Table I. Relative Rate Dependence of $Fe(CO)_5$-Catalyzed [4 + 1] Cycloaddition at 50 °C in THF[a]

[**1**], mM	[M], mM	[CO], mM	k_{obsd}, s^{-1}	k_{rel}
290	29	17	9.6×10^{-4}	1.00
70	29	17	1.8×10^{-4}	0.19
290	10	17	3.9×10^{-4}	0.41
290	29	64	7.8×10^{-5}	0.08

[a] Each entry represents the average of five kinetic experiments monitored to at least 80% completion by ^1H NMR (200 MHz). M = $Fe(CO)_5$.

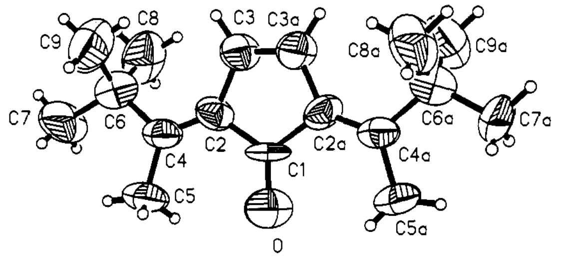
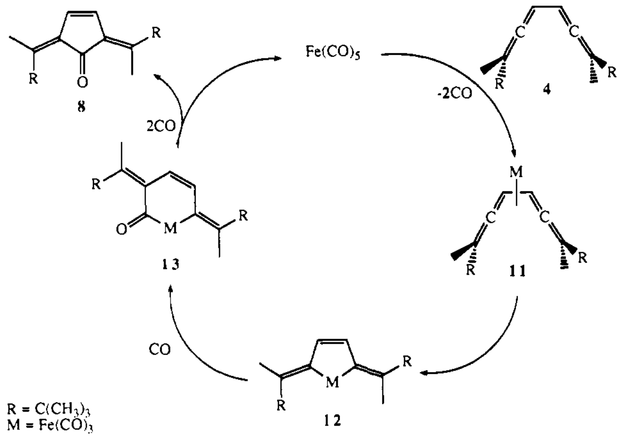


Figure 1. X-ray crystal structure analysis ORTEP view of **6**. Selected bond distances (Å): O–C1 1.232; C1–C2 1.508; C2–C3 1.467; C2–C4 1.319; C3–C3A 1.315; C4–C5 1.473; C4–C6 1.573.

Scheme I



and subsequent reductive elimination could form **8**[14] and regenerate the catalyst.

In summary, conjugated diallenes undergo stereoselective [4+1] cycloaddition with CO in the presence of $Fe(CO)_5$ or $Fe_2(CO)_9$ under preparatively useful conditions. Consistent with the first step being rate-limiting coordination of iron to the diallene, CO was found to be inhibitory. Facial selectivity of iron coordination may account for why meso diastereomers **2** and **3** yield only **6** and **7**. Surprisingly, sterically demanding diallene **4** gave some of **8** indicative of a stereospecific mechanism.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Grant-in-Aid from Washington State University is gratefully appreciated. NMR data were obtained from the WSU NMR Center supported in part by the NIH (RR0631401). B.E.E. thanks D. Matterson for guidance in preparing this manuscript.

Supplementary Material Available: Details of the X-ray crystal structure determination of **2** and **6** including solution and refinement, atomic coordinates, bond lengths, bond angles, isotropic and anisotropic displacement coefficients, and stereo ORTEP plots, together with experimental and analytical data (16 pages); tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Ring-Opening Polymerization of Strained, Ring-Tilted Ferrocenophanes: A Route to High Molecular Weight Poly(ferrocenylsilanes)†

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Received March 6, 1992

The development of new synthetic routes to macromolecules which contain inorganic elements or organometallic units is of considerable interest as a means of preparing materials with unusual and potentially useful properties.[1-5] Ring-opening polymerization represents an important, well-established route to organic polymers[6] and an increasingly successful method for the synthesis of inorganic macromolecules.[3-5] Ring-opening methods may also prove of great utility in the preparation of organometallic polymers, however, very few attempts to investigate this approach have been reported.[7] In this paper, we report the discovery of a novel, ring-opening route to organometallic polymers which provides access to the first examples of high molecular weight poly(ferrocenylsilanes).[8] These macromolecules possess a highly unusual main chain comprising ferrocene units and silicon atoms. Significantly, the synthetic route described is of potentially broad applicability as a similar methodology might also be successful with other strained organometallic monomers with related structures.[9,10]

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† Dedicated to Beverley John Morris.

