Coordination of Poly(methylphenylphosphazene) and Poly(dimethylphosphazene)

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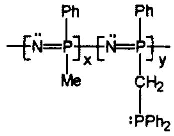
ABSTRACT: Lithium and silver complexes, $[\mathrm{Me(R)P{=}N}]_x[\mathrm{Me(R)P{=}N{\cdot}M^+BF_4^-}]_y$ (**5a**, M^+ = Ag, R = Ph, x = 0.83, y = 0.17; **5b**, M^+ = Ag, R = Ph, x = 0.70, y = 0.30; **6**, M^+ = Ag, R = Me, x = 0.85, y = 0.15; **8**, M^+ = Li, R = Ph, x = 0.84, y = 0.16; **9**, M^+ = Li, R = Me, x = 0.80, y = 0.20), were prepared from $[\mathrm{Me(Ph)PN}]_n$ (**3**) and $[\mathrm{Me_2PN}]_n$ (**4**) and $\mathrm{AgBF_4}$ or $\mathrm{LiBF_4}$. Each of these complexes had a single resonance in the ^{31}P NMR spectra suggesting mobility of the metal ions. However, two resonances were observed at −90 °C in the spectrum of **9**. A related polymer, $[\mathrm{Me(Ph)PN}]_{0.75}[\mathrm{Me(Ph)PN{\cdot}Ag(PPh_3)^+BF_4^-}]_{0.25}$, **7**, was also prepared. Treatment of **3** with $\mathrm{PtCl_2}$ resulted in both insoluble and soluble materials. Protonated forms of **3** and **4** were prepared by treatment with anhydrous HCl. Parent polymers were obtained from the proton complexes by washing with $\mathrm{K_2CO_3}$ and from the silver complexes by treatment with NaCl. The new poly(phosphazene) complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, and IR spectroscopy. Glass transition temperatures of these complexes range from −20 °C for **9** to 121 °C for **5b**.

Introduction

In the course of our studies of the derivatization of the methyl and phenyl substituents in poly(methylphenylphosphazene), $[\mathrm{Me(Ph)P{=}N}]_n$, we have frequently observed the tendency of the backbone nitrogens to coordinate to various Lewis acids. This is not surprising in view of the electron-releasing properties of the simple phenyl and methyl substituents, and this phenomenon has been studied on related cyclic phosphazenes.[2] While this backbone reactivity has been useful in purification of poly(phosphazene)-*graft*-polystyrene,[3] it has also precluded the synthesis of new polymers with pendant metal complexes, has sometimes resulted in significantly reduced thermal stability, and has limited our ability to use various reagents needed to accomplish certain functionalization reactions at the phosphorus substituents. We have, therefore, begun to more closely examine the coordinating ability of the simple poly(alkyl/arylphosphazenes), $[\mathrm{Me(Ph)P{=}N}]_n$, and $[\mathrm{Me_2P{=}N}]_n$, in order to better understand the scope, utility, and limitations of this phenomenon. In this paper we report (a) the preparation of soluble lithium, silver, and proton complexes of $[\mathrm{Me(Ph)P{=}N}]_n$ and $[\mathrm{Me_2P{=}N}]_n$, (b) evidence for movement of the cations along the backbone, (c) the preparation of cross-linked platinum complexes, and (d) coordination of and degradation of the backbone by methyl iodide.

