

Synthesis and Unexpected Coordination of a Silicon(II)-Based SiCSi Pincerlike Arene to Palladium**

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Dedicated to Professor Akira Sekiguchi on the occasion of his 60th birthday

Chelate ligands can be important for steering the reactivity of transition-metal complexes. Among multidentate ligands, pincer arenes, consisting of a central aromatic backbone linked to two-electron Lewis donor atoms (E) by different spacers, are particularly attractive because of their feasible structural tuning with many choices of donor groups.^[1,2] Recently, the chemistry of pincer-ligated transition-metal complexes underwent rapid developments and has been used for several intriguing chemical transformations.^[2,3] The coordination chemistry of the most common pincer ligands such as NCN-, PCP-, and SCS-type ligands toward transition metals in **A** (Figure 1) has been explored extensively.^[3] Pincer arenes

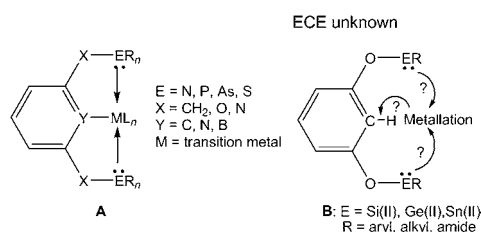
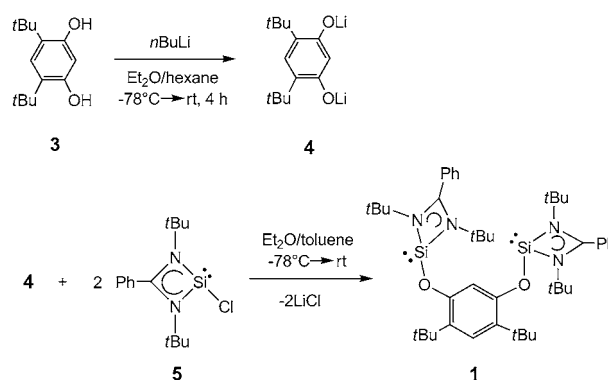


Figure 1. Pincer complexes **A** and currently unknown Group 14 metallylene-based ECE pincer arenes **B** for facile metallation of the benzene backbone.

with stronger σ -donor sites E than those provided by Group 15 and 16 atoms are very attractive for the synthesis of more electron-rich transition-metal complexes for activation of small molecules. Promising new ligands are pincer arenes **B** having divalent heavier Group 14 elements which could mediate facile C–H activation in the 2 position of the benzene ring by a metal (Figure 1). However, pincer arenes **B**

are currently unknown, despite the fact that isolable metallylenes^[4] are no longer laboratory curiosities and can serve at the same time as much stronger σ -donor and π -acceptor ligands toward transition metals than phosphine ligands.^[5,6] Up to now only a few isolable bis-silylenes with a Si–Si bond are known^[7a–d] and a 4,4'-biphenyl-bis-silylene^[7e] and Si₂N₂ four-membered ring bis-silylene^[7f] have been reported. Very recently we described the synthesis of an isolable bis-silylene oxide and its nickel complex.^[8] This encouraged us to attempt the synthesis of a silicon(II)-based pincer ligand **B** and to test its coordination ability towards a metal. We report herein the synthesis and characterization of the first bis-silicon(II)-based SiCSi pincer arene ligand **1** bearing amidinate chelate ligand for stabilizing the Si^{II} atom. Moreover, we describe the unusual coordination ability of **1** towards tetrakis(triphenylphosphine)palladium, which proceeds in the molar ratio of 2:1 to afford the unexpected bis-silylene-silyl(phenyl)-palladium(II) complex **2** through insertion of Pd⁰ into the C–H bond in 2 position of the benzene backbone of **1** and subsequent 1,2-hydride shift from palladium to a silicon atom of **1**.

The SiCSi pincer ligand **1** can be easily synthesized following the protocol as shown in Scheme 1. Dilithiation of 4,6-di-*tert*-butylresorcinol **3** with *n*BuLi gives the correspond-



Scheme 1. Synthesis of SiCSi pincer arene **1**.

ing 1,3-dilithium resorcinolate **4**. Its salt metathesis reaction with the N-donor stabilized chloro silylene LSiCl [L(amidinate) = PhC(NtBu)₂] **5**^[9] in the molar ratio of 1:2 furnishes the desired compound **1**, which could be isolated as pale yellow crystals in 79% yield (Scheme 1). The constitution and composition of **1** was established by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, and elemental analysis. The ¹H NMR spectrum

