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Synthesis of trans Bis-alkynyl Complexes of Co(III) Supported by a Tetradentate Macrocyclic Amine: A Spectroscopic, Structural, and Electrochemical Analysis of π -Interactions and Electronic Communication in the C=C-M-C=C Structural Unit

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Abstract

Alkynyl complexes of the type *trans*-[Co(cyclam)(CCR)₂]OTf have been prepared and characterized by UV-Vis spectroscopy, ¹H NMR, vibrational spectroscopy (infrared and Raman), and cyclic voltammetry. Where appropriate the data is compared to the corresponding Cr(III) and Rh(III) complexes. Though the arylalkynyl ligands have been shown to act as π -donors for the corresponding Cr(III) complexes, vibrational spectroscopy suggests that the π -interactions between the arylalkynyl ligands and Co(III) are quite weak, and that the more electron withdrawing trifluoropropynyl ligand likely behaves as a weak π -acceptor toward Co(III). X-ray crystal structures for *trans*-[Co(cyclam)(CCCF₃)₂]OTf and *trans*-[Cr(cyclam)(CCCF₃)₂]OTf are also reported and analysis of the M-C and C=C bond lengths are consistent with this understanding of the trifluoropropynyl ligand. Cyclic voltammetry of the trans-[Co(cyclam)(CCR)₂]OTf complexes demonstrates that when $R = C_6H_5$ or $p-C_6H_4CH_3$, the Co^{III/II} reduction wave is chemically irreversible. However, when $R = p-C_6H_4CF_3$, $p-C_6H_4CN$, or CF_3 , the Co^{III/II} reduction wave is chemically reversible. This suggests that the more electron withdrawing alkynyl ligands become π -acceptors toward the reduced form of cobalt. Finally, the ferrocenvl capped *trans*- $[M(cvclam)(CCFc)_2]OTf$ complexes (where M = Co(III) and Rh(III)) were prepared and studied. Cyclic voltammetry shows only a single 2ewave for the ferrocenyl termini, indicating little to no electronic communication through the organometallic backbone.

1. Introduction

The chemistry of transition metal σ -alkynyl complexes has been explored for use in applications such as molecular wires [1-5], molecular magnetism [5 -9], and non-linear optical materials [10]. Since the first reports of *trans*-bis(alkynyl) metal complexes of macrocyclic tetraamine ligands [11-13] several groups have explored this structural motif as a potential building block for molecular wires [3-4] and molecular magnets [8-9], in part due to this framework facilitating rigid-rod type applications. Our own interest in alkynyl complexes began with a desire to compare the emissive behavior of the *trans*-[M(cyclam)(CCR)₂]⁺ (cyclam = 1, 4, 8, 11tetraazacyclotetradecane, M = Cr³⁺ and Rh³⁺) cations with their isoelectronic dicyano analogues. This led us to develop a streamlined synthesis of the *trans*-[M(cyclam)(CCR)₂]⁺ complexes [13-14] that has now been applied successfully to the synthesis of Cr³⁺ [4, 8, 13-15], Rh³⁺ [14-15], Fe³⁺ [3], and now Co³⁺ (herein) complexes with a host of alkynyl ligands.

Particularly important in the design of systems for the applications named above is an understanding of the bonding interaction between the metal center and the alkynyl ligand [16]. In particular, strong π -interactions may facilitate communication between transition metal centers linked through an alkynyl bridging ligand. By analogy with the CN- ligand [17], the alkynyl ligands were conventionally thought be strong σ -donors and modest π -acceptors (weaker than CO). However, this simple analogy does not appear to apply in all cases [16]. For example, spectroscopic measurements and molecular orbital calculations for

FeCp(CCR)(CO)₂, (R = H, Ph, *t*-Bu, and CCH), and FeCp*(CC-Bu^{*t*})(CO)₂ suggests that the alkynyl ligand acts as a weak π -donor [18-19] Likewise, electronic spectroscopy and density functional theory calculations on [M(CCSiMe₃)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 [20]. We have recently shown for a series of *trans*-M(cyclam)(CCR)₂⁺ that RCC \rightarrow M π -donation plays a significant role in the M-CCR bond for the Cr(III) complexes, but much less of a role (if any) for the corresponding Rh(III) complexes [14]. Thus, it is clear that the metal plays a major role in determining whether the alkynyl ligand behaves as a π -donor or π -acceptor.

Herein we report the synthesis of a series of *trans*-Co(cyclam)(CCR)₂⁺ complexes along with their characterization by infrared, Raman, and UV-Vis spectroscopy and by electrochemistry. In addition, we report single crystal X-ray structures for *trans*-M(cyclam)(CCCF₃)₂⁺ (where M = Co(III) and Cr(III)). The data suggest that the alkynyl ligands act as weak π -donors in the case of the Cr(III) complexes but not for the low spin *d*⁶ Co(III) complexes. Co(III) complexes are also unlikely candidates for π -backbonding with alkynes due to their electron deficient nature. However, we observe some evidence for π -backbonding when the alkynyl ligand is trifluoropropynyl. We also have tested the ability of the Co(III) and Rh(III) complexes to act as organometallic molecular wires and observe no significant communication through the -C=C-M-C=C- structural motif.

