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Trimethylsilyl Esters of Phosphorus Acids. III. Esters of Difluoro- and Bis(trifluoromethyl)phosphinous and -thiophosphinous Acids

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The esters $R_2PESi(CH_3)_3$ (R = F, E = O; R = CF_3, E = O, S) have been prepared using one or more of four synthetic routes. $(CF_3)_2PSSi(CH_3)_3$ is the first known example of a P^{III}-S-Si bridged compound, but the analogous difluoro ester $F_2PSSi(CH_3)_3$ appears to be thermally unstable at 25°. Attempted syntheses of the P(V) isomers $R_2P(E)Si(CH_3)_3$ gave only the P(III) forms, indicating that these systems are susceptible to anti-Arbuzov rearrangements. The difference in the stability and polarity between the P-O-Si and P-S-Si bridge units was demonstrated by the reactions of the esters with HCl and $(CH_3)_2NH$. At least three different reactions of the esters with dimethylamine were observed: cleavage at the E-Si bond with or without concomitant subsequent reaction of $(CH_3)_3SiN(CH_3)_2$ with the ionic product R_2PE^- and, in the case of $(CF_3)_2POSi(CH_3)_3$, displacement of CF_3H to yield $CF_3[N(CH_3)_2]POSi(CH_3)_3$. The latter phosphine showed a temperature-dependent nmr spectrum consistent with conformational isomerism of the $N(CH_3)_2$ group.

Introduction

Whereas the P-O-Si structural unit is well known[1a] in compounds of both ter- and pentavalent phosphorus, the P-S-Si unit has been studied only for a small number of derivatives $R_2P(S)SSi(CH_3)_3$ of phosphorus(V).[1] The previous papers in this series[2,3] described the preparations and chemical and spectroscopic properties of the trimethylsilyl esters of the phosphinic acids $R_2P(E)E'H$ (R = F, CF_3; E, E' = O, S). We now report the syntheses and properties of the related esters $R_2PESi(CH_3)_3$ (I, R = F, E = O; III, R = CF_3, E = O; IV, R = CF_3, E = S) of the corresponding phosphinous acids. The synthesis and spectra of ester III have previously been reported[4] though few chemical properties were described.

Esters I, III, and IV were successfully synthesized using preparative routes similar to those used[3] in the preparation of the phosphorus(V) analogs. Attempts to prepare the P^V-Si bonded systems $R_2P(E)Si(CH_3)_3$ gave instead I, IV or $(CF_3)_2P(O)OSi(CH_3)_3$,[3] while attempted syntheses of the ester $F_2PSSi(CH_3)_3$ (II) were unsuccessful, probably due to its thermal instability.

Experimental Section

The reactions were carried out on a 0.2–5 m*M* scale in evacuated sealed tubes in the absence of solvent, and products were separated and purified where possible by fractional condensation *in vacuo*. In cases where separation could not be achieved, the compositions of the mixtures were determined by analysis of their nmr spectra. In some cases, however, the compositions could not be determined accurately due to the close similarity of the ^1H nmr spectra of the trimethylsilyl compounds. The reactions of phosphorus(III) halides with $[(CH_3)_3Si]_2O$ and $[(CH_3)_3Si]_2S$ are summarized in Table I.

Infrared and nmr spectroscopy and mass spectrometry were used for routine identification of products and characterization of new compounds. Infrared spectra were recorded on Perkin-Elmer 337, 457, and 421 and Beckmann IR-11 spectrometers, nmr spectra on Varian A-56/60 and HA-100 instruments, and mass spectra on an AEI MS-9 spectrometer. The nmr spectra were recorded using 10–30% solutions in $CFCl_3$ (liquids and gases) and water or CD_3CN (ionic products). ^1H chemical shifts were measured relative to a 5% solution of tetramethylsilane (TMS) in CCl_3F contained in a capillary as an external reference; ^{19}F shifts were measured relative to internal CCl_3F as solvent or external CCl_3F contained in a capillary when other solvents were employed. ^{31}P shifts were measured relative to an external capillary of P_4O_6. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Commercial samples of $[(CH_3)_3Si]_2O$, $[(CH_3)_3Si]_2NH$, HCl, $(CH_3)_2NH$, and PF_3 were used without further purification except for a single fractional condensation under vacuum to remove possible gross impurities. Literature methods were used to synthesize $(F_2P)_2O$,[5] SPF_2H,[6] OPF_2H,[6] $(CF_3)_2PF$,[7] $(CF_3)_2PCl$,[8] $(CF_3)_2P(S)Cl$,[9] $(CF_3)_2P(O)Cl$,[10] $[(CF_3)_2P]_2S$,[11] $[(CF_3)_2P]_2O$,[12] and $[(CH_3)_3Si]_2S$.[13] $(F_2P)_2S$ was prepared[14] from PF_2Br and $[(n\text{-}C_4H_9)_3Sn]_2S$. A sample of $Hg[Si(CH_3)_3]_2$ was kindly donated by Dr. D. Roark. $(CH_3)_3SiN(CH_3)_2$ was made by the reaction of $(CH_3)_3SiCl$ with 2 molar equiv of $(CH_3)_2NH$ and condensed *in vacuo* at −84°.

Trimethylsilyl Difluorophosphinite (I). (i) Hexamethyldisiloxane (0.327 g, 2.02 mmol) and μ-oxo-bis(difluorophosphine)[5] (0.411 g, 2.67 mmol) were heated to 60° for 16 days, an orange-brown solid gradually forming on the walls of the reaction tube. Separation of the volatile products under vacuum gave a mixture (0.129 g) of I, $(CH_3)_3SiF$, and unreacted $(PF_2)_2O$, trapped at −196°, and a mixture (0.496 g) of I and a little unreacted $[(CH_3)_3Si]_2O$, trapped at −95°. The latter was removed from the −95° fraction by slow redistillation through a −84° trap; I (0.419 g, 2.65 mmol, 66%) passed this trap and was collected at −196°. Mass spectrum: calcd for $F_2POSi(CH_3)_3$, *m/e* 158.0128 amu; found, *m/e* 158.0124 amu.

(ii) Hexamethyldisilazane (0.0657 g, 0.408 mmol) and OPF_2H[6] (0.092 g, 1.09 mmol, the purity of which was confirmed by nmr) reacted immediately on warming from −196° to room temperature, with rapid formation of a white solid. After 5 min the volatile products were removed and subjected to vacuum fractionation to yield I (0.089 g, 0.57 mmol, 78%, the purity of which was established as >98% by nmr) which was collected at −84°. Other products were PF_3 and $(CH_3)_3SiF$ collected at −196° and a small amount of impure I collected at −84°. The residual solid was insoluble in common solvents and decomposed in water.

A second reaction of hexamethyldisilazane (0.075 g, 0.465 mmol) and OPF_2H (0.135 g, 1.09 mmol), which contained a substantial amount of $OPF_2N(CH_3)_2$ impurity because of the difficulty of separating OPF_2H from this starting material, proceeded similarly to

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(13) E. W. Abel, *J. Chem. Soc.*, 4933 (1961).
(14) R. W. Rudolph, private communication.

