Preparation of $Mo(N_2)_2(DPPE)_2$ (1). DPPE (8.81 g, 22.1 mmol) and 250 mL of THF were combined in a round-bottom flask equipped with N_2 inlet and magnetic stirrer. $[MoCl_5]_2$ (2.52 g, 9.22 mmol of Mo(V)) was added to produce a brown suspension, followed by the addition of 1% Na/Hg (425 g, 185 mmol of Na). After stirring 16 h, the THF slurry was decanted, filtered over Celite, and washed through with 200 mL of benzene. Solvent was then removed using a rotary evaporator. The orange-brown residue was dissolved in 150 mL of benzene, followed again by Celite filtration and rinsing with 100 mL of benzene. Product was precipitated by the addition of 400 mL of methanol, collected by filtration, washed with methanol, and dried in vacuo. The bright orange product weighed 4.60 g (53% yield). Anal. Calcd for $MoN_4C_{52}H_{48}P_4$: N, 5.9. Found: N, 5.8. $\nu_{N\equiv N}$ 1978 cm^{-1} (vs).

Preparation of $Mo(N_2)_2(DEPE)_2$. DEPE (0.744 g, 3.61 mmol), 50 mL of THF, $[MoCl_5]_2$ (0.410 g, 1.50 mmol of Mo(V)), and 1% Na/Hg (69 g, 30 mmol of Na) were combined as above and stirred for 10 h. The reaction mixture was then decanted, Celite filtered, and washed through with 40 mL of benzene. After rotary evaporation of solvent, the residue was dissolved in 10 mL of benzene. This was filtered and rinsed with 20 mL of benzene. Methanol (60 mL) was added to the dark orange filtrate to precipitate product which was collected by filtration, washed with methanol, and dried in vacuo. The bright orange crystals weighed 0.415 g (49% yield). Anal. Calcd for $MoN_4C_{20}H_{48}P_4$: N, 9.9. Found: N, 9.6. $\nu_{N\equiv N}$ 1927 cm^{-1} (vs).

Preparation of $Mo(N_2)_2(ARPHOS)_2$. ARPHOS (4.70 g, 10.6 mmol), 125 mL of THF, $[MoCl_5]_2$ (1.21 g, 4.43 mmol of Mo(V)), and 1% Na/Hg (200 g, 87 mmol of Na) were combined as for compound **1** and stirred for 16 h. The THF slurry was decanted, Celite filtered, and rinsed through with 160 mL of benzene. Solvent was removed using a rotary evaporator, leaving an orange-brown residue to which 75 mL of benzene was then added. This was filtered over Celite and rinsed through with 90 mL of benzene. Methanol (250 mL) was added to precipitate product which was collected by filtration, washed with methanol, and then dried in vacuo. The yellow-orange product weighed 2.10 g (46% yield). Anal. Calcd for $MoN_4C_{52}H_{48}As_2P_2$: N, 5.4. Found: N, 4.8. $\nu_{N\equiv N}$ 1952 cm^{-1} (vs).

Preparation of $Mo(N_2)_2(Ph_2PCH_3)_4$. Ph_2PCH_3 (1.22 g, 6.09 mmol), 50 mL of THF, $[MoCl_5]_2$ (0.416 g, 1.52 mmol of Mo(V)), and 1% Na/Hg (70 g, 30 mmol of Na) were combined as for compound **1** and stirred 10 h. The THF slurry was then decanted, filtered over Celite, and rinsed through with 50 mL of benzene. Solvent was removed using a rotary evaporator, leaving a deep orange-red oil to which 20 mL of benzene was added. This was then Celite filtered and washed through with 30 mL of benzene. Ice-chilled methanol (100 mL) was then added, followed by further chilling (0 °C) of the resulting mixture. Product was collected by filtration, washed with methanol, and dried in vacuo. The orange-red crystals weighed 0.779 g (54% yield). Anal. Calcd for $MoN_4C_{52}H_{52}P_4$: N, 5.9. Found: N, 5.9. $\nu_{N\equiv N}$ 1922 cm^{-1} (vs).

