

Four-, Five-, and Six-Membered Silaplatinacycles Obtained from the Reaction of an Aryllallene with $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$

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Summary: The reaction of (4-fluorophenyl)allene with $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$ gives 2-sila-1-platinacyclobutane, 2,5-disila-1-platinacyclopentane, or 4-sila-1-platinacyclohexane, depending on the reaction conditions. All these complexes were characterized by X-ray crystallography and NMR spectroscopy.

2,5-Disila-1-metallacyclopentanes^{1–10} have attracted attention owing to their unique chemical properties and the important roles they play as an intermediate of transition metal complex catalyzed hydrosilylation and bis-silylation of unsaturated compounds.^{3,8} Most of these complexes were prepared by the oxidative addition of two Si–H bonds of 1,2-bis(silyl)alkanes, $\text{HSiR}_2\text{CH}_2\text{CH}_2\text{SiR}_2\text{H}$, to low-valent transition metal complexes. On the other hand, the reactions of alkene and alkyne with $\text{M}(\text{SiX}_3)_2(\text{PR}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Me}, \text{Ph}, \text{F}$) lead to the formation of their 1,2-disilylation products,^{11,12} which are closely related to the mechanism of bis-silylation of alkene, allene, and alkyne catalyzed by transition metal complexes.^{13–15} A similar reaction of alkene or allene

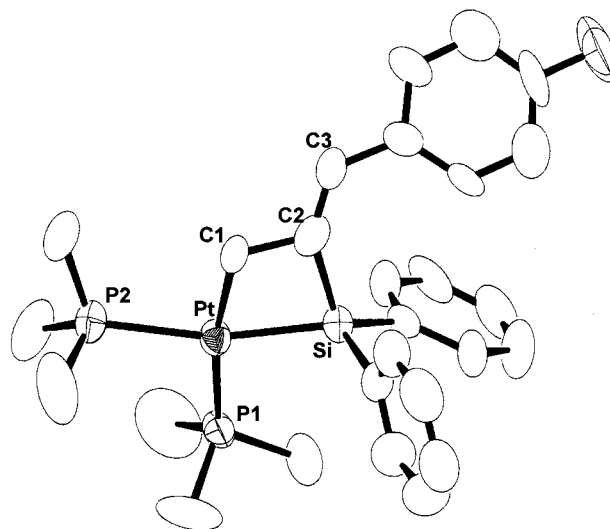


Figure 1. ORTEP drawing of **1** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt–P1 2.277(3), Pt–P2 2.349(4), Pt–Si1 2.367(3), Pt–C1 2.14(1), Si1–C2 1.87(1), C2–C3 1.31(2), C3–C4 1.48(2); P1–Pt–P2 99.4(1), P1–Pt–Si1 100.7(1), P1–Pt–C1 168.8(3), P2–Pt–Si1 159.6(1), P2–Pt–C1 91.7(3), Si1–Pt–C1 68.1(3), Pt–Si1–C2 85.3(4), Pt–C1–C2 103.2(7), Si1–C2–C1 95.8(8), Si1–C2–C3 141(1), C1–C2–C3 120(1), C2–C3–C4 128(1).

with Pt complexes having diorganosilyl ligands would lead to the formation of 1,2-bis(silyl)alkane or 2,5-disila-1-metallacyclopentane as its double oxidative addition product. Actually, $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_2\text{Ph})_2$ was reported to react with acetylene to afford $\text{Pt}(\text{SiPh}_2\text{CH=CH-SiPh}_2)(\text{PMe}_2\text{Ph})_2$.¹⁶ In this paper we report that the reaction of an aryllallene with a platinum complex with diphenylsilyl ligands gives not only a new disilaplatinacyclopentane but also four- or five-membered silaplatinacycles depending on the conditions.

(4-Fluorophenyl)allene reacts with an equimolar amount of $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$ ¹⁷ at room temperature to produce $\text{Pt}(\text{SiPh}_2\text{C(=CHC}_6\text{H}_4\text{-4)CH}_2)(\text{PMe}_3)_2$ (**1**),

