Macromolecules **1991,** *24,* 5208-5214

Synthesis and Characterization of Polyphosphazene (η^6-Arene)chromium Tricarbonyl Derivatives

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Received February 12, 1991; Revised Manuscript Received May 2, 1991

ABSTRACT: The synthesis and structure of a new class of poly(metallophosphazenes) is described. The polymers have the general formulas $[NP(OR)_2]_n$ and $[NP(OR)_x(OCH_2CF_3)_y]_n$, where the OR side group is (η^6-2-phenoxyethoxy)chromium tricarbonyl and $x + y = 2$. The single-substituent polymer is the first example of a poly(metallophosphazene) that has one transition-metal unit on every side group. Nonmetallo polymers with the general structures $[NP(OR')_2]_n$, $[NP(OR')_x(OCH_2CF_3)_y]_n$, and $[NP(OCH_2CF_3)_2]_n$, where the OR′ substituent is 2-phenoxyethoxy and $x + y = 2$, were prepared for comparison with the corresponding metallophosphazene polymers. Structural characterization for the high polymers was carried out by NMR spectroscopy, infrared spectroscopy, gel permeation chromatography, and elemental analysis. Thermal analysis of the polymers was investigated by differential scanning calorimetry and thermogravimetric analysis.

The expanding interest in transition-metal-functionalized macromolecules reflects the opportunities that exist for the development of advanced electroactive, optical, magnetic, or catalytic materials.[1,2]

The synthesis of phosphazenes that contain transition metals has been an area of growing interest.[3] In an earlier paper, we described the π-coordination of transition metals to pendent aryl ligands linked to cyclic phosphazenes.[4] In particular, we reported the synthesis of phosphazene (η^6-arene)$Cr(CO)_3$ complexes,[5] in which the arene ligand was bound either directly to the phosphazene skeleton, via an oxygen or nitrogen atom, or through an organic spacer group. Specifically, the earlier small-molecule studies involved the synthesis and structure of a new class of cyclotriphosphazene transition-metal complexes with the general structures $N_3P_3X_5[RCr(CO)_3]$ (1), $N_3P_3R_5[RCr(CO)_3]$ (2), and $N_3P_3[RCr(CO)_3]_6$ (3), in which the R substituents were aryl groups and the X substituents were fluoro, chloro, trifluoroethoxy, or *n*-propylamino groups (Figure 1). The substitutive method of synthesis available for phosphazenes allowed the facile incorporation of a diverse range of aryl side group structures and provided access to an interesting series of arene complexes.

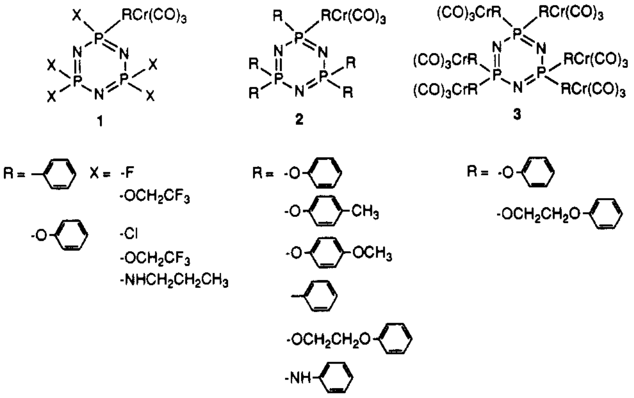


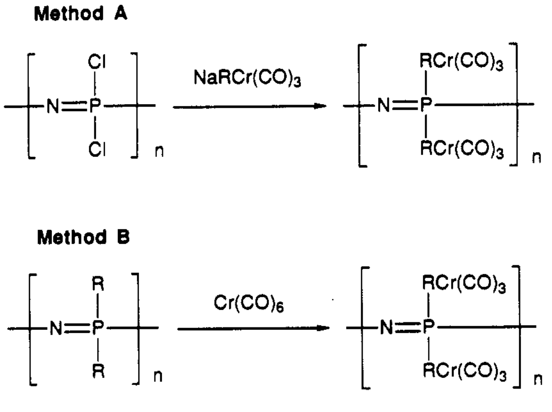
Figure 1. Structures of compounds 1-3.

The objective of the work described here was to extend the small-molecule synthesis of the cyclotriphosphazene (η^6-arene)$Cr(CO)_3$ complexes to the macromolecular level. Specifically, in this paper we describe the synthesis and characterization of a new class of poly(metallophosphazenes) that possess (η^6-2-phenoxyethoxy)chromium tricarbonyl substituent groups.

Results and Discussion

Overview of the Synthetic Approach. Two general synthetic approaches were explored in the preparation of the polyphosphazene (η^6-arene)$Cr(CO)_3$ complexes, as summarized in Scheme I. In method A, poly(dichlorophosphazene) was allowed to react with the sodium salt of an aryl oxide or aryl alkoxide chromium tricarbonyl complex. This approach paralleled closely the classical phosphazene synthesis methods.[6] Previously, this approach had been shown to be successful for the introduction of high loadings of $Cr(CO)_3$ units into the corresponding small-molecule cyclotriphosphazene systems.[4]

Scheme I



R = aryloxy or aryl-containing alkoxy group

In method B, an aryl-substituted polyphosphazene was allowed to react with $Cr(CO)_6$ in order to synthesize the macromolecular (η^6-arene)$Cr(CO)_3$ complex. This method was successful for the introduction of a moderate loading of $Cr(CO)_3$ units into the corresponding small-molecule cyclic species.[4]

Of the two approaches outlined, method A was found to be the most efficient and controlled route for the synthesis of soluble poly(metallophosphazenes) with high loadings of transition-metal units. Therefore, this synthetic approach is the primary focus of the following discussion.

