# Thermal Ring-Opening Polymerization (ROP) of Strained, Ring-Tilted, Phosphorus-Bridged [1]Ferrocenophanes: Synthesis of Poly(ferrocenylphosphines) and **Poly(ferrocenylphosphine sulfides)**

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A series of phosphorus(III)-bridged [1]ferrocenophanes  $Fe[(\eta-C_5H_3R)(\eta-C_5H_3R')]PX$  (X = Ph, R = R' = H (3); X = Cl, R = R' = H (4); X = Ph, R = H,  $R' = {}^{n}Bu$  (5); X = Ph, R = R'= SiMe<sub>3</sub> (6)) have been synthesized via the reaction of  $Fe[(\eta - C_5H_3RLi)(\eta - C_5H_3R'Li)]\cdot nTMEDA$ with  $PXCl_2$  (X = Cl, Ph). The reaction of **6** with an excess of elemental sulfur resulted in the quantitative formation of the phosphorus(V)-bridged species  $Fe[n-C_5H_3SiMe_3]_2P(S)Ph$ (7). The new compounds 4-7 were characterized by multinuclear NMR, by mass spectrometry and, in the cases of 4, 6, and 7, by single-crystal X-ray diffraction and elemental analysis. Ring-tilt angles ( $\alpha$ ) for **4** and **6** were found to be typical of phosphorus(III)-bridged [1]ferrocenophanes (4, 27.0(6)°; 6, 27.5(6)°) whereas in the case of the phosphorus(V)-bridged species 7 the tilt angle was slightly less ( $\alpha = 25.3(3)^\circ$ ). The thermal ring-opening polymerization of 3, 5, and 6 at 120-250 °C yielded the poly(ferrocenylphosphines) 8-10, respectively. These materials were characterized by multinuclear NMR and by elemental analysis. The molecular weight of the trimethylsilyl-substituted polymer 10 was determined by GPC in THF versus polystyrene standards to be  $M_{\rm w} = 66\ 000,\ {\rm PDI} = 1.98$ , whereas 8 and 9 failed to elute from the GPC column. The phosphorus(V)-bridged species 7 also underwent thermal ring-opening polymerization to yield the poly(ferrocenylphosphine sulfide) 13 which was analyzed by GPC ( $M_w = 22\ 000$ , PDI = 1.24); thermally-induced elimination of  $S(SiMe_3)_2$  from the ring-opened polymer was identified as a side reaction. The macromolecular reactions of 8-10 with elemental sulfur yielded the poly(ferrocenylphosphine sulfides) 11–13. These were structurally characterized by multinuclear NMR and elemental analysis and their molecular distributions were analyzed by GPC ( $M_{\rm w} = 18\ 000-65\ 000$ , PDI = 1.5 - 2.3).

# Introduction

Polymers with transition elements in the main chain structure are of current interest as a result of their novel physical and catalytic properties.<sup>1-5</sup> However, the synthesis of well-defined, high molecular weight, and soluble examples of these materials has posed a considerable synthetic challenge. With this in mind, we recently reported the discovery that strained ring-tilted [1]ferrocenophanes (e.g. 1) undergo thermal ring-opening polymerization (ROP) to yield high molecular weight poly(ferrocenylsilanes) (e.g. 2).<sup>6</sup> Subsequent studies have focused on the interesting properties of these materials. $^{2,5,7-10}$  We have also recently described that, in the presence of anionic initiators in solution, siliconbridged [1]ferrocenophanes yield linear oligo(ferrocenylsilanes). Moreover, in the presence of small quantities



possible.<sup>11</sup> This allows for the preparation of poly-(ferrocenylsilanes) with controlled molecular weights and end group structures and also permits access to novel block copolymers.<sup>11</sup> Recently, transition metalcatalyzed ROP of silicon-bridged [1]ferrocenophanes in solution at ambient temperatures has also been achieved.12

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We have also described the extension of the ROP approach to germanium-bridged [1]ferrocenophanes.<sup>13,14</sup> ROP of these species yields poly(ferrocenylgermanes) which have been shown to possess similar electrochemical and thermal transition behavior to their silicon analogues.<sup>2,15</sup> Strained, ring-tilted hydrocarbon-bridged [2]metallocenophanes also undergo thermally-induced ROP to yield new classes of organometallic polymers,  $poly(metallocenylethylenes).^{16}$ 

As part of our efforts to further extend this ROP methodology, we have studied the polymerization behavior of phosphorus-bridged [1]ferrocenophanes.<sup>17</sup> Polymers derived from these species are of interest as they possess phosphorus(III) centers which could function as coordination sites for the complexation of transition metals and as crosslinking sites through derivatization.<sup>18,19</sup> In this paper we report our studies of the thermal ring-opening polymerization behavior of [1]ferrocenophanes which possess either a phosphorus(III) or phosphorus(V) unit in the bridge.

## **Experimental Section**

Equipment. Reactions and manipulations were carried out strictly under an atmosphere of prepurified nitrogen (Canox) using either Schlenk techniques or an inert-atmosphere glovebox (VAC Atmospheres) where required. Solvents were all dried and distilled using standard methods, and all reactions were carried out with solvents that had been stored under an inert  $(N_2)$  atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using either a Varian XL 400 (400 and 100.5 MHz, respectively) or a Varian Gemini 200 spectrometer (200 and 50.3 MHz, respectively) and were referenced to SiMe<sub>4</sub> (TMS). <sup>31</sup>P NMR spectra were obtained using a Gemini 300 spectrometer (121.5 MHz) and were referenced externally to  $85\% \text{ H}_3\text{PO}_4$  in D<sub>2</sub>O. <sup>29</sup>Si NMR spectra were obtained on a Varian XL 400 spectrometer (79.4 MHz) using either a normal or a DEPT pulse sequence and were referenced externally to TMS. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer using an 70 eV electron impact ionization source. Molecular weights were determined by GPC (Waters 410 refractometer, Waters 510 HPLC pump, Waters 710 data module) on the basis of a comparison to polystyrene standards using a two column system in THF with 0.1% ["Bu<sub>4</sub>N]Br (w/ w) with Waters Ultrastyragel columns  $(1 \times 10^5, 1 \times 10^3)$ .

Materials. All reagents purchased from Aldrich were used as received (ferrocene, butylferrocene, 1.6 M butyllithium in hexanes, dichloro(phenyl)phosphine, TMEDA, S(SiMe<sub>3</sub>)<sub>2</sub>, and Grignard reagents). Inert-atmosphere nitrogen was supplied by Canox as prepurified N<sub>2</sub>. Trichlorophosphine was supplied by BDH Inc. and was used without further purification. Elemental sulfur was supplied by BDH and was sublimed

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before use. 1,1'-Bis(trimethylsilyl)ferrocene was synthesized using a literature procedure.<sup>20</sup>

Synthesis of  $Fe(\eta - C_5H_4)_2PPh$  (3). This procedure was adapted from that previously described by Seyferth and Withers.<sup>19</sup>

 $Fe[(\eta-C_5H_4)Li]_2 \cdot nTMEDA$  (2.33 g, 7.34 mmol) was slurried in 150 mL of hexanes with stirring and was cooled to -78 °C. To this mixture was added a 40 mL solution of PhPCl<sub>2</sub> (1.0 mL, 7.36 mmol) in hexanes dropwise by cannula. Stirring was continued as the reaction solution was slowly warmed to ca. 15 °C over which period (2.5 h) the color had become dark red. The resulting reaction solution was then filtered, the solvent was removed from the filtrate in vacuo, and the residue was dried overnight under high vacuum. The resulting solid was extracted with hexanes until the extracts were colorless. The washings were combined and concentrated by the removal of solvent under vacuum. The solution was cooled to -50 °C which resulted in the formation of red crystals. Yield of 3: 1.0 g (48%). These dark red crystals were identified as 3 by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy and by MS which afforded data in excellent agreement with those found in the literature.19

Data for 3: <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 13.1 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 7.7 - 7.5$  (m, o-Ph, 2H), 7.3-7.0 (m, p,m-Ph, 3H), 4.6-4.5 (m, Cp, 2H), 4.4-4.3 (m, Cp, 2H), 4.3-4.1 (m, Cp, 4H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 18.6 (d, ipso Cp,  $J_{PC}$  = 54.5 Hz), 78.2 (s, Cp), 77.3 (d, Cp,  $J_{PC}$  = 33.6 Hz), 77.6 (d, Cp,  $J_{PC}$  = 7.6 Hz), 77.2 (d,  $J_{\rm PC} = 8.0$  Hz), 137.9 (d, ipso Ph,  $J_{\rm PC} = 10.9$  Hz), 130.7 (d, o-Ph,  ${}^{2}J_{PC} = 13.9 \text{ Hz}$ , 128.8 (d, *m*-Ph,  ${}^{3}J_{PC} = 3.4 \text{ Hz}$ ), 127.7 (s, *p*-Ph) ppm.

