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Palladium and Platinum η^2-Disilyne Complexes Bearing an Isolable Dialkyldisilyne as a Ligand**

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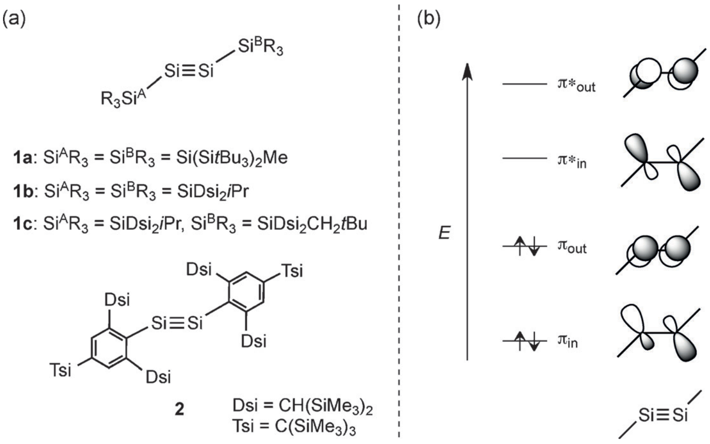
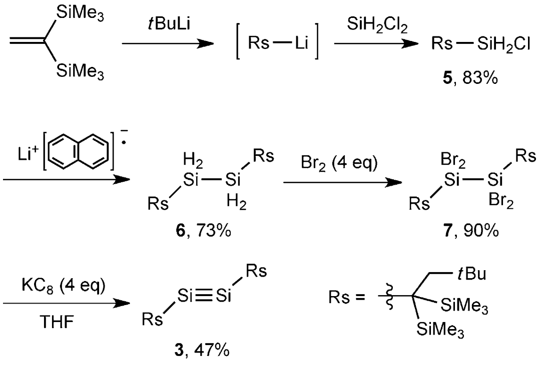
In the last decade, the chemistry of silicon–silicon triply bonded compounds (disilynes) has extensively developed since silyl- and aryl-substituted disilynes **1a**–**1c**[1–3] and **2**[4] are available as stable compounds (Scheme 1).[5,6] The detailed studies of disilynes unveiled that the silicon–silicon triple bonds adopt a *trans*-bent structure with two non-degenerate π bonds, these are the in-plane slipped π bond (π_{in}) and out-of-plane π bond (π_{out}), and the corresponding anti-bonding π^*_{in} and π^*_{out} orbitals as shown in Scheme 1b in contrast to alkynes which have two degenerated and orthogonal π(C≡C) bonds.[7] Consequently, disilyne should be a unique ligand for transition metals.[8] However, only theoretical studies on η^2-parent disilyne (HSi≡SiH) transition-metal complexes, such as [WCl$_4$(η^2-HSi≡SiH)],[9] [RhCl(PMe$_3$)$_2$(η^2-HSi≡SiH)],[10] and [Pt(PMe$_3$)$_2$(η^2-HSi≡SiH)],[10] and one experimental study on a η^1-(NHC-coordinated disilyne) zinc complex have been reported.[11] We report herein the synthesis and characterization of the missing dialkyl-substituted disilyne **3** (see Scheme 2) utilizing newly developed bulky alkyl group, 1,1-bis(trimethylsilyl)-3,3-dimethylbutyl (abbreviated as Rs group, hereafter) and its palladium and platinum η^2-disilyne complexes **4a** and **4b** showing a significant metallacycle character as the first η^2-disilyne complexes.



Scheme 1. a) Stable silicon–silicon triply bonded compounds. b) Schematic representation of π orbitals of disilyne.

Dialkyldisilyne **3** was synthesized from 1,1-bis(trimethylsilyl)ethylene as a starting material in four steps (Scheme 2). The regioselective carbolithiation of 1,1-bis(trimethylsilyl)ethylene with *t*BuLi and subsequent reaction with dichlorosilane gave RsSiH$_2$Cl (**5**).[12] Reductive coupling of **5** to form disilane **6** and the subsequent bromination provided tetrabromodisilane **7**. Finally, treatment of **7** with potassium graphite in THF at −78 °C afforded disilyne **3** in 47 % yield as a storable green crystalline solid.[13]

The molecular structure of disilyne **3** determined by X-ray structural analysis is shown in Figure 1.[14] The molecule has a crystallographic symmetry center at the



Scheme 2. Synthesis of disilyne **3**.

