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[17] [$Pd_2(dae)_3$] (405 mg, 0.8 mmol) were suspended in 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane (5 mL). The mixture was immediately cooled to − 30 °C and 1,3-dimesitylimidazol-2-ylidene (340 mg, 1.1 mmol) was added. After warming up to room temperature the solution was stirred for 1 h at this temperature. Then the white complex formed was collected by filtration, washed with pentane (2 × 5 mL), and dried in vacuo. X-ray structural analysis of **5**: STOE-IPDS diffractometer, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, structure solved by direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined with the full-matrix least-squares method against F^2 (SHELXL-93: G. M. Sheldrick, Göttingen, Germany, **1993**), structural representation: XP (Siemens), 0.4 × 0.3 × 0.2 mm, yellow prism, space group $P2_1/n$, monoclinic, $a = 13.100(3)$, $b = 18.235(4)$, $c = 13.467(3)$ Å, $\beta = 105.07(3)°$, $V = 3106.3(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.277$ g cm^{-3}, 6157 measured reflections, 3279 were independent of symmetry, of which 2412 were observed ($I > 2\sigma(I)$), $R = 0.033$, $wR2$ (all data) = 0.076, 316 parameters. CCDC-171440 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Simple Synthesis of Oligosilyl-α,ω-dipotassium Compounds**

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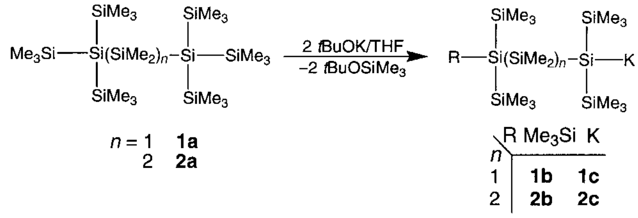
The chemistry of electrophilic silicon compounds is a well established and intensively studied area, whereas their nucleophilic counterparts, the so-called silyl anions, enjoyed much less attention for a long time. This is quite astonishing, considering the high popularity of the tris(trimethylsilyl)silyl group, which is mainly introduced through the respective silyl anion, in main group and organometallic chemistry. However, over the last few years this situation has changed and anionic silyl compounds are now the subject of increased investigations.[1] Recently, in this context, we have reported the synthesis of oligosilyl anions by cleavage of trimethylsilyl groups with potassium *tert*-butoxide.[2] This reaction can be regarded as a variation of the method developed by Gilman et al. for the synthesis of oligosilyllithium compounds by cleavage of trimethylsilyl groups with methyllithium.[3] An advantage of using potassium alkoxides instead of alkyllithium compounds becomes evident in the reaction with higher oligosilanes. In cases where there are additional Si–Si bonds besides the ones between the central silicon atom and the peripheral trimethylsilyl groups, these 'inner' bonds are cleaved exclusively by methyllithium,[3] whereas potassium *tert*-butoxide selectively removes a trimethylsilyl group.[2, 4] The access to these higher silyl anions opened the possibility of studying the prospects for the synthesis of multiply metalated oligosilanes.[4, 5]

Therefore, we treated bis[tris(trimethylsilyl)silyl] compounds, bridged with one (**1a**)[2, 6] or two (**2a**)[7] dimethylsilylene units with potassium *tert*-butoxide in THF at elevated temperatures (Scheme 1). Following a fast first metalation step,[2, 5, 8] the subsequent formation of the dianion takes place more easily when the negative charges are further apart. Whereas the reaction of **2a** to the dianion, occurs at a very low rate, even at room temperature, the conversion of **1a** requires prolonged heating to 60 °C.



Scheme 1. Synthesis of mono- and dipotassium compounds.

Concerning their reactivity **1c** and especially **2c** behave almost like isolated silyl anions. Derivatization reactions like hydrolysis (→**4**), alkylation with dimethyl sulfate (→**3**)[9] and the formation of homo- and heterocyclic rings by the reactions with dimethylsilyl (→**5**),[10] dimethyltin (→**6**),[11] and metallocene dihalides (→**7**, **8**) proceed very cleanly (Scheme 2). In contrast to what is found for lithium silanides,[12] the THF molecules of **1b,c** and **2b,c** are not bound very firmly. They can be removed in part in vacuum; therefore, depending on the conditions of isolation a different content of donor molecules can be observed for these compounds.

