monolabeled complex, after that the monolabeling was complete. The exchange rates for $[Fe(CO)_2L_2(COMe)NCS]$ were determined at 20 °C and p_{CO} = 1 atm. k_I was measured following the disappearance of the band of higher frequency of the unlabeled acetyl complex (ν_{CO} = 2024.4 cm^{-1}); k_{II} was measured by following both the disappearance of the band at higher frequency of the monolabeled complex (ν_{CO} = 1982.1 cm^{-1}) and the appearance of the band at lower frequency of the bilabeled complex (ν_{CO} = 1921 cm^{-1}), after that the monolabeling was completed.

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Registry No. **1**, 78240-85-4; **1′**, 89153-48-0; **2A**, 89153-50-4; **2A′**, 89153-51-5; **2B**, 89195-38-0; **2B′**, 89195-98-2; **3**, 89144-33-2; **3′**, 89153-49-1; **4**, 89153-47-9; **5**, 78250-85-8; **5′**, 89144-34-3; **6**, 89195-37-9; **8**, 91083-45-3; **9t**, 91083-46-4; **9c**, 91176-78-2; $[Fe(CO)_2(PMe_3)_2(Me)I]$, 33542-07-3; $[Fe(^*CO_a)(CO)(PMe_3)_2(Me)I]$, 91176-79-3; $[Fe(^*CO)_2(PMe_3)_2(Me)I]$, 88003-85-4; $[Fe(CO)_2(PMe_3)_2(COMe)I]$, 78306-61-3; $[Fe(^*CO)(CO)(PMe_3)_2(COMe)I]$, 89195-36-8; $[Fe(CO)_2(PMe_3)_2(Me)NCS]$, 78240-86-5; $[Fe(^*CO_a)(CO)(PMe_3)_2Me(NCS)]$, 91176-80-6; $[Fe(^*CO)_2(PMe_3)_2Me(NCS)]$, 89144-37-6; $[Fe(CO)_2(PMe_3)_2(COMe)(NCS)]$, 78688-00-3; $[Fe(^*CO)(CO)(PMe_3)_2(COMe)(NCS)]$, 89144-38-7; $[Fe(^*CO)_2(PMe_3)_2(^*COMe)(NCS)]$, 89144-39-8; CO, 630-08-0.

Contribution from The Research School of Chemistry,
The Australian National University, Canberra, ACT 2600, Australia

Synthetically Versatile (Trifluoromethanesulfonato)metal Amine Complexes

NICHOLAS E. DIXON, GEOFFREY A. LAWRANCE, PETER A. LAY, and ALAN M. SARGESON*

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Facile synthetic routes to complexes of the labile unidentate coordinated trifluoromethanesulfonate ($^-OSO_2CF_3$) ion are reported for $M(NH_3)_5(OSO_2CF_3)^{n+}$ (M = Rh(III), Ir(III), Cr(III), Ru(III) where n = 2; M = Pt(IV) where n = 3), $M(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ (M = Co(III), Rh(III), Cr(III)), *cis*-$M(en)_2(OSO_2CF_3)_2^+$ (M = Rh(III), Ir(III), Cr(III)), and *trans*-$M(en)_2Cl(OSO_2CF_3)^+$ (M = Rh(III), Ir(III)). The utility of these synthetically versatile intermediates in the preparation of a variety of complexes containing neutral ligands is illustrated. Rate constants for the aquation of the triflato complexes in 0.1 M CF_3SO_3H at 25 °C span 3 orders of magnitude and for the pentaammine complexes show a reactivity order of Ru(III) > Co(III) ~ Cr(III) ~ Rh(III) ≫ Ir(III) ≫ Pt(IV). For the pentakis(methylamine) complexes, the aquation rate is greater for Co(III), slightly greater for Rh(III), and smaller for Cr(III) in comparison to the corresponding pentaammine complexes. The aquations of $M(en)_2X(OSO_2CF_3)^+$ proceed largely without isomerization (<5%), and the triflato complexes are prepared stereospecifically by this route. For the *cis*-$M(en)_2(OSO_2CF_3)_2^+$ ions, consecutive first-order aquation processes are observed with rate constants $k_1 \sim 2k_2$.

Introduction

As a consequence of the large inductive effects of the CF_3– and $-SO_2$– groups, the (trifluoromethyl)sulfonyl group (CF_3SO_2) is one of the strongest electron-withdrawing groups known.[1-3] The trifluoromethanesulfonate anion ($CF_3SO_3^-$, triflate) has been shown to be a useful leaving group in organic chemistry.[3,4] The lability of coordinated triflate was established following the synthesis of $Cr(OH_2)_5(OSO_2CF_3)^{2+}$ by Scott and Taube.[5] Few other triflato complexes were reported until the recent synthesis of the complexes $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, and *fac*-$[Co(dien)(OSO_2CF_3)_3]$ (en = 1,2-ethanediamine; dien = 3-azapentane-1,5-diamine).[6,7] These complexes proved to be useful synthetic intermediates for reactions under mild conditions.[7-9] The triflate anion is only slightly less labile than perchlorate when coordinated in pentaamminecobalt(III) complexes (aquation rate constants are 0.1 and 0.027 s^{-1}, respectively, at 25 °C, μ = 1.0 M),[7,10] and its complexes are not potentially explosive as are the perchlorates. Triflate salts also have useful solubilities in a variety of nonaqueous solvents, which can be a synthetic advantage.

The present article reports syntheses of triflato complexes involving Co(III), Rh(III), Ir(III), Ru(III), Pt(IV), and Cr(III),[11] their reactivity, and use for further syntheses under mild conditions.

Experimental Section

Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, all molar absorptivities being reported in M^{-1} cm^{-1}. ^1H NMR spectra were measured with JEOL PMX60 or JEOL Minimar (100-MHz) spectrometers, at ~30 °C with neat CF_3SO_3H (for all triflato complexes) or D_2O as solvents and sodium (trimethylsilyl)propionate as internal reference. ^{13}C NMR spectra were recorded with a JEOL FX-60 spectrometer, using dioxane as reference. All chemical shifts (ppm) are reported as downfield shifts from these references. Infrared spectra were recorded (KBr disk) with a Perkin-Elmer Model 457 instrument. For the more labile triflato complexes, substitution of Br^- for $CF_3SO_3^-$ occurred in KBr disks. In these instances, chloroform mulls were prepared, and spectra were recorded after the chloroform had evaporated from the surface of the KBr disks.

Anhydrous trifluromethanesulfonic acid (CF_3SO_3H, 3M Co.) was vacuum distilled (bp 50 °C (10 mmHg)). The precursors $[Rh(NH_3)_5Cl]Cl_2$,[12] $[Cr(NH_3)_5Cl]Cl_2$,[13] $[Ir(NH_3)_5Cl]Cl_2$,[14] $[Ru(NH_3)_5$-

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$Cl]Cl_2$,[15] $[Pt(NH_3)_5Cl]Cl_3$,[16] $[Co(NH_2CH_3)_5Cl]Cl_2$,[17] $[Rh(NH_2CH_3)_5Cl]Cl_2$,[18] $[Cr(NH_2CH_3)_5Cl]Cl_2$,[19] and *cis*-$[Cr(en)_2Cl_2]Cl$[20] were synthesized by reported methods.[21]

cis- and *trans*-$[Rh(en)_2Cl_2]Cl$ were prepared by a modification of the published method.[22] $RhCl_3{\cdot}3H_2O$ (5.0 g) and en·2HCl (5.05 g) were dissolved in water (30 mL) by gentle warming. Aqueous 2 M NaOH (19 mL) was added and the solution refluxed with stirring until the suspension dissolved. More 2 M NaOH (19 mL) was added dropwise through the reflux condenser until the pH of the solution remained at ~7. The solution was evaporated to dryness, and the solid residue was heated at 170 °C for 24 h. The solid was dissolved in HCl (0.02 M, 1.5 L) and sorbed on a column of Dowex 50W-X2 resin (H^+ form, 25 × 4 cm). After being washed with 0.05 M HCl (2 L), the complexes were immediately eluted with 0.7 M HCl to give two clearly defined yellow bands. Each band was collected and evaporated to dryness under reduced pressure to yield the trans (3.0 g, first band eluted) and the cis isomers (3.1 g, second band), characterized spectroscopically. Anal. Calcd for *trans*-$[RhC_4H_{16}N_4Cl_2]Cl{\cdot}HCl{\cdot}2H_2O$: C, 11.95; H, 5.27; N, 13.94; O, 7.96; Cl, 35.28. Found: C, 11.9; H, 5.3; N, 13.7; O, 8.2; Cl, 35.3. ^1H NMR (0.1 M DCl): δ 4.86 (8 H, $-NH_2$), 2.91 (8 H, $-CH_2$). ^{13}C NMR (0.1 M DCl): δ −21.7. Anal. Calcd for *cis*-$[RhC_4H_{16}N_4Cl_2]Cl{\cdot}H_2O$: C, 13.71; H, 5.46; N, 15.99. Found: C, 14.0; H, 5.8; N, 15.7. ^1H NMR (0.1 M DCl): δ 2.88 (8 H, $-CH_2-$), 4.82 (4 H, $-NH_2$), 5.41 (4 H, $-NH_2$). ^{13}C NMR (0.1 M DCl): δ −20.2, −21.3.

