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Polyfluoroalkanediyl Bis(phosphates), 5,5,6,6-Tetrafluoro-2-hydroxy-1,3,2-dioxaphosphepane 2-Oxide, and Their Precursors

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Tetrabasic 2,2,3,3-tetrafluoro-1,4-butanediyl bis(phosphate) and 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediyl bis(phosphate), $(HO)_2P(O)OCH_2(CF_2)_nCH_2OP(O)(OH)_2$ (n = 2, 4), and monobasic 5,5,6,6-tetrafluoro-2-hydroxy-1,3,2-dioxaphosphepane 2-oxide, $HO\overline{P(O)OCH_2CF_2CF_2CH_2O}$, were prepared by controlled hydrolysis of the appropriate bis(phosphorodichloridates) and 2-chloro-5,5,6,6-tetrafluoro-1,3,2-dioxaphosphepane 2-oxide, i.e., $Cl_2P(O)OCH_2(CF_2)_nCH_2OP(O)Cl_2$ (n = 2, 4) and $Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}$. The last two compounds were obtained by the dinitrogen tetraoxide oxidation of $Cl_2POCH_2(CF_2)_nCH_2OPCl_2$ (n = 2, 4) and $Cl\overline{POCH_2CF_2CF_2CH_2O}$, which were synthesized from the reactions of PCl_3 with $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 4) and $HOCH_2(CF_2)_2CH_2OH$, respectively. When it was heated at 95 °C in the presence of excess water, $HO\overline{P(O)OCH_2CF_2CF_2CH_2O}$ was converted to H_3PO_4 and the parent diol. The tetrabasic bis(phosphates) were hydrolyzed at 175–200 °C to form H_3PO_4 and the respective diols.

Introduction

Although some mono cyclophosphoric esters and alkanediyl bis(phosphates) have been synthesized as mixtures, there appears to be little evidence of attempts to isolate and to purify them. No reports of their polyfluorinated analogues have been found. However, the latter compounds do have potential characteristics for serving a wide variety of roles such as electrolytes in fuel cells, polymerization inhibitors, and structural analogues of fructose diphosphates and in model studies of arrangements of phosphate and metal binding subsites in biological systems.

Synthesis and characterization of new materials as precursors to these mono- and bis(phosphates) were undertaken. These included initial syntheses of 2-chlorodioxaphosphepane and bis(phosphorodichloridites) and the resepctive 2-chlorodioxaphosphepane 2-oxide and bis(phosphorodichloridates). The last two compounds were hydrolyzed or otherwise converted to 2-hydroxy-1,3,2-dioxaphosphepane 2-oxide and bis(phosphates).

Results and Discussion

The 2-chlorodioxaphosphepane $Cl\overline{POCH_2(CF_2)_2CH_2O}$ and the bis(phosphorodichloridites) $Cl_2POCH_2(CF_2)_nCH_2OPCl_2$ (n = 2, 4) were obtained by the reaction of PCl_3 and polyfluorinated diols $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 4):

$$PCl_3 + HOCH_2(CF_2)_nCH_2OH \xrightarrow[-HCl]{-196\text{ to }+25\ ^\circ C} Cl\overline{POCH_2(CF_2)_nCH_2O} + Cl_2POCH_2(CF_2)_nCH_2OPCl_2$$

$$n = 2, 4$$

When n = 2, both the cyclic and acyclic compounds were obtained, whereas for n = 4 only an acyclic derivative was isolated. The HCl produced in the reactions was removed while the reaction vessel was maintained at −78 °C. Otherwise reaction occurred between HCl and the products to give Arbuzov-rearranged compounds. As indicated below, normally a base was used to remove HCl.

The first examples of a cyclic phosphorochloridite and bis(phosphorodichloridite) were reported from the reaction of PCl_3 and ethanediol.[1] Later reports[2-4] on the reaction of PCl_3 and ethanediol indicated that the cyclic phosphorochloridite was the only product. A solvent such as CH_2Cl_2 was required for better yields. However, when CCl_4 was used as a solvent, $Cl_2POCH_2CH_2OPCl_2$ was the only product obtained.[5]

Studies of reactions of polyfluorinated diols with PCl_3 in the presence of Et_3N were not found in the literature. When these reactions are carried out, the same products are obtained in the presence or absence of a base but in different yields. In the presence of Et_3N, when n = 2, the yield of the dioxaphosphepane is increased and that of the bis(phosphorodichloridite) is decreased. For n = 4, the cyclic compound is present but could not be isolated, whereas the yield of the bis(phosphorodichloridite) is the same as for n = 2. In both cases, the reactions proceed smoothly without solvent.

