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Group 4 Metallocene Complexes of Disilenes, Digermenes, and a Silagermene

Michaela Zirngast, Michaela Flock, Judith Baumgartner,* and Christoph Marschner*

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

Received July 9, 2009; E-mail: baumgartner@tugraz.at; christoph.marschner@tugraz.at

Abstract: Reactions of 1,2-dipotassiotetrakis(trimethylsilyl)disilane with group 4 metallocene dichlorides lead to the formation of the respective metallocene 1,1,2,2-tetrakis(trimethylsilyl)disilene complexes. While the disilene titanocene complex could be structurally characterized, the zirconocene and hafnocene compounds, which are believed to possess some degree of bis-[bis(trimethylsilyl)silylene] character, can only be isolated in substance as the respective trimethylphosphane adducts. Analogous metallocene 1,1,2,2-tetrakis(trimethylsilyl)digermene complexes and a tetrakis(trimethylsilyl)silagermene complex were prepared. Instead of metallocene 1,1,2,2-tetrakis(trimethylsilyl)distannene complexes, four-membered rings composed of a metallocene and three bis(trimethylsilyl)stannylene units were obtained.

Introduction

Compounds containing silicon-element bonds with a bond order higher than one were elusive for a long time. The analogy between carbon and silicon seemed to stop at this very point. This led to the formulation of the *double bond rule*, which stated that elements with a principal quantum number higher than two would not form $p\pi-p\pi$ bonds.[1] Eventually, the groups of West[2a] and Masamune[2b] were able to show that molecules with Si−Si double bonds can indeed be prepared. These compounds are, however, very reactive and can only be stabilized using bulky substituents, employing the principle of kinetic stabilization. Meanwhile, numerous examples of compounds with double-bonded silicon are known[3] and even the first examples of stable compounds with Si−Si triple bonds have been reported.[4] Even compounds with silicon−metal triple bond character are under investigation.[5]

Considering the lacking stability of disilenes, it was an interesting question, whether these reactive compounds could be stabilized by coordination to metals, in a way possible for other unstable compounds such as cyclobutadiene.[6]

This turned out to be possible, and a number of disilene metal complexes have been prepared.[7] The first example was reported by West and Pham.[8] Their synthetic strategy was to employ coordinatively unsaturated platinum fragments which undergo double oxidative insertion into a the Si−H bonds of 1,2-dihydrodisilane. The reactivity of these compounds is interesting in the sense that reactions with hydrogen, oxygen, and ammonia do not cleave the Si−metal bonds but in all cases a breaking of the Si−Si bond was observed. Later Berry and co-workers[9] reduced a chlorodisilanyl substituted group 6 metallocene chloride and were thus able to obtain disilene adducts of tungstenocene and molybdenocene. More recently, examples of disilene complexes were reported by Kira et al.,[10,11] who have treated a 1,2-disilanyldianion with platinum and palladium

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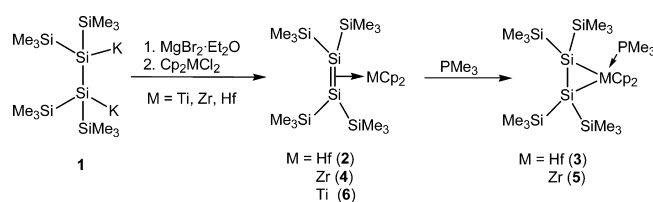
dichlorides to obtain metallacyclotrisilanes.[10] In an elegant study, they could show that switching the electron count at palladium, by removal or addition of a phosphane ligand, changes the character of the compound from a metallacycle to a π-complex.[10b] Kira and co-workers have also reported the first example of a complex of a chlorine substituted disilene from the reaction of tetracarbonylpotassium ferrate with the respective 2,2,3,3-tetrachlorotetrasilane.[11] While all the mentioned examples concern disilene complexes of late transition metals, the only example of coordination of a disilene to an early metal has been reported for hafnocene.[12] Reaction of a 1,2-dipotassiodisilane with hafnocene dichloride gave a hafnocene disilene complex, which was attributed to have some disilylene character. Adduct formation of this complex with trimethylphosphane changed the character of the compound to a more conventional metallacyclotrisilane.

Most of what was said above for disilenes is also true for digermenes. Compared to silicon, germanium chemistry in general has received less attention and so have digermene transition metal complexes. The only known examples concern digermene platinum complexes reported by Satgé and co-workers,[13] which have utilized both the double oxidative addition strategy of 1,2-dihydrodigermanes[13b] as well as the reaction of a 1,2-dilithiodigermane with a platinum chloride complex.[13a] The number of theoretical studies concerning disilene and digermene complexes[14] is also very small with an emphasis on palladium and platinum complexes. No distannene complexes of transition metals are known so far to the best of our knowledge.

Results and Discussion

Synthesis. Reactions of oligosilanyl anions in general and in particular of tris(trimethylsilyl)silanides with group 4 metallocene dichlorides are well established for zirconocene and hafnocene.[15,16] In the course of studies concerning the synthesis and reactivity of oligosilanyl dianions we have also investigated their behavior with zirconocene and hafnocene dichlorides. 1,3- and 1,4-dipotassio -tri- and tetrasilanes were found to react cleanly to the respective metallocyclotetra- and -pentasilanes, respectively.[17] The situation for reactions with titanocene

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Scheme 1

dichloride involves the reduction of titanium and subsequently the formation of silylated titanates.[18]

In principle, a simple access to 1,2-dipotassiodisilanes,[19] 1,2-dipotassiodigermanes[20] and 1,2-dipotassiodistannanes[21] should provide a convenient way to transition metal complexes of disilenes, digermenes and distannenes.
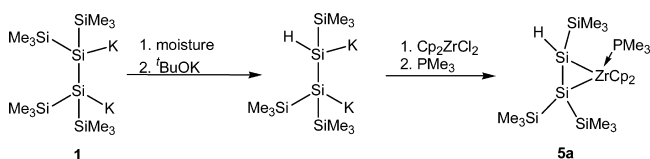
Transmetalation of 1,2-dipotassiotetrakis(trimethylsilyl)disilane[19] (**1**) with magnesium bromide[22] and subsequent reaction with hafnocene dichloride gave the hafnocene disilene complex **2** (Scheme 1), which exhibits a characteristic ^{29}Si NMR spectrum with the metalated silicon atoms resonating at +132.8 ppm.[12] Isolation of this compound in the solid state was not possible. However, upon addition of trimethylphosphane, the PMe₃ adduct **3** was formed, which could be isolated and subjected to crystal structure analysis (Scheme 1).[12] Repeating the reaction of **1** with zirconocene dichloride was possible but accompanied by the formation of approximately 10% byproducts, which seemed to be only monosilylated. Nevertheless, formation of the zirconocene disilene complex **4** could be observed by NMR spectroscopy. Again, isolation in the solid phase was not possible, but also in this case the PMe₃ adduct (**5**) could be obtained (Scheme 1) (discussion of NMR and X-ray data follows the synthetic section). For the reaction of the 1,2-dimagnesiumdisilane with titanocene dichloride, it was expected that the reaction products would exhibit titanium in the oxidation state +3.[18] However, much to our delight, the neutral titanocene disilene complex **6** was formed in some 30% yield along with some paramagnetic material. In this case, even isolation in solid phase was possible, and the structure assignment was confirmed by crystal structure analysis (Figure 3).

During the numerous attempts to obtain single crystals of zirconocene PMe₃ adduct **5**, some crystals of a related compound (**5a**) were isolated. Upon structure analysis, it became evident that the compound was a derivative of **5**, where one of the trimethylsilyl groups was replaced by a hydrogen atom. It is likely that the formation of this compound can be associated with the presence of an excess potassium *tert*-butoxide and some partial hydrolysis. Intermediately formed K(Me₃Si)₂SiSi(SiMe₃)₂H might have been converted to K(Me₃Si)₂SiSi(SiMe₃)(H)K, which eventually could react with Cp₂ZrCl₂ and PMe₃ to **5a** (Scheme 2). The compound is interesting, as it represents the first example of a disilene metal complex with a hydrogen substituent at a formal disilene silicon atom.

