Strain-Induced Ring-Opening Polymerization of Ferrocenylorganocyclotriphosphazenes: A New Synthetic Route to Poly(organophosphazenes)

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Abstract: The strained transannular ferrocenylcyclotriphosphazenes $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3R(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ [R = OPh, R = Me, R = Ph (R geminal to Cp), and R = Ph (nongeminal to Cp)], and $N_3P_3R_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ [R = Ph (geminal to Cp) and R = Ph (nongeminal to Cp)] undergo ring-opening polymerization when heated at 250 °C in the presence of a small amount (1%) of $(NPCl_2)_3$, which functions as a polymerization initiator. The cyclic trimers N_3P_3-$(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3Me(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$, and $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (Ph groups nongeminal to Cp) also polymerize at 250 °C but in the absence of $(NPCl_2)_3$. These transformations are the first examples of uncatalyzed ring-opening polymerization of cyclic phosphazenes that lack phosphorus–halogen bonds. By contrast, the sterically crowded cyclotriphosphazene $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ undergoes ring expansion to the corresponding cyclic hexamer when heated at 250 °C in the presence or absence of $(NPCl_2)_3$, but it does not polymerize. When heated in the absence of $(NPCl_2)_3$, $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$, $N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$, and $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (Ph nongeminal to Cp) also undergo ring expansion to form the corresponding cyclic hexamers. The Lewis acid BCl_3 initiates the ring-opening polymerization of $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ and catalyzes the ring expansion of $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$. Possible explanations for the differences in thermal behavior are given. The implications of these results for the mechanisms of phosphazene ring-opening polymerization and ring–ring equilibration are also discussed.

Ring-opening polymerization provides an important synthetic route to both organic and inorganic polymers.[1-4] In most cases, the presence of ring strain within the cyclic monomer provides a driving force for the polymerization process. We have utilized the deliberate introduction of ring strain as a means to enhance the polymerizability of cyclic phosphazenes. This provides a route for the polymerization of cyclic species that do not normally polymerize or that do so only at relatively high temperatures.[5-7] This methodology may also be useful for the polymerization of other cyclic inorganic or organic compounds that have so far resisted polymerization.

The main synthetic route to poly(organophosphazenes) involves the thermal ring-opening polymerization of hexachlorocyclo-triphosphazene (1) to yield poly(dichlorophosphazene) (2).[8-11] This macromolecular intermediate then serves as a substrate for chlorine atom replacement by organic nucleophiles to give polymers of general formula 3 (Scheme I, route A). An alternative route to a variety of poly(organophosphazenes) involves the condensation polymerization of N-silylphosphoranimines.[12-14] In principle, a third route to phosphazene polymers involves the introduction of organic or organometallic side groups at the cyclic trimer level (to give 4) followed by ring-opening polymerization

Scheme I
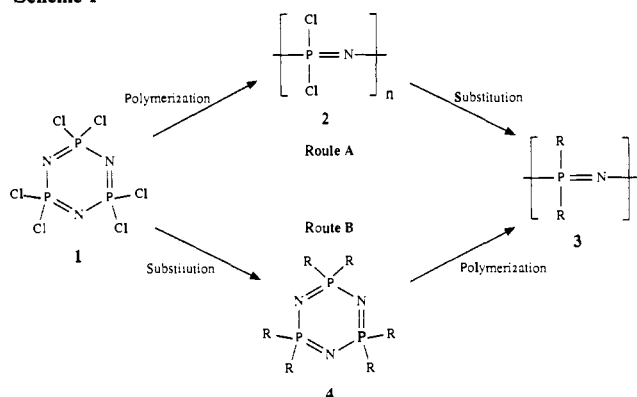
of these species (Scheme I, route B). Many substitution reactions, especially with organometallic or transition metal nucleophiles, are easier to perform at the small-molecule level due to the absence of side reactions that occur with the corresponding high polymers.[15,16] If synthesis route B could be exploited, the range of phosphazene high polymers might be broadened considerably. Many cyclic phosphazenes which possess *both* organic and halogen side groups can be induced to polymerize, but previous studies have shown that cyclotriphosphazenes of general structure $(NPR_2)_3$ (R = OCH_2CF_3, OPh, Ph, or Me), when heated, participate only in ring-expansion reactions to form higher cyclic species such as tetramers, pentamers, and hexamers.[17-19]

Recently, we reported the first ring-opening polymerization of a cyclic phosphazene which lacks halogen side groups.[7] The cyclic trimer, $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (5), polymerizes when heated at 250 °C in the presence of a small amount (1 mol %) of $(NPCl_2)_3$, which functions as a polymerization initiator. This provided the first access to the third synthetic route to poly-

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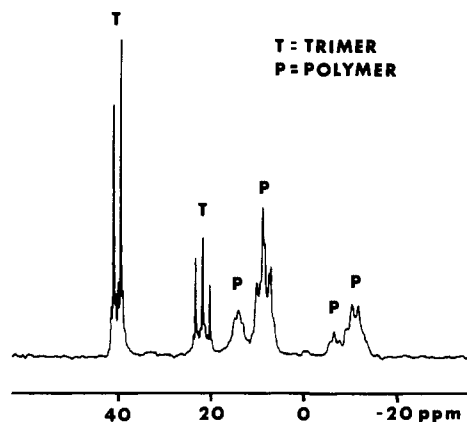(19) Allcock, H. R.; Riding, G. H. Unpublished results.

A New Synthetic Route to Poly(organophosphazenes)

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Figure 1. ^{31}P NMR spectrum (36.27 MHz) after heating **5** in the presence of 1% (NPCl$_2$)$_3$.

phosphazenes (Scheme 1, route B) discussed above. The ability of **5** to undergo polymerization is believed to result from ring strain imparted to the phosphazene ring by the transannular ferrocenyl group. The presence of ring strain is apparent from the non-planarity of the phosphorus–nitrogen ring as determined by an X-ray crystallographic study of **5**.[20]

By contrast, when the tetraphenoxy analogue N$_3$P$_3$(OPh)$_4$(η-C$_5$H$_4$)$_2$Fe (**19**) is heated at 250 °C in the presence of 1% (NPCl$_2$)$_3$, only ring expansion to the corresponding cyclic hexamer occurs.[7] Although structurally similar to **5**,[20] the inability of **19** to polymerize is attributed to the presence of the bulky phenoxy groups, which prevent the formation of a linear polymer. Thus, the nonferrocenyl side groups provide a means for a subtle control of polymerization versus ring expansion.

These contrasting results prompted us to study the influence of other side groups and substitution patterns on the thermal behavior of ferrocenylorganocyclotriphosphazenes. In addition to **5** and **19**, we have explored the polymerization of mixed substituent species that contain alkoxy side groups together with aryloxy (**11**), alkyl (**15**), and aryl (**7, 9, 13**, and **17**) moieties. The syntheses of these compounds are described elsewhere.[20]

