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Nickel(II) Complexes of Polydentate Fluorophosphine Ligands[1,2]

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Received February 24, 1972

Nickel(II) complexes of the new polydentate, polyfluoroarylphosphine ligands 1,2-bis(diphenylphosphino)tetrafluorobenzene (FDP) and bis(2-diphenylphosphino-3,4,5,6-tetrafluorophenyl)phenylphosphine (FTP) have been synthesized and characterized. In contrast to the behavior of similar nonfluorinated bidentate phosphine ligands, which readily give pentacoordinate $[Ni(bidentate)_2X]^+$ complexes, FDP gives only the planar, four-coordinate $Ni(FDP)X_2$ and $[Ni(FDP)_2]^{2+}$ compounds with nickel(II). However, both planar $[Ni(FTP)X]B(C_6H_5)_4$ and distorted square-pyramidal $Ni(FTP)X_2$ complexes were isolated with the tridentate ligand FTP. Although the introduction of the tetrafluoroaryl connecting linkage appears to decrease the tendency of the diphosphine ligand to form five-coordinate complexes, the positions of the electronic absorptions in the complexes of analogous fluorinated and unfluorinated ligands are surprisingly similar. These effects are discussed in terms of σ and π interactions of both the C_6F_4 linkage and the metal with the phosphorus atoms.

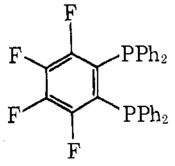
Introduction

Investigations in this laboratory have been concerned with the purposeful design and synthesis of new polydentate phosphorus, arsenic, and sulfur ligands that promote formation of transition metal complexes with unusual coordination numbers and geometries.[4-6] In order to compare the electronic effects of two ligands, it is best to choose a set of ligands whose donor groups and structural features are quite similar, but whose coordination properties can be influenced by changing the electronic properties of the molecule.

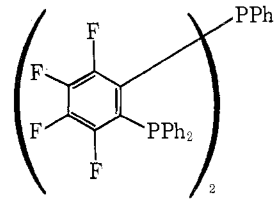
A variety of physical and chemical studies clearly show that the electronegativity of a C_6F_5 group is greater than that of a C_6H_5 group.[7,8] Thus, a pentafluorophenylphosphine should be a poorer σ-donor ligand than the corresponding C_6H_5 compound.

The synergic effect of the electronegative perfluoroaryl group might be expected to make a phosphine a better π-acceptor ligand, as is observed with PF_3. However, Graham and Hogben[7a] have concluded, on the basis of ^{19}F studies with pentafluorophenyl organic compounds, that the C_6F_5 ring functions as a net π-donor group to the empty 3d orbitals on phosphorus as a result of π back-bonding from the fluorine atoms. The observance of increased shielding of the ^{31}P nucleus with an increased number of C_6F_5 groups in $P(C_6H_5)_x(C_6F_5)_{3-x}$ compounds also indicates net π^* (aryl) $\rightarrow$ $d\pi$ (phosphorus) donation from the C_6F_5 ring.[8,9] Thus, the overall effect of the increased electronegativity and the $\pi^* \rightarrow d\pi$ donation of fluorinated aryl groups would be to reduce *both* the σ donor and the π acceptor properties in ligands such as FDP and FTP, as compared to the analogous unfluorinated ligands. Since the van der Waals radii of hydrogen and fluorine are very similar (1.2 and 1.35 Å, respectively),[10] steric considerations should be minimal in comparisons of such ligands.

To evaluate the effect of fluorine substitution, nickel(II) complexes of two new fluoro ligands (**1** and **2**) have been synthesized and characterized.



1, FDP



2, FTP

Experimental Section

Ligands and Reagents.—We have reported the detailed syntheses of the fluoro ligands.[11] All organic solvents and other reagents were the best commercial grades and were used without additional purification.

Preparation of the Complexes. **$Ni(FDP)X_2$ (X = Cl, Br, I, NCS).**—An ethanol solution of the appropriate hydrated nickel(II) halide was mixed with a dichloromethane solution of the ligand FDP in a 1:2 molar ratio. The $Ni(FDP)X_2$ compound precipitated rapidly from solution. Recrystallization from a mixture of ethanol and either dichloromethane or chloroform produced large crystalline platelets (microcrystals for $Ni(FDP)(NCS)_2$) that were suitable for elemental analyses.

