Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-03-2021-000707
Article Type:	Paper
Date Submitted by the Author:	02-Mar-2021
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Submitted to *Dalton Transactions*

A Unique Series of Chromium(III) Mono-alkynyl Complexes Supported by Tetraazamacrocycles †

Ashley J. Schuman [a], Sarah F. T. Robey [a], Eileen C. Judkins [a], Matthias Zeller [a] and Tong Ren*, [a]

Abstract

Described herein is the synthesis and characterization of macrocyclic Cr^{III} mono-alkynyl complexes. By using the *meso-* form of the tetraazamacrocycle HMC (HMC = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), *trans*-[Cr(HMC)(C_2Ph)Cl]OTf (**1a**), *trans*-[Cr(HMC)(C_2Np)Cl]OTf (**2a**), *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)Cl]OTf (**3a**), and *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))Cl]OTf (**4a**) complexes have been realized. These complexes were synthesized in high yield through the reaction of *trans*-[Cr(*meso*-HMC)($C_2Ar)_2$]OTf (**1b** – **4b**) with stoichiometric amounts of methanolic HCl. Single crystal X-ray diffraction showed that the *trans-* stereochemistry and pseudo-octahedral geometry is retained in the desired mono-alkynyl complexes. The absorption spectra of complexes **1a** – **4a** display *d-d* bands with distinct vibronic progressions that are slightly red shifted from *trans*-[Cr(HMC)($C_2Ar)_2]^+$ with approximately halved molar extinction coefficients. Time-delayed measurements of the emission spectra for complexes **1a** – **4a** at 77 K revealed phosphorescence with lifetimes ranging between 343 μs (**4a**) and 397 μs (**1a**). The phosphorescence spectra of **1a** – **4a** also exhibit more structuring than the

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†Electronic supplementary information (ESI) available. CCDC 2067384-2067389. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXXX

bis-alkynyl complexes due to a strengthened vibronic coupling between the Cr^{III} metal center and alkynyl ligands.

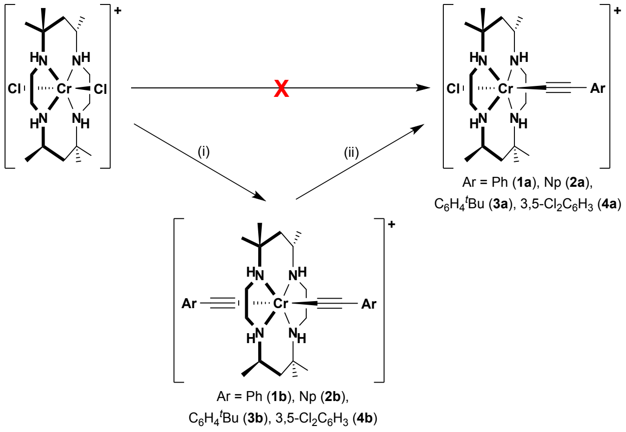
Introduction

Transition-metal alkynyl chemistry is a fascinating topic in the realms of both synthesis and materials applications.[1-3] Weinstein and co-workers have garnered attention for the study of donor-bridge-acceptor (D-B-A) complexes utilizing a *trans*-Pt^{II}-bis-alkynyl bridge, and demonstrated that the evolution of photoinduced electron transfer (PET) excited states, especially the formation of the charge-separated (CS) state, can be attenuated by vibrational excitation of the Pt bound C≡C bonds.[4] Expanding this chemistry to include earth abundant 3*d* metal complexes and investigating their PET processes is paramount in creating sustainable materials for optoelectronic applications. To accomplish this, D-B-A type complexes with dissymmetric alkynyl ligands need to be realized.

In the preparation of dissymmetric alkynyl D-B-A complexes, a mono-alkynyl species is first synthesized.[5, 6] Using this stepwise approach, it is possible to investigate the properties of each independent unit (D-B, B-A), the dissymmetric complex (D-B-A), and the symmetric complexes (D-B-D, A-B-A). Selective synthesis of mono-alkynyl species of Co^{III}(cyclam) complexes was first reported by Shores,[7] which proceeded under the weak base conditions. Our laboratory has published several examples of dissymmetric alkynyl complexes with Ru_2 and Co^{III}(cyclam) metal centers.[8-11] Femtosecond transient absorption and time-resolved IR spectroscopic studies of $[Co(cyclam)(C_2NAP^{iPr})(C_2D)]^+$ complexes (C_2NAP^{iPr} = 4-ethynyl-*N*-ispropyl-1,8-napthalimide, D = C_6H_4-4-NMe_2, Ph, or C_6H_4-4-$N(4\text{-}MeOPh)_2$), revealed the formation of desirable CS states, which were quickly deactivated by the low-lying Co-centered triplet states.[9] This necessitates further investigation of other macrocyclic 3*d* metal alkynyl bridges that sustain long-lived CS and metal-to-ligand charge transfer states.

Macrocyclic chromium alkynyl chemistry emerged with Taube and coworkers' $[Cr^{III}(phthalocyanine)(C_2Ph)_2]^-$ complex.[12] Following this, Berben and Long reported several $Cr^{III}(Me_3TACN)(C_2R)_3$ type complexes (Me_3TACN = *N,N',N"*-trimethyl-1,4,7-triazacyclononane, R = C_2SiMe_3, C_2H, C_4SiMe_3, and C_4H),[13] and Cr^{III}(cyclam) alkynyl complexes, *trans*-$[Cr(cyclam)(C_2R)_2]^+$ (R = C_2SiMe_3, C_2H) and *trans*-$[Cr(cyclam)(1,3\text{-}C_2C_6H_4C_2H)_2]^+$.[14] Additional Cr^{III}(cyclam) alkynyl complexes have been documented by the groups of Wagenknecht,[15] Nishijo,[16-19] and Ren.[20] Recent explorations of macrocyclic chromium alkynyl chemistry in our group include the study of *cis-/trans*-$[Cr^{III}(cyclam')(C_2R)_2]^+$ type complexes, where cyclam' is the C-substituted cyclam derivative DMC[21] (DMC = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) or HMC (HMC = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[22, 23] Thus far, all macrocyclic Cr^{III} alkynyl complexes feature symmetric bis-alkynyl ligands, while D-B-A type complexes have yet to be realized.