Table I. Reactions of Phosphorus(III) Halides with $[(CH_3)_3Si]_2O$ and $[(CH_3)_3Si]_2S$

Conditions	Starting reactants mmol	Ester mmol (%)	Other products mmol (%)	Recovered reactant mmol (%)
160°, 3 days	PF_3 $[(CH_3)_3Si]_2O$ 1.22 0.88		$(CH_3)_3SiF$ trace	PF_3 $[(CH_3)_3Si]_2O$ 1.19 (98) 0.83 (94)
25°, 16 hr	PF_3 $[(CH_3)_3Si]_2S$ 4.19 3.46		$(CH_3)_3SiF$ yellow solid 0.10 (3)	PF_3 $[(CH_3)_3Si]_2S$ 4.05 (97) 3.05 (88)
100°, 4 days	$(CF_3)_2PF$ $[(CH_3)_3Si]_2O$ 0.46 0.45	$(CF_3)_2POSi(CH_3)_3$ 0.42 (93)	$(CH_3)_3SiF$ $[(CF_3)_2P]_2O$ 0.47 (104) trace	$(CF_3)_2PF$ 0.02 (4)
110°, 4 days	$(CF_3)_2PCl$ $[(CH_3)_3Si]_2O$ 1.62 1.25	$(CF_3)_2POSi(CH_3)_3$ [a]	$(CH_3)_3SiCl$ [a]	$(CF_3)_2PCl$ [b] $[(CH_3)_3Si]_2O$ [c] 1.38 (85)
160°, 8 days	$(CF_3)_2PCl$ $[(CH_3)_3Si]_2O$ 1.04 0.93	$(CF_3)_2POSi(CH_3)_3$ 0.07 (8)	$(CH_3)_3SiCl$ [a]	$(CF_3)_2PCl$ [c] $[(CH_3)_3Si]_2O$ 0.85 (91)
100°, 7 days	$(CF_3)_2PCl$ $[(CH_3)_3Si]_2O$ 2.86 2.68	$(CF_3)_2PSSi(CH_3)_3$ 2.20 (82)	$(CH_3)_3SiCl$ $[(CF_3)_2P]_2S$ 2.87 (100) 0.30 (12)	

[a] Minor component in mixture. [b] This amount isolated pure. More was present as a minor component in a mixture. [c] Major component in mixture.

yield I contaminated with unreacted $OPF_2N(CH_3)_2$ which could not be separated easily.

Attempted Syntheses of II, Trimethylsilyl Difluorothiophosphinite. (i) Hexamethyldisilthiane[13] (0.616 g, 3.46 mmol) and PF_3 (0.369 g, 4.19 mmol) were allowed to react at room temperature for 16 hr, small amounts of yellow solid being produced. The volatile products consisted of PF_3 (0.357 g, 4.06 mmol, 97%), $(CH_3)_3SiF$ (0.009 g, 0.10 mmol, 3%), and $[(CH_3)_3Si]_2S$ (0.544 g, 3.05 mmol, 88%) while the yellow solid (20.9% S) remained in the reaction tube.

(ii) Hydrothiophosphoryl difluoride[6] (0.113 g, 1.11 mmol) reacted immediately with hexamethyldisilazane (0.059 g, 0.37 mmol) on warming from −196° to room temperature. The white solid and colorless liquid formed were rapidly converted to a mixture of white and yellow solids. After approximately 1 min of reaction time the products were separated *in vacuo* yielding PF_3 (0.0025 g, 0.028 mmol), which was trapped at −196°, a mixture of $(CH_3)_3SiF$ (0.0485 g, 0.53 mmol, 72%) and SPF_2H (0.0495 g, 0.485 mmol, 44% recovery) which was trapped at −132°, a mixture (0.019 g) of $(CH_3)_3Si$ groups and fluorine, which was trapped at −84°, and a colorless liquid which was trapped at −45°. This latter material rapidly decomposed (less than 1 min) during attempted spectral analysis to give $(CH_3)_3SiF$ (0.008 g, 0.09 mmol, 12%) and a yellow solid.

Yields are based on reactions 3 and 6 (*vide infra*).

(iii) Hexamethyldisilthiane (0.111 g, 0.625 mmol) and μ-thiobis(difluorophosphine)[14] (0.117 g, 0.69 mmol) reacted at room temperature during 30 min to give a colorless liquid and a considerable amount of yellow solid. Separation of the resultant volatile products gave PF_3 (0.0205 g, 0.23 mmol) which was trapped at −196°, a mixture of $(CH_3)_3SiF$ (0.0775 g, 0.84 mmol, 67% based on reaction 3) and SPF_2H (0.048 g, 0.47 mmol) which was trapped at −132°, and an unidentified compound (0.037 g) which was trapped at −84°. The yellow solid analyzed approximately as $(FPS)_n$. *Anal.* Calcd: F, 23.2; P, 37.7; S, 39.1. Found: F, 24.2; P, 38.6; S, 40.6.

Trimethylsilyl Bis(trifluoromethyl)phosphinite (III). (i) After heating to 100° for 4 days, $(CF_3)_2PF$[7] (0.086 g, 0.46 mmol) and $[(CH_3)_3Si]_2O$ (0.073 g, 0.45 mmol) gave unreacted $(CF_3)_2PF$ (0.003 g, 0.015 mmol, 3%) which was collected at −132° and III (0.108 g, 0.42 mmol, 93%, containing a trace of $[(CF_3)_2P]_2O$[12]) which was collected at −84°.

(ii) Hexamethyldisiloxane (0.21 g, 1.04 mmol) and $(CF_3)_2PCl$ (0.15 g, 0.93 mmol) were heated in a sealed tube at 160° for 7 days. Vacuum fractionation of the volatile products gave, as the least volatile fraction, a mixture of unreacted $[(CH_3)_3Si]_2O$ and $(CF_3)_2POSi(CH_3)_3$ (0.21 g; molar ratio 8.5:1 by nmr) and, as the most volatile fraction, a mixture (0.20 g) of unreacted $(CF_3)_2PCl$ with a small amount of $(CH_3)_3SiCl$. Further separation was not attempted in view of the low conversion. A similar experiment involving reaction of approximately equimolar proportions of $(CF_3)_2PCl$ and $[(CH_3)_3Si]_2O$ at 110° for 4 days gave at least 85% recovery of unchanged $(CF_3)_2PCl$ plus mixtures of $(CF_3)_2POSi(CH_3)_3$ and $[(CH_3)_3Si]_2O$ which were not separated.

On neutral aqueous hydrolysis, III (0.054 g, 0.21 mmol) gave $[(CH_3)_3Si]_2O$ (0.016 g, 0.10 mmol, 94%) and CF_3H (0.014 g, 0.20 mmol, 96%) while the $CF_3P(H)O_2^-$ ion, identified by nmr spectroscopy,[15] remained in solution. Alkaline hydrolysis of III (0.066 g, 0.26 mmol), using 1 ml of 20% NaOH solution, gave $[(CH_3)_3Si]_2O$ (0.019 g, 0.12 mmol, 92%) and CF_3H (0.037 g, 0.53 mmol, 103%). The resultant solution gave no ^{19}F nmr signal.

(15) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, **10**, 2720 (1971).

