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N-(Ferrocenylmethyl)-*N*-methylaminocyclotriphosphazenes

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The reactions of *N*-(ferrocenylmethyl)-*N*-methylamine, $C_5H_5FeC_5H_4CH_2(Me)NH$, with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, led to the formation of the *N*-(ferrocenylmethyl)-*N*-methylaminocyclotriphosphazene derivatives, $N_3P_3Cl_{6-n}[N(Me)CH_2C_5H_4FeC_5H_5]_n$ ($n = 1–3$). Only small amounts of higher degrees of substitution could be detected. In the case of the disubstituted products, the ratio of isomers was dependent on the polarity of the solvent. In nonpolar solvents the ratio was trans > geminal > cis while in acetonitrile only equal amounts of trans and cis isomers were observed. The reaction of *N*-(ferrocenylmethyl)-*N*-methylamine with (methacryloylbutenedioxy)pentachlorocyclotriphosphazene, $N_3P_3Cl_5O(CH_2)_4OC(O)C(Me)=CH_2$, gives the surprising geminal isomer 2,2-$N_3P_3Cl_4[O(CH_2)_4OC(O)C(Me)=CH_2]N(Me)CH_2C_5H_4FeC_5H_5$ and the tris derivative 2,2′,4-$N_3P_3Cl_3[O(CH_2)_4OC(O)C(Me)=CH_2][N(Me)CH_2C_5H_4FeC_5H_5]_2$. All of the phosphazene derivatives were characterized by elemental analyses, mass spectrometry, IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, and electrochemical techniques (cyclic, normal pulse, and differential pulse voltametry). The compounds all undergo a single, reversible oxidation reduction process.

Introduction

A variety of synthetic procedures are available for the construction of cyclophosphazenes containing organometallic and other metal-containing pendant groups.[1,2] The stability of the cyclophosphazene unit to redox processes[3] allows for utilization of redox active substituents without disruption of the core inorganic ring system. Examples of substituents which undergo oxidation−reduction without phosphazene degradation include cobalt and manganese[4] carbonyls as well as platinum[5] and ferrocene [6,7] containing species. A wide number of other cyclophosphazenes with various organometallic substituents[2] also have the potential for redox activity. Redox active phosphazene polymers including polyphosphazenes with directly bonded ferrocene groups[9] or ferrocene-containing side chains[10] and carbon chain polymers having cyclophosphazenes with cobalt carbonyl cluster substituents as side groups[11] have also been prepared. Often in organometallic electrochemistry, the goal is to explore interactions between multiple potential redox centers.[12] Our interest is in the construction of cyclophosphazenes which can serve as monomers or models for phosphazene-based polymers that can be used as electron transfer mediators. In order for optimal electron transfer properties to occur in a mediator, all redox center should have equivalent redox potentials. The strategy we have employed is the introduction of a stable, well-characterized redox center which is electronically isolated from the cyclophosphazene ring. In this investigation, we report the synthesis and electrochemical characterization of systems in which a redox active moiety (ferrocene) is bound to the cyclophosphazene through a saturated alkyl unit. Preliminary communications of certain aspects of this work have appeared previously.[13,14]

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Materials and Methods

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, **1**) was received from Nippon Soda Co. and purified by recrystallization from hexane followed by sublimation at 70 °C and 0.1 mmHg. Tetrahydrofuran was distilled over potassium using benzophenone as an indicator. Methanol was distilled over magnesium turnings. Diethyl ether was used as received (J.T. Baker). All reagents were purchased from Aldrich Chemical and used as received, except 4-hydroxybutyl methacrylate which was purchased from Polysciences Inc. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as delivered. Reactions which necessitated anhydrous conditions were carried out in magnetically stirred solutions under N_2 by utilizing standard Schlenk line techniques.

The NMR spectra were recorded on a Bruker ARX-500 spectrometer using Bruker UXNMR software. Operating frequencies were 500.13 MHz (^{1}H), 202.46 (^{31}P), and 125.76 (^{13}C). Phosphoric acid (85%) was used as an external reference for ^{31}P spectra with chemical shifts downfield of the reference assigned a positive sign. Broad-band ^{1}H decoupling was used for ^{13}C experiments. All ^{13}C and ^{1}H shifts are reported in ppm vs tetramethylsilane. NMR simulations were carried out using a locally modified version of DNMR-3[15] or the Brucker Win Daisey programs. Mass spectrometry was performed on a Finnegan 4610 spectrometer, and data are reported as monoisotopic peaks on the basis of ^{35}Cl. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR, and data handling was done with Grams Analyst 2000. All IR data are reported in wavenumbers (cm^{-1}). Electrochemical experiments were performed using a Princeton Applied Research model 273 potentiometer/galvanostat using an Ag/AgCl reference electrode. All voltammograms were recorded using PAR software. Normal pulse voltammetry experiments were conducted with a voltage range of 0 to +700 or +800 mV with a step height of 5 mV, at 1 pulse/s. Differential pulse voltammetry experiments were carried out with a pulse time of 1 s, a pulse height of 25 mV, and step height of 5 mV. Elemental analyses were performed by Robertson Microlit Laboratories.