Examples of Cr mono-alkynyl complexes are known but sparse. Smith's laboratory synthesized several $CpCr^{III}$-$[(ArNCMe)_2CH](R)$ complexes, including R = C_2H, in order to study Cr–R bond homolysis (Ar = *ortho*-disubstituted aryl).[24] Earlier work by Smith resulted in $CpCr(NO)(N^iPr_2)(R)$ type complexes (R = C_2CMe_3 and C_2Ph), where the stability of the complexes was attributed to the π-bonding interactions of the $[Cr(NO)(N^iPr_2)]^{2+}$ core.[25] Two $(\eta^5\text{-}C_5H_4R)Cr(NO)_2\text{-}C_2Ph$ complexes (R = H or $COOCH_3$) were synthesized (via CuI catalyzed coupling) and characterized.[26] Berben discovered a unique dinuclear complex *trans*-$[(Me_3SiCC)(dmpe)_2Cr]_2(\mu\text{-}N_2)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) from the reaction between *trans*-$Cr(dmpe)_2Cl_2$ and $LiCCSiMe_3$ under N_2,[27] and analogous compounds were further investigated by Shores.[28] Also based on $Cr^{II}(dmpe)_2$, Berke and coworkers synthesized a series of mono-alkynyl $Cr^{II}(dmpe)_2$ complexes using trimethylstannyl and sodium alkynyl reagents.[29, 30] Macrocyclic chromium mono-alkynyl complexes have thus far remained elusive. Reported herein are the syntheses and characterizations of a unique series of Cr^{III}(HMC) mono-alkynyl complexes **1a** – **4a**, and new bis-alkynyl complexes **3b** and **4b**.



Conditions: (i) ~3 equiv of LiC_2Ar, THF, RT, 2h, (ii) 1 equiv 0.12 M $HCl_{(MeOH)}$

Scheme 1. General synthesis of Cr^{III}(HMC) mono-alkynyl complexes through acid degradation of Cr^{III}(HMC) bis-alkynyl complexes.

Experimental

General methods

Phenylacetylene was purchased from Oakwood Chemical and used without further purification. HMC,[31] *trans*-[Cr(HMC)Cl_2]Cl/OTf,[32] *trans*-[Cr(HMC)$(C_2Ph)_2$]Cl/OTf,[23] *trans*-[Cr(HMC)$(C_2Np)_2$]Cl/OTf,[22] TMS-C_2Np,[33] TMS-$C_2C_6H_4{}^tBu$,[34] and TMS-C_2(3,5-$Cl_2C_6H_3$)[35] were prepared according to literature procedures. Tetrahydrofuran was freshly distilled over Na/benzophenone. The preparation of bis-alkynyl complexes **1b** and **2b** was performed under a dry N_2 atmosphere using standard Schlenk procedures,[21, 23] and new complexes **3b** and **4b** were synthesized similarly. Preparation of mono-alkynyl complexes **1a** – **4a** was carried out under ambient conditions. Unless specified, the counter anion is always triflate ($^{-}$OTf; $CF_3SO_3^-$) in this study.

Physical methods

Elemental analysis was performed by Atlantic Microlab, Inc in Norcross, GA. UV-vis spectra were obtained with a JASCO V-670 spectrophotometer in CH_2Cl_2 solutions. Emission data were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. FT-IR spectra were measured as neat samples with a JASCO FT/IR-6300 spectrometer equipped with an ATR accessory. ESI-MS were analyzed on an Advion Mass Spectrometer. Magnetic susceptibility was calculated via the Evans method[36] using ^{1}H NMR spectra that were recorded on a Varian Inova 300 spectrometer operating at 300 MHz. Single crystal X-ray diffraction data were collected on Nonius Kappa CCD and Bruker Quest instruments as detailed in the SI.

Synthesis

***trans*-[Cr(HMC)(C_2Ph)Cl]OTf (1a).** The reaction between 0.070 g (0.11 mmol) of *trans*-[Cr(HMC)(C_2Ph)$_2$]OTf and 1 equivalent of 0.12 M HCl in CH_3OH yielded a yellow solution, which was stirred for 20 minutes under ambient conditions. Solvent was removed by rotary evaporation, and a yellow solid (0.059 g, 93% based on Cr) was obtained after purification through a silica plug with **1a** eluded in 9:1 CH_2Cl_2:CH_3OH. An analogous procedure was used to obtain [**1a**]Cl from *trans*-[Cr(HMC)(C_2Ph)$_2$]Cl, from which a crystal was grown by slow diffusion of Et_2O into CH_3OH. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)(C_2Ph)Cl]OTf·3H_2O: C, 44.8 (44.5); H, 6.6 (6.7); N, 8.5 (8.3). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 365 (450), 375 (520), 388 (500), 402 (520), 417sh, 433 (260), 472 (90). FT-IR ν(C≡C) / cm^{-1}: 2088*w*. ESI-MS [M^+]: 472 *m/z* for the cationic species [**1a**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.85.

