Silylene Complexes

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Fourteen-Electron Bis(dialkylsilylene)palladium and Twelve-Electron Bis(dialkylsilyl)palladium Complexes**

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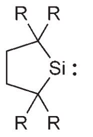
In memory of Hans Bock

Stable transition-metal complexes with divalent silicon ligands (silylene complexes) have been extensively studied because of their important role in many catalytic processes.[1] Since the pioneering works by Zybill et al.[2] and Tilley et al.,[3] various base-stabilized and base-free silylene complexes have been synthesized and their versatile reactivity has been well explored.[1] Although complexes with two or more silylene ligands are expected to show interesting bonding properties and reactivities that are not observed in monosilylene complexes, such complexes are still limited to donor-bridged bis(silylene) complexes[4] and complexes having cyclic diaminosilylenes as ligands.[5] During the course of our study on the application of dialkylsilylene **1**, which is the least electronically perturbed of the currently known stable silylenes,[6] to the synthesis of new stable unsaturated silicon compounds,[7] we successfully synthesized the bis(dialkylsilylene)palladium complex **2**, which is the first dicoordinate 14-electron palladium complex containing two silylene ligands.[8] The reaction of **2** with molecular hydrogen gives the first isolable 12-electron dicoordinate Pd complex **3**. Although these two complexes have similar bulky ligands, the Si-Pd-Si bond angle of **3** is much narrower than that of **2**. The structural difference between these two dicoordinate palladium complexes can be explained using a modified Walsh diagram.



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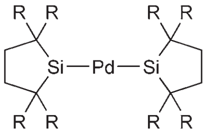

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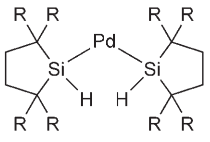

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R = SiMe$_3$

The bis(silylene) complex **2** was synthesized in 40 % yield by a simple ligand-exchange reaction between bis(tricyclohexylphosphine)palladium and silylene **1** in benzene [Eq. (1)].[9,10]

$$[(Cy_3P)_2Pd] \xrightarrow[C_6H_6,\ RT]{\mathbf{1}\ (2\ equiv)} \mathbf{2} \tag{1}$$

Recrystallization from toluene gave pure **2** as air- and moisture-sensitive dark red crystals with a decomposition temperature of 124 °C. The structure of **2** was determined by NMR spectroscopy, elemental analysis, and X-ray crystallography (see the Experimental Section). The ^{29}Si resonance of the two unsaturated silicon nuclei of **2** is found at $\delta =$ 448 ppm, which is more than 100 ppm to higher field than the corresponding resonance of the free silylene **1** ($\delta =$ 567 ppm)[6] but lower than those of known donor-free neutral silylene complexes ($\delta = 366$–414 ppm).[11] This value for the chemical shift indicates the donor-free nature of **2** in solution.

Figure 1 shows the molecular structure of **2**, as determined by X-ray analysis.[12] The two crystallographically independent molecules observed in the asymmetric unit have very

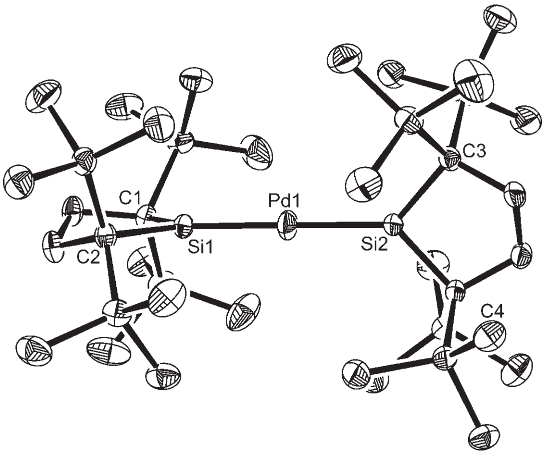

Figure 1. Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. One of the two crystallographically independent molecules with similar geometrical parameters that are present in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: Si1–Pd1 2.263(1), Si2–Pd1 2.260(1); Si1-Pd1-Si2 179.28(4), C1-Si1-Si2-C3 94.07(22).

