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Synthesis of cis and trans Bis-alkynyl Complexes of Cr(III) and Rh(III) Supported by a Tetradentate Macrocyclic Amine: A Spectroscopic Investigation of the M(III)−Alkynyl Interaction

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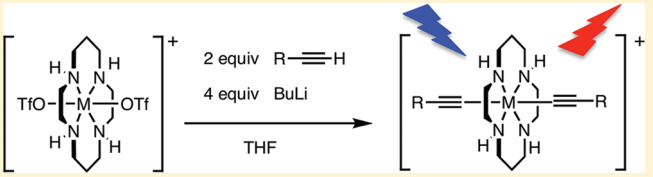
Supporting Information

ABSTRACT: Alkynyl complexes of the type $[M(cyclam)(CCR)_2]$-OTf (where cyclam = 1,4,8,11-tetraazacyclotetradecane; M = Rh(III) or Cr(III); and R = phenyl, 4-methylphenyl, 4-trifluoromethylphenyl, 4-fluorophenyl, 1-naphthalenyl, 9-phenanthrenyl, and cyclohexyl) were prepared in 49% to 93% yield using a one-pot synthesis involving the addition of 2 equiv of RCCH and 4 equiv of BuLi to the appropriate $[M(cyclam)(OTf)_2]$OTf complex in THF. The cis and trans isomers of the alkynyl complexes were separated using solubility differences, and the stereochemistry was characterized using infrared spectroscopy of the CH_2 rocking and NH bending region. All of the *trans*-$[M(cyclam)(CCR)_2]$OTf complexes exhibit strong Raman bands between 2071 and 2109 cm^{-1}, ascribed to $\nu_s(C{\equiv}C)$. The stretching frequencies for the Cr(III) complexes are 21−28 cm^{-1} lower than for the analogous Rh(III) complexes, a result that can be interpreted in terms of the alkynyl ligands acting as π-donors. UV−vis spectra of the Cr(III) and Rh(III) complexes are dominated by strong charge transfer (CT) transitions. In the case of the Rh(III) complexes, these CT transitions obscure the metal centered (MC) transitions, but in the case of the Cr(III) complexes the MC transitions are unobscured and appear between 320 and 500 nm, with extinction coefficients (170−700 L mol^{-1} cm^{-1}) indicative of intensity stealing from the proximal CT bands. The Cr(III) complexes show long-lived (240−327 μs), structureless, MC emission centered between 731 and 748 nm in degassed room temperature aqueous solution. Emission characteristics are also consistent with the arylalkynyl ligands acting as π-donors. The Rh(III) complexes also display long-lived (4−21 μs), structureless, metal centered emission centered between 524 and 548 nm in degassed room temperature solution (CH_3CN).



INTRODUCTION

Assemblies comprising two or more metal centers bridged by unsaturated organic ligands have been proposed as potential building blocks for molecular electronic devices, including wirelike structures. Alkynyl ligands such as $C{\equiv}C^{2-}$ and $C{\equiv}C{-}C{\equiv}C^{2-}$ are common building blocks in such assemblies,[1−9] and these ligands have, in many cases, been demonstrated to mediate electronic communication between metal centers. The prospect of inventing functional photochemical molecular devices (PMDs)[10,11] has prompted research on intramolecular energy transfer between transition metal centers bridged by ligands that facilitate such electronic communication.[12] We have had a long-term interest in the preparation and photophysical characterization of *trans*-$Cr(N_4)(CN)_2^+$ (where N_4 = a tetraazamarocyclic ligand) complexes[13] and in the study of the rates of intermolecular electronic energy transfer between them.[14] Our interest in the alkynyl ligands stems from their promise as isoelectronic substitutes for the CN^- ligand and the possibility of preparing photoactive complexes with bridging alkynyl ligands that might mediate intramolecular electron- and energy transfer. In addition, the dicyano complexes *trans*-$Rh(cyclam)(CN)_2^+$ and *trans*-$Cr(cyclam)(CN)_2^+$ (cyclam =1,4,8,11-tetraazacyclotetradecane) have relatively long excited state lifetimes in a room temperature fluid solution.[15,16] Consequently, it might be possible to intercept these excited states prior to deactivation, particularly if they can be bridged to an appropriate acceptor through an alkynyl type ligand.

Given our interest in the photochemistry of such systems and the possibility that the metallocyclam complexes might serve as building blocks for metal-alkynyl polymers, we sought a general synthetic method for complexes of the type $M(cyclam)(CCR)_2^{n+}$. The presence of the macrocyclic cyclam ligand provides stereochemical variability by virtue of the possibility of cis and trans isomers. Accordingly, M(cyclam) complexes might be used as building blocks for linear assemblies (as in the case of the trans complexes) or as corners (as in the case of the cis complexes).

An additional motivation for developing synthetic routes to $M(cyclam)(CCR)_2^{n+}$ complexes concerns the question of M−CCR π-bonding. By analogy with the CN^- ligand,[17] the alkynyl ligands were conventionally thought to be strong σ-donors

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and modest π-acceptors (weaker than CO). However, this simple analogy does not appear to apply in all cases.[18] For example, photoelectron spectroscopic measurements on FeCp(CCR)-$(CO)_2$ (R = H, Ph, *t*-Bu, and CCH) and $FeCp^*(CC\text{-}Bu^t)(CO)_2$ suggests that the alkynyl ligand acts as a weak π-donor,[19] a result that is supported by molecular orbital calculations.[19,20] More recently, a combination of electronic spectroscopy and density functional theory calculations on $[M(CCSiMe_3)_6]^{n-}$, where M = Cr(III), Fe(II), and Co(III), support the model that the alkynyl ligand acts as a π-donor in these cases.[21] Understanding M−CCR π-bonding is important not only from a theoretical perspective but also from a practical standpoint because π-delocalization is a prerequisite for electrical conductivity.

Herein we report a straightforward, high yield route to cis and trans $M(cyclam)(CCR)_2^{n+}$ complexes along with characterization by infrared, Raman, UV−vis, and emission spectroscopy. The results are consistent with the alkynyl ligands acting as π-donors.

EXPERIMENTAL SECTION

Materials and Methods. Tetrahydrofuran (THF) and diethyl ether were dried and degassed using an Innovative Technology Inc. solvent purification system before use. All other materials were reagent grade and used as received. Cis/trans mixtures and isomerically pure *cis*-$[Cr(cyclam)Cl_2]Cl$ were prepared by the method of Ferguson and Tobe.[22] Isomerically pure *trans*-$[Cr(cyclam)Cl_2]Cl$ was prepared by the method of Bakac and Espenson.[23] *trans*-$[Rh(cyclam)Cl_2]Cl$ and *cis*-$[Rh(cyclam)Cl_2]Cl$ were prepared according to the method of Bounsall and Koprich.[24] Triflato complexes were prepared from these chloro complexes by modifications of the literature procedures.[25,26] All other reactions were performed under a dry Ar atmosphere implementing standard Schlenk procedures unless otherwise noted. UV−vis absorption spectra were recorded using a Cary-50 spectrophotometer. NMR spectra were obtained using Varian INOVA 500 and 400-MR spectrometers. Raman spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR with an NXR FT-Raman module. Infrared spectra were measured on solid samples using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with an ATR accessory. Emission spectra were recorded using an SLM Aminco instrument running DataMax software. Emission lifetimes were measured using as the excitation source a Photon Technology International (PTI) GL-3300 pulsed nitrogen laser fed into a PTI GL-302 dye laser. Data were collected on an OLIS SM-45 EM fluorescence lifetime measurement system and analyzed using OLIS SpectralWorks. Elemental analyses were performed by Midwest Microlabs in Indianapolis, IN.

