Insertion of Phenylacetylene into $Pt(SnMe_3)_2(PMe_2Ph)_2$

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Oxidative addition of $Me_3SnSnMe_3$ to a platinum(0) complex, in situ generated from $Pt(nbe)_3$ (nbe = norbornene) and PMe_2Ph in Et_2O, gives a 72:28 mixture of cis and trans isomers of $Pt(SnMe_3)_2(PMe_2Ph)_2$ (**1**), which are rapidly interconverted with each other in solution in the presence of PMe_2Ph. The trans isomer is further converted to a five-coordinate species $Pt(SnMe_3)_2(PMe_2Ph)_3$ (**2**) by the coordination of PMe_2Ph. Treatment of an equilibrium mixture of **1** and **2** with phenylacetylene in CD_2Cl_2 forms two regioisomers of insertion complexes, *cis*-Pt{C(Ph)=CH($SnMe_3$)$_3$}($SnMe_3$)(PMe_2Ph)$_2$ (**5**) and *cis*-Pt{CH=C(Ph)($SnMe_3$)}($SnMe_3$)(PMe_2Ph)$_2$ (**6**). The product ratio varies with the amount of PMe_2Ph added to the system. Thus **6** is favorably formed in the absence of PMe_2Ph, whereas **5** is predominantly formed in the presence of PMe_2Ph. The formation processes of **5** and **6** are discussed.

Introduction

Catalytic addition of element−element bonds to unsaturated hydrocarbons has attracted a great deal of recent interest.[1] The addition of group 14 element bonds is among the central subjects of such reactions. Typical examples include bis-silylation,[2] bis-stannylation,[3] silyl-stannylation,[4] and silyl-borylation[5] of alkynes and dienes catalyzed by platinum-group metal complexes. While the catalytic reactions are commonly assumed to proceed via insertion of a C−C multiple bond into a group 14 element−platinum bond, detailed information about this elementary process has been extremely limited.[6,7] We have examined the mechanisms of alkyne insertion into bis(silyl), silyl(boryl), silyl(stannyl), and germyl(stannyl) complexes of platinum.[8] In this paper, we report a related study for $Pt(SnMe_3)_2(PMe_2Ph)_2$ (**1**). A bis(stannyl)platinum complex of this type was first synthesized by Clark et al. in 1970.[9a] They found that $Me_3SnSnMe_3$ is oxidatively added to $Pt(CH_2=CH_2)(PPh_3)_2$ or $Pt(PPh_3)_4$ to give $Pt(SnMe_3)_2(PPh_3)_2$. More recently, Tsuji et al. confirmed by X-ray diffraction analysis that the complex has a twisted square planar geometry around platinum, which is unusual for a four-coordinate Pt(II) complex having a d^8 metal center.[9b−d] They also found that bis(stannyl)platinum and related palladium complexes undergo twist-rotation via a tet-

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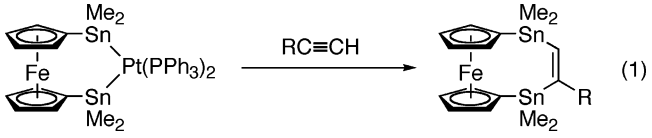
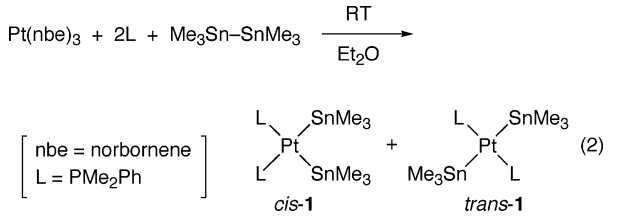
rahedral transition state in solution. Despite these interesting findings on the structures, insertion reactions of bis(stannyl) complexes have remained almost unexplored. Thus, although it has been shown that the bis(stannyl) complex given in eq 1 reacts with alkynes to give bis-stannylation products, no direct observation of intermediary platinum species has been reported.[10] In this study, we have succeeded for the first time in observing alkyne-insertion complexes derived from **1** and phenylacetylene.



(1)

Results

Preparation of Bis(stannyl)platinum(II) Complex. Complex **1** was synthesized by oxidative addition of $Me_3SnSnMe_3$ (1 equiv) to a platinum(0) complex generated in situ from $Pt(nbe)_3$ (nbe = norbornene) and 2 equiv of PMe_2Ph in Et_2O (eq 2). The reaction formed a 72:28 mixture of cis and trans isomers, which was obtained as a yellow solid in 93% yield from the reaction solution. Recrystallization of the crude product from Et_2O and pentane afforded **1** with a higher cis content (*cis*-**1**:*trans*-**1** = 95:5) in 56% yield.



(2)

When *cis*-**1** with a 95% isomeric purity was dissolved in CD_2Cl_2 at room temperature, the complex was again converted to a 72:28 mixture of the isomers. Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of this solution. Besides main signals of *cis*-**1** and *trans*-**1** and their ^{195}Pt satellites, small signals arising from $^2J_{SnP}$ couplings are observed. The trans isomer (δ −4.7) involves small couplings to ^{119}Sn (180 Hz) and ^{117}Sn (172 Hz), the values of which are consistent with the cis arrangement of phosphorus and tin atoms in *trans*-$Pt(SnMe_3)_2(PMe_2Ph)_2$. On the other hand, the cis isomer (δ 6.2) involves large and small couplings to ^{119}Sn (1600 and 178 Hz) and ^{117}Sn (1528 and 172 Hz), respectively, and each satellite is split further into a doublet by $^2J_{PP}$ coupling (24 Hz). This signal pattern is fully consistent with the *cis*-$Pt(SnMe_3)_2(PMe_2Ph)_2$ structure having $SnMe_3$ and PMe_2Ph ligands in mutually trans positions.

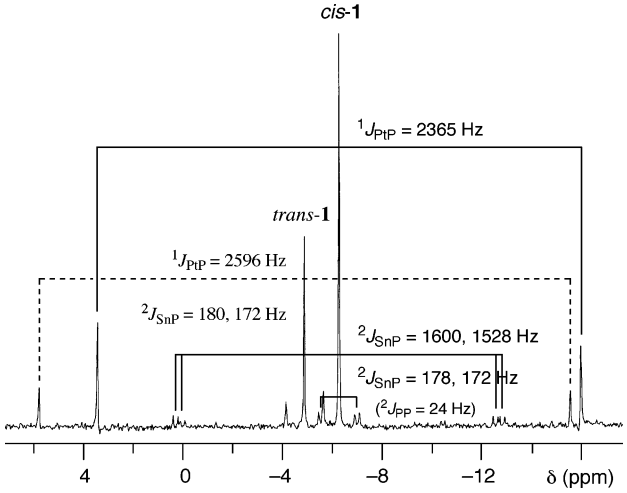


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a mixture *cis*-**1** and *trans*-**1** (72:28) in CD_2Cl_2 at −50 °C (121.49 MHz).