Attempted Synthesis of Poly(metallophosphazenes) with Phenoxychromium Tricarbonyl Substit-

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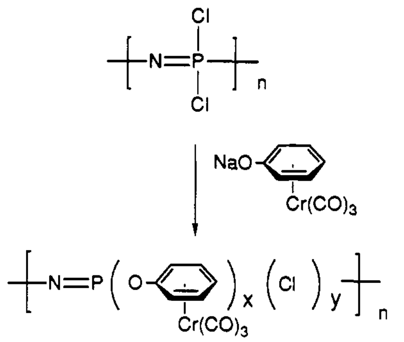
Scheme II



uents. In an earlier paper, small-molecule cyclotriphosphazene complexes of family $N_3P_3[RCr(CO)_3]_6$ (**3**) were prepared in which the R units were phenoxy and 2-phenoxyethoxy groups.[4] An extension of this research to the macromolecular level is described here.

The attempted synthesis of the single-substituent polymer $[NP((OC_6H_5)Cr(CO)_3)_2]_n$ is summarized in Scheme II. Poly(dichlorophosphazene), prepared by the thermal ring-opening polymerization of the cyclic trimer $(NPCl_2)_3$,[7] was allowed to react with sodium η^6-phenoxide chromium tricarbonyl in tetrahydrofuran. The progress of the substitution reaction was monitored by ^{31}P NMR spectroscopy. A loading of ca. 70% was achieved before gelation of the reaction mixture or precipitation of the polymer occurred. Extended warming did not bring about dissolution. Because of the high concentration of unreacted P–Cl bonds in the polymers, attempted purification led to hydrolysis and subsequent decomposition. The large steric size of the η^6-coordinated $Cr(CO)_3$ unit on the phenoxy substituent and its proximity to the backbone appear to inhibit complete halogen replacement.[8]

The synthesis of mixed-substituent poly(metallophosphazenes) with phenoxy chromium tricarbonyl side groups, and with trifluoroethoxy and phenoxy groups as cosubstituents, was then investigated. The syntheses were attempted by two sequences of nucleophile additions: (1) an initial addition of the arene nucleophile to poly(dichlorophosphazene), followed by reaction with an excess of the cosubstituent nucleophile, and (2) an initial addition of the cosubstituent nucleophile to poly(dichlorophosphazene), followed by reaction with an excess of the arene nucleophile. Pathways 1 and 2 are summarized in Scheme III.

In pathway 1, the reaction of the cosubstituent nucleophile with the partially substituted metallophosphazene resulted in a competition between replacement of the remaining P–Cl bonds and displacement of the arene units from the phosphazene backbone. This result is not surprising in view of the strong electron-withdrawing characteristics of the $Cr(CO)_3$ unit. (Similar displacement reactions have been detected for 4-nitrophenoxy side groups.)[6]

In pathway 2, the large steric size and low nucleophilicity of the phenoxy chromium tricarbonyl group severely limited attempts to replace all the chlorine atoms. As described previously for the single-substituent polymer, attempted purification led to hydrolysis and subsequent decomposition.

These results with phenoxy chromium tricarbonyl nucleophiles suggested that a spacer linkage was required in order to assist the substitution reaction. Thus, the use of (η^6-2-phenoxyethanol)chromium tricarbonyl as a substituent group was investigated. As shown in the following sections, introduction of an ethoxy spacer group reduced the restrictions associated with the large steric size and low nucleophilicity of the phenolic reagent.

Synthesis of Poly(metallophosphazenes) with (2-Phenoxyethoxy)chromium Tricarbonyl Substituents. The synthesis of single- and mixed-substituent poly(metallophosphazenes) with (η^6-2-phenoxyethoxy)-chromium tricarbonyl side groups was explored. The preparation of the single-substituent polymer $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (**4**) is summarized in Scheme IV. In the synthesis of **4**, poly(dichlorophosphazene) was allowed to react with an excess of (sodium η^6-2-phenoxyethoxide)chromium tricarbonyl, prepared by the reaction of the corresponding alcohol with sodium hydride. Complete replacement of the halogen atoms occurred to yield the fully substituted polymer even under mild reaction conditions (see Experimental Section). The polymer was isolated by precipitation from the concentrated reaction solution in tetrahydrofuran into diethyl ether and was purified by repeated precipitations into diethyl ether and water. As will be described in the following characterization section, no loss of the $Cr(CO)_3$ unit from the 2-phenoxyethoxy substituent was detected. Thus, polymer **4** represents the first example of a poly(metallophosphazene) that has *all* side-chain groups coordinated to a transition metal.

In order to study the effect of variations in the loading of $Cr(CO)_3$ units on the properties of the polymer, a series of mixed-substituent polyphosphazenes was prepared by using trifluoroethoxy groups as the cosubstituent. The synthesis of the mixed-substituent polymers **5**–**7** is outlined in Scheme V. The cosubstituents were present in the approximate ratios of one to three (**5**), one to one (**6**), and three to one (**7**). The trifluoroethoxy group was selected as a representative cosubstituent because of its unhindered steric size and hydrophobic character.

The synthesis of polymers **5**–**7** was carried out by the reaction of poly(dichlorophosphazene) with a stoichiometric deficiency of (sodium η^6-2-phenoxyethoxide)chromium tricarbonyl, followed by reaction with excess sodium trifluoroethoxide (see Scheme V). The sodium trifluoroethoxide was used to replace any remaining P–Cl bonds in order to obtain a halogen-free, hydrolytically stable derivative. No displacement of the $Cr(CO)_3$ unit from the arene ring by the trifluoroethoxide nucleophile was detected.[4]

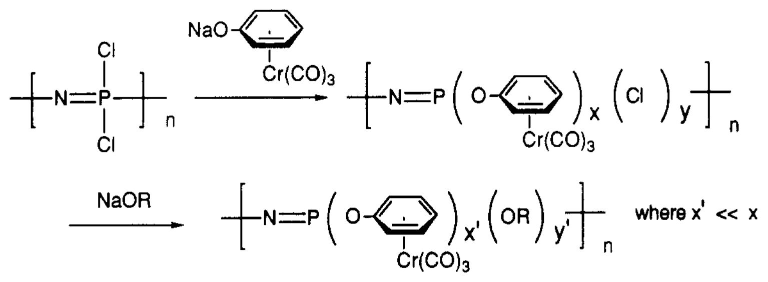
The preparation of polymers **5**–**7** was also accomplished by the reverse sequence of addition of the two nucleophiles. For example, poly(dichlorophosphazene) was first allowed to react with a deficiency of sodium trifluoroethoxide, followed by treatment with excess (sodium η^6-2-phenoxyethoxide)chromium tricarbonyl. The availability of both sequences of nucleophile addition allowed the ratio of the transition-metal-containing side group to be varied over a wide range, with the final ratio being controlled by the degree of substitution of the first nucleophile.

