α,ω-Oligosilyl Dianions and Their Application in the Synthesis of Homo- and Heterocyclosilanes

Roland Fischer, Dieter Frank, Walter Gaderbauer, Christian Kayser,
Christian Mechtler, Judith Baumgartner, and Christoph Marschner*

*Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 16,
A-8010 Graz, Austria*

Received March 31, 2003

The reactions of bridged tris(trimethylsilyl)silyl fragments with 2 molar equiv of potassium *tert*-butoxide allow the generation of α,ω-oligosilyl dianions (**1a**, **2a**, **3a**, **4a**). Depending on the nature of the spacer between the oligosilyl units, these compounds can be used to generate either linear or cyclic derivatives. They are especially attractive for the formation of homo- and heterocyclosilanes, as exemplified by the synthesis of sila-, stanna-, and zirconocenacyclosilanes. A linear bis(potassiumsilyl)acetylene (**4a**) was used to bridge two zirconocene units, ($Cp_2Zr(Cl)Si(SiMe_3)_2CCSi(SiMe_3)_2Zr(Cl)Cp_2$) (**11**).

1. Introduction

The synthesis of molecules with extended polysilane skeletons can be rather difficult. Compared to organic molecules with large frameworks consisting of connected carbon atoms, only relatively few compounds exist in which more than four or five silicon atoms are connected. If polymers, which often only exist as mixtures of molecules with a molecular weight distribution, are not taken into account, the number again shrinks. The remaining compounds usually are synthesized by Wurtz-type coupling[1] or Lewis acid-catalyzed rearrangement[2] reactions. The small number of defined compounds with all-silicon scaffolds is mainly due to the lack of adequate methods to connect molecular fragments that already contain silicon−silicon bonds. The lack of easily available silicon congeners of carbonyl compounds, olefins, and carbanions, which are essential reagents for the synthesis of extended organic systems, hinders the construction of molecules of even moderate complexity with all-silicon frameworks.

A rather straightforward strategy for the construction of more complex molecules is the use of multiply functionalized starting materials such as silyl dianions. These, however, thus far have been rather elusive species. The best strategy to date for their synthesis has been the cleavage of strained cyclosilanes.[3] Recently, some progress has been made, as 1,1-, 1,2-, and 1,4-dilithiooligosilanes have been prepared by the groups of Sekiguchi[4] and Okazaki,[5] Kira,[6] and Apeloig,[7] respectively.

Over the last 5 years we have developed an entry into the chemistry of silyl anions,[8] which opens a new perspective, permitting the relatively easy synthesis of larger oligosilanes. As an extension of these studies, we report here a quite general method for the preparation of α,ω-dianionic oligosilanes.

2. Results and Discussion

The easy access to oligosilyl potassium compounds[8,9b] provides a very simple route to compounds in which two tris(trimethylsilyl)silyl groups are linked to one or more silicon atoms. As has been shown for the case of the reaction with tris(trimethylsilyl)silyllithium,[10] oligosilyl anions can be reacted with α,ω-dihalosilanes (Scheme 1) to form bridged molecules with a variety of different spacer groups (**1**, **2**, **3**).[11]

To obtain also a compound with a rigid spacer between the tris(trimethylsilyl)silyl groups, we also prepared bis[tris(trimethylsilyl)silyl]acetylene[12] by a two-step sequence starting from tris(trimethylsilyl)-chlorosilane (Scheme 2).

---

* Corresponding author. Tel: ++43-316-873-8209. Fax: ++43-316-873-8701. E-mail: marschner@anorg.tu-graz.ac.at.

(1) West, R. Organopolysilanes. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Davies, A. G., Eds.; Elsevier: Oxford, U.K., 1995; Vol. II, Chapter 2, p 77ff. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

(2) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.

(3) (a) Jarvie, A. W.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1961**, *83*, 1921. (b) Gilman, H.; Tomasi, R. A. *Chem. Ind. (London)* **1963**, 954. (c) Hengge, E.; Wolfer, D. *J. Organomet. Chem.* **1974**, *66*, 413. (d) Becker, G.; Hartmann, H. M.; Hengge, E.; Schrank, F. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63.

(4) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231.

(5) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931.

(6) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910.

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

(8) (a) Marschner, Ch. *Eur. J. Inorg. Chem.* **1998**, 221. (b) Kayser, Ch.; Fischer, R.; Baumgartner, J.; Marschner, Ch. *Organometallics* **2002**, *21*, 1023.

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

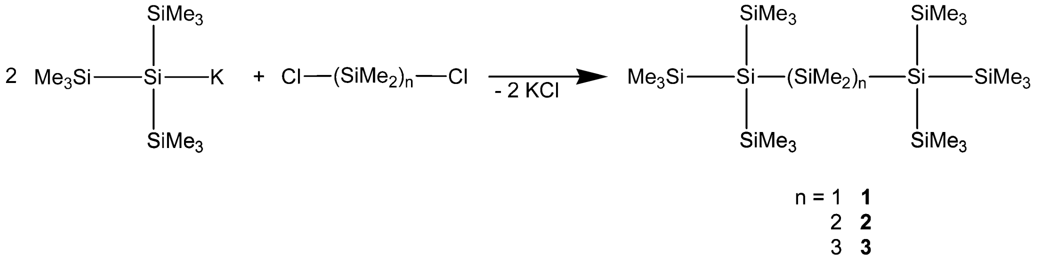
(10) (a) Whittaker, S. M.; Brun, M.-C.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1995**, *499*, 247. (b) Lambert, J. B.; Pflug, J. L.; Allgeier, A. M.; Campbell, D. J.; Higgins, T. B.; Singewald, E. T.; Stern, C. L. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 713.

(11) For alkylidene bridged di-oligosilyl compounds see: (a) Mechtler, Ch.; Marschner, Ch. *Tetrahedron Lett.* **1999**, *40*, 7777. (b) Blanton, J. R.; Diminnie, J. B.; Chen, T.; Wiltz, A. M.; Xue, Z. *Organometallics* **2001**, *20*, 5542.

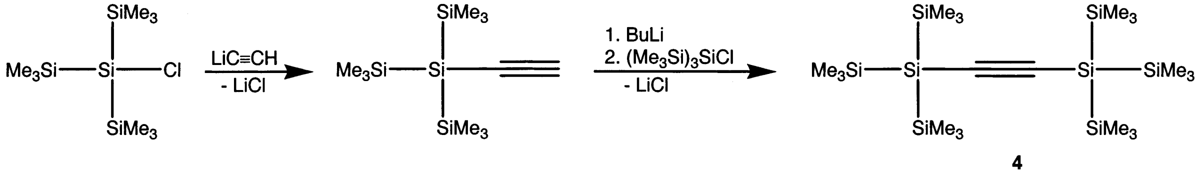
(12) For an alternative synthesis of **4** see: Bock, H.; Meuret, J.; Schödel, H. *Chem. Ber.* **1993**, *126*, 2227.

10.1021/om030233+ CCC: $25.00
Publication on Web 08/08/2003

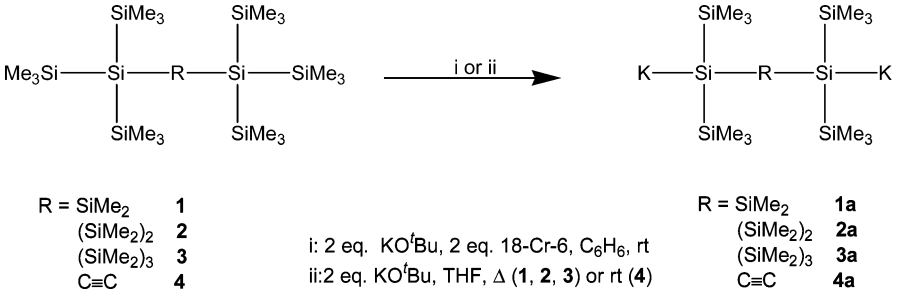
Scheme 1. Synthesis of α,ω-Bis[tris(trimethylsilyl)silyl]silanes



Scheme 2. Synthesis of Bis[tris(trimethylsilyl)silyl]acetylene (4)



Scheme 3. Preparation of α,ω-Oligosilyldianions 1a, 2a, 3a, and 4a



Recently, we described the reactions of **1** and **2** with 2 molar equiv of potassium *tert*-butoxide to give the respective dianions **1a** and **2a**.[13] These compounds are formed in THF at elevated temperature (60 °C) within a few days. The lability of THF toward ring cleavage makes it necessary to control the temperature precisely. An improvement of this protocol is the use of benzene or toluene as solvent in the presence of 2 equiv of 18-crown-6.[8b] These conditions facilitate the reactions dramatically, so that they occur at room temperature within a few hours (Scheme 3). An additional advantage gained is that the products usually crystallize from the used solvents so that isolated products and crystals suitable for X-ray structure analyses[14] of the crown ether adducts of compounds **1a**, **2a**, and **3a** (Figures 1–3) can be obtained.

