Insertion of Alkynes into the Pt–Si Bond of Silylplatinum Complexes Leading to the Formation of 4-Sila-3-platinacyclobutenes and 5-Sila-2-platina-1,4-cyclohexadienes

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Abstract: The reaction of dimethyl acetylenedicarboxylate (DMAD) with $[Pt(SiHPh_2)_2(PMe_3)_2]$ produces *cis*-$[Pt(CZ{=}CZ{-}SiHPh_2)(SiHPh_2)(PMe_3)_2]$ (*cis*-**1**, Z = COOMe) and $[Pt(CZ{=}CZ{-}SiPh_2)(PMe_3)_2]$ (**2**) depending on the reaction conditions. *cis*-**1** and **2** are equilibrated in solution at room temperature, and they are isolated by recrystallization of the mixtures. *cis*-**1** is converted slowly in solution into *trans*-$[Pt(CZ{=}CZ{-}SiHPh_2)(SiHPh_2)(PMe_3)_2]$ (*trans*-**1**) via intermediate **2** followed by reaction with H_2SiPh_2. DMAD also reacts with $[Pt(SiHPh_2)_2(dmpe)]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) to afford $[Pt(CZ{=}CZ{-}SiHPh_2)(SiHPh_2)(dmpe)]$ (**3**). Conversion of **3** into 4-sila-3-platinacyclobutene $[Pt(CZ{=}CZ{-}SiPh_2)(dmpe)]$ (**4**) takes place, accompanied by formation of H_2SiPh_2, to give an equilibrated mixture of the two complexes. Crystallographic and spectroscopic data of *cis*-**1**, *trans*-**1**, and **3** suggest the presence of an intramolecular interaction between the Si–H group of the 3-sila-1-propenyl ligand and Pt via an Si–H–Pt three-center-four-electron bond in the solid state and in solution. DMAD reacts with **2** to give 5-sila-2-platina-1,4-cyclohexadiene with π-coordinated DMAD, $[Pt(CZ{=}CZ{-}SiPh_2{-}CZ{=}CZ)(DMAD)(PMe_3)_2]$ (**5**), which is also obtained from the reaction of excess DMAD with $[Pt(SiHPh_2)_2(PMe_3)_2]$. Unsymmetrical six-membered silaplatinacycles without π-coordinated alkyne, $[Pt(CZ{=}CZ{-}SiPh_2{-}CH{=}CX)(PMe_3)_2]$ (**6**: X = COOMe; **7**: X = Ph), are prepared analogously from the respective reactions of phenyl acetylene and of methyl acetylene carboxylate with **2**. Methyl 2-butynolate reacts with **2** at 50 °C to form a mixture of the regioisomers $[Pt(CZ{=}CZ{-}SiPh_2{-}CMe{=}CZ)(PMe_3)_2]$ (**8**) and $[Pt(CZ{=}CZ{-}SiPh_2{-}CZ{=}CMe)(PMe_3)_2]$ (**9**).

Keywords: alkynes · metallacycles · platinum · Si ligands

Introduction

Pt and Pd complexes containing organosilyl ligands have attracted current attention with regard to the synthetic organic reactions of organosilanes catalyzed by complexes of these metals.[1] Several research groups have investigated the reactions of alkynes and alkenes with organosilanes catalyzed by Group 10 metal complexes as described below. Early studies by Kumada and Yamamoto revealed that Pt and Ni complexes catalyzed the addition of 1,1,2,2-tetramethyldisilane to diphenyl acetylene to afford 2,5-disila-1,4-cyclohexadienes and siloles, respectively.[2] They proposed a reaction mechanism which involves the intermediate platinum silylene complexes and 4-sila-3-platinacyclobutenes, based on the results of thermal conversion of the disilane to the oligosilane, $(SiMe_2)_n$, catalyzed by Pt complexes.[3] The silylene complexes of Pt^0 and Pt^{II} were isolated recently by Tilley et al.[4] The reaction of phenyl acetylene with $[Pt(SiHMe_2)_2(PEt_3)_2]$ was reported to produce 5-sila-2-platina-1,4-cyclohexadiene which liberated the silole upon heating.[5] The results suggest that the silole formation takes place via cycloaddition of $HSiMe_2SiMe_2H$ to alkynes to give the six-membered cyclic intermediate followed by expulsion of the Pt from the complex. Both Kumada and Tanaka proposed 4-sila-3-platinacyclobutene as the intermediate in the reactions. Addition of silacyclopropanes and silacyclopropenes to alkynes, catalyzed by Ni and Pd complexes, affords the four-, five-, and six-membered cyclic compounds containing Si.[6–9] Insertion of the metal center into a C–Si bond of the three-membered ring of the substrate, to give the 4-sila-3-metallacyclobutene intermediate, accounts for the formation of the products.

There have been only a limited number of the reports of such four-membered metallacycles that have been prepared and characterized in situ, although many reports of the above reactions proposed the 4-sila-3-metallacyclobutenes in the reaction mechanism. Fink reported the preparation of a silaplatinabenzocyclobutane that has a tendency to be hy-

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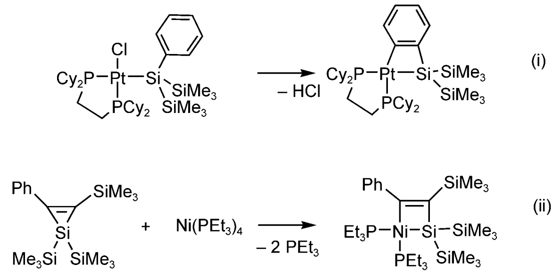
drolyzed during purification by column chromatography (Scheme 1i).[10] Ishikawa and Ohshita prepared the 4-sila-3-nickellacyclobutene via the reaction of a silacyclopropene with [Ni(PEt$_3$)$_4$] and characterized it based on the NMR spectroscopy and its chemical properties (Scheme 1ii). The complex is too unstable to be isolated.[11,12] In this paper, we report details of the reaction of alkynes with a bis(diphenylsilyl)platinum complex, which leads to the isolation of new 4-sila-3-platinacyclobutenes. We describe the full characterization of the metallacycles, the mechanism of its formation, and its further reaction with alkynes. Part of the work has already been reported in a preliminary form.[13]

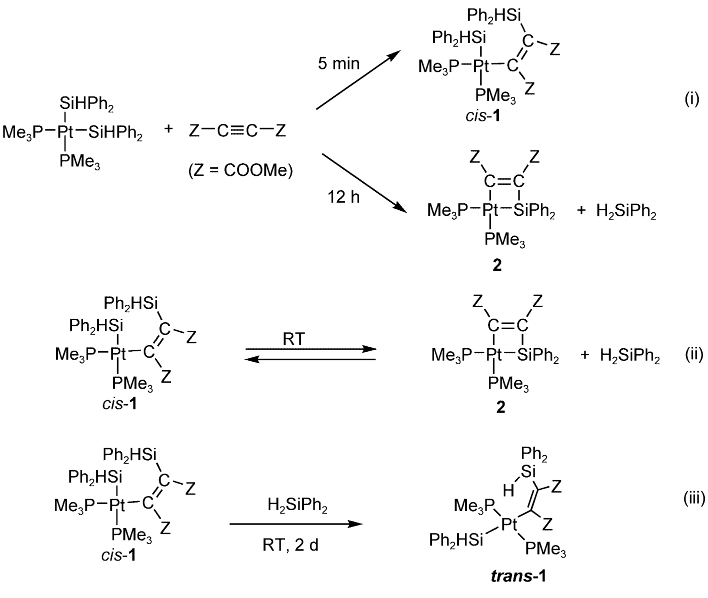


Scheme 1.

Results and Discussion

Formation of 4-sila-3-platinacyclobutenes: The reactions of dimethyl acetylenedicarboxylate (DMAD) with [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$][14] form the Pt-containing products as summarized in Scheme 2i. [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] reacts with equimolar DMAD in the presence of H$_2$SiPh$_2$ ([Pt] = 67 mM, [H$_2$SiPh$_2$] = 201 mM in THF) to produce *cis*-[Pt(CZ=CZ–SiHPh$_2$)(SiHPh$_2$)(PMe$_3$)$_2$] (*cis*-**1**, Z = COOMe), which is isolated in 93 % yield after reacting for 5 min at room temperature. The reaction did not give a *trans* isomer of *cis*-**1** under these conditions. Insertion of alkynes into the Pt–Si bond of bis(silyl)platinum(II) complexes, having no Si–H groups, was studied both experimentally and theoretically.[15] The reaction of DMAD with [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] in THF ([Pt] = 5.5 mM) for 12 h yielded 4-sila-3-platinacyclobutene, [Pt(CZ=CZ–SiPh$_2$)(PMe$_3$)$_2$] (**2**), as yellow crystals in 85 % yield, along with H$_2$SiPh$_2$. Products of both reactions contain *cis*-**1** and **2**, although each complex was isolated from the reaction mixtures under the above conditions.

