Four-, Five-, and Six-Membered Silaplatinacycles Obtained from the Reaction of an Arylallene with $Pt(SiHPh_2)_2(PMe_3)_2$

Makoto Tanabe, Hideto Yamazawa, and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Summary: The reaction of (4-fluorophenyl)allene with $Pt(SiHPh_2)_2(PMe_3)_2$ 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, $HSiR_2CH_2CH_2SiR_2H$, to low-valent transition metal complexes. On the other hand, the reactions of alkene and alkyne with $M(SiX_3)_2(PR_3)_2$ (M = Pd, Pt; X = Me, Ph, 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 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, $Pt(SiHPh_2)_2(PMe_2Ph)_2$ was reported to react with acetylene to afford $Pt(SiPh_2{-}CH{=}CH{-}SiPh_2)(PMe_2Ph)_2$.[16] In this paper we report that the reaction of an arylallene with a platinum complex with diphenylsilyl ligands gives not only a new disilaplatinacyclopentane but also four- or five-membered silaplatinacycles depending on the conditions.

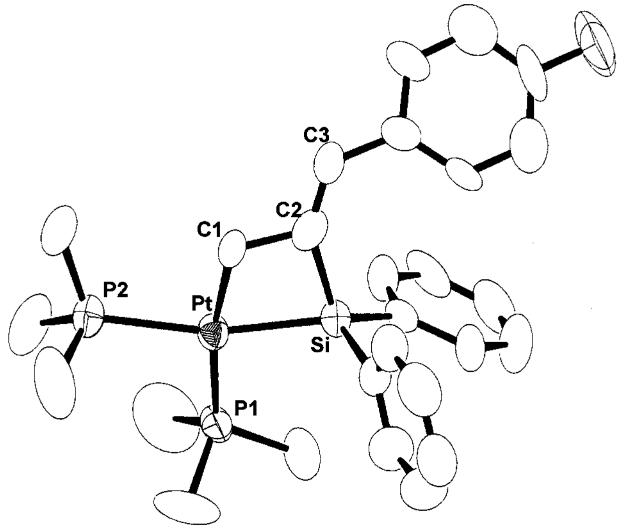

Figure 1. ORTEP drawing of **1** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt−P1 2.277(3), Pt−P2 2.349(4), Pt−Si1 2.367(3), Pt−C1 2.14(1), Si1−C2 1.87(1), C2−C3 1.31(2), C3−C4 1.48(2); P1−Pt−P2 99.4(1), P1−Pt−Si1 100.7(1), P1−Pt−C1 168.8(3), P2−Pt−Si1 159.6(1), P2−Pt−C1 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).

(4-Fluorophenyl)allene reacts with an equimolar amount of $Pt(SiHPh_2)_2(PMe_3)_2$[17] at room temperature to produce $Pt(SiPh_2C({=}CHC_6H_4F\text{-}4)CH_2)(PMe_3)_2$ (**1**),

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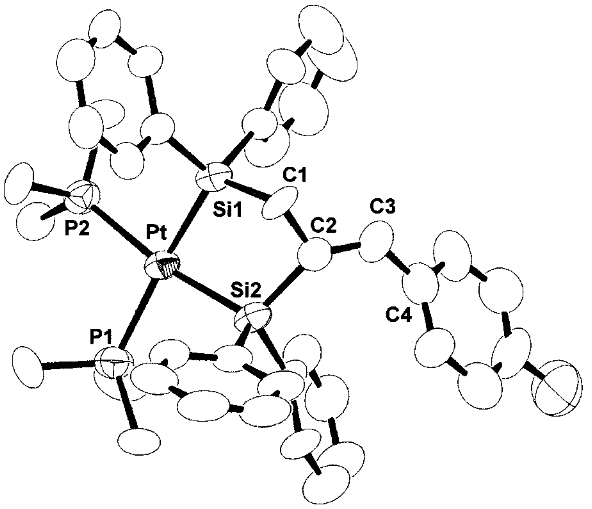
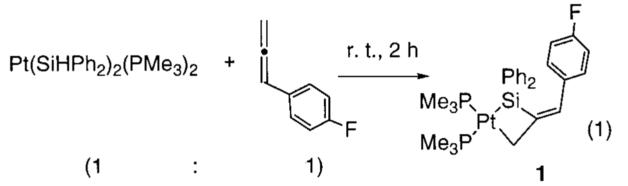