General Method for Synthesis of the Ethynyl Complexes. An oven-dried two-neck round-bottom flask (50 mL) under a positive pressure of Ar was charged with 1 equiv of $[M(cyclam)(OTf)_2]OTf$, 2 equiv of the appropriate acetylene, and THF (5 mL). After the mixture was cooled in a dry ice/acetone bath for 10 min, 4 equiv of butyllithium (2.5 M solution in hexanes) was added through a septum. The reaction mixture was stirred in the cold bath for 5 min, then removed, and allowed to warm to room temperature with stirring for 2 h. The mixture was quenched with ~0.5 mL of water, and the reaction mixture was loaded directly onto silica gel (4 cm in a 60 mL fritted glass funnel) and eluted using a 70:30 (v/v) mixture of methylene chloride and acetonitrile (200 mL or until the eluate became colorless). The solvent was removed using rotary evaporation. Cold diethyl ether (20 mL) was added to the residue, and the mixture was sonicated and kept in an ice bath for 5 min to maximize precipitation. The product was collected via vacuum filtration, washed with cold diethyl ether (2 × 10 mL), and dried under vacuum.

Synthesis of the Chromium Complexes. [Cr(cyclam)(OTf)$_2$]OTf. A solution of $[Cr(cyclam)Cl_2]Cl$ (1.50 g, 4.19 mmol) in trifluormethanesulfonic acid (10 g) was sparged for 24 h with nitrogen. The product mixture was poured into anhydrous ethyl ether (200 mL) that was being vigorously stirred. The resulting pink precipitate was collected by suction filtration on a coarse fritted glass funnel, washed with anhydrous ethyl ether, dried under vacuum, and stored in a desiccator for further use (yield = 2.67 g, 91%). Anal. Calcd (found) for $C_{13}H_{24}CrF_9N_4O_9S_3$: C, 22.32 (21.85); H, 3.46 (3.45); N, 8.01 (7.57).

[Cr(cyclam)(CCC$_6$H$_5$)$_2$]OTf (**1a**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), phenylacetylene (62.8 μL, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.159 g (92.2%) of analytically pure *cis/trans*-$[Cr(cyclam)(CCC_6H_5)_2]OTf\cdot{}^1/_2H_2O$. Anal. Calcd (found) for $C_{27}H_{34}CrF_3N_4O_3S\cdot{}^1/_2H_2O$: C, 52.93 (53.01); H, 5.76 (5.60); N, 9.15 (9.15). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 454.21.

[Cr(cyclam)(p-CCC$_6$H$_4$CH$_3$)$_2$]OTf (**1b**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), 4-ethynyltoluene (72.5 μL, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.148 g (82.0%) of analytically pure *cis/trans*-$[Cr(cyclam)(CCC_6H_4CH_3)_2]OTf$. Anal. Calcd (found) for $C_{29}H_{38}CrF_3N_4O_3S$: C, 55.14 (54.95); H, 6.06 (5.96); N, 8.87 (8.78). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 482.36.

[Cr(cyclam)(p-CCC$_6$H$_4$CF$_3$)$_2$]OTf (**1c**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), 4-ethynyl-α,α,α-trifluorotoluene (93.3 μL, 0.572 mmol)), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.160 g (75.7%) of analytically pure *trans*-$[Cr(cyclam)(CCC_6H_4CF_3)_2]OTf$. Anal. Calcd (found) for $C_{29}H_{32}CrF_9N_4O_3S$: C, 47.09 (47.06); H, 4.36 (4.29); N, 7.57 (7.44). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 590.19.

[Cr(cyclam)(p-CCC$_6$H$_4$F)$_2$]OTf (**1d**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), 1-ethynyl-4-fluorobenzene (65.5 μL, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.139 g (76.0%) of analytically pure *cis/trans*-$[Cr(cyclam)(CCC_6H_4F)_2]OTf$. Anal. Calcd (found) for $C_{27}H_{32}CrF_5N_4O_3S$: C, 50.70 (50.53); H, 5.04 (5.04); N, 8.76 (8.61). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 490.29.

[Cr(cyclam)(CCC$_6$H$_{11}$)$_2$]OTf (**1e**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), cyclohexylacetylene (74.7 μL, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.109 g (61.9%) of analytically pure *trans*-$[Cr(cyclam)(CCC_6H_{11})_2]OTf$. Anal. Calcd (found) for $C_{27}H_{46}CrF_3N_4O_3S$: C, 52.67 (52.47); H, 7.53 (7.39); N, 9.10 (8.98). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 466.30.

[Cr(cyclam)(CCC$_{10}$H$_7$)$_2$]OTf (**1f**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), 1-ethynylnaphthalene (81.3 μL, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.161 g (80.0%) of analytically pure *cis/trans*-$[Cr(cyclam)(CCC_{10}H_7)_2]OTf$. Anal. Calcd (found) for $C_{35}H_{38}CrF_3N_4O_3S$: C, 59.73 (59.46); H, 5.44 (5.45); N, 7.96 (7.84). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 554.22.

[Cr(cyclam)(CCC$_{14}$H$_9$)$_2$]OTf (**1g**). Using THF (5 mL), *cis/trans*-$[Cr(cyclam)(OTf)_2]OTf$ (200 mg, 0.286 mmol), 9-ethynylphenanthrene (0.116 g, 0.572 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) yielded 0.213 g (92.7%) of analytically pure *cis/trans*-$[Cr(cyclam)(CCC_{14}H_9)_2]OTf\cdot H_2O$. Anal. Calcd (found) for $C_{43}H_{42}CrF_3N_4O_3S\cdot H_2O$: C, 62.84 (62.50); H, 5.40 (5.32); N, 6.82 (6.88). ESI-MS: intense parent ion (M^+) at *m*/*z* value of 654.38.

Separation of cis and trans Isomers. A cis/trans mixture of $[Cr(cyclam)(CCR)_2]OTf$ (100 mg) was dissolved in dry THF (2 mL or desired amount). All dissolve completely except **1a**, **1f**, and **1g**. To precipitate the trans product, dry diethyl ether (8 mL) was added and the mixture was sonicated. The trans product was collected via vacuum filtration and washed with dry diethyl ether (2 × 10 mL). The filtrate was evaporated to afford the cis product.

trans-[Cr(cyclam)(CCC$_6$D$_5$)$_2$]OTf. The basic procedure for the synthesis of *trans*-$[Cr(cyclam)(CCC_6H_5)_2]OTf$ was followed, except that phenylacetylene-d_6 was used.

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N-Deuteration of trans-[Cr(cyclam)(CCC$_6$H$_5$)$_2$]OTf and trans-[Cr(cyclam)(CCC$_6$D$_5$)$_2$]OTf. A solution of the complex (0.021 g, 0.035 mmol) in anhydrous THF (1 mL) and D_2O (0.3 mL) was stirred under a nitrogen atmosphere for 24 h. After removal of the solvent under high vacuum, the solid was dissolved in a minimum amount of anhydrous THF (4 mL) and reprecipitated with anhydrous ether. The percent deuteration was determined to be >95% by relative integration using infrared spectroscopy (ν_{ND} = 2401 cm^{-1} and ν_{NH} = 3225 cm^{-1}).

Isolation of the Hydroamination Product of ***1c****.* To a solution of 4-ethynyl-α,α,α-trifluorotoluene (1.4 mL, 8.6 mmol) in THF (15 mL) at −78 °C was added *n*-BuLi (0.54 mL of a 2.5 M solution, 1.35 mmol). After the solution was allowed to warm to room temperature, *cis/trans*-[Cr(cyclam)(OTf)$_2$]OTf (0.250 g, 0.358 mmol) was added and the solution stirred for an additional hour. Following standard workup, half of the residue was separated using column chromatography (silica gel, 2% MeOH in CH_2Cl_2). The second (yellow) band was collected. After removal of the solvent, the residue was redissolved in a minimum of CH_3CN and precipitated with ether yielding 22 mg of a yellow/orange solid. ESI-MS: intense parent ion (M^+) at *m/z* value of 930.68. Crystals were grown by vapor diffusion of pentane/ether (1:1) into a solution of the complex in CH_3CN.

