanford University. I had a clear idea of pursuing a career of research in organic synthesis with some emphasis on transition-metal catalysis. Therefore, when I was approached by the late Professor Edwin Hengge to do some transition-metal catalysis work on organosilanes, I considered this to be a short-term excursion into the realm of organoelement chemistry. In Hengge's group much attention was focused on cyclosilane chemistry.[1] Some relatively recent work had utilized Vyazankin chemistry[2] to obtain (undecamethylcyclohexasilanyl)potassium (**2**) from the respective bis(undecamethylcyclohexasilanyl)mercury compound (**1**) (eq 1).[3,4] Such potassium derivatives proved to be very useful for the synthesis of higher polysilanes.



(1)

At the time I joined Hengge's group, a major improvement of the synthesis of (undecamethylcyclohexasilanyl)potassium (**2**) had been achieved by the simple reaction of dodecamethylcyclohexasilane (**3**) with a stoichiometric amount of potassium *tert*-butoxide.[5] This reaction avoided the use of air- and light-sensitive, toxic silyl mercurials. Nevertheless, the reaction was a strange one with an odd stoichiometry. What seemed to be at first glance a silicon−carbon cleavage reaction involved some fairly complicated rearrangement chemistry. The byproduct was not *tert*-butyl methyl ether but trimethylsilyl *tert*-butyl ether. This implied that in the reaction 7 equiv of dodecamethylcyclohexasilane was converted to 6 equiv of (undecamethylcyclohexasilanyl)potassium and trimethylsilyl *tert*-butyl ether (eq 2). In addition, the reaction was not completely selective as some



(2)

percentage of (nonadecamethylcyclopentasilanyl)potassium always was formed. It also did not matter whether the starting

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[1] Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495−1526.

[2] Vyazankin, N. S.; Razuvaev, G. A.; Gladyshev, E. N. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 830−832.

[3] (a) Mitter, F. K.; Pollhammer, G. I.; Hengge, E. *J. Organomet. Chem.* **1986**, *314*, 1−5. (b) Mitter, F. K.; Hengge, E. *J. Organomet. Chem.* **1987**, *332*, 47−52. (c) Hengge, E.; Jenkner, P. K. *Z. Anorg. Allg. Chem.* **1988**, *560*, 27−34. (d) Hengge, E.; Gspaltl, P.; Spielberger, A. *J. Organomet. Chem.* **1994**, *479*, 165−169.

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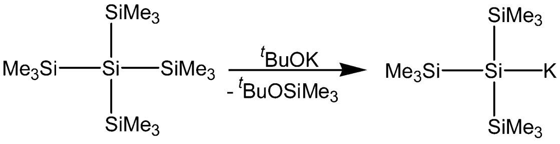
material was dodecamethylcyclohexasilane or decamethylcyclopentasilane.

This behavior aroused my curiosity, and I started some investigations of my own on linear polysilanes. My first experiment was the reaction of octamethyltrisilane with potassium *tert*-butoxide in dimethoxyethane (DME). Surprisingly, also in this reaction (undecamethylcyclohexasilanyl)potassium (**2**) was formed as a major product, accompanied by a high yield of hexamethyldisilane. The same reaction in THF revealed a stepwise formation of linear permethylated silanes up to the nonasilane, followed by a back-biting process to give cyclosilanes. Eventually almost exclusive formation of dodecamethylcyclohexasilane (**3**) and hexamethyldisilane was observed. In an attempt to do similar chemistry with branched polysilanes, I repeated the reaction of potassium *tert*-butoxide with tetrakis(trimethylsilyl)silane (**4**). The almost quantitative product of this clean reaction was [tris(trimethylsilyl)silyl]potassium (**5**) (eq 3).[6]



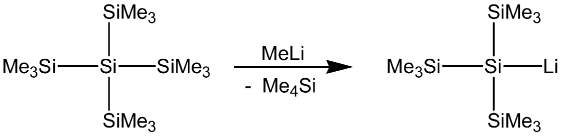
(3)

4 **5**

This result caused me to realize the limitations of my knowledge concerning organosilicon chemistry and to enquire about some of the roots of the chemistry I just had come upon.

Gilman's Branched Polysilanes

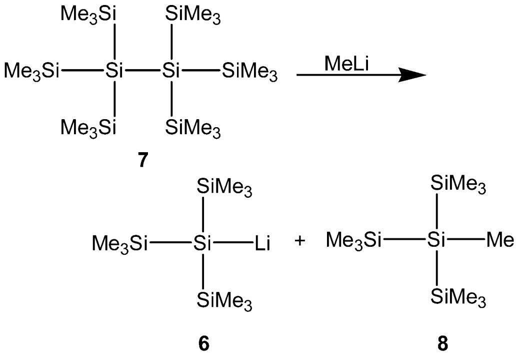
The story of polysilanyl anion chemistry starts with Henry Gilman, one of the giants of American organometallic chemistry. Gilman and co-workers made numerous contributions to organosilicon chemistry. In particular, the metalation of organosilicon compounds was a major field of interest. Gilman's group prepared the first examples of branched polysilanes[7] and tetrakis(trimethylsilyl)silane (**4**), the first tetrasilyl-substituted silane.[8] Reaction of **4** with methyllithium provided access to [tris(trimethylsilyl)silyl]lithium (**6**), the first branched silyl anion (eq 4).[9]



(4)

4 **6**

Compound **6** was used as a useful building block in the preparation of higher polysilanes such as hexakis(trimethylsilyl)disilane (**7**).[10] Attempts to subject **7** to the conditions required for the synthesis of **6** did not lead to cleavage of a terminal trimethylsilyl group but to the formation of **6** and tris(trimethylsilyl)methylsilane (**8**) (eq 5).

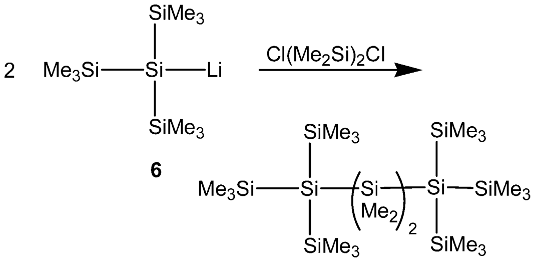


(5)

When, instead of methyllithium, either **6** or (triphenylsilyl)lithium was used as the metalating agent, [pentakis(trimethylsilyl)disilanyl]lithium (**9**) was formed. Reaction of **7** with 2 equiv of (triphenylsilyl)lithium gave 1,2-dilithiotetrakis(trimethylsilyl)disilane (**10**) (Scheme 1). The dianionic compound **10** is a very interesting, potentially useful building block for synthetic organosilicon chemistry. These results were described in what was Gilman's last publication on polysilanyl anion chemistry. The direction of his future research changed to completely other aspects of organosilicon chemistry.

[Tris(trimethylsilyl)silyl]lithium (**6**) became a popular building block in main-group and transition-metal chemistry.[11] Some years after Gilman's original publication Gutekunst and Brook published an improved procedure for the synthesis of **6**.[12] Brook had utilized **6** for the synthesis of acylpolysilanes, which eventually led to the synthesis of the first stable silene.[13]

The reaction of higher polysilanes with methyllithium had been reinvestigated by Apeloig and co-workers. They found that the susceptibility to cleavage of inner Si−Si bonds extends to 2,2,4,4-tetrakis(trimethylsilyl)octamethylpentasilane (**11**).[14] By reaction of 2 equiv of [tris(trimethylsilyl)silyl]lithium (**6**) with 1,2-dichlorotetramethyldisilane Pannell and co-workers obtained **12** (eq 6).[15]



(6)

12

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(4) In eq 1 and most of the following equations and schemes, anionic silicon compounds are drawn with a conventional bond between the negatively charged silicon atom and the metal counterion. It should be noted that it cannot be assumed that this interaction is therefore covalent. While the exact nature of the silicon−potassium bond is still a matter of investigation, reasons of convenience caused me to draw simple bonds between silicon and alkali-metal atoms: in particular, potassium. In addition, here it also should be noted that the equations and schemes do not reflect that potassium ions in fact are mostly coordinated by either ethereal (THF, DME, crown ether) or aromatic (benzene, toluene) solvent molecules. In cases of isolation without any donor molecules, the solid-state structures showed dimerization and coordination of the potassium ion to neighboring trimethylsilyl groups.

(5) Uhlig, F.; Gspaltl, P.; Trabi, M.; Hengge, E. *J. Organomet. Chem.* **1995**, *493*, 33−40.

(6) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221−226.

(7) Wittenberg, D.; George, M. V.; Gilman, H. *J. Am. Chem. Soc.* **1959**, *81*, 4812−4815.

(8) Gilman, H.; Smith, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 1454.

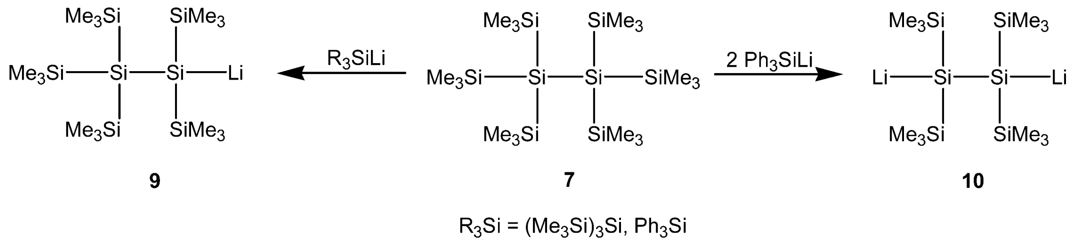
(9) (a) Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848−849. (b) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91−101.

(10) Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67−76.

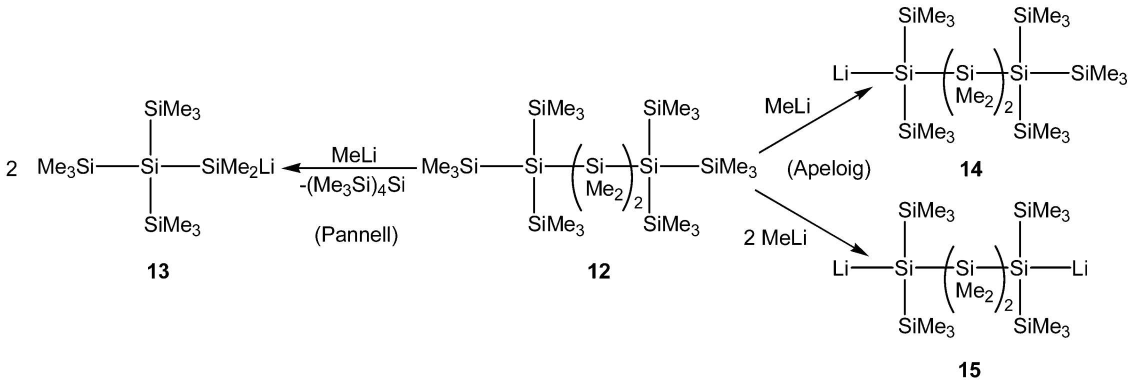
(11) Kornev, A. N. *Russ. Chem. Rev.* **2004**, *73*, 1065−1089.

(12) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1−3.