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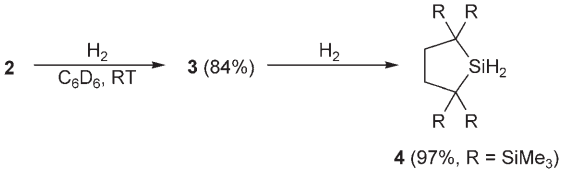
similar structural characteristics. Two dialkylsilylene ligands coordinate in an almost linear manner to the central palladium with a Si1-Pd1-Si2 angle of 179.28(4)°. The geometry around Si1 and Si2 is planar, with a sum of the bond angles of 359.99(12)° and 360.00(13)°, respectively. The two silacyclopentane rings in **2** are almost perpendicular to each other (C1-Si1-Si2-C3 dihedral angle of 94.07(22)°). The Si−Pd distances in **2** [2.263(1) and 2.260(1) Å] are almost equal to the corresponding Si−Pd distance (2.269(2) Å) in the bis(silyl)bis(diaminosilylene)palladium complex reported by Lappert et al.[5h] The linear and perpendicular arrangement of the two silylene ligands in **2** resembles that of the two cyclic carbene ligands in biscarbene complexes.[8a,c,d]

Although complex **2** has vacant coordination sites at the central palladium atom, no significant agostic interactions between Pd and the protons of the $SiMe_3$ groups are observed; the closest Pd···C distance of 3.95 Å is larger than the sum of the van der Waals radii of palladium and a methyl group.[13]

Complex **2** reacts with molecular hydrogen immediately in [D_6]benzene at room temperature to give the unprecedented bis(hydrosilyl)palladium complex **3**, which was isolated as orange crystals in 84% yield (see Scheme 1 and the Experimental Section); dialkylsilylene **1** does not react with molecular hydrogen. To the best of our knowledge, complex **3** is the first formal 12-electron dicoordinate palladium complex to be reported.[14] Complex **3** decomposes by slow reaction with the excess hydrogen to give the corresponding dihydrosilane **4**[15] in 97% yield (Scheme 1).[16]



Scheme 1. The reactions of **2** with molecular hydrogen.

The X-ray crystal structure of **3**[12] shows its remarkable bent structure, which is in contrast to the linear nature of complex **2**. The two dialkylsilyl groups of **3** coordinate to the central palladium with a Si1-Pd1-Si2 angle of 96.98(3)° (Figure 2). The Si−Pd distances in **3** (2.324(1) and 2.304(1) Å) are at the shorter end of known Si−Pd single-bond distances (2.300–2.565 Å).[17] The Si−H hydrogen atoms are bound to the silicon atoms and no significant interaction between these hydrogen atoms and the palladium center is observed. Significant agostic interactions between Pd and the hydrogen atoms of the $SiMe_3$ groups are, however, observed; the closest Pd···C distances are 2.709 and 2.832 Å.[12] The ^1H and ^{13}C NMR spectra of **3** show two singlets due to two types of Me_3Si groups, thereby indicating that rotation of the two hydridosilyl groups around the Si−Pd bonds is rapid in solution despite the agostic interactions found in the solid state.[18] The resonance for the SiH protons of **3** is observed at $\delta = 4.82$ ppm with a $^1J_{Si,H}$ coupling constant of 188.1 Hz, which is in the range of those typically found for hydridosilyl transition-metal complexes (143–219 Hz).[19] The ν_{SiH} band in the IR spectrum of **3** in hexane solution appears at higher wavenumber (2121 cm^{-1}) than those of *cis*-bis(phosphine)-bis(dialkylsilyl)palladium complexes (2008–2070 cm^{-1}).[20]

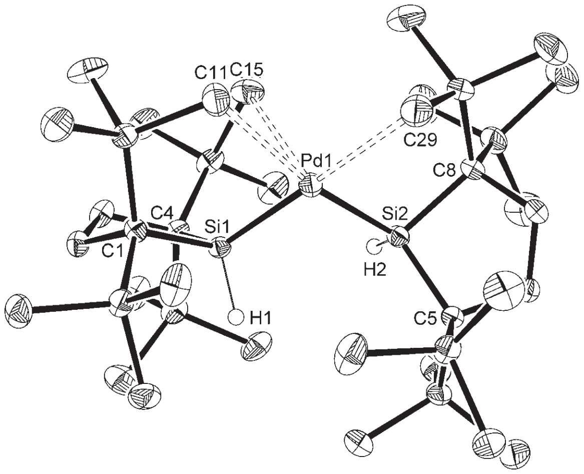
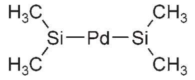