Trimethylsilyl Bis(trifluoromethyl)thiophosphinite (IV). (i) A mixture of $(CF_3)_2PCl$[8] (0.585 g, 2.86 mmol) and $[(CH_3)_3Si]_2S$ (0.477 g, 2.68 mmol) was heated to 100° for 7 days. Separation of the volatile products using a LeRoy still[16] gave $(CH_3)_3SiCl$ (0.310 g, 2.87 mmol, 100% based on reactions 4 and 5 (*vide infra*)), IV (0.602 g, 2.20 mmol, 82%), $[(CF_3)_2P]_2S$[11] (0.111 g, 0.30 mmol, 21%), and an unseparated mixture (0.024 g) of $[(CF_3)_2P]_2S$ and $(CH_3)_3SiCl$.

(ii) Hexamethyldisilthiane (0.057 g, 0.32 mmol) and $[(CF_3)_2P]_2S$[11] (0.107 g, 0.29 mmol) were heated to 100° for 16 hr. The volatile products were separated *in vacuo* yielding a mixture of IV and a little unreacted $[(CH_3)_3Si]_2S$ (0.060 g), which was trapped at −23°, and pure IV (0.100 g, 0.365 mmol, 63%) which was trapped at −45°. Traces of IV and $(CH_3)_3SiF$ passed this trap.

(iii) When a mixture of $(CF_3)_2P(S)Cl$[9] (0.123 g, 0.52 mmol) and $Hg[Si(CH_3)_3]_2$ (0.132 g, 0.38 mmol) was allowed to warm from −196° to room temperature, mercury was quickly deposited. After 12 hr, separation of the volatile products gave $(CF_3)_2PCl$ (0.008 g, 0.04 mmol, 10%, containing a little $(CH_3)_3SiH$) which was collected at −196°, a mixture (0.124 g) of $(CH_3)_3SiCl$ and $(CF_3)_2P(S)Cl$ which was collected at −116°, and IV (0.039 g, 0.14 mmol, 37%) which was collected at −45°. The residue was a mixture of mercury and an unidentified gray powder.

On neutral aqueous hydrolysis, IV (0.075 g, 0.27 mmol) gave $[(CH_3)_3Si]_2O$ (0.024 g, 0.15 mmol, 108%) which was collected at −84° and a mixture (0.032 g) of CF_3H and H_2S which was collected at −196°, while the $CF_3P(H)O_2^-$ ion[15] remained in solution. Treatment of the −196° fraction with lead acetate solution gave pure CF_3H (0.019 g, 0.27 mmol, 100%). Alkaline hydrolysis of IV (0.102 g, 0.37 mmol) gave $[(CH_3)_3Si]_2O$ (0.029 g, 0.18 mmol, 96%) and CF_3H (0.049 g, 0.70 mmol, 94%) as volatile products. The remaining solution, on treatment with aqueous lead acetate, gave white and black precipitates of $PbHPO_3$ and PbS, respectively.

Chemical Reactions. (a) Thermal Behavior. Ester I (0.184 g, 1.16 mmol) decomposed readily on heating to 220°, forming an orange-brown solid after an apparent induction period of about 1 day. After 7 days the volatile products were separated, yielding a small amount of a very volatile gas which passed −196°, PF_3 (0.020 g, 0.23 mmol, containing a little OPF_3) which was trapped at −196°, $(CH_3)_3SiF$ (0.0475 g, 0.52 mmol, 44%) which was trapped at −116°, and a mixture (0.071 g) of $[(CH_3)_3Si]_2O$ and an unidentified compound (ir: 1360, 1190, 945, 500 cm^{-1}; ^{19}F nmr: ϕ 74.0 ppm (singlet)) which was trapped at −95°. The involatile solid (18.5% Si) was shown to contain no methylsilyl or fluorophosphorus fragments by ir and mass spectroscopy.

Ester III (0.047 g, 0.18 mmol) was recovered almost quantitatively (0.046 g, 0.18 mmol) after 6 days at 195°.

Ester IV (0.081 g, 0.29 mmol), after 9 days at 195°, was largely recovered. Small amounts of several products, including $[(CF_3)_2P]_2S$, $(CH_3)_3SiF$, and at least three unidentified compounds were however detected by ^1H and ^{19}F nmr spectroscopy, and the glass wall of the reaction tube had been rendered opaque.

(b) Reactions with Anhydrous Hydrogen Chloride. Hydrogen chloride (0.022 g, 0.60 mmol) and I (0.104 g, 0.66 mmol) were allowed to react for 9 days at room temperature. The volatile products (0.101 g) contained PF_3, $(CH_3)_3SiF$, $(CH_3)_3SiCl$, $[(CH_3)_3Si]_2O$, and at least one unidentified compound (detected by ir spectroscopy), and a yellow residue remained in the reaction tube.

When III (0.060 g, 0.23 mmol) was treated with excess HCl for 7 days at room temperature, it was largely recovered unchanged

(16) D. J. LeRoy, *Can. J. Res., Sect. B*, **28**, 492 (1950).

(0.047 g, 0.18 mmol, 78%), but small amounts of $(CF_3)_2PCl$, $(CF_3)_2POH$, $[(CH_3)_3Si]_2O$, and $(CH_3)_3SiCl$ were identified as decomposition products by nmr spectroscopy.

Ester IV (0.059 g, 0.22 mmol) and HCl (0.013 g, 0.36 mmol), after 8 days at room temperature, gave unreacted HCl (0.004 g, 0.11 mmol), a mixture of $(CH_3)_3SiCl$ and $(CF_3)_2PSH$ (0.065 g, in the ratio 1:1.2 by nmr spectroscopy), and unreacted IV (0.001 g).

(c) **Reactions with Dimethylamine.** A mixture of I (0.121 g, 0.77 mmol) and dimethylamine (0.067 g, 1.50 mmol) reacted immediately on warming from $-196°$, the white solid which was first formed changing to an oil at room temperature. After 1 day at room temperature the volatile products were separated, yielding $(CH_3)_3SiF$ (0.0695 g, 0.755 mmol, 101%) and $F_2PN(CH_3)_2$ (0.018 g, 0.16 mmol). The involatile oil, dissolved in CD_3CN, gave the following nmr signals: ^1H: τ 7.54 (singlet), 7.51 (doublet) (J = 11.3 Hz); ^{19}F (ϕ *vs.* CCl_3F): 51.4 ppm (doublet of doublets) (J = 963 Hz, J = 129 Hz), 56.7 ppm (doublet of doublets of doublets) (J = 818 Hz, J = 127 Hz, J = 43 Hz).

Dimethylamine (0.052 g, 1.15 mmol) and III (0.062 g, 0.24 mmol) were allowed to react for 5.5 days at room temperature. The volatile products were then separated to give trimethylsilyl trifluoromethyl(dimethylamino)phosphinate, V (0.052 g, 0.23 mmol, 96%, containing a trace of $(CH_3)_3SiN(CH_3)_2$), which was collected at $-84°$, excess $(CH_3)_2NH$ (0.040 g, 0.89 mmol) collected at $-132°$, and CF_3H (0.015 g, 0.21 mmol, 89%) which was collected at $-196°$. The small amount of white solid remaining in the reaction tube was identified as $(CH_3)_2NH_2^+(CF_3)_2PO^-$ by treatment with excess HCl, whereupon $(CF_3)_2POH$ (0.001 g, 0.005 mmol, 2%) was evolved.[12] Alkaline hydrolysis of V (0.049 g, 0.21 mmol) gave a mixture (0.018 g) of $[(CH_3)_3Si]_2O$ and $(CH_3)_2NH$, which was collected at $-84°$, and CF_3H (0.015 g, 0.21 mmol, 100%) which was collected at $-196°$, while the residual solution gave no ^{19}F signal.

