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Activation of a Si═Si Bond by η^1-Coordination to a Transition Metal

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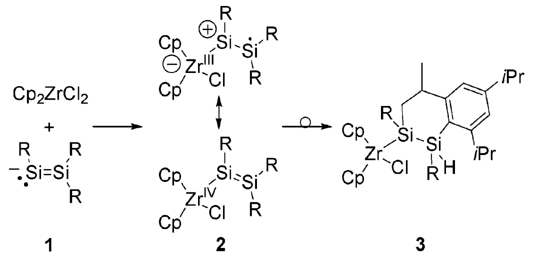
Since the ground breaking discovery of a stable disilene by West, Michl, and Fink in 1981[1], low-valent silicon compounds have received considerable attention.[2] In the meantime, numerous stable disilenes have been prepared, taking advantage of either kinetic stabilization by bulky substituents or electronic stabilization within the coordination sphere of transition metals. To date, examples of η^2-disilene complexes cover a wide range of transition metals from groups 4, 6, 8, and 10.[3] Conversely, no η^1-disilenide complexes, 3rd row analogues of the extensively studied η^1-vinyl complexes,[4] have yet been reported. The disilenides recently obtained by ourselves and others should be suitable precursors for such compounds.[5]

Here, we report the reaction of the lithium salt of disilenide **1**[5a] with Cp_2ZrCl_2, yielding the η^1-disilenide zirconium complex **2** almost quantitatively. Compared to that of the anionic precursor, the Si═Si bond of **2** appears to be far more reactive, as shown by its facile isomerization to the silyl complex **3** (Scheme 1).[6]

Scheme 1



R = 2,4,6-triisopropylphenyl

Compound **2** was characterized by means of ^{1}H, ^{13}C, and ^{29}Si NMR, and UV−vis spectroscopy. It shows an absorption band at $\lambda_{max} = 715$ nm, which is even more bathochromically shifted than the highest wavelength signal of the recently reported disilyne featuring a Si≡Si bond ($\lambda_{max} = 690$ nm).[7] Given its high extinction coefficient ($\epsilon \cong 7000$ L·mol^{-1}·cm^{-1}), the unusual red-shift of the absorption of **2** could be due to a ligand-to-metal $\pi \rightarrow$ d charge-transfer transition, as depicted by the resonance structures in Scheme 1.

A contribution by the upper resonance form might also explain the low-field ^{29}Si NMR resonances at 116.8 and 152.5 ppm. Compared to the signals of its precursor **1**,[5a] the latter is shifted more than 50 ppm to lower field. It is unambiguously assigned to the Si atom bonded to zirconium on the basis of 2D-^{29}Si−^{1}H experiments. On these grounds, a certain silylene character of the disilenide ligand in **2** can be considered. The ^{29}Si NMR shifts of cationic tungsten silylene complexes, for instance, have been observed between 277 and 314 ppm.[8]

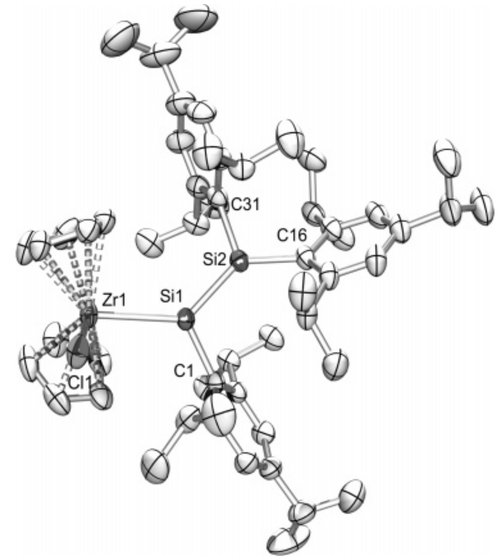


Figure 1. Structure of **2** in the solid state. H atoms and disordered hexanes are omitted for clarity. Ellipsoids at 50%. Selected bond lengths (Å): Si1−Si2 2.2144(7), Si1−Zr1 2.7611(6), Zr1−Cl1 2.4512(6), Si1−C1 1.925(2), Si2−C16 1.907(2), Si2−C31 1.884(2). Selected bond angles (°): Cl1−Zr1−Si1 99.912(18), Si2−Si1−Zr1 132.07(3), Zr1−Si1−C1 119.91(6), C1−Si1−Si2 107.70(6), Si1−Si2−C16 134.45(7), Si1−Si2−C31 116.64(7), C16−Si2−C31 108.42(9).

