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Ring-Opening Polymerization of [2]Ferrocenophanes with a Hydrocarbon Bridge: Synthesis of Poly(ferrocenylethylenes)

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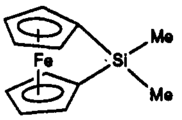
The synthesis of soluble, well-defined polymers which contain transition elements in the main chain represents a challenge of growing interest as a result of the unusual physical and chemical properties exhibited by these materials.[1,2] Ring-opening polymerization (ROP) provides a versatile route to organic[3] and, to an increasing extent, inorganic[4,5] polymers. In contrast, there are very few reports of the synthesis of transition metal-based polymers using ROP methodology.[2] We previously described that [1]ferrocenophanes with a single silicon atom in the bridge (such as **1**) and their germanium and phosphorus analogues polymerize thermally to yield high molecular weight organometallic polymers (such as **2**).[6–8] These [1]ferrocenophane monomers possess strained structures in which the cyclopentadienyl ligands are tilted by *ca.* 18–27° relative to one another.[9,10] However, our attempts to extend the ROP methodology to the [2]ferrocenophane **3**, which possesses two silicon atoms in the bridge, were unsuccessful.[7b] The lower propensity for **3** to polymerize was attributed to the lower degree of ring strain present in this species, which is reflected by the very small tilt angle of 4.19(2)°.[7b] In this paper we report that [2]ferrocenophanes with a hydrocarbon bridge, which are significantly more strained than **3** because of the smaller size of carbon relative to silicon, will undergo ROP. This provides access to polymers which, to our knowledge, represent the first examples of well-characterized poly(ferrocenylethylenes), with backbones consisting of alternating ferrocene groups and aliphatic C_2 units.[11]



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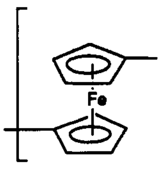

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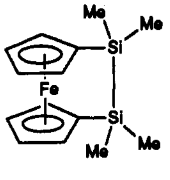

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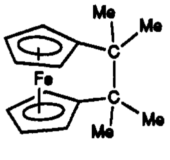

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Several examples of [2]ferrocenophanes with a hydrocarbon bridge have been synthesized to date.[12] The reported[12a] value for the tilt angle in the methylated compound **4** of 23°, which is even greater than for the polymerizable [1]ferrocenophane **1**, initially prompted us to investigate the polymerization behavior of selected examples of these species. Compound **5a** was prepared in moderate yield (*ca.* 30%) as an orange-red, moisture-sensitive, crystalline material by the previously reported method involving the reaction of the dilithium salt $Li_2[C_5H_4CH_2]_2$ with $FeCl_2$ in THF.[12b,13] When **5a** was heated at 300 °C in an evacuated,

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(1) See, for example: (a) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (b) Wright, M. E.; Sigman, M. S. *Macromolecules* **1991**, *25*, 6055. (c) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (d) Tenhaeff, S. C.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1459. (e) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allcock, H. R., Eds.; ACS Symp. Ser. 360; American Chemical Society: Washington, DC, 1988. (f) Manners, I. *J. Chem. Soc. Annu. Rep. Prog. Chem. A* **1991**, 77. (g) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (h) Struge, K. C.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D. *Organometallics* **1991**, *11*, 3056. (i) Sheats, J. E.; Carraher, C. E.; Pittman, C. U. *Metal Containing Polymer Systems*; Plenum: New York, 1985. (j) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703. (k) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709. (l) Gonsalves, K.; Zhan-ru, L.; Rausch, M. V. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (m) Dembek, A. A.; Fagan, P. J.; Marsi, M. *Macromolecules* **1993**, *26*, 2992.

(2) (a) Roesky, H. W.; Lucke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (b) Roesky, H. W.; Lucke, M. *J. Chem. Soc., Chem. Commun.* **1989**, 748. (c) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

(3) (a) *Ring Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984. (b) *Ring Opening Polymerization*; McGrath, J. E.; Ed.; ACS Symp. Ser. 286; American Chemical Society: Washington, DC, 1985.

(4) See, for example: (a) Sargeant, S. J.; Zhou, S. Q.; Manuel, G.; Weber, W. P. *Macromolecules* **1992**, *25*, 2832. (b) West, R.; Hayase, S.; Iwahara, T. *J. Inorg. Organomet. Polym.* **1991**, *4*, 545. (c) Anhaus, J. T.; Clegg, W.; Collingwood, S. P.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1720. (d) Manners, I.; Renner, G.; Allcock, H. R.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (e) Ngo, D. C.; Rutt, S. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1991**, *113*, 5075. (f) Wu, H. J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564. (g) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596. (h) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046. (i) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Engelwood Cliffs, NJ, 1992.