The overall objectives of this work were the following: (1) to explore the scope of this new synthetic route, (2) to determine the factors which influence the formation of linear polymers versus higher cyclic species, and (3) to examine the implications of the results with respect to the mechanism of phosphazene polymerization.
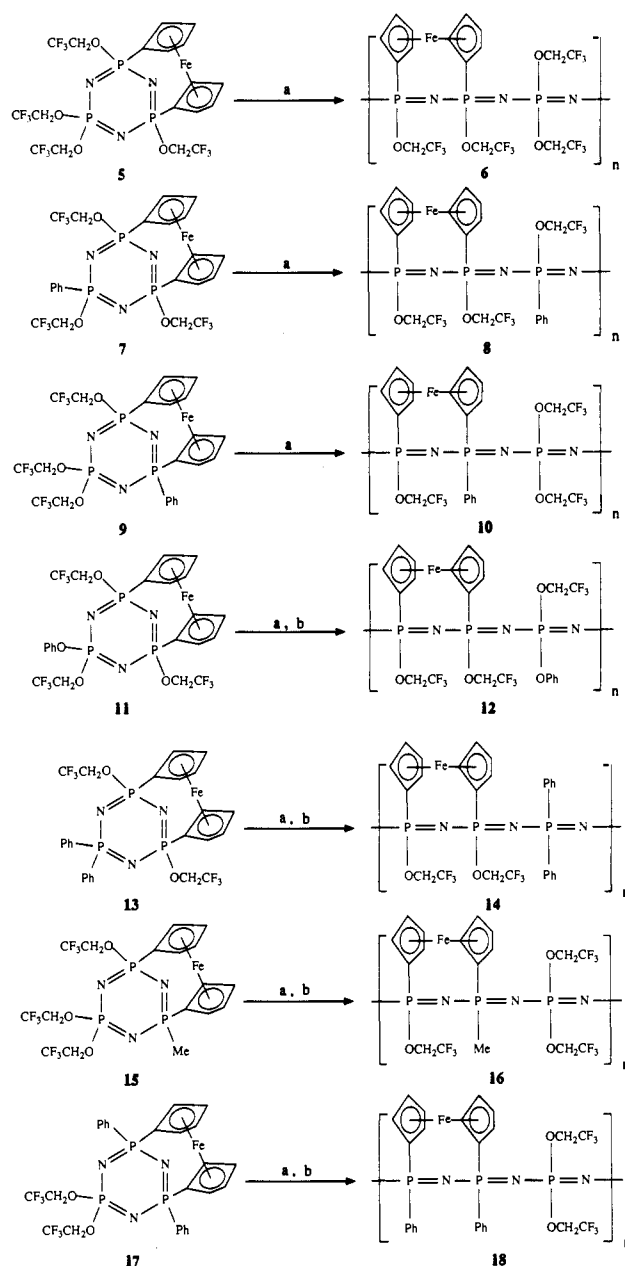
Results and Discussion

In the following discussion, the thermal behavior of ferrocenylorganocyclotriphosphazenes, both in the presence and absence of (NPCl$_2$)$_3$, is described first. Experiments involving the initiation of polymerization by BCl$_3$ and the concentration dependence of (NPCl$_2$)$_3$ will then be discussed. Following this, we will consider the significance of the results with regard to the phosphazene polymerization and ring–ring equilibration mechanisms.

Ring Expansion and Polymerization in the Presence of (NPCl$_2$)$_3$. Initial attempts to polymerize species **5** by heating this compound alone at 250 °C resulted in the formation of a cyclic hexamer (**21**) in low yield (see below). Subsequent experiments were carried out with the addition of a small amount of (NPCl$_2$)$_3$, which is known to act as a polymerization initiator for the pendent ferrocenylcyclotriphosphazene N$_3$P$_3$F$_5$(η-C$_5$H$_4$)Fe(η-C$_5$H$_5$).[5]

When cyclic trimer **5** was heated in the melt at 250 °C in the presence of a small amount (1%) of (NPCl$_2$)$_3$ a gradual increase in viscosity occurred, and this suggested that a polymerization process had taken place. The ^{31}P NMR spectrum of the reaction mixture (Figure 1) contained resonances that corresponded to unreacted starting trimer and linear polymer **6** (Scheme II).

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Scheme II^a

^{a}(a) 250 °C with 1 mol % (NPCl$_2$)$_3$. (b) 250 °C.

Several reprecipitations from THF into hexanes gave pure **6** as an amber-colored, film-forming material. The 36.27-MHz ^{31}P NMR spectrum of **6** consisted of four broad resonances at 13.0, 7.4, −8.7, and −13.5 ppm. These resonances appear to arise from two A$_2$X spin systems (fine structure unresolved). By contrast, related polymer **6a**, obtained by the polymerization of N$_3$P$_3$F$_4$-(η-C$_5$H$_4$)$_2$Fe followed by treatment with NaOCH$_2$CF$_3$, generates only one ^{31}P NMR A$_2$X spin system (8.3 and −11.8 ppm).[5] However, high-field ^{31}P NMR spectroscopic analysis of these polymers provides additional information regarding resonance assignments and polymer structure (see below).

The ^{1}H NMR spectrum of **6** contained a broad peak at 4.5 ppm, which corresponds to coincident resonances of the methylene and cyclopentadienyl protons. The weight-average molecular weight (M_w), as estimated by gel permeation chromatography (GPC), was 9.4 × 10^5, and the number-average molecular weight (M_n) was 1.8 × 10^5. There was no evidence for the presence of cyclic oligomers in the GPC chromatogram. Additional characterization was achieved by elemental analysis. The elemental ratios were consistent with the assigned structure, assuming that the small
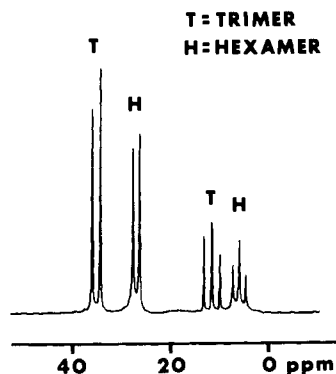
Figure 2. ^{31}P NMR spectrum (36.27 MHz) after heating **19** in the presence of 1% $(NPCl_2)_3$.

amount of $(NPCl_2)_3$ used as an initiator was incorporated into the polymer. Differential scanning calorimetry (DSC) analysis showed a glass transition temperature (T_g) at 68 °C. This is close to the value of 61 °C found previously for **6a**.[5]

Identical polymerization experiments were carried out with the other cyclic compounds (**7, 9, 11, 13, 15, 17**, and **19**). With the exception of **17** and **19**, all were found to behave similarly to yield, respectively, polymers **8, 10, 12. 14,** and **16**. These results are summarized in Scheme II. The polymeric products were isolated and characterized in a manner similar to that of **6**. Several of these polymers were selected for DSC analysis and were found to be amorphous glasses with glass transition temperatures ranging from 65 °C (for **12**) to 92 °C (for **16**). The reaction times for polymerization varied widely from 20 min (for **13**) to 7 days (for **9**).

By contrast, when the tetraphenoxy cyclic species **19** was heated at 250 °C in the presence of 1% $(NPCl_2)_3$ for 14 days, no significant increase in viscosity occurred. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed the presence of unreacted **19** and the cyclic hexamer **20** (Scheme III). The hexamer generated an A_2X spin pattern similar to that of **19** but shifted to higher field (Figure 2). Separation of **20** from **19** was achieved by column chromatography and recrystallization. The ^1H NMR spectrum of **20** showed slightly broadened resonances for the phenoxy and cyclopentadienyl protons but was otherwise identical to that of **19**.[20] The electron impact mass spectrum of **20** clearly showed the presence of the molecular ion at m/e 1382. The fast atom bombardment (FAB) mass spectrum of **20** also showed evidence for the formation of small amounts of the cyclic nonamer $[N_9P_9(OPh)_{12}\{(\eta-C_5H_4)_2Fe\}_3]$ (molecular ion at m/e 2073) and cyclic dodecamer $[N_{12}P_{12}(OPh)_{16}\{(\eta-C_5H_4)_2Fe\}_4]$ (molecular ion at m/e 2764).