The majority of the literature methods reported for oxidation of trialkyl phosphites involve air,[6] ozone,[7] hydrogen peroxide,[8] organic peroxides such as *tert*-butyl peroxide,[9] or dinitrogen tetraoxide[10] in a solvent (CH_2Cl_2) at −78 °C. We have used dinitrogen tetraoxide successfully at 25 °C without solvent to oxidize the chlorodioxaphosphepane as well as the bis(phosphorodichloridites) to their respective phosphorus(V) compounds.

$$2Cl\overline{POCH_2CF_2CF_2CH_2O} + N_2O_4 \xrightarrow{-196\text{ to }+25\ ^\circ C} \underset{\sim 100\%}{2Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}} + 2NO$$

$$Cl_2POCH_2(CF_2)_nCH_2OPCl_2 + N_2O_4 \xrightarrow{-196\text{ to }+25\ ^\circ C} \underset{\sim 100\%}{Cl_2P(O)OCH_2(CF_2)_nCH_2OP(O)Cl_2} + 2NO$$

$$n = 2, 4$$

The synthesis of $Cl\overline{P(O)OCH_2CF_2CF_2CF_2CH_2O}$ by the reaction of $OPCl_3$ and $HOCH_2(CF_2)_3CH_2OH$ in the presence of Et_3N and diethyl ether was reported, but no mention is made of the bis(phosphorodichloridate) $Cl_2P(O)OCH_2(CF_2)_3CH_2OP(O)Cl_2$.[11] In our reactions of $OPCl_3$ with $HOCH_2(CF_2)_2CH_2OH$ in the presence of CH_2Cl_2 or diethyl ether as solvent, only the dioxaphosphepane oxide containing a stabilizing seven-membered ring, $Cl\overline{P(O)OCH_2(CF_2)_2CH_2O}$, was formed. However, with $HOCH_2(CF_2)_4CH_2OH$, no cyclic compound was isolated and only

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$\mathrm{Cl_2P(O)OCH_2(CF_2)_4CH_2OP(O)Cl_2}$ was obtained. Apparently a nine-membered ring is of low stability relative to the acyclic bis(phosphorodichloridate).

$$\mathrm{OPCl_3 + HOCH_2(CF_2)_2CH_2OH \xrightarrow[CH_2Cl_2\ or\ ether]{Et_3N} Cl\overline{P(O)OCH_2CF_2CF_2CH_2O} + Et_3NHCl}$$

$$\mathrm{2OPCl_3 + HOCH_2(CF_2)_4CH_2OH \xrightarrow[CH_2Cl_2\ or\ ether]{2Et_3N} Cl_2P(O)OCH_2(CF_2)_4CH_2OP(O)Cl_2 + 2Et_3NHCl}$$

The synthesis of ethylene glycol esters from phosphorus acid esters has been achieved by thermal self-condensation reactions:[12]

$$\mathrm{2Ph(CH_3)P(O)OCH_2CH_2Cl \xrightarrow{200\text{–}240\ ^\circ C} Ph(CH_3)P(O)OCH_2CH_2OP(O)(CH_3)Ph + ClCH_2CH_2Cl}$$

Cyclic thiophosphorochloridates and bis(thiophosphorodichloridates) have been prepared from the reaction of the sodium salt of ethylene glycol with thiophosphoryl chloride.[13]

Various methods have been used to prepare cyclic phosphoric esters and alkanediyl bis(phosphates). For example, the reactions of P_4O_{10} with butanediol or ethanediol gave a mixture of acid phosphates, but none of them was separated.[14]

In our work, the reaction of $\mathrm{HOCH_2(CF_2)_2CH_2OH}$ with P_4O_{10} at 60 °C gave a mixture of cyclic and acyclic compounds as detected by ^{31}P NMR spectra. However, hydroxydioxaphosphepane could be isolated by bulb-to-bulb distillation (100 °C, 0.1 torr):

$$\mathrm{P_4O_{10} + HOCH_2CF_2CF_2CH_2OH \xrightarrow{60\ ^\circ C} HO\overline{P(O)OCH_2CF_2CF_2CH_2O} + (HO)_2P(O)OCH_2CF_2CF_2CH_2OP(O)(OH)_2 \xrightarrow{100\ ^\circ C,\ 0.1\ torr} \underset{50\%}{HO\overline{P(O)OCH_2CF_2CF_2CH_2O}}}$$

The bis(phosphates) reacted with the remaining P_4O_{10} at 100 °C and were not isolable. For the reaction of $\mathrm{HOCH_2CF_2CF_2CF_2CF_2CH_2OH}$ and P_4O_{10}, both cyclic and acyclic compounds were detected by their characteristic ^{31}P NMR chemical shifts, but both react with P_4O_{10} at 100 °C, so it was impossible to isolate either from this reaction.

Other methods for the syntheses of cyclic alkyl phosphates include reactions of the sodium salts of phosphoric acids and alcohols.[15] However, hydrolyses of $\mathrm{Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}}$ and $\mathrm{Cl_2P(O)OCH_2(CF_2)_nCH_2OP(O)Cl_2}$ (n = 2, 4) were carried out as reported for alkyl phosphorochloridates[16,17] with the exception that our polyfluoro compounds were isolated and purified before being hydrolyzed with a slight excess of water. The pure acids were isolated by freeze-drying.