Synthesis of the Rhodium Complexes. [Rh(cyclam)(OTf)$_2$]OTf. [Rh(cyclam)Cl$_2$]Cl (0.70 g, 1.71 mmol) in triflic acid (10.0 g) was heated at 110 °C for 3 days under a steady flow of argon. The reaction mixture was then added dropwise to a beaker of stirring anhydrous ethyl ether (200 mL) under a blanket of Ar. After stirring for an additional 5 min, the contents were transferred to a glovebag and the precipitate was collected by vacuum filtration using a course fritted glass funnel, washed with anhydrous ethyl ether (2 × 100 mL), and dried under vacuum. The product was stored in a desiccator due to its hygroscopic nature. Yield: 1.065 g (83.0%). Anal. Calcd (found) for $C_{13}H_{24}F_9N_4O_9RhS_3$: C, 20.81 (20.73); H, 3.22 (3.44); N, 7.47 (7.20).

*[Rh(cyclam)(CCC$_6$H$_5$)$_2$]OTf (**2a**).* Using THF (5 mL), [Rh(cyclam)(OTf)$_2$]OTf (0.164 g, 0.219 mmol), phenylacetylene (48.0 μL, 0.437 mmol), and BuLi (367 μL, 0.918 mmol) yielded 0.098 g (68.5%) of analytically pure [Rh(cyclam)(CCC$_6$H$_5$)$_2$]OTf. Anal. Calcd (found) for $C_{27}H_{34}F_3N_4O_3RhS$: C, 49.54 (49.39); H, 5.24 (5.23); N, 8.56 (8.38). ESI-MS: intense parent ion (M^+) at *m/z* value of 505.27. NMR data: *trans*-**2a**, ^{1}H NMR (500 MHz, CD_3CN) δ 1.49 (q, 2H), 2.04 (d, 2H), 2.64 (m, 4H), 3.03 (m, 12H), 4.50 (b, 4H), 7.17 (t, 2H), 7.26 (t, 4H), 7.38 (d, 4H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 30.5, 52.8, 54.5, 108.4 (d, J_{RhC} = 6.4 Hz, Rh−CCPh), 113.3 (d, J_{RhC} = 38 Hz, Rh−CCPh), 126.6, 129.0, 129.1, 132.2. *cis*-**2a**, ^{1}H NMR (500 MHz, CD_3CN) δ 1.81 (d, 2H), 2.60 (d, 2H), 2.71 (m, 4H), 3.01 (m, 8H), 3.35 (t, 2H), 3.47 (q, 2H), 4.44 (b, 2H), 4.88 (b, 2H), 7.15 (t, 2H), 7.25 (t, 4H), 7.33 (d, 4H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 24.4, 49.0, 49.9, 51.3, 53.7, 103.9 (d, J_{RhC} = 47 Hz, Rh−CCPh), 104.0 (d, J_{RhC} = 8.7 Hz, Rh−CCPh), 126.4, 129.21, 129.25, 131.9.

*[Rh(cyclam)(CCC$_6$H$_4$CH$_3$)$_2$]OTf (**2b**).* Using THF (5 mL), *trans*-[Rh(cyclam)(OTf)$_2$]OTf (0.224 g, 0.299 mmol), 4-ethynyltoluene (75.7 μL, 0.597 mmol), and BuLi (501 μL, 1.254 mmol) yielded 0.100 g (49.1%) of analytically pure [Rh(cyclam)(CCC$_6$H$_4$CH$_3$)$_2$]OTf·H_2O. Anal. Calcd (found) for $C_{29}H_{38}F_3N_4O_3RhS·H_2O$: C, 49.71 (49.98); H, 5.75 (5.47); N, 8.00 (7.78). ESI-MS: intense parent ion (M^+) at *m/z* value of 533.23. *trans*-**2b**. ^{1}H NMR (400 MHz, CD_3CN) δ 1.48 (q, 2H), 2.04 (d, 2H), 2.30 (s, 6H), 2.63 (m, 4H), 3.03 (m, 12H), 4.48 (b, 4H), 7.17 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 21.3, 30.5, 52.8, 54.5, 108.2 (d, J_{RhC} = 6.7 Hz, Rh−CCPh), 111.9 (d, J_{RhC} = 37 Hz, Rh−CCPh), 126.1, 129.8, 132.1, 136.4.

*[Rh(cyclam)(CCC$_6$H$_4$CF$_3$)$_2$]OTf (**2c**).* Using THF (5 mL), *trans*-[Rh(cyclam)(OTf)$_2$]OTf (0.175 g, 0.233 mmol), 4-ethynyl-α,α,α-trifluorotoluene (76 μL, 0.466 mmol), and BuLi (392 μL, 0.979 mmol) yielded 0.090 g (48.8%) of analytically pure [Rh(cyclam)(CCC$_6$H$_4$CF$_3$)$_2$]OTf. Anal. Calcd (found) for $C_{29}H_{32}F_9N_4O_3RhS$: C, 44.06 (44.39); H, 4.08 (4.16); N, 7.09 (7.00). ESI-MS: intense parent ion (M^+) at *m/z* value of 641.38. *trans*-**2c**, ^{1}H NMR (500 MHz, CD_3CN) δ 1.49 (q, 2H), 2.05 (d, 2H), 2.63 (m, 4H), 3.00 (m, 12H), 4.54 (b, 4H), 7.56 (m, 8H).

*[Rh(cyclam)(CCC$_6$H$_4$F)$_2$]OTf (**2d**).* Using THF (5 mL), *trans*-[Rh(cyclam)(OTf)$_2$]OTf (175 mg, 0.233 mmol), 1-ethynyl-4-fluorobenzene (53.5 μL, 0.466 mmol), and BuLi (392 μL, 0.979 mmol) yielded 0.098 g (60.9%) of analytically pure [Rh(cyclam)(CCC$_6$H$_4$F)$_2$]OTf. Anal. Calcd (found) for $C_{27}H_{32}F_5N_4O_3RhS$: C, 46.96 (46.47); H, 4.67 (4.58); N, 8.11 (7.91). ESI-MS: intense parent ion (M^+) at *m/z* value of 541.29. *trans*-**2d**, ^{1}H NMR (400 MHz, CD_3CN) δ 1.48 (q, 2H), 2.04 (d, 2H), 2.62 (m, 4H), 3.01 (m, 12H), 4.50 (b, 4H), 7.01 (t, 4H), 7.38 (m, 4H).

Separation of cis and trans Isomers. The same procedure was followed as for the Cr(III) complexes.

RESULTS AND DISCUSSION

General Synthesis. Recently we reported the syntheses of three complexes of the form *trans*-[Cr(cyclam)(CCR)$_2$]OTf, **1a**−**1c** (Figure 1, OTf = trifluoromethanesulfonate).[27] These were prepared by a method similar to that reported by Berben and Long for the preparation of (Me$_3$tacn)Cr(CCH)$_3$ (Figure 2).[28] In this synthetic method, *cis/trans*-[Cr(cyclam)(OTf)$_2$]OTf was treated with the ethynyllithium reagent. Following purification, **1a** and **1b** were obtained with isolated yields in the range of 50−60% (Figure 3).[27] Infrared spectroscopy provided evidence for the trans geometry in complexes **1a**−**1c**. Confirmation of this geometry for **1a** was obtained by X-ray crystallography.[27] Recently, this method has been exploited by the groups of Nishi[29] and Ren[30] for applications involving molecular magnetism and molecular wires. We have now broadened the scope of this synthetic method, determined the key side reactions in the synthesis, and discovered that the cis product can also be isolated in most instances.

Hydroamination Side Reaction. A complex mixture of species resulted when this synthetic method was performed using arylacetylenes where the aryl group has either an electron withdrawing group (i.e., CN or CF_3) in the para position or where the aryl group is one with extended aromaticity (i.e., naphthalene or phenanthrene). Mass spectrometry demonstrated that the mixture consisted of complexes containing two to five equivalents (n = 2−5) of the arylethynyl moiety. The complex (with n = 4) resulting from the synthesis of **1c** was isolated and a poorly resolved X-ray crystal structure demonstrated the connectivity shown in Figure 4. The additional two arylethynyl units appear to have added by hydroamination of the cyclam NHs across the arylethynyl CC triple bond.