The thermal behavior of **17** proved to be more complex. When **17** was heated at 250 °C in the presence of 1% $(NPCl_2)_3$ for 6 days, the reaction mixture became highly viscous. Analysis by ^{31}P NMR spectroscopy showed resonances that corresponded to unreacted **17** and a new A_2X spin system (δ 24.3 d, 12.9 t, $^2J_{PNP}$ = 29 Hz), which comprised approximately 10% of the reaction mixture (as determined by NMR integration). In addition, other broad resonances at 9.4, 5.3, and −20.0 ppm were present, which constituted another 10% of the reaction mixture. It is likely that these separate resonance systems correspond to cyclic hexamer and linear polymer (**18**), respectively. However, the two products could not be separated satisfactorily, and their structures could not be confirmed. The brown polymeric material obtained by repeated reprecipitations from THF into hexanes was shown by GPC analysis to have a very broad molecular weight distribution extending from 3.3×10^3 to 1.0×10^6 with a peak maximum at 5.0×10^3.

Ring Expansion and Polymerization in the Absence of $(NPCl_2)_3$. Each of the above experiments was conducted in conjunction with a control reaction which was a sample of identical trimer that contained no $(NPCl_2)_3$ initiator. In each case, the controls were subjected to exactly the same polymerization conditions. Because these pure materials also underwent thermal reactions, they are

Scheme III[a]
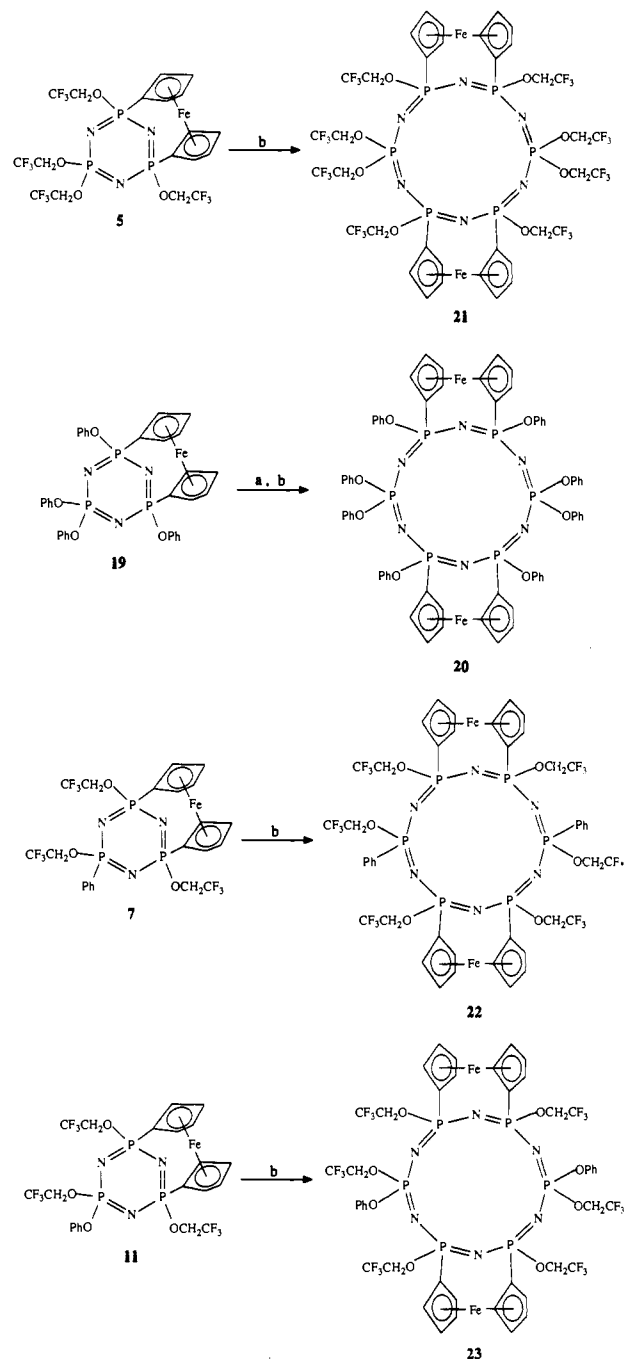
[a](a) 250 °C with 1 mol % $(NPCl_2)_3$. (b) 250 °C.

discussed here as a separate issue.

When $N_3P_3(OCH_2CF_3)_4(\eta-C_5H_4)_2Fe$ (**5**) was heated at 250 °C for 14 days, virtually no increase in the melt viscosity was detected. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed the presence of unreacted **5** and a small amount (ca. 3%) of the corresponding cyclic hexamer (**21**, Scheme III). The hexamer was isolated in low yield as a yellow-brown powder following column chromatography and recrystallization. The ^{31}P NMR spectrum of **21** consisted of an A_2X spin system (δ 32.7 d, 13.9 t, $^2J_{PNP}$ = 46 Hz) similar to that of **5** (δ 40.9 d, 21.2 t, $^2J_{PNP}$ = 59 Hz) but shifted to higher field. Further evidence for the structure of **21** was obtained by mass spectral analysis, which showed the molecular ion at m/e 1430.

Similar experiments were carried out with the other trimers (**7, 9, 11, 13, 15, 17,** and **19**). Species **7** and **19** behaved in a manner similar to **5** to give cyclic hexamers **22** and **20**, respectively (Scheme III). These products were isolated in low yield as

yellow-brown powders after column chromatography and recrystallization. Characterization was achieved by ^{31}P and ^1H NMR spectroscopy and mass spectrometry.

In marked contrast to the thermal behavior of **5**, **7**, and **19**, several of the trimers polymerized when heated in the *absence* of $(NPCl_2)_3$. For example, when diphenyl species **13** was heated alone at 250 °C, a rapid increase in viscosity occurred over a period of 30 min. The resultant polymeric product (**14**, Scheme II), when separated from unreacted **13**, yielded a ^{31}P NMR spectrum that consisted of a single, very broad peak centered at 16.1 ppm ($\nu_{1/2}$ = 140 Hz). This was assigned to the coincident resonances of the two phosphorus environments. The ^1H NMR spectrum contained broad resonances at 7.5 ppm (phenyl protons) and 3.7 ppm (methylene and cyclopentadienyl protons) in an approximately 5:6 ratio by integration. The macromolecular nature of the product was confirmed by GPC analysis, which showed a broad molecular weight distribution from 7.0×10^3 to 1.5×10^6 that was centered at 4.3×10^4.

Compounds **11** and **15** polymerized under similar conditions to form products **12** and **16**, respectively. However, during the conversion of **11** to polymer **12**, a significant amount of cyclic hexamer **23** was also formed. Although **23** could not be purified satisfactorily, the ^{31}P NMR spectrum (δ 31.9 d, 10.3 t, $^2J_{PNP}$ = 44 Hz) and FAB mass spectrum (m/e 1419 = M^+ + H) provide strong evidence for the proposed structure.

When **17** was heated at 250 °C for 11 days, the tube contents became nearly immobile. The ^{31}P NMR spectrum of the reaction mixture was virtually identical to that found for the thermal polymerization of **17** in the presence of $(NPCl_2)_3$, discussed above. As before, the products could not be separated or fully characterized.

By contrast, compound **9** underwent no detectable reaction under similar conditions. When heated at 250 °C for 14 days, no viscosity increase was observed, and analysis of the reaction mixture by ^{31}P NMR spectroscopy showed only the presence of unreacted **9**.

Each of the above experiments was repeated at least once in order to check the reproducibility of the results. Although the reaction times and product yields varied slightly, the same products were detected in the duplicate experiments.

Initiation of Polymerization. Boron trichloride is known to facilitate the ring-opening polymerization of $(NPCl_2)_3$.[21] It was of interest, therefore, to determine the influence of BCl_3 on the thermal behavior of ferrocenylcyclotriphosphazenes that lack phosphorus–halogen bonds.