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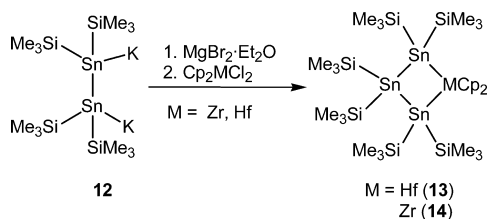
Scheme 2

Scheme 3
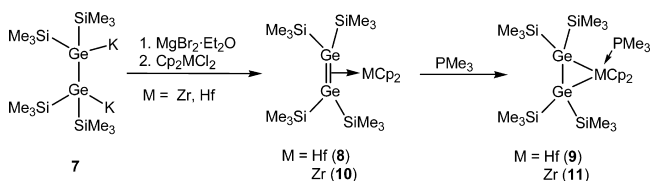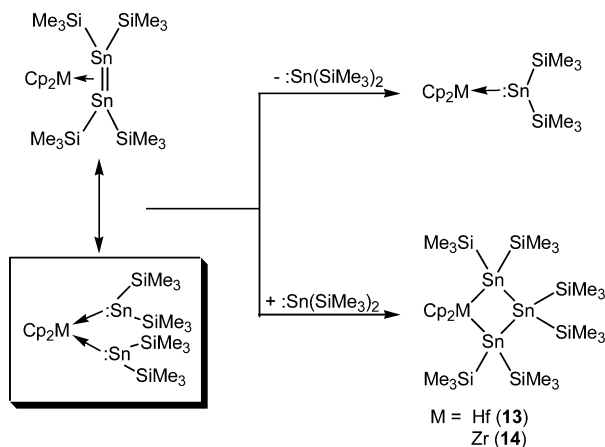

Scheme 4

Scheme 5

Scheme 6

Analogous reactions of hafnocene and zirconocene dichlorides with 1,2-dipotassiotetrakis(trimethylsilyl)digermane[20] (**7**) proceeded very much in the same manner. Formation of the respective digermene complexes **8** and **10** was detected by NMR spectroscopy (Scheme 3). Although the digermene complexes appeared to be more stable, compared to the disilene analogues, no solid state structural characterization was possible. Again isolation and structural characterization was possible upon PMe₃ adduct formation (**9**, **11**) (Scheme 3). The reaction of **7** with titanocene dichloride did not give the expected digermene complex. The two products obtained in this reaction were [Cp₂TiCl]₂, which is in line with our previous experience concerning reactions of oligosilylanions with titanocene dichloride[18] and octakis(trimethylsilyl)cyclotetragermane (**18**) which is the known dimerization product of tetrakis(trimethylsilyl)digermene.[23]

Attempts to apply the same strategy to obtain also distannene complexes, starting from 1,2-dipotassiotetrakis(trimethylsilyl)distannane[21] (**12**) took a different course. In both cases four-membered rings (**13**, **14**) consisting of three bis(trimethylsilyl)stannylene groups and the respective metallocene were obtained (Scheme 4). The outcome of these reactions was the same irrespective of the presence of PMe₃.

As the divalent state becomes more stable for heavier elements in the periodic table, it can be argued that digermene and distannene complexes would exhibit higher germylene or stannylene character. For the reactions of 1,2-dipotassiotetrakis-(trimethylsilyl)distannane with hafno- and zirconocene dichloride this proved to be true. It is assumed that the initially formed distannene complex possesses considerable distannylene character. Related examples for zirconocene distannylene complexes are known from work by Piers[24] and Ruzicka.[25] In addition stannylene ligand dissociation of Group 4 metallocene complexes has been studied in some detail by Tilley.[15c,26] It is therefore likely that a dissociated stannylene can insert into the
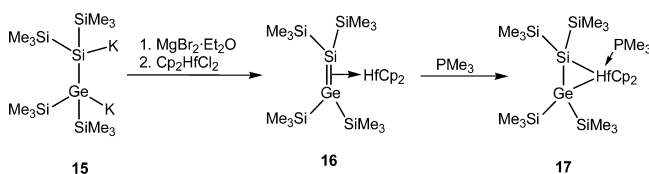
Sn–Sn bond of the initial complex and form the bisstannylated complexes **13** and **14** (Scheme 5). In the attempted reaction of **12** with titanocene dichloride, neither a distannene complex nor a titanacyclotetrastannane could be observed. Reduction of Cp₂TiCl₂ to paramagnetic species was observed.

The unusual low-field ²⁹Si NMR resonances of the metalated silicon atoms of **2**, **4**, and **6**, as well as the results of the computational investigation (see below) suggest partial silylene or germylene character of the ligands of compounds **2**, **4**, **6**, **8**, and **10** (see below). To verify that the connection between the two metalated atoms is not broken by the formation of transient free silylenes or germylenes, a mixed silicon–germanium ligand was prepared. Reaction of 1,2-dipotassio[bis(trimethylsilyl)-silylbis(trimethylsilyl)germane **15**[20] with hafnocene dichloride gave the expected silagermene complex **16**. No scrambling of the ligand was observed in solution. Again, the complex was only stable in solid phase as PMe₃ adduct **17** (Scheme 6).

NMR Spectroscopy. The ²⁹Si NMR resonances corresponding to the metalated atoms of compounds **2**, **4**, **6**, and **16** are substantially deshielded (Table 1), located close to the region typical for tetrasilylated disilenes,[27] which ranges from +140 to +155 ppm. Conversely are shifts for coordinated silicon atoms of isotetrasilanyl units of mono- or disilylated[15] hafno- and zirconocenes[7] found in the range between −50 and −100 ppm. Computational investigations of compounds **2**, **4**, and **6**

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Table 1. ^{29}Si NMR Shifts of Disilene–Group 4 Metallocene Complexes and Some Related Compounds

compound	^{29}Si NMR shifts of formal disilene silicon atoms
(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2^t$Bu)$_2$[27]	142.1
(Me$_3$Si)(^{i}Pr$_3$Si)Si=Si(SiMe$_3$)(Si^{i}Pr$_3$)[27b]	147.1
(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd.	155.1[12]
Cp$_2$Hf(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ (**2**)	132.8[12]
Cp$_2$Hf(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ (**3**)	−135.7/−159.7[12]
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ (**4**)	+129.7
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd.	127.5
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ (**5**)	−132.6/−158.1
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ calcd	−123.7/−86.8
Cp$_2$Ti(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ (**6**)	182.6
Cp$_2$Ti(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd	131.0
Cp$_2$Hf(Me$_3$Si)$_2$Si=Ge(SiMe$_3$)$_2$ (**16**)	164.2
Cy$_3$PPd(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2^t$Bu)$_2$[10b]	65.3
(Me$_3$P)$_2$Pd(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2^t$Bu)$_2$[10c]	−46.8

Figure 1. Molecular structure of **5** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Zr(1)−P(1) 2.7502(15); Zr(1)−Si(3) 2.8528(15), Zr(1)−Si(2) 2.8750(15), P(1)−C(23) 1.837(6), Si(1)−C(11) 1.887(6), Si(1)−Si(2) 2.366(2), Si(2)−Si(3) 2.336(2), Si(2)−Si(5) 2.385(2), P(1)−Zr(1)−Si(3) 79.88(4), Si(3)−Si(2)−Si(1) 117.40(8), Si(3)−Si(2)−Si(5) 121.75(8), Si(3)−Si(2)−Zr(1) 65.43(5).

(see below) showed that the character of the coordinated ligand is by no means that of a disilene but rather exhibits a bond order of less than unity. This indicates that the ligand possesses partial disilylene character. This is further supported by the fact that the ^{29}Si NMR shift of Sekiguchi's recently reported complex of a disilylated silylene coordinating to the Cp′$_2$Hf fragment is with 123.5 ppm very close to the 127.2 ppm found for **2**.[28]

The PMe$_3$ adducts **3** and **5** show a totally different NMR behavior compared to **2**, **4**, and **6**. Most likely due to a fast coordination/decoordination process of PMe$_3$, no resonances for the metalated silicon atoms can be obtained at ambient temperature. Measurement at −80 °C exhibited shifts of the metalated silicon atoms located more than 250 ppm upfield. Due to the additional coordination of the PMe$_3$ ligand to the metal, the two silicon atoms become nonequivalent and therefore two resonances are observed. The chemical shifts of −135.7/−159.7 ppm for **3** and −132.6/−158.1 for **5** are indicative of a metallacyclotrisilane, exhibiting the typical upfield shift behavior of three membered rings, close to the reported value of −174.4 ppm for [(Et$_3$Si)$_2$Si]$_3$.[29]

Structurally and spectroscopically (^{1}H-, and ^{13}C NMR) characterized examples of trimethylphosphane adducts of an ethylene titanocene complex[30] and isobutene complexes of hafnocene and zirconocene[31] provide evidence that also in these cases the metallacyclopropane description can be considered most appropriate.

The behavior of the ^{29}Si NMR resonances associated with the trimethylsilyl groups follows the trend that trimethylsilyl groups attached to strained cyclic compounds experience a shift to lower field.