Results and Discussion

The reduction of molybdenum(V) chloride in the presence of N_2 and a suitable phosphine ligand using sodium amalgam and THF as solvent has proven to be a very convenient route to the synthesis of bis(dinitrogen)molybdenum(0) complexes. The reaction proceeds readily and has provided good yields for the organophosphines employed.

The yields have been found to be dependent on the purity of the reactant materials. The highest yield obtained for compound **1** was 72% and involved the use of molybdenum(V) chloride purified by sublimation.[7] Yield was also found to increase when DPPE, recrystallized from benzene–methanol in order to remove phosphoryl species, was employed. Since small amounts of impurities do not appreciably affect the yield, purification of reactants is not employed for routine syntheses.[8]

Yields were found to be virtually unaffected by the amount of stirring time allowed for reaction. Reaction times varying from 3 to 47 h have been studied for compound **1** and have been found to produce no significant difference in yields. Thus, the reaction appears complete after only several hours of stirring.

The addition of molybdenum(V) chloride to the THF solvent prior to the addition of any organophosphine has been

found in the three trials thus conducted to cause solvent polymerization as evidenced by an intense infrared absorption for the reaction mixture at 1111 cm^{-1}. This absorption was absent in the spectra of those reaction mixtures containing dissolved phosphines prior to the addition of the molybdenum(V) chloride. Although product was formed in the presence of the polymer as indicated by the N–N absorption also in the spectra of the reaction mixture, the polymer prevented isolation of the product by the standard procedures employed for the complex containing Ph_2PCH_3 as coligand. The proper order of addition of reactants is therefore essential for facile workup.

Reactions using DPPE as coligand have been found to involve the formation of small quantities of $[MoH_4(DPPE)_2]$ in a competing process, the hydrogen source presumably arising from solvent decomposition. The tetrahydride can coprecipitate with the bis(dinitrogen) complex when higher methanol/benzene solution ratios or when chilling of the precipitating liquor are employed. Pure bis(dinitrogen) product can be obtained, however, by proper design of the final crystallization (see Experimental Section).

With the use of the presently described synthetic scheme, it is hoped that the study of dinitrogenmolybdenum(0) complexes will be facilitated.

References and Notes

(1) Avery Fellow (1976–1980).
(2) See, for example, E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 160 (1977).
(3) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 814 (1969); M. Hidai, K. Tominari, and Y. Uchida, *ibid.*, 1392 (1969); *J. Am. Chem. Soc.*, **94**, 110 (1972).
(4) J. Chatt and A. G. Webb, *J. Organomet. Chem.*, **27**, C15 (1971); J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074 (1975).
(5) M. Aresta and A. Sacco, *Gazz. Chim. Ital.*, **102**, 755 (1972).
(6) T. A. George and C. D. Seibold, *Inorg. Chem.*, **12**, 2544 (1973).
(7) R. Colton and I. B. Tomkins, *Aust. J. Chem.*, **18**, 447 (1965).
(8) The 72% yield for compound **1** was obtained on a small-scale synthesis (1.5 mmol of Mo(V)). For three reactions conducted on such a scale using the same sample of purified molybdenum(V) chloride, yields varied from 66 to 72%. Using unpurified $[MoCl_5]_2$ on the same scale, a 62% yield was obtained. Smaller yields have been generally found for larger scale syntheses (see Experimental Section).