Infrared spectroscopy confirms the presence of the alkene functionalities ($\nu_{C=C}$ = 1611, 1647), and the calculated mass spectrum (parent ion and isotopic distribution) matches that predicted by the formula associated with this structure (Supporting Information). Hydroamination of alkynes has received considerable attention because of the synthetic utility of this reaction.[31] It is likely that the side-reaction here is an example of a base catalyzed hydroamination, a reaction that has precedence in the CsOH catalyzed hydroamination of phenylacetylene.[32] The fact that the hydroamination reaction is most problematic for the synthesis of **1c** and **1f**−**1h** suggests that the presence of either electron withdrawing groups or extended aromaticity helps to stabilize charge buildup in the transition state. Mass spectroscopy shows that trace amounts of the hydroamination product were also formed for the other complexes, but these small amounts were removed in the final precipitation step.

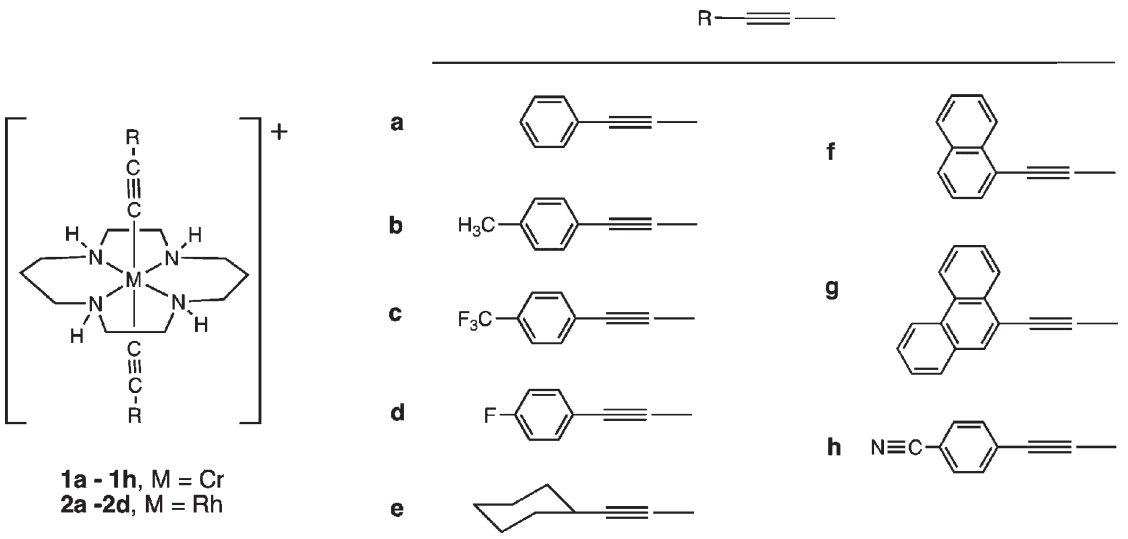

Figure 1. [M(cyclam)$(CCR)_2$]OTf complexes discussed in this paper. The abbreviations **1a**−**1h** and **2a**−**2d** are used to refer to the trans complexes. The cis complexes will be referred to as *cis*-**1a**−**1h**.

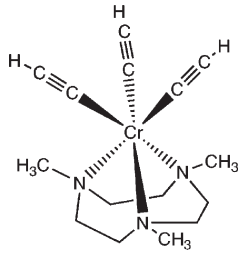

Figure 2. $(Me_3tacn)Cr(CCH)_3$.

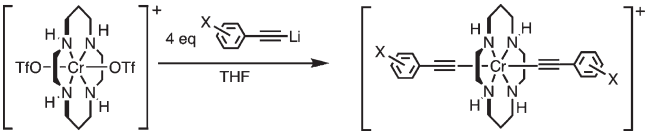

Figure 3. General synthetic scheme for **1a**−**1c**.

A likely mechanism for the hydroamination involves deprotonation of one of the cyclam NHs by the arylacetylide, yielding an amide coordinated to Cr(III). This results in an arylacetylene that is much more likely to undergo hydroamination than the corresponding (electron rich) arylacetylide. Decreasing the ethynyllithium to chromium ratio to 2:1 did give the desired product, albeit in significantly lower yields (15−30%). The lower yields for this stoichiometric ratio are consistent with the consumption of much of the ethynyllithium reagent through deprotonation of a macrocyclic amine. This suggested an alternate approach, namely, using excess *n*-BuLi for the deprotonation of the arylacetylene. When **1c** was prepared using a 4:2:1 ratio of *n*-BuLi to arylacetylene to Cr, the desired product was obtained in 75% yield, with the hydroamination product being barely detectable by mass spectroscopy. Notably, all reagents may be added in a single step with no decrease in yield, thus obviating the need to separately perform the deprotonation of the alkyne prior to the addition of the chromium complex.

This method has been successfully applied to the synthesis of **1a**−**1g** and **2a**−**2d**. The complexes are soluble in CH_3CN and

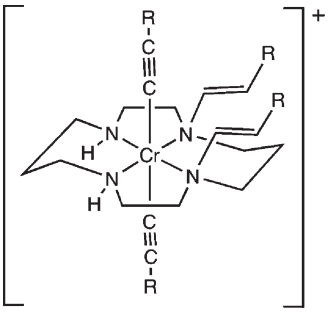

Figure 4. Structure of the product resulting from hydroamination.

THF (and have trace solubility in water) and are air stable both in the solid state and in solution. The preparation of **2a**−**2d** demonstrates that this synthesis is not restricted to Cr(III) nor to metals from the first transition series. Likewise, the synthesis of **1e** demonstrates that the synthesis is not restricted to arylethynyl complexes but can be applied to alkylethynyl complexes even though the alkylacetylides are much more basic than the corresponding arylacetylides. The only complex for which this method failed was **1h**, where mass spectral data indicated *n*-BuLi attack on the nitrile. Replacing *n*-BuLi with lithium diisopropylamide resulted in the desired product, albeit contaminated with an impurity that we have been unable to separate from **1h**.

It is important to note that these ethynyl complexes can be prepared in excellent yield using reagents that are very strong bases, even in the presence of the macrocyclic secondary amines. Consideration of relative pK_a values and the evidence cited above suggests that one or more macrocyclic amines are deprotonated during the synthesis of the cyclam complexes (presumably by the excess BuLi when a 4:2:1 ratio of BuLi to arylacetylene to Cr is used). The previously mentioned synthesis of (Me_3tacn)-$Cr(CCH)_3$ avoided this potential problem by using a macrocycle with tertiary amines.[28] Apparently, deprotonation of the macrocyclic amines does not inhibit the ethynyllithium reagent from binding to the metal. This is not surprising inasmuch as one of the mechanisms suggested for base hydrolysis of $M(NH_3)_5X^{2+}$ complexes involves prior deprotonation of the amine. This

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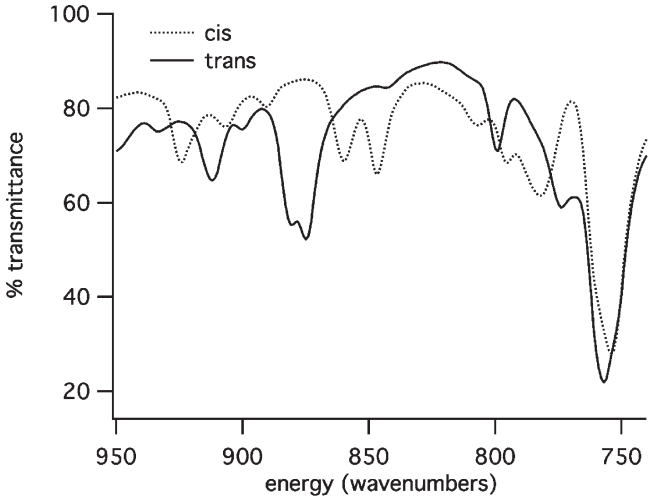

Figure 5. Infrared spectra in the CH_2 rocking and NH bending region for the cis and trans isomers of **1a**.

mechanism, termed S_N1CB, then proceeds via dissociative ligand exchange from this conjugate base (CB).[33] However, given the successful synthesis[28] of $(Me_3tacn)Cr(CCH)_3$ (a case in which there are no amine protons) under similar conditions as used for the cyclam complexes herein, it is unlikely that NH deprotonation is a requirement for OTf replacement.