When **5** was heated at 250 °C for 6 days in the presence of 1 mol % of BCl_3, both cyclic hexamer **21** and high polymer **6** were produced in 32% and 17% yields, respectively (as determined by ^{31}P NMR integration). The GPC chromatogram of the reaction mixture showed a broad molecular weight distribution centered at 2.9×10^4, which ranged from 3.0×10^3 to 3.2×10^6. By contrast, when **19** was heated at 250 °C with 1% BCl_3, ^{31}P NMR analysis showed the formation of cyclic hexamer **20** in 34% yield. Thus, BCl_3 initiates the polymerization of **5** and also facilitates the ring expansion of **19**. In this sense, BCl_3 mimicks the behavior of $(NPCl_2)_3$. The formation of cyclic hexamer **21** from the thermolysis of **5** under these conditions is probably a consequence of the longer reaction time (6 days). In general, longer reaction times favor equilibration to higher yields of cyclic hexamer.

Additional experiments were conducted to determine the minimum concentration of $(NPCl_2)_3$ required to initiate the polymerization of **5**. Samples of compound **5** were heated at 250 °C with varying concentrations of $(NPCl_2)_3$ (0.01, 0.1, 1.0, and 10.0 mol %). A concentration of 1% $(NPCl_2)_3$ was the minimum required to initiate polymerization, and no polymerization occurred when lower concentrations of $(NPCl_2)_3$ were used (0.01 or 0.1%). Interestingly, when a higher concentration was employed (10%), excess $(NPCl_2)_3$ remained in the reaction mixture (as determined by ^{31}P NMR spectroscopy). In both cases, elemental analysis

indicated the incorporation of approximately 1% $(NPCl_2)_3$ into the isolated polymer.

Mechanistic Implications: Ring-Opening Polymerization vs Ring–Ring Equilibration. Previous studies have shown that the ability of a cyclic phosphazene to polymerize at elevated temperatures or to participate in ring–ring equilibration reactions depends on the number and size of the organic side groups bonded to the ring. Thus, the halocyclotriphosphazenes, $(NPX_2)_3$ (X = F, Cl, Br), undergo ring-opening polymerization when heated,[22-25] but organocyclotriphosphazenes, $(NPR_2)_3$ (R = alkyl, aryl, alkoxy, aryloxy), instead participate in ring-expansion reactions to yield higher cyclic species.[17-19] On the other hand, organohalocyclotriphosphazenes undergo either ring-opening polymerization or ring–ring equilibration, depending on the number and size of the organic side groups present. For example, *non-gem*-$(NPClMe)_3$ polymerizes to a high molecular weight polymer at 250 °C, whereas *non-gem*-$(NPClEt)_3$ undergoes ring expansion to give cyclic tetramer, pentamer, and hexamer.[26]

In this work, the cyclic ferrocenylorganophosphazenes reacted at elevated temperatures to give cyclic hexamers and/or linear polymers depending on (1) the steric bulk of the organic substituents, (2) the presence or absence of a polymerization initiator, and (3) the reaction time. For example, the tetraphenoxy derivative, **19**, could not be induced to polymerize under any conditions. Even in the presence of $(NPCl_2)_3$ or BCl_3 as polymerization initiators, **19** yielded mainly the corresponding cyclic hexamer **20**. This suggests that the sterically demanding phenoxy groups of **19** prevent the formation of a linear polymer, regardless of the reaction conditions. Steric repulsions between side groups are expected to be more severe in a linear polymer than in the corresponding small-molecule cyclic species.[27,28] Therefore, bulky phenoxy substituents are likely to favor cyclic trimers and hexamers.

The trifluoroethoxy analogue, **5**, also yielded a cyclic hexamer (**21**) when heated at 250 °C. However, this reaction was slow (14 days) and the yield was very low (ca. 3%). The observation that **5** undergoes polymerization at 250 °C in the presence of 1% $(NPCl_2)_3$ indicates that the less sterically demanding trifluoroethoxy groups allow the formation of linear polymer. Nevertheless, the presence of an initiator is required for polymerization. Similar thermal behavior has been observed previously for the cyclic phosphazene, $N_3P_3F_5(\eta-C_5H_4)Fe(\eta-C_5H_5)$, which does not polymerize when heated alone at 250 °C, but does yield high polymer when heated with 1% $(NPCl_2)_3$.[5]

The introduction of other side groups in addition to trifluoroethoxy leads to significant changes in thermal behavior. For example, compound **11** represents a structural hybrid of **5** and **19** since it contains both trifluoroethoxy and phenoxy side groups. However, the observation that **11** reacts to yield both polymer **12** and hexamer **23** shows that its thermal reactivity is markedly different from that of both **5** and **19**. It is not clear why **11** polymerizes in the absence of an initiator whereas **5** does not. The bulky phenoxy group of **11** would probably generate even more steric resistance to polymerization as compared to the situation in **5**. However, compound **11** was isolated as an inseparable mixture of cis and trans isomers.[20] It is possible that the cis isomer is the more highly strained species due to transannular steric interactions between the phenoxy group and the ferrocenyl unit (this hypothesis is developed in more detail for **13** below). The cis isomer may therefore be responsible for the initiation of polymerization.

Contradictions begin to arise when comparing the thermal behavior of the other cyclic trimers. For example, diphenyl species

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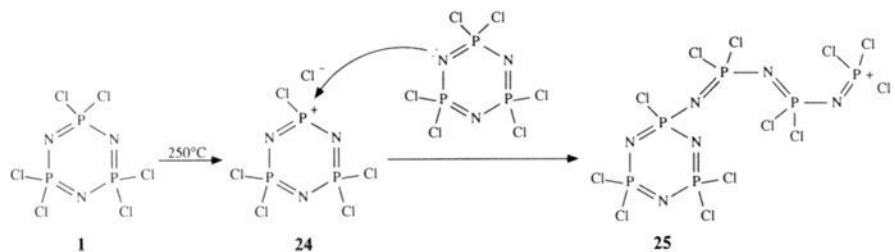(25) Cordischi, D.; Site, A. D.; Mele, A. *J. Macromol. Chem.* **1966**, *1*, 219.
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Scheme IV

13 polymerized when heated in the absence of an initiator, but monophenyl species **7**, when treated to the same conditions, underwent ring expansion to cyclic hexamer **22**. The two phenyl groups of **13** would be expected to inhibit polymerization relative to the single phenyl group of **7**. One possible explanation for this disparity is that **13** is more highly strained than **7** as a result of transannular steric interactions between the cis phenyl group and the cyclopentadienyl rings (**7** was isolated as a single isomer, presumably trans). Speculative evidence for this is provided by the X-ray crystal structure of **13**.[20] A lateral view of this species and a space-filling model are shown in Figure 3. Steric interactions may be possible between the cis phenyl protons and the cyclopentadienyl protons, especially when rotation of the cis aryl moiety about the P–C(phenyl) bond is considered. Such interactions may serve to further increase the enthalpy of **13**, thereby making polymerization more facile.

The methyl derivative, **15**, also polymerized when heated at 250 °C in the absence of an initiator. However, phenyl species **9** was completely unreactive under the same conditions. It seems unlikely that steric hindrance alone could explain this contrasting thermal behavior. It may also be that the electron-donating methyl group of **15** stabilizes cationic intermediates in the polymerization initiation and propagation steps. However, this explanation would not account for why **9** is unreactive when heated in the absence of (NPCl$_2$)$_3$, while diphenyl species **17** apparently polymerizes when treated to the same conditions.