Contribution from the Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

(Trifluoromethyl)sulfur Trifluoride. An Improved Synthesis, New NMR Data, and Stereochemistry

R. W. Braun, A. H. Cowley,* M. C. Cushner, and R. J. Lagow*

(Trifluoromethyl)sulfur trifluoride has been prepared by the action of F_2 or oxidative fluorinating agents on CS_2, CF_3SCl, or $(CF_3S)_2CS$.[1] However, the commercial availability of CF_3SSCF_3 renders this compound an ideal starting point for the one-step synthesis of CF_3SF_3. The conversion $CF_3SSCF_3 \rightarrow 2CF_3SF_3$ has, in fact, been accomplished previously by treatment with CF_3OF,[1c] ClF_3,[2] or F_2.[1c] However, the CF_3OF and ClF_3 reactions are difficult to control, and the direct fluorination involved a labor intensive batchwise method. The

Table I. NMR Data for CF_3SF_3 and Related Compounds[a]

Compound	F_a	F_e	$J_{F_aSF_e}$, Hz	Ref
CF_3SF_3	−52	+48	67	b
CH_3SF_3	−60	+51	72	c
$(CF_3)_2CFSF_3$	−61	+54	4.8	d
$C_6H_5SF_3$	−72	+26	53	e
$C_6F_5SF_3$	−73	+50	70	f

[a] [19]F chemical shifts in ppm relative to CCl_3F. Upfield shifts from CCl_3F are considered to be positive. [b] This work. These data are in essential agreement with earlier work. [c] Reference 4b. [d] R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, 1, 756 (1962). [e] Reference 1b. [f] P. Meakin, D. W. Ovenall, W. A. Sheppard, and J. P. Jesson, *J. Am. Chem. Soc.*, 97, 522 (1975).

present paper describes a greatly improved procedure for direct fluorination of CF_3SSCF_3 which avoids handling molecular fluorine in Pyrex glass.

(Trifluoromethyl)sulfur trifluoride is generally thought to possess an essentially trigonal-bipyramidal geometry in which the CF_3 moiety adopts an equatorial location. However, in view of the controversy which has surrounded the delineation of the ground-state geometry of the analogous phosphorane, CF_3PF_4,[3] it seemed appropriate to reinvestigate the stereochemical features of CF_3SF_3 by means of ^{19}F dynamical NMR (DNMR) spectroscopy.[4] Furthermore, since erroneous results had been obtained in DNMR studies of SF_4 in Pyrex glass NMR tubes[5] it was decided to employ quartz NMR tubes and an HF scavenger in the present study. Finally, we report the first ^{13}C NMR data for CF_3SF_3.

Experimental Section

The compound CF_3SSCF_3 was obtained commercially and purified by fractional vacuum condensation prior to use. The four-zone cold reactor fluorination system has been described previously.[6] A typical reaction involved the injection of 2.0 g of CF_3SSCF_3 into the reactor, the second zone of which was maintained at −120 °C by means of thermostatically controlled liquid nitrogen cooling. The helium flow was set at 60 mL/min and the fluorine flow at 1 mL/min. Various reaction times were investigated; the optimum time was discovered to be 38 h. Longer reaction times resulted in the production of CF_3SF_5. After 72 h of fluorination CF_3SF_5 was the only major product. After 38 h the fluorine flow was terminated and the reactor was allowed to assume ambient temperature. The products which had collected in a glass trap were transferred to a standard glass high-vacuum line and subjected to fractional distillation with U-traps held at −93, −110, and −196 °C. The −196 °C trap contained CF_3SOF plus traces of SF_6, SF_4, CF_4, and COF_2. The desired product condensed in the −110 °C trap. Based on the CF_3SSCF_3 consumed, the conversion to CF_3SF_3 was ~90%.

NMR samples were run both with and without $(C_6H_5)_3PNH$ present as HF scavenger. No spectral differences were discerned throughout the temperature ranges studied. In each experiment the CF_3SF_3 had been stored briefly over NaF prior to distillation into the quartz NMR cell. Preliminary ^{19}F NMR samples were run in 5-mm quartz tubes on a Varian 56/60 instrument. The variable-temperature ^{19}F NMR experiments were conducted on a Varian HA 100 spectrometer. The ^{13}C NMR measurements were made on 10-mm quartz tubes on a Brucker WH 90 spectrometer operating in the FT mode.

