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Coordination Chemistry

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 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 Si_2N_2 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 Pd^0 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**.

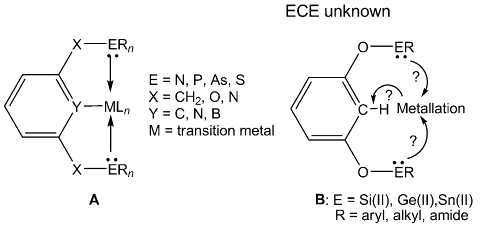
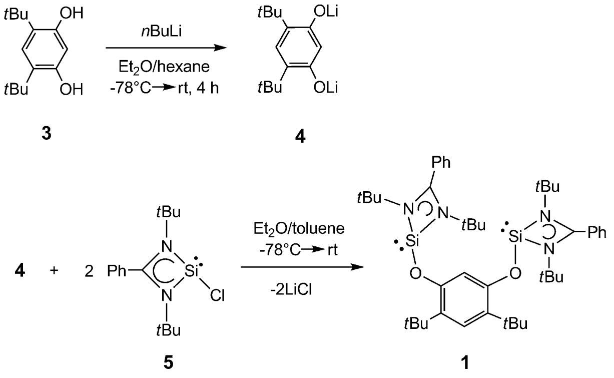


Figure 1. Pincer complexes **A** and currently unknown Group 14 metallylene-based ECE pincer arenes **B** for facile metallation of the benzene backbone.

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 corresponding 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, ^{13}C, and ^{29}Si NMR spectroscopy, and elemental analysis. The ^1H NMR spectrum



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

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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) ^{1}H 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 (R = *t*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 diplayed in Figure 2. The Si1-O1-C1 angle (141.79°) is larger than that 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°.

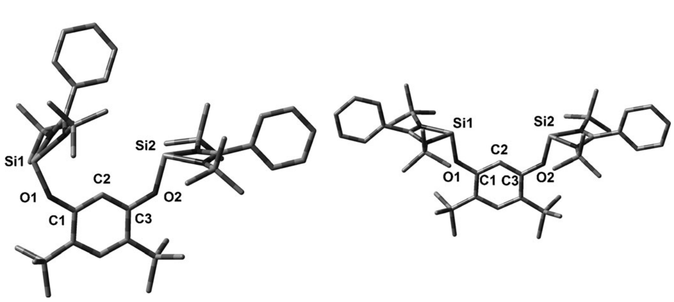
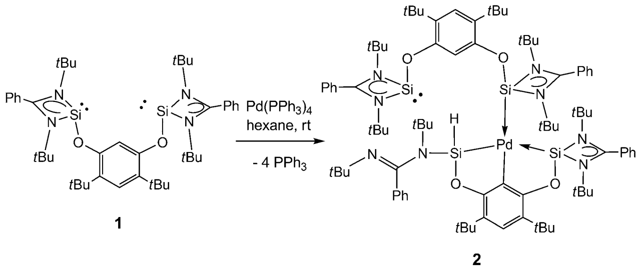


Figure 2. Optimized structures of bis(silylene)-like SiCSi pincer ligand **1** (left) and its rotational isomer **1′** (right) at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **1** and **1′**: compound **1**, Si1–O1 1.7056, Si2–O2 1.71905;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

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 (R = *t*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 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 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, Pd(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 Pd(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 ^{1}H 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)° in **2** is contrary to the linear X-Pd-C (X = Cl, I, Ph, 4-fluorophenyl,

