Reactivity of the Si-C Bond of [1]Silaferrocenophane: Palladium-Catalyzed Dimerization and Oxidative Addition to a Pt(0) Complex

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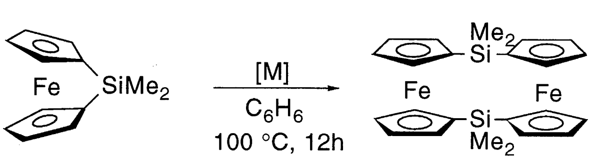
[1]Silaferrocenophanes (**1**) underwent dimerization reaction in the presence of palladium-trialkylphosphine complexes. A mechanistically-related [2]platinasilaferrocenophane complex was formed when **1** was treated with $Pt(PEt_3)_3$.

In the recent years, metallocenophanes have received increasing attention owing to the unique structure, bonding, reactivity and potential utility as precursors for metal-containing macromolecules.[1] Among them, [1]silaferrocenophanes have been under vigorous investigation as they were readily transformed into novel ferrocene-containing polymers under thermal or anionic conditions.[1,2] However, little is known about their reactivity in the presence of transition metal complexes. Recently, we found that [1]silaferrocenophanes were extremely reactive towards transition metals; they underwent a rapid ring-opening polymerization (ROP) in the presence of phosphine-free platinum or palladium complexes.[3] Further investigations indicated that [1]silaferrocenophanes are prone to other transformations similar to those of 1-silacyclobutanes.[4] In this report, we disclose the dimerization of a [1]silaferrocenophane catalyzed by palladium-phosphine complexes and the ability of the Si-C bond in this system to undergo oxidative addition with a Pt(0) complex, as a comment on the mechanism of dimerization and ROP reactions.[5]

Previously, we reported that palladium-triarylphosphine complexes such as $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_3$ could not promote either dimerization or ROP of dimethylsilylene bridged [1]silaferrocenophane **1**.[3] Similarly, $Pt(PPh_3)_4$ that was found to be efficient catalyst for the dimerization of 1-silacyclobutanes[4] could not induce any transformation of **1**. A systematic screening of the palladium and platinum complexes revealed that palladium-trialkylphosphine complexes promoted the dimerization of **1**.[6]



1 **2**

Conversion (%)	[M]	Yield (%)
100	$Pd(PCy_3)_2Cl_2$	90
77	$Pd(PBu_3)_2Cl_2$	63
15	$Pd(PEt_3)_2Cl_2$	10
5	$Pd(PMe_3)_2Cl_2$	< 2

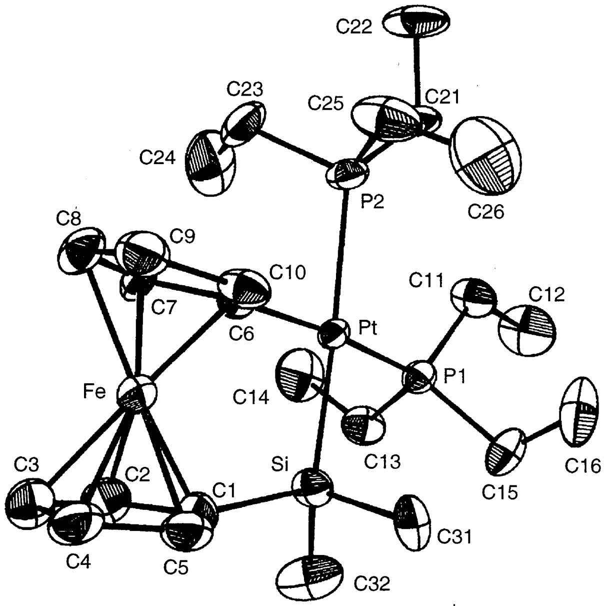


Figure 1. The molecular structure of complex **3**.

