Reactions of *cis*- and *trans*-Silyl(methyl)platinum(II) Complexes with Phenylacetylene. Remarkable Effect of Cis and Trans Configurations on the Reactivity

Fumiyuki Ozawa* and Toshihiko Hikida

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

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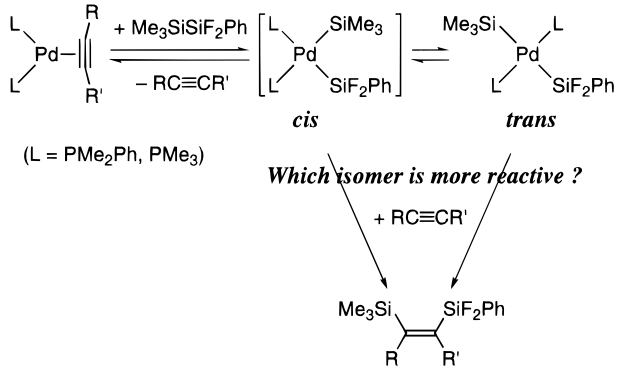
Two geometrical isomers of silyl(methyl)platinum complexes *cis*- and *trans*-PtMe($SiPh_3$)L_2 (L = PMe_2Ph, $PMePh_2$) exhibited entirely different reactivities toward phenylacetylene. Reactions of *cis*-PtMe($SiPh_3$)L_2 (L = PMe_2Ph (**1a**), $PMePh_2$ (**1b**)) with phenylacetylene readily proceeded at room temperature in benzene to give the acetylene-insertion products *cis*-PtMe{C(Ph)═CH($SiPh_3$)}L_2 (L = PMe_2Ph (**3a**), $PMePh_2$ (**3b**), respectively). In contrast, *trans*-PtMe($SiPh_3$)L_2 complexes (L = PMe_2Ph (**2a**), $PMePh_2$ (**2b**)) were totally inactive toward acetylene insertion. The *cis*-organo(silyl)platinum complexes *cis*-PtMe($SiPh_3$)(PMe_3)($PMePh_2$) (**1c**) and *cis*-Pt(COEt)($SiPh_3$)(PMe_2Ph)$_2$ (**6d**) also underwent the insertion of phenylacetylene into the Pt−$SiPh_3$ bond to provide quantitative yields of *cis*-PtMe{C(Ph)═CH($SiPh_3$)}(PMe_3)-($PMePh_2$) (**3c**) and *cis*-Pt(COEt){C(Ph)═CH($SiPh_3$)}(PMe_2Ph)$_2$ (**7**), respectively. The molecular structures of **3a**,**c** were determined by X-ray diffraction studies. Kinetic studies on the formation of **7** revealed the insertion process initiated by rate-determining displacement of one of the PMe_2Ph ligands in **6d** with phenylacetylene.

Introduction

Transition metal silyl complexes have attracted considerable recent interest because of their key roles in catalytic hydrosilylation and bis-silylation of unsaturated hydrocarbons.[1] Insertion of a C−C multiple bond into a transition metal−silyl bond is an important elementary process in such catalytic reactions. Although this process has been documented with some isolated transition metal silyl complexes,[2,3] the mechanistic details still remain to be explored.[4]

In the previous paper, we have shown that bis(silyl)-palladium complexes formed by the oxidative addition of unsymmetrical disilane Me_3SiSiF_2Ph to [Pd^0L_2] complexes (L = PMe_2Ph, PMe_3) exhibit extremely high reactivity toward insertion of acetylenes and olefins in catalytic and stoichiometric systems.[5] While bis(silyl) complexes observed in the reaction systems are *trans*-Pd($SiMe_3$)(SiF_2Ph)L_2, they are rapidly interconverted with the parent palladium(0) species and disilane (Scheme 1). Since it is accepted that the oxidative addition and the reductive elimination of disilane proceed via a concerted process,[6] the interconversion between palladium(0) complex and *trans*-bis(silyl)palladium(II) must involve an intermediate *cis*-bis(silyl)-palladium(II) species.

Scheme 1



In order to gain further insight into the insertion process, we tried in this study to compare the reactivity of *cis*- and *trans*-bis(silyl) complexes toward acetylenes. Because the two geometrical isomers of bis(silyl)palladium in Scheme 1 could not be prepared independently, we employed the platinum analogs *cis*- and *trans*-PtMe-($SiPh_3$)L_2 (L = PMe_2Ph, $PMePh_2$)[7] as models. We

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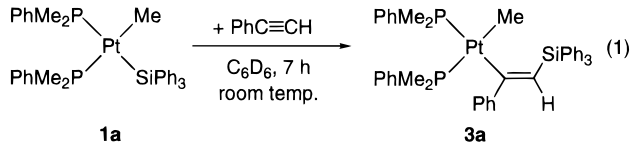
describe herein that the reactivity of silylplatinum complexes is significantly affected by the geometry about platinum and only the cis isomer undergoes insertion of phenylacetylene. A kinetic study on the mechanism of insertion is also reported. Portions of this work have been communicated.[8]

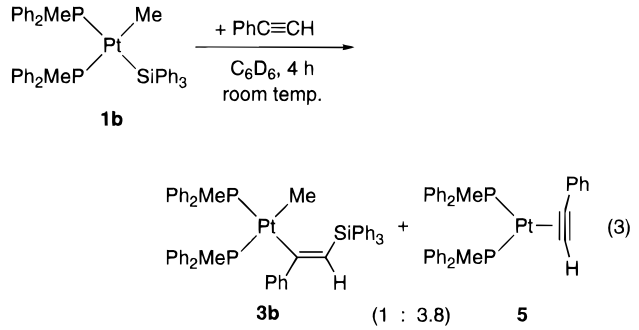
Results

Reactions of *cis*- and *trans*-PtMe(SiPh$_3$)L$_2$ with Phenylacetylene. A striking difference in the reactivity toward phenylacetylene was observed between the *cis*- and *trans*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ complexes (**1a** and **2a**, respectively). The reaction of *cis*-**1a** with phenylacetylene (5 equiv) in benzene-d_6 proceeded at room temperature for 7 h to give the insertion product **3a** in 70% yield together with some unidentified platinum species as confirmed by ^{31}P{^{1}H} NMR spectroscopy (eq 1). In contrast, *trans*-**2a** was inactive toward insertion



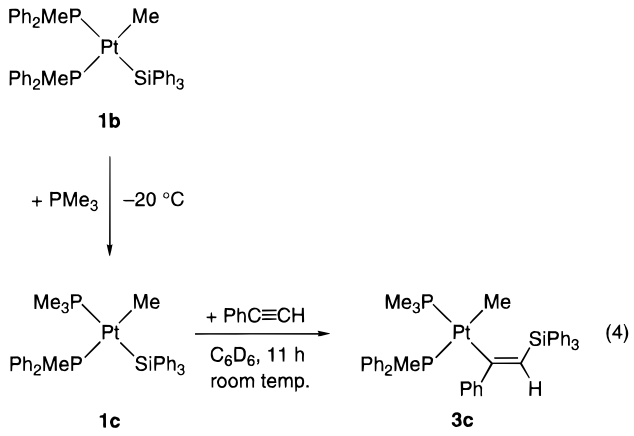
under similar reaction conditions, although *trans*-Pt(C≡CPh)(SiPh$_3$)(PMe$_2$Ph)$_2$ (**4**) was formed gradually when the system was allowed to stand at room temperature for 5 days (eq 2). Complexes **3a** and **4** were isolated as colorless crystals and characterized by NMR spectroscopy and elemental analysis. The structure of **3a** was confirmed by X-ray diffraction study (vide infra).

Similarly to *trans*-**2a**, *trans*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$ (**2b**) was inactive toward the insertion of phenylacetylene. On the other hand, *cis*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$ (**1b**) readily reacted with phenylacetylene (5 equiv) in benzene-d_6 at room temperature to afford two types of platinum complexes **3b** and **5** in a 1:3.8 ratio (eq 3).



Although these products could not be isolated, they were identified as *cis*-PtMe{C(Ph)=CH(SiPh$_3$)}(PMePh$_2$)$_2$ (**3b**) and Pt(PhC≡CH)(PMePh$_2$)$_2$ (**5**) on the basis of their ^{31}P{^{1}H} NMR data. Complex **3b** exhibited two sets of doublets ($^2J_{P-P}$ = 13 Hz) at δ 1.2 and 1.8 with $^1J_{Pt-P}$ values of 1961 and 1748 Hz, respectively, the values being comparable to those of **3a** (1961 and 1790 Hz). On the other hand, the ^{31}P{^{1}H} NMR signals of **5** appeared at δ 5.7 and 7.9 (each doublet, $^2J_{P-P}$ = 38 Hz) with $^1J_{Pt-P}$ values typical for platinum(0) complexes (3355 and 3481 Hz, respectively). Complexes **3b** and **5** are formed by the insertion of phenylacetylene into the Pt−SiPh$_3$ bond and by the reductive elimination of MeSiPh$_3$, respectively.