trans-[Cr(HMC)(C_2Np)Cl]OTf (**2a**). The reaction between *trans*-[Cr(HMC)(C_2Np)$_2$]OTf (0.050 g, 0.063 mmol) and 1 equivalent of 0.12 M HCl in 10 mL CH_3OH yielded an orange solution, which was stirred for 20 minutes under ambient conditions. Solvent was removed by rotary evaporation and an orange solid (0.039 g, 92% based on Cr) was obtained after purification through a silica gel plug, eluded with 9:1 CH_2Cl_2:CH_3OH. Single crystals suitable for X-ray diffraction were grown from vapor diffusion of Et_2O into CH_3CN. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)(C_2Np)Cl]OTf·0.5CH_3CN·0.5H_2O: C, 51.5 (51.4); H, 6.6 (6.4); N, 8.9 (9.0). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 442 (78), 467 (87), 498 (63), 528 (28), 542 (31). FT-IR $\nu(C\equiv C)$ / cm^{-1}: 2080*w*. ESI-MS [M^+]: 522 *m/z* for the cationic species [**2a**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.86.

trans-[Cr(HMC)($C_2C_6H_4{}^tBu$)Cl]OTf (**3a**). The reaction between 0.050 g (0.074 mmol) of *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)$_2$]OTf and 1 equivalent of 0.12 M HCl in CH_3OH yielded a yellow solution, which was stirred for 20 minutes under ambient conditions. Solvent was removed by rotary evaporation and a yellow solid (0.037 g, 88% based on Cr) was obtained after purification through a silica plug, with **3a** eluded with 9:1 CH_2Cl_2:CH_3OH. Single crystals suitable for X-ray diffraction were grown from slow diffusion of Et_2O into CH_3OH. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)Cl]OTf: C, 51.1 (51.4); H, 7.4 (7.3); N, 8.1 (8.3). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 379 (560), 393 (550), 407 (570), 423 (360), 438 (300). FT-IR $\nu(C\equiv C)$ / cm^{-1}: 2083*w*. ESI-MS [M^+]: 528 *m/z* for the cationic species [**3a**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.86.

trans-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))Cl]OTf (**4a**). The reaction between 0.080 g (0.12 mmol) of *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))$_2$]OTf and 1 equivalent of 0.12 M HCl in CH_3OH yielded a golden yellow solution, which was stirred for 20 minutes under ambient conditions. Solvent was removed by rotary evaporation and a golden yellow solid (0.057 g, 85% based on Cr) was obtained after purification through a silica gel plug, with **4a** eluding in 9:1 CH_2Cl_2:CH_3OH. Single crystals suitable for X-ray diffraction were grown from slow diffusion of Et_2O into CH_3CN. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))Cl]OTf·1CH_3OH·0.5H_2O: C, 42.85 (42.7); H, 5.9 (6.1); N, 7.8 (7.6). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 380 (290), 391 (290), 408 (300), 422sh, 439 (190). FT-IR ν(C≡C) / cm^{-1}: 2085*w*. ESI-MS [M^+]: 543 *m/z* for the cationic species [**4a**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.86.

trans-[Cr(HMC)($C_2C_6H_4{}^tBu$)$_2$]OTf (**3b**). A suspension of *trans*-[Cr(HMC)Cl_2]OTf (0.100 g, 0.180 mmol) in 15 mL THF was combined with 3 equivalents of $LiC_2C_6H_4{}^tBu$ (prepared from 0.543 mmol TMS-$C_2C_6H_4{}^tBu$ in THF and 0.75 mmol *n*-BuLi), and the reaction mixture was stirred for 2 hours at room temperature. After quenching the reaction in air, solvent was removed via rotary evaporation. A silica gel plug was used for purification and **3b** was eluded with 9:1 CH_2Cl_2:CH_3OH to yield (0.083 g, 58% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from slow diffusion of hexanes into CH_2Cl_2. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)$_2$]OTf·1.5H_2O·0.5CH_3CN: C, 57.3 (57.1); H, 7.6 (7.6); N, 7.2 (7.1). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 366 (1030), 377 (1070), 391 (1030), 404 (1080), 418 (700), 435 (620). FT-IR ν(C≡C) / cm^{-1}: 2082*w*. ESI-MS [M^+]: 650 *m/z* for the cationic species [**3b**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.89.

***trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))$_2$]OTf** (**4b**). A suspension of *trans*-[Cr(HMC)Cl_2]OTf (0.35 g, 0.63 mmol) and HC_2(3,5-$Cl_2C_6H_3$) (0.32 g, 1.9 mmol) in 25 mL THF was combined with 3.8 mL of 0.5 M LDA (1.9 mmol, prepared from the reaction of 0.6 mL diisopropylamine with 1.6 mL *n*-BuLi in 5.8 mL THF at 77 K), and the reaction mixture was stirred for 2 hours at room temperature. After quenching the reaction in air, solvent was removed via rotary evaporation. A silica gel plug was used for purification and **4b** was eluded with 9:1 CH_2Cl_2:CH_3OH (0.213 g, 41% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from slow diffusion of Et_2O into CH_3CN. Elem. Anal. Found (Calcd) for *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))$_2$]OTf: C, 48.0 (48.0); H, 5.1 (5.1); N, 6.8 (6.8). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 374 (540), 391 (450), 406 (490), 419sh, 438 (310). FT-IR ν(C≡C) / cm^{-1}: 2079*w*. ESI-MS [M^+]: 679 *m/z* for the cationic species [**4b**]$^+$. Magnetic susceptibility, μ_{eff} / μ_B: 3.76.