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of **1** shows one singlet for the *t*Bu groups and one set of resonances for the Ph groups of the amidinate ligands. The almost identical variable-temperature (VT) ^1H NMR spectra of **1** in C_7D_8 in the temperature range of 210 to 320 K indicates relatively low rotation barriers of the Si–O bonds on the NMR time scale. In the ^{29}Si NMR spectrum, a sharp singlet was detected at $\delta = -24.0$ ppm, which is comparable to that observed for alkoxy-substituted silylenes LSiOR ($\text{R} = t\text{Bu}$, *i*Pr, Me).^[10] The molecular structure of **1** was confirmed by a preliminary single-crystal X-ray diffraction analysis (see the Supporting Information); however the moderate crystal quality disallows discussion of metric parameters. Nevertheless, the analysis proves that the two silylene-like moieties in **1** face in the almost same direction (Scheme 1). To obtain detailed structural information of **1**, DFT calculations [B3LYP/6-31G(d)] were performed.^[17] The geometry of **1** obtained by X-ray crystallographic analysis was used as the initial structure. The optimized structure of **1** is displayed in Figure 2. The Si1–O1–C1 angle (141.79°) is larger than that

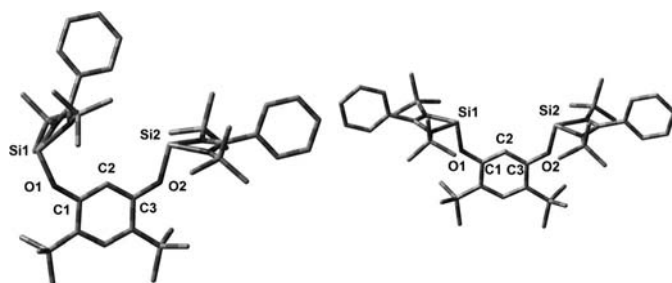
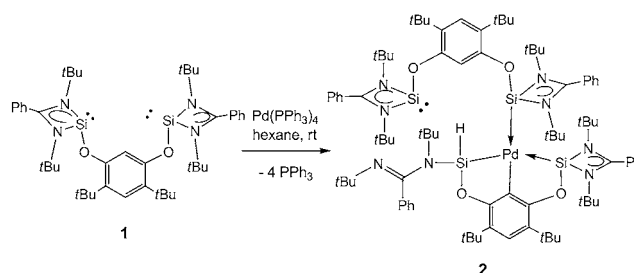


Figure 2. Optimized structures of bis(silylene)-like SiCSi pincer ligand **1** (left) and its rotational isomer **1'** (right) at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **1** and **1'**: compound **1**, Si1–O1 1.7056, Si2–O2 1.71905; Si1–O1–C1 141.79, Si2–O2–C3 132.17; compound **1'**, Si1–O1 1.7294, Si2–O2 1.7294; Si1–O1–C1 130.28, Si2–O2–C3 130.28.

of Si2–O2–C3 (132.17°). While the dihedral angle of Si1–O1–C1–C2 is 24.37° , the dihedral angle of Si2–O2–C3–C2 is 0.39° .

The Si–O single bond distances of 1.7056 and 1.7190 Å are little longer than those of bis-silylene oxide LSiOSiL [1.641(2) and 1.652(2) Å]^[8] and alkoxy silylenes LSiOR ($\text{R} = t\text{Bu}$, *i*Pr) [1.6442(3) and 1.6501(2) Å] owing to steric congestion.^[10] We could also identify the C_2 -symmetric rotational isomer **1'** as stable form on the hyperpotential energy surface which is only $1.8 \text{ kcal mol}^{-1}$ less stable than **1**. Interestingly, the Si–O distance of **1'** is even slightly longer than those of **1**. The bond rotation barrier of the Si–O bonds in **1** and **1'** are similar and estimated to be $+8.0 \text{ kcal mol}^{-1}$ by theoretical calculation.

Although bis-silylene **1** bearing an amidinate ligand may not serve as a π acceptor, bis-silylene **1** could work as a strong σ -donor ligand. To probe the pincer-type coordination ability of **1**, its reactivity towards phosphine palladium(0) complexes was investigated. Treatment of **1** with 0.5 equivalents of tetrakis(triphenylphosphine)palladium, $\text{Pd}(\text{PPh}_3)_4$, in hexane at room temperature afforded the unprecedented bis-silylene-silyl(phenyl)palladium(II) complex **2** as sole product, which could be isolated as orange crystals in 81 % yield (Scheme 2).



Scheme 2. Formation of **2** from reaction of **1** with $\text{Pd}(\text{PPh}_3)_4$ in the molar ratio of 2:1.