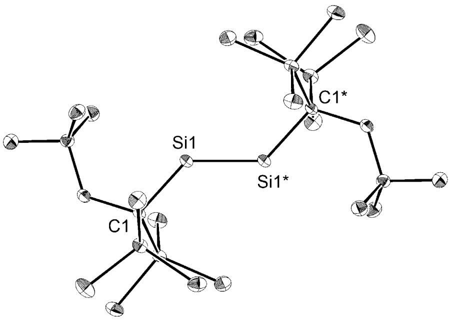


Figure 1. Molecular structure of **3**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si1* 2.0863(13), Si1–C1 1.8960(19); C1-Si1-Si1* 132.05(7), C1-Si1-Si1*-C1* 180.0.

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midpoint of the Si$\equiv$Si bond. Disilyne **3** has a *trans*-bent structure similar to disilynes **1b**, **1c**, and **2**. The C$-$Si$\equiv$Si angle of 132.05(7)° of **3** is slightly smaller than those of **1b** (137.44(4)°)[2] and **1c** (138.78(5)° and 137.89(5)°)[3] and comparable to that of diaryldisilyne **2** (133.0(3)°).[4] The two Rs groups are arranged in an anti-conformation with the dihedral angle C-Si-Si-C of 180°. The Si1–Si1* bond length is 2.0863(13) Å, which is much shorter than those of RsSiH$_2$–SiH$_2$Rs (**6**; 2.3706(9) Å), RsSiBr$_2$–SiBr$_2$Rs (**7**; 2.4776(9) Å), and within the range of the previously reported stable disilynes (2.0622(9) Å for **1b**, 2.0569(12) Å for **1c**, 2.108(5) Å for **2**). The ^{29}Si NMR spectrum obtained in C$_6$D$_6$ solution, showed a resonance signal for the unsaturated silicon nuclei in **3** was observed at $\delta = 31.8$ ppm similar to that of diaryldisilyne **2** ($\delta = 16.7$ ppm) and to the calculated value for $\mathbf{3}_{\text{fix}}$ at the GIAO/B3LYP/6-311+G(2df,p) level whose structural parameters are fixed to the experimentally determined structure ($\delta = 30.3$ ppm).[15]

A noticeable feature of **3** was found in UV/Vis spectrum (Figure 2). Disilyne **3** showed four absorption bands at 810 nm (ε 16, band I), 448 nm (ε 136, band II), 346 (ε 440, band III), and 309 nm (ε 3850, band IV) in hexane solution. The broad and very weak absorption band with the longest absorption maxima, band I, tails up to the near-IR region (1300 nm) and it can be assigned to $\pi_{\text{out}}\rightarrow\pi^*_{\text{in}}$ (HOMO→LUMO transition).[16] To our knowledge, this is the longest wavelength absorption band of diatomic chromophore of the main-group elements.[17] The absorption maxima of band I was remarkably red-shifted by 120 nm compared to that of **1b** (690 nm),[2] which can be explained by the higher-lying π_{out} orbital in **3** than in **1b**. The higher π_{out} orbital in **3** is due to the less-effective π-accepting character of alkyl groups compared to that of trialkylsilyl groups because trialkylsilyl groups adjacent to the π system effectively stabilize the π energy level due to the low-lying σ^*(Si-C) orbital.[18,19]

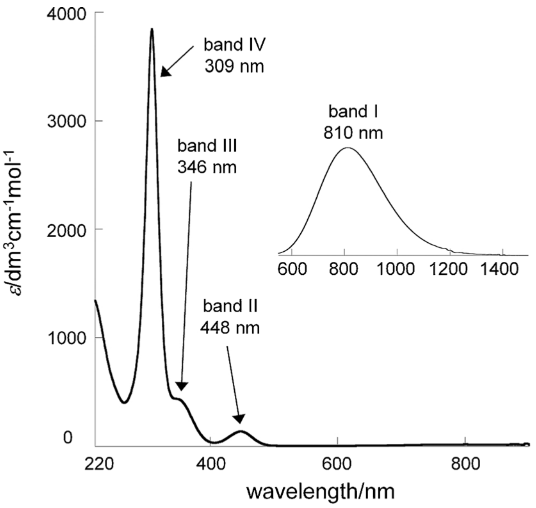
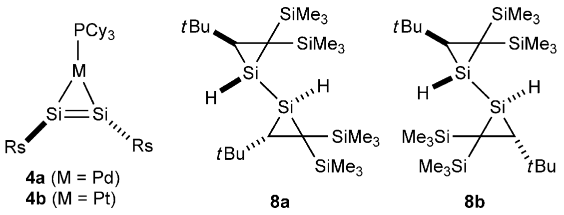


Figure 2. UV/Vis spectrum of **3** in hexane at room temperature. Inset: expansion of the region around 600–1400 nm.