Results and discussion

Synthesis

As shown in Scheme 1, the reaction between *trans*-[Cr(*meso*-HMC)Cl_2]OTf and three equivalents of the appropriate lithium arylalkynyl produced the bis-alkynyl complexes *trans*-[Cr(HMC)(C_2Ph)$_2$]OTf (**1b**),[23] *trans*-[Cr(HMC)(C_2Np)$_2$]OTf (**2b**),[22] *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)$_2$]OTf (**3b**), and *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))$_2$]OTf (**4b**). The bis-alkynyl complexes were filtered through celite and further purified over silica, with yields between 41-73% depending on the nature of arylalkynyl ligand. Mono-alkynyl complexes *trans*-[Cr(HMC)(C_2Ph)Cl]OTf (**1a**), *trans*-[Cr(HMC)(C_2Np)Cl]OTf (**2a**), *trans*-[Cr(HMC)($C_2C_6H_4{}^tBu$)Cl]OTf (**3a**), and *trans*-[Cr(HMC)(C_2(3,5-$Cl_2C_6H_3$))Cl]OTf (**4a**) were then synthesized by the reaction of the appropriate *trans*-[Cr(HMC)(C_2Ar)$_2$]OTf with a stoichiometric amount of HCl in CH_3OH. Purification over silica resulted in yields of *trans*-$[Cr(HMC)(C_2Ar)Cl]OTf$ ranging between 85-93%. A one-step synthesis of *trans*-$[Cr(HMC)(C_2Ph)Cl]Cl$ was attempted by combining a substoichiometric amount of LiC_2Ph with *trans*-$[Cr(HMC)Cl_2]Cl$, however, the yield of *trans*-$[Cr(HMC)(C_2Ph)Cl]Cl$ was < 12% based on Cr (see the Electronic Supplementary Information). The improved two-step synthesis of **1a** resulted in an overall percent yield of 48% (based on Cr in *trans*-$[Cr(HMC)Cl_2]OTf$), while other arylalkynyl ligands saw overall yields of up to 67%.

Previous studies on the alkynylation of the *cis*/*trans* isomers of $[Cr(HMC)Cl_2]^+$ have revealed the $[Cr(HMC)(C_2R)_2]^+$ products retain their *cis/trans* stereochemistry ($R = Ph$, C_2SiMe_3, and Np).[22, 23] This is in contrast to the alkynylation of Cr(cyclam) and Cr(DMC) complexes, which produced a mixture of *cis/trans* products when *cis*-$[Cr(cyclam/DMC)Cl_2]^+$ starting material was employed.[15, 21] We attempted to synthesize both *cis*- and *trans*-$[Cr(HMC)(C_2Ar)Cl]^+$ complexes, however, the *cis*- complexes were much less stable and often fully degraded to *cis*-$[Cr(HMC)Cl_2]Cl$ in acidified solution. At present, our focus is on the more robust *trans*-$[Cr(HMC)(C_2Ar)Cl]OTf$ complexes.

Like the corresponding bis-alkynyl complexes, mono-alkynyl species **1a** – **4a** are paramagnetic with room temperature effective magnetic moments (Evans method) corresponding to $S = 3/2$. While well resolved ^1H NMR spectra for complexes **1a** – **4a** are unattainable, their compositions were analyzed with ESI MS and elemental analysis.

Molecular structures

Mono-alkynyl complexes **1a** – **4a** have been characterized with single crystal X-ray diffraction. The cations were crystallized as the chloride (**1a**) or triflate (**2a**, **3a**, and **4a**) salts, and the molecular structures are shown in Figures 1 – 4. Selected bond lengths and bond angles are provided in Table 1. Molecular structures for **3b** and **4b** are presented in Figures S2 and S3 along with select bond lengths and angles in Table S2. All complexes have pseudo-octahedral geometry and retain *trans* stereochemistry.

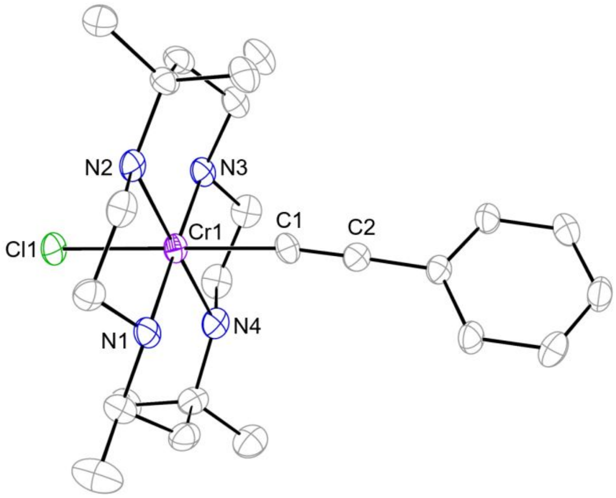


Figure 1. ORTEP plot of [**1a**]$^+$ at 30% probability level. H atoms and the Cl$^-$ counterion were omitted for clarity.

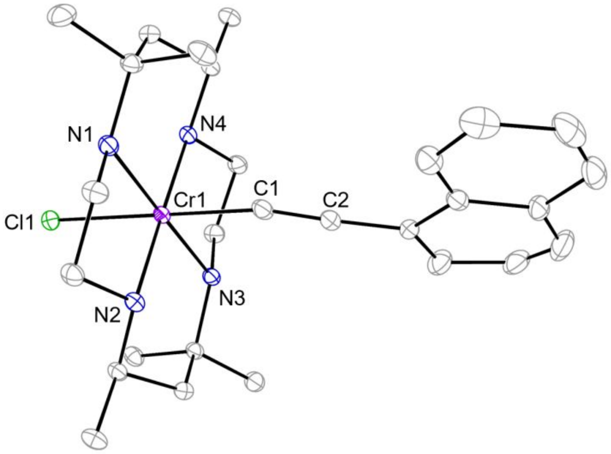


Figure 2. ORTEP plot of [**2a**]$^+$ at 30% probability level. H atoms, $^-$OTf counterion, and disorder were omitted for clarity.

