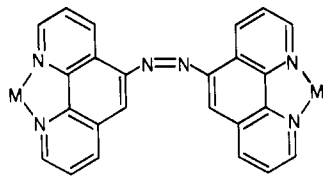
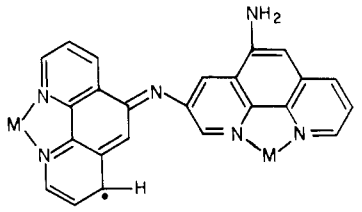


9



10

sites may exist in the polymer films is suggested by the broad MLCT visible absorption manifold. As noted above, spectral shifts are expected to occur if chemical changes occur at the periphery of the coordinated polypyridines. Evidence for imine coupling links was obtained in the IR spectra, but N=N stretches (1370 and 1150 cm^{-1})[20] were not seen, perhaps due to the intrinsic weakness of the stretching mode. The presence or absence of azo linkages should be explored further with Raman spectroscopy.

The polymerization reactions proposed for the complexes are a speculation based on aromatic amine oxidations, and further detailed insights into the polymerization chemistry and polymer structure are eventually needed. However, the available evidence does seem to point to polymers based on imine links of the type C—N=C. Based on this link, the phenanthroline ring system provides multiple coupling sites; note structure **10** above. Not accounted for in the above interpretation is the possible incorporation of 2,6-lutidine or pyridine into the polymer as suggested by the $E^{\circ\prime}_{surf}$ shift effects described earlier.

Finally, we should note that this work is the first example of what we suspect will be a general technique for oxidative electropolymerization to produce electrodes coated with electroactive polymers. The procedure described yields relatively stable, electroactive polymeric films in aerated solutions for a variety of monomeric complexes in addition to the cases reported here. On the basis of preliminary studies, oxidative electropolymerization also occurs with tetrakis(*o*-aminophenyl)porphine, *cis*-$Os(5\text{-phenNH}_2)_2Cl_2$, $[(bpy)_2Ru(3\text{-pyOH})_2]^{2+}$, and $[(bpy)_2Ru(4\text{-pyOH})_2]^{2+}$. Further work to support the implied generality of oxidative electropolymerization based on complexes containing amine or hydroxy substituents on bound ligands is currently under way.

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Registry No. $[(bpy)_2Ru(4\text{-pyNH}_2)_2](PF_6)_2$, 84537-84-8; $[(bpy)_2Ru(3\text{-pyNH}_2)_2](PF_6)_2$, 84558-23-6; $[(bpy)_2Ru(5\text{-phenNH}_2)](PF_6)_2$, 84537-86-0; $[(bpy)Ru(5\text{-phenNH}_2)_2](PF_6)_2$, 84537-88-2; $[Ru(5\text{-phenNH}_2)_3](PF_6)_2$, 84537-89-3; $[(bpy)_2Ru(4\text{-vpy})_2](PF_6)_2$, 84537-90-6; poly-$[(bpy)_2Ru(3\text{-pyNH}_2)_2](ClO_4)_2$, 84537-92-8; poly-$[(bpy)_2Ru(4\text{-pyNH}_2)_2](ClO_4)_2$, 84623-06-3; poly-$[(bpy)_2Ru(5\text{-phenNH}_2)](ClO_4)_2$, 84537-93-9; poly-$[(bpy)Ru(5\text{-phenNH}_2)_2](ClO_4)_2$, 84537-94-0; poly-$[Ru(5\text{-phenNH}_2)_3](ClO_4)_2$, 84537-95-1; poly-$[(bpy)_2Ru(4\text{-vpy})_2](ClO_4)_2$, 84537-96-2; $[Ru(5\text{-phenNH}_2)_3\cdot(bpy)_2Ru(5\text{-phenNH}_2)]$ (copolymer), 84537-97-3; *cis*-$Cl_2Ru(bpy)_2$, 19542-80-4; Pt, 7440-06-4; SnO_2, 18282-10-5; 2,6-lutidine, 108-48-5; pyridine, 110-86-1.

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Organophosphazenes. 16. Synthesis and Reactions of (1-Alkoxyvinyl)fluorocyclotriphosphazenes[1]

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The reactions of (1-lithioalkoxy)ethylenes with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to the case of similar reactions of propenyllithium with $N_3P_3F_6$, no evidence for degradation reactions via anionic attack on the olefinic center was observed and the reaction proceeds smoothly to yield $N_3P_3F_{6-n}[C(OR)=CH_2]_n$ (n = 1, 2; R = CH_3, C_2H_5). The reaction follows a geminal pathway at the stage of disubstitution. The mixed phenyl/ethoxyvinyl derivative 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ and dimethylamino/ethoxyvinyl derivatives 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ have been prepared. Evidence for both incoming group and ring substituent control of product stereochemistry has been observed. A model for ring substituent control is presented. The new (alkoxyvinyl)phosphazenes are characterized by mass spectrometry and NMR (^1H, ^{13}C, ^{19}F, ^{31}P) spectroscopy. Examination of the ^{13}C NMR spectra shows that the electron-withdrawing effect of the phosphazene results in a significant reduction of the electron-rich nature of the parent olefins.