Synthesis of  $Fe(\eta - C_5H_4)_2PCl(4)$ .  $Fe[\eta - C_5H_4Li]_2 \cdot nTMEDA$ (11.34 g, 36.1 mmol) was slurried in 700 mL of freshly distilled hexanes with stirring, and the suspension was cooled to -78°C. To this mixture was added a solution of PCl<sub>3</sub> (4.5 mL, 40 mmol) in 100 mL of hexanes dropwise by cannula. The resulting mixture was allowed to slowly warm (to ca. 15 °C) at which point it was filtered. The dark red filtrate was immediately cooled to -78 °C and stored at this temperature overnight. This resulted in the formation of a fine red powder which was decanted and dried under vacuum and found to be highly reactive to both air and moisture. This red powder which was found to decompose rapidly in solution (ca. 30 min) at room temperature was subsequently identified as 4 by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR and MS. Yield: 4.67 g (52%). Brick-red colored crystals of 4 suitable for a single-crystal X-ray diffraction study were grown from hexanes at -78 °C over several days.

Data for 4: <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 86.9 ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 19.2 \text{ ppm}$  (d, ipso,  ${}^{1}J_{PC} = 77.9 \text{ Hz}$ ), 72.2 (d, Cp, 37.3 Hz), 75.7 (d, Cp, 3.7 Hz), 77.8 ppm (d, Cp, 7.4 Hz), 79.4 ppm (s, Cp); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 4.0 (m, Cp, 4H), 4.2 (m, Cp, 2H), 4.6 (m, Cp, 2H) ppm; MS (EI, 70 eV) m/z (%) = 250 (M<sup>+</sup>, 100%),  $214 (M^+ - HCl, 90\%).$ 

Synthesis of  $Fe[(\eta - C_5H_3^nBu)(\eta - C_5H_4)]PPh$  (5). This species was prepared in a similar manner to **3** using  $Fe[(\eta - C_5H_3^n - C_5H_$ BuLi) $(\eta$ -C<sub>5</sub>H<sub>4</sub>Li)]·*n*TMEDA. However, since the product, which consisted of a mixture of isomers, proved to be a liquid even at low temperature (ca. -70 °C), 5 was isolated in vacuo as a red liquid, yield 6.0 g (71%). Purification beyond ca. 95% from n-butylferrocene impurity was not possible.

Data for 5: <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 15.6, 14.0, 12.0, 10.2 ppm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 7.8-7.2$  (br, Ph, 5H), 4.7-3.7 (br, Cp, 7H), 1.8-1.1 (br, CH<sub>2</sub> (butyl), 6H), 1.1-0.7 (br, CH<sub>3</sub>, 3H) ppm; MS (EI, 70 eV) m/z (%) 348 (M<sup>+</sup>, 100), 333 (M<sup>+</sup> - CH<sub>3</sub>, 8), 319  $(M^+ - C_2H_5, 25), 305 (M^+ - C_3H_7, 27), 291 (M^+ - C_4H_9, 13),$ 271 (M<sup>+</sup> – Ph, 10), 240 (M<sup>+</sup> – PPh, 18); HRMS (m/z) C<sub>20</sub>H<sub>21</sub><sup>56</sup>-FeP calcd 348.0730, found 348.0745.

Synthesis of  $Fe[\eta - C_5H_3SiMe_3]_2PPh$  (6). This species was prepared in a similar manner to **3** using  $Fe[\eta-C_5H_3SiMe_3 Li_{2}$ ·nTMEDA<sup>20</sup> except that the reaction solution was filtered

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and the solvent was then removed using high vacuum. The residue was placed under high vacuum for 3-4 h at 80 °C ensuring that all TMEDA and Fe( $\eta$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub> had been removed. The resulting dark-red oil was redissolved in a minimum of hexanes and cooled to -70 °C for 3 d. This resulted in the formation of a fine red powder. The product was filtered off at -70 °C resulting in the isolation of 2.0 g (yield 16%) of a fine rose-colored powder. Dissolution of this powder in hexanes and cooling to -70 °C for 3 d resulted in the formation of dark red-purple crystals suitable for a single-crystal X-ray diffraction study.

Data for 6: <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 10.0$  ppm; <sup>29</sup>Si NMR  $(\text{CDCl}_3) \delta = -4.4(\text{s}), -4.2 \text{ (s) ppm}; {}^{13}\text{C NMR} (\text{CDCl}_3) \delta = 137.0$ (d, ipso Ph,  $J_{PC} = 50.5$  Hz), 130.3 (d, o-Ph,  ${}^{2}J_{PC} = 13.9$  Hz), 128.5 (d, *m*-Ph,  ${}^{3}J_{PC} = 3.6$  Hz), 127.5 (s, *p*-Ph), 83.9 (s, ipso C–Si), 82.0 (s, ipso C–Si), 82.9 (s, Cp), 82.8 (d, Cp,  $J_{PC} = 6.6$ Hz), 81.7 (s, Cp), 81.6 (d, Cp,  $J_{PC} = 8.1$  Hz), 79.2 (d, Cp,  $J_{PC} =$ 2.9 Hz), 79.0 (d, Cp,  $J_{PC}$  = 2.9 Hz), 21.8 (d, ipso Cp-P,  $J_{PC}$  = 50.5 Hz), 21.3 (d, ipso Cp-P,  $J_{PC} = 49.8$  Hz), -0.03 (s, SiMe<sub>3</sub>), -0.04 (s, SiMe<sub>3</sub>) ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 7.7$  (tt, o-Ph, <sup>3</sup>J<sub>PH</sub> = 13.3 Hz,  ${}^{3}J_{HH} = 6.7$  Hz,  ${}^{4}J_{HH} = 1.5$  Hz, 2H), 7.3-7.0 (m, mand p-Ph, 3H), 4.7 (m, Cp, 1H), 4.6 (m, Cp, 1H), 4.56 (m, Cp, 1H), 4.5 (m, Cp, 1H), 4.3 (m, Cp, 1H), 4.2 (m, Cp, 1H), 0.2 (s, SiMe<sub>3</sub>, 9H), 0.1 (s, SiMe<sub>3</sub>, 9H) ppm; MS (EI, 70 eV) m/z (%) = 436 (100, M<sup>+</sup>), 421 (38, M<sup>+</sup> - CH<sub>3</sub>); HRMS (m/z) C<sub>22</sub>H<sub>29</sub><sup>56</sup>FeP<sup>28</sup>-Si<sub>2</sub> calcd 436.0895, found 436.0905. Anal. Calcd: C, 60.54; H, 6.70. Found: C, 60.12; H, 6.60.

Synthesis of  $Fe[\eta-C_5H_3SiMe_3]_2P(S)Ph$  (7). 6 (3.06 g, 6.9 mmol) was dissolved in 100 mL of THF, and an excess of elemental sulfur, 0.5 g (15.6 mmol), was added. After being stirred under nitrogen for 24 h, the solution was filtered. A <sup>31</sup>P NMR spectrum of this reaction solution showed the sulfurization to be quantitative. The solvent was then removed by vacuum, and the product was recrystallized from hexanes twice. This resulted in the isolation of a fine red powder, yield 2.2 g (68%). Bright red crystals suitable for single-crystal X-ray diffraction study were obtained by sublimation at 90 °C (0.02 mmHg) following recrystallization from a toluene/hexanes (1:2) mixture at -15 °C.

Data for 7: <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 46.1 ppm; <sup>29</sup>Si NMR  $(C_6D_6) \delta = -4.2$  (s, SiMe<sub>3</sub>), -4.4 (s, SiMe<sub>3</sub>) ppm; <sup>13</sup>C NMR  $(C_6D_6) \delta = 134.8$  (d, ipso Ph,  $J_{PC} = 87.9$  Hz), 132.1 (d, p-Ph,  ${}^{4}J_{PC} = 3.0 \text{ Hz}$ , 129.7 (d, *m*-Ph,  ${}^{3}J_{PC} = 12.5 \text{ Hz}$ ), 129.3 (d, *o*-Ph,  ${}^{2}J_{PC} = 14.0$  Hz), 86.6 (d, Cp ipso Si,  ${}^{3}J_{PC} = 7.3$  Hz), 85.3 (d, Cp ipso Si,  ${}^{3}J_{PC} = 5.8$  Hz), 84.9 (d, Cp,  $J_{PC} = 11.7$  Hz), 83.7 (d,  $Cp, J_{PC} = 9.5 Hz$ ), 81.7 (d,  $Cp, J_{PC} = 15.4 Hz$ ), 79.0 (d,  $Cp, J_{PC}$ = 2.9 Hz), 78.9 (d, Cp,  $J_{PC}$  = 2.9 Hz), 76.6 (d, Cp,  $J_{PC}$  = 11.0 Hz), 34.9 (d, P ipso Cp,  $J_{PC}$  = 34.4 Hz), 34.2 (d, P ipso Cp,  $J_{PC}$ = 35.1 Hz), -0.1 (s, SiMe<sub>3</sub>), -0.2 (s, SiMe<sub>3</sub>) ppm; <sup>1</sup>H NMR  $(C_6D_6) \delta = 7.9 \text{ (m, o-Ph, 2H)}, 7.3-7.0 \text{ (m, m- and p-Ph, 3H)},$ 5.2 (m, Cp, 1H), 5.13 (d, Cp, J = 1.5 Hz, 1H), 4.4 (m, Cp, 1H),4.3 (m, Cp, 1H), 4.0 (m, Cp, 1H), 3.9 (m, Cp, 1H), 0.2 (s, SiMe<sub>3</sub>, 9H), 0.1 (s, SiMe<sub>3</sub>, 9H), ppm; MS (EI, 70 eV) m/z (%) = 468  $(100, M^+), 453 (21, M^+ - CH_3), 436 (11, M^+ - S); HRMS (m/z)$  $C_{22}H_{29}{}^{56}FeP{}^{32}S{}^{28}Si_2$  calcd 468.0616, found 468.0606. Anal. Calcd: C, 56.40; H, 6.24. Found: C, 56.22; H, 6.17.