$$\mathrm{Cl\overline{P(O)OCH_2CF_2CF_2CH_2O} + H_2O \xrightarrow[-HCl]{} HO\overline{P(O)OCH_2CF_2CF_2CH_2O}(aq) \xrightarrow{freeze\text{-}dry} \underset{\sim 100\%}{HO\overline{P(O)OCH_2CF_2CF_2CH_2O}}}$$

$$\mathrm{Cl_2P(O)OCH_2(CF_2)_nCH_2OP(O)Cl_2 + 4H_2O \xrightarrow[-HCl]{25\ ^\circ C} \underset{\sim 100\%}{(HO)_2P(O)OCH_2(CF_2)_nCH_2OP(O)(OH)_2}}$$

$$n = 2, 4$$

As an indication of the ease of hydrolysis, when these phosphorochloridates were exposed to dry Idaho air, complete conversion to the respective acids had occurred in 48 h. The hydrolytic stabilities of the dioxaphosphepane and bis(phosphates) are shown:

$$\mathrm{HO\overline{P(O)OCH_2CF_2CF_2CH_2O} + excess\ H_2O \xrightarrow[10\ h]{95\ ^\circ C} H_3PO_4 + HOCH_2(CF_2)_2CH_2OH}$$

$$\mathrm{(HO)_2P(O)OCH_2(CF_2)_nCH_2OP(O)(OH)_2 + excess\ H_2O \xrightarrow{175\text{–}200\ ^\circ C} H_3PO_4 + HOCH_2(CF_2)_nCH_2OH}$$

$$n = 2, 4$$

The low hydrolytic stabilities of these materials will most likely preclude their utilization as fuel cell electrolytes. However, these interesting molecules may find applications as models for biological systems and as polymerization inhibitors.[18-20]

Experimental Section

Starting Materials. N_2O_4 (Air Products), PCl_3 (Baker), $OPCl_3$ (Baker), and $\mathrm{HOCH_2(CF_2)_nCH_2OH}$ (n = 2, 4) (3M) were used as received. Triethylamine was dried over KOH before use.

General Procedure. A conventional Pyrex glass vacuum line apparatus equipped with Heise Bourdon tube and thermocouple gauges was used for manipulation of gases and volatile materials. Trap-to-trap distillation was carried out to accomplish separation of volatile products. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer or Perkin-Elmer 1710 Fourier transform infrared spectrometer by using a 10-cm cell fitted with KBr windows. ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrometer with CCl_3F or H_3PO_4 (85%) as external reference and $CDCl_3$ or $(CD_3)_2SO$ as internal reference. Negative values are assigned to the signals that are upfield of the reference. Mass spectra were recorded on a VG 7070HS mass spectrometer. All fragments that contain chlorine had appropriate isotopic ratios.

Reaction of $\mathbf{(HOCH_2CF_2)_2}$ with $\mathbf{PCl_3}$. Under a nitrogen atmosphere, 0.81 g (5 mmol) of $(HOCH_2CF_2)_2$ was transferred into a thick-walled Pyrex glass tube equipped with a Teflon stopcock. With the tube at −196 °C, PCl_3 (1.37 g, 10 mmol) was condensed onto the diol. The tube was allowed to warm to 25 °C, and in a few minutes an exothermic reaction took place. After 20 min, the tube was cooled to −78 °C in order to remove any HCl that was produced. This process was repeated several times, and then the Pyrex tube was held at 25 °C for 10 h. Trap-to-trap distillation gave 3 mmol of $\mathrm{Cl\overline{POCH_2CF_2CF_2CH_2O}}$ in the trap at −40 °C (60% yield). The ^{1}H NMR spectrum in $CDCl_3$ consisted of a multiplet centered at δ 4.9. A multiplet in the ^{19}F NMR spectrum was centered at ϕ −126.02, and the ^{31}P{^{1}H} NMR spectrum showed a singlet at δ 166.06 that was a pentet (J_{P-H} = 20.7 Hz) in the nondecoupled spectrum. The infrared spectrum for $\mathrm{Cl\overline{POCH_2CF_2CF_2CH_2O}}$ contained bands at 2990 w, 2960 w, 2940 w, 2888 w, 1455 m, 1380 m, 1350 w, 1312 w, 1242 s, 1237 vs, 1150 vs, 1112 w, 1078 vs, 1040 s, 928 s, 769 vs, 710 m, 668 s, 569 m, 530 vs (ν_{P-Cl}), 508 w, 478 w, 430 w, and 380 m cm^{-1}. The positive CI mass spectrum showed peaks at *m/e* 227 (M^+ + 1, $C_4H_5F_4O_2PCl^+$) 6.9%, 226 (M^+, $C_4H_4F_4O_2PCl^+$) 28.5%, 191 ($C_4H_4F_4O_2P^+$) 91.6%, 171 ($C_4H_3F_3O_2P^+$) 6.9%, 147 ($C_2H_3ClF_2OP^+$) 2.6%, 141 ($C_3H_4F_2O_2P^+$) 3.8%, 111 ($C_2H_2F_2OP^+$) 8.9%, 99 (O_2PClH^+) 37.1%, 97 (CH_2OPClH^+) 3.3%, 77 ($CH_2O_2P^+$) 100%, and 66 (PCl^+) 7.2%.

The trap at −15 °C contained $\mathrm{Cl_2POCH_2CF_2CF_2CH_2OPCl_2}$ (1 mmol, 20%). The ^{1}H NMR spectrum showed a multiplet centered at δ 4.5, and the ^{19}F NMR spectrum had a multiplet centered at ϕ −120.76. The ^{31}P{^{1}H} NMR spectrum gave a singlet at δ 181.46 and a multiplet in the undecoupled ^{31}P NMR spectrum. The positive CI mass spectrum contained $M^+ - Cl$ at *m/e* 327 ($C_4H_4F_4O_2P_2Cl_3^+$) 3.3%, as well as peaks at *m/e* 282 ($C_4O_2P_2Cl_4^+$) 1.3%, 257 ($C_4H_4F_4O_2P_2Cl^+$) 1.1%, 245 ($C_4H_4F_4OPCl_2^+$) 0.8%, 226 ($C_4H_4F_4O_2PCl^+$) 12.9%, 222 ($C_4H_4F_4O_2P_2^+$) 2.6%, 191 ($C_4H_4F_4O_2P^+$) 100%, 181 ($C_2H_2F_2OPCl_2^+$) 1.4%, 163 ($C_2H_3FOPCl_2^+$) 1.1%, 131 ($CH_2OPCl_2^+$) 1.8%, 117 ($OPCl_2^+$) 3.4%, 101 (PCl_2^+) 19.5%, 66 (PCl^+) 62%, and 51 (CF_2H^+) 13.4%.