Ester IV (0.067 g, 0.24 mmol) and $(CH_3)_2NH$ (0.039 g, 0.87 mmol), after 7 days at room temperature, gave as volatile products $(CH_3)_3SiN(CH_3)_2$ (0.028 g, 0.24 mmol, 100%) and excess $(CH_3)_2NH$ (0.017 g, 0.38 mmol). The residual off-white solid was identified as $(CH_3)_2NH_2^+(CF_3)_2PS^-$ by treatment with excess HCl whereupon $(CF_3)_2PSH$ (0.044 g, 0.22 mmol, 92%) was evolved.[11a]

(d) **Reactions with Bis(trifluoromethyl)phosphorus(III) Halides.** When III (0.072 g, 0.28 mmol) and $(CF_3)_2PF$ (0.044 g, 0.23 mmol) were heated to 160° for 6 days, both reactants were recovered almost quantitatively. A very small amount of $(CH_3)_3SiF$ was produced, but the formation of $[(CF_3)_2P]_2O$ could not be detected by either ir or ^{19}F nmr spectroscopy.

A mixture of IV (0.075 g, 0.27 mmol) and $(CF_3)_2PCl$ (0.077 g, 0.38 mmol) was heated to 100° for 7 days. The volatile products were then separated, yielding $[(CF_3)_2P]_2S$ (0.059 g, 0.16 mmol, 59%), $(CH_3)_3SiCl$ (0.017 g, 0.155 mmol, 57%), IV (0.0215 g, 0.08 mmol, 30%), $(CF_3)_2PCl$ (0.044 g, 0.21 mmol), and a trace of $(CH_3)_3SiF$, while a little white solid remained in the reaction tube.

Reaction of $(CF_3)_2P(O)Cl$ with $Hg[Si(CH_3)_3]_2$. A mixture of $(CF_3)_2P(O)Cl$[10] (0.119 g, 0.54 mmol) and $Hg[Si(CH_3)_3]_2$ (0.060 g, 0.17 mmol) was allowed to warm slowly (12 hr) from $-84°$ to room temperature. Separation of the volatile products *in vacuo* then gave a mixture (0.003 g) of $(CH_3)_3SiH$ and a little $(CF_3)_2PCl$, which was collected at $-196°$, a mixture (0.104 g) of $(CF_3)_2P(O)Cl$ and $(CH_3)_3SiCl$, which was collected at $-116°$, and $(CF_3)_2P(O)OSi(CH_3)_3$ [3] (0.018 g, 0.065 mmol, 38%) which was collected at $-45°$. The residue consisted of mercury and an unidentified gray powder.

Reaction of the Adduct $(CH_3)_2NH\cdot OPF_2H$ with $(CH_3)_3SiN(CH_3)_2$. The adduct $(CH_3)_2NH\cdot OPF_2H$, prepared from OPF_2H[6] (0.083 g, 0.96 mmol) and $(CH_3)_2NH$ (0.0405 g, 0.93 mmol), reacted with $(CH_3)_3SiN(CH_3)_2$ (0.098 g, 0.84 mmol) at room temperature. After 5 min $(CH_3)_3SiF$ (0.066 g, 0.72 mmol, 86%) had been produced and the residual oil, dissolved in CD_3CN, showed the following nmr signals: ^1H: τ 7.54 (singlet), 7.51 (doublet) (J = 11.3 Hz); ^{19}F (ϕ *vs.* CCl_3F): 51.4 ppm (doublet of doublets) (J = 963 Hz, J = 129 Hz).

Results and Discussion

Synthetic Methods. Addition of hexamethyldisiloxane to the anhydride of the appropriate acid (eq 1), a proven synthetic method for obtaining the esters $R_2P(S)OSi(CH_3)_3$ (R = F, CF_3)[3] and $(CF_3)_2POSi(CH_3)_3$ (III),[4] has been successfully

$$(R_2P)_2E + [(CH_3)_3Si]_2E \rightarrow 2R_2PESi(CH_3)_3 \qquad (1)$$

I, R = F, E = O (66%)
IV, R = CF_3, E = S (63%)

utilized to obtain the new compounds $F_2POSi(CH_3)_3$ (I) and $(CF_3)_2PSSi(CH_3)_3$ (IV).

Ester III[4] and related compounds are stable to disproportionation in the manner of reversing eq 1. It has been suggested[4] that this stability is gained through variety in bonding of oxygen, since the acquisition of a better share of the oxygen π electrons by the better π acceptor, whether phosphorus or silicon, results in an increase in the total π-bond energy. Since thermal decomposition of esters I and IV by the reverse of reaction 1 (*vide infra*) occurs only at temperatures considerably higher than required for the syntheses, these three esters appear to behave similarly as might be expected.

A further test of this suggestion of stability from bond variety is provided by the reaction of $(CF_3)_2POP(CF_3)_2$ with F_2POPF_2 (eq 2) which gives an equilibrium mixture containing $(CF_3)_2POPF_2$ in yields[17] higher than predicted statistically.

$$F_2POPF_2 + (CF_3)_2POP(CF_3)_2 \rightleftarrows 2(CF_3)_2POPF_2 \qquad (2)$$

Considering the relative σ- and π-acceptor properties of the CF_3 group as compared to the σ-acceptor and π-donor properties of F[18-20] suggests that we can reasonably attribute the stabilization of the unsymmetrical compound to increased π bonding in the P–O–P structural unit when unsymmetrically substituted. Present data however do not permit exclusion of increased σ bonding in the unsymmetrical P–O–P structural unit as a reason for the observed effect.

Attempts to prepare $F_2PSSi(CH_3)_3$ (II) by reaction 1 (R = F, E = S) at room temperature were unsuccessful, the only products being $(CH_3)_3SiF$ (67%), PF_3, SPF_2H, and a yellow, apparently polymeric solid which analyzed approximately as $(FPS)_n$. Thermal decomposition of the initial product II (eq 3) would likely afford $(CH_3)_3SiF$, while PF_3 could be

$$F_2PSSi(CH_3)_3 \rightarrow (CH_3)_3SiF + (1/n)(FPS)_n \qquad (3)$$

formed by decomposition of either the solid $(FPS)_n$ or the unstable reactant $(F_2P)_2S$. The origin of SPF_2H is not clear and may suggest the presence of a very complex decomposition route involving CH_3 groups. The alternative possibility of inadvertent hydrolysis arising because of the instability of the $(F_2P)_2S$ and the thermal instability of the product suggested below cannot be excluded in spite of the considerable precautions taken to avoid such complications; however the quantity of SPF_2H obtained and the absence of P=O compounds suggests that hydrolysis is an unlikely reason for this result.

