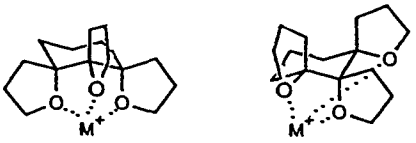
traction method[16a] and quantified in terms of extraction equilibrium constants (K_{ex}).[16b] As shown in Table I, the spiro furans exhibit coordinative abilities toward alkali-metal cations that are quite respectable for the limited number of oxygen atoms available for binding. Although **3** is expectedly the best ligand of its subset, with K_{ex} values approaching those of 12-crown-4 (four coordination sites), the precise geometry of the bridging oxygens in these complexes (1,3-diaxial as in A or diequatorial as in B) has yet to be established. Inversion of the *central* oxygen atom as in **5**



A B

is less detrimental to ion complexation than inversion of a *terminal* binding site (see **4**). This finding, when linked to the response of **6**, suggests that the host:guest stoichiometric ratio may be >1 in these circumstances. Whatever the case, the promise offered by completely spherical ligands of type **1** and **2** appears high.

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Poly(phosphazophosphazenes): A New Class of Inorganic Polymers with Short-Chain Branching

Dennis C. Ngo, J. Steven Rutt, and Harry R. Allcock*

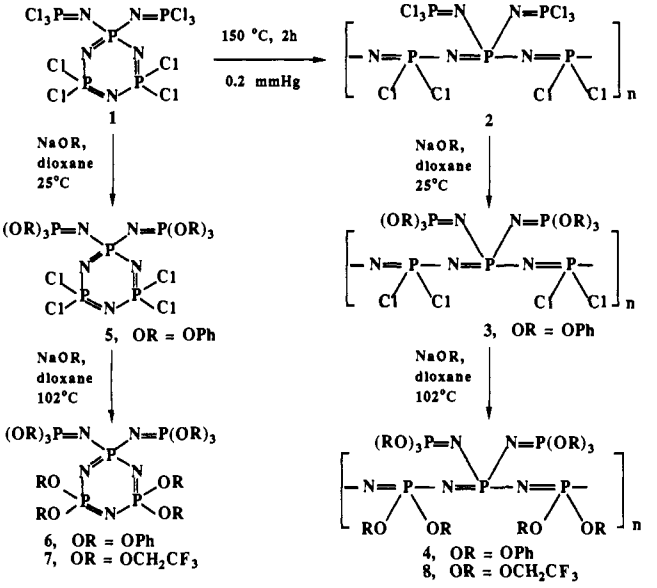
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
Received February 11, 1991

Most polyphosphazenes are prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, at 250 °C to high molecular weight poly(dichlorophosphazene), $[NPCl_2]_n$,[1] followed by replacement of the chlorine atoms in the polymer by organic groups.[2] These organophosphazene polymers are essentially linear and often have a symmetric structure that generates microcrystallinity.

Here we report a method for the introduction of molecular asymmetry and materials free volume at the polymerization stage to yield a new series of polyphosphazenes. *gem*-Bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (**1**) undergoes an unusual low-temperature, ring-opening polymerization to form a high molecular weight poly(phosphazophosphazene) (**2**) (Scheme I). This is the first example of a phosphazene polymer with well-defined short-chain branching. Polymer **2** can act as a macromolecular intermediate in selected cases and can be converted to hydrolytically stable, branched-structure poly(organophosphazenes).

Air-sensitive crystals of **1**[3] were placed in an airless flask, and the entire apparatus was evacuated through a vacuum line. Under

Scheme I



a dynamic vacuum, the flask and its contents were heated at 150 °C for 2 h with stirring. The molten **1** was slowly converted to an immobile gel. This was soluble in dichloromethane. The spectra of both **1** and **2** consisted of A_2B_2C spin systems (Figure 1). Upfield chemical shift changes in the ^{31}P NMR spectra were detected for polymer **2** relative to trimer **1**. This observation is similar to the polymerization of other cyclotriphosphazenes such as $(NPCl_2)_3$.[1] The close similarity of the spectra suggested that polymerization did not result in a side-unit rearrangement or loss of the geminal trichlorophosphazo side groups. Integration of the NMR peaks of **2** relative to **1** indicated a 50–60% conversion of trimer to polymer. No intermediate species or side products were detected from the NMR spectra.

Trimer **1** was removed from polymer **2** by extraction with heptane to yield an air-sensitive, colorless polymer. Further characterization of **2** was accomplished by replacement of the chlorine atoms by reaction with sodium phenoxide in dioxane (Scheme I). Similar substitutions with trimer **1** were also explored as model reactions.