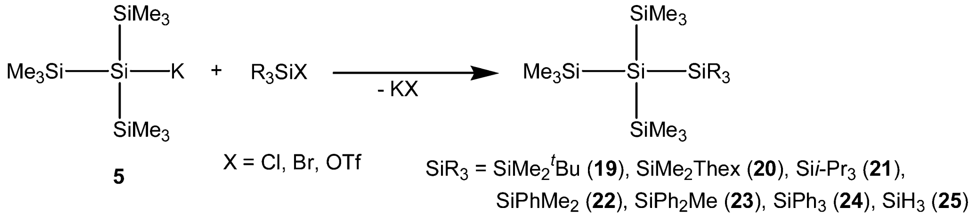
Scheme 1



Scheme 2



Scheme 3



The reaction of **12** with methyllithium was also investigated by the groups of Pannell and Apeloig, who came to different conclusions. While Pannell proposed cleavage of the central silicon−silicon bond to give the primary (polysilanyl)lithium compound **13**,[15] Apeloig found that cleavage of a terminal trimethylsilyl group afforded **14** and that the addition of another 1 equiv of methyllithium provided access to the 1,4-dilithiosilane **15** (Scheme 2).[16]

Polysilanylpotassium Chemistry Continued

After my synthesis of [tris(trimethylsilyl)silyl]potassium (**5**) and some research on previous work, I realized that by this time Gilman's chemistry was already 30 years old. Even **5** had been prepared in the meantime by Klinkhammer using transmetalation of bis[tris(trimethylsilyl)silyl]mercury and -cadmium with potassium.[17] Also, the use of potassium alkoxides for the synthesis of silyl anions had been established a long time before. This procedure had been used by Sakurai et al. to obtain (trimethylsilyl)potassium from hexamethyldisilane.[18]

Nevertheless, the reaction of tetrakis(trimethylsilyl)silane (**4**) with potassium *tert*-butoxide was a novel way to obtain the tris(trimethylsilyl)silyl anion. In comparison to the Gilman chemistry, the reaction is a real improvement. It does not require the use of alkyllithium solutions but makes use of readily available potassium alkoxides, which can easily be controlled in their stoichiometry. In addition, the reaction is rather fast in THF. Surprisingly, [tris(trimethylsilyl)silyl]potassium (**5**) is much more soluble, even in very nonpolar solvents, than its lithium counterpart (**6**).[19]

Attempts to repeat the reaction of tetrakis(trimethylsilyl)silane (**4**) with lithium and sodium *tert*-butoxide revealed that the reaction does not work at all with the lithium alkoxide but can be carried out under forcing conditions (DME, reflux) with sodium *tert*-butoxide.[19] Interestingly, [tris(trimethylsilyl)silyl]sodium (**16**) was found to be the least soluble compound of the series, precipitating from DME at room temperature. Reactions of tetrakis(trimethylsilyl)silane (**4**) with rubidium and cesium *tert*-butoxides in THF provided access to the expected [tris(trimethylsilyl)silyl]rubidium (**17**) and -cesium (**18**) in essentially quantitative yield.

In some of our studies done with [tris(trimethylsilyl)silyl]potassium (**5**) we reacted it with various silyl electrophiles in order to obtain derivatives of tetrakis(trimethylsilyl)silane (Scheme 3).[6]

Attempts to subject these compounds again to the reaction with potassium *tert*-butoxide in THF were successful when SiR_3

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(13) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191−192.

(14) Apeloig, Y.; Yuzefovich, M.; Bendikov, M.; Bravo-Zhivotovskii, D.; Klinkhammer, K. *Organometallics* **1997**, *16*, 1265−1269.

(15) Whittaker, S. M.; Brun, M.-C.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1995**, *499*, 247−252.

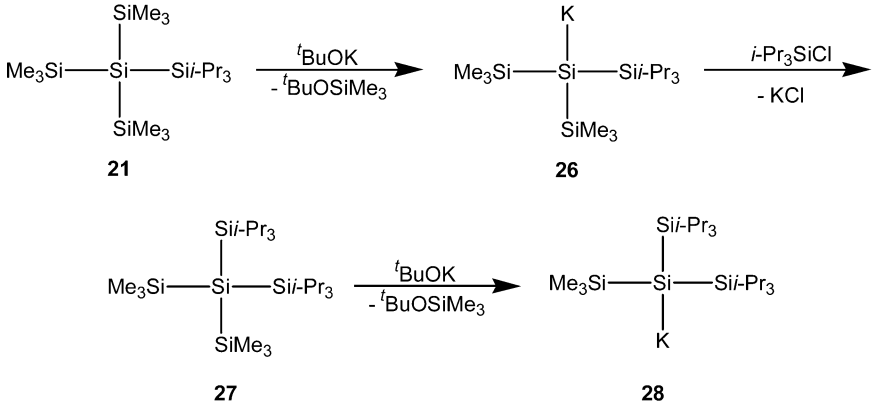
(16) Apeloig, Y.; Korogodsky, G.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *Eur. J. Inorg. Chem.* **2000**, 1091−1095.

(17) (a) Klinkhammer, K. W.; Schwarz, W. *Z. Anorg. Allg. Chem* **1993**, *619*, 1777−1789. (b) Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418−1432.

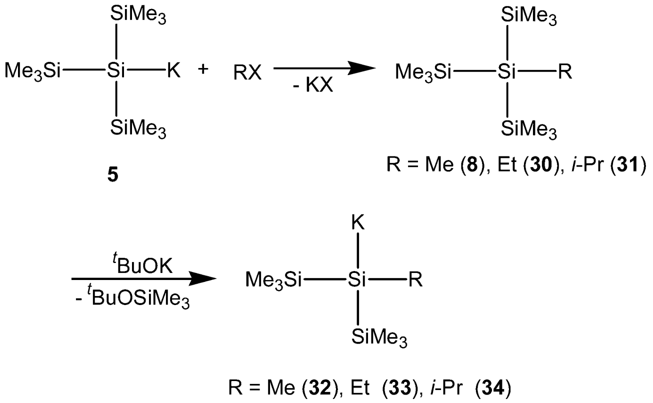
(18) (a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, *19*, 1511−1514. (b) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46−C48.

(19) Kayser, C. Dissertation, Technical University Graz, 2001.

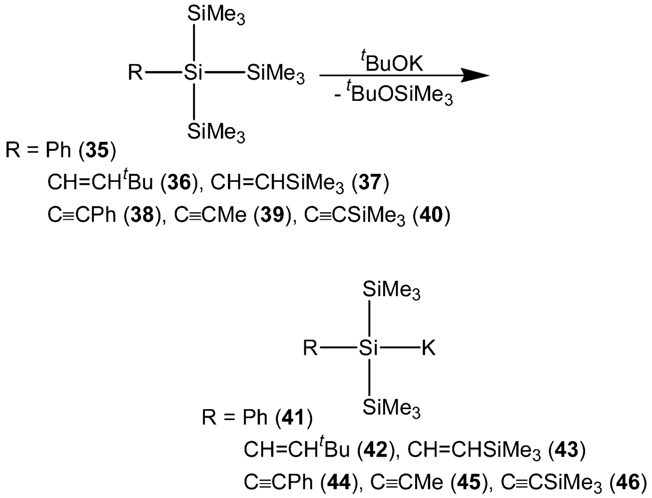
Scheme 4



Scheme 5



Scheme 6



was a trialkylsilyl group, sterically more demanding than the trimethylsilyl group (**19**−**21**). Tris(silyl)silyl anions (**26**, **28**) with one or two bulky silyl groups such as triisopropylsilyl could be obtained conveniently in this way (Scheme 4).[20,21] If the dimethylphenylsilyl-substituted compound **22** was treated with potassium *tert*-butoxide, a mixture of equal amounts of **5** and [bis(trimethylsilyl)(dimethylphenylsilyl)silyl]potassium (**29**) was obtained. This indicates a preferred reactivity of the potassium alkoxide with dimethylphenylsilyl compared to trimethylsilyl groups. Reactions of the higher phenylated neopentasilanes **23** and **24** with potassium *tert*-butoxide were not clean; always formation of some Ph_2MeSiK or Ph_3SiK, respectively, was observed.[20]

[Tris(trimethylsilyl)silyl]potassium (**5**) can be alkylated with dimethyl sulfate, ethyl bromide, or isopropyl chloride (Scheme 5). The isotetrasilanes **8**, **30**, and **31** could be in turn reacted cleanly with potassium *tert*-butoxide to give the respective silyl anions (**32**−**34**) (Scheme 5).[6,20]

To assess the scope of the method, a number of different substituents were attached to the tris(trimethylsilyl)silyl fragment, and the compounds thus obtained then were treated with potassium *tert*-butoxide.

It was found that phenyl substituents (**35**) facilitate the reaction, which is faster and seems to be more exothermic (Scheme 6). Similar behavior was observed when R = vinyl,[22] alkynyl.[23,24] In fact, (tris(trimethylsilyl)silyl)alkynes were the most reactive among all the investigated compounds substituted with organic groups (Scheme 6).[23]

(Polysilanyl)lithium compounds had been used for the synthesis of dendrimeric polysilanes.[25] It was therefore of interest to see whether the potassium compounds might be of similar use. To test this, tris(dimethylphenylsilyl)methylsilane (**47**) was selected as the starting material for both the core and the branching units of the dendrimer. Reaction with hydrogen bromide gave the tribromide **48**, while conversion with potassium *tert*-butoxide provided the trisilanyl anion **49**. Three equivalents of the silyl anion reacted with the tribromide (**48**) to give a first-generation dendrimer (**50**). With hydrogen bromide this compound could be converted to a hexabromide. Addition of 6 equiv of the silyl anion (**49**) generated a second-generation dendrimer (**51**) (Scheme 7).[26]

In a manner analogous to the reaction of [tris(trimethylsilyl)silyl]lithium (**6**), the reaction of [tris(trimethylsilyl)silyl]potassium (**5**) with 1,2-dibromoethane gave hexakis(trimethylsilyl)disilane (**7**).[6]

Reaction of **7** with potassium *tert*-butoxide proved to be an important issue. Thus far, the chemistry done with potassium alkoxides could be considered an improvement in comparison to Gilman's chemistry, but it was certainly not superior to the reaction with methyllithium. Therefore, it was the first real

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[20] Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023−1030.

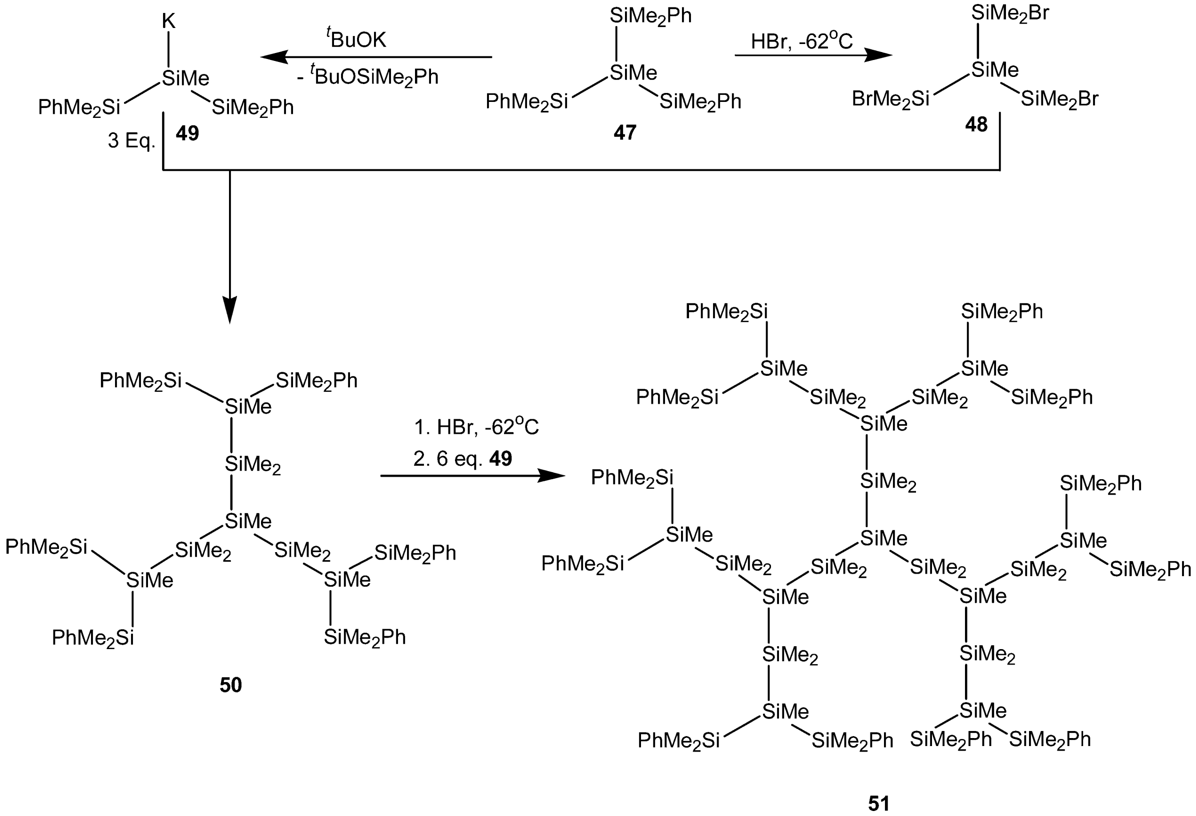
[21] For an example how bulky polysilanes can also be obtained using Gilman's chemistry, see: Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Blaser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228−12229.