We have previously confirmed that the reductive elimination of *cis*-**1b** involves prior displacement of the PMePh$_2$ ligand trans to the SiPh$_3$ group with acetylene.[7] Therefore, in order to prevent the reductive elimination path in eq 3 and to improve the selectivity for the insertion of phenylacetylene, we introduced PMe$_3$ with a higher coordination ability than the PMePh$_2$ ligand into the trans position of the SiPh$_3$ group (eq 4).



Treatment of *cis*-**1b** with 1 equiv of PMe$_3$ in a Et$_2$O−pentane mixture (1:4) led to the selective formation of one geometrical isomer of PtMe(SiPh$_3$)(PMe$_3$)(PMePh$_2$) (**1c**), which exhibited two sets of doublets ($^2J_{P-P}$ = 21 Hz) at δ 6.3 ($^1J_{Pt-P}$ = 2144 Hz) and −13.2 ($^1J_{Pt-P}$ = 1342 Hz) in the ^{31}P{^{1}H} NMR spectrum. On the basis of the chemical shifts and the magnitude of $^1J_{Pt-P}$ values as well as the fact that only the signal at the higher magnetic field (δ −13.2) involves the satellites due to the coupling to the ^{29}Si nucleus ($^2J_{Si-P}$ = 198 Hz), we assigned the PMe$_3$ and PMePh$_2$ ligands in **1c** to the trans and cis positions of the SiPh$_3$ ligand, respectively. Complex **1c** thus prepared underwent the insertion of phenylacetylene into the Pt−SiPh$_3$ bond to provide the corresponding insertion product **3c**, exclusively (eq 4).

X-ray Structures of 3a,c. The ORTEP diagrams of **3a**,**c** are shown in Figures 1 and 2, respectively. The crystal of **3a** contained two crystallographically independent molecules, which are essentially superposable with each other. Figure 1 shows one of the molecules for simplicity. Table 1 lists the selected bond distances and angles. The platinum atom has a square planar geometry in both complexes, the sum of four angles about platinum being 360.0° for **3a** and 360.3° for **3c**. The C(2)−C(3) distances (1.33(1) Å for **3a** and 1.34(2) Å for **3c**) are in the typical range of a carbon−carbon double bond. The cis arrangement of the platinum and silicon atoms around the C=C double bond clearly shows the occurrence of cis insertion of phenylacetylene into the platinum−silyl bond.

Reactions of *cis*- and *trans*-PtR(SiPh$_3$)L$_2$ (R = Me, Et) with Carbon Monoxide. We have demonstrated above that only *cis*-silylplatinum undergoes the insertion of phenylacetylene into the Pt−SiPh$_3$ bond. In contrast, toward CO insertion, *trans*-alkyl(silyl)platinum complexes exhibited much higher reactivity than

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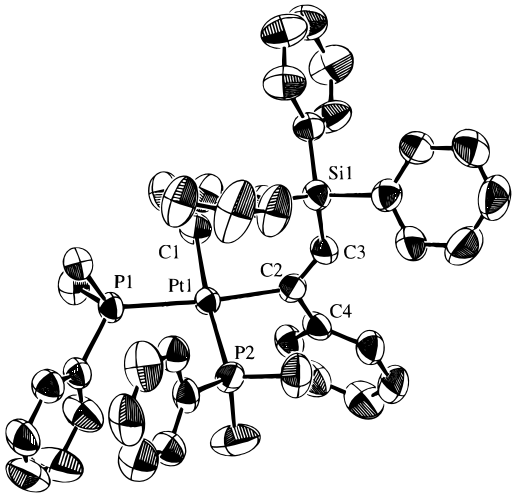


Figure 1. Molecular structure of *cis*-PtMe{C(Ph)═CH-($SiPh_3$)}(PMe_2Ph)$_2$ (**3a**). Only one of the two very similar but crystallographically independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level.

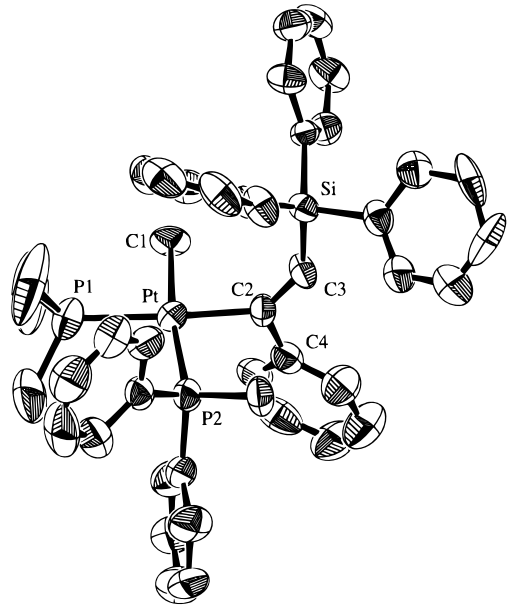
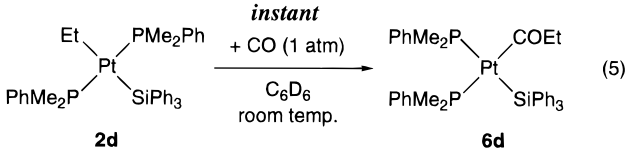


Figure 2. Molecular structure of PtMe{C(Ph)═CH($SiPh_3$)}-(PMe_3)($PMePh_2$) (**3c**). Thermal ellipsoids are drawn at the 50% probability level.

the cis isomers. For example, *trans*-PtEt($SiPh_3$)(PMe_2-Ph)$_2$ (**2d**) instantly reacted with CO (1 atm) in benzene-d_6 at room temperature to give propionyl−silyl complex **6d** (eq 5), whereas the reaction of cis isomer **1d** with



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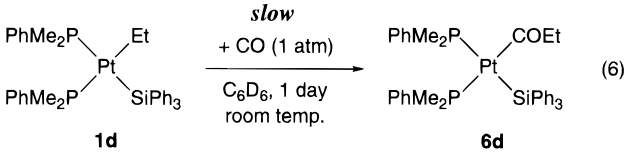


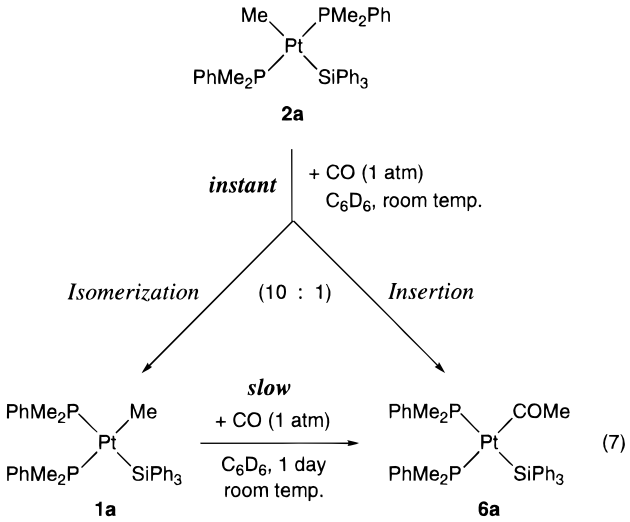
(6)

CO under the same reaction conditions took about 1 day for its completion (eq 6). In these reactions, the CO insertion occurs selectively at the Pt−C bond; no formation of the insertion product into Pt−Si bond was observed.

Table 1. Selected Bond Distances and Angles for 3a,c

3a		3c	
Distances (Å)			
Pt(1)−P(1)	2.313(2)	Pt−P(1)	2.311(4)
Pt(1)−P(2)	2.291(2)	Pt−P(2)	2.301(4)
Pt(1)−C(1)	2.122(8)	Pt−C(1)	2.09(1)
Pt(1)−C(2)	2.100(8)	Pt−C(2)	2.06(1)
C(2)−C(3)	1.33(1)	C(2)−C(3)	1.34(2)
C(2)−C(4)	1.48(1)	C(2)−C(4)	1.51(2)
Si(1)−C(3)	1.840(9)	Si−C(3)	1.83(1)
Angles (deg)			
P(1)−Pt(1)−P(2)	98.63(8)	P(1)−Pt−P(2)	97.2(1)
P(1)−Pt(1)−C(1)	87.3(2)	P(1)−Pt−C(1)	90.1(4)
P(1)−Pt(1)−C(2)	171.9(2)	P(1)−Pt−C(2)	171.6(4)
P(2)−Pt(1)−C(1)	174.1(2)	P(2)−Pt−C(1)	172.0(4)
P(2)−Pt(1)−C(2)	88.9(2)	P(2)−Pt−C(2)	89.7(3)
C(1)−Pt(1)−C(2)	85.2(3)	C(1)−Pt−C(2)	83.3(5)
Pt(1)−C(2)−C(3)	126.9(6)	Pt−C(2)−C(3)	131(1)
Pt(1)−C(2)−C(4)	113.4(6)	Pt−C(2)−C(4)	113.6(9)
C(3)−C(2)−C(4)	119.7(8)	C(3)−C(2)−C(4)	116(1)
Si(1)−C(3)−C(2)	137.6(7)	Si−C(3)−C(2)	137(1)

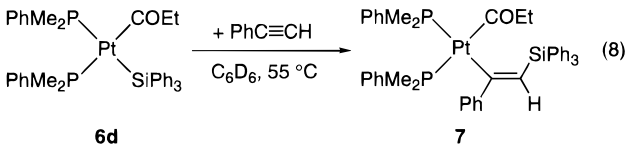
The much higher reactivity of trans complex than cis isomer toward CO-insertion was observed also with methyl−silyl complexes *cis*-**1a** and *trans*-**2a**, though the results were somewhat obscure due to the concomitantly occurring trans−cis isomerization (eq 7). When *trans*-



(7)

2a was treated with CO (1 atm) in benzene-d_6 at room temperature, complex **2a** disappeared within a few minutes to be replaced by the CO-insertion product (**6a**) and the isomerization product (*cis*-**1a**) in a 1:10 ratio. Thereafter, CO insertion of *cis*-**1a** gradually proceeded.