In contrast to the metalation of the silylidene-bridged precursors (**1**, **2**, **3**), forcing conditions are not required for the reaction of the compound with the alkynylidene spacer (**4**). Conversion to the dianion (**4a**) proceeds at room temperature in THF in the absence of crown ether. The alkynylidene bridge seems to enhance reactivity toward the alkoxide considerably.[15] The effect is so pronounced that it is rather difficult to achieve monometalation using only 1 equiv of potassium *tert*-butoxide. A similar but less marked effect could also be observed for phenyl substituted compounds.[8b]

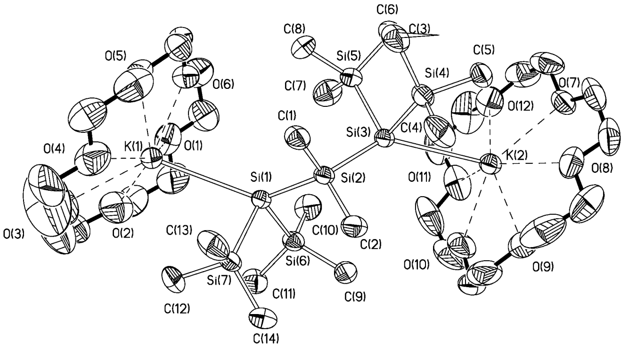


Figure 1. Molecular structure and numbering of **1a** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(1)–Si(1) 3.5011(18); K(2)–Si(3) 3.5836(18); Si(1)–Si(6) 2.3373(17); Si(1)–Si(7) 2.3518(17); Si(1)–Si(2) 2.3750(17); Si(2)–Si(3) 2.3846(16); Si(3)–Si(5) 2.3384(19); Si(3)–Si(4) 2.3511(19). Si(6)–Si(1)–Si(7) 97.08(6); Si(6)–Si(1)–Si(2) 104.21(7); Si(7)–Si(1)–Si(2) 101.80(6); Si(6)–Si(1)–K(1) 122.90(6); Si(2)–Si(1)–K(1) 130.60(5); Si(1)–Si(2)–Si(3) 118.70(7); Si(5)–Si(3)–Si(4) 96.57(7); Si(5)–Si(3)–Si(2) 105.32(7); Si(4)–Si(3)–Si(2) 101.21(7); Si(5)–Si(3)–K(2) 113.66(6); Si(4)–Si(3)–K(2) 87.91(5); Si(2)–Si(3)–K(2) 138.64(5).

Dianions **1a**–**3a** are excellent precursors for the synthesis of cyclic compounds by reaction with difunctional electrophiles. Reactions of **1a** and **2a** with zirconocene dichloride resulted in clean formation of the expected four- and five-membered rings (**5**, **6**) (Scheme 4).[13] Both compounds have been structurally characterized (Figure 4).[16]

---

(13) Kayser, Ch.; Kickelbick, G.; Marschner, Ch. *Angew. Chem.* **2002**, *114*, 1031; *Angew. Chem., Int. Ed.* **2002**, *41*, 989.

(14) Jenkins, D. M.; Teng, W.; Englich, U.; Stone, D.; Ruhlandt-Senge K. *Organometallics* **2001**, *20*, 4600.

(15) The effect of the high reactivity of alkynyl-substituted oligosilanes toward potassium alkoxides is not restricted to compound **4** but is rather general: Mechtler, Ch.; Marschner, Ch. Manuscript in preparation.

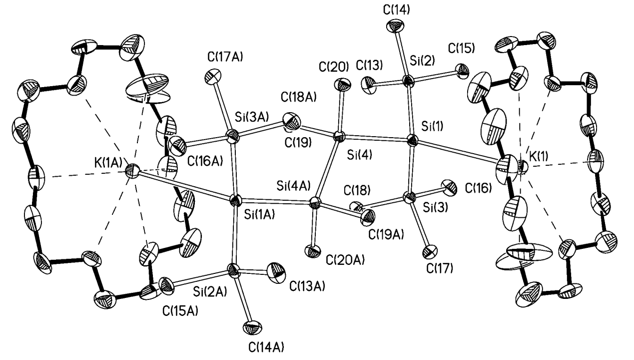


Figure 2. Molecular structure and numbering of **2a** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(1)−Si(1) 3.4458(14); Si(1)−Si(3) 2.3411(16); Si(1)−Si(2) 2.3672(15); Si(1)−Si(4) 2.3860(14); Si(3)−Si(1)−Si(2) 98.97(5); Si(3)−Si(1)−Si(4) 107.13(6); Si(2)−Si(1)−Si(4) 101.83(5); Si(3)−Si(1)−K(1) 96.10(4); Si(2)−Si(1)−K(1) 116.99(5); Si(4)−Si(1)−K(1) 130.68(5).

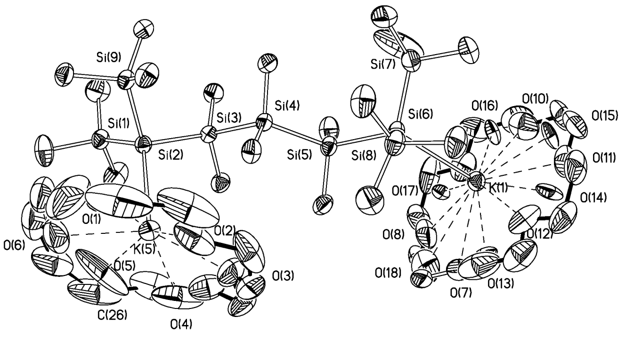
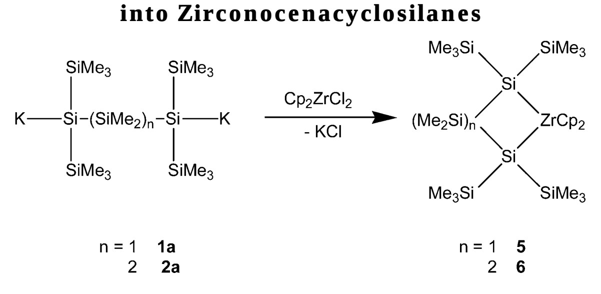


Figure 3. Molecular structure and numbering of **3a** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(5)−Si(2) 3.568(2); K(1)−Si(6) 3.461 (4); Si(1)−Si(2) 2.3517(18); Si(2)−Si(9) 2.3440(17); Si(2)−Si(3) 2.3565(17); Si(3)−Si(4) 2.3739(17); Si(4)−Si(5) 2.3657(18); Si(5)−Si(6) 2.3527(19); Si(6)−Si(8) 2.327(2); Si(6)−Si(7) 2.331(2); Si(9)−Si(2)−Si(1) 100.42(6); Si(9)−Si(2)−Si(3) 105.97(6); Si(1)−Si(2)−Si(3) 101.17(7); Si(9)−Si(2)−K(5) 108.22(6); Si(1)−Si(2)−K(5) 129.04(6); Si(3)−Si(2)−K(5) 109.87(6); Si(2)−Si(3)−Si(4) 112.09(7); Si(5)−Si(4)−Si(3) 113.77(6); Si(6)−Si(5)−Si(4) 125.35(7); Si(8)−Si(6)−Si(7) 104.08(8); Si(8)−Si(6)−Si(5) 106.80(7); Si(7)−Si(6)−Si(5) 109.52(8); Si(8)−Si(6)−K(1) 114.29(7); Si(7)−Si(6)−K(1) 104.51(6); Si(5)−Si(6)−K(1) 116.85(6).

Scheme 4. Conversion of α,ω-Oligosilyl Dianions into Zirconocenacyclosilanes



Both zirconacycles undergo clean insertion reactions with 2,6-dimethylphenylisonitrile to give the respective five- and six-membered rings (**5a**, **6a**).[17] As expected, only one insertion reactions occurs. The products show a coordinative interaction between the zirconium and nitrogen atoms (Figures 5 and 6). This interaction blocks the coordination site required for a further insertion step.

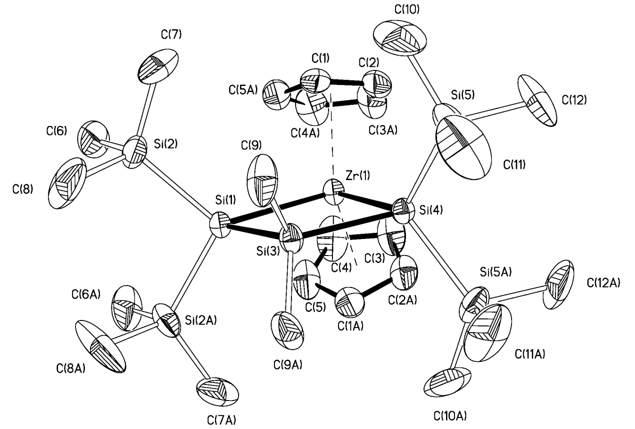


Figure 4. Molecular structure and numbering of **5** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Zr(1)−Si(4) 2.7429(16); Zr(1)−Si(1) 2.7563(16); Si(4)−Si(5) 2.3597(17); Si(4)−Si(3) 2.402(2); Si(3)−Si(1) 2.388(2); Si(1)−Si(2) 2.3534(17); C(4)−Zr(1)−Si(4) 135.20(17); C(3)−Zr(1)−Si(4) 108.35(16); C(5)−Zr(1)−Si(4) 118.81(18); C(1)−Zr(1)−Si(4) 87.20(15); C(2)−Zr(1)−Si(4) 81.78(14); C(4)−Zr(1)−Si(1) 106.72(17); C(3)−Zr(1)−Si(1) 134.31(15); C(5)−Zr(1)−Si(1) 80.73(15); C(1)−Zr(1)−Si(1) 87.85(12); C(2)−Zr(1)−Si(1) 119.96(14); Si(4)−Zr(1)−Si(1) 91.00(5); Zi(5)−Si(4)−Si(3) 107.76(6); Si(5)−Si(4)−Zr(1) 125.80(5); Si(3)−Si(4)−Zr(1) 79.54(6).

