Communication

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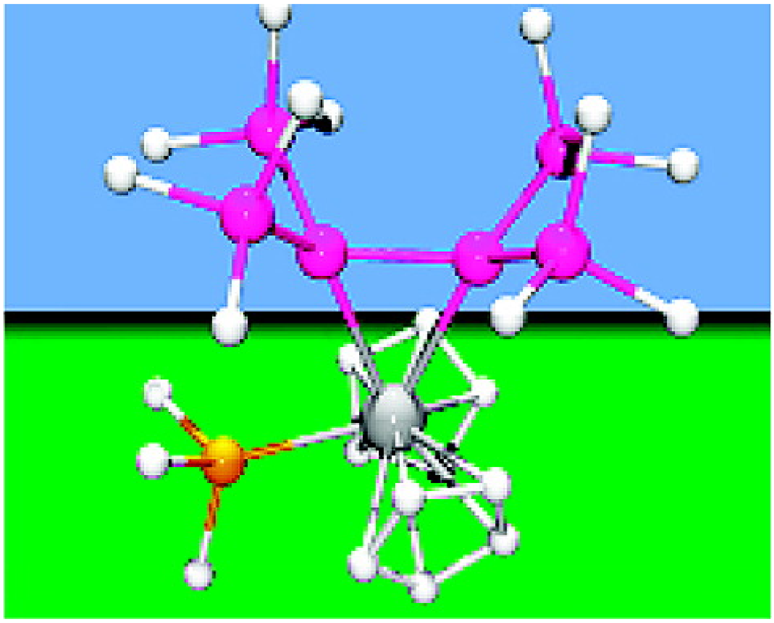

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Synthesis of a Hafnocene Disilene Complex

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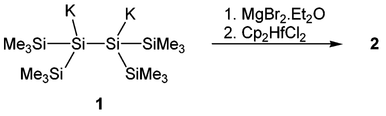
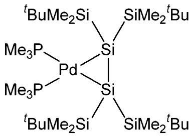
Disilenes, previously thought to be not stable, have now been known for some 20 years. Since the landmark synthesis by Fink and West,[1] numerous stable examples have been studied. Nonetheless, only a few examples of disilene transition-metal complexes[2−4] are known thus far. Interestingly, only examples of complexes with groups 10[3] and 6[4] have been reported. Disilene complexes of groups 4 or 5, however, have not been known until now.

In recent years, we have investigated the synthesis of oligosilyl potassium compounds by the reaction of oligosilanes with potassium alkoxides.[5] These studies provided simple access to dimetalated oligosilanes.[6] Some of the obtained silyl anions were reacted with zirconocene and hafnocene dichlorides to give bis-silylated group 4 metallocenes.[7] Most recently, we were able to extend our studies to the synthesis of 1,2-disilanyl dianions.[8] 1,2-Dipotassiumtetrakis(trimethylsilyl)disilane (**1**) proved to be a highly reactive compound that was difficult to derivatize. However, by addition of magnesium bromide the reactivity could be moderated.[9] Further addition of hafnocene dichloride effected the formation of the first example of a group 4 disilene complex (**2**) (Scheme 1).[10]

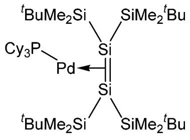
Scheme 1



In a series of recent publications, Kira et al.[3] used a conceptually similar approach for the syntheses of disilene complexes of platinum[3a] and palladium[3b,c] by reaction of a 1,2-dilithiotetrasilyldisilane[11] with the respective metal chlorides. In an elegant comparison, 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 (**A**) to a π-complex (**B**).



metallacycle (**A**)

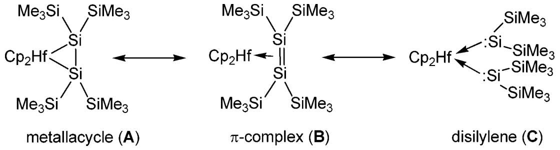


π-complex (**B**)

This change was reflected by the differences in the geometry of the disilene moiety, which displays sp^3 hybridization for the coordinated silicon atoms in the metallacycle (**A**) case and sp^2 hybridized silicon atoms in the π-complex (**B**). ^{29}Si NMR spectroscopy proved to be another good indicator for the degree of sp^2 hybridization. While the resonances of the coordinated silicon atoms of the metallacycles are in the typical range[14] for isotetrasilanylmetal compounds of around -50[3b] ppm, the π-complexation mode causes a downfield shift of some 110 ppm to $+65.3$[3c] ppm (Table 1).

The ^{29}Si NMR shift value for the coordinated atoms of **2** is $+132.8$ ppm. This is close to typical shifts for tetrasilyl substituted disilenes,[12] which range from $+140$ to $+155$ ppm. Chemical shifts for the coordinated silicon atom of the isotetrasilanyl unit of mono- or disilylated[7,13] hafno- and zirconocenes[14] lie in the range of -50 to -100 ppm. For known ethylene titanocene complexes,[15] ^{13}C NMR spectra show a similar upfield shift of some 20 ppm for the coordinated ethylene resonances compared to free ethylene.