[22] Markov, J.; Baumgartner, J.; Oehme, H.; Gross, T.; Marschner, C. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 309−313.

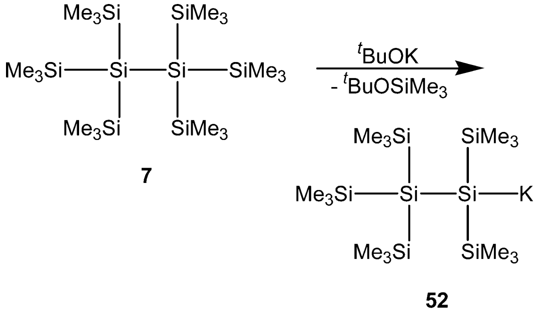
[23] Mechtler, C.; Baumgartner, J.; Marschner, C. In *Organosilicon Chemistry V*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 171−174.

[24] Mechtler, C.; Zirngast, M.; Baumgartner, J.; Marschner, C. *Eur. J. Inorg. Chem.* **2004**, 3254−3261.

Scheme 7

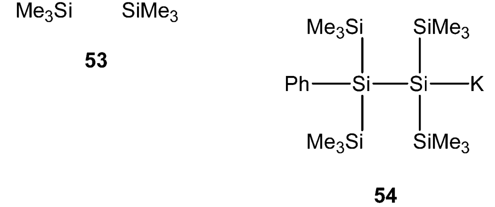


breakthrough of (polysilanyl)potassium chemistry when potassium *tert*-butoxide did not cleave the central silicon−silicon bond but selectively removed a trimethylsilyl group from hexakis(trimethylsilyl)disilane (**7**) to give [pentakis(trimethylsilyl)disilanyl]potassium **52** (eq 7).



(7)

When 1-phenylpentakis(trimethylsilyl)disilane (**53**) was reacted with potassium *tert*-butoxide under the same conditions, a regioselective conversion to the β-phenylsilyl anion (**54**) was observed (eq 8).[20]



(8)

One of the implications of the fact that cleavage of internal Si−Si bonds did not occur in the reaction with potassium *tert*-butoxide was that synthesis of di- or even trianions became a viable option. For this reason a number of compounds in which two tris(trimethylsilyl)silyl groups were bridged by difunctional groups were synthesized. Connection via alkylene chains was achieved by reaction of [tris(trimethylsilyl)silyl]potassium (**5**) with α,ω-ditosylalkanes (**56**−**58**).[27] Reaction of [tris(trimethylsilyl)silyl]potassium with α,ω-(dichloromethyl)polysilanes gave access to compounds in which the bulky tris(trimethylsilyl)silyl groups were separated by one, two, three, or four dimethylsilylene units (**11**, **12**, **59**, **60**).[28] A compound with a *trans*-1,2-ethenylidene bridge between two tris(trimethylsilyl)silyl groups (**61**) was obtained by the reaction of [tris(trimethylsilyl)silyl]lithium (**6**) with methyl formate.[29] Reaction of dilithioacetylene with 2 equiv of tris(trimethylsilyl)chlorosilanes (**62**) resulted in formation of bis[tris(trimethylsilyl)silyl]acetylene (**63**).[23,24,28]

Most of these compounds could be used to obtain α,ω-polysilanyl dianions. The ease of formation of the dianions was dependent on the degree of separation of the metalated silicon

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(25) (a) Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem.* **1995**, *107*, 106−108; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98−99. (b) Sekiguchi, A.; Nanjio, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195−4196. (c) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293−294. (d) Lambert, J. B.; Pflug, J. L.; Denari, J. M. *Organometallics* **1996**, *15*, 615−625.

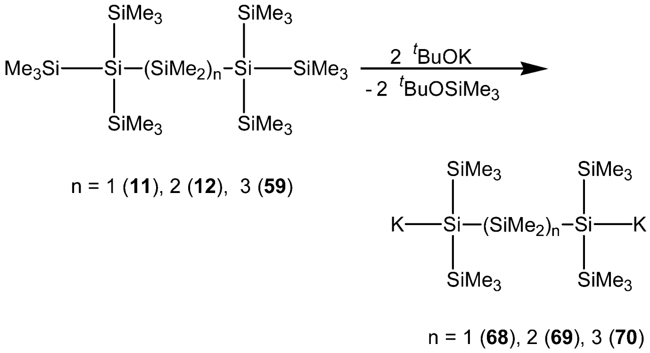
(26) Baumgartner, J.; Fischer, R.; Kickelbick, G.; Hassler, K.; Marschner, C. *Chem. Eur. J.* **2004**, *10*, 1021−1030.

(27) (a) Mechtler, C.; Marschner, C. *Tetrahedron Lett.* **1999**, *40*, 7777−7778. (b) Marschner, C.; Mechtler, C. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *168*−*169*, 517−520.

(28) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723−3731.

(29) Gross, T.; Kempe, R.; Oehme, H. *J. Organomet. Chem.* **1997**, *534*, 229−231.

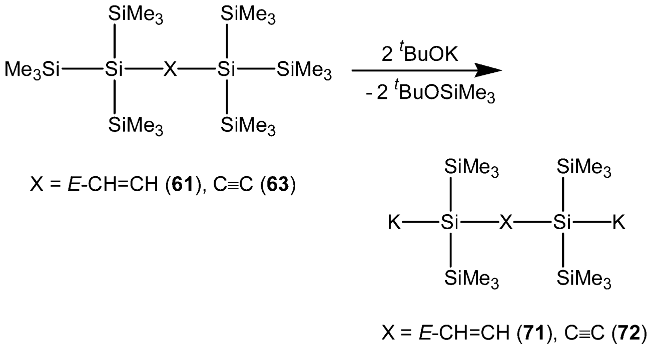
Scheme 8



n = 1 (**11**), 2 (**12**), 3 (**59**)

n = 1 (**68**), 2 (**69**), 3 (**70**)

Scheme 9



X = *E*-CH=CH (**61**), C≡C (**63**)

X = *E*-CH=CH (**71**), C≡C (**72**)

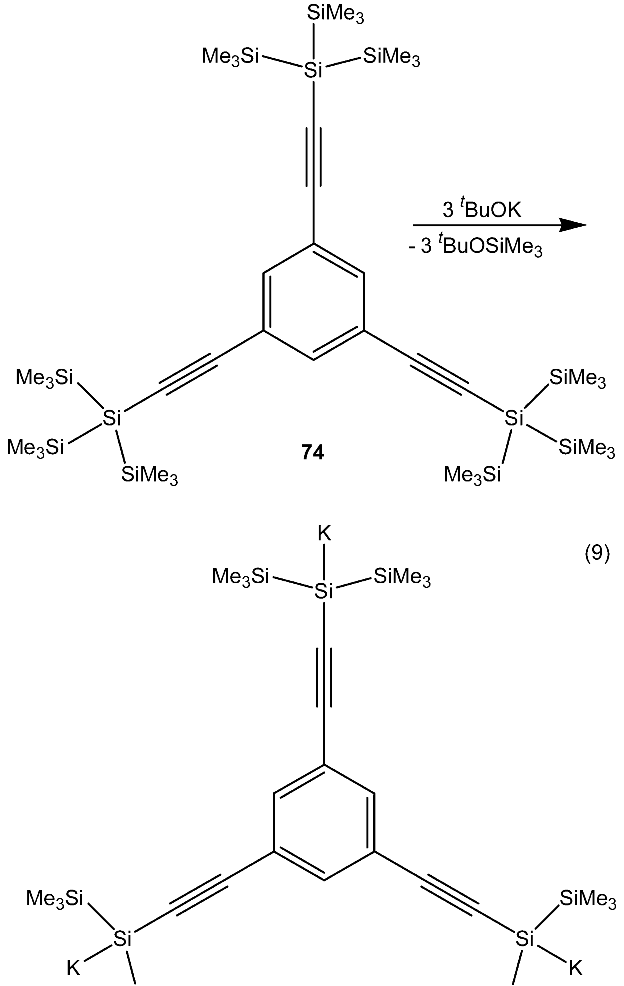
atoms. While the 1,3-, 1,4-, and 1,5-dipotassium compounds (**68**−**70**)[28,30] with dimethylsilylene spacers were formed in THF or DME at slightly elevated temperature (Scheme 8), the formation of 1,2-dipotassiotetrakis(trimethylsilyl)disilane (**73**) from **7** did not occur cleanly under these conditions but required the presence of 18-crown-6.[31]

Compounds with substituents or spacers such as vinylene or alkynylene groups which facilitate anion formation also formed dianions easily (Scheme 9).

The stabilization provided by the alkynylene unit allowed even the generation of a triply metalated polysilane, as shown by the reaction of 1,3,5-tris[(tris(trimethylsilyl)silyl)ethynyl]benzene (**74**) with 3 equiv of potassium *tert*-butoxide to give **75** (eq 9).[32]

As the formation of alkylated silyl anions is less favored, the same is true for alkylene-bridged dianions.[27] The conversion of bis[tris(trimethylsilyl)silyl]methane (**55**) to the respective 1,3-dianion (**64**) thus required the use of crown ether (Scheme 10).[33]

One of the intriguing prospects of polysilanyl dianions is their use in the synthesis of cyclosilanes. Reactions of 1,4-dipotassiotetrasilane **69** with either dimethyldichlorosilane or 1,2-dichlorotetramethyldisilane provided access to cyclopenta-[28,30] (**76**) and cyclohexasilanes (**77**) (Scheme 11).[34]



74

(9)

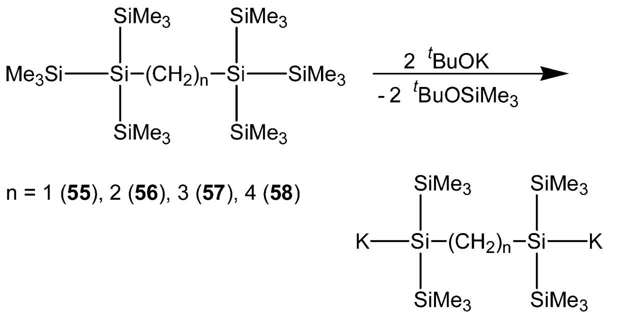
75

1,2-Dianions such as **73** are suited for the synthesis of small rings. They can not only be reacted with dielectrophiles to give three- (**78**) or four-membered (**79**) rings but can also be converted to disilenes which undergo [2 + 2] cycloaddition to four-membered rings (**80**)[35] (Scheme 12).[31]

Reaction of a 1,4-octamethyltetrasilylene-bridged bis[tris(trimethylsily)silyl] compound (**60**) with potassium *tert*-butoxide did not yield the expected monopotassium compound. Instead, 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (**81**) and [tris(trimethylsilyl)silyl]potassium (**5**) were formed.[32] **81** most likely was produced by back-biting of the initially formed silyl anion (Scheme 13).

The reactions of the 1,3-propylene- and 1,4-butylene-bridged dianions (**66**, **67**) with 1 equiv of H_2O gave cyclic anions (**82**, **83**) accompanied by the release of trimethylsilane (Scheme 14).[27] The reaction seemed to involve hydrolysis of one anionic center, which became sufficiently electrophilic to be attacked

Scheme 10



n = 1 (**55**), 2 (**56**), 3 (**57**), 4 (**58**)

n = 1 (**64**), 2 (**65**), 3 (**66**), 4 (**67**)

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(30) Kayser, C.; Kickelbick, G.; Marschner, C. *Angew. Chem.* **2002**, *114*, 1031−1034; *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 989−992.