Single- and mixed-substituent non-metal-containing polyphosphazenes were synthesized for comparison with the corresponding poly(metallophosphazenes). Species $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (**8**), $[NP(OCH_2CH_2OC_6H_5)_x(OCH_2CF_3)_y]_n$ (**9**–**11**), and $[NP(OCH_2CF_3)_2]_n$ (**12**), shown in Figure 2, were prepared by use of the procedures described previously.[6,7] Note that polymers **9**–**11** possess cosubstituents in the approximate ratios of one to three (**9**), one to one (**10**), and three to one (**11**).

General Properties. Chromium-containing polymers **4**–**7** are yellow compounds, while polymers **8**–**12** are white materials. The solubilities of polymers **4**–**7** were more limited than those of polymers **8**–**12**. Polymers **4**–**7** were

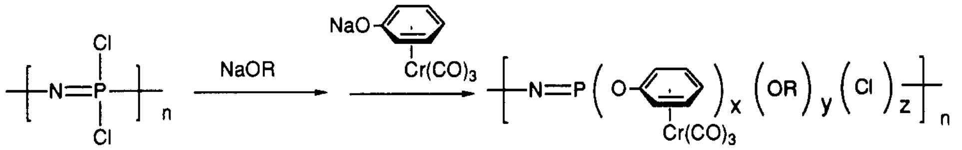
Scheme III

Pathway 1



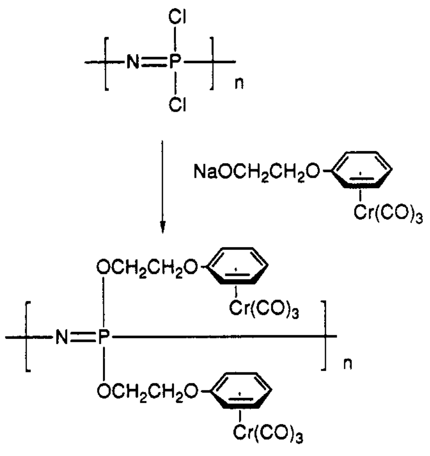
Displacement of the arene side group by the NaOR nucleophile.

Pathway 2



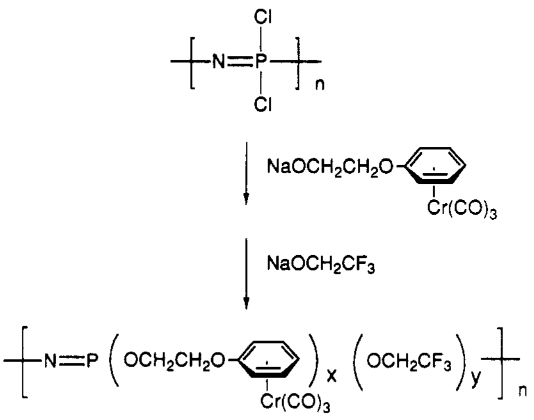
OR = OC_6H_5 or OCH_2CF_3

Scheme IV



4

Scheme V



5-7

5 x = 1.5, y = 0.5

6 x = 1.0, y = 1.0

7 x = 0.7, y = 1.3

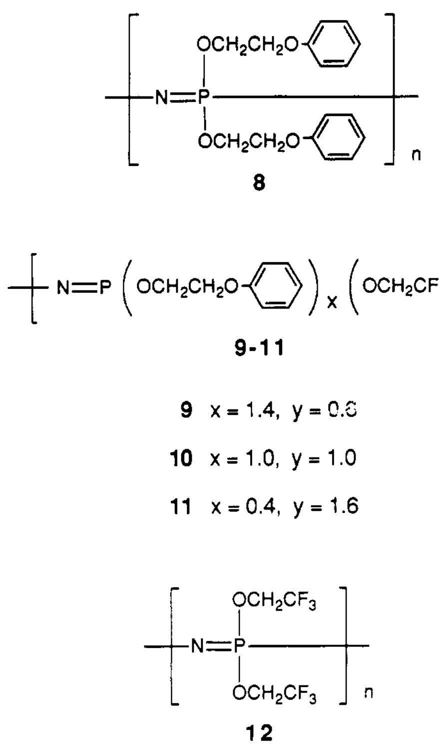
soluble initially in tetrahydrofuran and acetone. However, if the polymers were completely dried or were stored in the solid state for several days, their solubility decreased and they swelled without dissolving on attempted dissolution. For this reason, the polymers were always stored in tetrahydrofuran solution. This behavior may be a result of the enhanced opportunities for side group stacking in the solid state, which could generate microcrystalline domains and reduce the solubility. Similar characteristics were found in earlier work for polyphosphazenes that possessed nonlinear optical and liquid crystalline moieties.[9] Polymers 8–12 showed a normal solubility behavior in solvents such as tetrahydrofuran and acetone.

