

## Ferrocenyl Derivatives of Poly(methylphenylphosphazene)

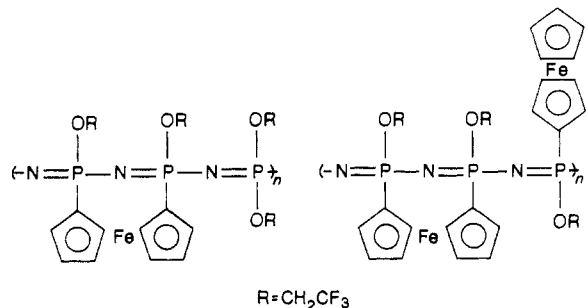
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**Summary:** Poly(alkyl/arylphosphazenes) with ferrocenyl units attached to the polymer backbone by two carbon spacer groups have been prepared by the sequential treatment of  $[\text{Ph}(\text{Me})\text{P}=\text{N}]_n$  with  $n\text{-BuLi}$ , followed by ferrocenecarboxaldehyde or acetylferrocene. The ferrocenyl-substituted polymers  $\{[\text{Ph}(\text{Me})\text{P}=\text{N}]_x[\text{Ph}(\text{R})\text{P}=\text{N}]_y\}$  {1,  $\text{R} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{OH})\text{CH}_2]$ , and 2,  $\text{R} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{Me})(\text{OH})\text{CH}_2]$ } have approximate  $x:y$  ratios of 1:1 for 1 and 2:1 for 2. The characterization of these new polymers by elemental analysis, size exclusion chromatography, and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectroscopy is discussed.

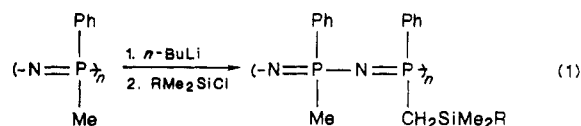
The incorporation of the ferrocenyl moiety into polymers has been of considerable interest for a number of years because the unusual thermal, electrical, mechanical, catalytic, and even biological properties of such materials offer numerous potential applications.<sup>1</sup> Recently, polyphosphazenes that have ferrocenyl and/or ruthenocenyl groups directly attached to the backbone phosphorus have been prepared by the ring-opening polymerization of fluorinated cyclic trimers to which the metallocenyl units are attached.<sup>2,3</sup> The polymers with only transannular-



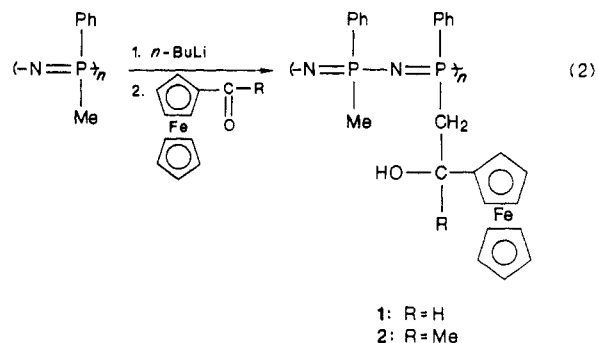
linked metallocenes generally have high molecular weights and contain one metallocene unit for every three  $\text{P}=\text{N}$  monomer units.<sup>2</sup> The materials with a higher metallocene content (i.e., two metallocene moieties for every three monomer units) have both transannular and pendent metallocene units but typically have medium molecular weights.<sup>3</sup> In both of these polymer systems the phosphorus atoms which are not bound to the metallocene ring are further substituted with the trifluoroethoxy group which makes the polymers hydrolytically stable.

In contrast to the polymerization of cyclic phosphazenes, simple alkyl/aryl-substituted phosphazenes can be prepared by a condensation process.<sup>4</sup> As part of our ongoing study of the derivative chemistry of the poly(alkyl/arylphosphazenes),<sup>5</sup> we have found that ferrocenyl units can be attached to polyphosphazenes through a two-carbon linkage. The synthesis and characterization of ferrocene-containing polyphosphazenes in which all phosphorus substituents are attached by direct  $\text{P}-\text{C}$  linkages are described below.

