Dimethylformamide was distilled from KOH and then from BaO and stored over 4-Å molecular sieves prior to use in electrochemical experiments.

NMR spectra were obtained on either a Varian XL-200, a Nicolet NT-360, or a GE GN-500 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR instrument. Electrochemical experiments were performed on a BAS 100 electrochemical analyzer with glassy carbon working and platinum auxiliary electrodes and a Ag/AgCl reference electrode. Electrochemical solutions were approximately 0.1 M in electrolyte and 0.01 M in analyte. Ultraviolet and visible spectra were recorded on a Hewlett Packard Model 8452 diode-array spectrophotometer.

$Ru(O)_2(C_5H_5N)_2(C_3H_4O_2S)$ (3). A solution of **1** (0.055 g, 0.17 mmol) in 25 mL of CH_2Cl_2 was cooled to −78 °C. A solution of 3-mercaptopropionic acid (16 μL, 0.18 mmol) in 10 mL of CH_2Cl_2 was added dropwise to the $Ru(O)_2(OH)_2(C_5H_5N)_2$. The reaction mixture was slowly warmed to room temperature with magnetic stirring. A light green solid precipitated. This solid was collected by filtration, redissolved in pyridine, and precipitated with diethyl ether. The residue was dried under vacuum to give 0.040 g (60%) of the solvated product $Ru(O)_2(C_5H_5N)_2(C_3H_4O_2S)\cdot 0.25C_5H_5N$. IR (KBr pellet, cm^{-1}): 802 (RuO_2), 1657 (CO). ^1H NMR (CD_3CN, 360 MHz, 18 °C): δ 7.1–9.0 (m, 12.5 H, C_5H_5N), 2.88 (t, J = 7.0 Hz, 2 H, CH_2), 2.66 (t, J = 7.0 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 90 MHz, 35 °C): δ 172.6 (CO), 149.5 (py), 136.0 (py), 123.8 (py), 33.9 (CH_2), 33.3 (CH_2). UV–vis (DMF, 0.0014 M in analyte, nm): λ 266 (ε = 5333), 308 (4180), 420 (2600), 580 (2220), 636 (3390). Anal. Calcd for $RuC_{13}H_{14}N_2O_4S\cdot 0.25C_5H_5N$: C, 41.23; H, 3.70; N, 7.59. Found: C, 41.41; H, 3.94; N, 7.52.

$Ru(O)_2(C_5H_4N)_2(C_4H_5NO_3S)$ (4). The compound was synthesized according to the method used for **3** in 69% yield from **2** and *N*-formyl-L-cysteine. The methylene chloride solvate $Ru(O)_2(C_5H_5N)_2(C_4H_5NO_3S)\cdot CH_2Cl_2$ was obtained. IR (KBr pellet, cm^{-1}): 835 (RuO_2), 1600 (CO), 1650 (C=O), 3360 (NH). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 18.4 °C): δ 8.10 (s, 1 H, *H*CO), 7.6–9.4 (m, 8 H, bpy), 5.60 (s, 2 H, CH_2Cl_2), 3.15 (dd, J = 4.4, 13.7 Hz, 1 H, CH_2), 2.95 (dd, J = 8.8 Hz, 13.7 Hz, 1 H, CH_2), 4.57 (m, 1 H, C*H*). Anal. Calcd for $RuC_{14}H_{13}N_3O_5S\cdot CH_2Cl_2$: C, 34.56; H, 2.90; N, 8.06; Cl, 13.6. Found: C, 34.76; H, 3.14; N, 8.03; Cl, 13.53.