$[Ni(FDP)_2](ClO_4)_2$.—A solution containing 0.366 g (1 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 10 ml of ethanol was added to a solution of 0.518 g (1 mmol) of FDP dissolved in 3 ml of dichloromethane. After the resulting solution had stirred for 1 min, a yellow orange precipitate began to separate. The solid was collected on a filter, washed with diethyl ether, and then dissolved in a few milliliters of dimethylformamide and filtered. A yellow-orange

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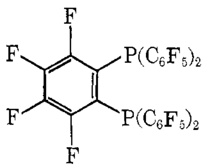
[1] The term "fluoro ligand" will be used to refer to a ligand in which some of the hydrogen atoms are replaced by fluorine, *e.g.*, FDP or FTP; the term "perfluoro ligand" will be reserved for those ligands in which *all* the hydrogen atoms are replaced by fluorine, *e.g.*, PF_3, $P(CF_3)_3$, or



[2] Presented at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June, 1970. Abstracted from the Ph.D. dissertation of P. G. Eller, The Ohio State University, Dec 1971.

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TABLE I

CHARACTERIZATION DATA FOR SOME NICKEL(II) COMPLEXES OF THE FLUORO LIGANDS FDP AND FTP

Compound[a]	Color	Elemental Analyses								Conductance Λ_M, cm^{-2} ohm^{-1} M^{-1} [b]
		% C		% H		% X		% P		
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Ni(FDP)Cl_2$	Orange	55.60	55.42	3.11	3.27			9.56	9.66	4.2
$Ni(FDP)Br_2$	Ochre	48.89	48.68	2.74	2.86			8.41	8.61	8.4
$Ni(FDP)I_2$	Purple	43.46	42.52	2.43	2.36	30.54	30.24			2.6
$Ni(FDP)(NCS)_2$	Tan	55.43	55.72	2.90	2.80	4.04(N)	4.00			1.0
$Ni(FDP)_2(ClO_4)_2$	Yellow	55.67	55.47	3.11	3.30	5.48	5.67	9.57	9.20	171
$Ni(FTP)Cl_2$	Olive green	55.80	55.89	2.79	3.04	7.89	7.84	10.28	9.92	15.1
$Ni(FTP)Br_2$	Dark green	50.79	51.05	2.53	2.40	16.09	15.87	9.35	9.40	17.4
$Ni(FTP)I_2$	Blue-black	46.41	46.46	2.32	2.43	23.35	23.45	8.54	8.67	28.6
$[Ni(FTP)Cl]BPh_4$	Yellow-orange	67.18	66.87	3.84	4.00	3.00	2.99	7.82	7.46	51.3

[a] All these compounds are diamagnetic, with corrected molar susceptibilities less than 205 cgsu. [b] Measured on ~10^{-3} M nitromethane solutions.

solid separated on addition of ether to the dimethylformamide solution.

$Ni(FTP)X_2$ (X = Cl, Br, I).—A solution containing 0.775 g (1 mmol) of FTP in 5 ml of dichloromethane was added to a warm solution of the appropriate hydrated nickel(II) halide (1 mmol) in 20–25 ml of ethanol. On cooling the resulting solution, the $Ni(FTP)X_2$ compound precipitated. Crystalline products were obtained by recrystallization of the solid from a dichloromethane–ethanol solvent mixture.

$[Ni(FTP)Cl]B(C_6H_5)_4$.—A solution containing 0.388 g (0.5 mmol) of FTP in 5 ml of dichloromethane was added to 10 ml of an ethanol solution containing 0.119 g (0.500 mmol) of $NiCl_2 \cdot 6H_2O$ and 0.342 g (1 mmol) of sodium tetraphenylborate. A red-brown precipitate formed immediately; however, the solid turned into a sticky brown oil within 1 min. Addition of ether to the solution and stirring produced a yellow-orange solid. The solid was collected on a filter and washed with ether, benzene, and ethanol. The powder was then dissolved in chloroform, filtered, and added to 15 ml of ethanol. The complex did not crystallize, so the solvents were evaporated to give a brown oil. Ether was added to the oil and after the solution had stood overnight, a yellow-orange solid precipitated. The compound was collected on a filter and washed with ether and ethanol.

