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1,1′-Oligosilylferrocene Compounds

Harald Wagner, Judith Baumgartner, and Christoph Marschner*

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

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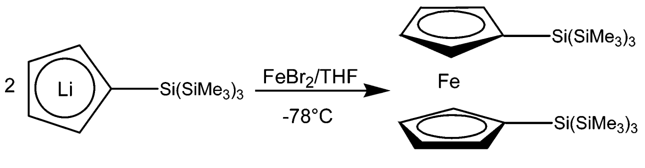
1,1′-Bis[tris(trimethylsilyl)silyl]ferrocene (**1**) was prepared by reaction of 2 equiv of lithiated tris(trimethylsilyl)silylcyclopentadiene with $FeBr_2$. Treatment of **1** with 2 equiv of potassium *tert*-butoxide gave 1,1′-bis[bis(trimethylsilyl)potassiosilyl]ferrocene (**2**). Reactions of **2** with several dielectrophiles led to the formation of a number of novel 1,1′-polysilyl *ansa*-ferrocenes with different heteroelements in the bridge.

Introduction

In recent years a main focus of our research has been on the synthesis and chemistry of polysilyl anions,[1,2] and especially polysilyl potassium compounds have been studied to a large degree.[3] One of the especially intriguing aspects of this chemistry was that it allowed the rather straightforward synthesis of polysilyl dianions.[4] While such compounds can also be prepared by some other methods,[5] the reaction of a suitable precursor with potassium alkoxides proved to be applicable to a wide array of compounds with different spacer elements[1] between the two negatively charged polysilyl units. In the current account we would like to disclose our results on the use of a 1,1′-ferrocenylene unit as the bridge between two polysilyl moieties.

Scheme 1. Synthesis of 1,1′-Bis[tris(trimethylsilyl)silyl]ferrocene (1)



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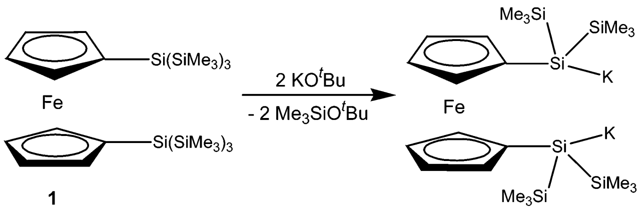
Scheme 2. Preparation of 1,1′-Bis[bis(trimethylsilyl)potassiosilyl]ferrocene (2)



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Silylated ferrocenes have been known since the first synthesis of mono- and bis(trimethylsilyl)ferrocene,[6] and also polysilylferrocenes were well established early by Kumada's seminal studies.[7,8] The *ansa*-ferrocene with a 1,1′-tetramethyldisilanylene bridge has been studied to some extent with respect to Si−Si insertion chemistry.[9,10] Poly-[11] and monomeric[12] polysilylferrocenes have been under investigation for their conducting and electrochemical properties. In recent years donor−acceptor-substituted polysilylferrocenes have gained

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* Corresponding author. Tel: ++43-316-873-8209; Fax: ++43-316-873-8701. E-mail: christoph.marschner@tugraz.at.

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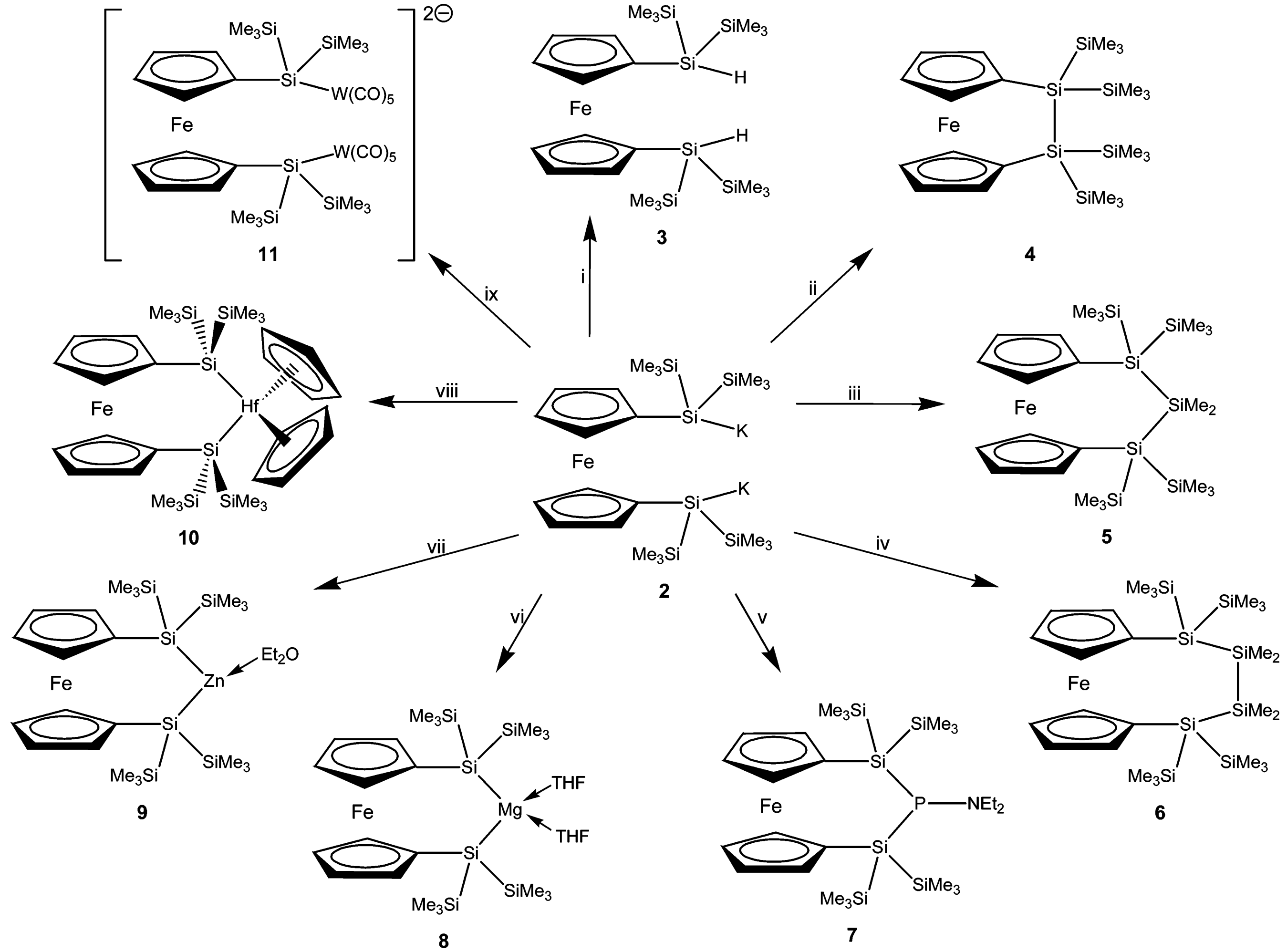
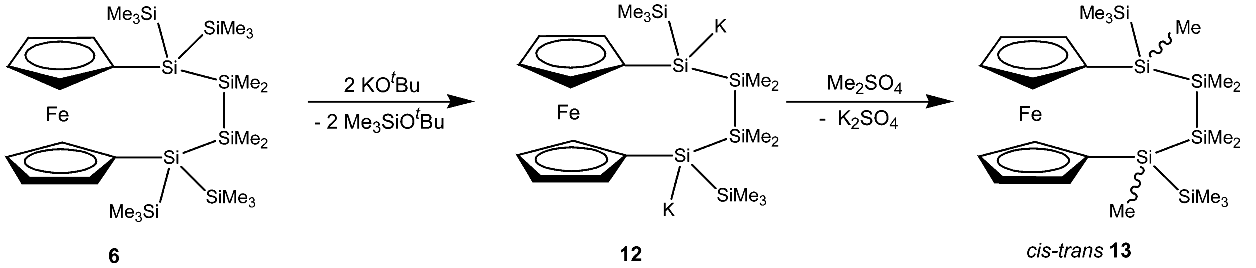
Scheme 3. Reactivity of 1,1′-Bis[bis(trimethylsilyl)silyl]ferrocene (2) with Several Electrophiles: (i) H_2SO_4; (ii) $Br(CH_2)_2Br$, −78 °C; (iii) Me_2SiCl_2; (iv) $Cl(Me_2Si)_2Cl$; (v) Et_2NPCl_2; (vi) $MgBr_2 \cdot Et_2O$; (vii) $ZnCl_2$; (viii) Cp_2HfCl_2; (ix) $Li[W(CO)_5I]$



