required only slight cooling before the A_2BX spectrum (Table I) was shown, whereas the CD_2Cl_2 solution of **2** (L = PMe_2Ph)[15] failed to give a slow-exchange spectrum at the lowest temperature available (173 K). However, the slow-exchange A_2MX spectrum (Table I) was achieved for **2** (L = PMe_2Ph) in acetone solvent, suggesting an important role for solvation in slowing the exchange process. The pattern of chemical shifts resembles that for the alkynyls, and assignment of square-pyramidal stereochemistry seems assured.

Our observations are therefore at variance with the conclusions drawn by McAuliffe and co-workers regarding the unequivocal establishment of the trigonal-bipyramidal geometry for a complex of ruthenium(II). The supposed mononuclear complexes $[RuCl(L_2)_2][BPh_4]$, which contain ^{31}P NMR signals at +45.7 ppm (L_2 = $Ph_2P(CH_2)_3PPh_2$) and +35.7 ppm (L_2 = $Ph_2P(CH_2)_3PMe_2$), may well be dimeric with chloride bridges analogous to those of the known complex $[RuCl(PMe_3)_4]_2Cl_2$[17] or at least undergo a rapid-exchange process with such a dimer, since *cis*-$[RuCl_2(Ph_2P(CH_2)_3PPh_2)_2]$ exhibits[18] a chemical shift value of +42.0 ppm for the phosphorus nuclei trans to chlorine and chloro complexes of ruthenium have a well-known tendency to form chloro-bridged species.[17-19] This interpretation would also explain the "absence" of fluxional behavior of the five-coordinate compounds reported in ref 7. We have synthesized $[Ru(C{\equiv}CCO_2Et)(Ph_2P(CH_2)_3PPh_2)_2][PF_6]$,[8] which is closely similar to $[RuCl(Ph_2P(CH_2)_3PPh_2)_2][BPh_4]$ except that the $-C{\equiv}CCO_2Et$ group would not be expected to bridge as readily as Cl^-. Our complex is fluxional in CD_2Cl_2 with a single ^{31}P resonance at 30 °C. At −80 °C, however, two triplets are observed, but rather than ascribing this to a trigonal-bipyramidal structure, we suggest two other possibilities: (i) a weak association of mononuclear units via coordination of the ketonic oxygen atom; (ii) a square-pyramidal structure with the alkynyl ligand at the apex and a pair of trans phosphorus atoms bent slightly away from the alkynyl group. The latter possibility has been described[20] for the compound *trans*-$[RuHCl(diop)_2]$. Of relevance to the proposals made herein is that the observed pair of triplets in the ^{31}P NMR spectrum of the latter complex was originally interpreted[21] as indicating a salt $[RuH(diop)_2][Cl]$ containing a trigonal-bipyramidal cation.

Finally, we have found that $[RuH(Ph_2P(CH_2)_3PPh_2)_2][PF_6]$[10] reacts with $CDCl_3$ to give a product that exhibits a doublet of triplets in the ^{31}P NMR (δ 43.2 and −3.8; J = 32 Hz), and it is very likely therefore that the similar pattern observed[7] for $[RuH(Ph_2P(CH_2)_3PMe_2)_2]^+$ is the result of reaction with the solvent.

We are continuing our studies on the solution structures of five-coordinate phosphine complexes of ruthenium(II) and hope to disclose further results in the near future; the evidence for a trigonal-bipyramidal geometry for such complexes remains inconclusive.

Registry No. **1** (L = PMe_2Ph), 96227-16-6; **1** (L = $PMe_2(oA)$), 96227-18-8; **2** (L = PMe_2Ph), 96211-42-6; **2** (L = $PMe_2(oA)$), 96227-20-2.