Mechanism of Polymerization. These studies are important with respect to the phosphazene ring-opening polymerization mechanisms. The generally accepted mechanism for the polymerization of (NPCl$_2$)$_3$ involves initiation via P–Cl bond ionization to form **24** (Scheme IV). This is followed by an attack by the resulting phosphazenium ion on another trimer molecule (to form **25**).[23,24] Species **25** thus begins propagation and chain polymerization.

The observation that compounds **5, 7,** and **9** require the presence of a small amount of (NPCl$_2$)$_3$ for polymerization is consistent with P–Cl bond ionization during the initiation step. Although initial CF$_3$CH$_2$O/Cl metathesis between the ferrocenylorganophosphazenes and (NPCl$_2$)$_3$ cannot be ruled out, because only a catalytic amount of (NPCl$_2$)$_3$ is required for polymerization, phosphorus–halogen bonds are clearly not necessary for chain propagation in these species.

By contrast, species **11, 13,** and **15** polymerized in the absence of an initiator. Thus, a different initiation mechanism must operate in these cases. One possibility involves the ionization of trifluoroethoxy side groups to generate species such as **26** (as il-
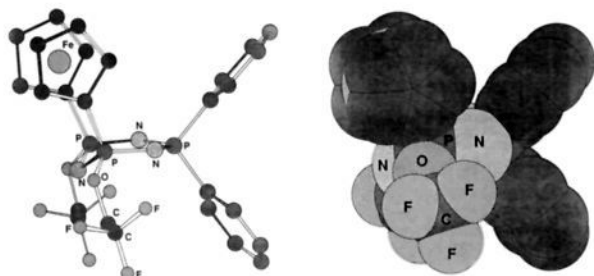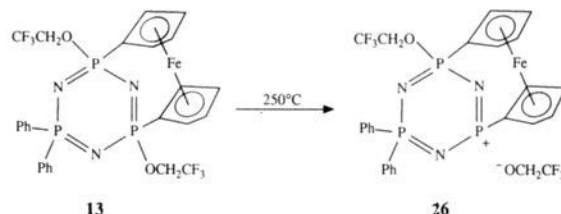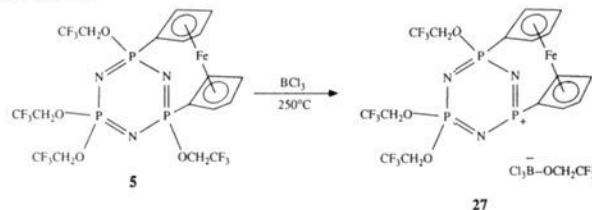
Scheme V

Scheme VI

lustrated for the polymerization of **13** in Scheme V). This would be consistent with the observation that the polymerization rates of **11, 13,** and **15** appeared to increase in the presence of (NPCl$_2$)$_3$, since the ionization of P–Cl bonds would be expected to be more facile than that of P–OCH$_2$CF$_3$ bonds because Cl⁻ is the better leaving group. Nevertheless, the observation that **11, 13,** and **15** (and presumably **17**) polymerize in the absence of an external initiator indicates that phosphorus–halogen bonds are not necessarily required for access to a phosphazene polymerization mechanism. It had been assumed previously that phosphorus–halogen bonds were required for both the initiation and propagation steps.

Boron trichloride is believed to function as a polymerization initiator for (NPCl$_2$)$_3$ either by acting as a halide ion acceptor or by facilitating the opening of the phosphazene ring.[21] It is probable that BCl$_3$ reacts in a similar manner with **5**. Thus, BCl$_3$ might assist in the abstraction of CF$_3$CH$_2$O⁻ groups (Scheme VI). Alternatively, BCl$_3$ might induce ring opening by coordination to a skeletal nitrogen atom. An additional possibility is that BCl$_3$ and N$_3$P$_3$(OCH$_2$CF$_3$)$_4$(η-C$_5$H$_4$)$_2$Fe undergo CF$_3$CH$_2$O/Cl metathesis, which would allow for P–Cl bond ionization as the initiation step. This mechanism would be consistent with previous observations of CF$_3$CH$_2$O/Cl metathesis in the thermal reactions of BCl$_3$ with [NP(OCH$_2$CF$_3$)$_2$]$_3$.[29]

Mechanism of Ring–Ring Equilibration. Any plausible mechanism for phosphazene ring–ring equilibration must be consistent with the observation that this process is accessible to cyclophosphazenes with nonionizable alkyl and aryl side groups. For example, the cyclic trimers (NPR$_2$)$_3$ (R = Ph or Me) give mixtures of the corresponding cyclic tetramer, pentamer, and hexamer when heated at elevated temperatures.[18,19] One possible mechanism for this ring expansion involves initial heterolytic cleavage of a skeletal phosphorus–nitrogen bond in the cyclic trimer to yield a zwitterionic intermediate (**28**, Scheme VII), which subsequently attacks another trimer molecule to yield a cyclic hexamer (**29**). Support for this mechanism was obtained previously from studies on the thermal behavior of organohalocyclotriphosphazenes.[26] In

Figure 3. Molecular structure of **13** derived from X-ray diffraction positional parameters using Chem3D.[20] Left: side view. Right: space-filling model.

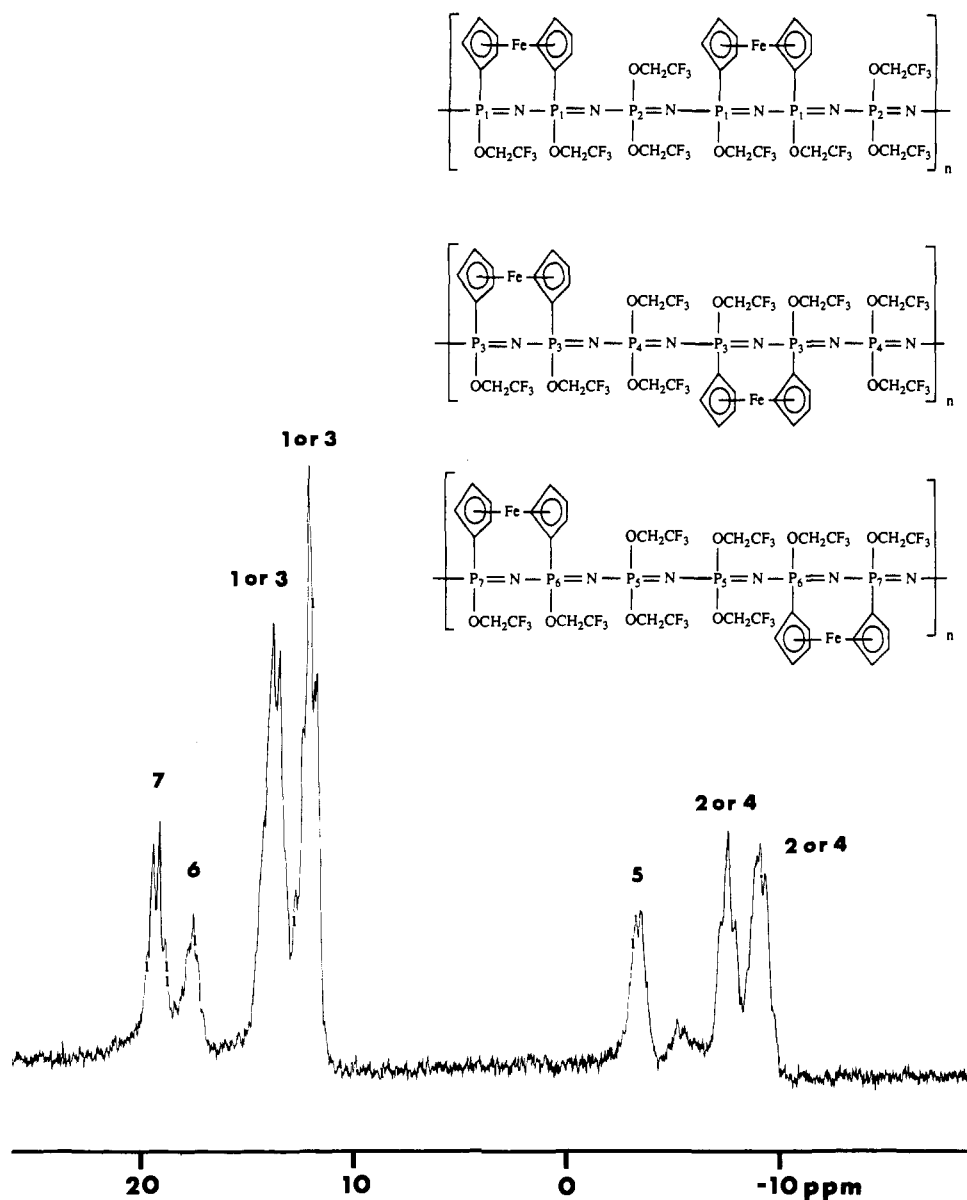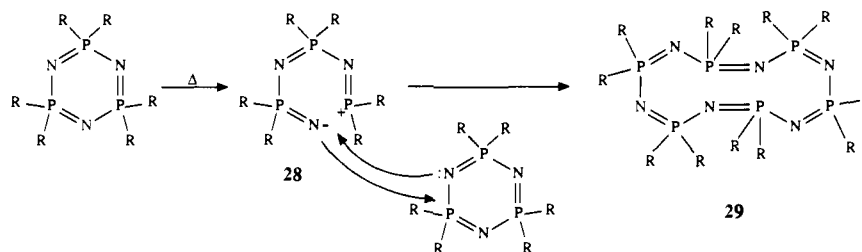(29) Horn, H. G.; Kolkmann, F. *Makromol. Chem.* **1982**, *183*, 1843.

