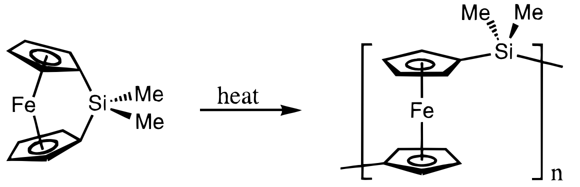
Spirocyclic [1]Ferrocenophanes: Novel Cross-Linking Agents for Ring-Opened Poly(ferrocenes)

Mark J. MacLachlan, Alan J. Lough, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 3H6, Ontario, Canada

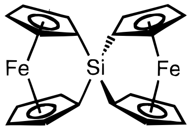
Received August 20, 1996

The incorporation of transition metals into the main chain of polymers is attracting attention as a means of generating materials with unusual and useful chemical and physical properties.[1,2] Ferrocene-based polymers are of considerable interest in this regard but, until recently, high molecular weight examples have been very rare.[3−5] We have previously described the synthesis of high molecular weight linear poly(ferrocenes) such as the poly(ferrocenylsilane) **2** ($M_n > 10^5$) via the thermal ring-opening polymerization of strained metallocenophane monomers such as **1**.[5] Materials such as **2** have attracted recent attention as a result of their intriguing physical properties.[6−8] As the cross-linking of polymers is necessary for the improvement of mechanical properties, thermal stability, and ceramic yields and is crucial for many applications (e.g. for poly(ferrocenes), the formation of redox-active gels[9]), a convenient means of cross-linking materials such as **2** is very desirable. In this paper we report that difunctional spirocyclic [1]ferrocenophanes function as convenient cross-linking agents for polymers such as **2** via ring-opening copolymerization reactions.

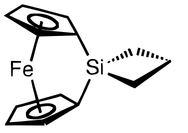


1 **2**

Very few studies of spirocyclic [1]ferrocenophanes have been previously reported in the literature.[10−13] We prepared the spirocyclic [1]silaferrocenophane **3** by a modification of the original method reported by Osborne and Whiteley[12] which involved the reaction of 2 equiv of dilithioferrocene−tetramethylethylenediamine (fcLi$_2$·TMEDA) with tetrachlorosilane.[14] Our yield of this potential cross-linking agent was ca. 56%, a considerable improvement over that reported previously (7 and 17%).[12,13] We also prepared the novel red crystalline spirocyclic carbosilane−[1]ferrocenophane **4** in 71% yield via the reaction of fcLi$_2$·TMEDA with an excess of the dichlorosilacyclobutane Cl$_2$Si(CH$_2$)$_3$.[14]



3



4

Both **3** and **4** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectrometry which afforded data consistent with the previously assigned structure of **3**[15] and that for the new compound **4**.[16] Because of the complete absence of any crystallographic data on spirocyclic [1]ferrocenophanes, single-crystal X-ray diffraction studies were perfomed on each compound. The molecular structures of **3** and **4** are shown in Figure 1.[17,18] The molecules of each compound are highly strained, as indicated by the tilt angles between the planes of the cyclopentadienyl (Cp) ligands of 19.4(2)° (in **3**) and 20.61(8)°(in **4**) which are similar to the value in **1** (20.8(5)°).[6] Significant structural distortions from planarity are also detected at the ipso carbon atoms of the Cp ligands bonded to silicon where the angles between the planes of the Cp ligands and the C(Cp)−Si bonds are 39.4−39.7° and 37.6° in **3** and **4**, respectively. The carbosilane ring in **4** is also clearly very strained with skeletal C−Si−C, C−C−Si, and C−C−C bond angles of 81.10(8), 86.4(1), and 102.6(1)°, respectively. Interestingly, the puckering of this ring, 20.6(2)°, is significantly less than that of the silacyclobutane derivative of bis(benzene)vanadium (23°)[19] and 4-sila-3,3-spiroheptane, (CH$_2$)$_3$Si(CH$_2$)$_3$, (30(2)° by electron diffraction[20]).