The esters $(CF_3)_2PESi(CH_3)_3$ were also prepared in high yields by the reaction (eq 4) of appropriate phosphorus(III) halides with $[(CH_3)_3Si]_2E$ at 100°. Results are summarized in Table I.

$$(CF_3)_2PX + [(CH_3)_3Si]_2E \rightarrow (CF_3)_2PESi(CH_3)_3 + (CH_3)_3SiX \qquad (4)$$

III, X = F, E = O (93%)
IV, X = Cl, E = S (82%)

Though esters III and IV were successfully synthesized in this manner from $(CF_3)_2PF$ and $(CF_3)_2PCl$, respectively, we were able to obtain only moderate to low yields of III from the reportedly quantitative[4] reaction of $(CF_3)_2PCl$ with $[(CH_3)_3Si]_2O$ at either 110 or 160°; most of the reactants were recovered unchanged. The presence of catalytic impurities in the former case[4] may account for the difference

(17) R. G. Cavell, A. R. Sanger, and A. J. Tomlinson, in preparation.
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(19) M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 91, 291 (1969).
(20) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 768 (1972).

in results, a view which is supported by the report of significant catalytic activity of adsorbed water in exchange reactions of phosphorus halides.[21] Successful preparation from the fluoride can be understood as a result of a larger difference in bond energy between reactants and products in the fluoro system relative to the chloro system.

The analogous reaction of PF_3 with $[(CH_3)_3Si]_2O$ at 160° gave no ester I while PF_3 and $[(CH_3)_3Si]_2S$ at 25° gave small amounts of $(CH_3)_3SiF$ but no ester II. The mechanism proposed[2] for the formation[2,3] of the P(V) esters $R_2P(E)E'Si(CH_3)_3$ from $R_2P(E)X$ involves addition of $[(CH_3)_3Si]_2E'$ to the phosphoryl compound and subsequent elimination of $(CH_3)_3SiX$. The relative ease of formation of these pentavalent esters is exemplified by the virtually quantitative production of $F_2P(O)OSi(CH_3)_3$ from OPF_3 and $[(CH_3)_3Si]_2O$ at room temperature.[3] The relative difficulty in preparing the P(III) esters by this route is probably due to the lack of an available site for a facile addition mechanism suggesting that reaction 4 is probably an SN2 type substitution reaction.

A substantial amount of $[(CF_3)_2P]_2S$ was formed as a by-product in the synthesis of IV when excess $(CF_3)_2PCl$ was used and was shown to result from reaction 5 by separate

$$(CF_3)_2PSSi(CH_3)_3 + (CF_3)_2PCl \rightarrow [(CF_3)_2P]_2S + (CH_3)_3SiCl \quad (5)$$

experiment. The reaction was not complete in this case under the conditions used and there was evidence for decomposition. In contrast III reacted with $(CF_3)_2PF$ to give only trace amounts of $(CH_3)_3SiF$ even at 160°. Furthermore very little of the by-product $[(CF_3)_2P]_2O$ was produced in the synthesis of III.

The hydrides EPF_2H react readily with hexamethyldisilazane as if the hydrogen were acidic. Good yields of ester I were obtained from OPF_2H according to eq 6 (which is

$$3OPF_2H + [(CH_3)_3Si]_2NH \rightarrow 2F_2POSi(CH_3)_3 + NH_4^+OPF_2^- \quad (6)$$

idealized because either the solid product did not dissolve or it decomposed and was therefore not characterized); however, the only volatile products afforded by SPF_2H were those expected from thermal decomposition of II, namely, $(CH_3)_3SiF$ and small amounts of PF_3, suggesting that our inability to obtain II arises from its thermal instability at ordinary temperatures. The fact that SPF_2H is a reagent in this case precludes a confirmation of the suggestion (*vide supra*) that this is a decomposition product of ester II.

This reaction (eq 6) may proceed *via* the P(III) isomer F_2POH although the P(V) structure has been established as the only detectable form[6] for these fluoro hydrides.

Ester IV was synthesized in moderate yield by the rapid reaction (eq 7) of $(CF_3)_2P(S)Cl$ with $Hg[Si(CH_3)_3]_2$ which

$$3(CF_3)_2P(S)Cl + 2Hg[Si(CH_3)_3]_2 \rightarrow 3(CF_3)_2PSSi(CH_3)_3 + (CH_3)_3SiCl + Hg + HgCl_2 \quad (7)$$

involves both substitution and reduction.

The mechanism of these reactions probably involves a multicenter intermediate, though an anti-Arbuzov rearrangement of the P(V) isomer $(CF_3)_2P(S)Si(CH_3)_3$ cannot be excluded (*vide infra*). The analogous reaction of $(CF_3)_2P(O)Cl$ gave no ester III, but instead the phosphinate ester $(CF_3)_2P(O)OSi(CH_3)_3$ was isolated in 38% yield. A secondary reaction of any ester III formed following eq 8 is a

$$(CF_3)_2POSi(CH_3)_3 + (CF_3)_2P(O)Cl \rightarrow (CF_3)_2P(O)OSi(CH_3)_3 + (CF_3)_2PCl \quad (8)$$

possible route to this product, though only very small amounts of $(CF_3)_2PCl$ were observed even with excess $(CF_3)_2P(O)Cl$ indicating that eq 8 is probably not an important process.

Spectroscopic Studies and Structures. The P(III) esters could exist in two isomeric forms, $R_2PESi(CH_3)_3$ and $R_2P(E)Si(CH_3)_3$, interconvertible by means of Arbuzov and anti-Arbuzov rearrangements.[12] The infrared spectra (Table II) and chemical behavior of esters I and III were entirely consistent with the trivalent phosphorus structure (E = O). The absence of any strong bands in the 1300-1500 cm^{-1} region of the infrared spectra precludes the existence of a phosphoryl system while strong bands at 1042 cm^{-1} (I) and 996 cm^{-1} (III) were present arising as expected[3] from stretching modes of the P-O-Si unit. Similarly the spectrum of IV showed no thiophosphoryl stretching mode in the 700-800-cm^{-1} region, whereas a band at 527 cm^{-1} is assignable as a stretching vibration of the P-S-Si system (*cf.*[3] $F_2P(S)SSi(CH_3)_3$, 525 cm^{-1}; $(CF_3)_2P(S)SSi(CH_3)_3$, 526 cm^{-1}). The ^{19}F nmr spectra (Table III) also supported the P(III) isomeric structures, with coupling constants $^1J_{FP}$(I) and $^2J_{FP}$(III, IV) in each case characteristic of coupling of fluorine to tervalent rather than pentavalent phosphorus.[22] The trimethylsilyl protons appeared as a singlet in the ^1H nmr spectra (τ 9.3-9.7). The ^1H chemical shift of these protons in III has been reported[4] as 7.38 ppm downfield from external TMS (τ 2.62), but as this value is substantially outside the typical range found in trimethylsilyl compounds, the present value is considered more reliable.