Reaction of $\mathbf{(HOCH_2CF_2CF_2)_2}$ with $\mathbf{PCl_3}$. This reaction was carried out as above. On Kugelrohr treatment at 65 °C $(Cl_2POCH_2CF_2CF_2)_2$ was obtained in 55% yield. The ^{1}H NMR spectrum of the compound in

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$\mathrm{CDCl_3}$ contained two overlapping triplets centered at δ 4.5 ($J_{\mathrm{H-P}} = 7.08$ Hz, $J_{\mathrm{H-F}} = 14.7$ Hz); the ^{19}F NMR spectrum had a complex triplet of triplets centered at ϕ −121.68 ($J_{\mathrm{F-F}} = 6.5$ Hz) and a complex triplet at ϕ −118.2. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum showed a singlet at δ 181.67. A triplet was found in the ^{31}P NMR spectrum. The infrared spectrum has bands at 2960 m, 2880 w, 2840 w, 1450 s, 1393 m, 1298 vs, 1242 vs, 1172 vs, 1140 vs, 1070 br, s, 995 w, 978 w, 958 s, 940 w, 895 w, 880 m, 853 m, 825 br, s, 752 w, 732 w, 710 m, 682 w, 640 w, 568 w, 545 m, 510 vs, 460 br, s, and 400 m $\mathrm{cm^{-1}}$.

The EI mass spectrum had a molecular ion peak at *m/e* 462 ($\mathrm{C_6H_4F_8O_2P_2Cl_4^+}$) 2.0%, as well as peaks at *m/e* 427 ($\mathrm{C_6H_4F_8O_2P_2Cl_3^+}$) 0.4%, 382 ($\mathrm{C_6F_4O_2P_2Cl_4^+}$) 14.7%, 322 ($\mathrm{C_6H_4F_8O_2P_2^+}$) 1.0%, 291 ($\mathrm{C_6H_4F_8O_2P^+}$) 2.4%, 271 ($\mathrm{C_6H_3F_7O_2P^+}$) 3.9%, 240 ($\mathrm{C_6H_3F_7O_2^+}$) 3.8%, 181 ($\mathrm{C_2H_2F_2OPCl_2^+}$) 0.5%, 161 ($\mathrm{C_2HFOPCl_2^+}$) 2.1%, 131 ($\mathrm{CH_2OPCl_2^+}$) 23.4%, 126 ($\mathrm{C_2HFOPCl^+}$) 10.5%, 117 ($\mathrm{OPCl_2^+}$) 11.7%, 101 ($\mathrm{PCl_2^+}$) 100%, 96 ($\mathrm{CH_2OPCl^+}$) 10.2%, 66 ($\mathrm{PCl^+}$) 25.4%, and 51 ($\mathrm{CF_2H^+}$) 16.1%. Anal. Calcd for $\mathrm{C_6H_4F_8O_2P_2Cl_4}$: C, 15.52; H, 0.86; P, 13.37; Cl, 30.60. Found: C, 14.56; H, 0.86; P, 13.52; Cl, 30.79.

Reaction of $\mathrm{(HOCH_2CF_2)_2}$ and $\mathrm{PCl_3}$ in the Presence of $\mathrm{Et_3N}$. A 1.9-g (12-mmol) sample of $\mathrm{(HOCH_2CF_2)_2}$ was transferred into a 1-L round-bottomed flask equipped with a Teflon stopcock and a magnetic stirring bar under an inert atmosphere. Triethylamine (24 mmol, 3.3 mL) was condensed at −196 °C onto the $\mathrm{(HOCH_2CF_2)_2}$. This reaction mixture was allowed to warm to 25 °C and then stirred for 30 min. Phosphorus trichloride (25 mmol, 3.43 g) was added at −196 °C. When the mixture was warmed to 25 °C, the reaction took place with the formation of $\mathrm{Et_3NHCl}$. After 24 h, trap-to-trap distillation gave ~11 mmol of $\mathrm{PCl_3}$ in a trap at −78 °C and 8 mmol (67% yield) of $\mathrm{Cl\overline{POCH_2CF_2CF_2CH_2O}}$ in a trap at −40 °C. The trap at −15 °C contained $\mathrm{Cl_2POCH_2CF_2CF_2CH_2OPCl_2}$ (2 mmol, 17% yield).