Scheme 4. Preparation and Derivatization of Bridged 1,1′-Bis[bis(trimethylsilyl)potassiosilyl]ferrocene, 12



some prominence for their electronic and nonlinear optic (NLO) properties.[12d,13−15]

Results and Discussion

In order to obtain 1,1′-bis[tris(trimethylsilyl)silyl]ferrocene (**1**), we initially decided to follow the original Kumada route for the synthesis of 1,1′-bis(pentamethyldisilanyl)ferrocene.[7] The synthesis was attempted as the silylation of 1,1′-dilithioferrocene with 2 equiv of tris(trimethylsilyl)silyl chloride.[7] However, in addition to the formation of **1** also several side products were observed. We therefore changed our strategy to the use of the known tris(trimethylsilyl)silylcyclopentadiene[16] as a precursor. Lithiation of the latter with BuLi and treatment with 0.5 equiv of ferrous bromide provided **1** in a clean reaction in an acceptable isolated yield of 65% (Scheme 1).

Related to Kumada's initial observation that disilanyl-substituted ferrocenes can undergo facile Si−Si bond cleavage,[8]

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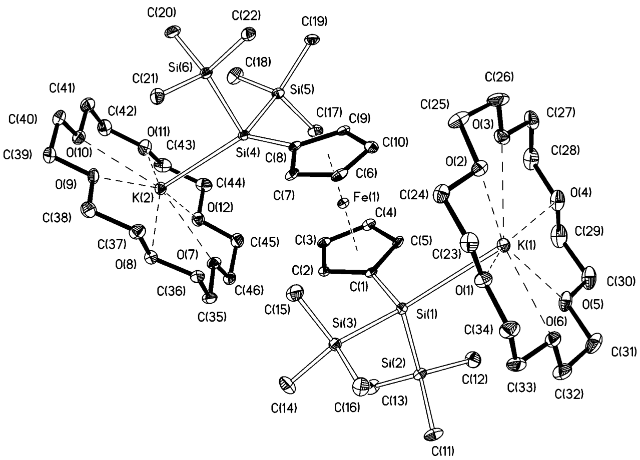

Figure 1. Molecular structure and numbering of **2**. Selected bond lengths [Å] and bond angles [deg] with SDs: Fe(1)−C(6) 2.031(4), Fe(1)−C(1) 2.092(4), Si(1)−C(1) 1.923(4), Si(1)−Si(3) 2.3373(16), Si(1)−K(1) 3.4640(15), Si(4)−C(8) 1.929(4), Si(4)−K(2) 3.4153(15), Si(1)−Si(2) 2.3503(15), Si(4)−Si(5) 2.3354(16), Si(4)−Si(6) 2.3397(15), C(8)−Si(4) 1.9286(39), Si(3)−Si(1)−Si(2) 99.28(6), C(1)−Si(1)−K(1) 114.12(12), Si(3)−Si(1)−K(1) 121.96(5), Si(2)−Si(1)−K(1) 118.12(5), C(8)−Si(4)−Si(5) 103.48(13), C(8)−Si(4)−Si(6) 96.94(12), Si(5)−Si(4)−Si(6) 99.41(6), C(8)−Si(4)−K(2) 142.70(12).

it was found that **1** is somewhat sensitive to atmospheric conditions. Slow decomposition was observed under air, and therefore all operations including aqueous workup were carried out under an inert gas atmosphere.

Compound **1** was then subjected to metalation conditions with potassium *tert*-butoxide either in THF[3] or in benzene in the presence of 18-crown-6.[4c] As observed in related previous cases,[4c,17] it was not possible to achieve selective monometalation under several different conditions. The treatment of **1** with 1 equiv of potassium alkoxide always resulted in a mixture of **1**, the monopotassium compound, and the dipotassium compound **2**. The latter was obtained selectively upon the reaction of **1** with 2 equiv of potassium *tert*-butoxide (Scheme 2).

The dianion **2** is a very useful starting material for the synthesis of a number of different 1,1′-polysilylferrocenes. Plain hydrolysis of **2** with aqueous sulfuric acid gave the bis(hydrosilane) **3**, which is a red oil at ambient temperature that can be crystallized at −35 °C to give a solid with a low melting point (33 °C). Reaction of **2** with 1,2-dibromomethane resulted in oxidative coupling of the two silylanionic units[18] and the formation of 1,1′-tetrakis(trimethylsilyl)disilanylene-bridged ferrocene (**4**) (Scheme 3). Treatment of **2** with dichlorodimethylsilane or 1,2-dichlorotetramethyldisilane led to the formation of compounds with trisilanylene (**5**) and tetrasilanylene (**6**) bridges, respectively, as products of the salt elimination reactions (Scheme 3). Similar cyclosilane formation had been observed before with other polysilyl dianions.[19] The introduction of a phosphorus atom into the bridge was accomplished in a similarly straightforward manner by reaction of **2** with diethylaminodichlorophosphane (Scheme 3).[20] This reaction was not completely selective but gave silylphosphane **7** in addition to 5% of **4** as a side product.

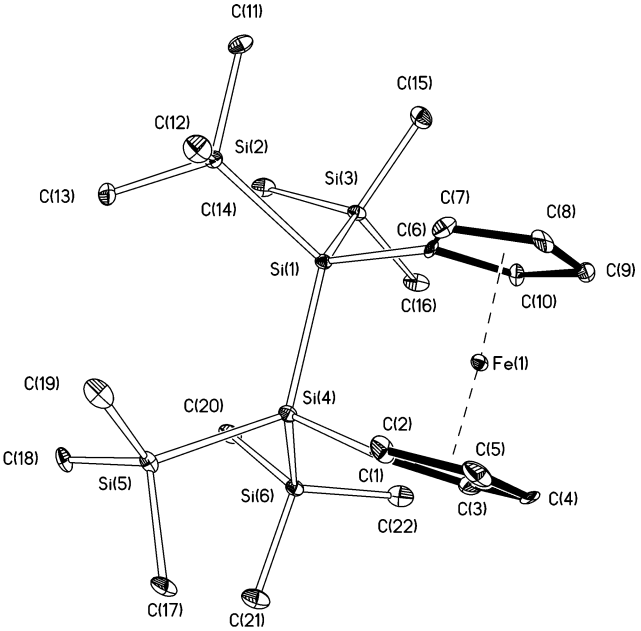

Figure 2. Molecular structure and numbering of **4**. Selected bond lengths [Å] and bond angles [deg] with SDs (only one of four crystallographically independent molecules shown): Fe(1)−C(6) 2.031(7), Fe(1)−C(1) 2.041(7), Si(1)−C(6) 1.907(7), Si(1)−Si(2) 2.360(3), Si(1)−Si(3) 2.371(3), Si(1)−Si(4) 2.390(3), Si(4)−C(1) 1.884(7), Si(4)−Si(5) 2.362(3), Si(4)−Si(6) 2.366(3), C(6)−Si(1)−Si(2) 109.6(2), C(6)−Si(1)−Si(3) 105.6(2), Si(2)−Si(1)−Si(3) 104.16(11), C(6)−Si(1)−Si(4) 101.6(2), Si(2)−Si(1)−Si(4) 114.31(11), Si(3)−Si(1)−Si(4) 121.04(11), Si(5)−Si(4)−Si(6) 104.40(11), C(1)−Si(4)−Si(1) 101.7(2), Si(5)−Si(4)−Si(1) 121.11(11), Si(6)−Si(4)−Si(1) 114.38(11).