Analytically pure crystals of *cis*-**1** and **2** were characterized unambiguously. These results have already been reported in the preliminary communication.[13] Complex **2** was also characterized by NMR (^{1}H, ^{31}P{^{1}H}, ^{29}Si{^{1}H}) spectroscopy in solution. The ^{29}Si{^{1}H} NMR spectrum contains a doublet of doublets at δ–63.6 accompanied by a ^{195}Pt satellite (J(Si,P) = 161 and 3 Hz, J(Si,Pt) = 778 Hz). 4-Sila-3-nickellacyclobutene, (Et$_3$P)$_2$Ni–C(Ph)=C(SiMe$_3$)-Si(SiMe$_3$)$_2$, exhibits the ^{29}Si{^{1}H} NMR signal of the Si in the four-membered metallacycle at δ–105.4.[11] The peak position of nickellacyclobutene at higher magnetic fields than **2** is partly due to the SiMe$_3$ groups bonded to the Si of the four-membered ring. The ^{13}C{^{1}H} NMR spectrum of **2** shows the signals of two vinylic carbons at δ = 152.7 and 170.4. The latter signal, which shows larger coupling constants (J(C,P) = 7 and 106 Hz, J(C,Pt) = 716 Hz) than the former (J(C,P) = 4 and 11 Hz, J(C,Pt) = 55 Hz), is assigned to the carbon attached directly to the Pt center.



Scheme 2.

The NMR spectra of isolated *cis*-**1** contain the signals not only of the complex but also of **2** formed in the solution. Concomitant formation of H$_2$SiPh$_2$ is noted in the ^{1}H NMR spectrum. The NMR signals of *cis*-**1** were assigned by comparison of the spectra with those of **2** and of H$_2$SiPh$_2$. The ^{29}Si{^{1}H} NMR signals of *cis*-**1** at δ = 13.3 and 2.5 are attributed to the Si nuclei of the 3-sila-1-propenyl ligand and of the SiHPh$_2$ ligand, respectively. The former signal shows smaller coupling constants (J(Si,P) = 8 Hz, J(Si,Pt) = 121 Hz) than the latter (J(Si,P) = 15 and 160 Hz, J(Si,Pt) = 1169 Hz). The ^{1}H NMR spectrum shows the signals at δ = 5.45 (J(H,Pt) = 40 Hz) and 6.35 (J(H,Pt) = 19 Hz), which were assigned to the Si–H hydrogens of SiHPh$_2$ ligand and 3-sila-1-propenyl ligand, respectively. Addition of H$_2$SiPh$_2$ to a solution of **2** decreases the amount of the complex accompanied by formation of *cis*-**1**. These results indicate the attainment of a rapid equilibrium of the complexes in solution (Scheme 2ii). Figure 1 shows the ^{1}H NMR spectra of the solutions of *cis*-**1** with [Pt] = 20 and 2 mM. The former spectrum shows the presence of a mixture of *cis*-**1**, **2**, and H$_2$SiPh$_2$ in similar amounts, while the latter exhibits much larger signals of **2** and H$_2$SiPh$_2$ than *cis*-**1**. The results are explained by a shift of the equilibrium towards the formation of **2** and H$_2$SiPh$_2$ in the more dilute solution.

Compound *cis*-**1**, which is in rapid equilibrium with **2** in a solution, changes gradually into *trans*-[Pt(CZ=CZ–SiHPh$_2$)-(SiHPh$_2$)(PMe$_3$)$_2$] (*trans*-**1**) at room temperature (Scheme 2iii). *trans*-**1** was isolated in 57 % yield after stirring a solution of *cis*-**1** in the presence of H$_2$SiPh$_2$ for 30 h and recrystallization of the products, while a change in the ^{1}H

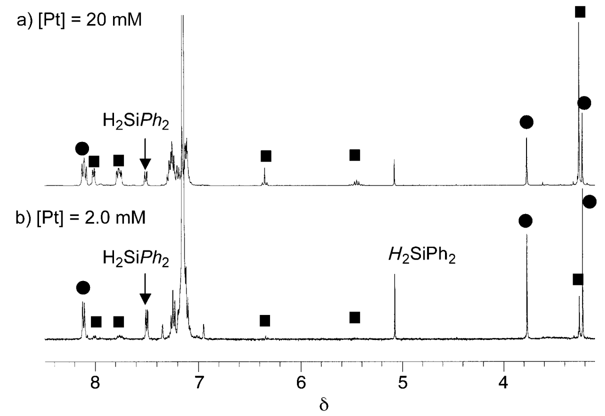
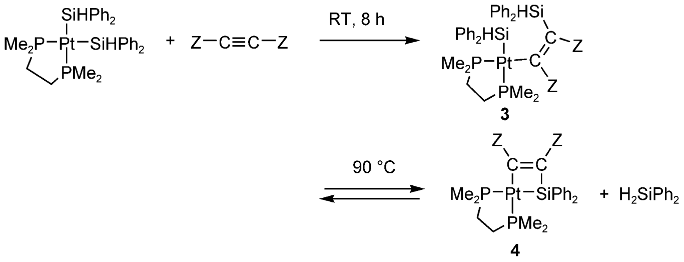


Figure 1. ^{1}H NMR spectra of C_6D_6 solutions of *cis*-**1** at a) [Pt] = 20 mM and b) [Pt] = 2.0 mM (400 MHz). The signals of *cis*-**1** (■) and those of **2** (●) and H_2SiPh_2 formed in the solution are observed.

NMR spectra during the reaction showed that conversion of *cis*-**1** into *trans*-**1** was complete within 2 d. The reaction probably took place by cyclization of the 3-sila-1-propenyl ligand of *cis*-**1** according to Scheme 2ii to give **2** and subsequent addition of H_2SiPh_2 to the Pt–C bond of **2** to regenerate *cis*-**1** or to form *trans*-**1**. Although the formation of *trans*-**1** was much slower than the mutual conversion of *cis*-**1** and **2**, once formed *trans*-**1** was not turned into **2** nor *cis*-**1**. This irreversible formation of *trans*-**1** prevented the determination of precise thermodynamic parameters of the reversible reactions in Scheme 2ii. Thus, the new Pt complexes shown in Scheme 2i are produced by the reactions among the above complexes. Insertion of the C–C triple bond of DMAD into a Pt–Si bond of $[Pt(SiHPh_2)_2(PMe_3)_2]$ gives *cis*-**1** as the initial product which is in rapid equilibrium with a mixture of **2** and H_2SiPh_2. *cis*-**1** was converted gradually into *trans*-**1** via formation of the intermediate **2** and its further reaction with H_2SiPh_2.

Complex [Pt(CZ=CZ–SiHPh$_2$)(SiHPh$_2$)(dmpe)] (**3**) was isolated in 64% yield from the reaction of excess DMAD with $[Pt(SiHPh_2)_2(dmpe)]$. The NMR (^{1}H and ^{31}P{^{1}H}) spectra of a solution of isolated **3** indicate partial liberation of H_2SiPh_2 and formation of a new Pt complex. The product complex shows no ^{1}H NMR signal from the Si–H hydrogen. Based on these results as well as a comparison of the ^{31}P{^{1}H} NMR signals of the mixture with those of **2**, the complex formed in the solution is assigned to the 4-sila-3-platinacyclobutene with a dmpe ligand **4** (Scheme 3). The conversion of **3** into **4** is rapid and reversible; the ratios between the complexes in a [D$_8$]toluene solution are 75:25 at 25 °C and 30:70 at 90 °C.