Reaction of 1 with PMe_2Ph. The interconversion between *cis*-**1** and *trans*-**1** is a slow process in a neat solvent (CD_2Cl_2), taking several hours to reach equilibrium at room temperature. On the other hand, the cis−trans isomerization proceeded very rapidly in the presence of PMe_2Ph.[11] Furthermore, *trans*-**1** underwent coordination of PMe_2Ph to form a five-coordinate complex, *trans*-$Pt(SnMe_3)_2(PMe_2Ph)_3$ (**2**) (Scheme 1).[12]

Figure 2 shows the ^1H NMR spectra of **1** in CD_2Cl_2 in the absence or presence of added PMe_2Ph at −50 °C. In the absence of PMe_2Ph, the signals of *cis*-**1** and *trans*-**1** are observed at δ 0.02 (SnMe) and 1.60 (PMe) and at δ −0.33 (SnMe) and 1.99 (PMe), respectively (a). On addition of 0.1 equiv of PMe_2Ph to the system, new

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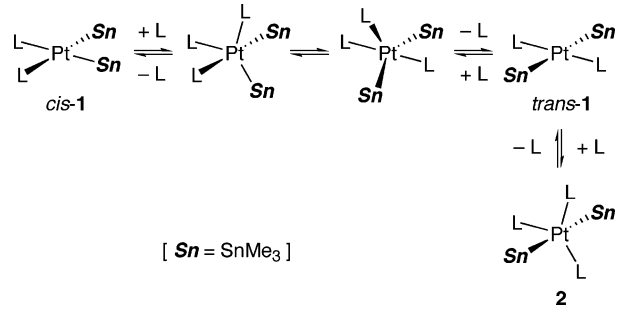
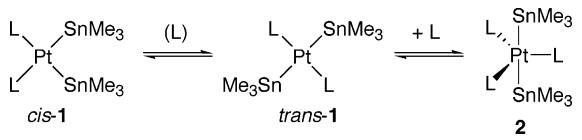
(11) The marked acceleration by added PMe_2Ph indicates the occurrence of a Berry pseudorotation process. Similar isomerization behavior has been reported for bis(germyl)platinum complexes: (a) Ref 6. (b) Yamashita, H.; Kobayashi, T.-a.; Tanaka, M.; Samuels, J. A.; Streib, W. E. *Organometallics* **1992**, *11*, 2330.

(12) Considering a high stability of **2** in solution, we believe that this five-coordinate species having two $SnMe_3$ ligands at apical positions is not the intermediate for cis−trans isomerization of **1**, as illustrated below. A similar situation has been observed for *trans*-$NiMe_2(PEt_3)_3$: Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1984**, *106*, 8181.



Scheme 1



signals assignable to **2** appear at δ −0.22 (SnMe) and 1.70 (PMe) (b). Since the signals of *trans*-**1** and **2** are more broadened than that of *cis*-**1**, the interconversion between *trans*-**1** and **2** takes place more rapidly than the cis−trans isomerization of **1**. Complex **2** increases with increasing amount of PMe_2Ph (c) and predominates in the presence of 1 equiv of PMe_2Ph (d). The $^{31}P\{^1H\}$ NMR spectrum of this solution (d) exhibited mainly a singlet assignable to **2** at δ −45.9 (s, $^1J_{PtP}$ = 2912 Hz, $^2J_{SnP}$ = 197 Hz); the chemical shift was much higher than that of *cis*-**1** and *trans*-**1** (δ 6.2 and −4.7, respectively).

Table 1 lists the ratio of *cis*-**1** to the sum of *trans*-**1** and **2**. The ratio was temperature-dependent. Thus, in the presence of over 1 equiv of added PMe_2Ph, *cis*-**1** was nearly negligible at −50 °C, but observed in a considerable amount at 20 °C.

The five-coordinate complex **2** was isolated as colorless crystals in 63% yield and characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. Figure 3 shows an ORTEP drawing of the X-ray structure. The complex has a trigonal bipyramidal structure having two $SnMe_3$ groups and three PMe_2Ph ligands at apical and equatorial positions, respectively. The sum of the three P−Pt−P angles is 359.58°, and