A DFT calculation study of the zirconocene analogue of **2**[16,17] provided further insight into the bonding situation of **2**. A calculated NMR shift value of $+127$ ppm was obtained, which compares nicely to the observed data. The geometry of the calculated structure, however, does not exhibit the expected shortened central Si−Si bond but rather an unusually long distance of 2.56 Å. Also, a back bending of the trimethylsilyl groups can be observed. Together with the unusually low NMR shift, this geometry suggests a partial disilylene[18] character (**C**) of the ligand. The nature of bonding between the disilene unit and the metal in **2** therefore should be assigned somewhere between the π-complex and disilylene resonance structures.



Reaction of **2** with hydrogen resulted in the almost quantitative formation of tetrakis(trimethylsilyl)disilane,[19] which most likely proceeds via a σ-bond metathesis mechanism.[20] The formation of 1,1,1,3,3,3-hexamethyltrisilane, which might be a product derived from a silylene ligand, was not detected.

Unfortunately, it was not possible to isolate **2** in the solid state. Evaporation of the solvent resulted in decomposition. NMR monitoring of the formation of **2** showed it to be a stepwise process with a monosilylated intermediate. Using ferrocene as an internal standard, the yield of **2** could be estimated to be around 60%.

Reaction of **2** with trimethylphosphane proceeded smoothly to give the phosphane adduct **3**,[21] which could be subjected to single-crystal X-ray diffraction analysis (Figure 1). The obtained structure consists of a hafnocene with the two Cp groups bent by 129.4°.[22] The plane Si(2)−Hf−Si(3) is almost orthogonal to the Cp−Hf−Cp plane (87.1°). Also, the phosphorus atom is close to the equatorial plane. The bond between the two coordinating silicon atoms (2.343(4) Å) is longer than those found for the structurally similar platinum[3a] (2.321(2) Å) and palladium[3b] (2.303(1) and 2.3180(8) Å) complexes. The Si−Si−Si angles around the coordinating silicon atoms add up to 329.1° for Si(2) and 338.6° for Si(3). The Si−Hf bond lengths of 2.8309(6) and 2.8332(5) Å compare well to related compounds with σ-bonded silyl ligands connected to the Cp$_2$Hf fragment ($Cp_2Hf[Si(SiMe_3)_3]_2$: 2.850 Å,[7] ($Cp_2Hf[Si(SiMe_3)_2SiMe_2]_2$: 2.826 and 2.791 Å[6a]).

These structural features clearly indicate a high degree of sp^3 character for the coordinating silicon atoms. Further evidence for the metallacycle character of **3** was provided by ^{29}Si NMR

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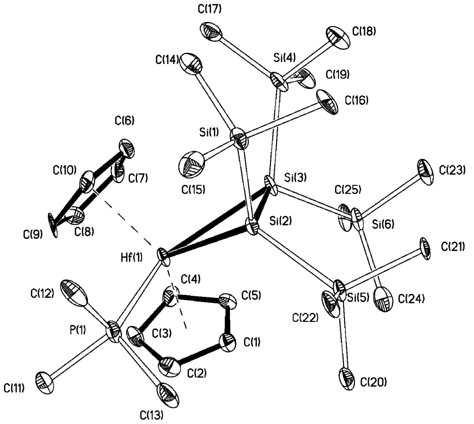

Figure 1. Molecular structure of **3** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms omitted for clarity.

Table 1. ^{29}Si NMR Data of Disilenes and Disilene Complexes

compound	^{29}Si NMR shift
$({}^t\text{BuMe}_2\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_2{}^t\text{Bu})_2$	142.1[12]
$(\text{Me}_3\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_3)_2$ calcd.	155.1[16]
$\text{Cp}_2\text{Hf}(\text{Me}_3\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_3)_2$ (**2**)	132.8
$\text{Cp}_2\text{Zr}(\text{Me}_3\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_3)_2$ calcd.	127.2[16]
$\text{Cy}_3\text{PPd}({}^t\text{BuMe}_2\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_2{}^t\text{Bu})_2$ (**B**)	65.3[3c]
$(\text{Me}_3\text{P})_2\text{Pd}({}^t\text{BuMe}_2\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_2{}^t\text{Bu})_2$ (**A**)	−46.8[3b]
$\text{Cp}_2\text{Hf}(\text{Me}_3\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_3)_2\cdot\text{PMe}_3$ (**3**)	−135.7/−159.7
$\text{Cp}_2\text{Zr}(\text{Me}_3\text{Si})_2\textit{Si}{=}\textit{Si}(\text{SiMe}_3)_2\cdot\text{PMe}_3$ calcd.	−86.8/−123.7[16]

spectroscopy. At ambient temperature it was only possible to detect a signal for the trimethylsilyl groups. The resonances belonging to the coordinated silicon atoms could not be obtained, most likely because of a fast coordination/decoordination process of trimethylphosphane. At −80 °C, however, two sets of resonances were observed for the trimethylsilyl groups (−0.7 and −1.3 ppm) and central silicon atoms (−135.7 and −159.7). All four resonances displayed couplings to phosphorus.