Cis and trans Isomers for the Cr(III) Complexes. The previously reported synthesis resulted in exclusive isolation of the trans isomers of **1a**−**1c**.[27] We have determined that this was due to the rather surprising solubility of the cis isomers in ether or mixtures of THF and ether. Because the final purification step had involved precipitation of the product from THF solution by the addition of ether, the trans isomer was obtained selectively. In the purification reported here, the crude residue obtained after elution through a silica gel plug is sonicated with a small amount of ether, resulting in a fine solid that is collected by filtration. In several cases, **1a**, **1b**, **1d**, **1f**, and **1g**, the resulting solid is a mixture of cis and trans isomers as demonstrated by IR spectroscopy. For **1c** and **1e**, the resulting solid is the trans isomer with the corresponding cis isomer remaining in the ether filtrate (as evidenced by mass spectrometry and IR spectroscopy) along with other minor impurities.

For **1a**, **1b**, **1d**, **1f**, and **1g**, the isomers are separated by dissolving the mixture in THF and precipitating the trans product with ether. The filtrate contains the cis isomer. Infrared spectroscopy in the region of N−H bending and CH_2 rocking vibrations has been used to differentiate between cis and trans isomers for cyclam complexes of Co(III).[34] The infrared spectra in this region for the cis and trans isomers of **1a** (Figure 5) are consistent with complete separation of the isomers.

The most diagnostic feature is the doublet from the N−H vibration centered at 878 cm^{-1} for the trans isomer, which gives way to a doublet centered at 853 cm^{-1} for the cis isomer. Similar spectra are observed for the other congeners (Supporting Information), though these doublets are sometimes obscured by the aromatic out of plane vibration(s).

For the sake of simplicity, these syntheses begin with a cis/trans mixture of $[Cr(cyclam)Cl_2]Cl$, prepared by the method of Ferguson and Tobe,[22] which typically contains no more than 10% of the trans isomer. IR evidence demonstrates that ligand exchange to the $[Cr(cyclam)(OTf)_2]OTf$ proceeds with retention of configuration (Supporting Information). For all of the ethynyl complexes of Cr(III), we obtain greater than 60% yield of the trans isomer after separation, suggesting that the reaction from *cis*-$[Cr(cyclam)(OTf)_2]OTf$ proceeds with isomerization (eq 1).

$$\underset{>90\%\ cis}{[Cr(cyclam)Cl_2]Cl} \rightarrow \underset{>90\%\ cis}{[Cr(cyclam)(OTf)_2]OTf} \rightarrow \underset{>60\%\ trans}{[Cr(cyclam)(CCR)_2]OTf} \quad (1)$$

Furthermore, starting with isomerically pure *cis*-$[Cr(cyclam)(OTf)_2]OTf$ for the synthesis of **1a** results in a 2:1 ratio of trans to cis product. Alternatively, starting with isomerically pure *trans*-$[Cr(cyclam)(OTf)_2]OTf$ results in isomerically pure *trans*-**1a**. Thus, the preparation of the ethynyl complexes proceeds with retention of configuration when starting with the trans precursor, whereas it proceeds with significant isomerization when starting with the cis precursor. This is not surprising inasmuch as a similar cis to trans isomerization occurs when preparing *trans*-$Cr(cyclam)(CN)_2^+$ from a cis/trans mixture of $Cr(cyclam)Cl_2^+$.[35] For the synthesis of the trans ethynyl complexes, **1a**−**1g**, we find it more facile to start with a cis/trans mixture of $[Cr(cyclam)Cl_2]Cl$ and to perform the isomeric separation of the ethynyl product than to prepare isomerically pure *trans*-$[Cr(cyclam)Cl_2]Cl$ starting material.

Cis and trans Isomers for the Rh(III) Complexes. In addition to IR spectroscopy,[24,34] ^1H and ^{13}C NMR spectroscopy have been useful in determining stereochemistry for cis and trans $Rh(cyclam)X_2^+$ complexes.[36] Starting with isomerically pure *cis*-$[Rh(cyclam)Cl_2]Cl$ results in isomerically pure *cis*-$[Rh(cyclam)(OTf)_2]OTf$ (Supporting Information). However, ^1H and ^{13}C NMR demonstrate that the $[Rh(cyclam)(CCPh)_2]OTf$, **2a**, prepared from *cis*-$[Rh(cyclam)(OTf)_2]OTf$ contains approximately 15% of the trans isomer, indicating some cis to trans isomerization in this final step (eq 2).

$$\underset{pure\ cis}{[Rh(cyclam)Cl_2]Cl} \rightarrow \underset{pure\ cis}{[Rh(cyclam)(OTf)_2]OTf} \rightarrow \underset{\sim 15\%\ trans}{[Rh(cyclam)(CCPh)_2]OTf} \quad (2)$$

The stereochemical progression starting with *trans*-$[Rh(cyclam)Cl_2]Cl$ is less apparent by IR or NMR, due to what appears to be multiple macrocyclic conformations of the cyclam ligand for the trans isomer of the chloro and triflato complexes.[37] In addition, ^1H NMR demonstrates that the *trans*-$[Rh(cyclam)Cl_2]Cl$ starting material is contaminated with at least a few percent of the cis isomer (Supporting Information). Regardless, the ratio of trans to cis **2a** prepared starting from *trans*-$[Rh(cyclam)Cl_2]Cl$ is approximately 2:1 (eq 3).

$$\underset{\sim 95\%\ trans}{[Rh(cyclam)Cl_2]Cl} \rightarrow \underset{??}{[Rh(cyclam)(OTf)_2]OTf} \rightarrow \underset{\sim 2:1\ trans/cis}{[Rh(cyclam)(CCPh)_2]OTf} \quad (3)$$

The tendency of *cis*-$Rh(cyclam)I_2^+$ (but not *cis*-$Rh(cyclam)Br_2^+$ or *cis*-$Rh(cyclam)Cl_2^+$) to isomerize in refluxing aqueous solution suggests a steric preference of bulkier ligands for the trans configuration.[24] This suggests that the isomerization shown in eq 2 is due to steric preferences, implying that the isomerization shown in eq 3 occurs during the (harsh) first step and is likely due to an electronic preference.

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Like the analogous Cr(III) complexes, the cis and trans isomers of the alkynyl complexes can be separated based on solubility. However, isomerically pure *cis*-**2a**−**2d** were more difficult to obtain due to a greater solubility of their trans isomers (in ether/THF) than the corresponding Cr(III) complexes. Even so, a quantity of *cis*-**2a** sufficient for spectroscopic characterization was obtained.

^{1}H and ^{13}C NMR spectra of the ethynyl complexes of Rh(III) confirm the cis and trans geometries and demonstrate that the cis and trans isomers each exist in a single conformation. For example, the ^{1}H NMR spectrum of *trans*-**2a** shows a single NH resonance indicative of four equivalent amine protons, whereas *cis*-**2a** shows two such resonances. Furthermore, the ^{13}C NMR spectrum of *trans*-**2a** displays two resonances (52.8 and 54.5 ppm) associated with N-bound methylene carbons and one assigned to the central carbon of the three-carbon linkage (30.5), whereas that of *cis*-**2a** displays four resonances (49.0, 49.9, 51.3, 53.7) associated with N-bound methylene carbons and, again, one assigned to the central carbon of the three-carbon linkage (24.4).

Alkynyl C≡C Vibrational Frequency. Tables 1 and 2 list ν(C≡C) for all complexes along with ν(C≡C) for the parent alkyne. Intense Raman bands near 2100 cm^{-1} are evident for all complexes. All of the Rh(III) complexes also have IR active stretches in this region, whereas ν(C≡C) for the majority of the Cr(III) complexes are IR silent, with the exception of [Cr(cyclam)(CCC$_6$H$_{11}$)$_2$]OTf for which this band is weak but observable. For all trans complexes, the Raman bands can be assigned to the symmetric C≡C stretch and the IR bands to the asymmetric C≡C stretch.