$Ru(O)_2(C_5H_5N)_2(C_5H_7NO_3S)$ (5). In a typical procedure, a solution of *N*-acetylcysteine (0.027 g, 0.16 mmol) in 5 mL of DMF was added dropwise over a period of 15–20 min to a solution of **1** (0.052 g, 0.16 mmol) in 35 mL of DMF and 5 mL of CH_2Cl_2. The reaction mixture was allowed to stir for an additional 1 h at room temperature. A dark green solid was precipitated by the addition of diethyl ether and was filtered out and dried under vacuum to give the product as a CH_2Cl_2/DMF solvate $Ru(O)_2(C_5H_5N)_2(C_5H_7NO_3S)\cdot CH_2Cl_2\cdot 2DMF$ in 70% yield. IR (KBr pellet, cm^{-1}): 3272 (NH), 1655 (CO), 1602 (CO), 800 (RuO_2). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 30 °C): δ 8.25 (d, J = 7.7 Hz, 2 H, py), 7.90 (s, 2.5 H, C*H*O), 7.76 (t, J = 7.7 Hz, 2 H, py), 7.37 (t, J = 6 Hz, 2 H, py), 5.65 (s, 2 H, CH_2Cl_2), 4.45 (m, J = 4.3 Hz, 1 H, C*H*), 3.14 (dd, J = 4.6 Hz, 13.7 Hz, 1 H, CH_2), 2.87 (dd, J = 9.0 Hz, 13.5 Hz, 1 H, CH_2), 2.80 (s, 7.5 H, NCH_3), 2.65 (s, 7.5 H, NCH_3), 1.83 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125.7 MHz, 30 °C): δ 171.9 (CO), 169.2 (CO), 149.4 (py), 136.0 (py), 123.7 (py), 57.0 (CH_2Cl_2), 51.7 (CH), 22.2 (CH_3). UV–vis (DMSO, 0.001 72 M in analyte, nm): λ 266 (ε 710), 336 (488), 388 (686), 658 (405). FABMS: m/z 453, $(M + H)^+$. Anal. Calcd for $RuC_{15}H_{17}N_3O_5S\cdot CH_2Cl_2\cdot 2DMF$: C, 38.66; H, 4.87; N, 10.25; Cl, 10.37. Found: C, 38.30; H, 4.63; N, 10.55; Cl, 10.53.

$Ru(O)_2(C_5H_4N)_2(C_5H_7NO_3S)$ (6). This compound was synthesized according to the method used for **5** from **2** and *N*-acetyl-L-cysteine. The product was isolated in 87% yield as the methylene chloride solvate $Ru(O)_2(C_5H_4N)_2(C_5H_7NO_3S)\cdot CH_2Cl_2$. IR (KBr pellet, cm^{-1}): 3267 (NH), 1666 (CO), 1600 (CO), 833 (RuO_2). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 18.0 °C): δ 9.40 (d, 2 H, bpy), 8.50 (t, 2 H, bpy), 8.10 (d, 2 H, bpy), 7.60 (t, 2 H, bpy), 5.60 (s, 2.2 H, CH_2Cl_2), 4.48 (m, 1 H, C*H*), 3.11 (dd, J = 4.6 Hz, 14 Hz, 1 H, CH_2), 2.90 (dd, J = 9.0 Hz, 14 Hz, 1 H, CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125.7 MHz, 30 °C): δ 172 (CO), 170 (CO), 159.8, 154.2, 137.3, 126.8, 123.4 (bpy), 57.0 (CH_2Cl_2), 52.0 (CH), 22.0 (CH_3). UV–vis (DMSO, 0.001 23 M in analyte, nm): λ 249 (ε 3090), 412 (1170), 586 (245), 666 (1.40). FABMS: m/z 451, $(M + H)^+$. Anal. Calcd for $Ru(C_{15}H_{15}N_3O_5S)\cdot CH_2Cl_2$: C, 35.56; H, 3.19; N, 7.73; Cl, 14.34. Found: C, 35.68; H, 3.22; N, 7.91; Cl, 14.33.

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Preparation of Novel Low-Coordinate Chloro and Azido P–N Compounds. Attempted Synthesis of Cyclodiphosphazenes

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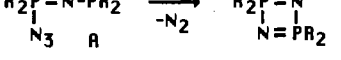
Introduction

Polyphosphazene chemistry is one of the most highly developed areas of phosphorus chemistry due to the large range of physical and chemical properties and to the wide industrial applications of these inorganic polymers. Various processes lead to the formation of such polymers, including, for example, the polymerization of cyclotriphosphazenes,[1] addition of phosphorus pentachloride to ammonium chloride,[2] polycondensation of *N*-(dichlorophosphoranyl)-*P*,*P*,*P*-trichloro-1λ⁵-phosphazene,[3] and polycondensation of monomeric species such as $Me_3SiN{=}P(R_2)OCH_2CF_3$.[4] We have shown[5] that the photolysis of phosphane azides led to transient phosphonitriles (R_2PN), which are in fact the monomeric units of polyphosphazenes. Depending on the nature of the phosphorus substituents, the phosphonitriles may trimerize, oligomerize, and/or polymerize.[5d] In only one case have we been able to isolate and fully characterize a dimer, namely, the tetrakis(diisopropylamino)cyclodiphosphazene **1** (Scheme I).[5b,c] Since that report, only one other synthesis of **1** has been published.[6] It also involves the dimerization of a phosphinonitrene, but the precursor, the nitrilimine **2**, is not readily available, making this new route of no synthetic utility (Scheme I). All attempts to prepare other isolable dimers failed.[5d,7]