Control of conversion and characterization of the silyl anions can be achieved most easily by ^{29}Si NMR spectroscopy. The formal exchange of one trimethylsilyl group for a potassium atom results in a shift of the resonance signal of the affected silicon atom of $\Delta\delta \approx 60$ to lower frequencies. At the same time the trimethylsilyl groups in β-position experience a shift of $\Delta\delta \approx 4 - 5$ in the opposite direction. The second metalation step from **2b** to **2c** effects an additional slight shift of the ^{29}Si resonance signal of the metalated nucleus to lower frequency ($\delta = -192$), which is in accordance with previous observations with alkylidene-bridged dianions.[5] In contrast to this **1c** exhibits an NMR signal for the metalated silicon

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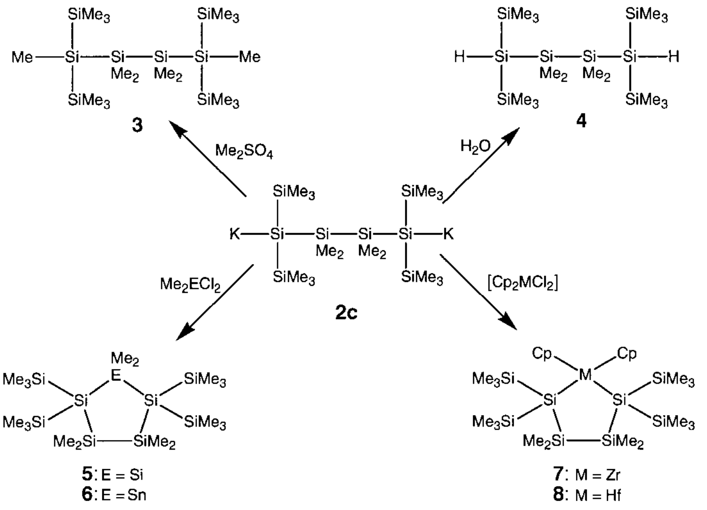
[**] This work was supported by the Austrian science fund (FWF). C. M. thanks the Austrian Academy of Science for an APART fellowship.



Scheme 2. Reactions of **2c**.

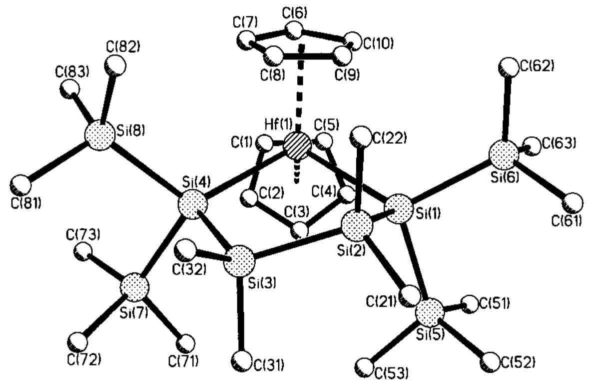


Figure 2. Structure of **8** in the crystal. Selected bond lengths [Å] and angles [°]: Si(1)-Hf(1) 2.791(14), Si(4)-Hf(1) 2.823(15), Si(2)-Si(3) 2.342(3), Si(1)-Si(2) 2.385(2), Si(3)-Si(4) 2.379(2), Si(1)-Si(5/6) 2.374(2)/2.371(3), Si(4)-Si(7/8) 2.382(2)/2.381(2), Si(1)-Si(2)-Si(3) 108.05(9), Si(2)-Si(3)-Si(4) 111.38(9), Si(6)-Si(1)-Si(5) 100.84(9), Si(8)-Si(4)-Si(7) 99.22(9), Si(1)-Si(5)-Hf(1) 119.90(7), Si(1)-Hf(1)-Si(4) 96.41(5).

atoms at $\delta = -173$. Compared to the resonance of the monometalated compound (**1b**) this corresponds to a shift of $\Delta\delta \approx 15$ to higher frequencies.[13]