Figure 2. Molecular structure of complex **3**. Carbon-bound hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si1−Pd1 2.324(1), Si2−Pd1 2.304(1); Si1-Pd1-Si2 96.98(3), C1-Si1-Pd1-Si2 166.26(10), C4-Si1-Pd1-Si2, −80.98(13), C5-Si2-Pd1-Si1 −94.01(12), C8-Si2-Pd1-Si1 156.69(11). Distances [Å] between Pd and methyl carbon atoms of $SiMe_3$: Pd1···C11 2.709, Pd1···C15 3.554, Pd1···C29 2.832.

The remarkable structural difference between the dicoordinate 14-electron complex **2** and the 12-electron complex **3**, which have similar bulky ligands, is worthy of discussion. The linear Si-Pd-Si arrangement observed for **2** is not surprising as 14-electron dicoordinate Group 10 metal complexes such as [$(R_3P)_2M$] (M = Pd, Pt) are known to adopt a linear geometry.[21] The reason for this geometry can readily be understood from the qualitative Walsh diagram for the change of P-M-P angle.[22] However, this discussion should be modified for bis(silylene) complex **2** to take into account the secondary effects of π back donation on the geometry. Density functional calculations[23] have shown that the optimized geometry of **5** is significantly bent, with a Si-Pd-Si bond angle of 116.7°,



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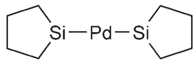

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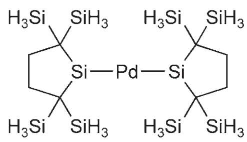

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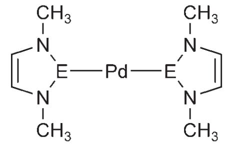
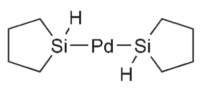


8, E = Si; **9**, E = C



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and that the angle at the optimized geometry increases with increasing bulkiness of silylene ligands; the Si-Pd-Si angles for **6** and **7**, for example, are 118.8° and 135.4°, respectively.[24] The theoretical calculations reported herein indicate that the skeleton of 14-electron palladium complexes coordinated by two silylene ligands is intrinsically bent due to the π back donation[25] and that it is rather flexible and sensitive to the steric bulkiness of the silylene ligands. The fact that the bis(silylene)palladium complex **2** has a linear skeleton is thus rationalized by the steric effects of the bulky silylene ligands overwhelming the secondary electronic effects.

Although the geometry of 12-electron dicoordinate palladium complexes ($[R_2Pd]$, R = alkyl, aryl, silyl) has not been explicitly discussed either experimentally or theoretically, the Si-Pd-Si skeleton is expected to primarily be bent, with a steeper bending potential surface, on the basis of the qualitative discussion using the Walsh diagram.[26] The strongly bent geometry of **3**, despite this complex having bulky silyl ligands, is compatible with this view. The Si-Pd-Si angle for the optimized geometry of bis(silyl)palladium complex **10**[23] is calculated to be 95.7°, which is much narrower than that for the bis(silylene)palladium complex **6**.

Experimental Section

2: Dry benzene (2.5 mL) was transferred by vacuum line onto a mixture of bis(tricyclohexylphosphine)palladium (50.0 mg, 0.0749 mmol) and **1** (61.5 mg, 0.165 mmol) in a Schlenk flask (30 mL) equipped with a magnetic stir bar. The mixture turned dark red after it had been stirred for 48 h under argon. The solvent was removed in vacuo and dry toluene was added. Recrystallization from toluene at −35 °C gave analytically pure complex **2** (25.4 mg, 0.0298 mmol, 40 % yield). Single crystals of **2** suitable for X-ray diffraction study were obtained by recrystallization from toluene at −35 °C. **2**: air-sensitive dark red crystals; m.p. 124 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 0.46$ (s, 72H; SiCH$_3$), 2.08 ppm (s, 8H; CH$_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene): $\delta = 3.5$ (SiCH$_3$), 35.4 (CH$_2$), 50.3 (C(SiCH$_3$)$_2$); ^{29}Si NMR (79 MHz, [D$_6$]benzene): $\delta = -1.14$ (SiCH$_3$), 447.7 ppm (Si); UV/Vis (hexane): $\lambda_{\max}$ (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 263 (11 000), 323 (9900), 402 (3300), 544 nm (1300); Elemental analysis (%) calcd for $C_{32}H_{80}PdSi_{10}$: C 45.10, H 9.46; found: C 44.99, H 9.20.