The molecules of *cis*-**1**, *trans*-**1**, and **3** contain an interaction of the γ-Si–H hydrogen of the 3-sila-1-propenyl ligand with the Pt center. Table 1 summarizes the bond parameters and spectroscopic data relating to this issue. The H1 hydrogens of *trans*-**1** and **3** are located at the apical position of the Pt center. The Pt···Si distances, 3.657(2) and 3.540(2) Å, are shorter than the sum of the van der Waals radii of Pt and Si (3.85 Å).[16] The IR spectra show peaks at $\tilde{\nu}$ = 2116–2078 cm^{-1}, which are assigned to the Si–H vibration of the 3-sila-1-propenyl ligand. The lower peak positions than those of an organosilyl compound with a vinyl group, Ph$_2$SiH(CH=CH$_2$) (2124 cm^{-1}),[17] suggest an interaction between the Si–H group and the Pt center in the solid state. The ^{1}H NMR signals of the Si–H hydrogen of *cis*-**1**, *trans*-**1**, and **3** appear at δ = 6.10–6.35, which are at lower field positions than that of Ph$_2$SiH(CH=CH$_2$) (δ = 5.11).[17] The signals accompany the splitting from H–Pt coupling (J(H,Pt) = 14–20 Hz). Coupling constants between Si and H of the complexes (J(H,Si) = 196–197 Hz at 25 °C) are smaller than that of Ph$_2$SiH(CH=CH$_2$) (206 Hz). The coupling constant of *cis*-**1** decreases slightly on lowering the temperature of the solution (198 Hz at 70 °C, 196 Hz at 25 °C, and 195 Hz at −30 °C). These results indicate that the agostic interaction exists in the complexes in both the solid state and in solution, although the observed change of the spectroscopic parameters caused by the interaction is much smaller than those observed in the compounds having a three-center-two-electron bond between the metal center and C–H or Si–H groups.[18]



Scheme 3.

Table 1. X-ray and NMR data of the γ-Si–H bond and Pt of *cis*-**1**, *trans*-**1**, and **3**.

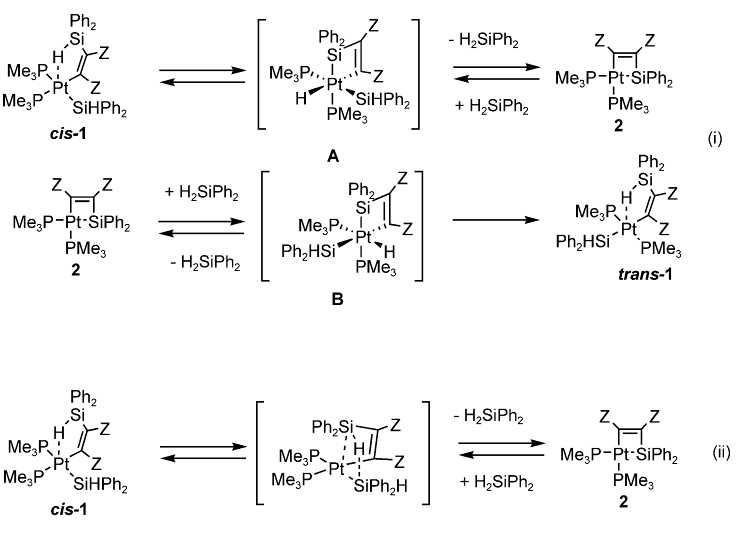
	cis-**1**	*trans*-**1**	**3**	Ph$_2$SiH(CH=CH$_2$)[a]
X-ray data				
d(Si–H) [Å^{-1}]	–	1.34	1.60	–
d(Pt···H) [Å^{-1}]	–	2.93	2.40	–
d(Pt···Si) [Å^{-1}]	–	3.657	3.540	–
IR data				
$\tilde{\nu}$(SiH) [cm^{-1}][c]	2098	2078	2116	2124
NMR data				
δ_{SiH} [ppm]	6.35	6.21	6.10	5.11
J(Pt,H) [Hz]	19	14	20	–
J(Si,H) [Hz]	197	196	196[b]	206

[a] Taken from ref. [17]. [b] At 25 °C, 198 Hz at 70 °C, 195 Hz at −30 °C. [c] Complexes *cis*-**1**, *trans*-**1**, and **3** show the $\tilde{\nu}$(Si–H) peak of the diphenylsilyl ligand at 2070, 2049, and 2043 cm^{-1}, respectively. The peak position of $[Pt(SiHPh_2)_2(PMe_3)_2]$ is 2026 cm^{-1}.

Albinati et al. investigated the interaction of a C–H bond of the ligand coordinated with square-planar d^8 metal center, which causes approach of the C–H group to the apical site of the metal center. Pt^{II} and Rh^{I} complexes with a formylquinoline or iminopyridine ligand show a shift of the ^{1}H NMR signal of the hydrogen to a low magnetic field position because of deshielding by the filled d$_{z^2}$ orbital of the metal center.[19] They proposed an interaction involving a three-center-four-electron bond to account for the spectroscopic results which differ from the complexes that have a three-center-two-electron bond. The 3-sila-1-propenylplatinum complexes in this study exhibit similar spectroscopic features to the above-mentioned Rh and Pt complexes in which there is an interaction between the C–H group and the metal in the form of a three-center-four-electron bond. C–H and N–H bond activation reactions, triggered by such an interaction of the ligand and the square-planar d$_8$ metal centers, have already been reported.[20] Recently, a Ta complex was reported to have a γ-Si-H-Ta interaction that was classified as a three-center-two-electron bond.[21]

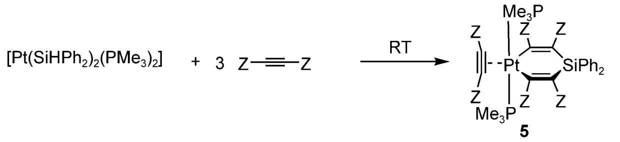
Scheme 4i depicts a plausible pathway for the conversion between *cis*-**1**, *trans*-**1**, and **2**. Intramolecular oxidative addition of the Si–H bond of *cis*-**1** to the Pt center forms an intermediate complex **A** with a 4-sila-3-platinacyclobutene ring and with hydrido and SiHPh$_2$ ligands. Reductive elimination of H$_2$SiPh$_2$ from the Pt^{IV} complex readily occurs to give the 4-sila-3-platinacyclobutene **2** with a Pt^{II} center. Oxidative addition of H$_2$SiPh$_2$ to **2** also gives **A**, which causes coupling of the hydrido and the Si atom of the four-membered ring to regenerate *cis*-**1**. Another oxidative addition product, **B**, which is an isomer of **A**, induces a similar Si–H formation to give *trans*-**1**. The Si–H bond activation of *trans*-**1** would form a hexacoordinated intermediate having two silyl ligands at the mutually *trans* positions. This structure is less favorable than intermediate **A** that has the two silyl ligands with a highly electron-releasing nature at the *cis* positions. Thus, according to this mechanism, *trans*-**1** is not converted into *cis*-**1** or **2**. Another possible pathway is shown in Scheme 4 (ii). Activation of the γ-Si–H bond and Pt–Si bond of *cis*-**1** takes place simultaneously with the formation of new Pt–Si and Si–H bonds to produce the 4-sila-3-platinacyclobutene and H$_2$SiPh$_2$. The concerted reaction pathway, which resembles that of σ-bond metathesis, also accounts for the smooth and reversible conversion between *cis*-**1** and **2**. Conversion of **2** into *trans*-**1** via this intermediate is sterically much less favorable than the conversion into *cis*-**1**.

Addition of alkyne to a platinum silylene intermediate was proposed for the formation of 4-sila-3-platinacyclobutene in the previous reports.[2,5] Although platinum silylene complexes could react with the unsaturated molecules to form the four-membered silaplatinacycles, the reactions of 3-sila-1-propenylplatinum complexes in this study do not involve the Pt silylene intermediate but occur following the direct pathway in Scheme 4. Insertion of DMAD into the Pt–Si bond of the [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$], giving the 3-sila-1-propenyl ligand bonded to the Pt center, takes place more rapidly than the α elimination of the diphenylsilyl ligand to form the Pt silylene intermediate.



Scheme 4.