Although several hundred cyclotri-, cyclotetra-, and cyclopolyphosphazenes are known,[8] **1** is, surprisingly, the only example of a cyclodiphosphazene reported so far. This type of four-membered ring is of great importance, since it may shed new light on the question of equilibria among monomers, rings, and chains in phosphazenes. Such equilibria could be important in understanding the formation of commercial phosphazene resins. The development of the chemistry of cyclodiphosphazenes has been hindered by the lack of large-scale multigram syntheses of these compounds. Here we report our attempts to prepare new cyclodiphosphazenes via an intramolecular Staudinger reaction, starting from derivatives of type A.



Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC80 or a Varian EM 360V spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer at 32.43 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 983 G spectrophotometer using a polystyrene film for calibration. Mass spectra were obtained on a Nermag R10-10H instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor.

Synthesis of [(Dichlorophosphanyl)imino]chlorobis(diisopropylamino)phosphorane (5). To a solution of 10 g (28.3 mmol) of [(trimethylsilyl)imino]chlorophosphorane **3** in dichloromethane (30 mL), maintained at −70 °C, was added dropwise a solution of 3.9 g (28.4

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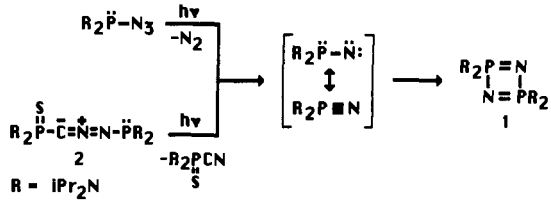
Scheme I



mmol) of trichlorophosphane in 5 mL of dichloromethane. The mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was washed with 5 mL of acetonitrile at 0 °C. Filtration and drying under vacuum afforded **5** (9.4 g, 87% yield) as a white powder. Mp: 42–43 °C. ^{31}P NMR (C_6D_6): 172.6 (d), 7.1 (d), J_{PP} = 38.7 Hz. ^1H NMR (C_6D_6): 1.07 (d, J_{HH} = 7.0 Hz, 12 H, CH_3), 1.16 (d, J_{HH} = 7.0 Hz, 12 H, CH_3), 3.37 (m, 4 H, CH). Anal. Calcd for $C_{12}H_{28}Cl_3N_3P_2$: C, 37.65; H, 7.32; N, 10.98. Found: C, 37.70; H, 7.28; N, 10.96.

Synthesis of [[(Diisopropylamino)phosphanyl]imino]chlorobis(diisopropylamino)phosphorane (6). An ethereal solution (30 mL) of lithium diisopropylamide (1.12 g, 10.48 mmol) was added dropwise, at −70 °C, to an ethereal solution (20 mL) of **5** (2 g, 5.23 mmol). The deep orange mixture obtained was stirred at room temperature for 2 h. After filtration and evaporation of the solvent, the residue was dissolved in 5 mL of dichloromethane. A precipitate was obtained by addition of acetonitrile. After filtration, two additional washings at 0 °C with 10 mL of acetonitrile, and drying under vacuum, 0.74 (35 % yield) of **6** was isolated as a white slightly deliquescent solid at room temperature. ^{31}P NMR (CD_2Cl_2): 41.4 (dd, J_{PH} = 217.7 Hz, J_{PP} = 117.7 Hz), 1.9 (d, J_{PP} = 117.7 Hz). ^1H NMR (CD_2Cl_2): 1.24 (m, 36 H, CH_3), 3.49 (m, 6 H, CH), 6.65 (dd, J_{PH} = 217.7 and 34.7 Hz, 1 H, PH). ^{13}C NMR (CD_2Cl_2): 22.16–24.24 (m, CH_3), 47.29 and 47.35 (d, J_{PC} = 5.3 Hz, CH), 50.43 (d, J_{PC} = 10.6 Hz, CH). Mass spectrum: *m/e* 412 (M^+), 369 (M^+ − iPr), 312 (M^+ − $NiPr_2$).