Characterization Measurements.—Electronic and infrared spectra and conductance and magnetic measurements were obtained as previously described.[6a]

Discussion

FDP Complexes.—The diphosphine ligand FDP reacts with nickel(II) perchlorate in ethanol to produce the yellow, sparingly soluble $[Ni(FDP)_2](ClO_4)_2$ (eq 1). Nitromethane solutions of the complex give conductivity values typical of 2:1 electrolytes and the infrared spectrum of the solid exhibits no evidence for coordination of the perchlorate group. From the conductivity and infrared data for $[Ni(FDP)_2](ClO_4)_2$ and the similarity of its electronic spectrum to the spectra of nickel(II) complexes of known planar geometry,[12] we infer the existence of planar $[Ni(FDP)_2]^+$ cations in $[Ni(FDP)_2](ClO_4)_2$.

The ligand FDP, even when present in excess, reacts with nickel(II) halides in ethanol to form the $Ni(FDP)X_2$ (X = Cl, Br, I, NCS) complexes (eq 2). The $Ni(FDP)X_2$ compounds are assigned planar structures on

$$Ni(ClO_4)_2 \cdot 6H_2O + 2FDP \longrightarrow [Ni(FDP)_2](ClO_4)_2 + 6H_2O \quad (1)$$

$$NiX_2 \cdot 6H_2O + FDP \longrightarrow Ni(FDP)X_2 + 6H_2O \ (X = Cl, Br, I, NCS) \quad (2)$$

the basis of their magnetic, conductance, and electronic spectral properties (Table I) which are typical for planar nickel(II). Infrared measurements in the C–N stretching region on dichloromethane solutions of the thiocyanate complex gave values for the half-band-widths (21.6 and 30.4 cm^{-1}), absorption frequencies (2093 and 2079 cm^{-1}), and integrated intensities (5.94×10^4 and 7.91×10^4 cm^{-2} M^{-1}) which are characteristic for nitrogen-bonded thiocyanate groups.[13] The observance of two C–N stretching frequencies is probably due to the cis geometry of the thiocyanate groups as a result of the chelating ligand.[14]

When halide ion is added slowly to acetone solutions of $[Ni(FDP)_2](ClO_4)_2$, one observes new bands in the electronic spectra which are similar to the transitions found in the corresponding $Ni(FDP)X_2$ complex. Apparently halide ion displaces one of the FDP ligands from $[Ni(FDP)_2]^+$ rather than forming five-coordinate $[Ni(bidentate)_2X]^+$ complexes as was observed for similar unfluorinated bidentate ligands.[5,6a] We conclude that FDP has little or no tendency to form pentacoordinate species such as $[Ni(FDP)_2X]^+$ under these conditions. Numerous other attempts to prepare five-coordinate nickel(II) complexes with FDP also failed.

It is interesting to note that the similar bidentate phosphorus ligand 1,2-bis(diphenylphosphino)ethane also gives only planar $Ni(bidentate)X_2$ complexes.[15–17] However, the closely related ligands *cis*-1,2-bis(diphenylphosphino)ethylene[15] and diphenyl-*o*-(diphenylarsino)phenylphosphine,[6a] both of which contain aryl or olefinic connecting linkages between the donor atoms, readily form pentacoordinate $[Ni(bidentate)_2X]^+$ complexes. The unfluorinated analog of FDP, 1,2-bis(diphenylphosphino)benzene, has been prepared but its nickel(II) complexes, unfortunately, have never been reported.[18,19] In related studies we have found that the fluorophosphine ligands 2-methylthio-3,4,5,6-tetrafluorophenyldiphenylphosphine[20] and dimethylpentafluorophenylphosphine[21] exhibit significantly reduced

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tendencies to form pentacoordinate nickel(II) compounds. Other workers have observed a similar effect in comparisons of 1,2-bis(dimethylarsino)benzene with its 3,4,5,6-tetrafluorophenyl analog.[22] Thus, the presence of a perfluorophenyl ring appears to reduce significantly the tendency of the ligands to stabilize pentacoordinate nickel(II) compounds. This effect may arise as a result of the poorer σ donor nature of the perfluorophenylphosphine ligand compared with an analogous unfluorinated ligand. We shall report soon an ^{19}F nmr study which seems to substantiate a reduced σ donor but an increased π acceptor nature of the perfluorophenylphosphine ligands in d^8 metal complexes.[23]