Polysilyl potassium compounds and especially dianions are frequently too reactive for selective reactions. One way to cope with this situation is the transmetalation from potassium to either lithium or more frequently magnesium.[21] For the case of **2**, by reaction with magnesium bromide another *ansa*-product was obtained with a magnesium atom in the bridge (**8**) (Scheme 3). As noted on some occasions before the magnesium atom is coordinated by two THF molecules. In a similar reaction of **2** with zinc chloride the *ansa*-product with zinc in the bridge (**9**) was formed (Scheme 3). Compared to **8**, the shorter Si−Zn bonding distance[22] seems to allow the coordination of only one ether donor molecule to the zinc atom. The reaction of **2** with 1 equiv of hafnocene dichloride gave the heterodimetallocene compound **10**[4b,c] as the product of the salt elimination reaction (Scheme 3). Reaction of **2** with 2 equiv of [Li(DIME)$_2$][W(CO)$_5$I][23] eventually gave the dianionic compound **11** with two pentacarbonyltungstenate groups attached to silicon (Scheme 3). The ^{1}H NMR spectrum of **11** indicated that lithium counterions are not coordinated by two DIME but by four THF

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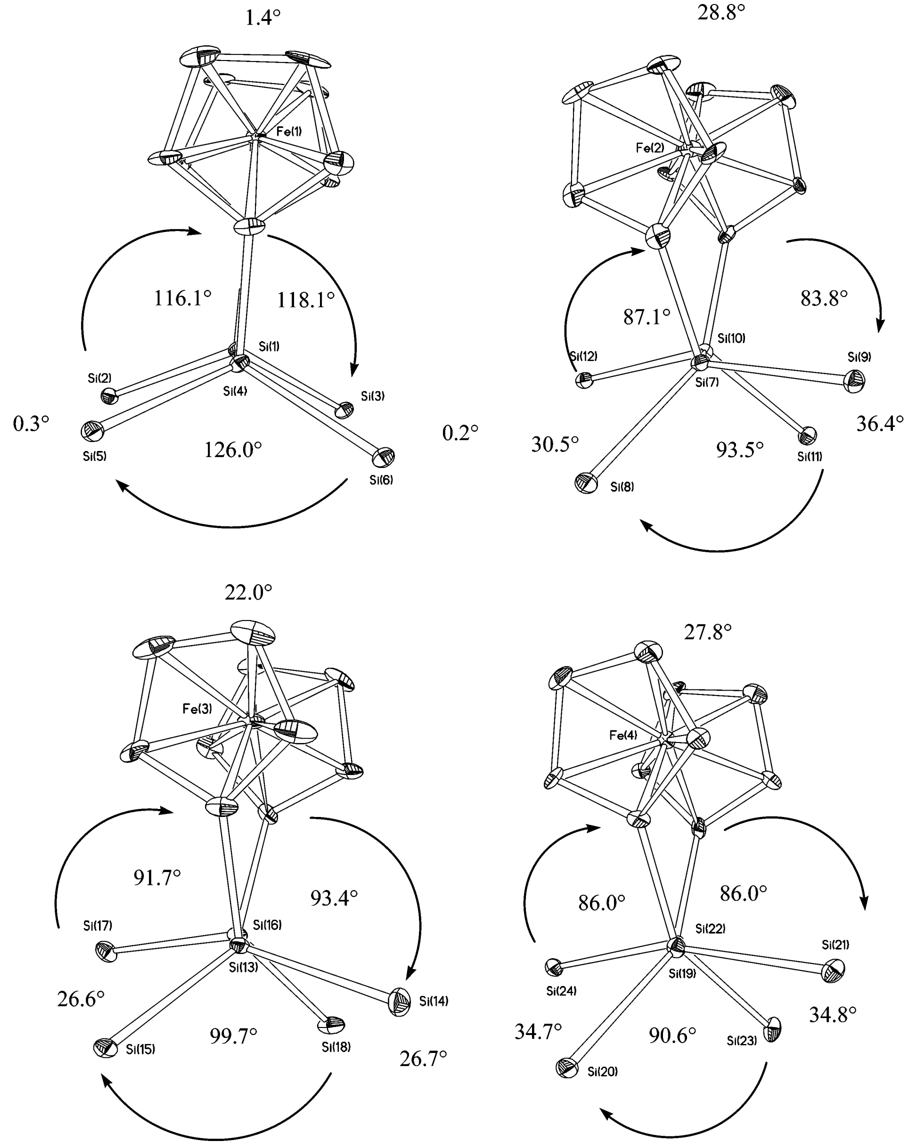

Figure 3. Different conformational properties of the four crystallographically independent molecules of **4**. The molecules are shown in Newman-type projections along the central Si−Si bond.

molecules. This assignment was confirmed by X-ray single-crystal analysis, which was of low quality but unambiguously displayed the coordination mode in the molecule.

Compounds **4**, **5**, and **6** are potential candidates for the synthesis of further examples of polysilyl dianions. Therefore, the conversion of these compounds with 2 equiv of potassium *tert*-butoxide was attempted. The reaction of the most strained substance **4** was not successful. While also the conversions of **5** was not completely clean, the reaction of **6** occurred in the expected manner and the cyclic polysilylferrocenyl dianion **12** was formed (Scheme 4).

Reaction of **12** with dimethyl sulfate gave a 2:5 mixture of the *cis*- and *trans*-isomers (**13**) (Scheme 5). After recrystallization the major isomer was obtained in pure form. A crystal structure analysis allowed assigning it to the *trans*-isomer (*trans*-**13**).

NMR Spectroscopy. The most useful nucleus for NMR spectroscopic investigation of the compounds in this paper was ^{29}Si, but also ^{13}C and, for the case of compound **7**, ^{31}P NMR spectroscopy could provide some valuable insight.

Compound **1**, with its two tris(trimethylsilyl)silyl groups should resemble $PhSi(SiMe_3)_3$, where we have another aromatic system connected to the bulky isotetrasilanyl group. The ^{29}Si NMR shifts of −82.3 and −13.5 ppm for **1** therefore are similar to values (−76.8, −12.8 ppm) for $PhSi(SiMe_3)_3$.[24] The upfield shift of almost 40 ppm upon metalation to −121.1 ppm (**2**) is definitely more pronounced for the ferrocene compound compared to −99.3 ppm for $PhSi(SiMe_3)_2K$.[3b] However, this comparison may not be completely valid, as compound **2** is a dianion in contrast to $PhSi(SiMe_3)_2K$. ^{13}C NMR spectra showed that the change from **1** to **2** is accompanied by a strong deshielding of the *ipso*-Cp carbon. While its shift for **1** is at 67.4 ppm, the corresponding resonance for **2** was found at 81.2 ppm. This behavior again resembles that of the couple $PhSi(SiMe_3)_3$/$PhSi(SiMe_3)_2K$.[25] The ^{29}Si resonances for the hydrosilane **3** (−67.6, −15.7) are in close accordance with the data for $HSi(SiMe_3)_3$. In both compounds a comparison with the respective trimethylsilylated analogue showed that the resonance of the central silicon atom is about 15 ppm deshielded, while that for the trimethylsilyl groups moves in the opposite direction

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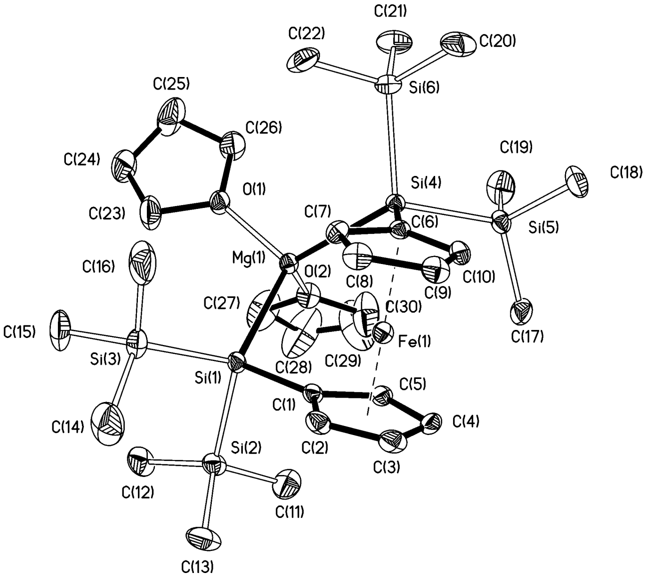

Figure 4. Molecular structure and numbering of **8**. Selected bond lengths [Å] and bond angles [deg] with SDs: Fe(1)−C(1) 2.073(2), Fe(1)−C(6) 2.084(2), Mg(1)−O(1) 2.054(2), Mg(1)−Si(1) 2.6572(13), Mg(1)−Si(4) 2.6691(12), Si(1)−C(1) 1.900(2), Si(1)−Si(2) 2.3431(11), Si(1)−Si(3) 2.3523(12), Si(4)−Si(5) 2.3512(10), Si(4)−Si(6) 2.3531(10), C(6)−Si(4) 1.8943(25), O(1)−Mg(1)−O(2) 91.19(9), O(1)−Mg(1)−Si(1) 112.42(6), O(1)−Mg(1)−Si(4) 115.35(7), Si(1)−Mg(1)−Si(4) 113.36(4), Si(2)−Si(1)−Si(3) 103.70(5), Si(2)−Si(1)−Mg(1) 120.77(4), Si(3)−Si(1)−Mg(1) 120.19(4), Si(5)−Si(4)−Si(6) 104.82(4), Si(5)−Si(4)−Mg(1) 121.95(4), Si(6)−Si(4)−Mg(1) 116.22(4).