Reaction of 4 with PhMgBr. Alternative Synthesis of 3. A cold (-78 °C) solution of 4 (3.7 g, 15.0 mmol) in 50 mL of ether was made as described above and used in situ. Once this solution had warmed to 15 °C, PhMgBr in ether (9.0 mL, 2.0 M, 18.0 mmol) was added quickly by syringe. A <sup>31</sup>P NMR spectrum of the reaction solution at this point revealed 2 singlet resonances at  $\delta = 86.9$  and 13.0 ppm assigned to 4 and 3, respectively. After 20 min reaction time SiMe<sub>3</sub>Cl (0.2 mL, 1.6 mmol) was added to destroy any remaining lithiated ferrocene products and/or excess Grignard reagent. The resulting solution was then filtered, and the solvent was removed in vacuo. The residue was extracted with dry hexanes until the washings were colorless. These washings were then combined and solvent was removed in vacuo to give 3.3 g (75%) of 3 which was identified by <sup>31</sup>P NMR spectroscopy and mass spectrometry.

Thermal Ring-Opening Polymerization of 3 and 5-7.

A general procedure was used for the thermal ROP of 3 and 5-7. The procedure for the synthesis of polymer 9 serves as a representative example.

A Pyrex tube was charged with **5** (1.50 g, 4.3 mmol) and was sealed under vacuum (0.01 mmHg). This was then heated in an oven to 175 °C for 2 h. The initially molten sample became immobile after 10 min. The tube was allowed to cool and was then opened, and the contents were dissolved in 50 mL of THF. The resulting solution was filtered, and the volume of THF was reduced to 5-6 mL using a water aspirator. The concentrated polymer solution was then slowly added to stirred hexanes (500 mL) which resulted in the formation of a fine tan powder precipitate (1.24 g, 83%). The precipitate was identified as **9** by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy.

Data for polymer 8: Thermal ROP conditions for 3 with 1 h at 120 °C, 15 min at 130 °C, precipitation into hexanes; <sup>31</sup>P NMR identical to literature.<sup>19</sup> <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 7.9-6.8$ (br, Ph, 5H), 4.7-3.6 (br, Cp, 8H) ppm. Polymer 8 was found not to elute from the GPC column. However GPC was performed on the sulfurized derivative 11, which confirmed 8 was polymeric indirectly. Yield: 60%.

Data for polymer 9: Thermal ROP conditions for 5 with 2 h at 175 °C, precipitation into hexanes; <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$ = -30.0 to -33.0 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 8.2-6.8 (br, Ph, 5 H), 4.8-3.1 (br, Cp, 7 H), 2.5-0.5 (br, <sup>n</sup>Bu, 9 H) ppm. Anal. Calcd: C, 68.99; H, 6.08. Found: C, 67.78; H, 6.13. Polymer 9 was found not to elute from the GPC column. However GPC was performed on the sulfurized derivative 12, which confirmed 9 was polymeric indirectly. Yield: 83%.

Data for polymer 10: Thermal ROP conditions for 6 with 1 h at 250 °C, precipitation into MeOH; <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta =$ -27.0 to -31.0 ppm; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta =$  8.3-6.6 (br m, Ph, 5 H), 5.2-3.5 (br m, Cp, 6 H), 0.9 to -0.3 (br, SiMe<sub>3</sub>, 18 H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta =$  140.0 (br, ipso Ph), 137.0-134.0 (br, p-Ph), 130.0-129.0 (o-, m-Ph), 87.3-73.0 (br, Cp), 0.9 (br, SiMe<sub>3</sub>) ppm; <sup>29</sup>Si NMR (CDCl<sub>3</sub>)  $\delta =$  -2.2 to -3.3 (br, SiMe<sub>3</sub>) ppm; GPC  $M_w =$  66 000, PDI = 1.98. Anal. Calcd: C, 60.54; H, 6.70. Found: C, 59.82; H, 6.44. Yield: 66%.

Data for polymer 13: Thermal ROP conditions for 7 with 15 min at 250 °C, precipitation into MeOH; <sup>31</sup>P NMR (CD<sub>2</sub>-Cl<sub>2</sub>)  $\delta = 38$  (br) ppm; GPC  $M_w = 22000$ , PDI = 1.24. For full characterization, see polymer prepared by sulfurization of 10.

**Note:** The thermal ROP of 4 was attempted at 250 °C and resulted in the detonation of the sample. Extreme care should be exercised if this experiment is to be repeated!

Reaction of the Poly(ferrocenylphosphines) 8-10 with Elemental Sulfur: Synthesis of the Poly(ferrocenylphosphine sulfide)s 11-13. All reactions were carried out in a similar fashion, and that for 10 serves as a representative example.

Polymer 10 (250 mg, 0.6 mmol,  $M_w = 66\ 000$ , PDI = 1.98) was dissolved in 2–3 mL of dry dichloromethane with stirring. To this solution was added an excess of elemental sulfur (100 mg, 0.4 mmol of S<sub>8</sub>). This reaction solution was allowed to stir overnight. There was no noticeable color change of the reaction solution over this time. The reaction mixture was then filtered, and solvent was removed. The resultant product was then redissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and filtered again. A <sup>31</sup>P NMR spectrum of this product revealed a broad resonance centered at  $\delta$  ca. 38 ppm characteristic of 13 (similar to the polymer produced via thermal ROP of 7). The molecular weight of 13 produced in this manner was  $M_w = 65\ 000$ , PDI = 1.90. The yield was quantitative (ca. 100%) as was indicated by <sup>31</sup>P NMR spectroscopy. The isolated yield was 95%.

Data for polymer 11: <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 37.5 ppm; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 9.1–7.5 (br, Ph, 5 H), 5.6–3.0 (br, Cp, 8 H) ppm;  $M_w$  = 18 000, PDI = 1.52. Anal. Found: C, 58.77; H, 4.04. Calcd: C, 59.28; H, 4.05. Yield: 95%

Data for polymer 12:  ${}^{31}$ P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 38.1$  ppm;  ${}^{13}$ C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 135.5 - 133.0$  (br, *ipso*-Ph), 132.6 - 130.5 (br, Ph), 129.0 - 128.5 (br, Ph), 94.7 (br, Cp ipso  $J_{PC} = 100$  Hz), 82-69 (br, Cp), 35.0 - 33.3 (br, CpCH<sub>2</sub>), 29.5 - 27.8 (br, CH<sub>2</sub>), 23.5 - 22.0 (br, MeCH<sub>2</sub>), 14.6 - 13.2 (br, CH<sub>3</sub>) ppm;  ${}^{1}$ H NMR

 $(CD_2Cl_2) \delta = 8.1-6.9 (br, Ph, 5 H), 4.5-3.5 (br, Cp, 7 H), 2.6-$ 2.0 (br, P-CH<sub>2</sub>, 2 H), 1.8-1.0 (br, CH<sub>2</sub>, 4H), 1.0-0.8 (d, CH<sub>3</sub>, 3H) ppm;  $M_{\rm w} = 19\ 000$ , PDI = 2.26. Anal. Calcd: C, 63.17; H, 5.57. Found: C, 62.50; H, 5.57. Yield: 90%.

Data for polymer 13: <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta = 36-39$  (br) ppm; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 8.2-7.1$  (br, Ph, 5 H), 5.1-4.5 (br, Cp, 6 H), 1.0 to -0.4 (br, SiMe<sub>3</sub>, 18 H) ppm; <sup>13</sup>C NMR (CD<sub>2</sub>- $Cl_2$ )  $\delta = 134-130$  (br, Ph), 130.0-127.0 (br, Ph), 84.0-70.0 (br, Cp), 3.5 to -2.0 (br, SiMe<sub>3</sub>) ppm;  $M_w = 65\ 000$ , PDI = 1.90. Anal. Calcd: C, 56.40; H, 6.24. Found: C, 55.51; H, 6.06. Yield: 95%.