Preparation of *N*-(Ferrocenylmethyl)-*N*-methylamine, $C_5H_5FeC_5H_4CH_2(CH_3)NH$ (2). A 1 L round-bottom flask was charged with 8.02 g (37.4 mmol) of ferrocenyl aldehyde (Aldrich) and dissolved in 400 mL of distilled methanol. Methylamine hydrochloride (12.6 g, 186 mmol) was added to this solution and allowed to stir for 15 min. To this solution, 1.40 g of sodium cyanoborohydride (22.3 mmol) was then added and allowed to react for 30 min. The solution was acidified with concentrated HCl to pH 2. The methanol was removed by flash evaporation, and the amine salt was redissolved in distilled water and washed with 30 mL of diethyl ether 5 times. The aqueous layer was made basic to pH 10 by adding KOH pellets, and the ferrocenylamine separated as an orange oil layer. The product was isolated by five extractions with 30 mL diethyl ether and evaporated to an orange oil at room temperature. The yield was 4.80 g (56% of theory) of product. MS (EI): *m*/*z* 229. ^{1}H NMR: δ 2.4 (s, CH_3); δ 3.4 (s, CH_2); δ 4.0, 4.1 (m, C_5H_4); δ 4.1 (C_5H_5). ^{13}C{^{1}H} NMR: δ 36.8 (CH_3); δ 51.7 (CH_2); δ 87.9, 68.3−68.9 (C_5H_4); δ 69.5 (C_5H_5). IR: 3322 cm^{-1} (w, NH stretch); 1626 cm^{-1} (m, NH bend); 820 cm^{-1} (s, NH wag); 1001 cm^{-1} (m, CH out of plane).

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Preparation of (*N*-(Ferrocenylmethyl)-*N*-methylamino)pentachlorocyclotriphosphazene, $N_3P_3Cl_5N(Me)CH_2C_5H_4FeC_5H_5$ (3). Under an inert atmosphere, 0.130 g (1.29 mmol) of triethylamine was added to 0.309 g (0.860 mmol) of **1** in 25 mL of anhydrous diethyl ether. A solution of 0.197 g (0.861 mmol) of **2** in 5 mL of Et_2O was added from an addition funnel. The resulting mixture was refluxed for 2 days, after which the ether was removed by evaporation. The product was washed with 20 mL of 0.1 M HCl, 20 mL of a saturated bicarbonate solution, and 20 mL of deionized water. The crude product was purified by flash chromatography using 60/40 medium boiling petroleum ether/diethyl ether as an eluent, and the first orange band was collected yielding 0.310 g of an orange oil (67% of theory). Anal. Calcd for $C_{12}H_{14}FeN_4P_3Cl_5$: C, 26.68; H,2.61; N,10.37; mol wt 538 (^{35}Cl). Found: C,-26.99; H, 2.69; N, 10.14; mol wt 538 (MS, ^{35}Cl). ^{1}H NMR: δ 2.6 (d, CH_3), $^3J_{PH}$ = 14.4; δ 4.02 (d, CH_2), $^3J_{PH}$ = 9.4; δ 4.1 (s, C_5H_5); δ 4.2 (s, C_5H_4). ^{13}C{^{1}H} NMR: δ 37.1 (CH_3); δ 52.0 (CH_2); δ 69.4, 68.6, 69.3 (C_5H_4); δ 69.2 (C_5H_5). ^{31}P{^{1}H} NMR: δ 20.6 (cmplex multiplet, *P*(Fc−amine)Cl); δ 21.3 (cmplex multiplet, N*P*Cl_2). IR: 1212 cm^{-1} (vs, PN str); 1197 cm^{-1} (vs, PN str); 3103 cm^{-1} (m, aromatic CH); 2922 cm^{-1} (m, CH str); 1114 cm^{-1} (m, CN str).

Preparation of Bis(*N*-(Ferrocenylmethyl)-*N*-methylamino)-tetrachlorophosphazenes, $N_3P_3Cl_4[N(Me)CH_2C_5H_4FeC_5H_5]_2$ (4, 5). The preparation was allowed to proceed as above, except that 2 equiv of **2** and triethylamine/mol of **1** and triethylamine were employed. In a typical experiment, a 100 mL round-bottom flask was charged with a solution of 0.400 g (1.15 mmol) of **1** dissolved in 25 mL of Et_2O. This was followed by addition of 0.349 mL (3.45 mmol) of triethylamine. A solution of **2** (0.527 g, 2.30 mmol) in 5 mL of Et_2O was added directly to the flask from an addition funnel, and the mixture was allowed to reflux for 2 days. Chromatographic separation was performed on 0.310 g of crude product using 50/50 methylene chloride/medium boiling (30−60 °C) petroleum ether as an eluent. Three orange bands were observed; the first (0.074 g, 32% of the combined product weights) was determined to be compound **3**, the second was determined to be the mixture of nongeminally substituted phosphazenes **4** (0.135 g, 23.8% of theory), and the third was determined to be the geminally disubstituted phosphazene **5** (0.023 g, 7.4% of theory). Anal. Calcd for $C_{24}H_{28}Fe_2N_5P_3Cl_4$: C, 39.33; H, 3.85; N, 9.56; mol wt 731 (^{35}Cl). Found for **4**: C, 39.52; H, 3.85; N, 9.46. MS (EI): *m*/*z* 731 (M^+, ^{35}Cl). Found for **5**: C, 39.33; H 3.85; N 9.57. MS (CI): *m*/*z* 732 (M^++ 1, ^{35}Cl). ^{1}H NMR for **4**: δ 2.6 (d, 6H, CH_3), $^3J_{PH}$ = 16.6; δ 4.03 (complex doublet, CH_2), $^3J_{PH}$ = 14.1; δ_{CH_2} 4.1 (complex doublet, CH_2), $^3J_{PH}$ = 13.8; δ 4.2 (s, C_5H_5); δ 4.3, 4.1 (C_5H_4). ^{1}H NMR for **5**: δ 2.4 (d, 6H, CH_3), $^3J_{PH}$ = 11.7; δ 3.9 (d, 4H, CH_2), $^3J_{PH}$ = 11.2; 4.1, 4.2 (C_5H_4); δ 4.1 (s, C_5H_5). ^{13}C{^{1}H} NMR for **4**: δ 33.3 (CH_3); δ 49.1 (CH_2); δ 69.1−69.3, 70.8, 82.7−82.8 (C_5H_4); δ 69.6 (C_5H_5). ^{13}C{^{1}H} NMR for **5**: δ 32.7 (CH_3); δ 48.6−48.7 (CH_2); δ 68.9, 70.5, 83.8 (C_5H_4); δ 69.2 (C_5H_5). ^{31}P{^{1}H} NMR for **4**: δ 23.7 (cmplx d, P(Fc−amine)Cl), $^2J_{PP}$ = 46.2; δ 21.5 (cmplex t, *P*Cl_2). ^{31}P NMR for **5**: δ 20.5 (d, *P*Cl_2), $^2J_{PP}$ = 41.4; δ 16.2 (t, *P*(Fc−amine)Cl), $^2J_{PP}$ = 41.4. IR for **4**: 1212 cm^{-1} (vs, PN str); 1196 cm^{-1} (vs, PN str). IR for **5**: 1231 cm^{-1} (vs, PN str); 1182 cm^{-1} (vs, PN str). The reaction was repeated under identical conditions in the following solvents: acetonitrile, tetrahydrofuran, and toluene. The relative amounts of each bis(*N*-(ferrocenylmethyl)-*N*-methylamino)cyclophosphazene was determined by ^{31}P NMR spectroscopy.