The silyl compounds of the early transition metals can be synthesized most easily by the salt elimination reaction of silyl anions with metal halides.[14] Because of the limited availability of silyl dianions, early metal compounds with bidentate silyl ligands are only scarcely known.[15] Therefore, **2c** was tested for its reactivity with zirconocene and hafnocene dichlorides (Scheme 2). The respective reactions proceeded very cleanly to give the expected zirconocena- (**7**) and hafnocenacyclopentasilanes (**8**), which, to the best of our knowledge, are the first examples of these types of compounds.[15] Both compounds could be characterized unambiguously by single-crystal X-ray structure analysis (Figures 1 and 2).[16, 17]

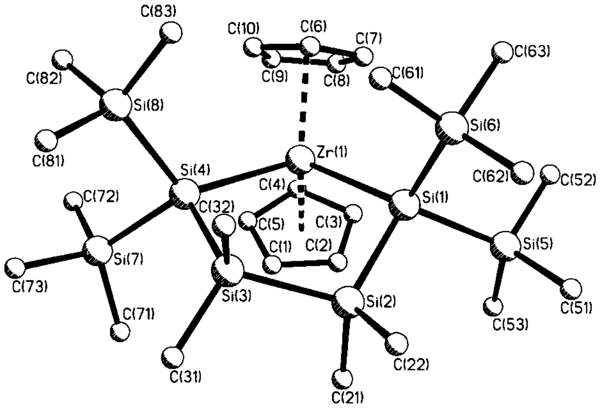
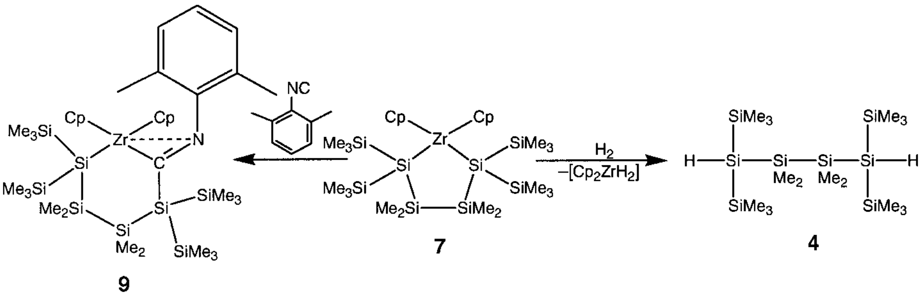


Figure 1. Structure of **7** in the crystal. Selected bond lengths [Å] and angles [°]: Si(1)-Zr(1) 2.8264(19), Si(4)-Zr(1) 2.8497(19), Si(2)-Si(3) 2.351(4), Si(1)-Si(2) 2.387(3), Si(3)-Si(4) 2.378(3), Si(1)-Si(5/6) 2.369(3)/2.376(3), Si(4)-Si(7/8) 2.380(3)/2.386(3), Si(1)-Si(2)-Si(3) 109.25(11), Si(2)-Si(3)-Si(4) 112.79(11), Si(6)-Si(1)-Si(5) 101.42(11), Si(8)-Si(4)-Si(7) 99.46(11), Si(1)-Si(5)-Zr(1) 121.09(9), Si(1)-Zr(1)-Si(4) 97.70(6).

We oriented our studies of the reactivity of these metallacyclopentanes on work by Tilley et al. on silyl metallocenes,[18, 19] and carried out reactions with hydrogen, 1-isocyano-2,6-dimethylbenzene, and carbon monoxide. As expected the reaction of **7** with hydrogen led to the quantitative formation of the dihydridometallocene and 1,4-dihydro-1,1,4,4-tetrakis(trimethylsilyl)tetramethylsilane (**4**) (Scheme 3). Reaction of **7** with the isonitrile also proceeded very cleanly to the insertion product (**9**) (Scheme 3). Even in the presence of excess isonitrile only one insertion step occurs. In contrast to this, reactions of **7** and **8** with CO did not lead to uniform products. However, it could be shown that the first reaction step of insertion of CO into a silcon–metal bond is reversible.[19a] This reaction is currently under investigation.



Scheme 3. Reactions of **7**.

Experimental Section

All manipulations were carried out under exclusion of oxygen and moisture, either by conventional Schlenk techniques or through the use of a glove box under a nitrogen atmosphere.