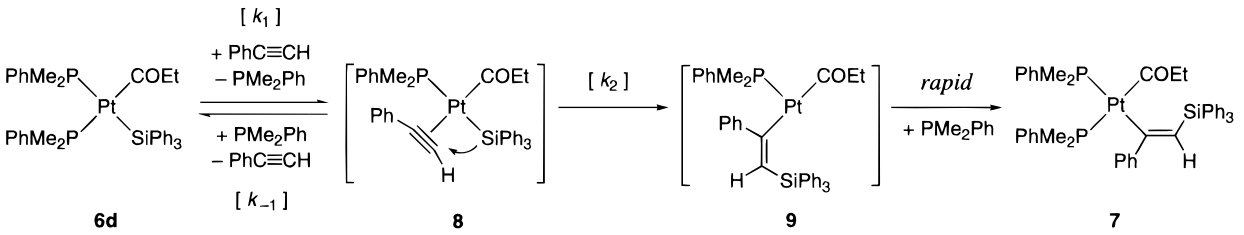
Kinetic Study on the Insertion of Phenylacetylene. Unlike the *cis*-methyl−silyl complexes, the *cis*-propionyl(silyl)platinum complex **6d** was fairly stable toward reductive elimination and cleanly reacted with phenylacetylene in benzene-d_6 to give the insertion product **7**, quantitatively (eq 8). In the presence of an



(8)

excess amount of phenylacetylene (10−25 equiv/**6d**), the

Scheme 2



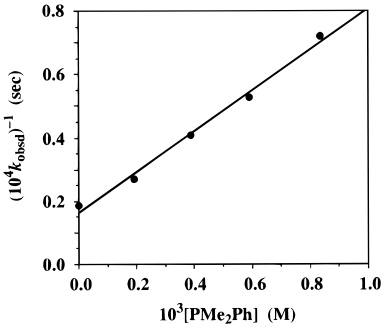


Figure 3. Effect of added PMe_2Ph on the reaction of **2d** with PhC≡CH in benzene-d_6 at 55 °C. Initial concentration: [**2d**] = (4.0 ± 0.2) × 10^{-2} M; [PhC≡CH] = 0.80 ± 0.01 M.

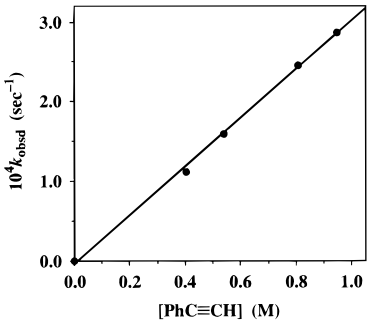


Figure 4. Effect of the concentration of PhC≡CH on the reaction of **2d** with PhC≡CH in benzene-d_6 in the presence of free PMe_2Ph at 55 °C. Initial concentration: [**2d**] = (4.0 ± 0.2) × 10^{-2} M; [PMe_2Ph] = (3.9 ± 0.1) × 10^{-4} M.

insertion reaction proceeded by obeying the first-order rate law in the concentration of **6d** over 70% conversion.

The reaction progress was effectively retarded by addition of free PMe_2Ph to the system; a plot of the reciprocals of rate constants ($1/k_{obsd}$) against the concentration of PMe_2Ph added to the system ([PMe_2Ph]) gave a straight line (r = 0.995) (Figure 3). On the other hand, the rate of insertion increased linearly as the concentration of phenylacetylene increased (r = 0.999) (Figure 4).[9]

These kinetic observations suggest the insertion mechanism depicted in Scheme 2. The first step is displacement of the PMe_2Ph ligand trans to the COEt group in **6d** with phenylacetylene, giving a four-coordinate silyl acetylene complex **8**, which successively undergoes insertion of the coordinated acetylene into the Pt−Si bond. Since the insertion most probably proceeds via a migration of the $SiPh_3$ group to the acetylene ligand, the initial product **9** must have a three-coordinate, *trans*-diorganoplatinum structure. Complex **9** is subsequently converted into the final product **7** by the trans−cis isomerization followed by coordination of the PMe_2Ph ligand.

Assumptions of the ligand displacement as the rate-determining step and of the steady-state approximation for the concentration of acetylene-coordinated silylplatinum species **8** in Scheme 2 lead to the kinetic expressions in eqs 9−11.

$$-\frac{\mathrm{d}[\mathbf{6d}]}{\mathrm{d}t} = \frac{k_1 k_2[\mathrm{PhC{\equiv}CH}]}{k_{-1}[\mathrm{PMe_2Ph}] + k_2}[\mathbf{6d}] \qquad (9)$$

$$k_{\mathrm{obsd}} = \frac{k_1 k_2[\mathrm{PhC{\equiv}CH}]}{k_{-1}[\mathrm{PMe_2Ph}] + k_2} \qquad (10)$$

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{k_{-1}[\mathrm{PMe_2Ph}]}{k_1 k_2[\mathrm{PhC{\equiv}CH}]} + \frac{1}{k_1[\mathrm{PhC{\equiv}CH}]} \qquad (11)$$

Equations 10 and 11 are consistent with the kinetic data represented by Figures 4 and 3, respectively. Using the values of slope (6.40 × 10^6 s M^{-1}) and intercept (1.65 × 10^3 s) of the plot in Figure 3, the following constants can be estimated from eq 11: $k_{-1}/(k_1k_2)$ = 5.12 × 10^6 s, k_1 = 7.57 × 10^{-4} s^{-1} M^{-1}. On the other hand, on the basis of eq 10 and the plot in Figure 4,

$$\frac{k_1 k_2}{k_{-1}[\mathrm{PMe_2Ph}] + k_2} = 3.06 \times 10^{-4}\ \mathrm{s^{-1}\ M^{-1}} \qquad (12)$$

Applying the experimental condition ([PMe_2Ph] = 3.9 × 10^{-4} M) for Figure 4 and the $k_{-1}/(k_1k_2)$ value (5.12 × 10^6 s) derived from Figure 3 to eq 12 provides the k_1 value of 7.87 × 10^{-4} s^{-1} M^{-1}, the value being in good agreement with that estimated from Figure 3 (7.57 × 10^{-4} s^{-1} M^{-1}).

Discussion

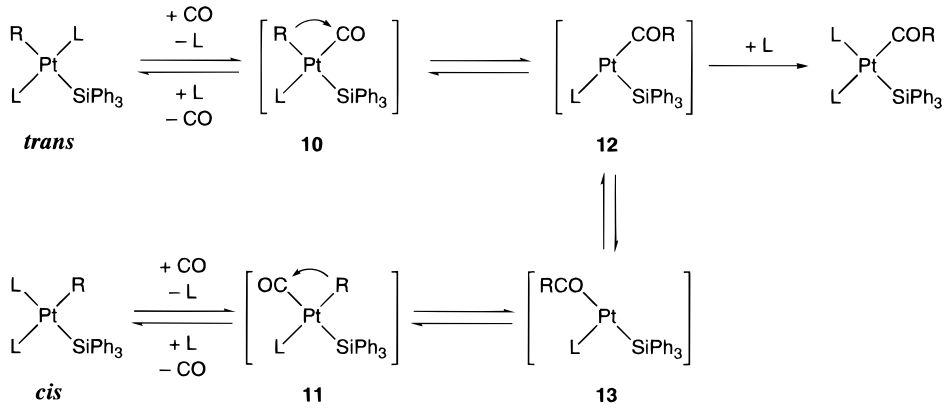
We have found that the reactivity of organo(silyl)-platinum complexes is strongly dependent upon the configuration about platinum. In addition, the relative reactivity of trans and cis isomers and the site of insertion varied dramatically with substrates. Thus, phenylacetylene reacted only with cis isomers, leading to the selective insertion into the Pt−Si bond. On the other hand, carbon monoxide inserted exclusively into the Pt−C bond and trans isomers exhibited much higher reactivity than cis isomers.