3: Exposure of a dry [D$_6$]benzene (0.5 mL) solution of **2** (20.0 mg, 0.0235 mmol) to one atmosphere of hydrogen pressure at 27 °C (2.2 mL, 0.089 mmol) resulted in immediate formation of an orange solution. Removal of the solvent in vacuo and then recrystallization from toluene at −35 °C gave analytically pure **3** (16.9 mg, 0.0198 mmol, 84 % yield). Single crystals of **3** suitable for X-ray diffraction study were obtained by recrystallization from toluene at −35 °C. Dihydrosilane **4** formed in 97 % yield when the solution of **2** was kept under one atmosphere of hydrogen pressure for 10 days, as determined by NMR spectroscopy. **3**: air-sensitive orange crystals; m.p. 103 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 0.35$ (s, 36H; SiCH$_3$), 0.41 (s, 36H; SiCH$_3$), 1.90 (s, 8H; CH$_2$), 4.82 ppm (s, $^1J_{\text{Si,H}} = 188.1$ Hz, 2H; Si-H); ^{13}C NMR (100 MHz, [D$_6$]benzene): $\delta = 3.2$ (SiCH$_3$), 4.5 (SiCH$_3$), 14.2 (C(SiCH$_3$)$_2$), 34.9 ppm (CH$_2$); ^{29}Si NMR (79 MHz, [D$_6$]benzene): $\delta = 1.3$ (SiCH$_3$), 3.8 ppm (SiCH$_3$), 25.8 ppm (SiH); Elemental analysis (%) calcd for $C_{32}H_{82}PdSi_{10}$: C 44.99, H 9.68; found: C 45.19, H 9.78; IR (n-hexane) $\tilde{\nu}_{\text{SiH}} = 2121\ \text{cm}^{-1}$.

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[17] The Si−Pd single bond distances were obtained from the Cambridge Crystallographic Database (http://www.ccdc.cam.ac.uk).

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[23] The basis sets used were 6-31G* for Si, C, N, and H and Lanl2dz for Pd. See the Supporting Information for details of the calculations.

[24] The linear geometries for bis(silylene)complexes **5**–**7**, which have approximate D_{2d} symmetry, are not local minima but a saddle point with two imaginary frequencies. As expected, the energy difference between the bent and linear geometries $[\Delta E = E(\text{linear}) - E(\text{bent})]$ decreases with increasing bulk of the silylene ligands: $\Delta E = 7.2$, 6.0, and 3.5 kcal mol^{-1} for **5**, **6**, and **7**, respectively.

[25] The low-lying vacant π orbital of silylene is indispensable for effective π back donation; the Si-Pd-Si angles in the optimized structures of palladium complexes **8** and **9**, which have rather higher vacant pπ orbitals due to the donation of the nitrogen lone-pair electrons, are 153.2° and 180.0°, respectively. Previous theoretical studies using a different density functional method have also shown that **9** and other bis(carbene)palladium complexes adopt similar linear skeletal geometries: J. C. Green, R. G. Scurr, P. L. Arnold, F. G. N. Cloke, *Chem. Commun.* **1997**, 1963; J. C. Green, B. J. Herbert, *Dalton Trans.* **2005**, 1214. The density funcitonal calculations reported herein show that the LUMO levels of dialkylsilylene, diaminosilylene, and diaminocarbene increase in this order.[23]

[26] See the Supporting Information for a qualitative explanation of the bent geometry as well as the significant agostic interaction in 12-electron dicoordinate metal complexes using the Walsh diagram.