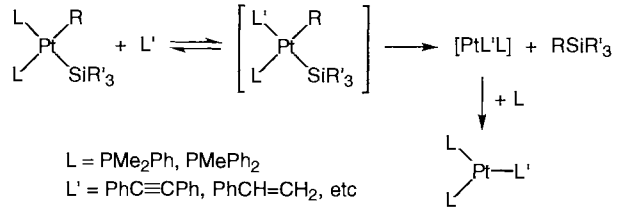
A New Process for C–Si Bond Formation from *cis*-Alkyl(silyl)platinum(II) Complexes

Fumiyuki Ozawa,* Masaya Kitaguchi, and Hiroyuki Katayama
Department of Applied Chemsitry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585

(Received September 2, 1999; CL-990760)

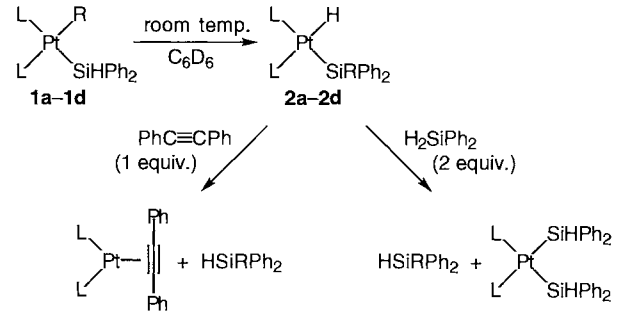
The complexes *cis*-PtR(SiHPh$_2$)(PMe$_2$Ph)$_2$ (R = Me, Et, Pr, Bu) have been found to undergo two types of C–Si bond formation process. One is a novel reaction process *via* isomerization to *cis*-PtH(SiRPh$_2$)(PMe$_2$Ph)$_2$, and the other is C–Si reductive elimination involving prior displacement of a PMe$_2$Ph ligand with diphenylacetylene added to the system.

The C–Si bond formation from alkyl(silyl)platinum complexes is commonly assumed as the product-forming step for platinum-catalyzed hydrosilylation of alkenes.[1,2] However, little is known about this elementary process.[3,4] We recently reported that the formation of MeSiPh$_3$ from *cis*-PtMe(SiPh$_3$)L$_2$ (L = PMe$_2$Ph, PMePh$_2$) proceeds readily at around ambient temperature *via* a reductive elimination process involving prior displacement of a phosphine ligand (L) with alkyne or alkene (L') added to the system (Scheme 1).[5] Thus the reaction is effectively accelerated by alkynes and alkenes, particularly by those with electron-withdrawing substituents. In this study, we found another type of C–Si bond formation process that is operative for alkyl–silyl complexes bearing a SiHPh$_2$ ligand (Scheme 2).



Scheme 1.

cis-PtR(SiHPh$_2$)(PMe$_2$Ph)$_2$ (**1a–1d**) dissolved in benzene-d_6 at room temperature changed within a few minutes into the corresponding hydrido–silyl complexes **2a–2d**, in which the R–Si bond is formed.[6,7] Addition of diphenylacetylene or diphenylsilane to the resulting solutions led to instant liberation of HSiRPh$_2$ in quantitative yields.



Scheme 2. R = Me (**1a**, **2a**), Et (**1b**, **2b**), Pr (**1c**, **2c**), Bu (**1d**, **2d**); L = PMe$_2$Ph.

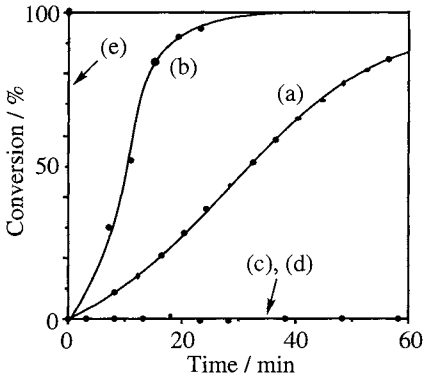
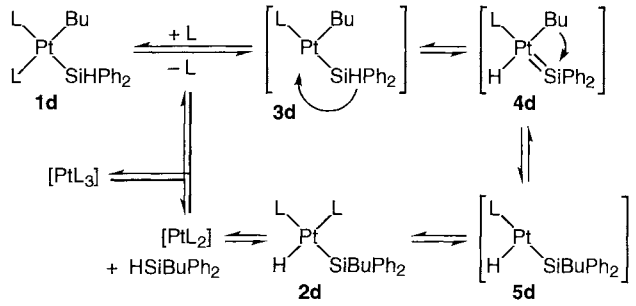


Figure 1. Time-conversion curves for the conversion of **1d** into **2d** in benzene-d_6 at 10 °C. Initial concentration: [**1d**]$_0$ = 20 mM (a, c–e) ; 40 mM (b). Additive: PMe$_2$Ph (2 mM) (c); PhC≡CPh (10 mM) (d); Pt(cod)$_2$ (1 mM) (e).