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(8) Low molecular weight (1400–7000), partially characterized poly(ferrocenylsilanes) have previously been prepared via a polycondensation reaction involving dilithioferrocene and dialkyl- and diaryldichlorosilanes. Rosenberg, H. U.S. Patent 3,426,053, 1969. In addition, Pannell and co-workers have reported the synthesis and characterization of polysilanes with ferrocenyl side groups. See ref 1b, p 329.

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The cycloferrocenylsilane **1a** is accessible in high yield (>60%) as an orange-red, moisture-sensitive, crystalline material via the reaction of dilithioferrocene·TMEDA (TMEDA = tetramethylethylenediamine) with dimethyldichlorosilane.[11] Previous work carried out with [1]ferrocenophanes such as **1a** indicates that molecules of this type are highly strained[12] and that stoichiometric ring-opening processes readily occur.[9a,13] The presence of ring strain in these species is indicated by the significant tilting of the cyclopentadienyl rings as shown by X-ray crystallography.[12] By contrast, in ferrocene derivatives or ferrocenophanes with bridges containing more than one atom the cyclopentadienyl ligands are virtually parallel.[14] Because ring strain provides an important driving force for ring-opening polymerization, we concluded that **1a** would be an excellent candidate for polymerization studies.

When **1a** was heated in an evacuated, sealed Pyrex tube at 130 °C, the tube contents became molten and then rapidly more viscous. After 10 min the tube contents were completely immobile. Heating was then continued for an additional 50 min at the same temperature. Subsequent analysis of the tube contents (see below) indicated that the polymeric product **2a** was formed essentially quantitatively as unreacted **1a** was not detected. In addition, the polymeric product dissolved slowly but completely in THF, which indicated that no appreciable crosslinking had taken place. The poly(ferrocenylsilane) **2a** was isolated as a yellow, fibrous material by repeated precipitation from THF into hexanes.[15] The ^{1}H NMR spectrum of **2a** (in C_6D_6) showed two broad resonances for the cyclopentadienyl protons at 4.25 and 4.10 ppm and a broad resonance at 0.5 ppm assigned to the methyl groups attached to silicon in the expected 4:4:6 ratio. The ^{13}C NMR spectrum of **2a** (in C_6D_6) showed that the unusual, high-field resonance at 33.5 ppm for the cyclopentadienyl carbon attached to silicon in the strained monomer **1a** was shifted to a more conventional value of 71.9 ppm in the polymer. The ^{29}Si NMR spectrum of **2a** consists of a single, singlet resonance at −6.4 ppm which is slightly shifted to high field compared to that of the monomer **1a** (δ = −4.6 ppm). Elemental analysis data for **2a** were consistent with the assigned structure. Gel permeation chromatography indicated that **2a** possessed an approximate weight average molecular weight (M_w) of 5.2×10^5 and a number average molecular weight (M_n) of 3.4×10^5.[16] Polymer **2a** appears indefinitely stable to the atmosphere and readily forms amber, free-standing films when cast from solution using solvents such as toluene.

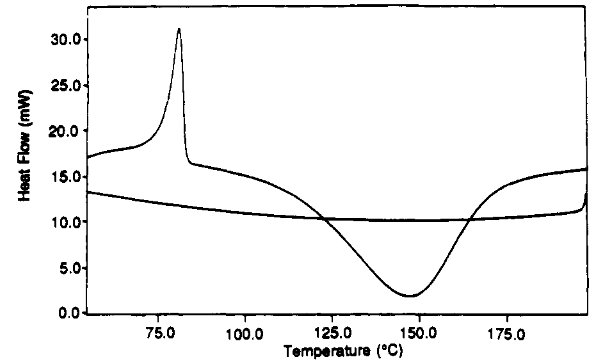
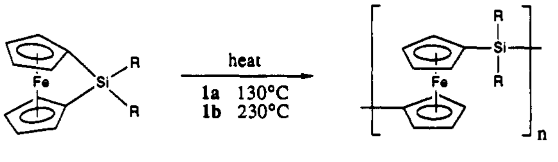


Figure 1. DSC thermogram for **1a**.

We have also found that the phenylated cycloferrocenylsilane **1b** polymerizes quantitatively at 200–235 °C, just above the melting point of the monomer (196 °C).[11] However, in this case characterization of the resulting polymer (which we presume to have the structure **2b**) was precluded by the insolubility of the material in all organic solvents tested to date.[17] However, the polymeric nature of **2b** was clearly indicated by the noticeable swelling of a sample of the material to form a gel in *N*-methylpyrrolidone.