FTP Complexes.—Nickel(II) halides and FTP give the diamagnetic, crystalline complexes $Ni(FTP)X_2$ (X = Cl, Br, I) from ethanol solutions. The $Ni(FTP)X_2$ complexes exhibit a slight dissociation of the halogen atom in nitromethane solutions, the degree of dissociation increasing in the order Cl < Br < I. In fact, addition of sodium tetraphenylborate to solutions that contain FTP and nickel(II) chloride leads to precipitation of the light yellow $[Ni(FTP)Cl]B(C_6H_5)_4$ (eq 3). The latter compound acts as a 1:1 electrolyte in nitromethane and exhibits an electronic spectrum that is characteristic of square-planar nickel(II).[12]

$$NiX_2 \cdot 6H_2O \xrightarrow{FTP} Ni(FTP)X_2 \xrightarrow{BPh_4^-} [Ni(FTP)X]BPh_4 \quad (3)$$
$$(X = Cl, Br, I)$$

The electronic spectra of the $Ni(FTP)X_2$ complexes are quite different from either of the planar species $Ni(FDP)X_2$ or $[Ni(FTP)Cl]^+$ (Figure 1). The spectra of the $Ni(FTP)X_2$ complexes are very similar both in solution and in the solid state, with a transition near 12,000 cm^{-1} and a more intense absorption near 20,000 cm^{-1} being observed. On the basis of spectral comparisons with low-spin pentacoordinate compounds of known trigonal-bipyramidal,[4,5] square-pyramidal,[6,12] and intermediate geometries,[24] we propose that the $Ni(FTP)X_2$ complexes have a distorted, square-pyramidal structure. Thus, the band near 12,000 cm^{-1} may be assigned to the $^1A' \rightarrow {}^1A'(d_{z^2} \rightarrow d_{x^2-y^2})$ transition, and the intense absorption near 20,000 cm^{-1} may contain both the $^1A' \rightarrow {}^1A''$ $(d_{xz} \rightarrow d_{x^2-y^2})$ and $^1A' \rightarrow {}^1A''$ $(d_{yz} \rightarrow d_{x^2-y^2})$ transitions in C_s microsymmetry.

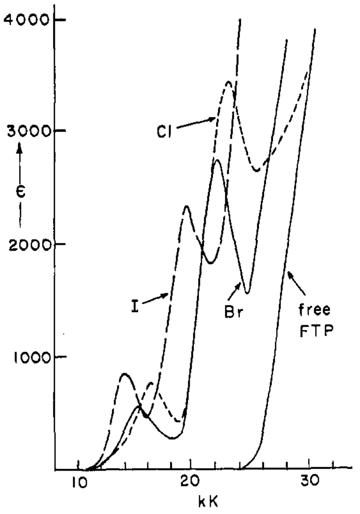

Figure 1.—The electronic spectra of *ca.* 10^{-3} *M* solutions of $Ni(FTP)I_2$ (— — —), $Ni(FTP)Br_2$ (——), $[Ni(FTP)Cl_2]$ (--------), and the free ligand FTP (——) in nitromethane.

Bis(2-diphenylphosphinophenyl)phenylphosphine (TP) forms nickel(II) complexes which are similar spectrochemically to the analogous FTP compounds.[25] Thus, Table II shows that the observed electronic transitions for analogous $Ni(TP)X_2$ and $Ni(FTP)X_2$ (X = Cl, Br, I) complexes are virtually identical in energy and that the FTP complexes exhibit slightly greater molar extinction coefficients. These observations may be compared with our studies with other pairs of related polyfluoroaryl and unfluorinated mono- and bidentate ligands, where the spectrochemical properties of corresponding polyfluoroaryl and unfluorinated ligands were found to be similar even though the tendency of the two ligands to stabilize pentacoordinate complexes was quite different.[20,21,23] Apparently, fluorine substitution in the *o*-phenylene part of the ligand changes the π acidity of the ligands sufficiently to more than compensate for the reduced σ donor character of the fluoro ligand donor atoms.