Results and Discussion

When the polymer $\{[\mathrm{Me(Ph)PN}]_3[\mathrm{Ph(Ph_2PCH_2)PN}]\}_n$, **1**,[4] was treated with $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2(NCMe)^+}]\mathrm{BF_4^-}$, **2**, simple displacement of acetonitrile by the phosphine group was expected.[5] Instead, the infrared spectrum of the products contained a complicated pattern in the ν_{CO} region (1600–2300 cm^{-1}). In order to determine if the iron carbonyl group was also interacting with the nitrogen in the polymer backbone, $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2(NCMe)^+}]\mathrm{BF_4^-}$ was treated with the simple parent polymer $[\mathrm{Me(Ph)PN}]_n$, **3**, under similar conditions. As the reaction progressed (ca. 1 week), the ^{31}P NMR spectrum of the mixture showed a single peak that moved downfield from 2 to 7 ppm. Simultaneously, several new bands appeared in the ν_{CO} region of the IR spectrum. We were not, however, able to isolate any polymeric materials that had typical CpFe(CO) signals in either the NMR or IR spectra. Because of the complexity of these reactions, we began to investigate the interaction of the backbone nitrogen with simple metal species (e.g., Li and Ag) that possess fewer potential coordination sites.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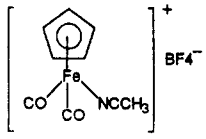
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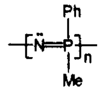
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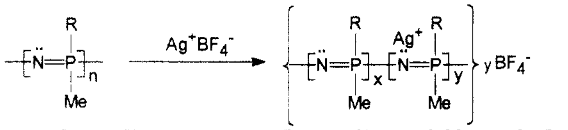
When $\mathrm{AgBF_4}$ was mixed with a $\mathrm{CH_2Cl_2}$ solution of either poly(methylphenylphosphazene), **3**, or poly(dimethylphosphazene), **4**, virtually all of the insoluble $\mathrm{AgBF_4}$ disappeared over a period of ca. 2 days (eq 1). Removal of the solvent afforded the new silver complexes **5a,b** and **6**. The polymer complexes remained soluble in $\mathrm{CH_2Cl_2}$ but had markedly different solubility properties than the parent polymers; i.e., **5a** and **5b** were completely insoluble in THF and $\mathrm{CHCl_3}$, which readily dissolve $[\mathrm{Me(Ph)PN}]_n$, and **6** was insoluble in $\mathrm{CHCl_3}$, a good solvent for the parent $[\mathrm{Me_2PN}]_n$. Moreover, the ^{31}P NMR spectra (Table II) of **5a** and **5b** showed single broad peaks at δ 12 and 17 relative to ca. δ 2 for $[\mathrm{Me(Ph)PN}]_n$. The chemical shift value of δ 16 for **6** was also significantly lower than that of $[\mathrm{Me_2PN}]_n$ (δ 8 ppm). These downfield shifts, which were expected due to deshielding by the transition metal, are also dependent on the amount of silver coordinated to the backbone (see discussion below). The degree of substitution (ratio of x to y) was determined by elemental analyses (Table I) and correlated roughly with the reaction stoichiometries.



(1)

3, R = Ph
4, R = Me

5a, R = Ph, x = 0.83, y = 0.17
5b, R = Ph, x = 0.70, y = 0.30
6, R = Me, x = 0.85, y = 0.15

Attempts to coordinate increased quantities of silver tetrafluoroborate to $[\mathrm{Me(Ph)PN}]_n$ were unsuccessful. For example, **5b**, where the ratio of polymer to silver salt is

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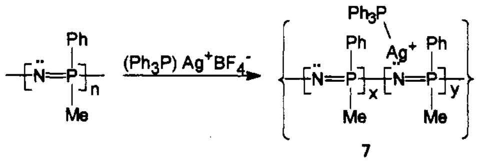
0.7:0.3, was soluble in CH_2Cl_2, but addition of 0.45 equiv of salt to the parent polymer resulted in complete precipitation of the polymer. This effect is similar to the insolubility observed when high concentrations of metal triflates were added to the poly(phosphazene) system known as MEEP, $\{[CH_3(OCH_2CH_2)_2]_2PN\}_n$.[6]

A related polymer complex, 7, was also prepared by treating $[Me(Ph)PN]_n$ with $(Ph_3P)Ag^+BF_4^-$ in THF (eq 2). The ^{31}P NMR (CD_2Cl_2) spectrum of 7 contained two broad peaks at δ 21 and 13. The first, which corresponds to the PPh_3 group, was downfield from that of the phosphorus in $(Ph_3P)Ag^+BF_4^-$ (δ 16). The second was that of the backbone phosphorus, which again was downfield from that of the parent polymer due to coordination of the nitrogen in the backbone.