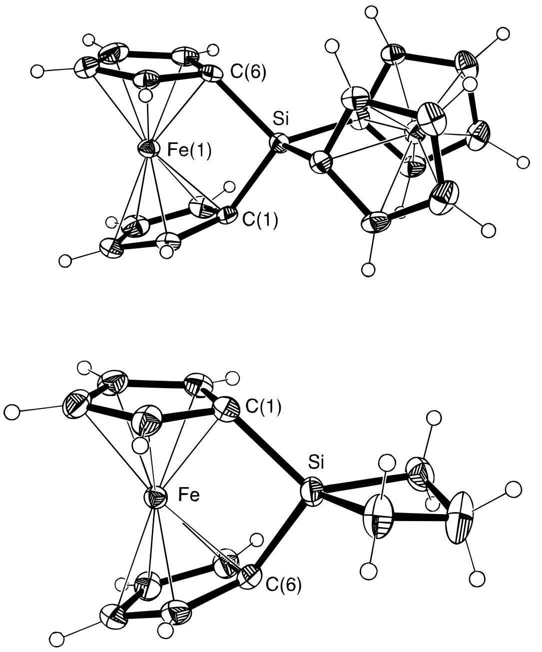


Figure 1. (Top) 50% probability thermal ellipsoid drawing of **3**. Selected interatomic distances (Å) and angles (deg): Si−C1 = 1.874(3), Si−C6 = 1.871(3), Fe1−Si = 2.6572(5), C1−Si−C6 = 98.5(1). (Bottom) 50% probability thermal ellipsoid drawing of **4**. Selected interatomic distances (Å) and angles (deg): Si−C1 = 1.884(2), Si−C6 = 1.883(2), Fe−Si = 2.7113(5), C1−Si−C6 = 95.83(6).

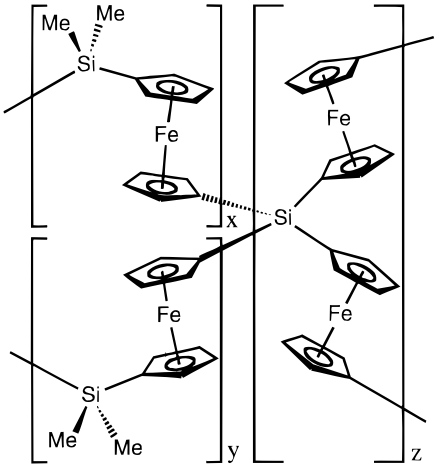
In order to probe the ROP behavior of **3** and **4** each compound was initially studied by differential scanning calorimetry (DSC). A DSC thermogram of **3** showed no melt endotherm, but two exothermic transitions were detected with onsets at 175 and 270 °C, respectively. A DSC thermogram of **4** displayed a melt at 92 °C followed immediately by an exotherm with two peaks. In contrast, a DSC thermogram of **1** shows a melt and a single ROP exotherm (onset = 130 °C). The presence of two exotherms for **3** and **4** suggested that the two rings present in each compound may open sequentially.

When **3** was heated in a sealed evacuated Pyrex tube at 320 °C for 30 min, the tube contents changed color slightly from orange-red to orange-brown. The resulting material was completely insoluble in THF and did not swell, which is consistent with the formation of a highly cross-linked polymer. Furthermore, the material formed

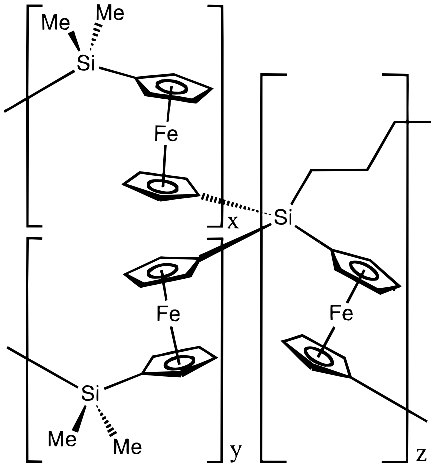
S0024-9297(96)01260-0 CCC: $12.00

was amorphous by wide-angle X-ray scattering (WAXS). Compound **4** became viscous then rapidly immobile when heated at 100−120 °C for 50 min. Again, the polymeric product was insoluble in THF and did not swell.

Despite the substantial temperature difference between the ROP onset temperature for **3** (270 °C) and **1** (130−150 °C), the two monomers were found to successfully copolymerize. Thus, when **1** and ≤15 mol % of **3** were heated at 100 °C, a homogeneous solution of **3** in the melt of **1** was formed. The monomers were then polymerized at 300−320 °C for 2 h, forming red-brown polymers **5** that were insoluble in THF but were observed to readily swell, forming orange gels. As **4** undergoes ROP at a similar temperature to **1**, this species appeared ideal for controlled thermal copolymerization experiments. By using 2, 5, 10, and 15 mol % of **4** polymers **6a**−**6d** were prepared at 140−180 °C. After stirring at room temperature in THF under N_2 for 16 h, the resulting insoluble polymers were recovered by suction filtration in air. The remaining solvent was removed under vacuum to afford orange-red powders. These materials were characterized by DSC, and their cross-linked nature was probed by swelling experiments. The homopolymer **2** possesses a T_g at 33 °C, and annealed samples, which are crystalline by WAXS, show a T_m at 122 °C.[6] In contrast, DSC of **6a**−**6d** showed no evidence for melt transitions. Polymers **6a** and **6b** showed a broad T_g at 38−40 °C, and no T_g was observed for polymers **6c,d**. This behavior is consistent with cross-linked structures for **6a**−**6d** in which ordered interchain packing is disrupted. Swelling experiments were performed in THF (Table 1). The results indicated that the cross-link density could be successfully controlled by altering the mole ratio of **1** and the spirocyclic cross-linking agent.



