$\rightarrow 3SeF_4 + 2Cl_2$, the yield was 87%, a value comparable to that found for ClF reactions.

SeF_5Cl.—Selenium chloride pentafluoride was prepared by first forming the solid complex $CsSeF_5$ from CsF and SeF_4.[8] Weighed samples of the complex were placed in prepassivated cylinders and $ClSO_3F$ was added at −196°. After warming to room temperature for several hours or more, the volatile products were separated by fractional condensation at −95, −112, and −196°. Unreacted $ClSO_3F$ was retained at −95° while by-products and impurities such as ClF, $FClO_2$, and Cl_2 passed into the trap cooled to −196°. Pure SeF_5Cl was found in the −112° fraction. From 4.50 mmol of $CsSeF_5$, 4.13 mmol of SeF_5Cl was obtained, corresponding to a yield of 91.7% for the equation $CsSeF_5 + ClSO_3F \rightarrow CsSO_3F + SeF_5Cl$. The presence of uncomplexed CsF in the salt does not inhibit the formation of SeF_5Cl directly but does result in the loss of some $ClSO_3F$ by reaction to form ClF.[5]

Because the system $CsF-SF_4-ClF$ was very effective[4] in producing SF_5Cl, it was expected that $CsF-SeF_4-ClF$ would behave similarly. Such was not the case and unreacted ClF was always fully recoverable after 1 day or several weeks in contact with $CsSeF_5$. However, in the course of preparing SeF_4 from Se and ClF or ClF_3, it was found that excesses of the chlorine fluorides gave detectable yields of SeF_5Cl. To determine the extent of this reaction, 4.19 mmol of SeF_4 and 4.21 mmol of ClF were placed in a 10-ml stainless steel cylinder and kept at ambient temperature for 8 days. Separation of the products by fractional condensation led to the recovery of unreacted SeF_4 and ClF (1.45 mmol of each), as well as trace amounts of SeF_6 and Cl_2. The main product was SeF_5Cl (2.62 mmol), representing a 95% yield based on the SeF_4 that had reacted. With ClF_3, up to 10% yields of SeF_5Cl were obtained but always accompanied by much greater amounts of SeF_6. Thus the direct reaction of SeF_4 and ClF affords an alternate, albeit less efficient, route to SeF_5Cl.

Properties of SeF_5Cl.—Selenium chloride pentafluoride is colorless as a gas, liquid, or solid. It is stable at ambient temperature when stored in clean, dry, passivated stainless steel cylinders. However, contact with glass always resulted in significant decomposition. Even glassware suitably dry and otherwise prepared for the manipulation of ClF_3 did not serve for handling SeF_5Cl. It seems likely that this property hindered the earlier discovery of this compound.

Analysis.—A 0.2001-g sample of SeF_5Cl was hydrolyzed with excess standardized NaOH solution in a glass ampoule fitted with a Teflon Fischer–Porter valve. Fluoride, selenium, and base consumption were determined as reported by Smith and Cady.[9] Fluoride was also determined by the usual thorium nitrate titration. The amount of base consumed was calculated, assuming the hydrolysis equation $SeF_5Cl + 8OH^- \rightarrow SeO_4^{2-} + 4H_2O + 5F^- + Cl^-$. *Anal.* Calcd for SeF_5Cl: Se, 37.71; F, 45.37; OH^- consumed, 8.00 equiv/mol. Found: Se, 37.98; F, 45.18; OH^- consumed, 7.82 equiv/mol.

Molecular Weight.—The molecular weight of the compound as determined by vapor density, assuming ideal gas behavior, was 208 (calcd 209.5).

Vapor Pressure, Boiling Point, and Melting Point.—The vapor (sublimation) pressures of SeF_5Cl over the temperature range −79 to +3° are as follows [T (°C), P (mm)]: −78.7, 6; −64.4, 19; −45.3, 66; −32.2, 142; −23.0, 220; 0.0, 630; 3.5, 729. The pressure–temperature relationship is described by the equation $\log P_{mm} = 7.779 - 1360/T°K$. The normal boiling point calculated from the equation is 4.5°, with a heat of vaporization of 6.22 kcal/mol and a Trouton constant of 22.4. Under its own vapor, the compound melts at −19°. Since part of the pressure–temperature data given are below the melting point, it is actually a sublimation pressure and not a vapor pressure. However, pressure values obtained above and below the melting point were nearly on the same line, indicating little difference in the heats of sublimation and vaporization and consequently a very low heat of fusion.