Elimination of S(SiMe<sub>3</sub>)<sub>2</sub> from (A) the Thermal ROP of 7 and (B) the Thermal Decomposition of Polymer 13. (A) From Thermal ROP of 7. A Pyrex tube was charged with 7 (0.5 g, 1.1 mmol) and was sealed under vacuum (0.01 mmHg). This was heated to 250 °C for 1 h. The tube was then opened under a nitrogen atmosphere, and the clear liquid contents were collected (ca. 10  $\mu$ L). Subsequent characterization of this liquid by <sup>29</sup>Si and <sup>1</sup>H NMR spectroscopy and mass spectrometry confirmed it was S(SiMe<sub>3</sub>)<sub>2</sub>.<sup>27</sup>

(B) From Thermal Decomposition of Polymer 13. A small glass capillary was loaded with ca. 5 mg of polymer 13. This was then placed into the mass spectrometer sample head and heated under vacuum to approximately 150 °C. Ions ascribable to  $S(SiMe_3)_2$  appeared as well as other peaks identifiable as polymer decomposition products. The residual sample was insoluble in THF. MS (EI, 70 eV) [m/z (%)]:  $S(SiMe_3)_2$ , 178 (10, M<sup>+</sup>), 163 (33, M<sup>+</sup> - Me), 105 (10, M<sup>+</sup> -SiMe<sub>3</sub>); other polymer decomposition products, 256 (100, Fe[ $(\eta$ - $C_5H_3SiMe_3(\eta-C_5H_3)]), 192 (55, Fe[(\eta-C_5H_3SiMe_3)]).$ 

Single-Crystal X-ray Diffraction Technique. Intensity data for 4 and 6 were collected on an Enraf-Nonius CAD-4 diffractometer whereas 7 was collected on a Siemens P4 diffractometer using graphite-monochromated Mo Ka radiation ( $\lambda = 0.710$  73 Å) with  $\omega$  scans. In each case the intensities of 3 standard reflections measured periodically showed no decay. Data were corrected for Lorentz and polarization effects and for absorption. The absorption corrections for all compounds were carried out using the SHELXA-90 routine in SHELXL. The structures were solved by direct methods. All structures were refined anisotropically by full-matrix least squares. For all structures the hydrogen atoms were visible in difference Fourier maps and were included in idealized positions. Crystal data and data collection parameters are listed in Table 2. All calculations were performed and all diagrams were created using SHELXTL-PC<sup>28</sup> and SHELXL-93<sup>29</sup> on a 486-66 personal computer.

#### **Results and Discussion**

Phosphorus-bridged [1]ferrocenophanes were first reported in 1980 by Osborne et al.<sup>21</sup> and by Seyferth and co-workers.<sup>22</sup> Important studies in this area have also been reported by Cullen.23 These species were prepared via the reaction of dilithioferrocene  $nTMEDA^{24}$ with dichloroorganophosphines  $PR'''Cl_2$  (R''' = Me, Ph) in nonpolar solvents such as hexanes (Scheme 1). Single-crystal X-ray diffraction studies have shown that phosphorus-bridged [1]ferrocenophanes such as 3 possess highly strained structures with tilt angles between the planes of the cyclopentadienyl rings of ca. 26-27°.<sup>23,25</sup> These compounds have been shown to undergo facile stoichiometric ring-opening reactions with aryllithium reagents.<sup>22</sup> Moreover, Seyferth et al. have reported that in the presence of small amounts of anionic initiator oligo(ferrocenylphosphines) with 2-5



repeat units are formed. However, attempts to generate high molecular weight poly(ferrocenylphosphines) via anionic ROP by using small quantities of initiator were reported to be unsuccessful and led only to the same oligomeric products. Low molecular weight poly(ferrocenylphosphines) were also formed (instead of the [1]ferrocenophane 3) by condensation polymerization reactions when the reaction of dilithioferrocene nTMEDAwith PPhCl<sub>2</sub> was carried out in ether solvents rather than in hexanes.<sup>19</sup> In addition, under certain conditions, these polycondensation reactions were reported to yield surprisingly<sup>26</sup> high molecular weight materials.

As part of our program to develop ROP as a route to transition metal-based macromolecules we initially focused on the [1]ferrocenophane 3 for our thermal polymerization studies.

Synthesis and Thermal ROP of  $Fe(\eta - C_5H_4)_2PPh$ (3). The synthesis of 3 was accomplished by the reaction of PPhCl<sub>2</sub> with 1,1'-dilithioferrocene•nTMEDA in hexanes.<sup>19</sup> This yielded red crystalline 3 in 48% yield. and the product gave <sup>31</sup>P and <sup>1</sup>H NMR and mass spectra in excellent agreement with those in the literature.<sup>22</sup> A Pyrex tube was charged with 3 and then sealed under vacuum. The tube was then heated to 120 °C for 1 h and then to 130 °C for 15 min. During this time the tube contents melted and then became viscous and subsequently immobile. The tube contents were then dissolved in CH<sub>2</sub>Cl<sub>2</sub> over 24 h. A <sup>31</sup>P NMR spectrum of the solution exhibited two broad resonances, one of high intensity at  $\delta = -30.5$  to -31.2 ppm, which was assigned to the internal phosphorus atoms of 8, and one

<sup>(21)</sup> Osborne, A. G.; Whiteley, R. H.; Meads, R. E. J. Organomet. Chem. 1980, 193, 345.

 <sup>(22)</sup> Withers, H. P.; Seyferth, D. Organometallics 1982, 1, 1275.
 (23) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. Organometallics 1983, 2, 128.

<sup>(24)</sup> Reaction of 2 equiv of BuLi and ferrocene in the presence of 2 equiv of TMEDA produces dilithioferrocene nTMEDA. A crystal structure has been reported for the species n = 1.5. However, the value of n in the isolated bulk product is not necessarily the same as in the crystal structure. See: Butler, I.R.; Cullen, W.R.; Ni, J.; Rettig, S. J. Organometallics 1985, 4, 2196 and references therein. For the purposes of this paper we have assumed that n = 1. (25) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. J. Organ-

omet Chem. 1980, 194, 91.

<sup>(26)</sup> The formation of high molecular weight products via polycondensation reactions using dilithioferrocene nTMEDA as a difunctional monomer would be highly unexpected as this reagent, which is generated via the reaction of ferrocene with n-butyllithium TMEDA, is generally only 90-95% pure. A major impurity is monolithiofer. rocene which serves as a polymer chain capping agent and therefore favors the formation of only low molecular weight products. On the basis of the hindsight provided by the recent discovery of the anionic ROP of silicon-bridged [1]ferrocenophanes, it appears far more likely to us that the high molecular weight poly(ferrocenylphosphines) are not formed by polycondensation but instead arise via a chain growth reaction, namely the anionically (i.e. lithiated ferrocene) induced ROP of the phosphorus-bridged [1]ferrocenophane 3 which is generated in situ. See: Manners, I. Adv. Organomet. Chem. 1995, 37, 131-136 and 153 - 154.

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of low intensity at  $\delta = -26.3$  ppm, which was assigned to the phosphorus atoms at the chain terminii. These assignments agree with those for the oligomers and polymers 8 generated by condensation routes.<sup>19</sup> Precipitation into hexanes yielded 8 as a fluffy, tan-colored solid in 60% yield. A <sup>1</sup>H NMR spectrum of 8 (in  $CD_2$ - $Cl_2$ ) showed broad resonances in the correct integration ratio for the Ph and Cp protons. However, an estimation of the molecular weight of 8 could not be obtained by gel permeation chromatography (GPC) as found previously by Seyferth and co-workers.<sup>19</sup> After injection onto the GPC column, no polymer was detected in the eluted solvent at any time. This result suggests that significant polymer-column interactions may be interfering with normal elution based on size exclusion. We were subsequently able to obtain molecular weight information for the sulfurized derivative of 8 (Scheme 2) which was found to be GPC-analyzable (see below).

Synthesis and Characterization of  $Fe(\eta - C_5H_4)_2$ -PCl (4). The synthesis of phosphorus-bridged [1]ferrocenophanes from dilithioferrocene  $\cdot n$ TMEDA involves reaction with dichlorophosphines PR"Cl<sub>2</sub>. Of these, only PPhCl<sub>2</sub> is readily available at reasonable cost, and this species, together with the other more expensive examples (especially alkyl derivatives), is extremely malodorous and toxic. We were therefore interested in investigating whether an alternative and potentially general approach to the synthesis of phosphorus-bridged [1]ferrocenophanes might be possible. An attractive approach would be to use readily available PCl<sub>3</sub> to react with dilithioferrocene nTMEDA to form the chloroderivative 4 and to subsequently react this with organometallic nucleophiles to form P-substituted derivatives (Scheme 1).