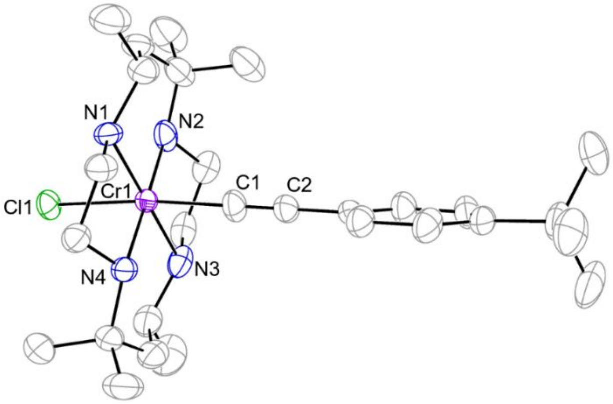


Figure 3. ORTEP plot of [**3a**]$^+$ at 30% probability level. H atoms, $^-$OTf counterion, and disorder were omitted for clarity.

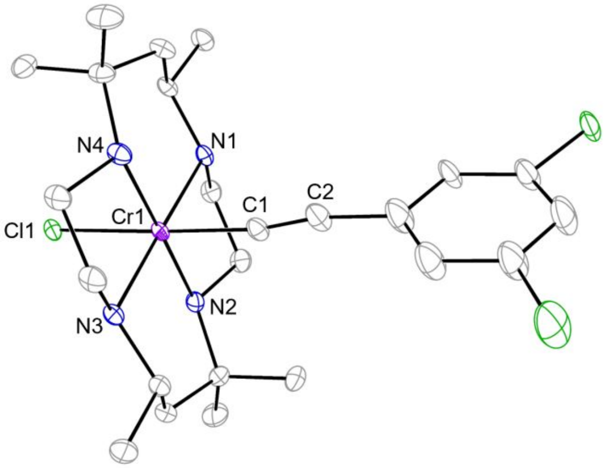


Figure 4. ORTEP plot of [**4a**]$^+$ at 30% probability level. H atoms, $^-$OTf counterion, and disorder were omitted for clarity.

The Cr–C bond length of 2.049(4) Å in [**1a**]Cl is comparable to those observed for *trans*-[Cr(cyclam)(C_2Ph)$_2$]$^+$ (*avg*. 2.073 Å) and **1b** (*avg*. 2.085 Å), but slightly shortened by *ca.* 0.024/0.036 Å, respectively.[23, 37] The shorter Cr–C bond distance is not unexpected, as acetylides are stronger donors than chloro ligands, and in both *trans*-[Cr(cyclam)(C_2Ph)$_2$]$^+$ and *trans*-[Cr(HMC)(C_2Ph)$_2$]Cl there is a distinct *trans*-influence by the two alkynyl ligands.[23, 37] A similar trend is observed for **2a** with a Cr–C bond length of 2.035(2) Å, while the average of those for *trans*-[Cr(HMC)($C_2Np)_2$]Cl is 2.078 Å;[21] and for **4a** with a Cr–C bond length of 2.028(2) Å (*ca.* 0.047 Å shorter than those of **4b**). A more significant contrast in the Cr–C bond length is observed between **3a** and **3b** (*ca.* 0.091 Å). This is attributed to the fact that *tert*-butylphenylacetylide is the strongest σ-donor in the series and forms the strongest Cr–C bond in its mono-alkynyl complex but exhibits the highest *trans*-influence in the bis-alkynyl complex.

The C≡C bond lengths of **1a**, **3a**, **4a** are comparable to one another, as well as to the corresponding bis-alkynyl complexes **1b**, **3b**, and **4b**. The C≡C bond length of **2a** is 1.251(3) Å, which is notably longer than the observed range (1.150 – 1.225 Å, esd ≤ 0.010 Å) for C≡C bonds in complexes containing MC≡CR (R = C, Si) bonds.[38] The ethynylnapthalene ligand in the crystal structure of **2a** is disordered (Figure S1) and was refined to have an occupancy ratio of 0.576(3) to 0.424(3). The disordered moiety has a C≡C bond length of 1.221(4) Å, which falls within the well-established range of metal-alkynyl bonds. The disordered moiety also possesses a Cr1–C1–C2 bond angle that is in better agreement with **1a**, **3a**, and **4a**, at 167.7(2)° compared to 159.0(2)° reported for **2a**.

Table 1. Selected bond lengths (Å) and bond angles (°) for **1a** – **4a**.

	[**1a**]Cl	**2a**	**3a**	**4a**
Cr1-N1	2.074(4)	2.077(1)	2.092(8)	2.077(2)
Cr1-N2	2.090(4)	2.096(1)	2.092(8)	2.092(2)
Cr1-N3	2.080(4)	2.074(1)	2.064(9)	2.075(2)
Cr1-N4	2.113(4)	2.088(1)	2.086(9)	2.107(2)
Cr1-C1	2.049(4)	2.035(2)	2.014(7)	2.028(2)
Cr1-Cl1	2.3678(13)	2.3704(4)	2.372(6)	2.3615(5)
C1-C2	1.205(7)	1.251(3)	1.192(4)	1.210(3)
C1-Cr1-Cl1	176.93(14)	179.81(5)	173.9(3)	178.11(7)
Cr1-C1-C2	168.1(5)	159.0(2)	174.2(4)	170.9(2)
N1-Cr1-N3	178.70(15)	171.19(5)	179.6(4)	179.11(7)
N2-Cr1-N4	179.55(16)	179.23(4)	178.3(4)	178.99(6)
N1-Cr1-N2	85.27(17)	85.15(6)	93.8(3)	84.38(4)
N1-Cr1-N4	94.85(18)	95.49(6)	84.6(4)	95.12(4)
N2-Cr1-N3	94.92(17)	94.50(7)	86.5(4)	95.28(4)
N3-Cr1-N4	84.95(18)	84.87(7)	95.2(4)	85.22(4)