Reaction of $\mathrm{(HOCH_2CF_2CF_2)_2}$ with $\mathrm{PCl_3}$ in the Presence of $\mathrm{Et_3N}$ and Diethyl Ether as a Solvent. This reaction was carried out as described above, except diethyl ether was used as a solvent. The $\mathrm{Et_3NHCl}$ was filtered out, and diethyl ether was evaporated under vacuum, leaving behind a mixture of $\mathrm{Cl\overline{POCH_2CF_2CF_2CF_2CF_2CH_2O}}$, $\mathrm{Cl_2POCH_2CF_2CF_2CF_2CF_2CH_2OPCl_2}$, and some other unidentified phosphorus(III) products as indicated by ^{31}P NMR. On Kugelrohr treatment at 55 °C, $\mathrm{Cl_2POCH_2(CF_2)_4CH_2OPCl_2}$ (4.8 mmol, 40%) was obtained.

Reaction of $\mathrm{OPCl_3}$ with $\mathrm{(HOCH_2CF_2)_2}$ in the Presence of $\mathrm{Et_3N}$ and Methylene Chloride. The diol $\mathrm{(HOCH_2CF_2)_2}$ (0.81 g, 5 mmol) was transferred under an $\mathrm{N_2}$ atmosphere into a 250-mL round-bottom flask equipped with a Teflon stopcock and a magnetic stirring bar. After evacuation at −196 °C, $\mathrm{Et_3N}$ (1.01 g, 10 mmol) and $\mathrm{CH_2Cl_2}$ (~20 mL) were transferred into the vessel. The mixture was allowed to warm to 25 °C and stirred for 30 min. It was cooled to −196 °C, and then $\mathrm{OPCl_3}$ (1.9 g, 12.5 mmol) was added. After 24 h at 25 °C, $\mathrm{CH_2Cl_2}$ was removed under vacuum, and dry diethyl ether was added and the $\mathrm{Et_3NHCl}$ was removed by filtering under an inert atmosphere. The ether was removed to leave $\mathrm{Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}}$, which sublimed at 40 °C and 0.1 torr (91% yield). The ^{1}H NMR spectrum of the sublimed white solid in $\mathrm{CDCl_3}$ gave a complex multiplet centered at δ 4.4. The ^{19}F NMR spectrum also showed a complex multiplet centered at ϕ −125.7. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum had a singlet at δ 7.7 and a pentet with additional fine structure in the ^{31}P NMR spectrum with $J_{\mathrm{P-H}} = 19.6$ Hz. The infrared spectrum had bands at 3021 w, 2971 w, 1460 m, 1397 m, 1353 w, 1284 s ($\nu_{\mathrm{P=O}}$), 1274 s, 1240 m, 1220 s, 1140 s, 1114 s, 1078 s, 1050 s, 924 vs, 862 vs, 833 vs, 709 m, 672 s, 604 s, 575 m, 569 m, 539 w, 481 m, and 466 m $\mathrm{cm^{-1}}$. The positive CI mass spectrum had a $\mathrm{M^+} + 1$ peak at *m/e* 243 ($\mathrm{C_4H_5F_4O_3PCl^+}$) 100%, as well as peaks at *m/e* 222 ($\mathrm{C_4H_3F_3O_3PCl^+}$) 20.7%, 207 ($\mathrm{C_4H_4F_4O_3P^+}$) 4.1%, 203 ($\mathrm{C_4H_3F_2O_3PCl^+}$) 11.3%, 177 ($\mathrm{C_3H_2F_4O_2P^+}$) 2.2%, 158 ($\mathrm{C_3H_2F_3O_2P^+}$) 9.6%, 113 ($\mathrm{CH_3O_2PCl^+}$) 10.5%, 107 ($\mathrm{C_2H_4O_3P^+}$) 7.4%, 93 ($\mathrm{CH_2O_3P^+}$) 13.0%, 80 ($\mathrm{HPO_3^+}$) 8.7%, 77 ($\mathrm{CH_2O_2P^+}$) 22.9%, and 51 ($\mathrm{CF_2H^+}$) 13.9%. Anal. Calcd for $\mathrm{C_4H_4ClF_4O_3P}$: C, 19.79; H, 1.65; P, 12.78. Found: C, 19.96; H, 1.77; P, 12.81.