Synthesis of [[(Diisopropylamino)chlorophosphanyl]imino]chlorobis(diisopropylamino)phosphorane (7). To a solution of 3.82 g (10 mmol) of [(dichlorophosphanyl)imino]chlorobis(diisopropylamino)phosphorane (**5**) in toluene (15 mL), maintained at −30 °C, was added dropwise 2.02 g (20 mmol) of diisopropylamine. The resulting mixture was allowed to warm to room temperature and was then stirred for 2 h. The mixture was filtered through Celite and the solvent removed under vacuum. The residue was washed with acetonitrile (5 mL) and then twice with pentane (5 mL). The product was then dried under vacuum, affording **7** as a white powder (3.49 g, 78% yield). Mp: 108 °C. ^{31}P NMR (C_6D_6): 11.8 (d), 162.7 (d), J_{PP} = 161.8 Hz. ^1H NMR (C_6D_6): 1.15–1.35 (m, 36 H, CH_3), 3.50 (m, 6 H, CH). ^{13}C NMR (C_6D_6): 21.70–22.84 (m, CH_3C), 47.42 (d, J_{PC} = 5.2 Hz, CH), 47.75 (d, J_{PC} = 4.9 Hz, CH). Anal. Calcd for $C_{18}H_{42}Cl_2N_4P_2$: C, 48.32; H, 9.40; N, 12.52. Found: C, 48.12; H, 9.36; N, 12.68.

Synthesis of [[Bis[bis(trimethylsilyl)amino]phosphanyl]imino]chlorobis(diisopropylamino)phosphorane (8). To an ether solution (6 mL) of 0.44 g (2.62 mmol) of the lithium salt of bis(trimethylsilyl)amine at −70 °C was added dropwise 0.501 g (1.31 mmol) of **5**. The mixture was stirred for 2 h at room temperature. According to ^{31}P NMR spectroscopy, a mixture of **8** (90%) and **9** (10%) was obtained. The minor compound, **9**, was characterized by NMR with comparison an authentic sample.[9] After filtration and evaporation of the solvent, the residue was washed three times with acetonitrile at −30 °C and **8** (0.496 g, 60% yield) was obtained as a white powder, only stable at low temperature (−30 °C). ^{31}P NMR (C_6D_6): 20.0 (d), 120.9 (d), J_{PP} = 171.6 Hz. ^1H NMR (C_6D_6): 0.54 (d, J_{PH} = 1.4 Hz, 36 H, $SiCH_3$), 1.21 (d, J_{HH} = 6.2 Hz, 12 H, CH_3), 1.29 (d, J_{HH} = 6.2 Hz, 12 H, CH_3), 3.90 (m, 4 H, CH). Mass spectrum: *m/e* 631 (M^+), 588 (M^+ − iPr), 523 (M^+ − Me_3SiCl).

Synthesis of [(Diphenylphosphanyl)imino]chlorobis(diisopropylamino)phosphorane (10). A solution of phenyllithium (10.46 mmol) in ether (20 mL) was added dropwise to an ether solution (30 mL) of **5** (2 g, 5.23 mmol) maintained at −70 °C. The resulting mixture was stirred at room temperature for 2 h. After filtration and removal of the solvent under reduced pressure, the residue was washed twice with 10 mL of acetonitrile and **10** (2.02 g, 83% yield) was obtained as a white powder. ^{31}P NMR ($CDCl_3$): 18.7 (d), 42.3 (d), J_{PP} = 147.7 Hz. ^1H NMR ($CDCl_3$): 1.09 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.12 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 3.51 (m, 4 H, CH), 7.30 (m, 10 H, C_6H_5). ^{13}C NMR ($CDCl_3$): 24.00–25.09 (m, CH_3CH), 49.6 (d, J_{PC} = 8.11 Hz, $CHCH_3$), 129.67 (s, *p*-C), 129.88 (d, J_{PC} = 5.24 Hz, *m*-C), 131.93 (d, J_{PC} = 13.5 Hz, PC), 133.28 (d, J_{PC} = 22.57, *o*-C). Anal. Calcd for $C_{24}H_{38}ClN_3P_2$: C, 61.87; H, 8.16; N, 9.02. Found: C, 61.98; H, 8.09; N, 8.94.

Synthesis of [(Dichlorophosphanyl)imino]azidobis(diisopropylamino)-phosphorane (12). To a solution of 1.08 g (2.99 mmol) of [(trimethylsilyl)imino]azidobis(diisopropylamino)phosphorane **11**[5a,c] in 8 mL of dichloromethane, maintained at −70 °C, was added dropwise 0.410 g (2.99 mmol) of trichlorophosphine. The mixture was stirred at room temperature for 2 h. After evaporation of the solvent and of the trimethylsilyl chloride, the residue was washed with 3 mL of acetonitrile at 0 °C and **12** (0.683 g, 59% yield) was obtained as a white powder. ^{31}P NMR (C_6D_6): 3.9 (d), 165.2 (d), J_{PP} = 21.0 Hz. ^1H NMR ($CDCl_3$): 1.23 (d, J_{HH} = 7.0 Hz, 12 H, CH_3), 1.30 (d, J_{HH} = 7.0 Hz, 12 H, CH_3), 3.50 (m, 4 H, CH). IR (KBr): 2150 cm^{-1} (N_3). Mass spectrum: *m/e* 388 (M^+), 353 (M^+ − Cl). Anal. Calcd for $C_{12}H_{28}Cl_2N_6P_2$: C, 37.02; H, 7.19; N, 21.59. Found: C, 36.72; H, 7.04; N, 21.68.