For M-CCR complexes, the frequency of the C≡C stretch relative to ν(C≡C) for the parent HCCR has been used to determine information about the bond between the metal and the alkynyl carbon. However, as pointed out by Manna et al., better reference compounds are those of the type R′CCR (R′ ≠ H) because of the fact that ν(C≡C) for the HCCR derivatives contains contributions from the terminal C−H coordinate.[18] For example, whereas ν(C≡C) for HCCPh is 2110 cm^{-1}, the corresponding R′CCPh can range from 2150 to 2280 cm^{-1}. However, for the sake of a common comparison we have included the HCCR data.

A closer look at the Raman active bands for each of the trans complexes reveals a slight reduction of ν(C≡C) relative to the analogous alkyne (Table 1), thus these ν(C≡C) values should all be significantly lower than the corresponding R′CCR compounds. This is consistent with a weakening of the C≡C bond. Two explanations have been put forth for this weakening. The first explanation involves π-interactions, either M → CCR π-backbonding or RCC → M π-bonding. The second explanation recognizes that the lone pair on the RCC$^-$ anion is antibonding with respect to the C≡C bond. Thus, an increased ionic character in the M−CCR bond will result in a weaker C≡C bond.[18] For example, the alkali metal salts of the phenylethynyl anion demonstrate decreased values for ν(C≡C) down the column (LiCCPh, 2030 cm^{-1}; NaCCPh, 2005 cm^{-1}; KCCPh, 1998 cm^{-1}).[38] Presumably, the C≡C bond weakening for the Cr(III) and Rh(III) ethynyl complexes is partly due to the ionic nature of the M(III)−CCR bond. However, can any reduction in bond order be ascribed to π-interactions and if so, π-bonding or π-backbonding?

A comparison of ν(C≡C) reveals that these values range from 21 to 28 cm^{-1} higher for the Rh(III) complexes than the analogous Cr(III) complexes (Table 1), indicating more C≡C bond weakening for the Cr(III) complexes. Note that, apart from a slight ionic radius difference [66.5 pm for Rh(III) vs 60.5 pm for Cr(III)], the chief difference between these metals is in the population of the orbitals of appropriate symmetry for π-interaction with the ethynyl ligands. Namely, these orbitals are half-filled for Cr(III) whereas they are filled for Rh(III). Thus, if the chief π-interaction were π-backbonding, this interaction would be favored for the Rh(III) complexes over the Cr(III) complexes, suggesting that the Rh(III) complexes should have the weaker C≡C bonds. In fact, the opposite is observed, which is consistent with π-donation from the ethynyl ligands to the half-filled t_{2g} orbitals of the Cr(III) complexes being more pronounced than π-donation to the filled t_{2g} orbitals of the Rh(III) complexes. Furthermore, if the difference in M(III) ionic radius here has any significant effect, it would be to weaken the C≡C bond of the Rh(III) complexes relative to the Cr(III) complexes, serving only to partly mitigate the effect of the observed π-interaction.

Though these spectroscopic results clearly indicate that the alkynyl ligands act as π-donors for the Cr(III) complexes, the nature of the interaction with the Rh(III) complexes is less obvious, though clearly weak. For the related *trans*-Ru(16-TMC)(CCAr)$_2$ complexes (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane), the Ru(II)-alkynyl interactions are discussed in terms of the alkynyl ligands being π-acceptors, albeit quite weak.[7] Such π-backbonding would be expected to be even weaker for Rh(III) complexes compared with Ru(II) complexes, due to the higher positive charge on Rh.

Photophysical Characterization. *Electronic Absorption Spectra of the Cr(III) Complexes.* As demonstrated in Figure 6, the UV−vis absorption spectra of the *trans*-[Cr(cyclam)(CCR)$_2$]OTf complexes exhibit intense ($\varepsilon \sim 5\,000-40\,000$ M^{-1} cm^{-1}) transitions at wavelengths below 320 nm. These likely involve charge

Table 1. Raman Vibrational Data (cm^{-1})

	ν(C≡C) complex (parent alkyne)	Δ
1a	2077 (2110)	33
1b	2079 (2108)	29
1c	2086 (2115)	29
1d	2083 (2112)	29
1e	2088 (2115)	27
1f	2073 (2100)	27
1g	2071 (2097)	26
2a	2105 (2110)	5
2b	2105 (2108)	3
2c	2107 (2115)	8
2d	2109 (2112)	3

Table 2. IR Vibrational Data (cm^{-1})

	ν(C≡C)
2a	2094
cis-**2a**	2110, 2123
2b	2098
2c	2103
2d	2103
cis-**2d**	2107, 2120

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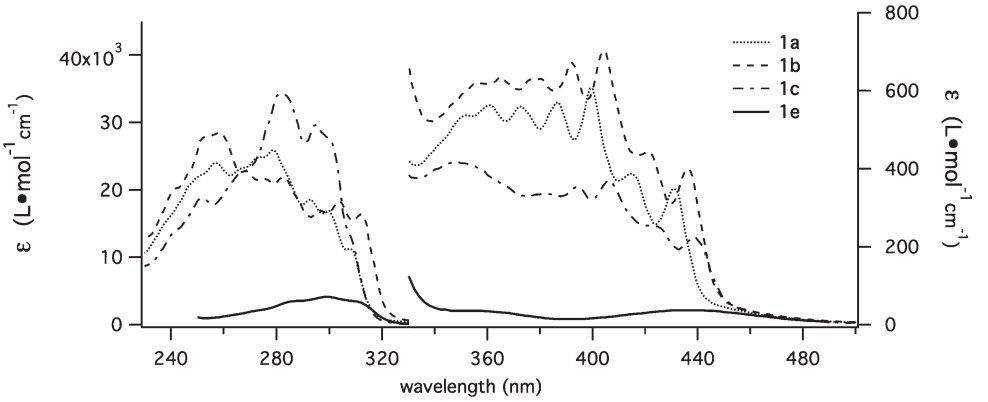

Figure 6. UV−vis absorption spectra (in CH_3CN) comparing selected *trans*-[Cr(cyclam)$(CCR)_2$]OTf complexes, **1a**−**1c** and **1e**.

transfer (CT)[39,40] and intraligand (IL) transitions. The absorbance spectra between 320 and 500 nm (typical region for transitions from the $^4A_{2g}$ ground state to the $^4T_{1g}$ and $^4T_{2g}$ (O_h) excited states) demonstrate extinction coefficients ranging from 170 to 700 M^{-1} cm^{-1} (Figures 6 and 7 and Table 3)

These molar extinction coefficients are much larger than is typical for d−d transitions involving centrosymetric species. For example, the isoelectronic *trans*-Cr(cyclam)$(CN)_2^+$ displays two absorption bands of modest intensity ($\varepsilon \sim 60$ L/mol cm) at 414 nm ($^4A_{2g} \rightarrow {}^4T_{2g}$) and 328 nm ($^4A_{2g} \rightarrow {}^4T_{1g}$).[35] The larger extinction coefficients for the arylethynyl complexes, along with the fine structure apparent in the absorption spectra suggest possible intensity stealing from the proximal CT band[41] as has been observed for other alkynyl complexes of Cr(III).[21] Here, this intensity stealing appears to require the aryl substituent, inasmuch as the electronic absorption spectrum of the related cyclohexylethynyl complex, **1e**, lacks either the fine structure or intensity observed for the arylethynyl complexes (Figure 6 and Table 3). The fact that these visible absorption bands for **1e** are shifted to lower energy relative to those of the *trans*-Cr(cyclam)-$(CN)_2^+$ cation also suggests that the ethynylcyclohexane ligand is a weaker field ligand than CN^-. This conclusion is consistent with the π-donor character of the alkynyl ligands that has previously been inferred for Cr(III) complexes.[21]

Figure 7 also demonstrates that extended aromaticity of the aryl group shifts the onset of absorption approximately 100 nm to the red. Furthermore, as demonstrated in Table 3 for **1a** vs *cis*-**1a** (and shown in the Supporting Information for several additional congeners), the cis isomers exhibit extinction coefficients approximately twice the magnitude of their corresponding trans isomers, with absorption maxima shifted 7−10 nm to lower energy. The larger extinction coefficients are consistent with the loss of centrosymmetry.