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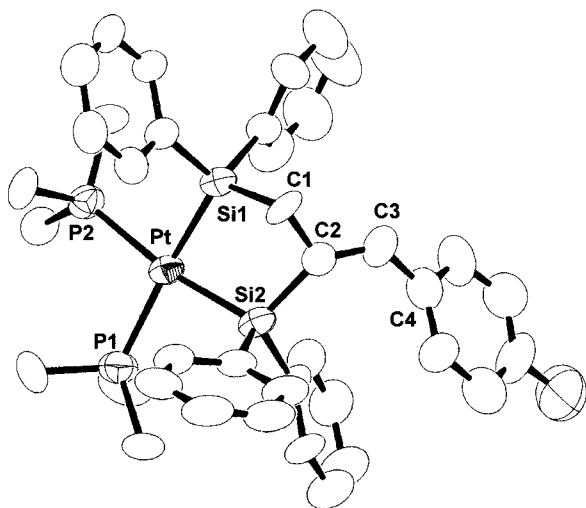
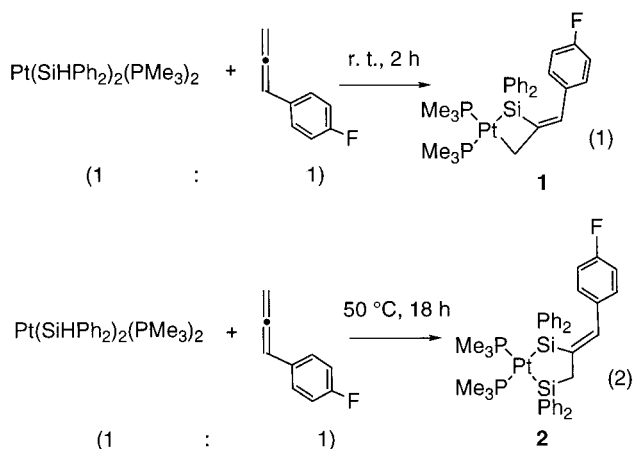


Figure 2. ORTEP drawing of **2** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt–P1 2.349(2), Pt–P2 2.344(2), Pt–Si1 2.365(2), Pt–Si2 2.374(2), Si1–C1 1.888(6), Si2–C2 1.892(7), C1–C2 1.498(8), C2–C3 1.346(8), C3–C4 1.479(9); P1–Pt–P2 96.06(7), P1–Pt–Si1 170.98(7), P1–Pt–Si2 93.95(7), P2–Pt–Si1 90.38(7), P2–Pt–Si2 169.96(7), Si1–Pt–Si2 79.74(7), Pt–Si1–C1 111.0(2), Pt–Si2–C2 110.2(2), Si1–C1–C2 105.6(4), Si2–C2–C1 106.1(5), Si2–C2–C3 134.1(6), C1–C2–C3 118.5(7), C2–C3–C4 130.6(7).

while the reaction at 50 °C affords $\text{Pt}(\text{SiPh}_2\text{C}(\text{=CHCHC}_6\text{H}_4\text{F-4})\text{CH}_2\text{SiPh}_2)(\text{PMe}_3)_2$ (**2**), as shown in eqs 1 and 2. Molecular structures of the four- and five-

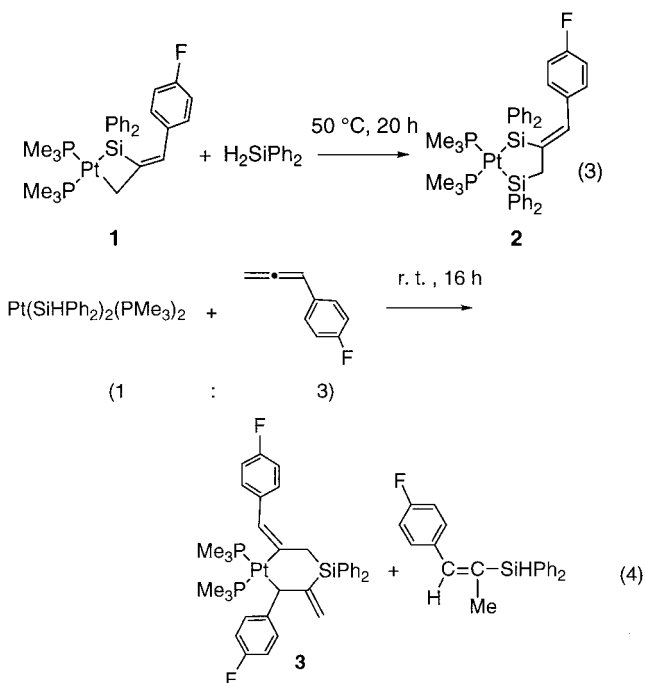


membered silaplatinacycles **1** and **2** were determined by X-ray crystallography (Figures 1 and 2). The crystallographic data are summarized in Table 1. Complex **1** contains a planar metallacycle ring with highly distorted bond angles, Si1–Pt–C1 68.1(3)°, Pt–Si1–C2 85.3(4)°, Pt–C1–C2 103.2(7)°, Si1–C2–C1 95.8(8)°. Despite the strained ring structure, **1** is stable at room temperature in the solid state and in solution. The square-planar Pt center of **2** is included in the five-membered disilametallacyclic ring and is bonded to two PMe_3 ligands. The C2–C3 bond distance (1.346(8) Å) is typical of the C=C double bond, while the Si–C2–C3 bond angle (134.1(6)°) is enlarged due to steric repulsion between the 4-fluorophenylmethylidene substituent and a phenyl substituent on the Si2 atom. The NMR spectra are also consistent with the proposed structures. The $^{13}\text{C}\{^1\text{H}\}$