The reaction of $(CF_3)_2P(E)Cl$ and $Hg[Si(CH_3)_3]_2$ which might have been expected to give the P(V) isomers $(CF_3)_2P(E)Si(CH_3)_3$ gave only P-E-Si esters through apparently rather complex reactions. It is possible that the desired esters are originally formed followed by an anti-Arbuzov rearrangement to ester IV or subsequent reaction to the P(V) oxy ester; however the experiments provide no support for such a proposal. Ester I was prepared in good yield from the reaction of OPF_2H with $[(CH_3)_3Si]_2NH$, no evidence for the formation of $F_2P(O)Si(CH_3)_3$ being found, while the existence of the bis(trifluoromethyl) analog of OPF_2H in the form $(CF_3)_2POH$ and not $(CF_3)_2P(O)H$[12] precludes a synthesis of $(CF_3)_2P(O)Si(CH_3)_3$ by this route. It thus appears that both I and IV are stable in the P(III) rather than the P(V) form and are probably capable of formation by anti-Arbuzov rearrangements of the P(V) isomers. The ester III probably behaves similarly since it is inert to the Arbuzov reaction when heated with CH_3I.[4] This behavior is in marked contrast to that of the carbon analogs $(CF_3)_2POC(CH_3)_3$ and $(CF_3)_2P(O)C(CH_3)_3$ where both isomeric forms have been isolated, and the Arbuzov rearrangement of the former to the latter under catalysis by methyl iodide[12] or hydrogen chloride[23] has been demonstrated.

Thermal Stability. The esters I, III, and IV are of similar or slightly reduced thermal stability relative to the pentavalent esters $R_2P(E)E'Si(CH_3)_3$. In the pentavalent series of esters, compounds containing the P-O-Si structural unit were generally stable to 200° while those containing P-S-Si unit decomposed fairly readily above 100°.[2,3] Ester III was thermally stable to 200° and only at this temperature did ester I undergo decomposition, an apparent induction period being followed by formation of PF_3, $(CH_3)_3SiF$, $[(CH_3)_3Si]_2O$, and an orange-brown solid. The products indicate that two decomposition processes occur (eq 9 and 10), with

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Table II. Infrared Spectral Data[a] for $R_2PESi(CH_3)_3$ (I, III, IV) and $CF_3P[OSi(CH_3)_3]N(CH_3)_2$ (V)

$F_2POSi(CH_3)_3$ I	$(CF_3)_2POSi(CH_3)_3$[b] III	$(CF_3)_2PSSi(CH_3)_3$ IV	$CF_3P[OSi(CH_3)_3]N(CH_3)_2$ V	Assignment
2970 w	2966 w	2965 w	2968 m	
2915 vs	2908 vw	2908 vw	2935 w, sh	ν_{C-H}
			2903 m	
			2855 w	
			2813 w	
1385 vw			1462 w	
1375 vw				
1265 m			1294 w	δ_{N-CH_3}
	1268 m	1262 m	1265 m	δ_{Si-CH_3}
	1224 s			
	1200 m, sh	1200 s	1190 s	
	1174 vs	1163 s	1122 vs	ν_{C-F}
	1149 s	1127 s		
	1109 s			
1122 m	1052 w		1027 w, sh	$\nu_{sym,P-O-Si}$
1042 vs	996 s		990 m	$\nu_{as,P-O-Si}$
			958 s	ν_{sym,C_2NP}
858 vs	858 s	850 s	855 s	ν_{Si-C}
	764 w	761 w	759 m	δ_{H-C-Si}
813 s				
				ν_{P-F}
800 w, sh				
763 w, sh				
695 vw	676 vw		688 m	
660 vw		633 w		
615 vw	607 vw		606 w	
515 m	557 vw	559 w	538 w	
		527 w		ν_{P-S-Si}
	457 m	457 m	470 w	ν_{P-CF_3}
383 vw				

[a] All frequencies in cm^{-1}. Abbreviations: ν, stretching; δ, deformation; s, strong; m, medium; w, weak; v, very; sh, shoulder; sym, symmetric; as, asymmetric. [b] Spectrum given in ref 4 is in good agreement with these data.

Table III. Nmr Spectral Data for Trivalent Esters $R_2PESi(CH_3)_3$ and $CF_3P[OSi(CH_3)_3]N(CH_3)_2$

	τ_H[a]	ϕ_F[b]	δ_P[c]	J_{FP}, Hz	J_{HP}, Hz	J_{HF}, Hz
$F_2POSi(CH_3)_3$	9.63	33.3		1303[d]		
$(CF_3)_2POSi(CH_3)_3$	9.62[f]	67.4	30.3[e]	85.0[d]		
$(CF_3)_2PSSi(CH_3)_3$	9.39	58.7	91.2[e]	79.5[d]	1.3[g]	
CF_3P $N(CH_3)_2$	7.22[h]				8.9[h]	0.9[h]
		72.2[j]	8.7[k]	81.5		
$OSi(CH_3)_3$	9.67[i]				0.3[i]	

[a] Chemical shift in ppm from external tetramethylsilane (TMS) (τ = 10.0). [b] In ppm from internal $CFCl_3$, positive values indicating resonances to high field of the standard. [c] In ppm from external P_4O_6, positive values indicating resonances to high field of the standard. [d] Doublet in ^{19}F nmr spectrum; no F–H coupling observed. [e] Septet in ^{31}P spectrum due to F–P coupling; no PH coupling resolved. [f] Reference 4 quotes a value of 7.38 ppm downfield from TMS (*i.e.*, τ = 2.62) for the ^1H chemical shift of this compound which is undoubtedly in error. [g] Doublet in ^1H spectrum; no F–H coupling observed. [h] Refers to $N(CH_3)_2$ group which appears as a doublet of quartets in the ^1H spectrum at 33°. [i] Refers to $OSi(CH_3)_3$ group which appears as a doublet in the ^1H spectrum at 33°. [j] The ^{19}F spectrum at 33° is a doublet of quartets. [k] The ^{31}P spectrum at 33° is a quartet with no further discernible splitting as a result of low signal to noise conditions.

$$2F_2POSi(CH_3)_3 \rightarrow (F_2P)_2O + [(CH_3)_3Si]_2O \quad (9)$$

$$F_2POSi(CH_3)_3 \rightarrow (CH_3)_3SiF + (1/n)(FPO)_n \quad (10)$$

the PF_3 arising from the known[5] thermal instability of $(F_2P)_2O$ (eq 11) and also possibly from the presumed pol-

$$(F_2P)_2O \rightarrow PF_3 + (1/n)(FPO)_n \quad (11)$$

ymer product $(FPO)_n$. The orange-brown solid, which may be a product of a further unknown decomposition route, was shown not to contain methylsilyl or fluorophosphorus fragments and is probably a mixed silicon-phosphorus oxide.

Ester IV decomposed incompletely at 200°, partially by a reversal of reaction 1 and partially by more complex routes, including cleavage of C–F bonds to give $(CH_3)_3SiF$. Ester II seems to be thermally unstable at room temperatures; however successful synthesis of this ester is required conclusively to demonstrate the validity of this proposal.

Chemical Reactions. The chemical reactivity of the esters is dominated by the polarity of the P–E–Si structural units and the relative strengths of the P–E and E–Si bonds. For instance, IV was almost quantitatively cleaved as the S–Si bond by anhydrous HCl at room temperature (eq 12). The

$$(CF_3)_2P\text{-}S\text{-}Si(CH_3)_3 + HCl \rightarrow (CF_3)_2PSH + (CH_3)_3SiCl \quad (12)$$

oxy esters I and III reacted much more slowly and less completely than the sulfur esters forming products such as $[(CH_3)_3Si]_2O$ and $(CF_3)_2PCl$ which are suggestive of P–O as well as O–Si bond cleavage as for example in eq 13.

$$R_2P\text{-}O\text{-}Si(CH_3)_3 + HCl \rightarrow R_2PCl + [(CH_3)_3Si]_2O + {}^1/_2H_2O \quad (13)$$

The difference in products between the oxygen and sulfur system is more likely a reflection of the greater reactivity (*e.g.*, $(CF_3)_2POH$) or instability (*e.g.*, $F_2P(O)H$) of the oxygen analogs which result from O–Si bond cleavage following eq 12.