(15) Complex **2** (L = PMe_2Ph) was generated in situ by warming either a CD_2Cl_2 or an acetone-d_6 solution of the formato complex $[Ru(O_2CH)(PMe_2Ph)_4][PF_6]$.[16] Alternatively, it may be obtained by reaction of **1** (L = PMe_2Ph) with H_2.
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Articles

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(Trifluoromethyl)sulfenyl, (Trifluoromethyl)sulfinyl, and (Trifluoromethyl)sulfonyl Derivatives of Heterocyclic Amines

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1,8-Bis((trifluoromethyl)sulfenyl)-1,8,10-triaza-9-boradecalin, 1,4,7,10-tetrakis((trifluoromethyl)sulfenyl)-1,4,7,10-tetraazacyclododecane, 1,5,9-tris((trifluoromethyl)sulfenyl)-1,5,9-triazacycloundecane, 1,5-bis((trifluoromethyl)sulfenyl)octamethylcyclotetrasilazane, 1,3,5-tris((trifluoromethyl)sulfenyl)hexamethylcyclotrisilazane, 1,4-bis((trifluoromethyl)sulfenyl)piperazine, and 1,4,8,11-tetrakis((trifluoromethyl)sulfenyl)-1,4,8,11-tetraazacyclotetradecane result when CF_3SCl is reacted with the respective heterocyclic amines. Piperazine and 1,4,8,11-tetraazacyclotetradecane form analogous compounds with CF_3SO_2Cl and with $CF_3S(O)Cl$. The latter also forms 1,3,5-tris((trifluoromethyl)sulfinyl)hexamethylcyclotrisilazene with hexamethylcyclotrisilazane.

Introduction

(Trifluoromethyl)sulfur(II, IV, VI)-containing molecules have attracted considerable attention because of their biologically active nature. To date this has been particularly true for compounds where a sulfur–nitrogen bond is present, e.g., as secondary or tertiary amine derivatives.[1] The substituted amines are most often acyclic or aromatic, and only rarely is the nitrogen atom found as the heteroatom in the latter ring or in a saturated ring system.[2,3]

In this paper we report the syntheses of a variety of (trifluoromethyl)sulfenyl, (trifluoromethyl)sulfinyl, and (trifluoromethyl)sulfonyl N-substituted heterocyclic amines. The reagents of choice for the introduction of these groups into such compounds

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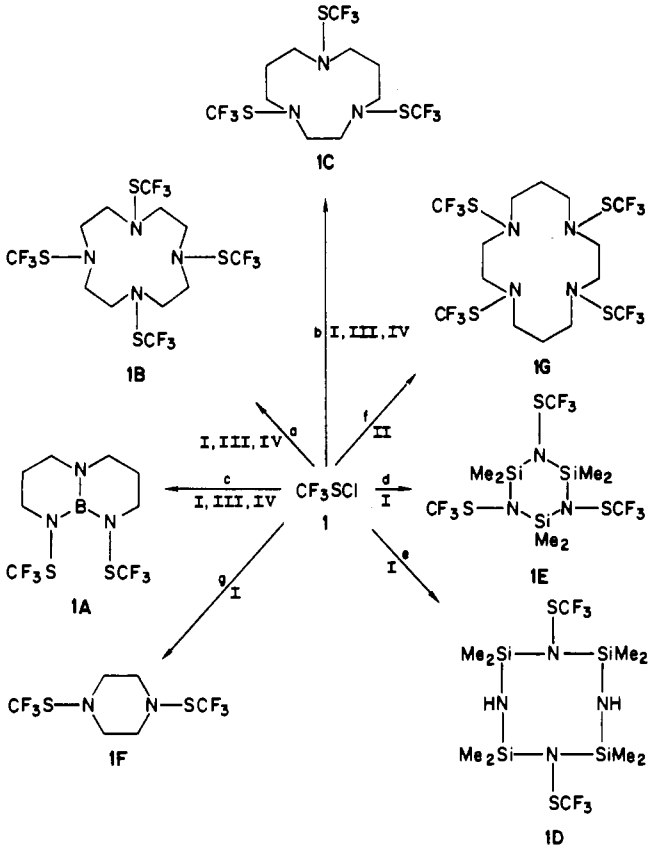
Scheme I[a]



[a] I-IV refer to the methods and a-g to the reactants outlined in the Experimental Section.

are the *S*-chloro derivatives. We and others have used CF_3SCl,[2-4] $CF_3S(O)Cl$,[5,6] and CF_3SO_2Cl[7] as excellent transfer reagents for the CF_3S–, $CF_3S(O)$–, and CF_3SO_2– moieties. Thus, we have demonstrated that heterocyclic amines including piperazine, 1,4,8,11-tetraazacyclotetradecane, hexamethylcyclotrisilazane, 1,8,10-triaza-9-boradecalin, and others react smoothly to give the N-substituted products. These metathetical reactions proceed usually directly with the amine in the presence of a base, but the lithiated or silylated amines are useful precursors also.