Analytically pure *cis*- and *trans*-$[Ir(en)_2Cl_2]Cl$ were prepared by the modification of Galsbøl[23] on the original method of Baranovskii.[24] Column chromatography as described for the Rh analogues may be used to separate the isomers. The complexes were characterized by their known spectral properties.[23]

Trifluoromethanesulfonato Complexes. *Caution*! The addition of CF_3SO_3H to the complexes causes a rapid evolution of HCl. All reactions should be performed in a well-ventilated fume hood. Perchlorate salts should not be used in the following reactions under any circumstances; dissolution of perchlorate salts in triflic acid results in the generation of a hot solution of anhydrous perchloric acid, an extreme explosion hazard.

$[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as described previously.[6,7] The isolation procedure may be simplified by the use of gravity filtration instead of centrifugation after addition of ether, as described below for the Rh analogue. ^1H NMR: δ 1.67 (3 H, trans NH_3), 3.33 (12 H, cis NH_3). $[Co(ND_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared analogously by using $[Co(ND_3)_5Cl]Cl_2$[25] as starting material.

$[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. Anhydrous CF_3SO_3H (60 mL) was added cautiously to $[Rh(NH_3)_5Cl]Cl_2$ (10 g). A steady stream of nitrogen was passed through the resulting solution while the flask was heated in an oil bath at 100 °C. After evolution of HCl had ceased[6] (~2 h), the flask was cooled to ~5 °C. The gas flow was discontinued, and diethyl ether (200 mL) was added slowly with vigorous stirring. The pale yellow suspension was filtered under gravity on a sintered frit (porosity 4); then, vacuum was applied and the precipitate washed thoroughly with ether and air-dried. The product was ground in a mortar and dried in a vacuum desiccator over P_2O_5 (21.5 g). Anal. Calcd for $C_3H_{15}N_5F_9O_9S_3Rh$: C, 5.67; H, 2.38; N, 11.03; S, 15.14. Found: C, 5.6; H, 2.5; N, 11.3; S, 14.9. ^1H NMR (60 MHz): δ 2.90 (3 H, trans NH_3), 3.16 (12 H, cis NH_3).

$[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. A solution of $[Cr(NH_3)_5Cl]Cl_2$ (1.0 g) in anhydrous CF_3SO_3H (30 mL) was allowed to stand at room temperature for 3 days while being gently flushed with N_2. Diethyl ether (230 mL) was added slowly with vigorous stirring. A fine pink precipitate was separated on a sintered frit (porosity 4), initially by gravity and after a bed of precipitate had formed, by suction. The precipitate was washed with ether (~250 mL) and dried overnight in vacuo over P_2O_5 (1.75 g). The pink powder is best stored in a desiccator and is stable for several months sealed from the atmosphere. Anal. Calcd for $C_3H_{15}N_5F_9O_9S_3Cr$: C, 6.17; H, 2.59; N, 11.98; S, 16.46. Found: C, 6.2; H, 2.5; N, 11.6; S, 16.2.

$[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. Anhydrous CF_3SO_3H (10 mL) was added to $[Ir(NH_3)_5Cl]Cl_2$ (0.5 g). A steady stream of nitrogen was passed through the resulting solution as it was warmed to and maintained at ~120 °C for 15 h. When the solution was cooled 20 °C and ether (80 mL) was added, a white product precipitated. This was separated as described for the Cr analogue. It was ground in a mortar and boiled in dry chloroform (~30 mL) for 15 min, filtered, washed with ether (~50 mL), and dried in vacuo over P_2O_5 (0.82 g). Anal. Calcd for $C_3H_{15}N_5F_9O_9S_3Ir$: C, 4.97; H, 2.09; N, 9.67; F, 23.60. Found: C, 4.8; H, 2.1; N, 9.1; F, 23.2. ^1H NMR (60 MHz): δ 3.85 (NH_3).

$[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. A solution of $[Ru(NH_3)_5Cl]Cl_2$ (0.4 g) in anhydrous CF_3SO_3H (8 mL) was heated under N_2 in an oil bath at 100 °C for 2 h. After it was cooled to 20 °C, ether (40 mL) was added with vigorous stirring, and the white precipitate was isolated and purified as described for the Ir analogue (0.82 g). Anal. Calcd for $C_3H_{15}N_5F_9O_9S_3Ru$: C, 5.69; H, 2.39; N, 11.06; S, 15.18; F, 27.00. Found: C, 5.7; H, 2.4; N, 10.8; S, 15.2; F, 26.5.

$[Pt(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$. A solution of $[Pt(NH_3)_5Cl]Cl_3$ (0.6 g) in anhydrous CF_3SO_3H (10 mL) was treated as described for the Ir analogue, and a white product was isolated (1.1 g). Anal. Calcd for $C_4H_{15}N_5F_{12}O_{12}S_4Pt$: C, 5.51; H, 1.73; N, 8.00; S, 14.63. Found: C, 5.2; H, 2.0; N, 7.4; S, 14.4. ^1H NMR (60 MHz): δ 4.70 ($^3J_{^{195}Pt-^1H} \sim 35$ Hz, $^2J_{^{14}N-^1H} \sim 55$ Hz).

$[Cr(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. A solution of $[Cr(NH_2CH_3)_5Cl]Cl_2$ (0.65 g) in anhydrous CF_3SO_3H (20 mL) was treated as described for the $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ ion (1.25 g). Anal. Calcd for $C_8H_{25}N_5F_9O_9S_3Cr$: C, 14.68; H, 3.85; N, 10.70; S, 14.70. Found: C, 15.0; H, 3.9; N, 10.4; S, 14.45.

$[Co(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. A solution of $[Co(NH_2CH_3)_5Cl]Cl_2$ (0.8 g) in anhydrous CF_3SO_3H (20 mL) was treated as described for the Cr analogue. Anal. Calcd for $C_8H_{25}N_5F_9O_9S_3Co$: C, 14.53; H, 3.81; N, 10.59; S, 14.54. Found: C, 14.2; H, 3.8; N, 10.2; S, 14.7. ^1H NMR (60 MHz): δ 1.24 (3 H, trans CH_3), 1.87 (12 H, cis CH_3), 3.08 (2 H, trans NH_2), 3.76 (8 H, cis NH_2).

$[Rh(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. A solution of $[Rh(NH_2CH_3)_5Cl]Cl_2$ (0.65 g) in anhydrous CF_3SO_3H (15 mL) was heated at ~110 °C for 3 h, while flushed gently with N_2. After it was cooled to 20 °C, ether (100 mL) was slowly added to the flask with mechanical stirring. The white precipitate was collected, washed with ether (100 mL), and dried in vacuo over P_2O_5 (1.2 g). Anal. Calcd for $C_8H_{25}N_5F_9O_9S_3Rh$: C, 13.62; H, 3.57; N, 9.93; S, 13.63. Found: C, 13.6; H, 3.5; N, 9.6; S, 13.8. ^1H NMR (60 MHz): δ 1.80 (3 H, trans CH_3), 2.10 (12 H, cis CH_3), 3.56 (10 H, $-NH_2$).

***cis*-$[Cr(en)_2(OSO_2CF_3)_2](CF_3SO_3)$.** A solution of *cis*-$[Cr(en)_2Cl_2]Cl$ (1.0 g) in anhydrous CF_3SO_3H (30 mL) was treated, and the product was isolated, exactly as described for the $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ complex (2.1 g). Anal. Calcd for $C_7H_{16}N_4F_9O_9S_3Cr$: C, 13.57; H, 2.60; N, 9.04; S, 15.53. Found: C, 13.45; H, 2.8; N, 8.8; S, 15.2.