Crystal Structure Analyses. Compounds **5**, **5a**, **6**, **9**, **11**, **13**, **14**, **17**, and **18** could be subjected to single crystal structure analysis. Compound **6** (Figure 3), the only disilene complex which was not obtained as a PMe$_3$ adduct, crystallizes in the triclinic space group $P\bar{1}$. Unfortunately, the quality of the
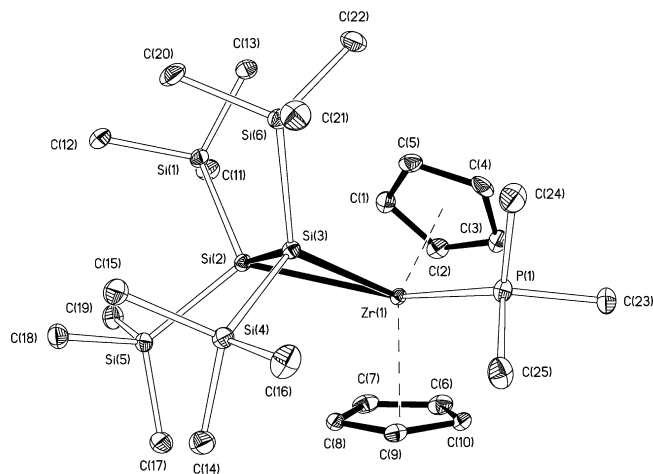
isolated crystals was not very good. Nevertheless, the structure is important as it provides evidence that the theoretical data obtained for **6** are fairly accurate. Thus, it also strengthens the confidence into the data calculated for **2** and **4**. The bond between the two coordinating silicon atoms (2.41 Å) in **6** is considerably longer than in the zirconocene PMe$_3$ complexes **5** and **5a** and quite similar to the value obtained for the central Si−Si bond (2.40 Å) of hexakis(trimethylsilyl)disilane.[32] Compound **5** (Figure 1) crystallizes in the monoclinic space group $P2(1)/c$ and together with a benzene molecule in the asymmetric unit, whereas **5a** (Figure 2), where one trimethylsilyl group is replaced by a hydrogen atom, crystallizes in the chiral orthorhombic space group $P2(1)2(1)2(1)$. The length of the central silicon−silicon bond in **5** is much shorter (2.33 Å) and very similar to the corresponding hafnocene complex **3** (2.34 Å),[12] which is slightly longer, indicating the increased back-donating properties of hafnocene.[33] The quality of the data of **5a** was sufficient to locate the hydrogen atom at the coordinating silicon atom. The reduction of the steric demand in **5a** around the central silicon atoms effects a further shortening of the Si−Si bond length from 2.33 Å in **5** to 2.30 Å in **5a**. The digermene complexes **9** (Figure 4) and **11** (Figure 5) crystallize in the monoclinic space group $P2(1)/c$ with a toluene molecule in the asymmetric unit and the triclinic space group $P\bar{1}$, respectively. The lengths of the Ge−Ge bonds for **9** (2.46 Å) and **11** (2.44 Å) are again similar to the values found for hexakis(trimethylsilyl)digermane (2.48 Å)[34] and hexakis(trimethylsilyl)cyclotrigermane.[35] The Si−Ge compound **17** (Figure 8) crystallizes in the same space group as **9** also with a toluene molecule in the asymmetric unit. Because of the small difference in the atomic radii of silicon and germanium, the two atoms in **17**

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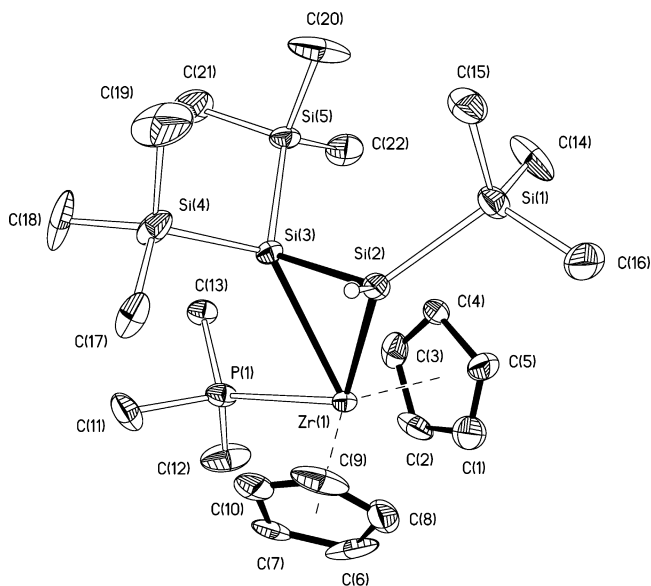
Figure 2. Molecular structure of **5a** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms (except the one at Si(2)) omitted for clarity (bond lengths in Å, angles in deg). Zr(1)−P(1) 2.740(2), Zr(1)−Si(2) 2.788(3), Zr(1)−Si(3) 2.895(3), P(1)−C(11) 1.819(9), Si(1)−C(14) 1.890(11), Si(1)−Si(2) 2.328(3), Si(2)−Si(3) 2.304(3), P(1)−Zr(1)−Si(2) 122.95(7), Si(3)−Si(2)−Si(1) 125.66(14), Si(3)−Si(2)−Zr(1) 68.55(8).
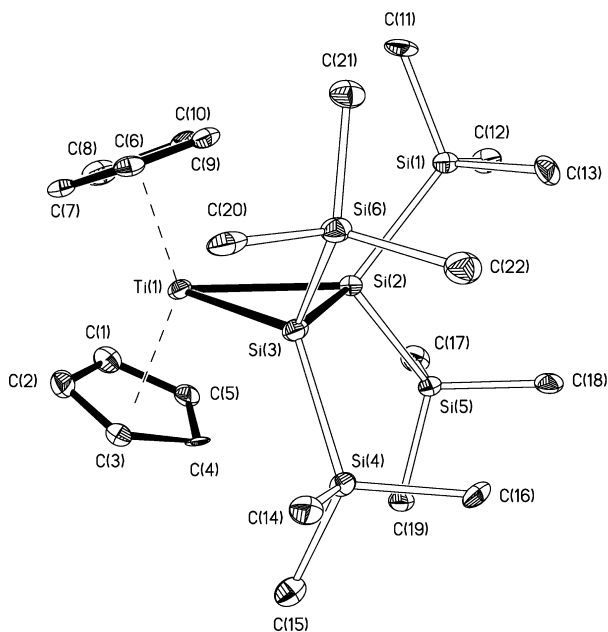

Figure 3. Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Ti(1)−C(1) 2.314(10), Ti(1)−Si(3) 2.596(3), Ti(1)−Si(2) 2.601(3), Si(1)−C(12) 1.856(11), Si(1)−Si(2) 2.368(4), Si(2)−Si(5) 2.371(4), Si(2)−Si(3) 2.411(4), Si(3)−Ti(1)−Si(2) 55.28(10), Si(1)−Si(2)−Si(5) 100.71(15), Si(1)−Si(2)−Si(3) 116.42(15), Si(5)−Si(2)−Si(3) 118.13(15).

share the same sites. In hexakis(trimethylsilyl)silylgermane, the central Si−Ge bond length is 2.43 Å, which is slightly longer than in complex **17** (2.40 Å).[34] In all the above cases, residual electron density is relatively high and located around the metal atoms. The coordinating PMe₃ groups are situated in the equatorial planes formed by the metal and the two coordinating group 14 atoms. The distances of the metal atom to the coordinating silicon or germanium atom are not equal and are
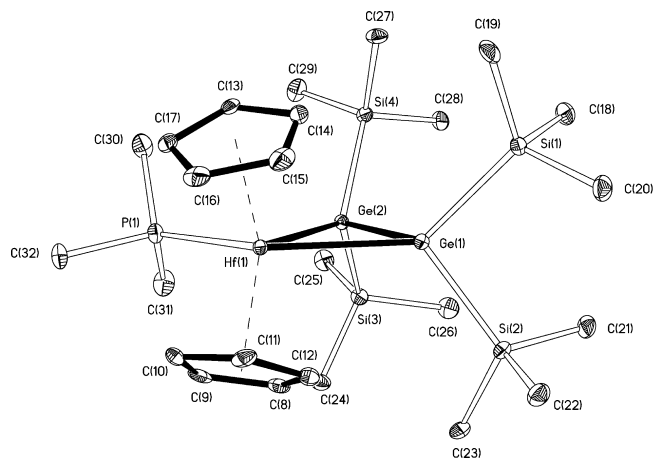

Figure 4. Molecular structure of **9** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Hf(1)−P(1) 2.7284(15), Hf(1)−Ge(2) 2.8413(8), Hf(1)−Ge(2) 2.8670(4), Ge(1)−Si(2) 2.3998(18), Ge(1)−Si(1) 2.4173(16), Ge(1)−Ge(2) 2.4538(9), Si(1)−C(18) 1.883(6), P(1)−C(31) 1.830(6), P(1)−Hf(1)−Ge(2) 78.64(3), Si(2)−Ge(1)−Ge(2) 115.73(5), Ge(1)−Ge(2)−Hf(1) 65.097(19).
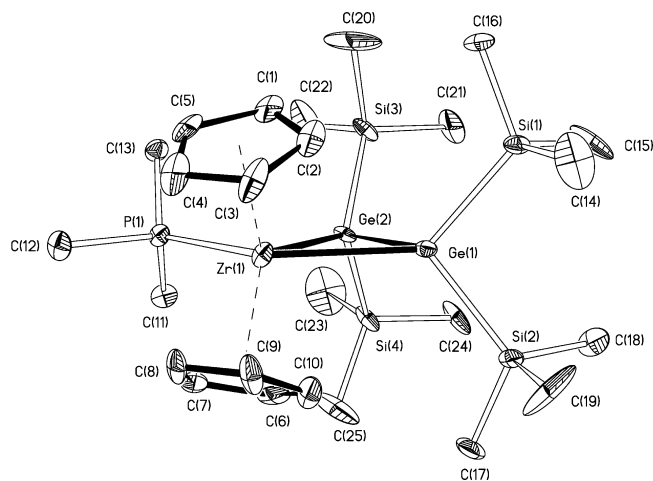

Figure 5. Molecular structure of **11** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Zr(1)−P(1) 2.733(2), Zr(1)−Ge(1) 2.8700(13), Zr(1)−Ge(1) 2.89502, Ge(1)−Si(2) 2.400(3), Ge(1)−Ge(2) 2.4337(14), P(1)−C(11) 1.835(8), Si(1)−C(14) 1.866(12), P(1)−Zr(1)−Ge(1) 124.71(6), Si(2)−Ge(1)−Ge(2) 118.45(8), Ge(2)−Ge(1)−Zr(1) 66.04(4).

in all cases shorter next to the PMe₃ group (Table 2). The crystallographic data for compounds **5**, **5a**, **6**, and **9** can be found in Table 3.

