Insertion of Phenylacetylene into *cis*-Silyl(stannyl)platinum Complexes

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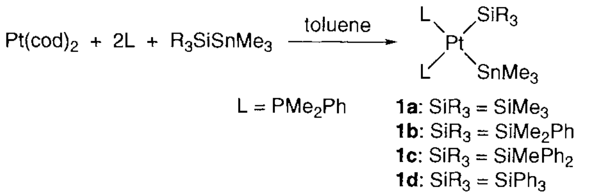
Silyl(stannyl)platinum(II) complexes *cis*-$Pt(SiR_3)(SnMe_3)(PMe_2Ph)_2$ ($SiR_3 = SiMe_3, SiMe_2Ph, SiMePh_2, SiPh_3$) undergo insertion of phenylacetylene into the Pt–Si or Pt–Sn bond. The site selectivity dramatically varies with silyl ligands under kinetic conditions, while under thermodynamic conditions the insertion into the Pt–Si bond exclusively takes place irrespective of silyl ligands.

Silylstannanes are known to be added to acetylenes or dienes in the presence of palladium catalysts.[1] The catalysis is considered to involve insertion of a C–C multiple bond into a silyl(stannyl)palladium intermediate. This elementary process has been examined theoretically.[2] On the other hand, owing to instability of silyl(stannyl) complexes, experimental study on the insertion reaction has been extremely limited, and only a particular system stabilized by inclusion of the silyl and stannyl ligands in a chelate ring has been investigated.[3]

In this study we prepared platinum analogs of the presumed silyl(stannyl)palladium intermediates (**1a**–**1d** in Scheme 1) and examined their reactions with phenylacetylene. A particular interest has been focused on site selectivity at the insertion. Thus, silyl(stannyl) complexes have two transition metal–element bonds capable of undergoing the insertion of acetylene. A previous theoretical study on the insertion of acetylene into *cis*-$Pd(SiH_3)(SnH_3)(PH_3)_2$ has predicted that the insertion into Pd–Sn is preferable to that into Pd–Si under kinetic conditions.[2] On the other hand, in the present platinum systems, relative ease of the insertion (Pt–Si vs Pt–Sn) has dramatically varied with silyl ligands.



Scheme 1.

Complexes **1a**–**1d** were prepared by oxidative addition of silylstannanes to a platinum(0) complex in situ generated from $Pt(cod)_2$ and 2 equivalents of PMe_2Ph in toluene. All reactions were completed instantly at room temperature to give the desired complexes, quantitatively, which were isolated as yellow crystalline solids by recrystallization from THF/Et_2O.[4]

Figure 1 shows X-ray structure of **1d**.[5] The complex has a twisted square planar geometry around platinum.[6] The Pt–Si and Pt–Sn bonds are tilted from the PtP_2 plane by 18.2 and 24.0°, respectively. Accordingly, deviation from the ideal coordination plane is more remarkable for the $SnMe_3$ ligand than the $SiPh_3$ ligand, indicating more flexible nature of the Pt–Sn bond. The Pt–P(1) bond trans to the silyl ligand is longer than the Pt–P(2) bond trans to the stannyl ligand, reflecting the higher trans influence of $SiPh_3$ than $SnMe_3$. The difference in trans influence was also suggested by Pt–P coupling constants in the $^{31}P\{^1H\}$ NMR spectrum.[7]

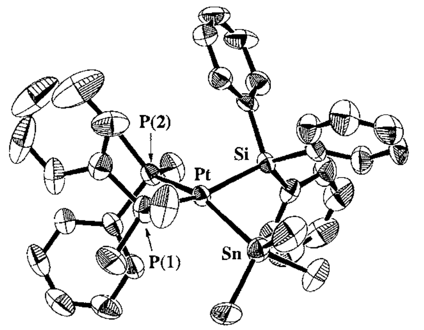
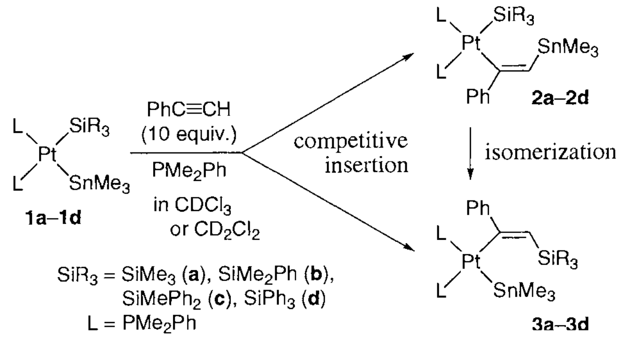


Figure 1. X-Ray structure of **1d**·THF. Selected bond distances (Å) and angles (deg): Pt–Si = 2.362(2), Pt–Sn = 2.6079(5), Pt–P(1) = 2.352(2), Pt–P(2) = 2.323(2), Si–Pt–Sn = 86.20(5), P(1)–Pt–P(2) = 96.60(7). The THF molecule is omitted for simplicity.