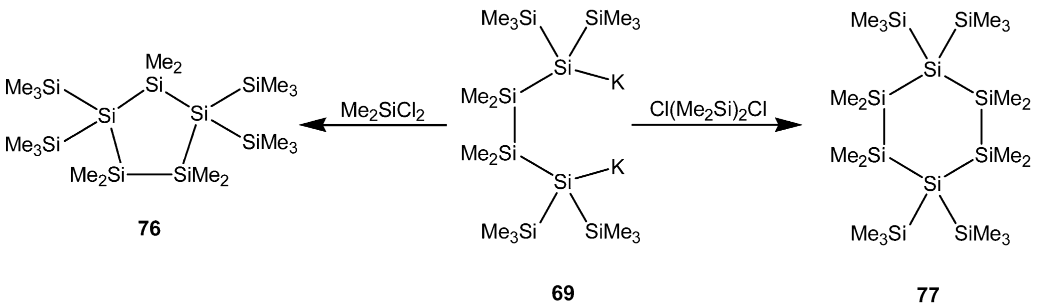
(31) Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. *Organometallics* **2004**, *23*, 1899−1907.

(32) Mechtler, C.; Zirngast, M.; Gaderbauer, W.; Wallner, A.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2006**, *691*, 150−158.

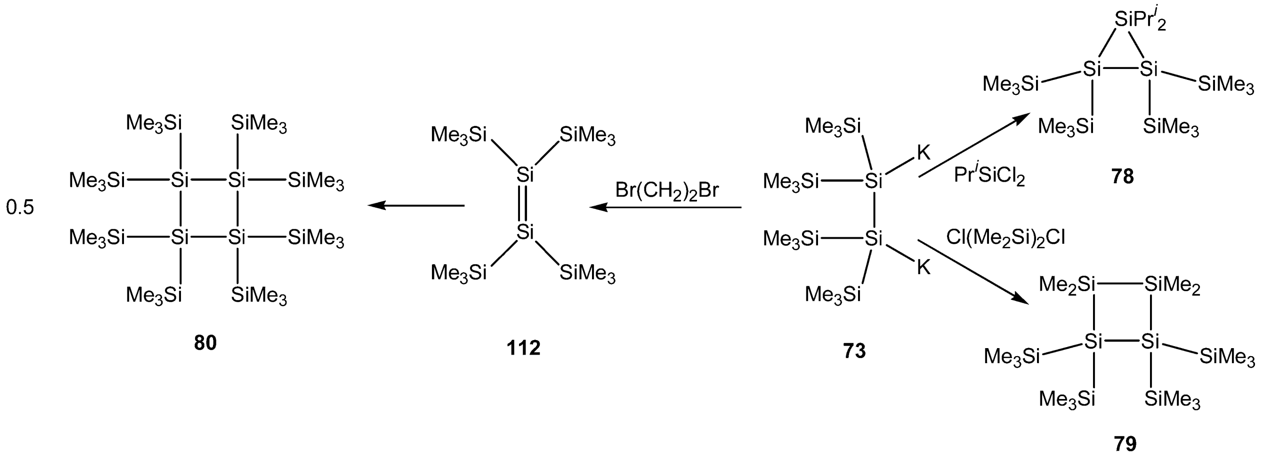
(33) Blanton, J. R.; Diminnie, J. B.; Chen, T.; Wiltz, A. M.; Xue, Z. *Organometallics* **2001**, *20*, 5542−5546.

(34) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, *685*, 79−92.

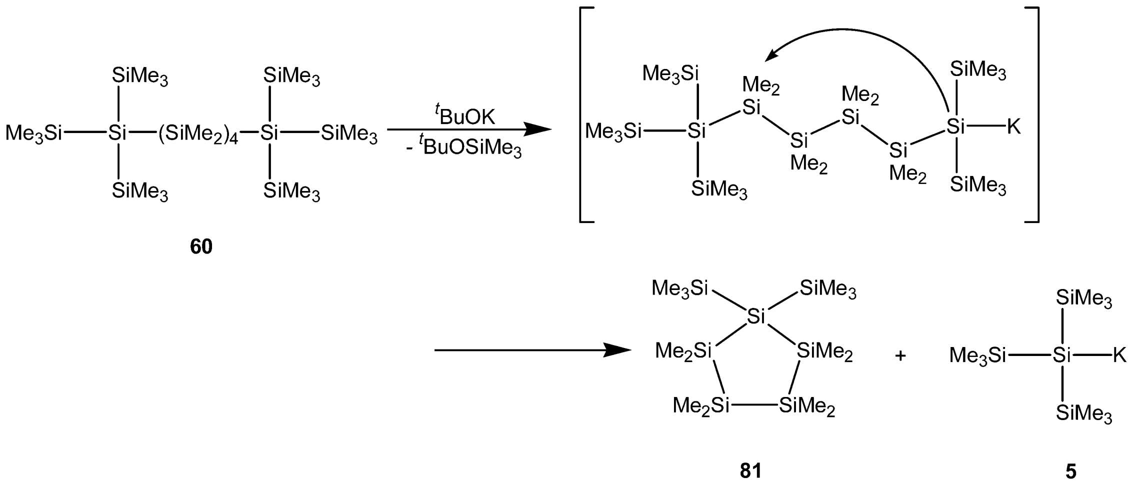
Scheme 11



Scheme 12



Scheme 13



by the remaining silyl anionic moiety. Reactions of the compounds **82** and **83** thus obtained with trimethylchlorosilane gave the quadruply trimethylsilylated compounds **84** and **85**, which could be obtained directly from **66** and **67** by reaction with 1,2-dibromoethane (Scheme 14).

Several of these four-, five-, and six-membered rings bearing trimethylsilyl groups were again subjected to the anion formation chemistry. Both mono- and dipotassium compounds could be prepared. The latter were employed in a way analogous to that used in the cyclosilane formation to yield bicyclic polysilanes.[34] Reaction of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (**77**) with 2 equiv of potassium *tert*-butoxide gave a 1,4-di-*trans*-diaxial dipotassium compound (**86**). Reaction of **86** with 1,2-dibromoethane, dichlorodimethylsilane, or 1,2-dichlorotetramethyldisilane yielded the [2.2.0]-, [2.2.1]-, and [2.2.2]-bicyclosilanes **87**−**89**, respectively (Scheme 15).[34,36]

Eventually, even the bicyclic silanes could be converted to (polysilanyl)potassium compounds. For **89** this step removed the last two trimethylsilyl groups originating from the starting tetrakis(trimethylsilyl)silane (**4**) to give the dianion **90**,[34] which was converted to the permethylated bicyclo[2.2.2]octasilane **91** (Scheme 16).[34,36,37]

Similar chemistry could be carried out with octakis(trimethylsilyl)cyclotetrasilane (**80**). Again a monoanion (**92**) or a dianion (**93**) could be obtained (Scheme 17).[31]

In contrast to this, the reaction of 1,1,2,2-tetrakis(trimethylsilyl)tetramethylcyclotetrasilane (**79**) with potassium *tert*-bu-

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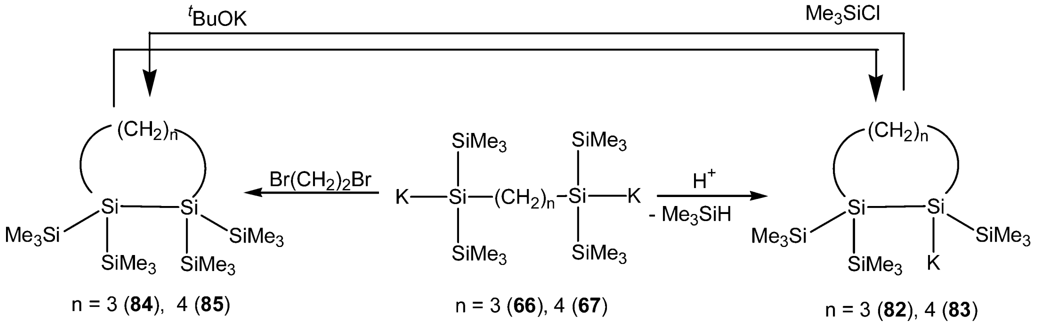
(35) Shen, Y.-S.; Gaspar, P. *Organometallics* **1982**, *1*, 1410−1412.

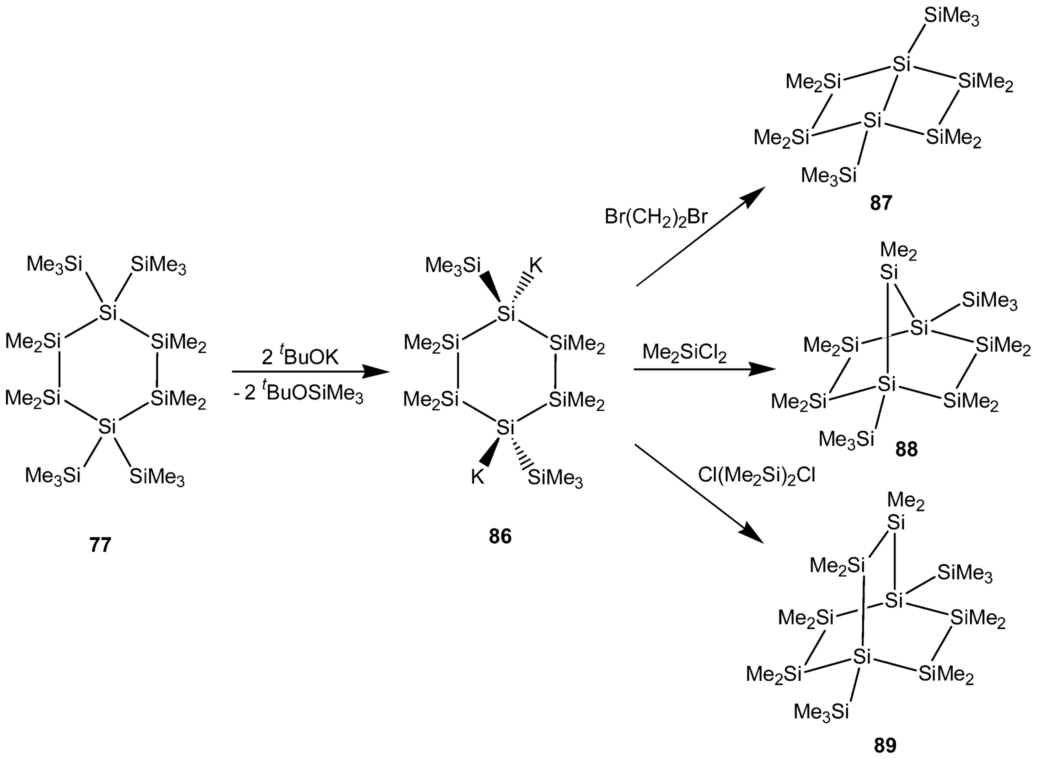
(36) Wallner, A. Dissertation, Technical University Graz, 2005.

(37) West, R.; Indriksons, A. *J. Am. Chem. Soc.* **1972**, *94*, 6110−6115.

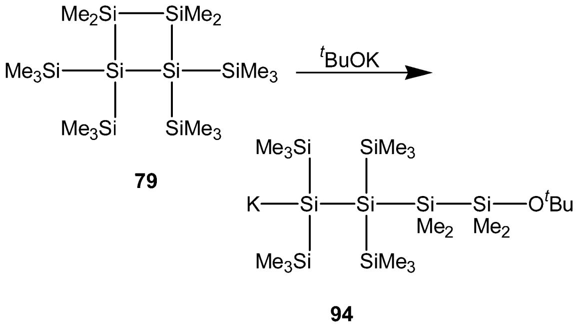
Scheme 14



Scheme 15



toxide did not give a cyclosilanyl anion but proceeded via ring opening by attack of the alkoxide at a dimethylsilylene group, giving the (4-alkoxypolysilanyl)potassium compound **94** (eq 10).[31]

 (10)

Polysilanyl dianions such as **69** also are well-suited for the synthesis of heterocyclosilanes. While there are numerous heterocyclosilanes known, most of them were obtained by reaction of α,ω-dichloroperalkylpolysilanes either with dinucleophiles such as H_2O, H_2S, and NH_3 or under Wurtz-type reaction conditions.[38] Reaction of polysilanyl dianions with dielectrophiles can be considered an interesting synthetic alternative. In this way it was possible to obtain five-membered rings with magnesium (**95**),[19] zirconium (**96**, **97**),[30] hafnium (**98**, **99**),[30,61] zinc (**100**),[39] boron (**101**),[40] aluminum (**102**),[41] germanium (**103**),[42] tin (**104**, **105**),[28,30,42] phosphorus (**106**),[40] and sulfur (**107**)[41] as heteroatoms (Scheme 18).