UV-vis spectroscopic analysis

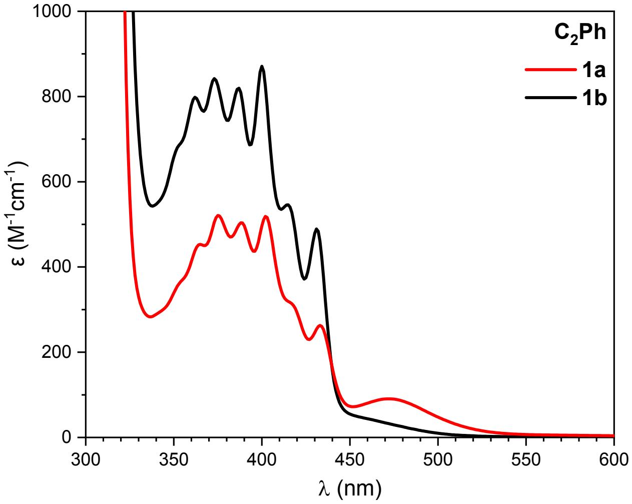


Figure 5. UV-vis absorption spectra of complexes **1a** and **1b** as CH_2Cl_2 solutions.

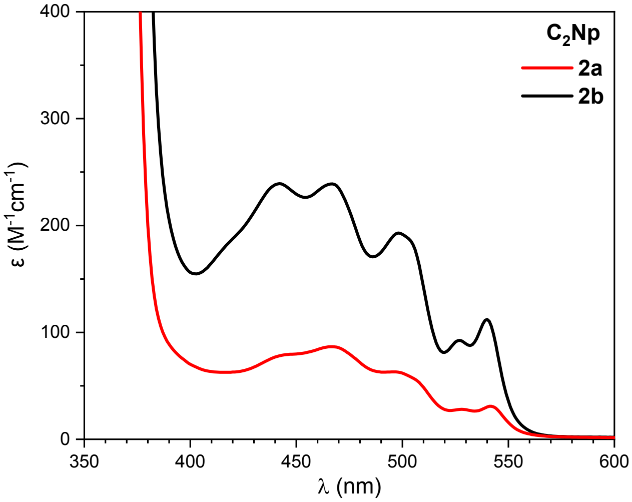


Figure 6. UV-vis absorption spectra of complexes **2a** and **2b** as CH_2Cl_2 solutions.

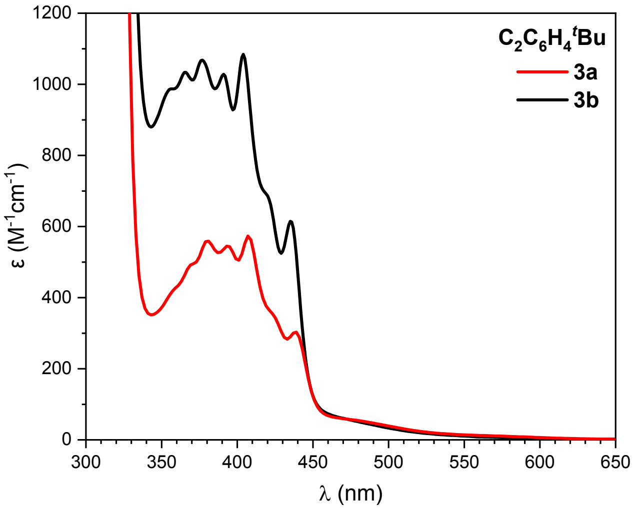


Figure 7. UV-vis absorption spectra of complexes **3a** and **3b** as CH_2Cl_2 solutions.

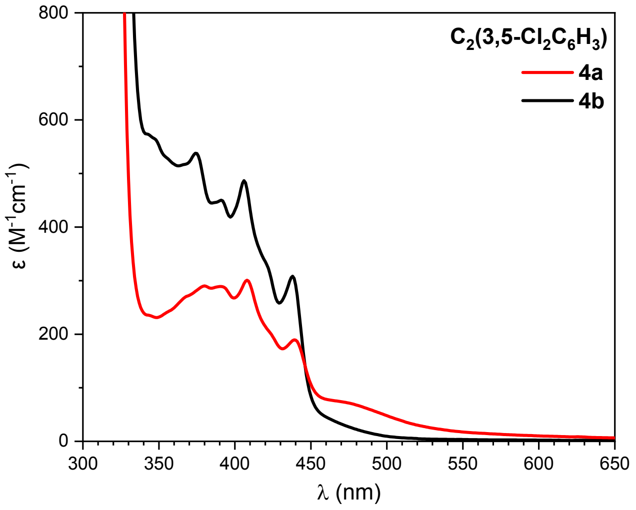


Figure 8. UV-vis absorption spectra of complexes **4a** and **4b** as CH_2Cl_2 solutions.

The UV-vis absorption spectra of mono-alkynyl complexes **1a** – **4a** compared to their bis-alkynyl counterparts, **1b** – **4b**, are shown in Figures 5 – 8. The absorption is assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}/{}^4T_{2g}$ (O_h) transition. Similar to the Cr bis-alkynyl complexes, all mono-alkynyl complexes display structured *d-d* bands between 300 and 450 nm for **1a**, **3a**, and **4a**, and between 400 – 550 nm for complex **2a**. The bathochromic shift of the metal-based absorption of **2a** is a result of increased ligand aromaticity and has been previously observed.[15, 22] The *d-d* bands of mono-alkynyl complexes are slightly red shifted from their bis-alkynyl analogues (< 5 nm) due to the chloro substituent being a weaker field ligand than the arylalkynyl ligand. The intensities of these *d-d* bands are rather high in comparison to those seen for halide complexes *trans*-$[Cr(HMC)X_2]^+$, which reinforces the previous presumption of a partial charge–transfer character due to strong $d\pi$–π(C≡C) mixing.[23] As shown in Figures 5 – 8, the molar extinction coefficients of the *d-d* bands in **1a** – **4a** are approximately half of those for their corresponding *trans*-$[Cr(HMC)(C_2Ar)_2]$OTf complexes, corroborating the presumption of significant contributions from $d\pi$–π(C≡C) mixing.