In a typical experiment, a benzene (0.5 ml) solution of **1** (0.2 mmol) was heated at 100 °C in an argon-purged sealed tube in the presence of $PdCl_2(PCy_3)_2$ (4 mol%) for 12 h. ^{1}H NMR of the reaction mixture showed complete conversion of **1** and a high yield (90%) formation of dimer **2**. The reaction mixture was filtered through florisil, concentrated and washed with a small amount of hexane (2 × 1 ml) to give 82% yield of pure dimer **2**.

The conversion of **1**[7] as well as the yield of **2** (^{1}H NMR) gradually decreased with the decrease in the basicity of phosphine ligands, indicating that highly electron-rich metal species promote the dimerization. Notably, the synthesis of **2** was recently reported which involved a tedious five step procedure.[8]

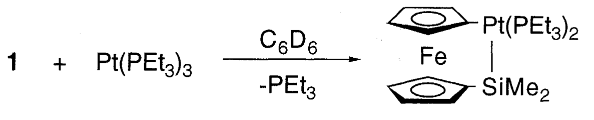
The metal-catalyzed dimerization and ROP[3] of **1** presumably proceed by a Si-C/Si-C bond metathesis. This assumption obviously invokes the possibility of oxidative addition of the Si-C bond across low-valent metal species. Although we have been unable to confirm such oxidative addition with palladium complexes, $Pt(PEt_3)_3$ did react with **1**. Thus, when a mixture of $Pt(PEt_3)_3$ (0.06 mmol) and **1** (0.062 mmol)

Table 1. Selected bond lengths (Å) and bond angles (°) in **3**

Bond lengths					
Pt-P1	2.291 (2)	Si-C1	1.900(9)	Pt-P2	2.407 (2)
Si-C31	1.90 (1)	Pt-Si	2.382 (2)	Si-C32	1.92 (1)
Pt-C6	2.073 (8)	Fe-C1	1.987 (9)	Fe-C6	2.067 (8)

Bond angles			
P1-Pt-P2	102.86 (8)	Pt-Si-C1	114.4 (3)
P1-Pt-Si	92.05 (8)	Pt-Si-C31	107.5 (4)
P1-Pt-C6	174.3 (3)	Pt-Si-C32	122.4 (3)
P2-Pt-Si	162.65 (9)	C1-Si-C31	102.7 (4)
P2-Pt-C6	82.0 (2)	C1-Si-C32	101.5 (5)
Si-Pt-C6	83.6(2)	C1-Fe-C6	96.0 (3)
Fe-C1-Si	113.1 (4)	Pt-C6-Fe	129.1 (4)

was dissolved in C_6D_6 (0.4 ml), ^{1}H NMR of the reaction mixture showed that more than 20% of the starting materials were selectively transformed to [2]ferrocenophane complex **3**, in which the two Cp rings are bridged by dimethylsilylene and Pt(II) moieties. The conversion increased to 60% after heating at 60 °C for 2h and > 95% at 80 °C for 3 h. ^{31}P NMR of **3** showed two signals centered at δ 11.1 (d, $^2J_{P-P}$ = 19.2 Hz, $^1J_{Pt-P}$ = 2160 Hz, P trans to C) and 10.4 (d, $^2J_{P-P}$ = 19.2 Hz, $^1J_{Pt-P}$ = 911 Hz, $^2J_{P-Si}$ = 185 Hz, P trans to Si) and ^{29}Si NMR showed a resonance at δ 5.2 (dd, $^2J_{P-Si}$ = 185, ≈ 18 Hz, $^1J_{Pt-Si}$ = 1304 Hz). In a preparative scale, the pure complex was isolated in 84% yield.[9]



3

(rt: ~20%; 60 °C/2h: ~60%; 80 °C/3h: ~95%)

X-ray diffraction study of **3**[10] unambiguously demonstrated the metal insertion into the Si-C bond of **1**. The crystals of **3** were obtained by dissolving in toluene-hexane mixture (1 : 3 v/v) followed by slow cooling to -30 °C. The molecular structure of **3** is given in Figure 1 and important bond distances and angles are summarized in Table 1. Complex **3** possesses a distorted square-planar structure around platinum. The Pt-Si and Pt-C bond lengths (Å) are 2.382 (2) and 2.073 (8) respectively. The trans influence of silicon is remarkably stronger than that of carbon (Cp); the Pt-P bond length trans to Si is 2.407 (2) and that trans to C is 2.291 (2).