Further indications that charge transfer from the disilenide ligand to Zr might contribute to satisfy the electron demand of the formal 16e$^-$ center are provided by X-ray crystallography (Figure 1).[9] While the Si1−Si2 bond in **2** is significantly longer than that in the precursor (**2**, 2.2144(7); **1**, 2.1920(6) Å), the Zr1−Si1 distance of 2.7611(6) Å is relatively short considering the bulkiness of the ligand. For instance, the Zr−Si distance in $Cp_2Zr(SiPh_3)Cl$ (**4**) was determined to 2.813(2) Å.[10] Nonetheless, the Zr1−Cl1 bond in **2** (2.4512(6) Å) is somewhat longer than that in **4** (2.430(3) Å). The Si1═Si2 bond of **2** is considerably twisted, as indicated by the angle of 20.24° between the planes defined by Zr1, Si1, C1 and C31, Si2, C16, respectively. Both silicon atoms are, however, only slightly pyramidalized (sum of angles: Si1 359.68, Si2 359.51). A strong twisting of a Si═Si bond was also observed in the blue disilene $[(t\text{Bu}_2\text{MeSi})_2\text{Si}]_2$ and its diradical nature discussed.[11]

To our knowledge, the facile rearrangement of **2** at room temperature to the zirconocene silyl complex **3** is without precedent in disilene chemistry.[12] On the other hand, the insertion of carbene analogues into C−H bonds is well-known, for example, for the germylene $GeAr_2$ (Ar = 2,4,6-tri-*tert*-butylphenyl).[13] The actual mechanism of the isomerization of green **2** to red **3**, which formally requires the 1,2-addition of a methyl C−H bond to the Si═Si bond, remains obscure. While an excess of **1** in the synthesis of **2** sped up the latter's rearrangement considerably (complete conversion after 1 h), a slight surplus of Cp_2ZrCl_2 stabilized **2** in benzene solution for at least 24 h at room temperature. Therefore, either a base-catalyzed mechanism or a radical pathway initiated by electron transfer from excess disilenide **1** can be envisaged.

As expected, **3** is formed as a diastereomeric mixture. However, presumably due to its favorable arrangement of the bulky substituents, the *l*,*l*-diastereomer[14] predominates and was crystallized from hexane in 57% yield.[6]

10.1021/ja052593p CCC: $30.25 © 2005 American Chemical Society

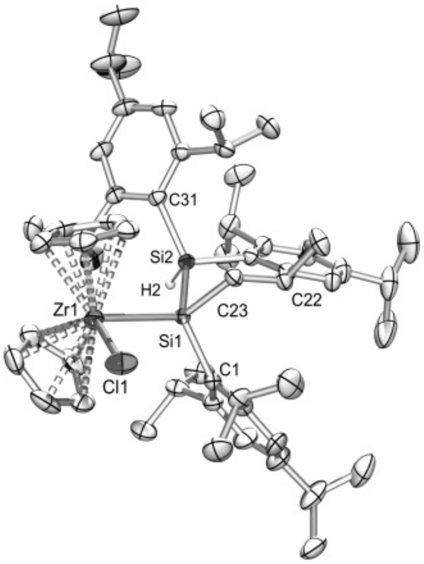


Figure 2. Structure of *l*,*l*-**3** in the solid state. H atoms, except for H2, are omitted for clarity. Ellipsoids at 50%. Selected bond lengths (Å): Si1−Si2 2.3827(6), Si2−H2 1.327(19), Si1−Zr1 2.8214(4), Si1−C23 1.9161(15), Zr1−Cl1 2.4181(5), Si1−C1 1.9527(15), Si2−C16 1.8937(16), Si2−C31 1.9189(15). Selected bond angles (°): Cl1−Zr1−Si1 101.461(17), Si2−Si1−Zr1 119.194(18), Zr1−Si1−C1 118.32(5), C1−Si1−Si2 109.71(5), C1−Si1−C23 103.45(7), Si2−Si1−C23 89.11(5), Zr1−Si1−C23 112.12(5).