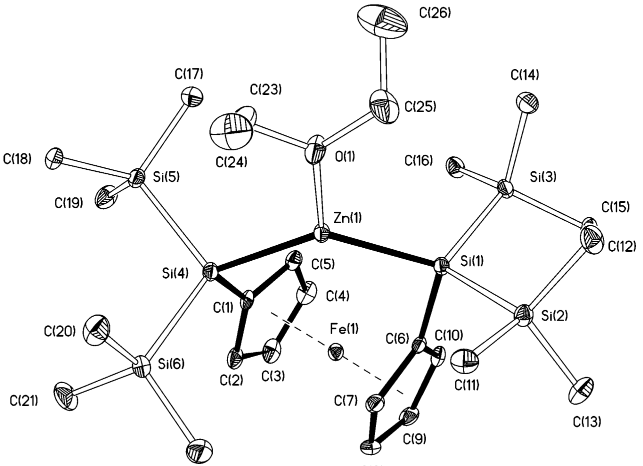

Figure 5. Molecular structure and numbering of **9**. Selected bond lengths [Å] and bond angles [deg] with SDs: Fe(1)−C(1) 2.079(3), Si(1)−C(6) 1.903(4), Si(1)−Si(2) 2.3431(15), Si(1)−Zn(1) 2.3855(13), Si(4)−C(1) 1.884(4), Si(4)−Si(5) 2.3465(16), Si(4)−Zn(1) 2.3846(12),− Zn(1)−O(1) 2.096(3), Si(3)−Si(1)−Si(2) 108.04(6), C(6)−Si(1)−Zn(1) 101.06(11), Si(3)−Si(1)−Zn(1) 120.40(5), Si(2)−Si(1)−Zn(1) 113.87(5), Si(6)−Si(4)−Si(5) 110.77(6), Si(6)−Si(4)−Zn(1) 117.37(6), Si(5)−Si(4)−Zn(1) 113.53(5), Si(4)−Zn(1)−Si(1) 128.33(4).

for about 2 ppm. The resonance for the central silicon atom of the *ansa*-compound **4** (−51.6 ppm) is shifted to lower field more than 30 ppm compared to **1** (−82.3 ppm). This is most likely due to the strained geometry in **4**. A very similar effect was observed for octakis(trimethylsilyl)cyclotetrasilane (−91.1 ppm),[26] where the ring atoms are also more than 40 ppm shifted to lower field compared to tetrakis(trimethylsilyl)silane (−135.6 ppm). Reduction of strain, as observed for the *ansa*-compounds **5** (−82.8 ppm) and **6** (−75.3 ppm), effects a return of the central silicon resonances to values close to that of **1** (−82.3 ppm).

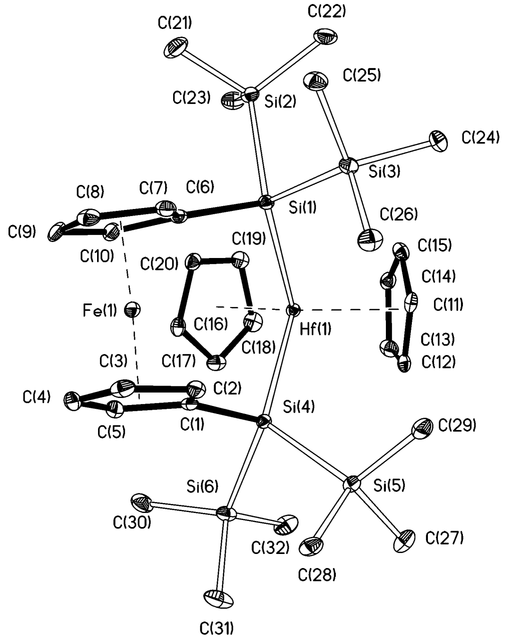

Figure 6. Molecular structure and numbering of **10**. Selected bond lengths [Å] and bond angles [deg] with SDs: Fe(1)−C(6) 2.105(5), Fe(1)−C(1) 2.130(4), Hf(1)−C(16) 2.484(5), Hf(1)−C(11) 2.498(5), Hf(1)−Si(1) 2.7825(13), Hf(1)−Si(4) 2.8016(16), Si(1)−C(6) 1.917(5), Si(1)−Si(3) 2.3791(19), Si(1)−Si(2) 2.3995(19), Si(4)−Si(6) 2.3798(18), Si(4)−Si(5) 2.3863(18), Si(1)−Hf(1)−Si(4) 99.23(4), Si(3)−Si(1)−Si(2) 98.50(7), Si(3)−Si(1)−Hf(1) 120.95(6), Si(2)−Si(1)−Hf(1) 118.11(6), Si(6)−Si(4)−Si(5) 97.17(7), Si(6)−Si(4)−Hf(1) 113.15(6), Si(5)−Si(4)−Hf(1) 122.87(6).

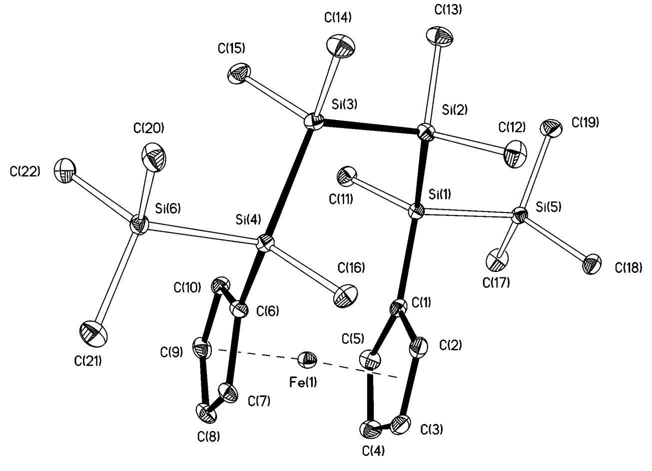

Figure 7. Molecular structure and numbering of *trans*-**13**. Selected bond lengths [Å] and bond angles [deg] with SDs: Fe(1)−C(4) 2.040(3), Si(1)−C(1) 1.876(3), Si(1)−C(11) 1.887(3), Si(1)−Si(2) 2.3339(11), Si(1)−Si(5) 2.3451(11), Si(4)−C(6) 1.880(3), Si(4)−C(16) 1.890(3), Si(4)−Si(6) 2.3488(11), C(1)−C(2) 1.433(4), C(1)−Si(1)−Si(2) 112.96(9), C(6)−Si(4)−Si(6) 106.23(9), Si(1)−C(1)−Fe(1) 130.88(14), Si(4)−C(6)−Fe(1) 130.09(14).

The central ^{29}Si resonance for the phosphorus compound **7** is at −61.2 ppm and displays a $^{1}J_{\mathrm{Si-P}}$ coupling constant of 87 Hz. These values compare well to a similar phosphacyclopentasilane[20] we prepared earlier. The same is true for the ^{31}P NMR resonance at −8.3 ppm. The fact that for the cyclopentadienyl part of **7** no symmetry break was observed in the ^{1}H and ^{13}C

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

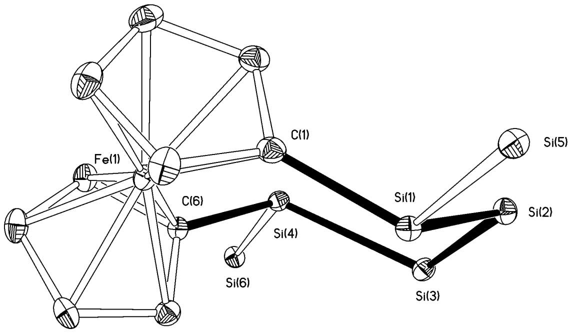

Figure 8. View of the *chair*-type conformation of *trans*-**13** (methyl groups and hydrogen atoms omitted for clarity).