The reactivity order observed for CO insertion (trans >> cis) may be rationalized by assuming the insertion mechanism involving a four-coordinate intermediate [PtR($SiPh_3$)(CO)L] (R = Et, Me; L = PMe_2Ph)[10] and by taking into account the great trans influence of the $SiPh_3$ ligand. As shown in Scheme 3, replacement of

(9) The activation parameters estimated from an Eyring plot of the rate constants measured at four different temperatures (45, 50, 55, and 60 °C) are as follows: $\Delta H^{\ddagger}$ = 25.5 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 3.9 ± 1.4 eu.

(10) It has been confirmed that the CO insertion of **2d** is effectively retarded by addition of free PMe_2Ph to the system.

Scheme 3



one of the tertiary phosphine ligands (L) in *trans*- and *cis*-$PtR(SiPh_3)L_2$ with CO forms CO-coordinated alkyl–silyl intermediates **10** and **11**, respectively. In these intermediates, owing to the greater trans influence of the $SiPh_3$ ligand than the phosphine ligand (L), the Pt–R bond must be more weakened in **10** than in **11**,[11] and thereby the activation barrier for the alkyl migration becomes lower in **10** than in **11**. On the other hand, alkyl migration reactions in **10** and **11** form T-shaped, three-coordinate complexes **12** and **13**, respectively. In this case, the greater trans influence of the $SiPh_3$ ligand than the phosphine ligand probably makes **13** to be more unstable than **12**. The overall situations give rise to the more facile CO-insertion of trans isomers than cis isomers. Similar discussions based on trans influence have been made by Anderson and Cross to explain the difference in the reactivities of three geometrical isomers of $[PtR(CO)Cl(PR'_3)]$ toward CO-insertion.[12,13]

On the other hand, an apparently different argument is required to cope with the opposite order of reactivity observed for the acetylene insertion (cis ≫ trans). As a possible explanation, we have proposed in the preliminary report the insertion processes via five-coordinate intermediates, which are formed by the coordination of phenylacetylene to *cis*- and *trans*-$PtMe(SiPh_3)L_2$ complexes without dissociation of phosphine ligand (L).[8] However, since the present kinetic study using **6d** clearly showed the insertion process via a four-coordinate intermediate **8**, the other explanation for the much higher reactivity of cis isomers than trans isomers toward acetylene insertion is now needed.

The kinetic data indicated the ligand displacement of silyl complexes with phenylacetylene as the rate-determining step. Although we could obtain no direct information on the relative ease of ligand displacement between cis and trans isomers, the reactivity order observed for the acetylene insertion may be rationalized if one assumes *cis*-$PtMe(SiPh_3)L_2$ is more reactive toward ligand displacement than the trans isomer. Previously, Tanaka and his co-workers reported that *cis*-$Pt(SiMe_2Ph)_2(PMePh_2)_2$ was highly reactive toward insertion of unsaturated hydrocarbons; the reactions with diphenylacetylene, phenylacetylene, and ethylene proceeded readily at room temperature.[3a] The reported reactivity of *cis*-bis(silyl)platinum is considerably higher than that of *cis*-organo(silyl)platinums examined in this study. For the sake of more direct comparison, we prepared *cis*-$Pt(SiPh_3)_2(PMe_2Ph)_2$ and examined its reaction with phenylacetylene.[14] The reaction proceeded rapidly even at low temperature (−20 °C), giving the insertion product *cis*-$Pt\{C(Ph)=CH(SiPh_3)\}(SiPh_3)(PMe_2Ph)_2$. Clearly, *cis*-$Pt(SiPh_3)_2(PMe_2Ph)_2$ is much more reactive than *cis*-$PtMe(SiPh_3)(PMe_2Ph)_2$ (**1a**). Since the only distinction between the bis(silyl) complex and **1a** is the ligand trans to the coordination site for phenylacetylene ($SiPh_3$ or Me), it is convincing that the difference in the reactivity toward acetylene insertion is due to the relative ease of ligand displacement originating from the greater trans effect of the $SiPh_3$ ligand compared to the methyl ligand.

In conclusion, we have confirmed that *cis*-silylplatinum complexes are much more reactive than the corresponding trans isomers toward acetylene insertion. This observation seems crucial to understanding the details of catalytic bis-silylation, though the relation of the present platinum systems to actual palladium catalysis remains to be explored.

Experimental Section

General Procedure and Materials. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^1H NMR, 399.65 MHz; ^{13}C NMR, 100.40 MHz; ^{31}P NMR, 161.70 MHz). Chemical shifts are reported in δ ppm referred to an internal $SiMe_4$ standard for ^1H and ^{13}C NMR and to an external 85% H_3PO_4 standard for ^{31}P NMR.

THF, Et_2O, benzene, pentane, and hexane were dried over sodium benzophenone ketyl and distilled just before using. CH_2Cl_2 was dried over CaH_2 and distilled just before using. Benzene-d_6 was dried over $LiAlH_4$ and vacuum transferred and stored under a nitrogen atmosphere. $PMePh_2$ and PMe_2Ph were prepared by the reactions of MeMgBr with $PClPh_2$ and PCl_2Ph, respectively. *trans*-$PtCl(SiPh_3)(PMe_2Ph)_2$[15] and *cis*- and *trans*-$PtMe(SiPh_3)(PMePh_2)_2$ (**1b** and **2b**, respectively)[7] were prepared as reported. All other compounds used in this study were obtained from commercial sources and used without further purification.

(11) Note that the $^1J_{Pt-C(Me)}$ value of *trans*-**2a** (372 Hz) having a $SiPh_3$ group trans to the methyl group is much smaller than the $^1J_{Pt-C(Me)}$ value of *cis*-**1a** (508 Hz), in which PMe_2Ph is trans to the methyl group. These data indirectly support the weaker Pt–R bond in **10** compared to that in **11**.

(12) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67. For a theoretical study, see: Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280.

(13) Predominant role of trans influence has been predicted by an ab-initio MO study on the insertion of ethylene into *trans*- and *cis*-$PtH(SiH_3)(PH_3)_2$ complexes.[4a]

(14) Ozawa, F.; Kamite, J. Unpublished results.

(15) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.

Preparation of *cis*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (1a). To a solution of *trans*-PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$ (1.01 g, 1.32 mmol) in THF (4 mL) was added an Et$_2$O solution of MeLi (1.4 M, 1.9 mL, 2.66 mmol) at 0 °C. The mixture was stirred at room temperature for 15 min and then cooled to −20 °C. Methanol (1 mL) was slowly added, and the solution was concentrated to dryness. The resultant solid was extracted with CH_2Cl_2 (2 × 4 mL) and filtered through a filter-paper-tipped cannula, and then the solution was concentrated to 1 mL. Et$_2$O (*ca.* 5 mL) was carefully layered on the CH_2Cl_2 solution and the solvent layers were allowed to stand at −20 °C to form colorless crystals of **1a** (0.80 g, 81%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.21 (dd, $^3J_{P-H}$ = 12.7 and 6.3 Hz, $^2J_{Pt-H}$ = 60.0 Hz, 3H, PtC*H*$_3$), 1.09 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 22.4 Hz, 6H, PC*H*$_3$), 1.33 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 15.6 Hz, 6H, PC*H*$_3$), 7.1−7.4 (m, 15H, Ph), 7.4−7.6 (m, 4H, Ph), 7.62 (m, 6H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 1.3 (dd, $^2J_{P-C}$ = 81 and 8 Hz, $^1J_{Pt-C}$ = 508 Hz, Pt*C*H$_3$), 13.4 (d, $^1J_{P-C}$ = 23 Hz, $^2J_{Pt-C}$ = 17 Hz, P*C*H$_3$), 17.1 (dd, J_{P-C} = 30 and 3 Hz, $^2J_{Pt-C}$ = 33 Hz, P*C*H$_3$), 127.0 (s, SiPh), 127.2 (s, SiPh), 128.4 (d, $^3J_{P-C}$ = 7 Hz, PPh), 128.5 (d, $^3J_{P-C}$ = 7 Hz, PPh), 129.7 (s, PPh), 129.9 (s, PPh), 131.3 (m, PPh), 137.3 (s, $^3J_{Pt-C}$ = 23 Hz, SiPh), 137.8 (d, $^1J_{P-C}$ = 36 Hz, $^2J_{Pt-C}$ = 12 Hz, PPh), 140.1 (dd, J_{P-C} = 43 and 3 Hz, PPh), 145.6 (d, $^3J_{P-C}$ = 5 Hz, $^2J_{Pt-C}$ = 48 Hz, SiPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −10.9 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 2048 Hz), −3.7 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 1330 Hz, $^2J_{Si-P}$ = 198 Hz). Anal. Calcd for $C_{35}H_{40}P_2PtSi$: C, 56.37; H, 5.41. Found: C, 56.18; H, 5.39.