The ^{29}Si NMR shifts of *l*,*l*-**3** at $\delta = -46.1$ and -8.4 ppm are indicative of the absence of a Si═Si bond. The formal addition of a methyl C−H bond of one of the *o*-isopropyl moieties was verified by 2D-^{29}Si−^{1}H experiments. The UV−vis absorption of *l*,*l*-**3** at 490 nm is in accordance with the deep-red color usually observed for zirconocene(chloro)silylcomplexes.[15]

X-ray crystallography proved the stereochemistry of *l*,*l*-**3** (Figure 2).[9] The achiral point group $P\bar{1}$ implies that both enantiomers are present as symmetry equivalents in the lattice. While Si1−Zr1 is significantly longer than that in **2**, Zr1−Cl1 is noticeably shorter. These changes could be attributed to a significantly weaker interaction between Zr1 and the σ-bonded silyl ligand in **3**. However, it has been shown that the Zr−Si and Zr−Cl distances in complexes such as **3** can depend on the steric congestion of the silyl group.[15]

In conclusion, we have shown that the Si═Si bond in the first η^1-disilenide transition metal complex **2** is considerably activated by the σ-coordination to zirconium. The enhanced reactivity leads to an unprecedented addition to a methyl C−H bond of the substituents, affording the silyl zirconocene complex **3**. Investigations of the reactivity of **2** toward nucleo- and electrophiles are currently underway.

Acknowledgment. Funding of this work by the Deutsche Forschungsgemeinschaft (DFG SCHE 906/3-1) is gratefully acknowledged. The author thanks Prof. H. Braunschweig for continuous support, and Dr. R. Bertermann for NMR spectroscopy.

Supporting Information Available: Details of the synthesis and structure determinations of **2** and **3**. The X-ray crystallographic data are supplied in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) For experimental details, see Supporting Information. Compound **2**: air-sensitive green solid; ^{1}H NMR (C_6D_6, 500 MHz) δ 7.11, 7.07, 6.97 (s, 2H each, Ar*H*), 5.91 (s, 10H, Cp*H*), 4.23, 4.10, 3.55, 2.79, 2.73, 2.64 (hept., 9H, *i*PrC*H*), 1.46, 1.39, 1.33, 1.20, 1.14, 1.08 (d, 54H, *i*PrCH_3); ^{13}C NMR (C_6D_6, 125 MHz) δ 155.14, 154.89, 154.73, 151.46, 150.42, 148.96, 142.24, 140.34, 138.14 (Ar*C*), 122.64, 122.28, 122.02 (Ar*C*H), 111.08 (Cp*C*), 38.30, 37.23, 36.17, 34.74, 34.68, 34.33 (*i*Pr*C*H), 26.43, 24.86, 24.13, 23.86 (*i*Pr*C*H_3); ^{29}Si NMR (C_6D_6, 99 MHz) δ 152.5 (Zr*Si*), 116.8 (*Si*Ar_2); UV−vis (hexane) λ_{max}/nm (ϵ) 416 (3000), 715 (7000). Compound **3**: air-sensitive red solid; mp 154 °C dec; ^{1}H NMR (C_6D_6, 500 MHz) δ 7.20, 7.11, 7.05, 6.93, 6.91 (s, 6H, Ar*H*), 5.914, 5.910 (s, 10H, Cp*H*), 5.74 (d, 1H, $^4J = 2.44$ Hz, Si*H*), 3.83, 3.66, 3.60, 3.35, 2.78, 2.73, 2.62 (hept., 9H, *i*PrC*H*), 2.31 (pseudo-dt, 1H, $^2J = 15.37$ Hz, SiCH_2), 2.18 (dd, dt, 1H, $^2J = 15.49$ Hz, SiCH_2), 1.64, 1.59, 1.51, 1.48 (d, 15H, *i*PrCH_3), 1.44, 1.36 (br, 9H, *i*PrCH_3), 1.25, 1.20, 1.19, 1.17, 1.10, 1.09, 0.90, 0.81 (d, 27H, *i*PrCH_3); ^{13}C NMR (C_6D_6, 125 MHz) δ 156.63, 156.30, 155.45, 155.23, 154.60, 152.16, 150.39, 148.85, 148.24, 137.32, 134.85, 130.35 (Ar*C*), 126.83, 122.94, 122.20, 121.64, 121.48, 120.67 (Ar*C*H), 111.62, 111.48 (Cp*C*), 38.88, 36.00, 35.10, 34.67, 34.57, 34.31, 34.12, 33.45, 33.06 (*i*Pr*C*H), 31.06 (*i*Pr*C*H_3), 30.67 (Si*C*H_2), 28.64, 27.39, 27.27, 26.36, 26.05, 25.48, 25.40, 24.84, 24.54, 24.30, 24.13, 24.05, 24.03, 24.00, 23.91 (*i*Pr*C*H_3); ^{29}Si NMR (C_6D_6, 99 MHz) δ -8.4 (*Si*CH_2), -46.1 (*Si*H); UV−vis (hexane) λ_{max}/nm (ϵ) 490 (1400). Anal. Calcd for $C_{55}H_{79}ClSi_2Zr$: C, 71.56; H, 8.63. Found: C, 71.42; H, 8.26.
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JA052593P