Another exciting issue concerning the synthesis of silyl anions with different substitution patterns is that it is readily possible to obtain chiral compounds. As most carbanions are not configurationally stable under ambient conditions, the question of the configurational stability of silyl anions was addressed early. Sommer[43] and Corriu[44] provided the first evidence for

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(38) Watanabe, H.; Suzuki, H.; Takahashi, S.; Ohyama, K.; Sekiguchi, Y.; Ohmori, H.; Nishiyama, M.; Sugo, M.; Yoshikawa, M.; Hirai, N.; Kanuma, Y.; Adachi, T.; Makino, M.; Sakata, K.; Kobayashi, K.; Kudo, T.; Matsuyama, H.; Kamigata, N.; Kobayashi, M.; Kijima, M.; Shirakawa, H.; Honda, K.; Goto, M. *Eur. J. Inorg. Chem.* **2002**, 1772−1793.

(39) Gaderbauer, W. Dissertation, Technical University Graz, ongoing.

(40) Markov, J.; Fischer, R.; Wagner, H.; Noormofidi, N.; Baumgartner, J.; Marschner, C. *Dalton Trans.* **2004**, 2166−2169.

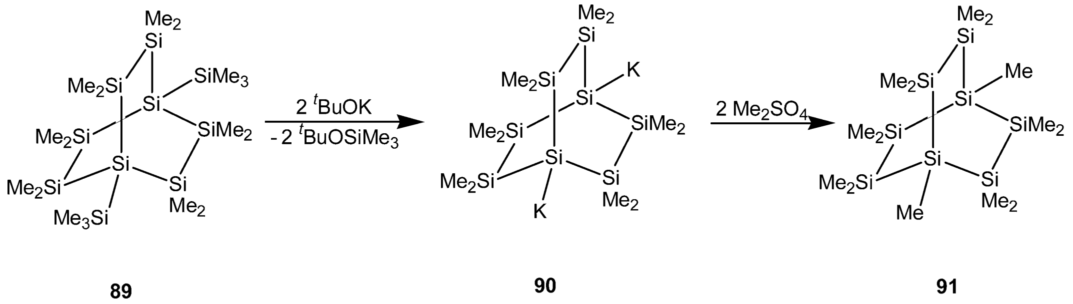
(41) Fischer, J. Dissertation, Technical University Graz, 2005.

(42) Fischer, J.; Gaderbauer, W.; Baumgartner, J.; Marschner, C. *Heterocycles* **2006**, *67*, 507−510.

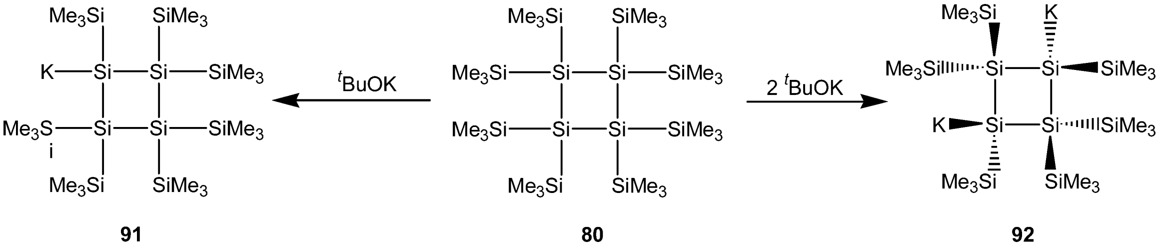
(43) Sommer, L. H.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 1619−1920.

(44) Colomer, E.; Corriu, R. *J. Chem. Soc., Chem. Commun.* **1976**, 176−177.

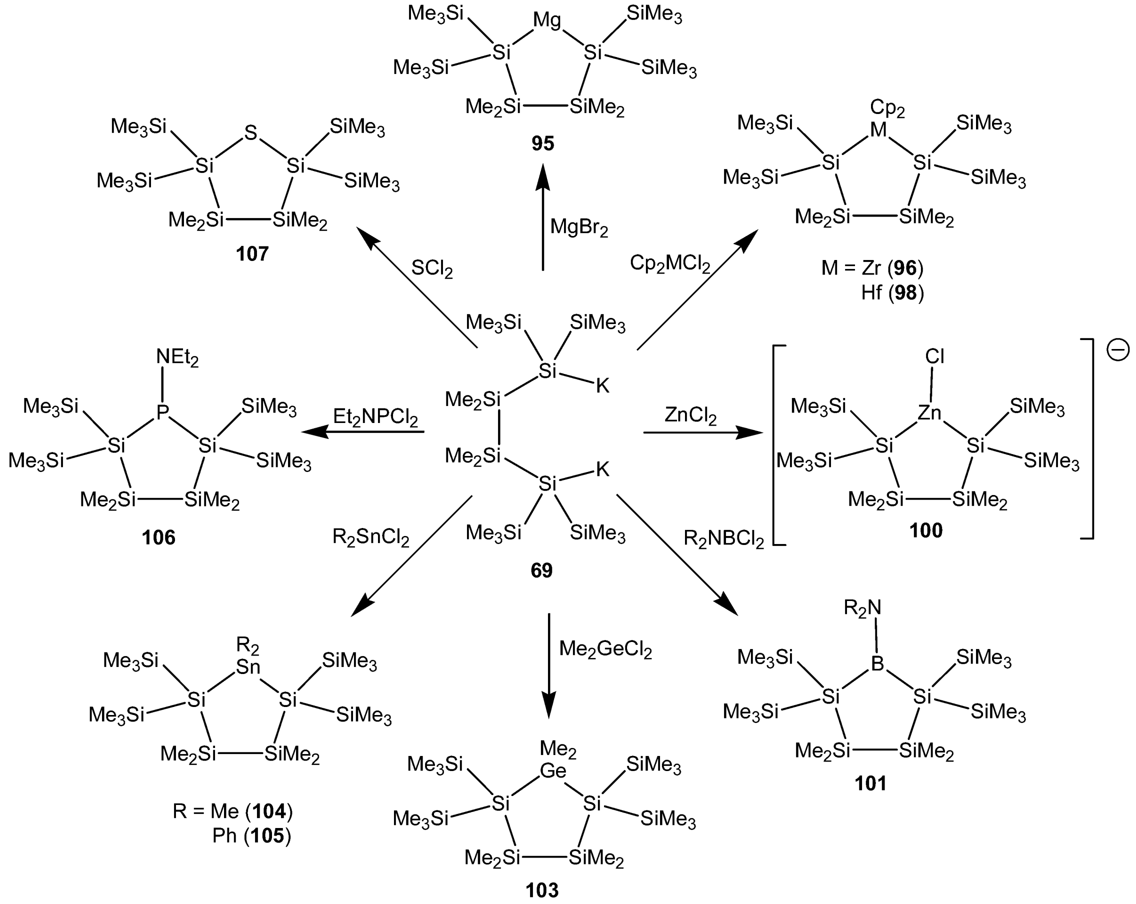
Scheme 16



Scheme 17



Scheme 18



some stability of silyllithium and -magnesium compounds. Lambert et al. were able to provide a lower limit of 23.8 kcal/mol for the inversion barrier of *i*-$Pr_2PhSiLi$.[45]

While a number of computational investigations of the inversion barrier of silyl anions have been reported,[46] we have begun a study of this behavior of oligosilyl anions with different substitution patterns. The results showed that all substituents which facilitate formation of silyl anions in the reaction with potassium *tert*-butoxide also contribute to a lowering of the

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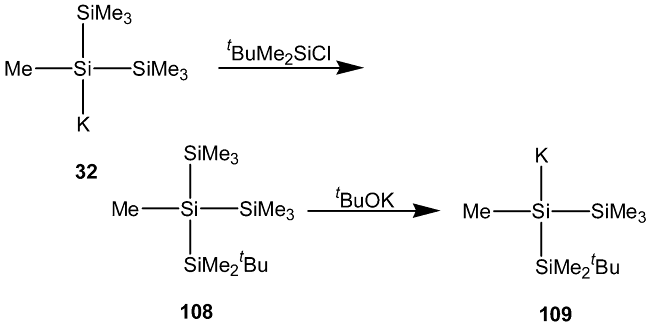
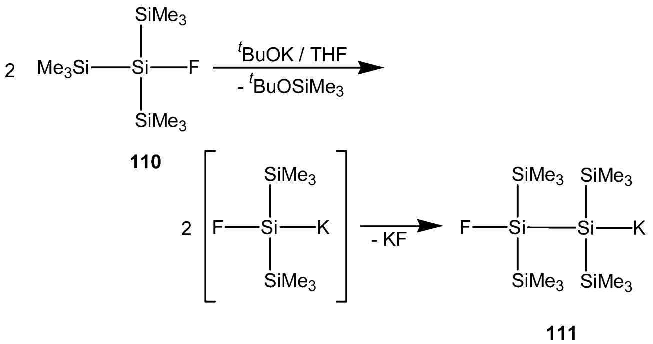
[45] Lambert, J. B.; Urdaneta−Pérez, M. *J. Am. Chem. Soc.* **1978**, *100*, 157−162.

[46] (a) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998−1003. (b) Hopkinson, A. C.; Lien, M. H. *Tetrahedron* **1981**, *37*, 1105−1112. (c) Damrauer, R.; Hankin, J. *Chem. Rev.* **1995**, *95*, 1137−1160. (d) Brinkmann, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304−8310. (e) Gordon, M. S.; Volk, D. E.; Gano, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 9273−9275.

Scheme 19



Scheme 20



111

inversion barrier.[47] To obtain experimental data, a number of chiral silyl anions such as **109** were synthesized (Scheme 19). Dynamic NMR spectroscopic investigations of the diastereotopic methyl groups allowed us to determine the inversion barriers.[48]

A systematic variation of substituents, counterions, and donor molecules was performed. The values obtained for the inversion barriers of the investigated compounds ranged from less than 8 to greater than 24 kcal/mol. Substituents were found to give decreased barriers in the order

$$\mathrm{Me} > \mathrm{Et} > i\text{-}\mathrm{Pr} > \mathrm{H} > \mathrm{SiR_3} > \mathrm{Ph} > \mathrm{C{\equiv}CR}$$

The counterion has also an important influence, and it was found that transmetalation from potassium to magnesium provided silyl anions that are configurationally stable at room temperature.

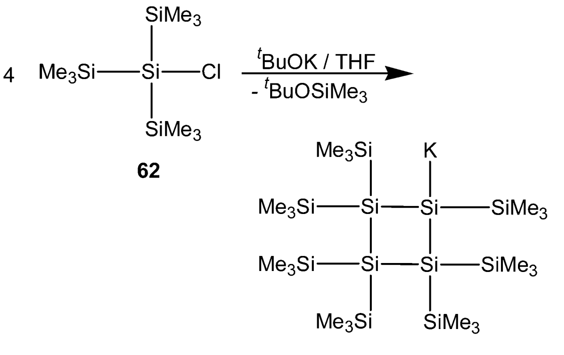
An interesting point which arose from the computational studies was that π-donating substituents such as halides, alkoxy, and amino groups raise the inversion barrier.[49]

As Tamao and Kawachi[50] have introduced silyl anions with attached amino and alkoxy substituents, we also wanted to study polysilanyl anions containing these groups.