The deprotonation of poly(methylphenylphosphazene) by  $n\text{-BuLi}$  has been demonstrated by the preparation of silylated polyphosphazenes from the sequential treatment of  $[\text{Ph}(\text{Me})\text{PN}]_n$  with  $n\text{-BuLi}$  and various chlorosilanes (eq 1).<sup>5</sup> The comparable reactivity of the polymer anion and



typical organolithium reagents is further demonstrated by the reactions of the anion with acetylferrocene and ferrocenecarboxaldehyde (eq 2). In this manner, the ferrocenyl



moiety was readily attached to the phosphazene via the reaction of the  $\text{CH}_2^-$  anion sites along the backbone with the carbonyl functionality in the ferrocene compounds. These reactions typically gave high yields of new ferrocenylpolyphosphazenes with almost one ferrocenyl moiety for every two  $\text{P}=\text{N}$  units. Both 1 and 2 were slightly orange-colored materials that were soluble in THF, chlorinated hydrocarbons, and benzene.

As in the previous work,<sup>5</sup> the polymer anion was generated by treatment of 2.0 g of  $[\text{Ph}(\text{Me})\text{PN}]_n$  in 20 mL of dry THF with 0.5 equiv of  $n\text{-BuLi}$  at  $-78^\circ\text{C}$ . After the mixture was stirred for 1 h at  $-78^\circ\text{C}$ , the polymer anion was treated with a solution of ferrocenecarboxaldehyde (1.7 g in ca. 20 mL of THF) at  $-78^\circ\text{C}$ , and the mixture was allowed to warm to room temperature before being quenched with 2 mL of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . Precipitation into  $\text{H}_2\text{O}$ , purification by several precipitations from THF into hexanes and Soxhlet extraction with hexanes and ethanol, and, finally, drying at  $50^\circ\text{C}$  in a vacuum oven gave 3.0 g (81%) of polymer 1, in

(1) See for example: (a) Critchley, J. P.; Knight, G. J.; Wright, W. W. *Heat Resistant Polymers*; Plenum: New York, 1984. (b) Pittman, C. U., Jr. *Organometallic Reactions and Synthesis*; Plenum: New York, 1977; Vol. 6. (c) Neuse, E. W.; Khan, F. B. D. *Macromolecules* 1986, 19, 269. (d) Rockett, B. W.; Marr, G. J. *Organomet. Chem.* 1987, 318, 231. (e) Butler, I. R.; Cullen, W. R. *Organometallics* 1986, 5, 2537. (f) Withers, H. P.; Seyferth, D.; Fellman, J. D.; Garrou, P. E.; Martin, S. *Organometallics* 1982, 1, 1283.

(2) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* 1985, 18, 1340.

(3) Allcock, H. R.; Riding, G. H.; Lavin, K. D. *Macromolecules* 1987, 20, 6.

(4) (a) Neilson, R. H.; Wislan-Neilson, P. *J. Macromol. Sci., Chem.* 1981, A16, 425. (b) Neilson, R. H.; Hani, R.; Wislan-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* 1987, 20, 910. (c) Wislan-Neilson, P.; Neilson, R. H. *Inorg. Synth.*, in press.

(5) Wislan-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* 1986, 19, 2089.