In recent years there have been a number of investigations involving organophosphazenes.[2] Factors such as the complexities of reactions leading to these materials,[3,4] electronic structure,[5] and thermal stability[6,7] all contribute to the interest in this class of compounds. We have been interested in the preparation and synthetic transformations of phosphazenes with organofunctional substituents.[8] These studies have led

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to new and interesting organophosphazenes and organophosphazene polymers.[9] One such species, 2-propenylpentafluorocyclotriphosphazene, $N_3P_3F_5C(CH_3)=CH_2$, is prepared by the reaction of the appropriate lithium reagent with hexafluorocyclotriphosphazene ($N_3P_3F_6$).[10] In addition, one also obtains considerable amounts of materials that apparently arise from the attack of the anionic lithium reagent on the olefinic center.[11] It has been shown by a variety of techniques that the $P_3N_3F_5$ moiety exhibits a strong electron-withdrawing effect when attached to organic substituents.[5,9] The olefinic center in $N_3P_3F_5C(CH_3)=CH_2$ would thus be highly polar and susceptible to anionic attack. In order to avoid these undesirable side reactions, we decided to prepare alkenylphosphazenes with strong electron-donating substituents on the olefinic center, thus counterbalancing the electron-withdrawing effect of the phosphazene. Due to their electron-rich nature, the vinyl ethers were considered to be favorable substituents for this study. A preliminary account of this work has appeared.[11]

Experimental Section

Materials and Methods. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Ethyl Corp.), was converted to hexafluorocyclotriphosphazene, $N_3P_3F_6$,[12] which in turn was converted to phenylpentafluorocyclotriphosphazene, $N_3P_3F_5C_6H_5$,[13] and (dimethylamino)pentafluorocyclotriphosphazene[14] by previously reported procedures. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Ethyl vinyl ether (Aldrich), methyl vinyl ether (Pfaltz and Bauer), *tert*-butyllithium (2.0 *m* in pentane, Aldrich), bromobenzene (Fisher), lithium metal (Alfa), and anhydrous dimethylamine (Eastman) were used without further purification. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 (^1H), 62.9 (^{13}C), 235.2 (^{19}F), and 101.2 MHz (^{31}P). Tetramethylsilane, Me_4Si (for ^1H and ^{13}C), and fluorotrichloromethane, $CFCl_3$ (for ^{19}F), were used as internal references. For ^{31}P NMR, 85% H_3PO_4 was used as an external reference. Chemical shifts upfield to the reference are assigned a negative sign. ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded under conditions of broad-band decoupling. Infrared (IR) spectra were obtained as their films (NaCl disks) or KBr pellets on a Beckman IR 20 A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Gas chromatography was performed on a Hewlett-Packard 5700A instrument equipped with a Chromasorb W (SE-30) column. NMR simultations were carried out with a locally modified version of the DNMR3 computer program.[15] Elemental analyses were performed by Integral Microanalytical Laboratories.

All reactions were carried out under anhydrous conditions in a three-necked round-bottomed flask fitted with a reflux condenser and a pressure-equalizing dropping funnel. The system was stirred magnetically and flushed with nitrogen, which exited through a mercury bubbler. Lithium reagents were transferred by using syringe techniques.

Preparation of $N_3P_3F_5C(OC_2H_5)=CH_2$. A previously described[16] vessel for the preparation and transfer of air-sensitive reagents was charged with ethyl vinyl ether (6 mL, 0.063 mol) and 100 mL of tetrahydrofuran (THF) flushed with N_2 and cooled to −78 °C. *tert*-Butyllithium (27 mL, 0.054 mol) was added over a 0.5-h period. The solution was allowed to stir for 1 h while warming to 0 °C, and stirring was continued for an additional 1 h. The lithiated vinyl ether was transferred[16] over a 0.5-h period to a solution of $N_3P_3F_6$ (15 g, 0.06 mol) in 75 mL of THF at −78 °C. The solution was allowed to come to room temperature, and the reaction proceeded for 18 h. The solvent was removed; the mixture was dissolved in petroleum ether, and the salts were removed by filtration. After treatment with activated carbon, the solvent was removed and the resulting oil was distilled to yield 5.4 g (33.2% theory) of a water-white liquid (bp 25–30 °C (0.02 mmHg)). Anal. Calcd for $N_3P_3F_5C_4H_7O$ (**1**): C, 15.95; H, 2.33; mol wt 301. Found: C, 15.71; H, 2.44; mol wt 301 (mass spectrum[17]).

^1H NMR:[18] δ_{H_c} 5.23 (d of d, 1 H), $^2J_{H_cH_t}$ = 3.66, $^3J_{H_cP}$ = 17.09; δ_{H_t} 4.96 (d of t, 1 H), $^2J_{H_tH_c}$ = 3.66, $^3J_{H_tP}$ = 47.61, $^4J_{H_tF}$; δ_{OCH_2} 3.91 (q, 2 H), $^3J_{HH}$ = 6.71; $\delta_{OCH_2CH_3}$ 1.38 (t, 3 H), $^3J_{HH}$ = 6.71. ^{13}C NMR:[19] δ_{C_1} 152.71, $^1H_{C_1P}$ = 246.28, $^2J_{C_1F}$ = 36.20; δ_{C_2} 99.03, $^2J_{C_2P}$ = 29.81; δ_{C_3} 65.66, $^3J_{C_3P}$ = 12.77; δ_{C_4} 14.08. ^{31}P NMR: $\delta_{=PF(C_4H_7O)}$ 25.18, $^1J_{PF}$ = 1001.8; $\delta_{=PF_2}$ 9.45, $^1J_{PF}$ = 919.7. ^{19}F NMR: $\delta_{=PF(C_4H_7O)}$ −68.25; $\delta_{=PFF}$ −68.11; $\delta_{=PFF}$ −69.20. IR:[20] 2970 (w, ν_{CH}), 1620 (s, $\nu_{C=C}$), 1450 (w), 1385 (m), 1360 (m), 1270 (vs, $\nu_{P=N}$), 1110 (w, COC asym), 1045 (s, COC, sym), 1010 (m), 940 (vs, PF asym), 855 (vs, PF sym), 760 (s, $=CH_2$ wag).