Preparation of Tris(*N*-(ferrocenylmethyl)-*N*-methylamino)-trichlorophosphazenes, $N_3P_3Cl_3[N(Me)CH_2C_5H_4FeC_5H_5]_3$ (6, 7). The preparation was allowed to proceed as above, except that 3

equiv of **2** and triethylamine/mol of **1** is employed. A round-bottom flask was charged with 0.444 g (1.28 mmol) of **1** dissolved in 50 mL of diethyl ether, to which 0.582 g (5.76 mmol) of triethylamine was added. After several minutes of stirring, 0.880 g (3.84 mmol) of **2** dissolved in 5 mL of diethyl ether was added dropwise through an addition funnel. The product was purified by column chromatography using 55/45 methylene chloride/medium boiling petroleum ether as the eluent. The products in order of elution were traces of **3**−**5**, the nongeminally substituted tris-substituted phosphazene **6** (50 mg, 4% of theory), and the geminally tris-substituted phosphazene **7** (20 mg, 2% of theory). Anal. Calcd: C, 46.72; H, 4.57; N,9.08; mol wt 926. Found for **6**: C, 46.71; H, 4.68; N, 8.41. MS (EI): *m*/*z* 727, (926 − 199, $M^+ - C_{10}H_9FeCH_2$, ^{35}Cl). Found for **7**: C, 45.40; H, 4.53; N, 8.15. MS (EI): *m*/*z* 727, (926 − 199, $M^+ - C_{10}H_9FeCH_2$, ^{35}Cl). ^1H NMR for **6**: δ 2.7 (d, CH_3), $^3J_{PH} = 16.1$; δ 2.8 (d, CH_3), $^3J_{PH} = 15.4$; δ 3.9−4.2 (CH_2); δ 4.2−4.4 (C_5H_4); δ 4.2 (s, C_5H_5). ^1H NMR for **7**: δ 2.4 (d, CH_3), $^3J_{PH} = 11.5$; δ 2.5 (d, CH_3), $^3J_{PH} = 11.7$; δ 2.6 (d, CH_3), $^3J_{PH} = 16.2$. $^{13}C\{^1H\}$ NMR for **6**: δ 33.3, 33.4 (*C*H_3); δ 49.1, 49.3 (*C*H_2); δ 69.1−69.3, 70.9−71.0, 83.4 (C_5H_4); δ 69.6−69.6 (C_5H_5). $^{13}C\{^1H\}$ NMR for **7**: δ 31−33 (*C*H_3); δ 48.2−48.6 (*C*H_2); δ 68.3−68.6, 70.0−70.3, 82.4−83.0 (C_5H_4); δ 68.7−69.0 (C_5H_5). $^{31}P\{^1H\}$ NMR for **6**: δ 25.8−26.0 (cmplex d); δ 26.4−26.8 (cmplex t). ^{31}P NMR for **7**: δ 18.7 (t, *P*(Fc−amine)$_2$), $^2J = 41.0$; δ 21.7 (d of d, *P*Cl$_2$), $^2J = 39.8$, $^2J = 56.5$; δ 25.2 (d of d, *P*Cl(Fc−amine), $^2J = 41.0$, $^2J = 56.5$. IR for **6**: 1204 cm^{-1} (vs, PN str); 888 cm^{-1} (w, PN). IR for **7**: 1224 cm^{-1} (vs, PN str); 1178 cm^{-1} (vs, PN str).

Attempted Preparation of Tetrakis(*N*-(ferrocenylmethyl)-*N*-methylamino)dichlorocyclotriphosphazenes, $N_3P_3Cl_2[N(Me)CH_2C_5H_4FeC_5H_5]_4$. The product of the reaction of 6 molar equiv of **2** with 6 molar equiv of sodium hydride was allowed to react with 1 equiv of **1**. NMR evidence was obtained for formation of some tetrasubstituted product which resisted attempts at purification. Evidence for very small amounts of higher order products was also obtained.