Reactions of **1a** and **2a** with diorganotin dichlorides produce stannacyclosilanes (**7**, **8**, **9**) (Scheme 6). The synthesis of the stannacyclotetrasilane (**7**) via **1a** is not very clean. Presumably, ring opening of the strained four-membered ring occurs. A major improvement in this case was the intermediate formation of a silylmagnesium[18] compound, which then very cleanly reacted with dimethyldichlorostannane. The diphenylstannacyclopentasilane (**9**) was structurally characterized (Figure 7). The only other reaction of this type that has been reported was that of 1,4-dilithiooctaphenyltetrasilane, derived from ring opening of octaphenylcyclotetrasilane,[3] with diphenyldichlorostannane.[19]

The reaction of **1a** with 1,2-dibromotetramethyldisilane gave 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane (**10**).[20] The same compound can be obtained by the reaction of **2a** with dimethyldichlorosilane.[13,21]

The dianion derived from the bisoligosilylacetylene (**4a**) is not suited for the preparation of cyclic com-

---

(16) For the discussion of the structural features of **6** cf. ref 13.

(17) (a) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (b) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (c) Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Organomet. Chem.* **1988**, *358*, 169.

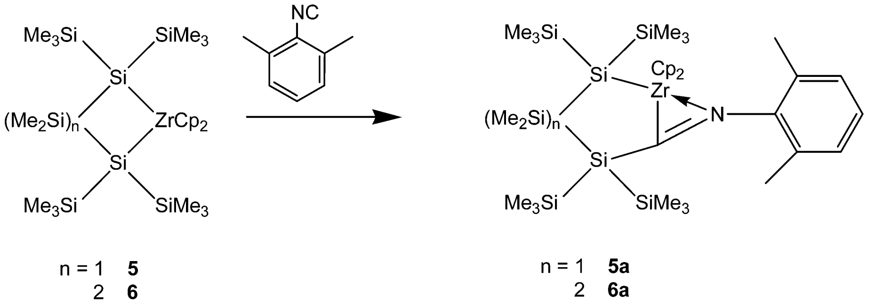
(18) (a) Krempner, C.; Reinke, H.; Oehme, H. *Chem. Ber.* **1995**, *128*, 143. (b) Farwell, J. D.; Lappert, M. F.; Marschner, Ch.; Strissel, Ch.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185.

(19) Hengge, E.; Brychy, U. *Monatsh. Chem.* **1966**, *97*, 84.

(20) Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128. The ^{29}Si NMR data reported for compound **10** in this reference contain a typographical error (−1.94 ppm instead of −19.4 ppm).

(21) For a more detailed study of the synthesis of cyclo- and bicyclosilanes starting from **2a** see: Fischer, R.; Konopa, T.; Ully, St.; Baumgartner, J.; Marschner, Ch. *J. Organomet. Chem.*, in press.

Scheme 5. Zirconocenacyclosilane Insertion Reactions



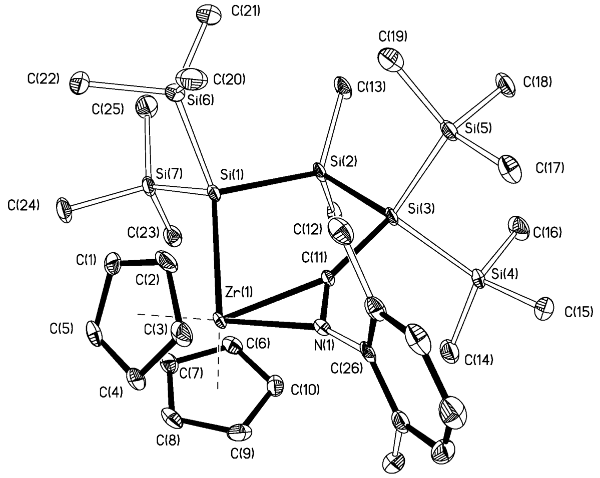


Figure 5. Molecular structure and numbering of **5a** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Zr(1)−N(1) 2.247(3); Zr(1)−Si(1) 2.875(2); Zr(1)−C(11) 2.286(4); Si(1)−Si(7) 2.3817(19); Si(1)−Si(6) 2.3894(18); Si(1)−Si(2) 2.3895(16); Si(2)−Si(3) 2.3690(19); Si(3)−Si(5) 2.3739(17); Si(3)−Si(4) 2.3761(18); N(1)−C(11) 1.272(5); N(1)−C(26) 1.439(5); N(1)−Zr(1)−C(11) 32.57(12); C(11)−Zr(1)−C(9) 103.09(15); C(11)−Zr(1)−C(10) 81.94(14); N(1)−Zr(1)−C(2) 87.52(15); N(1)−Zr(1)−C(8) 121.84(13); N(1)−Zr(1)−C(7) 138.93(13); N(1)−Zr(1)−C(6) 112.11(13); C(11)−N(1)−C(26) 132.4(3); C(11)−N(1)−Zr(1) 75.4(2); C(26)−N(1)−Zr(1) 150.6(2).

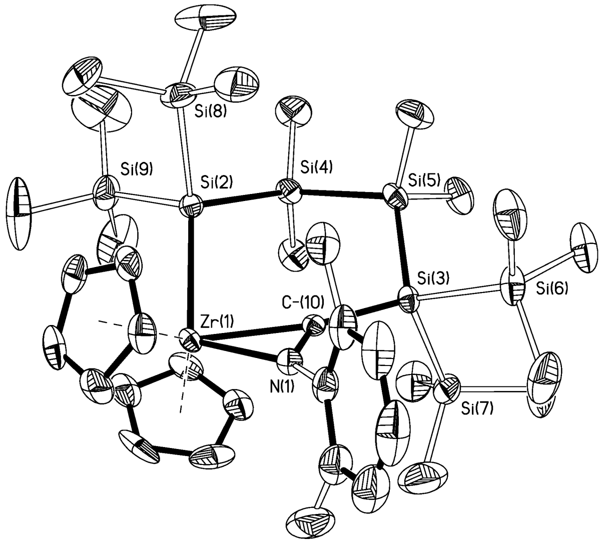
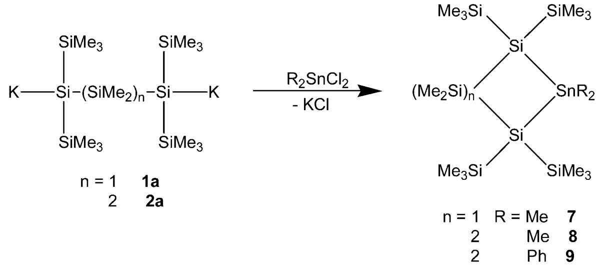


Figure 6. Molecular structure and numbering of **6a** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Zr(1)−N(1) 2.203(3); Zr(1)−C-10 2.318(3); Si(2)−Si(4) 2.3593(14); Si(2)−Si(9) 2.3898(17); Si(2)−Si(8) 2.3907(18); Si(3)−C−10 1.925(3); Si(3)−Si(5) 2.3479(16); Si(3)−Si(6) 2.3889(16); Si(3)−Si(7) 2.4058(18); Si(4)−Si(5) 2.3473(16); N(1)−C−10 1.274(4); N(1)−C−1 1.440(5); N(1)−Zr(1)−C−10 32.60(10); C(6)−Zr(1)−C(10) 31.16(14); N(1)−Zr(1)−C(8) 115.0(2); Si(4)−Si(2)−Si(9) 101.33(6); Si(4)−Si(2)−Si(8) 104.36(6); Si(9)−Si(2)−Si(8) 100.56(6); Si(4)−Si(2)−Zr(1) 112.89(5); Si(9)−Si(2)−Zr(1) 116.06(6); Si(8)−Si(2)−Zr(1) 119.32(6); C−10−Si(3)−Si(5) 106.27(10); C−10−Si(3)−Si(6) 122.98(11); Si(5)−Si(3)−Si(6) 108.25(6); C−10−Si(3)−Si(7) 107.41(11); Si(5)−Si(3)−Si(7) 109.27(6); Si(6)−Si(3)−Si(7) 102.16(6); Si(5)−Si(4)−Si(2) 114.97(6); Si(4)−Si(5)−Si(3) 111.86(6); N(1)−C−10−Si(3) 131.7(2); N(1)−C−10−Zr(1) 68.74(17); Si(3)−C−10−Zr(1) 159.38(17).

pounds. Nevertheless, it can be used, for example, to prepare bridged silylmetal compounds. Reaction of **4a** with 2 equiv of zirconocene dichloride gave the expected product containing two metallocene units bridged by a bissilylated acetylene (**11**). Again, transmetalation of **4a** to the dimagnesium compound improved the yield substantially. As we have demonstrated recently that two bulky silyl groups can be attached to a zirconocene unit,[22] it can be assumed that **11** might be the precursor for an interesting polymer consisting of Zr−Si−C≡C−Si units.