The synthesis of 4 involved the addition of  $PCl_3$  in hexanes to a slurry of dilithioferrocene nTMEDA in hexanes at -78 °C. However, once formed in solution this [1]ferrocenophane was found to quickly decompose at temperatures above -20 °C. Nevertheless, under certain conditions and appreciable care 4 can be isolated in moderate yield (ca. 50%). The structure of 4 was assigned on the basis of <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy as well as mass spectrometry. Once isolated, it was found that large brick red crystals of 4 could be grown





by first dissolving the species in hexanes at -20 °C and then cooling further to -78 °C. This permitted further characterization of 4 via a single-crystal X-ray diffraction study (see below).

**Reaction of 4 with PhMgBr. Alternative Synthesis of 3.** In order to investigate whether nucleophilic substitution of the chlorine substituent in 4 could be achieved, this species was reacted with PhMgBr in ether. The reaction was monitored in solution by <sup>31</sup>P NMR spectroscopy which showed that  $3 (\delta = 13.0 \text{ ppm})$ was formed from  $4 (\delta = 86.9 \text{ ppm})$  quantitatively. Furthermore, the isolated yield of 3 (75%) indicated that this type of reaction sequence might, in principle, be used in the future to generate a wide range of substituted phosphorus-bridged [1]ferrocenophanes.

Synthesis and ROP of  $Fe[(\eta-C_5H_3^nBu)(\eta-C_5H_4)]$ -PPh (5). One possible explanation for the GPCinactivity of 8 is the fairly poor solubility of this polymer in THF which might lead to adsorption to the GPC column. We therefore aimed to prepare a more soluble derivative via the attachment of alkyl chains to the cyclopentadienyl ligands. The synthesis of the monomer  $Fe[(\eta-C_5H_3^nBu)(\eta-C_5H_4)]PPh$  (5) was therefore investigated.

The synthesis of 5 involved the dilithiation of nbutylferrocene and the subsequent reaction of the product with PPhCl<sub>2</sub>. This led to an overall crude yield of 71% of 5 which was isolated as a red liquid. A  $^{31}P$ NMR spectrum of 5 (in  $CH_2Cl_2$ ) revealed four unique resonances at  $\delta = 15.6$ , 14.0, 12.0, and 10.2 with the two lower field peaks of greater intensity than the others. This result was consistent with the formation of four different structural isomers. The formation of these isomers can be explained by the lithiation of the n-butyl ferrocene at both the  $\alpha$  and  $\beta$  positions in combination with the possible cis or trans relation of the Ph group to that of the n-butyl group in 5. The formation of isomers with the Ph and "Bu groups trans to one another is likely to be favored (Figure 1). Further characterization of 5 was achieved by high-resolution mass spectrometry, which showed the expected molecular ion, and <sup>1</sup>H NMR, which clearly showed broad resonances in the correct intensity ratios which were assigned to the Ph, Cp, and to the n-butyl group, respectively.

When 5 was heated in an evacuated Pyrex tube to 175 °C for 2 h, the sample immediately became free flowing and then increasingly viscous and finally immobile. The tube was then opened under nitrogen, and the entire contents were dissolved in THF. Purification yielded 9, which presumably contains a mixture of monomer units derived from the various isomers of 5, as a light brown powder in 83% yield. The poly-(ferrocenylphosphine) 9 was characterized by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy. The <sup>31</sup>P NMR spectrum of 9 (in CH<sub>2</sub>Cl<sub>2</sub>) consisted of a single, broad resonance at  $\delta =$ -30 to -33 ppm which was similar to that for polymer 8. The <sup>1</sup>H NMR spectrum of 9 (in C<sub>6</sub>D<sub>6</sub>) consisted of broad resonances in the correct integration ratio for the



**Figure 2.** <sup>1</sup>H NMR spectrum of **10** in  $CD_2Cl_2$ .

phenyl, Cp, and alkyl regions. Polymer 9, which showed good solubility in polar solvents, formed well-defined but brittle films when cast from a solution in  $CH_2Cl_2$ . However, attempts to estimate the molecular weight of 9 by GPC were unsuccessful as in the case of 8. Again, sulfurization provided a GPC-analyzable derivative (see below) which confirmed that 9 was indeed polymeric.

Synthesis and ROP of  $Fe[\eta - C_5H_3SiMe_3]_2PPh$  (6). An alternative precursor to more soluble poly(ferrocenylphosphines), the bis(trimethylsilyl)-substituted species  $Fe[\eta-C_5H_3SiMe_3]_2PPh$ , 6, was also synthesized. This was accomplished by the dilithiation of 1,1'-bis(trimethylsilyl)ferrocene with 2 equiv of BuLi·TMEDA in hexanes and the subsequent reaction of the product with 1 equiv of PPhCl<sub>2</sub>. The [1]ferrocenophane 6 was isolated as a rose-colored solid which was characterized by <sup>31</sup>P, <sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H NMR and high-resolution mass spectrometry. The spectroscopic data were all consistent with the assigned structure for 6. However, in contrast to the situation for 5, the NMR data indicated the presence of a single structural isomer. For example, a single <sup>31</sup>P NMR resonance at 10.0 ppm (in  $CD_2Cl_2$ ) was detected for both the bulk product and for that of the single crystals of 6. The formation of a single structural isomer is consistent with the previously noted regiospecifically  $\beta$ - and stereospecifically *anti*-dilithiation of 1,1'bis(trimethylsilyl)ferrocene which has been attributed to the bulky nature of the  $SiMe_3$  groups.<sup>20</sup> Additional characterization of 6 was obtained by X-ray diffraction (see below).

The thermal ROP of 6 was carried out at 250 °C over 1 h. A <sup>31</sup>P NMR spectrum of the products showed a small singlet resonance at  $\delta = 10$  ppm assigned to unreacted **6** and a very broad resonance from  $\delta = -27$ to -31 ppm which was assigned to the polymer 10. Precipitation into methanol resulted in the isolation of a tan solid in a 66% yield. A <sup>1</sup>H NMR spectrum of this polymer revealed broad resonances for the Ph, Cp, and SiMe<sub>3</sub> groups in the correct intensity ratios (Figure 2). As noted above and by others previously,<sup>19</sup> molecular weight analysis of poly(ferrocenylphosphines) by GPC techniques has until now been complicated by the fact the polymers do not elute from the column properly.<sup>19</sup> However, we found that the introduction of the trimethylsilyl groups allowed us to overcome this difficulty and a GPC investigation of 10 in THF revealed that the material possessed a  $M_{\rm w}$  of 66 000 and a polydispersity (PDI) of 1.98 versus polystyrene standards.

Synthesis and Polymerization Behavior of Fe- $[\eta$ -C<sub>5</sub>H<sub>3</sub>SiMe<sub>3</sub>]<sub>2</sub>P(S)Ph (7). In order to investigate whether phosphorus (V)-bridged [1]ferrocenophanes would also undergo thermally-induced ROP, we synthesized the phosphine sulfide 7 via the reaction of 6 with an excess of  $S_8$  in THF. The reaction was monitored by <sup>31</sup>P NMR which after 24 h showed a single, new singlet resonance at  $\delta = 44$  ppm. Species 7 was isolated as a red powder and was characterized by multinuclear NMR and high-resolution mass spectrometry. As in the case of 6, each hydrogen atom bound to the cyclopentadienyl (Cp) ligands was found to be unique. Thus 6 signals were observed in the Cp region of the <sup>1</sup>H NMR spectrum, and a set of 10 resonances were assigned to the Cp carbons in the <sup>13</sup>C NMR spectrum. As with other strained, ring-tilted [1]ferrocenophanes, the Cp-P ipso carbon <sup>13</sup>C NMR resonances are considerably upfield at  $\delta = 34.9$  (d,  $J_{PC} = 34.4$  Hz) and 34.2 ppm (d,  $J_{PC} = 35.1$  Hz) whereas the other 8 Cp resonances appear in the typical region between 76 and 87 ppm. Further characterization of 7 was achieved by single-crystal X-ray diffraction (see below).

In a manner similar to that for the other [1]ferrocenophanes, 7 was sealed in an evacuated Pyrex tube and was then heated (to 250 °C). The sample became molten, viscous, and then immobile after 15 min. However, only a small fraction of the tube contents were found to be soluble in THF. Furthermore, a clear colorless liquid was observed within the Pyrex tube before the products were analyzed. Isolation and characterization of this liquid showed it to be the sulfide,  $S(SiMe_3)_2$ . This was confirmed by mass spectrometry and a comparison of the <sup>29</sup>Si and <sup>1</sup>H NMR spectra of this species to those of an authentic sample.<sup>27</sup> The soluble polymer fraction exhibited a broad <sup>31</sup>P NMR resonance centered at  $\delta = 38$  ppm. The insoluble material was presumably crosslinked polymer having further P-Cp bonds. However, this has not been established and the insoluble products may be poorly defined decomposition products. Studies of polymer 13 synthesized by an alternative route (i.e. the sulfurization of 10) have shown that the elimination of  $S(SiMe_3)_2$ occurs at temperatures below that needed to generate polymer by thermal ROP (see below).