Figure 2. ORTEP drawing of **2** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt−P1 2.349(2), Pt−P2 2.344(2), Pt−Si1 2.365(2), Pt−Si2 2.374(2), Si1−C1 1.888(6), Si2−C2 1.892(7), C1−C2 1.498(8), C2−C3 1.346(8), C3−C4 1.479(9); P1−Pt−P2 96.06(7), P1−Pt−Si1 170.98(7), P1−Pt−Si2 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 $Pt(SiPh_2C(=CHC_6H_4F\text{-}4)CH_2SiPh_2)(PMe_3)_2$ (**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 $^{13}C\{^1H\}$ 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**, $^1J_{CPt}$ = 400 Hz; **2**, $^2J_{CPt}$ = 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).



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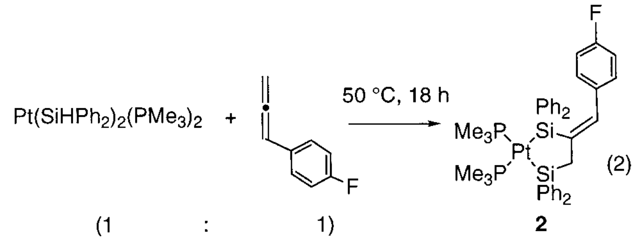

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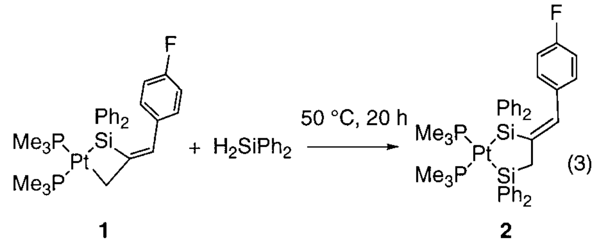
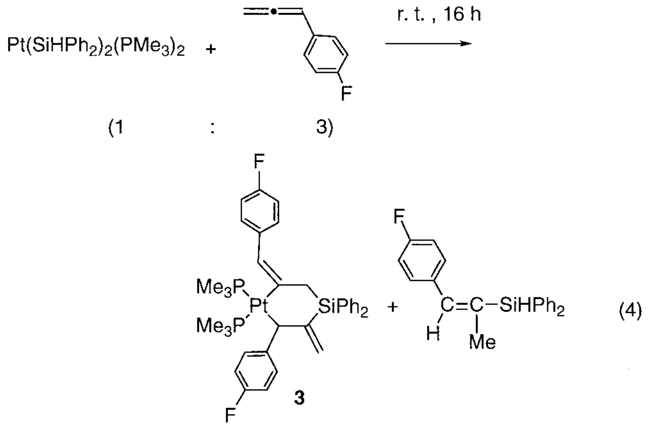
Table 1. Crystallographic Data of Complexes 1−3

	1	2	3
chemical formula	$C_{27}H_{35}FP_2PtSi$	$C_{39}H_{45}FP_2PtSi$	$C_{36}H_{42}F_2P_2PtSi$
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)
a, Å	16.803(3)	11.517(2)	9.792(2)
b, Å	8.349(2)	27.949(3)	18.710(3)
c, Å	20.434(8)	12.952(2)	19.296(2)
β, deg	103.17(2)	111.52(1)	94.95(2)
V, Å^3	2791(1)	3878(1)	3499.1(8)
Z	4	4	4
μ, mm^{-1}	5.184	3.778	4.153
F(000)	1312	1696	1592
D_{calcd}, 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
2θ 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>3.0σ(I))	3444	4447	5024
no. of variables	289	406	379
R	0.052	0.037	0.035
R_w	0.035	0.024	0.024