Treatment of **1d** with phenylacetylene (10 equiv.) in $CDCl_3$ at 50 °C led to two types of products **2d** and **3d**, which were formed by the insertion of phenylacetylene into Pt–Sn and Pt–Si, respectively (Scheme 2).[4] The site of insertion could be unequivocally assigned by $^{31}P\{^1H\}$ NMR spectroscopy. Thus the ^{117}Sn–P and ^{119}Sn–P couplings observed for **1d**[7] disappeared in the spectrum of **2d**,[8] showing that the insertion into the Pt–Sn bond takes place. In contrast, **3d** exhibited the Sn–P couplings consistent with the insertion into the Pt–Si bond.[9]



Scheme 2.

The ratio of **2d** to **3d** significantly varied with reaction conditions, especially with the concentration of free PMe_2Ph added to the system. Thus, in the absence of added PMe_2Ph, selective formation of **3d** was observed; the complex was isolated in 61% yield. In contrast, **2d** and **3d** were obtained in a 93:7 ratio at high concentration of PMe_2Ph (20 mM, 1 equiv./**1d**). At low concentration of PMe_2Ph (2.0 mM, 0.1

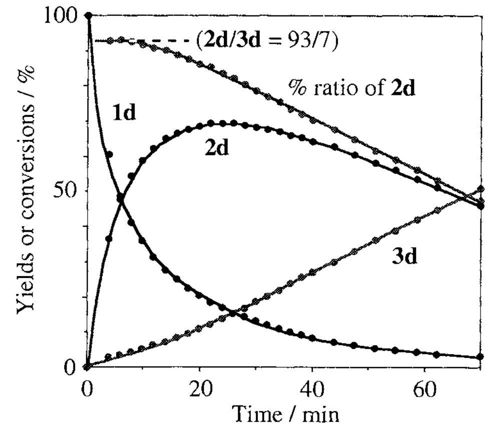


Figure 2. Time-course of the reaction of **1d** with phenylacetylene in $CDCl_3$ at 50 °C in the presence of free PMe_2Ph (2.0 mM).

equiv./**1d**), the reaction initially afforded a 93:7 mixture of **2d** and **3d**, while the relative ratio of **2d** gradually decreased with reaction progress (see Figure 2).

These observations clearly indicate the presence of two reaction stages as depicted in Scheme 2. At the first stage, **1d** undergoes competitive insertion of phenylacetylene into the Pt–Sn or Pt–Si bond, the ratio of which is 93:7 at 50 °C irrespective of the concentration of PMe_2Ph. At low concentration of PMe_2Ph or in the absence of added PMe_2Ph, **2d** generated in the reaction system successively undergoes isomerization to **3d**. However, since the isomerization is strongly suppressed by free PMe_2Ph, **2d** is stable at high concentration of PMe_2Ph.

The reactions of **1a**–**1c** were similarly examined. Table 1 summarizes the results. Complex **1a** is reactive even at –70 °C, and the insertion took place selectively at the Pt–Si bond. In the reaction of **1b**, **2b** and **3b** were formed in the ratio of 34:66 at –5 °C. Complex **2b** was stable toward the isomerization at this temperature but totally converted into **3b** at room temperature. The reaction of **1c** in the presence of 2.0 mM of PMe_2Ph proceeded at 15 °C to give a 59:41 mixture of **2c** and **3c**. In this system, isomerization of **2c** to **3c** was observed at a later stage of the reaction.

Table 1. Reactions of **1a**–**1d** with phenylacetylene in the presence of PMe_2Ph[a]

Complex	Temp	k_{initial}[b]	Product ratio[c]	
1a	-70 °C	rapid	**2a/3a**	= 0/100
1b	-5 °C	$1.5 \times 10^{-3}\ s^{-1}$	**2b/3b**	= 34/66
1c	15 °C	$3.3 \times 10^{-4}\ s^{-1}$	**2c/3c**	= 59/41
1d	50 °C	$2.5 \times 10^{-3}\ s^{-1}$	**2d/3d**	= 93/7

[a] All reactions were run in the presence of added PMe_2Ph (2.0 mM). Solvent: CD_2Cl_2 (**1a**, **1b**, **1c**), $CDCl_3$ (**1d**). Initial concentration: [**1**] = 20 mM, [PhC≡CH] = 200 mM. [b] Initial rate estimated from the time-conversion curve of **1**. [c] Ratio under the condition without isomerization of **2** to **3**.