5 (x+y>>z)



6 (x+y>>z)

Table 1. Swelling Experiments for Samples of the Thermally-Generated Cross-Linked Poly(ferrocenylsilanes) 6a−6d[a]

polymer	mol % of **4**	dry mass, mg	wet mass	% mass increase
6a	2	36	130	260
6b	5	12	36	200
6c	10	43	116	170
6d	15	12	17	40

[a] THF was chosen as a solvent for swellability measurement since the homopolymer **2** is very soluble in this solvent. Small pieces of **6a**−**6d** were weighed and immersed in THF under N_2 for 48 h. The swollen pieces of polymer were then removed from the THF, the surface solvent was removed, and the samples were reweighed.

We have also carried out preliminary experiments on the transition metal catalyzed copolymerization of **1** with **3** or **4** at ambient and elevated (60 °C) temperatures. However, no reaction was detected when **3** was treated with small quantitities of $PtCl_2$ in CH_2Cl_2 or C_6D_6 or Karstedt's catalyst in C_6D_6, conditions under which ROP of **1** to afford **2** is readily observed.[21,22] Consistent with this, reaction of a mixture of **1** and **3** with either Pt catalyst afforded a polymer product which was soluble in THF and was indistinguishable from **2** spectroscopically. Compound **4**, on the other hand, underwent homopolymerization with catalytic quantities of Pt(0), in the form of either Karstedt's catalyst or $Pt(1,5\text{-}COD)_2$, to give yellow, insoluble material. In addition, when ca. 10 mol % **4** was combined with **1** and a catalytic amount of Karstedt's catalyst in toluene, gelation was observed after about 30 min. The physical properties of this cross-linked polymer are under investigation.

In summary, we have shown that spirocyclic [1]-ferrocenophanes function as convenient cross-linking agents for poly(ferrocenes) via thermal ring-opening copolymerization reactions. The use of **4** in transition metal catalyzed copolymerizations also appears promising. Further studies of these reactions and products (including the use of small amounts of **3** and **4** to afford soluble, branched poly(ferrocene) materials) are in progress.

Acknowledgment. M.J.M. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Graduate Fellowship. I.M. thanks the Ontario Centre of Materials Research (OCMR) for funding and the Alfred P. Sloan Foundation for a Research Fellowship (1994−1998). M.J.M. thanks T. Peckham for assistance with initial cross-linking studies and R. Rulkens for helpful discussions.

Supporting Information Available: Details of the synthesis of **6a**−**d** and general procedures (3 pages) and tables of crystallographic details for **3** and **4** (15 pages); tables of *hkl* values for **3** and **4** (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent examples of transition metal based polymeric materials, see, for example: (a) Dembek, A. A.; Fagan, P.

J.; Marsi, M. *Macromolecules* **1993**, *26*, 2992. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (c) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596. (d) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055. (e) Roesky, H. W.; Lücke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (f) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (g) Tenhaeff, S C.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1459. (h) Sturge, K. C.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D. *Organometallics* **1992**, *11*, 3056. (i) Bayer, R.; Pöhlmann, T.; Nuyken, O. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 359. (j) Altman, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (k) Rosenblum, M.; Nugent, H. M.; Jang, K. -S.; Labes, M. M.; Cahalane, W.; Klemarczyk, P.; Reiff, W. M. *Macromolecules* **1995**, *28*, 6330. (l) Patterson, W. J.; McManus, S. P.; Pittman, C. U. *J. Polym. Sci. A* **1974**, *12*, 837. (m) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (n) Gonsalves, K.; Zhanru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (o) Morán, M.; Pascual, M. C.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 811. (p) Chen, H.; Archer, R. D. *Macromolecules* **1995,** *28*, 1609. (q) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713.

(2) (a) Manners, I. *Chem. Br.* **1996**, *32*, 46 (b) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

(3) (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Galloway, C. P.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1319. (c) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (d) Compton, D. L.; Brandt, P. F.; Rauchfuss, T. B.; Rosenbaum, D. F.; Zukoski, C. F. *Chem. Mater.* **1995**, *7*, 2342.

(4) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848.

