

Dichotomous Reactivity of Halodisilanes in Oxidative Addition with $\text{Pt}(\text{PEt}_3)_3$.

Formation of Bis(silyl)- or (Disilanyl)platinum Complexes

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The Si-Si bond in $\text{XSiMe}_2\text{SiMe}_2\text{Y}$ (X, Y = F, F; Cl, Cl; Cl, Me; Br, Me) was readily cleaved with $\text{Pt}(\text{PEt}_3)_3$ to give *cis*-(XMe_2Si)(YMe_2Si) $\text{Pt}(\text{PEt}_3)_2$ complexes. On the other hand, $\text{ISiMe}_2\text{SiMe}_3$ selectively underwent oxidative addition at the Si-I bond to result in the formation of *trans*-($\text{Me}_3\text{SiMe}_2\text{Si}$) $\text{PtI}(\text{PEt}_3)_2$.

In the previous papers, we reported that olefins underwent double silylation¹⁾ and/or dehydrogenative single silylation²⁾ with disilanes in the presence of platinum(0) complex catalysts. These reactions as well as other double silylation reactions are considered to be initiated by oxidative addition of the Si-Si bond of the disilanes. However, the oxidative addition of non-cyclic strain-free disilanes with low valent transition metal complexes has not been observed except for the cases of $\text{Cl}_3\text{SiSiCl}_3$ and $\text{Br}_3\text{SiSiBr}_3$,³⁾ and the reactivity of other disilanes and the stereochemistry of the products have not been elucidated. On the other hand, platinum(0) complexes undergo oxidative addition with halosilanes to give *trans*-halogeno(silyl)platinum complexes.⁴⁾ We now report further examples of clean oxidative addition of Si-Si bonds and the first example of oxidative addition of a halogen-silicon bond in a halodisilane.

When $\text{FSiMe}_2\text{SiMe}_2\text{F}$ (**1a**, 0.10 mmol) was treated with $\text{Pt}(\text{PEt}_3)_3$ (0.05 mmol) in benzene- d_6 (0.25 ml), the color of the solution readily changed from orange to yellow at room temperature within 10 min. ^1H NMR showed new signals assignable to the formation of $\text{FMe}_2\text{Si-Pt}$ species emerging at 0.77 ppm ($J_{\text{H-F}} = 9.4$ Hz, $J_{\text{H-Pt}} = 18.8$ Hz). In addition, the ^{31}P NMR signal of the phosphine bound to the platinum center cleanly shifted from 40.7 ($J_{\text{P-Pt}} = 4216$ Hz) to 21.9 ppm ($J_{\text{P-Pt}} = 1533$ Hz, $J_{\text{P-F}} = 40.3$ Hz). In a separate experiment,

a mixture of **1a** (80 mg, 0.52 mmol), Pt(PEt₃)₃ (190 mg, 0.285 mmol), and benzene (0.8 ml) was stirred at room temperature for 15 min. Concentration of the reaction mixture followed by recrystallization from pentane afforded *cis*-(FMe₂Si)₂Pt(PEt₃)₂ (**2a**) as yellow crystals (125 mg, 75% isolated yield).⁵⁾ The analytical and spectral data were in good agreement with the proposed structure, the coupling constant value ($J_{P-Pt} = 1533$ Hz) of the satellite bands being indicative of *cis*-configuration.⁶⁾ The structure of the product was further confirmed by the following observations. Firstly, when treated with PhLi, **2a** could be converted to the known *cis*-(PhMe₂Si)₂Pt(PEt₃)₂.⁶⁾ Secondly, **2a** reacted (90 °C, 15 min) with 2 equivalents of diphenylacetylene to give (Z)-1,2-bis(fluorodimethylsilyl)-1,2-diphenylethene in 93% yield.⁷⁾

Other disilanes with at least one halogen atom placed on the silicon reacted at room temperature (Eq. 1).