1a R = Me
1b R = Ph

2a R = Me
2b R = Ph

We have followed the polymerization of **1a** by differential scanning calorimetry in order to obtain an estimate of the strain energy present in the monomer.[18] A DSC thermogram for **1a** is shown in Figure 1. Compound **1a** melts at 78 °C and then polymerizes exothermically at 120–170 °C. Integration of the latter exotherm for a known amount of **1a** indicated the strain energy of **1a** to be ca. 80 kJ mol^{-1}. A similar DSC for **1b** gave a strain energy of ca. 60 kJ mol^{-1}.

Because of their novel backbone structure, which comprises potentially conjugated σ, $p\pi$, and $d\pi$ units, poly(ferrocenylsilanes) such as **2a** are of considerable interest with respect to their electrical and electrochemical properties. In addition, they might be expected to exhibit high thermooxidative stability and function as ceramic precursors. We have made a preliminary investigation of the electrochemistry of **2a** by cyclic voltammetry in CH_2Cl_2 which showed the presence of two reversible oxidation processes at −0.035 and 0.121 V (in CH_2Cl_2 vs ferrocene).[19] In addition, polymer **2a** appears thermally stable to over 350 °C by thermogravimetric analysis.[20] These and other aspects of the material properties of poly(ferrocenylsilanes) together with studies aimed at extending this novel ring-opening route to both subtly and

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(9) A variety of [1]ferrocenophanes analogous to **1a** with other bridging atoms such as Ge, P, As, and transition metals in the place of silicon are also known. However, to our knowledge, no successful ring-opening polymerization of any of these species to yield high molecular weight polymers has been reported. See, for example: (a) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275. (b) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817. (c) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128. (d) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91 and references cited therein.

(10) The ring-opening polymerization of strained ferrocenylphosphazenes has also been reported. In these species the strain is manifested in the nonplanarity of the phosphazene ring, and polymerization yields polymers with ferrocene groups in the side group structure. See: Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596 and references cited therein.

(11) Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501.

(12) The X-ray crystal structure of $Fe(\eta\text{-}C_5H_4)_2(SiPh_2)$ (**1b**) has been determined, and this species contains a strained structure with a tilt angle of 19.2° between the planes of the cyclopentadienyl rings. See: Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402. We have also determined the X-ray structure of **1a**, and the corresponding tilt angle is slightly larger in this species with a value 20.8 (5)°: Tang, B. Z.; Foucher, D. A.; Lough, A.; Manners, I. Unpublished results.

(13) The stoichiometric ring-opening reactions of **1a** and related species have been used to derivatize surfaces. See, for example: Fischer, A. B.; Bruce, J. A.; McKay, D. R.; Maciel, G. E.; Wrighton, M. S. *Inorg. Chem.* **1982**, *21*, 1766.

(14) In ferrocene itself the cyclopentadienyl rings are parallel. See: Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373.

(15) For polymer **2a**: yield 90%; ^{29}Si NMR (in C_6D_6) δ −6.4 ppm; ^{13}C NMR (in C_6D_6) δ 73.6 (Cp), 71.9 (Cp, C–Si), 71.8 (Cp), −0.51 ppm ($SiMe_2$); ^{1}H NMR (in C_6D_6) δ 4.25 (br s, 4 H, Cp), 4.10 (br s, 4 H, Cp), 0.53 (s, 6 H, $SiMe_2$) ppm; GPC $M_w = 5.2 \times 10^5$, $M_n = 3.4 \times 10^5$, polydispersity = 1.5. Anal. Calcd: C, 59.5; H, 5.8. Found: C, 58.8; H, 5.6. The ^{1}H (400 MHz), $^{13}C\{^1H\}$ (100.6 MHz), and $^{29}Si\{^1H\}$ (39.7 MHz) NMR chemical shift values are relative to TMS.

(16) GPC data were recorded in THF; they are relative to polystyrene standards and are therefore considered estimates.

(17) Further characterization of **2b** by solid-state NMR and X-ray diffraction is in progress in order to elucidate possible reasons for insolubility such as the presence of crystallinity.

(18) This data was collected at a scan rate of 10 °C/min. The completion of the reaction was checked by the complete loss of the melting endotherm for the monomer on the reverse scan (see Figure 1). The strain energies were estimated from the detected thermogram by integration.

(19) Rauchfuss and Brandt have recently reported the synthesis of polyferrocenylene persulfides via the reaction of trithiaferrocenophanes with PBu_3. Two reversible oxidation waves were also detected for these polymers, and the authors proposed that the first oxidation occurs at alternating iron sites along the polymer chain. See: Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

(20) Recorded at a heating rate of 10 °C/min under N_2.

significantly different organometallic monomer structures are under active investigation in our group.