The reaction of fluorotris(trimethylsilyl)silane (**110**) with potassium *tert*-butoxide is surprisingly selective. A (β-fluorodisilanyl)potassium compound (**111**) was formed as the sole product (Scheme 20). The mechanism of the formation of this compound seems to involve the self-condensation of the initially formed α-fluorosilyl anion.[51]

The final product **111** is surprisingly thermally stable. Even at 80 °C the elimination of potassium fluoride is very slow. However, attempts to achieve transmetalation from potassium to lithium, magnesium, or zirconium caused immediate elimination to the disilene **112**, which could be trapped with anthracene to yield **113** or which, in the absence of a trapping reagent, underwent [2 + 2] cycloaddition to form the cyclotetrasilane **80** (Scheme 21).[51]

It is likely that the stabilization of the β-fluorosilyl anion is caused by the strong Si−F bond. Attempts to repeat this chemistry with chlorotris(trimethylsilyl)silane (**62**) gave [heptakis(trimethylsilyl)cyclotetrasilanyl]potassium (**92**) as a major product (eq 11).[52] It was assumed that the same chemistry



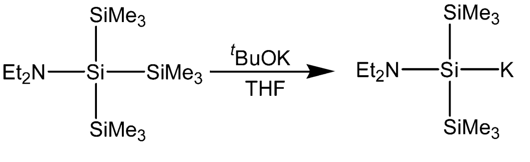
92

(11)

occurred as in the case of the fluoride. However, the condensation product underwent elimination to the disilene and, subsequently, [2 + 2] cycloaddition to octakis(trimethylsilyl)cyclotetrasilane (**80**), which then was attacked by the potassium alkoxide.[52]

The reaction of methoxytris(trimethylsilyl)silane (**114**) with potassium *tert*-butoxide was similar to that of the tris(trimethylsilyl)silyl halides, but the tendency to self-condense was less pronounced.[53] This was observed when the experiment was carried out either in THF or in toluene in the presence of 18-crown-6. While in THF self-condensation led to the formation of a β-methoxysilyl anion (**115**), the crown ether stabilized the α-methoxysilyl anion **116**, which is the primary reaction product (Scheme 22).

Reaction of (diethylamino)tris(trimethylsilyl)silane (**117**) with potassium *tert*-butoxide was also studied. No self-condensation was observed in this case, only clean formation of [(diethylamino)bis(trimethylsilyl)silyl]potassium (**118**) (eq 12).[54]



117 **118**

(12)

Reactivity Change

To obtain selective reactions, sometimes a moderation of the reactivity of the silylpotassium compounds was desirable. A solution to this problem was found in transmetalation, using metathetical reactions with halides of metals of less electropositive character. Most important was the reaction of [tris(trimethylsilyl)silyl]potassium (**5**) with magnesium bromide.[55]

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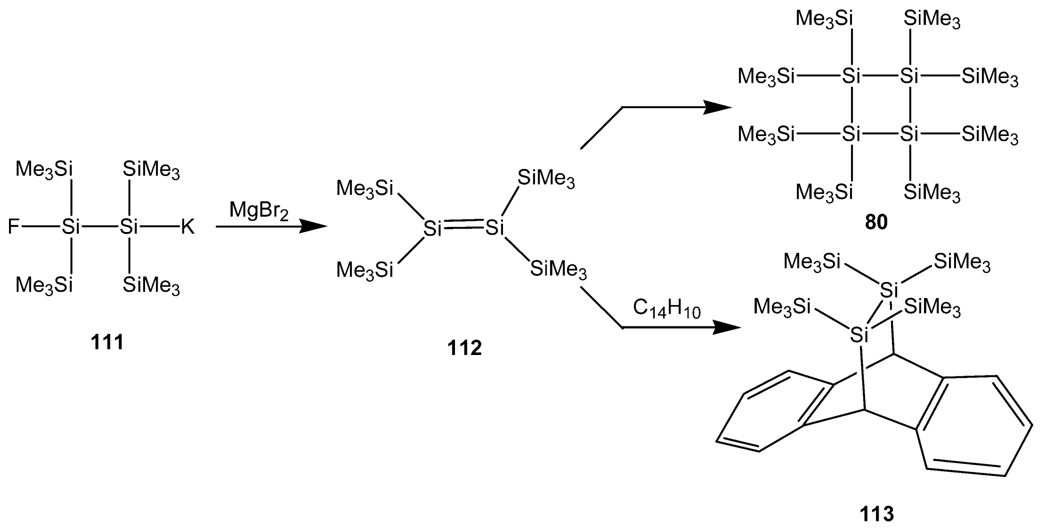
(47) Flock, M.; Marschner, C. *Chem. Eur. J.* **2002**, *8*, 1024−1030.

(48) (a) Fischer, R.; Marschner, C. In *Organosilicon Chemistry V*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 190−194. (b) Fischer, R.; Fischer, J.; Baumgartner, J.; Marschner, C. Manuscript in preparation.

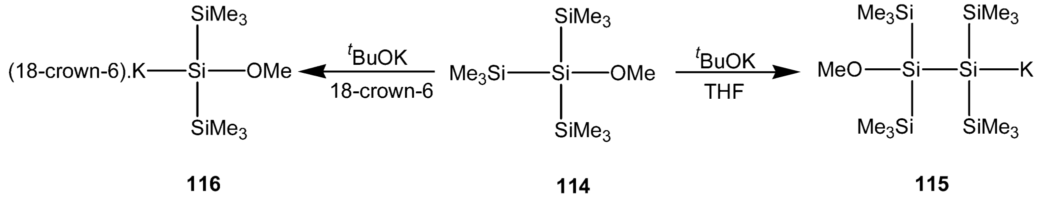
(49) Flock, M.; Marschner, C. *Chem. Eur. J.* **2005**, *11*, 4635−4642.

(50) (a) Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, 818−820. (b) Tanaka, Y.; Hada, M.; Kawachi, A.; Tamao, K.; Nakatsuji, H. *Organometallics* **1998**, *17*, 4573−4577. (c) Tamao, K.; Kawachi, A. *J. Am. Chem. Soc.* **1992**, *114*, 3989−3990. (d) Tamao, K.; Kawachi, A.; Tanaka, Y.; Ohtani, H.; Ito, Y. *Tetrahedron* **1996**, *52*, 5765−5772. (e) Kawachi, A.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 1919−1926. (f) Kawachi, A.; Maeda, H.; Tamao, K. *Organometallics* **2002**, *21*, 1319−1321.

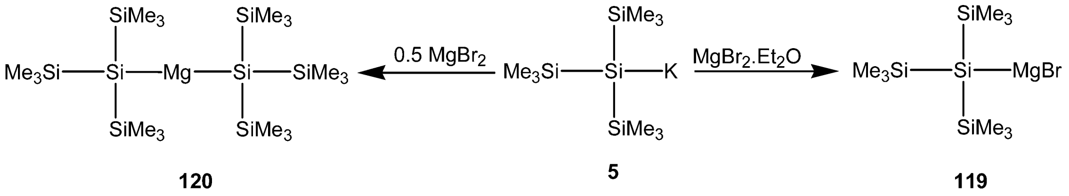
Scheme 21



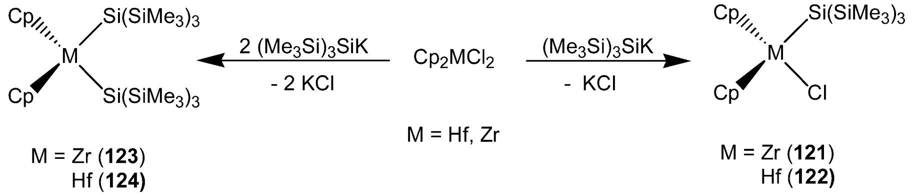
Scheme 22



Scheme 23



Scheme 24



Depending on the stoichiometry, either [tris(trimethylsilyl)silyl]magnesium bromide (**119**) or bis[tris(trimethylsilyl)silyl]magnesium (**120**) can be obtained (Scheme 23).[55]

Transmetalation to magnesium proved to be especially useful in the case of dianions. Reaction of the 1,4-dianionic compound **69** with magnesium bromide gave the five-membered magnesacycle **95** (Scheme 18).[19] In the case of the extremely reactive 1,2-dipotassium compound **73** transmetalation was found to be the only way to observe clean follow-up chemistry. A structural determination of this particular magnesium compound was not possible yet.[31]

Polysilanyl Transition-Metal Compounds

Tilley and co-workers have pioneered the synthesis of polysilanyl-substituted early-transition-metal compounds.[56] Since they have used mainly **6** as the silyl anion source, it was of interest to see whether (polysilanyl)potassium compounds could also be used.

Reaction of [tris(trimethylsilyl)silyl]potassium (**5**) and some other (polysilanyl)potassium compounds with hafnocene or zirconocene dichlorides gave the respective compounds such as **121** and **122** in clean reactions and good yield (Scheme 24).[57] The enhanced reactivity of the potassium compounds allows

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(51) Fischer, R.; Baumgartner, J.; Kickelbick, G.; Marschner, C. *J. Am. Chem. Soc.* **2003**, *125*, 3414−3415.

(52) Fischer, R.; Likhar, P. R.; Baumgartner, J.; Marschner, C. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 319−322.

(53) Likhar, P. R.; Zirngast, M.; Baumgartner, J.; Marschner, C. *Chem. Commun.* **2004**, 1764−1765.

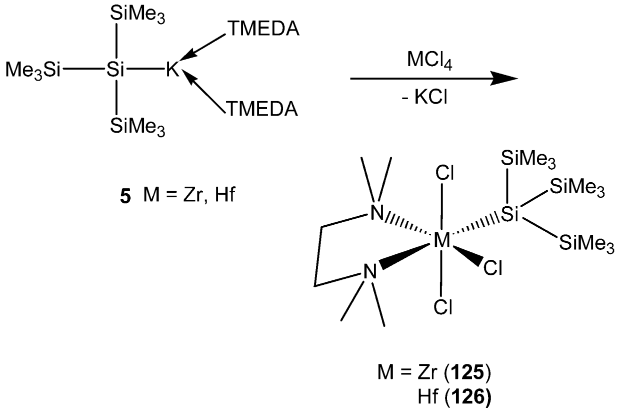
(54) Marschner, C. Unpublished results.

(55) Farwell, J. D.; Lappert, M. F.; Marschner, C.; Strissel, C.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185−188.

(56) (a) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409−6410. (b) Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084−4085. (c) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284−2286. (d) Woo, H. G.; Tilley, T. D. *J. Organomet. Chem.* **1990**, *393*, C6−C9.

(57) Kayser, C.; Marschner, C. *Monatsh. Chem.* **1999**, *130*, 203−206.

Scheme 25



even the double silylation of the metallocenes to **123** and **124** (Scheme 24).[58]

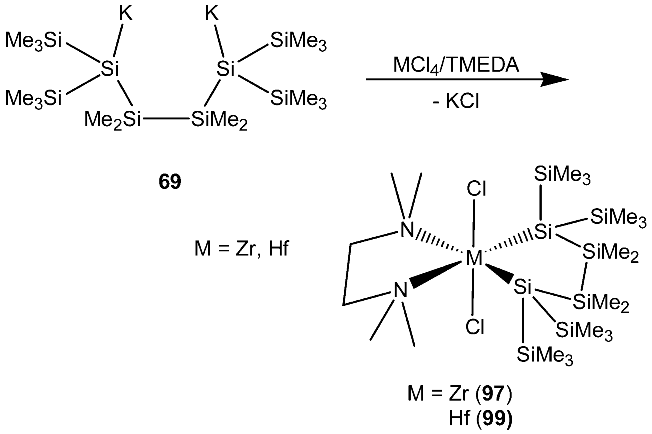
Reactions of group 4 tetrahalides with silyl anions have been found to be difficult. The reason for this is the strong Lewis acidic character of the metal salts, which promotes the cleavage of ether molecules present from the generation of silyl anions. This facilitates the formation of metal alkoxides instead of silylmetal compounds.[59] To avoid the use of ethereal solvents, the formation of silylpotassium compounds was carried out in the presence of tetramethylethylenediamine (TMEDA) in toluene. The resulting TMEDA adduct of [tris(trimethylsilyl)silyl]-potassium (**5**) was reacted with zirconium and hafnium tetrachlorides. The products, however, were TMEDA adducts with only one chloride being exchanged by a tris(trimethylsilyl)silyl unit (**125**, **126**) (Scheme 25).[60]

The fact that two bulky silyl groups could be attached to the group 4 metallocene fragment prompted the synthesis of metallacycles from silyl dianions. Reaction of the 1,4-dipotassium compound **69** with hafnocene or zirconocene dichlorides gave the respective metallocenacyclotetra- and -pentasilanes (**96**, **98**) (Scheme 18).[28] The reaction with group 4 tetrahalides has also been carried out with the TMEDA adduct of the 1,4-dipotassium compound **69**. The products (**97**, **99**) have the two bidentate ligands in the equatorial positions and the chlorides in the apical positions (Scheme 26).[61]

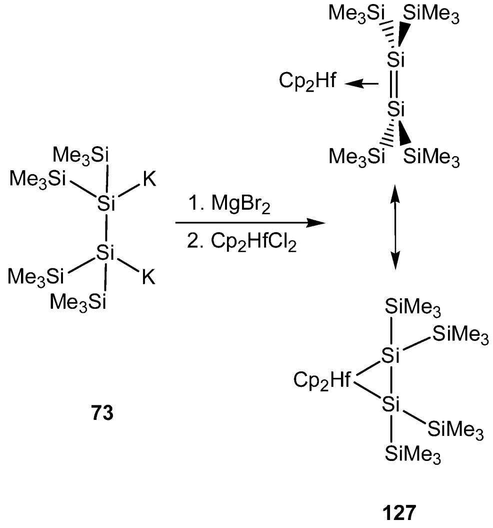
The reaction of hafnocene dichloride with the magnesium derivative of the 1,1,2,2-tetrakis(trimethylsilyl)disilanyl dianion (**73**) gave the first early-metal disilene complex (**127**) (Scheme 27) with a rather unusual ^{29}Si NMR shift of +132.8 ppm. Unfortunately, the compound could not be isolated in the solid state and a crystal structure could be obtained only of its trimethylphosphine adduct (**128**).[62]

Polysilanylpotassium compounds could also be employed for the synthesis of polysilanyl group 6 pentacarbonylmetalates.[63] These were obtained either by reaction of the silyl anions with group 6 iodopentacarbonylmetalates or, more conveniently, directly from group 6 hexacarbonyls (Scheme 28).