The two tin containing compounds **13** (Figure 6) and **14** (Figure 7) both crystallize in the triclinic space group *P*1̄ and the obtained crystallographic data are of low quality (Table 4). The four-membered rings (M−Sn−Sn−Sn) in both structures are approximately planar. The angles between the planes Sn−Sn−Sn and Sn−M−Sn and thus the deviation from planarity are 5.8 and 6.4° for **13** and **14**. No other four-membered rings with three Sn-atoms and a heterometal atom could be found in the CCDC database while cyclotetrastannane rings are a well established class of compounds.[36] The Sn−Sn bond lengths observed for cyclotetrastannanes are around 2.85 Å,[36] close to the values found in compounds **13** and **14**.

The respective Sn−metal distances are 2.91/2.92 Å for **13** (Hf−Sn) and Å 2.93/2.95 Å for **14** (Zr−Sn). The Hf−Sn bonds

Table 2. Calculated and Observed Structure Properties of Some Disilenes and Disilene Transition Metal Complexes

compound	Cp–M–Cp angle	E–E/M–E (Å) bond lengths
(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2$^{t}Bu)$_2$[27a]		2.201
(Me$_3$Si)(^{i}Pr$_3$Si)Si=Si(SiMe$_3$)(Si^{i}Pr$_3$)[27b]		2.197
(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd.		2.229
Cp$_2$Hf(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd		2.571
Cp$_2$Hf(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ (**3**)[12]		2.343(4)/2.8309(6), 2.8332(5)
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd.		2.563
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ (**5**)	129.9	2.336(2)/2.8528(15), 2.8750(15)
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ calcd		2.366/2.937, 2.913
Cp$_2$Zr(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$·PMe$_3$ (**5a**)	130.2	2.304(3)/2.788(3), 2.895(3)
Cp$_2$Ti(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ (**6**)	138.1	2.411(4)/2.601(3)
Cp$_2$Ti(Me$_3$Si)$_2$Si=Si(SiMe$_3$)$_2$ calcd		2.494/2.621
Cp$_2$Hf(Me$_3$Si)$_2$Ge=Ge(SiMe$_3$)$_2$·PMe$_3$ (**9**)	129.5	2.4538(9)/2.8413(8), 2.8670(4)
Cp$_2$Zr(Me$_3$Si)$_2$Ge=Ge(SiMe$_3$)$_2$·PMe$_3$ (**11**)	128.5	2.4337(14)/2.8700(13), 2.89502)
Cp$_2$Hf(Me$_3$Si)$_2$Si=Ge(SiMe$_3$)$_2$ (**17**)	129.6	2.3987(11)
Cy$_3$PPd(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2$^{t}Bu)$_2$[10b]		2.2740(11)
(Me$_3$P)$_2$Pd(^{t}BuMe$_2$Si)$_2$Si=Si(SiMe$_2$^{t}Bu)$_2$[10c]		2.303(1)

Table 3. Crystallographic Data for Compounds **5**, **5a**, **6**, and **9**

	5	5a	6	9
Empirical formula	ZrPSi$_6$C$_{31}$H$_{61}$	ZrPSi$_5$C$_{22}$H$_{47}$	TiSi$_6$C$_{22}$H$_{46}$	HfPGe$_2$Si$_4$C$_{32}$H$_{63}$
M_w	724.53	574.24	527.03	914.82
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.34 × 0.28 × 0.22	0.35 × 0.28 × 0.20	0.38 × 0.28 × 0.26	0.40 × 0.34 × 0.24
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2(1)/c$	$P2(1)2(1)2(1)$	$P\bar{1}$	$P2(1)/c$
a [Å]	16.861(3)	11.365(2)	9.878(2)	16.908(3)
b [Å]	10.925(2)	15.798(3)	10.085(2)	10.926(2)
c [Å]	23.401(5)	17.117(3)	16.779(3)	23.415(5)
α [deg]	90	90	90.47(3)	90
β [deg]	110.76(3)	90	90.22(3)	110.94(3)
γ [deg]	90	90	117.42(3)	90
V [Å^3]	4031(2)	3073(2)	1483(2)	4040(2)
Z	4	4	2	4
ρ_{calc} [gcm^{-3}]	1.194	1.241	1.180	1.504
Absorption coefficient [mm^{-1}]	0.510	0.613	0.539	4.220
$F(000)$	1544	1216	568	1848
θ range	$1.85 < \theta < 25.00$	$1.75 < \theta < 25.00$	$2.28 < \theta < 23.50$	$1.85 < \theta < 26.35$
Reflections collected/unique	28324/7066	21943/5417	9504/4376	31022/8201
Completeness to θ [%]	99.9	99.9	99.7	99.7
Data/restraints/parameters	7066/0/367	5417/0/279	4376/6/274	8201/0/377
Goodness of fit on F^2	1.05	0.89	1.01	1.073
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.061$	$R1 = 0.065$	$R1 = 0.098$	$R1 = 0.045$
	$wR2 = 0.160$	$wR2 = 0.111$	$wR2 = 0.218$	$wR2 = 0.090$
R indices (all data)	$R1 = 0.076$	$R1 = 0.111$	$R1 = 0.170$	$R1 = 0.058$
	$wR2 = 0.1715$	$wR2 = 0.127$	$wR2 = 0.258$	$wR2 = 0.095$
Largest diff. Peak/hole [e$^-$/ Å^3]	5.54/−0.54	0.74/−0.54	0.86/−0.55	3.25/−0.89

are relatively short considering related examples[26,37] [f.i. (C$_5$H$_4$Me)$_2$Hf(SnMe$_3$)$_2$: 2.952 Å][37] cover a range from 2.95 to 3.00 Å. Compared to the known Sn–Zr distances which range from 2.97 to 3.04 Å,[38] the respective bond lengths in **14** are again rather short. Only for cases where the Sn–Zr bond involves stannylene ligands shorter distances of 2.87 and 2.82 Å have been observed.[24,25]

The four-membered ring of compound **18** (Figure 9) was found to be planar and isomorphous to the analogous cyclotetrasilane.[39,40] Ge–Ge bond distances of around 2.49 Å and Ge–Si

bond distances between 2.40 and 2.42 Å are slightly longer than in related compounds.[34,35]

Computational Results. For a better understanding of the unexpected ^{29}Si NMR behavior of compounds **2**, **4**, and **6** a theoretical study concerning these compounds was carried out. Compounds **2**, **4**, **5**, and **6** were investigated using two different methods: RI-BP/TZVP (ECP on Zr, Hf) implemented in Turbomole 5.7.1[41] and MPW1PW91/SDD (DV95 for Si, P, C, H; Stuttgart-Dresden ECPs on M) as implemented in Gaussian03 (see Tables 2, 5, and 6).[42] NMR chemical shifts were calculated