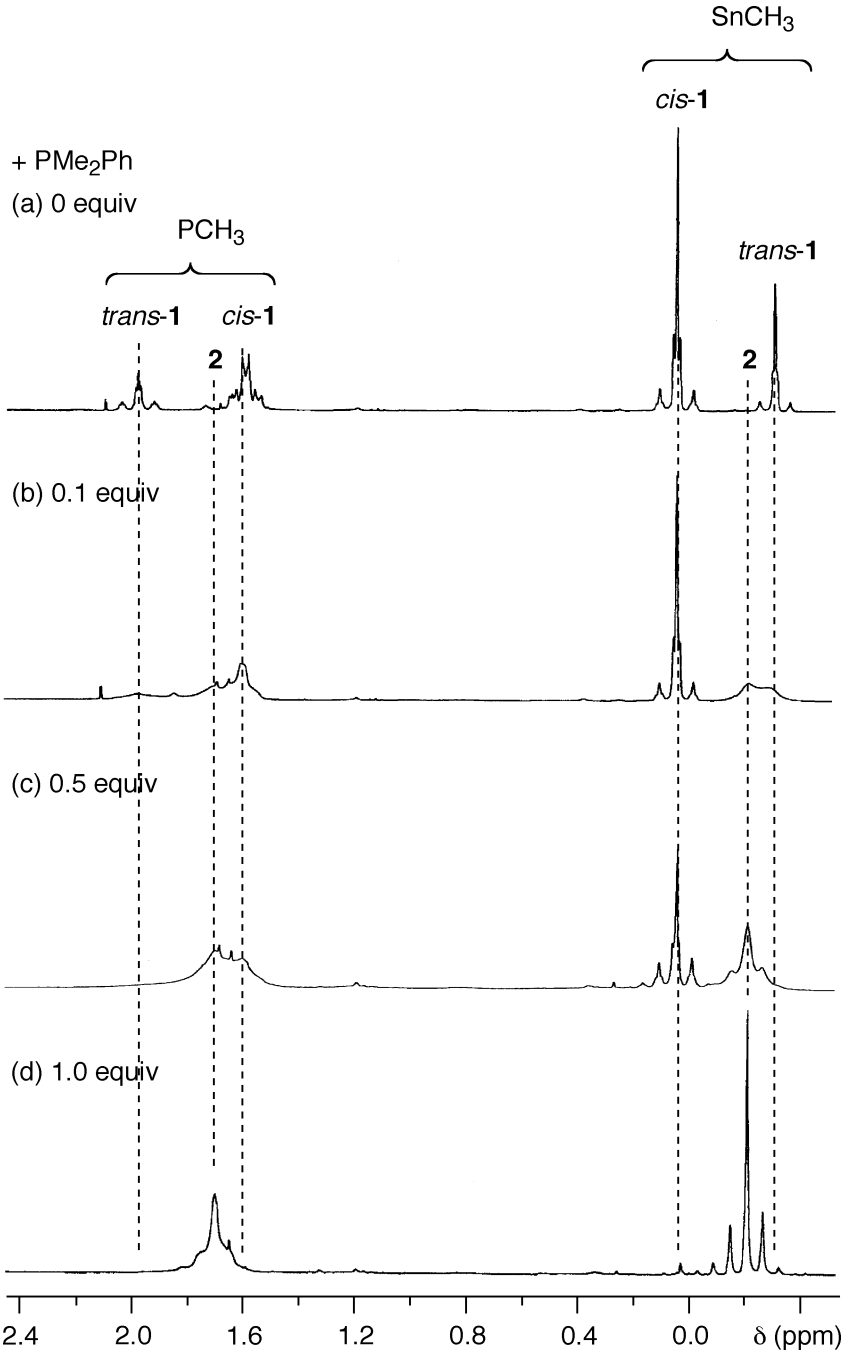


Figure 2. ^1H NMR spectra of **1** (25 mM) in CD_2Cl_2 at −50 °C in the absence or presence of added PMe_2Ph (300.10 MHz).

Table 1. Effect of Added PMe_2Ph on the Ratio of Platinum Complexes[a]

	[*cis*-**1**]:[*trans*-**1** + **2**]	
[PMe_2Ph] (equiv/**1**)	−50 °C	20 °C
0.0	72:28	72:28
0.1	65:35	68:32
0.5	40:60	51:49
1.0	2:98	36:64
2.0	1:99	21:79
3.0	0:100	2:98

[a] All measurements were carried out by ^1H NMR spectroscopy using a CD_2Cl_2 solution of **1** (25 mM).

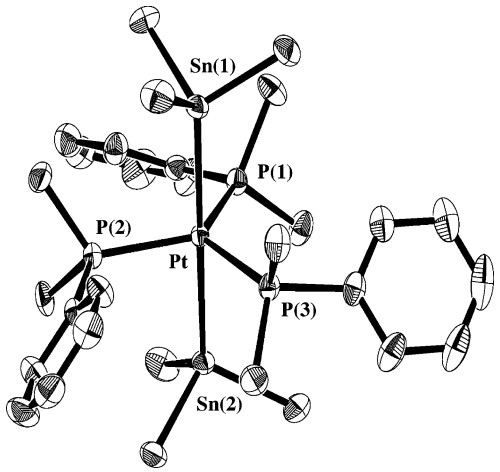


Figure 3. ORTEP drawing of the X-ray structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt−Sn(1) = 2.6623(3), Pt−Sn(2) = 2.6568(3), Pt−P(1) = 2.327(1), Pt−P(2) = 2.328(1), Pt−P(3) = 2.320(1), Sn(1)−Pt−Sn(2) = 177.62(1), P(1)−Pt−P(2) = 115.77(4), P(1)−Pt−P(3) = 121.21(4), P(2)−Pt−P(3) = 122.60(4).

the Sn(1)−Pt−Sn(2) angle is 177.62°. The two Pt−Sn distances are almost identical with each other. Variation in the three Pt−P distances is small.

Complex **1** combined also with CO and Bu^tNC to form five-coordinated complexes, $Pt(SnMe_3)_2(CO)(PMe_2Ph)_2$ (**3**) and $Pt(SnMe_3)_2(CNBu^t)(PMe_2Ph)_2$ (**4**), respectively, which were isolated as analytically pure white solids in 74% yields. The $^{31}P\{^1H\}$ NMR spectrum of **3** measured in CD_2Cl_2 at −50 °C exhibited a sharp singlet at δ −44.9 ($^1J_{PtP}$ = 2851 Hz, $^2J_{SnP}$ = 152 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, a triplet signal assignable to the CO ligand was observed at δ 180.7 with the couplings to ^{31}P and ^{195}Pt nuclei ($^2J_{PC}$ = 60 Hz, $^1J_{PtC}$ = 1538 Hz), showing a high coordination stability of the CO ligand in solution at low temperature. On the other hand, the isonitrile ligand in **4** underwent reversible dissociation in solution. Thus, the NMR signals remained broadened even at −70 °C.

Insertion of Phenylacetylene into 1. An equilibrium mixture of *cis*-**1** and *trans*-**1** (72:28, 25 mM) was treated with phenylacetylene (10 equiv, 0.25 M) in CD_2Cl_2 at 20 °C and examined by ^1H NMR spectroscopy at intervals. Complex **1** decreased over 30 min to be replaced by three kinds of species having an $SnMe_3$ group. As described below in detail, two of them were assigned to regioisomers of insertion complexes, *cis*-Pt{C(Ph)=CH($SnMe_3$)}($SnMe_3$)(PMe_2Ph)$_2$ (**5**) and *cis*-Pt{CH=C(Ph)($SnMe_3$)}($SnMe_3$)(PMe_2Ph)$_2$ (**6**), respectively,

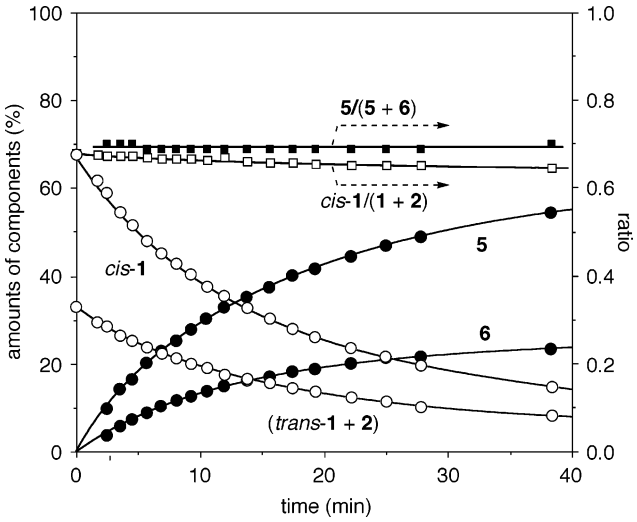


Figure 4. Time-course of the reaction of **1** (25 mM) with phenylacetylene (0.25 M) in CD_2Cl_2 at 20 °C in the presence of PMe_2Ph (2.5 mM).

Table 2. Dependence of Product Distribution and Insertion Rate upon the Amount of Added PMe_2Ph[a]

run	PMe_2Ph (mM)	**5**:**6**	10^4k_{obsd} (s^{-1})[b]
1	0.0	39:61[c]	16.2(1)
2	2.5	70:30	8.7(2)
3	12.5	92:8	2.54(1)
4	25	99:1	1.17(2)
5	50	100:0	0.471(4)

[a] All runs were performed in CD_2Cl_2 at 20 °C using **1** (25 mM) and phenylacetylene (0.25 M). [b] Estimated by first-order plots for total conversion of bis(stannyl)platinum complexes (**1** and **2**). [c] The reaction involved the formation of an unidentified species (see text).

which were formed in 39:61 ratio (eq 3). Although the other species, showing a singlet signal at δ 0.08 ($^2J_{^{119}SnH}$ = 51.8 Hz, $^2J_{^{117}SnH}$ = 49.8 Hz), could not be identified, its formation became negligible by addition of PMe_2Ph to the system. In the following sections, **5** and **6** are defined as α- and β-isomers, respectively, on the basis of the position of the phenyl substituent in the alkenyl ligand.