Sulfurization of the Poly(ferrocenylphosphines) 8-10 with Elemental Sulfur. Synthesis of the Poly(ferrocenylphosphine sulfides) 11-13. In order to investigate the ability of 8 to undergo macromolecular reactions and in order to attempt to obtain a derivative that could be analyzed by GPC, we reacted 8 with an excess of elemental sulfur in THF. The reaction was monitored by <sup>31</sup>P NMR which showed a singlet resonance at  $\delta = ca. 37$  ppm which was dramatically downfield shifted from that of  $8 (\delta = ca. -30 \text{ ppm})$ . The polymer product was identified as 11 by <sup>31</sup>P and <sup>1</sup>H NMR and elemental analysis. Furthermore, analysis by GPC showed that this species successfully eluted from the column and that it possessed  $M_{\rm w} = 18\ 000$  and PDI = 1.52.

The poly(ferrocenylphosphines) 9 and 10 were similarly reacted with sulfur to yield 12 and 13, respectively. Similar ca. 60 ppm downfield shifts in the  ${}^{\bar{3}1}P$  NMR spectra of the sulfurized polymers were noted. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and elemental analysis provided additional characterization for 12 and 13. Both poly-

<sup>(27)</sup> The elimination product exhibited chemical shifts as follows: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 0.28$  ppm (0.28); <sup>28</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 14.3$  ppm (14.3). Those of the authentic sample are in parentheses. (28) Sheldrick, G. M. SHELXTL-PC, Siemens Analytical X-ray

Instruments Inc., Madison, WI, 1990.

<sup>(29)</sup> Sheldrick, G. M. SHELXL-93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1994.



**Figure 3.** Alternative views of the molecular structure of **4** with thermal ellipsoids at the 50% probability level.

Table 1. Selected Structural Data for Phosphorus-Bridged [1]Ferrocenophanes, with Esd's in Parentheses (Where Available)

	compd					
	3	4	6	7		
Fe-P dist (Å)	2.774(3)	2.715(6)	2.784(2)	2.688(2)		
Fe displacement (Å)		0.277(8)	0.291(7)	0.259(2)		
ring tilt α (deg)	26.7	27.0(6)	27.5(6)	25.3(3)		
$\beta(av) (deg)$	32.5	31.9(7)	32.0(3)	35.0(4)		
$\theta$ (deg)	90.6(3)	90.1(7)	95.7(4)	95.0(2)		
δ (deg)	159.8	160.4(6)	159.5(3)	161.8(2)		
$C_{ipso} - C'_{ipso} (Å)$	2.619(12)	2.606(17)	2.638(9)	2.673(7)		

 Table 2.
 Summary of Crystal Data and Intensity

 Collection Parameters for 4, 6, and 7

	4	6	7
formula	C <sub>10</sub> H <sub>8</sub> ClFeP	C <sub>22</sub> H <sub>29</sub> FePSi <sub>2</sub>	C <sub>22</sub> H <sub>29</sub> FePSi <sub>2</sub> S
$M_{ m r}$	250.4	436.5	468.5
cryst class	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
temp, K	292	223	173
a, Å	7.306(1)	8.0748(8)	11.580(2)
b, Å	19.442(8)	11.4391(14)	13.472(2)
c, Å	7.421(1)	12.7716(17)	15.314(3)
α, deg	90	103.46(1)	90
$\beta$ , deg	118.870(12)	93.87(1)	90.89(1)
$\gamma$ , deg	90	97.51(1)	90
V, Å <sup>3</sup>	923.1(4)	1131.54(24)	2388.8(7)
Ζ	4	2	4
$D_{\rm calcd}, {\rm g} {\rm cm}^{-3}$	1.802	1.281	1.303
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	2.036	0.846	0.891
$\lambda$ (Mo K $\alpha$ ), Å	0.709 30	0.710 73	0.710 73
$R_{ m int}, \%$	3.43	0.00	5.23
$R,^a \%$	5.08	5.90	4.98
$R_{ m w}^{st,a}$ %	4.23	7.55	8.74
abs cor	1.175/0.843	1.1640/0.8120	0.9353/0.6018

<sup>a</sup> Definition of R factors:  $R = \sum \Delta \sum (F(\text{obs}))$ .  $R_w = [\sum(\text{weight} \times \Delta)^2 / \sum(\text{weight} \times F(\text{obs})^2)]^{1/2}$ , where  $\Delta = [F(\text{obs}) - F(\text{calc})]$ .

(ferrocenylphosphine sulfides) were also found to elute from the GPC column (12,  $M_w = 19\ 000$ , PDI = 2.26; 13,  $M_w = 65\ 000$ , PDI = 1.90). In the case of 11 and 12 the GPC activity allowed an estimation of the molecular weights of their poly(ferrocenylphosphine) precursors 8 and 9. Comparison of the value for 13 ( $M_w = 65\ 000$ , PDI = 1.90) with that for the sole example of a GPC-

Table 3. Atomic Coordinates  $(\times 10^4)$  and Equivalent Isotropic Displacement Coefficients  $(\dot{A}^2 \times 10^3)$  for the Non-Hydrogen Atoms of 4 with Esd's in Parentheses

atom	x	У	z	$U(eq)^a$
Fe	7382(3)	8960(1)	1938(3)	28(1)
Cl	12953(6)	8414(2)	6333(5)	<b>53</b> (2)
Р	10731(7)	8069(2)	3492(7)	<b>46</b> (2)
C(1)	10070(21)	8870(8)	1988(20)	30(7)
C(2)	8454(24)	8857(8)	-98(22)	<b>41</b> (8)
C(3)	7310(23)	9465(7)	-547(22)	<b>40</b> (8)
C(4)	8265(21)	9875(8)	1214(22)	39(9)
C(5)	9949(20)	9536(7)	2750(21)	<b>32</b> (7)
C(6)	8362(23)	8157(7)	3760(22)	38(9)
<b>C</b> (7)	6389(23)	7981(7)	1932(22)	36(9)
<b>C</b> (8)	4884(23)	8449(8)	1890(22)	39(9)
C(9)	5779(27)	8874(8)	3556(26)	53(10)
C(10)	7889(24)	8706(7)	4743(20)	26(7)

<sup>*a*</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $\mathbf{U}_{ij}$  tensor.

Table 4.	Bond Lengths (Å) for 4 with Esd's in				
Parentheses					

Fe-P	2.755(5)	Fe-C(1)	1.954(17)
Fe-C(2)	2.019(20)	Fe-C(3)	2.068(18)
Fe-C(4)	2.052(16)	Fe-C(5)	2.011(14)
Fe-C(6)	1.960(14)	Fe-C(7)	2.036(15)
Fe-C(8)	2.063(18)	Fe-C(9)	2.050(24)
Fe-C(10)	1.992(16)	Cl-P	2.055(5)
P-C(1)	1.840(15)	P-C(6)	1.843(20)
C(1) - C(2)	1.423(17)	C(1) - C(5)	1.431(21)
C(2) - C(3)	1.393(21)	C(3) - C(4)	1.397(20)
C(4) - C(5)	1.376(17)	C(6) - C(7)	1.465(17)
C(6) - C(10)	1.427(23)	C(7) - C(8)	1.415(24)
C(8) - C(9)	1.364(22)	C(9) - C(10)	1.396(22)

analyzable poly(ferrocenylphosphine) precursor 10 ( $M_w$  = 66 000, PDI = 1.98) is significant. This suggests sulfurization occurs without significant molecular weight decline assuming that the hydrodynamic volumes of each species are similar. This suggests that GPC analysis of the sulfurized derivatives provided a good method for evaluating the molecular weights of poly-(ferrocenylphosphines) which adsorb to the GPC column and removes the necessity of resorting to the use of light scattering (or other) techniques which are considerably more time consuming.

The facile formation of soluble 13 via the sulfurization of 10 compares favorably with the small amount of soluble material formed in the thermal ROP of the phosphine sulfide 7 discussed previously. In the latter reaction the other products were  $S(SiMe_3)_2$  and insoluble material. The possibility that  $S(SiMe_3)_2$  was formed by the thermal decomposition of the ring-opened polymer 13 was investigated by heating a well-characterized sample of 13, prepared by the sulfurization of 10, from 25 to 150 °C under vacuum. The formation of the sulfide  $S(SiMe_3)_2$  was detected by simultaneous mass spectrometry. Furthermore, the resulting polymeric product was rendered insoluble. Thus, the thermal treatment of the soluble polymer 13 might allow the introduction of controlled degrees of crosslinking.