Table II

Electronic Spectra of Some Nickel(II) FTP, FDP, and TP Complexes[a]

Compound	Solution (cm^{-1})[b]	Solid state (cm^{-1})[c]
$Ni(FDP)(NCS)_2$	22,450 (3110)	
$Ni(FDP)Cl_2$	21,800 (1670)	
$Ni(FDP)Br_2$	21,100 (1970)	
$Ni(FDP)I_2$	18,750 (1600)	
$[Ni(FDP)_2](ClO_4)_2$	23,050 (733), 27,300 (5500)	
$Ni(FDP)Cl_2$	16,400 (760), 23,000 (3460)	15,600, 23,100
$Ni(TP)Cl_2$	16,800 (300), 22,650 (3200)	15,900, 23,550
$Ni(FTP)Br_2$	15,400 (560), 22,200 (2730)	15,300, 22,200
$Ni(TP)Br_2$	15,300 (280), 22,000 (2400)	16,150, 22,200
$Ni(FTP)I_2$	14,300 (850), 19,800 (2320)	16,700, 20,100
$Ni(TP)I_2$	14,450 (530), 20,050 (1700)	14,710, 20,000
$[Ni(FTP)Cl]BPh_4$	22,470 (2820)	
$[Ni(TP)Cl]BPh_4$	22,500 (2800)	

[a] Extinction coefficients listed in parentheses. The estimated experimental error in band positions for FTP and FDP complexes are ±40 cm^{-1} for solution spectra and ±120 cm^{-1} for mull spectra. [b] Taken in approximately 10^{-3} *M* dichloromethane solutions. [c] Taken as Nujol mulls. [d] Data for the TP complexes are taken from ref 25. We thank Professor L. M. Venanzi for permission to use these data.

The ^{19}F nmr resonance positions in FDP occur from 1 to 18 ppm farther downfield than in similar $o\text{-}C_6F_4X_2$ (X = Cl, Br, H) compounds.[23] In the complex $Ni(FDP)X_2$, the ^{19}F nuclei of FDP are deshielded even more. These data indicate a net π delocalization from the tetrafluoroaryl ring to vacant d orbitals on phosphorus, as Graham observed in his studies with simple pentafluorophenyl derivatives.[7a,b,c] Apparently, the synergic effect of the electronegative C_6F_4 group increases the π acidity of the donor atoms to more than compensate for a loss in π acidity caused by π^* (fluoroaryl) → d(phosphorus) back-bonding from the perfluoroaryl ring. Other ^{19}F nmr studies in our labora-

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tories[23] involving various metal complexes and several fluoroarylphosphine ligands further substantiate these conclusions concerning the effect of fluorine substitution on the donor properties of the arylphosphine ligands.

Acknowledgments.—The authors are grateful for financial support of the National Science Foundation. We thank Professor L. M. Venanzi for permitting us to use his data on the TP complexes prior to publication.

CONTRIBUTION FROM THE ANORGANISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT GÖTTINGEN, GÖTTINGEN, GERMANY

Some Reactions of Sulfur Difluoride Imides and Sulfur Dichloride Imides

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Received September 28, 1971

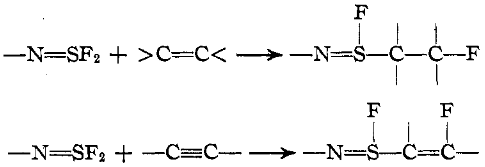
The fluorine atoms of the NSF_2 group in sulfur difluoride *N*-perhaloalkylimides are readily exchanged using $R_2NSi(CH_3)_3$, $RN[Si(CH_3)_3]_2$, or RONa to give compounds of the general formula $R_{HAL}{-}N{=}S(NR_2)F$, $R_{HAL}{-}N{=}S(NR_2)_2$, $R_{HAL}{-}N{=}S{=}N{-}R$, $R_{HAL}{-}N{=}S(OR)F$, and $R_{HAL}{-}N{=}S(OR)_2$. In the interaction of sulfur dichloride imides with *N*-silylated secondary amines, monochlorosulfur imides $R_{HAL}{-}N{=}S(NR_2)Cl$ are formed. These compounds show physical and chemical relationships to analogs in the $O{=}S(X)Y$ system.

