

Isolation and Ring-Opening of New 1-Sila-3-metallacyclobutanes ($\eta^5\text{-C}_5\text{H}_4\text{Fe}$)(CO) $_2\text{CH}_2\text{SiR}_2$ Leading to A New Class of Organometallic Polymer

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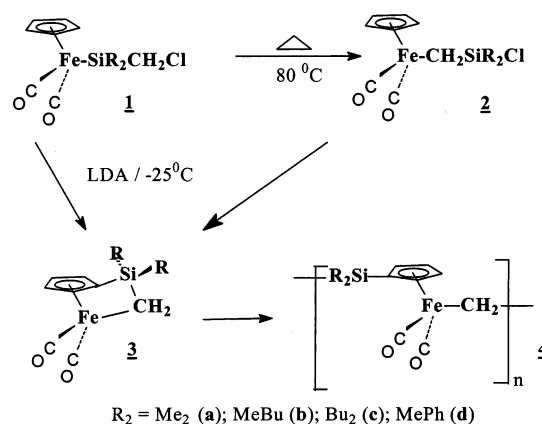
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Well-defined polymers containing transition metal atoms in the backbone are attractive materials owing to their potential applications as catalysts,¹ ion-exchange resins,² polymeric support materials,³ precursors for ceramic materials,⁴ conducting polymers,^{5,6} and chemical sensors.⁶ Excellent examples of such materials are the high-molecular-weight poly-silyleneferrocenylenes obtained from the ring-opening of the appropriate strained [1]-sila-ferrocenophanes.^{5,6} There are reports on the synthesis and reactivity of 1-sila-3-metallacyclobutanes (metal = Zr,⁷ Nb,⁷ and Mo,⁷ and Ir⁸) that undergo ring expansion upon reaction with paraformaldehyde,^{7c} isocyanides,^{7d} and CO.^{7e} Furthermore, a recent example of 1-sila-2-platinacyclobutanes that exhibits a diphenylsilane insertion has been reported.⁹ We now report the synthesis, isolation, characterization, and unprecedented ring-opening polymerization of 1-sila-3-metallacyclobutanes of the type ($\eta^5\text{-C}_5\text{H}_4\text{Fe}$)(CO) $_2(\text{CH}_2\text{SiR}_2)$ (**3**).

As originally reported by the Giering group, thermolysis of FpSiR₂CH₂Cl [Fp = ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) $_2$, R₂ = Me₂ (**1a**)] at 80 °C in benzene in sealed NMR tube results in clean and quantitative formation of the isomeric iron complex containing a direct Fe–C bond, FpCH₂SiR₂Cl (**2a**).¹⁰ We find that similar chemistry occurs with complexes in which R₂ = MeⁿBu (**1b**), ⁿBu₂ (**1c**), and MePh (**1d**). The rearrangement of **1** to **2** is facile; even storing **1** at low temperature (–5 °C) for a few days resulted in the formation of **2** in 20–30% yield along with black decomposed material. NMR spectroscopy and infrared spectra are useful to distinguish between the Fe–Si bond in **1** and the Fe–C bond in **2**.¹¹ The ²⁹Si NMR signal for the Fe–CH₂Si, β -Si in **2** with respect to the Fe atom is downfield shifted in the range of 6–8 ppm from the Fe–Si, α -Si in **1a–d**. The two isomers **1** and **2** are also distinguishable by the ¹³C resonances of the CH₂ group, ~35–37 ppm in **1** vs ~–26.0 ppm for **2**, and the carbonyl stretching frequencies for the Fp–Si complexes are ~15 cm^{–1} lower frequency than the corresponding Fp–C complexes.¹²

Treatment of either **1** or **2** with lithium diisopropylamide (LDA) results in the formation of 1-sila-3-metallacyclobutanes **3a–d** (Scheme 1). The formation of the metallacycles **3** from **2** presumably results from an initial metalation of the cyclopentadienyl ring followed by a ring-closing salt elimination reaction. For the transformation of **1** \rightarrow **3**, we suggest that after the initial metalation of the cyclopentadienyl ring a well-documented silyl group migration to the ring occurs,¹³ generating an iron-based anionic species that performs the final intramolecular ring-closing salt elimination. To date, we have not performed any detailed study to further delineate this aspect of the research. The new silametallacycle **3a** could not be isolated and was characterized by NMR and infrared spectroscopy. A special spectroscopic feature of the metallacycles is the unusual high-field resonance at ~–53 ppm for the CH₂ carbon in ¹³C NMR spectra. Complex **3a** is reasonably stable in solution for several hours; however, attempts to isolate it as a

Scheme 1



molecular species were uniformly unsuccessful since removal of the solvent resulted in the formation of the ring-opened polymer **4a**.

Progressive replacement of the methyl groups by *n*-butyl groups increases the thermal stability of the new metallacycles, and the di-*n*-butyl complex **3c** can be isolated as a pure red viscous oil in 70% yield after column chromatography on silica gel. This simple substitution, dibutyl for dimethyl, results in a metallacycle **3c** that is stable in air and has not, to date, exhibited any thermal, anionic, or transition-metal-catalyzed ring-opening polymerization. Photochemical treatment of a hexane solution of **3c** in a quartz tube for 2 h in the presence of Ph₃P resulted in the formation of the red crystalline phosphine-substituted silametallacycle **5** in 41% yield, thereby permitting a structural analysis of the new metallacycle ring.