Infrared Spectrum.—The infrared spectrum of SeF_5Cl in the range 4000–250 cm^{-1} shows several absorptions with the most prominent ones occurring at 745 (vvs), 440 (vs), 420 (s), 385 (w), and 335 cm^{-1} (m). The two highest frequencies and the strongest bands noted are comparable to those of bands of similar intensity and position in related hexacoordinate selenium fluorides. Thus, the two strongest bands for SeF_6[10] occur at 780 and 430 cm^{-1} and for SeF_5OF[11] at 750 and 422 cm^{-1}. That these bands are typical of the SeF_5 group is shown by their presence in a series of substituted SeF_5 compounds.[11] A detailed analysis of the vibrational spectrum of SeF_5Cl is in progress.[12]

Nuclear Magnetic Resonance Spectrum.—The ^{19}F nmr spectrum of SeF_5Cl is shown in Figure 1. It is an AB_4 spectrum and resembles that of SF_5Cl[13] so closely as to be virtually identical. The reported[13] chemical shifts for SF_5Cl when converted to a $CFCl_3$ reference point are −62.3 and −125.8 ppm, respectively, for the axial and equatorial fluorines. For SeF_5Cl, the corresponding values taken from Figure 1 are −71.3 and −132.0 ppm. The only part of the spectrum of SeF_5Cl not identical with the SF_5Cl example is the appearance of the small satellite lines due to $^{77}Se-^{19}F$ coupling. The observed coupling constant of 629 Hz is furthermore comparable to selenium–fluorine coupling in compounds which contain a chlorine bonded to the selenium central atom as in SeOFCl, where a value of 647 Hz was reported.[14]

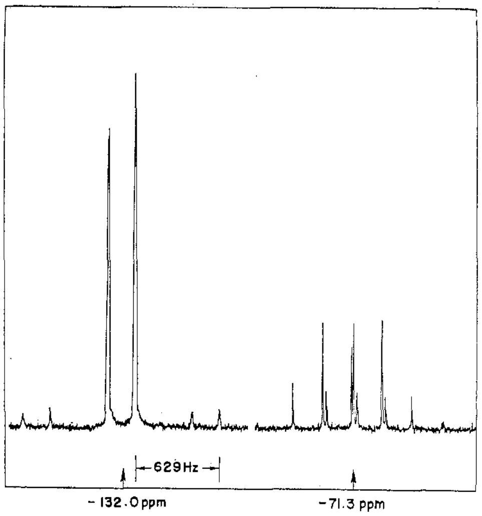

Figure 1.—The ^{19}F nmr spectrum of SeF_5Cl.

Acknowledgment.—The authors gratefully acknowledge support for this work by the Office of Naval Research, Power Branch. We are also indebted to Drs. D. Pilipovich and K. O. Christe for helpful discussion.

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A New Cyclotriphosphazene from a Ring-Closure Reaction

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Received June 4, 1971

Considerable work has been done on exchange reactions involving tris(dimethylamino)phosphine with various primary[1] and secondary[2,3] amines ("transamination"), amides,[2,3] imines,[4] amino alcohols,[5] and carbonyl compounds.[3] Iminobis(aminodiphenylphosphonium) chloride,[6] $[(C_6H_5)_2P(NH_2)\text{=}N\text{=}P(NH_2)(C_6H_5)_2]^+Cl^-$ (I), and the corresponding free phosphinimine (II) offer a preformed five-membered chain for a ring-closure reaction as well as amino groups, and therefore we have investigated the reaction between $P[N(CH_3)_2]_3$ and II.

Experimental Section

Materials.—All solvents used were Spectrograde quality and practically water free. Compound I was made by ammonolysis of $(C_6H_5)_2PCl_3$ with dry ammonia[6] followed by dehydrochlorination to the corresponding phosphinimine (II) with a freshly prepared sodium methoxide solution.[7] Melting point and nmr spectra agreed with the published data. $P[N(CH_3)_2]_3$ was also prepared following a literature procedure.[8] All operations were carried out under nitrogen.

Analyses.—Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained in sealed glass capillaries on a Mel-Temp melting point block and are uncorrected.

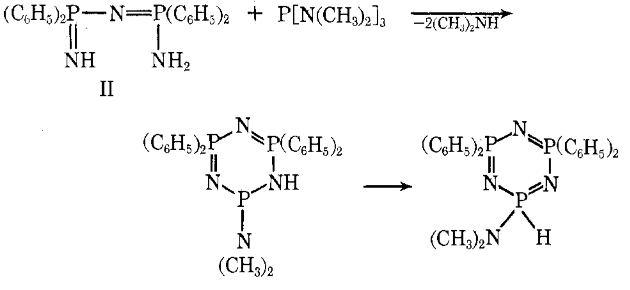
Spectra.—Infrared (ir) spectra were recorded in solution (CCl_4–CS_2) with a Beckman IR-10 spectrometer. The ^1H nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ solution, using TMS as an internal standard. The ^{31}P nmr spectra were run with a Varian XL-100-15 spectrometer, operating at a frequency of 40.55 MHz and locked onto the deuterium resonance of D_2O. The samples were contained in 5-mm o.d. tubes (solvent CH_2Cl_2) which were concentrically inserted, using Teflon spacers, into a thin-wall 12-mm o.d. tube containing the D_2O.

