the bromo complexes reported here. The non-halide ligands are treated as monodentate ammines, while the complexes involved have two bidentate amines; not all geometries are possible for {[Ru(en)$_2$X]$^{2+}$}. For example, a TBP with an apical halide (Figure 2A) forces one ethylenediamine to span the 120° angle between equatorial sites, a highly strained, if not impossible, configuration for ethylenediamine. (One of the distortions from that TBP would force the ethylenediamine to span trans sites in the resulting SPY.) This has the effect of raising the energy of the ^{4}E state (Figure 1 of ref 16) and makes isomerization through the C_{3v} form of the TBP impossible. (This is analogous to the restriction in the d^6 case, brought on by electronic considerations.) In addition, the three TBP → SPY distortions of the TBP with the equatorial halide (Figure 2B) need not be equally probable, as all three equatorial ligands are not identical.

Photolysis of *cis*-[Ru(en)$_2$Cl$_2$]$^+$ is fundamentally stereoretentive, with a cis/trans photoproduct ratio near 5/1; the analogous *cis*-[Ru(en)$_2$Br$_2$]$^+$ ion is much less stereoretentive upon photolysis, with a slight preponderance of the isomerized trans product (the cis/trans ratio is about 0.9/1). Both *trans*-[Ru(en)$_2$X$_2$]$^+$ ions photoisomerize, with a cis/trans ratio of 2/1 for X = Cl and 3/1 when X = Br. Lowering the average ligand field, by replacing chloride with bromide, leads to increased photoisomerization, rather than the increased stereoretention predicted.[16]

At this early stage in the study of Ru(III) photochemistry, we do not understand the seemingly chaotic stereophotochemistry observed. Available models, based on rearrangements of coordinately unsaturated species, seem inadequate, which again raises the question of whether these photoaquations should be considered to be dissociative processes, with no place for the incoming water until the stereochemistry of the 5-coordinate species has been established. More experimental work is necessary to determine whether a pattern in the stereophotochemistry of Ru(III) complexes will emerge.

Registry No. *cis*-[Ru(en)$_2$Br$_2$]$^+$, 55822-57-6; *trans*-[Ru(en)$_2$Br$_2$]$^+$, 73238-27-4; *cis*-[Ru(en)$_2$Br(H$_2$O)]$^{2+}$, 53368-48-2; *trans*-[Ru(en)$_2$Br(H$_2$O)]$^{2+}$, 15337-42-5.

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(Trifluoromethanesulfonato)pentaammineruthenium(III): A Relatively Labile Synthetic Intermediate[1]

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Typical syntheses of ruthenium(III) complexes involve the use of relatively labile ruthenium(II) intermediates (for example, [Ru(NH$_3$)$_5$(H$_2$O)]$^{2+}$ or [Ru(NH$_3$)$_4$(SO$_3$)(H$_2$O)]).[2,3] After a ligand on the Ru(II) complex (H$_2$O in the two examples above) has been replaced by the desired ligand, a Ru(III) complex is obtained by oxidation with reagents such as Ag(I),[4] Ce(IV),[4] Br$_2$,[5] and H$_2$O$_2$.[5] Unfortunately, in some

instances, these convenient methods are inappropriate: in the synthesis of bimetallic complexes in which a second atom, for example Co(III), is reducible by Ru(II); in situations when the ligands themselves are oxidizable; in cases where these methods require that the ligand compete successfully against the solvent, water, in binding to Ru(II). Recently, Sargeson and co-workers described a facile general method for the preparation of Co(III) complexes using the trifluoromethanesulfonate anion as a noncompeting leaving group.[6] We have adapted this method for the syntheses of Ru(III) complexes. The reaction involves substitution of Ru(III), which is normally highly inert,[7] without the necessity for Ru(II) intermediates or oxidizing agents.

In this report we describe the synthesis and some kinetics of formation of several classes of pentaammine complexes of Ru(III) that have received considerable attention in recent years: nitrile complexes, halide complexes, and complexes of aromatic nitrogen heterocycles.

Experimental Section

Reagents. Commercially available ACS grade reagents (Fisher) or redistilled solvents were used unless otherwise specified. Anhydrous trifluoromethanolsulfonic acid hydrate and tetramethylene sulfone (Alfa) were distilled under reduced pressure twice.

