Synthesis and Characterization of Metallophosphazene Derivatives: Solution State and Surface Reactions

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The small-molecule cyclotriphosphazenes $N_3P_3(OPh)_5OC_6H_4R$ and $N_3P_3(OC_6H_4R)_6$ where R = $FeCp(CO)_2$ were synthesized by reaction of the corresponding [(lithioaryl)oxy]phosphazenes with cyclopentadienyliron dicarbonyl iodide in the absence of moisture, oxygen, and light. Molecular structural characterization for the cyclic trimers was achieved by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, infrared spectroscopy, elemental microanalysis, and FAB mass spectrometry. These small-molecule reactions were used as models for the preparation of the corresponding high polymeric analogues. The synthesis of the poly(metallophosphazene), $[NP(OC_6H_4R)_x(OC_6H_4X)_{2-x}]_n$, where X = H or Br and R = $FeCp(CO)_2$, via the metal–halogen exchange reaction of $[NP(OC_6H_4Br)_2]_n$ with n-BuLi at −78 °C, is described. Structural characterization for this polymer was carried out by solid-state ^{13}C NMR spectroscopy, KBr infrared spectroscopy, and elemental microanalysis. Thermal properties were investigated via differential scanning calorimetry, thermogravimetric analysis (TGA), and TGA/mass spectrometry. The organometallic-containing polymers showed solid-state paramagnetic behavior. Modification reactions at the surface interfacial region of cross-linked films of $[NP(OC_6H_4Br)_2]_n$ were also investigated. Controlled exposure of these films to lithiation and metal–halogen exchange conditions, as described above, allowed the preparation of surface-metalated materials. These surface-metalated films were characterized by the use of X-ray microanalysis and scanning electron microscopy (SEM), transmission electron microscopy (TEM), contact angle measurements, and attenuated transmission reflectance infrared spectroscopy (ATR-IR).

Polymers containing transition metals have received considerable attention in recent years. Such materials have potential catalytic, magnetic, electroactive, or preceramic applications.[1-3] For example, cross-linked polystyrene bearing a side-group coordinated catalyst system forms the basis of many studies.[2] Conductive polymer systems such as metallo(tetraphenylporphyrins) or metal–(tris)–bipyridine complexes are well-known. Furthermore, polymers that contain inorganic elements within the backbone have been investigated as high-temperature or preceramic materials.[4]

Polyphosphazenes are macromolecules that are especially suited for metallo–polymer studies because of the substitutive method used for their synthesis. This allows the facile incorporation of a diverse range of side group structures.[5] Previous research in our laboratory has identified several methods for the synthesis of polyphosphazenes that bear transition-metal-containing side groups.[6] Incorporation of metallo species is possible via coordination to the skeletal nitrogen atoms,[7] to exocyclic phosphorus atoms in phosphino groups,[8] or to arene units in an η^6-manner.[9] Alternatively, covalent linkage of metals to skeletal phosphorus atoms is possible either directly or through use of pendent organic spacer groups.[10,11]

In this paper we describe the covalent attachment of an organo–iron unit to aryloxy side groups pendent to a phosphazene chain. The aryloxy group was chosen (a) for ease of attachment to the phosphazene skeleton, (b) because of the known stability of aryloxy-substituted phosphazenes, and (c) for efficient insulation of the metallo species from the electron-withdrawing phosphorus–nitrogen backbone. In particular, it was of interest to examine the effect of changes in the loading of the transition-metal species on the properties of the resultant polymers.

Initial studies were carried out at the small-molecule level to allow optimization of the reaction conditions and to facilitate molecular characterization. The stability of these species was also investigated via model studies of the behavior of phenylcyclopentadienyldicarbonyliron, which was synthesized by the reaction between PhLi and

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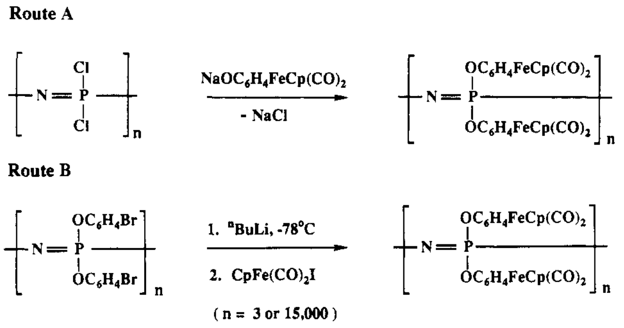
Scheme I



$CpFe(CO)_2I$. Slight oxidative, moisture, and light sensitivities were detected. Consequently, all reaction mixtures were protected from the atmosphere and ambient light.

Specifically, we describe here the synthesis, characterization, and properties of cyclotriphosphazene transition-metal complexes of structures $N_3P_3(OPh)_5(OC_6H_4R)$ (**5**) and $N_3P_3(OC_6H_4R)_6$ (**6**) and the high polymeric analogues $[NP(OC_6H_4R)_x(OC_6H_4X)_{2-x}]_n$ (**8**), where R = $FeCp(CO)_2$ and X = H or Br. The polymeric metalation processes were also investigated for reactions at the surface interfacial region.

Results and Discussion

General Solution-State Synthetic Approach. The formation of an iron–carbon σ bond can be achieved through a variety of synthetic routes.[12] Two variations of this methodology were investigated for phosphazenes, as outlined in Scheme I. The first approach (route A) involves the synthesis of an organo–iron phenoxy side-group moiety, followed by linkage of this to the phosphazene skeleton. This route was attractive for a number of reasons. Independent preparation of an organometallic-aryloxy side group and subsequent linkage of it to the polymer by nucleophilic substitution follow a well-established procedure.[13] Furthermore, this route would minimize the formation of side products and allow facile control of the degree of incorporation of the organometallic species. This protocol is particularly attractive for use at the high polymeric level where it could, in principle, give high loadings of the organometallic species.