Introduction

Sulfur difluoride imides, $RN{=}SF_2$, may undergo the following reactions to give other sulfur–nitrogen compounds:[1] (a) cleavage of the R–N bond and transfer of the NSF_2 group, (b) addition to the N=S double bond, (c) oxidation of the sulfur(IV) to sulfur(VI), and (d) exchange of the fluoride atoms to give other S-substituted sulfur(IV) imides.

The first reaction type is found in the cleavage of acyl-,[2–4] metal-,[2,3,5] or *N*-halogeno sulfur difluoride imides.[6–9] Fluorination of $R{-}N{=}SF_2$ gives $R{-}NF{-}SF_5$[10,11] (addition and oxidation) or $R{-}N{=}SF_2{=}N{-}R$ (oxidation and S=N bond cleavage).[10,12] The interaction (c) is brought about by the photochemical oxidation of $RNSF_2$ with OF_2 to give sulfur oxydifluoride imides.[13]

Fluorine–chlorine exchange according to (d) is achieved using the Lewis chloro acids $AlCl_3$,[14] PCl_5,[15] and $SiCl_4$.[16] In the reaction of phenylsulfur difluoride imide with nitrogen bases, alcoholates, or phenyllithium also both fluorine atoms of the $N{=}SF_2$ group were exchanged and the appropriate fluorine-free sulfur(IV) imides were generated.[17] Starting from sulfur difluoride imides only their addition across the carbon–carbon double[18] and triple bond[19] gave S-substituted sulfur monofluoride imides



$$-N{=}SF_2 + {>}C{=}C{<} \longrightarrow -N{=}\overset{F}{\overset{|}{S}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-F$$

$$-N{=}SF_2 + -C{\equiv}C- \longrightarrow -N{=}\overset{F}{\overset{|}{S}}-\overset{|}{C}{=}\overset{F}{\overset{|}{C}}-$$

We have investigated the value of sulfur difluoride imides as precursors for S-substituted monofluoride imides and whether the procedures given for phenylsulfur difluoride imide may be generally applied. We have also investigated the influence of substituents at the sulfur (other than fluorine) upon the stability of the compounds.

Experimental Section

General Methods.—$CF_2ClCF_2NSF_2$,[6] $CFCl_2CF_2NSF_2$,[8] $(CH_3)_2NSi(CH_3)_3$,[20] $(C_2H_5)_2NSi(CH_3)_3$,[21] and $CH_3N[Si(CH_3)_3]_2$.[22] were prepared by the literature methods. All reactions were carried out in Pyrex-glass flasks under an atmosphere of dry nitrogen.

Ir spectra were obtained in the liquid phase (KBr windows) with a Leitz infrared spectrometer. Nmr spectra were measured with a Varian A-56/60 spectrometer. Tetramethylsilane and trichlorofluoromethane were used as external standards. Mass spectra were recorded with an Atlas UFCH 4 spectrometer. Elemental analyses (Table I) were performed by Beller Microanalytical Laboratory, Göttingen, Germany.

Preparation of $CF_2ClCF_2N{=}S(F)N(CH_3)_2$ (I).—The reaction was carried out in a two-necked 100-ml Pyrex-glass flask, equipped with a magnetic stirrer, dropping funnel, and reflux condenser with a nitrogen T adapter. At room temperature 7.4 g (69.1 mmol) of $(CH_3)_3SiN(CH_3)_2$ was slowly added to 14.8 g (67.5 mmol) of $CF_2ClCF_2NSF_2$. Upon warming, the reaction mixture turned orange. The volatile products were removed at 12–14 Torr. Distillation of the residue gave 9.5 g of $CF_2ClCF_2N{=}S(F)N(CH_3)_2$, bp 76–78° (14 Torr) with slight decomposition (yield 57%). Nmr spectrum: δ_{SF} −33.3, δ_{CF_A} +77.6, δ_{CF_B} +80.1, δ_{CF_2Cl} +73.7, δ_{CH} −2.94 ppm; J_{SF-CF_A} = 13.4, J_{SF-CF_B}

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