Figure 4. ^{31}P NMR spectrum (145.81 MHz) of polymer **6**.

Scheme VII

that work, the detection of an initial increase and a subsequent decrease in the concentration of cyclic hexamers during equilibration reactions provided evidence that the initial step involved a fusion of two cyclic trimer molecules. The results of the present work provide additional support for this trimer fusion process. Thus, a number of ferrocenylorganocyclotriphosphazenes (**5**, **7**, and **19**) were found to yield cyclic hexamer almost exclusively when heated. The detection of small amounts of the cyclic nonamer and cyclic dodecamer in the case of **19** suggests that the cyclic hexamer and cyclic nonamer are also capable of undergoing fusion with trimer molecules.

Molecular Structures of 6 and 6a. Analysis of **6** by high-field ^{31}P NMR spectroscopy allowed for more precise resonance as-

signments and also provided information about the polymer structure. The 145.81-MHz ^{31}P NMR spectrum of **6** is shown in Figure 4. The resonances at 14.1, 12.2, −7.5, and −9.0 ppm are present in an approximately 2:2:1:1 ratio, respectively, and appear to result from two overlapping A_2X spin systems (fine structure unresolved) arising from different stereoisomers of the head-to-tail structure. One set of resonances is assigned to an isomer in which adjacent ferrocenyl groups are trans to one another, and the other set is assigned to the analogous cis arrangement. The remaining three resonances (19.5, 17.5, and −3.4 ppm) are believed to result from head-to-head polymerization. There is no evidence to suggest that they arise from macrocyclic species. The presence of only three resonances for the head-to-head

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structural arrangement suggests that a single stereoisomer is present. This may be trans because the cis isomer would probably be more sterically hindered.

By contrast. polymer **6a**. obtained via the ring-opening polymerization of $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ to give $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]_n$ followed by treatment of this species with $NaOCH_2CF_3$,[5] consists almost exclusively of the head-to-tail positional arrangement. The 145.81-MHz ^{31}P NMR spectrum of this polymer contains broad resonances at 14.1, 12.2, -7.5, and -9.0 ppm, which were assigned to the head-to-tail structure as discussed above. Resonances at 19.5, 17.7, and -3.7 ppm, arising from the head-to-head isomer, are present only in trace amounts. Thus, the head-to-tail structure is predominant.

These spectra suggest that the head-to-tail or head-to-head preference of the polymerization process is strongly influenced by the bulky ferrocenyl group. However, the resultant polymer structure also appears to depend on the size of the cosubstituents. Thus, the presence of the small fluorine atoms in $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$ seems to favor the less hindered head-to-tail polymer structure. By contrast, the formation of **6** from **5** may be less regiospecific because the head-to-tail and head-to-head isomers are more equally encumbered due to the presence of the relatively bulky trifluoroethoxy groups. However, even here the head-to-tail placement still appears to predominate.

Conclusions

The results described here demonstrate that, by generating ring strain through the use of transannular ferrocenyl groups, it is possible to induce the ring-opening polymerization of a range of cyclotriphosphazenes which might otherwise be expected to resist polymerization. Use of this method has led to the development of a new synthetic route to phosphazene polymers.

The finding that several fully organo-substituted ferrocenyl-phosphazenes polymerize thermally in the absence of any added initiator is of particular mechanistic significance. These species provide the first examples of the uninitiated ring-opening polymerization of cyclotriphosphazenes which lack phosphorus–halogen bonds. These results are notable because it had been assumed previously that phosphorus–halogen bonds were required for both the initiation *and* propagation steps in the polymerization of cyclic phosphazene compounds.

The high-field ^{31}P NMR analysis of polymer **6** reveals the first example, to our knowledge, of a phosphazene polymer with both head-to-tail and head-to-head structural arrangements. Thus, the ring-opening polymerization of cyclophosphazenes is not necessarily regiospecific and may be influenced by side group steric interactions.

The methodology described here also has important implications for the synthesis of polymers from other cyclic inorganic or organic compounds which have so far resisted polymerization. The introduction of ring strain into such species should be a challenging area for future exploration.

Experimental Section

Materials. Cyclic trimers **5, 7, 9, 11, 13, 15, 17,** and **19** were prepared by methods reported elsewhere.[20] Polymer **6a** was synthesized as described previously.[5] Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by sublimation (0.05 mmHg, 40 °C). BCl_3 (Aldrich) was used as received.

Analytical Equipment and Techniques. Polymerizations were carried out by sealing samples under vacuum (0.01 mmHg) in thick-walled Pyrex tubes (5 cm × 0.5 cm). The tubes were cleaned and dried before use by soaking for at least 1 day in concentrated 2-propanol/KOH, followed by rinsing with distilled/deionized water and then drying overnight at 125 °C. All experiments were carried out at 250 °C using thermoregulated ovens which were equipped with mechanical rocking devices to provide continuous tube agitation. NMR spectra were recorded for $CDCl_3$ (^1H) or THF (^{31}P) solutions using either a JEOL FX-90Q or a Bruker WM-360 NMR spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or internal $CHCl_3$ (^1H). Glass transition temperatures were determined with the use of a Perkin-Elmer DSC 7 instrument. Sample weights were between 8 and 11 mg. The samples were heated initially to 115 °C to remove any residual solvent and were then rapidly cooled to 0 °C. Measurements were made at a heating rate of 20°/min. Polymer molecular weights were estimated by means of a Hewlett-

Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 3392 refractive index detector. A calibration curve was established using polystyrene standards. Fractionated samples of poly[bis(trifluoroethoxy)phosphazene] of known molecular weight averages (as determined by light scattering and membrane osmometry) were provided by Drs. R. Singler, M. Sennett, and G. Hagnauer (Army Materials Technology Laboratory, Watertown, MA) and were used as controls for our GPC work. Satisfactory agreement was obtained between the polystyrene calibration curve and the poly[bis(trifluoroethoxy)phosphazene] controls. Polymer samples were prepared at a concentration of 0.1% w/w and were eluted with a 0.1% w/w solution of tetra-*n*-butylammonium bromide in tetrahydrofuran through Polymer Laboratories PLgel columns (10^6, 10^6, 10^4 Å pore sizes, 10 μm particle size). Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Mass spectral data were obtained by using a Kratos MS-9/50 (electron impact) or a Kratos MS-50 (fast atom bombardment). Column chromatography was carried out by using silica gel (60–200 mesh, VWR) as the packing material.