Thus, the tetrahydropyran (THP)-*p*-bromophenol was prepared as a starting material. The THP protecting group was essential to ensure a clean reaction of this species with *n*-BuLi. Addition of cyclopentadienyliron dicarbonyl iodide to the lithiated derivative yielded the THP protected phenoxy organo–iron group in low yield. Preparation of the lithiated species and purification via washing with diethyl ether and hexane, before slow addition to a solution of the organometallic halide, improved the yield only minimally.

Complications were encountered during the attempted deprotection of this transition-metal-bearing aryloxy group. Although the typical conditions required for regeneration of the phenol and 3,4-dihydro-2*H*-pyran (DHP) are quite mild (10 mol % pyridinium *p*-toluenesulfonate in EtOH at 55 °C),[14] these conditions did not bring about deprotection when applied to this organometallic species. Decomposition occurred when more forcing conditions were employed. Thus, further work was focused on the alternative approach outlined in route B (see Scheme I).

The second approach (route B), involves a metal–halogen exchange reaction between *n*-BuLi and poly[bis(*p*-bromophenoxy)phosphazene]. Subsequent addition of cyclopentadienyliron dicarbonyl iodide to the [(lithioaryl)-oxy]phosphazene intermediate would yield the organo–iron bearing phosphazene polymer. It is important to note that the (lithioaryl)oxy intermediate is extremely sensitive to trace amounts of water due to the ease of protonation at the lithio site.[15,16]

A significant limitation of this route is that the lithiation reaction is incomplete. At high levels of lithiation the polymer becomes insoluble in tetrahydrofuran and other etheric solvents, presumably as a result of lithioaryloxy unit aggregation and the increased ionic character of the polymer. Thus, the efficiency of the lithiation step and the effectiveness of the subsequent metal–halogen exchange reaction are impaired. However, during exposure to the organo–iron electrophile the lithiated polymer redissolves to yield a material that bears a mixture of bromo, hydrogen, and organo–iron units at the para positions of the aryloxy side groups.

Small Molecule Synthesis. Syntheses related to route B have been investigated previously in our laboratory.[16] Use of a difunctional reagent such as *p*-bromophenol, is the key to this approach. The bromo unit remains unreactive during the initial nucleophilic replacement of the chlorine atoms, but it can be utilized later as a reactive site.

For simplicity the monosubstituted cyclic trimer, $N_3P_3(OPh)_5(OC_6H_4Br)$ (**3**), was studied first as a model system to facilitate optimization of both the reaction conditions and the purification techniques (see Scheme II). These small-molecule transition-metal-bearing species were moderately unstable to oxidation both in the solid and solution states. The cyclotriphosphazenes were isolated (the monosubstituted as a yellow oil and the hexasubstituted as a yellow powder) and characterized fully by nuclear magnetic resonance and infrared spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section).

High Polymer Solution-State Reactions: Synthetic Methodology. The synthetic procedure outlined in route B can impose limits on the level of incorporation of the organo–iron side groups due to the insolubility of the lithiated polymers. Initially, the lithiation and iron metalation of a series of polymers bearing 25, 50, 75, and 100% loadings of *p*-bromophenoxy groups were investigated (the remainder of the side groups being phenoxy units). However, after purification and isolation in the solid state, the organo–iron-bearing polymers were found to be insoluble in a range of solvents, including concentrated sulfuric acid. Moreover, the loading of the organometallic species, as determined by elemental microanalysis, was lower than would be expected on the basis of the amount of bromo units in the original polymer. In

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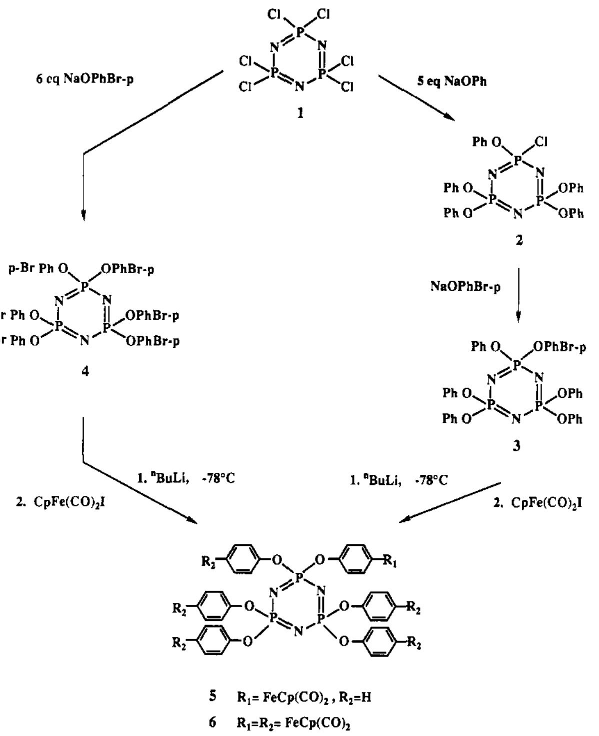
Scheme II



addition, these iron-substituted polymers showed a marked paramagnetism in the solid state. The homogeneous reaction solution, before isolation of the polymer, was not paramagnetic. Thus, it is proposed that a change in oxidation state of the Fe(II) species occurs via an intramolecular solid-state reaction. The paramagnetic character was detected regardless of the method of polymer isolation and purification, by either dialysis or precipitation, under argon or in the atmosphere.

To examine the possibility that formation of the paramagnetic species was due to a reduction of the iron by the phosphazene backbone, a control reaction was carried out. $CpFe(CO)_2I$ was added to a solution of poly[bis(*p*-bromophenoxy)phosphazene] (7) in THF, and the mixture was stirred under argon in the absence of light for 2 days. A magnetic susceptibility measurement of the reaction solution showed no evidence of paramagnetism. Following removal of the solvent in vacuo and storage for 3 weeks in the solid state under argon in the absence of light, this mixture remained nonparamagnetic. Thus the paramagnetism may be a result of *oxidation* of the iron species. The formation of Fe–O–Fe groups is one possible oxidation route.