Preparation of *trans*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (2a). To a solution of *trans*-PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$ (2.0 g, 2.61 mmol) in THF (10 mL) was added an Et$_2$O solution of Me$_2$Mg (2.3 M, 1.13 mL, 2.60 mmol) at 0 °C. The mixture was stirred at room temperature for 15 min and then cooled to −20 °C. Methanol (1 mL) was added, and the solution was concentrated to dryness. The resultant solid was extracted with CH_2Cl_2 (3 mL × 3) and filtered through a filter-paper-tipped cannula, and the combined extracts were concentrated to ca. 1 mL. Et$_2$O (*ca.* 5 mL) was carefully layered on the CH_2Cl_2 solution, and the solvent layers were allowed to stand at −20 °C to give colorless crystals of **2a** (1.31 g, 66%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.04 (t, $^3J_{P-H}$ = 6.8 Hz, $^2J_{Pt-H}$ = 43.9 Hz, 3H, PtC*H*$_3$), 1.33 (virtual triplet, J = 3.2 Hz, $^3J_{P-H}$ = 31.2 Hz, 12H, PC*H*$_3$), 7.13 (m, 9H, Ph), 7.35 (m, 6H, Ph), 7.55 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 6.9 (t, $^2J_{P-C}$ = 9 Hz, $^1J_{Pt-C}$ = 372 Hz, Pt*C*H$_3$), 14.7 (virtual triplet, J = 19 Hz, $^2J_{Pt-C}$ = 38 Hz, P*C*H$_3$), 127.0 (s, SiPh), 127.1 (s, SiPh), 128.2 (virtual triplet, J = 5 Hz, PPh), 129.9 (s, PPh), 131.9 (virtual triplet, J = 6 Hz, PPh), 136.8 (virtual triplet, J = 28 Hz, $^2J_{Pt-C}$ = 28 Hz, PPh), 137.2 (s, SiPh), 148.2 (s, $^2J_{Pt-C}$ = 26 Hz, SiPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −3.6 (s, $^1J_{Pt-P}$ = 2778 Hz). Anal. Calcd for $C_{35}H_{40}P_2PtSi$: C, 56.37; H, 5.41. Found: C, 56.18; H, 5.29.

Preparation of PtMe(SiPh$_3$)(PMe$_3$)(PMePh$_2$) (1c). The complex *cis*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$ (**1b**) (167 mg, 0.18 mmol) was suspended in a mixture of Et$_2$O (1 mL) and pentane (4 mL) at −20 °C, and a solution of PMe$_3$ in Et$_2$O (0.3 M, 1.2 mL, 0.36 mmol) was added by means of a syringe. The white heterogeneous mixture was stirred at room temperature for 17 h, and the solvent was removed under reduced pressure. The resultant solid was washed with Et$_2$O at −20 °C and dried under vacuum (72 mg, 53%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.37 (dd, $^3J_{P-H}$ = 12.7 and 6.3 Hz, $^2J_{Pt-H}$ = 59.5 Hz, 3H, PtC*H*$_3$), 0.94 (d, $^2J_{P-H}$ = 7.8 Hz, $^3J_{Pt-H}$ = 16.6 Hz, 9H, P(C*H*$_3$)$_3$), 1.32 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 28.3 Hz, 3H, P(C*H*$_3$)Ph$_2$), 7.04−7.14 (m, 9H, Ph), 7.36 (m, 6H, Ph), 7.50 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 1.9 (dd, $^2J_{P-C}$ = 79 and 8 Hz, $^1J_{Pt-C}$ = 536 Hz, Pt*C*H$_3$), 14.1 (d, $^1J_{P-C}$ = 24 Hz, $^2J_{Pt-C}$ = 18 Hz, P*C*H$_3$), 16.7 (dd, J_{P-C} = 35 and 5 Hz, P(*C*H$_3$)Ph$_2$), 126.8 (s, SiPh), 126.9 (s, SiPh), 128.6 (d, $^3J_{P-C}$ = 10 Hz, PPh), 130.1 (s, PPh), 132.7 (d, $^2J_{P-C}$ = 12 Hz, $^3J_{Pt-C}$ = 18 Hz, PPh), 137.1 (s, $^3J_{Pt-C}$ = 22 Hz, SiPh), 137.9 (dd, J_{P-C} = 40 and 3 Hz, PPh), 145.5 (d, $^3J_{P-C}$ = 7 Hz, $^2J_{Pt-C}$ = 41 Hz, SiPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 6.3 (d, $^2J_{P-P}$ = 21 Hz,^{1} J_{Pt-P} = 2144 Hz), −13.2 (d, $^2J_{P-P}$ = 21 Hz, $^1J_{Pt-P}$ = 1342 Hz, $^2J_{Si-P}$ = 198 Hz). Anal. Calcd for $C_{35}H_{40}P_2PtSi$: C, 56.37; H, 5.41. Found: C, 56.13; H, 5.39.

Preparation of *cis*-PtEt(SiPh$_3$)(PMe$_2$Ph)$_2$ (1d). A solid of EtLi (43.7 mg, 1.21 mmol) was placed in a Schlenk tube and cooled to 0 °C. A solution of *trans*-PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$ (205 mg, 0.27 mmol) in THF (4 mL) was added, and the mixture was stirred for 30 min at room temperature. The mixture was cooled to −20 °C, and methanol (*ca.* 0.5 mL) was slowly added. The solution was concentrated to dryness to give a pale yellow solid, which was extracted two times with 3 mL of CH_2Cl_2 and filtered through a filter-paper-tipped cannula. The combined extracts were concentrated to 1 mL, and Et$_2$O (ca. 5 mL) was carefully layered on the CH_2Cl_2 solution. The solvent layers were allowed to stand at −20 °C to form colorless crystals of **1d** (115 mg, 56%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.65 (q, $^3J_{H-H}$ = 7.8 Hz, $^2J_{Pt-H}$ = 59.5 Hz, 2H, PtC*H*$_2$CH$_3$), 1.02 (d, $^2J_{P-H}$ = 7.8 Hz, $^3J_{Pt-H}$ = 20.5 Hz, 6H, PC*H*$_3$), *ca.* 1.05 (3H, PtCH$_2$C*H*$_3$, the coupling pattern and the exact chemical shift were obscured due to overlap with the PC*H*$_3$ signals), 1.31 (d, $^2J_{P-H}$ = 7.3 Hz, $^3J_{Pt-H}$ = 15.6 Hz, 6H, PC*H*$_3$), 7.20 (m, 9H, Ph), 7.3−7.4 (m, 6H, Ph), 7.5−7.6 (m, 4H, Ph), 7.63 (m, 6H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 11.0 (dd, $^2J_{P-C}$ = 79 and 7 Hz, $^1J_{Pt-C}$ = 533 Hz, PtCH$_2$CH$_3$), 13.4 (d, $^1J_{P-C}$ = 23 Hz, P*C*H$_3$), 16.8 (dd, J_{P-C} = 28 and 3 Hz, P*C*H$_3$), 16.8 (s, PtCH$_2$*C*H$_3$), 126.8 (s, SiPh), 126.9 (s, SiPh), 128.2 (d, $^3J_{P-C}$ = 8 Hz, PPh), 129.5 (s, PPh), 129.7 (s, PPh), 131.2 (m, PPh), 137.0 (s, $^3J_{Pt-C}$ = 22 Hz, SiPh), 137.8 (d, $^1J_{P-C}$ = 36 Hz, PPh), 140.0 (dd, J_{P-C} = 36 and 2 Hz, PPh), 145.5 (d, $^3J_{P-C}$ = 5 Hz, $^2J_{Pt-C}$ = 46 Hz, SiPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −4.0 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 1437 Hz, $^2J_{Si-P}$ = 193 Hz), −12.9 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 1792 Hz). Anal. Calcd for $C_{36}H_{42}P_2PtSi$: C, 56.91; H, 5.57. Found: C, 56.81; H, 5.68.