Preparation of 2,2-$N_3P_3F_4[C(OC_2H_5)=CH_2]_2$ (2). This preparation was allowed to proceed as above except that the following quantities of reagents were used: ethyl vinyl ether, 9 mL (0.095 mol); *tert*-butyllithium, 42.5 mL (0.088 mol). An aliquot of the lithiated vinyl ether was quenched with distilled water and titrated with a standard HCl solution. The solution was found to contain 0.066 mol of the reagent and consequently required 8.2 g (0.033 mol) of $N_3P_3F_6$ (in 100 mL of THF). The resulting product was recrystallized twice from hexane to afford 2.37 g (20.4% of theory) of a milk-white solid, mp 51–52 °C. Anal. Calcd for $N_3P_3F_4C_8H_{14}O_2$: C, 27.20; H, 3.97; N, 11.90; mol wt 353. Found: C, 27.02; H, 4.08; N, 11.78; mol wt 353 (mass spectrum[17]).

^1H NMR:[18] δ_{H_c} 5.17 (d of d, 2 H), $^2J_{H_cH_t}$ = 3.42, $^3J_{H_cP}$ = 14.16; δ_{H_t} 4.92 (d of d, 2 H), $^2J_{H_tH_c}$ = 3.42, $^3J_{H_tP}$ = 38.57; δ_{OCH_2} 3.90 (q, 4 H), $^3J_{HH}$ = 6.84; $\delta_{OCH_2CH_3}$ 1.35 (t, 6 H), $^3J_{HH}$ = 6.84. ^{13}C NMR:[19] δ_{C_1} 155.29, $^1J_{C_1P}$ = 174.59; δ_{C_2} 97.94, $^2J_{C_2P}$ = 25.55; δ_{C_3} 65.25, $^3J_{C_3P}$ = 9.94; δ_{C_4} 14.06. ^{31}P NMR: $\delta_{=P(C_4H_7O)_2}$ 15.03; $\delta_{=PF_2}$ 8.95, $^1J_{PF}$ = 895.03. ^{19}F NMR: δ_{PF_2} −68.16. IR:[20] 2990 (s, ν_{CH}), 2950 (m, ν_{CH}), 1630 (m, $\nu_{C=C}$), 1610 (s, $\nu_{C=C}$), 1485 (m), 1465 (m), 1450 (m, CH_3 asym), 1390 (s, CH_3 sym), 1365 (m), 1255 (vs, $\nu_{P=N}$), 1155 (m, COC asym), 1045 (s, COC sym), 975 (s, $=CH_2$ wag), 950 (m), 920 (vs, PF asym), 855 (s), 810 (vs, PF sym), 760 (s), 745 (s, $=CH_2$ wag).

Preparation of $N_3P_3F_5C(OCH_3)=CH_2$ (3) and $N_3P_3F_5[C(OCH_3)=CH_2]_2$ (4). The procedure used was identical with that described above except that the methyl vinyl ether was condensed at −78 °C and subsequently transferred to the reaction vessel. In a typical experiment, the following quantities of reagents were used: 8 mL (0.107 mol) of methyl vinyl ether, 45 mL (0.09 mol) of *tert*-butyllithium, and 23 g (0.092 mol), $N_3P_3F_6$. The resulting oil was distilled to yield 3.38 g (13% of theory) of a water-white liquid, bp 25 °C (0.02 mmHg). Anal. Calcd for $N_3P_3F_5C_3H_5O$: C, 12.45; H, 1.74; mol wt 287. Found: C, 13.06; H, 1.54; mol wt 287 (mass spectrum[17]).

^1H NMR:[18] δ_{H_c} 5.27 (d of d, 1 H), $^2J_{H_tH_c}$ = 3.97, $^3J_{H_cP}$ = 16.48; δ_{H_t} 5.00 (d of t, 1 H), $^2J_{H_tH_c}$ = 3.97, $^3J_{H_tP}$ = 46.35, $^4J_{H_tF}$ = 3.66; δ_{OCH_3} 3.73 (s, 3 H). ^{13}C NMR:[19] δ_{C_1} 152.75, $^1J_{C_1P}$ = 250.09, $^2J_{C_1F}$ = 36.47; δ_{C_2} 98.77, $^2J_{C_2P}$ = 29.77; δ_{C_3} 53.68, $^3J_{C_3P}$ = 12.65. ^{31}P NMR: $\delta_{=PF(C_3H_5O)}$ 25.49, $^1J_{PF}$ = 1003.65; $\delta_{=PF_2}$ 9.09, $^1J_{PF}$ = 933.46, $^2J_{PF}$ = 82.00, $^3J_{PF}$ = 18.75, $^4J_{PF'}$ = 5.15. ^{19}F NMR: $\delta_{=PF(C_3H_5O)}$ −66.85, $^1J_{PF}$ = 989.87; δ_{PFF} −67.85; δ_{PFF} −69.23. IR:[20] 2970 (w, ν_{CH_3}), 1620 (m, $\nu_{C=C}$), 1460 (w), 1380 (w), 1280 (vs, $\nu_{P=N}$), 1195 (w), 1045 (s, COC sym), 1015 (m, $=CH_2$ wag), 945 (s, PF asym), 910 (m), 865 (s), 840 (s, PF sym), 760 (s, $=CH_2$ wag), 720 (w).