In view of these findings, further work was concentrated on the use of the *p*-bromophenoxy single-substituent polymer (7) in an effort to obtain the maximum incorporation of the iron species. Even if the organometallic-bearing polymer proved to be insoluble, it should still have interesting solid-state properties (see Scheme III).

High Polymer Solution-State Reactions: Characterization. Structural characterization of the poly[bis(*p*-bromophenoxy)phosphazene] (7) was achieved by NMR spectroscopy and gel permeation chromatography. Solution NMR and GPC could not be used as characterization techniques because of the low solubility of the organo–iron-derivatized polymer 8 in a wide variety of solvents. However, infrared (KBr) and solid-state ^{13}C NMR spectroscopy were utilized to investigate the molecular structure of this polymer. The thermal properties of polymers 7 and 8 were investigated by differential scanning calorimetry, thermogravimetric analysis (TGA), and TGA/mass spectrometry. Compositional information was obtained by elemental microanalysis. The characterization data are summarized in the Experimental Section.

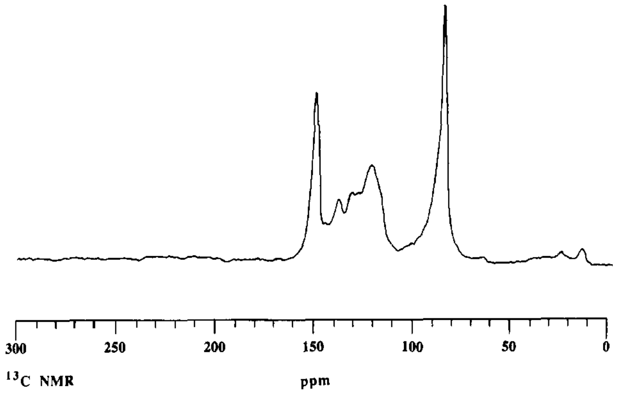
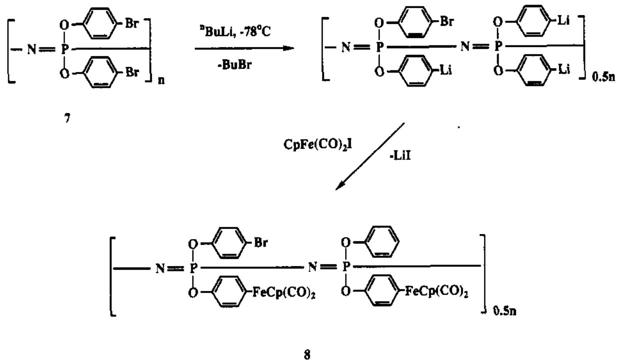


Figure 1. The 75-MHz solid-state ^{13}C NMR spectrum of polymer 8 (16 000 scans) with use of cross polarized magic angle spinning and total sideband suppression.

Scheme III



Solid-State ^{13}C Analysis. Careful manipulation of polymer 8 under an inert atmosphere, and isolation by precipitation into dried, deoxygenated solvents, minimized the degree of paramagnetism displayed initially and allowed "same-day" preparation and ^{13}C solid-state NMR analysis to be carried out (see Figure 1).

The cross-polarization magic angle spinning (CPMAS) technique was employed with total sideband suppression (toss).[17] The aromatic carbon atoms were detected as a series of broad resonances ranging from 151–118 ppm. The cyclopentadienyl carbon atoms appeared at 86 ppm as a broad peak. The carbonyl carbon atoms were not detected under these conditions. As a control experiment, a solid-state ^{13}C NMR study of $CpFe(CO)_2I$ was carried out with use of CPMAS toss conditions. Although the cyclopentadienyl carbons were visible, again the carbonyl carbon atoms were not clearly discernible. However, when the toss technique was not utilized for the $CpFe(CO)_2I$ sample, the isotropic shift for the carbonyl carbons was assignable (216 ppm) by systematic alteration of the sample spin rate.

Thermal Analysis. The glass transition temperatures (T_g) of polymers 7 and 8 were determined by differential scanning calorimetry. The effect of the incorporation of the organo–iron derivative is reflected by an increase in

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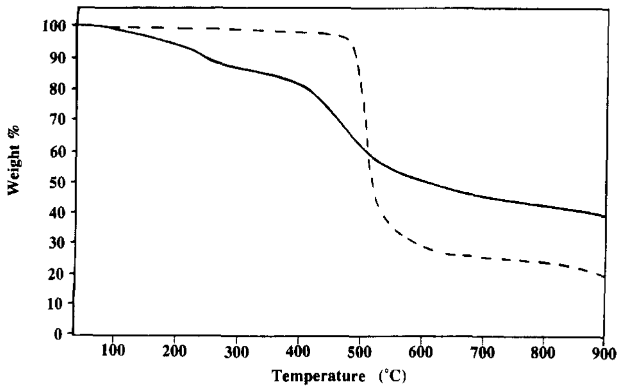

Figure 2. Thermogravimetric analysis curves for $[NP(OC_6H_4Br)_2]_n$ (7) (- - -) and $[NP(OC_6H_4FeCp(CO)_2)_x(OC_6H_4X)_{2-x}]_n$ (8) (—) where X = Br or H measured under a nitrogen atmosphere (heating rate = 20 °C/min).

the meausred T_g. Polymer 7 has a T_g of 10 °C while the poly(metallophosphazene), 8, has a T_g of 41 °C. The higher T_g may result from both the increased steric bulk of the cyclopentadienyliron dicarbonyl group and a presumed cross-linking reaction via bridging carbonyl formation (vide infra).