Results and Discussion

We have found that CF_3SF_3 can be prepared in approximately 90% yields by the direct fluorination of CF_3SSCF_3 in a continuous-flow reactor which features helium dilution and maintenance of the substrate at −120 °C. The reaction times were found to be critically important. Optimum yields of CF_3SF_3 are produced after a 38-h run; extension of reaction times beyond 38 h generates progressively larger quantities of CF_3SF_5. After 72 h essentially complete conversion to CF_3SF_5 occurs.

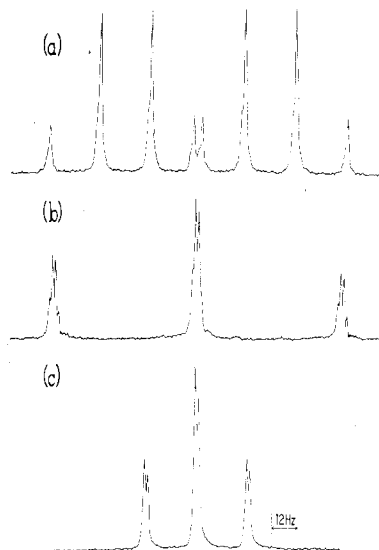The ^{19}F NMR data for CF_3SF_3 are displayed in Figure 1, and the F axial (F_a) and F equatorial (F_e) chemical shift and

Figure 1. The 94.1-MHz ^{19}F NMR spectra of CF_3SF_3 at 29 °C: (a) axial (F_a) region, (b) equatorial (F_e) region, and (c) CF_3 region (+69.9 ppm relative to internal CCl_3F).
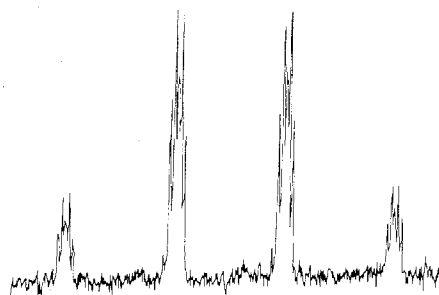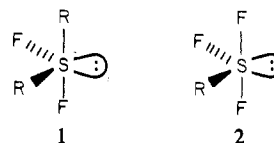

Figure 2. The 22.6-MHz ^{13}C NMR spectrum of CF_3SF_3 at 30 °C.

$J_{F_aSF_e}$ coupling constant data have been assembled in Table I, along with those for analogous RSF_3 sulfuranes which feature sulfur–carbon bonds, viz., alkyl, perfluoroalkyl, C_6H_5, or C_6F_5 substituents.

Two trigonal-bipyramidal models can be considered for RSF_3 molecules (**1**, **2**). It is clear that both the axially

substituted model, **1**, and the equatorially substituted model, **2**, will yield AX_2 (or AB_2) ^{19}F NMR spectral patterns under the condition of slow ligand permutation. The differentiation of the structures must, consequently, rely on ^{19}F chemical shift data. The F_a and F_e chemical shift assignments in Table I exhibit a very consistent pattern. The premise upon which these assignments are based is that CH_3SF_3 must adopt structure **2** because of the very small apicophilicity of the CH_3 group.[7] It may, therefore, be concluded that CF_3SF_3, like the other C–S bonded compounds, prefers structure **2**.

The ^{19}F NMR spectra of CF_3SF_3 are unchanged up to 75 °C, thus implying a barrier to intramolecular fluorine exchange in excess of 17 kcal/mol. The conformational stability of CF_3SF_3 is remarkable in view of the fact that fluorine exchange in the phosphorane analogues, CF_3PF_4 and $(CF_3)_2PF_3$, persists down to −150 °C.[3]

The ambient-temperature ^{13}C NMR spectrum of CF_3SF_3 consists of the anticipated 24-line spectrum centered at 122 ppm relative to external $(CH_3)_4Si$ (Figure 2) with J_{CF} = 323.6, J_{F_aSC} = 11.8, and J_{F_eSC} = 19.1 Hz. These data confirm the

stereochemical rigidity of CF_3SF_3 at ambient temperature. The fact that J_{F_eSC} is slightly larger than J_{F_aSC} may be a reflection of the fact that the equatorial plane of a trigonal bipyramid features more sulfur 3s character than the axes. The differences in the axial and equatorial F–S–C couplings may be useful for the stereochemical assay of fluorosulfuranes.