Synthesis of [[(Diisopropylamino)chlorophosphanyl]imino]azidobis(diisopropylamino)phosphorane (16). Diisopropylamine, 0.698 g (6.9 mmol), was added dropwise to a toluene (15 mL) solution of [(dichlorophosphanyl)imino]azidobis(diisopropylamino)phosphorane (**12**), 1.345 g (3.45 mmol), maintained at −30 °C. The resulting mixture was allowed to warm to room temperature and was then stirred for 2 h. After filtration on Celite and evaporation of the solvent, the residue was washed twice with pentane (2 mL), and **16** (1.36 g, 87% yield) was obtained as a white powder. Mp: 76 °C. ^{31}P NMR (C_6D_6): 11.1 (d), 175.5 (d), J_{PP} = 139.2 Hz. ^1H NMR (C_6D_6): 1.08–1.27 (m, 36 H, CH_3), 3.35 (m, 6 H, CH). IR (KBr): 2149 cm^{-1} (P–N_3). Anal. Calcd for $C_{18}H_{42}ClN_7P_2$: C, 47.63; H, 9.26; N, 21.61. Found: C, 47.54; H, 9.20; N, 21.78.

Synthesis of [[(Dimethylamino)chlorophosphanyl]imino]azidobis(diisopropylamino)phosphorane (17). (Dimethylamino)dichlorophosphane, 0.153 g (1.05 mmol), was added dropwise to a solution of [(trimethylsilyl)imino]azidobis(diisopropylamino)phosphorane, 0.378 g (1.05 mmol), in dichloromethane (8 mL) at −70 °C. The resulting mixture was stirred for 2 h at room temperature. After evaporation of the solvent and trimethylchlorosilane, 0.393 g (94% yield) of **17** was obtained as a slightly yellow viscous liquid. ^{31}P NMR (C_6D_6): 11.8 (d), 181.8 (d), J_{PP} = 116.7 Hz. ^1H NMR (CD_2Cl_2): 1.20 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 1.27 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 2.57 (d, 13.0 Hz, 6 H, CH_3N), 3.50 (m, 4 H, CH). IR (CH_2Cl_2): 2151 cm^{-1} (P–N_3). Anal. Calcd for $C_{14}H_{34}ClN_7P_2$: C, 42.26; H, 8.55; N, 24.65. Found: C, 42.30; H, 8.35; N, 24.50.

Synthesis of the [[(Dialkylamino)phosphonio]imino]azidobis(diisopropylamino)phosphoranyl Trifluoromethanesulfonates (19, 20). To a solution of [[(dialkylamino)chlorophosphanyl]imino]azidobis(diisopropylamino)phosphorane **16** or **17** (1.73 mmol) in dichloromethane (7 mL), maintained at −70 °C, was added dropwise 1.80 mmol of trimethylsilyl trifluoromethanesulfonate. The resulting mixture was allowed to warm to room temperature and was then stirred for 2 h. After evaporation of the solvent and trimethylchlorosilane, phosphenium salts **19** and **20** were obtained as slightly yellow oils. **19**: ^{31}P NMR (C_6D_6) 22.9 (d), 309.5 (d), J_{PP} = 87.2 Hz; ^1H NMR (CD_2Cl_2) 1.13–1.30 (m, 36 H, CH_3), 3.45 (m, 6 H, CH). **20**: ^{31}P NMR (C_6D_6) 20.53 (d), 294.29 (d), J_{PP} = 80.5 Hz. ^1H NMR (CD_2Cl_2) 1.25 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 1.32 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 2.65 (d, 13.0 Hz, 6 H, CH_3N), 3.55 (m, 4 H, CH).