Electronic Absorption Spectra of the Rh(III) Complexes. UV−vis spectra for the corresponding Rh(III) complexes, **2a**−**2c** and *cis*-**2a**, are shown in Figure 8. These are dominated by CT transitions that are red-shifted approximately 40−70 nm relative to the corresponding transition for the Rh(cyclam)-$(CN)_2^+$ complex.[42] As a result of this red-shift, the metal centered (MC) ligand field transitions for the Rh(III) alkynyl complexes are obscured (for reference, the lowest energy MC transition for Rh(cyclam)$(CN)_2^+$ occurs at 267 nm). The MC transitions are also likely to be red-shifted due to the alkynyl ligand being a weaker field ligand than cyanide, but apparently this shift is not large enough to reveal this transition.

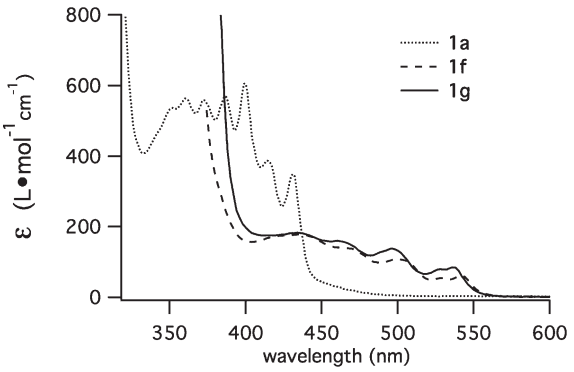

Figure 7. UV−vis absorption spectra (in CH_3CN) comparing **1a** with **1f** and **1g**. Note that the expanded aromaticity shifts the onset of absorption to longer wavelengths.

Steady State and Transient Emission Data for the Cr(III) Complexes. The Cr(III) alkynyl complexes are emissive in the red region of the visible spectrum, the emission being solvent and concentration independent (Table 4). The excitation spectrum for each complex resembles the UV−vis absorption spectrum, indicating that emission is not due to an impurity.

By analogy with the isoelectronic *trans*-Cr(cyclam)$(CN)_2^+$ complexes, emission from the alkynyl complexes could be expected to originate from the ^2E_g (O_h) excited state. However, the steady-state room temperature emission spectra for most of these complexes are broad and structureless (Supporting Information), with emission maxima red-shifted relative to the 650−710 nm region characteristic of ^2E_g emission.[43] Such spectra are characteristic of $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h) transitions.[44] Typical $^2T_{1g}$ emitters of similar structure (e.g., *trans*-[Cr(cyclam)$(OH)_2]^+$ and *trans*-[Cr(tet a)$F_2]^+$ where tet a is *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) can be characterized as having axial ligands that are both σ and π donors.[45] However, assignment of the emission as originating from the $^2T_{1g}$ excited state does not necessitate that the ligands be π-donors but only that there exists an asymmetry of π effects (π-donating or π-withdrawing) between the axial and equatorial ligands.[46] Regardless, the vibrational data discussed above clearly point toward the asymmetry arising from π-donation from the alkynyl ligand.

The cyclohexylethynyl complex, **1e**, on the other hand, displays an emission spectrum that is not as red-shifted and that shows evidence of fine structure (Supporting Information). This suggests

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Table 3. UV−Visible Spectral Data (Visible Region) for [Cr(cyclam)(CCR)$_2$]OTf Complexes in CH$_3$CN[a]

complex	λ_{max} (ε)[b]	ref
1a	352 (528), 360 (554), 373 (550), 387 (560), 400 (597), 414 (380), 432 (343)	27
cis-**1a**	354 sh (753), 369 (794), 382 (943), 395 (1025), 408 (1091), 424 (669), 441 (582)	this work
1b	355 (620), 365 (635), 376 (629), 380 (631), 392(673), 404 (703), 421 (443), 436 (400)	27
1c	348 (452), 382 (358), 394 (363), 406 (369), 424 (258), 438 (224)	27
1d	359 (576), 373 (569), 385 (598), 397 (594), 414 (401), 428 (327)	this work
1e	354 (36), 438 (37)	this work
1f	434 (178), 466 sh (141), 500 (109), 528 (56), 542 (63)	this work
1g	434 (183), 464 sh (158), 496 (139), 528 (80), 536 (85)	this work

[a] The spectrum for **1a** was also recorded in THF and water (Supporting Information), demonstrating that the spectra are largely solvent independent. The Beer's Law dependence was also demonstrated for **1a** in CH$_3$CN. [b] Absorption wavelengths are in nanometers, and the extinction coefficients are in units of molarity^{-1} centimeters^{-1}.

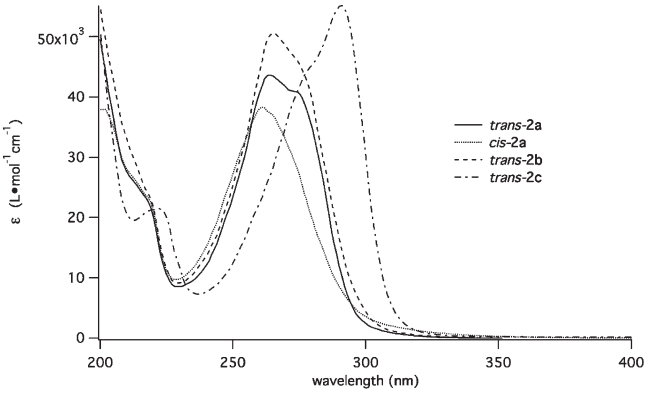

Figure 8. UV−vis absorption spectra of Rh(III) alkynyl complexes in CH$_3$CN. The spectrum for *trans*-**2a** was also recorded in THF and water, demonstrating that the spectra are largely solvent independent. The Beer's Law dependence was also demonstrated for *trans*-**2a** in CH$_3$CN.

Table 4. Photophysical Data for *trans*-[Cr(cyclam)(CCR)$_2$]$^+$

	λ_{max} (nm)[a]			τ (μs)		
	20 °C		77 K	20 °C, air saturated (N$_2$)		77 K
complex	CH$_3$CN	H$_2$O[b]	glass	CH$_3$CN	H$_2$O[b]	glass
trans-**1a**	748	745	745[c]	6 (225)	37 (293)	343[c]
trans-**1b**	749	746	746[c]	5 (259)	30 (285)	340[c]
trans-**1c**	748	746	745[c]	6 (203)	32 (313)	370[c]
trans-**1e**	727	731	735[d,e]	51 (331)	187 (327)	179,[d,f] 341[d,g]
trans-**1f**	749	748	748[d]	3 (250)	13 (240)	343[d]
trans-**1g**	750	747	750[d]	3 (238)	*h* (273)	345[d]

[a] The emission spectra are concentration independent. [b] An ion-exchange resin, Dowex 2-X8, chloride form, 20-50 mesh, was used to assist the solubility of the complexes in H$_2$O. [c] H$_2$O/DMSO glass. [d] CH$_3$OH/DMSO glass. [e] The spectrum exhibits significant fine structure with peaks between 719 and 756 nm. [f] Emission monitored at 718 nm. [g] Emission monitored at 756 nm. [h] Because of low solubility in water and oxygen quenching, this lifetime could not be measured.

that emission in this case may originate from the ^{2}E$_g$ (O$_h$) excited state or perhaps from both the ^{2}T$_{1g}$ and ^{2}E$_g$ (O$_h$) excited states as is observed for Cr(bpy)$_3^{3+}$.[47] Consistent with this latter suggestion, an analysis of the lifetimes for **1e** in a CH$_3$OH/DMSO glass at 77 K (a temperature below that at which thermal equilibration might occur) reveals two different lifetimes: 179 μs at 719 nm, compared with 341 μs at 756 nm. At room temperature, the excited state lifetime is independent of emission wavelength. If these results indeed demonstrate at least some emission from the ^{2}E$_g$ (O$_h$) excited state, it implies that the cyclohexylethynyl ligand is a poorer π-donor than any of the arylethynyl ligands, an assertion that seems reasonable considering that the aryl ring can contribute π-electron density to the alkynyl bond.