Reaction of alkynes with the silaplatinacycle: Reaction of excess DMAD with [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] affords a 5-sila-2-platina-1,4-cyclohexadiene with π-coordinated DMAD, [$\overline{\text{Pt(CZ=CZ–SiPh}_2\text{–CZ=C}}$Z)(DMAD)(PMe$_3$)$_2$] (**5**), as shown in Equation (1). Complex **5** has a trigonal bipyramidal structure with two PMe$_3$ ligands at the apical positions. Figure 2 depicts the structure of this molecule which has a crystallographic *C*2 symmetry around the Si–Pt axis and a flat six-membered ring. The Pt–P bond (2.346 Å) is longer than that of square-planar Pt^{II} complexes with the phosphine ligands at mutually *trans* positions. Tanaka reported the preparation of the 5-sila-2-platina-1,4-cyclohexadiene



$$[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}] + 3\ \mathrm{Z{-}{\equiv}{-}Z} \xrightarrow{\mathrm{RT}} \mathbf{5} \quad (1)$$

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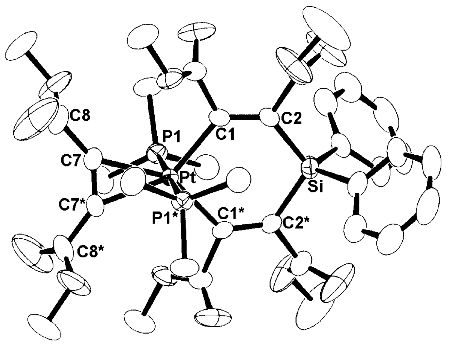
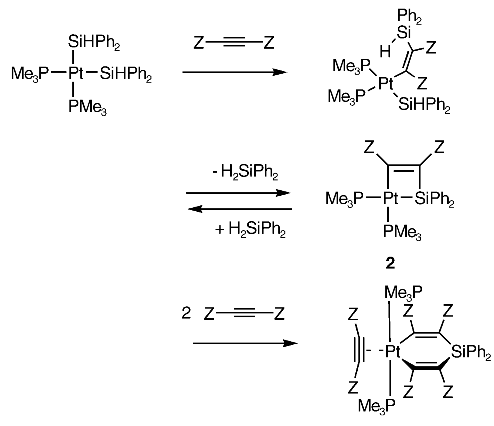


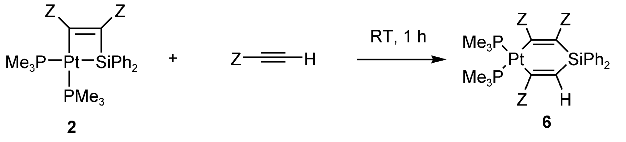
Figure 2. ORTEP drawing of **5** with 50 % thermal ellipsoid. One of the two crystallographically independent molecules is shown. The molecule has a symmetrical axis between Pt and Si. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected bond lengths [Å] and angles [°]: Pt–P1 2.346(1), Pt–C1 2.119(4), Pt–C7 2.128(4), C1–C2 1.337(5), Si–C2 1.871(4), C7–C7* 1.28(1), P1-Pt-P1* 180.00(7), C1-Pt-C1* 97.6(2), P1-Pt-C1 91.2(2), P1-Pt-C1* 88.8(2), C2-Si-C2* 110.4(3), Pt-C1-C2 128.5(3), Si-C2-C1 127.1(3), C7*-C7-C8 142.0(3).

without a coordinated alkyne ligand, [Pt(CPh=CH–SiMe$_2$–CH=CPh)(PEt$_3$)$_2$], from the reaction of phenyl acetylene with [Pt(SiHMe$_2$)$_2$(PEt$_3$)$_2$].[5] We also reported the reaction of ferrocenyl acetylene with [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] to give 5-sila-2-platina-1,4-cyclohexadienes with ferrocenyl pendants.[22] The five-coordinated structure of **5** is stabilized by π-back donation of Pt to the DMAD ligand that has electron-withdrawing COOMe substituents. Formation of complex **5** probably involves the intermediate complex **2** which causes insertion of DMAD into the Pt–Si bond of the four-membered cycle as proposed in the previous report.[5] Scheme 5 depicts the pathway for the formation of **5** in this study based on the above results. The initial reaction of DMAD with the bis(silyl)platinum complex forms the intermediate 3-sila-1-propenylplatinum complex that is in equilibrium with the 4-sila-3-platinacyclobutene. Further insertion of the alkyne into the Pt–Si bond of the 4-sila-3-platinacyclobutene and coordination of another alkyne molecule to the Pt center give the product. The reaction of DMAD with complex **2** also affords the six-membered metallacycle **5** in high yields.



Scheme 5.

Terminal alkynes, such as phenyl acetylene and methyl acetylenecarboxylate, react with **2** to give unsymmetrical six-membered silaplatinacycles, [Pt(CZ=CZ–SiPh$_2$–CH=CZ)(PMe$_3$)$_2$] (**6**) and [Pt(CZ=CZ–SiPh$_2$–CH=CPh)(PMe$_3$)$_2$] (**7**), respectively, as shown in Equations (2) and (3). Complex **7** contains a puckered six-membered 5-platina-2-sila-1,4-cyclohexadiene ring (Figure 3). Phenyl acetylene shows a lower reactivity than methyl acetylenecarboxylate; completion of the latter reaction requires 24 h at 50 °C. Both reactions give the complexes with the substituents at the *α* carbon of the metallacycle selectively. A preliminary result of the reaction of 1-hexyne with **2** also produces a similar complex with a butyl group at the *α* position of the six-membered metallacycle, although isolation of the product is not feasible because of the low yield of the product. The reaction of methyl 2-butynolate with **2** affords an equimolar mixture of the regioisomers [Pt(CZ=CZ–SiPh$_2$–CMe=CZ)(PMe$_3$)$_2$] (**8**) and [Pt(CZ=CZ–SiPh$_2$–CZ=CMe)(PMe$_3$)$_2$] (**9**) as shown in Equation (4). Repeated recrystallization of the products gives single crystals of complex **8**. Figure 4 shows the molecular structure of the complex which has the COOMe group in the *α* position. Comparison of the ^{1}H NMR spectrum of **8** and the mixture of **8** and **9** enabled the assignment of the signals of both complexes (Figure 5). The alkyne having both an electron-withdrawing COOMe group and an electron-donating Me group inserts into the Pt–Si bond without selectivity to give the two possible products in equal amounts. The results suggest that the direction of the alkyne insertion is influenced by the steric bulkiness of the substituents on the alkyne more significantly than their electronic factors.



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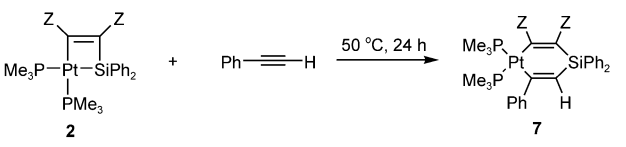


(3)

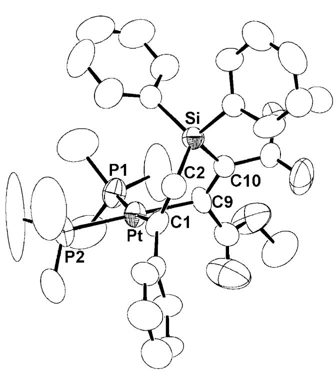
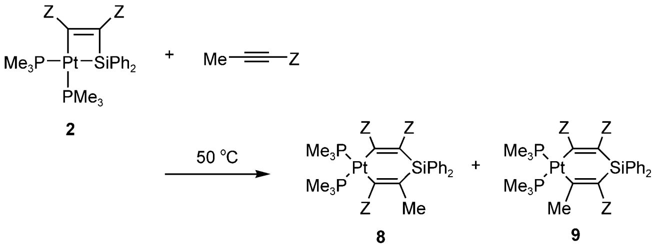


Figure 3. ORTEP drawing of **7** with 50 % thermal ellipsoids. Selected bond lengths [Å] and angles [°]: Pt–P1 2.315(4), Pt–P2 2.304(4), Pt–C1 2.08(1), Pt–C9 2.06(1), Si–C2 1.84(1), Si–C10 1.90(1), C1–C2 1.35(2), C1–C3 1.47(2), C9–C10 1.32(2), P1-Pt-P2 95.7(1), P1-Pt-C9 91.1(3), P2-Pt-C1 88.4(4), C1-Pt-C9 84.7(5), C2-Si-C10 102.7(5), Pt-C1-C2 116(1), Si-C2-C1 120(1), Pt-C9-C10 125(1), Si-C10-C9 113(1).