Table 1. Crystallographic Data of Complexes **1–3**

	1	2	3
chemical formula	$\text{C}_{27}\text{H}_{35}\text{FP}_2\text{PtSi}$	$\text{C}_{39}\text{H}_{45}\text{FP}_2\text{PtSi}$	$\text{C}_{36}\text{H}_{42}\text{F}_2\text{P}_2\text{PtSi}$
fw	663.70	845.97	797.85
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
<i>a</i> , Å	16.803(3)	11.517(2)	9.792(2)
<i>b</i> , Å	8.349(2)	27.949(3)	18.710(3)
<i>c</i> , Å	20.434(8)	12.952(2)	19.296(2)
β , deg	103.17(2)	111.52(1)	94.95(2)
<i>V</i> , Å ³	2791(1)	3878(1)	3499.1(8)
<i>Z</i>	4	4	4
μ , mm ^{−1}	5.184	3.778	4.153
<i>F</i> (000)	1312	1696	1592
<i>D</i> _{calc} , g cm ^{−3}	1.579	1.449	1.514
cryst size, mm × mm × mm	0.64 × 0.32 × 0.26	0.58 × 0.32 × 0.29	0.52 × 0.34 × 0.32
2 θ range, deg	5.0–55.0	5.0–55.0	5.0–55.0
no. of unique reflns	6801	9084	8281
no. of used reflns (<i>I</i> > 3.0 σ (<i>I</i>))	3444	4447	5024
no. of variables	289	406	379
<i>R</i>	0.052	0.037	0.035
<i>R</i> _w	0.035	0.024	0.024

NMR signals of the CH_2 carbon of **1** and **2** are observed at δ 20.8 and 38.0, respectively, flanked by ^{195}Pt satellite peaks (**1**, $^1J_{\text{CPt}} = 400$ Hz; **2**, $^2J_{\text{CPt}} = 88$ Hz), while the signals of the sp^2 carbons of the metallacycles appear at δ 157.8 and 150.0. The NMR analyses of reaction **1** revealed generation of H_2SiPh_2 in the solution. The reaction of H_2SiPh_2 with **1** was conducted in order to clarify the route of formation of **2**. Heating a benzene solution of a mixture of **1** and H_2SiPh_2 in 1:3 molar ratio at 50 °C caused formation of **2** in 34% (eq 3).



The reaction of (4-fluorophenyl)allene with $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$ in a 3:1 molar ratio affords $\text{Pt}\{\text{C}(\text{=CHCHC}_6\text{H}_4\text{F-4})\text{CH}_2\text{SiPh}_2\text{C}(\text{=CH}_2)\text{CH}(\text{C}_6\text{H}_4\text{F-4})\}(\text{PMe}_3)_2$ (**3**) in 73% yield (eq 4). The organic product, $\text{FC}_6\text{H}_4\text{CH}=\text{C}(\text{Me})\text{SiPh}_2\text{H}$, was obtained from the reaction mixture (34% isolated yield based on Pt) and characterized by NMR spectroscopy. Figure 3 shows the molecular structure of **3**, which contains the puckered 4-sila-1-platinacyclohexane ring