***cis*-$[Rh(en)_2(OSO_2CF_3)_2](CF_3SO_3)$.** While being flushed with N_2, *cis*-$[Rh(en)_2Cl_2]Cl{\cdot}1.5H_2O$ (1.0 g) in anhydrous CF_3SO_3H (5 mL) was heated at ~110 °C for 4 h. When the evolution of HCl had ceased,[6] the viscous solution was cooled to 20 °C and ether (25 mL) was added cautiously with stirring. The yellow solid was collected on a sintered-glass funnel (porosity 4), washed with ether (~50 mL), and then boiled in chloroform (~20 mL) for 1 h. The suspension was collected, washed with ether (~50 mL), and dried in vacuo over P_2O_5 (1.6 g). Anal. Calcd for $C_7H_{16}N_4F_9O_9S_3Rh$: C, 12.54; H, 2.14; N, 8.36; S, 14.35; F, 25.51. Found: C, 12.4; H, 2.5; N, 8.0; S, 13.8; F, 25.0. ^1H NMR (100 MHz): δ 2.22–2.80 ($-CH_2-$), 4.11, 4.36, 4.75 ($-NH_2$, ratio 1:1:2).

***cis*-$[Ir(en)_2(OSO_2CF_3)_2](CF_3SO_3)$.** Reaction of *cis*-$[Ir(en)_2Cl_2]Cl{\cdot}H_2O$ (0.5 g) in anhydrous CF_3SO_3H (5 mL) at 120 °C for 15 h and isolation as described for the Rh analogue yielded the white product (0.85 g). Anal. Calcd for $C_7H_{16}N_4F_9O_9S_3Ir$: C, 11.07; H, 2.12; N, 7.38; S, 12.66. Found: C, 11.2; H, 2.0; N, 7.4; S, 12.8. ^1H NMR (100 MHz): δ 2.24, 2.34 ($-CH_2-$), 4.8, 5.0 ($-NH_2$).

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***trans*-$[Rh(en)_2Cl(OSO_2CF)](CF_3SO_3)$.** *trans*-$[Rh(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ (1.0 g) in anhydrous CF_3SO_3H (5 mL) was reacted and the yellow product isolated exactly as described for the cis analogue (1.55 g). Anal. Calcd for $C_6H_{16}N_4ClF_6O_6S_2Rh$: C, 12.94; H, 2.89; N, 10.06; S, 11.52; F, 20.48; Cl, 6.37. Found: C, 13.0; H, 3.2; N, 9.8; S, 11.6; F, 20.2; Cl, 6.1. ^1H NMR (100 MHz): δ 2.46 ($-CH_2-$), 4.08 ($-NH_2$).

***trans*-$[Ir(en)_2Cl(OSO_2CF_3)](CF_3SO_3)$.** Reaction of *trans*-$[Ir(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ (0.5 g) in anhydrous CF_3SO_3H (5 mL), at 120 °C for 24 h, yielded the pale yellow product (0.85 g). Anal. Calcd for $C_6H_{16}N_4ClF_6O_6S_2Ir$: C, 11.16; H, 2.50; N, 8.67; S, 9.93; Cl, 5.49. Found: C, 11.2; H, 2.3; N, 8.6; S, 9.8; Cl, 5.6. ^1H NMR (100 MHz): δ 2.31 ($-CH_2-$), 4.62 ($-NH_2$).

Derivative Complexes. $[Cr(NH_3)_5(OH_2)](ClO_4)_3\cdot H_2O$. $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.3 g) was dissolved in water (10 mL), the pH was adjusted to $\sim$4 with $HClO_4$, and excess solid $LiClO_4$ was added. Refrigeration gave large orange crystals, which were collected, washed with ethanol, and dried in air (0.17 g). Anal. Calcd for $H_{19}N_5Cl_3O_{14}Cr$: H, 4.06; N, 14.85; Cl, 22.55. Found: H, 3.8; N, 14.4; Cl 22.4. Visible spectrum (λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})): in 0.01 M CF_3SO_3H, 480 (36.8), 360 (31.6); in 1.0 M $HClO_4$, 480 (35.1), 359 (30.3).[26]

$[Cr(NH_3)_5(NCCH_3)](CF_3SO_3)_3$. A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.3 g) in dry acetonitrile (15 mL) was stirred at 20 °C for 1 h. Evaporation under reduced pressure gave crystals of the complex, which were collected, washed with ether, and dried. The yellow product was sufficiently pure for use without recrystallization (0.3 g). Anal. Calcd for $C_5H_{18}N_6F_9O_9S_3Cr$: C, 9.60; H, 2.90; N, 13.44; S, 15.38. Found: C, 9.4; H, 3.2; N, 13.1; S, 15.7. Visible spectrum (λ_{max} (ϵ_{max})) in water: 468 (35), 351 (34). IR: $\nu(C\equiv N)$ 2333 cm^{-1}.

$[Cr(NH_3)_5(OC(NH_2)_2)](S_2O_6)_{3/2}\cdot 2H_2O$. A solution of recrystallized urea (1.0 g) and $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.4 g) in dry sulfolane (30 mL) was stirred for 1 h at 20 °C and then washed into a large flask with ethanol ($\sim$20 mL). Addition of ether ($\sim$300 mL) with vigorous stirring precipitated an oily red-pink product. The clear solution was decanted, and the precipitate was redissolved in ethanol ($\sim$30 mL) and reprecipitated with ether ($\sim$300 mL) (twice). Finally the powdery precipitate was dissolved in methanol ($\sim$40 mL) and an aqueous solution of lithium dithionate added with stirring to give crystals of the red dithionate salt. These were collected, washed with ice-cold water and then methanol and ether, and dried in air (0.22 g). Anal. Calcd for $CH_{23}N_7O_{12}S_3Cr$: C, 2.54; H, 4.89; N, 20.71; S, 20.32. Found: C, 2.5; H, 4.5; N, 20.6; S, 20.6. Visible spectrum (λ_{max} (ϵ_{max})) in water: 504 (58.6), 370 (38.2).

$[Rh(NH_3)_5(OH_2)](ClO_4)_3$. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (1.0 g) was dissolved in water (8 mL). The solution was filtered and warmed to $\sim$80 °C on a steam bath, and $HClO_4$ (70% w/v) was added until the first sign of persistent cloudiness. Slow cooling of the solution gave pale yellow crystals, which were collected, washed with ethanol and diethyl ether, and dried in air (0.7 g). A small second crop was obtained by the addition of more $HClO_4$ to the filtrate and cooling. Anal. Calcd for $H_{17}N_5Cl_3O_{13}Rh$: H, 3.40; N, 13.88; Cl, 21.08. Found: H, 3.5; N, 13.7; Cl, 20.9. Absorption spectrum (λ_{max} (ϵ_{max})) in water: 315 (104), 262 (90). ^1H NMR (60 MHz): δ 3.83 (NH_3).

$[Rh(NH_3)_6](CF_3SO_3)_3$. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) was dissolved in liquid ammonia ($\sim$50 mL), and the solvent was immediately removed by evaporation at reduced pressure. A quantitative yield of a white crystalline product was collected, washed with diethyl ether, and dried in vacuo over P_2O_5. Anal. Calcd for $C_3H_{18}N_6F_9O_9S_3Rh$: C, 5.52; H, 2.78; N, 12.88. Found: C, 5.7; H, 2.9; N, 12.7. The product was converted to the perchlorate salt by dissolution in hot water ($\sim$80 °C, 150 mL), addition of concentrated $HClO_4$ (3 mL), and slow cooling (1.5 g). Anal. Calcd for $H_{18}N_6Cl_3O_{12}Rh$: H, 3.60; N, 16.69; Cl, 21.12. Found: H, 3.7; N, 16.7; Cl, 21.05. Absorption spectrum (λ_{max} (ϵ_{max})) in water: 305 (131), 256 (94). ^1H NMR (60 MHz): δ 3.84 (NH_3).

$[Ir(NH_3)_5(OH_2)](CF_3SO_3)_3$. $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.2 g) was dissolved in water (2 mL) and the solution heated at 80 °C for 10 min. The solvent was removed by evaporation to give a quantitative yield of the white product, which was collected, washed with ether, and dried in vacuo over P_2O_5. Anal. Calcd for $C_3H_{17}N_5F_9O_{10}S_3Ir$: C, 4.85; H, 2.31; N, 9.42; S, 12.95. Found: C, 4.7; H, 2.2; N, 9.3; S, 13.1. Absorption spectrum (λ_{max} (ϵ_{max})) in water: 333 (12, sh), 258 (86), 213 (128).

$[Ru(NH_3)_5(HOCH_3)](CF_3SO_3)_3$. $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.3 g) was stirred in warm methanol ($\sim$50 mL, 40 °C) for 30 min. Then, the solution was evaporated to near dryness under reduced pressure. The white product was separated, washed with ether, and dried in vacuo (0.3 g). Anal. Calcd for $C_4H_{19}N_5F_9O_9S_3Ru$: C, 7.22; H, 2.88; N, 10.52; S, 14.54. Found: C, 7.1; H, 3.0; N, 11.0; S, 14.5.