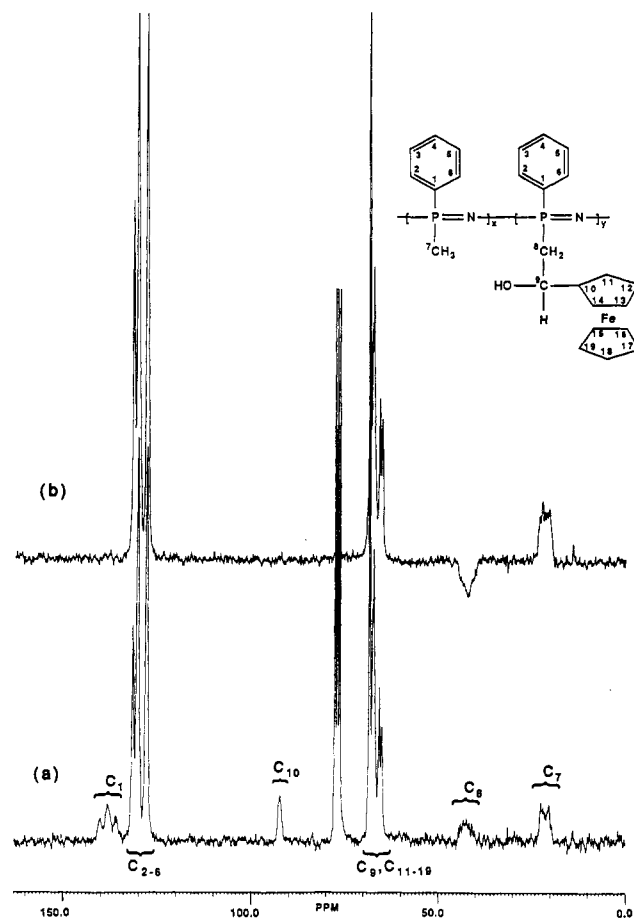


Figure 1.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of polymer 1 in  $\text{CDCl}_3$ : (a) normal spectrum; (b) DEPT spectrum with the signals for the  $\text{CH}_3$  and  $\text{CH}$  carbons up and the signals for the  $\text{CH}_2$  carbons down.

which the values of  $x$  and  $y$  are nearly equal. Integration of the phenyl and ferrocenyl protons in the  $^1\text{H}$  NMR spectrum<sup>6</sup> of 1 indicates that 45–50% of the pendant methyl groups have been substituted with the ferrocenyl group. This corresponds to a 90–100% reaction yield based on the amount of  $n\text{-BuLi}$  used. The elemental analyses<sup>6</sup> confirm the degree of substitution. Although the carbon and hydrogen analyses are not particularly informative due to the fact that the calculated values do not vary more than 0.5% over a range of 10–70% substitution, the nitrogen and iron analyses, which do vary significantly with the number of substituents, indicate a degree of substitution similar to that obtained from NMR integration.

The reaction of the acetylferrocene with the polymer anion at  $-78^\circ\text{C}$  was less successful since a lower degree of substitution was obtained. Typically, both integrations of the  $^1\text{H}$  NMR spectra and the elemental analyses<sup>7</sup> of 2 prepared in this manner showed that the degree of substitution was approximately 23%.

However, when the polymer anion was generated at  $-78^\circ\text{C}$ , stirred for 1 h, warmed to  $0^\circ\text{C}$ , and then allowed to react with a solution of acetylferrocene, the number of ferrocenyl moieties in polymer 2 was much higher. In fact,

(6) Polymer 1 (all NMR signals are broad singlets unless noted otherwise):  $^1\text{H}$  NMR  $\delta$  7.72, 7.24 (Ph), 3.92, 3.82 ( $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{H}_4$ ), 4.49 (H-CO), 5.91 (OH), 2.23–0.87 (m, Me,  $\text{CH}_2$ );  $^{31}\text{P}$  NMR  $\delta$  2.7, 0.5;  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  140.1, 138.2, 136.1 ( $\text{C}_1$ ), 131.5, 130.3, 127.9 ( $\text{C}_{2-6}$ ), 92.2 ( $\text{C}_{10}$ ), 65.0 ( $\text{C}_9$ ), 68.4, 67.6, 67.3, 65.7, ( $\text{C}_{11-19}$ ), 42.2 (m,  $\text{C}_8$ ), 22.1–20.5 (m,  $\text{C}_7$ ); GPC molecular weight,  $M_w$ , 187 000 (parent 135 000). Anal. Calcd for 45% substitution: C, 61.48; H, 5.40; N, 6.00; Fe, 10.76. Found: C, 60.90; H, 5.58; N, 5.48; Fe, 10.34.

integration of the  $^1\text{H}$  NMR spectrum indicated that approximately 32% of the methyl groups were now derivatized and elemental analyses gave a range of 36–40% substitution.<sup>7</sup> The thermal stability of the polymer anion is apparently greater than expected and certainly higher than that of the related monomer anion  $[\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{Me})\text{CH}_2^-]$  which begins to disappear at approximately  $-50^\circ\text{C}$ .<sup>8</sup> At the higher temperature nucleophilic attack at the carbonyl carbon by the polymer anion is apparently favored over quenching of the anion by abstraction of a proton from the methyl group of the acetylferrocene<sup>9</sup>—a problem which does not exist with ferrocenecarboxaldehyde.