(4)

Scheme 6 depicts the mechanism of insertion of the monosubstituted alkyne into the Pt–Si bond of **2**. Initial coordination of alkyne to an apical position of the square-planar Pt center of **2** is followed by insertion of the alkyne into the Pt–Si bond. The insertion leads to the product with the sub-

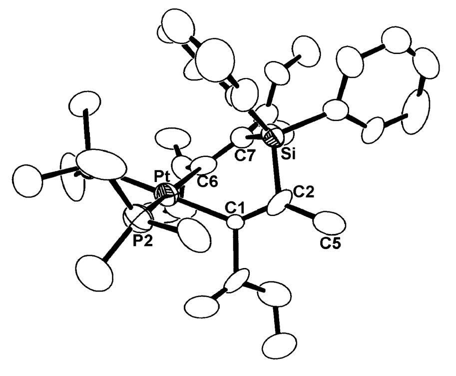


Figure 4. ORTEP drawing of **8** with 50 % thermal ellipsoids. Selected bond lengths [Å] and angles [°]: Pt–P1 2.29(1), Pt–P2 2.305(8), Pt–C1 1.99(2), Pt–C6 2.08(2), C1–C2 1.29(5), C6–C7 1.36(4), C2–C5 1.49(4), Si–C2 1.91(3), Si–C7 1.90(3), P1-Pt-P2 95.9(4), P2-Pt-C1 86.3(9), P1-Pt-C6 92.8(9), C1-Pt-C6 85.3(12), Si-C2-C1 107.3(20), Si-C7-C6 117.9(20), C2-Si-C7 103.4(14)

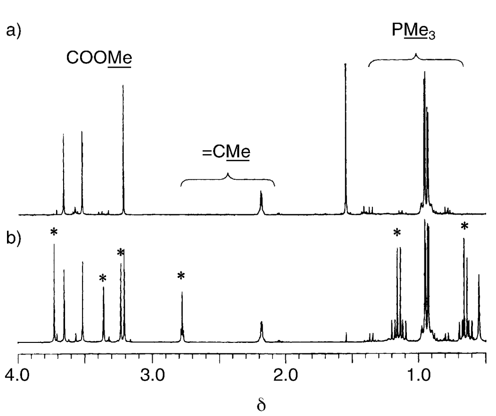
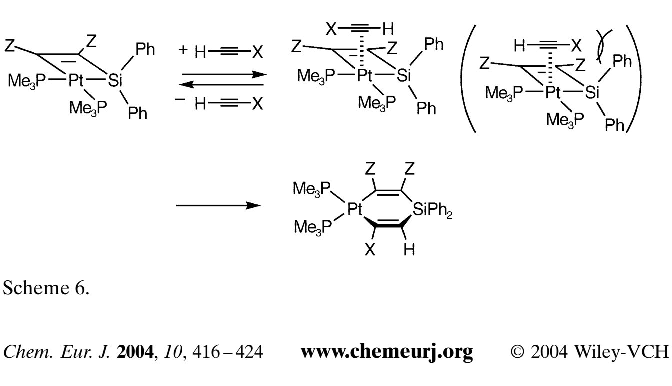


Figure 5. ^{1}H NMR spectra of a) isolated **8** and b) a mixture of **8** and **9**. (400 MHz, $\mathrm{C_6D_6}$). Peaks with an asterisk in (b) are assigned to **9**.

stituent at the α position because alkyne insertion in the opposite direction causes severe steric repulsion between the substituent of the alkyne and the $\mathrm{SiPh_2}$ group. The steric interaction between the substituent and the metal center or $\mathrm{PMe_3}$ ligand in the pathway in Scheme 6 is less severe because of the long Pt–P bond. Results of the reactions of alkynes with alkyl complexes of late transition metals, leading to the alkyne insertion into the M–C bond, were often explained by means of the steric factors of the substituents on the alkynes.[23]



Scheme 6.

In summary, this study revealed that the 4-sila-3-platinacyclobutene does exist and reacts with the alkynes to form the six-membered cyclic silaplatinacyclohexdiene. The reaction of the bissilylplatinum complex with alkynes to give 4-sila-3-platinacyclobutene involves the formation of the 3-sila-1-propenylplatinum intermediate and subsequent intramolecular γ-Si–H bond activation by the Pt center.

Experimental Section

General methods: All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. Hexane, toluene, and THF were distilled from sodium/benzophenone and stored under nitrogen. NMR spectra (^{1}H, ^{13}C, ^{29}Si, and ^{31}P) and IR spectra were recorded on JEOL EX-400 and Varian Mercury300 spectrometers and a Shimadzu FTIR-8100A spectrophotometer, respectively. $\mathrm{[Pt(SiHPh_2)_2(PMe_3)_2]}$ was prepared according to the literature method.[14] $\mathrm{[Pt(SiHPh_2)_2(dmpe)]}$ was prepared by heating a 2:1 mixture of $\mathrm{H_2SiPh_2}$ and $\mathrm{[PtMe_2(dmpe)]}$[24] in toluene for 24 h at 90 °C. DMAD and $\mathrm{H_2SiPh_2}$ were purchased and used as received. Peak positions of the ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectra were referenced to external 85 % $\mathrm{H_3PO_4}$ and external $\mathrm{SiMe_4}$, respectively. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of *cis*-$\mathbf{[Pt(CZ{=}CZSiHPh_2)(SiHPh_2)(PMe_3)_2]}$ (*cis*-1): DMAD (82 µL, 0.67 mmol) was added to a THF (10 mL) solution of $\mathrm{H_2SiPh_2}$ (374 µL, 2.01 mmol) and $\mathrm{[Pt(SiHPh_2)_2(PMe_3)_2]}$ (479 mg, 0.67 mmol) at room temperature. After stirring the reaction mixture for 5 min, the solvent was removed under reduced pressure. Addition of hexane (3 mL) caused separation of a pale orange solid which was collected by filtration, washed with hexane (4 × 3 mL), and dried in vacuo (533 mg, 93 %); elemental analysis calcd (%) for $\mathrm{C_{36}H_{46}O_4P_2PtSi_2}$: C 50.52, H 5.42; found: C 51.08, H 5.40. The NMR data of *cis*-**1** were obtained from the spectra of a mixture of **2**, *cis*-**1**, and $\mathrm{H_2SiPh_2}$, because once isolated *cis*-**1** was soon equilibrated with **2** and $\mathrm{H_2SiPh_2}$ in solution. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ = 0.92 (d, 9 H, *J*(H,P) = 9 Hz, *J*(H,Pt) = 25 Hz, P(CH_3)$_3$ *cis* to Si), 1.06 (d, 9 H, *J*(H,P) = 8 Hz, *J*(H,Pt) = 19 Hz, P(CH_3)$_3$ *trans* to Si), 3.25 (s, 3 H, OCH_3), 3.26 (s, 3 H, OCH_3), 5.45 (appt, 1 H, *J*(H,Pt) = 40 Hz, PtSi*H*), 6.35 (s, 1 H, *J*(H,Pt) = 19 Hz, *J*(H,Si) = 197 Hz, =CSi*H*), 7.08–7.28 (m, 12 H, C$_6H_5$-*m* and *p*), 7.74 (d, 2 H, *J*(H,H) = 7 Hz, C$_6H_5$-*o*), 7.77 (d, 2 H, *J*(H,H) = 7 Hz, C$_6H_5$-*o*), 8.00 (d, 2 H, *J*(H,H) = 7 Hz, C$_6H_5$-*o*), 8.08 (d, 2 H, *J*(H,H) = 7 Hz, $\mathrm{C_6H_5}$-*o*); ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{C_6D_6}$): δ = −30.7 (d, *J*(P,P) = 23 Hz, *J*(P,Pt) = 2089 Hz, *P* *cis* to Si), −19.3 (d, *J*(P,P) = 23 Hz, *J*(P,Pt) = 1455 Hz, *P* *trans* to Si); ^{29}Si{^{1}H} NMR (79 MHz, $\mathrm{CD_2Cl_2}$): δ = 13.3 (appt, *J*(Si,P) = 8 Hz, *J*(Si,Pt) = 121 Hz, C*Si*), 2.51 (dd, *J*(Si,P) = 15 and 160 Hz, *J*(Si,Pt) = 1169 Hz, Pt*Si*); IR (KBr): $\tilde{\nu}$ = 2098, 2070 (Si–H), 1700, 1684 (C=O) cm^{-1}.