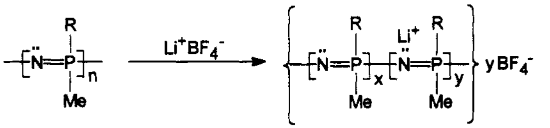
$$-[\ddot{N}=\overset{Ph}{\underset{Me}{P}}]_n- \xrightarrow{(Ph_3P)Ag^+BF_4^-} \left\{ -[\ddot{N}=\overset{Ph}{\underset{Me}{P}}]_x-[\overset{Ph_3P\diagdown Ag^+}{N}=\overset{Ph}{\underset{Me}{P}}]_y- \right\} yBF_4^- \quad (2)$$

7

x = 0.75, y = 0.25

In a separate experiment a simple blend of $(n\text{-}Bu)_4N^+BF_4^-$ and $[Me(Ph)PN]_n$ was prepared in CH_2Cl_2. The ^{31}P NMR chemical shift of this blend, in which backbone coordination is minimal, was virtually that of the pure parent polymer (δ 2). This indicates that the BF_4^- anion is not responsible for changes in the ^{31}P NMR spectra of the metal complexes.

Poly(methylphenylphosphazene) and $[Me_2PN]_n$ also reacted with $LiBF_4$ in CH_2Cl_2 to yield the lithium complexes, $[Me(R)PN]_x[Me(R)PN{\cdot}Li^+]BF_4^-$, 8 and 9 (eq 3). The solubility behavior of the new polymer complexes was similar to that of the silver complexes in that 8 was no longer soluble in THF and 9 was not soluble in $CHCl_3$.



$$-[\ddot{N}=\overset{R}{\underset{Me}{P}}]_n- \xrightarrow{Li^+BF_4^-} \left\{ -[\ddot{N}=\overset{R}{\underset{Me}{P}}]_x-[\overset{Li^+}{N}=\overset{R}{\underset{Me}{P}}]_y- \right\} yBF_4^- \quad (3)$$

3, R = Ph
4, R = Me

8, R = Ph, x = 0.84, y = 0.16
9, R = Me, x = 0.80, y = 0.20

The ^{31}P NMR spectra of the lithium complexes also exhibited single signals (8, δ 8; 9, δ 15) that were shifted significantly downfield from the signals of the parent polymers (δ 2 and 8, respectively). Low-temperature ^{31}P NMR spectra provided evidence for movement of the cations along the backbone. The ^{31}P NMR spectra of complex 9 (Figure 1) first broadened below room temperature and eventually split into two signals (δ 18 and 8) at ca. −90 °C. This suggests that the lithium cation is moving from nitrogen to nitrogen along the polymer backbone at room temperature, but such movement is eliminated at lower temperatures. Moreover, this accounts for the increasingly downfield shift that is observed with increasing concentrations of the metal (Table III) in both the silver and lithium tetrafluoroborate complexes. When more metal was coordinated to the backbone, the proportion of the downfield signal increased, causing the averaged room temperature signal to appear at a lower field. It should be noted that the effect was smaller for the lithium complexes than for the silver complexes.

Less straightforward results were obtained when $[Me(Ph)PN]_n$ was treated with platinum dichloride in benzene. When no reaction was observed at room temperature, the mixture was refluxed for 10 h. During this time, the polymer completely precipitated from the benzene. Extraction of the insoluble products with CH_2Cl_2 gave a 43% yield of the sparingly soluble complex, $[Me(Ph)PN]_{10}[Me(Ph)PN{\cdot}PtCl_2]$, 10, whose composition was determined by elemental analysis (Table I). The ^{31}P NMR spectrum of 10 contained signals at δ 6 and 2 suggesting that the platinum is not able to move along the backbone. It is likely that this is caused by coordination of more than one backbone nitrogen to each platinum. This also explains the formation of significant quantities of insoluble material, presumably highly cross-linked polymer in this reaction. The insolubility could also be due to the increased polarity of a more highly substituted polymer. Elemental analysis indicated that this material contained more than 1 equiv of $PtCl_2$/PN unit, suggesting that $PtCl_2$ was trapped in the cross-linked polymer. Platinum complexes of $[(MeNH)_2PN]_n$ have also been reported, and model compounds indicated that coordination occurred only at the backbone nitrogen.[7]