2. Experimental Section

2.1 Materials and Methods.

Tetrahydrafuran (THF) was dried and degassed using an Innovative Technology Inc. solvent purification system. Lithium diisopropylamide (2.0 M solution in THF and heptane) and *n*-butyllithium (2.5 M solution in hexanes) were purchased from Aldrich. Infrared spectra were recorded on solid samples using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with an ATR accessory. UV-Vis absorption spectra were collected using a Cary-50 spectrophotometer. NMR spectra were obtained using a Varian INOVA 400-MR spectrometer, Raman spectra were recorded using either a Thermo Scientific Nicolet 6700 FT-IR with an NXR FT-Raman module or a Spectra-Physics model 2017 with an argon ion laser, a Spex 750m monochrometer, and a Symphony CCD Detector from Horiba. Cyclic voltammograms were recorded using a BAS epsilon electrochemical work station and a BASi cell stand. Cell resistance was measured by the instrument and iR compensation applied accordingly. Parameters for iR compensation were evaluated on solutions of ferrocene to avoid over compensation. Elemental analyses were performed by Midwest Microlabs in Indianapolis, IN.

2.2 Syntheses

2.2.1 General synthetic methods.

The complexes *trans*-[Co(cyclam)Cl₂]Cl [21], *trans*-[Co(cyclam)(CN)₂]Cl [22], *trans*-[Co(cyclam)(CCC₆H₅)Cl]Cl [9]; and *trans*-[Cr(cyclam)(CCCF₃)₂]OTf, **1e**, and *trans*-[Co(cyclam)(CCCF₃)₂]OTf, **2e** [15], were prepared according to the literature procedures. *trans*-[Co(cyclam)(CN)₂]PF₆ was prepared by anion metathesis in water from the chloride salt. Alkynyl complexes of the type *trans*-

[M(cyclam)(CCR)₂]OTf were prepared using a modification of the literature procedure [14].

2.2.2 trans-[Co(cyclam)(OTf)₂]OTf

A slight modification of the literature synthesis of $[Co(en)_2(OTf)_2]OTf$ was followed [23]. A solution of *trans*- $[Co(cyclam)Cl_2]Cl (1.0 g, 2.73 mmol) in$ trifluoromethanesulfonic acid (10 g) was heated at 100°C for 3 hours under argon.The resulting mixture was then added to 200 mL of anhydrous diethyl ether thatwas being stirred vigorously. A light green precipitate formed which was thencollected by vaccum filtration. The solid was washed with anhydrous diethyl ether(20 mL), dried under vacuum, and stored in a desiccator until further use. (Yield = $1.59 g, 82 %) Anal. Calcd (found) for <math>CoC_{13}N_4F_9S_3O_9H_{24}$: C, 22.10 (21.59); N, 7.93 (7.51); H, 3.42 (3.38); Cl, 0 (none found).

2.2.3 trans-[Co(cyclam)(CCC₆H₅)₂]OTf (**2a**).

Using the general procedure [14], THF (5 mL), *trans*-[Co(cyclam)(OTf)₂]OTf (200 mg, 0.283 mmol), phenylacetylene (65 μL, 0.592 mmol), and *n*-butyllithium (480 μL, 1.20 mmol) resulted in 0.104 g (60 %) of analytically pure *trans*-[Co(cyclam)(CCC₆H₅)₂]OTf. Anal. Calcd. (found) for CoC₂₇N₄F₃SO₃H₃₄ : C, 53.13 (52.84); N, 9.18 (9.25); H, 5.61 (5.54). ESI-MS: intense parent ion (M⁺) at *m/z* value of 461.51. IR: v_a(C≡C) 2098 cm⁻¹. Raman: v_s(C≡C) 2102 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.33 (q, 2H), 1.86 (d, 2H), 2.54 (m, 12H), 2.83 (q, 4H), 4.19 (b, 4H), 7.23 (t, 2H), 7.34 (t, 4H), 7.51 (d, 4H). UV-Vis CH₃CN: λ_{MAX} (ε) 272 (53,069), 354(sh) (450), 452 (106).