Preparation of (Methacryloylbutenedioxy)pentachlorocyclotriphosphazene, $N_3P_3Cl_5(OC_4H_8OC(O)C(Me)CH_2)$ (8). This preparation is based on a previously reported procedure.[16] A 250 mL round-bottom flask was charged with 11.9 g (3.42 mmol) of **1** and then evacuated and backfilled with N_2. To this flask 125 mL of diethyl ether was added by syringe and cooled to 0 °C. Following the addition of 2.70 g (3.41 mmol) of pyridine, a solution of 5.4 g (3.4 mmol) of 4-hydroxybutyl methacrylate in diethyl ether was introduced dropwise. The solution was allowed to warm to room temperature and allowed to reflux for 48 h. The crude mixture was washed with 50 mL of 0.01 M HCl and two washings of saturated aqueous bicarbonate solution. Purification was achieved with flash chromatography on silica gel with 82/18 low boiling petroleum ether/diethyl ether. Total yield: 7.22 g (45% of theory). Mol wt: 469; found 470 (M +1, MS CI). ^1H NMR: δ 1.8 (complex m, CH_2CH_2); δ 1.9 (s, CH_3); δ 4.1 (t, CH_2OC), $^3J_{HH} = 6$ Hz; δ 4.2 (d of t, POCH_2), $^3J_{PH} = 9$ Hz; δ 5.5 (d of q, CH_2, H trans to CH_3), $^4J_{HH} = 1$ Hz; 6.0 (s, CH_2, H cis to CH$_3$). $^{13}C\{^1H\}$ NMR: δ 19.2 (*C*H_3); δ 26.0, 28.2 (*C*H_2CH_2); δ 65.0 (*C*HOC); δ 70.5 (*C*H_2OP); δ 127.1 (*C*CH$_2$); δ 138.1 (*C*H$_2$); δ 168.0 (C═O). ^{31}P NMR: δ 15.7 (t of t, POCl), $^2J_{PP} = 63$ Hz, $^3J_{PH} = 9$ Hz; δ 23.3 (d, *P*Cl$_2$).

Preparation of (Methacryloxybutenedioxy)(*N*-(ferrocenylmethyl)-*N*-methylamino)tetrachlorocyclotriphosphazene, $N_3P_3Cl_4[O(CH_2)_4OC(Me)CH_2][C_5H_5FeC_5H_4CH_2NMe]$ (9), and (Methacryloylbutenedioxy)bis(*N*-(ferrocenylmethyl)-*N*-methylamino)-trichlorocyclotriphosphazene, $N_3P_3Cl_3[O(CH_2)_4OCMeCH_2][C_5H_5FeC_5H_4CH_2NMe]_2$ (10). A 100 mL round-bottom flask was evacuated and filled with N_2, and a solution of 3.78 g (0.806 mmol) of **8** in 40 mL of diethyl ether was added by syringe into the vessel. Triethylamine (1.46 g, 1.44 mmol) was added, and the solution was cooled to 0 °C. A solution of 3.33 g of **2** (1.45 mmol) in 10 mL of ether was added dropwise, and the flask was allowed to warm to room temperature and then allowed to reflux for 48 h. The crude mixture was washed once with 25 mL of 0.01 M HCl and twice with 25 mL of saturated aqueous bicarbonate solution. The product was purified by flash chromatography with silica gel and a solvent system of 92/8 low boiling petroleum ether/ethyl acetate. Product weights: 3.28 g of **9** (29.7% of theoretical yield) and 1.92 g of **10** (35.3% of theoretical yield). Anal. Calcd for 9: C, 36.28; H, 4.11: N, 8.46. Found: C, 36.54; H, 4.30; N, 8.33. Mol. wt (MS El): 658 (^{35}Cl); found 658. Anal. Calcd for **10**: C, 44.97; H, 4.84; N, 8.19. Found: C, 45.63; H, 5.04; N, 8.05. ^1H NMR for **9**: δ 1.8 (m, CH_2CH_2); δ 1.9 (s, CH_3); δ 2.5 (d, NCH_3), $^3J_{PH} = 12$ Hz; δ 3.9 (m, POCH_2); δ 4.0 (d, NCH_2), $^3J_{PH} = 12$ Hz; δ 4.1 (s, C_5H_5); 4.1 (C_5H_4); δ 4.2−4.3 (C_5H_4, COCH_2); δ 5.5 (cmplex m, CH_2, H trans to CH$_3$); δ 6.1 (s, CH_2). $^{13}C\{^1H\}$ NMR: δ 19.1 (*C*CH$_3$); δ 25.9, 27.4 (*C*H$_2$CH$_2$); 48.7 (*C*H$_3$); 64.7 (*C*H$_2$-OC); 65.8 (d, *C*H$_2$OP); 69.1 (C_5H_5); δ 69−70, 83.0 (C_5H_4); δ 126.2 (alkene *C*H$_2$); δ 137.1 (alkene *C*CH$_3$); δ 168.1 (*C*═O). ^{31}P NMR: δ 12.4 (cmplex multiplet, P(Fc−amine)O); δ 22.2 (d, PCl$_2$), $^2J_{PP} = 50.4$ Hz. ^1H NMR for **10**: δ 1.7 (m, *C*H$_2$*C*H$_2$); δ 1.9 (s, *C*H$_3$); δ 2.5, 2.6 (NCH$_3$), $^3J_{PH} = 11$, 16 Hz; δ 3.7−4.4 (−POCH$_2$, NCH$_2$, C_5H_5, C_5H_4); δ 5.5 (cmplex multiplet, *C*H$_2$, H trans to CH$_3$); δ 6.1 (s, *C*H$_2$).$^{13}C\{^1H\}$ NMR: δ 19.1 (C*C*H$_3$); δ 25.8, 27.3 (*C*H$_2$*C*H$_2$); δ 33.0 (N*C*H$_2$); δ 48.7 (*C*H$_3$); δ 64.7 (*C*H$_2$OC); δ 65.8 (d, *C*H$_2$-OP); δ 69.1 (C_5H_5); δ 69−70, 83.0 (C_5H_4); δ 126.2 (*C*H$_2$); δ 137.1 (*C*CH$_3$); δ 168.1 (*C*═O). ^{31}P NMR: δ 15.3 (m, *P*NO), $^2J = 50$ Hz, $^2J = 46$ Hz; δ 23.1 (d of d, *P*Cl$_2$), $^2J = 56$ Hz; δ 26.7 (m, *P*NCl). IR for **9**: 1720 cm^{-1} (C═O), 1641 cm^{-1} (C═C), 1179, 1232 cm^{-1} (P═N). IR for **10**: 1720 cm^{-1} (C═O), 1640 cm^{-1} (C═C), 1231 cm^{-1} (P═N).