Reaction of $\mathrm{(HOCH_2CF_2CF_2)_2}$ with $\mathrm{OPCl_3}$ in the Presence of $\mathrm{Et_3N}$. This reaction was carried out as above. After the ether was removed from the filtrate, a sublimable white solid (70 °C, 0.1 torr) was found, which proved to be $\mathrm{Cl_2P(O)OCH_2CF_2CF_2CF_2CF_2CH_2OP(O)Cl_2}$ (3.5 mmol, 70% yield). The ^{1}H NMR spectrum of this compound in $\mathrm{CDCl_3}$ consisted of overlapping triplets centered at δ 4.6 ($J_{\mathrm{P-H}} = 8.79$ Hz; $J_{\mathrm{H-F}} = 15.13$ Hz). The ^{19}F NMR spectrum showed a complex triplet at ϕ −122.26 and a complex multiplet at ϕ −119. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum had a singlet at δ 9.9 and a complex triplet in the ^{31}P NMR spectrum. The infrared spectrum had bands at 3019 w, 2981 w, 1453 w, 1290 br, s ($\nu_{\mathrm{P=O}}$), 1240 m, 1170 s, 1131 s, 1064 s, 956 m, 881 s, 827 m, 692 m, 626 s, 602 m, 562 m, and 531 m $\mathrm{cm^{-1}}$. The positive CI mass spectrum showed a peak assigned to $\mathrm{M^+} + 1$ at *m/e* 495 ($\mathrm{C_6H_5F_8O_4P_2Cl_4^+}$) 32.8%, as well as peaks at *m/e* 475 ($\mathrm{C_6H_4F_7O_4P_2Cl_4^+}$) 1.8%, 459 ($\mathrm{C_6H_4F_7O_3P_2Cl_4^+}$) 46.9%, 439 ($\mathrm{C_6H_3F_6O_3P_2Cl_4^+}$) 2.9%, 361 ($\mathrm{C_6H_4F_8O_2PCl_2^+}$) 36.7%, 325 ($\mathrm{C_6H_3F_8O_2PCl^+}$) 1.3%, 278 ($\mathrm{C_5H_3F_8O_2P^+}$) 1.2%, 228 ($\mathrm{C_4H_3F_6O_2P^+}$) 2.2%, 177 ($\mathrm{C_3H_2F_4O_2P^+}$) 0.6%, 147 ($\mathrm{CH_2O_2PCl_2^+}$) 100%, 117 ($\mathrm{OPCl_2^+}$) 56.4%, 100 ($\mathrm{C_2F_4^+}$) 6.2%, 82 ($\mathrm{OPCl^+}$) 1.1%, 64 ($\mathrm{C_2H_2F_2^+}$) 20.7%, and 51 ($\mathrm{CF_2H^+}$) 8.4%. Anal. Calcd for $\mathrm{C_6H_4Cl_4F_8O_4P_2}$: C, 14.52; H, 0.81; P, 12.5. Found: C, 13.90; H, 0.88; P, 12.44.

Oxidation of $\mathrm{Cl_2POCH_2(CF_2)_2CH_2OPCl_2}$ with $\mathrm{N_2O_4}$. The bis(phosphorodichloridite) $\mathrm{Cl_2POCH_2(CF_2)_2CH_2OPCl_2}$ (1.09 g, 3 mmol) was transferred into a 100-mL round-bottom flask under an inert atmosphere. Then, 3 mmol of $\mathrm{N_2O_4}$ was condensed in at −196 °C. The flask was warmed slowly to 25 °C and allowed to remain for 12 h. After all the volatile materials were removed, a sublimable white solid remained, $\mathrm{Cl_2P(O)OCH_2(CF_2)_2CH_2OP(O)Cl_2}$ (55 °C, 0.1 torr; 85% yield). The ^{1}H NMR spectrum showed a multiplet centered at δ 4.7. The ^{19}F NMR spectrum had a multiplet at ϕ −120.6. A singlet at δ 9.8 was observed in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum, and the ^{31}P NMR spectrum had a multiplet. The positive CI mass spectrum had peaks at *m/e* 395 ($\mathrm{M^+} + 1$, $\mathrm{C_4H_5F_4O_4P_2Cl_4^+}$) 13.7%, 359 ($\mathrm{C_4H_4F_4O_4P_2Cl_3^+}$) 32.7%, 261 ($\mathrm{C_4H_4F_4O_2PCl_2^+}$) 100%, 225 ($\mathrm{C_4H_3F_4O_2PCl^+}$) 2.0%, 197 ($\mathrm{C_2H_2F_2O_2PCl_2^+}$) 5.4%, 147 ($\mathrm{CH_2O_2PCl_2^+}$) 56.8%, 117 ($\mathrm{OPCl_2^+}$) 36.1%, 101 ($\mathrm{C_2F_4H^+}$, $\mathrm{PCl_2^+}$) 2.2%, 82 ($\mathrm{OPCl^+}$) 1.8%, 77 ($\mathrm{CH_2O_2P^+}$) 17.4%, and 51 ($\mathrm{CF_2H^+}$) 10.0%.

Oxidation of $\mathrm{Cl_2POCH_2(CF_2)_4CH_2OPCl_2}$ with $\mathrm{N_2O_4}$. This was carried out as described above. After the volatile materials were removed, a white solid remained behind, which sublimed at 70 °C (0.1 torr), and its spectroscopic data confirmed it to be $\mathrm{Cl_2P(O)OCH_2(CF_2)_4CH_2OP(O)Cl_2}$ (90%).

Oxidation of $\mathrm{Cl\overline{POCH_2(CF_2)_2CH_2O}}$ with $\mathrm{N_2O_4}$. The oxidation was accomplished as described above. After removal of the volatile materials, NO and $\mathrm{N_2O_4}$, a white sublimable solid (40 °C, 0.1 torr) was obtained, and comparison of its spectroscopic data showed it to be $\mathrm{Cl\overline{P(O)OCH_2(CF_2)_2CH_2O}}$ (92%).