NMR spectra indicates that the configurational stability of the phosphorus in **7** is low on the NMR time scale.

The cyclic magnesium compound **8** shows the expected deshielding effect compared to **2**. The resonance of its metalated silicon atom was found at −108.5 ppm, which is a shift of about 13 ppm to lower field. For the zinc compound **9** the situation is similar. Zinc is less electropositive than magnesium; therefore, the ^{29}Si resonance of the metalated silicon atom shifts further to −92.2 ppm. For the bimetallocenic compound **10** the central silicon resonance of −15.3 ppm is significantly at lower field compared to the −29.9 ppm found for $Cp_2Zr(Cl)Si(SiMe_3)_2$-Me.[21b,27] The resonance at −80.8 ppm found for the ditungstenate **11** is close to the value of −87.1 ppm observed for the related compound $Li[(CO)_5WSi(SiMe_3)_2Me]$.[23] The ^{29}Si NMR resonance for the anionic silicon atoms of compound **12** (−118.6 ppm), which is another dianion, resembles that of **2** (−121.1 ppm). The ^{29}Si NMR values of **13** (−15.3, −40.4, −43.0 ppm) eventually are in the typical range for peralkylated polysilanes.

X-ray Crystallography. A number of polysilylferrocens have already been structurally characterized.[9a,b,28,29] During this study we have been able to determine the crystal structures of compounds **2**, **4**, **8**, **9**, **10**, and *trans*-**13** at a temperature of 100 K. The dipotassium compound **2** was crystallized as the 18-crown-6 adduct with two molecules of benzene in the asymmetric unit (Figure 1). The cyclopentadienyl rings of the ferrocene part are parallel and almost perfectly eclipsed. The silicon atoms connected to the cyclopentadienyl units, which are separated by an angle of 151° around the iron atom, bear one axial and one equatorial trimethylsilyl group. The potassium atoms, which are coordinated by crown ethers, are also in equatorial positions with respect to the negatively charged silicon atoms. Si−Si bond distances were found to be in the expected range between 2.33 and 2.35 Å. The Si−K distances of 3.41 and 3.46 Å are also similar to related previous examples.[4c] The Si−Si−Si bond angles are both close 99° and indicate the typical pyramidalization of a silyl anion.

The crystal structure of the coupling product **4** (Figure 2) is somewhat unusual, as it contains four crystallographically independent molecules in the asymmetric unit. The four molecules are rotamers and distinctly different with respect to their conformational properties. The Newton-type projections along the central Si−Si bonds in Figure 3 show conformations ranging from *eclipsed* to different degrees of *gauche.*

The disilylmagnesium compound **8** (Figure 4) was found to crystallize with one molecule of cyclohexane in the asymmetric unit. The cyclopentadienyl rings of the ferrocene are again parallel, and an almost eclipsed arrangement is observed. The angle between the planes consisting of the iron atom, the *ipso*-carbon, and the ferrocene-connected silicon atom is 52°. The Si−Si bond lengths are all close to 2.35 Å, and also the Si−Mg distances of about 2.66 Å are close to what we have found previously.[21] The possibility of free rotation of the cyclopentadienyl rings around the iron atom in conjunction with the sufficiently long Si−Mg bonds allows for a totally nonstrained

Table 1. Crystallographic Data for Compounds 2, 4, 8, 9, 10, and *trans*-13

	2	**4**	**8**	**9**	**10**	*trans*-**13**
empirical formula	$FeK_2O_{12}Si_6C_{58}H_{104}$	$Fe_4Si_{24}C_{88}H_{176}$	$FeMgSi_6C_{33}H_{66}$	$FeZnSi_6C_{26}H_{54}$	$FeHfSi_6C_{32}H_{54}$	$FeSi_6C_{22}H_{44}$
M_w	1296.00	2131.85	743.56	672.45	841.63	532.96
temperature [K]	100(2)	100(2)	133(2)	100(2)	100(2)	100(2)
size [mm]	0.48 × 0.35 × 0.28	0.42 × 0.31 × 0.20	0.50 × 0.40 × 0.40	0.40 × 0.35 × 0.30	0.30 × 0.25 × 0.15	0.44 × 0.34 × 0.24
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$	$P2(1)$	$P2(1)/n$	$P2(1)$
a [Å]	23.402(5)	10.354(2)	13.692(3)	10.947(2)	16.670(3)	8.675(2)
b [Å]	11.500(2)	12.174(2)	18.305(4)	15.391(3)	11.827(2)	18.203(4)
c [Å]	28.474(6)	46.891(9)	17.250(3)	11.461(2)	20.571(4)	9.524(2)
α [deg]	90	93.28(3)	90	90	90	90
β [deg]	107.86(3)	91.27(3)	92.00(3)	107.01(3)	113.38(3)	98.71(3)
γ [deg]	90	91.24(3)	90	90	90	90
V [Å ^{3}]	7294(3)	5897.9(2)	4320.8(2)	1846.5(6)	3722.6(2)	1486.6(5)
Z	4	2	4	2	4	2
ρ_{calc} [g cm^{-3}]	1.180	1.200	1.143	1.209	1.502	1.191
absorp coeff [mm^{-1}]	0.470	0.764	0.556	1.254	3.390	0.758
F(000)	2784	2288	1608	716	1712	572
θ range	$1.50 < \theta < 24.00$	$1.31 < \theta < 24.00$	$1.62 < \theta < 26.37$	$1.86 < \theta < 26.33$	$2.02 < \theta < 26.37$	$2.16 < \theta < 26.36$
no. of reflns collected/ unique	46 812/11 440	39 372/18 406	33 659/8774	14 675/7326	28 958/7608	11 605/5884
completeness to θ [%]	100	99.5	99.3	99.5	99.9	99.4
no. of data/ restraints/ params	11 440/0/724	18 406/30/1093	8774/0/400	7326/1/331	7608/0/373	5884/1/275
goodness of fit on F^2	1.31	1.20	1.06	1.08	1.25	1.08
final R indices [$I > 2\sigma(I)$]	R1 = 0.071, wR2 = 0.130	R1 = 0.097, wR2 = 0.177	R1 = 0.048, wR2 = 0.131	R1 = 0.042, wR2 = 0.082	R1 = 0.042, wR2 = 0.080	R1 = 0.034, wR2 = 0.083
R indices (all data)	R1 = 0.077, wR2 = 0.133	R1 = 0.131, wR2 = 0.190	R1 = 0.063, wR2 = 0.138	R1 = 0.045, wR2 = 0.083	R1 = 0.046, wR2 = 0.081	R1 = 0.036, wR2 = 0.084
largest diff peak/ hole [e$^-$/ Å^3]	0.50/−0.33	0.78/−0.51	0.54/−0.36	0.71/−0.41	1.34/−1.79	1.17/−0.24

molecule, which is also reflected by the parallel cyclopentadienyl rings. In accordance with the more covalent character of the Si−Mg bond, the Si−Si−Si angles are widened to 104−105° and the Si−Mg−Si angle is close to 113°. As already mentioned, the coordination of magnesium is tetrahedral with two THF molecules as donors at a distance of 2.05 Å.

The structure of the zinc compound **9** (Figure 5) resembles that of **8**. The planes of the cyclopentadienyl rings are almost parallel (3°), and the angle between the planes consisting of the iron atom, the *ipso*-carbon, and the ferrocene-connected silicon atom is, at 45°, slightly smaller. All Si−Si bond lengths are close to 2.34 Å, and the Si−Zn bonds are also in this range (2.38 Å). The zinc atom is tricoordinated with Zn(1), Si(1), Si(4), and O(1) in a plane. The Si−Zn−Si angle is 128°, while the two O−Zn−Si angles are 115° and 116°. Compared to **8** the Si−Si−Si angle is, at 111°, less pyramidalized.