Instrumentation. Visible absorption spectra were recorded with thermostated Cary 14 or Beckman DU-8 spectrophotometers. Infrared spectra (KBr disk) were recorded with a Beckman Model 4240 spectrometer. Cyclic voltammograms were obtained with a Bioanalytical Systems CV-1 three-electrode system (Ag/AgCl reference electrode).

(Trifluoromethanesulfonato)pentaammineruthenium(III) Trifluoromethanesulfonate, [Ru(NH$_3$)$_5$(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$. This synthesis proceeds as described by A. M. Sargeson et al.[6] for the analogous cobalt complex, [Co(NH$_3$)$_5$(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$, with the following exceptions: (1) the ruthenium precursor, [Ru(NH$_3$)$_5$Cl]Cl$_2$·^{2}/$_3$H$_2$O,[8] was allowed to react for 2 h at 95 °C instead of 1 h and (2) the product was filtered by equally dividing the reaction mixture into three medium-porosity fritted filter funnels of 2.5-cm diameter and 10.5-cm height fitted with a septum cap and kept under positive pressure of dry nitrogen gas. The most convenient scale for this preparation is 5–10 g of product. Anal. Calcd for RuC$_3$H$_{15}$N$_5$F$_9$O$_9$S$_3$: C, 5.68; H, 2.38; N, 11.05; F, 26.97; S, 15.16; O, 22.70. Found (Galbraith Laboratories, Knoxville, TN): C, 5.56; H, 2.73; N, 10.72; F, 26.79; S, 14.96; O, 22.91. Visible spectrum: 285 nm, ϵ = 890 (in anhydrous HCF$_3$SO$_3$); 284 nm, ϵ = 870 (in sulfolane).

Halopentaammineruthenium(III), Pyridylpentaammineruthenium(III), and (Organonitrile)pentaammineruthenium(III) Complexes. In a typical preparation of these complexes, a solution containing [Ru(NH$_3$)$_5$(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$ (0.01–0.10 M) was prepared in doubly distilled sulfolane and an excess of the ligand was added. For reactions involving relatively neutral ligands such as the halides and organonitriles, a stoichiometric amount of trifluoromethanesulfonic anhydride was added. The vessel was stoppered to eliminate moisture. After the reaction was complete and the reaction mixture allowed to cool, the product was isolated by extraction. An equal volume of water was added, and excess ligand and sulfolane were extracted with several portions of dichloromethane, each of which was 10 times the volume of the original reaction mixture. The volume of the water layer was then reduced with use of a rotary evaporator until the product had precipitated. The solid was washed with methanol or acetone, rinsed with diethyl ether, and air-dried.

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Reactions to form iodo-, bromo-, and chloropentaammineruthenium(III) complexes are best carried out at 40–50 °C. A slight excess (less than 10%) of the appropriate halide salt is used to obtain the product as the trifluoromethanesulfonate salt, and a large excess (5–10-fold) is used to obtain the product as the halide salt. Product formation was monitored by UV–visible spectroscopy, and the product showed appropriate spectral properties.[9]

Complexes of substituted pyridines were prepared at 40–60 °C with use of no $(CF_3SO_2)_2O$ and a large (5–20 fold) excess of the ligand. Products were identified by visible–UV spectroscopy.[10]

A number of (organonitrile)pentaammineruthenium(III) complexes that have previously been reported have now been prepared with use of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$, including complexes of acetonitrile, benzonitrile, and o-, m-, and p-dicyanobenzenes. For these species, it has proven convenient to carry out the reaction at 60–70 °C and to monitor the reactions by cyclic voltammetry. The UV–visible and infrared spectra of these complexes match those that have been reported.[11]