Preparation of *trans*-PtEt(SiPh$_3$)(PMe$_2$Ph)$_2$ (2d). To a solution of *trans*-PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$ (518 mg, 0.676 mmol) in THF (17 mL) was added an Et$_2$O solution of Et$_2$Mg (0.93 M, 1.09 mL, 1.01 mmol) at 0 °C. The solution was stirred at room temperature for 15 min and then cooled to −20 °C. MeOH (2 mL) was added, and the mixture was concentrated to dryness under vacuum. The resultant solid was extracted with CH_2Cl_2 and filtered through a filter-paper-tipped cannula. The extract was concentrated to dryness, and the resultant solid was dissolved in a minimum amount of CH_2Cl_2 at room temperature, diluted with Et$_2$O, and cooled at −20 °C to give white crystals of **2d** (516 mg, 70%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.64 (q, $^3J_{H-H}$ = 7.8 Hz, $^2J_{Pt-H}$ = 43.7 Hz, 2H, PtC*H*$_2$-CH$_3$), 0.97 (t, $^3J_{H-H}$ = 7.8 Hz, $^3J_{Pt-P}$ = 35.6 Hz, 3H, PtCH$_2$C*H*$_3$), 1.32 (virtual triplet, J = 3.4 Hz, $^3J_{Pt-H}$ = 31.2 Hz, 12H, PC*H*$_3$), 7.09 (m, 9H, Ph), 7.30 (m, 6H, Ph), 7.43 (m, 6H, Ph), 7.56 (m, 4H, Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ −3.5 (s, $^1J_{Pt-P}$ = 2919 Hz). Anal. Calcd for $C_{36}H_{42}P_2PtSi$: C, 56.91; H, 5.57. Found: C, 56.84; H, 5.47.

Preparation of *cis*-PtMe{C(Ph)=CH(SiPh$_3$)}(PMe$_2$Ph)$_2$ (3a). To a solution of *cis*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (**1a**) (108 mg, 0.15 mmol) in benzene (3 mL) was added phenylacetylene (50 μL, 0.46 mmol) at room temperature. The homogeneous solution was stirred at room temperature for 26 h and concentrated to dryness. The orange solid was dissolved in Et$_2$O (ca. 1 mL), and a small amount of pentane (1 drop) was added. The solution was cooled in a refrigerator for 1 day to give colorless crystals of **3a**, suitable for X-ray diffraction study (34.2 mg, 32%). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 0.39 (dd, $^3J_{P-H}$ = 7.8 and 4.8 Hz, $^2J_{Pt-H}$ = 67.8 Hz, PtC*H*$_3$), 0.88 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 22.4 Hz, PC*H*$_3$), 0.96 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 22.4 Hz, PC*H*$_3$), 1.00 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 22.4 Hz, PC*H*$_3$), 1.31 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 22.4 Hz, PC*H*$_3$), 6.61 (t, 2H, Ph), 7.20 (m, 4H, Ph), 7.15−7.40 (m, 16H, Ph), 7.55 (d, $^4J_{P-H}$ = 17.1 Hz, 1H, PtC=C*H*), 7.72 (m, 8H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 0.67 (dd, $^2J_{P-C}$ = 93 and 10 Hz, $^1J_{Pt-C}$ = 581 Hz, Pt*C*H$_3$), 13.2 (d, $^1J_{P-C}$ = 33 Hz, P*C*H$_3$), 13.4 (d, $^1J_{P-C}$ = 33 Hz, P*C*H$_3$), 13.9 (d, $^1J_{P-C}$ = 33 Hz, P*C*H$_3$), 14.9 (d, $^1J_{P-C}$ = 33 Hz, P*C*H$_3$), 123.9 (br, $^2J_{Pt-C}$ = 51 Hz, PtC=*C*H), 125.6 (s, Ph), 127.6 (m, Ph), 128.0 (s, Ph), 128.3 (s, Ph), 128.9

(s, Ph), 129.2 (s, Ph), 130.6 (s, Ph), 137.0 (s, Ph), 138.9 (s, Ph), 155.5 (s, $^2J_{Pt-C}$ = 37 Hz, Ph), 195.0 (dd, $^2J_{P-C}$ = 118 and 15 Hz, $^1J_{Pt-C}$ = 854 Hz, Pt*C*═CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −15.5 (d, $^2J_{P-P}$ = 15 Hz, $^1J_{Pt-P}$ = 1961 Hz), −15.5 (d, $^2J_{P-P}$ = 15 Hz, $^1J_{Pt-P}$ = 1790 Hz). Anal. Calcd for $C_{43}H_{46}P_2PtSi$: C, 60.91; H, 5.47. Found: C, 60.33; H, 4.99.

Preparation of *trans*-Pt(C≡CPh)(SiPh$_3$)(PMe$_2$Ph)$_2$ (4). The complex *trans*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (**2a**) (65.2 mg, 0.0874 mmol) was placed in a Schlenk tube and dissolved in benzene (1 mL) at room temperature. Phenylacetylene (30 μL, 0.27 mmol) was added, and the mixture was allowed to stand at 20 °C for 5 days. The $^{31}P\{^1H\}$ NMR spectrum of the solution exhibited a singlet signal at δ −11.5 ($^1J_{Pt-P}$ = 2582 Hz) assignable to **4**; no peaks due to the starting complex **2a** were observed. The solution was concentrated to dryness, and the resultant pale yellow solid was dissolved in CH_2Cl_2 (ca. 0.5 mL), diluted with Et_2O (4 mL), and allowed to stand at −20 °C for 1 day to give colorless crystals of **4** (48.2 mg, 66%). ^1H NMR (CD_2Cl_2, −20 °C): δ 1.57 (virtual triplet, J = 3.2 Hz, $^3J_{Pt-H}$ = 31.7 Hz, 12H, PC*H*$_3$), 7.06−7.20 (m, 14H, Ph), 7.26−7.38 (m, 6H, Ph), 7.44 (d, 6H, Ph), 7.52 (q, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 16.4 (virtual triplet, J = 20 Hz, $^2J_{Pt-C}$ = 83 Hz, P*C*H$_3$), 111.4 (s, $^1J_{Pt-C}$ = 198 Hz, PtC≡*C*Ph), 125.6 (s, Ph), 126.3 (t, $^2J_{P-C}$ = 19 Hz, $^1J_{Pt-C}$ = 758 Hz, Pt*C*≡CPh), 127.2 (s, SiPh), 127.5 (s, SiPh), 128.2 (virtual triplet, J = 5 Hz, PPh), 128.3 (s, Ph), 130.0 (s, PPh), 130.7 (s, Ph), 131.8 (virtual triplet, J = 6 Hz, PPh), 136.4 (virtual triplet, J = 28 Hz, $^2J_{Pt-P}$ = 28 Hz, PPh), 137.3 (s, $^3J_{Pt-C}$ = 17 Hz, SiPh), 145.7 (s, $^2J_{Pt-C}$ = 30 Hz, SiPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −11.4 (s, $^1J_{Pt-P}$ = 2551 Hz). IR (Nujol): $\nu_{C\equiv C}$ = 2080 cm^{-1}. Anal. Calcd for $C_{42}H_{42}P_2PtSi$: C, 60.64; H, 5.09. Found: C, 60.41; H, 4.90.

Reaction of *cis*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$ (1b) with Phenylacetylene. Complex **1b** (28.8 mg, 0.0306 mmol) was placed in an NMR sample tube equipped with a rubber septum and dissolved in benzene-d_6 (0.6 mL) at room temperature. Phenylacetylene (17.0 μL, 0.154 mmol) was added, and the solution was allowed to stand at room temperature for 4 h. The $^{31}P\{^1H\}$ NMR spectrum exhibited two sets of AB patterns in a ratio of 1:3.8 together with some unidentified small peaks: δ 1.2 ($^2J_{P-P}$ = 13 Hz, $^1J_{Pt-P}$ = 1961 Hz) and 1.8 ($^2J_{P-P}$ = 13 Hz, $^1J_{Pt-P}$ = 1748 Hz); δ 5.7 ($^2J_{P-P}$ = 38 Hz, $^1J_{Pt-P}$ = 3355 Hz) and 7.9 ($^2J_{P-P}$ = 38 Hz, $^1J_{Pt-P}$ = 3481 Hz). On the basis of the magnitude of the $^1J_{Pt-P}$ values, the former AB signals were assigned to *cis*-PtMe{C(Ph)═CH(SiPh$_3$)}(PMePh$_2$)$_2$ (**3b**) and the latter to Pt(PhC≡CH)(PMePh$_2$)$_2$ (**5**). Several attempts for isolation of **3b** and **5** from the reaction mixture were unsuccessful.

Complex **5** was independently synthesized and identified. To a solution of Pt(cod)$_2$ (56 mg, 0.15 mmol) in benzene (1 mL) were added PhC≡CH (50 μL, 0.45 mmol) and PMePh$_2$ (57 μL, 0.306 mmol) at 0 °C. The solution was stirred for 1 h at room temperature and concentrated to dryness. The residue was washed with a small amount of Et_2O at −50 °C and dried under vacuum (97.4 mg, 93%). ^1H NMR (C_6D_6, 23 °C): δ 1.60 (d, $^2J_{P-H}$ = 7.3 Hz, $^3J_{Pt-H}$ = 28.3 Hz, 3H, PC*H*$_3$), 1.74 (d, $^2J_{P-H}$ = 6.8 Hz, $^3J_{Pt-H}$ = 27.3 Hz, 3H, PC*H*$_3$), 6.85−7.05 (m, 15H, Ph), 7.57 (m, 10H, Ph), 7.83 (dd, $^2J_{P-H}$ = 24.2 and 12.4 Hz, $^2J_{Pt-H}$ = 51.7 Hz, 1H, PhC≡C*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ 5.7 (d, $^2J_{P-P}$ = 38 Hz, $^1J_{Pt-P}$ = 3355 Hz), 7.9 (d, $^2J_{P-P}$ = 38 Hz, $^1J_{Pt-P}$ = 3481 Hz). Anal. Calcd for $C_{34}H_{32}P_2Pt$: C, 58.53; H, 4.62. Found: C, 58.72; H, 4.55.