Discussion and Comparison of the X-ray Structures of 4, 6, and 7. Crystals of 4 suitable for a singlecrystal X-ray diffraction study were obtained from hexanes at -78 °C. Two views of the molecular structure of 4 are shown in Figure 3. Table 1 gives selected structural data for important features for this and related [1]ferrocenophanes. The angles  $\alpha$ ,  $\beta$ , and  $\theta$  are defined in Figure 6.

The summary of the crystal data and collection parameters is found in Table 2. Tables of the fractional



Figure 4. Alternative views of the molecular structure of 6 with thermal ellipsoids at the 50% probability level.

Table 5. Selected Bond Angles (deg) for 4 withEsd's in Parentheses

Cl-P-C(1)	101.1(4)	P-C(6)-C(7)	115.7(13)
Cl-P-C(6)	100.2(5)	P-C(6)-C(10)	126.6(11)
C(1) - P - C(6)	90.1(7)	C(2)-C(1)-C(5)	105.6(12)
P-C(1)-C(2)	118.8(11)	C(7) - C(6) - C(10)	106.0(13)
P - C(1) - C(5)	125.0(12)		

coordinates, bond lengths, and selected angles for 4 are found in Tables 3-5, respectively. X-ray diffraction quality crystals of 6 were grown from hexanes at -70°C over several days. Views of the molecular structure of 6 are shown in Figure 4. Fractional coordinates, bond lengths, and selected angles can be found in Tables 6-8, respectively. Suitable crystals of 7 were grown by vacuum sublimation. Views of the molecular structure are shown in Figure 5, and fractional coordinates, bond lengths, and selected bond angles can be found in Tables 9-11, respectively.

The single-crystal X-ray diffraction studies confirmed the structures of 4, 6, and 7 as phosphorus-bridged [1]ferrocenophanes. Although both 6 and 7 consisted of a single structural isomer, both are chiral. Two enantiomers were found for each species in the crystals as indicated by the symmetries of the unit cells (6, P1,Z = 2; 7,  $P2_1/c$ , Z = 4). The most notable features of the phosphorus(III)-bridged [1]ferrocenophanes 4 and **6** are the large ring tilt angles ( $\alpha$ ) of ca. 27° compared to their silicon-bridged analogs ( $\alpha = ca. 21^{\circ}$ ). This phenomenon has been previously noted and analyzed by Cullen<sup>23</sup> and by Osborne.<sup>30</sup> A significant difference between the structures of the molecules is the larger  $\theta$ angle for the trimethylsilyl-substituted species 6 and 7 compared to 4. Average  $\theta$  angles for phosphorus(III)bridged [1]ferrocenophanes are normally within the range  $90.5-91.5^{\circ}$  (e.g. for 3,  $\theta = 90.7(2)^{\circ}$ ). However, none exceed 94° and values of this magnitude are more

Table 6. Atomic Coordinates  $(\times 10^4)$  and Equivalent Isotropic Displacement Coefficients  $(\dot{A}^2 \times 10^3)$  for the Non-Hydrogen Atoms of 6 with Esd's in Parentheses

atom	x	У	z	$U(eq)^a$
Fe	2190(1)	8521(1)	1744(1)	34(1)
Р	-296(3)	10003(2)	2026(2)	47(1)
Si(1)	3465(3)	7034(2)	-768(2)	47(1)
Si(2)	4708(3)	7617(2)	3716(2)	<b>43(1)</b>
<b>C</b> (1)	413(9)	8883(7)	2717(6)	<b>41</b> (3)
C(2)	56(9)	7628(8)	2125(6)	47(3)
C(3)	1410(9)	7047(7)	2362(6)	43(3)
C(4)	2659(9)	7893(7)	3127(6)	<b>39(3</b> )
C(5)	2026(9)	9006(7)	3342(6)	39(3)
C(6)	1473(10)	9858(7)	1162(6)	<b>42(3)</b>
C(7)	1312(10)	8784(7)	309(6)	45(3)
C(8)	2939(10)	8394(7)	166(6)	<b>44(3)</b>
C(9)	4087(10)	9292(7)	976(7)	48(3)
C(10)	3193(10)	10172(7)	1587(6)	45(3)
C(11)	443(9)	11443(8)	3025(7)	48(3)
C(12)	1174(11)	12440(8)	2711(8)	58(4)
C(13)	1561(12)	13567(9)	3459(9)	<b>68</b> ( <b>4</b> )
C(14)	1145(12)	13692(10)	4514(9)	71(4)
C(15)	407(12)	12720(9)	4827(8)	64(4)
C(16)	38(10)	11603(9)	4082(7)	58(4)
C(21)	1909(14)	5692(8)	-728(9)	93(5)
C(22)	5653(12)	6847(10)	-365(8)	81(5)
C(23)	3333(11)	7183(8)	-2187(7)	62(4)
C(31)	5378(12)	6247(9)	2825(8)	77(5)
C(32)	6284(10)	8962(8)	3794(7)	62(4)
C(33)	4476(11)	7399(10)	<b>5097</b> (7)	75(5)

<sup>*a*</sup> Equivalent isotropic U defined as one-third of the trace of the orthogonalized  $\mathbf{U}_{ij}$  tensor.



Figure 5. Alternative views of the molecular structure of 7 with thermal ellipsoids at the 50% probability level.

common in silicon-bridged ferrocenophanes. Both 6 and 7 have  $\theta$  values greater than 94° (6, 95.7(4)°; 7, 95.0(2)°).

The tilt angle ( $\alpha$ ) of **6** was found to be 27.5(6)° whereas the  $\alpha$  angle of **7** was significantly smaller (25.3(3)°). Interestingly, this difference was not accompanied by a significant change in the  $\theta$  angle in the two complexes.

<sup>(30)</sup> Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. J. Organomet. Chem. 1980, 194, 91.

 
 Table 7. Bond Lengths (Å) for 6 with Esd's in Parentheses

Fe-P	2.784(2)	Si(2)-C(31)	1.868(9)
Fe-C(1)	1.987(7)	Si(2) - C(32)	1.859(9)
Fe-C(2)	2.033(7)	Si(2) - C(33)	1.859(9)
Fe-C(3)	2.067(8)	C(1) - C(2)	1.447(10)
Fe-C(4)	2.086(7)	C(1) - C(5)	1.455(9)
Fe-C(5)	2.004(6)	C(2) - C(3)	1.406(11)
Fe-C(6)	1.980(8)	C(3) - C(4)	1.436(8)
Fe-C(7)	2.024(7)	C(4) - C(5)	1.420(10)
Fe-C(8)	2.123(7)	C(6) - C(7)	1.425(9)
Fe-C(9)	2.084(8)	C(6) - C(10)	1.425(9)
Fe-C(10)	2.009(7)	C(7) - C(8)	1.443(10)
P-C(1)	1.846(8)	C(8) - C(9)	1.447(9)
P-C(6)	1.869(7)	C(9) - C(10)	1.423(10)
P-C(11)	1.831(7)	C(11) - C(12)	1.379(12)
Si(1) - C(4)	1.864(7)	C(11) - C(16)	1.379(11)
Si(1) - C(21)	1.860(9)	C(12) - C(13)	1.389(11)
Si(1) - C(22)	1.845(8)	C(13) - C(14)	1.378(14)
Si(1) - C(23)	1.851(9)	C(14) - C(15)	1.360(14)
Si(2) - C(8)	1.842(7)	C(15) - C(16)	1.379(11)

Table 8. Selected Bond Angles (deg) for 6 with<br/>Esd's in Parentheses

C(1) - P - C(6)	90.5(3)	C(21)-Si(1)-C(22)	108.5(4)
C(1) - P - C(11)	102.8(3)	C(31)-Si(2)-C(33)	109.6(4)
C(3)-Si(1)-C(22)	108.2(3)	P-C(1)-C(2)	116.9(5)
C(3)-Si(1)-C(21)	111.0(4)	P-C(1)-C(5)	123.4(5)
C(6) - P - (C) 11	102.0(3)	P-C(6)-C(7)	116.5(5)
C(9)-Si(2)-C(31)	109.2(3)	P-C(6)-C(10)	125.8(5)
C(9) - Si(2) - C(33)	108.6(4)		



**Figure 6.** Definition of structural parameters for [1]metallocenophanes.

However, a significant increase in the  $\beta$  angle was observed. This angle, which represents a distortion from planarity for the ipso carbon atoms of the cyclopentadienyl rings bonded to phosphorus, increased from  $32.0(3)^{\circ}$  in **6** to  $35.0(4)^{\circ}$  in **7**. The difference in the  $\beta$ angle may be a consequence of the change in the length of the ipso carbon-phosphorus bonds which shorten from an average value of 1.857(8) Å in **6** to a value of 1.799(5) Å in **7**.