Results and Discussion

The products that result from the reactions of CF_3SCl, $CF_3S(O)Cl$, and CF_3SO_2Cl with heterocyclic amines are indicated in Schemes I–III, respectively. The various experimental conditions and methods employed are outlined in the Experimental Section. Although the techniques used in carrying out these reactions were essentially similar, a number of points should be noted. (1) In order to ensure high yields of products when changing reactants from piperazine to larger rings such as 1,4,8,11-tetraazacyclotetradecane, it is important to mix the base (triethylamine) and the heterocycle prior to the addition of the sulfur-containing reactant. (2) Purification becomes more difficult in moving from the CF_3S– to CF_3SO_2– derivatives as the solubilities of the product and the triethylammonium chloride become more similar; e.g., the difficulty is enhanced since compounds **2C** and **3B** are also insoluble in most of the polar solvents tried. (3) As might be anticipated, the rate of reaction decreases with an increase in the oxidation state of the sulfur and the concomitant decrease in reactivity of the S–Cl bond.

When trifluoromethanesulfenyl chloride was reacted with 1,4,7,10-tetraazacyclododecane in the presence of triethylamine at 25 °C, the tetrasubstituted compound **1B** was obtained. It was observed that if a reaction time of less than 12 h was used, complete substitution on nitrogen did not occur and lower substituted products were observed. When the reaction was carried out in the absence of the base, a white solid (85% yield) that decomposed at >220 °C and corresponded to the composition $C_8H_{19}N_4 \cdot CF_3S \cdot HCl$ was formed. **1B** was also obtained in good yield by methods III and IV.

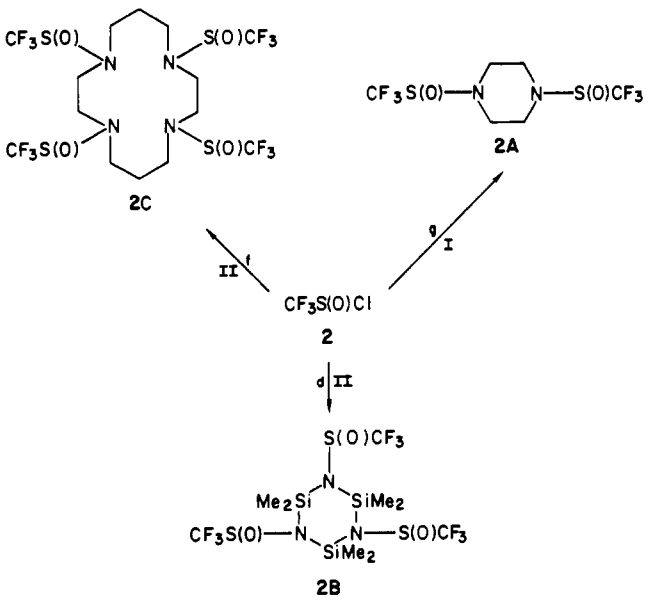
With 1,5,9-triazacycloundecane, CF_3SCl formed the colorless liquid **1C** in high yield. It does not decompose at 90 °C and is insensitive to the ambient air. In the absence of Et_3N, an insoluble white solid was observed.

A stable yellow liquid **1A**, which was insensitive to air, was obtained in good yield when 1,8,10-triaza-9-boradecalin was treated with CF_3SCl. A salt that formed in the absence of Et_3N was analyzed to be $C_7H_{12}N_3BF_3Cl$ and found to decompose at >230 °C. When **1A** was reacted with COF_2 for 2 h at 25 °C and 8 h at 45 °C, no reaction occurred and **1A** was recovered unchanged. *m*-Chloroperbenzoic acid did not oxidize S(II) to either of its higher oxidation states even after 12 h at 25 °C in CH_2Cl_2. However, fuming nitric acid did convert the S(II) in **1A** to S(IV) and S(VI), and no unreacted **1A** was recovered after 1 h.

Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane formed **1E** and **1D**, respectively, when reacted with CF_3SCl at 25 °C. Surprisingly, it was not possible to obtain the tetrasubstituted derivative of octamethylcyclotetrasilazane. When compound **1E** was heated at 80 °C, a yellow liquid was formed, which corresponded to the disubstituted derivative.