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(8) (a) After the paper listed as ref 6 was received by *J. Am. Chem. Soc.*, Pannell and co-workers made an independent report of the polymerization of **1** at the XXV Silicon Symposium, Los Angeles, CA, April 3–4, 1992: Pannell, K., private communication. (b) Seyferth and co-workers have synthesized polymers of formula $[Fe(\eta\text{-}C_5H_4)_2(PPh)]_n$ using condensation routes, see: Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P.; Martin, S. *Organometallics* **1982**, *1*, 1283.

(9) (a) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402. (b) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91. (c) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275. (d) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128. (e) Fischer, A. B.; Bruce, J. A.; McKay, D. R.; Maciel, G. E.; Wrighton, M. S. *Inorg. Chem.* **1982**, *21*, 1766. (f) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345.

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

(11) Poly(ferrocenylmethylenes), $[Fe(\eta\text{-}C_5H_4)_2CH_2]_n$, have been previously prepared via condensation routes. These materials are generally of low molecular weight, and a mixture of 1,2-, 1,3-, and 1,1′-disubstituted ferrocene units are present in the main chain. See, for example: Neuse, E. W.; Khan, F. B. D. *Macromolecules* **1986**, *19*, 269. To our knowledge, no well-characterized poly(ferrocenylethylenes) of substantial molecular weight have been reported, although oligomers as well as cyclics are formed in the synthesis of **5a**, See: Luttringhaus, A.; Kullick, W. *Angew. Chem.* **1958**, *70*, 438 and ref 12b.

(12) (a) Burke Laing, M.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *19*, 373. (b) Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1971**, *27*, 4343. (c) Yasufuku, K.; Aoki, K.; Yamzaki, H. *Inorg. Chem.* **1977**, *16*, 624.

(13) We have also determined the X-ray structure of **5a**, and the corresponding tilt angle, 21.6(5)°, is slightly less than in **4**: Rengel, H.; Nelson, J. M.; Lough, A.; Manners, I., unpublished results.

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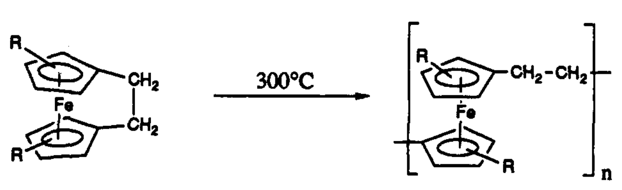

5a R = H

5b R = Me

6a R = H

6b R = Me

sealed Pyrex tube, the reaction mixture became molten and then rapidly more viscous and, after 1 h, completely immobile. Subsequent analysis of the products was precluded by the insolubility of virtually all of the material in all organic solvents tested to date. However, the probable polymeric nature of the insoluble product **6a** was suggested by its filmlike appearance and the identification of the cyclic oligomers $[Fe(\eta^5\text{-}C_5H_4)_2(CH_2)_2]_x$ (x = 2–5) in CH_2Cl_2-soluble extracts of the material by mass spectrometry.[14] In order to prepare a soluble polymeric product, the [2]ferrocenophane **5b**, which consisted of a complex mixture of isomers, was synthesized via reaction of the dilithiated salt $Li_2[MeC_5H_3CH_2]_2$ with $FeCl_2$.[15] When **5b** was heated under the same conditions as **5a**, a rapid increase in viscosity was also detected. However, in this case the polymeric product dissolved slowly but completely in THF, which indicated that no appreciable cross-linking had taken place. The poly(ferrocenylethylene) **6b** was isolated as a mustard colored, fibrous material by repeated precipitation from THF into methanol.[16,17] The ^1H NMR spectrum of **6b** (in C_6D_6) showed broad resonances for the cyclopentadienyl protons, the CH_2CH_2 protons, and the methyl groups attached to the cyclopentadienyl rings at 3.6–4.1, 2.3–2.8, and 1.6–2.1 ppm, respectively. The ratio of these three resonances determined by integration was 6:4:6, as expected. The ^{13}C NMR spectrum for **6b** was complex due to the structural isomerism involving the methyl substituents attached to the cyclopentadienyl rings but was also consistent with the assigned structure.[16] Elemental analysis provided additional evidence for the structure proposed.[17] Gel permeation chromatography (GPC) indicated that **6b** possessed a bimodal molecular weight distribution. The first fraction possessed an approximate weight average molecular weight (M_w) of 8.1×10^4 and a number average molecular weight (M_n) of 6.6×10^4, while the second, essentially oligomeric fraction was characterized by values of $M_w = 4.8 \times 10^3$ and $M_n = 3.5 \times 10^3$.[16]