1c, **2c**: The starting material (**1a**, **2a**; 0.61 mmol) was mixed with two equivalents (0.135 g, 1.22 mmol) of potassium *tert*-butoxide, THF (2 mL) and C_6D_6 (1 mL) were added, and the mixture was heated to 60 °C in a 10-mm NMR tube, either with an attached teflon stop cock or flame sealed. The conversion was monitored by ^{29}Si NMR spectroscopy.

1c: ^1H NMR (300 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = 0.91$ (s, 6H; $SiMe_2$), 0.51 (s, 36H; $SiMe_3$); ^{13}C-NMR (75.4 MHz, THF, C_6D_6, 25 °C, TMS):

$\delta = 8.50$ (SiMe$_3$), 2.28 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = -5.3$ (SiMe$_3$), -16.5 (SiMe$_2$), -172.0 (SiK).

2c: ^{1}H NMR (500 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = 0.67$ (s, 12H; SiMe$_2$), 0.57 (s, 36H; SiMe$_3$); ^{13}C-NMR (125.9 MHz, THF, C_6D_6, 25 °C, TMS): $\delta =$ 8.66 (SiMe$_3$), 3.33 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = -4.1$ (SiMe$_3$), -26.7 (SiMe$_2$), -191.6 (SiK).

7: Zirconocene dichloride (0.50 g, 1.90 mmol, 30% excess) and **2c** (1.46 mmol) were dissolved at room temperature with toluene (5 mL), and the reaction mixture immediately became deep red. After two hours the solvent was removed at reduced pressure, and the residue was dissolved in pentane. After filtration the product was crystallized at -30 °C and obtained as deep red crystals. Yield: 0.90 g (1.30 mmol, 89%). A suitable single crystal was used for an X-ray structure analysis. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 6.29$ (s, 10H; Cp–H), 0.45 (s, 12H; SiMe$_2$), 0.43 (s, 36H; SiMe$_3$); ^{13}C NMR (125.9 MHz, C_6D_6, 25 °C, TMS): $\delta = 108.80$ (Cp), 6.93 (SiMe$_3$), 2.19 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, pentane/D_2O capillary, 25 °C, TMS): $\delta = -2.4$ (SiMe$_3$), -29.2 (SiMe$_2$), -65.2 (SiZr); elemental analysis(%) calcd for $C_{26}H_{58}Si_8Zr$ ($M_r = 686.65$): C 45.48, H 8.51; found: C 45.01, H 8.47; UV (cyclohexane): λ_{max} (ε) = 302 (4000), 466 (800), 556 nm (250).

8: Synthesis and isolation of **8** ([Cp_2HfCl_2] (0.64 g, 1.68 mmol); **2c** (1.28 mmol)) were accomplished analogously to that of **7**. Compound **8** was obtained as deep red crystals in 85% yield (0.84 g; 1.08 mmol), which were suitable for a single crystal X-ray structure analysis. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 6.21$ (s, 10H; Cp), 0.49 (s, 12H; SiMe$_2$), 0.44 (s, 36H; SiMe$_3$); ^{13}C NMR (125.9 MHz, C_6D_6, 25 °C, TMS): $\delta = 108.32$ (Cp), 7.05 (SiMe$_3$), 2.43 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, pentane/D_2O capillary, 25 °C, TMS): $\delta = -2.0$ (SiMe$_3$), -27.8 (SiMe$_2$), -52.2 (SiHf); elemental analysis (%) calcd for $C_{26}H_{58}HfSi_8$ ($M_r = 773.91$): C 40.35, H 7.55; found: C 39.79, H 7.56; UV (cyclohexane): λ_{max} (ε) = 210 (50000), 344 (3100), 412 (3100), 504 nm (250).