X-ray Crystallography. The structures of the crown ether adducts of compounds **1a**, **2a**, and **3a** were determined by X-ray diffraction analyses (Table 1, Figures 1−3). All three compounds cocrystallize with benzene molecules in the cell, **1a** with six, **2a** with two, and **3a** with four molecules. Obtaining data sets at 100 K was only successful in the case of **2a**. The other crystals lost their structural integrity upon cooling to this temperature, so that we were forced to do the measurement at higher temperature (223 K). As expected, all three dianions are very air-sensitive and the crystals were difficult to mount. The crown ethers parts are well resolved except for one in molecule **3a**, where

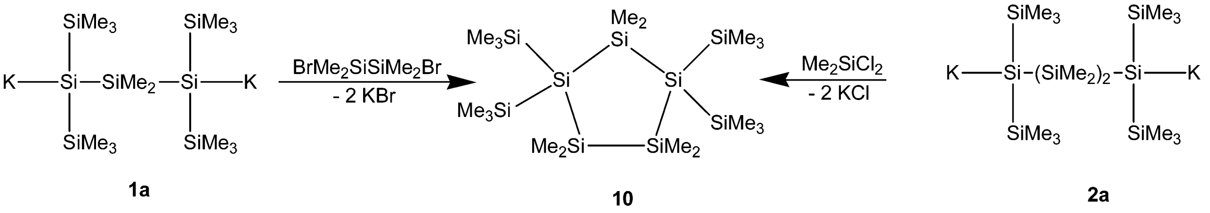
Scheme 6. Synthesis of Stannacyclosilanes



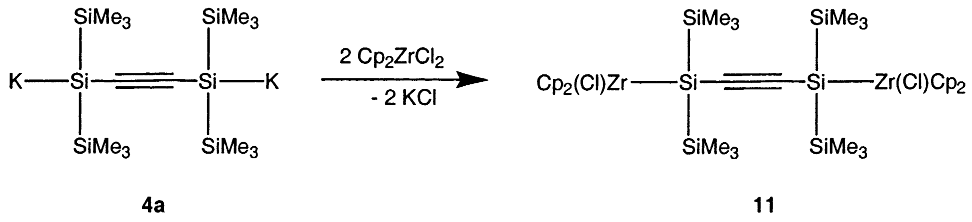
---

(22) Kayser, Ch.; Frank, D.; Baumgartner, J.; Marschner, Ch. *J. Organomet. Chem.* **2003**, *667*, 149.

Scheme 7. Synthesis of 1,1,3,3-Tetrakis(trimethylsilyl)hexamethylcyclopentasilane (10)



Scheme 8. Synthesis of a Bissilylacetylene-Bridged Dizirconocene Compound (11)



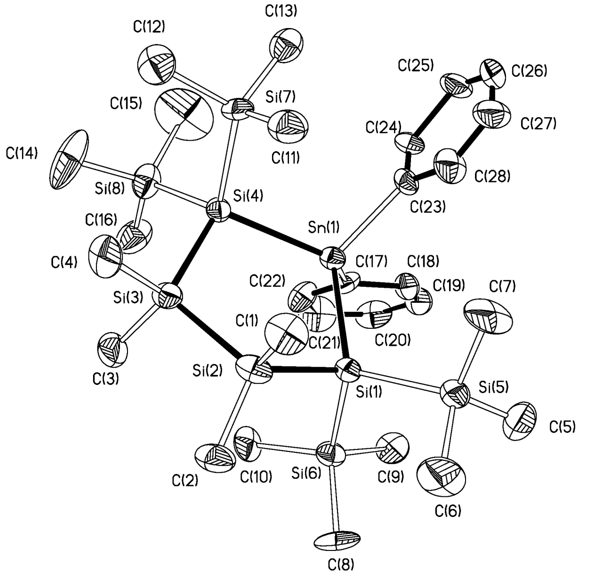


Figure 7. Molecular structure and numbering of **9** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Sn(1)−Si(4) 2.594(4); Sn(1)−Si(1) 2.620(4); Sn(1)−C(17) 2.162(12); Sn(1)−C(23) 2.161(11); Si(1)−Si(5) 2.353(5); Si(1)−Si(6) 2.357(5); Si(1)−Si(2) 2.364(5); Si(2)−C(2) 1.825(14); Si(2)−Si(3) 2.3484(18); Si(3)−Si(4) 2.347(5); Si(4)−Si(8) 2.341(5); Si(4)−Si(7) 2.370(5); C(17)−Sn(1)−C(23) 99.16(16); C(17)−Sn(1)−Si(4) 119.4(3); C(23)−Sn(1)−Si(4) 108.5(3); C(17)−Sn(1)−Si(1) 107.0(3); C(23)−Sn(1)−Si(1) 118.4(3); Si(4)−Sn(1)−Si(1) 105.19(4); Si(5)−Si(1)−Si(6) 107.4(2); Si(5)−Si(1)−Si(2) 110.1(2); Si(6)−Si(1)−Si(2) 109.5(2); Si(5)−Si(1)−Sn(1) 119.57(19); Si(6)−Si(1)−Sn(1) 107.07(17); Si(2)−Si(1)−Sn(1) 102.98(17); Si(3)−Si(2)−Si(1) 109.9(2); Si(4)−Si(3)−Si(2) 110.3(2); Si(8)−Si(4)−Si(3) 108.8(2); Si(8)−Si(4)−Si(7) 107.3(2); Si(3)−Si(4)−Si(7) 108.8(2); Si(8)−Si(4)−Sn(1) 120.8(2); Si(3)−Si(4)−Sn(1) 103.64(17); Si(7)−Si(4)−Sn(1) 106.98(17).

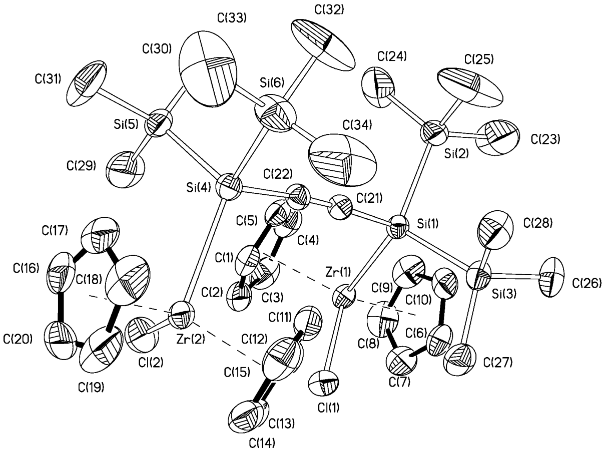


Figure 8. Molecular structure and numbering of **11** with 30% probability thermal ellipsoids. All hydrogens have been removed for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Zr(1)−Cl(1) 2.4252(8); Zr(1)−C(1) 2.497(3); Zr(1)−C(6) 2.517(3); Zr(1)−Si(1) 2.7849(8); Zr(2)−Cl(2) 2.4293(10); Zr(2)−C(16) 2.499(4); Zr(2)−C(11) 2.502(3); Zr(2)−Si(4) 2.7964(8); Si(1)−C(21) 1.856(3); Si(1)−Si(2) 2.3671(12); Si(1)−Si(3) 2.3705(11); Si(4)−C(22) 1.861(3); Si(4)−Si(6) 2.3610(13); Si(4)−Si(5) 2.3725(13); C(21)−C(22) 1.204(3); Si(2)−Si(1)−Si(3) 106.49(4); Si(6)−Si(4)−Si(5) 106.53(5); Cl(2)−Zr(2)−C(11) 116.28(9); Cl(2)−Zr(2)−C(17) 111.56(15); Cl(1)−Zr(1)−C(3) 111.13(12); Cl(1)−Zr(1)−C(4) 135.60(10); Cl(1)−Zr(1)−C(8) 112.98(13); Cl(1)−Zr(1)−C(9) 136.80(10); Cl(1)−Zr(1)−C(5) 115.92(9); Cl(1)−Zr(1)−C(10) 115.98(10); C(3)−Zr(1)−Si(1) 128.37(10); C(4)−Zr(1)−Si(1) 98.24(10); C(8)−Zr(1)−Si(1) 126.83(11); C(9)−Zr(1)−Si(1) 96.38(12); C(2)−Zr(1)−Si(1) 120.91(10); C(7)−Zr(1)−Si(1) 120.09(10); Cl(2)−Zr(2)−C(20) 86.93(18); Cl(2)−Zr(2)−C(19) 117.3(2); Cl(2)−Zr(2)−C(13) 111.69(13).

the oxygen atoms were found to be doubled because of disorder. The two potassium atoms in **2a** are exactly anti to each other [torsional angle K(1)−Si(1)−Si′(1)−K′(1): 180°]. In the case of **1a** the angle is 147.7° [K(2)−Si(3)−Si(1)−K(1)], and it diminishes further to 84.8° [K(1)−Si(6)−Si(2)−K(5)] for **3a** (Figure 9). The distance between the two potassium atoms of one molecule is surprisingly constant for all three compounds. It is 10.27 Å [K(1)−K(2)] for **1a**, 11.14 Å [K(1)−K′(1)] for **2a**, and 10.99 Å [K(1)−K(5)] for **3a**. The Si−K bond length varies from 3.4458(14) Å in **2a** to 3.5836(18) Å in **1a**. All Si−Si bonds of the backbone of the molecules are elongated compared to the Si−(SiMe$_3$) bonds.