(1-Adamantanecarbonitrile)pentaammineruthenium(III) Trifluoromethanesulfonate. A 500-mg amount of $[Ru(NH_3)_5(CF_3S-O_3)](CF_3SO_3)_2$ was dissolved in 10 mL of sulfolane at 60 °C containing a stoichiometric amount of $(CF_3SO_2)_2O$. A twofold excess of 1-adamantanecarbonitrile (250 mg) was added, and the reaction was periodically monitored with use of cyclic voltammetry. To obtain a voltammogram, 10 μL of the reaction mixture was withdrawn with an automatic micropipettor and added to 2.5 mL of dimethylformamide containing 0.10 M tetrabutylammonium perchlorate. This complex shows a reversible peak at 0.467 V vs. the NHE. The reaction is complete in 30 min. The crude product was obtained by addition of an equal volume of acetone followed by addition of a volume of diethyl ether approximately 10 times the original volume of the reaction mixture. The product is then obtained in approximately 65% overall yield by dissolving the crude product in a minimum amount of water, filtering, and adding 5 M aqueous trifluoromethanesulfonic acid drop by drop until the acid concentration is approximately 1 M. Anal. Calcd for $RuC_{14}H_{30}N_6F_9S_3O_9$: C, 21.15; H, 3.77; N, 10.57. Found (MicAnal, Tucson, AZ): C, 20.22; H, 3.44; N, 10.01. Visible–UV spectrum: 229 nm, $\epsilon = 626$ (in 0.01 M trifluoromethanesulfonic acid). Infrared spectrum: CN stretch at 2290 cm^{-1}.

(1,4-Dicyanobicyclo[2.2.2]octane)bis(pentaammineruthenium(III)) Trifluoromethanesulfonate. Preparation of a complex with two pentaammineruthenium(III) moieties simply requires the addition of 2 equiv of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ and a longer reaction time than is required for a corresponding mono(pentaammineruthenium(III)) complex. There is a limitation in this method in that the two pentaammineruthenium(III) moieties cannot be immediately adjacent to one another (i.e. the title complex and complexes with two $(NH_3)_5Ru^{III}$ moieties bound to trans-1,4-dicyanocyclohexane and to p-dicyanobenzene can be made, but only one $(NH_3)_5Ru^{III}$ unit could be bound to o-dicyanobenzene or to 1,2-dicyanocyclobutane). In a typical synthesis of (μ-1,4-dicyanobicyclo[2.2.2]octane)bis(pentaammineruthenium(III)) trifluoromethanessulfonate, 0.100 mg of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ and 0.0127 g of 1,4-dicyanobicyclo[2.2.2]octane were dissolved in 2.0 mL of double-distilled sulfolane containing 30 μL of trifluoromethanesulfonic anhydride. The reaction, monitored by cyclic voltammetry, required 2 h at 60 °C. The yield, with use of the precipitation and crystallization procedure described for the 1-adamantanecarbonitrile complex, was 49%. Anal. Calcd for $RuC_{16}H_{42}N_{12}F_{18}S_6O_{18}$: C, 13.50; H, 2.95; N, 11.81. Found (MicAnal, Tucson, AZ): C, 13.55; H, 2.78; N, 11.34. Visible–UV spectrum: 298 nm, $\epsilon = 1367$. Infrared spectrum: CN stretch at 2300 cm^{-1}.

((1,4-Dicyanobicyclo[2.2.2]octane)pentaammineruthenium(III))-aquotetraamminecobalt(III) Trifluoromethanesulfonate. Bimetallic complexes of 1,4-dicyano[2.2.2]octane, trans-1,4-dicyanocyclohexane, and m- and p-dicyanobenzene were prepared by the general route of first adding the cobalt(III) moiety $(NH_3)_4(H_2O)_2Co^{III}$ by removal of a chloride ligand (a shift of 10–15 nm in the band near 500 nm can be monitored as the reaction proceeds) and isolation of the corresponding (organonitrile)cobalt(III) complex followed by addition of $(NH_3)_5Ru^{III}$ with use of the $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$