I. Polymerization Behavior in the Presence of 1% (NPCl$_2$)$_3$. (a) $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ **(5).** Samples of **5** (2.2 g, 3.0 mmol) and $(NPCl_2)_3$ (10.4 mg, 0.03 mmol) were placed in a Pyrex tube. The tube was evacuated, sealed, and then heated at 250 °C. After 8 h, the molten material had become nearly immobile. The tube was opened and the contents were dissolved in THF (ca. 5 mL). The mixture was concentrated to a highly viscous solution and was poured slowly into stirred hexanes. A yellow polymeric material, $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$ **(6)**, precipitated from solution. The polymer was purified further by five additional reprecipitations from THF into hexanes (0.74 g, 34%). For **6**: ^1H NMR (360.13 MHz) δ 4.50 (br, m); ^{31}P NMR (36.27 MHz) δ 13.0, 7.4, -8.7, -13.5 (all br, m); M_w, 9.4 × 10^5; M_n, 1.8 × 10^5; T_g = 68 °C. See also ref 5.

The following experiments were carried out and the resulting polymer products were isolated in a manner similar to that described for **5** above.

(b) $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ **(7).** Samples of **7** (1.0 g, 1.4 mmol) and $(NPCl_2)_3$ (4.9 mg, 0.014 mmol) were sealed in a Pyrex tube. After 8 h at 250 °C, the tube contents were nearly immobile. ^{31}P NMR analysis showed the products to consist of unreacted cyclic trimer **7** and linear polymer **8**. The polymer product was isolated by several reprecipitations from THF into hexanes (0.20 g, 20%). For **8**: ^1H NMR δ 7.52 (br, 5 H), 4.35 (br, 14 H); ^{31}P NMR δ 9.2, 4.4, 0.6, -3.9 (all br); M_w, 4.0 × 10^5; M_n, 5.3 × 10^4; T_g = 90 °C. Anal. Calcd: C, 38.12; H, 2.74; N, 6.06; Cl, 0.00. Found: C, 37.28; H, 2.73; N, 5.99; Cl, 0.72.

(c) $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ **(9).** After 7 days at 250 °C, a mixture of **9** (0.8 g, 1.2 mmol) and $(NPCl_2)_3$ (4.2 mg, 0.012 mmol) became nearly immobile. Yield of **10** = 0.1 g (13%). For **10**: ^1H NMR δ 7.52 (br, 5 H), 4.39 (br, 14 H); ^{31}P NMR δ 39.9, 30.5, 23.8, 11.9, 4.8, 0.8, -9.8, -14.9 (all br); M_w, 5.9 × 10^5; M_n, 9.5 × 10^4. Anal. Calcd: C, 38.10; H, 2.74; N, 6.06; Cl, 0.00. Found: C, 39.14; H, 3.14; N, 6.09; Cl, 0.02.

(d) $N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ **(11).** A mixture of **11** (1.2 g, 1.7 mmol) and $(NPCl_2)_3$ (5.9 mg, 0.017 mmol) was heated at 250 °C, and after 8 h, the tube contents had become nearly immobile. Unreacted cyclic trimer was separated from polymer **12** by several reprecipitations. Yield of **12** = 0.3 g (25%). For **12**: ^1H NMR δ 7.15 (br, 5 H), 4.34 (br, 14 H); ^{31}P NMR δ 12.1, 5.8, -12.8, -19.0 (all br); M_w, 1.8 × 10^6; M_n, 2.9 × 10^5; T_g = 65 °C. Anal. Calcd: C, 37.26; H, 2.68; N, 5.92; Cl, 0.0. Found: C, 36.41; H, 2.54; N, 5.94; Cl, 0.7.

(e) $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ **(13).** A sample of **13** (0.9 g, 1.3 mmol) was heated at 250 °C with $(NPCl_2)_3$ (4.5 mg. 0.013 mmol), and a rapid increase in viscosity was observed until, after 20 min, the tube contents were nearly immobile. The resultant yellow polymer (**14**) was isolated by reprecipitation. Yield = 0.11 g (12%). For **14**: ^1H NMR δ 7.45 (br, 10 H), 3.75 (br, 12 H); ^{31}P NMR δ 16.1 (br). Anal. Calcd: C, 46.50; H, 3.28; N, 6.26. Found: C, 47.03; H, 4.15; N, 5.28. GPC: very broad molecular weight distribution centered at 4.3 × 10^4.

(f) $N_3P_3Me(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ **(15).** Samples of **15** (0.6 g, 0.95 mmol) and $(NPCl_2)_3$ (3.5 mg, 0.01 mmol) were sealed in a Pyrex tube and heated at 250 °C. After 8 h, the mixture had become nearly immobile. Unreacted cyclic trimer and linear polymer **16** were separated by multiple reprecipitations. Yield = 0.11 g (18%). For **16**: ^1H NMR δ 4.31 (br, 14 H), 1.65 (br, 3 H); ^{31}P NMR δ 10.0, 6.3, -8.7, -14.5 (all br); M_w, 1.5 × 10^6; M_n, 1.3 × 10^5; T_g = 92 °C. Anal. Calcd: C, 32.36; H, 2.69; N, 6.66; Cl, 0.00. Found: C, 30.59; H, 3.09; N, 6.44; Cl, 0.60.

(g) $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ **(17).** A sample of **17** (0.53 g, 0.8 mmol) was heated at 250 °C in the presence of $(NPCl_2)_3$ (2.8 mg, 0.008 mmol). After 6 days, the tube contents were nearly immobile. Analysis by ^{31}P NMR showed that the contents consisted of unreacted cyclic trimer **17** plus a species with a new A_2X spin system (24.3 (d), 12.9 (t) ppm, $^2J_{PNP}$ = 29 Hz, 10% of the total mixture by ^{31}P NMR integration), possibly corresponding to cyclic hexamer. Broad resonances at 9.4, 5.3, and -20.0 ppm were also present (ca. 10% of total), probably

corresponding to polymer **18**. GPC analysis of the powder obtained by repeated reprecipitations showed a very broad molecular weight distribution centered at 5.0×10^3. These products could not be separated satisfactorily by reprecipitation, and their structures could not, therefore, be confirmed.

(h) $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (19). A mixture of **19** (0.58 g, 0.8 mmol) and $(NPCl_2)_3$ (2.8 mg, 0.008 mmol) was heated at 250 °C, but after 14 days, no increase in viscosity was detected. ^{31}P NMR analysis indicated the presence of unreacted **19** plus the corresponding cyclic hexamer **20**. Product **20** was isolated as a yellow powder using column chromatography (1:1 THF/diethyl ether) and multiple recrystallizations (THF/hexanes). Yield = 0.38 g (33%). For **20**: ^1H NMR (360.13 MHz) δ 7.13, 7.04, 6.86 (all m, 40 H), 4.36, 4.26 (both m, 16 H); ^{31}P NMR (145.81 MHz) δ 27.5 (d), 5.9 (t) ($^2J_{PNP}$ = 48 Hz); EIMS calcd for $C_{34}H_{28}N_3O_4P_3Fe_2$ 1382, found 1382. Anal. Calcd: C, 59.06; H, 4.09; N, 6.08. Found: C, 56.73; H, 4.10; N, 5.61.