Table 5. Effect of Deuteration on Lifetime (μs) of 1a

	room temperature		77 K	
	H$_2$O[a]	D$_2$O[a]	H$_2$O/DMSO	D$_2$O/DMSO
trans-[Cr(cyclam)(CCC$_6$H$_5$)$_2$]OTf	293	318	343	
trans-[Cr(cyclam)(CCC$_6$D$_5$)$_2$]OTf	290	303	367	
trans-[Cr(d_4-cyclam)(CCC$_6$H$_5$)$_2$]OTf		1086		1380
trans-[Cr(d_4-cyclam)(CCC$_6$D$_5$)$_2$]OTf		1019		1420

[a] An ion-exchange resin, Dowex 2-X8, chloride form, 20-50 mesh, was used to assist the solubility of the complexes in H$_2$O and D$_2$O.

The excited state lifetimes of the alkynyl Cr(III) complexes are slightly solvent dependent and also sensitive to the presence of oxygen (Table 4). The oxygen sensitivity stands in contrast to *trans*-[Cr(cyclam)(CN)$_2$]$^+$[16] but is consistent with observations for *trans*-[Cr(cyclam)(NCS)$_2$]$^+$.[48] Such oxygen sensitivity for the lifetimes of Cr(III) complexes has been attributed to the presence of π-electron density on the coordinated ligand.[49] Consistent with this, the excited state lifetime of **1e** is the least oxygen sensitive of the series (Table 4).

In an attempt to better understand the excited state deactivation process, the lifetime of **1a** was studied (under deaerated conditions) as a function of deuteration of the macrocyclic amines and/or the aryl ring (Table 5).

Because phosphorescence quantum yields are typically quite small for Cr(III) complexes,[50] excited state relaxation must be dominated by nonradiative processes. Electronically coupled vibrational modes (typically N−H and C−H vibrations) are typical channels for nonradiative release of this excited state energy.[11,51] Note that there is roughly a 4-fold increase in the excited state lifetime of **1a** upon macrocyclic N−H deuteration (both at 77 K and at room temperature). Such an isotope effect indicates the significant role that the N−H vibrations play in excited state relaxation.[11,51] Deuteration of the aryl ring, on the other hand,

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Table 6. Photophysical Data for *trans*-[Rh(cyclam)(CCR)$_2$]$^+$

	λ_{max} (nm)[a]			τ (μs)	
	ambient		77 K	ambient	77 K
complex	CH_3CN[b]	H_2O[b]	glass[c]	CH_3CN[b]	glass[c]
trans-**2a**	548	546	526	5.4	19
trans-**2b**	546	544	524	3.8	17
trans-**2c**	524	520	*d*	21	*d*

[a] The emission spectra are concentration independent. [b] N_2 purged. [c] H_2O/DMSO/CH_3OH glass. [d] The 77 K emission spectrum is dominated by an emission at 460 nm with a lifetime of 22 ms, typical of organic triplet emission. We cannot rule out impurity emission at this time.

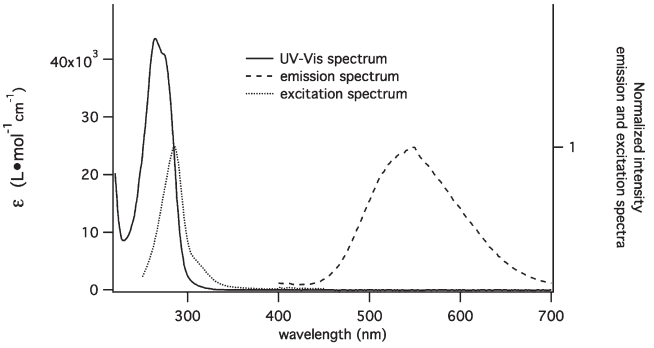

Figure 9. Absorption, emission (λ_{ex} = 290 nm), and excitation (λ_{em} = 548 nm) spectra for **2a** in degassed acetonitrile.

has no observable effect, clearly indicating that the aryl C−H bonds are not electronically coupled to the metal in the $^2T_{1g}$ excited state. The observation of a deuterium isotope effect upon amine deuteration for Cr(III) complexes is commonly cited as evidence for a weak coupling mechanism for excited state relaxation, that is, a mechanism involving tunneling between nested electronic states.[11]

The independence of the emission energy of the arylethynyl Cr(III) complexes as a function of the identity of the aromatic group suggests that there is very little electronic communication between Cr(III) and the aromatic ring in the doublet excited state. This is supported by the absence of a deuterium isotope effect upon aryl C−H bond deuteration.

Steady State and Transient Emission Data for the Rh(III) Complexes. Emission from acidoam(m)ine Rh(III) complexes in room temperature fluid solutions is typically short-lived (1−50 ns),[52] but *trans*-Rh(cyclam)$(CN)_2^+$ exhibits long-lived (8 μs) broad structureless emission centered at 470 nm in room temperature aqueous solutions. This behavior is attributed to the presence of stronger field CN^- ligands along the *z*-axis (both a better σ-donor and π-acceptor than the in-plane amine ligands), which results in the $^3A_{2g}$ (D_{4h}) state being the lowest energy MC excited state.[15] This restricts nonradiative and photochemical deactivation to the *xy*-plane (due to population of the $d_{x^2-y^2}$ orbital), and such deactivation is inhibited by the rigid macrocyclic ligand.[11,26] The isoelectronic Rh(III) alkynyl complexes, **2a**−**2c**, exhibit similar behavior, though emission is shifted to lower energy relative to *trans*-Rh(cyclam)$(CN)_2^+$ (Table 6, Figure 9, and Supporting Information). The red-shift in emission demonstrates that the alkynyl ligands are weaker-field ligands than cyanide, consistent with prior observations for the Cr(III) complexes. At the same time, the emissive behavior is consistent with excited state population of the $d_{x^2-y^2}$ orbital, supporting the understanding that alkynyl ligands are stronger σ-donors than the in-plane amines. In contrast to *trans*-Rh(cyclam)$(CN)_2^+$, **2a**−**2c** are quenched by oxygen, reminiscent of the analogous Cr(III) complexes. The slight red shift of the excitation spectrum from the absorption spectrum (<20 nm, e.g., Figure 9) is likely an artifact from the precipitous drop in the excitation lamp intensity at 270 nm.

SUMMARY

A high-yield one-pot synthesis for complexes of the type [M(cyclam)$(CCR)_2$]OTf has been developed. Both the cis and trans complexes can be isolated, though the trans complexes (which are typically more desirable as building blocks for molecular electronic devices) are typically obtained in substantially higher yields (due both to isomerization and solubility). Like their corresponding *trans*-M(cyclam)$(CN)_2^+$ complexes, both the Cr(III) and Rh(III) complexes exhibit long-lived MC phosphorescence. Analysis of ν(C≡C) suggests that RCC → M π-donation plays a significant role in the M−CCR bond for the Cr(III) complexes but much less of a role for the corresponding Rh(III) complexes. The MC electronic absorption bands of arylalkynyl complexes of Cr(III) show significant fine structure and unusually high intensities, indicative of intensity stealing from a proximal charge transfer band. This behavior appears to require the aryl ring, inasmuch as the MC absorption bands for the cyclohexylethynyl complex, **1e**, have normal intensities and lack fine structure. This indicates that the presence of the aryl ring enhances the electronic communication between Cr(III) and the alkynyl ligand. The presence of these π-interactions suggests the possibility of long-range electronic communication between metal centers connected by arylalkynyl ligands. We are currently working on extending this chemistry to the preparation of complexes with other transition metals as well as the synthesis of dimers and trimers for studies of intramolecular energy transfer.

ASSOCIATED CONTENT

Supporting Information. Characterization data for the hydroamination product; infrared spectra and analysis supporting the stereochemical assignments for the Cr(III) and Rh(III) starting materials and their alkynyl complex products; overlaid UV−vis spectra of the cis and trans isomers of **1a**, **1d**, **1f**, and **1g**; comparison of the UV−vis spectra of **1a** in CH_3CN, THF, and H_2O; room temperature and 77 K emission spectra of **1a**−**1c** and **1e**−**1g**; and room temperature emission and excitation spectra for **2b** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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