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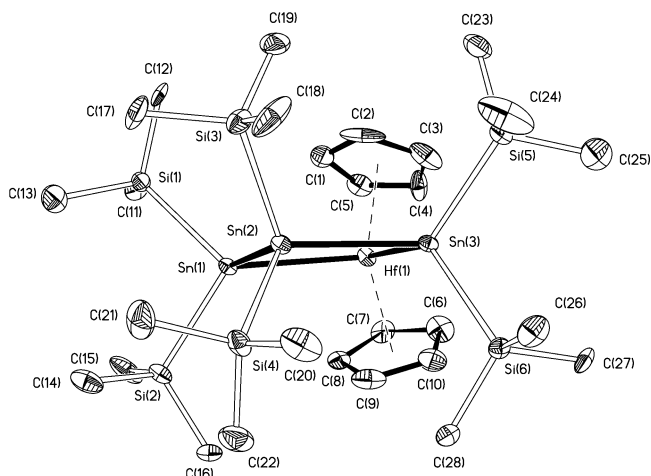
Figure 6. Molecular structure of **13** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Hf(1)−Sn(3) 2.9105(13), Hf(1)−Sn(1) 2.9238(13), Sn(1)−Si(2) 2.582(4), Sn(1)−Si(1) 2.600(5), Sn(1)−Sn(2) 2.8378(15), Sn(2)−Sn(3) 2.8505(15), Si(1)−C(12) 1.867(16), Sn(3)−Hf(1)−Sn(1) 99.56(4), Sn(2)−Sn(1)−Hf(1) 78.53(4), Sn(1)−Sn(2)−Sn(3) 103.11(5), Sn(2)−Sn(3)−Hf(1) 78.55(4).
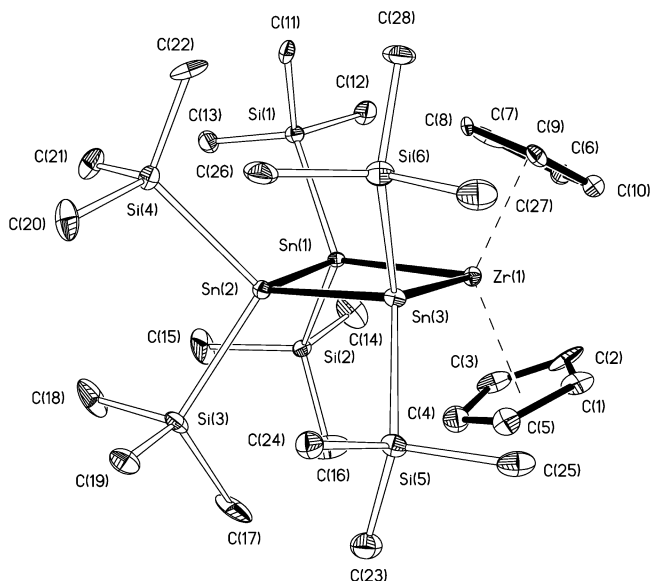

Figure 7. Molecular structure of **14** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Zr(1)−Sn(1) 2.9297(19), Zr(1)−Sn(3) 2.9454(18), Sn(1)−Si(1) 2.584(4), Sn(1)−Si(2) 2.587(4), Sn(1)−Sn(2) 2.8561(14), Sn(2)−Sn(3) 2.8480(16), Si(1)−C(11) 1.849(14), Sn(1)−Zr(1)−Sn(3) 102.67(6), Sn(2)−Sn(1)−Zr(1) 75.05(5), Sn(3)−Sn(2)−Sn(1) 107.07(5), Sn(2)−Sn(3)−Zr(1) 74.93(5).

according to SOS-DFPT PW91/Iglo-II (see Tables 1, 5, and 6) using deMon.[43]

The calculation of compound **4** is particularly interesting as the calculated ^{29}Si NMR data are matching the observed resonances very well. According to the calculations the central Si−Si bond distance of the formal disilene ligand is 2.56 Å, which is 0.15 Å longer than the central bond length in (Me₃Si)₃SiSi(SiMe₃)₃.[32] The same distance in compound **2** was found to be even slightly longer (2.57 or 2.59 Å, depending on

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the method). For the titanocene complex **6** this distance was calculated to be 2.46 Å (MPW1PW91/SDD) or 2.49 Å (RI-BP/TZVP). Both calculated values exceed the distance found in the crystal structure analysis (2.41 Å). Also the calculated ^{29}Si NMR resonances (calculated 132 ppm vs observed 182 ppm) do not fit as nicely as for **4**. The observed values for the Si−SiMe₃ distances of **2**, **4**, and **6** are all around 2.41 Å (RI-BP/TZVP) or 2.43 Å (MPW1PW91/SDD). In the crystal these distances were found to be around 2.37 Å. The same trend can be observed for the phosphane adduct **5**, where the Si−SiMe₃ distances were found to be 2.35 Å to the silicon atom next to the phosphane and 2.37 and 2.39 Å to the other silicon atom. The calculations confirm that the Si−SiMe₃ distance is shorter on the phosphane side but again overestimate the length [2.41 Å (P side) and 2.43 Å (RI-BP/TZVP), 2.42 Å (P side) and 2.44 Å (MPW1PW91/SDD)]. The central Si−Si bond of **5** in the crystal was found to be 2.33 Å, while the calculations gave values of 2.37 Å (RI-BP/TZVP) and 2.38 Å (MPW1PW91/SDD). From these comparisons it appears that both methods overestimate the Si−Si distances in the complexes. Therefore, it seems likely that the actual Si−Si distances of compounds **2** and **4** may also be somewhat shorter than the calculated ones.

Conclusion

It has been found that examples of disilene complexes of all three group 4 metallocenes can be prepared by reactions of a 1,2-disilanyldianion with the respective metallocene dichlorides. The zircono- and hafnocene complexes could only be observed spectroscopically and not be isolated in solid phase. Their isolation could be accomplished after conversion to the respective trimethylphosphane adducts. The base-free titanocene disilene complex on the other hand could be isolated and was subjected to single crystal X-ray structure analysis. The reactions of a 1,2-digermanyldianion proceeded along a similar line. Again the free zircono- and hafnocene complexes could only be detected spectroscopically, while their isolation and characterization was possible as trimethylphosphane adducts. Attempts to obtain the analogous metallocene distannene complexes by reactions of a 1,2-distannyldianion with the metallocene dichlorides led to the isolation of the respective metallacyclotetrastannanes of zirconium and hafnium.

The results of the structure analysis of the base-free titanocene disilene complex together with computational results suggest that the long Si−Si bond between the two metal-coordinating silicon atoms has a bond order of less than one. It can thus be concluded that the compound has a (small) resonance contribution from the respective bis[bis(trimethylsilyl)silylene] metallocene complex. Further evidence for this is provided by the unusual low-field ^{29}Si NMR chemical shifts. It is assumed that this unusual bond situation arises by the ability of the disilene to function both as a π- and σ-donor to the unsaturated metallocene fragment. Upon addition of trimethylphosphane as a base, the π-interaction between the metallocene and the disilene is shut down and the bond order of the silicon bond is raised and the distance is thus substantially shortened.

This situation is quite different from the picture known for metallocene olefin complexes, where we distinguish between π-complexes and metallcyclopropanes. π-Complexes donate electron density from the π-system of the olefin to the metal. The bond order is thus slightly reduced. In the metallcyclopropane case a more electron rich metal donates electron density back to the π*-system. As the bond order of the olefin is further reduced the C−C bond length is elongated. We believe that

Table 4. Crystallographic Data for Compounds **11**, **13**, **14**, **17**, and **18**

	11	13	14	17	18
Empirical formula	$ZrPGe_2Si_4C_{25}H_{55}$	$HfSn_3Si_6C_{28}H_{64}$	$ZrSn_3Si_6C_{28}H_{64}$	$HfPGeSi_5C_{32}H_{63}$	$Ge_4Si_8C_{24}H_{72}$
M_w	735.42	1103.89	1016.62	870.32	875.90
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Size [mm]	$0.38 \times 0.28 \times 0.22$	$0.30 \times 0.30 \times 0.18$	$0.35 \times 0.28 \times 0.20$	$0.32 \times 0.28 \times 0.22$	$0.42 \times 0.40 \times 0.40$
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$C2$
a [Å]	11.461(2)	10.982(2)	10.916(2)	16.865(3)	19.289(4)
b [Å]	11.770(2)	11.835(2)	11.849(2)	10.921(2)	12.751(3)
c [Å]	13.139(3)	17.500(4)	17.496(3)	23.394(5)	10.290(2)
α [deg]	84.00(3)	86.81(3)	87.04(3)	90	90
β [deg]	84.43(3)	87.77(3)	87.75(3)	110.88(3)	117.74(3)
γ [deg]	86.36(3)	75.29(3)	76.30(3)	90	90
V [Å^3]	1752(2)	2196(2)	2195(2)	4026(2)	2240(2)
Z	2	2	2	4	2
ρ_{calc} [gcm^{-3}]	1.394	1.670	1.538	1.436	1.299
Absorption coefficient [mm^{-1}]	2.192	4.222	2.098	3.532	2.886
$F(000)$	760	1076	1012	1776	912
θ range	$1.56 < \theta < 25.00$	$1.17 < \theta < 25.00$	$1.17 < \theta < 24.00$	$1.85 < \theta < 26.37$	$1.99 < \theta < 26.38$
Reflections collected/unique	12560/6077	12276/6576	14513/6849	31082/8193	8886/2397
Completeness to θ [%]	98.6	85.3	99.3	99.5	99.8
Data/restraints/parameters	6077/0/313	6576/12/361	6849/30/361	8193/0/378	2397/1/177
Goodness of fit on F^2	1.03	1.11	1.20	1.14	1.06
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.071$ $wR2 = 0.146$	$R1 = 0.070$ $wR2 = 0.218$	$R1 = 0.089$ $wR2 = 0.150$	$R1 = 0.044$ $wR2 = 0.094$	$R1 = 0.053$ $wR2 = 0.117$
R indices (all data)	$R1 = 0.100$ $wR2 = 0.161$	$R1 = 0.080$ $wR2 = 0.233$	$R1 = 0.120$ $wR2 = 0.162$	$R1 = 0.053$ $wR2 = 0.098$	$R1 = 0.063$ $wR2 = 0.124$
Largest diff. Peak/hole [e$^-$/ Å^3]	1.32/−1.57	2.27/−1.79	1.25/−2.04	2.31/−0.98	0.97/−0.73