The structure of **5** has been confirmed by NMR spectroscopy and by single-crystal X-ray crystallography (Figure 1). The structure was solved using X-ray data collected at 173 K and still shows significant disorder in one of the *n*-butyl groups. Structural analyses of several 1-metalla-3-silacyclobutanes are reported in the literature;^{7e,14} however, **5** represents the first in which one of the C atoms is part of a coordinated cyclopentadienyl ring. Thus, **5** may be regarded as intermediate between the class of 1-metalla-3-silacyclobutane metallacycles and the well-studied 1-sila-ferrocenophanes. These latter complexes exhibit significant ring strain and a rich vein of ring-opened polymerization chemistry.^{5,6} The ring Si–C bond distances of **5**, 1.840(3) and 1.874(3) Å, are in the range for such silacyclobutanes, while the C–Si–C angle of 94° is relatively small for such angles, and the C–Fe–C angle of 80° illustrates a degree of ring strain for this new structural arrangement. Further evidence for a level of ring strain is the Cp(centroid)–Fe–CH₂ angle of 115.6° in **5**, which is smaller than literature values for related ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)CH₂R systems (R = CH₃, 118.7°;^{15a} R = CH₂OCH₃, 120.4°;^{15b} R = CH₂SCH₂Ph, 121.6°).^{15b}

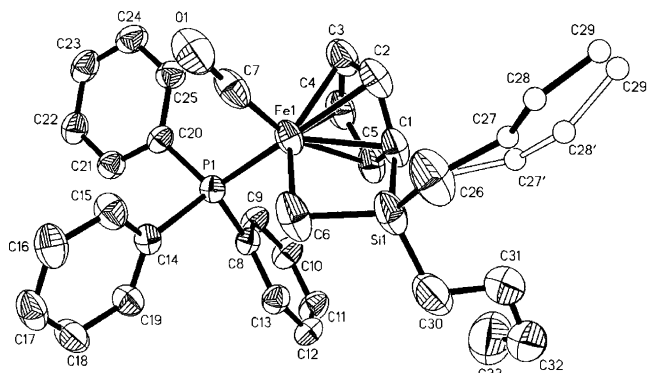


Figure 1. Structure of **5**, space group $P2_1/n$. Selected bond lengths (Å): Fe–C6 = 2.113(3), C6–Si = 1.839(3), Si–C1 = 1.871(3), Si–C26 = 1.867(3), Si–C30 = 1.892(4). Selected bond angles (°): C26–Si–C30 = 114.7(2), C1–Si–C6 = 94.06(11), Fe–C6–Si = 93.24(10), Si–C1–Fe = 92.45(11). The thermal ellipsoids are drawn at the 50% probability level.

An enlarged exocyclic C–Si–C angle of 114° is correspondingly observed. Overall the ring is almost planar, with a dihedral angle between the planes Fe1–Si1–C1 and Fe1–Si1–C6 of 5.9° .

The ^{13}C NMR of **5** exhibited a doublet at -52.6 ppm ($J_{\text{p-c}} = 13.5$ Hz) due to coupling between the C of the CH_2 group and the ^{31}P nucleus. The ^1H NMR signals of the two diastereotopic CH_2 hydrogens were observed as two ABX ($X = ^{31}\text{P}$) quartets due to inequivalent coupling between the phosphorus nucleus and the two H atoms ($J_{\text{AB}} = 11.2$ Hz, $^3J_{\text{AX}} = 13.0$ Hz, $^3J_{\text{BX}} = 1.0$ Hz). The related acyclic compounds, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{SiR}_3$, exhibit the same pattern.¹⁶

A characteristic property of silacyclobutanes is their ability to undergo ring-opened polymerization; however, none of the previously reported 1-metalla-3-silacyclobutanes exhibited such polymerization. Evaporation of the THF from **3a,b** gave the corresponding polymers **4a,b** in an almost quantitative yield, thus more closely resembling the 1-sila-ferrocenophanes. The thermal polymerization can be conveniently monitored by ^{29}Si NMR and ^{13}C NMR spectroscopy. In particular, the carbon resonance of the CH_2 moiety in for silametallacycles at ~ -53.0 ppm shifts to a more conventional value of -26.10 for **4a** and -29.98 ppm for **4b**. The polymeric materials dissolve slowly but completely in THF, suggesting that no appreciable cross-linking has taken place at this stage. Multi-angle laser light scattering analysis of the polymer **4a** revealed a bimodal molecular weight distribution with a predominant high-molecular-weight fraction ($M_w = 1.75 \times 10^5$, $M_n = 7.2 \times 10^4$). The molecular weight (M_w) for **4b** was found to be relatively low, 9500, with polydispersity of 6.3, suggesting that the introduction of the butyl group significantly retards the propagation of a polymer chain. The polymers are amorphous, as determined by WAXS.

The polymers are stable to the atmosphere, and films can be cast from THF solutions. Over a period of time their solubility is decreased, presumably via cross-linking. The glass transition temperature for **4a** was detected to be 3°C by DSC. Thermogravimetric analysis (TGA) of both **4a** and **4b** indicated that they undergo $\sim 45\%$ weight loss between 100 and 200°C and that a 25% residue remains at 700°C . Further study on the ring-opening reactions of **5** and related group 14 analogues of other transition metals are underway, together with studies on the new polymeric species.

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Supporting Information Available: Experimental procedures for the synthesis of **1–5** and NMR data (PDF). Full X-ray crystallographic data for **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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