$[Ir(NH_3)_6](CF_3SO_3)_3$. A solution of $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.5 g) in liquid ammonia ($\sim$30 mL) was allowed to stand for 14 h and then evaporated to dryness. The off-white product was slurried in ether ($\sim$50 mL), collected, washed with ether, and air-dried (0.5 g). Anal. Calcd for $C_3H_{18}N_6F_9O_9S_3Ir$: C, 4.86; H, 2.45; N, 11.13. Found: C, 5.0; H, 2.3; N, 11.0. ^1H NMR (60 MHz): δ 4.60. It is recrystallized as the chloride salt from 3 M HCl. Anal. Calcd for $H_{18}N_6Cl_3Ir$: H, 4.53; N, 20.97; Cl, 26.54. Found: H, 4.4; N, 20.8; Cl, 26.6. Absorption spectrum (λ_{max} (ϵ_{max})) in water: 314 (14), 251 (92), 214 (160).

***cis*-$[Rh(en)_2(NH_3)_2](CF_3SO_3)_3$.** A solution of *cis*-$[Rh(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (0.2 g) in liquid ammonia ($\sim$10 mL) was allowed to evaporate to dryness. The white product was slurried with ether ($\sim$30 mL), collected, washed with ether, and air-dried (0.2 g). Anal. Calcd for $C_7H_{22}N_6F_9O_9S_3Rh$: C, 11.94; H, 3.15; N, 11.93. Found: C, 12.1; H, 3.0; N, 11.8. ^{13}C NMR: δ −21.0, −21.25 (vs. dioxane). Absorption spectrum (λ_{max} (ϵ_{max})) in water: 302 (241), 256 (183).

***trans*-$[Rh(en)_2(NH_3)Cl](CF_3SO_3)_2$.** Reaction of *trans*-$[Rh(en)_2Cl(OSO_2CF_3)](CF_3SO_3)$ (0.2 g) exactly as above yielded the required product quantitatively. Anal. Calcd for $C_6H_{19}N_5ClF_6O_6S_2Rh$: C, 12.55; H, 3.33; N, 12.20; Cl, 6.18; F, 19.86. Found: C, 12.8; H, 3.1; N, 11.7; Cl, 5.8; F, 19.9. ^{13}C NMR: δ −21.75 (vs. dioxane). ^1H NMR (60 MHz): δ 3.15 ($-CH_2-$), 5.4 ($-NH_2$, NH_3, br). Absorption spectrum (λ_{max} (ϵ_{max})) in water: 342 (80), 275 (113).

$[Rh(en)_3]Cl_3\cdot 3H_2O$. *cis*-$[Rh(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (0.5 g) was dissolved in dry 1,2-ethanediamine ($\sim$2 mL) and heated on a steam bath for 10 min. Ethanol (5 mL) and ether (50 mL) were added to the cooled solution with stirring, and the white precipitate was collected, boiled in chloroform (50 mL), and collected again. The air-dried complex was recrystallized from aqueous HCl as the chloride salt (0.23 g). Anal. Calcd for $C_6H_{30}N_6Cl_3O_3Rh$: C, 16.24; H, 6.82; N, 18.94. Found: C, 16.2; H, 6.5; N, 18.7. ^1H NMR (60 MHz): δ 2.75 ($-CH_2-$). ^{13}C NMR: δ −21.0. Absorption spectrum (λ_{max} (ϵ_{max})) in water: 301 (242), 255 (144). The complex was prepared in higher yield by equimolar addition of the ligand and the complex in dry sulfolane. After 5 min, the solution was mixed with hot aqueous HCl to precipitate the desired complex.

$[Ir(en)_3]Cl_3\cdot 3H_2O$. The complex was prepared from *cis*-$[Ir(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (0.4 g) as described for the Rh analogue except a longer reaction time ($\sim$2 h) was used (0.27 g). Anal. Calcd for $C_6H_{30}N_6Cl_3O_3Ir$: C, 13.52; H, 5.67; N, 15.77. Found: C, 13.8; H, 5.5; N, 15.7. ^1H NMR (60 MHz): δ 2.80 ($-CH_2-$), 5.45, 5.75 ($-NH_2$). ^{13}C NMR: δ −18.9.

Kinetic Measurements. The kinetics of spontaneous aquation were determined at 25 ± 0.1 °C usually at the absorbance maximum for the triflato complex by using a Cary 118C recording spectrophotometer. Reactions were initiated by direct dissolution in the temperature-equilibrated solvent or, for faster runs, by injecting prequilibrated solvent from a thermostated syringe through a mixing chamber containing the solid complex on a sintered frit directly into a spectrophotometer cell.[27] This mixer allows the progress of the reaction to be monitored within a few seconds of dissolution. Reactions were followed for at least 4 half-lives, and rate constants were evaluated by least-squares computer fitting to a single exponential term (for first-order processes) or by graphical separation (for those reactions showing consecutive first-order processes).[28] Quoted rate constants are the mean values obtained from three or more identical experiments.

Results

Syntheses and Characterization. The complexes $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_n$ ($n = 2$, M = Co(III),[6,7] Rh-

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Table I. Infrared Frequencies (cm^{-1}) of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_n$ Complexes

Co(III)[a]		Rh(III)[a]	Ir(III)[a]	Cr(III)[a,c]	Ru(III)[a]	Os(III)[c,d]	Pt(IV)[a,c]	assignt[e]
3300 (s)	[2600][b]	3200 (s)	3290 (s)	3250 (s)	3250 (s)	3300 (s)	3150 (s)	ν(N-H)
			3250 (s)				3080 (sh)	
1610 (m)	[1400]	1620 (m)	1618 (m)	1620 (m)	1600 (m)	1620 (m)	1560 (m)	δ_{as}(N-H)
			1413 (w)			1400 (m)		
1390 (m)		1387 (m)	1379 (s)	1390 (m)	1385 (m)	1370 (s)	1380 (m)	
1360 (s)	[1355]	1348 (s)	1365 (sh)	1350 (s)	1350 (s)	1355 (m)	1348 (s)	δ_s(N-H) + ν_{as}(OSO, ligand)
		1333 (s)	1347 (m)	1347 (m)	1330 (s)	1338 (m)	1325 (sh)	
		1314 (s)				1320 (s)		
1250 (s)	[1250]	1250 (s)	1250 (s)	1250 (s)	1250 (s)	1280 (s)	1290 (sh)	ν_{as}(OSO, anion)
			1230 (s)			1235 (s)	1255 (s)	
			1216 (s)			1220 (s)	1205 (m)	
1170 (s)	[1175]	1170 (s)	1182 (s)	1180 (s)	1175 (s)	1185 (s)	1178 (s)	ν(C-F)
			1160 (s)			1160 (sh)		
1030 (s)	[1030]	1033 (sh)	1031 (s)	1038 (s)	1030 (s)	1032 (s)	1033 (s)	
		1026 (s)	1023 (s)	1030 (s)		1018 (s)	1025 (s)	ν_s(OSO)
		1020 (s)	1018 (s)					
830 (m)	[700]	890 (sh)	890 (sh)	805 (sh)	795 (m)	873 (m)	905 (m, br)	
		850 (s)	881 (m)	770 (m)		850 (sh)		$\rho_r(NH_3)$
						838 (s)		
640 (s)	[635]	640 (s)	639 (s)	650 (s)		638 (s)	652 (s)	
		630 (s)	628 (s)	630 (s)	635 (s)	630 (s)	640 (s)	anion bending, str δ(OSO)
572 (m)	[580]	580 (m)	578 (m)	575 (m)	580 (m)	582 (m)	580 (m)	
520 (s)	[520]	520 (m)	518 (s)	515 (s)	520 (s)	523 (s)	520 (s)	
				480 (w)		500 (w)		ν(M-N) + δ(N-M-N)
			367 (w)			370 (w)		
			352 (w)			360 (w)	352 (w)	
			322 (w)	321 (w)		324 (w)	322 (w)	γ(M-O)

[a] Obtained from dried chloroform mulls. Resolution was poor, but KBr disks showed some substitution of coordinated triflate by bromide in some cases. [b] $[Co(ND_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. [c] KBr disk. [d] References 42 and 74. [e] Assignments made by analogy to usual assignments for pentaammine and trifluoromethanesulfonate compounds, supported by deuteration experiments with Co(III).