Complex **3** is highly stable towards moisture and air. It did not decompose when **3** in the solid state was exposed to open air for several weeks. When treated with compound **1** (2 equiv., 90-100 °C in C_6D_6), complex **3** remained in the reaction mixture without any appreciable conversion to dimer **2** or polymer of **1**.

In conclusion, we have demonstrated that [1]silaferrocenophane dimerizes in the presence of basic trialkylphosphine-palladium complexes. The Si-C bond of **1** undergoes a facile oxidative addition reaction with a Pt(0) complex. The detailed studies on the reactivity of complex **3** and other catalytic transformations[11] of [1]silaferrocenophanes are in progress.

References and Notes

1 D. A. Foucher, C. H. Honeyman, J. M. Nelson, B. Z. Tang, and I. Manners, *Angew. Chem., Int. Ed. Engl.*, **32**, 1709 (1993); I. Manners, *Adv. Organomet. Chem.*, **37**, 131 (1995); M. Herberhold, *Angew. Chem., Int. Ed. Engl.*, **34**, 1837 (1995).

2 a) D. A. Foucher, B. Z. Tang, and I. Manners, *J. Am. Chem. Soc.*, **114**, 6246 (1992); b) M. T. Nguyen, A. F. Diaz, V. V. Dement'ev, and K. H. Pannell, *Chem. Mater.*, **6**, 952 (1994); c) R. Rulkens, Y. Ni, and I. Manners, *J. Am. Chem. Soc.*, **116**, 12121 (1994); d) J. K. Pudelski and I. Manners, *J. Am. Chem. Soc.*, **117**, 7265 (1995) and the references cited therein.

3 a) N. P. Reddy, H. Yamashita, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1995**, 2263; b) Y. Ni, R. Rulkens, J. K. Pudelski, and I. Manners, *Macromol. Chem. Rapid Commun.*, **16**, 637 (1995).

4 Recently, we reported that 1-silacyclobutanes undergo platinum-catalyzed dimerization and ROP reactions and also oxidative addition reaction with a Pt(0) complex. H. Yamashita , M. Tanaka, and K. Honda, *J. Am. Chem. Soc.*, **117**, 8873 (1995).

5 Preliminary results were presented at the 69th Spring Annual Meeting of Chemical Society of Japan, Abstract 2C743, Kyoto, March 27-30, 1995.

6 It was reported that the transition metal-catalyzed ROP of **1** affords a small amount of dimer **2** as a byproduct (ref. 3b).

7 A small amount of polymer of **1** was formed (< 5%), presumably, due to high temperature reaction conditions. It can be noted that the thermal ROP of **1** proceeds at 120 °C (Ref. 2a).

8 D. L. Zechel, D. A. Foucher, J. K. Pudelski, G. P. A. Yap, A. L Reingold, and I. Manners, *J. Chem. Soc., Dalton Trans.*, **1995**, 1893.