For the bimetallocenic hafnium compound **10** (Figure 6) the cyclopentadienyl units are almost eclipsed but tilt to an angle of 9°. The Si−Si bonds are, in general, longer (2.38−2.40 Å) than in the other compounds, and the Si−Si−Si angles are, at 97° and 98°, very small. Both effects are likely to result from a high degree of steric crowding in the molecule. The Si−Hf bond lengths of 2.78 and 2.80 Å are exactly in the range of what we have observed previously for related compounds.[4b]

Compound *trans*-**13** (Figure 7) is relatively unstrained, as can be seen from the Si−Si bond lengths of 2.34−2.35 Å. The cyclopentadienyl units are again tilted to an angle of 13°. The cyclosilanyl part exhibits a *chair*-type conformation with the bulky trimethylsilyl groups in the equatorial positions (Figure 8). This situation is very similar to what we have observed previously for 1,4-disubstituted cyclohexasilanes.[4d,30]

Conclusion

The current study constitutes another extension of our program on the synthesis of polysilyl anions. The preparation of 1,1′-bis[tris(trimethylsilyl)silyl]ferrocene (**1**) starting from tris(trimethylsilyl)silylcyclopentadiene provides a convenient entry into the chemistry of ferrocenylpolysilanes. The facile formation of the dianion **2** allows the synthesis of a several *ansa*-ferrocenyl polysilanes with different bridge regions. Besides a number of compounds with all-silicon bridges, also heteroatoms such as phosphorus, zinc, hafnium, and magnesium could be incorporated in a straightforward way. The dianion **2** is likely to possess some potential as a building block for polymeric materials. The same is probably true for the very reactive compounds with incorporated phosphorus, zinc, hafnium, and magnesium atoms and the strained compound **4**. The second dianionic compound **12** may also have a potential as the backbone of a chiral ligand. Work in these directions is currently in progress.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents were dried and freshly distilled prior to use. Potassium *tert*-butanolate was purchased exclusively from Merck. All other chemicals were bought from different suppliers and were used without further purification.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.3 MHz), and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si spectra were either dissolved in a deuterated solvent or 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, the INEPT pulse sequence was used for the amplification of the signal.[31] Elementary analyses were carried out using a Heraeus Vario Elementar. UV absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer in heptane solution.

$CpSi(SiMe_3)_3$,[16] Et_2NPCl_2,[32] $MgBr_2{\cdot}Et_2O$,[33] and $[Li(DIME)_2][W(CO)_5I]$[34] were prepared according to literature procedures.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of a glass fiber, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F^2_o and corrected for absorption effects with SAINT[35] and SADABS,[36] respectively. The structures were solved by direct methods and refined by the full-matrix least-squares method (SHELXL97).[37] If not noted otherwise, 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. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately the obtained crystal quality of some substances (**2**, **4**) was poor. This fact is reflected by quite high R and low θ values.

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **4**, **8**, **9**, **10**, and *trans*-**13** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-607962 (**2**), 607961 (**4**), 607958 (**8**), 607959 (**9**), 607960 (**10**), and 628364 (*trans*-**13**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int.) ++44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

1,1′-Bis[tris(trimethylsilyl)silyl]ferrocene (1). Tris(trimethylsilyl)silylcyclopentadiene (6.11 g, 19.56 mmol) was dissolved in THF and cooled to −78 °C. Over a period of 15 min *n*-BuLi (19.56 mmol, 2 M in pentane) diluted with THF was added. The solution was stirred for 30 min at −78 °C, was allowed to come to rt, and was stirred for another 30 min. $FeBr_2$ (2.11 g, 0.5 equiv) was added again at −78 °C in small portions, and the orange solution was stirred for another 12 h. For workup the reaction mixture was added to 2 M H_2SO_4. The aqueous phase was extracted several times with diethyl ether, and the combined organic layers were dried with Na_2SO_4 before the solvent was evaporated. The residue was crystallized from pentane/acetone (both degassed), and orange crystals were obtained (65%; mp 272−274 °C). ^{29}Si NMR (C_6D_6, δ ppm): −13.5 (*Si*Me$_3$); −82.3 (*Si*Fc). ^{13}C NMR (C_6D_6, δ ppm): 74.8 (*Cp*); 71.8 (*Cp*); 67.4 (*Cp*-Si); 1.5 (Si*Me$_3$*). ^{1}H NMR (C_6H_6, δ ppm): 4.37

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(pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 4.04 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 0.30 (s, 54H, Si*Me*$_3$). Anal. Calcd for $C_{28}H_{62}Si_8Fe$ (679.33): C 49.51, H 9.20. Found: C 49.30, H 9.23. UV absorption: 227 nm (2.1 × 10^4 M^{-1} cm^{-1}); 275 nm (6.6 × 10^3 M^{-1} cm^{-1}); 448 nm (1.8 × 10^2 M^{-1} cm^{-1}).

1,1′-Bis[bis(trimethylsilyl)silyl]ferrocenyldipotassium. (18-crown-6)$_2$ (2). To a mixture of **1** (106 mg, 0.156 mmol), 18-crown-6 (84 mg, 2 equiv), and potassium *tert*-butanolate (37 mg, 2.10 equiv) was added benzene (2 mL). The solution immediately turned dark red. After 12 h complete conversion was observed by ^{29}Si NMR spectroscopy. During this time the solution had became orange and a dark red crystalline product of **2** (169 mg, 94%) precipitated. ^{29}Si NMR (C_6D_6, δ ppm): −9.1 (*Si*Me$_3$); −121.1 (*Si*K). ^{13}C NMR (C_6D_6, δ ppm): 81.2 (*Cp*-Si); 75.7 (*Cp*); 71.5 (*Cp*); 70.1 (*18-cr-6*); 5.4 (Si*Me*$_3$). ^{1}H NMR (C_6H_6, δ ppm): 4.18 (s, 8H, Cp-*H*); 3.32 (s, 48H, *18-cr-6*); 0.48 (s, 36H, Si*Me*$_3$). The reaction could be carried out also in THF without the use of crown ether. While the isolation of the THF adduct of **2** is not as convenient as that for the crown ether derivative, the THF solution could easily be used for follow-up chemistry as described below.

1,1′-Bis[bis(trimethylsilyl)silyl]ferrocene (3). A solution of dipotassium compound **2** (0.256 mmol) in THF (2 mL) was poured into 2 M H_2SO_4 (3 mL). The reaction mixture was extracted several times with diethyl ether, the organic layers were dried with Na_2SO_4, and the solvent was evaporated. The orange residue was dissolved in degassed 2-propanol, and an orange crystalline product was obtained upon cooling to −35 °C (114 mg, 83%, mp: 32−33°). ^{29}Si NMR (C_6D_6, δ ppm): −15.7 (*Si*Me$_3$); −67.6 ($^1J_{Si-H}$ = 169 Hz, *Si*H). ^{13}C NMR (C_6D_6, δ ppm): 75.7 (*Cp*); 72.8 (*Cp*); 63.3 (*Cp*-Si); 0.4 (Si*Me*$_3$). ^{1}H NMR (C_6D_6, δ ppm): 4.28 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 4.12 (distorted pseudotriplet, 6H, J = 2 Hz, Cp-*H* and Si-*H*); 0.27 (s, 36H, Si*Me*$_3$). IR (film): 2066 cm^{-1} (Si−H). Anal. Calcd for $C_{22}H_{46}Si_6Fe$ (534.97): C 49.39, H 8.67. Found: C 49.03, H 8.40. UV absorption: 226 nm (1.9 × 10^4 M^{-1} cm^{-1}); 275 nm (4.9 × 10^3 M^{-1} cm^{-1}); 329 nm (1.5 × 10^2 M^{-1} cm^{-1}); 450 nm (1.8 × 10^2 M^{-1} cm^{-1}).