Preparation of $\mathbf{[P\overline{t(CZ{=}CZSi}Ph_2)(PMe_3)_2]}$ (2): DMAD (19 µL, 0.14 mmol) at room temperature was added to a THF (25 mL) solution of $\mathrm{[Pt(SiHPh_2)_2(PMe_3)_2]}$ (98 mg, 0.14 mmol). A ^{1}H NMR spectrum of the solution showed formation of $\mathrm{H_2SiPh_2}$. After stirring the solution for 12 h, the solvent was evaporated to dryness. Addition of hexane (3.5 mL) to the residue caused separation of a yellow solid which was collected by filtration, washed with hexane (2 × 3 mL), and dried in vacuo. Recrystallization from THF/hexane gave **2** as yellow crystals (79 mg, 85 %). ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 1.38 (d, 9 H, *J*(H,P) = 9 Hz, *J*(H,Pt) = 32 Hz, P(CH_3)$_3$ *cis* to Si), 1.51 (d, 9 H, *J*(H,P) = 8 Hz, *J*(H,Pt) = 16 Hz, P(CH_3)$_3$ *trans* to Si), 3.50 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 7.32–7.33 (m, 6 H, C$_6H_5$-*m* and *p*), 7.72 (m, 4 H, C$_6H_5$-*o*); ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_2Cl_2}$): δ = 17.2 (d, *J*(C,P) = 22 Hz, *J*(C,Pt) = 17 Hz, P(CH$_3$)$_3$ *trans* to Si), 20.0 (dd, *J*(C,P) = 4 Hz, *J*(C,P) = 33 Hz, *J*(C,Pt) = 45 Hz, P(CH$_3$)$_3$ *cis* to Si), 51.0 (OCH$_3$), 51.3 (OCH$_3$), 127.7 (C_6H$_5$-*m*), 128.6 (C_6H$_5$-*p*), 136.6 (C_6H$_5$-*o*, *J*(C,Pt) = 22 Hz), 138.7 (br, *J*(C,P) = 5 Hz, C_6H$_5$-*i*), 152.7 (dd, *J*(C,P) = 4 Hz, *J*(C,P) = 11 Hz, *J*(C,Pt) = 55 Hz, Si*C*=C), 167.3 (dd, *J*(C,P) = 4 Hz, *J*(C,P) = 9 Hz, *J*(C,Pt) = 161 Hz, PtC*C*=O), 170.4 (dd, *J*(C,P) = 7 Hz, *J*(C,P) = 106 Hz, *J*(C,Pt) = 716 Hz, Pt*C*), 178.2 (dd, *J*(C,P) = 4 Hz, *J*(C,P) = 11 Hz, *J*(C,Pt) = 29 Hz, SiC*C*=O); ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CD_2Cl_2}$): δ = −30.7 (d, *J*(P,P) = 16 Hz, *J*(P,Pt) = 2357 Hz, *P* *cis* to Si), −17.2 (d, *J*(P,P) = 16 Hz,

J(P,Si) = 161 Hz, J(P,Pt) = 1384 Hz, *P trans* to Si); ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2): δ = −63.6 (dd, J(Si,P) = 3 Hz, J(Si,P) = 161 Hz, J(Si,Pt) = 778 Hz); IR (KBr): $\tilde{\nu}$ = 1690, 1703 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{34}O_4P_2PtSi$: C 42.92, H 5.10; found: C 42.91, H 5.02.

Preparation of *trans*-[Pt(CZ=CZSiHPh$_2$)(SiHPh$_2$)(PMe$_3$)$_2$] (*trans*-1): H_2SiPh_2 (264 µL, 1.41 mmol) at room temperature was added to a toluene (20 mL) solution of *cis*-**1** (122 mg, 0.14 mmol). After 30 h, solvent was removed under reduced pressure. Addition of hexane (3 mL) to the residue caused separation of a yellow solid which was collected by filtration, washed with hexane repeatedly, and dried in vacuo (69 mg, 57 %). Recrystallization from toluene/hexane afforded single crystals of *trans*-**1**. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.17 (vt, 18 H, J(H,P) = 4 Hz, J(H,Pt) = 32 Hz, P(CH_3)$_3$), 3.31 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 4.98 (t, 1 H, J(H,P) = 14 Hz, J(H,Pt) = 28 Hz, PtSi*H*), 6.21 (s, 1 H, J(H,Pt) = 14 Hz, J(H,Si) = 196 Hz, =CSi*H*), 7.17–7.30 (m, 12 H, C$_6H_5$-*m* and *p*), 7.93 (d, 4 H, J(H,H) = 7 Hz, C$_6H_5$-*o*), 8.01 (d, 4 H, J(H,H) = 7 Hz, C$_6H_5$-*o*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 15.6 (vt, J(C,P) = 40 Hz, J(C,Pt) = 40 Hz, P(CH$_3$)$_3$), 50.5 (OCH$_3$), 50.9 (OCH$_3$), 127.3 (C$_6$H$_5$-*m*), 127.7 (Si*C*=, J(C,Pt) = 37 Hz), 127.9 (C$_6$H$_5$-*m*), 129.4 (C$_6$H$_5$-*p*), 130.2 (C$_6$H$_5$-*p*), 134.3 (C$_6$H$_5$-*i*), 135.7 (C$_6$H$_5$-*o*), 136.9 (J(C,Pt) = 16 Hz, C$_6$H$_5$-*o*), 141.5 (J(C,Pt) = 24 Hz, C$_6$H$_5$-*i*), 167.7 (J(C,Pt) = 72 Hz, PtC*C*=O), 177.5 (J(C,Pt) = 41 Hz, SiC*C*=O), 214.7 (J(C,P) = 13 Hz, J(C,Pt) not determined, Pt*C*=); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ = −22.7 (s, J(P,Pt) = 2511 Hz); ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$): δ = −16.9 (br, J(Si,Pt) = 83 Hz, Pt*Si*), −12.5 (br, J(Si,Pt) = 33 Hz, C*Si*); IR (KBr): $\tilde{\nu}$ = 2078, 2049 (Si–H), 1707, 1690 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{46}O_4P_2PtSi$: C 50.52, H 5.42; found: C 51.19, H 5.43.

Preparation of [Pt(CZ=CZ–SiHPh$_2$)(SiHPh$_2$)(dmpe)] (3): DMAD (192 µL, 1.51 mmol) at room temperature was added to a THF (3 mL) solution of [Pt(SiHPh$_2$)$_2$(dmpe)] (234 mg, 0.31 mmol). A white solid was precipitated during the reaction. After 8 h, the solid product was collected by filtration, washed with hexane, and dried in vacuo. Recrystallization from THF/hexane gave **3** as colorless crystals (179 mg, 61 %). The ^{1}H NMR spectrum exhibited the signals of not only **3** but also **4** and H_2SiPh_2 formed in the solution. The NMR data of **3** and **4** were obtained from the solution containing a mixture of the complexes. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.73 (d, 3 H, J(H,P) = 10 Hz, J(H,Pt) = 25 Hz, P(CH_3)$_2$ *trans* to Si), 0.80 (d, 3 H, J(H,P) = 9 Hz, J(H,Pt) = 19 Hz, P(CH_3)$_2$ *trans* to Si), 0.95 (d, 3 H, J(H,P) = 10 Hz, J(H,Pt) = 29 Hz, P(CH_3)$_2$ *cis* to Si), 1.03 (d, 3 H, J(H,P) = 10 Hz, J(H,Pt) = 39 Hz, overlapped with the methyl hydrogen signals, P(CH_3)$_2$ *cis* to Si), 1.41 (CH_2–THF), 3.25 (s, 3 H, PtC=CCOOCH_3), 3.33 (s, 3 H, J(H,Pt) = 3 Hz, PtCCOOCH_3), 3.56 (OCH_2–THF), 5.60 (appt, 1 H, J(H,Pt) = 36 Hz, PtSi*H*), 6.10 (s, 1 H, J(H,Pt) = 20 Hz, J(H,Si) = 196 Hz, =CSi*H*), 7.08–7.23 (m, 10 H, C$_6H_5$-*m* and *p*) 7.30 (t, 2 H, J(H,H) = 7 Hz, C$_6H_5$-*p*), 7.70 (d, 4 H, J(H,H) = 7 Hz, C$_6H_5$-*o*), 7.96 (d, 1 H, J(H,H) = 7 Hz, C$_6H_5$-*o*), 7.97 (d, 1 H, J(H,H) = 7 Hz, C$_6H_5$-*o*), 8.07 (d, 2 H, J(H,H) = 7 Hz, C$_6H_5$-*o*), methylene and methyl hydrogen signals overlapped severely; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, at −50 °C): δ = 10.2 (d, J(C,P) = 22 Hz, J(C,Pt) = 28 Hz, P(CH$_3$)$_2$), 11.4 (d, J(C,P) = 26 Hz, J(C,Pt) = 31 Hz, P(CH$_3$)$_2$), 12.2 (d, J(C,P) = 35 Hz, J(C,Pt) = 33 Hz, P(CH$_3$)$_2$), 12.6 (d, J(C,P) = 31 Hz, J(C,Pt) = 51 Hz, P(CH$_3$)$_2$), 26.6 (dd, J(C,P) = 31 Hz, J(C,P) = 11 Hz, PCH$_2$), 29.1 (dd, J(C,P) = 35 Hz, J(C,P) = 18 Hz, PCH$_2$), 25.5 (CCH$_2$–THF), 49.9 (OCH$_3$), 50.7 (OCH$_3$), 67.7 (OCH$_2$–THF), 126.9 (C$_6$H$_5$-*m*), 127.0 (C$_6$H$_5$-*m*), 127.1 (C$_6$H$_5$-*p*), 127.2 (C$_6$H$_5$-*m*), 127.3 (C$_6$H$_5$-*p*), 127.7 (C$_6$H$_5$-*m*), 128.5 (C$_6$H$_5$-*p*), 129.4 (C$_6$H$_5$-*p*), 135.0 (C$_6$H$_5$-*o*), 135.1 (C$_6$H$_5$-*i*), 135.4 (C$_6$H$_5$-*i*), 135.5 (J(C,Pt) = 24 Hz, C$_6$H$_5$-*o*), 135.9 (C$_6$H$_5$-*o*), 137.3 (J(C,Pt) = 28 Hz, C$_6$H$_5$-*o*), 141.3 (d, J(C,P) = 6 Hz, J(C,Pt) = 39 Hz, C$_6$H$_5$-*i*), 143.7 (appt, J(C,P) = 6 Hz, J(C,Pt) = 35 Hz, C$_6$H$_5$-*i*), 167.0 (d, J(C,P) = 9 Hz, J(C,Pt) = 103 Hz, PtC*C*=O), 177.5 (d, J(C,Pt) = 22 Hz, SiC*C*=O), 205.9 (dd, J(C,P) = 11 Hz, J(C,P) = 94 Hz, J(C,Pt) = 738 Hz, Pt*C*); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 20.1, (d, J(P,P) = 14 Hz, J(P,Pt) = 1921 Hz, *P cis* to Si), 37.7 (d, J(P,P) = 14 Hz, J(P,Si) = 160 Hz, J(P,Pt) = 1406 Hz, *P trans* to Si); ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$): δ = −15.7 (appt, J(Si,P) = 4 Hz, J(Si,Pt) = 125 Hz, =C*Si*), −1.18 (dd, J(Si,P) = 13 Hz, J(Si,P) = 160 Hz, J(Si,Pt) = 1167 Hz, Pt*Si*); IR (KBr): $\tilde{\nu}$ = 2116, 2043 (Si–H), 1703, 1690 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{44}O_4P_2PtSi_2 \cdot C_4H_8O$: C 51.88, H 5.66; found: C 51.90, H, 5.66.

