Chromium(III) Bis-alkynyl complexes supported by *C*-substituted cyclam MPC

Ashley J. Schuman, Madeline M. Mills, Leobardo Rodriguez Segura, Lyndsy A. Miller-Clark, Tong Ren*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

ARTICLE INFO

ABSTRACT

Macrocyclic Cr^{III} bis-alkynyl complexes have recently been used as a precursor in the synthesis of mono-alkynyl complexes, which can serve as synthetic intermediates towards the formation of dissymmetric bis-alkynyl complexes. The *trans* stereochemistry is essential to generate stable macrocyclic Cr^{III} mono-alkynyl complexes, however, previously explored cyclam (1,4,8,11-tetraazacyclotetradecane) and its derivatives heavily favor the *cis* isomer after Cr insertion. The *C*-substituted cyclam MPC (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane) has shown a noteworthy preference towards the *trans* isomer upon insertion of Cr, making it desirable for the pursuit of dissymmetric bis-alkynyl complexes in significant quantity. Reported herein are the synthesis and characterization of *trans*-$[Cr(MPC)(C_2Ar)_2]^+$ complexes, where Ar is Ph (**1**), Np (**2**), or $C_6H_4{}^tBu$ (**3**). Complexes **1** – **3** have structural and optical properties similar to previous Cr^{III} bis-alkynyl complexes based on single-crystal X-ray diffraction, UV-vis and phosphorescence spectroscopical characterizations.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

Transition-metal alkynyl complexes have attracted interest for applications as molecular wires, molecular memory devices, and optoelectronic materials due to their π-delocalization, redox activity of the metal center, and ease of synthesis [1–4]. Based on donor-bridge-acceptor (D-B-A) complexes containing a *trans*-Pt^{II}-bis-alkynyl bridge, it has been demonstrated recently that the evolution of photo-induced electron transfer (PET) states, notably the formation of the charge-separated (CS) state, can be attenuated by vibrational excitation of the Pt bound C≡C bonds [5,6]. In an effort to expand D-B-A alkynyl chemistry to include more sustainable 3*d* metals, our group has investigated the PET properties of *trans*-$[Co(cyclam)(C_2NAP^{iPr})(C_2D)]^+$ complexes (cyclam = 1,4,8,11-tetraazacyclotetradecane; D = C_6H_4-4-NMe_2, Ph, or C_6H_4-4-N(4-MeOPh)$_2$) [7,8]. Femtosecond transient absorption and time-resolved IR spectroscopic studies revealed the formation of desirable CS states; however, they were quickly deactivated by the low-lying Co-centered triplet state. Thus, there is a need to further investigate other D-B-A dyads with macrocyclic 3*d* metal bridges that could potentially sustain long-lived CS and metal-to-ligand charge transfer states.

Macrocyclic chromium alkynyl chemistry emerged with Taube and co-workers' $[Cr^{III}(phthalocyanine)(C_2Ph)_2]^-$ complex [9] in the late 70's and has gained traction over the past few decades. Several $Cr^{III}(Me_3TACN)(C_2R)_3$ complexes ($Me_3TACN = N,N',N''$-trimethyl-1-4-7-triazacyclononane; R = C_2SiMe_3, C_2H, C_4SiMe_3, C_4H) and Cr^{III}(cyclam) bis-alkynyl complexes *trans*-$[Cr(cyclam)(C_2R)_2]^+$ (R = C_2SiMe_3, C_2H, 1,3-$C_2C_6H_4C_2H$) were reported by Berben and Long [10,11]. The groups of Wagenknecht [12–14], Nishijo [15–18], and Ren [19] have documented additional Cr^{III}(cyclam) bis-alkynyl complexes. To date, all examples of macrocyclic Cr^{III} alkynyl complexes feature symmetric alkynyl ligands, while D-B-A type complexes remain elusive. D-B-A complexes may be accessed in a stepwise manner, as shown in Scheme 1: a mono-alkynyl intermediate is generated, followed by subsequent addition of a different alkynyl ligand. There are limited literature examples of Cr mono-alkynyl complexes that can undergo further alkynylation. Berke and co-workers' Cr^{II} and Cr^{III} *trans*-$[Cr(dmpe)_2(C_2R)_2]^n$ complexes (R = C_2Ph, $SiMe_3$, $SiEt_3$, and C_2SiMe_3; n = 0, 1) [20] and our *trans*-$[Cr^{III}(HMC)(C_2Ar)Cl]^+$ complexes (HMC = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Ar = Ph, Np (naphthalene), $C_6H_4{}^tBu$, and 3,5-$Cl_2C_6H_3$) [21] are both viable candidates. Although the analogous *cis*-Cr(HMC) mono-alkynyl complexes can be prepared [22], they are less robust in solution than the *trans* isomer, demonstrating the need for isomeric control of the reactions in the pursuit of D-B-A complexes. The supporting macrocyclic ligand plays an essential role in determining the stere-