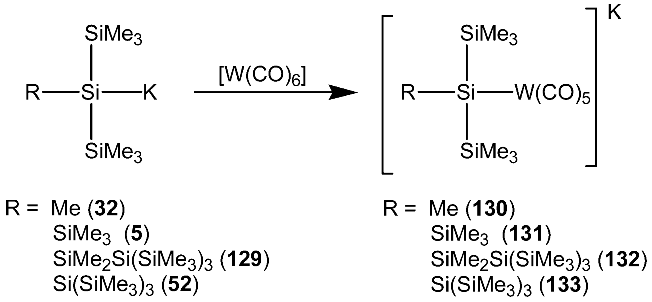
Scheme 26



Scheme 27



Scheme 28



Potassium Polysilanyls as Reagents

A number of chemists have adopted the potassium alkoxide generated polysilanyl anions in the meanwhile. Ruhlandt-Senge and her group have demonstrated their use for the synthesis of tris(trimethylsilyl)silyl−alkaline-earth-metal compounds.[64] Tilley and co-workers have used (polysilanyl)potassium chemistry for the preparation of early-transition-metal compounds.[65] Ottosson et al. have employed [tris(trimethylsilyl)silyl]pivalate[6,66] (**134**)

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(58) Kayser, C.; Frank, D.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, *667*, 149−153.

(59) Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 69.

(60) Frank, D.; Baumgartner, J.; Marschner, C. *J. Chem. Soc., Chem. Commun.* **2002**, 1190−1191.

(61) Frank, D.; Baumgartner, J.; Marschner, C. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 452−456.

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(63) Wagner, H.; Baumgartner, J.; Marschner, C. *Organometallics* **2005**, *24*, 4649−4653.

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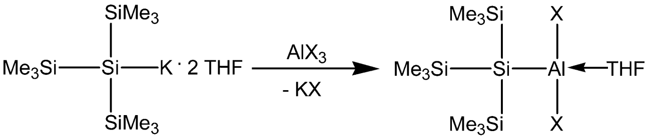
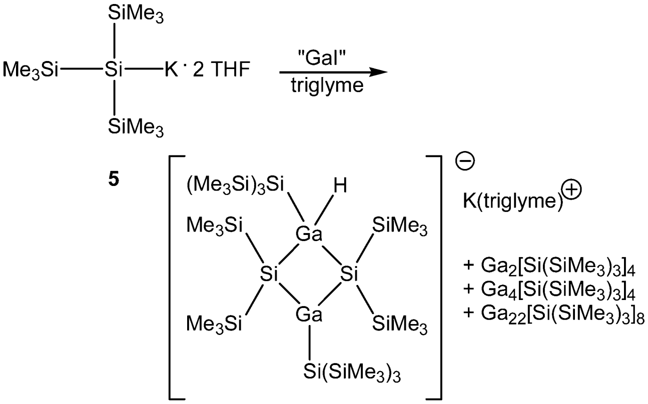
Scheme 29



5

X = Cl (**137**)
Br (**138**)
I (**139**)

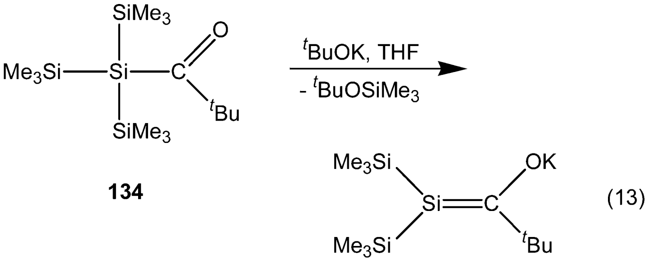
Scheme 30



5

140

for the synthesis of the first structurally characterized silenolate, **135** (eq 13).[67]



134

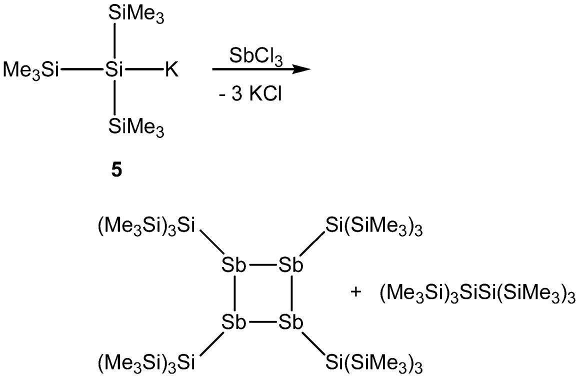
135

(13)

Roesky and co-workers have reacted 2 equiv of **5** with hexachlorodisilane to obtain 1,2-bis[tris(trimethylsilyl)silyl]-tetrachlorodisilane (**136**).[68] The Roesky group also reacted **5** with aluminum halides to avoid formation of lithium aluminates and obtained THF adducts of [tris(trimathylsilyl)silyl]aluminum dihalides (**137**−**139**) (Scheme 29).[69]

Linti et al. also observed a different reaction behavior of **5** compared to that of **6** in the reaction with gallium subiodide. In addition to a number of already known gallium cluster molecules, they isolated as a main product the hydrogallanate **140** (Scheme 30), which does not form in the reaction with **6**.[70]

By reaction of 3 equiv of **5** with antimony trichloride Garcia et al. obtained tetrakis[tris(trimethylsilyl)silyl]cyclotetrastibine (**141**) and hexakis(trimethylsilyl)disilane (**7**) (eq 14).[71]

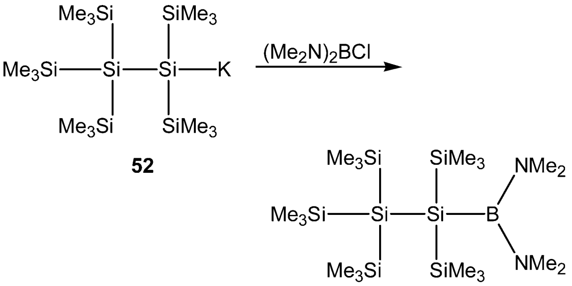


5

141

(14)

Braunschweig et al. reacted [pentakis(trimethylsilyl)disilanyl]-potassium (**52**) with chlorobis(dimethylamino)borane to obtain the corresponding disilanylborane **142** (eq 15).[72]



52

142

(15)

Herzog and co-workers have reacted **5** and **52** with elemental sulfur, selenium, and tellurium to give the corresponding potassium [tris(trimethylsilyl)silyl]- and [pentakis(trimethylsilyl)disilanyl]chalcogenolates (**143**−**148**) (Scheme 31).[73]

Krempner has reacted **5** and **41** with 1,2-dimethyltetrachlorodisilane to obtain dichlorosilanes that could be converted to the respective 1,2-disilanediols, which were used as ligands for transition metals.[74] In an interesting attempt to obtain more bulky silyl anions, Reinke and Krempner have reacted 3 equiv of [methylbis(trimethylsilyl)silyl]potassium (**32**) with trichlorosilane to obtain tris[bis(trimethylsilyl)methylsilyl]silane (**149**). This compound was brominated (**150**) and converted to [tris-(bis(trimethylsilyl)methylsilyl)silyl]lithium (**151**) (Scheme 32).[75]

Steel and co-workers recently have used [phenylbis(trimethylsilyl)silyl]potassium (**41**) and other silylpotassium compounds to obtain silenes such as those shown in Scheme 33, which they used as novel reagents, for example; in Diels−Alder reactions.[76]

Kira and co-workers have utilized the 1,3-dipotassium compound **68** to obtain 1,1-dichloro-2,2,4,4-tetrakis(trimethylsilyl)diethylcyclotetrasilane (**152**), which subsequently was

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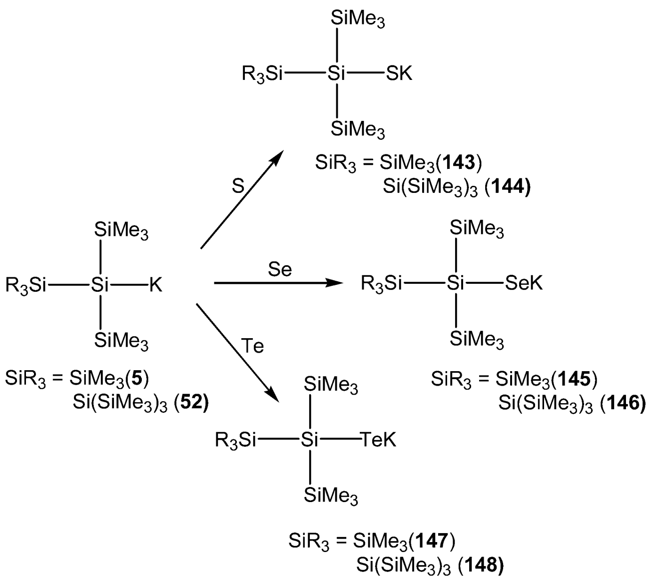
Scheme 31

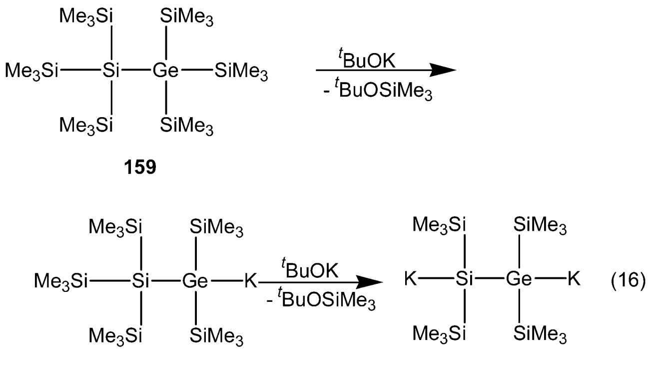


reacted with lithium to give a fused bicyclic disilene (**153**) (Scheme 34).[77]

The most recent use of polysilanyl anion chemistry was provided by our synthesis of a undecamethylcyclohexasilanyl-substituted bicycloheptasilane (**154**), which served as a precursor for the aluminum trichloride catalyzed rearrangement to a silicon analogue of adamantane (**155**) (Scheme 35).[78]