Heating of [[(Diisopropylamino)chlorophosphanyl]imino]azidobis(diisopropylamino)phosphorane (16). A 1.610-g sample (3.55 mmol) of azidophosphorane **16** in 30 mL of toluene was heated at 110 °C with stirring for 3 h. It could be seen from the ^{31}P NMR spectrum that the

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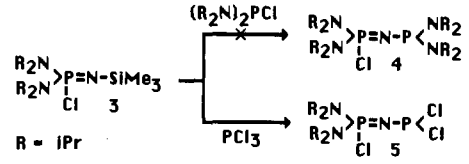
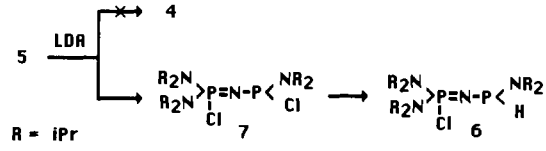
Scheme II



Scheme III



main products were polymeric (~80%) whereas cyclodiphosphazene **18** was formed in a yield of only 20%. After removal of the solvent in vacuo, the residue no longer exhibited the characteristic infrared absorption band of the azido group (P–N_3). All attempts to isolate **18** in pure form were unsuccessful. ^{31}P NMR (C_6D_6): 52.2 (d), 41.6 (d), J_{PP} = 71.8 Hz; complex multiplet centered at 0 ppm.

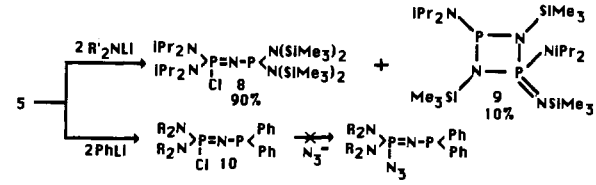
Results and Discussion

The first problem in our strategy was to synthesize the starting phosphane–iminophosphorane azides of type A. We first tried to prepare the corresponding chloride by treatment of chloroiminophosphorane **3** with the bis(diisopropylamino)chlorophosphane in order to obtain a precursor **4** of the known cyclodiphosphazene **1**. Even on heating, however, no reaction was observed, and in fact, **3** does not appear to react with monochlorophosphanes. In contrast, a dichloromethane solution of **3** did react with trichlorophosphane, affording the desired phosphane–iminophosphorane complex **5**, in nearly quantitative yield (Scheme II). Since lithium diisopropyl amide is known to substitute chlorophosphane, we attempted the reaction of **5** with LDA. We did not obtain the totally substituted product **4** but a novel phosphane **6**. The ^{31}P NMR spectrum of **6** gave a signal in the form of a doublet of doublets at 41.4 ppm (λ^3-P, J_{PH} = 217.7 Hz, J_{PP} = 117.7 Hz) and a doublet at 1.9 ppm (λ^5-P, J_{PP} = 117.7 Hz). The proposed structure was confirmed by ^1H and ^{13}C NMR as well as mass spectroscopy. To rationalize the formation of **6**, it seems reasonable to postulate that a chlorine substitution first occurred, giving **7**, followed by a lithium–chlorine exchange and subsequent hydrolysis, giving **6** (Scheme III). In order to provide further evidence for the proposed mechanism, we first prepared **7** by addition of 2 molar equiv of diisopropylamine to **5**. The monoamino-substituted product **7** was then characterized by ^{13}C, ^1H, and ^{31}P NMR spectroscopy together with elemental analysis. The addition of LDA to **7** in ether at −78 °C was monitored by ^{31}P NMR spectroscopy, and two signals which are believed to correspond to the lithio derivative (73.15 (d), 8.17 (d), J_{PP} = 134.6 Hz) were observed. However, this extremely water-sensitive compound was seen to rapidly transform, giving **6**.

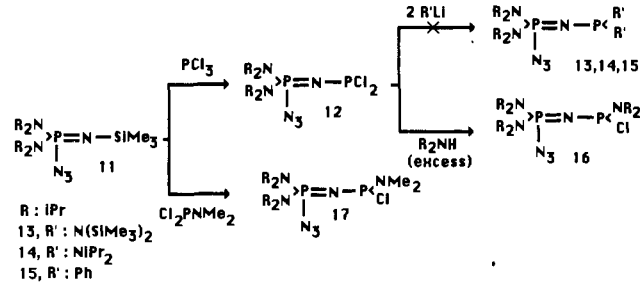
In contrast, treatment of **5** with lithium bis(trimethylsilyl)amide led to the expected substituted derivative **8**, as the major product (90%), along with a small amount (10%) of diazadiphosphetidine **9**. Formation of the four-membered ring **9**, already obtained in the reaction of bis(diisopropylamino)phosphonitrile with [bis(trimethylsilyl)amino][(trimethylsilyl)imino]phosphane, probably involves a multistep mechanism.[9] When 2 equiv of phenyllithium was added to **5**, a straightforward reaction occurred, leading to the substituted phosphane–iminophosphorane complex **10**, isolated in 83% yield. Unfortunately, we were not able to substitute the chlorine atom of **8** or **10** with an azido group. Steric hindrance due to the diisopropylamino groups is probably responsible for the lack of reactivity of these compounds (Scheme IV).