---

* Corresponding author.
 E-mail address: tren@purdue.edu (T. Ren).
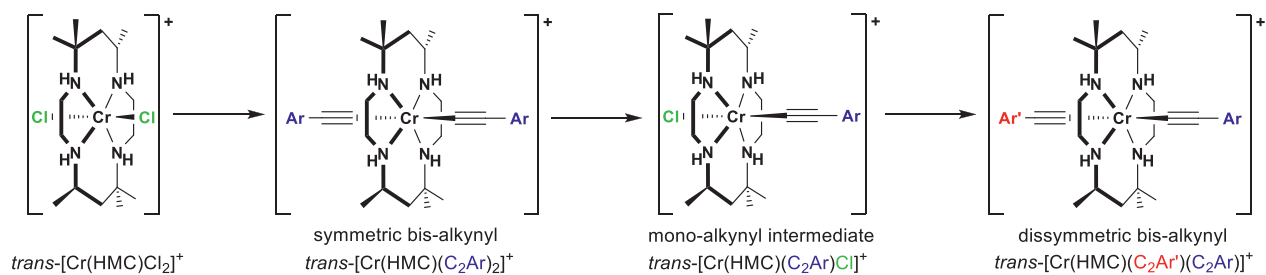
**Scheme 1.** Synthetic pathway for macrocyclic Cr^{III} alkynyl complexes

Ar = Ph (**1**), Np (**2**), C$_6$H$_4$^{t}Bu (**3**)
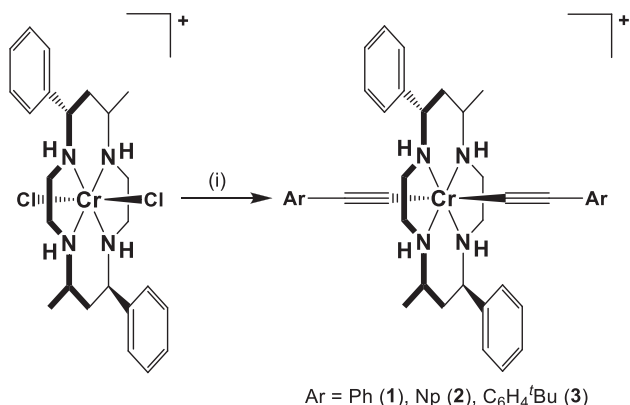
Scheme 2. Synthesis of trans-[Cr(MPC)(C$_2$Ar)$_2$]$^+$ complexes. Conditions: (i) 5 eq LiC$_2$Ar in THF, 2 h.

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

ochemistry of these complexes and further fine-tuning should be pursued.