Isonitrile insertion into compound **7**: Compound **7** (0.057 g, 0.08 mmol) was dissolved in C_6D_6 (2 mL) and treated with 1-isocyano-2,6-dimethylbenzene (0.011 g, 0.08 mmol). The initially deep red solution turned orange immediately. NMR spectroscopy showed the exclusive formation of the expected insertions product. Addition of a second equivalent of isonitrile did not lead to another insertion step. The solvent and excess isonitrile were removed in vacuum; the residue was dissolved in pentane and crystallized at -35 °C as yellow crystals. Yield of **9**: 0.030 g (0.04 mmol, 50%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 6.85$ (m, 3H; Ar–H), 5.69 (s, 10H; Cp), 1.94 (s, 6H; Ar–Me), 0.78 (s, 6H; SiMe$_2$), 0.52 (s, 18H; SiMe$_3$), 0.51 (s, 6H; SiMe$_2$), 0.10 (s, 18 H SiMe$_3$); ^{13}C NMR (125.9 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = 279.6$ (C=N), 154.16 (NC$_{ar}$), 129.56 (C$_{ar}$), 128.96 (C$_{ar}$), 128.36 (C$_{ar}$), 106.46 (Cp), 21.56 (C$_{ar}$Me), 7.16 (SiMe$_3$), 4.36 (SiMe$_3$), 2.16 (SiMe$_2$), -0.16 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, pentane/D_2O capillary): -4.36 (SiMe$_3$), -10.06 (SiMe$_3$), -33.06 (SiMe$_2$), -36.36 (SiMe$_2$), -79.06 (ZrSi), -117.26 (NCSi); elemental analysis(%) calcd for $C_{35}H_{67}NSi_8Zr$ ($M_r =$ 817.82): C 51.40, H 8.26; found: C 50.97, H 8.37.

Reactions of **7** and **8** with hydrogen and of **2c** with acid to give dihydrosilane **4**: The respective metallacyclosilane (0.07 mmol) was dissolved in C_6D_6 in an NMR tube. The solution was frozen with liquid nitrogen, evacuated, and flushed with hydrogen. After warming up to ambient temperature the tube was shaken whereupon the red color disappeared. For the isolation of the hydrosilane the solvent was removed in vacuum, the residue dissolved in pentane, and after filtration to remove the insoluble metallocene hydride, the sample was evaporated and the residue **4** crystallized as colorless crystals from acetone. Yield: 0.029 g (0.06 mmol, 85%). Alternatively, **4** was obtained from **2c**, analogously to the previously described hydrolysis procedure with sulfuric acid[2] in almost quantitative yield. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 2.68$ (s, 2H; Si–H), 0.42 (s, 12H; SiMe$_2$), 0.27 (s, 54H; SiMe$_3$); ^{13}C NMR (125.9 MHz, THF, C_6D_6, 25 °C, TMS): $\delta = 2.47$ (SiMe$_3$), -1.40 (SiMe$_2$); ^{29}Si NMR (99.3 MHz, pentane/D_2O capillary): $\delta = -11.1$ (SiMe$_3$), -36.4 (SiMe$_2$), -116.4 (Si–H, $J = 155.9$ Hz); MS (70 eV): m/z (%): 392 (9) [$M^+ -$ HSiMe$_3$], 318 (89) [$M^+ - H_2Si_2Me_6$], 218 (25) [$M^+ -$ HSi(SiMe$_3$)$_3$], 73 (100) [SiMe$_3$]; elemental analysis (%) calcd for $C_{16}H_{50}Si_8$ ($M_r = 467.25$) C 41.13, H 10.79; found: C 40.82, H 10.78.

Received: April 23, 2001
Revised: November 28, 2001 [Z16976]

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[3] a) H. Gilman, J. M. Holmes, C. L. Smith, *Chem. Ind. (London)* **1965**, 848; b) Y. Apeloig, M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, K. Klinkhammer, *Organometallics* **1997**, *16*, 1265.

[4] Recently Apeloig et al. showed that in the reaction of **2a** with methyllithium also no cleavage of the inner Si–Si bonds occurs and that the dilithio analogue of **2c** is obtained. Y. Apeloig, G. Korogodsky, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *Eur. J. Inorg. Chem.* **2000**, 1091. But Pannell et al.[7a] have reported previously the cleavage of the inner Si–Si bonds of **2a** under the same conditions. Also the reaction of hexamethyldisilane with methyllithium yields either trimethylsilyllithium or pentamethyldisilanyllithium depending on conditions (K. Krohn, K. Khanbabaee, *Angew. Chem.* **1994**, *106*, 100; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 99). This leads to the assumption that the different results reported by Apeloig et al. and Pannell et al. are caused by subtle differences in the conditions which lead to different reaction mechanisms.