Polymers 7 and 8 were also examined by thermogravimetric analysis to explore the overall influence of the $CpFe(CO)_2$ unit on the thermal stability of the polymer, as well as to probe the nature of the cross-linking process. As shown in Figure 2, the onset temperature for volatilization differed for the two polymers. However, both systems appear to undergo cross-linking reactions during thermolysis. The thermogram of polymer 7 reveals a dramatic mass loss near 500 °C. Under the same conditions, the organometallic bearing polymer 8 underwent a gradual weight decline as the material was heated from 100 to 600 °C. The percentage of nonvolatile residue which remained after heating to 900 °C was higher for 8 (43%) than for 7 (24%). The higher weight retention from 8 may be a consequence of the incorporation of the $CpFe(CO)_2$ units, which appear to favor cross-linking rather than depolymerization.

Thermogravimetric/mass spectral (TGA/MS) analysis experiments were conducted to determine the identity of the volatile species.[18] Previous research has shown that extended heating of related phenoxy-substituted polymers produces significant amounts of small-molecule cyclic analogues via cyclization/depolymerization reactions.[19] Although TGA/MS analysis of both 7 and 8 detected fragments derived from such substituted cyclics, the corresponding molecular ions were not found. For the trimer 6 and high polymeric analogue 8, the loss of CO, Cp, and CpFe fragments were detected from 200 to 250 °C. The loss of these fragment ions over this temperature range is consistent with the TGA trace of polymer 8.

Infrared Analysis. Further characterization of the polymers was carried out via KBr FTIR spectral analysis. The poly(metallophosphazene) 8 showed characteristic stretching absorption peaks at 2012 and 1957 cm^{-1} from the carbonyl groups. In addition, a band at 1794 cm^{-1} was detected, which suggests the presence of a bridging carbonyl species. For comparison, KBr FTIR analysis of the hexaorganoiron trimer (6) was carried out, and no absorbances assignable to a *bridging* carbonyl were detected. Furthermore, infrared analysis of the pyrolysis residue formed from the thermolysis of polymer 8 showed loss of the terminal carbonyl stretches, but provided clear evidence for the presence of a bridging carbonyl at 1796 cm^{-1}.

These data support the TGA/MS results which suggested a loss of carbonyl groups during thermolysis. The presence of a bridging carbonyl group before and after thermolysis implies that these units serve as cross-link sites which stabilize the resultant pyrolyzed ultrastructure material.

High Polymer Surface Reactions: Synthetic Methodology. It is often useful to be able to alter the surface properties and surface functionalities of a polymeric material while retaining the original properties of the bulk material.[20–23] Three methods are typically used to attain this goal: chemical modification of surfaces,[24] surface grafting of polymers,[25] and plasma modification of surfaces.[26]

In this study, the metalation of a poly(organophosphazene) at the surface interfacial region was investigated by chemical modification methods. For the purposes of this study, we will use the term "surface" to describe the polymer surface interfacial region which undergoes metalation. A fundamental consideration in surface reaction chemistry is control of the depth and degree to which the reaction proceeds. The effects of systematic variations in the surface reaction conditions were examined in order to optimize the degree of metalation, without affecting the bulk material (see Experimental Section).

Films of polymer 9 were first cross-linked to further limit the degree of swelling in contact with solvents at −78 °C and to facilitate their subsequent purification. In a typical reaction, a ^{60}Co γ-radiation cross-linked film of $[NP(OC_6H_4Br)_2]_n$ (9) was immersed in a minimum amount of dry THF and was immediately cooled to −78 °C under an inert atmosphere. The film was then exposed to an excess of *n*-BuLi. Subsequent removal of the *n*-BuLi/THF, and exposure of the film to a solution of $CpFe(CO)_2I$ in THF at −78 °C, yielded the surface modified polymer films 10 (see Scheme IV). The duration of both the lithiation and metal–halogen exchange reaction times was altered systematically, and the effects of solvent and temperature variations were also investigated.

After the optimum temperature and solvent conditions had been established, a series of surface reactions were

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[18] Solid-state samples of polymers 7 and 8, and the derivatized trimer 6, were examined via the direct insertion probe method and ionization by electron impact. The sample-filled capillary tubes were heated from 200 to 400 °C, and mass spectral data were obtained at 50 °C intervals.

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[25] Allcock, H. R.; Fitzpatrick, R. J.; Visscher, K.; Salvati, L. *Chem. Mater.* **1992**, *4*, 775.

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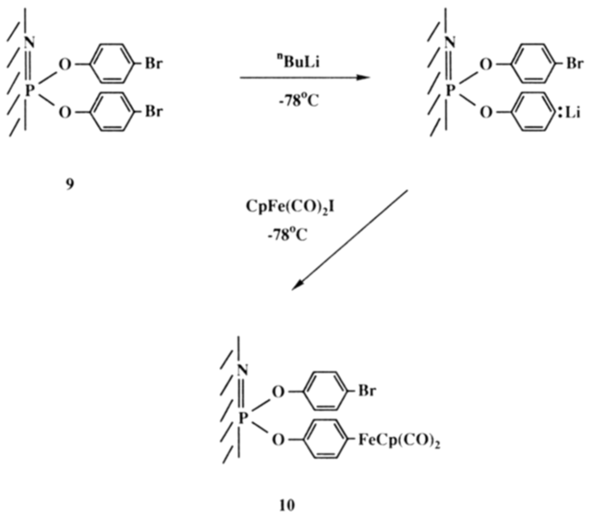
Scheme IV



carried out using lithiation times of 30 s (**10a**), 1 min (**10b**), 2.5 min (**10c**), and 5 min (**10d**). The first and final films in this series were characterized in the greatest detail in an attempt to determine the degree to which the depth of metalation could be controlled (see Experimental Section).