The X-ray structure analysis of **5** shows that the four-membered ring is planar, as has already been found for octakis(trimethylsilyl)cyclotetrasilane,[23] and the two Me$_3$Si groups on one Si are totally aligned with the two

---

[23] Shen, Y.-S.; Gaspar, P. *Organometallics* **1982**, *1*, 1410.

Table 1. Crystallographic Data for Compounds 1a, 2a, and 3a

	1a	**2a**	**3a**
empirical formula	$C_{74}H_{126}K_2O_{12}Si_7$	$C_{52}H_{108}K_2O_{12}Si_8$	$C_{66}H_{126}K_2O_{12}Si_9$
M_w	1482.58	1228.29	1442.67
temp [K]	223(2)	100(2)	223(2)
wavelength [Å]	0.71073	0.71073	0.71073
size [mm]	0.51 × 0.32 × 0.25	0.65 × 0.43 × 0.30	0.58 × 0.50 × 0.20
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$
a [Å]	11.851(2)	17.870(4)	12.468(3)
b [Å]	22.358(5)	18.619(4)	16.654(3)
c [Å]	29.679(6)	11.315(2)	19.927(4)
α [deg]	90	90	74.34(3)
β [deg]	96.84(3)	105.59(3)	73.76(3)
γ [deg]	90	90	86.83(3)
V [Å^3]	7808(3)	3626.0(3)	3824.0(13)
Z	4	2	2
ρ_{calc} [g cm^{-3}]	1.062	1.125	1.029
abs coeff [mm^{-1}]	0.275	0.311	0.307
$F(000)$	2704	1332	1283
θ range [deg]	$1.66 < \theta < 24.71$	$1.61 < \theta < 24.72$	$1.75 < \theta < 23.25$
no. of reflns collected/unique	53 828/13287	24 490/6183	23 519/10 882
completeness to θ [%]	99.8	99.9	99.0
abs corr	empirical	empirical	empirical
no. of data/restraints/params	13287/55/689	6183/0/342	10882/249/719
extinction coeff	0.0000(2)	none	none
goodness of fit on F^2	1.032	1.031	1.011
final R indices [$I > 2\sigma(I)$]	R1 = 0.0814, wR2 = 0.2283	R1 = 0.0735, wR2 = 0.1706	R1 = 0.0672, wR2 = 0.1842
R indices (all data)	R1 = 0.1246, wR2 = 0.2643	R1 = 0.0826, wR2 = 0.1772	R1 = 0.1006, wR2 = 0.2114
largest diff peak/hole [e$^-$/Å^3]	0.626/−0.404	1.369/−0.908	0.433/−0.239

Table 2. Crystallographic Data for Compounds 5, 5a, 6a, 9, and 11

	5	**5a**	**6a**	**9**	**11**
empirical formula	$ZrSi_7C_{24}H_{52}$	$ZrSi_7NC_{33}H_{61}$	$ZrSi_8NC_{35}H_{67}$	$SnSi_8C_{28}H_{58}$	$Zr_2Si_6Cl_2C_{34}H_{56}$
M_w	628.51	759.68	817.84	738.15	886.67
temp [K]	223(2)	100(2)	223(2)	233(2)	292(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
size [mm]	0.10 × 0.10 × 0.06	0.30 × 0.25 × 0.10	0.54 × 0.32 × 0.09	0.78 × 0.54 × 0.30	0.60 × 0.29 × 0.23
cryst syst	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
space group	$Cmca$	$P\bar{1}$	$P\bar{1}$	Cc	$P2(1)/c$
a [Å]	16.387(3)	11.350(2)	11.452(2)	14.027(3)	25.9502(17)
b [Å]	20.111(4)	11.971(2)	13.279(3)	16.638(3)	13.6249(9)
c [Å]	21.438(4)	17.035(3)	16.809(3)	18.058(4)	26.0480(17)
α [deg]	90	95.72(3)	85.11(3)	90	90
β [deg]	90	91.10(3)	85.26(3)	103.29(3)	95.0260(10)
γ [deg]	90	112.89(3)	65.20(3)	90	90
V [Å^3]	7065(2)	2117.5(7)	2309.1(8)	4101.6(14)	9174.3(10)
Z	8	2	2	4	4
ρ_{calc} [g cm^{-3}]	1.182	1.191	1.176	1.195	1.284
abs coeff [mm^{-1}]	0.560	0.480	0.469	0.873	0.748
$F(000)$	2672	808	872	1552	3664
θ range (deg)	$1.86 < \theta < 23.25$	$1.95 < \theta < 23.25$	$1.69 < \theta < 20.81$	$1.93 < \theta < 24.71$	$1.57 < \theta < 27.59$
no. of reflns collected/unique	14859/2645	12855/6002	9028/4601	9879/4861	63205/19631
completeness to θ [%]	99.9	98.6	94.9	99.8	92.5
abs corr	empirical	empirical	none	empirical	none
no. of data/restraints/params	2645/0/158	6002/0/423	4601/0/464	4861/2/350	19 631/0/817
goodness of fit on F^2	1.050	1.007	0.911	1.025	0.895
final R indices [$I > 2\sigma(I)$]	R1 = 0.0484, wR2 = 0.1010	R1 = 0.0508, wR2 = 0.1281	R1 = 0.0323, wR2 = 0.0713	R1 = 0.0328, wR2 = 0.0758	R1 = 0.0390, wR2 = 0.0940
R indices (all data)	R1 = 0.0667, wR2 = 0.1083	R1 = 0.0619, wR2 = 0.1350	R1 = 0.0430, wR2 = 0.0739	R1 = 0.0398, wR2 = 0.0795	R1 = 0.0672, wR2 = 0.1041
largest diff peak/hole [e$^-$/Å^3]	0.489/−0.257	1.191/−1.118	0.231/−0.324	0.692/−0.220	1.051/−0.301

on the other side (Figure 4). The Si−Si distances in the ring are slightly elongated compared to the ones in the $Si-(SiMe_3)_2$ units.

The five-membered ring of **5a** was found in an envelope conformation, with the $Si(SiMe_3)_3$ group next to the zirconium atom being 22° out of plane (Figure 5). The nitrogen atom of the fused three-membered ring (N(1)−Zr(1)−C(11)) also lies in the plane of the envelope. In contrast to this, the situation for **6a** is that the six-membered ring displays a slightly twisted chair conformation, with the fused nitrogen atom extending further out of plane (Figure 6). It is interesting to compare the distances between the Zr atom and the carbon and nitrogen atoms of the isonitrile. Compared with the insertion product of $CpCp^*Zr(Cl)Si(SiMe_3)_3$[17c] (Zr−N: 2.250 Å, Zr−C: 2.310 Å), it was found that both values are slightly shorter for **5a** (Zr−N: 2.247 Å, Zr−C: 2.286 Å). For **6a**, however, the Zr−N distance (2.203 Å) is about 0.05 Å shorter, while the Zr−C bond (2.318 Å) does not change very much.

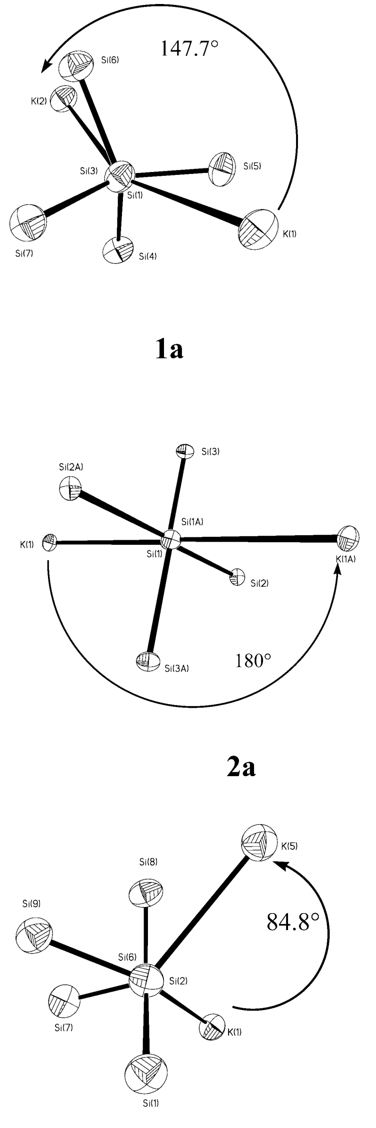


Figure 9. Comparison of conformational differences between **1a**, **2a**, and **3a**. View along the axis between the negatively charged silicon atoms. Dimethylsilylene and methyl groups as well as crown ethers omitted for clarity.