Results and Discussion

Hexachlorocyclotriphosphazene (**1**) was treated with *N*-(ferrocenylmethyl)-*N*-methylamine (**2**) to produce the product (*N*-(ferroocenylmethyl)-*N*-methylamino)pentachlorocyclotriphosphazene (**3**) in good yield. Product **3** is an orange oil which was purified by flash chromatography. It, and all of the other ferrocenylamine derivatives, were characterized by ^1H, ^{13}C, and ^{31}P NMR as well as infrared spectroscopy, mass spectrometry, elemental analysis, and voltammetry. The ^1H NMR spectrum of the *N*-methyl and *N*-methylene peaks showed downfield shifts relative to **2,** and the presence of phosphorus−proton coupling split each peak into a doublet. The ferrocenyl protons were not significantly affected. The ^{31}P NMR was an A_2B second-order spectrum which was simulated to give the reported ^{31}P NMR parameters. The mass spectrum of **3** shows the parent ion and fragment ions arising from cleavage of exocyclic groups from the phosphazene ring. Fragmentation associated with the amine moiety was dominated by the $CpFe^+$ and $CpFeC_5H_4CH_2^+$ ions. The well-known stability of the ferrocenylmethyl carbocation (*m*/*z* 199) accounts for the dominance of this species in the mass spectrum. When **1** is allowed to react with 2 equiv of **2**, three disubstituted compounds are formed, the non-geminal 2,4-bis(*N*-(ferrocenylmethyl)-*N*-methylamino)-

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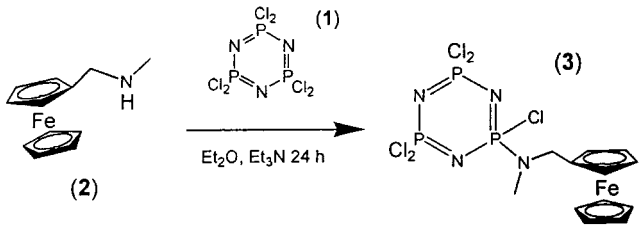

Figure 1. (*N*-(Ferocenylmethyl)-*N*-methylamino)pentachlorocyclotriphosphazene.

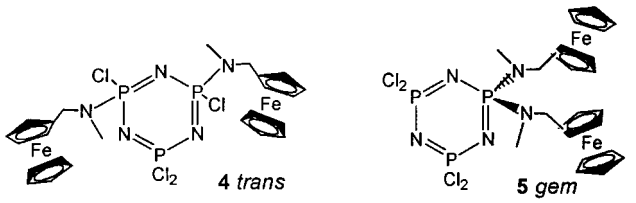

Figure 2. Bis(*N*-(ferrocenylmethyl)-*N*-methylamino)tetrachlorcyclotriphosphazenes.

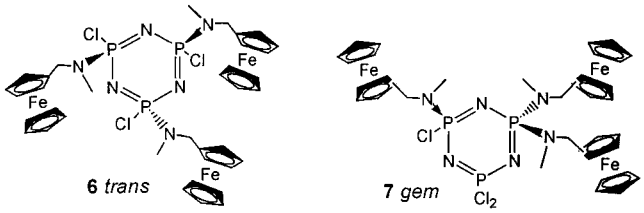

Figure 3. Tris(*N*-(ferrocenylmethyl-*N*-methylamino)trichlorocyclotriphosphazenes.

phosphazenes (**4**) and the 2,2-geminal isomer (**5**)**.** All of these compounds were orange oils. Two non-geminal isomers were obtained in the reaction; the major form of **4** is assigned to the trans isomer, and the minor, the cis isomer. The cis species generally formed in relatively low yields compared to the trans isomer or **5** and could not be separated from **4**. The parent ions are observed in the mass spectra of both **4** and **5**. The ^{31}P NMR spectrum of **4** shows two AB_2 components with the B centers showing coupling to the protons in the (ferrocenylmethyl)amino substituent thus establishing the non-geminal structure. The A ($\equiv PCl_2$) centers of the two non-geminal isomers are clearly resolved in the spectrum. The spectrum of **5** is a first-order AX_2 with proton coupling to the A center thus establishing the geminal structure. The ^{1}H NMR spectra are analogous to those observed for monosubstituted compound **3** in that the chemical shifts of the methyl and methylene peaks are downfield from **2**. Also, the presence of phosphorus−proton coupling split each peak into a doublet. However, the *N*-methyl peak shape differed in the trans and gem isomers. In **5** the peak is a simple doublet with a phosphorus−proton coupling of 16.6 Hz. However, in **4** the doublet contains a smaller rounded peak between the two main peaks which were separated by 11.7 Hz. This virtual coupling phenomenon is typical for non-geminal disubstituted aminophosphazenes.[17] The identification of the trans vs cis components in **4** was based on the ^{1}H NMR shifts of the *N*-methyl peaks in the mixture. It is known that protons in the corresponding dimethylamino derivatives cis isomer are more shielded than the trans and thus have a smaller shift relative to the free amine.[18,19] If this criteria is applied to **4**, the *N*-methyl peaks of the more abundant component can be assigned to the trans isomer. The dominance of the trans isomer in the bis(dimethylamino)tetrachlorocyclotriphosphazenes and in **4** has a common origin in the well-established mechanism of the aminolysis reaction.[1,20]

When **1** was allowed to react with 3 equiv of **2** in the presence of triethylamine, low yields of the trans-2,4,6 (**6**) and 2,2,4-geminal (**7**) trisubstituted isomers were obtained. The mass spectra of **6** and **7** show low-intensity parent ion peaks but are dominated by the ferrocenylmethyl carbocation. Product **7** was identified from the AMX ^{31}P NMR spectrum where one phosphorus resonance was free of proton coupling. Product **6** gives rise to a second-order AB_2 spectrum. In a cis isomer all phosphorus atoms are equivalent given rise to an A_3 system while the trans isomer gives the observed AB_2 spectrum. The dominance of the trans isomer is consistent with the trans preference at the disubstituted stage. The ^{1}H of **6** spectrum showed two sets of doublets for the methyl protons; one doublet had an intensity twice that of the other. The larger doublet was upfield and displayed "virtual coupling". The relative positions of these doublets match the analagous nongeminal *trans*-tris(dimethylamino)trichlorocyclophosphazene.[19] There appeared to be a similar pattern for the methylene protons with two sets of doublets with the "virtual coupling". The ^{1}H spectrum of **7** showed three simple doublets for each set of CH_3 protons.