2.2.4 trans-[Co(cyclam)(p-CCC₆H₄CH₃)₂]OTf (2b)

Using the general procedure [14], THF (5 mL), *trans*-[Co(cyclam)(OTf)₂]OTf (200 mg, 0.283 mmol), 4-ethynyltoluene (78 µL, 0.615 mmol), and *n*-butyllithium (480 µL, 1.20 mmol) resulted in 0.120 g (66 %) of analytically pure *trans*-[Co(cyclam)(CCC₆H₄CH₃)₂]OTf. Anal. Calcd. (found) for CoC₂₉N₄F₃SO₃H₃₈: C, 54.54 (54.92); N, 8.77 (8.78); H, 5.99 (6.12). ESI-MS: intense parent ion (M⁺) at *m/z* value of 489.56. IR: v_a(C≡C) 2102 cm⁻¹. Raman: v_s(C≡C) 2104 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.30 (q, 2H), 1.86 (d, 2H), 2.33 (s, 6H), 2.50 (m, 12H), 2.82 (q, 4H), 4.16 (b, 4H), 7.13 (d, 4H), 7.40 (d, 4H). UV-Vis CH₃CN: λ_{MAX} (ε) 272 (64,200), 455 (115).

2.2.5 trans-[Co(cyclam)(p-CCC₆H₄CF₃)₂]OTf (2c).

Using the general procedure [14], THF (5 mL), *trans*-[Co(cyclam)(OTf)₂]OTf (200 mg, 0.283 mmol), 4-ethynyl- α , α , α -trifluorotoluene (91 µL, 0.56 mmol), and *n*-butyllithium (480 µL, 1.20 mmol) resulted in 0.143 g (68 %) of analytically pure *trans*-[Co(cyclam)(CCC₆H₄CF₃)₂]OTf. Anal. Calcd. (found) for CoC₂₉N₄F₉SO₃H₃₂ : C, 46.66 (46.61); N, 7.50 (7.47); H, 4.32 (4.30). ESI-MS: intense parent ion (M⁺) at *m/z* value of 597.51. IR: v_a(C=C) 2106 cm⁻¹. Raman: v_s(C=C) 2111 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.30 (q, 2H), 1.85 (d, 2H), 2.46 (m, 8H), 2.60 (m, 4H), 2.75 (q, 4H), 4.18 (b, 4H), 7.66 (s, 8H). UV-Vis CH₃CN: λ_{MAX} (ϵ) 289 (52,000), 447 (120).

2.2.6 trans-[Co(cyclam)(p-CCC₆H₄CN)₂]OTf (2d)

Using the general procedure [14], THF (5 mL), *trans*-[Co(cyclam)(OTf)₂]OTf (200 mg, 0.283 mmol), 4-ethynylbenzonitrile (72 mg, 0.566 mmol), and lithium diisopropylamide (600 µL, 1.20 mmol) resulted in a crude product that was purified using silica gel column chromatography (70/30 CH₂Cl₂/CH₃CN, 20 cm x 2.5 cm). Yield: 0.103 g (55 %). Anal. Calcd. (found) for CoC₂₉N₆F₃SO₃H₃₂ : C, 52.73 (52.92); N, 12.72 (12.77); H, 4.88 (4.93). ESI-MS: intense parent ion (M⁺) at *m/z* value of 511.53. IR: v_a(C=C) 2104 cm⁻¹. Raman: v_s(C=C) 2108 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.31 (q, 2H), 1.86 (d, 2H), 2.48 (m, 8H), 2.61 (m, 4H), 2.78 (q, 4H), 4.19 (b, 4H), 7.63 (dt, 4H), 7.69 (dt, 4H). UV-Vis CH₃CN: λ_{MAX} (ϵ) 206 (52,000), 251 (24,000), 308 (79,000), 441 (157).

2.2.7 trans-[Co(cyclam)(CCFc)₂]OTf (**2f**)

Using the general procedure [14], THF (7 mL), *trans*-[Co(cyclam)(OTf)₂]OTf (200 mg, 0.283 mmol), ethynylferrocene (119 mg, 0.57 mmol), and *n*-butyllithium (460 µL, 1.15 mmol) resulted in 0.110 g (47 %) of analytically pure *trans*-[Co(cyclam)(CCFc)₂]OTf. Anal Calcd. (found) for CoFe₂C₃₅N₄F₃SO₃H₄₂ : C, 50.81 (50.52); N, 6.78 (6.48); H, 5.12 (5.16). IR: v_a (C≡C) 2114 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.29 (q, 2H), 1.92 (d, 2H), 2.54 (m, 12H), 2.90 (q, 4H), 4.04 (b, 4H), 4.15 (s, 4H), 4.23 (s, 10H), 4.40 (d, 4H). UV-Vis CH₃CN: λ_{MAX} (ε) 220 (77,000), 275 (26,000), 306 (21,000), 446 (766).