Compound **9** exhibits a twisted half-chair conformation, in which the two $SiMe_2$ groups lie about 8° under or above the ring plane (Figure 7). The Si−Sn bond lengths of 2.594(4) and 2.620(4) Å are in the expected range.[24] The same is true for the Si−Si bond lengths.[24]

The X-ray analysis of **11** shows two different independent molecules in the cell (only one is shown in Figure 8). Both molecules exhibit a gauche-type conformation with respect to the zirconocene units. The torsional angles for Zr(2)−Si(3)−Si(6)−Zr(1) and Zr(3)−Si(1)−Si(2)−Zr(4) are 53.4° and 38.4°, respectively (Figure 10). The distance of the two Zr atoms in both molecules is approximately the same [6.784 Å for Zr(1)−Zr(2) and 6.801 Å for Zr(3)−Zr(4)].

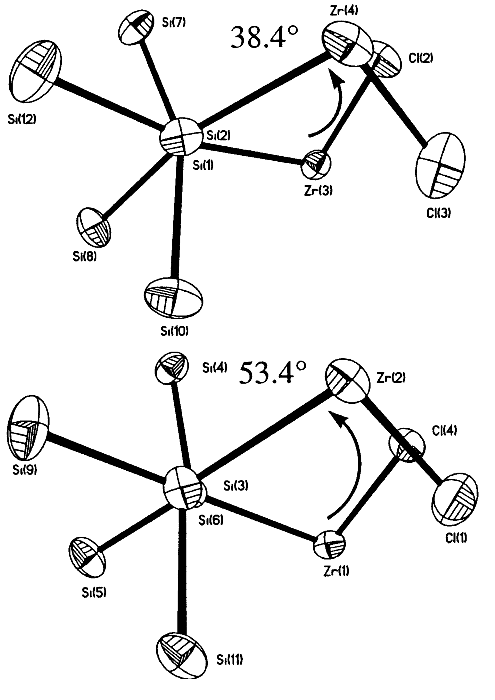


Figure 10. Conformational differences between the two crystallographically independent molecules of **11**. View along the SiCCSi axis. Methyl and cyclopentadienyl groups omitted for clarity.

Conclusion. In summary the present study can be considered as an extension of our work concerning the formation of oligosilyl potassium compounds via the reaction of oligosilanes with potassium *tert*-butoxide. As this reaction does selectively cleave off trimethylsilyl groups, it bears the potential for the synthesis of multiply charged silanes. This has been demonstrated already for α,ω-alkylidene-bridged bis(trimethylsilyl)silyl compounds.[11] We have studied this for similar compounds with one and two dimethylsilylene units in the bridge.[13] The current study extends this further to tris(dimethylsilylene)- and alkynylidene-bridged examples. A protocol employing crown ether was established for improved synthesis of the dianions. The dimethylsilylene-bridged dianions are structurally characterized. The synthetic potential of **1a** and **2a** for the formation of homo- and heterocyclosilanes has been demonstrated by the reactions with dihalides of group 4 and 14 element compounds. The alkynylidene-bridged dianion (**4a**) was converted to a bis(zirconocenylsilyl)alkyne (**11**).

3. Experimental Section

All reactions were carried out under an atmosphere of dry argon or nitrogen. Solvents were dried over sodium/potassium alloy and freshly distilled before use. Potassium *tert*-butoxide was purchased from Merck and sublimed prior to use (140 °C, 0.1 mbar). 18-Crown-6 was used as purchased from Fluka. All other chemicals were used as received from chemical suppliers. Compounds **1**[8a] and **2**[10] were obtained using slight variations of published procedures.

---

[24] A survey of compounds containing a Si−Sn bond in the Cambridge Crystallographic Database gave 50 compounds and Si−Sn bond lengths ranging from 2.50 to 2.75 Å with a mean value of 2.61 Å. The same survey was also conducted for compounds with Si−Si bonds, giving 1004 entries with a significant range from 2.29 to 2.53 Å with a mean value of 2.37 Å.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.3 MHz), and ^{119}Sn (111.8, MHz) NMR spectra were recorded on either a Bruker MSL 300 or a Varian Unity INOVA 300. Samples for ^{29}Si spectra were either dissolved in deuterated solvents or in the case of reaction samples measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, an INEPT pulse sequence was used for the amplification of the signal. The completeness of the reactions was usually controlled by NMR spectroscopy.

For X-ray structure analysis the crystals were mounted onto the tip of a glass fiber, and data collection was performed with a Bruker-AXS Smart Apex CCD diffractometer. The data were reduced to F_o^2 and corrected for absorption effects with SAINT[25] and SADABS,[26] respectively. The structures were solved by direct methods and refined by a full-matrix least-squares method (SHELXL97).[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles.

No satisfactory elemental analyses of the silyl potassium compounds could be obtained. This is in accordance with the observations of other authors, who experienced similar problems with alkali silyl compounds.[9b,14]

3.1. Synthesis of Starting Materials 3 and 4. 3.1.1. 2,2,3,3,4,4-Hexamethyl-1,1,1,3,3,3-hexakis(trimethylsilyl)-pentasilane (3). To 1,3-dichlorohexamethyltrisilane (8.60 g, 35.0 mmol) in toluene (60 mL) at −70 °C was added a solution of tris(trimethylsilyl)silylpotassium[8] in toluene (20 mL) within 30 min. After stirring for 2 h at room temperature the mixture was subjected to aqueous workup (dilute sulfuric acid, extraction with ether, drying over sodium sulfate). After removal of the solvent the white residue was recrystallized from acetone/ether to obtain colorless plates (19.7 g, 29.4 mmol, 84%). Mp: 202−204 °C. ^{1}H NMR (C_6D_6, δ ppm): 0.18 (s, 12 H, 2 × Si*Me*$_2$); 0.05 (s, 6 H, 1 × Si*Me*$_2$); 0.00 (s, 54 H, 6 × Si*Me*$_3$). ^{13}C NMR (C_6D_6, δ ppm): 3.5 (Si*Me*$_3$); 1.0 (2 × Si*Me*$_2$); −1.8 (Si*Me*$_2$). ^{29}Si NMR (C_6D_6, δ ppm): −9.9 (*Si*Me$_3$); −30.41 (2x *Si*Me$_2$); −37.4 (1 × *Si*Me$_2$); −128.3 (*Si*(SiMe$_3$)$_3$). Anal. Calcd for $C_{24}H_{72}Si_{11}$: C 43.04, H 10.83. Found: C 43.20, H 10.99.

3.1.2. Bis[tris(trimethylsilyl)silyl]acetylene (4). Over a stirred solution of *n*-butyllithium (45.0 mL of a 2 M solution in pentane, 90.0 mmol) in ether (45 mL) at −70 °C a stream of acetylene was introduced such that all the gas was consumed. After 2 min the solution became cloudy, and after about 20 min the gas consumption ceased. After stirring for 10 min the temperature was raised to −50 °C and tris(trimethylsilyl)-chlorosilane (25.0 g, 88.3 mmol) in ether (50 mL) was added dropwise over 30 min. The solution was allowed to warm to room temperature and was stirred for another 16 h. After aqueous workup (dilute sulfuric acid, extraction with ether, drying over sodium sulfate) and removal of the solvent the residue was purified by short-path distillation (100 °C, 10^{-2} mbar) to give ethynyltris(trimethylsilyl)silane as a colorless solid (21.3 g, 78.1 mmol, 88%) with a mp near room temperature. ^{1}H NMR (C_6D_6, δ ppm): 2.10 (s, 1 H, C≡C*H*); 0.28 (s, 27 H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, δ ppm): 96.8 (C≡*C*Si); 83.4 (C≡*C*H); 0.3 (Si*Me*$_3$). ^{29}Si NMR (THF/D_2O capillary, δ ppm): −11.5 (*Si*Me$_3$); −100.7 (*Si*(SiMe$_3$)$_3$). MS: mz(%): 272(2) M$^+$; 257(70) M$^+$ − Me; 199(20) (Me$_3$Si)$_2$Si(CCH); 183(45) (Me$_3$Si)$_2$-Si(CC) − Me; 116(30) Si$_2$Me$_4$; 73(100) Me$_3$Si.

To a solution of ethynyltris(trimethylsilyl)silane (10.0 g, 36.7 mmol) in ether (50 mL) at −70 °C was added dropwise within 30 min *n*-butyllithium (23.0 mL of a 1.6 M solution in hexane, 36.8 mmol). After stirring for a further 30 min the temperature was raised to room temperature. The solution was cooled to −20 °C and tris(trimethylsilyl)chlorosilane (10.4 g, 36.7 mmol) in ether (50 mL) was added dropwise over 30 min. After a workup analogous to that described above, the solvent was removed and the residue Kugelrohr distilled to remove residual ethynyltris(trimethylsilyl)silane and tris(trimethylsilyl)-chlorosilane. The remaining residue was recrystallized from 2-propanol to give bis[tris(trimethylsilyl)silyl]acetylene (**4**) (15.4 g, 29.7 mmol, 81%) as colorless crystals. Mp: 188−190 °C (acetone). ^{1}H NMR (CDCl$_3$, δ ppm): 0.19 (s, 54 H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, δ ppm): 109.6 (*C*≡*C*); 0.4 (Si*Me*$_3$). ^{29}Si (C_6D_6, δ ppm): −11.2 (*Si*Me$_3$); −100.6 (*Si*(SiMe$_3$)$_3$). MS: mz(%): 518-(3) M$^+$; 348(33) (Me$_3$Si)$_4$Si$_2$; 73(100) Me$_3$Si. Anal. Calcd for $C_{20}H_{54}Si_8$: C 46.25; H 10.48. Found: C 43.63; H 10.54.