In the solid state, the arene polymers 4–7 were air- and moisture-stable. However, after several days storage in solution in contact with air or moisture, the yellow polymer solutions became green. This was presumably due to oxidation of the chromium from Cr(0) to a paramagnetic Cr(III) species.[5] Similar decomposition characteristics were detected previously for the corresponding cyclic species.[4]

Characterization of Polyphosphazenes. Structural characterization of polymers 4–12 was achieved by NMR spectroscopy, infrared spectroscopy, gel permeation chromatography, and elemental analysis. Thermal analysis was investigated by differential scanning calorimetry and thermogravimetric analysis. The characterization data are summarized in Tables I and II.

(a) Spectroscopic Analysis. The ^{31}P NMR spectra of polymers 4–12 consisted of a sharp, singlet resonance at ca. −8 ppm (see Table I). In the mixed-side-group systems, the singlet resonance is a consequence of the similar environment at the ethoxy- and trifluoroethoxy-linked phosphorus atoms. The ^{31}P NMR spectrum of the single-substituent poly(metallophosphazene) 4 was a sharp, singlet resonance at −8.8 ppm. The singlet was indicative of a high degree of chlorine replacement, and this was supported by the elemental microanalysis data.

The ^1H NMR spectra of polymers 4–7 confirmed the η^6-coordination of the $Cr(CO)_3$ unit to the 2-phenoxyethoxy substituent.[5] The aromatic protons on the complexed sub-



8

9-11

9 x = 1.4, y = 0.6

10 x = 1.0, y = 1.0

11 x = 0.4, y = 1.6

12

Figure 2. Structures of polymers 8–12.

stituent in 4–7 resonated in the region from 6.0 to 5.0 ppm, which is at a significantly higher field than the resonance for the corresponding uncomplexed side group in polymers 8–11 (7.3–6.5 ppm) (see Table I). In addition, ^{1}H NMR analysis, together with elemental microanalysis, was important for estimation of the composition ratios for the mixed-substituent polymers. The ratios were estimated by a comparison of the integration of the aromatic resonances with the trifluoroethoxy resonance at 4.5 ppm.

The ^{13}C NMR spectrum of polymer 4 provided additional evidence for the presence of one transition-metal unit on every side group structure. This is illustrated clearly in Figure 3, by a comparison of the aromatic region of the ^{13}C NMR spectra of species $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4) and $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8). The characteristic upfield shift of ca. 16–35 ppm in the resonances of the complexed phenoxy carbon atoms of 4 (144–80 ppm) can be compared with the resonances from the uncomplexed phenoxy carbon atoms of 8 (160–115 ppm).[5]

In the ^{13}C NMR spectrum of polymer 4, the CO ligands were detected as a singlet resonance at 232 ppm. The singlet arises from the equivalence of the three CO ligands. The ethoxy units in polymers 4 and 8 were detected as two singlet resonances in the region 68–65 ppm.

The IR spectra of polymers 4–7 in solution showed two intense C–O stretching absorptions, one in the region 1970–1965 cm^{-1} and the other at 1888–1887 cm^{-1}. The specific ν_{CO} absorption values for 4–7 are listed in Table II. The presence of these two bands is a characteristic feature of (η^6-arene)$Cr(CO)_3$ complexes[5]. In our previous study of cyclotriphosphazene (η^6-arene)$Cr(CO)_3$ complexes, the frequency of the stretching absorption was correlated with the electron density on the arene ligand, which in turn was determined by the electronic properties of the phosphazene cosubstituents and the arene para substituents.[4]

The ν_{CO} absorption values for 4–7 (ca. 1967, 1887 cm^{-1}) can be compared directly to the value for the starting reagent, η^6-2-phenoxyethanol chromium tricarbonyl (1968, 1887 cm^{-1}). The similarity in the ν_{CO} absorption values confirms the ability of the ethoxy group to decouple the electronic characteristics of the phosphazene backbone from the arene.

The molecular weights of polymers 4–12 were estimated by gel permeation chromatography to be in the range M_n 1.2×10^5–1.4×10^6, $M_w > 1.5 \times 10^6$, with M_w/M_n values in the region 2–15 (see Table II). The broad, bimodal molecular weight distribution is typical of polyphosphazenes.

(b) Thermal Analysis. The glass transition temperatures (T_g) were determined by differential scanning calorimetry and are listed in Table II. The T_g of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4) is 43 °C. The DSC thermogram is shown in Figure 4. Since the T_g of $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8) is −8 °C, the η^6-coordination of the $Cr(CO)_3$ unit to the 2-phenoxyethoxy side groups increases the T_g by ca. 50 °C.

A comparison of the T_g's of the metallo (5–7) and nonmetallo (9–11) mixed-substituent polymers confirms the trend that η^6-coordination of the $Cr(CO)_3$ unit increases the T_g significantly. For example, the T_g's of polymers 5, 6, and 7 were 31, 8, and 0 °C, respectively, while the T_g's of the corresponding polymers 9, 10, and 11 were −18, −24, and −45 °C, respectively. The T_g of the single-substituent polymer $[NP(OCH_2CF_3)_2]_n$ (12) is −66 °C.[6] The higher T_g values for the metallophosphazenes are presumably a consequence of restricted skeletal torsion due to the steric bulk of the $Cr(CO)_3$ group at the 2-phenoxyethoxy substituent.[8]

The thermal behavior of polymers 4–12 was examined by thermogravimetric analysis. The objective of these experiments was to gain insight into the overall influence of the $Cr(CO)_3$ unit on the thermal stabilities of the polymers, as well as to identify any potential metal-containing ultrastructure systems. The emphasis in these experiments was on the pattern of loss of volatile thermolysis products and on the percentage of nonvolatile ultrastructure material remaining at a specific temperature. A comparison of the results obtained from the metallo- (4–7) and nonmetallo-substituted (8–12) macromolecules was particularly interesting.