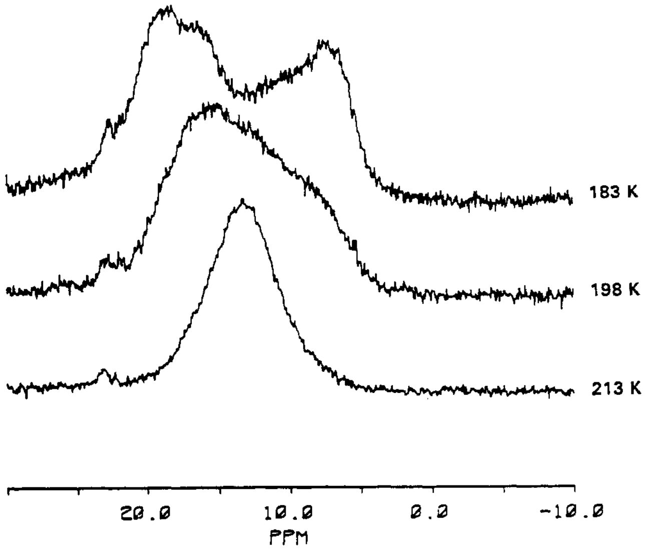
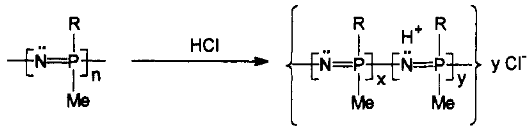


Figure 1. Low-temperature ^{31}P NMR spectra of 9.

The coordination of simple protons to the polymer backbone has frequently been observed in our labs, but has not been closely investigated. In this study excess anhydrous HCl was bubbled through CH_2Cl_2 solutions of the parent polymers 3 and 4 (eq 4). This resulted in complete precipitation of 11 and 12, respectively, which were isolated by filtration and carefully dried at ambient temperatures. The ^{31}P NMR spectra of these new polymers showed very downfield shifts of δ 18.9 (CD_2Cl_2) for 11 and δ 32 (D_2O) for 12. Not only were these polymer complexes no longer soluble in $CHCl_3$ but also 11 was no longer soluble in THF and 12 was very soluble in H_2O. Elemental analysis of 11, obtained by solvent removal and extensive drying under vacuum at ambient temperature, indicated that ca. 65% of the backbone units were coordinated to HCl (i.e., $x = 0.35$, $y = 0.65$).



$$-[\ddot{N}=\overset{R}{\underset{Me}{P}}]_n- \xrightarrow{HCl} \left\{ -[\ddot{N}=\overset{R}{\underset{Me}{P}}]_x-[\overset{H^+}{N}=\overset{R}{\underset{Me}{P}}]_y- \right\} yCl^- \quad (4)$$

3, R = Ph
4, R = Me

11, R = Ph,
12, R = Me

When glacial acetic acid was added to a CH_2Cl_2 solution of 3, similar downfield shifts were observed in the ^{31}P NMR spectra. A large excess produced the most downfield shift (δ 9). It was not possible to isolate this protonated polymer since precipitation and washing with Et_2O resulted in the removal of all the glacial acetic acid. The starting material 3 was recovered virtually unchanged after this process as