The size exclusion chromatography analyses indicated that no degradation of the polymer backbone occurred in the preparation of either 1 or 2 since the molecular weight distributions (i.e.,  $M_w/M_n$ ) of the parent polymer and the new derivatives were nearly identical and significant molecular weight increases were observed.<sup>6,7</sup>

While the IR spectra of both 1 and 2 exhibited the expected O–H stretching frequency at  $3300\text{ cm}^{-1}$ , the most definitive spectral evidence for incorporation of the ferrocenyl moiety was the  $^{13}\text{C}$  DEPT NMR experiments.<sup>10</sup> As shown in Figure 1, the  $\text{CH}_2$  carbon at 42.2 ppm is clearly distinguished from all other carbons in polymer 1 because each of those carbons is attached to an odd number of protons. Since neither unreacted ferrocenecarboxaldehyde or the parent polyphosphazene contain a  $\text{CH}_2$  group, the presence of the  $\text{CH}_2$  signal clearly indicates that substitution has occurred. Furthermore, the DEPT spectrum aids in the assignment of the  $^{13}\text{C}$  chemical shifts of the quaternary carbons in both 1 and 2<sup>6,7</sup> and of the COH carbon in 2<sup>7</sup> because these signals are not observed in a DEPT spectrum.

By thermogravimetric analysis, the onsets of the major decomposition of both 1 and 2 occur between 350 and 380  $^\circ\text{C}$ , but slight deflections occur as early as 100  $^\circ\text{C}$ . Interestingly, the weight retained above 800  $^\circ\text{C}$  is remarkably high for polyphosphazenes which tend to form cyclics that sublime leaving very little residue. In fact 53% of the weight of 1 and 26% of the weight of the 23% substituted sample of 2 were retained.

Finally, the alcohol functionality in these polymers offers the potential for further derivatization of these materials. Preliminary experiments indicate that treatment of the polymers with  $\text{H}_2\text{SO}_4$  or heating above 200  $^\circ\text{C}$  for several hours results in insoluble, presumably cross-linked materials. Further studies of these types of reactions are in progress.

**Acknowledgment.** We thank the United States Army Research Office for generous financial support of this project.

(7) Polymer 2 (all NMR signals are broad singlets unless noted otherwise):  $^1\text{H}$  NMR  $\delta$  7.70, 7.14 (Ph), 6.5 (OH), 4.04, 3.89 ( $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{H}_4$ ), 2.30, 1.37, 0.89 (m,  $\text{CH}_2$ );  $^{31}\text{P}$  NMR  $\delta$  1.3, -0.9;  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  140.7, 138.1 ( $\text{C}_1$ ), 131.4, 130.5, 129.6, 127.6 ( $\text{C}_{2-6}$ ), 100.9 ( $\text{C}_{10}$ ), 69.8 ( $\text{C}_9$ ), 68.4, 66.8, 65.6, 65.2 ( $\text{C}_{11-19}$ ), 47.7 (m,  $\text{C}_8$ ), 30.7 ( $\text{H}_3\text{C-COH}$ ), 22.8–20.9 (m,  $\text{C}_7$ ); GPC molecular weight,  $M_w$ , 154 000 (parent 135 000). Anal. Calcd for 23% substitution: C, 61.84; H, 5.72; N, 7.39; Fe, 6.77. Found: C, 61.71; H, 5.97; N, 6.87; Fe, 6.71. Calcd for 36% substitution: C, 62.02; H, 5.66; N, 6.39; Fe, 9.17. Found: C, 61.85; H, 5.94; N, 6.39; Fe, 9.38.

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