2.2.8 trans-[Rh(cyclam)(CCFc)₂]OTf (**3f**)

The general procedure [14] using THF (7 mL), *trans*-[Rh(cyclam)Cl₂]Cl (100 mg, 0.244 mmol), ethynylferrocene (103 mg, 0.490 mmol), and *n*-butyllithium (410

μL, 1.0 mmol) was applied, followed by a modified purification. The reaction mixture was first eluted through a silica gel plug with 100 mL of 50/50 CH₃CN/CH₂Cl₂ followed by 100 mL of pure CH₃CN. The solvent was removed from the second fraction resulting in 180 mg of crude chloride salt which was converted to the triflate by metathesis with NaOTf in acetone. The crude product was washed with water resulting in 0.127 g (71%) of analytically pure *trans*-[Rh(cyclam)(CCFc)₂]OTf•2H₂O. Anal Calcd. (found) for RhFe₂C₃₅N₄F₃SO₃H₄₂•2H₂O: C, 46.38 (46.88); N, 6.18 (6.21); H, 5.12 (4.82). IR: v_a(C≡C) 2110 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 1.46 (q, 2H), 2.10 (d, 2H), 2.65 (m, 4H), 3.07 (q, 12H), 4.11 (s, 4H), 4.18 (s, 10H), 4.29 (s, 4H), 4.34 (b, 4H). UV-Vis CH₃CN: λ_{MAX} (ε) 230 (36,000), 275 (18,000), 447 (634).

2.2.9 trans-[Co(cyclam)(CCC₆H₅)(CN)]PF₆

An oven-dried, two-neck, round-bottom flask (100mL) was charged with a stir bar, a filtered aqueous (50 mL) solution of *trans*-[Co(cyclam)(CCC₆H₅)Cl]Cl (308 mg, 0.714 mmol) and sodium cyanide (86 mg, 1.8 mmol). The reaction mixture was heated at reflux for 4 hours during which the color changed from red to yellow. The solution was then cooled to room temperature and the solvent volume was reduced to 5 mL. The mixture was then cooled overnight and filtered to remove dark impurities. To the filtrate was added an aqueous solution of ammoium hexafluorophosphate and the solid was collected via vacuum filtration and washed with diethyl ether (3 x 5 mL). The precipitate was eluted down a column of alumina (15 x 1 in) using a 50:50 mixture of CH_3CN/CH_2Cl_2 . The yellow band was collected

and evaporated to dryness. Yield: 0.254g (66 %). ESI-MS: intense parent ion (M+) at m/z value of 386.40. IR: v_a (C=C) 2129 cm⁻¹. Anal Calcd. (found) for CoC₁₉N₅F₆PH₂₉•H₂O : C, 41.54 (41.75); N, 12.75 (12.58); H, 5.69 (5.27). ¹H NMR (400 MHz, CD₃CN) 1.34 (q, 2H), 1.89 (d, 2H), 2.52 (m, 12H), 2.83 (q, 4H), 4.27 (b, 4H), 7.25 (t, 1H), 7.34 (t, 2H), 7.51 (d, 2H). UV-Vis CH₃CN: λ_{MAX} (ϵ) 218 (28,400), 254 (25,600), 264 (sh) (22,100), 356 (214), 445 (125).

2.3 X-ray structure determinations

Crystals of **1e** and **2e** were grown by slow evaporation of solvent from a concentrated acetonitrile solution. All single crystal measurements were performed on a Rigaku AFC8S diffractometer with a Mercury CCD detector at 173 ± 2 K, with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected to a maximum 2 θ value of 52.8° in 0.5° oscillations (in ω) with two exposures (to identify detector anomalies) of 15s (1e) or 30s (2e). Corrections for Lorentz and polarization effects and absorption [24] were applied to the data. The structures were solved by direct methods and refined by using full-matrix least-squares techniques. The triflate anion is disordered about an inversion center, and an acetonitrile solvent molecule shares occupancy with the anion. The trifluoromethyl groups of the alkynyl ligands of the cation were rotationally disordered in both compounds, with a major component occupancy in both compounds of 82.5%. The major component fluorine atoms were refined with anisotropic displacement parameters and the minor component fluorine atoms were refined isotropically. All non-hydrogen atoms other than the minor component fluorine atoms were refined

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anisotropically. Hydrogen atoms of the cyclam ligands were included in optimized positions with riding displacement parameters (20% greater than U_{eq} of host atom). Structure solution, refinement and the calculation of derived results were performed with the *SHELXTL-Plus* package of computer programs [25]. Crystallographic parameters are reported in Table 1.

		6
	1e	2e
Formula	C ₁₉ H ₂₇ N ₅ O ₃ F ₉ SCr	C ₁₉ H ₂₇ N ₅ O ₃ F ₉ SCo
Mw	628.52	635.45
Crystal System	Monoclinic	Monoclinic
Space Group	<i>P2₁/c</i> (No. 14)	<i>P2₁/c</i> (No. 14)
a, Å	8.9746(18)	8.9019(16)
b, Å	11.229(4)	11.179(3)
c, Å	14.081(4)	14.0286(19)
β, (°)	107.542(15)	108.570(13)
<i>V</i> , Å ³	1353.1(7)	1323.4(5)
Ζ	2	2
D _{calc} , g cm ⁻³	1.54	1.60
μ, mm ⁻¹	0.592	0.822
Transmission coefficients	0.76-1.00	0.83-1.00
Reflections collected	10827	10227
Reflections unique (<i>R</i> _{merge})	2759 (0.114)	2693 (0.0609)
Reflections observed (I>2σ(I))	1331	1810
R_1^a	0.0769 (0.1533)	0.0656 (0.0960)
wR_{2}^{b}	0.1484 (0.1850)	0.1323 (0.1503)

Table 1.Crystal data

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$ for observed data; number in parentheses is for all data.