Given the low yields obtained at the trisubstituted stage, attempts were made at obtaining higher-order substitution by deprotonating the ferrocenylmethamine (**2**) with sodium hydride and allowing a large excess of the resulting ion to react with **1** under reflux conditions. Some of the geminal tetrasubstituted product was formed, as shown by a doublet−triplet pattern in the ^{31}P NMR where the triplet did not show any proton coupling. Some of this product could be partially purified but not sufficiently to be unambiguously identified. The dominance of geminal isomers at the tetrakis stage of substitution is common in a variety of phosphazene aminolysis reactions and is believed to result from a change to a dissociation process in the substitution reaction.[1,21] The mass spectra showed extensive fragmentation and no parent peak. Higher-order products were also seen in the spectra but in such small amounts that they could not be isolated in sufficient amount for analysis. In all of the reactions between **1** and **2**, yields decrease significantly with increased degrees of substitution. This is due to the inherent bulkiness of **2** which inhibits further substitution. The reactions of other large secondary amines such as dibenzylamine[1,22] with **1** have been shown to lead to incomplete substitution.

The nature of the solvent plays a significant role in the observed isomer distribution. The results of these studies for

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(21) Goldschmidt, J. M. E., Licht, E. J. *J. Chem. Soc. A* **1971**, 2429.
(22) Hasan, M.; Shaw, R. A.; Woods, M. *J. Chem. Soc. A* **1970**, 2202.

Table 1. Relative of Amounts of Disubstituted Isomers in Disubstitution Reactions

solvent	ratio trans:cis:gem[a]	solvent	ratio trans:cis:gem[a]
MeCN	1.0:1:0	diethyl ether	5.8:1:1.4
THF	3.7:1:0	toluene	6.2:1:2.3

[a] Determined by ^{31}P NMR integration.

the disubstituted materials are summarized in Table 1 and show significant variations in both the regio- and steroisomer ratios.

The geminal to non-geminal ratio increases with decreased solvent polarity. It is well established that in the case of primary amines, the geminal isomer arises from a dissociative process at a rate independent of solvent.[1] The non-geminal isomers arise from a solvent sensitive associative process with increased rates observed in more polar solvents.[23] Evidence also exists that geminal and non-geminal isomers obtained from secondary amines arise from dissociative and associative pathways, respectively. In the present investigation, the reaction of the sterically demanding *N*-(ferrocenylmethyl)-*N*-methylamine is sufficiently slow that in nonpolar solvents the geminal isomer is competitive with the formation of the non-geminal isomers. Similar results have been observed in the reactions of 2-haloethylamines with **1**.[24] The increase in the rate of the associative process in polar solvents leads to exclusive formation of the non-geminal regioisomers in acetonitrile. The variation in the ratio of the stereoisomers is related to follow-up isomerization reactions. In the reactions of dimethylamine with **1**, the *trans*-2,4-$N_3P_3Cl_4(NMe_2)_2$ isomer is initially formed with the thermodynamically stable cis isomer arising from isomerization.[25] The amounts of *cis*-2,4-$N_3P_3Cl_4[N(CH_3)CH_2C_5H_4FeCp]_2$ isomer increases with solvent polarity. The more polar solvents can act as nucleophiles displacing a chloride ion leading to the isomerization process.

To provide materials to continue our studies of hybrid organic−inorganic polymers with redox active cyclophosphazenes,[11] we investigated the synthesis of mixed substituent cyclophosphazenes containing both **2** and an olefin-containing substituent. To accomplish this, (methacyloylbutenedioxy)pentachlorocyclotriphosphazene, **8**, was allowed to react with 2 equiv of **2**. A mixture of the monosubstituted *N*-(ferrrocenylmethyl)-*N*-methylaminophosphazene, **9**, and the disubstituted *N*-(ferrocenylmethyl)aminophosphazene, **10,** was obtained. Product **9** was a mixture of non-geminal and geminal isomers in a 1:2 ratio. Upon disubstitution the (ferrocenylmethyl)amine preferentially attacked the ≡P(OR)Cl center in the non-geminal isomer of **9** to yield mostly **10** with one ferrocenyl group geminal to the methacryl ligand. Significant amounts of other isomers of **10** were not observed. It is interesting that the ≡P(OR)Cl center is the preferential site of attack by **2**. In the reaction of **1** and **2** carried out in THF (the solvent used in the syntheses of **9** and **10**), a non-geminal pathway is followed exclusively. A non-geminal pathway is also observed in the reactions of alkoxide ions with **1**.[1,26] Therefore, there must be another influence at work in the mixed substituent system. One possibility is that hydrogen bonding between the carbonyl oxygen atom on the ester would place the amine nitrogen closer to the substituted phosphorus center, resulting in the geminal substitution pattern. Alternatively, the carbonyl group may interact with the substituted phosphorus center, enhancing chloride ion displacement. A similar effect has been proposed to account for geminal isomer formation in the reactions of 2-haloethylamines with **1**.[24]

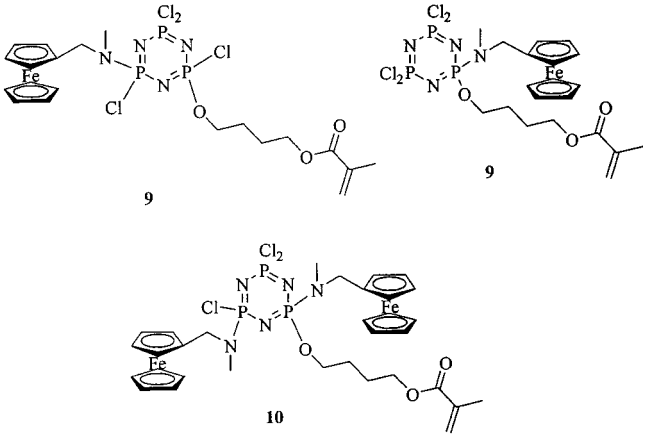

Figure 4. Mixed-substituent cyclophosphazene derivatives.