In conclusion, we have succeeded for the first time in observing thermodynamic and kinetic ratio of the insertion of phenylacetylene into Pt–Sn and Pt–Si bonds of silyl(stannyl)-platinum complexes. The insertion product into Pt–Si bond (**3**) is thermodynamically more stable than that into Pt–Sn bond (**2**). This fact is in fair agreement with the theoretical conclusion for *cis*-$Pd(SiH_3)(SnH_3)(PH_3)_2$.[2] On the other hand, kinetically, both insertion reactions can compete with each other and the relative ratio is highly sensitive to the nature of silyl ligands. As seen from the k_{initial} values in Table 1, the reactivity toward the insertion is markedly affected by silyl ligands. The difference is much larger than that previously observed for *cis*-$Pt(SiR_3)_2(PMe_2Ph)_2$ complexes.[10] Details of the insertion mechanism and the factors governing the reactivity are the subjects to be clarified in due course.

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4 Complexes **1a–1d**, **2b–2d**, and **3a–3d** were characterized by NMR spectroscopy and/or elemental analysis. These data are available as a supporting information (PDF) on request to the author by e-mail: ozawa@a-chem.eng.osaka-cu.ac.jp.

5 Crystallographic data for **1d**·THF: $C_{37}H_{46}P_2PtSiSn \cdot C_4H_8O$, fw = 966.69, orthorhombic, space group $P2_12_12_1$, a = 17.8553(4) Å, b = 19.7769(6) Å, c = 11.8019(3) Å, V = 4167.5(2) Å^3, Z = 4, d_{calcd} = 1.541 g cm^{-3}, μ(Mo K_α) = 40.73 cm^{-1}, T = 294 K, $R(F^2)$ ($R_w(F^2)$) = 0.046 (0.061) for 4562 data with $I > 3\sigma(I)$.

6 Similar distortion from planarity has been observed for X-ray structures of bis(silyl), bis(germyl), and bis(stannyl) complexes of platinum and/or palladium: Y. Tsuji, K. Nishiyama, S. Hori, M. Ebihara, and T. Kawamura, *Organometallics*, **17**, 507 (1998); Y. Obora, Y. Tsuji, Y. Nishiyama, M. Ebihara, and T. Kawamura, *J. Am. Chem. Soc.*, **118**, 10922 (1996); H. Yamashita, T. Kobayashi, and M. Tanaka, *Organometallics*, **11**, 2330 (1992); W. Hatanaka, T. Wada, K. Mochida, and A. Yamamoto, 45th Symposium on Organometallic Chemistry, Japan, Tokyo, September 1998, Abstr., No. PA 137.

7 $^{31}P\{^1H\}$ NMR data for **1d** (CD_2Cl_2, –50 °C): δ –5.4 (d, $^2J_{P-P}$ = 25 Hz, $^1J_{Pt-P}$ = 1663 Hz, $^2J_{^{119}Sn-P}$ = 185 Hz, $^2J_{^{117}Sn-P}$ = 177 Hz), –9.7 (d, $^2J_{P-P}$ = 25 Hz, $^1J_{Pt-P}$ = 2331 Hz, $^2J_{^{119}Sn-P}$ = 1559 Hz , $^2J_{^{117}Sn-P}$ = 1499 Hz).

8 Selected NMR data for **2d** (CD_2Cl_2, 24 °C). $^{31}P\{^1H\}$ NMR: δ –10.9 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 1324 Hz), –15.5 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{Pt-P}$ = 1889 Hz). $^{13}C\{^1H\}$ NMR: δ 169.4 (dd, $^2J_{P-C}$ = 99 and 17 Hz, $^1J_{Pt-C}$ = 713 Hz, Pt*C*(Ph)=CH), 125.7 (d, $^3J_{P-C}$ = 5 Hz, $^2J_{Pt-C}$ = 26 Hz, PtC(Ph)=*C*H).

9 Selected NMR data for **3d** (CD_2Cl_2, 24 °C). $^{31}P\{^1H\}$ NMR: δ –15.3 (d, $^2J_{P-P}$ = 18 Hz, $^1J_{Pt-P}$ = 2081 Hz, $^2J_{^{119}Sn-P}$ = 1736 Hz, $^2J_{^{117}Sn-P}$ = 1659 Hz), –18.6 (d, $^2J_{P-P}$ = 18 Hz, $^1J_{Pt-P}$ = 1975 Hz, $^2J_{^{119}Sn-P}$ = 171 Hz , $^2J_{^{117}Sn-P}$ = 165 Hz). $^{13}C\{^1H\}$ NMR: δ 184.3 (dd, $^2J_{P-C}$ = 101 and 13 Hz, $^1J_{Pt-C}$ = 719 Hz, Pt*C*(Ph)=CH), 125.8 (t, $^3J_{P-C}$ = 6 Hz, $^2J_{Pt-C}$ = 56 Hz, PtC(Ph)=*C*H).

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