The thermal behavior of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4) was significantly different from that of $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8), as illustrated in the thermogravimetric analysis curve in Figure 5. Although both systems underwent cross-linking reactions during thermolysis, the percentage of nonvolatile residue at 800 °C was higher for 4 (43%) than for 8 (20%). The higher weight retention may be associated with the incorporation of chromium-containing species. In addition, the thermal behavior of polymers 4 and 8 differed in the onset temperature for volatilization. Polymer 4 underwent a gradual weight decline in the temperature range 200–400 °C, while polymer 8 underwent a dramatic decline at ca. 350 °C.

A control experiment was carried out with $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$, in an attempt to understand the effect of the $Cr(CO)_3$ unit on the thermal properties of the polymers. The thermogravimetric analysis curve is shown in Figure 6. Surprisingly, thermolysis of the phosphazene-free system yielded a nonvolatile ultrastructure of 32% weight retention at 800 °C. The calculated weight percent of chromium in the small molecule is 19%. The thermal events had an onset temperature of ca. 180 °C and continued to a temperature of ca. 400 °C.

The thermolysis behavior for (η^6-2-phenoxyethanol)chromium tricarbonyl was explored further by solid-state ^{13}C NMR spectroscopy. Solid-state ^{13}C NMR spectra were obtained before and after pyrolysis to 500 °C. The

Table I
Polyphosphazene Characterization Data. Part 1

compd[a]	^{31}P NMR, ppm[b]	^{1}H NMR, ppm[b]	elem anal. calcd	elem anal. found
4	−8.8 (s)[c]	5.9–5.0 (m, Ar H, 5 H), 4.5–4.0 (m, OCH_2, 4 H)[c]	C, 44.68; H, 3.07; N, 2.37; Cl, 0.00	C, 44.20; H, 3.42; N, 2.42; Cl, 0.14
5	−8.6 (s)	5.9–5.1 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.4–3.9 (m, OCH_2)	C, 41.68; H, 2.90; N, 2.78; Cl, 0.00	C, 41.10; H, 3.65; N, 2.64; Cl, 0.23
6	−8.5 (s)	6.0–5.2 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.5–3.9 (m, OCH_2)	C, 37.42; H, 2.66; N, 3.36; Cl, 0.00	C, 36.51; H, 3.21; N, 3.08; Cl, 0.08
7	−8.5 (s)	6.0–5.1 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.4–3.0 (m, OCH_2)	C, 33.90; H, 2.46; N, 3.84; Cl, 0.00	C, 34.46; H, 3.47; N, 3.48; Cl, 0.14
8	−7.7 (s)	7.1–6.5 (m, Ar H, 5 H), 4.4–4.2 (d, OCH_2, 2 H), 3.9–3.7 (d, OCH_2, 2 H)	C, 60.18; H, 5.68; N, 4.39; Cl, 0.00	C, 60.00; H, 5.63; N, 4.01; Cl, 0.01
9	−8.2 (s)	7.2–6.6 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.4–3.9 (m, OCH_2)	C, 50.24; H, 4.69; N, 4.73; Cl, 0.00	C, 48.72; H, 4.16; N, 4.84; Cl, 0.06
10	−8.1 (s)	7.2–6.6 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.4–3.8 (m, OCH_2)	C, 42.71; H, 3.94; N, 4.98; Cl, 0.00	C, 43.15; H, 3.84; N, 4.99; Cl, 0.25
11	−8.1 (s)	7.3–6.7 (m, Ar H), 4.5 (br s, OCH_2CF_3), 4.4–3.9 (m, OCH_2)	C, 29.76; H, 2.65; N, 5.42; Cl, 0.00	C, 30.24; H, 2.75; N, 5.60; Cl, 0.10
12	−7.9 (s)	4.5 (br s, OCH_2CF_3)	C, 19.77; H, 1.66; N, 5.76; Cl, 0.00	C, 19.80; H, 1.46; N, 5.53; Cl, 0.06

[a] See Schemes IV and V and Figure 2 for structures. [b] In acetone-d_6. [c] In THF-d_8.

Table II
Polyphosphazene Characterization Data. Part 2

compd[a]	T_g, °C	IR, ν_{CO}, cm^{-1} [b]	molecular weight (GPC) M_n	M_w	M_w/M_n
4	43	1965, 1887[c]	5.7×10^5	$>2 \times 10^6$	5
5	31	1968, 1887	1.8×10^5	$>2 \times 10^6$	14
6	8	1970, 1888	6.9×10^5	$>2 \times 10^6$	4
7	0	1969, 1887	1.4×10^6	$>2 \times 10^6$	3
8	−8		5.9×10^5	$>2 \times 10^6$	4
9	−18		1.1×10^6	$>2 \times 10^6$	2
10	−24		1.2×10^5	1.6×10^6	13
11	−45		1.4×10^6	$>2 \times 10^6$	3
12	−66, $T(1)$ = 65		4.2×10^5	1.5×10^6	6

[a] See Schemes IV and V and Figure 2 for structures. [b] In CH_2Cl_2 solution. [c] In THF solution.

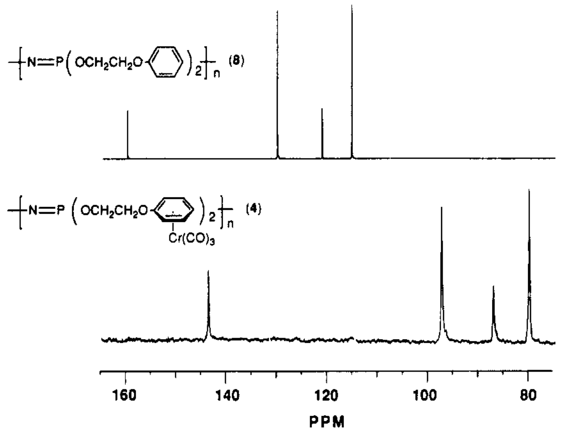


Figure 3. Aromatic region of the ^{13}C (90.0 MHz) NMR spectra of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4) and $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8) in THF-d_8.