Acknowledgment. We thank the Ontario Centre for Materials Research (OCMR) Seed Funding Program and the Natural Science and Engineering Research Council of Canada (NSERC) Operating Grants Program for the financial support of this work. We also thank the University of Toronto for an open fellowship for D.A.F. We are also grateful to Mr. Nick Plavac for obtaining the ^{29}Si NMR spectra.

Synthesis of a New Small-Cage Carborane *nido*-4,5-$C_2B_6H_{10}$ and Structural Characterization of Its Conjugate Anion *nido*-4,5-$C_2B_6H_9^-$

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We have previously shown that nitrile carbons are susceptible to nucleophilic attacks by polyhedral borane anions and that these reactions can result in either CN or monocarbon cage-insertion products in high yields.[2] For example, the reaction of *arachno*-6,8-$C_2B_7H_{12}^-$ with acetonitrile was found to produce the new tricarbon carborane *nido*-6-CH_3-5,6,9-$C_3B_7H_9^-$. We have now found that the reaction of acetonitrile with the isomeric carborane anion *arachno*-4,5-$C_2B_7H_{12}^-$ proceeds in a different fashion to form the new carborane anion *nido*-4,5-$C_2B_6H_9^-$ in high yields.[3]

$$\textit{arachno}\text{-}4,5\text{-}C_2B_7H_{12}^- + CH_3CN \xrightarrow{\Delta} \textit{nido}\text{-}4,5\text{-}C_2B_6H_9^- + \tfrac{1}{3}Et_3B_3N_3H_3 \quad (1)$$

In a typical reaction, *arachno*-4,5-$C_2B_7H_{13}$[4] was deprotonated with KH in THF at −50 °C. An excess of dry CH_3CN was then added, and the solution was refluxed for ~1 day. Removal of the volatiles left a slightly air-sensitive off-white solid, K^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$), in essentially quantitative yield.[5] Fractionation of the volatile materials also gave an equivalent amount of *N*,-*N*,*N*-triethylborazine.

The *arachno*-4,5-$C_2B_7H_{12}^-$ anion, unlike the *arachno*-6,8-$C_2B_7H_{12}^-$ isomer, contains a BH_2 structural unit.[4a] Thus, the differences observed in the reactivity of these two carborane anions with acetonitrile undoubtedly arise because of the base-induced cleavage of a BH_3 group[6] from the 4,5-isomer with subsequent rearrangement of the resulting $CH_3CN{\cdot}BH_3$ adduct to 1,3,5-$Et_3B_3N_3H_3$.[7]

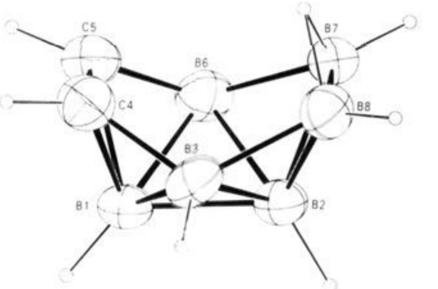
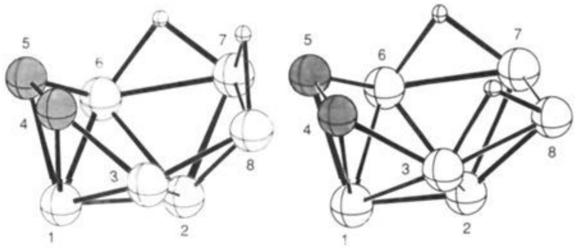


Figure 1. ORTEP drawing of the cage structure of Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$). Selected bond distances (Å): B1–B2, 1.749 (7); B1–B3, 1.794 (7); B1–C4, 1.687 (7); B1–C5, 1.686 (6); B1–B6, 1.805 (7); B2–B3, 1.792 (7); B2–B6, 1.833 (7); B2–B7, 1.715 (6); B2–B8, 1.710 (7); B3–C4, 1.566 (7); B3–B8, 1.699 (7); C4–C5, 1.400 (7); C5–B6, 1.562 (7); B6–B7, 1.709 (7); B7–B8, 1.666 (7); B7–H78, 1.219 (35); B8–H78, 1.294 (35).



1a 1b

Figure 2. Possible structures for *nido*-4,5-$C_2B_6H_{10}$: HF/3-21G optimized geometries[18-20] for the asymmetric (**1a**) and symmetric (**1b**) isomers. Terminal hydrogens have been omitted from the figure for clarity.