High Polymer Surface Reactions: Characterization. The surface-reacted samples were cleaned by sonication in THF. The films were then dried thoroughly and were characterized via advancing contact angle measurements and attenuated transmission reflectance infrared spectroscopy (ATR-IR). X-ray microanalysis and scanning electron microscopy (SEM) were utilized in tandem to confirm the presence of the iron at the modified film surface, to examine the surface topography and surface interfacial region of the metallated films, and to evaluate the depth of the reaction zone. Transmission electron microscopy (TEM) of cross sections of the polymer films was used to study the surface deposition of the organometallic species. An estimation of the extent of metalation was obtained by an elemental microanalytical determination of the percent iron present in the films (see Experimental Section).

Contact Angle Measurements. The contact angle of a sessile drop of water on the surface of films of polymer **9** and modified films of **10a** and **10d** was measured. The films were attached to glass slides with use of double-sided adhesive tape. Measurements of both the air- and glass-cast polymer surfaces were carried out. The contact angles of the films did not depend on the surface examined, and the droplets did not display a detectable spreading behavior after 10–15 min exposure to the film surface.

A contact angle of 120° was measured for the cross-linked poly[bis(*p*-bromophenoxy)phosphazene] film (**9**). Surface reaction of these films resulted in visible surface roughening. Because of the surface roughness of the metalated films, the use of contact angle measurements was considered to be a qualitative technique only. However, a marked difference was detected between the contact angles of the reacted films and those of their precursors. An average value of 54° was found for both the **10a**- and **10d**-reacted film surfaces. These data suggest a significant increase in the surface free energy of the metalated films.

Attenuated Transmission Reflectance Infrared Spectroscopy (ATR-IR). ATR-IR analysis of films of **9** and **10** was performed with use of either a KRS (45°) or a Ge (45°) internal reflectance element. The most characteristic spectra were obtained with the KRS (45°) crystal with measurements made under an inert atmosphere. The ATR-IR spectra of the modified films **10a** and **10d** showed a new band for the cyclopentadienyl C–C stretches at 1410 cm^{-1}. Further evidence for the modification of these film surfaces by CpFe(CO)$_2$I was provided by detection of the characteristic solid-state carbonyl stretching absorbances at 2013 and 1957 cm^{-1}.

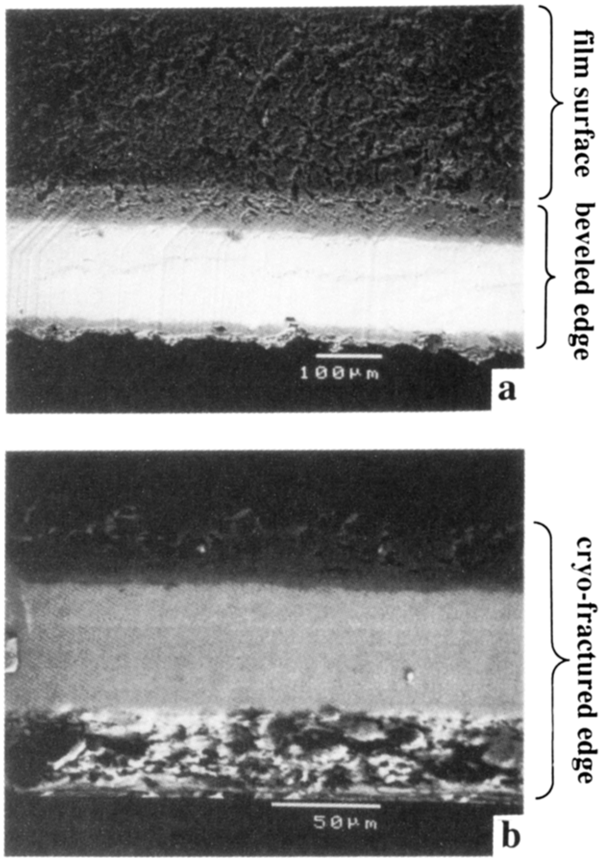


Figure 3. Scanning electron micrographs (backscattered detection) of the surface metalated films **10a** (30-s lithiation) with a razor-beveled cross-cut edge (a) and a sharp cryofractured edge (b).

Electron Microscopy. Scanning electron microscopy (SEM) of the modified films **10a** and **10d** was used to examine the surface topography. Cross sections of the metalated films were mounted on carbon stubs and sputter-coated with carbon. The images obtained using a backscatter detector for films of **10a** are shown in Figure 3. The preparation of sections with a beveled edge enabled a study to be made of the roughening effects of the metalation reaction on the film surface (see Figure 3a). In addition, the absence of bulk modification is clearly visible. Selective X-ray microanalysis of the metalated surface and the unmodified bulk revealed the presence of iron *only* at the surface.

Cryofracturing of the modified films allowed the preparation of a sharp edge for depth of modification measurements (see Figure 3b). The average overall thickness of the films was 100 μm. No significant change in the depth of modification was detected for the metalated films **10d** (with 5-min lithiation) with a measured value of 30 μm as compared to **10a** (30 s treatment) with a value of 27 μm.