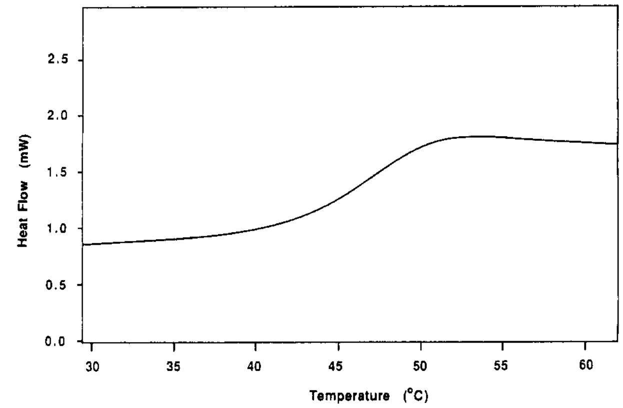


Figure 4. Differential scanning calorimetry thermogram of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4). (Heating rate = 15 °C/min.)

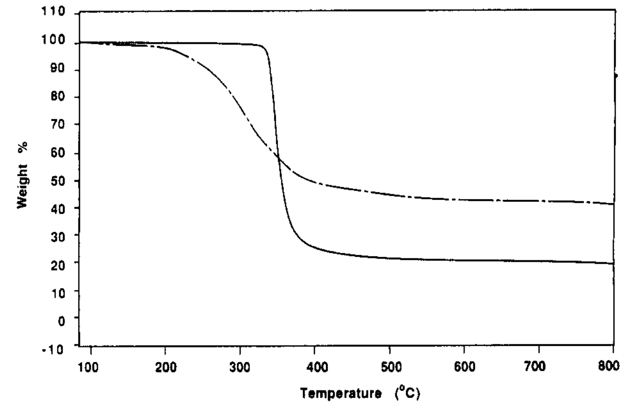


Figure 5. Thermogravimetric analysis curves for $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4) (- - -) and $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8) (—) under a nitrogen atmosphere. (Heating rate = 10 °C/min).

spectrum obtained before pyrolysis was consistent with the resonances described previously for the solution ^{13}C NMR spectrum.[11] The spectrum of the black, porous material obtained after pyrolysis to 500 °C indicated the presence of a paramagnetic species, presumably Cr(III). Because of the paramagnetic nature of the sample, no additional NMR information on the nonvolatile residue could be obtained.

The thermal profiles were not changed significantly when the single-substituent polymers 4 and 8 were replaced by the mixed-substituent trifluoroethoxy polymers 5–7 and 9–11. The percentage of nonvolatile residue at 800 °C was in the range from 38 to 43% for 5–7 (compared to 43% for 4) and from 13 to 18% for 9–11 (compared to 20% for 8). These thermogravimetric analyses for the mixed-substituent systems are interesting in comparison to the analysis for the single-substituent polymer $[NP(OCH_2CF_3)_2]_n$ (12). As shown in earlier studies, complete depolymerization to cyclic oligomers and volatilization of the material occurs by 450 °C, with no evidence for cross-linking reactions during thermolysis.[12] Thus, the present results suggest that the 2-phenoxyethoxy substituent plays a major role in stabilizing the mixed-substituent polymers against complete depolymerization.

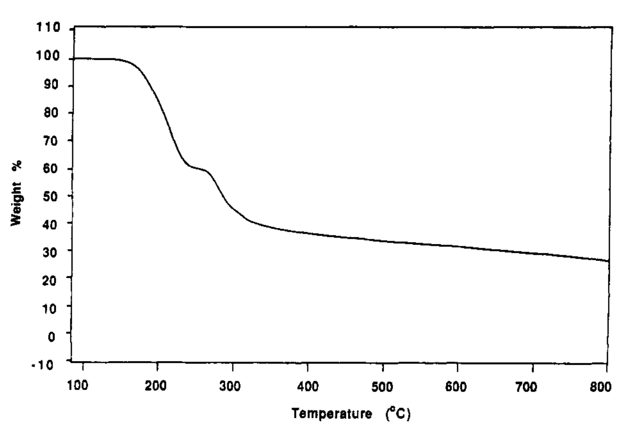


Figure 6. Thermogravimetric analysis curve for $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$ under a nitrogen atmosphere. (Heating rate = 10 °C/min.)

Attempted Synthesis of Polyphosphazenes via Method B. As mentioned previously, the interaction of aryl-substituted polyphosphazenes with $Cr(CO)_6$ was explored as an alternative route to poly(metallophosphazenes). These reactions are summarized as method B in Scheme I. The potential advantage of this approach is its synthetic simplicity. Specifically, $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (**8**) and $[NP(OCH_2CH_2OC_6H_5)_{1.0}(OCH_2CF_3)_{1.0}]_n$ (**10**) were allowed to react with $Cr(CO)_6$ in solvents such as tetrahydrofuran, ethylene glycol dimethyl ether, and dioxane. The reactions were allowed to proceed at reflux temperatures for different periods of time (12–60 h). Attempts to isolate the polymeric products by concentration of the reaction mixture often resulted in gelation of the solution. Precipitation of the gel into nonpolar solvents (i.e., *n*-hexane and *n*-pentane) yielded green, elastomeric materials, which were subsequently insoluble.

^{31}P NMR spectra of the reaction mixtures, before attempted isolation of the polymer, contained very broad resonances (line width ca. 4 ppm). η^6-Coordination of the $Cr(CO)_3$ unit to the arene ring should not affect the ^{31}P NMR resonance of the polymer, since the aryl substituents were insulated from the polymer backbone by the ethoxy spacer groups (see NMR characterization discussion). Thus, these NMR characteristics suggest that coordination of a chromium species occurs to the polyphosphazene backbone together with production of paramagnetic Cr(III) species. Thus, at its present level of synthesis development, method A has marked advantages over method B.