Figure 1 shows the time-course of the conversion of **1d** into **2d** at 10 °C. The reaction showed S-shaped time-conversion curves and proceeded more rapidly at higher concentration of the starting complex (curves a and b), indicating the occurrence of a reaction process promoted by a product. Addition of free PMe$_2$Ph or diphenylacetylene to the system effectively suppressed the reaction progress (curves c and d). On the other hand, the reaction was dramatically accelerated by addition of a Pt(0) complex (Pt(cod)$_2$) (curve e).

These observations can be rationalized by the mechanism depicted in Scheme 3. The first step is dissociation of the PMe$_2$Ph ligand cis to the SiHPh$_2$ group. Free PMe$_2$Ph added to the system prevents this step. The three-coordinate species **3d** thus formed isomerizes to a hydrido–butyldiphenylsilyl complex **5d**, probably *via* a hydrido–butyl–silylene intermediate **4d**.[8] Coordination of PMe$_2$Ph to **5d** forms **2d**.

As suggested by the instant conversion of **2d** into Pt(PhC≡CPh)(PMe$_2$Ph)$_2$ by the treatment with diphenylacetylene (Scheme 2), **2d** is in an equilibrium with an



Scheme 3.

coordinatively unsaturated species $[Pt(PMe_2Ph)_2]$, which may serve as a phosphine sponge to facilitate the dissociation of PMe_2Ph from **1d**. Consequently, the rate of the conversation of **1d** to **2d** is enhanced with reaction progress and this tendency should be more remarkable at higher concentration of the starting complex. $Pt(cod)_2$ may trap PMe_2Ph liberated from **1d** more efficiently than the $[Pt(PMe_2Ph)_2]$ species, causing the extremely high reaction rate. In contrast, diphenylacetylene, which converts the $[Pt(PMe_2Ph)_2]$ species into stable $Pt(PhC{\equiv}CPh)(PMe_2Ph)_2$, inhibits the reaction.

It is noted that the effect of diphenylacetylene on the reaction rate of the present C–Si bond formation process is opposite to that observed for the C–Si reductive elimination from *cis*-$PtMe(SiPh_3)L_2$ complexes (Scheme 1). Thus the former is retarded by addition of diphenylacetylene while the latter is accelerated. This tendency is more clearly observed from Figure 2, in which the rate constants for the thermolysis of **1d** are plotted against the concentration of diphenylacetylene added to the system. At high concentration (>0.20 M), the reaction was first-order in the concentration of **1d** over 80% conversion. On the other hand, since the reaction did not obey the first-order kinetics at low concentration of diphenylacetylene (*vide infra*), initial rate constants estimated from the time-conversion curves are plotted instead.

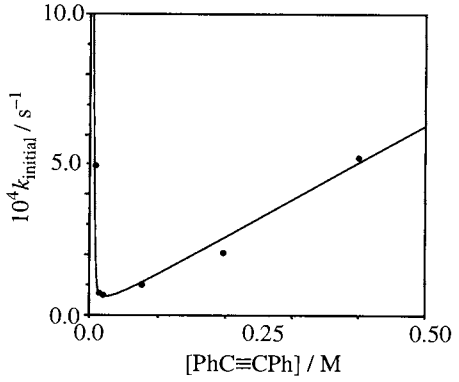


Figure 2. Dependence of the thermolysis rate of **1d** on the concentration of diphenylacetylene at 50 °C in benzene-d_6. Initial concentration: $[\mathbf{1d}]_0 = 20$ mM.

It is clearly seen that in low concentration region, the reaction rate dramatically increases as the concentration of diphenylacetylene decreases. This tendency is compatible with the mechanism in Scheme 3. In contrast, in the region of high acetylene concentration, the thermolysis rate linearly increases with increasing amount of diphenylacetylene. This tendency is in fair agreement with the mechanism in Scheme 1. Accordingly, we may conclude that **1d** undergoes two types of C–Si bond formation process given in Schemes 1 and 3. The C–Si bond formation by the reductive elimination (Scheme 1) is a rather slow process and takes place only under heated conditions even at high concentration of diphenylacetylene (Figure 2). In contrast, the C–Si bond formation according to the mechanism in Scheme 3 occurs under much milder conditions. Relevance of the latter process to catalytic hydrosilylation is now under investigation.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area "The Chemistry of Inter-element Linkage" (No. 09239105) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965); J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **87**, 1133 (1965); P. Brunstein and M. Knorr, *J. Organomet. Chem.*, **500**, 21 (1995); C. A. Recatto, *Aldrichimica Acta*, **28**, 85 (1995); T. D. Tilley, in "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley, Chichester (1989), p. 1415.