complex. For the synthesis of ((μ-1,4-dicyanobicyclo[2.2.2]octane)pentaammineruthenium(III))aquotetraamminecobalt(III) trifluoromethanesulfonate, 100 mg of $[Co(NH_3)_4(H_2O)Cl]$ was dissolved in 1 mL of tetramethylene sulfone at 80 °C and 40 μL of $(CF_3SO_3)_2O$ and 33.5 mg of 1,4-dicyanobicyclo[2.2.2]octane were added. After 15 min the reaction mixture was allowed to cool to room temperature. This complex, as well as other Co(III) complexes with aquo ligands, does not precipitate as well as pentaammineruthenium(III) complexes. Therefore, aquotetraammine(1,4-dicyanobicyclo[2.2.2]octane)cobalt(III) was isolated by addition of 10 mL of water to the reaction mixture and extraction with 10 100-mL portions of CH_2Cl_2. Then, 100 mg (67% yield) of this complex was dissolved in 2 μL of sulfolane at 60 °C to which were added 25 μL of $(CF_3SO_2)_2O$ and 84 mg of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ and formation of the complex was monitored by cyclic voltammetry. After 2 h the mixture was cooled to room temperature and isolated by addition of an equal volume of acetone and a 10-fold volume of diethyl ether. It was recrystallized by dissolution in a minimum amount of water and addition of 10 M aqueous trifluoromethanesulfonic acid until the total acid concentration was about 4 M. Anal. Calcd for $RuCoC_{16}H_{41}N_{11}F_{18}S_{16}O_{19}$: C, 13.88; H, 2.96; N, 11.13. Found (MicAnal, Tucson, AZ): C, 13.71; H, 2.72; N, 11.30. Visible–UV spectrum: 498 nm, $\epsilon = 62$; 380 nm, shoulder; 295 nm, $\epsilon = 613$. IR spectrum: CN stretch at 2300 cm^{-1}.

Kinetics of Complex Formation. To monitor the kinetics of formation of nitrile and halide complexes of pentaammineruthenium(III), $[Ru(NH_3)_5(CF_3SO_3)_3]^{2+}$ was dissolved in acidic tetramethylene sulfone (0.01 M in trifluoromethanesulfonic acid) with warming and stirring. The Ru(III) concentration was typically about 1 mM. All reactions were carried out with the ligand in pseudo-first-order excess. Solutions were allowed to equilibrate in the thermostated cuvette holder of the spectrophotometer before the reaction was initiated. The changes in concentration were monitored continuously at a single wave length. Data were analyzed with use of least-squares fitting programs available with the PROPHET computing system.[12]

The formation of the 4-phenylpyridine complex was monitored differently because the spectral changes in the visible–UV region upon complexation were small. In this case, aliquots of the reaction mixture were removed periodically and the complex was reduced to give the characteristic spectrum ($\lambda_{max} = 446$ nm) of the pentaammine(4-phenylpyridine)ruthenium(II) complex.[10] The procedure was as follows: a 1 mM solution of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ in tetramethylene sulfone with no added acid was deaerated in a 10-mL bubbler flask on an argon line. The ligand, 4-phenylpyridine (twice recrystallized from methanol), was dissolved in tetramethylene sulfone and deaerated in a separate 10-mL bubbler flask. When the two solutions had been mixed, the progress of the reaction was monitored by reducing an aliquot of the reaction mixture with $[Ru(NH_3)_6]^{2+}$ (produced from $[Ru(NH_3)_6](CF_3SO_3)_3$ in acetone over amalgamated zinc) and recording the visible absorption spectrum. The temperature of the reaction mixture was maintained at 48 °C (to facilitate handling of the tetramethylene sulfone solutions, which can solidify at room temperature) with use of an oil bath.

Results and Discussion

Sargeson and co-workers published the first applications of trifluoromethanesulfonate complexes as relatively labile precursors for synthesis involving normally inert metal ions. Their initial work concerned cobalt(III) complexes.[6] Taube and co-workers applied this strategy for the synthesis of osmium(III) complexes shortly thereafter.[13] Since this work was first presented[1] and submitted for publication, Sargeson and co-workers have reported the preparation of a number of trifluoromethanesulfonate complexes, including pentaammine complexes of Rh(III), Ir(III), Ru(III), and Os(III).[14] In this work, we have used (trifluoromethanesulfonato)pentaammineruthenium(III) to prepare a variety of complexes that are of general interest to ruthenium chemists and we have

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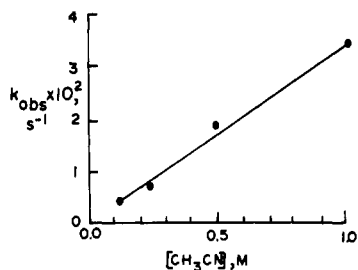
Figure 1. Plot of the pseudo-first-order rate constant for the formation of (acetonitrile)pentaammineruthenium(III) trifluoromethanesulfonate from (trifluoromethanesulfonato)pentaammineruthenium(III) in sulfolane as a function of the initial concentration of acetonitrile (at 37 °C).

obtained some kinetics data that are useful in predicting rates of reactions for synthetic purposes.