the situation of the phosphane adducts of the disilene complexes is quite similar to the metallcyclopropane cases. A description as metallcyclotrisilanes seems appropriate. However, the π-complex case of the disilenes or digermenes (or even distannenes) is different in the sense that the Si—Si σ-bond is capable of interacting with the metal, serving as an additional source of electron density. This way not only the bond order of the π-bond but also of the σ-bond is reduced. A complete acceptance of the σ-bond is leading to an -ylene complex, a situation which likely occurs for the distannene ligand. Even the dissociation of free stannylenes, which in a subsequent step can insert into
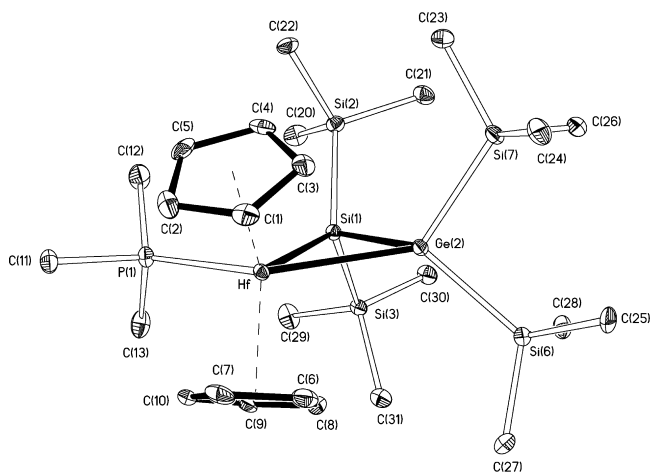
the Sn—Sn or Sn—M bond of the distannylene complex seems to be facilitated. This way a metallacyclotetrastannane is formed.

Experimental Section

Figure 8. Molecular structure of **17** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Si(1)—Si(3) 2.3692(16), Si(1)—Si(2) 2.3770(15), Si(1)—Ge(2) 2.3987(11), Si(2)—Hf 2.8369(8), Ge(2)—Hf 2.8613(9), Hf—P(1) 2.7264(14), P(1)—C(12) 1.828(5), Si(2)—C(21) 1.876(5), Si(3)—Si(1)—Ge(2) 111.67(5), Ge(2)—Si(1)—Hf 65.63(2).
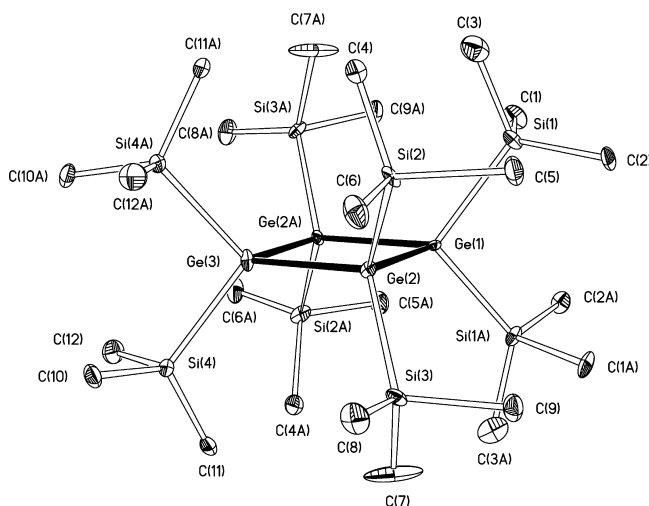

Figure 9. Molecular structure of **18** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity (bond lengths in Å, angles in deg). Ge(1)—Si(1) 2.419(5), Ge(1)—Ge(2) 2.490(2), Ge(2)—Si(2) 2.397(2), Ge(2)—Si(2) 2.415(3), Ge(2)—Ge(3) 2.485(2), Ge(3)—Si(4) 2.415(5), Si(1)—C(3) 1.808(14), Ge(2)—Ge(1)—Ge(2A) 89.79(9), Ge(3)—Ge(2)—Ge(1) 90.09(4), Ge(2)—Ge(3)—Ge(2A) 90.03(9), Ge(1)—Ge(2)—Ge(3)—Ge(2A) 0.0.

Table 5. Optimization of **2**, **4**, **6** and **5** using RI-BP/TZVP (ECP for Zr, Hf) with Turbomole 5.7.1 NMR: SOS-DFPT PW91/Iglo-II (TMS: $\sigma =$ 362.4 ppm)

6   **4**   **2**
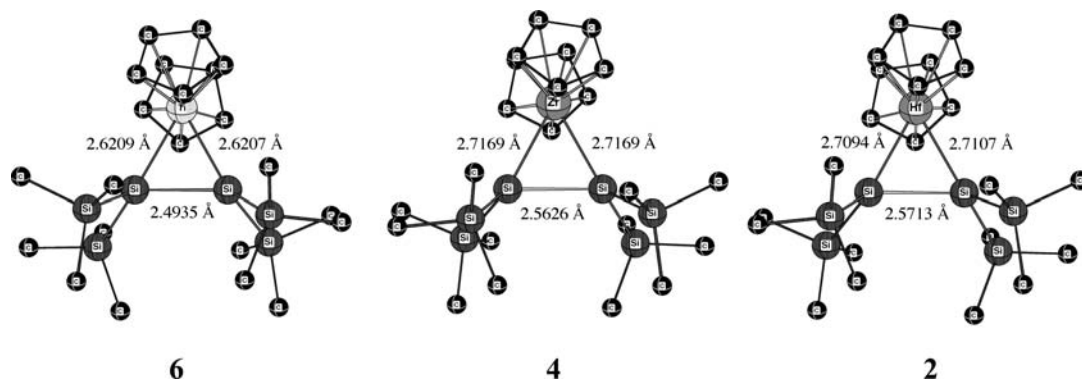
	2	4	6
Si−Si′	2.5713	2.5626	2.4935
M−Si	2.7094	2.7169	2.6209
M−Si′	2.7107	2.7169	2.6207
Si−SiMe$_3$	2.4143	2.4150	2.4161
Si−SiMe$_3$	2.4092	2.4099	2.4226
Si′−SiMe$_3$	2.4154	2.4145	2.4161
Si′−SiMe$_3$	2.4096	2.4098	2.4226
δ^{29}Si (Si$_3$)^a		127.2	130.6
δ^{29}Si (Si$_3$)^a		127.8	131.4
δ^{29}Si (SiMe$_3$)^b		5.0/1.3	4.0/0.3
δ^{29}Si (SiMe$_3$)^b		5.0/1.3	4.1/0.2

5
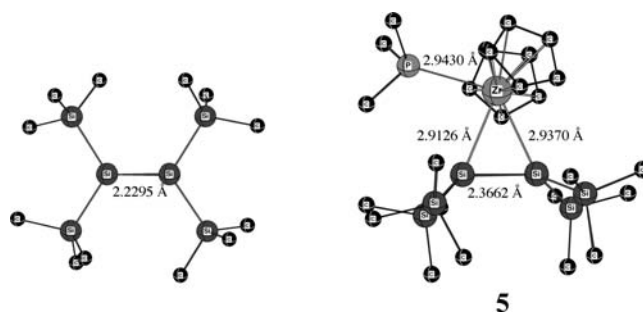
^{a} δ^{29}Si (Si$_3$) 157.4, 152.8 ppm −123.7 ppm, −86.8 ppm. ^{b} δ^{29}Si (SiMe$_3$) −4.4/−3.7, −4.0/−3.5 ppm 2.1/1.2, 4.0/2.1 ppm.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{31}P (124.4 MHz), ^{119}Sn (111.8 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded either on a Varian INOVA 300 spectrometer. If not noted otherwise, for all samples, C$_6$D$_6$ was used or in case of reaction samples they were measured with a D$_2$O capillary 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.[44] Elementary analysis was carried out using a Heraeus VARIO ELEMENTAR.

X-Ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, 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[45] and SADABS,[46] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[47] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were located at 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 was poor. This fact is reflected by quite high R and low theta values.

Crystallographic data (excluding structure factors) for the structures of compounds **5**, **5a**, **6**, **9**, **11**, **13**, **14**, **17**, and **18** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-709576 (**5**), 709575 (**5a**), 709577 (**6**), 709570 (**9**), 709571 (**11**), 709572 (**13**), 709574 (**14**), 709573 (**17**), and 738853 (**18**). Copies of the data can be obtained free of charge at http://www.ccdc. cam.ac.uk/products/csd/request/.

1,1,2,2-Tetrakis(trimethylsilyl)disilanyl-1,2-dipotassium,[19] 1,1,2,2-tetrakis(trimethylsilyl)digermanyl-1,2-dipotassium,[20] bis(trimethylsilyl)[potassiobis(trimethylsilyl)silyl]germylpotassium,[20] 1,1,1,2,2,2-hexakis(trimethylsilyl)distannane,[48] tris(trimethylsilyl)-stannylpotassium·18-crown-6,[21] and MgBr$_2$·Et$_2$O[49] were prepared and found to have spectral properties according to reported procedures.

