Insertion into the Strained Silicon−Carbon Bond of a Silicon-Bridged [1]Ferrocenophane: Synthesis and Structure of a [2]Platinasilaferrocenophane

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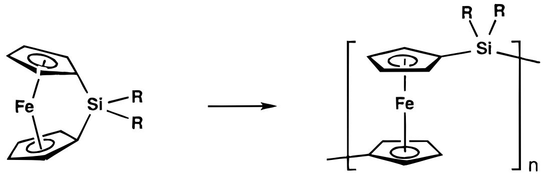
Summary: The first example of a well-characterized insertion of a transition-metal fragment into a strained silicon-carbon bond of a silicon-bridged [1]ferrocenophane is reported. Reaction of $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (**3**) *with* $Pt(PEt_3)_3$ *yields the novel amber crystalline [2]platinasilaferrocenophane* $Fe(\eta\text{-}C_5H_4)_2Pt(PEt_3)_2SiMe_2$ (**4**). *An X-ray diffraction study of* **4** *indicated that the cyclopentadienyl rings in this species are tilted with respect to one another by an angle of 11.6(3)°. Complex* **4** *is of interest as a model of the proposed intermediate during the transition-metal-catalyzed ring-opening polymerization of species such as* **3** *to yield poly(ferrocenylsilanes).*

Since their discovery in 1975, [1]ferrocenophanes have attracted attention because of their interesting structures and reactivity,[1] their applications as surface derivatization agents,[2] and very recently as precursors to novel transition metal-based polymers via ring-opening polymerization (ROP).[3] These unusual species can generally be prepared via the reaction of dilithioferrocene−tmeda (tmeda = tetramethylethylenediamine) with organoelement dihalides and possess strained structures in which, depending on the bridging element (silicon, phosphorus, sulfur, zirconium, etc.), the planes of the cyclopentadienyl (Cp) ligands are tilted with respect to one another by ca. 6−31°.[3−8]



1 **2** (n = ca 1,200 - 3,000)

Stoichiometric ring-opening reactions for silicon-bridged [1]ferrocenophanes (**1**) were described in the late 1970s,[2] whereas thermally induced ROP to yield high molecular-weight poly(ferrocenylsilanes) (**2**) was first reported in 1992.[9] This ROP methodology has now been extended to a variety of strained [1]- and [2]metallocenophanes[3,8,10−12] and yields materials with a range of interesting physical properties.[3,13−18] Anionic ROP of silicon-bridged [1]ferrocenophanes which proceeds at ambient temperature has also been described.[19] Very recently transition-metal-catalyzed ROP, which also operates at room temperature, has been achieved using a variety of Rh^I, Pd^0, Pd^{II}, Pt^0, and Pt^{II} catalysts.[20,21] By analogy with proposed mechanisms for the transi-

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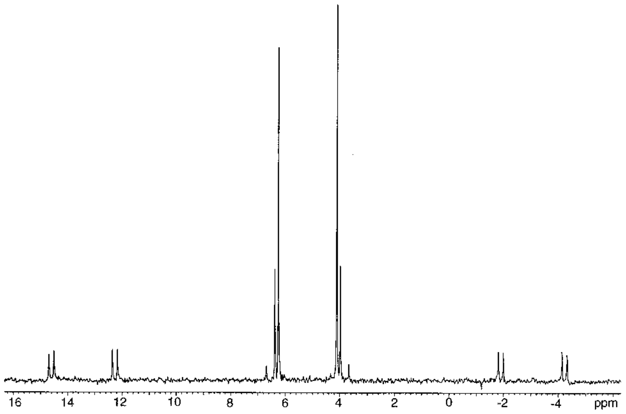
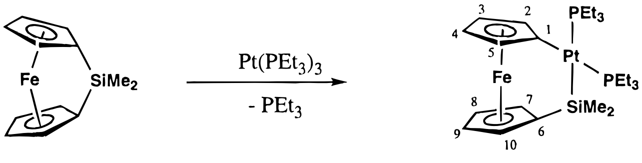


Figure 1. ^{29}Si NMR spectrum (79.5 MHz, C_6D_6) of **4**.

tion-metal-catalyzed ROP of silacyclobutanes, the initial step might be expected to involve insertion of the transition metal into the strained Si−C bond.[22−25] In this communication we report the insertion of platinum into the strained silicon-carbon bond of the $SiMe_2$-bridged species **3**, which represents the first well-characterized example of an insertion of a transition metal into the cyclopentadienyl carbon−bridging atom bond of a strained [1]silaferrocenophane.