(5) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(6) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131.

(7) (a) Foucher, D. A.; Ziembinski, R.; Tang, B. Z.; Macdonald, P. M.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878. (b) Foucher, D. A.; Ziembinski, R.; Petersen, R.; Pudelski, J. K.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992. (c) Pudelski, J. K.; Rulkens, R.; Foucher, D. A.; Lough, A. J.; Macdonald, P. M.; Manners, I. *Macromolecules* **1995**, *28*, 7301. (d) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Macdonald, P. M.; Manners, I.; Barlow, S.; O'Hare, D. *Macromolecules* **1996**, *29*, 1894.

(8) (a) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389. (b) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (c) Barlow, S.; Rohl, A. L.; Shi, S.; Freeman, C. M.; O'Hare D. *J. Am. Chem. Soc.* **1996**, *118*, 7578. (d) Hmyene, M.; Yassar, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564.

(9) Tatsuma, T.; Takada, K.; Matsui, H.; Oyama, N. *Macromolecules* **1994**, *27*, 6687.

(10) Blake, A. J.; Mayers, F. R.; Osborne, A. G.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2379.

(11) Mayers, F. R.; Osborne, A. G.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1990**, 3419.

(12) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

(13) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345.

(14) Complete experimental details are given in the Supporting Information.

(15) **3:** ^{13}C NMR (C_6D_6) $\delta = 78.3$ (Cp), 75.5 (Cp), 31.1 (*ipso*-Cp) ppm; ^{1}H NMR (C_6D_6) $\delta = 4.47$ (s, 16H, Cp) ppm; ^{29}Si NMR (C_6D_6) $\delta = -16.6$ ppm; MS (EI, 70 eV) m/z (%) = 397 (41, $M^+ + 1$), 396 (100, M^+); cyclic voltammetry (5×10^{-3} M in CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$) 0.14 (**3**/**3**$^+$, rev), 0.51 (**3**$^+$/**3**$^{2+}$, irrev) V vs FcH.

(16) **4:** ^{13}C NMR (C_6D_6) $\delta = 78.0$ (Cp), 74.7 (Cp), 31.9 (*ipso*-Cp), 18.3 ($CH_2CH_2CH_2$), 16.0 ($SiCH_2$) ppm; ^{1}H NMR (C_6D_6) $\delta = 4.39$ (s, 4H, Cp), 4.04 (s, 4H, Cp), 2.38 (qt, $^{3}J_{HH} = 8.2$ Hz, 2H, $CH_2CH_2CH_2$), 1.44 (t, $^{3}J_{HH} = 8.2$ Hz, 4H, $SiCH_2$) ppm; ^{29}Si NMR (C_6D_6) $\delta = 3.6$ ppm; MS (EI, 70 eV) m/z (%) = 255 (34, $M^+ + 1$), 254 (100, M^+), 226 (62, $M^+ - C_2H_4$), 148 (38); mp 92 °C; cyclic voltammetry (5×10^{-3} M in CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$): 0.11 (**4**/**4**$^+$, rev) V vs FcH.

(17) Crystal data for **3**: $a = 20.771(2)$ Å, $b = 10.304(1)$ Å, $c = 7.424(1)$ Å, $\beta = 100.99°$, $V = 1559.8(3)$ Å^3, space group $C2/c$ (monoclinic), $Z = 4$, mol wt = 396.12 for $C_{20}H_{16}Fe_2Si$, $T = 168(2)$ K, $R = 0.0317$, $R_w = 0.0677$, GOF = 0.838.

(18) Crystal data for **4**: $a = 10.603(2)$ Å, $b = 6.085(1)$ Å, $c = 17.210(2)$ Å, $\beta = 98.60°$, $V = 1097.9(3)$ Å^3, space group $P2_1/n$ (monoclinic), $Z = 4$, mol wt = 254.18 for $C_{13}H_{14}FeSi$, $T = 168(2)$ K, $R = 0.0266$, $R_w = 0.0692$, GOF = 1.012.

(19) Elschenbroich, C.; Bretschneider-Hurley, A.; Hurley, J.; Behrendt, A.; Massa, W.; Wocadlo, S.; Reijerse, E. *Inorg. Chem.* **1995**, *34*, 743.

(20) Mastryukov, V. S.; Dorefeeva, O. V.; Vilkov, L. V.; Cyvin, S. J.; Cyvin, B. N. *J. Struct. Chem. (Engl. Transl.)* **1975**, *16*, 438.

(21) Ni, Y.; Rulkens, R.; Pudelski, J. K.; Manners, I. *Macromol. Rapid Commun.* **1995**, *16*, 637−641.

(22) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263.

MA961260X