Data of 4: ^{1}H NMR (400 MHz, [D$_8$]toluene, 90 °C): δ = 0.85 (d, 2 H, J(H,P) = 10 Hz, P(CH_2)$_2$P), 0.90 (d, 2 H, J(H,P) = 10 Hz, P(CH_2)$_2$P), 1.01 (d, 6 H, J(H,P) = 9 Hz, J(H,Pt) = 32 Hz, P(CH_3)$_2$ *cis* to Si), 1.16 (d, 6 H, J(H,P) = 9 Hz, J(H,Pt) = 17 Hz, P(CH_3)$_2$ *trans* to Si), 3.40 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 7.11–7.20 (C$_6H_5$-*m* and *p* and H_2SiPh_2), 7.87 (d, 4 H, J(H,H) = 7 Hz, C$_6H_5$-*o*); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, 90 °C): δ = 21.2 (J(P,Pt) = 2177 Hz, *P cis* to Si), 37.3 (J(P,Pt) = 1345 Hz, *P trans* to Si).

Preparation of [Pt(CZ=CZ–SiPh$_2$–CZ=CZ)(ZC≡CZ)(PMe$_3$)$_2$] (5): DMAD (82 µL, 0.67 mmol) at room temperature was added to a THF (3 mL) solution of [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] (160 mg, 0.22 mmol); during the course of the reaction the color of the solution turned from yellow to orange. After stirring for 1.5 h, the solvent was evaporated to dryness. Addition of hexane to the residue caused separation of the product as an orange solid which was collected by filtration, washed with hexane (5 mL) and Et$_2$O (5 mL), and dried in vacuo to give **5** (208 mg, 96 %). Recrystallization from Et$_2$O and hexane gave yellow crystals. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.39 (appt due to virtual coupling, 18 H, apparent splitting 5 Hz, J(H,Pt) = 19 Hz, P(CH_3)$_3$), 3.20 (s, 6 H, OCH_3), 3.45 (s, 6 H, OCH_3), 3.70 (s, 6 H, OCH_3), 7.20–7.28 (m, 6 H, C$_6H_5$-*m* and *p*), 8.03 (d, 4 H, J(H,H) = 8 Hz, C$_6H_5$-*o*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.0 (appt due to virtual coupling, J(C,Pt) = 20 Hz, P(CH$_3$)$_3$), 50.6 (s, OCH$_3$), 50.8 (br, OCH$_3$), 52.0 (s, OCH$_3$), 93.8 (d, J(C,P) = 6 Hz, J(C,Pt) = 195 Hz, *C*≡*C*), 126.9 (C$_6$H$_5$-*m*), 128.9 (C$_6$H$_5$-*p*), 134.3 (C$_6$H$_5$-*i*), 136.2 (J(C,Pt) = 69 Hz, PtC=*C*), 136.5 (C$_6$H$_5$-*o*), 161.2 (J(C,Pt) = 20 Hz, *C*=O), 165.5 (t, J(C,P) = 9 Hz, J(C,Pt) = 758 Hz, Pt*C*=C), 167.4 (J(C,Pt) = 70 Hz, *C*=O), 177.3 (J(C,Pt) = 13 Hz, *C*=O); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = −24.7 (J(P,Pt) = 1791 Hz); ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$): δ = −19.5 (J(Si,Pt) = 103 Hz); elemental analysis calcd (%) for $C_{36}H_{46}O_{12}P_2PtSi$: C 45.24, H 4.85; found: C 45.59, H 5.05.

Preparation of [Pt(CZ=CZ–SiPh$_2$–CH=CZ)(PMe$_3$)$_2$] (6): Methyl propiolate (12.0 µL, 0.14 mmol) at room temperature was added to a toluene (4 mL) solution of **2** (80.6 mg, 0.12 mmol). The NMR spectra of the reaction mixture after 1 h showed consumption of **2**. The solvent was evaporated to dryness. Addition of hexane (5 mL) to the residue caused separation of a solid which was collected by filtration, washed with hexane (2×1 mL), and dried in vacuo to give **6** (72 mg, 61 %). The complex contained water which might be contained in the alkyne or solvent used in the reaction. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.80 (d, 9 H, J(H,P) = 9 Hz, P(CH_3)$_3$), 0.95 (d, 9 H, J(H,P) = 8 Hz, J(H,Pt) = 20 Hz, P(CH_3)$_3$), 3.21 (s, 3 H, OCH_3), 3.52 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 7.12 (m, 6 H, C$_6H_5$-*m* and *p*), 7.64 (m, 2 H, C$_6H_5$-*o*), 7.84 (m, 2 H, C$_6H_5$-*o*), 8.44 (dd, 1 H, J(H,P) = 3, 13 Hz, J(H,Pt) = 113 Hz, =C*H*); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 16.7 (d, J(C,P) = 6 Hz, J(C,Pt) = 28 Hz, P(CH$_3$)$_3$), 16.9 (d, J(C,P) = 7 Hz, J(C,Pt) = 27 Hz, P(CH$_3$)$_{33}$), 50.9 (OCH$_3$), 51.6 (OCH$_3$), 51.8 (OCH$_3$), 127.6 (C$_6$H$_5$-*m*), 128.0 (C$_6$H$_5$-*m*), 129.2 (C$_6$H$_5$-*p*), 129.3 (C$_6$H$_5$-*p*), 134.7 (Si*C*(Z)=), 135.4 (C$_6$H$_5$-*o*), 135.9 (C$_6$H$_5$-*o*), 136.7 (C$_6$H$_5$-*i*), 138.5 (C$_6$H$_5$-*i*), 140.7 (Si*C*(H)=), 170.6 (d, *C*=O, J(C,P) = 9 Hz, J(C,Pt) = 105 Hz), 173.9 (appt, J(C,P) = 7 Hz, J(C,Pt) = 42 Hz, *C*=O), 176.5 (appt, J(C,P) = 6 Hz, J(C,Pt) not determined, *C*=O), 181.3 (dd, J(C,P) = 17, 112 Hz, J(C,Pt) not determined, Pt*C*=), 187.4 (dd, J(C,P) = 17, 112 Hz, J(C,Pt) not determined, Pt*C*=); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = −29.5 (d, J(P,P) = 20 Hz, J(P,Pt) = 1904 Hz), −28.5 (d, J(P,P) = 20 Hz, J(P,Pt) = 2119 Hz); elemental analysis calcd (%) for $C_{28}H_{38}O_6P_2PtSi \cdot H_2O$: C 43.47, H 5.21; found: C 43.28, H 4.92.