Although disilyne **3** in the solid state did not decompose in an inert atmosphere at ambient temperature for several months, it isomerizes in solution quantitatively to a diastereomeric mixture of bi(silacyclopropane)s[20] **8a** and **8b** (Scheme 3) in approximately 1:1 ratio within 10 h at ambient temperature.[21,22] Similar C$-$H insertion was observed in thermal reaction of diaryldisilyne **2**.[4]



Scheme 3. Reaction products of disilyne **3** (see text for details).

Treatment of **3** with [(Cy$_3$P)$_2$Pd][23] gave a ligand-exchange product, mono(phosphine)palladium η^2-disilyne complex (**4a**) as a red crystalline solid in 76 % yield. Similarly, the reaction of **3** with [(Cy$_3$P)$_2$Pt][23] afforded the corresponding platinum complex **4b** in 36 % yield.

X-ray structural analysis revealed the striking features of complex **4a** (Figure 3) and **4b** (Figure S16 in Supporting Information). Complex **4a** is a hitherto unknown transition-metal η^2-disilyne complex; the disilyne moiety coordinates almost symmetrically to the palladium atom with Pd$-$Si distances of 2.3590(9) and 2.3398(9) Å for **4a**. Palladium atom adopts a planar Y-shaped tricoordinate geometry (Si1-Pd1-P1 153.95(3)°, Si2-Pd1-P1 151.04(3)°, and the sum of the bond angles around Pd atom Σ(Pd)[24] 360.0(1)°). The disilyne moiety still has a *trans*-bent structure upon complexation and tricoordinate silicon atoms are highly pyramidalized; the sum of the bond angles around Si1 and Si2 [Σ(Si1) and Σ(Si2)] were 322.0(1)° and 319.0(1)°, respectively. It should be noted that the Si1$-$Si2 bond length of 2.1702(13) Å is significantly elongated by 4.0 %[24] compared to that of **3** and is within the range of those of cyclotrisilenes (2.118–2.186 Å).[25] Two Rs substituents are bent back away from the palladium center: the bent-back angles of Si1–C1 and Si2–C13 were found to be considerable (14.9° and 16.6°)[23] and the dihedral angle of C1-Si1-Si2-C13 of 134.95(19)° is smaller than that of free disilyne **3** (180°). Platinum complex **4b** shows very similar structural features (Figure S16 in Supporting Information).

The ^{29}Si NMR spectrum of **4a** obtained in C$_6$D$_6$ shows resonance signals arising from the η^2-disilyne moiety at $\delta = 93.3$ ppm as a doublet signal owing to coupling to the ^{31}P nuclei ($^2J_{\text{PSi}} = 14.3$ Hz). The signal of **4a** is considerably downfield shifted compared to that of free **3** ($\delta = 31.8$ ppm) and similar to those of cyclotrisilenes ($\delta = 37$ to 143 ppm).[25] The resonance signals of **4b** appeared at $\delta = 109.8$ ppm as a doublet signal owing to coupling to the ^{31}P nuclei accompanied by a doublet satellite signal owing to coupling to the ^{195}Pt nuclei ($^2J_{\text{PSi}} = 18.9$ Hz and $^1J_{\text{PtSi}} = 666$ Hz). The observed $^1J_{\text{PtSi}}$ is much smaller than in bis(phosphine)platinum (η^2-R$_2$Si=SiR$_2$) (R = Me, Ph, *i*Pr) complexes (1125 to 1252 Hz),[26] suggesting that the silicon orbital in the Pt–Si bonds has a larger p character compared to those in η^2-disilene platinum complexes.

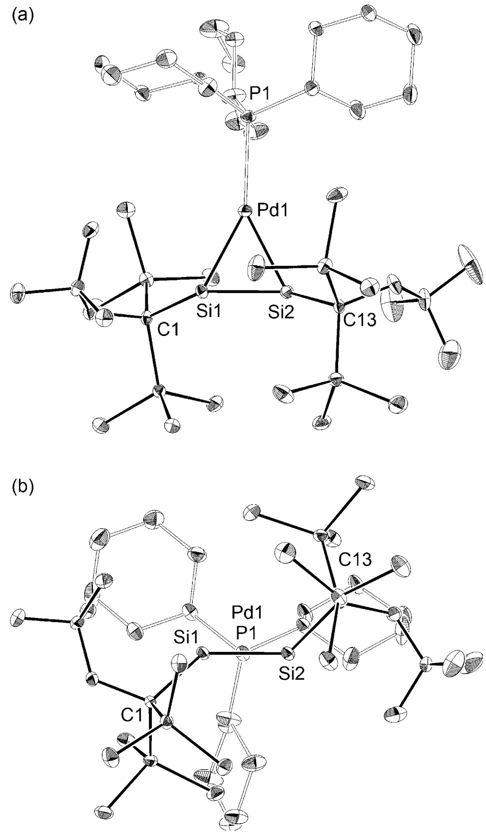
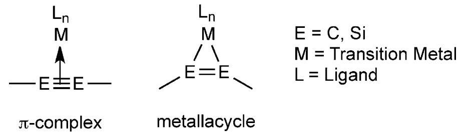