The residue from the distillation was subjected to column chromatography using hexanes as the eluting solvent. A small amount of 2,2-$N_3P_3F_4[C(OCH_3)=CH_2]_2$, as identified by the mass spectrum and NMR spectroscopy, was isolated.

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(18) All NMR (^1H, ^{13}C, ^{31}P, ^{19}F) chemical shifts are in ppm, and coupling constants in Hz. H_c is the olefinic hydrogen atom cis to the phosphazene and H_t is trans to the phosphazene
(19) Numbers refer to $\equiv PFC^1(OC^3H_2C^4H_3)=C^2H_3$.
(20) In cm^{-1}.

^{1}H NMR:[18] δ_{H_c} 5.22 (d of d, 2 H), $^2J_{H_cH_t}$ = 3.66, $^3J_{H_cP}$ = 13.67; δ_{H_t} 4.97 (d of d, 2 H), $^2J_{H_tH_c}$ = 3.66, $^3J_{H_tP}$ = 37.60; δ_{OCH_3} 3.70 (s, 3 H), ^{13}C NMR:[19] δ_{C_1} 156.26, $^1J_{C_1P}$ = 176.41; δ_{C_2} 97.78, $^2J_{C_2P}$ = 25.31; δ_{C_3} 56.63, $^3J_{C_3P}$ = 10.42. ^{31}P NMR: $\delta_{\equiv P(C_3H_3O)_2}$ 13.88; $\delta_{\equiv PF_2}$ 8.32, $^1J_{PF}$ = 892.89. ^{19}F NMR: $\delta_{\equiv PF_2}$ −67.86. IR:[20] 2950 (m, ν_{CH}), 2860 (w, ν_{CH}), 1620 (s, $\nu_{C=C}$), 1460 (m, CH_3 asym), 1375 (m, CH_3 sym), 1255 (vs, $\nu_{P=N}$), 1190 (w), 1000 (m, $=CH_2$ wag), 960 (m), 925 (s, PF asym), 895 (m), 855 (m), 820 (s, PF sym), 740 (s, $=CH_2$ wag).

Preparation of 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ (5) from $N_3P_3F_5C_6H_5$. The procedure used was identical with that described above except that $N_3P_3F_5C_6H_5$ was used in place of $N_3P_3F_6$. In a typical experiment, the following quantities of reagents were used: 4.5 mL (0.047 mol) of ethyl vinyl ether, 23 mL (0.046 mol) of *tert*-butyllithium, and 14.2 g (0.046 mol) of $N_3P_3F_5C_6H_5$. The resulting oil was distilled to yield 2.80 g (17% theory) of a water-white liquid (bp 80–90 °C (0.02 mmHg)). Anal. Calcd for $N_3P_3F_4C_{10}H_{12}O$: C, 33.43; H, 3.34; mol wt 359. Found: C, 32.92; H, 3.07; mol wt 359 (mass spectrum[17]).

^{1}H NMR:[18] δ_{Ar} 7.54 (m, 5 H); δ_{H_c} 4.86 (d of d, 1 H), $^2J_{H_cH_t}$ = 3.43, $^3J_{H_cP}$ = 14.23; δ_{H_t} 4.78 (d of d, 1 H), $^2J_{H_tH_c}$ = 3.43, $^3J_{H_tP}$ = 38.40; δ_{OCH_2} 3.82 (q, 2 H), $^3J_{HH}$ = 6.86; $\delta_{OCH_2CH_3}$ 1.27 (t, 3 H). ^{13}C NMR:[19] δ_{C_1} 157.74, $^1J_{C_1P}$ = 168.65; δ_{C_2} 96.60, $^2J_{C_2P}$ = 25.70; δ_{C_3} 65.18, $^3J_{C_3P}$ = 8.03; δ_{C_4} 13.99; δ_{C_o} 128.61, $^2J_{C_oP}$ = 14.46; δ_{C_m} 131.11, $^3J_{C_mP}$ = 11.24; δ_{C_p} 133.07. ^{31}P NMR: $\delta_{\equiv P(C_6H_5)(C_4H_7O)}$ 21.11; $\delta_{\equiv PF_2}$ 9.03, $^1J_{PF}$ = 923.6. ^{19}F NMR: $\delta_{\equiv PFF}$ −68.98; $\delta_{\equiv PFF}$ −67.30. IR:[20] 3080 (w, ν_{CH}), 2950 (w, ν_{CH}), 1620 (s, $\nu_{C=C}$), 1450 (m), 1250 (vs, $\nu_{P=N}$), 1190 (m), 1130 (m, COC asym), 1050 (m, CH bend), 1000 (w, $=CH_2$ wag), 980 (w), 925 (s, PF asym), 860 (m), 820 (s, PF sym), 740 (s, $=CH_2$ wag), 690 (m, CH bend).