1a: X = Y = F

b: X = Y = Cl

c: X = Cl, Y = Me

d: X = Br, Y = Me

2a: X = Y = F

b: X = Y = Cl

c: X = Cl, Y = Me

d: X = Br, Y = Me

Thus, **1b** similarly reacted to afford **2b** (66% isolated yield),⁹⁾ albeit at somewhat lower rate; it took about 45 min to complete the reaction. The reaction of **1c** and **1d** required 1 d, but selectively afforded **2c** and **2d**, respectively.¹⁰⁾ As estimated by NMR of the reaction mixture, the yield of each reaction of Eq. 1 was always in excess of 90%. On the other hand, XSiMe₂SiMe₂Y (**1e**: X = Y = Me; **1f**: X = Y = Ph) seemed apparently unreactive toward Pt(PEt₃)₃ not only at room temperature but at 120 °C as judged by ¹H and ³¹P NMR. The results of Eq. 1 combined with those of the unsuccessful reactions of **1e** and **1f** reveal the reactivity order of FSiMe₂SiMe₂F > ClSiMe₂SiMe₂Cl > ClSiMe₂SiMe₃, BrSiMe₂SiMe₃ >> PhSiMe₂SiMe₂Ph, Me₃SiSiMe₃. In Pd- and Pt-catalyzed double silylation reactions, the reactivity of disilanes is significantly enhanced by electronegative substituents attached to the silicon atoms.^{1,11)} This is entirely consistent with the above-mentioned trend of the reactivity of disilanes toward Pt(PEt₃)₃.

In striking contrast with **1a-d**, when $\text{ISiMe}_2\text{SiMe}_3$ (**1g**) (0.95 mmol) was treated with $\text{Pt}(\text{PEt}_3)_3$ (0.38 mmol) in benzene- d_6 (0.6 ml) at 90 °C for 10 min, *trans*- $\text{Me}_3\text{SiMe}_2\text{SiPtI}(\text{PEt}_3)_2$ (**4**) was formed in nearly quantitative yield (^1H NMR). In ^{31}P NMR of the reaction mixture, signals assignable to other platinum-



phosphine species were not observed at all. Accordingly, the Si-I bond seemed to have selectively undergone oxidative addition while the Si-Si bond remained intact. In a separate reaction using $\text{Pt}(\text{PEt}_3)_3$ (1.02 mmol) and **1g** (1.80 mmol) in benzene (1 ml) at 60 °C for 1 h, reasonably pure **4** could be isolated as yellow crystals in 68% yield after recrystallization from benzene-pentane.¹²⁾ The dissociation energy of $\text{Me}_3\text{Si-X}$ bond (kJ/mol) decreases in the order of X; F (590) > Cl (410) > Br (320) > SiMe_3 (284) > I (240).¹³⁾ The exclusive cleavage of the Si-I bond is presumably associated with the weakness of the bond as compared with the Si-Si bond.

In summary, the rate and the course of the reactions of disilanes remarkably depend on the nature of the substituent attached to the silicon atoms. The reactions herein described provide convenient methods to synthesize bis(silyl) and disilanyl transition metal complexes. Full details of the reactivity of disilanes as well as those of the resulting complexes are the subjects of coming papers.

References

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- 5) Compound **2a**: mp 75-76 °C; ^1H NMR (C_6D_6 , TMS) δ 0.78 (d, $J_{\text{H-F}} = 9.4$ Hz, $J_{\text{H-Pt}} = 18.8$ Hz, 12H, SiCH_3), 0.90 (dt, $J_{\text{H-P}} = 15.8$ Hz, $J = 7.9$ Hz, 18H, PCH_2CH_3), 1.78 ppm (dq, $J_{\text{H-P}} = J = 7.9$ Hz, 12H,