The relative strength of the O–Si bond compared to the S–Si bond in these compounds is further demonstrated by the reactivity of IV with $(CF_3)_2PCl$ (eq 5) compared to the inertness of III to $(CF_3)_2PCl$[4] or $(CF_3)_2PF$ (above).

The most straightforward aminolysis reaction (eq 14) is

$$(CF_3)_2PSSi(CH_3)_3 + 2(CH_3)_2NH \rightarrow (CH_3)_3SiN(CH_3)_2 + (CH_3)_2NH_2^+(CF_3)_2PS^- \quad (14)$$

that of the trifluoromethyl thio ester (IV) which was quantitatively cleaved with dimethylamine to yield the $(CF_3)_2PS^-$ adduct,[11] the presence of which was demonstrated by treatment with anhydrous HCl to give $(CF_3)_2PSH$ nearly quantitatively (eq 15).[11] The behavior of ester IV is thus analogous[3]

$$(CH_3)_2NH_2^+(CF_3)_2PS^- + HCl \rightarrow (CF_3)_2PSH + (CH_3)_2NH_2^+Cl^- \quad (15)$$

to the pentavalent phosphinate esters $(CF_3)_2P(E')ESi(CH_3)_3$. In contrast, reflecting the greater chemical stability of the Si-O bond, the oxy ester (III) reacted according to eq 14 to the extent of only ~2% (confirmed by treatment of the resultant salt with anhydrous HCl and identification of $(CF_3)_2POH$). The majority of the reaction (>95%) followed eq 16 to yield CF_3H and a new aminophosphinite (V) which

$$(CF_3)_2POSi(CH_3)_3 + (CH_3)_2NH \rightarrow CF_3H + CF_3P[OSi(CH_3)_3]N(CH_3)_2 \quad (16)$$

is discussed below.

Most complex of all was the reaction of the fluorooxy ester (I) with dimethylamine which yielded $F_2PN(CH_3)_2$, $(CH_3)_3SiF$, and a fluorine-containing oil which, when dissolved in CD_3CN, gave nmr spectra indicative of $N(CH_3)_2$ and fluorine groups attached to phosphorus as well as perhaps a P-H function. This same species was also obtained when the adduct[6] $(CH_3)_2NH \cdot OPF_2H$ was allowed to react separately with $(CH_3)_3SiN(CH_3)_2$ giving in addition $(CH_3)_3SiF$. A second involatile species present in nearly equal proportion to the first was also obtained from the fluorooxy ester reaction but not from the reaction of the OPF_2H adduct. Since the reactions involved different time spans, this second product may be a decomposition product of a common involatile species. This reaction is also analogous to the reaction of the pentavalent esters which gave[3] initially $(CH_3)_3SiN(CH_3)_2$ and thiophosphinate salts $R_2PEE'^-$ (eq 17)

$$R_2P(E)E'Si(CH_3)_3 + 2(CH_3)_2NH \rightarrow (CH_3)_2NH_2^+R_2PEE'^- + (CH_3)_3SiN(CH_3)_2 \quad (17)$$

which in the case of the fluorothio ester suffered subsequent reaction with $(CH_3)_3SiN(CH_3)_2$[3] (eq 18) to give amino-

$$F_2PE'E^- + (CH_3)_3SiN(CH_3)_2 \rightarrow (CH_3)_3SiF + FPEE'[N(CH_3)_2]^- \quad (18)$$

substituted anions in the salt products. By analogy then, the amine reacts with ester I to yield the OPF_2H-amine adduct (eq 19) which then reacts (eq 20) with $(CH_3)_3SiN$-

$$F_2POSi(CH_3)_3 + 2(CH_3)_2NH \rightarrow (CH_3)_2NH \cdot OPF_2H + (CH_3)_3SiN(CH_3)_2 \quad (19)$$

$$(CH_3)_2NH \cdot OPF_2H + (CH_3)_3SiN(CH_3)_2 \rightarrow (CH_3)_3SiF + (CH_3)_2NH \cdot OPF[N(CH_3)_2]H \quad (20)$$

$(CH_3)_2$ generated in the first step to yield P(III) anionic salts analogous to the above which are however unstable and decompose slowly to $F_2PN(CH_3)_2$ (eq 21). The $F_2PN(CH_3)_2$

$$\text{"OPFH[N(CH}_3)_2]\text{"} \rightarrow F_2PN(CH_3)_2 + ? \quad (21)$$

product cannot be formed directly by eq 22 since $[(CH_3)_3$-

$$F_2POSi(CH_3)_3 + (CH_3)_2NH \rightarrow F_2PN(CH_3)_2 + {}^1/_2[(CH_3)_3Si]_2O + {}^1/_2H_2O \quad (22)$$

$Si]_2O$ was not present among the products.

The Aminophosphinite $CF_3P[N(CH_3)_2]OSi(CH_3)_3$ (V). The structure of the new trimethylsilyl aminophosphinite V was confirmed by alkaline hydrolysis (yielding 1 mol of CF_3H/mol of V), by mass spectroscopy (parent ion: calcd for $C_6H_{15}F_3PON^{28}Si$, *m/e* 233.0613 amu; found, *m/e* 233.0610 amu), by infrared spectroscopy (Table II), and by nmr (Table III) spectroscopy. The infrared spectrum showed peaks typical of a trifluoromethylphosphorus-siloxy compound, including symmetric and asymmetric stretching modes of the P-O-Si structural unit in the 950-1050-cm^{-1} region (*cf.* I, 1042 (vs) cm^{-1}; III, 1052 (w), 996 (s) cm^{-1}).

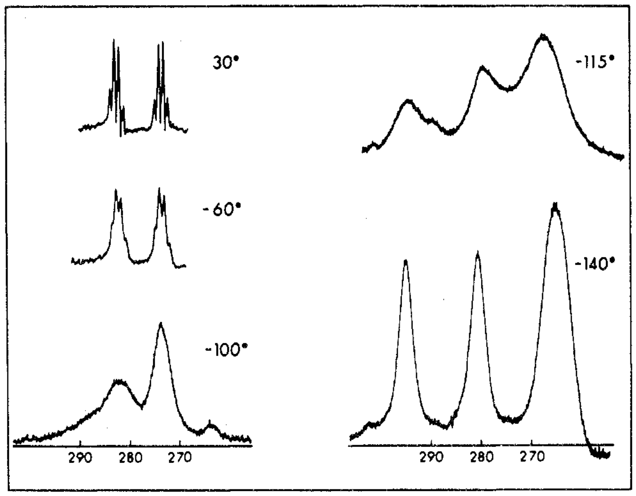

Figure 1. The 100-MHz ^1H nmr spectra of the $N(CH_3)_2$ region of $CF_3P[OSi(CH_3)_3]N(CH_3)_2$. The scale gives shifts in hertz from external TMS. The spectra were obtained from approximately 20% solutions in the mixed solvent $CFCl_3$-CF_2Cl_2. Increased spectral amplitudes were used for the low-temperature spectra (−100 to −140°).