Transmission electron microscopy (TEM) of cross sections of the unmodified polymer film **9** and the surface-metalated films **10** was also investigated. The phosphorus–

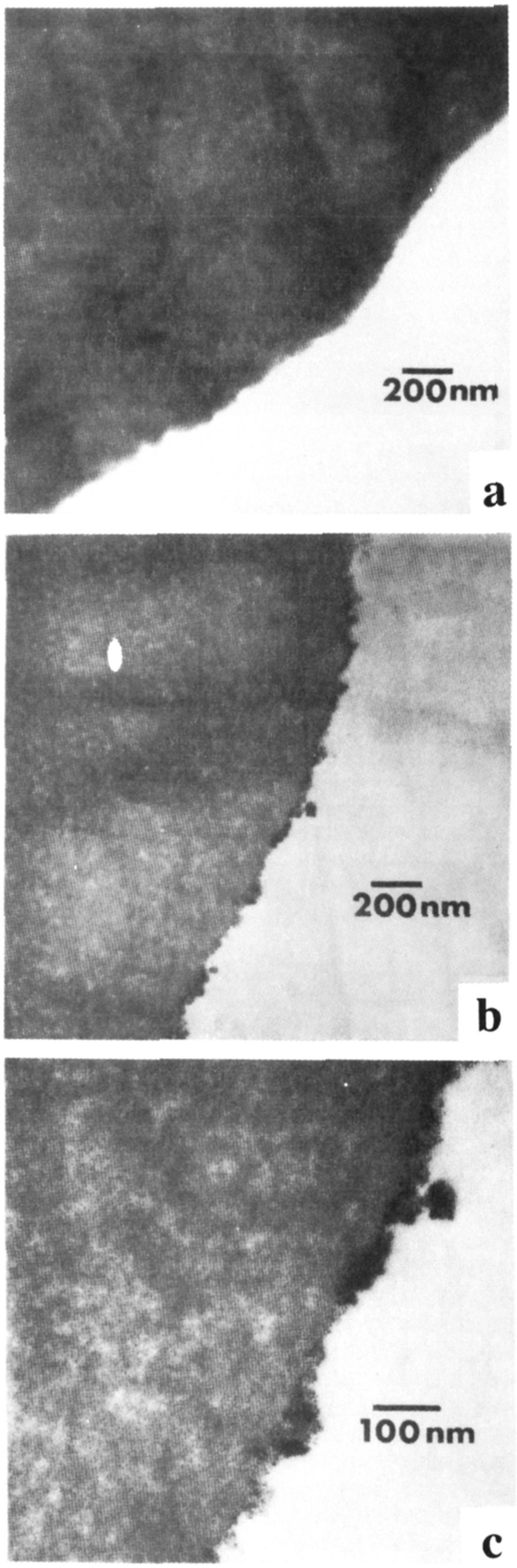


Figure 4. Transmission electron micrographs of microtomed, cross sections of the cross-linked precursor film $[NP(OC_6H_4Br)_2]_n$ (**9**) at 30000× (a), and of the surface-metalated film **10d** (5 min lithiation) at 30000× (b) and 75000× (c).

nitrogen backbone of polyphosphazenes allows TEM evaluation without the use of specialized contrast agents. The micrographs of samples **9** and **10d** are shown in Figure 4. The roughening effects of the modification reaction, as seen in the SEM study, were also detected here. Again the selectivity of the process is clearly evident, with the deposition of the organometallic species being apparent *only* at the surface of the modified films, as shown in the micrographs.

Conclusions

The synthesis and characterization of metallophosphazene derivatives which possess covalent iron–carbon linkages has been accomplished. The polymeric species displayed paramagnetic behavior in the solid state, which may be a consequence of oxidation of the iron species. The formation of bridging carbonyl units may account for the observed cross-linking and reduced solubility and also play a role in the increased thermal stability. This explanation is supported by the KBr infrared analysis data of the poly(metallophosphazene) which shows the characteristic bridging carbonyl stretch before and following pyrolysis to 900 °C under $N_2(g)$.

Reactions at the surface interfacial region of radiation cross-linked films of poly[bis(*p*-bromophenoxy)phosphazene] (**9**) were used to prepare surface-metalated materials. Investigation of these films by use of ATR-IR and contact angle analyses provided an insight into the effects of the surface metalation. An estimate of the depth of reaction (approximately 30 μm) was obtained by the use of scanning electron microscopy of cross sections of the films. Transmission electron microscopy was utilized to delineate clearly the reaction boundaries of the surface interfacial region. Studies to probe the extention of this methodology to other organometallic systems are currently in progress.

Experimental Section

Equipment. ^{1}H NMR (360.0 MHz), ^{13}C NMR (90.0 MHz), and ^{31}P NMR (145.8 MHz) spectra were obtained using a Bruker WM-360 MHz spectrometer. Solid-state ^{13}C NMR (74.78 MHz) spectra were recorded with use of a Chemagnetics CMX-300 NMR spectrometer. A broad-band CPMAS (cross-polarization magic angle spinning) pencil probe was employed and data were obtained under $N_2(g)$ purge. Chemical shifts are relative to tetramethylsilane at $\delta = 0$ for proton and carbon. The phosphorus chemical shifts are relative to external 85% H_3PO_4 at $\delta = 0$ with positive shift values downfield from the reference. All heteronuclear NMR spectra were proton decoupled. Infrared spectra were recorded on a Perkin-Elmer Model 1710 FTIR spectrophotometric instrument interfaced with a Perkin-Elmer 3600 data station. A Harrick variable-angle twin parallel mirror reflection attachment equipped with a 45° Ge or KRS crystal (50 × 10 × 3 mm) was used to obtain all ATR-IR spectra. A Rame-Hart Model 100 goniometer equipped with an environmental chamber was used to measure contact angles. The microscopy work was carried out at the electron microscope facility for the Life Sciences in the Biotechnology Institute at The Pennsylvania State University. Transmission electron microscopy (TEM) was performed with use of a JEOL JEM-1200 EXII transmission electron micrograph with an accelerating voltage of 80 kV. Magnifications of the photographs were 30000× and 75000× with an exposure time of 1.8 s. The TEM samples were sectioned with use of an LKB Ultratome III microtome. Scanning electron microscopy (SEM) was carried out using a JEOL JSM-5400 scanning electron micrograph with X-rays accelerated at 20 kV. The backscattered images were obtained by use of a Robinson backscatter detector (RBJ-5400 FML). X-ray microanalyses were determined via the SEM interfaced with a Princeton Gamma-Tech (PGT) IMIX (integrated microanalyzer for imaging and X-ray) system. Magnetic susceptibility readings were measured on a Johnson Matthey susceptibility balance. The balance was zeroed initially to an empty quartz sample tube (for solid samples) or a solvent-filled tube (for solution measurements).