(III), Ir(III), Cr(III), Ru(III); $n = 3$, M = Pt(IV)) and $[M(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (M = Co(III), Rh(III), Cr(III)) containing coordinated triflate have been prepared from the appropriate chloro precursors in essentially quantitative yield and were characterized by microanalysis and IR, electronic, and NMR spectroscopic methods. The pentaammine complexes of Co(III), Rh(III), Ir(III), Cr(III), Ru(III), and Pt(IV) show simple infrared spectra with bands due to ammine and triflate only (Table I). In particular, the region of 1300–1400 cm^{-1} exhibits bands that are due to neither ionic triflate nor NH_3 vibrational modes, the latter being identified by deuteration of the cobalt complex. This IR spectral window is where the asymmetric S=O stretch occurs for organic triflate esters[29] and is assigned the same mode in the complexes. Other assignments are based on tabulated IR data for ammine complexes[30] and triflate salts and esters.[29] Additional peaks adjacent to those normally attributed to the triflate anion were observed, and these are also assigned as deriving from the triflato ligand.

The pentaammines aquate in dilute acid to yield only one product, detected chromatographically, with an electronic absorption spectrum consistent with the formation of the aqua complex. No chloride ion could be detected in the complexes. Dissolution of the $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ ion in water or acetonitrile yielded the corresponding aqua and acetonitrile complexes in quantitative yield; methanol and ammonia solvates of the Ru(III) and Ir(III) analogues, respectively, were also prepared. Aqua and ammonia solvates of the Rh(III) complex were isolated. These observations are consistent with complete replacement of coordinated and ionic chloride ion by triflate ion, while retaining the ammonia ligands. Absorption spectra of triflate complexes, recorded in anhydrous triflic acid, are recorded in Table II.

Table II. Absorption Spectra of Trifluoromethanesulfonato Complexes[a]

complex	λ, nm (ϵ, M^{-1} cm^{-1})[b]	ref
$Co(NH_3)_5(OSO_2CF_3)^{2+}$	524 (45.8), 465 sh (33), 345 (40.6)	7
$Rh(NH_3)_5(OSO_2CF_3)^{2+}$	333 (103), 267 (84)	*c*
$Ir(NH_3)_5(OSO_2CF_3)^{2+}$	315 sh (150), 270 (220)	*c*
$Cr(NH_3)_5(OSO_2CF_3)^{2+}$	499 (36.8), 364 (31.7)	*c*
$Ru(NH_3)_5(OSO_2CF_3)^{2+}$	284 (790)	*c*
$Os(NH_3)_5(OSO_2CF_3)^{2+}$	447 (50), 290 sh (108), 235 (843)	42
$Pt(NH_3)_5(OSO_2CF_3)^{3+}$	299 (186)	*c*
$Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	542 (58.9), 490 sh (51), 362 (67.3)	*c*
$Rh(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	335 (142), 275 (144)	*c*
$Cr(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	506 (49.1), 374 (45.8)	*c*
cis-$Co(en)_2(OSO_2CF_3)_2^+$	590 sh (33), 508 (80.1), 374 (105.3)	*c*
cis-$Rh(en)_2(OSO_2CF_3)_2^+$	321 (193), 271 (142)	*c*
cis-$Ir(en)_2(OSO_2CF_3)_2^+$	464 sh (10), 368 sh (34), 296 sh (142), 272 (184), 243 (156)	*c*
cis-$Cr(en)_2(OSO_2CF_3)_2^+$	497 (69.8),[d] 380 (42.7)	*c*
trans-$Rh(en)_2Cl(OSO_2CF_3)^+$	407 (43), 270 sh (127)	*c*
trans-$Ir(en)_2Cl(OSO_2CF_3)^+$	502 sh (16), 428 sh (25), 334 (51), 275 sh (60), 241 (110)	*c*

[a] Measured in anhydrous triflic acid. All complexes are triflate salts. [b] sh = shoulder. [c] This work. [d] Asymmetric band, but no clear shoulder.

The $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ complex could not be prepared by the usual practice of heating the chloro precursor in anhydrous CF_3SO_3H. Under these conditions, loss of some ammine ligands was also apparent, and a mixture of products that could not be purified conveniently was obtained. However, allowing the reaction in acid to proceed at room temperature for 3 days led to a quantitative conversion to the triflato complex. This particular approach was also adopted for the synthesis of $Cr(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ and $Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ ions. While the $Co(NH_3)_5$-

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$(OSO_2CF_3)^{2+}$ complex can also be prepared by allowing the reaction to proceed at room temperature for several days, the previously described synthesis at high temperature[7] is to be preferred.

The complexes *cis*-$[M(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (M = Cr(III), Rh(III), Ir(III)) were synthesized by reaction of the *cis*-$[M(en)_2Cl_2]Cl$ precursors in CF_3SO_3H at elevated temperatures (~100 °C). Although we cannot discount the possibility that these complexes contain chelating triflate with two triflate anions, this mode of substitution is unlikely to occur in neat CF_3SO_3H. The stereochemical course of the substitution reactions for Rh(III) and Ir(III) was followed by NMR spectroscopy in neat CF_3SO_3H; both ^{13}C and ^1H NMR indicated the reactions were largely stereoretentive (>95%). The stereoretentive nature of these reactions was evident also from the solvolysis of the products in water or ammonia, since only cis-$M(en)_2(OH_2)_2{}^{3+}$ and *cis*-$M(en)_2(NH_3)_2{}^{3+}$ were observed (>95%; M = Rh, Ir). They were characterized where possible by spectroscopic comparison with authentic samples.[31-34] The product of solvolysis of cis-$[Cr(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ in water was consistent with authentic *cis*-$Cr(en)_2(OH_2)_2{}^{3+}$ [absorption spectrum λ_{max} (ϵ_{max}) in 1.25 M perchlorate: 486 (64.2), 368 (41.2)],[35] and only one band was detected chromatographically upon elution on SP-Sephadex C-25 or Dowex 50W-X2 cation-exchange resins.

It is notable that the reaction of either *cis*- or *trans*-$Co(en)_2Cl_2{}^+$ with anhydrous triflic acid yielded only *cis*-$Co(en)_2(OSO_2CF_3)_2{}^+$,[7] consistent with the cis complexes being more stable in polar solvents than the trans isomers.[36] However, reaction of *trans*-$M(en)_2Cl_2{}^+$, where M = Rh or Ir, produced the intermediate complexes *trans*-$M(en)_2Cl(OSO_2CF_3)^+$, which were stable to isomerization and exceptionally slow in substituting the second chloride ligand. Apparently the $CF_3SO_3{}^-$ ion has little effect in labilizing anions trans to it. These complexes were characterized by microanalyis and ^{13}C NMR spectroscopy. Stereoretentive solvolysis in water and ammonia yielded *trans*-$M(en)_2Cl(OH_2)^{2+}$ and *trans*-$M(en)_2(NH_3)Cl^{2+}$ complexes (95%; M = Rh or Ir), characterized where possible by comparison of their spectral properties with those of authentic samples. An intermediate, presumably *trans*-$Co(en)_2Cl(OSO_2CF_3)^+$, has been observed in the reaction of *trans*-$Co(en)_2Cl_2{}^+$ and CF_3SO_3H at low temperature, but it is apparently not stable to isomerization even in the solid state.[37] These observations are consistent with the general belief that reactions of Rh(III) and Ir(III) are more stereoretentive than those of Co(III).[38] They do not exclude the possibility, however, that some rearrangement takes place in the substitution, albeit a small amount.

Most other aqua, solvent, and acido complexes can be treated in a like manner to generate the desired triflato complex. The powerful protonating ability of neat CF_3SO_3H presumably assists the ligands in leaving when they have a site to protonate. All the triflato complexes are air-stable and react only slowly with atmospheric moisture; no special precautions in their storage and handling are necessary over short periods of time, and they may be stored for months in a desiccator. Partially hydrated samples may be dehydrated by heating the solid under a vacuum at 110 °C overnight (see also ref 9).