Addition of equimolar quantities of **3** to toluene solutions of $Pt(PEt_3)_3$ followed by heating to 60 °C for 4 h led to a gradual disappearance of **3**, as monitored by ^1H NMR spectroscopy and formation of the adduct **4**.



3 **4**

Complex **4** crystallizes from hexane solutions as an air-stable orange crystalline solid and was isolated in ca. 60% yield. The new species was characterized using ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy.[26] Noteworthy is the ^{29}Si signal at 5.18 ppm (Figure 1), which shows a large 1312 Hz coupling to Pt as well as couplings of 181 and 14.5 Hz to phosphorus nuclei of the trans and cis phosphine ligands, respectively. The ^{31}P NMR data show Pt−P couplings of 2160 and 910 Hz, the latter being smaller due to the strong trans influence of the silyl substituent. The proton and ^{13}C NMR data are consistent with a [2]platinasilaferrocenophane structure in that four and six cyclopentadienyl resonances are observed, respectively. Of these, the $^{13}C\{^1H\}$ NMR signals for C_1 and C_6 are of particular interest. Thus, C_1 appears as a multiplet centered at 73.3 ppm with a large Pt−C coupling of 850 Hz, whereas that for C_6 is a multiplet at δ 85 with a much smaller J_{PtC} value of 60 Hz. The downfield chemical shift of C_6 is notably different from that of 33.5 ppm observed for the ipso carbons in the highly strained parent [1]ferrocenophane (**3**).

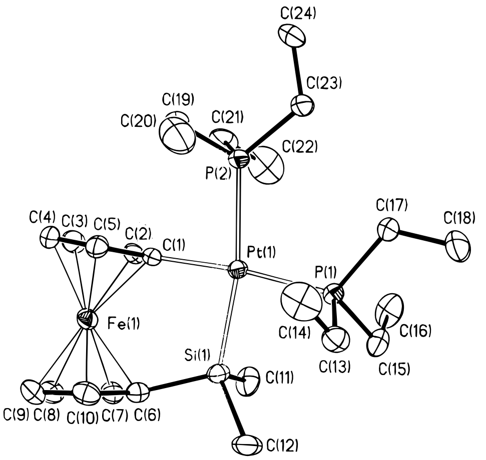


Figure 2. Molecular structure of complex **4** showing the atom labeling (30% thermal ellipsoids are shown).

In order to more fully investigate the novel structure of **4**, an X-ray diffraction study was undertaken.[27] Suitable crystals were grown from hexane solution at ca. −10 °C over 2 days, and a labeled thermal ellipsoid plot of **4** is shown in Figure 2. The structure reveals that the molecule is slightly strained with a tilt angle of 11.6(3)° between the Cp planes. The platinum center is in a distorted-square-planar environment with a larger than expected P−Pt−P angle of 102.74(5)° and somewhat compressed P−Pt−Cp and Cp−Pt−Si angles of 82.48(13) and 83.28(13)°, respectively. Interestingly, the angle β between the plane of the cyclopentadienyl ligand and the C-Pt bond is only 1.2(3)°, whereas the analogous angle for the ipso C−Si bond is 12.8(3)°. The Pt−Si bond is also twisted with respect to the Cp−Fe−Cp vector, as revealed by a stagger in the Cp rings of 7.6(5)°.