Preparation of PtMe{C(Ph)═CH(SiPh$_3$)}(PMe$_3$)(PMePh$_2$) (3c). The complex PtMe(SiPh$_3$)(PMe$_3$)(PMePh$_2$) (32.0 mg, 0.0429 mmol) was placed in an NMR sample tube equipped with a rubber septum and dissolved in benzene-d_6 (0.6 mL). Phenylacetylene (23.6 μL, 0.214 mmol) was added to the solution, and the mixture was allowed to stand at 20 °C for 11 h. $^{31}P\{^1H\}$ NMR analysis of the solution revealed the selective formation of **3c**. The solution was transferred into a Schlenk tube and concentrated to dryness. The resultant orange solid was dissolved in Et_2O (*ca.* 0.5 mL), and a small quantity of pentane was added (1 drop). The solution was allowed to stand in a refrigerator for 1 day to give colorless crystals of **3c**, suitable for X-ray diffraction study (26 mg, 71%). ^1H NMR ($CDCl_3$, 23 °C): δ 0.60 (dd, $^3J_{P-H}$ = 9.8 and 6.3 Hz, $^2J_{Pt-H}$ = 68.8 Hz, 3H, PtC*H*$_3$), 0.89 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 20.5 Hz, 9H, P(C*H*$_3$)$_3$), 1.62 (d, $^2J_{P-H}$ = 8.3 Hz, $^3J_{Pt-H}$ = 21.5 Hz, P(C*H*$_3$)Ph$_2$), 6.8−7.8 (m, 30H, Ph), 7.47 (dd, $^4J_{P-H}$ = 21.5 and 2.9 Hz, 1H, PtC═C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 2.4 (dd, $^2J_{P-C}$ = 91 and 8 Hz, $^1J_{Pt-C}$ = 579 Hz, Pt*C*H$_3$), 14.7 (d, $^1J_{P-C}$ = 25 Hz, P(*C*H$_3$)$_3$), 15.3 (d, $^1J_{P-C}$ = 31 Hz, P(*C*H$_3$)Ph$_2$), 125.1 (s, PtC═*C*H), 194.7 (dd, $^1J_{PtC}$ = 827 Hz, $^2J_{PC}$ = 116 and 12 Hz, Pt*C*═CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C): δ 1.1 (d, $^2J_{P-P}$ = 16 Hz, $^1J_{Pt-P}$ = 1980 Hz), −27.5 (d, $^2J_{P-P}$ = 16 Hz, $^1J_{Pt-P}$ = 1729 Hz). Anal. Calcd for $C_{43}H_{46}P_2PtSi$: C, 60.91; H, 5.47. Found: C, 60.52; H, 5.50.

Preparation of *cis*-Pt(COMe)(SiPh$_3$)(PMe$_2$Ph)$_2$ (6a). A solution of *cis*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (**1a**) (50 mg, 0.067 mmol) in benzene (3 mL) was stirred under carbon monoxide (1 atm) at room temperature for 1 day. The solution was concentrated to dryness under reduced pressure to give a white solid, which was dissolved in CH_2Cl_2 (1 mL). Et_2O (5mL) was layered on the CH_2Cl_2 solution, and the solvent layers were allowed to stand at −20 °C to form colorless crystals of **6a** (30 mg, 58%). ^1H NMR (CD_2Cl_2, −20 °C): 0.89 (br, 3H, PC*H*$_3$), 1.24 (br, 3H, PC*H*$_3$), 1.53 (s, PtCOC*H*$_3$), 7.2−7.5 (m, 19H, Ph), 7.7−7.8 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20°C): δ 14.4 (br, P*C*H$_3$), 15.9 (d, $^1J_{P-C}$ = 22 Hz, P*C*H$_3$), 46.6 (d, $^3J_{P-C}$ = 24 Hz, $^2J_{Pt-C}$ = 244 Hz, PtCO*C*H$_3$), 127.2 (s, SiPh), 127.7 (s, SiPh), 128.7 (s, PPh), 129.9 (s, PPh), 130.2 (s, PPh), 131.0 (m, PPh), 136.6 (d, $^1J_{P-C}$ = 39 Hz, PPh), 137.2 (s, SiPh), 138.2 (d, $^1J_{P-C}$ = 44 Hz, PPh), 145.1 (s, $^2J_{Pt-C}$ = 54 Hz, SiPh), 252.7 (dd, $^2J_{P-C}$ = 105 and 12 Hz, $^1J_{Pt-C}$ = 781 Hz, Pt*C*OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −19.2 (d, $^2J_{P-P}$ = 23 Hz, $^1J_{Pt-P}$ = 1422 Hz), −7.3 (d, $^2J_{P-P}$ = 23 Hz, $^1J_{Pt-P}$ = 1609 Hz, $^2J_{Si-P}$ = 144 Hz). IR (Nujol): 1605 cm^{-1}. Anal. Calcd for $C_{36}H_{40}OP_2PtSi$: C, 55.88; H, 5.21. Found: C, 55.73; H, 5.39.

Preparation of *cis*-Pt(COEt)(SiPh$_3$)(PMe$_2$Ph)$_2$ (6d). A solution of *cis*-PtEt(SiPh$_3$)(PMe$_2$Ph)$_2$ (54 mg, 0.071 mmol) in benzene (3 mL) was stirred under carbon monoxide (1 atm) at room temperature for 1 day and then concentrated to dryness. The resultant white solid was dissolved in CH_2Cl_2 (1 mL). Et_2O (5mL) was carefully layered on the CH_2Cl_2 solution, and the solvent layers were allowed to stand at −20 °C to form colorless crystals of **6d** (56 mg, 76%). ^1H NMR (CD_2Cl_2, −20 °C): δ 0.20 (t, $^3J_{H-H}$ = 7.1 Hz, PtCOCH$_2$C*H*$_3$), 0.87 (br, PC*H*$_3$), 1.21 (br, PC*H*$_3$), 1.6−2.3 (br, PtCOC*H*$_2$CH$_3$), 7.2−7.5 (m, 19H, Ph), 7.7 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 8.0 (s, $^3J_{Pt-C}$ = 29 Hz, PtCOCH$_2$*C*H$_3$), 14.3 (br, P*C*H$_3$), 15.9 (br, P*C*H$_3$), 53.3 (d, $^3J_{P-C}$ = 27 Hz, $^2J_{Pt-C}$ = 225 Hz, PtCO*C*H$_2$CH$_3$), 127.2 (s, SiPh), 127.6 (s, SiPh), 128.6 (d, $^3J_{P-C}$ = 7 Hz, PPh), 128.7 (d, $^3J_{P-C}$ = 7 Hz, PPh), 129.9 (s, PPh), 130.1 (s, PPh), 130.9 (d, $^2J_{P-C}$ = 12 Hz, PPh), 131.1 (d, $^2J_{P-C}$ = 12 Hz, PPh), 136.8 (d, $^1J_{P-C}$ = 39 Hz, PPh), 137.2 (s, SiPh), 138.3 (d, $^1J_{P-C}$ = 39 Hz, PPh), 145.1 (s, $^2J_{Pt-C}$ = 51 Hz, SiPh), 251.9 (dd, $^2J_{P-C}$ = 103 and 12 Hz, $^1J_{Pt-C}$ = 791 Hz, Pt*C*OEt). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −19.0 (d, $^2J_{P-P}$ = 23 Hz, $^1J_{Pt-P}$ = 1422 Hz), −6.2 (d, $^2J_{P-P}$ = 23 Hz, $^1J_{Pt-P}$ = 1606 Hz, $^2J_{Si-P}$ = 146 Hz). IR (Nujol): ν_{CO} = 1605 cm^{-1}. Anal. Calcd for $C_{37}H_{42}OP_2PtSi$: C, 56.41; H, 5.37. Found: C, 55.84 ; H, 5.37.