Table III. Rate Constants for Spontaneous Aquation of Trifluoromethanesulfonato Complexes at 25 °C in Aqueous 0.1 M CF_3SO_3H

complex	k_1,[a] s^{-1}	k_2,[b] s^{-1}	ref
$Co(NH_3)_5(OSO_2CF_3)^{2+}$	2.68×10^{-2}		7
$Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	1.13×10^{-1}		*c*
$Rh(NH_3)_5(OSO_2CF_3)^{2+}$	1.87×10^{-2}		*c*
$Rh(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	3.28×10^{-2}		*c*
$Ir(NH_3)_5(OSO_2CF_3)^{2+}$	2.61×10^{-4}		*c*
$Cr(NH_3)_5(OSO_2CF_3)^{2+}$	1.24×10^{-2}		*c*
$Cr(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	6.3×10^{-4}		*c*
$Ru(NH_3)_5(OSO_2CF_3)^{2+}$	9.3×10^{-2}		*c*
$Os(NH_3)_5(OSO_2CF_3)^{2+}$	1.8×10^{-3}		42, 74
$Pt(NH_3)_5(OSO_2CF_3)^{3+}$	$\sim 10^{-5}$ (80 °C)		43
cis-$Co(en)_2(OSO_2CF_3)_2{}^+$	2.2×10^{-2}	8.6×10^{-3}	7
cis-$Rh(en)_2(OSO_2CF_3)_2{}^+$	3.7×10^{-2}	1.7×10^{-2}	*c*
cis-$Ir(en)_2(OSO_2CF_3)_2{}^+$	3.0×10^{-4}	1.8×10^{-4}	*c*
cis-$Cr(en)_2(OSO_2CF_3)_2{}^+$	5.7×10^{-2}	3.2×10^{-2}	*c*
trans-$Rh(en)_2Cl(OSO_2CF_3)^+$	3.5×10^{-2}		*c*
trans-$Ir(en)_2Cl(OSO_2CF_3)^+$	6.9×10^{-4}		*c*

[a] Average of at least three independent runs; average standard error <8%. [b] Consecutive rates determined as described in ref 28. [c] This work.

Since anhydrous CF_3SO_3H does not absorb in the visible and near-ultraviolet region of the spectrum and exhibits only a single signal above ~9 ppm in the ^1H NMR spectrum and a weak quartet centered 53 ppm downfield from dioxane in the ^{13}C NMR spectrum, it is a versatile solvent for spectroscopy of the otherwise labile triflato complexes. Absorption spectra of the complexes are reported in Table II, and NMR spectra are included in the Experimental Section. The positions of the d–d absorption bands of the triflato complexes are moved to considerably lower energies in comparison to the aqua analogues. For example, $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ and $Cr(NH_3)_5(OH_2)^{3+}$ have their first d–d band maxima at 499 and 480 nm, respectively. Marked asymmetry was observed in the lowest energy band of $Co(NH_3)_5(OSO_2CF_3)^{2+}$ and of $Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$. These observations are consistent with a weak ligand field contribution from the triflato ligand.

The ^1H NMR spectra of the $M(NH_2R)_5(OSO_2CF_3)^{2+}$ ions gave distinct resonances for the cis and trans amines when M = Co and Rh; however, only a single resonance was observed for M = Ir and Pt although the last exhibited ^{195}Pt–^1H and ^{14}N–^1H coupling of comparable magnitude (~40–50 Hz). The *trans*-$M(en)_2Cl(OSO_2CF_3)^+$ complexes (M = Rh, Ir) displayed only two broad resonances due to $-NH_2$ and $-CH_2-$ protons; by contrast, *cis*-$M(en)_2(OSO_2CF_3)^+$ ions (M = Co, Rh, Ir) gave complex multiplet for the $-CH_2-$ groups and three signals for the $-NH_2$ groups in the ratio 2:1:1. ^{13}C NMR spectra of cis and trans isomers exhibited two and one $-CH_2-$ resonances, respectively. These observations are entirely consistent with the expectations for pentaamine and *cis*- and *trans*-bis(1,2-ethanediamine) low-spin d^6 complexes. NMR spectroscopy was also employed to follow the stereochemical course of the substitution reactions.

Reactions in the poorly coordinating solvent sulfolane are usually appropriate for syntheses of complexes such as $Cr(NH_3)_5(OC(NH_2)_2)^{3+}$ where the entering ligand is not the solvent. This complex in particular has been characterized as O-bound urea, with $\nu(H_2N\cdots C\cdots O)$ at 1580 and 1640 cm^{-1}, by comparison with the O- and N-bound isomers of the corresponding Rh(III) complex.[39] The *cis*-$M(en)_2(OSO_2CF_3)_2{}^+$ complexes also react with chelates such as 1,2-ethanediamine, either as neat ligands or in sulfolane, to yield $M(en)_3{}^{3+}$ species

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(M = Rh, Ir). This ease of substitution of the triflato ligand in normally substitution-inert metal centers makes such complexes versatile synthetic precursors.

Kinetic Measurements. Rate constants of spontaneous aquation of the (triflato)metal amine complexes are collected in Table III. For the triflato pentaammine complexes of Co, Rh, and Ir, the ratios of aquation rates at 25 °C are 103:72:1. (The aquation rate for the Ir and Pt complexes was incorrectly reported previously.[11]) This can be compared with data for chloro pentaammine analogues, where the ratio Co:Rh:Ir is 17 000:600:1.[40] At 25 °C, the $-OSO_2CF_3$ ligand aquates $\sim 10^4$ times faster than Cl^- from Co, $\sim 10^5$ times faster from Rh, and $\sim 10^6$ times faster from Ir; i.e., the relative lability of triflate is enhanced down the d^6 triad. The (triflato)pentaamminechromium(III) ion aquates at approximately half the rate of the cobalt(III) analogue, 1.7×10^3 times faster than $Cr(NH_3)_5Cl^{2+}$,[41] and approximately 20 times faster than $Cr(OH_2)_5(OSO_2CF_3)^{2+}$ (7.6×10^{-4} s^{-1}; 25 °C).[5] However, the general reactivity sequence[40] Co(III) $\sim$ Cr(III) > Rh(III) $\gg$ Ir(III) is maintained for the triflato pentaammine complexes. The approximately 100-fold decrease in rate from second-row Rh(III) to third-row Ir(III) is also observed between the Ru(III) and Os(III)[42] complexes. The Pt(IV) complex was surprisingly stable with $t_{1/2} \sim 24$ h at 80 °C in 0.1 M CF_3SO_3H.[43]

The reactivity trends for the $M(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ and $M(NH_3)_5(OSO_2CF_3)^{2+}$ ions (M = Co, Rh, Cr) differ, with $k(NH_2CH_3):k(NH_3)$ ratios of 4.2 (Co), 1.7 (Rh), and 0.051 (Cr). The analogous chloro complexes show ratios of 22 (Co), 0.5 (Rh), and 0.030 (Cr).[17,44]

For the *cis*-$M(en)_2(OSO_2CF_3)_2^+$ complexes (M = Cr, Rh, Ir) two sequential first-order aquations were observed that differed in rate by a factor of approximately 2, similar to the ratio observed for the cobalt(III) analogue[7] (Table III). Only one fast reaction of *trans*-$M(en)_2Cl(OSO_2CF_3)^+$ to form *trans*-$M(en)_2(OH_2)Cl^{2+}$ (M = Rh, Ir) was observed, with the subsequent chloro loss being very slow. All these reactions were stereoretentive (>95%).

Discussion

Syntheses. The substitution-inert chloro complexes of Cr(III), Co(III), Rh(III), Ir(III), Ru(III), and Pt(IV) amines are converted readily into the corresponding triflato complexes by reaction in neat CF_3SO_3H. The synthetic advantages of reacting such well-characterized, isolable salts containing a labile ligand has already been illustrated for the cobalt(III) amine triflates.[7] For the complexes reported in this paper, the triflato ligand is sufficiently labile to allow similar reactions to be performed. The poor coordinating ability of the triflate ion is reflected in the long Pd–O (2.27 Å) bond observed in the crystal structure of the $Pd(3\text{-}(diethylamino)\text{-}propanalato)(Et_2NH)(OSO_2CF_3)$ compound, which is considerably longer than other Pd–O bonds (typically 2.1 Å).[45] Similarly, an Au–O bond length of 2.20 Å has been reported for triflate in $Au(CH_3)_2(OH_2)(OSO_2CF_3)$, compared with 2.16 Å for the coordinated water.[46]

The weak M–O bond of coordinated $-OSO_2CF_3$ is also reflected in the rates of acid hydrolysis of $Co(NH_3)_5X^{n+}$ complexes where, of the extensive series of reported compounds, the triflate ligand ranks a close second to the perchlorate ligand in terms of lability.[5,7] Although the fluorosulfonate ligand exhibits a similar lability, its substitution by other ligands is complicated by decomposition reactions resulting in fluoro complexes.[47] Further, the potentially explosive nature of perchlorate complexes limits their synthetic usefulness, leaving the triflate complexes as the best synthetic intermediates in terms of lability, safety, ease of synthesis, and ease of use. Apart from complexes reported in this paper, triflato pentaammine complexes of Co(III),[6,7,9] Os(III),[42] and Ru(II)[48] have been prepared. The versatility of these complexes is reflected in the synthesis of a range of derivatives.[7,9,39,48-55] The use of triflato complexes for the synthesis of $^{17}OH_2$- and $^{18}OH_2$-labeled complexes is also the method of choice, since it is facile and results in no isotopic dilution of the residual labeled water.[55]