Therefore, the synthetic pathway to the target molecule $R_2P(N_3)$=NPR′$_2$ from $R_2P(Cl)$=$NPCl_2$ implies the following contradiction: the steric hindrance of the substituents R must be sufficient enough to prevent the substitution reaction with the lithium salt at the tetracoordinated phosphorus, but must also be weak enough to allow the chlorine–azide exchange reaction.

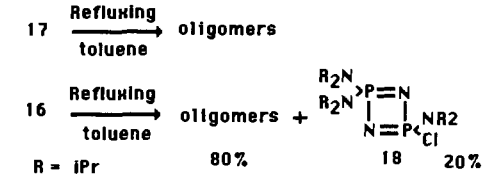
Scheme IV



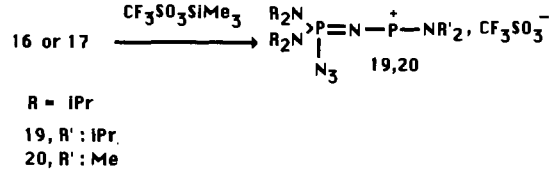
Scheme V



Scheme VI



Scheme VII



Taking into account all these observations, a second approach was developed whereby we tried to prepare the desired precursor of type A starting from (trimethylsilylimino)azidophosphorane **11**.[5a,c] Elimination of chlorotrimethylsilane was easily effected by the addition of trichlorophosphane to **11**. The azido derivative **12** was obtained as a stable white powder which exhibited a characteristic infrared absorption at 2150 cm^{-1}. Apparently, formation of the disubstituted species **13–15** did not take place when 2 equiv of R′Li (R = $N(iPr)_2$, $N(SiMe_3)_2$, Ph) was added to **12**. On the other hand, addition of 4 equiv of diisopropylamine led to the monosubstituted compound **16**. A similar compound **17** was prepared by reacting azidophosphorane **11** with (dimethylamino)dichlorophosphane (Scheme V).

Only oligomeric material was obtained when a toluene solution of **17** was refluxed (^{31}P NMR: very broad signal centered at 0 ppm, fwhh = 800 Hz). There was no evidence for the formation of a cyclodiphosphazene arising from the expected intramolecular Staudinger reaction. Analogous oligomeric species were also obtained, under the same experimental conditions, from **16**. However, in this case a minor compound (20% yield according to ^{31}P NMR: +52.3 (d), +41.6 (d), J_{PP} = 71.8 Hz) was tentatively assigned to cyclodiphosphazene **18**. Indeed, the high-field signal of **18** appeared in the same range as the ^{31}P chemical shift of cyclodiphosphazene **1** (+40 ppm). As far as the low-field signal is concerned, a deshielding of 10 ppm is usual when an amino group is replaced by a chlorine atom, and the value of the phosphorus–phosphorus coupling constant is as would be expected. All attempts to isolate **18** in pure form failed (Scheme VI).

It has been shown that a Staudinger reaction can also occur with dicoordinated phosphonium salts,[10] but in contrast to phosphane reactions, this reaction is supposed to involve the nu-

(10) Marre, M. R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur* **1982**, *13*, 327.

cleophilicity of the azide.[11] Thus, we prepared the iminophosphorane–phosphenium salts **19** and **20**[12] by treatment of **16** and **17** with trimethylsilyl trifluoromethanesulfonate. **19** and **20** exhibited characteristic ^{31}P NMR chemical shifts for cationic dicoordinated phosphorus species. **19**: 22.95 (d), 309.51 (d), J_{PP} = 87.2 Hz. **20**: 20.53 (d), 294.30 (d), J_{PP} = 80.5 Hz (Scheme VII). Thermolysis and UV photolysis of **19** and **20** led to oligomers featuring broad ^{31}P NMR signals at around 0 ppm.

In conclusion, it appears that intermolecular Staudinger reactions are favored compared to intramolecular ones. The only evidence for the formation of cyclodiphosphazene has been obtained with the bulky diisopropylamino groups on both phosphorus atoms. It is reasonable to think that such bulky substituents slow down the intramolecular process and thus allow the intramolecular reaction. These observations suggest that the use of small substituents at both phosphorus atoms could make the (phosphanylimino)azidophosphoranes interesting monomers for synthesis of polyphosphazenes. These results once more emphasize the difficulty of synthesizing cyclodiphosphazenes. The large-scale preparation of such compounds remains a challenge.