A different type of silylene–silyl metal complexes has been described by Ogino and co-workers.^[11] Compound **2** was fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis. The formation of **2** implies that two equivalents of **1** were consumed. When a 1:1 molar ratio of starting materials was applied, a smaller yield of **2** ($< 40\%$) was obtained but no other product or intermediate could be detected by ^1H NMR spectroscopy. The molecular structure of **2** is shown in Figure 3.^[12] Remarkably, compound **2** crystallizes as racemic mixture of its *R* and *S* enantiomers, of which only the *S* form is presented in Figure 3. The Pd^{II} atom adopts a typical distorted square-planar configuration defined by the two silylene Si^{II} atoms, Si2 and Si3, the silyl Si^{IV} atom Si1, and the carbon atom C1 of the central aryl ring. Interestingly, during the complexation, the former Si1–N2 bond in **1** is disrupted because of the formation of a Si–H silyl group through 1,2-hydride shift from palladium to silicon. Owing to the coordinative saturation of the Pd center, one silylene subunit (Si4) remains “free”. The bent Si3–Pd1–C1 angle of $167.83(12)^\circ$ in **2** is contrary to the linear X–Pd–C ($\text{X} = \text{Cl}$, I, Ph, 4-fluorophenyl,

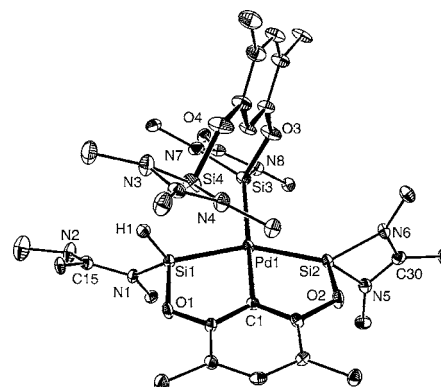
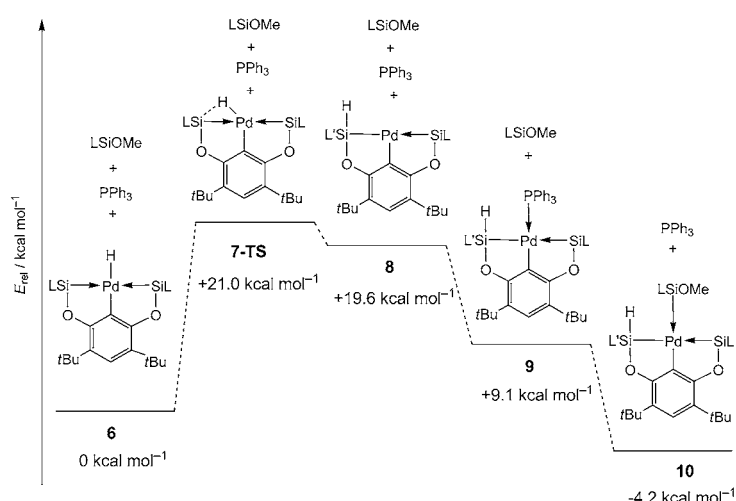


Figure 3. Molecular structure of **2**. The compound crystallizes as racemic mixture of its *S* and *R* enantiomers. Only the *S* form is shown. Thermal ellipsoids are drawn at a probability level of 30%. Hydrogen atoms, *t*Bu groups, and phenyl groups are omitted for clarity, except for the H1 atom. Selected bond lengths [Å] and angles [°]: Pd1–C1 2.125(3), Pd1–Si1 2.3561(12), Pd1–Si2 2.3271(12), Pd1–Si3 2.3038(11), Si1–O1 1.694(3), Si1–N1 1.789(4), Si2–O2 1.675(3), Si2–N5 1.862(3), Si2–N6 1.840(4), Si3–O3 1.662(3), Si3–N7 1.888(3), Si3–N8 1.860(3), Si4–O4 1.704(3), Si4–N3 1.893(4), Si4–N4 1.892(4); Si1–Pd1–Si2 155.03(4), Si1–Pd1–C1 78.61(11), Si2–Pd1–C1 76.81(11), Si3–Pd1–C1 167.83(12).