The reaction scheme of eq 1 for M = Rh(III) and Ir(III) is a more facile and higher yielding route to the $Rh(NH_3)_6^{3+}$ and $Ir(NH_3)_6^{3+}$ compounds than conventional techniques,[56,57] which have not changed much since the original methods of Jørgensen[58] and Palmaer.[59] Other approaches to the hexa-

$$M(NH_3)_5Cl^{2+} \xrightarrow[110\ °C]{CF_3SO_3H} M(NH_3)_5(OSO_2CF_3)^{2+} \xrightarrow{NH_3(l)} M(NH_3)_6^{3+} \quad (1)$$

ammines such as the conversion of the $M(NH_3)_5N_3^{2+}$ complexes to $M(NH_3)_6^{3+}$ via a $M(NH_3)_5(NH_2Cl)^{3+}$ intermediate are not as convenient, since they involve several steps.[60,61] The reaction sequence of eq 2 for M = Rh and Ir offers a new route

$$cis\text{-}M(en)_2Cl_2^+ \xrightarrow[110\ °C]{CF_3SO_3H} cis\text{-}M(en)_2(OSO_2CF_3)_2^+ \xrightarrow{en} M(en)_3^{3+} \quad (2)$$

to the $M(en)_3^{3+}$ complexes. Although $Rh(en)_3^{3+}$ and $Ir(en)_3^{3+}$ are conveniently prepared from $RhCl_3 \cdot H_2O$[62] and $IrCl_3 \cdot 3H_2O$[64] and 1,2-ethanediamine, eq 2 outlines the most convenient route for the synthesis of $M(en)_2(diamine)^{3+}$ ions.[63]

While solvolysis reactions of triflato complexes are clearly facile, reactions in a poorly coordinating solvent containing another ligand have been developed for cobalt(III), rhodium(III), ruthenium(III), and osmium(III) amines.[7,9,39,42,53,54] The facile synthesis of the O-bond (urea)pentaamminechromium(III) complexes reported here further illustrates the as yet largely untapped synthetic potential of triflato complexes.

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Electronic Spectroscopic Properties. The low-spin d^6 complexes $M(NH_2R)_5(OSO_2CF_3)^{n+}$, M = Co(III), Rh(III), Ir(III), and Pt(IV), should exhibit spin-allowed ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h) ligand field transitions. The effective C_{4v} symmetry of the ions gives rise to the asymmetry in the first ligand field envelope for d^6 Co(III) with both R = H and CH_3, where the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ level is split in the lowered symmetry into the ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$ component transitions. The large splitting of the low-energy band of the Co(III) complex (Table II) indicates a weak-field Co(III)–O bond in the CoN_5O chromophore. The position of the ${}^1A_1 \rightarrow {}^1E$ component of the first spin-allowed transition in $Co(NH_3)_5(OSO_2CF_3)^{2+}$ places the ${}^-OSO_2CF_3$ ligand between Cl^- and N_3^- in the spectrochemical series, by comparison with other pentaammine complexes.[65]

No splitting of the low-energy absorption envelope is observed in the spectrum of $Rh(NH_3)_5(OSO_2CF_3)^{2+}$; therefore, the ligand field parmaeters Δ and B can be estimated from the energies of the first two ligand field bands ${}^1A_1 \rightarrow {}^1T_1$ and ${}^1A_1 \rightarrow {}^1T_2$ by assuming the complexes approximate the O_h transitions ($\Delta - 4B + 86B^2/\Delta$ and $\Delta - 20B + 2B^2/\Delta$, respectively, where $C = 4B$).[66,67] Calculated Δ and B values are 31 300 and 506 cm^{-1}, respectively, giving a nephelauxetic ratio $\beta_{35} = 0.70$. The high value of β_{35}, in comparison with other pentaamminerhodium(III) complexes,[68] which range from 0.64 for $Rh(NH_3)_5NO_2^{2+}$ to 0.39 for $Rh(NH_3)_5SCN^{2+}$, is indicative of the very low nephelauxetic effect of $CF_3SO_3^-$. Values of β for $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5(ONO)^{2+}$ of ~0.7 have been shown to be an artifact due to mixing of charge-transfer bands with the ${}^1A_1 \rightarrow {}^1T_2$ component,[68] since the nephelauxetic effects of Cl^- and ONO^- are much lower in MX_6^{3-} complexes in comparison with $M(NH_3)_6^{3+}$ species.[66] No such problems arise in the $Rh(NH_3)_5(OSO_2CF_3)^{2+}$ complex, since the spin-allowed transitions are far removed from charge-transfer bands and exhibit normal intensities for spin-allowed d–d transitions. The value of 31 300 cm^{-1} for Δ is in keeping with the placement of Δ for ${}^-OSO_2CF_3$ as approximately equal to that of N_3^-.

The above analysis is consistent with the triflato ligand being an excellent leaving group in the substitution chemistry of the transition elements. The low energy of the purely electrostatic component of bonding (evident from the observed Δ) combined with a very low covalent contribution to bonding (evident from the high β_{35}) allows $CF_3SO_3^-$ to be removed easily. Normally, weak field ligands such as the halo ligands, N_3^- and ${}^-SCN$ are comparatively soft ligands (evident from low values of β_{35} in ML_6^{n+} species), and hence the kinetic stability of the M–L bond is enhanced by covalent bonding.

Approximate empirical calculations[66,67] incorporating the Δ and β_{35} values obtained for other triflato complexes and comparison with the spectra of other pentaammineiridium(III) complexes[69] indicate that the shoulder at 315 nm for d^6 $Ir(NH_3)_5(OSO_2CF_3)^{2+}$ can be assigned to the spin-forbidden ${}^1A_1 \rightarrow {}^3T_1$ transition, while the absorption at 270 nm arises from the spin-allowed ${}^1A_1 \rightarrow {}^1T_1$ transition (in O_h symmetry). Assignments of the band at 299 nm in the spectrum of d^6 $Pt(NH_3)_5(OSO_2CF_3)^{3+}$ and of the band at 284 nm in the spectrum of d^5 $Ru(NH_3)_5(OSO_2CF_3)^{2+}$ are more difficult; the former may be due to a spin-forbidden ${}^1A_1 \rightarrow {}^3T_1$ transition, but the intensity of the latter suggests that it is not purely d–d in nature. The spectrum of the d^3 pentaamminechromium(III) complex exhibits two spin-allowed transitions of ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$ parentage; values of Δ and B are consistent with those calculated empirically from the rhodium(III) spectra. No asymmetry in the two characteristic ligand field bands of the d^3 Cr(III) analogues was observed, although a shift in the maximum of the first ligand field envelope for O-bound triflate (499 nm in the pentaammine) compared with coordinated OH_2 (480 nm in the pentaammine) was observed. It parallels a similar shift reported for the Co(III) analogues.[7] This type of shift for triflate vs. water ligands was observed to a variable extent throughout the range of complexes prepared. Similar effects are observed for Cl^- and N_3^-. The lower molecular symmetry (C_2) relative to O_h is evident from the asymmetry of the lowest energy band in the chromium(III) and cobalt(III) *cis*-bis(1,2-ethanediamine) complexes, although no asymmetry was observed in the spectra of the rhodium(III) or iridium(III) complexes.

Substitution Kinetics. The increase in relative inertness of the metal–ligand bond down the Co triad for Cl^- compared with ${}^-OSO_2CF_3$ as ligands may reflect greater covalency in bonding in the former ligand. The general lability of triflato complexes is reflected in their greater reactivity (>10^3-fold) compared with complexes containing ligands of similar ligand field strength (e.g., Cl^-). However, the general reactivity sequence Co(III) ~ Cr(III) > Rh(III) > Ir(III)[40] is maintained for the triflato pentaammine complexes.

In the substitution reactions of the pentaammine complexes, the rate constant ratios for $k(M(NH_2CH_3)_5Cl^{2+}):k(M(NH_3)_5Cl^{2+})$ for M = Co, Rh and Ir have been interpreted as support for largely dissociative reactions for Co and more associative pathways for Rh and Cr.[18] Clear reactivity differences between Co and Cr are evident also in aquation for the labile triflato complexes. The Rh methylamine and ammonia complexes only differ in minor ways, and the only general conclusion that we can extract from the data is that the degree of association in the aquation process follows the order Co(III) < Rh(III) < Cr(III).