Treatment of solutions of **2** in dioxane with *excess* sodium phenoxide at 25 °C resulted in the facile formation of the partially substituted, but hydrolytically stable, polymer **3** (Scheme I), which was isolated by precipitation into water and hexane as a white, film-forming elastomer. The elasticity of the polymer is maintained when the polymer is stored under an inert atmosphere. Evidence for the structure of **3** was provided by the ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy and elemental analysis.[4] Despite the presence of excess sodium phenoxide, steric hindrance by the bulky, geminal triphenoxyphosphazo side groups appeared to prevent replacement of the main-chain P–Cl bonds of **3** at 25 °C and also retarded hydrolysis of the protected P–Cl bonds. This regioselective substitution by sodium phenoxide at 25 °C promises to allow a precisely controlled side-group incorporation for poly(organophosphazenes) prepared by the reaction of **2** with nucleophiles.

The residual P–Cl bonds in **3** were replaced by treatment with excess sodium phenoxide at 102 °C in dioxane for 7 days in the presence of tetra-*n*-butylammonium bromide as a phase-transfer agent to form **4**. This polymer was also isolated by precipitation into water and hexane as a white, film-forming material (Scheme I). The structure was confirmed by ^{31}P, ^{13}C, and ^{1}H NMR

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(4) Characterization data for **3**: ^{31}P NMR (A_2BC_2 spin system, δ_A = −29 ppm, δ_B = −30 ppm, δ_C = −35 ppm); ^{13}C NMR (δ = 121, 125, 130, 151 ppm); ^{1}H NMR (m, δ = 6.8–7.4 ppm). Elemental anal. Calcd: C, 46.70; H, 3.24; N, 7.57; Cl, 15.35. Found: C, 47.06, H, 3.79; N, 6.99; Cl, 14.81.

(5) Characterization data for **5**: ^{31}P NMR (A_2BC_2 spin system, δ_A = 14 ppm, δ_B = −19 ppm, δ_C = −28 ppm); ^{13}C and ^{1}H NMR same as for **3**; mass spectrum calcd 925, found 925.

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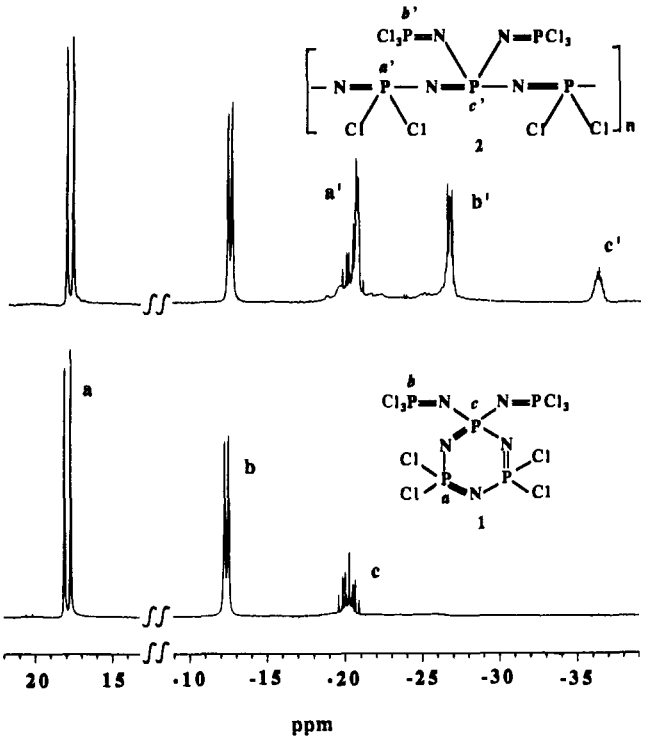

Figure 1. ^{31}P NMR spectra of compounds **1** and **2**.

spectroscopy and elemental analysis.[6] Films of **4** were significantly less flexible than films of classical poly[bis(phenoxy)phosphazene], $[NP(OC_6H_5)_2]_n$, which contains no branching. The small-molecule analogues **5**[5] and **6**[7] were also prepared as model compounds.

Treatment of model compound **1** with excess sodium trifluoroethoxide in dioxane at 102 °C resulted in complete replacement of the chlorine atoms by trifluoroethoxy side groups to form *gem*-$N_3P_3(OCH_2CF_3)_4[NP(OCH_2CF_3)_3]_2$ (**7**).[8] The corresponding high polymeric reaction of **2** with sodium trifluoroethoxide yielded the fully substituted polymer **8**.[9] Polymer **8** was isolated as a white, film-forming, fibrous material.

Gel permeation chromatograph (GPC) analysis of the hydrolytically stable polymers **3** ($M_n = 6 \times 10^4$, $M_w = 9 \times 10^5$), **4** ($M_n = 1 \times 10^5$, $M_w = 7 \times 10^5$), and **8** ($M_n = 4 \times 10^4$, $M_w = 1 \times 10^5$) indicated that high molecular weight materials were formed by the polymerization of **1** at a relatively low temperature, and that the polymers can be prepared without extensive chain cleavage. The glass transition temperatures (T_g) of these polymers are as follows: **3**, $T_g = -6$ °C; **4**, $T_g = 28$ °C; and **8**, $T_g = -69$ °C.