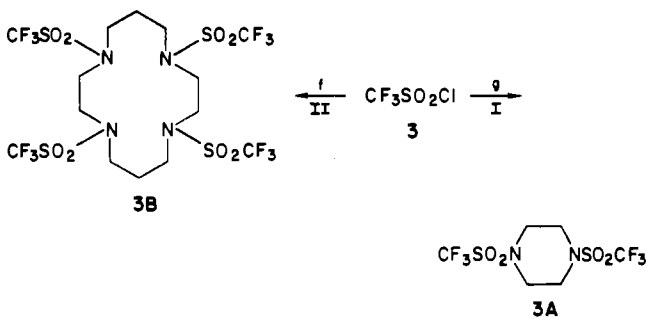
The compounds **1A**, **1B**, and **1C** have been prepared by methods III and IV in yields comparable to those via method I. Due to

Scheme II[a]



[a] I and II refer to the methods and d, f, and g to the reactants outlined in the Experimental Section.

Scheme III[a]



[a] I and II refer to methods and f and g to reactants outlined in the Experimental Section.

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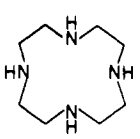
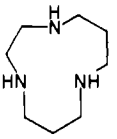
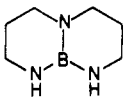
Chart I



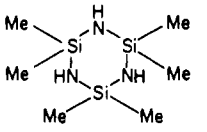
1,4,7,10-tetraazacyclododecane (a)



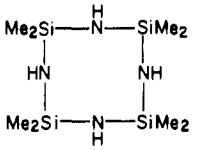
1,5,9-triazacycloundecane (b)



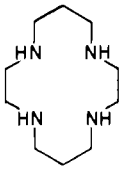
1,8,10-triaza-9-boradecalin (c)



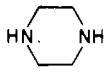
hexamethylcyclotrisilazane (d)



octamethylcyclotetrasilazane (e)



1,4,8,11-tetraazacyclotetradecane (f)



piperazine (g)

decomposition, **1D** and **1E** were obtained only by using method I.

The majority of the products obtained were stable in ambient air and with the exception of the silazane derivatives were hydrolytically stable.

Although it is possible to form $CF_3S(O)-$ and CF_3SO_2- derivatives from the oxidation of the CF_3S-substituted amines, a more straightforward route to the former is the metathetical reactions between $CF_3S(O)Cl$ and CF_3SO_2Cl and the respective amines. These new compounds are shown in Schemes II and III. The yields of these sulfur(IV) and -(VI) derivatives were lowered primarily because of the difficulty in purification.

Experimental Section

Trifluoromethanesulfenyl chloride[8] and trifluoromethanesulfinyl chloride[6] were prepared by the methods described in the literature. 1,4,7,10-tetraazacyclododecane,[9] 1,5,9-triazacycloundecane,[10] and 1,8,10-triaza-9-boradecalin[11] were synthesized by the literature procedures. The other reagents were used as received from commercial suppliers without further purification. The sources are as follows: 1,4,8,11-tetraazacyclotetradecane, Strem Chemicals; piperazine, Aldrich Chemical; hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, and trifluoromethanesulfonyl chloride, PCR.

General Procedure. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Volatile compounds were measured quantitatively by using PVT techniques. Infrared spectra were recorded with a Perkin-Elmer 599 spectrometer as liquid films between KBr disks. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz. $CDCl_3$ was used as the solvent with $CFCl_3$ as an external reference. Chemical shifts upfield from $CFCl_3$ were assigned negative values. ^{11}B NMR and ^1H NMR spectra were obtained at operating frequencies of 28.70 and 89.94 MHz, respectively. ^{11}B NMR spectra were recorded with reference to boric acid. Melting points were obtained with a Thomas-Hoover apparatus. Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU-6E or a VG 7070 HS mass spectrometer with an ionization potential of 17 or 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

The cyclic secondary amines shown in Chart I were employed in this study.

