A Remarkable Difference in the Reactivity between *cis*- and *trans*-Silylplatinum Complexes toward Insertion of Acetylene

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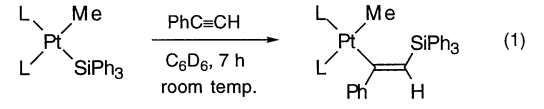
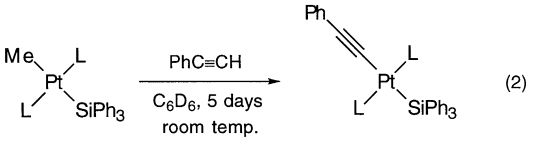
Reaction of *cis*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (**1**) with phenylacetylene in benzene readily proceeds at room temperature to give the acetylene-insertion product *cis*-PtMe{C(Ph)=CH(SiPh$_3$)}(PMe$_2$Ph)$_2$, while *trans*-PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (**2**), which is the geometrical isomer of **1**, is inactive toward acetylene-insertion. A mechanism of insertion involving a five-coordinate intermediate is proposed to account for the marked difference in the reactivity between the cis and trans isomers.

Insertion of a C–C multiple bond into a transition metal–silyl bond is assumed to be a crucial process in the catalytic hydrosilylation and bis-silylation of olefins and acetylenes.[1] Although such a reaction has recently been documented with isolated transition metal silyl complexes,[2] the details of mechanism of this elementary process still remain to be clarified. In this study we examined the reactions of two geometrical isomers (cis and trans) of PtMe(SiPh$_3$)L$_2$ with phenylacetylene and found only the cis isomer exhibiting the reactivity to give the insertion product PtMe{C(Ph)=CH(SiPh$_3$)}L$_2$. The marked difference in the reactivity between the cis and trans isomers toward insertion can be accounted for most consistently by assuming the insertion process via a five-coordinate intermediate PtMe(SiPh$_3$)(PhC≡CH)L$_2$.

The two geometrical isomers of PtMe(SiPh$_3$)(PMe$_2$Ph)$_2$ (*cis*-**1** and *trans*-**2**) were independently prepared[3] and subjected to the reaction with phenylacetylene (5 equiv.) in benzene-d_6 at room temperature. ^{31}P NMR analysis of the reaction solution revealed that the cis isomer **1** undergoes insertion of phenylacetylene into the Pt–Si bond to give *cis*-PtMe{C(Ph)=CH(SiPh$_3$)}(PMe$_2$Ph)$_2$ (**3**) in 70% yield (eq. 1).[4] In contrast, the trans isomer **2** was inactive toward insertion, while gradual formation of *trans*-Pt(C≡CPh)(SiPh$_3$)(PMe$_2$Ph)$_2$ (**4**) took place (eq. 2).





Complex **3** was unequivocally identified by X-ray diffraction study.[5] The X-ray structure in Figure 1 indicates the insertion process in a syn 1,2-addition manner with retention of the cis configuration of **1**.

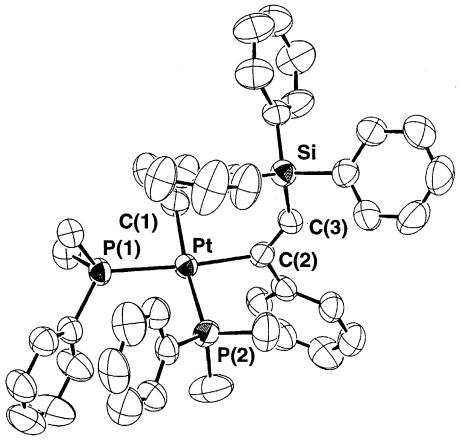
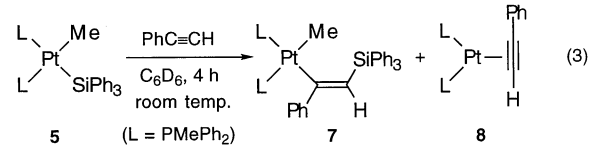
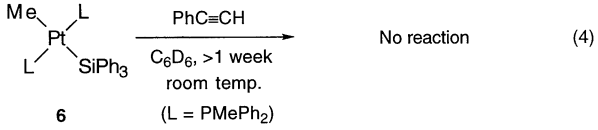


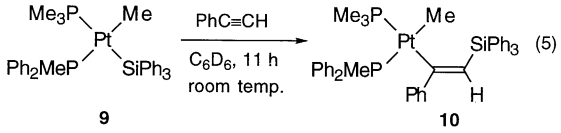
Figure 1. The X-ray structure of complex **3**. Selected bond distances (Å) and angles (deg): Pt–C(1) = 2.122(8), Pt–C(2) = 2.100(8), C(2)–C(3) = 1.33(1), C(3)–Si = 1.840(9), Pt–P(1) = 2.313(2), Pt–P(2) = 2.291(2), Pt–C(2)–C(3) = 126.9(6), C(2)–C(3)–Si = 137.6(7), C(1)–Pt–P(1) = 87.3(2), C(1)–Pt–C(2) = 85.2(3), P(1)–Pt–P(2) = 98.63(8), C(2)–Pt–P(2) = 88.9(2).