1,1-Bis(cyclopentadienyl)-2,2,3,3-tetrakis(trimethylsilyl)-1-zirconacyclotrisilane·PMe$_3$ (5). 1,1,1,2,2,2-Hexakis(trimethylsilyl)-disilane (200 mg, 0.404 mmol), 18-crown-6 (213 mg, 2 equiv), and KO^{t}Bu (91 mg, 2 equiv) were dissolved in benzene (4 mL).

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(45) *SAINTPLUS: Software Reference Manual, Version 6.45*; Bruker-AXS: Madison, WI, 1997−2003.
(46) Blessing, R. H. *Acta Cryst. A* **1995**, *51*, 33–38. *SADABS: Version 2.1*; Bruker-AXS: Madison, WI, 1998.
(47) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112–122.

(48) Mallela, P.; Geanangel, R. A. *Inorg. Chem.* **1993**, *32*, 5623–5625.

Table 6. Optimization of **2**, **4**, **6** and **5** using MPW1PW91/SDD (DV95 for Si, C, H, ECPs for M) with Gaussian03 NMR: SOS-DFPT PW91/Iglo-II (TMS: σ= 366.7 ppm)
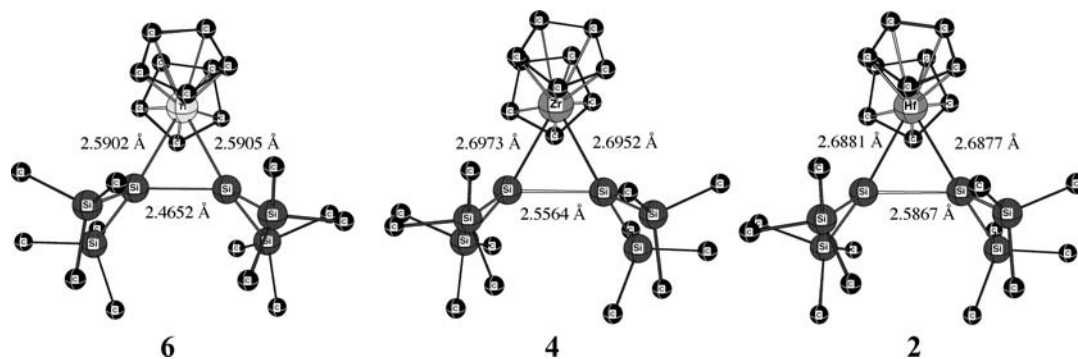
	2	4	6
Si−Si′	2.5867	2.5564	2.4652
M-Si	2.6881	2.6973	2.5902
M-Si′	2.6877	2.6952	2.6207
Si-SiMe$_3$	2.4352	2.4334	2.4343
Si-SiMe$_3$	2.4223	2.4264	2.4419
Si′-SiMe$_3$	2.4343	2.4370	2.4341
Si′-SiMe$_3$	2.4223	2.4288	2.4414
δ^{29}Si (Si$_3$)^a		137.1	131.9
δ^{29}Si (Si$_3$)^a		140.3	134.1
δ^{29}Si (SiMe$_3$)^b		11.2/7.3	10.5/6.0
δ^{29}Si (SiMe$_3$)^b		11.5/7.4	10.6/6.2

5
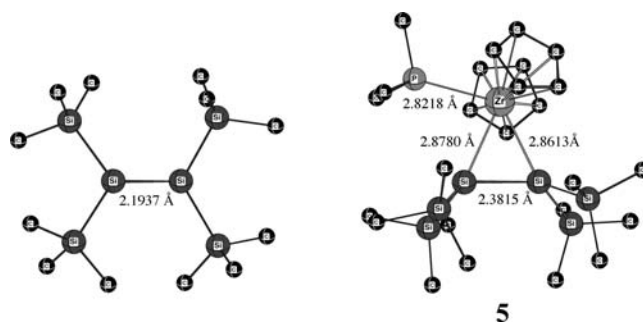
^{a} δ^{29}Si (Si$_3$) 152.0 ppm, 160.1 ppm −106.7 ppm, −72.3 ppm. ^{b} δ^{29}Si (SiMe$_3$) 2.2/1.5 ppm, 1.9/1.2 ppm 27.9/27.2 ppm, 31.1/26.1 ppm.

After 20 h formation of dianion **1** was complete (checked by ^{29}Si NMR). MgBr$_2$·Et$_2$O (104 mg, 1 equiv) was added and stirring continued for another 30 min. Cp$_2$ZrCl$_2$ (118 mg, 0.404 mmol) was added and the red solution was stirred for 3 h. Formation of compound **4** was detected by NMR spectroscopy. [**4**: ^{29}Si NMR (δ in ppm): 129.8, 2.6. ^{1}H NMR (δ in ppm): 6.35 (s, 10H, *Cp*), 0.67 (s, 36H)]. After addition of PMe$_3$ (31 mg, 1 equiv) and stirring for another 3 h the precipitate was removed by centrifugation and the solution cooled to −70 °C. Orange crystals of **5** were obtained (52 mg, 20%) (mp: decomposition over 135 °C). ^{29}Si NMR (δ in ppm, −80 °C): −1.5 (bs), −1.6 (bs), −132.6 (d, $^2J_{Si-P}$ = 14.6), −158.1 (d, $^2J_{Si-P}$ = 31.9). ^{1}H NMR (δ in ppm): 5.22 (s, 10H, *Cp*); 0.94 (d, J_{Si-P} = 5.8 Hz, 9H, P*Me*$_3$); 0.59 (bs, 36H, Si*Me*$_3$). ^{13}C NMR (δ in ppm): 97.9 (Cp); 20.2 (d, J_{Si-P} = 18.7, P*Me*$_3$); 7.7 (Si*Me*$_3$). ^{31}P NMR (δ in ppm, −80 °C): −4.0. Anal. Calcd for C$_{25}$H$_{55}$Si$_6$PZr (646.43): C 46.45, H 8.58. Found: C 45.60, H 8.16.

During one of the attempts to obtain good quality single crystals of **5**, a crystal of 1,1-bis(cyclopentadienyl)-2,2,3-tris(trimethylsilyl)-1-zirconacyclotrisilane·PMe$_3$ (**5a**) was isolated and subjected to crystal structure analysis.

1,1-Bis(cyclopentadienyl)-2,2,3,3-tetrakis(trimethylsilyl)-1-titanacyclotrisilane (6). 1,1,1,2,2,2-Hexakis(trimethylsilyl)disilane (200 mg, 0.404 mmol), 18-crown-6 (213 mg, 2 equiv), and KO^{t}Bu (91

mg, 2 equiv) were dissolved in benzene (3 mL). After 18 h formation of **1** was complete (checked by ^{29}Si NMR), MgBr$_2$·Et$_2$O (104 mg, 1 equiv) was added and stirring continued for another 5 min. The suspension was added to a solution of Cp$_2$TiCl$_2$ (101 mg, 0.404 mmol) in a mixture of benzene (3 mL) and pentane (1 mL). The green solution was stirred for 4 h and then monitored by ^{29}Si NMR, which indicated only formation of oktakis(trimethylsilyl)-cyclotetrasilane and *tert*-butoxytrimethylsilane. The precipitate was removed by centrifugation and half of the solvent in vacuum. Two different kinds of crystals could be obtained namely colorless crystals of Cp$_2$TiCl$_2$K·18-crown-6[18] and dark blue ones of **6** (15 mg, 27%). ^{29}Si NMR (δ in ppm): 182.6, 2.9. ^{1}H NMR (δ in ppm): 6.22 (s, 10H, *Cp*), 0.53 (s, 36H, Si*Me*$_3$). ^{13}C NMR (δ in ppm): 110.0 (Cp), 6.1 (Si*Me*$_3$).

1,1-Bis(cyclopentadienyl)-2,2,3,3-tetrakis(trimethylsilyl)-1-hafnacyclotrigermane·PMe$_3$ (9). Reaction was carried out analogously to the preparation of **5** using 1,1,1,2,2,2-hexakis(trimethylsilyl)digermane (150 mg, 0.257 mmol), 18-crown-6 (136 mg, 2 equiv), KO^{t}Bu (58 mg, 2 equiv), MgBr$_2$·Et$_2$O (66 mg, 1 equiv), and Cp$_2$HfCl$_2$ (97 mg, 0.257 mmol) in C$_6$D$_6$. Formation of **8** was confirmed as a red solution after 3 h by NMR [**8**: ^{29}Si NMR (δ in ppm): 9.2. ^{1}H NMR (δ in ppm): 5.98 (s, 10H, *Cp*); 0.57 (s, 36H). ^{13}C NMR (δ in ppm): 103.9 (*Cp*); 6.6 (Si*Me*$_3$)]. Addition of PMe$_3$ (0.027 mL, 1 equiv) provided orange crystals of **9** (97 mg, 46%) obtained after removal of the precipitate and cooling to −70 °C. ^{29}Si NMR (δ in ppm): 8.2. ^{1}H NMR (δ in ppm): 5.83 (s, 10H, *Cp*);

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0.82 (d, J_{Si-P} = 1.5 Hz, 9H, P*Me*₃) 0.60 (s, 36H, Si*Me*₃). ¹³C NMR (δ in ppm): 102.8 (*Cp*); 17.3 (P*Me*₃); 6.9 (Si*Me*₃).