Method I. A 100- or 125-mL round-bottomed Pyrex flask equipped with a 14/20 ground-glass joint, a glass stopcock, and a magnetic stirring bar was used. The starting material was first dissolved in 25 mL of dry CH_2Cl_2, and a stoichiometric amount of dry triethylamine was then added. An equimolar amount of CF_3SCl, $CF_3S(O)Cl$, or CF_3SO_2Cl was condensed into the reaction flask at −196 °C. The reaction vessel was allowed to warm to 25 °C and to remain overnight with stirring. The solvent was removed under vacuum, 50 mL of dry benzene (pentane or hexane) was added to the solid remaining, and the mixture was stirred for 10 min. Any undissolved white solid was then removed by filtering, and the filtrate was concentrated to ~5 mL and subjected to Kugelrohring, which resulted in the isolation of the final product.

Method II. This method is as described in method I, except that after the triethylamine was added, the reaction vessel was allowed to warm to 25 °C and to remain with stirring for about 2 h before the CF_3SCl, $CF_3S(O)Cl$, or CF_3SO_2Cl was added.

Method III. The starting material was lithiated by stirring under nitrogen in 50 mL of anhydrous tetrahydrofuran at −78 °C and adding a stoichiometric amount of 1.6 M *n*-butyllithium. The resulting slurry was warmed to 25 °C and stirred for 15 min. Then it was cooled to −78 °C and treated with an equimolar amount of trimethylchlorosilane. After the mixture was stirred 30 min at 25 °C, the solvent was replaced with cyclohexane by distillation. This slurry was filtered, and the filtrate was concentrated and distilled bulb to bulb. The pure material that was recovered was then dissolved in 50 mL of CH_2Cl_2, and an equivalent amount of CF_3SCl was transferred into the flask at −196 °C. It was allowed to warm to 25 °C and to stir overnight. The procedure continues as in method I.

Method IV. Method III is followed to the stage of lithiation. The reaction mixture is cooled to −196 °C, and CF_3SCl is added in the requisite amount. The mixture is warmed to 25 °C and stirred overnight. The procedure continues as in method I.

1,8-Bis((trifluoromethyl)sulfenyl)-1,8,10-triaza-9-boradecalin (1A) (Methods I, III, IV). After the benzene solvent was concentrated, the product was distilled at 60 °C (1 torr) to give a pale yellow liquid (80%) that decomposed at >250 °C. The mass spectrum showed a molecular ion at *m/e* 339. ^{19}F NMR spectrum: ϕ −51.43 (s). ^{11}B NMR spectrum: +4.995 (s) ppm. Anal. Calcd for $C_8H_{12}N_3BS_2F_6$: C, 28.31; H, 3.53; N, 12.38. Found: C, 29.10; H, 3.75; N, 12.66.

1,4,7,10-Tetrakis((trifluoromethyl)sulfenyl)-1,4,7,10-tetraazacyclododecane (1B) (Methods I, III, IV). The product is a white solid (mp 86 °C, 85%) obtained after bulb-to-bulb distillation at 60 °C (1 torr). The mass spectrum showed a molecular ion peak at *m/e* 572 and peaks that correspond to the stepwise loss of CF_3S- groups. ^{19}F NMR spectrum: ϕ −46.04 (s). Anal. Calcd for $C_{12}H_{16}N_4S_4F_{12}$: C, 25.17; H, 2.79; N, 9.79. Found: C, 25.25; H, 2.96; N, 9.71.

1,5,9-Tris((trifluoromethyl)sulfenyl)-1,5,9-triazacycloundecane (1C) (Methods I, III, IV). The compound was obtained as a colorless liquid (90%) after bulb-to-bulb distillation at 60 °C (1 torr). The mass spectrum showed a molecular ion at *m/e* 457 and peaks corresponding to successive loss of CF_3S- groups. ^{19}F NMR spectrum: ϕ −44.88 (s). Anal. Calcd for $C_{11}H_{16}N_3S_3F_9$: C, 28.88; H, 3.52; N, 9.19. Found: C, 29.05; H, 3.76; N, 9.41.

1,5-Bis((trifluoromethyl)sulfenyl)octamethylcyclotetrasilazene (1D) (Method I). The product is a white solid (mp 88 °C, 70%) obtained after bulb-to-bulb distillation at 80 °C (1 torr). ^{19}F NMR spectrum: ϕ −51.25 (s). The mass spectrum showed a molecular ion peak at *m/e* 492 and peaks corresponding to the loss of CF_3S- groups. Anal. Calcd for $C_{10}H_{26}N_4Si_4S_2F_6$: C, 24.39; H, 5.28; N, 11.38. Found: C, 24.63; H, 5.17; N, 11.14.