We next examined the reactions of *cis*- and *trans*-PtMe(SiPh$_3$)(PMePh$_2$)$_2$ (**5** and **6**)[3] with phenylacetylene (5 equiv.) in benzene-d_6 at room temperature (eqs. 3 and 4). The trans isomer **6** was totally inactive in the reaction system for 1 week (eq. 4), whereas *cis*-**5** was smoothly converted into two platinum species **7** and **8** (1:3.8) as confirmed by ^{31}P NMR spectroscopy (eq. 3). The latter species **8** was identified as Pt(PhC≡CH)(PMePh$_2$)$_2$ formed by the reductive elimination of MeSiPh$_3$. On the other hand, the former species **7** was assigned to be the insertion product *cis*-PtMe{C(Ph)=CH(SiPh$_3$)}(PMePh$_2$)$_2$ on the basis of the $^1J_{PtP}$ coupling constants.[6]





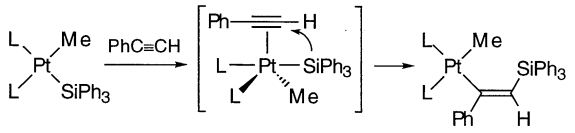
We have already shown that the reductive elimination of **5** involves prior displacement of the $PMePh_2$ ligand trans to the $SiPh_3$ group with acetylene to give the $PtMe(SiPh_3)$(acetylene)-($PMePh_2$) intermediate.[3] Therefore, in order to improve the selectivity for the acetylene-insertion, we introduced PMe_3 of higher coordinating ability than the $PMePh_2$ ligand into **5** and examined the reaction with phenylacetylene (eq. 5). Treatment of **5** with 1 equivalent of PMe_3 in Et_2O gave the desired complex $PtMe(SiPh_3)(PMe_3)(PMePh_2)$ (**9**), in which the PMe_3 and $PMePh_2$ ligands coordinate to trans and cis to the $SiPh_3$ ligand, respectively. Complex **9** thus obtained selectively formed insertion product **10** without concomitant reductive elimination.[7]



(5)

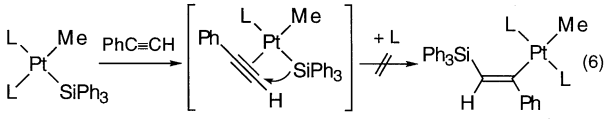
9 10

We described here that only the *cis*-silyl complexes possess the reactivity toward acetylene-insertion. It was also found that the silyl complexes bearing tertiary phosphine ligands of the higher coordinating ability provide the higher selectivity for the acetylene-insertion. These findings strongly suggest the insertion process via a five-coordinate intermediate (Scheme 1). The retention of cis geometry at the platinum center during the insertion is also consistent with the associative process in Scheme 1.



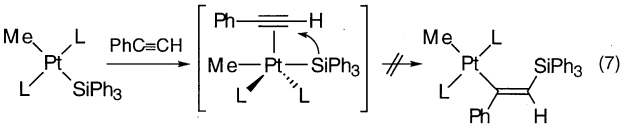
Scheme 1. Proposed mechanism for the acetylene-insertion.

On the other hand, the alternative process that involves the displacement of one of the phosphine ligands with acetylene followed by the migratory insertion of acetylene into the Pt–Si bond (eq. 6) may not accord with the experimental results, because this process must provide the insertion product bearing trans configuration.[8]



(6)

The lack of reactivity of *trans*-silyl complexes toward the acetylene-insertion can be understood also by assuming the process via a five-coordinate intermediate (eq. 7). In this case *trans*-PtMe{C(Ph)=CH($SiPh_3$)}L_2 is expected to be formed with retention of the trans geometry.[9] However, the great trans influence of methyl ligand would make the insertion product unstable and inhibit the insertion to proceed. In contrast, in the insertion of cis isomer (Scheme 1), such a labilizing effect of methyl ligand does not directly affect stability of the insertion product because of the cis orientation. Hence, the facial insertion of acetylene into the Pt–Si bond proceeds.