Reaction of II with $P[N(CH_3)_2]_3$.—In a typical reaction, 10.0 g of II and 3.92 g of $P[N(CH_3)_2]_3$ in 40 ml of bromobenzene were heated slowly to reflux. The reaction started at *ca.* 120° and the split-off dimethylamine was collected in a −78° trap. After 4 hr, 2.17 g of $(CH_3)_2NH$ (96% of theory) was collected; the yellow solution was concentrated to about 20 ml and chilled to 0°, and the unreacted II was filtered off. Evaporation to dryness yielded a heavy oil (III); addition of acetonitrile gave, upon standing, white crystals which were recrystallized from acetonitrile; yield 8.05 g (61% of theory based upon the quantity of II consumed); dec pt *ca.* 110°. *Anal.* Calcd for $C_{28}H_{30}N_5P_3$: C, 63.51; H, 5.71; N, 13.23; P, 17.55. Found: C, 63.07; H, 5.53; N, 13.29; P, 17.70. Nmr: proton spectrum: $\tau_{C_6H_5}$ 2.08, 2.30, 2.62 (complex multiplet); τ_{PH} 2.45 (d); τ_{CH_3} 7.48 (d); τ_{CH_3CN} 8.22; $^3J_{PNCH}$ = 13.5 Hz, $^1J_{PH}$ = 611 Hz; phosphorus spectrum: $\delta_{PC_6H_5}$ −14.1 ppm (s); $\delta_{PN(CH_3)_2}$ −7.5 (d, d); ratio $P_{C_6H_5}:P_{N(CH_3)_2} = 2:1$ (calcd 2:1).

The above compound represents an acetonitrile adduct of $(C_6H_5)_4P_3N_3H[N(CH_3)_2]$. This adduct may be destroyed by recrystallization from benzene to give the unsolvated compound; mp 179–181°. *Anal.* Calcd for $C_{26}H_{27}N_4P_3$: C, 63.93; H, 5.57; N, 11.47; P, 19.02. Found: C, 63.42, H, 5.04; N, 11.56; P, 19.28. Ir: 3080 (s, sh), 3060 (vs), 3020 (m), 2940–2920 (s), 2890 (m), 2840 (m), 2800 (m), 2370/2340 (s), 1480 (m), 1440 (s), 1200–1160 (vs), 1120 (vs), 1070 (s), 1030 (s), 970 (vs), 855 (s), 715 (s), 690 (vs), 605 cm^{-1} (m). Nmr: as above but without the acetonitrile peak.

Results and Discussion

As in the case of the reaction of $RP(OC_6H_5)_2$ with II,[9] the isolated product is not the phospha(III)diphospha(V)triazine derivative IV but its tautomer V, a PH phosphazene. Evidence for the ring closure is given by the infrared spectrum which shows at 1200–1160 and at 1120 cm^{-1} the characteristic P=N bands. Evidence for V is provided by the insensitivity of the compound to oxygen, by the ir frequencies at 2370 and 2340 cm^{-1} (ν_{PH} vibrations), and by the high coupling constant J_{PH} = 611 Hz. The observed ^{31}P chemical shifts are also in accord with this structure.



II

IV V

It should be noted that in one experiment out of nine carried out, the ^{31}P nmr spectrum of a CH_2Cl_2 solution of III was found to exhibit only two peaks of δ_P −63.0 ppm and δ_P −40.9 ppm (ratio: calcd, 1:2; found, 1:2.1), the former being split into a multiplet (theoretical septet) with $^3J_{PNCH}$ = 14.0 Hz. This experiment could, however, not be repeated, but it seems we have here observed form IV as the sole product which then transformed into V upon crystallization.

It is further interesting to note that V gives an adduct with acetonitrile as do the related phosphazatriene derivatives $(C_6H_5)_4P_3N_3Cl_2$[10] and $[(C_6H_5)_2PN]_3$[11] (the latter with *sym*-$C_2H_2Cl_4$); no such adduct was reported for the previously mentioned[9] PH phosphazenes.

Acknowledgment.—We wish to thank the National Science Foundation (Grant No. GP-9525) for partial financial support and Dr. A. D. F. Toy of the Stauffer Chemical Co. for a generous gift of diphenylphosphinous chloride.

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The Synthesis of Tetrafluorodiphosphine–Bis(borane(3))

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Received June 30, 1971

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