Again this spectral behavior was in accordance with a calculation for the zirconium analogue of **3**, which predicted slightly less pronounced upfield shifts to −86.8 and −123.7 ppm (Table 1). Structurally and spectroscopically (^{1}H- and ^{13}C NMR) characterized examples of trimethylphosphane adducts of an ethylene titanocene complex[23] and isobutene complexes of hafnocene and zirconocene[24] provide evidence that also in these cases a metallacyclopropane description can be considered most appropriate.

Further studies concerning the insertion chemistry of **2** and related compounds are currently under way.

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Supporting Information Available: The coordinates of the calculated Zr analogue of **2** and a CIF file of compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) 1,1,2,2-Tetrakis(trimethylsilyl)disilyl-1,2-dipotassium·2 × 18cr6 (200 mg, 0.20 mmol)) (caution: extremely sensitive and frequently pyrophoric!) was dissolved in THF (5 mL), and magnesiumbromide etherate (53 mg, 0.20 mmol) was added to yield the silylmagnesium derivative. Solvents were removed in vacuo, and toluene (4 mL) was added. Upon addition of 77 mg (0.20 mmol) of hafnocene dichloride, the reaction mixture acquired a dark red color. NMR data (δ in ppm): ^{1}H (toluene-d_8): 6.11 (s, 10H, C*H*), 0.55 (s, 36H, (C*H*$_3$)$_3$Si); ^{13}C (toluene-d_8): 105.7 (*C*H), 6.4 (*Me*$_3$Si); ^{29}Si (toluene-d_8): 132.7 ((Me$_3$Si)$_2$*Si*), 3.1 (Me$_3$*Si*).
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(16) Calculation carried out with RI-BP/TZVP (ECP-28-MWB pseudopotential on Zr) as implemented in Turbomole: Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346−354. NMR chemical shifts were calculated with deMon at the PW91/IGLO_II level using a (633321/53211*/531+) basis set on Zr. For reasons of computational convenience not the hafnium but rather the chemically similar zirconium compounds were calculated.
(17) Attempts to obtain the zirconium analogue of **2** by reaction of Cp$_2$ZrCl$_2$ with **1** and MgBr$_2$ indicated formation of the expected product as seen by ^{29}Si NMR shifts at 129.7 and 2.6 ppm. However, the reaction is not as clean as in the hafnium case.
(18) For an example of a related zirconocene distannylene complex, see: (a) Whittal, R. M.; Ferguson, G.; Gallagher, J. F.; Piers, W. E. *J. Am. Chem. Soc.* **1991**, *113*, 9867−9868. (b) Piers, W. E.; Whittal, R. M.; Ferguson, G.; Gallagher, J. F.; Froese, R. D. J.; Stronks, H. J.; Krygsman, P. H. *Organometallics* **1992**, *11*, 4015−4022.
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(21) To the reaction solution of **2**[10] PMe$_3$ (30 μL) was added, causing a color change to brownish green. After removal of the solvent in a vacuum, the residue was extracted with pentane. At −30 °C yellowish crystals (87 mg, 59%) were obtained. NMR data (δ in ppm): ^{1}H (benzene-d_6): 5.23 (s, 10H, Cp); 0.82 (d, 9H, PMe$_3$); 0.64 (s, 36H, (C*H*$_3$)$_3$Si)); ^{29}Si (toluene-d_8, −80 °C): −0.7 (d, ^3J(Si−P) = 1.6 Hz), −1.3 (d, ^3J(Si−P) = 1.8 Hz), −135.7 (d, ^2J(Si−P) = 12.3 Hz), −159.7 (d, ^2J(Si−P) = 23.6 Hz); ^{31}P (toluene-d_8, −80 °C): −20.6. Anal. Calcd for $C_{25}H_{55}HfPSi_6$: C, 40.93; H, 7.56. Found: C, 40.81; H, 7.39.
(22) Crystallographic data for **3**: $C_{25}H_{55}HfPSi_6$ orthorhombic space group *Pbcn*, $a = 16.487(3)$ Å, $b = 22.667(5)$ Å, $c = 18.672(4)$ Å, $V = 6978(2)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.397$ Mg/m^3, R1 = 0.071, wR2 = 0.1264, GOF = 1.107. CCDC 233774.
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