1,1′-*ansa*-[Tetrakis(trimethylsilyl)disilanylene]ferrocene (4). To a solution of dipotassium compound **2** (0.318 mmol) in THF (2 mL) at −78 °C was added slowly dibromethane (60 mg, 1 equiv), and the mixture was allowed to come to rt and stirred for another 12 h. For workup 2 M H_2SO_4 was added, the reaction mixture was extracted several times with diethyl ether, the organic layers were dried with Na_2SO_4, and the solvent was removed. The orange residue was treated with hot and degassed 2-propanol and slowly cooled to rt. Three batches of orange crystals were obtained (158 mg, 93%; mp: dec over 130 °C). ^{29}Si NMR (C_6D_6, δ ppm): −13.5 (*Si*Me$_3$); −51.6 (*Si*Fc). ^{13}C NMR (C_6D_6, δ ppm): 78.0 (*Cp*); 71.0 (*Cp*); 70.0 (*Cp*-Si); 2.4. ^{1}H NMR (C_6D_6, δ ppm): 4.77 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 4.12 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 0.42 (s, 36H, Si*Me*$_3$). Anal. Calcd for $C_{22}H_{44}Si_6Fe$ (532.94): C 49.58, H 8.32. Found: C 48.83, H 8.18. UV absorption: 226 nm (2.0 × 10^4 M^{-1} cm^{-1}); 275 nm (2.5 × 10^3 M^{-1} cm^{-1}); 451 nm (9.3 × 10^1 M^{-1} cm^{-1}).

1,1′-*ansa*-[1,1,3,3-Tetrakis(trimethylsilyl)-2,2-dimethyltrisilanylene]ferrocene (5). A procedure similar to that for the preparation of **4** was followed, but instead of dibromoethane dichlorodimethylsilane (34 mg, 1 equiv) was added to **2** (0.263 mmol). Crystallization from degassed 2-propanol at 0 °C gave orange crystals (141 mg, 91%; mp 128−133 °C). ^{29}Si NMR (C_6D_6, δ ppm): −12.3 (*Si*Me$_3$); −22.0 (*Si*Me$_2$); −82.8 (*Si*Fc). ^{13}C NMR (C_6D_6, δ ppm): 76.00 (*Cp*); 71.10 (*Cp*); 67.10 (*Cp*-Si); 3.2 (Si*Me*$_2$); 2.0 (Si*Me*$_3$). ^{1}H NMR (C_6D_6, δ ppm): 4.19 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 4.07 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 0.65 (s, 8H, Si*Me*$_2$); 0.32 (s, 36H, Si*Me*$_3$). Anal. Calcd for $C_{24}H_{50}Si_7Fe$ (591.11): C 48.77, H 8.53. Found: C 46.98, H 8.34. UV absorption: 226 nm (2.9 × 10^4 M^{-1} cm^{-1}); 275 nm (4.0 × 10^3 M^{-1} cm^{-1}); 447 nm (1.4 × 10^2 M^{-1} cm^{-1}).

1,1′-*ansa*-[1,1,4,4-Tetrakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilanylene]ferrocene (6). A solution of dipotassium compound **2** (0.309 mmol) in THF (2 mL) was added at −40 °C to dichlorotetramethyldisilane (58 mg, 1 equiv) in THF. After a workup procedure as described for **4** orange crystals (193 mg, 96%, mp: dec over 130 °C) were obtained. ^{29}Si NMR (C_6D_6, δ ppm): −12.7 (*Si*Me$_3$); −36.5 (*Si*Me$_2$); −75.3 (*Si*Fc). ^{13}C NMR (C_6D_6, δ ppm): 75.7 (*Cp*); 71.1 (*Cp*); 66.1 (*Cp*-Si); 2.4 (Si*Me*$_2$); 1.5 (Si*Me*$_3$). ^{1}H NMR (C_6D_6, δ ppm): 4.17 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 3.96 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 0.50 (s, 12H, Si*Me*$_2$); 0.26 (s, 36H, Si*Me*$_3$). Anal. Calcd for $C_{26}H_{56}Si_8Fe$ (649.25): C 48.10, H 8.69. Found: C 47.28, H 8.71.

1,1′-*ansa*-[1,1,3,3-Tetrakis(trimethylsilyl)-2-(dimethylamino)-phosphatrisilanylene]ferrocene (7). To a suspension of the crown ether adduct of **2** (0.241 mmol) in benzene (2 mL) was added Et_2NPCl_2 (42, mg, 1 equiv). The dianion was slowly dissolved, and after 12 h a bright red solution was obtained. The solvent was removed and an orange solid was obtained (140 mg, 91% contaminated with 5% **4**; mp: dec over 130 °C). ^{29}Si NMR (C_6D_6, δ ppm): −13.0 ($^2J_{Si-P}$ = 19 Hz, *Si*Me$_3$); −61.2 ($^1J_{Si-P}$ = 87 Hz, *Si*P). ^{13}C NMR (C_6D_6, δ ppm): 75.3 ($^3J_{C-P}$ = 4 Hz, *Cp*); 71.3 ($^4J_{C-P}$ = 1 Hz, *Cp*); 64.7 ($^2J_{C-P}$ = 11 Hz, *Cp*-Si); 53.3 ($^2J_{C-P}$ = 6 Hz, *C*H$_2$CH$_3$); 15.6 ($^3J_{C-P}$ = 5 Hz, CH$_2$*C*H$_3$); 1.5 ($^3J_{C-P}$ = 2 Hz, Si*Me*$_3$). ^{1}H NMR (C_6D_6, δ ppm): 4.19 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 4.15 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 2.98 (dq, 4H, $^3J_{H-H}$ = 7 Hz, $^3J_{H-P}$ = 10 Hz, C*H*$_2$CH$_3$); 1.11 (t, 6H, $^3J_{H-H}$ = 7 Hz, CH$_2$C*H*$_3$); 0.40 (s, 36H, Si*Me*$_3$). ^{31}P NMR (C_6D_6, δ ppm): −8.3 ($^1J_{P-Si}$ = 87 Hz). Anal. Calcd for $C_{26}H_{54}Si_6NPFe$ (636.05): C 49.10, H 8.56. Found: C 47.91, H 8.26.

1,1′-*ansa*-[1,1,3,3-Tetrakis(trimethylsilyl)-2-magnesatrisilanylene]ferrocene·2[THF] (8). To a solution of dipotassium compound **2** (0.246 mmol) in THF (2 mL) was added $MgBr_2{\cdot}Et_2O$ (64 mg, 1 equiv). After 1 h the reaction mixture was filtered and the solvent evaporated. The residue was dissolved in pentane/THF, and after crystallization at −40 °C orange crystals were obtained (170 mg, 98%; mp: dec over 240 °C). ^{29}Si NMR (THF/D_2O capillary, δ ppm): −11.2 (*Si*Me$_3$); −108.5 (*Si*Mg). ^{13}C NMR (THF/D_2O capillary, δ ppm): 77.8 (*Cp*); 72.3 (*Cp*-Si); 69.0 (*Cp*); 3.0 (Si*Me*$_3$). ^{1}H NMR (THF-d_8/C_6D_6, δ ppm): 4.21 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 3.84 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 3.53 (m, 8H, C*H*$_2$O); 1.47 (m, 8H, C*H*$_2$CH$_2$O); 0.27 (s, 36H, Si*Me*$_3$). Anal. Calcd for $C_{30}H_{60}O_2Si_6FeMg$ (701.47): C 51.37, H 8.62. Found: C 50.54, H 8.56. UV absorption: 238 nm (1.2 × 10^4 M^{-1} cm^{-1}); 292 nm (2.2 × 10^3 M^{-1} cm^{-1}); 452 nm (1.6 × 10^2 M^{-1} cm^{-1}).