Molecular weights were determined using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-

1037A refractive index detector and Polymer Laboratories PL gel 10-μm columns. The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. Thermal analyses were carried out by use of a Perkin-Elmer thermal analysis system 7 equipped with a Perkin-Elmer 7500 computer. For the determination of glass transition temperatures by differential scanning calorimetry, a heating rate of 15 °C/min under a nitrogen atmosphere was used, with a sample size between 10 and 30 mg. For thermogravimetric analyses, heating rates of 20 °C/min under a nitrogen atmosphere were used. Sample sizes were between 3–5 mg. Thermogravimetric/mass spectral data were obtained with use of a KRATOS MS-25 GC/MS magnetic instrument. Samples were analyzed in the solid state via the direct insertion probe (DIP) method and ionized via electron impact (approximately 50 eV) within capillary tubes. Fast atom bombardment (FAB) mass spectra were obtained with the use of a Kratos MS9/50 spectrometer. Chromatography was carried out with the use of activity III neutral alumina under inert atmosphere.

Materials and Procedures. All reactions were carried out under an atmosphere of dry argon or nitrogen (Matheson), with use of standard Schlenk and drybox techniques. Tetrahydrofuran (THF), dioxane (Omnisolv), and diethyl ether were dried and distilled from sodium benzophenone ketyl. Hexane was distilled from CaH_2. Fractional sublimation at 30 °C/10 μm was utilized to purify the hexachlorocyclotriphosphazene which was provided by Ethyl Corp. Compounds **2**–**4** were prepared as reported previously.[27] Poly(dichlorophosphazene) was prepared by the thermal ring opening polymerization of the trimer at 250 °C.[28] The *p*-bromophenol (Eastman Kodak) was purified by sublimation at 20 °C/10 μm and was stored in vacuo. The *n*-butyllithium (Aldrich), a 2.5 M solution in hexane, was used as received. Cyclopentadienyliron dicarbonyl iodide (Aldrich) and ammonium hexafluorophosphate (Aldrich) were used as received. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory in Woodside, NY, and Galbraith Laboratories in Knoxville, TN.

Pentaphenoxychlorocyclotriphosphazene (2). This compound was synthesized by previously reported methods.[16,27] For **2**: mp 54–60 °C; MS *m/z* calcd 635, *m/z* found 635; ^{31}P NMR ($CDCl_3$) δ_A 21.9 ppm (t) δ_B 6.5 ppm (d) J_{PNP} = 83.0 Hz.

Pentaphenoxy(*p*-bromophenoxy)cyclotriphosphazene (3). Preparation of the compound followed the procedure reported by us previously.[16,27] For **3**: MS *m/z* calcd 772, *m/z* found 771; ^{31}P NMR ($CDCl_3$) δ 9.4 ppm (s).

Hexakis(*p*-bromophenoxy)cyclotriphosphazene (4). Synthesis of this compound was reported previously.[16,27] For **4**: FAB MS *m/z* calcd 1167, *m/z* found 1168; ^{1}H NMR (THF-d_8) δ 7.4 (d, Ar), 6.85 ppm (d, Ar); ^{13}C NMR (THF-d_8) δ 150.4, 133.5, 123.6, 119.1 ppm (Ar); ^{31}P NMR (THF-d_8) δ 9.6 ppm (s).

Pentaphenoxy(*p*-(cyclopentadienyldicarbonyliron)phenoxy)cyclotriphosphazene (5). $N_3P_3(OC_6H_5)_5(OC_6H_4Br\text{-}p)$ (**3**, 1.02 g, 1.3 mmol was dissolved in dry THF (50 mL) in a 100-mL three-necked round-bottomed flask and $CpFe(CO)_2I$ (0.64 g, 2.1 mmol, 1.6 equiv) was dissolved in dry THF (25 mL) in an attached addition funnel. To a second addition funnel, *n*-BuLi (0.6 mL, 1.1 equiv) was added via syringe. The reaction apparatus was cooled to −78 °C and was covered with foil in a darkened hood. The *n*-BuLi solution was added slowly to the cooled phosphazene solution and, after 5 min, the organo–iron reagent solution was added dropwise to the cooled reaction mixture over a 30-min period. When the addition was complete, the reaction solution was allowed to warm to room temperature. The solution was concentrated in vacuo to a brown oil and was purified under argon by chromatography on activity III neutral alumina (1 Et_2O:2 hexane). The product was isolated as a noncrystallizable dark yellow oil (57% yield). For **5**: FAB MS *m/z* calcd 869, *m/z* found 870; FTIR (THF) ν 2023, 1972 (CO's); ^{31}P NMR ($CDCl_3$) δ 9.6 ppm (s); ^{1}H NMR ($CDCl_3$) δ 7.4–6.7 (m, Ar) 4.9–4.8 ppm (m, Cp); ^{13}C NMR ($CDCl_3$) δ 216.0 (CO), 148.0, 144.7, 139.3, 120.2, (Fe, Ar), 85.7 (Cp), 150.6, 129.3, 124.7, 121.0 ppm (Ph, Ar). Anal. Calcd: C, 59.40; H, 3.94; N, 4.83; Fe, 6.42. Found: C, 58.38; H, 4.12; N, 4.54; Fe, 6.16.