Figure 3. Molecular structure of **4a**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. a) A top view; b) A view along with Pd1–P1 bond. Selected bond lengths [Å] and angles [°]: Pd1–Si1 2.3590(9), Pd1–Si2 2.3398(9), Pd1–P1 2.4340(8), Si1–Si2 2.1702(13), Si1–C1 1.915(3), Si2–C13 1.912(3); Si1-Pd1-Si2 55.01(3), Si2-Si1-Pd1 62.05(3), Si1-Si2-Pd1 62.94(3), Si1-Pd1-P1 153.95(3), Si2-Pd1-P1 151.04(3), C1-Si1-Si2 135.27(11), C13-Si2-Si1 131.96(11), C1-Si1-Si2-C13 134.95(19).

On the basis of Dewar–Chatt–Duncanson model,[27] two possible canonical structures, a π-complex and a metallacycle, can be drawn for η^2-disilyne complex (Scheme 4).[28] The observed elongation of the silicon–silicon bond, considerable bent-back angles, and downfield-shift of the ^{29}Si resonance signal upon complexation indicate that η^2-disilyne complexes **4a** and **4b** have a significant metallacycle character with an intact π_{in}-type Si=Si bond. Theoretical studies of $\mathbf{4a}_{\text{fix}}$, whose structural parameters are fixed to those obtained by X-ray analysis were carried out. Wiberg bond index (WBI) of the Si–Si bond in $\mathbf{4a}_{\text{fix}}$ (1.99) is significantly lower than that of $\mathbf{3}_{\text{fix}}$ (2.45), which indicates that silicon–silicon bond in **4a** has a double bond character. The HOMO−6 and HOMO−1 of $\mathbf{4a}_{\text{fix}}$ displayed in Figure 4 correspond to π-back-donation and σ-donation orbitals, while the HOMO and LUMO are mainly slipped π_{in} and π^*_{in} orbitals, respectively. Because δ-bonding by orbital overlap between d and π^*_{in} orbitals that should favor a planar structure is weak,[8] complexes **4a** and **4b** would keep *trans*-bent structures.[29]



Scheme 4. Two canonical structures of η^2-disilyne and η^2-alkyne complexes.

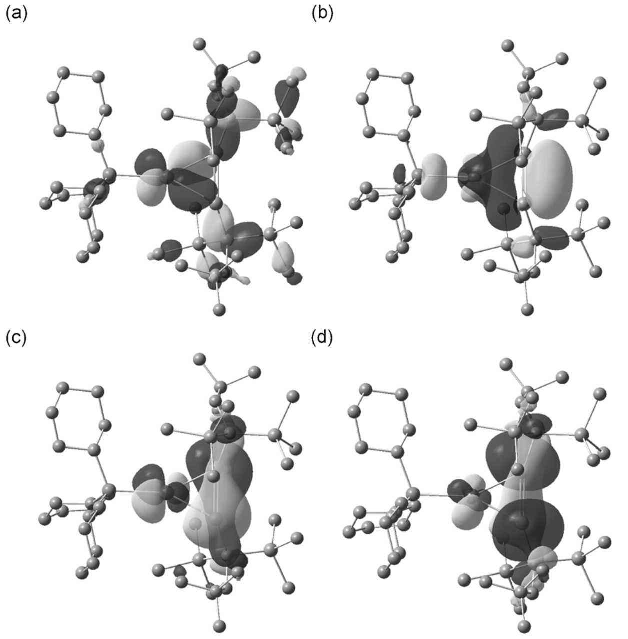
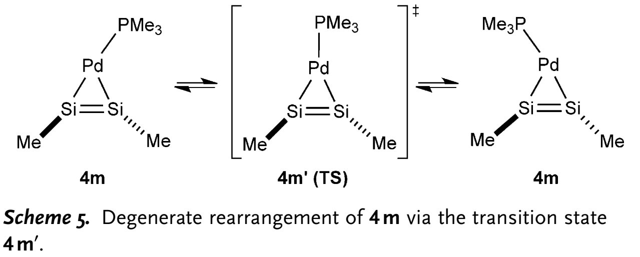


Figure 4. Selected orbitals of $\mathbf{4a}_{\text{fix}}$. a) HOMO−6 (d + π^*_{out}) b) HOMO−1 (d + π_{out}) c) HOMO (slipped π_{in}) d) LUMO (slipped π^*_{in}) calculated at the B3LYP/B1 level (basis B1:SDD for Pd atom and 6-31G(d) for P, Si, C, H atoms).