Preparation of *cis*-Pt(COEt){C(Ph)═CH(SiPh$_3$)}(PMe$_2$Ph)$_2$ (7). To a solution of *cis*-Pt(COEt)(SiPh$_3$)(PMe$_2$Ph)$_2$ (109 mg, 0.14 mmol) in benzene (5 mL) was added phenylacetylene (270 mg, 2.6 mmol) at room temperature. The mixture was stirred at 60 °C for 2.5 h, cooled to room temperature, and then concentrated to dryness under reduced pressure. The resultant yellow solid was washed with Et_2O (2 mL × 2) at −20 °C and recrystallized from a CH_2Cl_2−Et_2O mixture to give colorless crystals of **7** (60 mg, 48%). ^1H NMR (CD_2Cl_2, −20 °C): δ 0.47 (t, $^3J_{H-H}$ = 7.1 Hz, PtCOCH$_2$C*H*$_3$), 0.72 (d, $^2J_{P-H}$ = 8.8 Hz, 3H, PC*H*$_3$), 0.85 (d, $^2J_{P-H}$ = 8.8 Hz, PC*H*$_3$), 1.03 (d, $^2J_{P-H}$ = 8.8 Hz, PC*H*$_3$), 1.27 (d, $^2J_{P-H}$ = 8.8 Hz, PC*H*$_3$), 2.2−2.6 (m, PtCOC*H*$_2$CH$_3$), 6.28 (dd, J = 9.3 and 8.3 Hz, 2H, Ph), 6.95−7.45 (m, 20H, Ph), 7.53 (dd, $^4J_{P-H}$ = 18.1 and 4.4 Hz, 1H, PtC═C*H*), 7.77 (d, J = 6.8 Hz, 6H, Ph), 8.15 (d, J = 7.8

Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 7.8 (s, $PtCOCH_2CH_3$), 12.4 (d, $^1J_{P-C}$ = 29 Hz, PCH_3), 13.5 (d, $^1J_{P-C}$ = 29 Hz, PCH_3), 15.9 (d, $^1J_{P-C}$ = 29 Hz, PCH_3), 51.3 (d, $^3J_{P-C}$ = 27 Hz, $^2J_{Pt-C}$ = 217 Hz, $PtCOCH_2CH_3$), 126.2 (s, Ph), 127.0 (br, $^2J_{Pt-C}$ = 66 Hz, PtC≡*C*H), 127.7 (s, Ph), 127.8 (s, Ph), 128.1 (d, $^2J_{P-C}$ = 10 Hz, Ph), 128.3 (d, $^2J_{P-C}$ = 10 Hz, Ph), 128.8 (s, Ph), 129.2 (s, Ph), 129.5 (s, Ph), 130.1 (s, Ph), 130.2 (s, Ph), 136.8 (s, Ph), 137.0 (s, Ph), 137.2 (s, Ph), 138.5 (s, $^2J_{Pt-C}$ = 68 Hz, Ph), 154.6 (s, Ph), 184.3 (dd, $^2J_{P-C}$ = 117 and 12 Hz, $^1J_{Pt-C}$ = 887 Hz, Pt*C*≡CH), 246.9 (dd, $^2J_{P-C}$ = 117 and 12 Hz, $^1J_{Pt-C}$ = 889 Hz, Pt*C*OEt). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ −20.8 (d, $^2J_{P-P}$ = 16 Hz, $^1J_{Pt-P}$ = 1415 Hz), −12.0 (d, $^2J_{P-P}$ = 16 Hz, $^1J_{Pt-P}$ = 2054 Hz). IR (Nujol): ν_{CO} = 1600 cm^{-1}. Anal. Calcd for $C_{45}H_{48}OP_2PtSi$: C, 60.73; H, 5.44. Found: C, 60.56; H, 5.35.

Kinetic Studies. A typical procedure for measuring the rate of insertion of *cis*-**6d** is as follows. *cis*-Pt(COEt)-($SiPh_3$)(PMe_2Ph)$_2$ (**6d**) (19.2 mg, 0.025 mmol) was placed in an NMR sample tube equipped with a rubber septum, and the system was replaced with nitrogen gas at room temperature. PhC≡CH (49.0 mg, 0.48 mmol) and benzene-d_6 (0.60 mL), which contains toluene (0.020 M) as an internal reference, were added. The sample was placed in an NMR sample probe controlled to 55 ± 0.1 °C and examined by ^1H NMR spectroscopy. The amount of insertion product **7** produced with time was determined by measuring the relative peak integration of the methylene signals of *cis*-**6d** (δ 2.31) and **7** (δ 2.51) and the methyl signal of toluene (δ 2.10).

X-ray Diffraction Studies. (a) Data Collection. 3a. A single crystal of dimensions *ca.* 0.5 × 0.4 × 0.4 mm was sealed in a glass capillary tube. Intensity data were collected on a Rigaku AFC5R four-circle diffractometer. Unit cell dimensions, obtained from a least-squares treatment of the setting angles of 25 reflections in the range 34.5 < θ < 35.0°, and a statistical analysis of intensity distribution indicated the space group $P\bar{1}$ (No. 2). Diffraction data were collected at 23 °C in the range 3.0 < 2θ < 50.1° using the ω−2θ scan technique at a scan rate of 16° min^{-1} in ω. Three standard reflections, monitored at every 150 reflection measurements, showed no significant decay in their intensities. The data was corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans of three reflections). Of the 13 901 unique reflections measured, 8800 were classed as observed ($I > 3\sigma(I)$), and these were used for the solution and refinement of the structure.

3c. A single crystal of dimensions ca. 0.20 × 0.20 × 0.13 mm was sealed in a glass capillary tube. Intensity data were collected on a Rigaku AFC7R four-circle diffractometer. Unit cell dimensions were obtained from a least-squares treatment of the setting angles of 23 reflections in the range 32.1 < 2θ < 35.0°. The cell dimensions suggested a monoclinic cell, and systematic absences in the diffractometer data indicated the space group $P2_1/c$ (No. 14). Diffraction data were collected at 23 °C in the range 6.0 < 2θ < 50.0° using the ω−2θ scan technique at a scan rate of 16° min^{-1} in ω. Three standard reflections, monitored at every 150 reflection measurements, showed a linear decay in the intensity by 4.4%. The data was corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans of three reflections). Of the 7254 unique reflections measured, 3455 were classed as observed ($I > 2\sigma(I)$), and these were used for the solution and refinement of the structure.

(b) Structure Solution and Refinement. All calculations were performed with the TEXSAN crystal structure analysis package provided by Rigaku Corp.[16] The scattering factors were taken from ref 17. The structures were solved by heavy-atom Patterson methods (PHASE for **3a**; SAPI91 for **3c**) and expanded using Fourier techniques (DIRDIF). Each structure was refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. In the final cycles of refinement, hydrogen atoms were located at idealized positions (d(C−H) = 0.95 Å) with isotropic temperature factors ($B_{iso} = 1.20B_{bonded\ atom}$) and were included in calculation without refinement of their parameters. The function minimized in least-squares was $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1/[\sigma^2(F_o)]$). The final R indexes were 0.040 (R_w = 0.042, S = 1.37) for **3a** and 0.050 (R_w = 0.049, S = 1.39) for **3c**. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o is the number of observed data and N_p is the number of parameters varied. Crystal data and details of data collection and refinement are summarized in Table 2. Additional information is available as Supporting Information.

Table 2. Crystal Data and Details of the Structure Determination for 3a and 3c

	3a	**3c**
formula	$C_{43}H_{46}P_2PtSi$	$C_{43}H_{46}P_2PtSi$
fw	847.97	847.97
habit	prismatic	prismatic
cryst size, mm	0.5 × 0.4 × 0.4	0.2 × 0.2 × 0.1
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	16.668(3)	13.317(4)
b, Å	21.114(5)	14.363(4)
c, Å	11.595(3)	20.871(4)
α, deg	100.74(2)	
β, deg	90.98(2)	97.35(2)
γ, deg	79.26(2)	
V, Å^3	3938(2)	3959(1)
Z	4	4
d_{calcd}, g cm^{-3}	1.430	1.423
μ(Mo Kα), cm^{-1}	37.35	37.35
F(000)	1704	1704
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite	graphite
data collcd	$+h,\pm k,\pm l$	$+h,+k,\pm l$
2θ range, deg	3.0−50.1	4.0−50.0
scan type	w-2q	w-2q
$\Delta\omega$, deg	1.05 + 0.30 tan θ	1.21 + 0.30 tan θ
scan speed, deg min^{-1}	16, fixed	16, fixed
temp, K	296	293
abs corr	empirical	empirical
min and max transm factors	0.89, 1.00	0.913, 1.000
no. of reflcns collcd	14 422	7583
no. of unique reflcns	13 901 (R_{int} = 0.029)	7254 (R_{int} = 0.044)
no. of obsd reflcns	8800 ($I \geq 3\sigma(I)$)	3455 ($I \geq 2\sigma(I)$)
no. of variables	847	424
R	0.040	0.050
R_w	0.042	0.049
goodness of fit	1.37	1.39
max Δ/σ in final cycle	0.46	0.02
max and min peak, e Å^{-3}	1.17, −1.24 (near Pt)	1.54, −1.05 (near Pt)

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Supporting Information Available: Details of the structure determinations, including figures showing atomic numbering schemes and tables of atomic coordinates, thermal parameters, and bond distances and angles for **3a**,**c** (24 pages). Ordering information is given on any current masthead page.

OM960506J

(16) TEXSAN Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.