Reaction of $\mathrm{(HOCH_2CF_2)_2}$ with $\mathrm{P_4O_{10}}$. Powdered $\mathrm{P_4O_{10}}$ (2.84 g, 10 mmol) was transferred into a dry 50-mL round-bottom flask equipped with a Teflon stopcock and a magnetic stirring bar. Five millimoles of $\mathrm{(HOCH_2CF_2)_2}$ was added. After the reaction vessel was evacuated, the mixture was heated to 60 °C for 10 h. On Kugelrohr treatment at 110 °C and 0.1 torr for 2 h a colorless solid, $\mathrm{HO\overline{P(O)OCH'_2CF'_2CF''_2CH''_2O}}$, was obtained in 50% yield. The ^{1}H NMR spectrum in $\mathrm{Me_2SO}$-d_6 had a singlet peak at δ 13.08 (OH) and an overlapping doublet of triplets of triplets ($J_{\mathrm{P-H}} = 16.30$ Hz, $J_{\mathrm{F'-H'}} = J_{\mathrm{F''-H''}} = 7.08$ Hz, $J_{\mathrm{F'-H''}} = J_{\mathrm{F''-H'}} = 5.37$ Hz) centered at δ 4.4. The ^{19}F NMR spectrum is a triplet of triplets centered at ϕ −125.4. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectrum had a singlet peak at δ −3.01, and in the ^{31}P NMR spectrum a pentet was observed. In the positive CI mass spectrum, a peak assigned to $\mathrm{M^+} + 1$ was observed at *m/e* 225 ($\mathrm{C_4H_6F_4O_4P^+}$) 5.6%, as well as peaks at *m/e* 204 ($\mathrm{C_4H_4F_3O_4P^+}$) 56.9%, 194 ($\mathrm{C_3H_3F_4O_3P^+}$) 2.4%, 184 ($\mathrm{C_4H_3F_2O_4P^+}$) 0.9%, 160 ($\mathrm{C_4H_4F_4O_2^+}$) 11.6%, 144 ($\mathrm{C_2H_3F_2O_3P^+}$) 1.8%, 127 ($\mathrm{C_2H_2F_2O_2P^+}$) 3.3%, 100 ($\mathrm{C_2F_4^+}$) 7.2%, 81 ($\mathrm{C_2F_3^+}$) 21.4%, 79 ($\mathrm{PO_3^+}$) 11.8%, 77 ($\mathrm{CH_2O_2P^+}$) 14.4%, 64 ($\mathrm{HO_2P^+}$) 100%, and 51 ($\mathrm{CF_2H^+}$) 14.8%. Anal. Calcd for $\mathrm{C_4H_5F_4O_4P}$: C, 21.42; H, 2.23; P, 13.8. Found: C, 21.40; H, 2.27; P, 14.30.

Hydrolysis of $\mathrm{Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}}$. $\mathrm{Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}}$ (0.73 g, 3 mmol) was transferred to a 50-mL round-bottom flask under anhydrous conditions, and distilled water (0.07 g, 4 mmol) was added at −196 °C. The reaction mixture was warmed to ambient temperature. After 24 h volatile materials such as HCl and $\mathrm{H_2O}$ were removed under vacuum. Kugelrohr treatment of the remaining material at 110 °C and 0.1 torr gave $\mathrm{HO\overline{P(O)CH_2CF_2CF_2CH_2O}}$ (90%), which was confirmed by its ^{1}H, ^{19}F, and ^{31}P NMR spectra. Similar results were observed when the acid chloride was exposed to ambient air for 48 h.

Hydrolysis of $\mathrm{Cl_2P(O)OCH_2(CF_2)_2CH_2OP(O)Cl_2}$. The hydrolysis of this bis(phosphorodichloridate) was carried out as described for its cyclic analogue above, except 13 mmol of water was used. After HCl and $\mathrm{H_2O}$ were removed, the solid left behind was characterized as $\mathrm{(HO)_2P(O)OCH_2(CF_2)_2CH_2OP(O)(OH)_2}$ (mp 108 °C). The ^{1}H NMR spectrum showed a peak at δ 7.0 (OH) and a triplet of doublets centered at δ 4.3 (CH; $J_{\mathrm{P-CH_2}} = 6.59$ Hz, $J_{\mathrm{H-F}} = 14.65$ Hz). The ^{19}F NMR spectrum showed a triplet centered at ϕ −122.3. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum gave a singlet peak at δ −1.5. The ^{31}P NMR spectrum was a triplet. The FAB spectrum had a molecular ion peak at *m/e* 322 ($\mathrm{C_4H_8F_4O_8P_2^+}$) 0.7%, as well as peaks at *m/e* 321 ($\mathrm{C_4H_7F_4O_8P_2^+}$) 12.8%, 318 ($\mathrm{C_4H_4F_4O_8P_2^+}$), 28.8%, 301 ($\mathrm{C_4H_6F_3O_8P_2^+}$) 1.5%, 287 ($\mathrm{C_4H_5F_4O_6P_2^+}$) 0.8%, 264 ($\mathrm{C_2H_4F_2O_7P_2^+}$) 2.1%, 225 ($\mathrm{C_4H_6F_4O_4P^+}$) 1.0%, 211 ($\mathrm{C_3H_4F_4O_4P^+}$) 1.1%, 194 ($\mathrm{C_3H_3F_4O_3P^+}$) 1.8%, 177 ($\mathrm{C_3H_2F_4O_2P^+}$) 4.0%, 160 ($\mathrm{C_4H_4F_4O_2^+}$)

5.3%, 144 ($C_4H_4F_4O^+$) 31.1%, 140 ($C_4H_3F_3O_2^+$) 61.6%, 127 ($C_2H_2F_2O_2P^+$) 1.6%, 105 ($C_2H_2O_3P^+$) 100%, 98 ($H_3PO_4^+$) 7.1%, and 63 (PO_2^+) 13.9%. Air hydrolysis of $Cl_2P(O)OCH_2(CF_2)_2CH_2OP(O)Cl_2$ also gave the bis(phosphate).