Registry No. **3**, 90670-65-8; **5**, 135665-16-6; **6**, 135665-17-7; **7**, 135665-18-8; **8**, 135665-19-9; **9**, 117874-63-2; **10**, 135665-20-2; **11**, 96455-38-8; **12**, 135665-21-3; **16**, 135665-22-4; **17**, 135665-23-5; **18**, 135695-47-5; **19**, 135665-25-7; **20**, 135665-27-9; trichlorophosphine, 7719-12-2; (dimethylamino)dichlorophosphane, 683-85-2.

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A Mononuclear Zinc Hydroxide Complex Stabilized by a Highly Substituted Tris(pyrazolyl)hydroborato Ligand: Analogies with the Enzyme Carbonic Anhydrase

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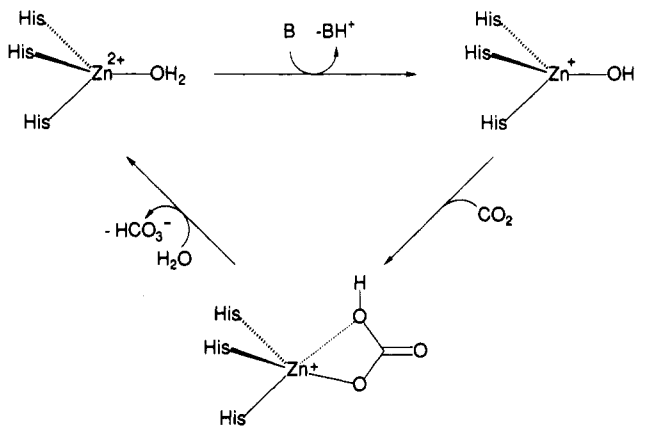
The enzyme carbonic anhydrase has a remarkably simple function, namely to catalyze the hydration of CO_2 to bicarbonate (eq 1). The catalytic site consists of a deceptively simple tetrahedral coordination environment in which a zinc center is bound to three histidine imidazole groups and a water molecule, $[His_3Zn–OH_2]^{2+}$ (His = histidine), and the initial stages of the catalytic cycle are considered to involve initial deprotonation of the coordinated water to give the active zinc hydroxide derivative $[His_3Zn–OH]^+$, followed by reaction with CO_2 to give a zinc bicarbonate derivative $[His_3Zn–OCO_2H]^+$ (Scheme I).[1] However, attempts to mimic structurally the zinc coordination environment in carbonic anhydrase by the synthesis of simple model compounds have met with only limited success,[2] while investigations to model the enzyme's function using other zinc complexes have generally been confined to ester hydrolysis studies.[3] At present there is no report of a fully characterized mononuclear tetrahedral $L_3Zn–OH$ complex, in spite of the facts that (i) basic salts are a common feature of the inorganic chemistry of zinc[4] and (ii) several hydroxide-bridged oligonuclear zinc complexes are known.[3d,5]

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad (1)$$

Scheme I. Simplified Catalytic Cycle for Hydration of CO_2



For studies designed to model structurally the active site of carbonic anhydrase, the tris(pyrazolyl)hydroborato ligand system, $\{HB(3,5\text{-}RR'pz)_3\}^-$ (RR'pz = substituted pyrazole), would appear to be an almost ideal choice for several reasons: (i) the three nitrogen atom donors of the $\{HB(3,5\text{-}RR'pz)_3\}^-$ ligand have the ability to bind to the zinc center in a manner analogous to that proposed for carbonic anhydrase, (ii) the sterically demanding tris(pyrazolyl)hydroborato derivatives, e.g. $\{HB(3\text{-}Bu^tpz)_3\}^-$, effectively restrict the maximum coordination of zinc to 4, and (iii) the uninegative nature of $\{HB(3,5\text{-}RR'pz)_3\}^-$ indicates that the tetrahedral hydroxide derivative $\{\eta^3\text{-}HB(3,5\text{-}RR'pz)_3\}ZnOH$ would be a neutral complex, which would thereby greatly simplify isolation procedures.[6] Indeed, our previous independent investigations of [tris(pyrazolyl)hydroborato]zinc chemistry have illustrated the validity of the aforementioned points,[5d,e,6c,d,7] and this paper reports the first result of our joint effort to synthesize and characterize a complex designed to model structurally the active site of the enzyme carbonic anhydrase.

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