Preparation of 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ (5) from $N_3P_3F_5C(OC_2H_5)=CH_2$. A solution of phenyllithium was prepared[13] from bromobenzene (2 mL, 0.019 mol) and lithium (0.35 g, 0.05 mol) in the air sensitive reagent transfer vessel[16] with diethyl ether as the solvent. The lithium reagent was added to a solution of 5.75 g (0.019 mol) of $N_3P_3F_5C(OC_2H_5)=CH_2$ in 50 mL of diethyl ether at 0 °C. Workup was as described as above with the addition of a column chromatography step using petroleum ether as the eluent. The resulting oil was distilled (80–90 °C (0.02 mmHg)) to give 1.44 g (21% of theory) of a product, which was shown by NMR spectroscopy to be equivalent to that obtained in the preceding preparation.

Preparation of 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ (6) from $N_3P_3F_5N(CH_3)_2$. The procedure was identical with that described for the preparation of **1** except that $N_3P_3F_5N(CH_3)_2$ was used in place of $N_3P_3F_6$. In a typical experiment the following quantities of reagents were used: 4.75 mL (0.05 mol) of ethyl vinyl ether, 20 mL (0.04 mol) of *tert*-butyllithium, and 11.0 g (0.04 mol) of $N_3P_3F_5N(CH_3)_2$. The resulting oil was distilled to yield 0.99 g (7.6% of theory) of a water-white liquid (bp 32–37 °C (0.02 mmHg)). Anal. Calcd for $N_4P_3F_4C_6H_{13}O$: C, 22.09; H, 3.99; N, 17.17; mol wt 326. Found: C, 22.01; H, 3.90; N, 17.17; mol wt 326 (mass spectrum[17]).

^{1}H NMR:[18] δ_{H_c} 5.19 (d of d, 1 H), $^2J_{H_cH_t}$ = 3.36, $^3J_{H_cP}$ = 16.18; δ_{H_t} 4.87 (d of t, 1 H), $^2J_{H_tH_c}$ $^2J_{H_tH_t}$ = 3.36, $^3J_{H_tP}$ = 46.08, $^4J_{H_tF}$ = 3.97; δ_{OCH_2} 3.88 (q, 2 H), $^3J_{HH}$ = 7.02; δ_{NCH_3} 2.74 (d, 6 H), $^3J_{HP}$ = 12.51; $\delta_{CH_2CH_3}$ 1.37 (t, 3 H), $^3J_{HH}$ = 7.02. ^{13}C NMR:[19] δ_{C_1} 153.82, $^1J_{C_1P}$ = 269.64, $^2J_{C_1F}$ = 36.54; δ_{C_2} 97.41, $^2J_{C_2P}$ = 28.11; δ_{C_3} 64.99, $^3J_{C_3P}$ = 11.24; δ_{C_4} 14.10; δ_{NCH_3} 35.85, $^2J_{CP}$ = 4.82. ^{31}P NMR: $\delta_{\equiv PF(C_2H_6N)}$ 23.75; $^1J_{PF}$ = 908.69; $\delta_{\equiv PF(C_4H_7O)}$ 23.75, $^1J_{PF}$ = 993.20; $\delta_{\equiv PF_2}$ 8.12, $^1J_{PF}$ = 922.00. ^{19}F NMR: $\delta_{\equiv PF(C_2H_6N)}$ −61.72; $\delta_{\equiv PF(C_2H_6N)}$ −62.53; $\delta_{\equiv PF(C_4H_7O)}$ −65.76; $\delta_{\equiv PF(C_4H_7O)}$ −66.56; $\delta_{\equiv PF_2}$ −67.56; $\delta_{\equiv PF_2}$ −69.12. IR:[20] 2950 (m, ν_{CH}), 1620 (s, $\nu_{C=C}$), 1490 (m, CH_3 sym), 1465 (m, CH_3 sym), 1450 (m), 1385 (m), 1365 (m), 1260 (vs, $\nu_{P=N}$), 1170 (m, ν_{CN}), 1115 (w, COC asym), 1050 (s, CH bend), 1015 (s, $=CH_2$ wag), 980 (s), 920 (vs, PF asym), 845 (vs, PF sym), 770 (s), 730 (s, $=CH_2$ wag), 710 (s).

Preparation of 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ (6) from $N_3P_3F_5C(OC_2H_5)=CH_2$. A dropping funnel equipped with a cold jacket was maintained at 0 °C and charged with 2.0 mL (0.03 mol) of anhydrous dimethylamine in 30 mL of diethyl ether. The resulting solution was added dropwise to a solution of 4.0 g (0.013 mol) of $N_3P_3F_5C(OC_2H_5)=CH_2$ in 50 mL of diethyl ether at 0 °C. The reaction mixture was allowed to come to room temperature and continued to react, with stirring, for 24 h. The salts were separated, and the solvent was removed. Distillation (32–37 °C (0.02 mmHg)) of the crude material yielded 1.15 g (26.5% of theory) of a product, which was shown, by NMR spectroscopy, to be identical with that obtained in the preceding preparation.