As stated above, complexes **4a** and **4b** show metallacycle character, whereas [WCl$_4$(η^2-HSi≡SiH)] is theoretically predicted to have π-complex character.[9] The electron-rich d^{10} character of the palladium and platinum compared to the W$^{\text{IV}}$ center would favor π-back-donation to low-lying π^*_{out} orbitals of disilyne moiety in **4a** and **4b**, which is responsible for the significant metallacycle character.

Model compound [Me$_3$PPd(η^2-MeSi≡SiMe)] (**4m**) optimized at the B3LYP/6-31G(d) level adopts a T-shaped geometry where the Me$_3$P ligand coordinates to Pd unsymmetrically with the Si-Pd-P angles of 125.6° and 168.4°, respectively. Symmetric **4m′** resembling **4a** is located as a transition state for the swinging motion of the Me$_3$P ligand in **4m** with a very small barrier of 0.56 kJ mol^{-1} (Scheme 5) and the *trans*-bent character of **4m** and **4m′** is essentially unchanged during the swinging motion. Steric effects would favor Y-shaped structures in **4a** and **4b**.[30]



Scheme 5. Degenerate rearrangement of **4m** via the transition state **4m′**.

In conclusion, we successfully synthesized and characterized the first isolable dialkyldisilyne **3**. The longest absorption band due to HOMO–LUMO transition of **3** appeared at 810 nm and tailed up to 1300 nm in the near-infrared region. Ligand exchange reactions of $[(Cy_3P)_2M]$ (M = Pd, Pt) with **3** afforded η^2-disilyne complexes **4a** and **4b**. Spectroscopic and structural features of these complexes and theoretical studies indicates that **4a** and **4b** have a significant metallacyclic character.

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Keywords: disilyne · metallacycle · palladium · platinum · silicon

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[13] Disilyne **3** has the lowest molecular weight among the reported isolable disilynes. Formula weight of disilynes: **3** 514, **1a** 940, **1b** 836, **1c** 864, **2** 1306.

[14] Synthetic details, characterization, and molecular structures obtained by X-ray structural analysis of compounds **3**, **4a**, **4b**, **6**, **7**, **8a**, and **8b** are described in Supporting Information. CCDC 957867 (**3**), 957868 (**6**), 957869 (**7**), 957870 (a single crystal of a 2:1 mixture of **8a** and **8b**), 957871 (**4a**), 957872 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] The ^{29}Si resonance signals of **2** and **3** were considerably upfield shifted from symmetrically substituted disilyldisilynes ($\delta = 91.5$ ppm for **1a** and $\delta = 89.9$ ppm for **1b**).[1,2] Magnetic anisotropic effect is suggested for the reason of the upfield shift.[4,5]

[16] Assignments of the transitions based on the computational study of 3_{fix} at the TD-B3LYP/SDD for Pd, 6-311+G(2df,p) for H, C, Si: band II is a mixed transition of $\pi_{in}\rightarrow\pi^*_{in}$ and $\pi_{out}\rightarrow\pi^*_{out}$ (HOMO−1 to LUMO and HOMO to LUMO+1); band III, $\pi_{out}\rightarrow\sigma^*$ (HOMO to LUMO+2); band IV, $\pi_{out}\rightarrow\pi^*_{out}$ (HOMO to LUMO+1), respectively.

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[21] Recrystallization of a 1:1 mixture of **8a** and **8b** formed single crystals of **8a** and **8b** with a 2:1 ratio which was analyzed by X-ray diffraction study. As well as the reported bi(silacyclopropane) compounds, compounds **8a** and **8b** have short Si–Si bonds of 2.2928(11) Å and 2.3126(16) Å in comparison with the standard Si–Si single bond length (2.34 Å)[22] owing to the increased s character of the exocyclic Si–Si bond. Separation of **8a** and **8b** has not been possible.

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[30] A Y-shaped structure with planar silicon–silicon double bond (**4m″**) was found as a second-order saddle point and to be 75.0 kJ mol^{-1} higher in energy than **4m**.