 ${}^{b}wR_{2} = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2}$ for observed data; number in parentheses is for all data.

3. Results and Discussion

3.1 General synthesis and characterization

The syntheses of **1a** – **1f**, **3a** – **3c** and **3e** have been previously reported using the procedure summarized in Figure 1 [4, 13-15]. The syntheses of the corresponding Co(III) complexes, **2a** – **2f** and the Rh(III) complex, **3f**, are herein reported using this method. Though Figure 1 shows the starting material and



Figure 1. General synthesis of the complexes discussed in this paper

product in the trans configuration, for the Cr(III) and Rh(III) complexes, cis/trans mixtures of the starting material result in cis/trans product mixtures which can be separated by taking advantage of solubility differences [14]. In the case of the Co(III) complexes, the *trans*-[Co(cyclam)Cl₂]Cl precursor undergoes ligand exchange to the triflato complex, *trans*-[Co(cyclam)(OTf)₂]OTf, with retention of configuration. Replacement of the triflato ligands with the alkyne ligands (Figure 1) also proceeds with retention of configuration, thus requiring no separation of cis and trans isomers. The isomeric purity was confirmed by analysis of the CH₂

rocking and NH bending region of the IR spectra (supplementary material) according to the method of Poon et al [26]. The products are air stable in the solid state and in solution, with the triflate salts demonstrating good solubility in CH₃CN and THF.

Asymmetrically substituted *trans*-[Co(cyclam)(CCC₆H₅)CN]PF₆ was prepared by ligand substitution from *trans*-[Co(cyclam)(CCC₆H₅)Cl]Cl. The ¹H NMR spectra of all Co(III) complexes are well resolved, indicating the expected low-spin d^6 configuration.

UV-Vis absorption spectra for 2a - 2e are compared with that of *trans*-[Co(cyclam)(CN)₂]PF₆, **2g** (Figure 2). For **2g**, excitation from the ¹A_{1g} ground state



Figure 2. UV-Vis absorption spectra comparing the charge transfer bands (left) and the metal centered bands (right) for the Co(III) complexes, **2a** – **2e**, and **2g**.

into the ${}^{1}T_{1g}$ and ${}^{1}T_{2g}$ (O_{h}) ligand field excited states is observed. Likwise, both ligand field absorptions are observed for the trifluoropropynyl complex, **2e**, though these absorptions are slightly red shifted [15]. For the corresponding arylethynyl complexes, **2a** – **2d**, the higher energy ${}^{1}A_{1g}$ to ${}^{1}T_{2g}$ absorptions are obscured by the tails of charge transfer bands with maxima between 272 nm and 308 nm. In

addition, the lowest energy ligand field absorption bands of the arylethynyl complexes are two to three times as intense as that for the dicyano analogue, **2g**. Increased intensity was also observed for the corresponding arylethynyl Cr(III) complexes, **1a** – **1d**, and attributed to intensity borrowing from the charge transfer bands [14].

A comparison of the lowest energy absorption bands in Figure 2 suggests that the arylethynyl ligands are weaker field than either trifluoropropynyl or cyano ligands. It is also noteworthy that the addition of an electron withdrawing group to the aryl ring ($2c = -CF_3$; 2d = -CN) slightly blue-shifts the lowest energy absorption band relative to 2a and 2b. This mild increase in ligand field strength for these Co(III) complexes might reflect a slight reduction in π -donation from the alkynyl ligand (or possibly switching on some π -acceptor nature).

3.2 Analysis of the $C \equiv C$ stretching frequencies

All of the trans bis-ethynyl complexes discussed herein have v(C=C) near 2100 cm⁻¹. For such complexes, one would expect v_s(C=C) to be Raman active and v_a(C=C) to be IR active. In fact, all of the previously studied trans bis-ethynyl Cr(III) and Rh(III) complexes studied show intense Raman bands attributed to v_s(C=C). In addition, whereas v_a(C=C) for the Rh(III) complexes are observable by IR spectroscopy, for most of the Cr(III) complexes these vibrations are too weak to observe [14]. Not surprisingly, the Co(III) complexes synthesized herein show behavior similar to the Rh(III) complexes in having Raman observable v_s(C=C), and

IR observable $v_a(C=C)$. The following discussion will focus on the Raman data so that cross comparisons can be made between all three metals.