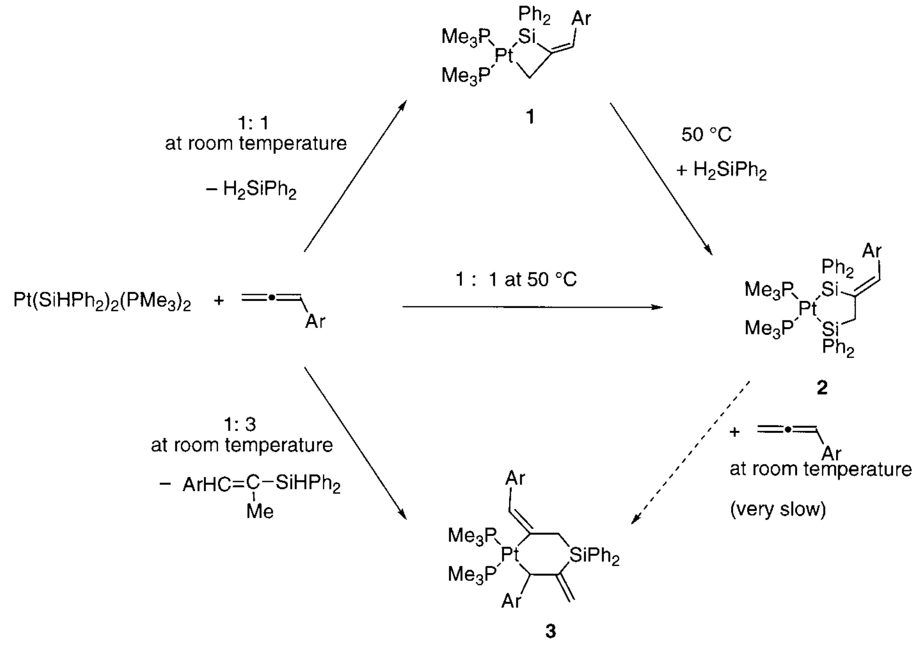
1 **2**



3

The reaction of (4-fluorophenyl)allene with $Pt(SiHPh_2)_2(PMe_3)_2$ in a 3:1 molar ratio affords $Pt\{C(=CHC_6H_4F\text{-}4)CH_2SiPh_2C(=CH_2)CH(C_6H_4F\text{-}4)\}(PMe_3)_2$ (**3**) in 73% yield (eq 4). The organic product, $FC_6H_4CH=C(Me)SiPh_2H$, 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



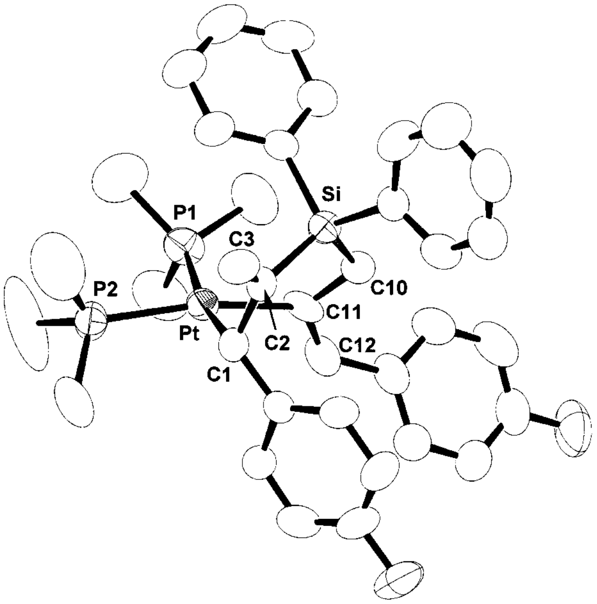


Figure 3. ORTEP drawing of **3** at the 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt−P1 2.286(2), Pt−P2 2.308(2), Pt−C1 2.148(5), Pt−C11 2.061(5), C1−C2 1.512(7), C1−C4 1.500(7), C2−C3 1.335(7), Si−C2 1.879(5), Si−C10 1.863(5), C10−C11 1.540(7), C11−C12 1.343(7); P1−Pt−P2 98.49(6), 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 $\mathrm{Pt(PMe_3)_2}$ moiety are at the opposite side of the plane formed by a Si and four carbon atoms in the metallacycle. The ^{1}H NMR signals of two $=\mathrm{CH_2}$ hydrogens appear at δ 5.57 and 5.73, while the signals of Pt−CH− and $\mathrm{Si{-}CH_2{-}}$ 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 $\mathrm{H_2SiPh_2}$ 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 $\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}$ 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.