Hydrolysis of $Cl_2P(O)OCH_2(CF_2)_4CH_2OP(O)Cl_2$. The hydrolysis was carried out as above. The white solid remaining after the volatile materials were removed had a melting point of 170 °C. The ^1H NMR of $(HO)_2P(O)OCH_2(CF_2)_4CH_2OP(O)(OH)_2$ had a peak at δ 7.6 (OH) and a triplet of doublets centered at δ 4.4 (J_{P-CH_2} = 6.91 Hz, J_{H-F} = 13.9 Hz). The ^{19}F NMR spectrum had two complex triplets centered at ϕ −117.97 and −121.16. The $^{31}P\{^1H\}$ NMR spectrum had a resonance at δ −1.9, and the ^{31}P NMR spectrum was a triplet. The FAB mass spectrum has peaks at *m/e* 423 ($M^+ + 1$, $C_6H_9F_8O_8P_2^+$) 0.4%, 405 ($C_6H_7F_8O_7P_2^+$) 0.1%, 325 ($C_6H_6F_8O_4P^+$) 0.2%, 161 ($C_2H_4F_2O_4P^+$) 0.1%, 127 ($C_2H_2F_2O_2P^+$) 0.1%, 102 ($HF_2O_2P^+$) 100%, 81 ($H_2O_3P^+$) 1.1%, 77 ($CH_2O_2P^+$) 0.6%, 64 ($C_2H_2F_2^+$) 1.1%, and 51 (CF_2H^+). Air hydrolysis of the tetrachloro compound also results in the bis(phosphate).

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Kinetics and Mechanism for Reduction of Ammine and Haloammine Complexes of Gold(III) by Iodide

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The rate-determining step in the reduction of $Au(NH_3)_4^{3+}$ by iodide in acidic aqueous solution is the ligand substitution

$$Au(NH_3)_4^{3+} + I^- \rightarrow Au(NH_3)_3I^{2+} + NH_3$$

with $k^{298} = (1.52 \pm 0.03) \times 10^3\ M^{-1}\ s^{-1}$, $\Delta H^* = 54.6 \pm 1.1$ kJ mol^{-1}, and $\Delta S^* = -1 \pm 4$ J mol^{-1} K^{-1} in 1.0 M $NaClO_4$ with pH 2.3, as determined by stopped-flow spectrophotometry. In a subsequent rapid reductive elimination, attack by free iodide on $Au(NH_3)_3I^{2+}$ or *trans*-$Au(NH_3)_2I_2^+$ (the latter formed in a rapid trans substitution) leads to the final products AuI_2^- and iodine. The same products are formed when *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br) reacts with iodide. For X = Br reduction of the complex probably takes place by direct reductive elimination via one of the bromide ligands, without any initial substitution. This reaction is too fast for the stopped-flow technique at 25.0 °C: $k^{277.3} = (3.4 \pm 0.5) \times 10^6\ M^{-1}\ s^{-1}$. For X = Cl, reduction takes place with the parameters $k^{298} = (2.91 \pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$, $\Delta H^* = (32.8 \pm 1.5)$ kJ mol^{-1}, and $\Delta S^* = -30 \pm 6$ J mol^{-1} K^{-1}, which probably correspond to a rate-determining substitution of chloride by iodide followed by rapid reduction via the iodide ligand. However, it cannot be excluded that this reaction represents a borderline case, where direct reduction and substitution have very similar rates.

Introduction

Reduction of square-planar gold(III) complexes takes place as reductive eliminations via an attack by the reducing agent on a coordinated ligand and concomitant two-electron transfer to the metal.[3-6] However, many good reductants featuring nonmetal centers are also efficient nucleophiles, and when gold(III) complexes are allowed to react with e.g. iodide, thiocyanate, or thioethers, it is often a close run as to whether the approach of a reducing ligand to the square-planar gold(III) complex results in a ligand substitution via a pentacoordinated transition state (followed eventually by reductive elimination in a subsequent step) or in a direct reductive elimination.[7] It is known that substitution is faster than reduction for the reactions between tetrachloroaurate(III) and thiocyanate[4] and thiosulfate.[8]

The presence in the gold(III) substrate complex of ligands capable of acting as efficient bridges for electron transfer favor direct reduction. For instance, in the reaction between tetrabromoaurate(III) and thiocyanate, direct reduction by thiocyanate proceeds at a rate comparable to the rate for bromide/thiocyanate substitution.[4] Examples of gold(III) substrate/reductant combinations for which the direct reduction clearly dominates include the reactions between tetrachloroaurate(III) and triphenylarsine[9] and hydroxylammonium.[10]

The reductions of tetrachloroaurate(III) and tetrabromoaurate(III) by iodide represent borderline cases for which it has been difficult to establish whether the rate-determining step is a ligand substitution or a direct reduction.[5,11] Comparison with the rate of bromide/chloride exchange in tetrahaloaurate(III)[12] has led to the conclusion that direct reduction of tetrabromoaurate(III) with iodide is faster than substitution of bromide by iodide, whereas for tetrachloroaurate(III) the question still remains unsettled.[5] The present study of the reaction between iodide and the series of well-characterized[13-18] ammine gold(III) complexes $Au(NH_3)_4^{3+}$, *trans*-$Au(NH_3)_2Cl_2^+$, and *trans*-$Au(NH_3)_2Br_2^+$ was

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