Similar to the bis-alkynyl complexes, the mono-alkynyl complexes also exhibit intense absorptions below 330 nm (not shown) that are associated with charge transfer and intraligand π-π^* transitions. Also like the bis-alkynyl complexes, replacement of one of the halide ligands leads to a stronger ligand field, thus the $^4T_{1g}$ term seen for halide $[Cr(HMC)X_2]^+$ complexes is likely beyond the UV-vis window or hidden beneath the charge transfer bands.[23]

The highly-structured nature of the *d–d* bands is still the most prominent feature of the spectra, and ideally, the origin of the vibronic progressions may be determined from the FT-IR of the complexes. The vibronic progressions have been calculated for **1a** – **4a** (see Figure S7 and Table S4). For **1a**, **3a**, and **4a**, the progressions average between 860 – 980 cm^{-1}, similar to the *trans*-$[Cr(HMC)(C_2Ar)_2]$Cl complexes. It is difficult to determine the vibrational mode(s) responsible for the vibronic progressions due to the possible occurrence of aromatic C-H bending, N-H bending and methylene vibrations within the same region.[23] The irregularly spaced progressions for **2a** average a spacing of around 1043 cm^{-1}, which aligns more closely with aromatic C=C stretching modes or phenyl ring deformations in the Np ligand, as previously suggested for **2b**.[22]

Emission studies

Complexes **1a** – **4a** exhibit Cr^{III} emission centered around 725 nm, as shown in Figures 9 – 12. Phosphorescence in octahedral Cr^{III} complexes occurs as a result of intersystem crossing from the ${}^4T_{1g}$ or ${}^4T_{2g}$ excited states to two possible lower-lying doublet states, ${}^2T_{1g}$ and ${}^2E_g$.[39] The emission of complexes **1a** – **4a** is attributed to a ${}^2T_{1g} \rightarrow {}^4A_{2g}$ transition, which is consistent with the previous report of emissions by bis-alkynyl complexes **1b** and **2b**. This assignment is partially based on the red shift from where ${}^2E_g$ emission is usually observed.[40] The phosphorescence spectra of complexes **1a** – **4a** exhibit fine-structuring at 77 K, which is believed to be vibronic in origin.[41] Stronger vibronic coupling between the alkynyl ligand and the Cr metal center results in more defined structuring of complexes **1a** – **4a** in comparison to complexes **1b** – **4b**. This interpretation is supported by the shorter Cr–C bond lengths observed in the mono-alkynyl species. For complexes **1a** – **4a**, a blue shift of approximately 20 nm is observed compared to **1b** – **4b** (Table 2). This can be attributed to the nephelauxetic effect as the electron cloud is more localized between the Cr metal center and the alkynyl ligand in complexes **1a** – **4a**, resulting in higher energy emission. While the new mono-alkynyl complexes **1a** – **4a** display a single ${}^2T_{1g} \rightarrow {}^4\mathrm{A}_{2g}$ emission, a weaker secondary emission of ${}^2E_g \rightarrow {}^4A_{2g}$ origin was previously noted for bis-alkynyl complex **2b** at 77 K.[22] A secondary emission is also identified for the new bis-alkynyl complex **3b** at 726 nm.

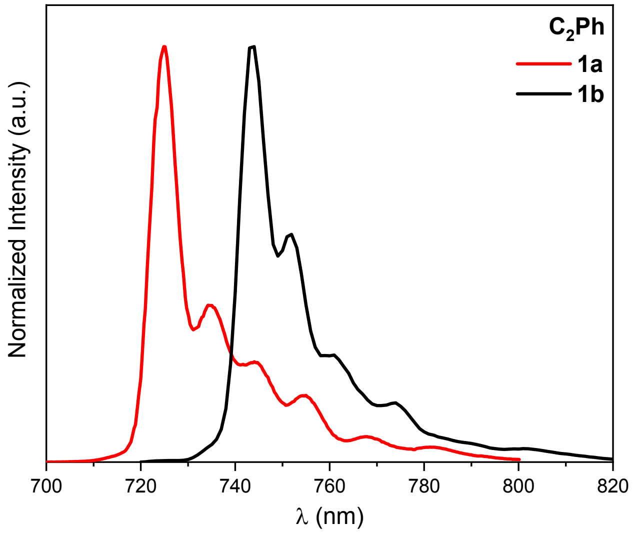


Figure 9. Normalized emission spectra of complexes **1a** and **1b** in a 4:1 CH_3CH_2OH/CH_3OH glass measured at 77 K.

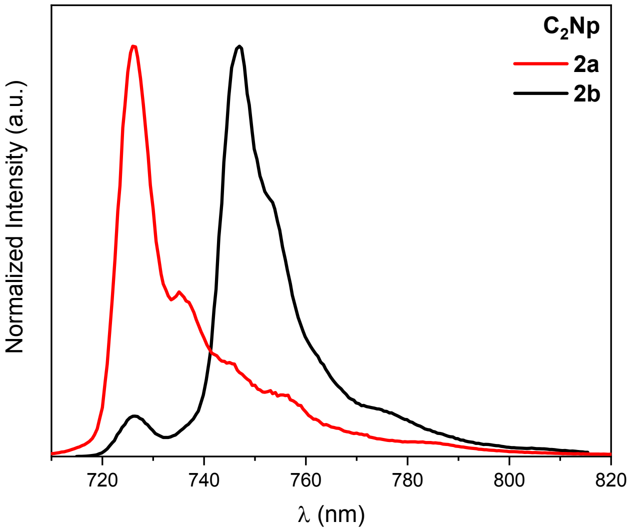


Figure 10. Normalized emission spectra of complexes **2a** and **2b** in a 4:1 CH_3CH_2OH/CH_3OH glass measured at 77 K.