Table 2. Cyclic Voltammetry Data

compd	$E_{1/2}$ vs Cp_2Fe in mV[a]	ΔE_p at 100 mV/s	$E_{pa} - E_{1/2pa}$
2	54	92	68
3	50	80	52
4	26	100	63
5	23	74	53
6	42	73	56
7	4	82	58
9	24	93	67
10	7	78	56

[a] The $E_{1/2}$ values were calculated with the following formula: $E_{1/2} = (E_{pa} - E_{pc})/2$ and are in millivolts relative to ferrocene.[27]

The series of *N*-(ferrocenylmethyl)-*N*-methylaminocyclophosphazene derivatives (**3**−**7, 9**, and **10**) were characterized by a variety of voltammetric methods to gain an understanding of the electrochemical behavior of ferrocene-modified cyclophosphazenes. Phosphazenes with more than one ferrocene center may undergo either a concurrent oxidation or each ferrocene center may be oxidized successively at different potentials. The voltammetry experiments were conducted to address this question.

A summary of the $E_{1/2}$ values (relative to ferrocene[27]) obtained from the cyclic voltammetry experiments may be found in Table 2. The cyclic voltamogram of compound **3** is shown in Figure 5. In all cyclic voltamograms only one

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(24) Allen, C. W.; MacKay, J. A. *Inorg. Chem.* **1986**, *25*, 4628.
(25) Lingley, D. J.; Shaw, R. A.; Woods, M.; Krishnamurthy, S. S. *Phosphorus Sulfur* **1978**, *4*, 379. Brian, Z.; Goldschmidt, J. M. E. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 185. Lingley, D. J.; Shaw, R. A.; Yu, H. S. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 219.
(26) Sorokin, M. F.; Latou, V. K. *Kinet. Catal.* **1966**, *7*, 35. Schmutz, J. L.; Allcock, H. R. *Inorg. Chem.* **1975**, *14*, 2433.
(27) Connelly, N.; Geiger, W. *Chem. Rev.* **1996**, *96*, 6, 877. Gennett, T.; Milner, D.; Weaver, M. *J. Phys. Chem.* **1985**, *89*, 2787. Decamethylferrocene was used as a standard ($E_{1/2} = -590$ mV relative to ferrocene).

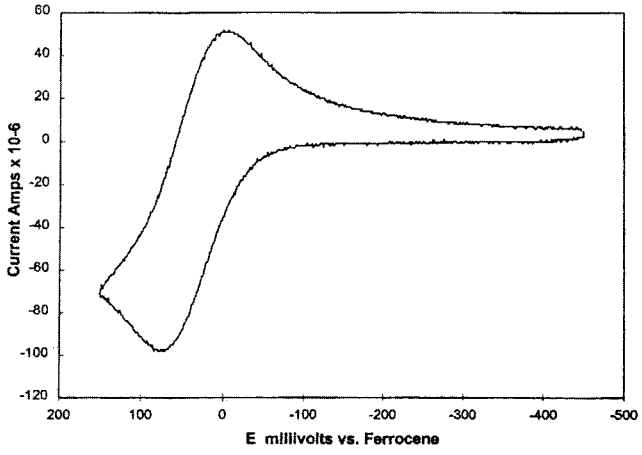

Figure 5. Cyclic voltammogram of **3** in CH_2Cl_2 at 200 mV/s.

oxidation−reduction wave was seen, even in compounds **4**−**7** which contain more than one ferrocene center. This observation suggests that the oxidation of one of the ferrocenyl moieties does not significantly affect the oxidation of other ferrocene units. A complete set of data for selected compounds is presented as Supporting Information. All of the compounds displayed larger peak separations at higher scan rates, which may be due to a relatively slow electron-transfer rate between the oxidized species and the electrode.[28] The ratio of the oxidation and reduction currents (i_{pc}/i_{pa})[29] is close to 1, which indicates the electrochemical reversibility of the electron transfer. All of the products displayed diffusion-controlled behavior as evidenced by the linear relationship between i_{pa} versus the square root of the scan rate ($v^{1/2}$) for all products.

A typical normal pulse voltammogram (Figure 6) shows that decamethyl ferrocene is oxidized at the more negative potential followed by the oxidation of product **7**. The small upward slope on the left of the plot, at a potential positive to the $E_{1/2}$ value, is indicative of some precipitation of the oxidized species on the electrode surface. The limiting current i_d, observed current i, and potential E_{appl} are plotted according to the relationship

$$\log \frac{i_d - i}{i} \text{ vs } E_{appl}$$

for the voltammetric wave. For a reversible oxidation, a line with a slope of $n/59$, where n equals the stoichiometric amount of electrons in each oxidation, is observed. The values summarized in Table 3 are close to the value of $n = 1$ per ferrocene unit expected for these systems, if oxidations of the ferrocene moieties are sequential but at indistinguishable potentials.