Results and Discussion

The reactions of lithiated methyl or ethyl vinyl ether with hexafluorocyclotriphosphazene, $N_3P_3F_6$, proceed to give moderate yields of the appropriate monosubstituted phosphazenes (eq 1). In addition to the expected products, trace

$$N_3P_3F_6 + LiC(OR)=CH_2 \rightarrow N_3P_3F_5C(OR)=CH_2 + LiF \quad (1)$$
$$R = C_2H_5\ (\mathbf{1}),\ CH_3\ (\mathbf{3})$$

amounts of the compound derived from metalation of ethyl vinyl ether at the β position, i.e. $N_3P_3F_5CH=CHOC_2H_5$, were detected in the ^{1}H NMR spectrum of the crude product. The desired material, **1**, could be obtained in the pure state by distillation. Significantly, one does not obtain any of the degradation products arising from anionic attack on the olefinic center in **1** or **3**. This is in contrast to the results obtained in the 2-propenyllithium system, where such degradative processes play a dominant role in the reaction.[11] This observation confirms, at the synthetic level, our postulation of the reduction of olefin polarity in **1** and **3** by the incorporation of a strong electron-donating substituent on the olefin, which counterbalances the strong electron-withdrawing effect[5] of the phosphazene. The new compounds were characterized by elemental analyses and mass and NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) spectra.

The ^{1}H NMR spectrum of **1** shows multiplets in the β-hydrogen region but none in the region assigned to the α-hydrogen atoms in ethyl vinyl ether. A complex multiplet in the α-hydrogen region does appear in the spectrum of the trace byproduct described above. Simulation of the ^{1}H NMR spectrum of **1** requires, in addition to the expected interactions, fluorine coupling with the β-hydrogen atom trans to the phosphazene. The ^{13}C NMR spectrum also confirms the position of attachment of the phosphazene. The α-carbon resonance is of very low intensity with large one-bond phosphorus–carbon coupling along with two-bond fluorine–carbon coupling and some possible additional long-range phosphorus coupling. The ^{31}P and ^{19}F NMR spectra confirm a monosubstituted phosphazene by showing two $\equiv PF_2$ centers and one $\equiv PF[C(OR)=CH_2]$ center.

Certain features of the NMR parameters require additional discussion. The phosphorus atom chemical shifts are relatively constant on going from **1** to **3**, thus implying no significant bond angle changes at the phosphorus center. The chemical shift of the fluorine atom in a $\equiv PF[C(OR)=CH_2]$ environment varies with the nature of the alkyl group. The magnitude of this variation (1.4 ppm) is such that it could be ascribed to solvent or related effects. There is no long-range fluorine coupling to the alkyl group. The β-carbon chemical shifts of olefins can be correlated to substituent electron donor/acceptor effects.[21] The β-carbon chemical shift goes from 84.6 ppm in ethyl vinyl ether to 99.0 ppm in **1**. This latter value is in the general range of olefins with weak electron-withdrawing substituents (e.g., vinyl acetate). Thus the effect of the phosphazene has been to significantly reduce the electron-rich nature of the vinyl ether. The net result is a slightly electron-deficient olefin, which may be contrasted to the very polarized propenylphosphazene.[9,11] The qualitative difference in polarity between **1** and the corresponding propenyl derivative is in agreement with the differences observed in their reactivity toward lithium reagents.

The addition of 2 molar equiv of $LiC(OR)=CH_2$ to $N_3P_3F_6$ produces the geminally substituted derivatives 2,2-$N_3P_3F_4[C(OR)=CH_2]_2$, **2** and **4**. The corresponding reaction using 2-propenyllithium yielded only degradation products,[10] pre-

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sumably from anionic attack on the electron-deficient olefin.[11] These observations further demonstrate the validity of the reduction of polarity hypothesis in the synthetic chemistry of alkyl vinyl ether–phosphazene derivatives. The geminal configurations were unambiguously deduced from the NMR spectroscopic data. The absence of fluorine coupling in both the ^1H and ^{13}C NMR spectra of **2** and **4** suggests a geminal configuration since such coupling was observed for a $\equiv PFC(OR)=CH_2$ center in **1** and **3**. The phosphorus–carbon ($^1J_{PC}$) and phosphorus–hydrogen ($^3J_{PCCH}$) coupling constants all decrease on going from the mono- to the disubstituted derivatives. Similar trends have been observed in the ^1H[5c,22] and ^{13}C[5b,e] NMR spectra of a wide variety of geminal organo- and aminophosphazenes. The geminal assignment can be confirmed by ^{19}F and ^{31}P NMR spectroscopy. The complex ^{19}F NMR spectra observed for **1** and **3** reduce to a doublet in **2** and **4**, indicating a single fluorine environment. The second-order fine structure is of the type expected for an ABB′$X_2X'_2$ system. The ^{31}P NMR spectra of **2** and **4** show a large triplet due to $\equiv PF_2$ centers and a small triplet due to a phosphorus atom in a $\equiv P[C(OR)=CH_2]_2$ center coupling with two equivalent phosphorus atoms. The fine structure on the $\equiv P[C(OR)=CH_2]_2$ resonance is clarified by broad-band proton decoupling and results (in the decoupled spectra) from long-range phosphorus–fluorine coupling. The chemical shift of the olefinic β-carbon undergoes a small ($\sim$1 ppm) shift on going from the mono- to the disubstituted derivatives. The direction of the shift[21] is consistent with a small decrease in electron-withdrawing ability as a fluorine atom is replaced by a less electronegative organic group.[5a] A substantive shift ($\sim$10 ppm) is observed for the organosubstituted phosphorus resonance on going from the mono- to the disubstituted derivatives. The origins of this variation are complex, but the major contributions would be expected to be electron release from the olefin and change in bond angle at the phosphorus atom.

Attempts to introduce additional ethyl vinyl ether substituents on to the phosphazene ring have proved unsuccessful. The NMR and mass spectra of the small amounts of product mixtures obtained suggest that these materials arise from displacement of the ethoxy function from the olefin in **2**.