The C=C vibrational frequencies have often been used to determine relative C=C bond strengths and make determinations regarding the nature of metal alkynyl bonding. As has been thoroughly discussed elsewhere [14, 16], the strength of the C=C bond in an alkynyl complex depends both on the ionic character of the M–CCR bond, and on the metal alkynyl π -interactions. In our previous study comparing a set of [M(cyclam)(CCR)₂]⁺ complexes, the vibrational data suggested that the differences in v_s(C=C) between complexes where M = Cr³⁺ and Rh³⁺ was chiefly due to π -interactions, not the ionic character of the bond [14]. A comparison of v_s(C=C) values as a function of ionic radius of the metal (Table 2) further supports this contention. Namely, complexes of the two metal ions with the most disparate

	$v_{s}(C \equiv C) (\Delta v^{a})$			
	parent	Cr(III) 1	Co(III) 2	Rh(III) 3
	alkyne	r = 62 pm ^b	r = 55 pm ^b	r = 67 pm ^b
$[M(cyclam)(CCC_6H_5)_2]OTf (a)$	2110	2077 (-33)	2102 (-8)	2105 (-5)
$[M(cyclam)(CCC_6H_4CH_3)_2]OTf$ (b)	2108	2079 (-29)	2104 (-4)	2105 (-3)
$[M(cyclam)(CCC_6H_4CF_3)_2]OTf$ (c)	2115	2086 (-29)	2111 (-4)	2107 (-8)
$[M(cyclam)(CCC_6H_4CN)_2]OTf$ (d)	2111	2084 (-27)	2108 (-3)	-
$[M(cyclam)(CCCF_3)_2]OTf$ (e)	2165	2126 (-39)	2137 (-28)	-

Table 2. Raman vibrational data (cm⁻¹) for trans-[M(cyclam)(CCR)₂]OTf

^a Difference in stretching frequencies = (metal complex – parent alkyne).
^b Effective ionic radius [27].

effective ionic radii, Co(III) and Rh(III), and thus the largest difference in ionic character, have nearly identical v_s (C=C) values. In contrast, the Cr(III) complexes have lower stretching frequencies than either the Rh(III) or Co(III) complexes by approximately 25 cm⁻¹. This suggests that it is the *d*-electron count of the metal

that has the greatest impact on $v_s(C=C)$ and that the ionic character of the M-C bond is of relatively little importance. The lower energy C=C stretch for the d^3 configuration compared with that of the low spin d^6 configuration is consistent with the alkynyl ligands acting as π -donors and that the π -donation to the half-filled t_{2g} orbitals of the Cr(III) complexes is more pronounced than that to the filled t_{2g} orbitals of the Rh(III) and Co(III) complexes.

Though π -donation to Cr(III) is clearly implicated, it is unclear whether there is any significant π -donation to the low spin d^6 metals, or if the alkynyl ligands might even be behaving as very weak π -acceptors. Thus we also prepared *trans*- $[Co(cyclam)(CCC_6H_5)X]^+$, where X = CN⁻, to compare with the literature value for the complex where $X = Cl^{-}[9]$. Given that the Co^{III/II} reduction wave for the cyano complex is more negative than the chloro complex by 240 mV (supplementary material), the Co(III) center is clearly more electron rich when X = CN⁻, a very potent σ -donor. Thus, if the alkynyl ligand were acting as a π -acceptor, v(C=C) should be lower for the more electron-rich cyano complex than for the chloro complex. If the alkynyl ligand is acting as a π -donor, the opposite should be observed. We observe a slightly higher v(C=C) for the complex where X = CN⁻ (2129 cm⁻¹) than where X = Cl⁻ (2125 cm⁻¹) [9]. Though this difference is in the direction consistent with the alkynyl ligand acting as a π -donor, the difference in these frequencies is within experimental error, and thus suggests there are very minimal π -interactions between the arylethynyl ligand and Co(III).

Finally, in an attempt to increase the π -acceptor nature of the alkynyl ligand, we also prepared complexes from 4-ethynyl- α , α , α -trifluorotoluene, 4-

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ethynylbenzonitrile, and trifluoropropyne. However, as demonstrated in Table 2, the CF₃ and CN substituents on **2c** and **2d** did not reduce v_s (C=C) relative to the parent alkyne (Δv) any more than for **2a** and **2b**, indicating these substituents didn't significantly increase the π -acceptor nature of the ligand toward Co(III). Likewise, Δv for **1c** and **1d** is in line with that found for **1a** and **1b**. In contrast, the trifluoropropynyl complexes behave differently. Namely, the magnitude of Δv is notably increased relative to those of the arylalkynyl complexes. In addition, this increase is markedly greater for the Co(III) complex, **2e**, than for the Cr(III) complex, **1e**, which is consistent with turning on a slight π -acceptor nature of the ligand for these complexes. Not surprisingly, this is more accentuated for the low spin *d*⁶ configuration than the *d*³ configuration. The ability of trifluoropropynyl to act as a π -acceptor is consistent with earlier studies showing that this ligand is a very good electronic surrogate for cyanide [15]. However, this π -interaction is expected to be relatively weak due to the electron deficient nature of M³⁺ ions.