The synthesis of C-substituted tetraazamacrocycles has been discussed in-depth in the work of Curtis [23–25], Lloyd [26,27], and Hay [28]. Our group has previously explored Cr^{III}(cyclam') alkynyl complexes, where cyclam' is the C-substituted cyclam derivative HMC or DMC (5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) [29–31]. In contrast to cyclam, HMC and DMC are inexpensive to synthesize and allow for the facile separation of cis/trans-[Cr(cyclam')Cl$_2$]Cl starting materials. HMC and DMC heavily favor the generation of cis-[Cr(cyclam')Cl$_2$]Cl upon Cr insertion, with DMC producing a 9:1 ratio of cis/trans isomers [32]. Although the trans stereochemistry of trans-[Cr(HMC)Cl$_2$]$^+$ is retained throughout the synthesis of trans-[Cr(HMC)(C$_2$Ar)$_2$]$^+$ and trans-[Cr(HMC)(C$_2$Ar)Cl]$^+$ [21,29], the low yield of trans starting material limits its potential to produce D-B-A complexes in practical quantities. It was reported that trans-[Cr(DMC)(C$_2$R)$_2$]$^+$ can be generated through arylalkynylation of cis-[Cr(DMC)Cl$_2$]$^+$, however, the product must be separated from cis-[Cr(DMC)(C$_2$R)$_2$]$^+$ which has similar solubility, and the ratio of trans- product synthesized depends on the C$_2$R ligand employed. Initial interest in the MPC (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane) ligand in our laboratory stems from the use of its Ni(II) complex as a electrocatalyst for CO$_2$ reduction [33]. Subsequently, alkynyl complexes based on Co^{III}(MPC) were investigated and the MPC ligand was noted for enabling an energy order of $d_{x2-y2} < d_{z2}$, which led to (quasi)reversible Co(III/II) reduction [34,35]. Ford and co-workers reported the synthesis of cis/trans-[Cr(MPC)Cl$_2$]Cl [36]. The aforementioned starting material has a significant preference for the trans isomer after Cr insertion (7:1), making Cr(MPC) a worthwhile ligand framework to pursue in the synthesis of D-B-A complexes. Herein, we report the alkynylation of trans-[Cr(MPC)Cl$_2$]$^+$ (Scheme 2) to generate the novel bis-alkynyl
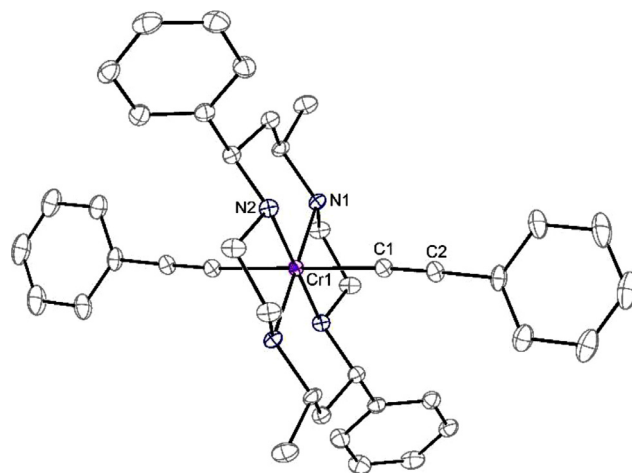
complexes trans-[Cr(MPC)(C$_2$Ar)$_2$]$^+$, where Ar = Ph (**1**), Np (**2**), and C$_6$H$_4$^{t}Bu (**3**).

2. Results and discussion

2.1. Synthesis

Complexes **1** – **3** were synthesized as depicted in Scheme 2. trans-[Cr(MPC)Cl$_2$]X (X = Cl$^-$ or PF$_6$$^-$) was dried in vacuo and reacted with 5 equivalents of the appropriate lithiated arylalkynyl ligand, LiC$_2$Ar, in THF. After 2 hours, the reaction was quenched in air and purified over a silica gel plug. In general, the desired product band was collected and a solid was obtained upon trituration with Et$_2$O. Recrystallization from minimal CH$_2$Cl$_2$ and Et$_2$O afforded yellow crystalline materials of trans-[Cr(MPC)(C$_2$Ph)$_2$]Cl (**1**) and trans-[Cr(MPC)(C$_2$C$_6$H$_4$^{t}Bu)$_2$]PF$_6$ (**3**), and orange crystalline materials of trans-[Cr(MPC)(C$_2$Np)$_2$]Cl (**2**), with yields ranging between 41-57%. The characteristic ν(C≡C) peak observed in the FTIR spectra indicated the successful incorporation of the alkynyl ligands. The identity and purity of complexes **1** – **3** were verified by ESI-MS and elemental analysis.