In addition, peaks typical of vibrations of the dimethylamino group could be identified in the C-H stretching, methyl deformational, and dimethylaminophosphine stretching regions. The nmr spectra provided convincing proof of the formulation V. The siloxy protons appeared as a doublet ($^4J_{HP}$ = 0.3 Hz) and the dimethylamino protons as a doublet ($^3J_{HP}$ = 8.9 Hz) of quartets ($^5J_{HF}$ = 0.9 Hz); on decoupling by irradiation with the ^{31}P resonance frequency these collapsed to a singlet and a quartet, respectively. The ^{31}P spectrum showed a quartet ($^2J_{PF} \approx 80$ Hz) with poorly resolved fine structure but the resonance signal due to the fluorine atoms was clearly resolved into a doublet ($^2J_{FP}$ = 81.5 Hz) of septets ($^5J_{FH}$ = 0.9 Hz).

The dimethylamino region of the ^1H spectrum showed interesting behavior on cooling (Figure 1). The doublet of quartets at τ 7.22 broadened and collapsed on cooling to −100° and was replaced by two chemically shifted regions of equal intensity which were well resolved at −140°. The low-field region at τ 7.12 was a doublet ($^3J_{HP}$ = 14.5 Hz) while the high-field region at τ 7.35 was a rather broad singlet. Cooling to −147° resulted only in a slight broadening and loss of the long-range F-H coupling between CF_3 and $N(CH_3)_2$ of 0.9 Hz in the ^{19}F spectrum of the CF_3 group. Similarly the $OSi(CH_3)_3$ proton nmr spectrum was unaffected by cooling to the same temperatures. These observations are in accord with the freezing of the molecule into a configuration in which the two nitrogen methyl groups are in different environments (as a result of restricted rotation of either the $N(CH_3)_2$ or $OSi(CH_3)_3$ substituents) and differ in their coupling with the phosphorus atom. Thus the motion of one of the methyl groups is quenched at −140° (the lower temperature limit available). It is possible that the second may resolve further into a doublet on further cooling. A coupling constant $^3J_{HP}$ = 3.3 Hz would be expected if the overall average coupling constant is unchanged from that at room temperature; the width at half-height of this signal at −140° was 6 Hz. The behavior of the aminophosphinite is similar to that of analogous aminophosphorus compounds discussed elsewhere and a similar rotational barrier is indicated by the above coalescence temperatures.[24]

(24) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 92, 5206 (1970).

Registry No. $[(CH_3)_3Si]_2O$, 107-46-0; F_2POF_2, 13812-07-2; $[(CH_3)_3Si]_2NH$, 999-97-3; OPF_2H, 14939-34-5; $(CF_3)_2PF$, 1426-40-0; $(CF_3)_2PCl$, 650-52-2; $[(CH_3)_3Si]_2S$, 3385-94-2; $[(CF_3)_2P]_2S$, 1486-20-0; $(CF_3)_2P(S)Cl$, 18799-82-1; $Hg[Si(CH_3)_3]_2$, 4656-04-6; HCl, 7647-01-0; $(CH_3)_2NH$, 124-40-3; $(CF_3)_2P(O)Cl$, 646-71-9; $(CH_3)_2NH{\cdot}OPF_2H$, 38680-92-1; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; $F_2POSi(CH_3)_3$, 38680-94-3; $(CF_3)_2POSi(CH_3)_3$, 19738-46-6; $(CF_3)_2PSSi(CH_3)_3$, 38680-96-5; $CF_3P[OSi(CH_3)_3]N(CH_3)_2$, 38822-36-5.

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Synthesis of Nine-Vertex Monocarbon Metallocarboranes by Polyhedral Contraction

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The base degradation of orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ has been found to effect a polyhedral contraction reaction to give $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$. This reaction constitutes the first reported example of a small metallocarborane formed by the removal of a carbon atom and three boron atoms from the polyhedral framework of a larger metallocarborane.

Introduction

The polyhedral contraction reaction developed in this laboratory[1,2] has been used to convert certain metallocarboranes to their next smaller homolog by the removal of one formal BH^{2+} unit by base degradation followed by a two-electron oxidation back to a neutral carborane. We

$$(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_nC_2H_{n+2}) \xrightarrow[2.\ -2e^-]{1.\ -BH^{2+}} (\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{n-1}C_2H_{n+1}) \quad (n = 8 \text{ or } 9)$$

have reported in a recent communication[3] that an attempt to effect a polyhedral contraction reaction with the orange[4-6] $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ gave an unusual product. A total of three BH units and one CH unit was removed from the 13-vertex parent metallocarborane giving, as the principal product, an anionic complex formulated as $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$ which contained a metallocarborane moiety with only nine vertices. We report here further details of this reaction and discuss more fully the unique nature of the products.

Results and Discussion

Preparation and Characterization of the Cyclopentadienylcobalt(III) Complexes of the $B_7CH_8{}^{3-}$ Ion and Its *C*-Methyl Derivative. The reaction of orange π-cyclopentadienyl-π-dodecahydro-6,7-dicarba-*nido*-dodecaboratocobalt(III) with excess potassium hydroxide in an ethanol solution at reflux resulted in the formation of π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobaltate(1−), $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$, I, in high yield. The ion I could be isolated and recrystallized as either its tetramethylammonium or cesium salt.

The 100-MHz ^1H nmr spectrum of the cesium salt of I, Table I, consisted of a sharp singlet of area 5 and a broad singlet of area 1. These were assigned to the cyclopentadienyl protons and to a single carborane CH unit, respectively. The spectrum was scanned to τ 30 but showed no evidence of BHB bridging protons. The 80.5-MHz ^{11}B nmr spectrum of I (Figure 1 and Table II) contained doublets of area ratios 2:2:2:1 indicating that the carborane framework consisted of one unique boron atom and three pairs of equivalent boron atoms.

The chemical analyses of I (Table III) are consistent with the formulations of $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$ and $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. Both salts contain a formal cobalt(III) species. The electronic spectrum and the infrared spectrum of the tetramethylammonium salt of I appear in Tables III and IV, respectively.

Other products isolated from the contraction of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ included trace amounts of the previously reported isomers of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$,[4,5] $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_9C_2H_{11})$,[7] and $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_8C_2H_{10})$.[8] These complexes were identified by their mass spectra and not characterized further.

As of this writing, the two isomers of the monomethyl derivative of the parent metallocarborane, $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$, prepared from $1,2\text{-}B_{10}C_2H_{11}(CH_3)$, have not been separated. The 6-methyl and the 7-methyl isomers are present in approximately equimolar amounts as evidenced by their nmr spectra. It was not surprising, then, that the base degradation of $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$ gave two products. One was identified as compound I and the other as compound II, a dark green monoanionic complex indicated by elemental analysis (Table III) to be $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_7(CH_3))]$.

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(6) Pending the results of an X-ray crystal structure determination, we have tentatively assigned the carbon atoms to positions 6 and 7 in the metallocarborane framework and to positions 5 and 7 for the red-orange isomer. These structures will be discussed in a future publication.
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