1,3,5-Tris((trifluoromethyl)sulfenyl)hexamethylcyclotrisilazane (1E) (Method I). The colorless liquid product (70%) was obtained after bulb-to-bulb distillation at 60 °C (1 torr). ^{19}F NMR spectrum: ϕ −50.73 (s). The mass spectrum showed a molecular ion at *m/e* 519 and peaks that correspond to the loss of CF_3S- groups. Anal. Calcd for $C_9H_{18}N_3Si_3S_3F_9$: C, 20.80; H, 3.66; N, 8.09. Found: C, 21.15; H, 3.79; N, 8.22.

1,4-Bis((trifluoromethyl)sulfenyl)piperazine (1F) (Method I). Benzene was used as the solvent. A colorless crystalline solid (mp 25 °C, 65%) was obtained by Kugelrohring at 35 °C (1 torr). ^{19}F NMR spectrum: ϕ −46.2 (s). The mass spectrum gave a molecular ion at *m/e* 286, $(M - CF_3)^+$, and peaks assigned to the subsequent loss of CF_3S- groups. Anal. Calcd for $C_6H_8N_2S_2F_6$: N, 9.79; S, 22.38; F, 39.8. Found: N, 9.41; S, 21.79; F, 38.2.

1,4,8,11-Tetrakis((trifluoromethyl)sulfenyl)-1,4,8,11-tetraazacyclotetradecane (1G) (Method II). The compound was obtained after Kugelrohring at 60 °C (1 torr) for 8 h. It is a light brown solid (mp 75 °C, 60%). ^{19}F NMR spectrum: ϕ −46.6 (s). The mass spectrum showed the molecular ion at *m/e* 600 and peaks arising from subsequent loss of CF_3S- groups. Anal. Calcd for $C_{14}H_{20}N_4S_4F_{12}$: C, 28.00; H, 3.30; F, 38.00. Found: C, 27.27; H, 3.12; F, 37.32.

1,4-Bis((trifluoromethyl)sulfinyl)piperazine (2A) (Method I). The benzene was removed under vacuum until white crystals appeared (mp

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40 °C, 60%). ^{19}F NMR spectrum: ϕ −73.3 (s). The mass spectrum showed a molecular ion peak at m/e 318 and loss of CF_3– and CF_3SO– groups. Anal. Calcd for $C_6H_8N_2S_2O_2F_6$: C, 22.64; H, 2.51; S, 20.16. Found: C, 22.50; H, 2.40; S, 17.32.

1,3,5-Tris((trifluoromethyl)sulfinyl)hexamethylcyclotrisilazane (2B) (Method II). Hexane was used as solvent. Although most of the salt was insoluble in hexane, the liquid product obtained after the decanted solvent was evaporated was contaminated with traces of the salt; yield 50%. ^{19}F NMR spectrum: ϕ −78.58. The mass spectrum contains peaks at m/e 498, $(M - CF_3)^+$, and peaks assigned to fragments resulting from subsequent loss of $CF_3S(O)$– groups.

1,4,8,11-Tris((trifluoromethyl)sulfinyl)-1,4,8,11-tetraazacyclotetradecane (2C) (Method II). After the solvent was concentrated to 5 mL, the solution was placed into a sublimation apparatus and sublimed under vacuum at 65 °C for 24 h. After the Et_3NHCl sublimed onto the cold finger, a brown solid (mp 113 °C) remained. ^{19}F NMR spectrum: ϕ −72.4 (s). The mass spectrum contains peaks at m/e 595, $(M - CF_3)^+$, and peaks assigned to fragments resulting from stepwise loss of four $CF_3S(O)$– groups.

1,4-Bis((trifluoromethyl)sulfonyl)piperazine (3A) (Method I). Piperazine was dissolved in benzene. The white crystalline product was obtained after Kugelrohring at 53 °C (1 torr) (mp 53 °C, 60%). ^{19}F NMR spectrum: ϕ −85.2 (s). The mass spectrum showed a molecular ion at m/e 350 and peaks that were assigned to stepwise loss of two CF_3SO_2– groups. Anal. Calcd for $C_6H_8N_2S_2O_4F_6$: N, 8.00; S, 18.28; F, 32.57. Found: N, 7.90; S, 18.00; F, 31.50.