The new carborane *nido*-4,5-$C_2B_6H_{10}$ (**1**) was obtained by protonation of a dry CH_2Cl_2 suspension of K^+*nido*-4,5-$C_2B_6H_9^-$ with gaseous HCl at −78 °C. Unoptimized, isolated yields of >60% of this colorless air-sensitive liquid that slowly decomposes at room temperature were obtained using standard vacuum fractionation techniques at a −50 °C trap.[8]

$$K^+\textit{nido}\text{-}4,5\text{-}C_2B_6H_9^- + HCl \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} \underset{\mathbf{1}}{\textit{nido}\text{-}4,5\text{-}C_2B_6H_{10}} + KCl \quad (2)$$

The carbons apart isomer of this carborane, 4,7-$C_2B_6H_{10}$, was first isolated in 1973 by Williams[9] in <5% yields, and later by Burg[10] in 37% yields, from the reactions of *closo*-1,5-$C_2B_3H_5$ and diborane. The two $C_2B_6H_{10}$ carboranes are examples of 8-vertex, 20 skeletal electron, nido cluster systems and, on the basis of skeletal electron counting rules,[11] would be expected to adopt open-cage structures based on a tricapped trigonal prism missing one high coordination vertex. However, the only structurally characterized 8-vertex nido cluster with this geometry is *nido*-

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[1] Department of Chemistry, Korea University, Seochang 208 Jochiwon, Choongnam, Korea, 339-800.

[2] (a) Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339–2347. (b) Kang, S. O.; Sneddon, L. G. *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 195–213.

[3] Onak has also recently synthesized the isomeric *nido*-3,5-$C_2B_6H_9^-$ anion: T. Onak, personal communication.

[4] (a) Hermanek, S.; Jelinek, T.; Plesek, J.; Stibr, B.; Fusek, J. *J. Chem. Soc., Chem. Commun.* **1987**, 927–928. (b) Stibr, B.; Hermanek, S.; Plesek, J. *Inorg. Synth.* **1983**, *22*, 237–238.

[5] Spectroscopic data for K^+*nido*-4,5-$C_2B_6H_9^-$: ^{11}B NMR (160.5 MHz, THF) (ppm, *J*, Hz) 4.9 (d, B7,8, J_{BH} = 135), −15.7 (d, B2, J_{BH} = 129), −17.1 (d, B3, 6, J_{BH} = 124), −36.4 (d, B1, J_{BH} = 157, J_{BB} = 20), 2D ^{11}B–^{11}B established the connectivities B7,8–B2, B7,8–B3,6, B2–B1, B2–B3,6; ^{13}C NMR (50.3 MHz, THF-d_8) (ppm, *J*, Hz) 108.4 (br); ^{1}H NMR (500 MHz, THF-d_8) (ppm, *J*, Hz) 5.5 (s, CH), 3.9 (q, BH, J_{BH} = 128), 2.1 (q, BH, J_{BH} = 123), 0.8 (q, BH, J_{BH} = 123), −0.3 (q, BH, J_{BH} = 158), −6.3 (br, BHB); mp 92–93 °C ($Bu_4N^+C_2B_6H_9^-$).

[6] *arachno*-4,5-$C_2B_7H_{13}$ also undergoes a one-boron degradation upon reaction with aqueous sodium cyanide to give the *hypho*-$C_2B_6H_{12}^-$ anion. See: Jelinek, T.; Plesek, J.; Hermanek, S.; Stibr, B. *Main Group Met. Chem.* **1987**, *10*, 397–398.

[7] Emeleus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614–2617.

[8] Spectroscopic data for *nido*-4,5-$C_2B_6H_{10}$: ^{11}B NMR (160 MHz, CD_2Cl_2) (ppm, *J*, Hz) 7.8 (br, B7,8), −7.3 (d, B1, J_{BH} = 176), −12.4 (d, B3,6, J_{BH} = 143), −26.6 (d, B2, J_{BH} = 146); 2D ^{11}B–^{11}B NMR established the connectivities B7,8–B3,6, B7,8–B2, B1–B3,6, B1–B2, B3,6–B2; ^{1}H NMR (200 MHz, toluene-d_8, ^{11}B spin decoupled) (ppm) 6.2 (CH), 3.0 (BH), 2.6 (BH), 2.0 (BH), 1.2 (BH), −3.4 (BHB); exact mass calcd for $^{12}C_2{}^{11}B_6{}^1H_{10}$ 100.1341, found 100.1349; mp ≈ −50 °C.

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