9 In a pyrex Schlenk tube, a mixture of $Pt(PEt_3)_3$ (0.49 mmol, generated from 327 mg of $Pt(PEt_3)_4$ and **1** (121 mg, 0.5 mmol) in benzene (3 ml) was heated at 80 °C with stirring for 5h. The reaction mixure was concentrated and 6 ml of hexane was added to afford the deposition of complex **3** as orange colored crystalline solid. The solvents were decanted and the complex was washed with cold hexane (2 × 3 ml) and dried under vacuum to give 277 mg (84% yield) of **3**. **3**: ^{1}H NMR δ 0.77 (dt, 1/2 × $^3J_{P-H}$ ≈ $^3J_{H-H}$ ≈ 7.5 Hz, 9H, $PCCH_3$), 0.82 (d, $^4J_{P-H}$ = 2.3 Hz, $^3J_{P-H}$ was overlapped by $PCCH_3$ resonances, 6H, $SiCH_3$), 0.89 (dt, 1/2 × $^3J_{P-H}$ ≈ $^3J_{H-H}$ ≈ 7.5 Hz, 9H, $PCCH_3$), 1.26 and 1.61 (each dq, $^2J_{P-H}$ ≈ $^3J_{H-H}$ ≈ 7.5 Hz, $^3J_{Pt-H}$ ≈ 15 Hz, each 6H, PCH_2), 4.13 (pseudo t, $^3J_{Pt-H}$ = 23.5, 2H, Cp), 4.37 (t, $^3J_{H-H}$ = 1.3 Hz, 2H, Cp), 4.51 (br s, 2H, Cp), 4.78 (t, $^3J_{H-H}$ = 1.3, 2H, Cp); ^{13}C NMR δ 8.15 ($^3J_{Pt-C}$ = 12.8 Hz, 3C, $PC\underline{C}$), 8.75 ($^3J_{Pt-C}$ = 23.7 Hz, 3C, $PC\underline{C}$), 8.91 (d, $^3J_{P-C}$ = 12 Hz, $^2J_{Pt-C}$ = 85.5 Hz, 2C, $SiCH_3$), 15.72 (d, $^1J_{P-C}$ = 17.4 Hz, $^2J_{Pt-C}$ = 11.9 Hz, 3C, PC), 18.49 (dd, $^1J_{P-C}$ = 27.5 Hz, $^3J_{P-C}$ = 5.3 Hz, $^2J_{Pt-C}$ = 27.9 Hz, 3C, PC), 70.06 (2C, SiCp), 70.41 (d, $^4J_{P-C}$ = 5.6 Hz, $^3J_{Pt-C}$ = 52 Hz, 2C, 3, 4 position of PtCp), 74.25 (dd, $^3J_{P-C}$ = 5.3, 1.8 Hz, $^2J_{Pt-C}$ = 58.2 Hz, 2C, 2,5 position of PtCp), 74.87 (2C, SiCp); ^{31}P NMR δ 10.4 (d, $^2J_{P-P}$ = 19.2 Hz, $^1J_{Pt-P}$ = 911 Hz, $^2J_{P-Si}$ = 185 Hz, P trans to Si), 11.1 (d, $^2J_{P-P}$ = 19.2 Hz, $^1J_{Pt-P}$ = 2160 Hz, P trans to C) and ; ^{29}Si NMR δ 5.2 (dd, $^2J_{P-Si}$ = 185, ≈ 18 Hz, $^1J_{Pt-Si}$ = 1304 Hz); ^{195}Pt NMR δ -4630 (dd, $^1J_{Pt-P}$ = 2160, 911 Hz). Analysis Calcd. for $C_{24}H_{44}FeP_2PtSi$: C, 42.80; H, 6.58. Found: C, 43.32; H, 6.54.

10 Crystallographic data for **3**: $C_{24}H_{44}FeP_2PtSi$, F.W. = 673.59, monoclinic, space group $P2_1/c$, a = 8.262(1) Å, b = 18.971(1) Å, c = 17.687(2) Å, β = 100.58(1)°, V = 2725.1 Å^3, Z = 4, D_{calc} = 1.64 g/cm^3, μ (Mo Kα) = 58.8 cm^{-1}. Intensity data were measured on a Enraf-Nonius CAD4 diffractometer. The 3699 unique reflections ($|F_o| > 3\sigma|F_o|$) were observed (2θ < 50°) using Mo Kα radiation and ω-2θ scan. The structure was solved by direct methods and all non-hydrogens were refined anisotropically by full-matrix least-squares to R = 0.036 and R_w = 0.042.

11 We have found that the Si-C bond of 1-silacyclobutanes or [1]sialferrocnophanes undergo a selective Si-C/Si-Si cross-metathesis reactions with disilanes. The details will be published elsewhere.