Scheme 1

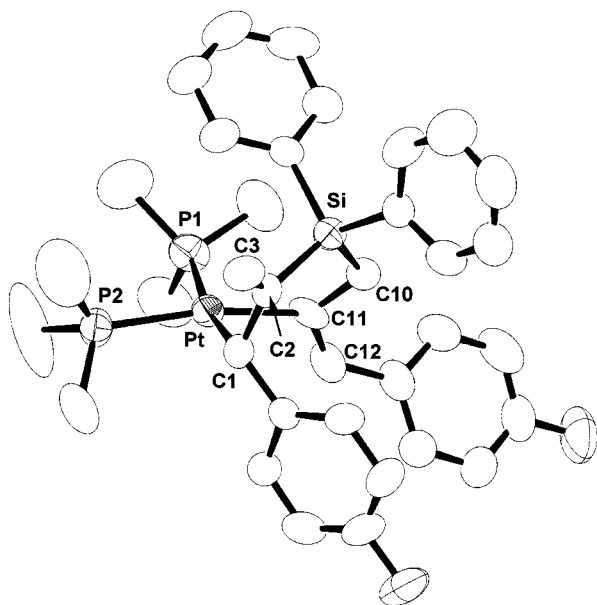
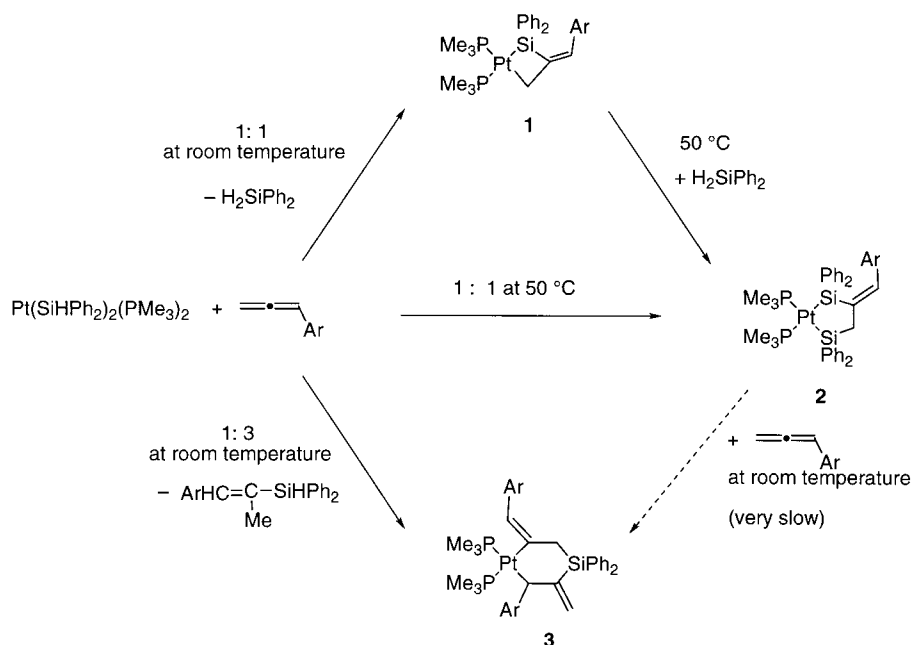


Figure 3. ORTEP drawing of **3** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt–P1 2.286(2), Pt–P2 2.308(2), Pt–C1 2.148(5), Pt–C11 2.061(5), C1–C2 1.512(7), C1–C4 1.500(7), C2–C3 1.335(7), Si–C2 1.879(5), Si–C10 1.863(5), C10–C11 1.540(7), C11–C12 1.343(7); P1–Pt–P2 98.49(6), P1–Pt–C1 170.0(1), P1–Pt–C11 88.1(1), P2–Pt–C1 88.9(1), P2–Pt–C11 168.7(1), C1–Pt–C11 85.7(2), Pt–C1–C2 103.8(3), Pt–C1–C4 114.6(4), C1–C2–C3 121.3(5), C2–C1–C4 115.7(5), Si–C2–C1 119.9(4), C2–Si–C10 110.9(2), Si–C2–C3 118.3(4), Si–C10–C11 111.9(4), C10–C11–C12 119.4(5), Pt–C11–C10 122.1(4), Pt–C11–C12 118.1(4).

with 4-fluorophenyl and 4-fluorophenylmethylidene substituents at each of the two α -carbons. The two 4-fluorophenyl groups and the $\text{Pt}(\text{PMe}_3)_2$ moiety are at the opposite side of the plane formed by a Si and four carbon atoms in the metallacycle. The ^1H NMR signals of two $=\text{CH}_2$ hydrogens appear at δ 5.57 and 5.73, while the signals of Pt–CH– and Si–CH₂– hydrogens are observed at δ 4.27 and δ 3.36 and 2.31, respectively. The

reaction of **1** with (4-fluorophenyl)allene would give a platinacycle with different stereochemistry at the C=C double bond than what is observed in compound **3**.¹⁸ The reaction of (4-fluorophenyl)allene with **2** at room temperature caused formation of **3** but at a very slow reaction rate; the conversion is not completed after stirring a 10:1 mixture of the allene and **2** after 140 h. This suggests that complex **2** is not a major contributor for the formation of compound **3** in the reaction in eq 4. Scheme 1 summarizes the reactions for formation of several silaplatinacycles. The formation of **2** in reaction 2 probably involves initial formation of **1** and subsequent reaction of **1** and H_2SiPh_2 at 50 °C. Reaction 4, which produces compound **3**, does not involve compounds **1** or **2** as intermediates. The reaction of (4-fluorophenyl)allene with **2** is much slower than the reaction shown in eq 2. At present, the mechanism of formation of **3** is not clear.

In summary, this study proposed a unique reaction mechanism for formation of 2,5-disilaplatinacyclopentane via initial formation of silaplatinacyclobutane and its reaction with diorganosilane. The insertion of a C=C double bond of the arylallene into the Pt–Si bond of $\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2$ takes place smoothly and selectively to cause the formation of unique platinacycles.

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Supporting Information Available: Experimental procedures and crystallographic data of **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) The complex exists as an equilibrium mixture of the cis and trans isomers in solution. See: Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349.

(18) The reaction of (4-fluorophenyl)allene with **1** at 50 °C does not give **3** but produces an uncharacterized Pt complex.