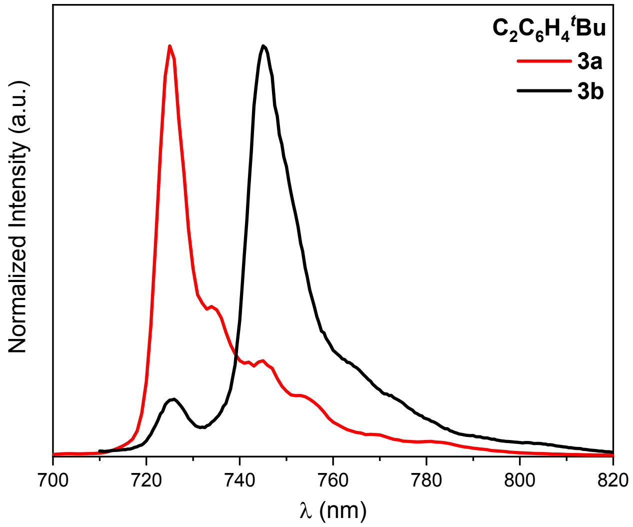


Figure 11. Normalized emission spectra of complexes **3a** and **3b** in a 4:1 CH_3CH_2OH/CH_3OH glass measured at 77 K.

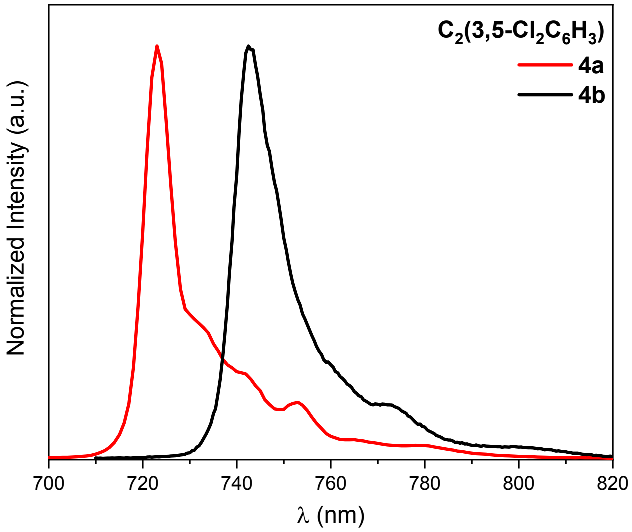


Figure 12. Normalized emission spectra of complexes **4a** and **4b** in a 4:1 CH_3CH_2OH/CH_3OH glass measured at 77 K.

Table 2. Photophysical data for mono-alkynyl complexes **1a** – **4a** and bis-alkynyl complexes **1b** – **4b**.

	Frozen Glass[a]			***Room Temperature***[b]		
	λ_{ex} (nm)	**λ_{em} (nm)**	**τ (μs)**	**λ_{ex} (nm)**	**λ_{em} (nm)**	**τ (μs)**
1a	400	725	397	400	725	123
2a	466	735	367	466	728	78
3a	406	725	383	406	728	87
4a	408	723	343	408	725	22
1b	425	744	469	425	746	164
2b	445	747	447	445	747	218
		727 [c]	362			
3b	403	745	479	403	748	117
		726 [c]	345			
4b	406	743	354	406	747	51

[a] Measured at 77 K in a 4:1 CH_3CH_2OH/CH_3OH glass

[b] Measured at room temperature in degassed CH_3CN

[c] $^2E_g \rightarrow {}^4A_{2g}$ emission

Relevant parameters for the emissions of **1a** – **4a** and **1b** – **4b** are compiled in Table 2. Complexes **1a** – **4a** have fairly long lifetimes, ranging between 343 μs to 397 μs. The lifetimes of **1b**, **2b**, and **3b** are between 70 – 89 μs longer than those of **1a**, **2a**, and **3a**, respectively. In the case of **4b**, the lifetime is only 11 μs longer than that of **4a**, which can likely be attributed to the presence of two heavy chloride atoms leading to increased non-radiative decay. All four *trans* mono-alkynyl complexes have longer lifetimes than *cis*-[Cr(HMC)(C_2Ph)$_2$]Cl and *cis*-[Cr(HMC)(C_2Np)$_2$]Cl, which is unsurprising when considering that the distortions in the CN_2R_2 plane of *cis*- complexes often result in larger non-radiative decay rates, and thus shorter lifetimes.[42]

Conclusion

Cr^{III} mono-alkynyl complexes supported by the HMC macrocycle have been realized with the synthesis of complexes **1a** – **4a**, thus expanding the repertoire of Cr^{III} alkynyl chemistry. All complexes display structured *d-d* bands like the bis-alkynyl complexes, with approximately halved molar absorptivity values. As with the bis-alkynyl complexes, complexes **1a** – **4a** exhibit long-lived phosphorescence at 77 K. The emission spectra of **1a** – **4a** are more structured than their bis-alkynyl counterparts as a result of stronger vibronic coupling between the Cr^{III} metal center and the alkynyl ligand, which is supported by the mono-alkynyl complexes displaying shorter Cr–C bond lengths than their bis-alkynyl counterparts. With these mono-alkynyl complexes of Cr(HMC) being realized, synthetic efforts can be made toward dissymmetric bis-alkynyl complexes based on Cr(HMC).

Conflicts of interest

The authors have no conflicts of interest to declare.

Acknowledgements

We thank the National Science Foundation (CHE 1764347) for generously supporting this work.

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