3.2. Preparation of the Dipotassium Compounds 1a, 2a, and 3a. The respective oligosilane (**1**, **2**, **3**), potassium *tert*-butoxide (2 equiv), and 18-crown-6 (2 equiv) were dissolved in a small amount of benzene. The reaction mixture immediately turned yellow and finally afforded an intensely red solution from which the product precipitated within 24 h as highly air- and moisture-sensitive dark red crystals.

3.2.1. 1,3-Dipotassium-2,2-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilane·2 18-crown-6 (1a). Starting from 2,2-dimethyl-1,1,3,3-hexakis(trimethylsilyl)trisilane (**1**) **1a** was obtained in 95% yield. ^{1}H NMR (C_6D_6, δ ppm): 3.29 (s, 48 H, C*H*$_2$O); 1.17 (s, 6 H, Si*Me*$_2$); 0.80 (s, 36 H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, δ ppm): 70.0 (*C*H$_2$O); 13.3 (Si*Me*$_2$); 9.4 (Si*Me*$_3$). ^{29}Si NMR (C_6D_6, δ ppm): −4.6 (*Si*Me$_3$); −14.5 (Si*Me*$_2$); −172.5 (*Si*K).

3.2.2. 1,4-Dipotassium-2,2,3,3-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)tetrasilane·2 18-crown-6 (2a). Starting with 2,2,3,3-tetramethyl-1,1,1,4,4,4-hexakis(trimethylsilyl)tetrasilane (**2**) **2a** was obtained in 98% yield. ^{1}H NMR (C_6D_6, δ ppm): 3.29 (s, 48 H, C*H*$_2$O); 0.87 (s, 12 H, Si*Me*$_2$); 0.77 (s, 36 H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, δ ppm): 70.1 (*C*H$_2$O); 8.8 (Si*Me*$_3$); 5.5(Si*Me*$_2$). ^{29}Si (C_6D_6, δ ppm): −3.7 (*Si*Me$_3$); −24.5 (*Si*Me$_2$); −190.2 (*Si*K).

3.2.3. 1,5-Dipotassium-2,2,3,3,4,4-hexamethyl-1,1,5,5-tetrakis(trimethylsilyl)pentasilane·2 18-crown-6 (3a). Starting from 2,2,3,3,4,4-hexamethyl-1,1,1,3,3,3-hexakis(trimethylsilyl)pentasilane (**3**) **3a** was obtained in 98% yield. ^{1}H NMR (C_6D_6, δ ppm): 3.27 (s, 48 H, C*H*$_2$O); 0.65 (s, 36 H, Si*Me*$_3$); 0.60 (s, 18 H, 3x Si*Me*$_2$). ^{13}C NMR (C_6D_6, δ ppm): 70.0 (*C*H$_2$O); 8.5 (Si*Me*$_3$); 7.7 (2 × Si*Me*$_2$); 5.4 (Si*Me*$_2$). ^{29}Si NMR (C_6D_6, δ ppm): −4.3 (*Si*Me$_3$); −23.1 (2 × *Si*Me$_2$); −40.1 (*Si*Me$_2$); −184.6 (*Si*K).

3.3. Bis[bis(trimethylsilyl)potassiosilyl]acetylene (4a). Bis[tris(trimethylsilyl)silyl]acetylene (**4**) (74 mg, 0.14 mmol) and potassium *tert*-butoxide (34 mg, 0.30 mmol) were mixed in toluene (1 mL), and 18-crown-6 (80 mg, 0.30 mmol) was added. Immediately the solution turned yellow. After 1 h complete conversion was detected using ^{29}Si NMR spectroscopy. Removal of the solvent in a vacuum leaves **4a** as an orange amorphous solid (135 mg, 98%). ^{1}H NMR (C_6D_6, δ ppm): 3.37 (s, 48 H, C*H*$_2$O); 0.66 (s, 36 H, SiMe$_3$). ^{13}C NMR (C_6D_6, δ ppm): 117.7 (*C*≡*C*); 70.2 (*C*H$_2$O); 5.1 (Si*Me*$_3$). ^{29}Si NMR (THF/C_6D_6, δ ppm): −7.3 (*Si*Me$_3$); −150.1 (*Si*K).

In contrast to compounds **1a**, **2a**, and **3a,** which do not form cleanly at room temperature in the absence of crown ether, **4a** can be prepared also in THF without 18-crown-6 at room temperature, which is clearly the preferred method for its in situ preparation.

3.4. Synthesis of Zirconasilacyclopentanes 5 and 6. Zirconocene dichloride (1.3 equiv) and the dipotassium silyl

---

[25] *SAINTPLUS*: Software Reference Manual, Version 5.054; Bruker-AXS: Madison, WI, 1997−1998.

[26] Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33−38. *SADABS*; Bruker AXS: Madison, WI, 1998.

[27] Sheldrick, G. M. *SHELX97*, Program for Crystal Structure Analysis (Release 97-2); Universität Göttingen: Göttingen, Germany, 1998.

[28] Crystallographic data (excluding structure factors) for the structures of compounds **1a**, **2a**, **3a**, **5**, **5a**, **6a**, **8**, and **9** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-194099 for **1a**, 194101 for **2a**, 194098 for **3a**, 194097 for **5**, 194100 for **5a**, 194102 for **6a**, 194103 for **9**, and 194096 for **11**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK [fax: (internat.) +44−1223/336−033; e-mail: deposit@chemcrys.cam.ac.uk].

compound were dissolved in toluene. The deep red solution was stirred at room temperature for 6 h. The solvent was removed in a vacuum, and the residue dissolved in pentane. The resulting solution was filtered and cooled to −30 °C to obtain the crystalline product.

3.4.1. 1,1-Dicyclopentadienyl-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)-1-zirconacyclotetrasilane (5). Using dianion **1a** deep red crystals of **5** were obtained in 47% yield. ^{1}H NMR (C_6D_6, δ ppm): 5.87 (s, 10 H, 2 × *Cp*); 0.46 (s, 6 H, Si*Me₂*); 0.45 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 102.5 (*Cp*); 5.7 (Si*Me₃*); −0.1 (Si*Me₂*). ^{29}Si NMR (C_6D_6, δ ppm): −1.4 (*Si*Me₃); −22.6 (*Si*Me₂); −120.3 (*Si*Zr). Anal. Calcd for $C_{24}H_{52}Si_7Zr$: C 45.86; H 8.34. Found: C 45.29; H 8.33.

3.4.2. 1,1-Dicyclopentadienyl-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)-1-zirconacyclopentasilane (6). Using dianion **2a** deep red crystals[16] of **6** were obtained in 90% yield. Mp: 167−170 °C (dec). ^{1}H NMR (C_6D_6, δ ppm): 6.29 (s, 10 H, *Cp*); 0.45 (s, 12 H, Si*Me₂*); 0.43 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 108.8 (*Cp*); 6.9 (Si*Me₃*); 2.2 (Si*Me₂*). ^{29}Si NMR (pentane, D_2O, δ ppm): −2.4 (*Si*Me₃); −29.2 (*Si*Me₃); −65.2 (*Si*Zr). Anal. Calcd for $C_{26}H_{58}Si_8Zr$: C 45.48; H 8.51. Found: C 45.01, H 8.47.

3.5. Reactions of Zirconacycles with Isonitrile (5a, 6a). Zirconacyclosilanes (0.08 mmol) and 1-isocyano-2,6-dimethylbenzene (11.0 mg, 0.08 mmol) were dissolved in 2 mL of C_6D_6. The color changed immediately from deep red to orange. The solvent was removed in a vacuum, and the residue was dissolved in pentane and cooled to −30 °C to obtain crystals suitable for single-crystal analysis.

3.5.1. Insertion into 5 (5a). Yellow crystals were obtained in 50% yield. Mp: 199−202 °C. ^{1}H NMR (C_6D_6, δ ppm): 6.85 (m, 3 H, *H*$_{Ar}$); 5.69 (s, 10 H, *Cp*); 2.05 (s, 6 H, 2 × *Me*$_{Ar}$); 0.86 (s, 6 H, Si*Me₂*); 0.58 (s, 18 H, Si*Me₃*); 0.10 (s, 18 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 281.2 (*C*=N); 154.7 (*C*$_{ipso}$); 129.7 (*C*$_{Ar}$); 128.4 (*C*$_{Ar}$); 127.9 (*C*$_{Ar}$); 105.0 (*Cp*); 18.5 (*Me*$_{Ar}$); 7.2 (Si*Me₃*); 5.3 (Si*Me₂*); 3.7 (Si*Me₃*). ^{29}Si NMR (C_6D_6, δ ppm): −2.9 (*Si*Me₃); −3.1 (*Si*Me₃); −11.4 (*Si*Me₂); −76.0 (Si); −92.5 (). Anal. Calcd for $C_{33}H_{61}NSi_7Zr$: C 52.17; H 8.09; N 1.84. Found: C 51.97; H 8.13; N 1.94.