Hydrolysis of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ in 0.1 M CF_3SO_3H occurred as two rapid consecutive first-order processes (eq 3;

$$cis\text{-}M(en)_2(OSO_2CF_3)_2^{+} \xrightarrow{k_1} cis\text{-}M(en)_2(OSO_2CF_3)(OH_2)^{2+} \xrightarrow{k_2} cis\text{-}M(en)_2(OH_2)_2^{3+} \quad (3)$$

M = Co).[7] While it is not possible to decide a priori which step is the faster,[28] several lines of evidence strongly favor $k_1 > k_2$. The rate constants for M = Co correspond closely with the purely statistical expectation $k_1 = 2k_2$; this was also observed for M = Rh, Ir, and Cr. Arguments and observations advanced for the cobalt complex can be applied in part or whole to the other complexes. The final products for M = Cr, Rh, and Ir were *cis*-$M(en)_2(OH_2)_2^{3+}$ (97 ± 3%), consistent with the generally stereoretentive nature of the hydrolysis of amine complexes of these metal ions.[38,70]

The observation that $k_1 \sim 2k_2$ for M = Co, Rh, and Cr (Table III) differs from the general behavior for *cis*-$M(en)_2X_2^+$ complexes, where often $k_1 \gg k_2$. For example, when X = Cl and M = Co, then $k_1:k_2 = 150$;[71] while for X = CF_3SO_3, $k_1:k_2 = 2.6$. The effect is less marked with M = Cr, since for X = Cl $k_1:k_2 = 12$,[72] while $k_1:k_2 = 1.8$ for CF_3SO_3. These observations are consistent with the triflato ligand having a weaker contribution to bonding, so that the strength of the second metal–triflato bond is less affected by loss of the first

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anion from the coordination sphere. Alternatively, but less likely, a chelating triflate is involved, and the first step involves a ring-opening reaction.

The aquation kinetics of *trans*-$M(en)_2Cl(OSO_2CF_3)^+$, M = Rh and Ir, exhibited only one fast aquation step; plots of log $(A_t - A_\infty)$ vs. time were linear over at least 5 half-lives. This observation is consistent with their formation as chloro triflato complexes, since aquation of coordinated chloride is very slow for these metal centers. In each case, ^{13}C NMR evidence indicated aquation was stereoretentive. The behavior of the Rh and Ir complexes is consistent with the general observation of largely stereoretention during aquation of these complexes in contrast to the cobalt chemistry.[73]

The synthetic utility of a large range of triflate complexes including osmium and ruthenium polypyridines and osmium pentaammine is presently being explored. They are not only valuable intermediates for the synthesis of mononuclear complexes but are being used extensively in these laboratories and elsewhere for the synthesis of binuclear and polynuclear species for use in studies of mixed-valence complexes and intramolecular electron transfer. Clearly, their potential uses are many-fold and their utility in preparative inorganic chemistry has only just begun to be explored. They also allow comparative studies on the substitution kinetics of a wide range of analogous series of complexes.

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Registry No. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-61-5; $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-59-1; $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84278-98-8; $[Pt(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$, 84254-63-7; $[Cr(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 90065-87-5; $[Co(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 90065-88-6; $[Rh(NH_2CH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 90065-89-7; *cis*-$[Cr(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, 90065-91-1; *cis*-$[Rh(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, 90065-93-3; *cis*-$[Ir(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, 90065-95-5; *trans*-$[Rh(en)_2Cl(OSO_2CF_3)](CF_3SO_3)$, 90065-97-7; *trans*-$[Ir(en)_2Cl(OSO_2CF_3)](CF_3SO_3)$, 90065-99-9; *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, 75522-52-0; $[Cr(NH_3)_5(OH_2)](ClO_4)_3$, 32700-25-7; $[Cr(NH_3)_5(NCCH_3)](CF_3SO_3)_3$, 90066-01-6; $[Cr(NH_3)_5(OC(NH_2)_2)](S_2O_6)_{3/2}$, 87564-83-8; $[Rh(NH_3)_5(OH_2)](ClO_4)_3$, 15611-81-1; $[Rh(NH_3)_6](CF_3SO_3)_3$, 90084-45-0; $[Ir(NH_3)_5(OH_2)](CF_3SO_3)_3$, 90084-46-1; $[Ru(NH_3)_5(HOCH_3)](CF_3SO_3)_3$, 90066-03-8; $[Ir(NH_3)_6](CF_3SO_3)_3$, 90066-04-9; *cis*-$[Rh(en)_2(NH_3)_2](CF_3SO_3)_3$, 90066-05-0; *trans*-$[Rh(en)_2(NH_3)Cl](CF_3SO_3)_2$, 90130-09-9; $[Rh(en)_3]Cl_3$, 14023-02-0; $[Ir(en)_3]Cl_3$, 29031-66-1; $[Rh(NH_3)_5Cl]Cl_2$, 13820-95-6; $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Ir(NH_3)_5Cl]Cl_2$, 15742-38-8; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[Pt(NH_3)_5Cl]Cl_3$, 16893-11-1; $[Cr(NH_2CH_3)_5Cl]Cl_2$, 15351-84-5; $[Co(NH_2CH_3)_5Cl]Cl_2$, 15392-59-3; $[Rh(NH_2CH_3)_5Cl]Cl_2$, 64459-98-9; *cis*-$[Cr(en)_2Cl_2]Cl$, 14240-29-0; *cis*-$[Rh(en)_2Cl_2]Cl$, 15444-62-9; *cis*-$[Ir(en)_2Cl_2]Cl$, 15444-47-0; *trans*-$[Rh(en)_2Cl_2]Cl$, 15444-63-0; *trans*-$[Ir(en)_2Cl_2]Cl$, 15444-46-9.

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nei bassi stati di ossidazione, Via G. Venezian 21, 20133 Milano, Italy, Dipartimento di Chimica
Inorganica e Metallorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy,
and Chemical Laboratory, University of Kent, Canterbury CT2 7NH, England

Mixed Pt–Rh Carbonyl Clusters. 1. Synthesis, Reactivity, and Solution Structures of $[PtRh_5(CO)_{15}]^-$, $[PtRh_4(CO)_{14}]^{2-}$, and $[PtRh_4(CO)_{12}]^{2-}$

ALESSANDRO FUMAGALLI,*[1a] SECONDO MARTINENGO,[1a] PAOLO CHINI,[1b,d] DANIELE GALLI,[1b]
BRIAN T. HEATON,[1c] and ROBERTO DELLA PERGOLA[1c]

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The reductive carbonylations of mixtures of Na_2PtCl_6 and $RhCl_3{\cdot}xH_2O$ (at room temperature and 1 atm CO) are reported. From the reaction mixtures $[PtRh_5(CO)_{15}]^-$ and $[PtRh_4(CO)_{14}]^{2-}$ have been isolated; the latter is in equilibrium, through the release and absorption of CO, with $[PtRh_4(CO)_{12}]^{2-}$. Solution structures and fluxional behavior of all these anions have been established by multinuclear (^{13}C, $^{13}C\{^{103}Rh\}$, ^{103}Rh, ^{195}Pt) variable-temperature NMR measurements.

Introduction

We reported, in a preliminary communication,[2] the isolation of $[PtRh_5(CO)_{15}]^-$, which reacted further under CO with an alkaline methanolic solution or Na–anthracene in THF to give an orange-yellow anion. This was formulated on the basis of partial analytical data to be $[PtRh_2(CO)_x]^{n-}$, which we now show to be $[PtRh_4(CO)_{14}]^{2-}$. This reversibly loses CO to give the related dianion $[PtRh_4(CO)_{12}]^{2-}$. The general features of the reductive carbonylation of mixtures containing Na_2PtCl_6 and $RhCl_3{\cdot}xH_2O$ are discussed in connection with the preparation of the above clusters. Multinuclear NMR studies (^{13}C, $^{13}C\{^{103}Rh\}$, ^{103}Rh, and ^{195}Pt) are reported which establish their structures and fluxional behavior in solution.

Results and Discussion

1. Generalities on the Reductive Carbonylation of Pt–Rh Systems. In an attempt to develop synthetic routes to mixed Pt–Rh clusters in good yields from readily available materials, we have carried out a systematic investigation of the reductive carbonylation of mixtures of Na_2PtCl_6 and $RhCl_3{\cdot}xH_2O$ in methanol under CO (1 atm pressure) at room temperature. The reduction was carried out by a stepwise addition of NaOH (1 M in methanol) to a vigorously stirred solution with various ratios of Pt:Rh (1:1, 1:2, 1:4, 1:5) under an atmosphere of CO; the reactions were monitored by IR after each addition of NaOH or at regular intervals. When an unambiguous interpretation of the spectra was not possible, excess bulky cations were added to precipitate the equilibrium mixture, which was then subjected to fractional crystallization. In every case, the same species were always formed first, though in different proportions. The final distribution of products, however, depends on both the ratios of OH^-:metals and Pt:Rh;

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(1) (a) CNR. (b) Università di Milano. (c) University of Kent. (d) Deceased.

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