Table I. Preparative and Thermal Data for Poly(phosphazene) Complexes

polymer	parent, mmol	salt, mmol	yield, %	analysis[a] % C (calcd)	analysis[a] % H (calcd)	analysis[a] % N (calcd)	T_g, °C
5a	3, 5.3	$AgBF_4$, 0.9	61	49.19 (49.39)	4.84 (4.74)	7.96 (8.23)	95
5b	3, 3.9	$AgBF_4$, 1.2	66	46.70 (46.22)	4.74 (4.43)	7.14 (7.70)	121
6	4, 13.3	$AgBF_4$, 2.0	52	23.28 (23.03)	6.28 (5.80)	12.18 (13.43)	10
7	3, 3.9	$[(Ph_3P)Ag]BF_4$, 1.0	8.5	55.33 (54.95)	4.93 (4.71)	5.29 (5.57)	88
8	3, 7.0	$LiBF_4$, 1.5	64	55.45 (55.27)	5.54 (5.30)	8.79 (9.21)	55
9	4, 13.2	$LiBF_4$, 2.6	55	25.29 (25.61)	7.32 (6.45)	13.89 (14.93)	−20
10	3, 5.9	$PtCl_2$, 1.5	42[b]	52.55 (52.41)	5.18 (4.63)	7.95 (8.79)	92
11	3, 7	HCl, excess	95	52.74 (52.28)	8.19 (8.71)	5.83 (5.42)	63
12	4, 13.8	HCl, excess	94				7

[a] Calculated values in parentheses. [b] Soluble portion. See Experimental Section for information on insoluble material.

Table II. Spectroscopic Data for Poly(phosphazene) Complexes

polymer	^{31}P NMR, δ[a]	^1H NMR, δ	IR,[b] ν (cm^{-1})
$[Me(Ph)PN]_{0.83}Me(Ph)PN\cdot Ag^+BF^-]_{0.17}$, **5a**	12.4	7.4, 7.2 (br, Ph), 1.23 (br, Me)	1060 (BF_4^-)[e]
$[Me(Ph)PN]_{0.7}[Me(Ph)PN\cdot Ag^+BF_4^-]_{0.3}$, **5b**	16.5	7.5, 7.3 (br, Ph), 1.3 (br, Me)	1050 (BF_4^-)
$[Me_2PN]_{0.85}[Me_2PN\cdot Ag^+BF_4^-]_{0.15}$, **6**	16.4	1.6 (d, J_{PH} = 13 Hz, Me)	1050, 527 (BF_4^-)
$[Me(Ph)PN]_{0.75}[Me(Ph)PN\cdot Ag(PPh_3)^+BF_4^-]_{0.25}$, **7**	21.2, 13.0	6.9–7.4 (m, Ph), 1.3, 1.5 (br m)	1052 (BF_4^-)
$[Me(Ph)PN]_{0.84}[Me(Ph)PN\cdot Li^+BF^-]_{0.16}$, **8**	8.4[c]	7.7, 7.4, 7.3 (br, Ph), 1.5 (m, Me)	1055 (BF_4^-)
$[Me_2PN]_{0.8}[Me_2PN\cdot Li^+BF_4^-]_{0.20}$, **9**	15.4	1.6 (d, J_{PH} = 13 Hz, Me)	1055, 527 (BF_4^-)
$[Me(Ph)PN]_{0.91}[Me(Ph)PN\cdot PtCl_2]_{0.09}$, **10**	6.1, 2.1	7.6, 7.2 (br, Ph), 1.3 (br, Me)	
$[Me(Ph)PN]_{0.35}[Me(Ph)PN\cdot H^+Cl^-]_{0.65}$, **11**	18.9	10.8 (H^+), 7.4, 7.3 (br, Ph), 1.8 (br, Me)	2634 (PN–H)
$[Me_2PN]_x[Me_2PN\cdot H^+Cl^-]_y$, **12**	32.0[d]	2.1, 2.0 (d, Me), 4.9 (H_3O^+)	2653 (PN–H)

[a] Solvent: CD_2Cl_2 unless specified otherwise. [b] KBr pellet unless noted otherwise. [c] Solvent: $CDCl_3$. [d] Solvent: D_2O. [e] Nujol mull.

Table III. ^{31}P NMR Chemical Shifts versus Weight Percent of Metal Tetrafluoroborate in $[Me(Ph)PN]_n$

salt	weight %	^{31}P NMR, δ
$AgBF_4$	0	2.1
$AgBF_4$	2.1	2.7
$AgBF_4$	3.5	3.7
$AgBF_4$	6.5	5.2
$LiBF_4$	0	2.1
$LiBF_4$	2.4	2.8
$LiBF_4$	5.1	2.9
$LiBF_4$	8.3	3.1

noted by the ^{31}P NMR spectra and GPC molecular weight measurements. (See Experimental Section.)