II. Polymerization Behavior in the Absence of $(NPCl_2)_3$. (a) $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (5). A sample of **5** (1.0 g, 1.4 mmol) was sealed under vacuum in a Pyrex tube and was heated at 250 °C. After 14 days, no increase in viscosity was observed. Analysis by ^{31}P NMR showed the presence of unreacted **5** and a small amount (ca. 3%) of cyclic hexamer **21**. The hexameric product was isolated in very low yield by column chromatography (THF/diethyl ether) and recrystallization (THF/hexanes) as a yellow-brown powder. For **21**: ^{31}P NMR (145.81 MHz) δ 32.7 (d), 13.9 (t) ($^2J_{PNP}$ = 46 Hz); EIMS calcd for $C_{36}H_{32}N_6O_8F_{24}P_6Fe_2$ 1430, found 1430.

(b) $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (7). Compound **7** (1.1 g, 1.6 mmol) was heated in the molten state at 250 °C. After 5 days, the tube contents were nearly immobile. Analysis by ^{31}P NMR showed the reaction mixture to consist of unreacted **7** and cyclic hexamer **22**. The amount of polymer formed was below the limit of detectability of the ^{31}P NMR analysis (ca. 3%). Product **22** was isolated by column chromatography (THF/diethyl ether) and by multiple recrystallizations from THF/hexanes. For **22**: ^1H NMR (360.13 MHz) δ 7.97 (4 H), 7.51 (6 H), 4.55 (16 H), 3.91 (12 H) (all m); ^{31}P NMR δ 29.3 (3 P), 23.9 (2 P) (both br, m); FABMS calcd for $C_{44}H_{38}N_6O_6P_6F_{18}Fe_2$ 1386, found 1387 ($M^+ + H$).

(c) $N_3P_3Ph(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (9). A sample of **9** (0.8 g, 1.2 mmol) was heated in the molten state at 250 °C. After 14 days, no increase in the melt viscosity was noted. Analysis of the tube contents by ^{31}P NMR showed virtually no change. Gel permeation chromatography showed only a small amount of high molecular weight material to be present (3.2×10^4 and 1.0×10^6, both trace amounts).

(d) $N_3P_3(OPh)(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (11). A sample of **11** (0.4 g, 0.6 mmol) was heated at 250 °C. After 14 days, the tube contents were completely immobile. Analysis by ^{31}P NMR spectroscopy showed the mixture to consist of unreacted **11**, cyclic hexamer **23**, and linear polymer **12** (ca. 13%, 13%, and 74%, respectively, by integration). Polymer **12** was isolated by several reprecipitations. Attempts were made to isolate **23** by column chromatography, reprecipitation, and recrystallization techniques, but the product could not be fully purified. For **12**: See above. Anal. Found: C, 35.83; H, 2.58; N, 5.87. M_w, 6.9×10^5; M_n, 1.2×10^5. Yield = 0.1 g (25%).

For **23**: ^{31}P NMR δ 31.9 (d), 10.3 (t, $^2J_{PNP}$ = 44 Hz); FABMS m/e calcd for $C_{44}H_{38}N_6O_2P_6F_{18}Fe_2$ 1418, found 1419 ($M^+ + H$).

(e) $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (13). Compound **13** (0.9 g, 1.3 mmol) was heated at 250 °C; after 30 min the tube contents had become nearly immobile. The resultant polymer product (**14**) was isolated by multiple reprecipitations. Yield = 0.05 g (6%). For **14**: See above.

Anal. Found: C, 44.72; H, 4.32; N, 7.18. GPC: broad molecular weight distribution centered at 4.3×10^4.

(f) $N_3P_3Me(OCH_2CF_3)_3(\eta\text{-}C_5H_4)_2Fe$ (15). A sample of **15** (0.6 g, 1.1 mmol) was heated for 10 days as the tube contents gradually became highly viscous. Linear polymer **16** was separated from unreacted **15** by multiple reprecipitations. Yield = 0.07 g (12%). For **16**: See above. Anal. Found: C, 33.46; H, 4.08; N, 6.44. M_w, 1.6×10^6; M_n, 1.4×10^5.

(g) $N_3P_3Ph_2(OCH_2CF_3)_2(\eta\text{-}C_5H_4)_2Fe$ (17). A sample of **17** (0.47 g, 0.7 mmol) was heated at 250 °C. After 11 days, the tube contents were nearly immobile. The ^{31}P NMR spectrum and GPC chromatogram were virtually identical to those obtained from the thermolysis of **17** with $(NPCl_2)_3$ as described above. However, as before, the resultant products could not be isolated and their identity was not confirmed.

(h) $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (19). Compound **19** (2.0 g, 2.9 mmol) was heated at 250 °C, but after 14 days, no increase in viscosity was observed. ^{31}P NMR analysis indicated that the tube contained a mixture of cyclic trimer and hexamer, **19** and **20**. By ^{31}P NMR integration, the amount of **20** formed was small (ca. 10%) and the product was not isolated. For **20**: ^{31}P NMR, see above.

III. Polymerization Behavior of 5 and 19 in the Presence of BCl_3. (a) $N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$ (5). A sample of **5** (0.6 g, 0.8 mmol) was placed in a Pyrex tube under argon, and gaseous BCl_3 (0.2 mL, 0.008 mmol) was added. The tube was immediately stoppered, and the lower half was cooled to −196 °C for 30 min. The tube was evacuated (0.010 mmHg), sealed, warmed to room temperature, and then heated at 250 °C. After 6 days, the contents of the tube were nearly immobile. The tube was cooled and, the contents were dissolved in THF (ca. 5 mL). Analysis by ^{31}P NMR indicated the presence of unreacted **5**, cyclic hexamer **21**, and linear polymer **6** (51%, 32%, and 17%, respectively, by integration). GPC analysis of this mixture showed a very broad molecular weight distribution centered at 2.9×10^4.

(b) $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ (19). A sample of **19** (0.4 g, 0.58 mmol) was sealed in a Pyrex tube with BCl_3 (0.2 mL, 0.006 mmol) according to the procedure used for **5** above. After 10 h at 250 °C, the contents of the tube had become nearly immobile. ^{31}P NMR analysis of the tube contents indicated the presence of **19** and cyclic hexamer **20** (66% and 34%, respectively, by integration).

IV. Determination of the Minimum Concentration of $(NPCl_2)_3$ Required for the Polymerization of 5. Identical samples of **5** were heated at 250 °C in the presence of various amounts of $(NPCl_2)_3$ (10, 1, 0.1, and 0.01 mol %) according to the polymerization procedures described above. After 14 days, the samples with 0.1% and 0.01% $(NPCl_2)_3$ showed no signs of polymerization either by viscosity increase or by ^{31}P NMR analysis. The samples treated with 10% and 1% $(NPCl_2)_3$, however, both polymerized within 8 h. Following isolation by reprecipitation, elemental analysis of both polymers showed the incorporation of almost the same amount of Cl. Anal. Found (10% $(NPCl_2)_3$ system) for polymer **6**: C, 28.89; H, 2.14; N, 5.91; Cl, 0.48. Anal. Found (1% $(NPCl_2)_3$ system) for **6**: C, 29.84; H, 2.17; N, 5.73; Cl, 0.84.