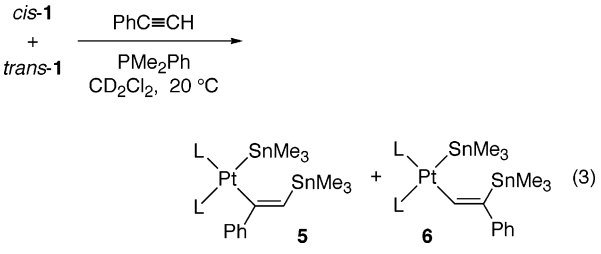


Figure 4 shows the time-course of the reaction in the presence of 0.1 equiv of PMe_2Ph (2.5 mM). The insertion complexes **5** and **6** were simultaneously formed in a constant ratio of 70:30. Since the **5**:**6** ratio changed to 29:71 upon prolonged heating, the product distribution observed in Figure 4 may be considered as a kinetic one.

Table 2 lists the results of insertion reactions in the presence of several amounts of PMe_2Ph. The rate constants (k_{obsd}) were estimated from first-order plots for total conversions of bis(stannyl) complexes (i.e., *cis*-**1** + *trans*-**1** + **2**). It is seen that the amount of **6**

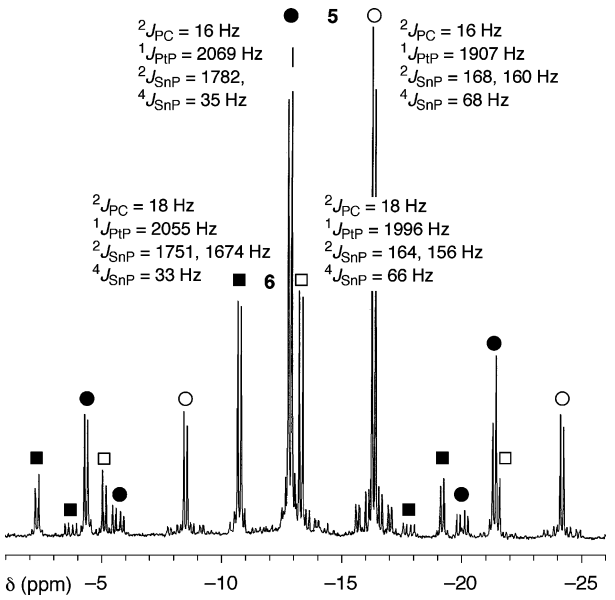


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of a mixture **5** and **6** (70:30) in CD_2Cl_2 at 20 °C (121.49 MHz).

significantly decreases as the amount of PMe_2Ph increases. Since the reaction rate also decreases, it is considered that the formation of **6** is more effectively hindered by added PMe_2Ph than that of **5**.

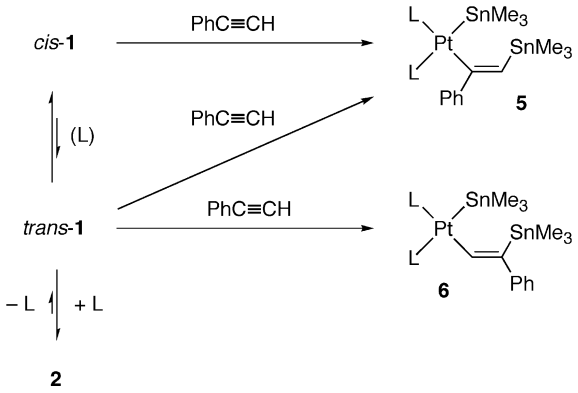
Since the insertion complexes **5** and **6** could not be separated from each other and from added PMe_2Ph, they were characterized by NMR spectroscopy. Figure 5 shows the $^{31}P\{^1H\}$ NMR spectrum of a 70:30 mixture of **5** and **6**. Each complex exhibits two sets of doublets with platinum and tin satellites. For the major isomer **5**, the doublet at δ −12.8 involves significantly large $^2J_{^{119}SnP}$ (1782 Hz) and $^2J_{^{117}SnP}$ (1704 Hz) values, consistent with the phosphine trans to the $SnMe_3$ ligand. On the other hand, the other doublet at δ −16.3 involves relatively small $^2J_{^{119}SnP}$ (168 Hz) and $^2J_{^{117}SnP}$ (160 Hz) couplings, assignable to the phosphine cis to the $SnMe_3$ ligand. Complex **6** exhibits almost the same signal patterns.

The regiochemistry of the insertion (i.e., α- or β-isomer) was determined by $^{13}C\{^1H\}$ NMR spectroscopy. The α- and β-carbon signals of the alkenyl ligand in **5** were observed at δ 176.7 (dd, $^2J_{PC}$ = 101 and 13 Hz, $^1J_{PtC}$ = 707 Hz) and 133.0 (dd, $^3J_{PC}$ = 8 and 5 Hz, $^2J_{PtC}$ = 58 Hz), respectively. The former disappeared in the DEPT NMR, but the latter remained unchanged. Therefore, **5** was characterized as the α-isomer having a phenyl group at the α-vinylic carbon. On the other hand, the α- and β-carbon signals of **6** appeared at δ 167.1 (dd, $^2J_{PC}$ = 104 and 15 Hz, $^1J_{PtC}$ = 671 Hz) and 148.3 (dd, $^3J_{PC}$ = 10 and 6 Hz, $^2J_{PtC}$ = 40 Hz), respectively. In this case, the latter signal disappeared in the DEPT NMR, and therefore **6** was assigned to the β-isomer.

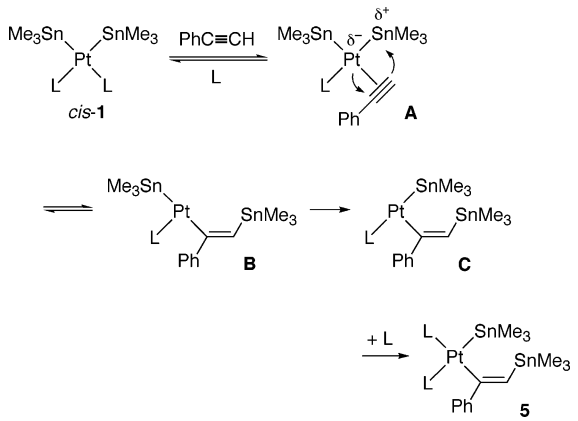
Discussion

It has been found that bis(stannyl)platinum(II) (**1**) forms three types of complexes in solution in the presence of added PMe_2Ph; the cis and trans isomers of four-coordinate complexes (*cis*-**1** and *trans*-**1**, respectively) and the five-coordinate complex **2**. These complexes are rapidly interconverted with each other according to the process given in Scheme 1. As seen from the data listed in Table 1, *cis*-**1** is the major species at low concentration of PMe_2Ph, while the equilibrium is significantly shifted to the side of **2** at higher concentration of PMe_2Ph. This equilibrium is correlated with the regioselectivity for the insertion of phenylacetylene to give **5** or **6** (Table 2). Thus the β-isomer **6** is preferably formed in the absence of PMe_2Ph (run 1). On the other hand, since the formation of **6** is suppressed by PMe_2Ph, the relative ratio of α-isomer **5** increases as the amount of added PMe_2Ph increases.