1,1-Bis(cyclopentadienyl)-2,2,3,3-tetrakis(trimethylsilyl)-1-zirconacyclotrigermane·PMe₃ (11). 1,1,1,2,2,2-Hexakis(trimethylsilyl)digermane (274 mg, 0.469 mmol), 18-crown-6 (254 mg, 2.05 equiv), and KO'Bu (108 mg, 2.05 equiv) were dissolved in toluene (3 mL). After 16 h formation of **7** was complete (checked by ²⁹Si NMR), MgBr₂·Et₂O (121 mg, 1 equiv) was added and stirring continued for another 1 h. Cp₂ZrCl₂ (137 mg, 0.469 mmol) was added and the red solution was stirred for 4 h. Formation of **10** observed by NMR: [**10**: ²⁹Si NMR (δ in ppm): 4.9. ¹H NMR (δ in ppm): 6.13 (s, 10H, *Cp*); 0.57 (s, 36H, Si*Me*₃). ¹³C NMR (δ in ppm): 105.0 (*Cp*); 6.3 (Si*Me*₃)]. The precipitate was removed by centrifugation and then the solvent removed in vacuum. The residue was treated with pentane and the insoluble part removed again by centrifugation. To the red solution PMe₃ (0.049 mL, 1 equiv) was added. Orange crystals of **11** (154 mg, 42%) were obtained by cooling to −70 °C. ²⁹Si NMR (δ in ppm): 3.7. ¹H NMR (δ in ppm): 5.43 (s, 10H, *Cp*); 0.88 (d, J_{Si-P} = 2.6 Hz, 9H, P*Me*₃) 0.62 (s, 36 H, Si*Me*₃). ¹³C NMR (δ in ppm): 99.9 (*Cp*); 17.9 (P*Me*₃); 7.7 (Si*Me*₃).

Attempted Synthesis of 1,1-Bis(cyclopentadienyl)-2,2,3,3-tetrakis(trimethylsilyl)-1-titanacyclotrigermane. The reaction was carried out in an analogous way as described for the synthesis of **6** with 1,1,1,2,2,2-hexakis(trimethylsilyl)digermane (150 mg, 0.257 mmol), 18-crown-6 (136 mg, 2 equiv), and KO'Bu (58 mg, 2 equiv). After removal of the salts and crystallization from toluene, orange crystals of [Cp₂TiCl]₂ and colorless crystals of [(Me₃Si)₂Ge]₄ (**18**) were obatined. The structures of both types of crystals were determined by single crystal X-ray diffraction analysis. **18**: NMR-data: ²⁹Si (δ in ppm): −4.0. ¹H (δ in ppm): 0.38 (s, 72H). ¹³C (δ in ppm): 4.6.

1,1-Bis(cyclopentadienyl)-2,2,3,3,4,4-hexakis(trimethylsilyl)-1-hafnacyclotetrastannane (13). Reaction was done according to **5** using hexakis(trimethylsilyl)distannane (105 mg, 0.155 mmol), 18-crown-6 (82 mg, 2 equiv), KO'Bu (35 mg, 2 equiv) in toluene. MgBr₂·Et₂O (40 mg, 1 equiv) was added after 4 h and Cp₂HfCl₂ (59 mg, 0.370 mmol) after additional 1 h. Dark-red crystals of **13** (62 mg, 54%) were obtained after cooling to −70 °C in pentane. By dissolving the crystals in benzene within 1 d decomposition could be observed by deposition of elemental tin. ²⁹Si NMR (*d*₈-toluene, δ in ppm): −9.5 (¹$J_{119/117Sn-29Si}$ = 175/168 Hz, ²$J_{119/117Sn-29Si}$ = 39/37 Hz), −9.8 (¹$J_{119/117Sn-29Si}$ = 160/152 Hz, ²$J_{119/117Sn-29Si}$ = 40/42 Hz). ¹H NMR (*d*₈-toluene, δ in ppm): 5.99 (s, 10H, *Cp*), 0.60 (s, ³$J_{119/117Sn-1H}$ = 8 Hz, ²$J_{119/117Sn-1H}$ = 11 Hz, 36H), 0.55 (s, ³$J_{119/117Sn-1H}$ = 4 Hz, ²$J_{119/117Sn-1H}$ = 11/12 Hz, 18H). ¹³C NMR (δ in ppm): 109.5 (*Cp*), 5.8 (²$J_{119/117Sn-13C}$ = 20 Hz), 4.5 (²$J_{119/117Sn-13C}$ = 19 Hz). ¹¹⁹Sn NMR (*d*₈-toluene, δ in ppm): −665.0, −678.3.

1,1-Bis(cyclopentadienyl)-2,2,3,3,4,4-hexakis(trimethylsilyl)-1-zirconacyclotetrastannane (14). Reaction was done according to **5** using hexakis(trimethylsilyl)distannane (70 mg, 0.103 mmol), 18-

crown-6 (55 mg, 2 equiv), KO'Bu (23 mg, 2 equiv) in toluene. MgBr₂·Et₂O (27 mg, 1 equiv) was added after 2 h and Cp₂ZrCl₂ (30 mg, 0.370 mmol) after additional 1 h. Dark-red crystals of **14** (38 mg, 54%) were obtained by cooling to −70 °C using pentane. By dissolving the crystals in benzene within 1 d decomposition could be observed by deposition of elemental tin. ²⁹Si NMR (*d*₈-toluene, δ in ppm): −9.5 (¹$J_{119/117Sn-29Si}$ = 175/167 Hz, ²$J_{119/117Sn-29Si}$ = 41/47 Hz), −9.8 (¹$J_{119/117Sn-29Si}$ = 159/152 Hz, ²$J_{119/117Sn-29Si}$ = 56/65 Hz). ¹H NMR (*d*₈-toluene, δ in ppm): 6.07 (s, 10H, *Cp*), 0.59 (s, ³$J_{119/117Sn-1H}$ = 10/9 Hz, ²$J_{119/117Sn-1H}$ = 17/16 Hz, 36H), 0.55 (s, ³$J_{119/117Sn-1H}$ = 3/4 Hz, ²$J_{119/117Sn-1H}$ = 11/12 Hz, 18H). ¹³C NMR (*d*₈-toluene, δ in ppm): 110.1 (*Cp*), 4.9 (²$J_{119/117Sn-13C}$ = 21 Hz), 4.4 (²$J_{119/117Sn-13C}$ = 20 Hz). ¹¹⁹Sn NMR (*d*₈-toluene, δ in ppm): −665.9, −679.3.

1,1-Bis(cyclopentadienyl)-2,2,3, 3-tetrakis(trimethylsilyl)-1-hafna-2-sila-cyclotrigermane-PMe₃ (17). Reaction was done according to **5** using tris(trimethylsilyl)silyltris(trimethylsilyl)germane (200 mg, 0.370 mmol), 18-crown-6 (196 mg, 2 equiv), KO'Bu (83 mg, 2 equiv), MgBr₂·Et₂O (96 mg, 1 equiv), and Cp₂HfCl₂ (141 mg, 0.370 mmol) in C₆H₆. The red solution was controlled after 3 h by NMR [**16**: ²⁹Si NMR (C₆H₆/D₂O, δ in ppm): 164.2; 9.5; 2.4. ¹H NMR (C₆H₆/D₂O, δ in ppm): 5.94 (s, 10H, *Cp*); 0.46 (s, 18H); 0.43 (s, 18H)]. Further procedure is identically as for **5** adding PMe₃ (0.038 mL, 1 equiv). Red crystals of **17** (93 mg, 32%) were obtained by cooling to −70 °C. ²⁹Si NMR (δ in ppm): 3.9 (Me₃*Si*-Ge); −0.1 (Me₃*Si*−Si); at 25 °C no signal for the central Si could be detected. ¹H NMR (δ in ppm): 5.36 (s, 10H, *Cp*); 0.96 (d, J_{Si-P} = 4.2 Hz, 9H, P*Me*₃) 0.61 (s, 36H, Si*Me*₃). ¹³C NMR (δ in ppm): 98.8 (*Cp*); 19.3 (d, J_{Si-P} = 14.6 Hz, P*Me*₃); 7.9 and 7.6 (Si*Me*₃). ³¹P NMR (δ in ppm): −30.6.

Note Added after ASAP Publication. The wrong images were published as Figures 6 and 7 in the version published ASAP October 2, 2009. The corrected version was published October 9, 2009.

Supporting Information Available: Details for the calculated structures of compounds **2**, **4**, **5** and **6** together with the complete ref 42, as well as X-ray crystallographic information for compounds **5**, **5a**, **6**, **9**, **11**, **13**, **14**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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