3.3 Structural data for the Co and Cr complexes

Vibrational data suggests that the arylethynyl ligands act as weak π -donors toward Cr(III) but likely have little to no π -interactions with Co(III), and that trifluoropropynyl may behave as a weak π -acceptor, particularly toward the low spin d^6 Co³⁺ complex. To further understand the metal-ligand π -interactions in the trifluoropropynyl complexes, X-ray structures (Figure 3, and supporting information) of the two trifluoropropynyl complexes, **1e** and **2e**, were determined

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in order to analyze the M-C and C \equiv C bond lengths (Table 3). Compounds **1e** and **2e** are isomorphous, both crystallizing in the monoclinic space group, $P2_1/c$. For each, the complex cation is situated upon an inversion center at (1/2 1/2 1/2). The triflate anion is disordered about an inversion center at (1/2 0 1/2), and an acetonitrile molecule shares occupancy with the anion, sitting opposite to it across the inversion center.



Figure 3. Thermal ellipsoid plot at the 35% probability level for the cation of *trans*- $[Co(cyclam)(CCCF_3)_2]OTf$, **2e**. The structure of the corresponding Cr complex, **1e**, is quite similar and appears in the supplementary material.

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Compound	M-C length (Å)	C≡C length (Å)			
$Cr(cyclam)(CCPh)_{2^+}$ 1a [13]	2.073 ^a	1.216ª			
$Cr(cyclam)(CCCF_3)_{2^+}$ 1e	2.071(5)	1.223(7)			
$Co(cyclam)(CCPh)_{2^+}$ 2a [9]	2.001(3)	1.113(4)			
$Co(cyclam)(CCCF_3)_{2^+}$ 2e	1.917(4)	1.217(6)			

Table 3. Selected bond lengths for *trans*-[M(cyclam)(CCR)₂]⁺ cations

^a The Cr does not occupy a center of inversion so these values are an average of the two distances; for Cr-C = 2.079(4) and 2.067(4); for C=C = 1.214(5) and 1.218(5).

A simple comparison of the trifluoropropynyl complexes of Cr(III) and Co(III), **1e** and **2e**, demonstrates that the C=C bond lengths for these two complexes are nearly identical. One explanation would be that there is no difference in the π interactions for these two complexes. However, another is that weakening of the C=C bond in **1e** due to ligand-to-metal π -donation is of similar magnitude to the weakening caused by metal-to-ligand π back bonding in **2e**. Extracting such information requires a comparison of the M-C and C≡C bond lengths of the two trifluoropropynyl complexes, **1e** and **2e**, with those of the phenylethynyl complexes, **1a** and **2a**. For the Cr(III) complexes, there is less than a 0.01 Å change in the Cr-C bond length when replacing CCPh with CCCF₃ (Table 3). Likewise, there is less than a 0.01 Å change in the respective $C \equiv C$ bond lengths. It is also worth noting that the C=C bond lengths in the parent alkynes, HCCPh (1.188 Å)[28] and HCCCF₃ (1.201 Å) [29], also differ very little (< 0.02Å). However, for the Co(III) complexes there is a 0.1 Å lengthening of the C=C bond upon the same replacement of the CCPh ligand with the CCCF₃ ligand, and a concomitant shortening of the M-C bond by nearly 0.1Å (Table 3). Thus, this structural data at least hints that the CCCF₃ ligand is acting as a

weak π -acceptor for Co(III), inasmuch as this shortening occurs only for the metal with filled t_{2g} orbitals, and thus is consistent with the vibrational data.

3.4 Voltammetry

The phenylethynyl, **2a**, and tolylethynyl, **2b**, complexes show irreversible

Co^{III/II} reduction waves (Figure 4).



Figure 4. Cyclic voltammograms for [Co(cyclam)X₂]⁺ complexes (2-5mM) in CH₃CN / 0.1 M Bu₄NClO₄ at a glassy carbon working electrode (3.0 mm). Scan rate = 100 mV/s; reference electrode = Ag/Ag⁺(0.005M) in CH₃CN. Under these conditions the $Fc^{+/0}$ couple appears at +0.133 V.

The irreversible reduction for **2a** was first reported by Shores' group and likely involves ligand dissociation from the resulting substitutionally labile Co(II) [9]. Addition of electron withdrawing groups on the aryl ring (2c and 2d) results in a

slight anodic shift, and chemical reversibility. Likewise, the bis-trifluoropropynyl (2e) and dicyano (2g) [15] complexes show reversible Co^{III/II} reduction waves that are further anodically shifted relative to the arylethynyl complexes. To test whether reversibility is more a function of the electron density on the metal or the nature of the ligand, the cyclic voltammograms of trans-[Co(cyclam)(CCC₆H₅)Cl]+ [9] and trans-[Co(cyclam)(CCC₆H₅)CN]⁺ were also recorded (supplementary material). Though the Co^{III/II} reduction waves for these complexes are anodically shifted relative to **2c**, and **2d**, they are chemically irreversible. Thus, we conclude that it is *not* the net electron density on the metal but rather the nature of the ligand that confers reversibility. Those ligands that are more capable of acting as π -acceptors $(C=N^-, C=CCF_3^-, C=CC_6H_4CF_3^-, C=CC_6H_4CN^-)$ are not as labile upon reduction to Co(II). This suggests that, even though these ligands are not terribly good π -acceptors toward the electron deficient Co(III), they are, not surprisingly, much more capable π -acceptors toward Co(II). A similar conclusion was drawn from the comparison of Rh(III) and Rh(II) alkynyl complexes of the type Rh(PP₃)(CCR)ⁿ⁺. [30]