- CH₂); ³¹P NMR (C₆D₆, H₃PO₄) δ 21.9 ppm (*J*_{P-Pt} = 1533 Hz); IR (nujol); 1248, 1236, 1032, 832, 800, 768, 746, 714, 668, 646, 634 cm⁻¹. Anal. Found: C, 32.90; H, 7.28%. Calcd for C₁₆H₄₂F₂P₂PtSi₂: C, 32.81; H, 7.23%.
- 6) T. -a. Kobayashi, T. Hayashi, H. Yamashita, and M. Tanaka, *Chem. Lett.*, **1988**, 1411.
- 7) We have reported that *cis*-(PhMe₂Si)₂Pt(PPh₂Me)₂ (**3**) reacts with acetylenes to give *cis*-1,2-bis(silyl)ethenes. See T. -a. Kobayashi, T. Hayashi, H. Yamashita, and M. Tanaka, *Chem. Lett.*, **1989**, 467. It is interesting to note that the reactivity of **2a** toward diphenylacetylene is lower than **3**; the reaction of **3** was almost completed in 15 min at room temperature while **2a** did not react under the same conditions. This is presumably due to the stabilization of the Si-Pt bond caused by the electronegative fluorine atom.⁸⁾
- 8) B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, **25**, 1 (1982).
- 9) Compound **2b**: mp 69-75 °C; ¹H NMR (C₆D₆, TMS) δ 0.93 (dt, *J*_{H-P} = 14.6 Hz, *J* = 7.3 Hz, 18H, PCH₂CH₃), 1.07 (s, *J*_{H-Pt} = 20.2 Hz, 12H, SiCH₃), 1.75 ppm (dq, *J*_{H-P} = *J* = 7.3 Hz, 12H, CH₂); ³¹P NMR (C₆D₆, H₃PO₄) δ 13.2 ppm (*J*_{P-Pt} = 1750 Hz); IR (nujol); 1238, 1034, 838, 796, 760, 718, 654, 416 cm⁻¹. Anal. Found: C, 30.23; H, 6.59%. Calcd for C₁₆H₄₂Cl₂P₂PtSi₂: C, 31.07; H, 6.84%.
- 10) In ¹H NMR the signals assignable to the methyl groups of XMe₂Si-Pt and Me₃Si-Pt moieties appeared at 1.15 (*J*_{H-Pt} = 21.6 Hz) and 0.59 ppm (*J*_{H-Pt} = 22.3 Hz) for **1c**, and 1.28 (*J*_{H-Pt} = 21.5 Hz) and 0.55 ppm (*J*_{H-Pt} = 21.4 Hz) for **1d**, respectively. The ³¹P NMR signal of Pt(PEt₃)₃ was replaced upon the reaction by new signals at 14.0 ppm (*J*_{P-Pt} = 1694 Hz) for **1c**, and 13.8 ppm (*J*_{P-Pt} = 1758 Hz) for **1d**.
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- 12) Compound **4**: mp 76-80 °C; ¹H NMR (C₆D₆, TMS) δ 0.29 (s, 9H, PtSiSiCH₃), 0.54 (s, *J*_{H-Pt} = 33.5 Hz, 6H, PtSiCH₃), 1.01 (tt, *J*_{H-P} = *J* = 7.8 Hz, 18H, PCH₂CH₃), 2.09 ppm (tq, *J*_{H-P} = 3.9 Hz, *J* = 7.8 Hz, 12H, CH₂); ³¹P NMR (C₆D₆, H₃PO₄) δ 14.4 ppm (*J*_{P-Pt} = 2822 Hz); IR (nujol); 1236, 1036, 836, 790, 764, 718, 684, 646, 620 cm⁻¹. Anal. Found: C, 28.15; H, 6.55%. Calcd for C₁₇H₄₅IP₂PtSi₂: C, 29.61; H, 6.58%. Despite of repeated attempts, isolation of analytically pure **4** failed owing to the instability. However, the lack of satellite bands associated with coupling between ¹⁹⁵Pt and the methyl protons at 0.29 ppm strongly supports that the Si-Si bond remained intact.
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