Scheme 2



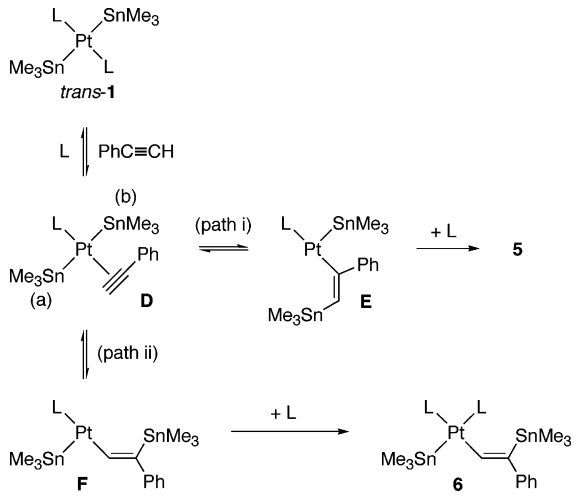
Scheme 3



These tendencies appear to suggest that **5** and **6** are formed from *trans*-**1** and *cis*-**1**, respectively. However, in view of the previous observations that insertion of phenylacetylene into related *cis*-bis(silyl)-, *cis*-silyl(boryl)-, *cis*-silyl(stannyl)-, and *cis*-germyl(stannyl)platinum(II) complexes forms α-isomers exclusively,[8] an alternative process depicted in Scheme 2 must be considered. Thus, *cis*-**1** is converted to **5**, whereas *trans*-**1** to **6** (and possibly to **5**). It is seen from Figure 2 that the equilibrium between *trans*-**1** and **2** is far on the side of **2**. Thus, the amount of *trans*-**1** observed in part (b) is much smaller than that of **2** and negligible in part (c). In this situation, the formation of **6** from *trans*-**1** is effectively suppressed by addition of PMe_2Ph to the system, because **2** is coordinatively saturated and unable to undergo coordination and the subsequent insertion of phenylacetylene.

The formation of **5** from *cis*-**1** may be rationalized by Scheme 3. This process is proposed on the basis of previous mechanistic observations for related silyl and stannyl complexes.[8] Ligand displacement of one of the phosphines (L) with phenylacetylene gives **A**, which

Scheme 4



subsequently undergoes migratory insertion of phenylacetylene into the Pt−$SnMe_3$ bond adjacent to the acetylene ligand.[13] Since the resulting complex **B** bears alkenyl and stannyl ligands with relatively strong trans influence in mutually trans positions, it must be isomerized to **C** to avoid electronic repulsion between the ligands.[14] In this case, the stannyl ligand with weaker trans influence is assumed to move to the trans position of L. Finally, coordination of L to **C** affords **5**. In this scheme, the regioselective formation of α-isomer **B** is due to an electronic reason.[7a] Thus, since the Pt−Sn bond is polarized as Pt(δ^-) and Sn(δ^+), the β-acetylenic carbon of phenylacetylene with higher π-electron density combines preferably with the $SnMe_3$ ligand, rather than the platinum center.

The reaction of *trans*-**1** with phenylacetylene provides an acetylene-coordinated complex **D** at the first stage (Scheme 4). Since this intermediate bears two $SnMe_3$ groups at the cis positions of the phenylacetylene ligand, there are two possible courses of migratory insertion (path (i) and path (ii)), which afford α- and β-isomers **5** and **6** via intermediates **E** and **F**, respectively. Path (i) should be kinetically preferable to path (ii) as described above. On the other hand, since **F** has the phenyl substituent at the more remote position from the bulky Pt($SnMe_3$)L moiety, this species must be sterically less demanding than **E**, and therefore path (ii) is thermodynamically more favorable than path (i). In Scheme 3, the kinetic selectivity for migratory insertion giving α-isomer **B** is preserved in the final product **5**, because **B** is irreversibly converted to **C** by trans-to-cis isomerization. On the other hand, the kinetic intermediate **E** formed in Scheme 4 already has a cis configuration and may undergo β-stannyl elimination to regenerate **D**.[15] That is, path (i) is very probably a reversible process, and this situation enables the thermodynamic path (ii) giving **6** to be operative.

(13) An insertion process involving prior displacement of a phosphine ligand with alkyne has been suggested by theoretical calculations for related platinum and palladium systems.[7a−g]

(14) While **B** and **C** in Scheme 3 and **E** and **F** in Scheme 4 are shown by T-shaped three-coordinate species, they are very probably stabilized by agostic interaction between $SnMe_3$ and platinum. Such stabilization has been observed by theoretical studies.[7]

(15) β-Stannyl elimination from *cis*-Pt{C(Ph)═CH($SnMe_3$)}(ER_3)(PMe_2Ph)$_2$ complexes (ER_3 = $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, $GeMe_3$) has been observed.[8d,f]

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents, or to the ^{31}P signal of external 85% H_3PO_4 standard. Elemental analysis was performed on a Perkin-Elmer 2400II CHN analyzer. Et_2O and pentane were dried over sodium benzophenone ketyl and distilled prior to use. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. CD_2Cl_2 was dried over $LiAlH_4$, vacuum transferred, and stored under a nitrogen atmosphere. Pt(nbe)$_3$ (nbe = norbornene) was prepared according to literature.[16] All other chemicals were obtained from commercial suppliers and used without purification.

Preparation of Pt($SnMe_3$)$_2$(PMe_2Ph)$_2$ (1). To a solution of Pt(nbe)$_3$ (500 mg, 1.05 mmol) in Et_2O (20 mL) were successively added PMe_2Ph (289 mg, 2.09 mmol) and $Me_3SnSnMe_3$ (343 mg, 1.05 mmol). The colorless solution was stirred at room temperature for 1 h to give a yellow solution containing *cis*-**1** and *trans*-**1** in a 72:28 ratio as confirmed by ^{31}P{^{1}H} NMR spectroscopy. The solution was filtered through a short column of Celite, and the filtrate was concentrated to dryness by pumping. The orange oily material thus obtained was dissolved in Et_2O (0.5 mL), and pentane (2 mL) was added at −78 °C. The mixture was stirred at the same temperature to give a yellow precipitate, which was collected by filtration, washed with pentane (2 mL × 2), and dried under vacuum (777 mg, 93%). The crude product was dissolved in a minimum amount of Et_2O (ca. 0.5 mL), layered with pentane (2 mL), and allowed to stand at −70 °C for 1 day to give a yellow crystalline solid containing *cis*-**1** and *trans*-**1** in a 95:5 ratio (468 mg, 56%). Anal. Calcd for $C_{22}H_{40}P_2PtSn_2$: C, 33.07; H, 5.05. Found: C, 33.14; H, 4.99.