As mentioned above, it is likely that the initial step in the platinum-catalyzed ROP of **3**[20,21] involves insertion of a Pt^{II} or Pt^0 atom into one of the Cp−Si bonds of

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(26) **4**: ^1H NMR (δ, 400 MHz, C_6D_6) 0.78 (9H, m, PEt_3), 0.84 (6H, d, J_{PH} = 2.2 Hz, $SiMe_2$), 0.89 (9H, m, PEt_3), 1.26 (6H, m, PEt_3), 1.61 (6H, m, PEt_3), 4.14 (2H, m, J_{PtH} = 23.5 Hz, $H_{2,5}$), 4.40 (2H, t, $H_{7,10}$), 4.52 (2H, m $H_{3,4}$), 4.80 (2H, t, $H_{8,9}$); ^{13}C $\{^1H\}$ NMR (δ, 100 MHz, Cp peaks only, C_6D_6) 70.0 ($C_{7,10}$), 70.5 (m, J_{PtC} = 52 Hz, J_{PC} = 15 Hz, $C_{2,5}$), 73.3 (m, J_{PtC} = 850 Hz, J_{PC} = 104 and 14 Hz, C_1), 74.3 (m, J_{PtC} = 65 Hz, J_{PC} = 4.5 and 2 Hz, $C_{3,4}$), 74.9 ($C_{8,9}$), 84.9 (m, J_{PtC} = 60 Hz, J_{PC} = 4.5 and 2 Hz, C_6); $^{31}P\{^1H\}$ NMR (δ, 121.5 MHz, C_6D_6), 10.4 (J_{PtP} = 910 Hz, J_{PP} = 19 Hz), 11.2 (J_{PtP} = 2160 Hz, J_{PP} = 19 Hz); $^{29}Si\{^1H\}$ NMR (δ, 79.5 MHz, C_6D_6), 5.18 (J_{PtSi} = 1312 Hz, J_{PSi} = 181 and 14.5 Hz). Anal. Calcd for $C_{24}H_{44}FeP_2PtSi$: C, 42.80; H, 6.53. Found: C, 42.77; H, 6.68.

(27) Crystal data for $C_{24}H_{44}FeP_2PtSi$ (**4**): monoclinic, $P2_1/c$, a = 8.2699(14) Å, b = 19.008(3) Å, c = 17.719(2) Å, β = 100.565(11)°, V = 2738.1(7) Å^3, Z = 4, μ = 5.803 mm^{-1}, Mo Kα radiation (λ = 0.710 73 Å), d_{calcd} = 1.634 Mg/m^3, 293(2) K, Siemens P4 diffractometer with graphite monochromator, orange crystal (0.05 × 0.53 × 0.60 mm). Of 6368 reflections collected ($2.51 \leq 2\theta \leq 27.00°$), 5959 were independent (R_{int} = 0.0387) and 4337 were observed with $F_o \geq 4\sigma(F_o)$. Solution was by direct methods and refinement on F^2 using SHELXTL-PC 5.0 (Sheldrick, G. M., Siemens Analytical X-ray Instruments Inc., Madison, WI, 1995). Absorption correction was carried out by indexing crystal faces and integration: minimum and maximum transmission coefficients 0.1383 and 0.7624. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and treated as riding atoms. R1 = 0.0293, wR2 = 0.0577 ($R1 = \sum(F_o - F_c)/\sum F_o$ observed data, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, all data), GOF = 0.886, N_o/N_v = 21.8, and $\Delta\rho_{max}$ = 1.02 e Å^{-3} (largest three peaks in residual electron density map within 1.0 Å from the Pt atom).

the ferrocenophane. Hence, complex **4** represents the first direct evidence that such a step can occur, and its isolation is also consistent with the fact that phosphine derivatives of the group 9 and 10 metals do not polymerize **3**. This is in contrast with the active catalysts that have weakly coordinated ligands (e.g. $PtCl_2$, Pt(1,5-cyclooctadiene)$_2$, [Rh(cyclooctene)$_2$(μ-Cl)]$_2$), which allow further addition of ferrocenophane substrate to species akin to **4**, leading to the high-molecular-weight organometallic polymers **2**.[20,21]

Preliminary studies of the reactivity of **4** have shown that the complex is stable up to 100 °C in C_6D_6 and that it does not react with **3** at 95 °C in the same solvent over a period of 20 h. Further studies on the mechanism of the transition-metal-catalyzed ROP of strained ferrocenophanes are in progress and will be reported in due course.

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Supporting Information Available: Complete tables of X-ray structural data, positional parameters, anisotropic thermal parameters, and bond lengths and angles and text giving a description of the preparation of **4** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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