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[6] M. Ishikawa, J. Iyoda, H. Ikeda, K. Kotake, T. Hashimoto , M. Kumada, *J. Am. Chem. Soc.* **1981**, *103*, 4845.

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

[8] The conversion of **2a** with one equivalent of potassium *tert*-butoxide leads, similarly as reported in reference [2] for **1a** very cleanly to the monopotassium compound **2b**: ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 3.67$ (m, 8H; THF), 1.45 (m, 8H; THF), 0.66 (s, 6H; SiMe$_2$), 0.55 (s, 6H; SiMe$_2$), 0.47 (s, 18H; KSi(SiMe$_3$)$_2$), 0.40 (s, 27H; Si(SiMe$_3$)$_3$); ^{29}Si NMR (59.6 MHz, THF/D_2O capillary, 20 °C, TMS): $\delta = -4.34$, -9.24, -20.62 (SiMe$_2$), -34.58 (SiMe$_2$), -130.70 (Si(SiMe$_3$)$_3$, -189.77 (SiK).

[9] Compound **3** was obtained by reaction of **2c** with dimethyl sulfate in toluene at -78 °C in about 85% yield. ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 0.40$ (s, 12H; SiMe$_2$), 0.24 (s, 36H; SiMe$_3$), 0.23 (s, 6H; SiMe); ^{13}C NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 1.01$ (SiMe$_3$), -1.58 (SiMe$_2$), -11.32 (SiMe); ^{29}Si NMR (59.6 MHz, THF/D_2O capillary, 20 °C, TMS): $\delta = -12.15$ (SiMe$_3$), -34.80 (SiMe$_2$), -82.08 (Si(SiMe$_3$)$_3$). The same compound was obtained by treatment of (Me$_3$Si)$_2$(Me)SiMe$_2$H with di-*tert*-butyl peroxide: M. Ishikawa, A. Nakamura, M. Kumada, *J. Organomet. Chem.* **1973**, *59*, C11.

[10] The homocyclic five-membered ring **5** was obtained in 62% yield by reaction of **2c** with dimethyldichlorosilane at room temperature in toluene. Spectroscopic and physical data correspond to those of the compound obtained by Blinka and West by AlCl$_3$-catalyzed rearrangement of octadecamethylcyclononasilane: T. A. Blinka, R. West, *Organometallics*, **1986**, *5*, 128.

[11] Compound **6** was obtained analogously to **5** in the reaction of **2c** with dimethyldichlorostannane. ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 0.57$ (s, 6H; SnMe$_2$), 0.37 (s, 12H; SiMe$_2$), 0.30 (s, 36H; SiMe$_3$); ^{29}Si NMR (59.6 MHz, hexane/D_2O capillary, 20 °C, TMS): $\delta = -5.4$ ($^2J_{^{29}Si\text{-}^{119}Sn}$44 Hz, SiMe$_3$), -22.2 ($^2J_{^{29}Si\text{-}^{119}Sn}$ 61 Hz, SiMe$_2$), -137.5 ($^1J_{^{29}Si\text{-}^{119}Sn/^{117}Sn}$ 192/186 Hz, SiSn); ^{119}Sn NMR (186.4 MHz, hexane/D_2O capillary, 20 °C): $\delta = -118.6$ ($^1J_{^{29}Si\text{-}^{119}Sn}$ 196.6 Hz, $^2J_{^{29}Si\text{-}^{119}Sn}$ 65.5 Hz).

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[13] This anomaly in the behavior of the ^{29}Si NMR spectra can be interpreted as a mutual perturbation of charge stabilization. Ab initio calculations (MP2/6−31 + G*) of the dilithio analogues of **1c** and **2c** and subsequent calculation of ^{29}Si NMR shift (DFT/IGLO-B2) reproduce the phenomenon of the relative shift of **1c** to higher frequencies (M. Flock, Ch. Marschner, unpublished results).

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port), Wiley, Chichester, **1989**, Chap. 24, p. 1415; b) T. D. Tilley in *The Silicon-Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1991**, Chap. 10, p. 309; c) M. S. Eisen in *The chemistry of Organic Silicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chap. 35, p. 2037.