Hexa(*p*-(cyclopentadienyldicarbonyliron)phenoxy)cyclotriphosphazene (6). $N_3P_3(OC_6H_4Br\text{-}p)_6$ (**4**, 0.5 g, 0.43 mmol) was utilized to prepare **6** in a manner similar to that described for **5**. Purification was accomplished by column chromatography under argon, on activity III neutral alumina (1 Et_2O:1 hexane). The product was isolated as a dark yellow powder (<20% yield). For **6**: FAB MS *m/z* calcd 1748, *m/z* found 1749; FTIR (THF) ν 2014, 1959 (CO's); ^{1}H NMR ($CDCl_3$) δ 7.25, 6.7 (d, Ar), 4.8 ppm (s, Cp); ^{13}C NMR ($CDCl_3$) δ 216.1 (CO), 148.6, 144.6, 138.2, 120.7, (Ar), 85.8 ppm (Cp); ^{31}P NMR ($CDCl_3$) δ 10 ppm (s); Anal. Calcd: C, 54.18; H, 3.18; N, 2.67; Fe, 17.75. Found: C, 49.54; H, 3.67; H, 2.03; N, 2.03; Fe, 14.58.

Poly[bis(*p*-bromophenoxy)phosphazene] (7). Poly(dichlorophosphazene) (15.0 g, 0.129 mol) dissolved in dry dioxane (500 mL) was added to an excess of sodium *p*-bromophenoxide (3 equiv/PCl) in dry dioxane (500 mL) and was refluxed for 3 days. The product polymer was isolated by precipitations into H_2O (2×) and was purified via Soxhlet extraction with 100% EtOH (2.5 days) and hexane (1.5 days). The polymer was dried under vacuum to yield a white, fibrous material (66%). For **7**: ^{31}P NMR ($CDCl_3$) δ −19.7 ppm (s); ^{1}H NMR ($CDCl_3$) 7.3–6.4 ppm (m, Ar); ^{13}C NMR ($CDCl_3$) δ 149.8, 132.2, 122.1, 118.0 ppm (Ar); $T_g = 10$ °C; $M_w = 2.5 \times 10^6$, $M_n = 1.2 \times 10^6$, $M_w/M_n = 2.1$. Anal. Calcd: C, 37.00; H, 2.07; N, 3.61; Cl, 0.09. Found: C, 38.59; H, 1.91; N, 3.79; Cl, <0.5.

Poly[(*p*-(cyclopentadienyldicarbonyliron)phenoxy)(*p*-bromophenoxy)(phenoxy)phosphazene] (8). Polymer **7** (0.5 g, 1.3 mmol) was dissolved in dry, deoxygenated THF (350 mL) in a 1-L flame-dried three-necked round-bottomed flask. $CpFe(CO)_2I$ (4.69 g, 15.4 mmol, 6 equiv/site) was dissolved in dry, deoxygenated THF (50 mL) and then transferred to an attached addition funnel. The *n*-BuLi (2.6 mL, 6.4 mmol, 2.5 equiv/site) was introduced via syringe into a second addition funnel. The whole reaction apparatus was cooled to −78 °C and covered with foil in a darkened hood. The *n*-BuLi was then added slowly to the cooled polymer solution and allowed to stir for 5 min. Subsequently, the $CpFe(CO)_2I$ solution was added in a dropwise manner over 30 min. When the addition of the electrophile was complete, the reaction solution was allowed to warm to room temperature. The solution was then concentrated in vacuo and precipitated repeatedly, under argon, into dry, deoxygenated Et_2O and THF, until clear solvent was extracted. A red-brown, fibrous polymer was obtained after high vacuum drying (approximately 70% yield). The use of NH_4PF_6 to quench the unreacted lithio sites prior to isolation of the polymer was also investigated. However, the resultant metallophosphazene was also found to be paramagnetic and insoluble upon isolation. For **8**: $T_g = 41$ °C; FTIR (KBr) ν 2012, 1957, 1794 (CO's). Anal. Calcd: C, 46.72; H, 2.80; N, 3.61; Fe, 6.48; Br, 20.39. Found: C, 42.65; H, 3.33; N, 2.82; Fe, 6.06; Br, 20.39 (ca. 23% metalation).

Preparation of Cross-Linked Films (9). Films of polymer **7** were prepared by a solution-casting method from THF/dioxane on a glass plate. The solvent was allowed to evaporate slowly in a dust-free, solvent-saturated environment, to give a homogeneous film. The films were then cross-linked by exposure to 10 Mrad of ^{60}Co γ-radiation at the Breazeale Nuclear Reactor at The Pennsylvania State University.

Preparation of the Surface-Metalated Films (10). A number of variations to this procedure were investigated, such as choice of solvent (hexane, Et_2O, THF), lithiation reaction conditions, temperature variations for different steps, duration of lithiation, and metalation reactions, etc. After these conditions were optimized, a single set of conditions was used, and the effect of variation of the lithiation time studied. In a typical reaction, the cross-linked polymer film **9** was immersed in dry THF (5 mL), in a flame-dried 100-mL, three-necked, round-bottomed flask, which was maintained under an inert atmosphere. The whole reaction apparatus was cooled immediately to −78 °C, and an excess of *n*-BuLi solution (5 mL, 2.5 M) added via syringe. Lithiation times were varied from 30 s (**10a**), 1 min (**10b**), 2.5 min (**10c**), to 5 min (**10d**) exposure. The cooled *n*-BuLi/THF solutions

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[27] Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.

[28] Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

were then removed via syringe and a solution of $CpFe(CO)_2I$ (10 equiv/Br) at −78 °C in dry THF (10 mL) was added all at once, from a previously attached, jacketed addition funnel. After an elapsed time of 15 min, the reaction was terminated by repeated washing of the film with THF. Purification of these films was carried out by sonication in THF (4 days). The films were then dried to constant weight and those films lithiated for 30 s (**10a**) and 5 min (**10d**) were characterized fully. Elemental microanalysis detected 1.4% Fe present for both of these films.

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