3.5.2. Insertion into 6 (6a). Yellow crystals were obtained in 62% yield. ^{1}H NMR (C_6D_6, δ ppm): 6.85 (m, 3 H, *H*$_{Ar}$); 5.69 (s, 10 H, *Cp*); 1.94 (s, 6 H, *Me*$_{Ar}$); 0.78 (s, 6 H, Si*Me₂*); 0.52 (s, 18 H, 2 × Si*Me₃*); 0.51 (s, 6 H, Si*Me₂*); 0.10 (s, 18 H, 2x Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 279.6 (*C*=N); 154.1 (*C*$_{ipso}$); 129.5 (*C*$_{Ar}$); 128.9 (*C*$_{Ar}$); 128.3 (*C*$_{Ar}$); 106.4 (*Cp*); 21.5 (*Me*$_{Ar}$); 7.1 (Si*Me₃*); 4.3 (Si*Me₃*); 2.1 (Si*Me₂*); −0.1 (Si*Me₂*). ^{29}Si NMR (pentane, D_2O, δ ppm): −4.3 (*Si*Me₃); −10.0 (*Si*Me₃); −33.0 (*Si*Me₂); −36.3 (*Si*Me₂); −79.0 (Zr*Si*); −117.2 (NC*Si*). Anal. Calcd for $C_{35}H_{67}NSi_8Zr$: C 51.40, H 8.26. Found: C 50.97, H 8.37.

3.6. Synthesis of Tin-Containing Cyclosilanes (7, 8, and 9). 3.6.1. 1,1,3,3-Tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1-stannacyclotetrasilane (7). 1,3-Dipotassium-2,2-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilane·2 18-crown-6 (**1a**) (0.20 mmol) and $MgBr_2\cdot Et_2O$ (77 mg, 0.30 mmol) were dissolved in toluene (5 mL). After 5 min dimethyldichlorostannane (66 mg, 0.30 mmol) was added. The solution was stirred at room temperature for 1 h. Then the solution was concentrated and the residue was extracted with pentane. The extracts were filtered and cooled to −30 °C to obtain colorless crystals. Mp: 114−116 °C. ^{1}H NMR (C_6D_6, δ ppm): 0.63 (s, 6 H, Si*Me₂*); 0.54 (s, 6 H, $^2J(^1H-^{119}Sn) = 6$ Hz, Sn*Me₂*); 0.33 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 4.3 (Si*Me₂*); 3.3 (Si*Me₃*); −9.0 (Sn*Me₃*). ^{29}Si NMR (C_6D_6, δ ppm): −7.8 ($^2J(^{29}Si-^{119}Sn) =$ 45 Hz, *Si*Me₃); −13.0 ($^2J(^{29}Si-^{119}Sn/^{117}Sn) = 54/52$ Hz, *Si*Me₂); −89.0 ($^1J(^{29}Si-^{119}Sn/^{117}Sn) = 188/180$ Hz, *Si*Sn). ^{119}Sn (C_6D_6, δ ppm): −174.0 [$^1J(^{29}Si-^{119}Sn) = 188$ Hz, $^2J(^{29}Si-^{119}Sn) = 55$ Hz, $J(^{13}C-^{119}Sn) = 11$ Hz]. Anal. Calcd for $C_{16}H_{48}Si_7Sn$: C 34.57; H 8.70. Found: C 34.59; H 8.99.

3.6.2. Stannacyclopentasilanes (8 and 9). 1,4-Dipotassium-2,2,3,3-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)tetrasilane·2 18-crown-6 (**2a**) (0.40 mmol) and the respective diorganotin dichloride (0.52 mmol) were dissolved in toluene (6 mL). The solution was stirred at room temperature for 12 h. The solution was concentrated, and the residue was dissolved in pentane, filtered, and cooled to −30 °C to obtain crystals.

3.6.2.1. 1,1,3,3,4,4-Hexamethyl-2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentasilane (8). Colorless crystals were obtained in 55% yield. Mp: 137−138 °C. ^{1}H (C_6D_6, δ ppm): 0.57 (s, 6 H, Sn*Me₂*); 0.37 (s, 12 H, Si*Me₂*); 0.30 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 3.7 (Si*Me₂*); −1.4 (Si*Me₃*); −8.3 (Sn*Me₂*). ^{29}Si NMR (hexane/THF/D_2O, δ ppm): −5.4 ($^2J(^{29}Si-^{119}Sn) = 44$ Hz, *Si*Me₃); −22.2 ($^2J(^{29}Si-^{119}Sn) = 61$ Hz, *Si*Me₂); −137.5 ($^1J(^{29}Si-^{119}Sn/^{117}Sn) = 192/186$ Hz, *Si*Sn). ^{119}Sn NMR (hexane/THF/D_2O, δ ppm): −118.6 ($^1J(^{29}Si-^{119}Sn) = 197$ Hz, $^2J(^{29}Si-^{119}Sn) = 66$ Hz). Anal. Calcd for $C_{18}H_{54}Si_8Sn$: C 35.21; H 8.86. Found: C 34.84; H 8.77.

3.6.2.2. 3,3,4,4-Tetramethyl-1,1-diphenyl-2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentasilane (9). Colorless crystals were obtained in 48% yield. Mp: 124−126 °C. ^{1}H NMR (C_6D_6, δ ppm): 7.76 (m, 4 H, *H*$_{Ar}$); 7.14 (m, 6 H, *H*$_{Ar}$); 0.50 (s, 12 H, Si*Me₂*); 0.27 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 154.0 (*C*$_{ipso}$); 141.9 (*C*$_{Ar}$); 138.8 (*C*$_{Ar}$); 128.4 (*C*$_{Ar}$); 3.9 (Si*Me₂*); −1.3 (Si*Me₃*). ^{29}Si NMR (toluene/D_2O, δ ppm): −3.6 ($^2J(^{29}Si-^{119}Sn) = 48$ Hz, *Si*Me₃); −21.2 ($^2J(^{29}Si-^{119}Sn) = 71$ Hz, *Si*Me₂); −132.0 ($^1J(^{29}Si-^{119}Sn/^{117}Sn) = 184/176$ Hz, *Si*Sn). ^{119}Sn NMR (hexane/THF/D_2O, δ ppm): −85.9 ($^1J(^{29}Si-^{119}Sn) = 186$ Hz, $^2J(^{29}Si-^{119}Sn) = 75$ Hz). Anal. Calcd for $C_{28}H_{58}Si_8Sn$: C 45.56; H 7.92. Found: C 45.21; H 7.97.

3.7. 1,1,3,3-Tetrakis(trimethylsilyl)hexamethylcyclopentasilane (10). 1,3-Dipotassium-2,2-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilane·2 18-crown-6 (**1a**) (0.23 mmol) and $MgBr_2\cdot Et_2O$ (77 mg, 0.30 mmol) were dissolved in toluene (5 mL). After 5 min 1,2-dibromotetramethyldisilane (91 mg, 0.33 mmol) was added. The solution was stirred at room temperature for 1 h. After aqueous workup (dilute sulfuric acid, extraction with ether, drying over sodium sulfate) and removal of the solvent a colorless compound (95 mg, 0.18 mmol, 79%) was obtained, which was found to exhibit identical spectral properties as reported.[20] Mp: 142−144 °C. ^{29}Si NMR (C_6D_6, δ ppm): −7.6 (*Si*Me₃); −19.9 (*Si*Me₂); −24.8 (*Si*Me₂); −129.4 (*Si*(SiMe₃)₂).[20]

3.8. Bis[(chlorozirconocenyl)bis(trimethylsilyl)silyl]acetylene (11). **4** (350 mg, 0.68 mmol) and potassium *tert*-butoxide (160 mg, 1.43 mmol) were dissolved in 1 mL of THF. After stirring for 1 h $MgBr_2\cdot Et_2O$ (380 mg, 1.48 mmol) was added. The solution was concentrated and the residue redissolved in 2 mL of toluene. The solution was filtered, and zirconocene dichloride (288 mg, 1.43 mmol) was added. After filtration of the salt, the remaining solution was cooled to −30 °C, and the product was isolated as deep red crystals by filtration (73%). ^{1}H NMR (C_6D_6, δ ppm): 5.29 (s, 20 H, *Cp*); 0.35 (s, 36 H, Si*Me₃*). ^{13}C NMR (C_6D_6, δ ppm): 102.8 (*Cp*); 97.5 (*C*≡*C*); 3.3 (Si*Me₃*). ^{29}Si (C_6D_6, δ ppm): −6.1 (*Si*Me₃); −54.8 (*Si*Zr). Anal. Calcd for $C_{34}H_{56}Cl_2Si_6Zr_2$: C 46.06; H 6.37. Found: C 45.37; H 6.33.

Acknowledgment. This study was carried out within the Forschungsschwerpunkt Siliciumchemie (S7902) supported by the Austrian Science Foundation (FWF) and the START project Chiral polysilanes (Y120)-funded by the Austrian Ministry of Education, Science and Culture.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM030233+