Summary

The synthesis and characterization of a new class of phosphazene macromolecules with $(\eta^6\text{-arene})Cr(CO)_3$ groups as the side-group structure have been described. The single-substituent polymer $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ is the first example of a 100% loading of side-group transition metals on any polyphosphazene. Although this methodology was developed for the (η^6-2-phenoxyethoxy)chromium tricarbonyl substituent group, the synthetic strategy should be applicable to a wide variety of aryl alcohols.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (provided by Ethyl Corp.), phenol (Aldrich), and chromium hexacarbonyl (Strem) were purified by vacuum sublimation before use. 2-Phenoxyethanol (Aldrich) and 2,2,2-trifluoroethanol (Halocarbon) were distilled from calcium hydride. All other reagents (Aldrich) were used as received. Poly(dichlorophosphazene) and poly[bis(trifluoroethoxy)phosphazene] (**12**) were prepared by procedures reported in the literature.[6,7] Column chromatography was carried out under an atmosphere of argon with the use of dry *n*-hexane/THF as elution solvents and with the use of silica gel (60–200 mesh, Fisher) as packing material. Solvents were dried and distilled under nitrogen by standard methods. All reactions and manipulations were carried out under an atmosphere of dry argon or nitrogen by using standard Schlenk and drybox techniques.

Equipment. ^{31}P (36.23 MHz) NMR spectra were recorded with use of a JEOL FX90Q NMR spectrometer. ^1H (360.0 MHz) and ^{13}C (90.0 MHz) NMR spectra were recorded with use of a Bruker WM360 spectrometer. Solid-state ^{13}C (74.78 MHz) NMR spectra were recorded with use of a Chemagnetics CMX-300 NMR spectrometer, which used a broad-band CPMAS pencil probe. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or tetramethylsilane (^1H and ^{13}C). All heteronuclear NMR spectra were proton decoupled. Infrared spectra were recorded with the use of a Perkin-Elmer Model 1710 FTIR instrument interfaced with a Perkin–Elmer 3600 data station. Electron-impact mass spectra were obtained with the use of a Kratos MS9/50 spectrometer. Molecular weights were determined by using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1037A refractive index detector and a Polymer Laboratories PL gel 10-μm column. The samples were eluted with a 0.1% by weight 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 using a Perkin-Elmer-7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. For the determination of glass transition temperatures by differential scanning calorimetry, heating rates of 10–25 °C/min under a nitrogen atmosphere were used, and sample sizes were between 10 and 30 mg. For thermogravimetric analyses, heating rates of 10 °C/min under a nitrogen atmosphere were used, and sample sizes were between 2 and 6 mg. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $(\eta^6\text{-}HOC_6H_5)Cr(CO)_3$. (Phenol)chromium tricarbonyl was prepared by following a modified literature procedure.[13] A solution of phenol (6.0 g, 0.064 mol) and $Cr(CO)_6$ (15.5 g, 0.071 mol, 10% excess) in di-*n*-butyl ether/THF (250 mL) was stirred and heated at reflux for 48–72 h. The solvent was removed in vacuo and the residue was transferred to a water-cooled sublimator, which was evacuated to 10^{-3} mmHg. After the mixture was warmed at 30 °C for 2 h, phenol and $Cr(CO)_6$ were collected on the cold finger and removed. Additional warming at 45 °C for 16 h allowed the isolation of the product as yellow crystals. Yield 35–70%; MS, *m/z* calcd 230, *m/z* found 230; ^1H NMR ($CDCl_3$) 5.8–4.6 (m, Ar H) ppm; ^{13}C NMR ($CDCl_3$) 233.3 (CO), 139.3, 95.4, 85.2, 79.6 ppm; IR (CH_2Cl_2) ν_{CO} 1969, 1887 cm^{-1}. Anal. Calcd for $C_9H_6O_4Cr$: C, 46.97; H, 2.63. Found: C, 47.06; H, 2.79.

Synthesis of $(\eta^6\text{-}HOCH_2CH_2OC_6H_5)Cr(CO)_3$. A solution of $C_6H_5OCH_2CH_2OH$ (20.0 g, 0.145 mol) and $Cr(CO)_6$ (35 g, 0.159 mol, 10% excess) in di-*n*-butyl ether/THF (300 mL) was stirred and heated at reflux for 48–72 h. The solvent and excess $Cr(CO)_6$ were removed in vacuo, and the excess $C_6H_5OCH_2CH_2OH$ was removed by vacuum distillation (ca. 70 °C at 10^{-3} mmHg). The residue was dissolved in THF (50 mL) and purified by column chromatography. The solvent was removed in vacuo, and the product was further purified by recrystallization from *n*-hexane/methylene chloride to yield $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$ as yellow crystals. Yield 45–80%; MS, *m/z* calcd 274, *m/z* found 274; ^1H NMR ($CDCl_3$) 5.6–5.4 (m, 2 H, Ar H), 5.2–5.0 (m, 2 H, Ar H), 4.9–4.7 (m, 1 H, Ar H), 4.1–3.8 (m, 4 H, OCH_2) ppm; ^{13}C NMR ($CDCl_3$) 233.1 (CO), 142.1, 95.0, 85.5, 78.6, 70.0, 60.9 ppm; IR (CH_2Cl_2) ν_{CO} 1968, 1887 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_5Cr$: C, 48.18; H, 3.68. Found: C, 47.96; H, 3.77.

Synthesis of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_2]_n$ (4). To a solution of poly(dichlorophosphazene) (0.25 g, 2.16 mmol) in THF (70 mL) was added slowly a solution of (sodium 2-phenoxyethoxide)chromium tricarbonyl, which was prepared from the reaction of (2-phenoxyethanol)chromium tricarbonyl (2.13

g, 7.77 mmol) and NaH (0.34 g, 8.54 mmol) in THF (80 mL) at room temperature for 6 h. The reaction mixture was warmed at 45–50 °C for 24 h. The reaction mixture was concentrated in vacuo, and the polymer was isolated by precipitation into diethyl ether and was purified by successive precipitations from THF into diethyl ether (two times), water (two times), and *n*-pentane (one time). Characterization data for 4 are listed in Tables I and II.