References and Notes

(1) (a) E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, **75**, 3523 (1953); (b) W. A. Sheppard, *ibid.*, **84**, 3058 (1962); (c) C. T. Ratcliffe and J. M. Shreeve, *ibid.*, **90**, 5403 (1968).
(2) G. H. Sprenger and A. H. Cowley, *J. Fluorine Chem.*, **7**, 333 (1976).
(3) For a summary of this controversy, see R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, **99**, 7841 (1977).
(4) For previous ¹⁹F NMR data on CF₃SF₃ at ambient temperature or below, see (a) ref 1c and (b) W. Gombler and R. Budenz, *J. Fluorine Chem.*, **7**, 115 (1976), and references therein.
(5) W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muetterties, D. D. Traficante, and G. M. Whitesides, *J. Am. Chem. Soc.*, **97**, 7023 (1975), and references therein.
(6) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
(7) For phosphoranes the order of apicophilicity is (in part) F > Cl > Br > CF₃ > alkyl. See ref 3.

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

Preparation and Raman Spectra of Tribromosulfur(IV) Hexafluoroarsenate(V) and Hexafluoroantimonate(V), (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻

Jack Passmore,* E. Keith Richardson, and Peter Taylor

Sulfur tetrachloride is stable only in the solid phase (mp −30 °C), binary sulfur bromides are less stable than their corresponding chlorides, and at the present there is no evidence for sulfur tetrabromide.[1-3] However, OSBr₂,[2,4] has been well characterized and a number of salts with cations of the type R₂SBr⁺ are known.[5] The cations SF₃⁺[6] and SCl₃⁺[7] with weakly basic anions such as AsF₆⁻ and SbF₆⁻ are well established. We now report the preparation and characterization by Raman spectroscopy of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻.

Experimental Section

Apparatus. Except where stated, apparatus and materials are the same as those described in ref 8. Raman spectra were obtained with exciting wavelengths 5145 Å (green) and 6471 Å (red).

Reagents. Reagent grade sulfur (B. D. H. Chemicals) was evacuated to dryness. Bromine (Matheson Gas Co.) was stored over tetraphosphorus decaoxide (P₄O₁₀) in a glass vessel until ready for use. Sulfur dioxide (Matheson Gas Co.) was stored over calcium hydride in a glass vessel. Antimony pentafluoride (Ozark-Mahoning) was twice distilled before use.

Spectra. All solid Raman samples were loaded into dry melting point capillaries in a drybox and flame sealed immediately on removing from the drybox. Solution samples were prepared in 5-mm o.d. glass tubing using either sulfur dioxide or arsenic trifluoride as the solvent and then sealed. Solution Raman spectra were obtained at room temperature with the 6471-Å (red) line and at a temperature just low enough to prevent bubbling with the 5145-Å (green) line, using an evacuated condenser type low temperature cell.

Reactions. All reactions were carried out in a one-piece glass apparatus, consisting of two arms linked by a tube incorporating a sintered-glass filter disk. One arm was fitted with a Teflon "Rotaflo" or a Whitey 1KS4 valve. Typically sulfur was loaded into one arm of the apparatus, which was then evacuated, and the solvent (SO₂ or AsF₃), bromine, and then AsF₅ or SbF₅ were condensed in separately at −196 °C (with thermal cycling to room temperature between each addition).