(7)

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References and Notes

1 T. D. Tilley in "The Chemistry of Organic Silicon Compounds" ed by S. Patai and Z. Rappoport, Wiley-Interscience, Chichester, U.K. (1989).

2 J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Organomet. Chem.*, **23**, 109 (1970); C. L. Randolph and M. S. Wrighton, *J. Am. Chem. Soc.*, **108**, 3366 (1986); H. Yamashita, M. Tanaka, and M. Goto, *Organometallics*, **12**, 988 (1993), and references cited therein.

3 F. Ozawa, T. Hikida, and T. Hayashi, *J. Am. Chem. Soc.*, **116**, 2844 (1994).

4 ^{1}H NMR (CD_2Cl_2, –20 °C): δ 7.46 (d, $^4J_{PH}$ = 17.1 Hz, PtC=C*H*, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2, –20 °C): δ 123.9 (s, $^2J_{PtC}$ = 48 Hz, PtC=*C*), 195.0 (dd, $^1J_{PtC}$ = 854 Hz, $^2J_{PC}$ = 118 and 15 Hz, Pt*C*=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, –20 °C): δ –15.5 (d, $^1J_{PtP}$ = 1961 Hz, $^2J_{PP}$ = 15 Hz), –15.5 (d, $^1J_{PtP}$ = 1790 Hz, $^2J_{PP}$ = 15 Hz).

5 Crystallographic data for **3**: $C_{43}H_{46}P_2PtSi$, *FW* = 847.96, triclinic, space group $P\bar{1}$, a = 16.668(3) Å, b = 21.114(5) Å, c = 11.595(3) Å, α = 100.74(2)°, β = 90.98(2)°, γ = 79.26(2)°, V = 3938(2) Å^3, Z = 4, d_{calcd} = 1.430 g cm^{-3}, μ(Mo Kα) = 37.35 cm^{-1}, T = 296 K, R (R_w) = 0.040 (0.042) for 8800 data with $I > 3\sigma(I)$. There are two essentially superposable molecules in each asymmetric unit. Figure 1 shows one of the molecules for simplicity.

6 Complex **7** could not be isolated because of its low contents in the reaction system. ^{31}P{^{1}H} NMR (C_6D_6, room temp.): δ 1.2 (d, $^1J_{PtP}$ = 1961 Hz, $^2J_{PP}$ = 13 Hz), 1.8 (d, $^1J_{PtP}$ = 1748 Hz, $^2J_{PP}$ = 13 Hz). The coupling constants are comparable to those of **3**.[4]

7 ^{1}H NMR ($CDCl_3$, room temp.): δ 0.60 (dd, $^2J_{PtH}$ = 68.8 Hz, $^3J_{PH}$ = 9.8 and 6.3 Hz, PtC*H*$_3$, 3H), 0.89 (d, $^2J_{PH}$ = 8.3 Hz, $^3J_{PtH}$ = 20.5 Hz, PC*H*$_3$, 9H), 1.62 (d, $^2J_{PH}$ = 8.3 Hz, $^3J_{PtH}$ = 21.5 Hz, PC*H*$_3$, 3H), 7.47 (dd, $^4J_{PH}$ = 21.5 and 2.9 Hz, PtC=C*H*, 1H). ^{13}C{^{1}H} NMR (C_6D_6, room temp.): δ 2.4 (dd, $^1J_{PtC}$ = 579 Hz, $^2J_{PC}$ = 91 and 8 Hz, Pt*C*H$_3$), 14.7 (d, $^1J_{PC}$ = 25 Hz, P(*C*H$_3$)$_3$), 15.3 (d, $^1J_{PC}$ = 31 Hz, P(*C*H$_3$)Ph$_2$), 125.1 (s, PtC=*C*), 194.7 (dd, $^1J_{PtC}$ = 827 Hz, $^2J_{PC}$ = 116 and 12 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.): δ –27.5 (d, $^1J_{PtP}$ = 1729 Hz, $^2J_{PP}$ = 15 Hz), 1.1 (d, $^1J_{PtP}$ = 1980 Hz, $^2J_{PP}$ = 15 Hz).

8 Recent theoretical study predicted that the ethylene insertion into the Pt–Si bond of *cis*-PtH(SiH_3)(PH_3)$_2$ via a dissociative mechanism analogous to eq. 6 is an energetically unlikely process: S. Sakaki, M. Ogawa, Y. Musashi, and T. Arai, *J. Am. Chem. Soc.*, **116**, 7258 (1994).

9 The retention of trans geometry in eq. 7 was assumed based on the theoretical study reported by Thorn and Hoffmann: D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2079 (1978).