***cis*-1b.** ^{1}H NMR (CD_2Cl_2, −50 °C): δ 0.02 (s, $^3J_{PtH}$ = 6.9 Hz, $^2J_{SnH}$ = 37.2 Hz, 18H, SnMe), 1.60 (d, $^2J_{PH}$ = 5.7 Hz, $^3J_{PtH}$ = 27.6 Hz, 12H, PMe), 7.2−7.7 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −2.7 (t, $^3J_{PC}$ = 8 Hz, $^2J_{PtC}$ = 67 Hz, $^1J_{SnC}$ = 189 Hz, SnMe), 18.7 (dd, $^1J_{PC}$ = 18 Hz, $^3J_{PC}$ = 16 Hz, $^2J_{PtC}$ = 42 Hz, PMe), 128.0 (t, $^3J_{PC}$ = 5 Hz, PPh), 129.6 (s, PPh), 130.8 (t, $^2J_{PC}$ = 6 Hz, $^3J_{PtC}$ = 30 Hz, PPh), 138.7 (d, $^1J_{PC}$ = 45 Hz, PPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −6.2 (s, $^1J_{PtP}$ = 2365 Hz, $^2J_{^{119cis}SnP}$ = 178 Hz, $^2J_{^{117cis}SnP}$ = 172 Hz, $^2J_{^{119trans}SnP}$ = 1600 Hz, $^2J_{^{117trans}SnP}$ = 1528 Hz).

***trans*-1b.** ^{1}H NMR (CD_2Cl_2, −50 °C): δ −0.33 (s, $^3J_{PtH}$ = 4.8 Hz, $^2J_{SnH}$ = 33.7 Hz, 18H, SnMe), 1.99 (virtual triplet, $^2J_{PH}$ = 5.7 Hz, $^3J_{PtH}$ = 35.4 Hz, 12H, PMe), 7.2−7.7 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −3.7 (s, $^2J_{PtC}$ = 48 Hz, $^1J_{SnC}$ = 135 Hz, SnMe), 21.2 (virtual triplet, $^1J_{PC}$ = 20 Hz, $^2J_{PtC}$ = 43 Hz, PMe), 127.9 (t, $^3J_{PC}$ = 5 Hz, PPh), 130.2 (s, PPh), 132.1 (t, $^2J_{PC}$ = 7 Hz, $^3J_{PtC}$ = 32 Hz, PPh), 137.5 (d, $^1J_{PC}$ = 28 Hz, PPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −4.7 (s, $^1J_{PtP}$ = 2596 Hz, $^2J_{^{119cis}SnP}$ = 180 Hz, $^2J_{^{117cis}SnP}$ = 172 Hz).

Preparation of Pt($SnMe_3$)$_2$(PMe_2Ph)$_3$ (2). To a solution of Pt($SnMe_3$)$_2$(PMe_2Ph)$_2$ (**1**; cis:trans = 72:28, 250 mg, 0.313 mmol) in CH_2Cl_2 (2 mL) was added PMe_2Ph (43.2 mg, 0.313 mmol) at −78 °C. The mixture was warmed to −30 °C and gradually concentrated by pumping until a small amount of crystalline solid appeared. The system was then allowed to stand at −70 °C for 3 days to afford white crystals of **2** (185 mg, 63%). ^{1}H NMR (CD_2Cl_2, −50 °C): δ −0.22 (s, $^2J_{SnH}$ = 35.5 Hz, 18H, SnMe), 1.70 (br, 18H, PMe), 7.2−7.6 (m, 15H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −2.1 (s, $^2J_{PtC}$ = 25 Hz, $^3J_{SnC}$ = 52 Hz, $^1J_{SnC}$ = 153 Hz, SnMe), 25.0 (br, PMe), 127.8 (br, PPh), 128.1 (br, PPh), 129.5 (br, PPh), 144.4 (br, PPh). ^{31}P-{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −45.9 (s, $^1J_{PtP}$ = 2912 Hz, $^2J_{SnP}$

(16) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 126.

= 197 Hz). Anal. Calcd for $C_{30}H_{51}P_3PtSn_2$: C, 38.45; H, 5.49. Found: C, 38.64; H, 5.48.

Preparation of Pt(SnMe$_3$)$_2$(CO)(PMe$_2$Ph)$_2$ (3). Complex **1** (cis:trans = 72:28, 380 mg, 0.475 mmol) was dissolved in CH_2Cl_2 (4 mL) and cooled to −78 °C. CO gas was passed through the solution for 15 min. The colorless solution thus obtained was concentrated to dryness by pumping at −30 °C to give a white solid of **3**, which was washed with a mixture of Et_2O (0.5 mL) and pentane (1.5 mL) at −78 °C and dried under vacuum (292 mg, 74%). ^{1}H NMR (CD_2Cl_2, −50 °C): δ −0.05 (s, $^2J_{SnH}$ = 41.0 Hz, 18H, SnMe), 1.76 (virtual triplet, $^2J_{PH}$ = 3.7 Hz, $^3J_{PtH}$ = 23.4 Hz, 12H, PMe), 7.3−7.6 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −5.5 (t, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 27 Hz, $^1J_{SnC}$ = 192 Hz, SnMe), 23.9 (t, $^1J_{PC}$ = 14 Hz, $^2J_{PtC}$ = 25 Hz, PMe), 128.0 (t, $^3J_{PC}$ = 5 Hz, PPh), 129.2 (s, PPh), 130.2 (t, $^2J_{PC}$ = 8 Hz, PPh), 139.5 (t, $^1J_{PC}$ = 25 Hz, $^2J_{PtC}$ = 35 Hz, $^3J_{SnC}$ = 9 Hz, PPh), 180.7 (t, $^2J_{PC}$ = 60 Hz, $^1J_{PtC}$ = 1538 Hz, CO). ^{31}P{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −44.9 (s, $^1J_{PtP}$ = 2851 Hz, $^2J_{SnP}$ = 152 Hz). IR (KBr): ν(CO) = 1939 cm^{-1}. Anal. Calcd for $C_{23}H_{40}OP_2PtSn_2$: C, 33.40; H, 4.88. Found: C, 33.64; H, 4.88.