1,4,8,11-Tetrakis((trifluoromethyl)sulfonyl)-1,4,8,11-tetraazacyclotetradecane (3B) (Method II). Both the product and the ammonium salt are insoluble in hexane. The brown product (mp 135 °C) has a ^{19}F NMR resonance peak at ϕ −85.82. The mass spectrum gave a molecular ion at m/e 728 and peaks that reflect the stepwise loss of three CF_3SO_2– groups.

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Equilibria between Monohydroxo- and Dihydroxo-Bridged Binuclear Amminerhodium(III) Complexes

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The binuclear ion $(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$ (diol) equilibrates in acidic solution according to Scheme I. The kinetics and equilibria have been studied in 1 M $(Na,H)ClO_4$ at 25 and 34.5 °C and in the hydrogen ion concentration range 10^{-5}–0.1 M. The results at 25 °C are as follows: $k_1 = 4.26 \times 10^{-5}$ s^{-1}, $\Delta H^* = 91$ kJ mol^{-1}; $k_{-1} = 1.41 \times 10^{-5}$ s^{-1}, $\Delta H^* = 89$ kJ mol^{-1}; $k_{-2} = 9.6 \times 10^{-6}$ s^{-1}; $\Delta H^* = 109$ kJ mol^{-1}; $k_2/K_{a3} = 7.4 \times 10^{-2}$ s^{-1} M^{-1}, $\Delta H^*(k_2) - \Delta H^\circ(K_{a3}) = 58$ kJ mol^{-1}; $k_1 = k_1/k_{-1} = 3.03$, $\Delta H^\circ = 1.6$ kJ mol^{-1}. The acid dissociation constants for the diaqua monool, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$, at 25 °C are $pK_{a1} = 3.41$ and $pK_{a2} = 8.80$. The aqua hydroxo monool has been isolated as a solid salt, *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$.

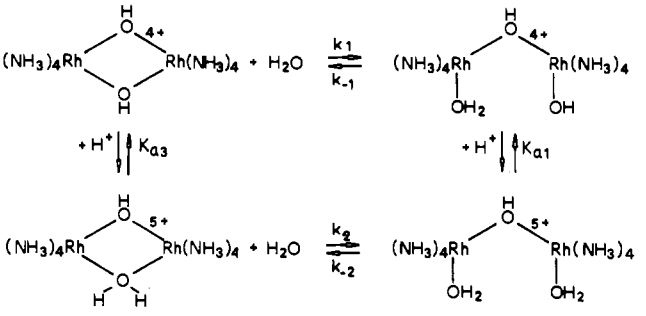
Introduction

Salts of the dihydroxo-bridged cations, diols, $(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$ and Δ,Λ-$(en)_2Rh(OH)_2Rh(en)_2^{4+}$ have been synthesized recently at this laboratory.[1-3] In analogy with the corresponding Cr(III) complexes[4-6] these Rh(III) diols equilibrate comparatively fast with their parent monohydroxo-bridged cations (monools). The thermodynamics and kinetics for the equilibration reaction between monools and diol in the Δ,Λ-ethylenediaminerhodium(III) system were published recently,[2] and we now report here our results for the tetraammine system.

Results

Synthesis and Properties of the Complexes. The diol, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$, dissolves rapidly in strongly acidic solution and gives nearly quantitatively the acid form of the monool, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$ (diaqua monool). The latter ion was obtained only in solution, but addition of the appropriate amount of base leads to the precipitation of pure aqua hydroxo monool salt, *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$.

Scheme I



Absorption spectra of the monool salt were measured in the $[H^+]$ region $1.0 \geq [H^+] \geq 10^{-14}$ M. All the spectral measurements could be interpreted in terms of the following two consecutive acid–base equilibria:

$$cis,cis\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+} \overset{K_{a1}}{\rightleftharpoons} cis,cis\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+} + H^+ \quad (1)$$

$$cis,cis\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+} \overset{K_{a2}}{\rightleftharpoons} cis,cis\text{-}(OH)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{3+} + H^+ \quad (2)$$

Spectral data for the three monool cations are reported in Table I. The results show that deprotonation of the hydroxo bridge to form an oxo-bridged species is unimportant for pH ≤14. The

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