OCOCF₃, etc.) angles of reported palladium(II) complexes supported by a PCP type pincer arene ligand.^[3,13] The Si1-Pd1-Si2 angle of 155.03(4)° deviates from the linear alignment, and is smaller than the respective P-Pd-P angle of the PCP pincer-type palladium complex.^[3,13] The Si2-Pd1 and Si3-Pd1 bond lengths (2.3271(12) and 2.3038(11) Å) of **2** are shorter than that of the Si1-Pd1 distance (2.3561(12) Å), reflecting the difference between a silyl ligand (Si1) with a Si^{IV}-Pd single bond vs. a silylene ligand (Si2 and Si3) with a Si^{II}→Pd dative bond. However, the Si2-Pd1 and Si3-Pd1 distances in **2** are similar with those of other silylene→palladium complexes.^[14,15] Furthermore, the Pd1-Cl_(aryl) bond length of **2** (2.125(3) Å) is longer than those of reported PCP pincer-type palladium(II) complexes, presumably because of steric congestion.^[3,13]

Consistent with its crystallographic analysis, the ¹H and ¹³C NMR spectra of **2** show twelve sets of nonequivalent *t*Bu groups. Moreover, the resonance for the Si-H proton is observed at δ = 6.59 ppm. The ²⁹Si NMR spectrum of **2** in C₆D₆ displays four signals at δ = -8.7 (L(Si:), Si4), 39.7 (SiH, Si1), 62.3 and 65.8 ppm (L(Si:)-Pd, Si2 and Si3), respectively. The chemical shift of the Si-H Si^{IV} atom (Si1) is shifted upfield in comparison to those of a related HSi→Pd complex reported by Kira, Iwamoto and co-workers because of the electronegative N and O atoms bound to the Si1 atom.^[14] The ²⁹Si resonances of the two Si^{II} atoms, Si2 and Si3, coordinated to the palladium center are comparable to those of other amidinate-based silylene complexes^[16] and significantly shifted to higher field in comparison to those reported for donor-free silylene palladium complexes owing to the additional N-donor coordination of the amidinate ligand to the Si^{II} atom. In addition, the infrared spectrum of **2** shows a weak Si-H stretching vibration band at 2135 cm⁻¹. The observed stretching frequency of **2** is higher than those of other reported palladium hydridosilyl complexes (2008–2121 cm⁻¹).^[13c,g,14]

To rationalize the peculiar reactivity of **1** towards Pd(PPh₃)₄, quantum chemical calculations using density functional theory (DFT) at the B3LYP level using 6-31G(d) basis set for H, C, N, O, P, and Si atoms and the LANL2DZ level for the Pd atom with the Gaussian 03 program for model compounds **6–10** have been performed.^[17] A schematic representation of the potential energy surface of the proposed pathway for the formation of **2** is given in Scheme 3. We assume that **6** is formed as initial intermediate, resulting from stepwise dissociation of phosphine ligands of Pd(PPh₃)₄ and insertion reaction of Pd⁰ into the pincer C-H bond of the central aryl ring of **1**. Subsequently, the 16-valence electron Pd^{II} complex **6** can undergo 1,2-hydride migration from palladium to a silicon(II) donor atom to form the 14-valence electron silylene silyl(aryl)palladium(II) complex **8** as second intermediate. The latter process occurs through transition state **7-TS** with a barrier of +21.0 kcal mol⁻¹, and **8** is only 1.4 kcal mol⁻¹ more stable than **7-TS**. The electron-deficient Pd^{II} complex **8** could easily undergo coordination with a phosphine ligand or silylene donor moiety of “free” **1**,



Scheme 3. DFT-derived relative energies of model compounds **6–10** [L = 1,3-μ₂-PhC(N*t*Bu)₂, L' = μ₁-(N*t*Bu)C(Ph)=N*t*Bu].

resulting in the formation of more stable 16-electron complexes. Accordingly, the calculated relative energies of P→Pd complex **9** stabilized by PPh₃ and Si→Pd complex **10** stabilized by methoxy silylene LSiOMe (L = PhC(N*t*Bu)₂) as model silylene donor are +9.1 and -4.1 kcal mol⁻¹, respectively. Since Si^{II} of intramolecular N-donor stabilized silylenes is a stronger σ donor than P^{III} of phosphines, complex **10** is 13.3 kcal mol⁻¹ more stable than **9**. Overall, the stepwise transformation of **6** into **10** in the presence of PPh₃ and the model silylene LSiOMe is exothermic by 4.2 kcal mol⁻¹.

In conclusion, we have reported the synthesis and isolation of the first Si^{II}-based SiCSi pincer arene **1** and its unusual coordination behavior towards palladium. The enormous electron-rich Lewis donor character of Si^{II} in pincer arene **1** gives facile access to new oligosilylene silyl(phenyl) transition-metal complexes with potential application in catalytic chemical transformations. Further investigations using **1** for the synthesis of SiCSi pincer complexes with other transition metals and their use in homogeneous catalysis are currently in progress.

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