This result prompted us to study the potential for recovery of starting material from all of the new polymer adducts. When a CH_2Cl_2 solution of **5b** was washed with an aqueous NaCl solution, the parent polymer **3** was also recovered unchanged as noted by comparisons of the GPC traces and ^{31}P NMR spectra. Presumably the driving force in this reaction is the formation and precipitation of AgCl. Similarly, the ^{31}P NMR spectrum of the polymer isolated when a CH_2Cl_2 solution of **11** was washed with K_2CO_3 was that of the parent polymer **3**. The GPC trace of this material was slightly narrower than that of the parent and had a higher M_w value. This has also been observed in the nitration of phenyl substituents in **3**.[8] Thus, the coordination of both protons and metal cations appears to occur without chain degradation. These data also indicate that it is reasonable to assume that the molecular weights of the coordinated polymers, which could not be measured due to their insolubility in THF, are comparable to those of the parent polymers. In contrast to the silver and proton complexes, $LiBF_4$ was not readily removed from the polymers. For example, washing a CH_2Cl_2 solution of **8** with water resulted in a complex for which the ^{31}P NMR signal (δ 6) was upfield from polymer complex **8** (δ 8) but was still somewhat lower than that of the parent polymer **3** (δ 2).

An interesting feature of the protonation of these poly(phosphazenes) is that the addition of very small amounts of either acetic acid or dilute aqueous HCl (<4%) results in rather complicated fine structure in the ^{31}P NMR spectra. For example, the spectrum of a solution prepared by adding 1 mL of aqueous HCl (0.01 N) to **3** (0.97 g, 0.1 mmol) in $CDCl_3$ (4 mL) consisted of signals at δ 3.0, 3.5, and 3.8. Similar results were observed when acetic acid was added and for a poly(phosphazene) with carboxylic acid substituents, $\{[Ph(Me)PN][Ph(CH_2COOH)PN]\}_n$.[9] In both cases, the concentration of protons available to the polymer is extremely low, since RCOOH is only partially dissociated and because of the immiscibility of aqueous HCl and $CDCl_3$ solutions of the polymer. Addition of ca. 4% anhydrous HCl to a CH_2Cl_2 solution of **3** gave a single broad, asymmetric signal in the ^{31}P NMR spectrum ($\Delta w_{1/2}$ = 162 Hz, 2 ppm). In fact, for a similar concentration of silver tetrafluoroborate $[Me(Ph)PN]_{0.96}[Me(Ph)PN\cdot AgBF_4]_{0.04}$ ($\Delta w_{1/2}$ = 130 Hz, 1.6 ppm), the bandwidths were also broad. A somewhat narrower bandwidth was observed for the lithium tetrafluoroborate complex, $[Me(Ph)PN]_{0.96}[Me(Ph)PN\cdot LiBF_4]_{0.04}$ ($\Delta w_{1/2}$ = 24 Hz, 0.4 ppm).

Polymers **3** and **4** also reacted with MeI at room temperature in CH_2Cl_2, but the process was complicated by the formation of several products as noted in the ^{31}P NMR spectra of the reaction mixtures. In the case of **3** signals at δ 30, 10, and 3 (very broad) were observed when 0.3 equiv of MeI was added. Reasonable assignments of these signals are cyclic products[10] formed by degradation of the backbone, polymer with methyl groups coordinated to nitrogen, and uncoordinated polymer with broadening possibly due to oligomer formation, respectively. When 4 was treated with MeI, signals at δ 40,[11] 16, and 8–10 were observed, and analogous assignments are reasonable. Degradation of the backbone has also been observed in the presence of I_2 and other halogens.[11]

The glass transition temperatures, T_g, of the new polymer adducts were determined by differential scanning calorimetry (DSC) (Table I). As expected, these values were higher than those of the parent polymers (3, T_g = 37 °C; 4, T_g = −40 °C) and increased degrees of coordination were accompanied by increased T_g values. The size of the coordinating Lewis acid was also proportional to the increase in T_g; e.g., silver complexes had higher T_g values than corresponding lithium complexes. The T_g of 3 mixed with $(n\text{-Bu})_4N^+BF_4^-$ was unchanged by the presence of the salt. Because backbone coordination cannot occur here, this provides additional evidence that the transition metals are coordinated to the polymer backbone.