Preparation of [Pt(CZ=CZ–SiPh$_2$–CH=CPh)(PMe$_3$)$_2$] (7): Phenyl acetylene (39.1 µL, 0.36 mmol) was added to a THF (5 mL) solution of **2** (79.8 mg, 0.12 mmol). The reaction was carried out at 50 °C for 24 h. The ^{1}H NMR spectrum after the reaction showed consumption of **2**. The solvent was removed by evaporation. Addition of hexane (3 mL) to the residue caused separation of the product as a solid which was collected by filtration, washed with hexane (2×1 mL), and dried in vacuo to give **7**. Recrystallization from THF/hexane afforded pale yellow crystals (61 mg, 66 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.58 (d, 9 H, J(H,P) = 9 Hz, J(H,Pt) = 20 Hz, P(CH_3)$_3$), 0.95 (d, 9 H, J(H,P) = 8 Hz, J(H,Pt) = 18 Hz, P(CH_3)$_3$), 3.26 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 7.12–7.20 (the signals of C$_6H_5$-*p*, SiC$_6H_5$-*m* and *p* are overlapped), 7.26 (t, 2 H, J(H,H) = 7.4 Hz, C$_6H_5$-*m*), 7.48 (dd, 1 H, J(H,P) = 3, 18 Hz, J(H,Pt) = 118 Hz, =C*H*), 7.62 (m, 2 H, SiC$_6H_5$-*o*), 7.85 (d, 2 H, J(H,H) = 7 Hz, CC$_6H_5$-*o*), 8.00 (m, 2 H, SiC$_6H_5$-*o*); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 16.8 (dd, J(C,P) = 6 Hz, J(C,Pt) = 27 Hz, P(CH$_3$)$_3$), 16.9 (dd, J(C,P) = 6 Hz,

J(C,Pt) = 24 Hz, P(CH_3)$_3$), 50.7 (OCH_3), 51.3 (OCH_3), 125.8 (J(C,Pt) = 9 Hz, SiC(Z)=), 126.6 (CC_6H_5-*p*), 127.5 (SiC_6H_5-*m*), 127.9 (CC_6H_5-*m*), 128.0 (SiC_6H_5-*m*), 128.1 (SiC_6H_5-*p*), 128.8 (SiC_6H_5-*p*), 128.9 (CC_6H_5-*o*), 135.4 (SiC_6H_5-*o*), 136.0 (SiC_6H_5-*m*), 138.0 (CC_6H_5-*i*), 139.9 (SiC_6H_5-*i*), 140.3 (SiC_6H_5-*i*), 151.9 (J(C,P) = 6 Hz, J(C,Pt) = 18 Hz, =CH), 170.7 (d, J(C,P) = 12 Hz, SiCC=O), 176.6 (dd, J(C,P) = 4 and 33 Hz, PtCC=O) 187.2 (d, J(C,P) = 18 and 116 Hz, PtC=), 195.2 (d, J(C,P) = 18 and 121 Hz, PtC=); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = −29.0 (d, J(P,P) = 20 Hz, J(P,Pt) = 2158 Hz), −28.5 (d, J(P,P) = 20 Hz, J(P,Pt) = 1724 Hz); elemental analysis calcd (%) for $C_{32}H_{40}O_4P_2PtSi$: C 49.67, H 5.21; found: C 49.61, H 5.37.

Table 2. Crystal data and details of structure refinement of **5**, **7**, and **8**.

	5	**7**	**8**
formula	$C_{36}H_{46}O_{12}P_2PtSi$	$C_{32}H_{40}O_4P_2PtSi$	$C_{29}H_{40}O_6P_2PtSi$
M_w	1179.06	773.79	769.75
crystal system	orthorhombic	orthorhombic	monoclinic
space group	*Pbcn* (no. 60)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
a [Å]	14.005(3)	17.143(9)	14.860(10)
b [Å]	23.515(4)	26.251(14)	11.582(5)
c [Å]	12.076(3)	14.723(11)	19.254(6)
β [°]			101.08(4)
V [Å^3]	3991	6626	3252
Z	4	8	4
μ [mm^{-1}]	7.175	4.384	4.470
F(000)	2288	3088	1536
ρ_{calcd} [g cm^{-3}]	1.962	1.551	1.572
crystal size [mm^3]	0.31 × 0.35 × 0.45	0.16 × 0.18 × 0.22	0.25 × 0.32 × 0.55
2θ range [°]	5.0–55.0	5.0–50.0	5.0–55.0
no. unique reflns[a]	5120	5921	2516
no. used reflns	2601	2650	5229
no. variables	236	361	392
R	0.025	0.044	0.111
R_w	0.021	0.039	0.144
GOF	1.98	1.41	1.40

[a] $I > 3\sigma(I)$.

Reaction of methyl 2-butynolate with 2: Methyl 2-butynolate (22.6 mg, 0.22 mmol) at room temperature was added to a THF (3 mL) solution of **2** (78.5 mg, 0.11 mmol). The reaction was carried out at 50 °C for 12 h. The solvent was evaporated to dryness. Addition of hexane (3 mL) to the residue caused separation of a solid which was collected by filtration, washed with hexane (2 × 3 mL), and dried in vacuo to give an equimolar mixture of [Pt(CZ=CZ–SiPh$_2$–CMe=CZ)(PMe$_3$)$_2$] (**8**) and [Pt(CZ=CZ–SiPh$_2$–CZ=CMe)(PMe$_3$)$_2$] (**9**). Repeated recrystallization of the mixture gave single crystals of **8**. X-ray crystallography and ^{1}H NMR spectroscopy showed the structure of **8** unambiguously, although analytically pure samples were not obtained. The NMR data of **9** was obtained as a mixture with **8**.

*Data for **8***: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.93 (d, 9H, J(H,P) = 9 Hz, P(CH_3)$_3$), 0.94 (d, 9H, J(H,P) = 9 Hz, P(CH_3)$_3$), 2.18 (dd, 3H, J(H,P) = 1 and 2 Hz, =CCH_3), 3.21 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.65 (s, 3 H, OCH_3), 7.10 (m, 6H, C_6H_5-*m* and *p*), 7.52 (m, 2H, C_6H_5-*o*), 7.91 (m, 2 H, C_6H_5-*o*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −28.7 (d, J(P,P) = 20 Hz, J(P,Pt) = 1985 Hz), −27.9 (d, J(P,P) = 20 Hz, J(P,Pt) = 2134 Hz).

*Data for **9***: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.64 (d, 9H, J(H,P) = 9 Hz, J(H,Pt) = 29 Hz, P(CH_3)$_3$), 1.14 (d, 9H, J(H,P) = 9 Hz, J(H,Pt) = 32 Hz, P(CH_3)$_3$), 2.78 (s, 3H, J(H,Pt) = 7 Hz, =CCH_3), 3.23 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 7.33 (t, 6H, J(H,H) = 7 Hz, C_6H_5-*m* and *p*), 8.02 (m, 2H, C_6H_5-*o*) 8.19 (m, 2H, J(H,H) = 7 Hz, C_6H_5-*o*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −28.3 (d, J(P,P) = 16 Hz, J(P,Pt) = 3237 Hz), −24.3 (d, J(P,P) = 16 Hz, J(P,Pt) = 3752 Hz).

Crystal structure determination: Crystals of **5**, **7**, and **8** were mounted in glass capillary tubes under argon. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R or AFC-7R automated four-cycle diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71069 Å) and $\omega - 2\theta$ scan method. An empirical absorption correction (ψ scan) was applied. Calculations were carried out with the program package teXsan for Windows. Atomic scattering factors were obtained from the literature.[25] Table 2 summarizes the crystal data and results of the refinement.

CCDC-214718 (**5**), -214719 (**7**) and -214720 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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