Previous structural studies on [1]ferrocenophanes have provided evidence for a possible dative interaction between the iron center and the bridging element. Further evidence for this Fe····E interaction has also been provided by physical methods such as Mössbauer spectroscopy.<sup>31,32</sup> A comparison of the structures of 6 and 7 offers some additional insight. The sulfurization of 6 to yield 7 formally alters the oxidation state of the phosphorus center. Thus an increase in the magnitude in the dative interaction between the iron atom and the phosphorus center might be expected. Indeed, the Fe···P distance in 7 (2.688(2) Å) is shorter than in 6 (2.784(2) Å). By comparison, in the previously studied phosphorus(III)-bridged [1]ferrocenophanes the Fe---P distances range from 2.715(6) to 2.784(2) Å. This shortening of the Fe···P distances in 7 relative to 6 was also accompanied by a decrease in the displacement of the Fe (in an opposite direction to the phosphorus atom)

Table 9. Atomic Coordinates  $(\times 10^4)$  and Equivalent Isotropic Displacment Coefficients  $(\mathring{A}^2 \times 10^3)$  for the Non-Hydrogen Atoms of 7 with Esd's in Parentheses

atom	x	у	z	$U(eq)^a$
Fe	2470(1)	446(1)	2348(1)	27(1)
Si(1)	2393(2)	1337(1)	131(1)	42(1)
Si(2)	-292(2)	798(1)	3217(1)	<b>55</b> (1)
Р	4350(1)	-337(1)	3135(1)	25(1)
S	<b>5922</b> (1)	155(1)	3125(1)	35(1)
C(1)	3686(4)	-534(4)	2069(3)	25(1)
C(2)	3735(4)	295(4)	1461(3)	30(1)
C(3)	2672(4)	385(4)	992(3)	32(1)
C(4)	1970(4)	-414(4)	1285(3)	32(1)
C(5)	2578(4)	-972(4)	1937(3)	<b>31</b> (1)
C(6)	3264(4)	<b>529</b> (4)	3502(3)	27(1)
C(7)	3190(5)	1501(4)	3112(3)	31(1)
C(8)	2010(5)	1744(4)	2987(3)	32(1)
C(9)	1301(5)	933(4)	3286(4)	38(2)
C(10)	2089(4)	207(4)	3603(3)	<b>32</b> (1)
C(11)	4099(4)	-1436(4)	3756(3)	<b>26</b> (1)
C(12)	3974(4)	-2367(4)	3380(4)	30(1)
C(13)	3762(4)	-3188(4)	3881(4)	35(1)
C(14)	3701(4)	-3096(4)	4764(4)	38(2)
C(15)	3869(5)	-2200(4)	5158(4)	<b>41</b> (2)
C(16)	4049(5)	-1363(4)	4661(3)	32(1)
C(21)	3312(7)	1014(5)	-821(4)	<b>92</b> (3)
C(22)	873(6)	1281(6)	-198(5)	114(4)
C(23)	2783(5)	2571(4)	538(4)	<b>50(2)</b>
C(31)	-847(6)	1574(5)	2323(5)	102(3)
C(32)	-938(6)	1188(7)	4245(5)	112(3)
C(33)	-653(5)	-507(5)	2997(5)	67(2)

<sup>*a*</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $\mathbf{U}_{ii}$  tensor.

Table 10.	Bond Lengths	(Å) for	7	with	Esd's	in
	Parenth	0202				

		-meses	
Fe-C(1)	1.981(5)	Fe-C(6)	1.984(5)
Fe-C(10)	2.005(5)	Fe-C(7)	2.013(5)
Fe-C(5)	2.015(5)	Fe-C(2)	2.024(5)
Fe-C(4)	2.072(5)	Fe-C(8)	2.078(5)
Fe-C(3)	2.094(5)	Fe-C(9)	2.095(5)
Fe···P	2.688(2)	Si(1) - C(22)	1.824(6)
Si(1) - C(23)	1.829(6)	Si(1) - C(3)	1.864(6)
Si(1) - C(21)	1.869(7)	Si(2)-C(32)	1.831(7)
Si(2) - C(31)	1.831(7)	Si(2) - C(33)	1.838(7)
Si(2) - C(9)	1.855(6)	P-C(11)	1.785(5)
P-C(6)	1.811(5)	P - C(1)	1.814(5)
P-S	1.938(2)	C(1) - C(5)	1.424(6)
C(1) - C(2)	1.455(7)	C(2)-C(3)	1.421(6)
C(3) - C(4)	1.426(7)	C(4) - C(5)	1.426(7)
C(6) - C(10)	1.439(7)	C(6) - C(7)	1.443(7)
C(7) - C(8)	1.415(7)	C(8)-C(9)	1.444(7)
C(9) - C(10)	1.417(7)	C(11) - C(12)	1.387(7)
C(11) - C(16)	1.392(6)	C(12) - C(13)	1.370(7)
C(13) - C(14)	1.360(7)	C(14) - C(15)	1.361(7)
C(15) - C(16)	1.378(7)		

Table 11.Selected Bond Angles (deg) for 7 with<br/>Esd's in Parentheses

$\begin{array}{c} C(1)-P-C(6) \\ C(1)-P-C(11) \\ C(3)-Si(1)-C(22) \\ C(3)-Si(1)-C(21) \\ \end{array}$	95.0(2) 106.8(2) 108.8(3) 107.3(3)	$\begin{array}{c} C(21) - Si(1) - C(22) \\ C(31) - Si(2) - C(33) \\ P - C(1) - C(2) \\ P - C(1) - C(5) \\ P - C(1) - C(5) \end{array}$	$109.5(4) \\109.4(3) \\116.3(4) \\123.8(4)$
C(3)-Si(1)-C(21) C(6)-P-C(11) C(9)-Si(2)-C(31) C(9)-Si(2)-C(33)	$107.3(3) \\104.4(2) \\108.9(3) \\109.1(3)$	P-C(1)-C(3) P-C(6)-C(7) P-C(6)-C(10) C(1)-P-S	$123.8(4) \\119.6(4) \\120.1(4) \\115.3(2)$

from the line joining the Cp centroids. Thus, in 7 this displacement is 0.259(2) Å, significantly less than in 6 (0.291(7) Å). This also provides evidence that the phosphorus(V) center in 7 may be acting as a better acceptor of electron density than the phosphorus(III) center in 6. However, it should be noted that the decreased length of the ipso carbon-phosphorus bonds in 7 relative to 6 mentioned above would also be expected to decrease the Fe···P distance. Thus, as noted

<sup>(31)</sup> Clemance, M.; Roberts, R. M. G.; Silver, J. J. Organomet. Chem. **1983**, 243, 461.

<sup>(32)</sup> Silver, J. J. Chem. Soc., Dalton Trans. 1990, 3513.

<sup>(33)</sup> Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. Organometallics **1995**, *14*, 2470.

elsewhere,<sup>33</sup> the different structural parameters in [1]ferrocenophanes are interrelated and it is difficult to distinguish definitively between which structural change is a "cause" which is an "effect".

Cullen has suggested that the ring strain in phosphorus-bridged [1]ferrocenophanes is manifest in different structural distortions compared to their silicon or germanium analogues.<sup>23</sup> Thus, on the basis of an analysis of the structures available at that time, it was noted that phosphorus-bridged [1]ferrocenophanes exhibit higher tilt angles  $(\alpha)$  whereas the silicon and germanium complexes have higher  $\theta$  and  $\beta$  angles. It is therefore interesting to note that, while the characteristics of 4 agree with this assessment, the  $\theta$  and  $\beta$ angles for 6 and in particular 7 are between those typically found in silicon-bridged and phosphorusbridged [1] ferrocenophanes. Thus, the  $\theta$  and  $\beta$  angles in 7 ( $\theta$  = 95.0(2)°,  $\beta$  = 35.0(4)°) are intermediate between those found in 3 ( $\theta = 90.6(3)^\circ$ ,  $\beta = 32.5^\circ$ ) and  $Fe(\eta - C_5H_4)_2SiPh_2 \ (\theta = 99.2(5)^\circ, \beta = 40.0(9)^\circ).$ 

### Summary

A series of strained, ring-tilted phosphorus(III)bridged [1]ferrocenophanes have been shown to undergo thermal ROP to yield poly(ferrocenylphosphines). Sulfurization of these materials yielded poly(ferrocenylphosphine sulfides) which were GPC-analyzable and which were completely characterized. The phosphorus(V)bridged [1]ferrocenophane 7 also underwent thermallyinduced ROP, but the resulting polymer partially decomposed under the thermolysis conditions.

Future work will be focused on detailed studies of the properties of the polymers, and we recently reported electrochemical studies of **9** which showed that the iron centers interact with one another in a similar manner to those in poly(ferrocenylsilanes) and poly(ferrocenylgermanes).<sup>2</sup> We are also investigating alternative methods for the initiation of the ROP of phosphorus-bridged [1]ferrocenophanes, and our results of this study will be reported in the near future.

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**Supporting Information Available:** Tables of crystallographic details, bond angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters (17 pages). Ordering information is given on any current masthead page.

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