It is noteworthy that the glass transition temperature of 9 is well below room temperature. This fact and the ^{31}P NMR data, which indicate that the lithium cation is moving along the polymer chain at ambient temperature, suggest that these complexes may behave like ionic conductors such as polyether complexes.[12]

Experimental Section

General. All reactions were carried out under an atmosphere of nitrogen. The metal salts were weighed and transferred in a glovebag. The polymers $[Me(Ph)PN]_n$ and $[Me_2PN]_n$ were prepared by published procedures[13] and were dried under vacuum at 50 °C for 24 h before use. Dichloromethane and Et_2O were distilled from CaH_2. Glacial acetic acid, $AgBF_4$, $LiBF_4$, $PtCl_2$, anhydrous HCl, MeI, PPh_3, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and CD_2Cl_2 were used as received from commercial sources.

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$ or CD_2Cl_2. Positive ^1H and ^{31}P NMR chemical shifts are downfield from Me_4Si and H_3PO_4, respectively. Elemental analyses were performed on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. The size exclusion (gel permeation) chromatography measurements were performed on a Waters Associates GPC instrument using a Maxima data handling system and 500-, 10^4, 10^5, and 10^6 Å μ-Styragel columns. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-Bu})_4N^+Br^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of a 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of ca. 10^3–10^6. Infrared spectra were recorded as CD_2Cl_2 solutions on a Perkin-Elmer Series 1600 Fourier transform infrared spectrometer. Differential scanning calorimetry (DSC) measurements were made under nitrogen against an aluminum reference on a Du Pont Model 910 instrument, and the inflection point is listed for all transitions. Each experiment was repeated at least once on the same sample.

Preparation of $[Me(R)PN]_x[Me(R)PN\cdot M^+BF_4^-]_y$, 5a,b, 6, 8 and 9. In a typical procedure silver tetrafluoroborate (0.180 g, 0.92 mmol), $[Me(Ph)PN]_n$ (0.721 g, 5.26 mmol), and CH_2Cl_2 (10 mL) were placed in a two-neck, round-bottom flask equipped as above. After stirring for 2 days, all reagents had completely dissolved, but the solution was filtered through Celite to remove undetectable traces of $AgBF_4$. The solvent was evaporated, and the residue was dried under vacuum at ambient temperature for 5 days. Yield and analytical data are given in Table I.

A CH_2Cl_2 (5 mL) solution of 5b (40 mg) was washed with 3 × 5 mL of nearly saturated aqueous NaCl. The CH_2Cl_2 portions were combined, solvent was removed, and the polymer was dried under vacuum for 2 days. ^{31}P NMR: δ 2.5. GPC: M_w = 74 000, M_w/M_n = 2.3; parent, M_w = 70 000, M_w/M_n = 2.3. A CH_2Cl_2 solution (5 mL) of 8 (40 mg) was washed with water (3 × 5 mL), and the polymer was isolated as above. ^{31}P NMR: δ 6.

Preparation of $[Me(Ph)PN]_3[Me(Ph)PN\cdot Ag(PPh_3)^+BF_4^-]_n$, 7. Silver tetrafluoroborate (0.195 g, 1.0 mmol), Ph_3P (0.263 g, 1.0 mmol), and $[Me(Ph)PN]_n$, 3 (0.536 g, 4.0 mmol), were placed in a 100-mL, two-neck, round-bottom flask equipped with a N_2 inlet and septum. Freshly distilled THF (5 mL) was added, and the mixture was stirred for 10 min. Then 25 mL of CH_2Cl_2 was added, and the solution was stirred for 3 days. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2. After filtering through Celite, the solvent was removed and the residue was dried under vacuum, washed with 2 × 20 mL of Et_2O to eliminate any remaining Ph_3P, and dried under vacuum at ambient temperature for 5 days. Yield: 0.85 g, 85%. Glass transition temperature (T_g): 88 °C.