Preparation of (SBr₃)⁺(AsF₆)⁻. In a typical reaction, S₈ (0.703 mmol) and Br₂ (26.65 mmol) were allowed to react with AsF₅ (10.65 mmol) in sulfur dioxide (5.95 g) solution. The product was a saturated purple solution with a copious yellow precipitate. The soluble product was isolated by repeated washings through the frit. The volatiles were identified as a mixture of SO₂, some AsF₅ containing traces of AsF₃ from infrared spectra. A light yellow insoluble solid (0.02 g) and a bright yellow soluble solid (2.405 g or 5.22 mmol assuming (SBr₃)⁺(AsF₆)⁻) were isolated following removal of the volatiles with brief pumping. A chemical analysis of the product was not obtained since it gave off bromine on standing in a sealed glass sample tube in an atmosphere of dry nitrogen.

Raman spectra were obtained from the yellow soluble product in the solid state and in both arsenic trifluoride and sulfur dioxide solutions using both exciting wavelengths.

Preparation of (SBr₃)⁺(SbF₆)⁻. In a typical reaction S₈ (0.86 mmol) and Br₂ (11.06 mmol) were allowed to react with SbF₅ (11.63 mmol) in sulfur dioxide (5.76 g) solution. The product was a saturated purple solution with a copious yellow precipitate. The soluble product was separated by repeated washings through the frit. The volatiles were removed leaving 0.828 g of an insoluble white solid and 3.302 g or 6.50 mmol (assuming (SBr₃)⁺(SbF₆)⁻) of soluble yellow crystalline solid.

The yellow solid gave elemental analysis consistent with the formulation (SBr₃)⁺(SbF₆)⁻. Anal. Calcd for (SBr₃)⁺(SbF₆)⁻: S, 6.30; Br, 47.23; Sb, 23.99; F, 22.46. Found: S, 6.13; Br, 46.80; Sb, 24.16; F, 22.77.

Raman spectra were obtained for both solids. The spectrum of the white insoluble solid is similar to that obtained when SbF₃·SbF₅ (A)[9] was reacted with excess PF₃ in arsenic trifluoride solution for 2 days.[10] Raman spectra were also obtained from the yellow soluble product in the solid state and in arsenic trifluoride and sulfur dioxide solutions using both exciting wavelengths.

In another experiment S₈ (2.52 mmol) and Br₂ (30.6 mmol) were allowed to react with SbF₅ (34.46 mmol) in SO₂ (7.57 g) solution yielding 19.91 mmol of soluble (SBr₃)⁺(SbF₆)⁻ and 2.27 g of a reduced antimony fluoride. The products were characterized by their Raman spectra.

Results and Discussion

Preparation of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻. Sulfur reacts with excess bromine and a slight excess of AsF₅ in arsenic trifluoride to give a bright yellow solid (SBr₃)⁺(AsF₆)⁻ according to the equation

$$^1/_4S_8 + 3Br_2 + 3AsF_5 \rightarrow 2(SBr_3)^+(AsF_6)^- + AsF_3$$
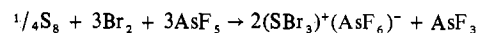
The salt was identified from Raman spectra in the solid state, in arsenic trifluoride solution, and also in sulfur dioxide solution. The solid gave some bromine on standing, in a sealed glass sample tube under an atmosphere of dry nitrogen. The (SBr₃)⁺(SbF₆)⁻ cation salt made in a similar fashion was stable and good analyses were obtained. The nature of the insoluble reduced antimony fluoride product given in the S₈/Br₂/SbF₅ reaction is presently under investigation. Elemental analysis and Raman spectroscopy were used to characterize the (SBr₃)⁺(SbF₆)⁻.

We note that the analogous reactions with iodine and sulfur lead to S₇I⁺ containing salts[11] and related species; whereas SeBr₃⁺ and TeBr₃⁺ can be made in a similar manner.[12]

Raman Spectra. Raman spectra of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻ in the solid state and in solution are given in Figure 1, and Table I lists the frequencies and assignments by comparison with the corresponding anions[6,13] and PBr₃.[14] Solvent peaks[15,16] and a weak peak at 319 cm⁻¹ observed in the solution spectra and attributed to bromine[17] are not included in Table I.