Synthesis of $[NP((OCH_2CH_2OC_6H_5)Cr(CO)_3)_x(OCH_2CF_3)_y]_n$ (5–7). Polymer composition ratios are shown in Scheme V. Polymers 5–7 were prepared in the same manner. The following procedure for the preparation of 6 is typical. To a solution of poly(dichlorophosphazene) (0.40 g, 3.45 mmol) in THF (75 mL) was added slowly a solution of (sodium 2-phenoxyethoxide)chromium tricarbonyl, which was prepared from the reaction of (2-phenoxyethanol)chromium tricarbonyl (0.95 g, 3.45 mmol) and NaH (0.15 g, 3.80 mmol) in THF (60 mL) at room temperature for 6 h. The reaction mixture was warmed at 45–50 °C for 24 h. A solution of sodium trifluoroethoxide was prepared from trifluoroethanol (0.61 mL, 8.35 mmol) and NaH (0.30 g, 7.59 mmol) in THF (50 mL). The sodium salt was added to the polymer reaction mixture, and the solution was warmed at 35–40 °C for 24 h. The reaction mixture was concentrated in vacuo, and the polymer was isolated by precipitation into diethyl ether and was purified by successive precipitations from THF into diethyl ether (two times), water (two times), and *n*-pentane (one time). Characterization data for 5–7 are listed in Tables I and II.

Synthesis of $[NP(OCH_2CH_2OC_6H_5)_2]_n$ (8). Polymer 8 was prepared from 2-phenoxyethanol by following the same procedure described for polymer 4. Polymer 8 was isolated by precipitation into methanol and was purified by successive precipitations from THF into methanol (two times), water (two times) and *n*-hexane (one time). Characterization data for 8 are listed in Tables I and II.

Synthesis of $[NP(OCH_2CH_2OC_6H_5)_x(OCH_2CF_3)_y]_n$ (9–11). Polymer composition ratios are shown in Figure 2. Polymers 9–11 were prepared from 2-phenoxyethanol by following the same procedure described for polymer 6. Polymers 9–11 were isolated by precipitation into water and were purified by successive precipitations from THF into water/methanol (3:1) (three times) and *n*-hexane (one time). Characterization data for 9–11 are listed in Tables I and II.

Acknowledgment. We thank the U.S. Army Research Office for financial support. We also thank Dr. I. Manners and J. Bennett for helpful discussions and Dr. A. Benesi and E. Fernandes for the solid-state ^{13}C NMR spectra.

References and Notes

(1) Reviews: (a) Andrews, M. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 174. (b) Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds. *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus, and Other Inorganic Elements*; ACS Symposium Series, Vol. 360; American Chemical Society: Washington, DC, 1988. (c) Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds. *Metal-Containing Polymeric Systems*; Plenum: New York, 1985.

(2) (a) Wright, M. E. *Macromolecules* **1989**, *22*, 3256. (b) Chaudret, B.; Chung, G.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 749. (c) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1990**, *2*, 224. (d) Andrews, M. P.; Ozin, G. A. *Inorg. Chem.* **1986**, *25*, 2587. (e) St. Clair, A. K.; Carver, V. C.; Taylor, L. T.; Furtsch, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 876.

(3) For examples of metallophosphazenes, see: (a) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316. (b) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267. (c) Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5561. (d) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1986**, *5*, 460. (e) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060. (f) Allcock, H. R.; Manners, I.; Mang, M. N.; Parvez, M. *Inorg. Chem.* **1990**, *29*, 522.

(4) Allcock, H. R.; Dembek, A. A.; Bennett, J. B.; Manners, I.; Parvez, M. *Organometallics* **1991**, *10*, 1965.

(5) For a review of organometallic chromium chemistry, see: (a) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Permagon: Oxford, 1982; Vol. 3, p 1001 and references cited therein. (b) Sneeden, R. P. A. *Organochromium Compounds*; Academic: New York, 1975. (c) Silverthorn, W. E. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1975; Vol. 13, p 48.

(6) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972; and references cited therein.

(7) (a) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216. (b) Allcock, H. R.; Kugel, R. L.; Valen, K. J. *Inorg. Chem.* **1966**, *5*, 1709. (c) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716. (d) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

(8) For discussions of structure/thermal property relationships in polyphosphazenes, see: (a) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323. (b) Allcock, H. R.; Mang, M. N.; Dembek, A. A.; Wynne, K. J. *Macromolecules* **1989**, *22*, 4179.

(9) (a) Allcock, H. R.; Dembek, A. A.; Kim, C.; Devine, R. L. S.; Shi, Y.; Steier, W. H.; Spangler, C. W. *Macromolecules* **1991**, *24*, 1000. (b) Allcock, H. R.; Kim, C. *Macromolecules* **1989**, *22*, 2596.

(10) (a) Mills, O. S. *Pure Appl. Chem.* **1969**, *20*, 117. (b) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314. (c) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 2271.

(11) The solid-state ^{13}C NMR spectrum obtained before pyrolysis was consistent with the presence of two ethoxy carbon atoms (72 and 61 ppm) and at least seven aromatic carbon atoms (145, 99, 97, 88, 82, 81, and 77 ppm). The number of aromatic carbon resonances indicated that two solid-state conformations are available for the molecule and are presumably the staggered and eclipsed configurations of the $Cr(CO)_3$ unit with respect to the carbon atoms of the arene ring. The CO ligands were not detected in the solid-state spectrum.

(12) Allcock, H. R.; McDonnell, G. S.; Riding, G. H.; Manners, I. *Chem. Mater.* **1990**, *2*, 425.

(13) Heppert, J. A.; Boyle, T. J.; Takusagawa, F. *Organometallics* **1989**, *8*, 461.