The wave height for the oxidation of a molecule is expected to be proportional to its concentration. Table 3 shows the ratio of ferrocene moieties which should approximate the ratio of their respective oxidation wave heights. However, for compounds **5**−**9** this is not so. Some of the current deficit is due to the difficulty of purification of **5**−**7**,

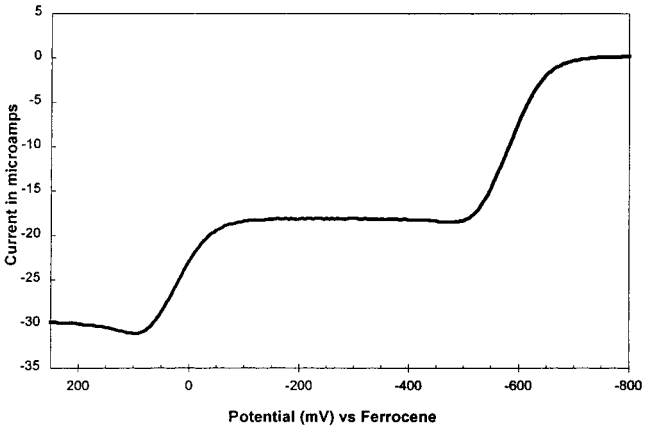

Figure 6. Normal pulse voltammogram of **7** vs decamethylferrocene.

Table 3. Values of *n* from Normal Pulse Voltammetry

compd	n[a]	[Fe][b] concn std	wave ht compared to wave ht std
3	1.04	0.50	0.44
4	0.80	0.97	1.02
5	1.28	0.98	0.50
6	0.97	0.99	0.73
7	1.04	1.0	0.74
9	1.34	0.90	0.48
10	1.14	0.94	0.50

[a] From the slope of the normal pulse voltammetry curve. [b] Concentration of ferrocene in compound

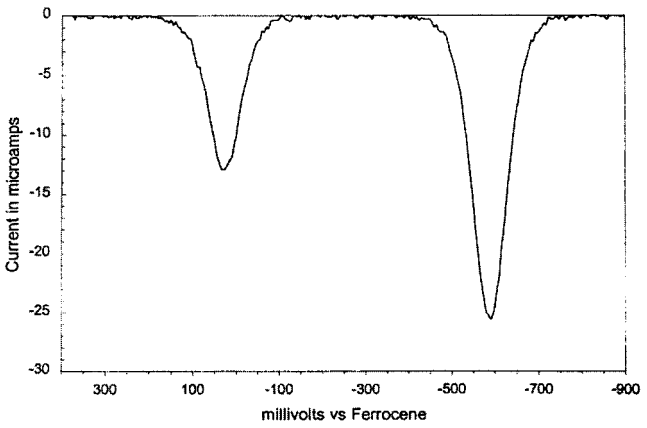

Figure 7. Differential pulse voltammogram (left) of **7** vs decamethylferrocene (right).

which are hydroscopic. Thus, in samples of **6** and **7** adventitious hydration occurred in the preparation of the solutions examined by electrochemistry. Products **5**−**7** behave as if they contain about 15% impurities. An additional source shortfall of current is due to precipitation of the oxidized compound on the electrode surface, which would in effect decrease the electrode surface area and thus the current. In an attempt to overcome this problem, voltammograms of **5** and **7** were obtained using a different supporting electrolyte, tetrakis(perfluorophenyl) borate, which has been shown to increase the solubility of oxidized analytes and prevent electrode precipitation.[30] Some improvement in the normal pulse voltammograms was observed, but the upward turn at the end of the normal pulse voltammogram of **7** remained

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Table 4. Differential Pulse Voltammetry Data for *N*-(Ferrocenylmethyl)-*N*-methyl-Substituted Phosphazenes

compd	$w_{1/2}$ (mV)	concn compared to concn std	wave ht compared to wave ht std
3	83	0.50	0.48
4	119	0.97	1.06
5	88	0.98	0.54
6	95	0.99	0.81
7	90	1.0	0.79
9	123	0.90	0.49
10	94	0.94	0.58

indicating some precipitations still occurred. The oxidation of multiple ferrocenyl centers will give rise to multicharged cations which will have a greater propensity to precipitation.

In differential pulse voltammetry the relationship between the width of the peak at half-height, $w_{1/2}$, and the stoichiometry of the electron-transfer reaction is such that, for $n = 1$ and $T = 298$ K, $w_{1/2} = 90$ mV. The differential pulse voltammogram scan for **7** vs decamethylferrocene is shown in Figure 7.

Products **3, 5**−**7,** and **10**, have $w_{1/2}$ values close to 90 mV (Table 4) suggesting a one-electron process, even in the bis- and trisubstituted phosphazenes. Compounds **4** and **9** have somewhat higher values. This observation indicates that, in higher order substituted phosphazene rings, the ferrocenyl groups are oxidized at nearly equivalent potentials, giving the appearance of one peak.

All of the compounds studied displayed behavior consistent with a one-electron transfer. The cyclic voltammograms showed only one anodic and cathodic peak, and the differential voltammograms had peak widths of about 90 mV. This is evidence that the ferrocenes are electronically isolated from the phosphazene ring. The peak heights for **5**−**7** were lower than expected for reasons outlined in the discussion of the normal pulse voltammetric data. The methacryoylphosphazenes containing ferrocenyl side chains also yielded much lower currents than expected, possibly due to precipitation of the oxidized and/or electropolymerized compound on the electrode surface.

In summary, we have prepared a series of *N*-(ferrocenylmethyl)-*N*-methylamine (**2**) derivatives of **1** and **8**. An unusual sensitivity to solvent effects was noted in the regio- and stereoisomer distribution for the disubstituted derivatives of **1**. The reactions of **2** with **8** show an unexpected and unprecented preference for a geminal substitution pathway. The electrochemical investigations demonstrate that we can successfully design cyclophosphazenes with noninteracting multiple redox centers. This characteristic allows for the use of polyphosphazene derivatives of **2** to be utilized as redox mediators in detection of glucose.[14]

Acknowledgment. The authors wish to thank the Vermont EPSCoR for partial funding of this work. We are also grateful to Dr. William E. Geiger for guidance and generosity in the use of his electrochemical instrumentation.

Supporting Information Available: A table of cyclic voltammetry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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