The fact that the reduced polarity of the olefinic centers in **1** and **3** allows for further ring substitution reactions by $LiC(OR)=CH_2$ without exocyclic group attack has led us to examine the synthesis of mixed-substituent derivatives of **1**. These reactions are summarized as follows:

$$\underset{\mathbf{1}}{N_3P_3F_5C(OC_2H_5)=CH_2} + LiC_6H_5 \rightarrow \underset{\mathbf{5}}{2,2\text{-}N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2}$$

$$N_3P_3F_5C_6H_5 + LiC(OC_2H_5)=CH_2 \rightarrow \mathbf{5}$$

$$\mathbf{1} + HN(CH_3)_2 \rightarrow \underset{\mathbf{6}}{2,4\text{-}N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2}$$

$$N_3P_3F_5N(CH_3)_2 + LiC(OC_2H_5)=CH_2 \rightarrow \mathbf{6}$$

The same mixed phenyl/ethoxyvinyl derivative (**5**) is formed independent of the order of introduction of the substituents. The geminal configuration for **5** is established by NMR spectroscopy. The ^1H and ^{13}C NMR spectra show the same characteristic shifts and absence of fluorine coupling as was observed in the preceding geminal derivatives **2** and **4**. The ^{19}F NMR spectrum is complicated since even in a geminal configuration the fluorine atoms in a $\equiv PF_2$ center are inequivalent; hence, one observes two sets of complex doublets. The structure is unambiguously confirmed by the ^{31}P NMR spectrum, which is very similar to those of the other geminal derivatives except for a substantive shift in the organosubstituted phosphorus atom over the divinyl ether derivatives. One would expect that the size difference between a phenyl and a vinyl ether substituent would effect bond angle changes at the phosphorus atom and hence be reflected in ^{31}P chemical shifts. The olefinic β-carbon ^{13}C NMR shift in **5** suggests a slightly more electron-rich olefinic environment in **5** than in **2**.

The same mixed dimethylamino/ethoxyvinyl derivative (**6**) is also obtained independent of the order of introduction of substituents. Examination of **6** by gas chromatography shows the existence of two components in similar (but not exactly equivalent) amounts. The relative amounts of each component do not vary significantly with the order of introduction of the substituent. The ^1H and ^{13}C NMR data are suggestive of a nongeminal configuration in that the coupling constants resemble **1** and **3** and fluorine coupling is observed. The ^{19}F and ^{31}P NMR spectra are complex due to the presence of the isomeric mixture; however, in each case the expected features of $\equiv PF_2$ and $\equiv PFR$ environments are observed. Thus, it can be concluded that sample **6** is a mixture of *cis*- and *trans*-2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$.

The results presented above are of interest in the continuing question of the basis of the stereoregulation effects observed in the substitution reactions of the cyclophosphazenes. In recent years, careful studies of the cross reactions of various amines with $N_3P_3Cl_6$ have clearly demonstrated the importance of incoming group control over the stereochemistry of phosphazene derivatives.[23] Evidence for incoming group control is also noted in this investigation. If one considers various reactions of the same monosubstituted phosphazene (**1**), one observes geminal isomer formation when the incoming moiety is an organolithium reagent and nongeminal isomer formation when the incoming group is dimethylamine. By using the same lithium reagent and changing the phosphazene, one also observes evidence for phosphazene substituent control over the stereochemistry of the product. Thus the reaction of $LiC(OC_2H_5)=CH_2$ with **1** and $N_3P_3F_5C_6H_5$ leads to geminal products while the comparable reaction with $N_3P_3F_5N(CH_3)_2$ yields nongeminal products.

The reactions examined in this investigation bridge the balance point between incoming reagent and substituent control. While many of the mechanistic features of incoming reagent control in the reactions of amines with $N_3P_3Cl_6$ are understood,[23d] similar details for the reactions of organolithium reagents with $N_3P_3F_6$ are lacking. However, a consistent model for ring substituent control is beginning to emerge. The clear predilection for geminal isomer formation for organophosphazenes[2] can be related to the σ-electron-releasing ability[5a] of the organic group. The preferential shift of ring nitrogen lone-pair electron density to the $\equiv PF_2$ center[24] results in occupation of phosphorus acceptor orbitals at that center, which otherwise would serve as sites for an incoming reagent in a bimolecular reaction. This leaves more acceptor orbitals for an incoming reagent at the $\equiv PFR$ center, and consequently geminal subtitution is formed. In the case of aminophosphazenes such as $N_3P_3F_5N(CH_3)_2$ the substituent is a π donor;[22] hence, acceptor orbitals at the $\equiv PFN(CH_3)_2$ center are occupied, and attack occurs at the $\equiv PF_2$ site, giving nongeminal products.

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Registry No. **1**, 80297-67-2; **2**, 80297-88-7; **3**, 80297-86-5; **4**, 80297-87-6; **5**, 80297-89-8; *cis*-**6**, 84624-30-6; *trans*-**6**, 84624-31-7; hexachlorocyclotriphosphazene, 940-71-6; hexafluorocyclotriphosphazene, 15599-91-4; methyl vinyl ether, 107-25-5; phenylpentafluorocyclotriphosphazene, 2713-48-6; phenyllithium, 591-51-5; (dimethylamino)pentafluorocyclotriphosphazene, 23208-17-5; dimethylamine, 124-40-3; ethyl vinyl ether, 109-92-2.