We are currently exploring the polymerization of **1** and $N_3P_3Cl_5(N{=}PCl_3)$ in detail and their copolymerization with unbranched cyclotriphosphazenes. The reaction of **2** with other nucleophiles to yield poly(organophosphazophosphazenes) is also under investigation.

Acknowledgment. This work was supported by the U.S. Army Research Office.

(6) Characterization data for **4**: ^{31}P NMR (A_2B_2C spin system, $\delta_A = -7$ ppm, $\delta_B = -19$ ppm, $\delta_C = -36$ ppm); ^{13}C NMR (122 (d), 127 (d), 131 (d), 152 (d) ppm); ^1H NMR (m, δ 6.9-7.5 ppm). Elemental anal. Calcd: C, 62.34; N, 6.06; H, 4.33; Cl, 0.00. Found: C, 59.97; N, 7.08; H, 4.14; Cl, 0.75.

(7) Characterization data for **6**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = 11$ ppm, $\delta_B = -4$ ppm, $\delta_C = -25$ ppm); ^{13}C and ^1H NMR same as for **4**; mass spectrum (calcd 1155, found 1155). Elemental anal. Calcd: C, 62.34; H, 4.33; N, 6.06. Found: C, 62.35; H, 4.31; N, 5.92.

(8) Characterization data for **7**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = 18$ ppm, $\delta_B = -5$ ppm, $\delta_C = -8$ ppm); ^1H NMR (multiplets, $\delta = 4.5$ ppm, $\delta = 4.8$ ppm); ^{13}C NMR (quartets, $\delta = 64$, 124 ppm); mass spectrum (calcd 1215, found 1215). Elemental anal. Calcd: C, 19.77; H, 1.66; N, 5.76. Found: C, 19.94; H, 1.66; N, 5.89.

(9) Characterization data for **8**: ^{31}P NMR (br resonances, $\delta = -3$ ppm (br) to -9 ppm (multiplets)); ^{13}C NMR (quartets, $\delta = 64$, 124 ppm); ^1H NMR (unresolved multiplets $\delta = 4.5$ ppm, $\delta = 4.8$ ppm). Elemental anal. Calcd: C, 19.77; H, 1.66; N, 5.76; Cl, 0.00. Found: C, 19.49; H, 1.59; N, 5.96; Cl, 0.094.

Template-Directed Diastereoselectivity. Cyclizations to Contrathermodynamic Products

Barry M. Trost* and Phil Ho Lee

Department of Chemistry, Stanford University
Stanford, California 94305-5080

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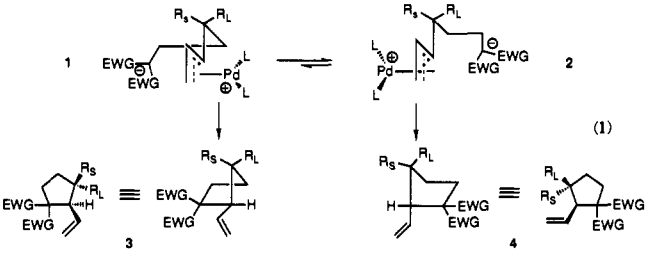
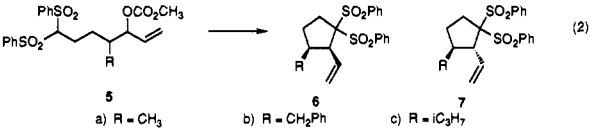
A major concern of synthetic chemistry during the past decade focused on diastereoselectivity. In cyclization reactions wherein stereochemistry is developed at one of the termini, intrinsic factors such as nonbonded interactions generally favoring 1,2-trans isomers normally dominate.[1] Developing approaches to force such groups to favor a thermodynamically less favorable cis orientation would be an important adjunct to existing methodology. Introduction of extrinsic factors that may dominate over such intrinsic ones provides a strategy to achieve this goal. Transition metal template directed reactions may offer one approach, as outlined in eq 1, provided the rates of the various steps depicted are appropriate to allow differential steric interaction between R_S and R_L and the metal template to dominate.[2] Further, the problem is complicated



(1)

by the question of regioselectivity in metal-catalyzed reactions which could lead to formation of the terminal substituted product **6**.[3-7]

Cyclization of the methyl substrate **5a** was explored in depth to examine the effect of catalyst and solvent (see Table I).



(2)

Gratifyingly, the cyclization generated the cyclopentyl products **6a**[8] and **7a**[8] in excellent yields with most catalysts. Somewhat surprisingly, electron-rich ligands that frequently prove ineffectual in promoting allyl alkylation, like trialkylphosphines and especially TTMPP, are very effective in promoting cyclization.[9,10]

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