1,1′-*ansa*-[1,1,3,3-Tetrakis(trimethylsilyl)-2-zincatrisilanylene]-ferrocene·[Et$_2$O] (9). A solution of dipotassium compound **2** (0.309 mmol) in THF (2 mL) was added dropwise to a solution of $ZnCl_2$ (42, mg, 1 equiv) in THF at rt. After 2 h the solvent was evaporated and the residue dissolved in Et_2O. After filtration the solvent was again evaporated and an orange solid was obtained, which was recrystallized from Et_2O at −40 °C (185 mg, 89%; mp: dec over 170 °C). ^{29}Si NMR (Et_2O/D_2O capillary, δ ppm): −11.0 (*Si*Me$_3$); −92.2 (*Si*Zn). ^{13}C NMR (Et_2O/D_2O capillary, δ ppm): 77.0 (*Cp*); 70.6 (*Cp*); 70.0 (*Cp*-Si); 2.4. ^{1}H NMR (Et_2O/D_2O capillary, δ ppm): 4.80 (pseudotriplet, 4H, J = 2 Hz, Cp−); 4.37 (pseudotriplet, 4H, J = 2 Hz, Cp-*H*); 0.76 (s, 36H, Si*Me*$_3$). Anal. Calcd for $C_{26}H_{54}Si_6FeOZn$ (672.46): C 44.10, H 7.41. Found: C 43.80, H 7.30. UV absorption: 240 nm (2.5 × 10^4 M^{-1} cm^{-1}); 288 nm (5.4 × 10^3 M^{-1} cm^{-1}); 305 nm (5.5 × 10^3 M^{-1} cm^{-1}); 385 nm (3.6 × 10^2 M^{-1} cm^{-1}); 457 nm (2.2 × 10^2 M^{-1} cm^{-1}).

1,1′-*ansa*-[1,1,3,3-Tetrakis(trimethylsilyl)-2-hafnocenatrisilanylene]ferrocene (10). To a solution of dipotassium compound **2** (0.253 mmol) in THF (2 mL) was added dropwise a solution of hafnocene dichloride (96 mg, 1.0 equiv) in THF (1 mL). After 12 h the solvent was evaporated and the dark residue diluted with pentane and filtrated. The pentane was slowly evaporated, and dark crystalline plates were obtained (55 mg, 26%; mp: dec over 170 °C). ^{29}Si NMR (C_6D_6, δ ppm): −5.3 (*Si*Me$_3$); −15.3 (*Si*Hf). ^{13}C NMR (C_6D_6, δ ppm): 108.1 (*Cp*-Hf); 75.7 (*Cp*-Fe); 69.8 (*Cp*-Fe); 69.1 (*Cp*-Si); 5.0 (Si*Me$_3$*). ^{1}H NMR (C_6D_6, δ ppm): 6.33 (s, 10H, HfCp-*H*); 4.12 (pseudotriplet, 4H, $J = 2$ Hz, FeCp-*H*); 4.04 (pseudotriplet, 4H, $J = 2$ Hz, FeCp-*H*); 0.36 (s, 36H, Si*Me$_3$*). Anal. Calcd for $C_{32}H_{54}Si_6FeHf$ (841.63): C 45.67, H 6.47. Found: C 44.06, H 6.14. UV absorption: 226 nm (3.2×10^4 M^{-1} cm^{-1}); 274 nm (2.0×10^4 M^{-1} cm^{-1}); 364 nm (2.0×10^3 M^{-1} cm^{-1}); 425 nm (1.4×10^3 M^{-1} cm^{-1}); 504 nm (4.0×10^2 M^{-1} cm^{-1}); 642 nm (4.4×10^2 M^{-1} cm^{-1}).

Reaction of 2 with 2 equiv of [Li(DIME)$_2$][W(CO)$_5$I] Leading to the Formation of [Li(THF)$_4$]$_2$[Fe{C$_5$H$_4$Si(SiMe$_3$)$_2$W(CO)$_5$}$_2$] (11). To a solution of dipotassium compound **2** (0.247 mmol) in THF (2 mL) was added [Li(DIME)$_2$][W(CO)$_5$I] (359 mg, 2.0 equiv). After 12 h the solvent was evaporated and the residue dissolved again in THF. After filtration the solvent was again evaporated and an orange solid was obtained, which was recrystallized from pentane/THF at −40 °C to give [Li(THF)$_4$]$_2$[Fe{C$_5$H$_4$Si(SiMe$_3$)$_2$-W(CO)$_5$}$_2$] (385 mg, 88%; mp: dec over 160 °C). ^{29}Si NMR (THF/D$_2$O capillary, δ ppm): −8.2 (*Si*Me$_3$); −80.8 (*Si*W). ^{13}C NMR (THF/D$_2$O capillary, δ ppm): 207.7 (*trans*-CO); 206.7 (*cis*-CO), 78.8 (*Cp*-Si), 76.0 (*Cp*), 70.5 (*Cp*), 3.3 (Si*Me$_3$*). ^{1}H NMR (THF/D$_2$O capillary, δ ppm): 4.28 (pseudotriplet, 4H, $J = 2$ Hz); 4.07 (pseudotriplet, 4H, $J = 2$ Hz); 3.66 (m, 32H, C*H$_2$*O); 1.82 (m, 32H, C*H$_2$*CH$_2$O); 0.20 (s, 36H). Anal. Calcd for $C_{64}H_{108}O_{18}Si_6FeW_2Li_2$ (1771.49): C 43.39, H 6.14. Found: C 43.53, H 6.08. UV absorption: 239 nm (6.6×10^4 M^{-1} cm^{-1}); 288 nm (2.4×10^4 M^{-1} cm^{-1}); 346 nm (7.7×10^3 M^{-1} cm^{-1}); 450 nm (3.8×10^2 M^{-1} cm^{-1}).

1,1′-*ansa*-[1,4-Bis(trimethylsilyl)-2,2,3,3-tetramethyl-1,4-dipotassiotetrasilanylene]ferrocene. (18-crown-6)$_2$ (12). To a solution of **6** (210 mg, 0.323 mmol) in benzene (3 mL) were added 18-crown-6 (171 mg, 2.0 equiv) and potassium *tert*-butanolate (72 mg, 2.0 equiv). The solution immediately turned to dark red. After 12 h **12** precipitated as deep red crystals (323 mg, 79%). ^{29}Si NMR (C_6D_6/THF, δ ppm): −7.6 (*Si*Me$_3$); −31.7 (*Si*Me$_2$); −118.6 (*Si*K). ^{1}H NMR (C_6D_6, δ ppm): 4.49 (m, 2H, Cp-*H*); 4.35 (m, 2H, Cp-*H*); 4.22 (m, 2H, Cp-*H*); 4.00 (m, 2H, Cp-*H*); 3.39 (s, 48H, 18-crown-6); 1.03 (s, 6H, Si*Me*); 0.80 (s, 6H, Si*Me*); 0.61 (s, 18H, Si*Me$_3$*).

1,1′-*ansa*-[1,4-Bis(trimethylsilyl)-1,2,2,3,3,4-hexamethyltetrasilanylene]ferrocene (13). To an ice cold solution of dipotassium compound **12** (0.215 mmol) in THF was added dropwise dimethyl sulfate (41 μL, 2 equiv). The red solution became orange and was then poured on 2 M H_2SO_4. The mixture was extracted with diethyl ether and washed with a saturated $NaHCO_3$ solution. After drying over Na_2SO_4 the solvent was removed in vacuum and an orange residue was obtained. NMR spectroscopic analysis indicated a 5:2 mixture of *cis*- and *trans*-**13**. Crystallization from a small amount of diethyl ether at −40 °C gave pure *trans*-**13** as indicated by crystal structure analysis.

trans-**13**: ^{29}Si NMR (C_6D_6, δ ppm): −15.3 (*Si*Me$_3$); −40.4 and −43.0 (*Si*Me). ^{13}C NMR (C_6D_6, δ ppm): 75.2 (*Cp*); 72.7 (*Cp*); 70.9 (*Cp*); 70.4 (*Cp*); 70.0 (*Cp*-Si); −1.0 (Si*Me$_3$*); −2.7 (Si*Me*); −5.4 (Si*Me*); −7.1 (Si*Me*). ^{1}H NMR (C_6D_6, δ ppm): 4.20 (m, 2H, Cp-*H*); 4.16 (m, 4H, Cp-*H*); 3.91 (m, 2H, Cp-*H*); 0.47 (s, 6H, Si*Me*); 0.45 (s, 6H, Si*Me*); 0.34 (s, 6H, Si*Me*); 0.10 (s, 18H, Si*Me$_3$*). Mp: 146−148 °C. Anal. Calcd for $C_{22}H_{44}Si_6Fe$ (532.95): C 49.58 H 8.32. Found: C 49.11, H 8.32. UV absorption: 225 nm (2.9×10^4 M^{-1} cm^{-1}); 274 nm (4.6×10^3 M^{-1} cm^{-1}); 463 nm (1.7×10^2 M^{-1} cm^{-1}).

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