Preparation of $[Me(Ph)PN]_x[Me(R)PN\cdot PtCl_2]_y$, 10. Platinum dichloride, (0.393 g, 1.5 mmol) was added to a benzene (25 mL) solution of $[Me(Ph)PN]_n$ (0.809 g, 5.9 mmol), and the mixture was heated under reflux for ca. 10 h. During this time precipitation occurred on the walls of the flask and the supernatant became clear and colorless when precipitation was complete. After removal of the benzene by decantation, the residue was extracted with 3 × 40 mL of CH_2Cl_2. The combined extracts were filtered through Celite, solvent was removed under vacuum, and the residue, 10, was dried under vacuum at ambient temperature for 5 days. Yield: 0.5 g, 42% (see Table I). The insoluble material remaining after extraction with CH_2Cl_2 was washed with hexane and dried as described above. Yield: 0.3 g. Elemental analysis: C, 17.98; H, 1.45; N, 2.56. T_g = 202 °C.

Preparation of $[Me(R)PN]_x[Me(R)PN\cdot H^+]_yCl^-$, 11 and 12. Dry HCl was bubbled through a CH_2Cl_2 solution (50 mL) of $[Me(Ph)PN]_n$ (0.989 g, 7.2 mmol) until precipitation was complete. Then nitrogen was bubbled through the mixture to remove excess HCl. Solvent was evaporated, and the residue was dried in an oven for 5 days under vacuum at room temperature.

A sample of 11 was dissolved in CH_2Cl_2, and then an aqueous solution of K_2CO_3 was added to eliminate HCl. After vigorous stirring for several min, the aqueous layer was removed. This process was repeated three times. The CH_2Cl_2 portions were combined and dried over Na_2SO_4. After solvent removal the polymer was dried under vacuum for 2 days. ^{31}P NMR: δ 2.4. GPC: M_w = 131 000, M_w/M_n = 1.5; parent, M_w = 70 000, M_w/M_n = 2.3.

Reaction of $HC_2H_3O_2$ with $[Me(Ph)PN]_n$. In a preliminary experiment, a sample of 3 was dissolved in CH_2Cl_2 and the ^{31}P NMR spectrum was recorded (δ 2.3). The spectrum was recorded again after the addition of dilute acetic acid (ca. 0.01 N in $CDCl_3$): 3 drops (δ 2.8), 6 drops (δ 3.0, 3.3, 3.7), 12 drops (δ 3.5, 4.0, 4.6), and a large excess (δ 9.0) of glacial acetic acid. In a separate experiment glacial acetic acid (0.167 mL, 2.9 mmol) was added to a stirred CH_2Cl_2 (8 mL) solution of 3 (0.80 g, 5.8 mmol). The solution was concentrated on a rotary evaporator and then poured into 300 mL of Et_2O. The precipitate that formed was recovered, dissolved in fresh CH_2Cl_2, and again precipitated into Et_2O. After washing with 2 × 100 mL of Et_2O and solvent removal, the polymer was dried for 3 h under vacuum at ambient temperature. ^{31}P NMR: δ 2. GPC: M_w = 98 000, M_w/M_n = 2.1; parent, M_w = 70 000, M_w/M_n = 2.3.

Reaction of $[Me(R)PN]_n$ with MeI. Methyl iodide (0.13 mL, 0.21 mmol) was added to a CH_2Cl_2 (10 mL) solution of $[Me(Ph)PN]_n$ (0.99 g, 7.2 mmol), and the mixture was stirred for 2 days. The solvent was evaporated, and the residue was dried under vacuum at room temperature for 5 days. A similar procedure was used for $[Me_2PN]_n$. ^{31}P NMR: from reaction of 3; δ 30, 10, and 3 (very broad); from reaction of 4, δ 40, 16, and 8–10.

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References and Notes

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