Supplementary Material Available: Table I showing major mass spectral fragments and their relative intensities (6 pages). Ordering information is given on any current masthead page.

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Stereochemically Nonrigid Paramagnetic Tris Chelate Complexes of Cobalt(II) with Octamethylpyrophosphoramide and Nonamethylimidodiphosphoramide. An NMR Study

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The terminal *N*-methyl substituents of the title ligands, OMPA and NIPA, are shown to be diastereotopic in the D_3 hexacoordinated complex ions $Co(OMPA)_3^{2+}$ (**1**) and $Co(NIPA)_3^{2+}$ (**2**), prepared as solutions of their perchlorates in a CD_3NO_2/CD_2Cl_2 solvent mixture. Contact and pseudocontact contributions to the isotropic shifts have been analyzed, with the assumption of a known geometry and identical contact shifts for both sets of diastereotopic protons. Ambiguities in line assignments are removed by a comparison of contact shifts in **1** and **2** and an examination of the temperature dependence of contact shifts and of paramagnetic line broadenings. Two types of exchange are revealed on raising the temperature from −20 to +100 °C: (i) an intramolecular optical inversion between the Λ and Δ enantiomers of **1** and **2** at the lower temperatures with $k_i(25\ °C) = 1.63 \times 10^4$ and $0.17 \times 10^4\ s^{-1}$, $\Delta H^{\ddagger}_i = 13.5$ and 10.9 kcal·mol^{-1}, and $\Delta S^{\ddagger}_i = 5.9$ and −7.3 eu, respectively, and (ii) a bimolecular ligand exchange in complex **1** at the higher temperatures, with $k_e(25\ °C) = 3.80$ s^{-1} mol^{-1}·dm^3, $\Delta H^{\ddagger}_e = 13.0$ kcal·mol^{-1}, and $\Delta S^{\ddagger}_e = -12.4$ eu. The rate-determining step for both processes involves the detachment of one end of one bidentate ligand from the metal atom to yield a pentacoordinated intermediate, which then either returns quickly to the initial complex molecule or to its enantiomer (optical inversion) or fastens a new ligand molecule from the bulk solution.

Introduction

In previous reports,[1-4] we have shown the possibility of using ^1H or ^{31}P DNMR to study the structure and dynamics of six-coordinate tris chelates of bivalent and trivalent diamagnetic cations with a diphosphorylated symmetrical bidentate ligand, nonamethylimidodiphosphoramide (NIPA, $(NMe_2)_2P(O)NMeP(O)(NMe_2)_2$). An important feature of the ^1H spectra of these compounds is the existence of diastereotopic terminal *N*-methyl substituents,[1] as is expected for D_3 complexes. Solutions of D_3 tris chelates contain equal quantities of two chiral isomers, Δ and Λ,[5-7] which yield identical spectra. Within each isomer, the terminal *N*-methyl substituents are not mutually interchanged through any symmetry operation (C_3, $3C_2$) of the D_3 symmetry point group. Two signals are therefore observed at low temperature ($T \approx -80$ °C) for the two nonequivalent *N*,*N*-dimethyl substituents $N(1)Me_2$ and $N(2)Me_2$ (Figures 1 and 3), attached to each phosphorus atom. At higher temperatures, optical inversion, $\Delta \rightleftarrows \Lambda$, brings about a rapid interchange, $N(1)Me_2 \rightleftarrows N(2)Me_2$, on the NMR time scale. However, the very small chemical shift differences between the diastereotopic protons in diamagnetic chelates,[1] e.g. $\Delta\delta = 0.01$, 0.004, and 0.005 for $Al(NIPA)_3^{3+}$, $Ga(NIPA)_3^{3+}$, and $In(NIPA)_3^{3+}$, respectively, prevent accurate measurements of the optical inversion rate. Moreover the NMR window is so narrow that the exchange rate is immeasurably slow on the NMR time scale up to the boiling point of the solutions (for most trivalent cations) or immeasurably fast down to the freezing point of the solutions (for most divalent cations). Finally, no simple relationship can be found between the structure of the diamagnetic complexes and the value of the observed shifts $\Delta\delta$, thus preventing us from assigning individual resonances to the two sets of diastereotopic protons.

These difficulties prompted us to investigate paramagnetic cobalt(II) octahedral chelates where the triply degenerate $^4T_{1g}$ ground state is expected to produce magnetic anisotropy and significant dipolar shifts,[8] as was pointed out by La Mar for the (4,7-dimethyl-1,10-phenanthroline)bis(acetylacetonate)-cobalt(II) complex.[9] The octamethylpyrophosphoramide ligand (OMPA, $(NMe_2)_2P(O)-O-P(O)(NMe_2)_2$) was preferred in a first step to the NIPA ligand, since only the crystal structure of the complex ion $Co(OMPA)_3^{2+}$ is described in the literature.[10] The complexes $Co(OMPA)_3^{2+},2ClO_4^-$ (**1**) and $Co(NIPA)_3^{2+},2ClO_4$ (**2**) are prepared in the solid state[11-13] and are then dissolved in an inert solvent, either in pure nitromethane or in a 2:1 v/v mixture of methylene chloride and nitromethane ("C_2N"). Two lines are effectively obtained at low temperatures (−60 and −20 °C), one of which is located upfield and the second one downfield, by several ppm, with respect to the signal of a diamagnetic analogue, the complex ion[14] $Mg(OMPA)_3^{2+}$. An inspection of the isotropic shifts and

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