The substitution reactions of Ru(III) ammine complexes are notoriously slow, and few kinetic data are available for such reactions. The hydrolysis rate for $[Ru(NH_3)_5Cl]^{2+}$ has been reported to be 3.1×10^{-6} s^{-1} at 35 °C[15] and 3.6×10^{-6} s^{-1} at 37.3 °C[16] while that for $[Ru(NH_3)_5Br]^{2+}$ has been reported to be 4.0×10^{-6} s^{-1} at 37.3 °C.[16] The trifluoromethanesulfonate ligand is a much better leaving group, as shown by the hydrolysis rate of $[Ru(NH_3)_5(CF_3SO_3)]^{2+}$, 9.3×10^{-2} s^{-1} at 25 °C.[14] The complex $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ is a relatively labile precursor for synthesis of a wide variety of ligands when used in the inert solvent sulfolane at moderate temperatures. Figure 1 shows the dependence of the rate of formation of (acetonitrile)pentaammineruthenium(III) at 37 °C on the concentration of CH_3CN. The calculated second-order rate constant for this reaction is 6.4×10^{-2} M^{-1} s^{-1}. Comparable rate constants were obtained for other neutral ligands: 3.2×10^{-2} M^{-1} s^{-1} for the formation of (1-adamantanecarbonitrile)pentaammineruthenium(III) at 37 °C and 0.19 M^{-1} s^{-1} for formation of (4-phenylpyridine)pentaammineruthenium(III) at 48 °C. The formation rate for the bromide complex, $[Ru(NH_3)_5Br]^{2+}$, is considerably greater, 6.7 M^{-1} s^{-1} at 30 °C and 9.5 M^{-1} s^{-1} at 40 °C. This result is consistent with the favorable formation of an ion pair prior to the substitution step. Reactions with iodide ion are rapid. Even at a KI concentration of 5×10^{-4} M, the formation of $[Ru(NH_3)_5I]^{2+}$ was complete on mixing. This rapid reaction of iodide ion with the Ru(III) complexes has been previously observed by Ford and co-workers[17] and Taube and co-workers[18] and has been attributed to the ability of I$^-$ to reduce Ru(III) to produce labile Ru(II) intermediates. Unfortunately, catalytic substitution of $[Ru(NH_3)_5(CF_3SO_3)]^{2+}$ in the presence of I$^-$ is not a useful synthetic procedure since I$^-$ coordinates preferentially in the presence of other potential ligands (i.e., in the presence of excess CH_3CN, $[Ru(NH_3)_5I]^{2+}$ is formed predominantly), the I$^-$ is thereby sequestered, and $[Ru(NH_3)_5I]^{2+}$ is inert.

Our results indicate that $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ can be made readily, is stable for months with minor precautions (storage in a common desiccator over P_2O_5), and is useful for a variety of synthetic applications. Rates of reaction can be reliably estimated. The preliminary kinetic data indicate that this complex may be useful for establishing the nature of substitution reactions of Ru(III) and for comparing with data available for other robust ions such as Co(III), Rh(III), and Ir(III).[19]

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$[(Ph_2MeP)_3Cu(NC)_2BH_2]$ and $P^3Cu(NC)_2BH_2$ (P^3 = 1,1,1-Tris((diphenylphosphino)methyl)ethane): The First Metal Complexes of Dicyanodihydroborate

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The synthetic and structural chemistry of the cyanotrihydroborate anion, H_3BCN^-, with several transition-metal complexes is known.[2] Depending upon reaction conditions, it has been found that either the cyano alone may coordinate to the metal or the cyano and hydroborate may both coordinate, resulting in a H_3BCN^- bridging ligand.[2a,b] The recent success of McPhail and Spielvogel in synthesizing the new substituted hydroborate, dicyanodihydroborate, $(H_2B(CN)_2^-)$,[3] allowed us to investigate the Cu(I) complexes of this interesting ligand. The dicyanodihydroborate offers the possibilities, by analogy with the cyanohydroborate, that only one cyano will coordinate or that a cyano *and* hydrogen will coordinate. In addition, the second cyano group offers additional interesting possiblities for coordination.

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