Beyond Polysilanyl Anions

[Tris(trimethylsilyl)germyl]lithium (**156**)[79] has been prepared by following Gilman's procedure with methyllithium. We[80] and others[81] have investigated the synthesis of (polysilylgermyl)-potassium compounds. [Tris(trimethylsilyl)germyl]potassium (**157**) was formed by the reaction of tetrakis(trimethylsilyl)-germane (**158**) with potassium *tert*-butoxide. It readily reacts with silyl halides such as tris(trimethylsilyl)silyl chloride (**62**) to give [tris(trimethylsilyl)silyl]tris(trimethylsilyl)germane (**159**). This compound was used to demonstrate the ease of formation of germylpotassium compounds compared to that of silylpotassium compounds. In the reaction of **159** with potassium *tert*-butoxide the exclusive formation of the germylpotassium compound **160** was observed (eq 16).[80d]

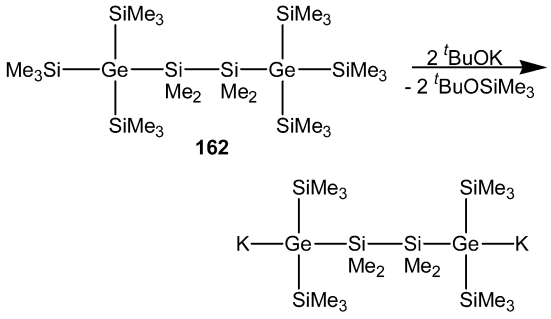


159

160 **161**

(16)

Further reaction of **160** with another 1 equiv of potassium alkoxide gave the respective 1,2-dianionic compound **161** (eq 16).[80] Reaction of **157** with 1,2-dichlorotetramethyldisilane proceeded analogously to the formation of **12** to give **162**. This compound was also converted to the dianion **163** (eq 17). **163**



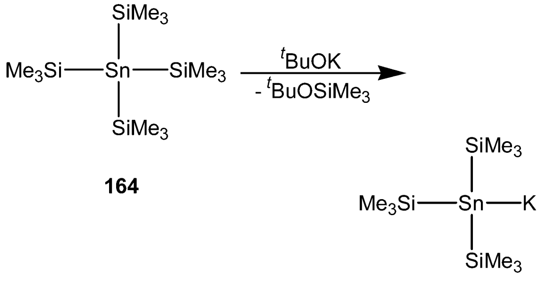
162

163

(17)

was, in a way analogous to the reactions with **69** (Scheme 18), the precursor for a number of heterosilacyclogermanes.[80]

Eventually, it was also shown that [tris(trimethylsilyl)stannyl]-potassium (**165**) could be obtained by employing the reaction of tetrakis(trimethylsilyl)stannane (**164**) with potassium *tert*-butoxide (eq 18).[82]

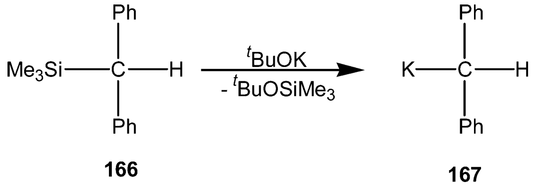


164

165

(18)

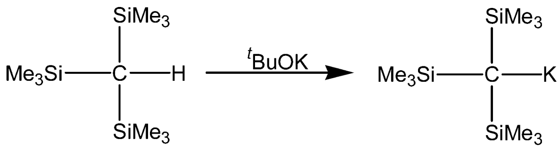
Recently, potassium *tert*-butoxide was used to abstract the trimethylsilyl group from diphenyl(trimethylsilyl)methane (**166**) to obtain the corresponding methylpotassium compound **167** (eq 19).[83]



166 **167**

(19)

In a similar attempt, tris(trimethylsilyl)methane (**168**) was reacted with *tert*-butoxide (eq 20). Instead of the expected [bis-(trimethylsilyl)methyl]potassium (**169**)[84] we obtained [tris-(trimethylsilyl)methyl]potassium (**170**),[85] which had been pre-



168 **170**

(20)

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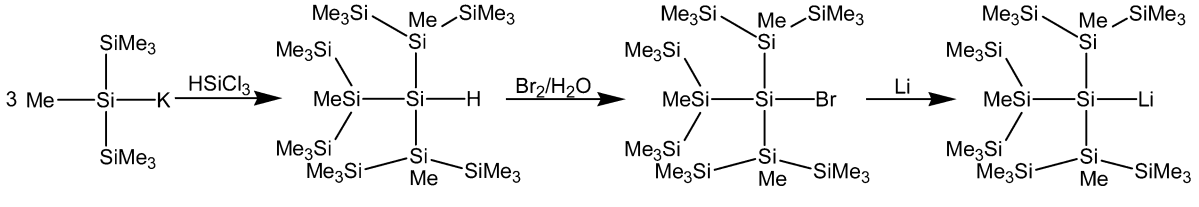
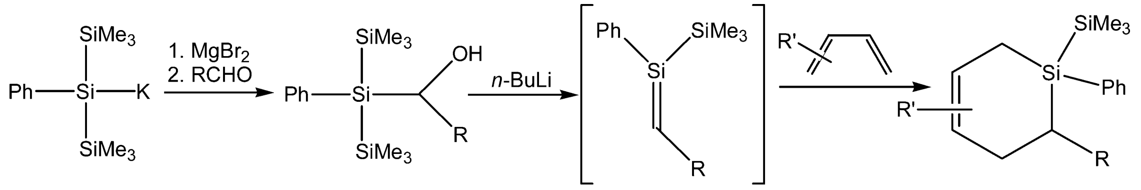
Scheme 32



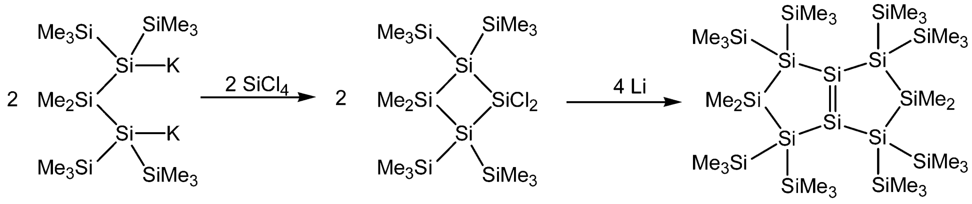
32 **149** **150** **151**

Scheme 33



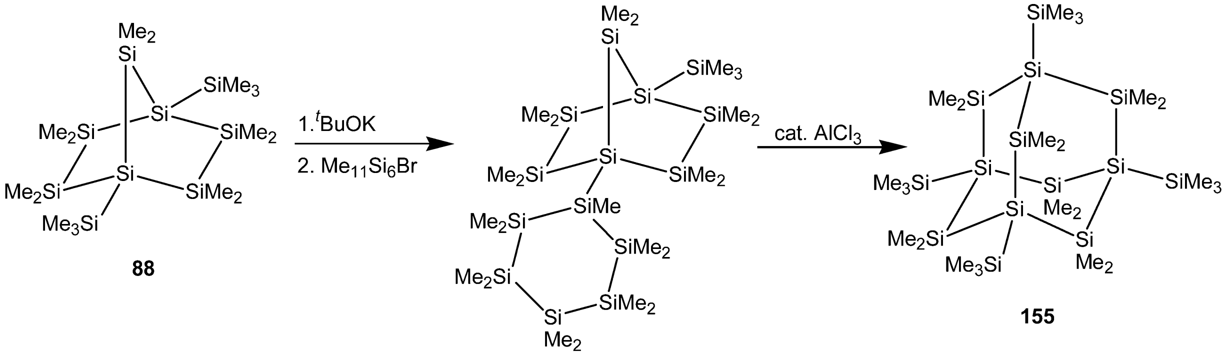
41

Scheme 34



68 **152** **153**

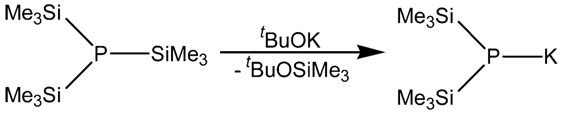
Scheme 35



88 **154** **155**

pared previously by reaction of [tris(trimethylsilyl)methyl]lithium (**171**) with potassium *tert*-butoxide.[86]

The reaction of tris(trimethylsilyl)phosphine (**172**) with potassium *tert*-butoxide afforded clean formation of the corresponding potassium phosphide **173**[87] (eq 21), thus demonstrating that the concept of anion preparation by alkoxysilane formation with a potassium alkoxide can also be employed for group 15 anions.



(21)

172 **173**

Concluding Remarks and Outlook

The (polysilanyl)potassium chemistry which triggered my transition from an organic to an organometallic chemist is still keeping my research group busy. The extraordinary selectivity and the good yields encountered in most of the reactions described in this review also allow multistep syntheses. Therefore, the construction of relatively complex polysilanes can be accomplished in a fairly straightforward way. A new major field of interest, Lewis acid catalyzed rearrangement reactions of polysilanes,[88] which helped us to prepare an all-silicon analogue

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of adamantane (Scheme 35),[78] is producing branched polysilanes which are perfectly suited to do further silyl anion chemistry. This way we expect to continue our exciting journey through the realm of organosilicon clusters.

In this review I have tried to give an overview on our work concerning the synthesis and reactivity of polysilanyl anions. Nevertheless, this field is also very rewarding with respect to structural chemistry. Over the years Dr. Judith Baumgartner has solved hundreds of crystal structures for us. Many of the investigated compounds have been very reactive and were quite a challenge to mount on the diffractometer. Of the compounds mentioned in this review, the following were structurally characterized by us and the data can be retrieved from the Cambridge Crystallographic Data Centre using the deposition number given in parentheses: **5** (CCDC238890),[61] **11** (CCDC 244010),[89] **38** (CCDC 226889),[24] **40** (CCDC 226890),[24] **43** (CCDC 238897),[22] **52** (CCDC 167978),[20] **54** (CCDC 174658),[20] **59** (CCDC 244009),[89] **60** (CCDC 244013),[89] **68** (CCDC 194099),[28] **69** (CCDC 194101),[28] **70** (CCDC 194098),[28] **73** (CCDC 211904),[31] **76** (CCDC 278678),[42] **77** (CCDC 238999),[90] **78** (CCDC 211905),[31] **79** (CCDC 216727),[31] **86** (CCDC 199637),[34] **89** (CCDC 239000),[90] **93** (CCDC 211906),[31] **95** (CCDC 290183),[91] **96** (CCDC 162781),[30] **98** (CCDC 162782),[30] **99** (CCDC 238891),[61] **101** (CCDC 229581),[40] **103** (CCDC 278677),[42] **105** (CCDC 194103),[28] **106** (CCDC 229580),[40] **111** (CCDC 196311),[51] **113** (CCDC 201304),[51] **115** (CCDC 232701),[53] **116** (CCDC 232700),[53] **120** (CCDC 141763, 290184),[55,91] **123** (CCDC 192913),[58] **124** (CCDC 192912),[58] **126** (CCDC 177994),[60] **128** (CCDC 233774),[62] **131** (CCDC 260991),[63] **155** (CCDC 269317, 269318),[78] **159** (CCDC 273400),[80] **163** (CCDC 253310),[80] **165** (CCDC 279492).[82] In the silanylpotassium compounds listed above, the potassium ions were coordinated with ether molecules, 18-crown-6 (as in the cover molecule) or THF, such that there were four or six K•••O interactions. From NMR studies we know that in solution (e.g., DME or THF) such coordination is also present. In presenting the chemistry of the polysilanyl anions in this review, such K/ether interactions have been ignored. In those crystal structures in which no ether was present, as mentioned earlier, there was indication of interaction of K with nearby trimethylsilyl groups.

Acknowledgment. I thank Dietmar Seyferth for his continued encouragement and support and for providing me with the opportunity to summarize much of the chemistry which has been carried out in my research group over the last 10 years. During this time I had the privilege to work with a number of very talented and motivated co-workers. They have carried out most of the experimental work described, and their names can be found in the references. I am most grateful to Judith Baumgartner, not only for being the mother of my daughters but also for her numerous crystal structure analyses and her energetic support in every conceivable situation. All of our work covered in this account was supported generously by the Austrian Science Foundation (FWF) within the research program *Siliciumchemie* (S7902) and especially the START project *Chiral polysilanes* (Y120). I am also grateful to the Austrian Academy of Science (ÖAW) for an APART scholarship. Finally, I am indebted to the Wacker Chemie AG (Burghausen, Germany) for their continued generous gifts of chlorosilanes.

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