Preparation of Pt(SnMe$_3$)$_2$(CNBu^t)(PMe$_2$Ph)$_2$ (4). This complex was prepared similarly to **3**, starting from **1** (300 mg, 0.375 mmol) and Bu^{t}NC (31.2 mg, 0.375 mmol) (281 mg, 85%). ^{1}H NMR (CD_2Cl_2, −50 °C): δ −0.13 (s, $^2J_{SnH}$ = 37.7 Hz, 18H, SnMe), 1.38 (s, 9H, *t*-BuNC), 1.68 (br, 12H, PMe), 7.2−7.6 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −5.6 (s, $^2J_{PtC}$ = 38 Hz, $^1J_{SnC}$ = 160 Hz, SnMe), 24.2 (br, PMe), 30.3 (s, CNC(CH$_3$)$_3$), 56.4 (s, CNC(CH$_3$)$_3$), 127.7 (s, PPh), 128.3 (s, PPh), 129.9 (s, PPh), 142.5 (br, PPh). ^{31}P{^{1}H} NMR (CD_2Cl_2, −50 °C): δ −44.7 (s, $^1J_{PtP}$ = 2896 Hz). IR (KBr): ν(CN) = 2097 and 2063 cm^{-1}. Anal. Calcd for $C_{27}H_{49}NP_2PtSn_2$: C, 36.76; H, 5.60; N, 1.59. Found: C, 36.57; H, 5.62; N, 1.52.

Insertion of Phenylacetylene into 1 (NMR Experiments). Complex **1** (cis:trans = 72:28, 12.0 mg, 15.0 μmol) was placed in an NMR sample tube equipped with a rubber septum cup and dissolved in CD_2Cl_2 (0.6 mL). Phenylacetylene (15.3 mg, 0.150 mmol) and hexane as an internal standard (2.00 μL, 15.3 mmol) were added, and the sample tube was placed in an NMR sample probe controlled at 20.0 ± 0.1 °C. The amounts of complexes at intervals were determined on the basis of peak integrations of SnMe signals and the Me signal of hexane in ^{1}H NMR spectra: *cis*-**1** (d 0.09 (s), $^3J_{PtH}$ = 7.3 Hz, $^2J_{SnH}$ = 37.7 Hz), *trans*-**1** (δ −0.26 (s), $^3J_{PtH}$ = 4.9 Hz, $^2J_{SnH}$ = 33.7 Hz), **5** (δ 0.27 (s), $^2J^{119}_{SnH}$ = 52.4 Hz, $^2J^{117}_{SnH}$ = 50.2 Hz), **6** (δ 0.29 (s), $^2J^{119}_{SnH}$ = 51.3 Hz, $^2J^{117}_{SnH}$ = 49.1 Hz), an unknown product (δ 0.08 (s), $^2J^{119}_{SnH}$ = 51.8 Hz, $^2J^{117}_{SnH}$ = 49.8 Hz), hexane (δ 0.88 (t)). A typical time-course was given in Figure 4.

Characterization of *cis*-Pt{C(Ph)=CH(SnMe$_3$)}(SnMe$_3$)(PMe$_2$Ph)$_2$ (5). A sample solution for NMR measurements was prepared by the reaction of **1** (cis:trans = 72:28, 60.0 mg, 75.0 μmol) with 1 equiv of phenylacetylene (7.67 mg, 75.0 μmol) in CD_2Cl_2 (0.6 mL) in the presence of PMe_2Ph (5.19 mg, 37.5 μmol) at room temperature. The system formed a 92:8 mixture of **5** and **6** after 10 h. The following NMR signals were observed for **5** at clearly distinct chemical shifts from free PMe_2Ph. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −0.17 (s, $^3J_{PtH}$ = 7.3 Hz, $^2J_{SnH}$ = 36.1 Hz, 9H, SnMe), 0.27 (s, $^2J^{119}_{SnH}$ = 52.4 Hz, $^2J^{117}_{SnH}$ = 50.2 Hz, 9H, SnMe), 1.18 (d, $^2J_{PH}$ = 8.6 Hz, $^3J_{PtH}$ = 25.1 Hz, 3H, PMe), 1.37 (d, $^2J_{PH}$ = 8.2 Hz, $^3J_{PtH}$ = 23.4 Hz, 3H, PMe), 1.41 (d, $^2J_{PH}$ = 7.9 Hz, $^3J_{PtH}$ = 21.2 Hz, 3H, PMe), 1.68 (d, $^2J_{PH}$ = 7.9 Hz, $^3J_{PtH}$ = 26.0 Hz, 3H, PMe), 7.0−7.8 (m, 15H, Ph), 7.83 (dd, $^4J_{PH}$ = 20.0 and 4.2 Hz, $^3J_{PtH}$ = 118.3 Hz, 1H, PtC=CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −7.3 (s, $^1J^{119}_{SnC}$ = 327 Hz, $^1J^{117}_{SnC}$ = 312 Hz, SnMe), −4.5 (dd, $^3J_{PC}$ = 10 and 2 Hz, $^2J_{PtC}$ = 77 Hz, $^1J_{SnC}$ = 194 Hz, SnMe), 13.7 (dd, $^1J_{PC}$ = 28 Hz, $^3J_{PC}$ = 2 Hz, $^2J_{PtC}$ = 30 Hz, PMe), 14.4 (dd, $^1J_{PC}$ = 29 Hz, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 37 Hz, PMe), 18.5 (dd, $^1J_{PC}$ = 29 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 25 Hz, PMe), 19.5 (dd, $^1J_{PC}$ = 32 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 43 Hz, PMe), 125.8 (s, Ph), 127.7 (s, Ph), 128.5 (s, PPh), 128.6 (s, PPh), 128.7 (d, $^4J_{PC}$ = 2 Hz, $^3J_{PtC}$ = 44 Hz, Ph), 129.8 (s, PPh), 130.9 (d, $^2J_{PC}$ = 12 Hz, PPh), 131.1 (d, $^2J_{PC}$ = 11 Hz, PPh), 133.0 (dd, $^3J_{PC}$ = 8 and 5 Hz, $^2J_{PtC}$ = 58 Hz, PtC=CH), 138.1 (dd, $^1J_{PC}$ = 36 Hz, $^3J_{PC}$ = 2 Hz, $^2J_{PtC}$ = 16 Hz, PPh), 139.0 (dd, $^1J_{PC}$ = 43 Hz, $^3J_{PC}$ = 4 Hz, $^2J_{PtC}$ = 10 Hz, PPh), 152.8 (dd, $^3J_{PC}$ = 6 and 2 Hz, Pt*C*Ph=CH), 176.7 (dd, $^2J_{PC}$ = 101 and 13 Hz, $^1J_{PtC}$ = 707 Hz, Pt*C*=CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −16.3 (d, $^2J_{PC}$ = 16 Hz, $^1J_{PtP}$ = 1907 Hz, $^2J^{119}_{SnP}$ = 168 Hz, $^2J^{117}_{SnP}$ = 160 Hz, $^4J_{SnP}$ = 68 Hz), −12.8 (d, $^2J_{PC}$ = 16 Hz, $^1J_{PtP}$ = 2069 Hz, $^2J^{119}_{SnP}$ = 1782 Hz, $^2J^{117}_{SnP}$ = 1704 Hz, $^4J_{SnP}$ = 35 Hz).