Because of the strong Ru(II) mediated coupling observed between the ferrocenyl termini in *trans*-Ru(dppm)₂(CCFc)₂ [31], we have been interested in studying related cyclam complexes (Figure 5). For *trans*-Ru(dppm)₂(CCFc)₂ the communication is measured electrochemically, and oxidation waves for the two ferrocenyl termini are separated in the cyclic voltammogram by $\Delta E_{1/2} = 220$ mV. [31] Ren's group first reported the Cr(III) complex, **1f**, which demonstrated minimal communication between the ferrocenyl termini [4]. We have now prepared the Co(III) complex, **2f**, and the Rh(III) complex, **3f**, to determine whether or not

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communication between the ferrocenyl termini could be increased by replacing the

 d^3 metal with a d^6 metal.



1f, M = Cr(III); 2f, M = Co(III); 3f, M = Rh(III)





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In the cyclic voltammograms for **2f** (Figure 6) and **3f** (supplementary material) only a single two-electron wave was observed for the ferrocenyl termini, thus demonstrating little to no communication through the Co(III) or Rh(III) centers. Differential pulse voltammograms [32] of the two-electron ferrocenyl oxidation for both the Co(III) and Rh(III) complexes also show no evidence of splitting (supplementary material).



Figure 6. Cyclic voltammogram of **2f** showing the 2e⁻ oxidation wave (A) corresponding to the two ferrocenyl termini and the one electron Co^{III/II} reduction. For experimental conditions, see Figure 4 caption.

4. Conclusions

Previous work in our group has suggested that arylalkynyl ligands behave as π -donors towards Cr(III). Herein we have explored what, if any, π -interactions can be demonstrated with low-spin *d*⁶ metals, chiefly Co(III). For the arylethynyl ligands, there is little evidence to suggest that the arylalkynyl ligands are behaving as either π -donors or π -acceptors toward Co(III). This is perhaps not surprising given that the low-spin *d*⁶ configuration leaves little room for donation even though the +3 oxidation state leaves the metal fairly electron deficient. Only in the case of trifluoropropynyl as a ligand is there evidence for the ligand behaving as a weak π -acceptor. The lack of π -interactions between Co(III) and the arylalkynyl ligands inhibits π -conjugation through the metal and thus it should not be surprising that no communication is observed between the ferrocenyl termini of **2f** and **3f**. Even for the Cr(III) complex, **1f**, there is no significant communication between the ferrocenyl termini, even though this system likely involves π -donation from the

alkynyl ligand to Cr(III) [4, 14]. For *trans*-Ru(dppm)₂(CCFc)₂, the magnitude of $\Delta E_{1/2}$ is attributed to metal-to-ligand π -backbonding [31] which has clearly been demonstrated with the more electron rich Ru(II) alkynyl complexes [11]. Our electrochemical results suggest that there is metal to alkynyl ligand π -back bonding in the Co(II) oxidation state, particularly for more electron withdrawing alkynyl ligands. However, due to the irreversibility of the Co^{III/II} reduction wave for **2f**, and fact that this reduction is more negative than for Fc^{+/0} (Figure 6) it is not possible to determine whether electronic communication occurs through the Co(II) form of **2f**. Finally, it may yet be possible to observe significant electronic coupling in systems where the ethynylferrocene ligands are behaving as π -donors, but clearly the metal center should be more electron poor than [Cr(cyclam)]³⁺.

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Appendix A. Supplementary material CCDC 964986 and 964987 contain the supplementary crystallographic data for **1e**, and **2e**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk. Additional supplementary data for this article includes infrared spectra for **2a-2d**, **2f**, and **3f**; cyclic voltammograms of *trans*-[Co(cyclam)(CCC₆H₅)(X)]⁺ and **3f**; and a thermal ellipsoid plot for **1e**. These can be found in the online version at doi 10.1016/j.ica.xxxx.

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1f, M = Cr(III); 2f, M = Co(III); 3f, M = Rh(III)









Highlights

• Alkynyl complexes of the type *trans*-Co(cyclam)(CCR)₂⁺ are prepared using a single pot reaction.

• Evidence suggests that the arylalkynyl ligands behave neither as π -donors nor as π -acceptors.

• The trifluoropropynyl ligand behaves as a weak π -acceptor in these complexes.

The ferrocenyl capped alkynyl complexes, trans-M(cyclam)(CCFc)₂+ show little Fc to Fc coupling.