The ROP of [2]ferrocenophanes provides access to macromolecules such as **6b**, in which the ferrocene units are further separated from one another than for polymers derived from [1]-ferrocenophanes such as the poly(ferrocenylsilane) **2**. For the latter, electrochemical evidence for substantial cooperative interactions between the iron centers has been provided by cyclic voltammetry, which shows that these materials possess two reversible oxidation waves.[6,7e,h,18] In contrast, a preliminary study of the electrochemistry of **6b** showed the presence of only a single reversible oxidation wave (E^0 = –0.275 V in CH_2Cl_2 vs ferrocene). This indicates that the ferrocene groups interact to a lesser extent in **6b** than in **2**.[18] Based on these results we anticipate that detailed studies of the properties of poly(ferrocenylethylenes) such as **6b** and comparisons with related materials (such as **2**)[6,7] will provide an interesting contribution to the understanding of structure–property relations for metal-containing polymers.

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(14) MS (EI, 70 eV) m/e: 1060 (x = 5, 18%), 848 (x = 4, 15%), 636 (x = 3, 32%), 424 (x = 2, 100%), 212 (x = 1, 90%).

(15) $Li_2[MeC_5H_3CH_2]_2$ was prepared from $Na[C_5H_4Me]$ and 1,2-dibromoethane followed by treatment with BuLi in an analogous way to the non-methylated analog (see ref 12b). For **5b**: MS (EI, 70 eV) m/e 240 (M^+, 100); ^1H NMR (200 MHz, C_6D_6) δ 4.4–4.7 (br m, 3H, Cp), 3.7–4.1 (br m, 3H, Cp), 2.5–2.7 (s, 4H, CH_2CH_2), 1.7–2.2 (s, 6H, Me); ^{13}C NMR (100.5 MHz, C_6D_6) δ 85.6–91.5 (ipso, Cp), 67.0–80.7 (α,β Cp), 32.3–34.8 (CH_2CH_2), 13.9–15.5 (Me). Because of the existence of different isomers, the NMR spectra of **5b** consisted of numerous peaks in the regions indicated.

(16) For polymer **6b**: ^1H NMR (200 MHz, C_6D_6) δ 3.6–4.1 (br, 6H, Cp), 2.3–2.8 (br, 4H, CH_2CH_2), 1.6–2.1 (br, 6H, Me); ^{13}C NMR (100.5 MHz, C_6D_6) δ 83.3–88.5 (ipso, Cp), 67.0–72.5 (α,β Cp), 31.4–33.4 (CH_2CH_2), 13.9–15.5 (Me). Because of the existence of different isomers, the ^{13}C NMR spectra of **6b** consisted of numerous peaks in the regions indicated. The resonances for the different isomers were unresolved in the ^1H NMR spectrum. GPC: for the first fraction, $M_w = 8.1 \times 10^4$, $M_n = 6.6 \times 10^4$, polydispersity = 1.2. For second fraction, $M_w = 4.8 \times 10^3$, $M_n = 3.5 \times 10^3$, polydispersity = 1.4. GPC data were recorded in THF, relative to polystyrene standards, and are therefore considered estimates.

(17) Anal. Calcd for **6b**: C, 70.0; H, 6.7. Found: C, 68.7; H, 6.5. The slightly low value for the carbon analysis is attributed to incomplete combustion due to ceramic formation. Similar problems were encountered with poly(ferrocenylsilanes) (see refs 7a,c).

(18) (a) Rauchfuss and Brandt have recently reported that poly(ferrocenylene persulfides), $[Fe(\eta^5\text{-}C_5H_3Bu)_2S_2]_n$, which were synthesized via the reaction of trithiaferrocenophanes with PBu_3, possess two reversible oxidation waves. The authors proposed that the first oxidation occurs at alternating iron sites along the polymer chain. See ref 2c. (b) The molecular species $FcSiMe_2Fc$ ($Fc = Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$) shows two one-electron oxidation waves, which indicates that oxidation of one ferrocene unit influences the oxidizability of the other. In contrast, for $Fc(CH_2)_2Fc$, where the ferrocene groups are further apart, only one wave is detected, which is indicative of a negligable interaction. See: Dong, T. Y.; Hwang, M. Y.; Wen, Y.; Hwang, W. S. *J. Organomet. Chem.* **1990**, *391*, 377 and references cited therein.