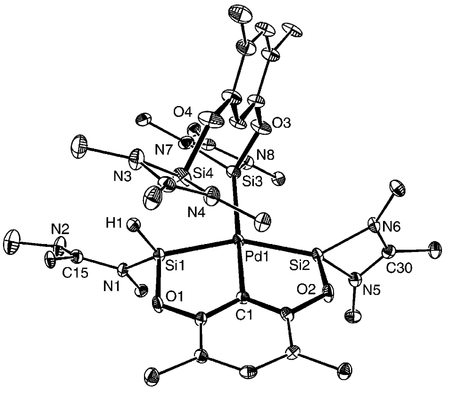
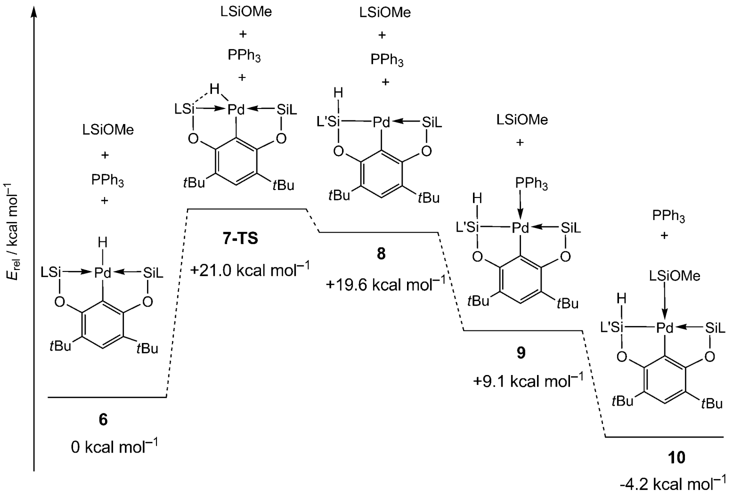


Figure 3. Molecular structure of **2**. The compound crystallizes as racemic mixture of its *S* and *R* enantiomers. Only the *S* form is shown. Thermal ellipsoids are drawn at a probability level of 30 %. Hydrogen atoms, *t*Bu groups, and phenyl groups are omitted for clarity, except for the H1 atom. 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).



Scheme 3. DFT-derived relative energies of model compounds **6–10** [L=1,3-μ_2-PhC(N*t*Bu)$_2$, L′=μ_1-(N*t*Bu)C(Ph)=N*t*Bu].

OCOCF$_3$, 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 $\mathrm{Si^{IV}}$–Pd single bond vs. a silylene ligand (Si2 and Si3) with a $\mathrm{Si^{II}}$→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–$\mathrm{C1_{(aryl)}}$ 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 ^{1}H and ^{13}C NMR spectra of **2** show twelve sets of nonequivalent *t*Bu groups. Moreover, the resonance for the Si–H proton is observed at $\delta = 6.59$ ppm. The ^{29}Si NMR spectrum of **2** in C_6D_6 displays four signals at $\delta = -8.7$ (L(*Si*:), Si4), 39.7 (*Si*H, Si1), 62.3 and 65.8 ppm (L(*Si*:)Pd, Si2 and Si3), respectively. The chemical shift of the Si–H $\mathrm{Si^{IV}}$ 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 ^{29}Si resonances of the two $\mathrm{Si^{II}}$ 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 $\mathrm{Si^{II}}$ 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(PPh$_3$)$_4$, 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(PPh$_3$)$_4$ and insertion reaction of Pd^0 into the pincer C–H bond of the central aryl ring of **1**. Subsequently, the 16-valence electron $\mathrm{Pd^{II}}$ 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 $\mathrm{Pd^{II}}$ complex **8** could easily undergo coordination with a phosphine ligand or silylene donor moiety of "free" **1**, resulting in the formation of more stable 16-electron complexes. Accordingly, the calculated relative energies of P→Pd complex **9** stabilized by PPh$_3$ 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 $\mathrm{Si^{II}}$ of intramolecular N-donor stabilized silylenes is a stronger σ donor than $\mathrm{P^{III}}$ 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 PPh$_3$ 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 $\mathrm{Si^{II}}$-based SiCSi pincer arene **1** and its unusual coordination behavior towards palladium. The enormous electron-rich Lewis donor character of $\mathrm{Si^{II}}$ 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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Keywords: chelates · pincer ligands · silicon · silylene complexes · transition metals

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