2 J. Stein, L. N. Lewis, Y. Gao, and R. A. Scott, *J. Am. Chem. Soc.*, **121**, 3693 (1999), and references cited therein.

3 M. E. van der Boom, J. Ott, and D. Milstein, *Organometallics*, **17**, 4263 (1998).

4 For theoretical studies, see: S. Sakaki, N. Mizoe, and M. Sugimoto, *Organometallics*, **17**, 2510 (1998).

5 F. Ozawa, T. Hikida, and T. Hayashi, *J. Am. Chem. Soc.*, **116**, 2844 (1994); F. Ozawa, T. Hikida, K. Hasebe, and T. Mori, *Organometallics*, **17**, 1018 (1998).

6 Complexes **1a–1d** were prepared from *trans*-$PtCl(SiHPh_2)(PMe_2Ph)_2$ and alkyllithiums by a procedure similar to the synthesis of *cis*-$PtMe(SiPh_3)L_2$ ($L = PMe_2Ph$, $PMePh_2$).[5]

7 Complexes **1a–1d** and **2a–2d** were identified by NMR and IR spectroscopy and/or elemental analysis. Characteristic data for **1d** and **2d** are as follows. The other data (PDF) are available on request to the author by e-mail: ozawa@a-chem.eng.osaka-cu.ac.jp. [**1d**] ^{1}H NMR (CD_2Cl_2, –30 °C): δ 0.51 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, $PtCH_2CH_2CH_2CH_3$), 0.75 (br, 2H, $PtCH_2CH_2CH_2CH_3$), 0.85 (qui, $^3J_{H-H}$ = 7.2 Hz, 2H, $PtCH_2CH_2CH_2CH_3$), *ca.* 1.3 (m, 2H, $PtCH_2CH_2CH_2CH_3$), 1.47 (d, $^2J_{P-H}$ = 7.8 Hz, $^3J_{Pt-H}$ = 22.8 Hz, 6H, PCH_3) 1.51 (d, $^2J_{P-H}$ = 7.2 Hz, $^3J_{Pt-H}$ = 14.7 Hz, 6H, PCH_3), 4.72 (dd, $^3J_{P-H}$ = 15.3 Hz and 22.2 Hz, $^2J_{Pt-H}$ = 48.6 Hz, 1H, SiH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, –30 °C): δ –10.8 (d, $^2J_{P-P}$ = 17 Hz, $^1J_{Pt-P}$ = 1780 Hz, $^2J_{Si-P}$ = 31 Hz), –4.0 (d, $^2J_{P-P}$ = 17 Hz, $^1J_{Pt-P}$ = 1574 Hz, $^2J_{Si-P}$ = 187 Hz); IR (KBr): ν_{Si-H} = 2032 cm^{-1}. Found: C, 53.87; H, 5.87%. Calcd for $C_{32}H_{42}P_2PtSi$: C, 54.00; H, 5.95%. [**2d**] ^{1}H NMR (C_6D_6): δ –2.17 (dd, $^2J_{P-H}$ = 160.6 Hz and 21.6 Hz, $^1J_{Pt-H}$ = 970 Hz, 1H, PtH), 0.99 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, $SiCH_2CH_2CH_2CH_3$), 1.07 (d, $^2J_{P-H}$ = 8.1 Hz, 6H, PCH_3), 1.28 (d, $^2J_{P-H}$ = 7.8 Hz, 6H, PCH_3), 1.59 (m, 2H, $SiCH_2CH_2CH_2CH_3$), 1.70 (m, 2H, $SiCH_2CH_2CH_2CH_3$), 1.92 (m, 2H, $SiCH_2CH_2CH_2CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ –6.1 (d, $^2J_{P-P}$ = 17 Hz, $^1J_{Pt-P}$ = 2294 Hz), –3.2 (d, $^2J_{P-P}$ = 17 Hz, $^1J_{Pt-P}$ = 1481 Hz); IR (KBr): ν_{Pt-H} = 2050 cm^{-1}.

8 The formation of silylene complexes *via* α-elimination of silylplatinum complexes bearing a $SiHAr_2$ ligand has been reported: G. P. Mitchell and T. D. Tilley, *Angew. Chem., Int. Ed.*, **37**, 2524 (1998); G. P. Mitchell and T. D. Tilley, *J. Am. Chem. Soc.*, **120**, 7635 (1998).