[15] Interestingly, there are two titanacyclosilanes, which were obtained by the reaction of titanocene dichloride with the corresponding 1,4- or 1,5- dilithiosilanes:a) V. A. Igonin, Yu. E. Ovchinnikov, V. V. Dement'ev, V. E. Shklover, T. V. Timofeeva, T. M. Frunze, Yu. T. Struchkov, *J. Organomet. Chem.* **1989**, *371*, 187; b) M. S. Holtman, E. P. Schram, *J. Organomet. Chem.* **1980**, *187*, 147.

[16] X-ray analyses: Crystals of **7** and **8** were mounted in glass capillaries and measured on a Bruker SMART Platform/CCD diffractometer at temperatures of 213 K (**7**) and 296 K (**8**), respectively. Crystal data for **7**: $C_{26}H_{58}Si_8Zr$, $M_r = 686.66$, monoclinic, $P2_1/c$; $a = 11.2474(13)$, $b = 16.5181(18)$, $c = 21.959(3)$ Å; $\beta = 103.770(2)$; $V = 3962.4(8)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.151\ \mathrm{Mg\,m^{-3}}$, $F(000) = 1464$, 317 parameters: $R1 = 0.0528$, $wR2 = 0.1465$, GOF = 1.038 for all 4123 data ($I > \sigma(I)$); max./min. residual electron density: $1.061/-0.440\ \mathrm{e^-A^{-3}}$. Crystal data for **8**: $C_{26}H_{58}HfSi_8$, $M_r = 773.93$, monoclinic, $P2_1/c$; $a = 11.292(2)$, $b = 16.518(3)$, $c = 21.975(4)$ Å; $\beta = 104.191(4)$; $V = 3973.7(13)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.294\ \mathrm{Mg\,m^{-3}}$, $F(000) = 1592$, 317 parameters: $R1 = 0.0351$, $wR2 = 0.0915$, GOF = 1.084 for all 6771 data ($I > \sigma(I)$); max./min. residual electron density: $2.006/-0.793\ \mathrm{e^-A^{-3}}$. CCDC-162782 (**7**) and CCDC-162781 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[17] The Si−Zr bond lengths of **7** are 2.8264(19) Å and 2.8497(19) Å, which is within the range of previously found values: a) W. Muir, *J. Chem. Soc. (A)* **1971**, 2663; b) T. Imori, R. H. Heyn, T. D. Tilley, A. L. Rheingold, *J. Organomet. Chem.* **1995**, *493*, 83; c) L. H. McAlexander, J. B. Diminnie, Z. Xue, *Organometallics* **1998**, *17*, 4853; d) R. H. Heyn, T. D. Tilley, *Inorg. Chem.* **1989**, *28*, 1768; e) K. A. Kreutzer, R. A. Fisher, W. M. Davis, E. Spaltenstein, S. L. Buchwald, *Organometallics* **1991**, *10*, 4031; f) T. Takahashi, M. Hasegawa, N. Suzuki, M. Saburi, C. J. Rousset, P. E. Fanwick, E.-i. Negishi, *J. Am. Chem. Soc.* **1991**, *113*, 8564; g) T. D. Tilley, *Organometallics* **1985**, *4*, 1452. Similarly the Si−Hf bond lengths in **8** (2.791(14) Å and 2.823(15) Å) are also within the range of previously found data; h) H. G. Woo, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 5698; i) G. L. Casty, C. G. Lugmair, N. S. Radu, T. D. Tilley, J. F. Walzer, D. Zargarian, *Organometallics* **1997**, *16*, 8; j) J. Arnold, D. M. Roddick, T. D. Tilley, A. L. Rheingold, S. J. Geib, *Inorg. Chem.* **1988**, *27*, 3510. In compound **7** the metallacyclopentasilane ring exhibits a twisted half-chair conformation, in which the two $Si(SiMe_3)_2$ groups lie 10° or −26°, respectively, under or above the ring plane. In contrast to this compound **8** exists in an envelope conformation with one trimethylsilyl-substituted silicon atom 20° above the plane.

[18] H. G. Woo, J. F. Walzer, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 7047.

[19] a) B. K. Campion, J. Falk, T. D. Tilley, *J. Am. Chem. Soc.* **1987**, *109*, 2049; b) F. H. Elsner, T. D. Tilley, A. L. Rheingold, S. J. Geib, *J. Organomet. Chem.* **1988**, *358*, 169.