Characterization of *cis*-Pt{CH=C(Ph)(SnMe$_3$)}(SnMe$_3$)(PMe$_2$Ph)$_2$ (6). A solution containing a 70:30 ratio of **5** and **6** was prepared by the treatment of **1** (cis:trans = 72:28, 80.0 mg, 100 μmol) with phenylacetylene (10.2 mg, 100 μmol) in CD_2Cl_2 (0.6 mL) in the presence of PMe_2Ph (0.69 mg, 5.00 μmol) at room temperature. The NMR signals of **6** were assigned by comparison with the data of **5** and free PMe_2Ph. ^{1}H NMR (CD_2Cl_2, 20 °C): δ −0.10 (s, $^3J_{PtH}$ = 7.5 Hz, $^2J_{SnH}$ = 37.4 Hz, 9H, SnMe), 0.29 (s, $^2J^{119}_{SnH}$ = 51.3 Hz, $^2J^{117}_{SnH}$ = 49.1 Hz, 9H, SnMe), 1.45 (d, $^2J_{PH}$ = 13.4 Hz, $^3J_{PtH}$ = 26.0 Hz, 3H, PMe), 1.48 (d, $^2J_{PH}$ = 12.2 Hz, $^3J_{PtH}$ = 22.7 Hz, 3H, PMe), 1.48 (d, $^2J_{PH}$ = 12.2 Hz, $^3J_{PtH}$ = 25.3 Hz, 3H, PMe), 1.69 (d, $^2J_{PH}$ = 12.3 Hz, $^3J_{PtH}$ = 24.2 Hz, 3H, PMe), 7.0−7.8 (m, 15H, Ph), 8.85 (dd, $^3J_{PH}$ = 5.7 and 3.8 Hz, $^2J_{PtH}$ = 27.6 Hz, $^3J^{119}_{SnH}$ = 219.8 Hz, $^3J^{117}_{SnH}$ = 210.5 Hz, 1H, PtCH=C). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −6.4 (s, $^1J^{119}_{SnC}$ = 320 Hz, $^1J^{117}_{SnC}$ = 307 Hz, SnMe), −6.0 (dd, $^3J_{PC}$ = 10 and 2 Hz, $^2J_{PtC}$ = 74 Hz, $^1J_{SnC}$ = 194 Hz, SnMe), 13.5 (dd, $^1J_{PC}$ = 25 Hz, $^3J_{PC}$ = 2 Hz, $^2J_{PtC}$ = 27 Hz, PMe), 15.8 (dd, $^1J_{PC}$ = 32 Hz, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 27 Hz, PMe), 18.9 (dd, $^1J_{PC}$ = 32 Hz, $^3J_{PC}$ = 5 Hz, $^2J_{PtC}$ = 43 Hz, PMe), 19.4 (dd, $^1J_{PC}$ = 31 Hz, $^3J_{PC}$ = 6 Hz, $^2J_{PtC}$ = 44 Hz, PMe), 124.0 (s, Ph), 126.1 (d, $^5J_{PC}$ = 3 Hz, $^3J_{SnC}$ = 23 Hz, Ph), 128.2 (s, PPh), 128.7 (s, PPh), 129.9 (s, Ph), 129.9 (s, PPh), 130.0 (s, PPh), 130.8 (d, $^2J_{PC}$ = 12 Hz, PPh), 131.4 (d, $^2J_{PC}$ = 12 Hz, PPh), 138.3 (dd, $^1J_{PC}$ = 37 Hz, $^3J_{PC}$ = 2 Hz, $^2J_{PtC}$ = 17 Hz, PPh), 139.1 (dd, $^1J_{PC}$ = 43 Hz, $^3J_{PC}$ = 3 Hz, $^2J_{PtC}$ = 11 Hz, PPh), 148.3 (dd, $^3J_{PC}$ = 10 and 6 Hz, PtC=CPh), 152.9 (dd, $^4J_{PC}$ = 6 and 3 Hz, PtC=CPh), 167.1 (dd, $^2J_{PC}$ = 104 and 15 Hz, $^1J_{PtC}$ = 671 Hz, PtC=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ −13.3 (d, $^2J_{PC}$ = 18 Hz, $^1J_{PtP}$ = 1996 Hz, $^2J^{119}_{SnP}$ = 164 Hz,

Table 3. Crystallographic Data and Details of Structure Determination for 2

formula	$C_{30}H_{51}P_3PtSn_2$
fw	937.12
cryst appearance	colorless, platelet
cryst size/mm	0.20 × 0.10 × 0.05
cryst syst	monoclinic
space group	$P2_1/c$ (#14)
a/Å	16.070(5)
b/Å	10.480(4)
c/Å	21.130(7)
β/deg	90.590(5)
V/Å^3	3558.4(1)
Z	4
d_{calcd}/g cm^{-3}	1.749
μ(Mo Kα)/cm^{-1}	54.50
temp/°C	−100
2θ max/deg	55.0
no. of reflns collected	29 354
no. of unique reflns	8125 (R_{int} = 0.059)
abs corr	numerical
transmn factors	0.3488−0.8262
no. of obsd reflns	6018 ($I \geq 2.0\sigma(I)$)
no. of variables	325
R^a ($I \geq 2\sigma(I)$)	0.028
$R_w{}^b$ (all data)	0.070
GOF	0.75
max. and min. peak/e Å^{-3}	2.41, −1.06 (near Pt)

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

$^2J_{^{117}SnP}$ = 156 Hz, $^4J_{SnP}$ = 66 Hz), −10.8 (d, $^2J_{PC}$ = 18 Hz, $^1J_{PtP}$ = 2055 Hz, $^2J_{^{119}SnP}$ = 1751 Hz, $^2J_{^{117}SnP}$ = 1674 Hz, $^4J_{SnP}$ = 33 Hz).

X-ray Structural Analysis. A colorless crystal of **2** having approximate dimensions of 0.20 × 0.10 × 0.05 mm was grown from a CH_2Cl_2 solution and mounted on a glass fiber. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The intensity data were collected at −100 °C and corrected for Lorentz and polarization effects and absorption (NUMABS). All calculations were performed with the TEXSAN Crystal Structure Analysis Package provided by Rigaku Corp. The structure was solved by heavy atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically (SHELXL-97). 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} = 1.20$B_{bonded\ atom}$) and were included in calculation without refinement of their parameters. Crystallographic data and details of data collection and refinement are summarized in Table 3.

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Supporting Information Available: Details of the structure determination of **2**, including an atomic numbering scheme and tables of atomic coordinates, thermal parameters, and full bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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