2.2. Molecular structures

Complexes **1** – **3** have been characterized with single crystal X-ray diffraction. The cations were crystallized as the chloride and hexafluorophosphate salts. Selected bond lengths and angles are provided in Table 1 and the molecular structures are shown in Figs. 1–3. All complexes have pseudo-octahedral geometry and the bis-alkynyl products retain the trans stereochemistry of the starting material. The MPC macrocycle adopts the C-meso configuration, while the macrocyclic N centers adopt a trans-III configuration

Table 1
Selected bond lengths (Å) and bond angles (°) for **1 – 3** and *trans*-[Cr(HMC)(C$_2$Ph)$_2$]Cl.

	1[a]	2	3[a]	*trans*-[Cr(HMC)(C$_2$Ph)$_2$]Cl
Cr1-N1	2.079(2)	2.088(2)	2.085(4)	2.086(1)
Cr1-N2	2.080(2)	2.080(2)	2.081(3)	2.078(1)
Cr1-N3				2.101(1)
Cr1-N4				2.074(1)
Cr1-C1	2.076(2)	2.069(2)	2.059(3)	2.078(2)
Cr1-C9				2.092(2)
C1-C2	1.214(3)	1.213(3)	1.202(5)	1.213(2)
C9-C10				1.209(2)
Cr1-C1-C2	173.9(2)	176.3(2)	177.4(3)	173.2(1)
Cr1-C9-C10				168.5(1)
N1-Cr1-N1'/N3	180.0	180.0	180.0	179.1(1)
N2-Cr1-N2'/N4	180.0	180.0	180.0	179.3(1)
N1-Cr1-N2	94.24(9)	85.59(7)	95.02(14)	95.6(1)
N1-Cr1-N2'/N4	85.76(9)	94.41(7)	84.98(14)	85.1(1)
N2-Cr1-N3				85.1(1)
N3-Cr1-N4				94.2(1)

[a] The unit cell revealed two (**1**) or four (**3**) crystallographically independent moities; geometric parameters for only one of them are listed here.
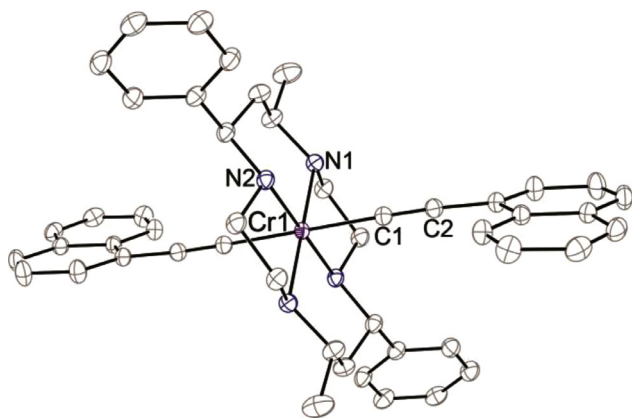
Fig. 2. ORTEP plot of [**2**]$^+$ at 30% probability level. H atoms and counterions (PF$_6^-$) were omitted for clarity.
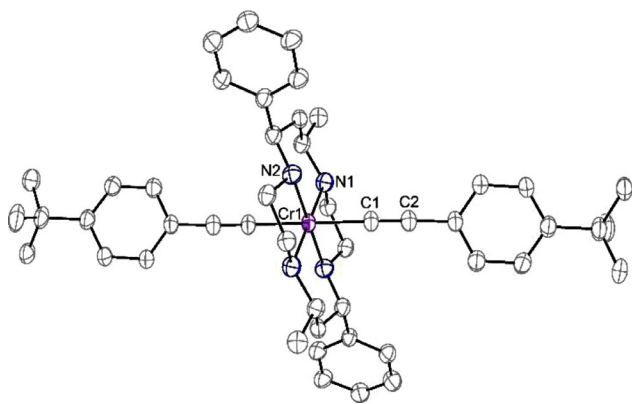
Fig. 3. ORTEP plot of [**3**]$^+$ at 30% probability level. H atoms, PF$_6^-$ counterion, and disorder were omitted for clarity.

(*R,R,S,S*), as depicted in Figs. S1 – S3. Complexes **1 – 3** all contain a crystallographic inversion center.

The initial crystal structure for **2** contained 50:50 counteranion disorder between Cl$^-$ and NO$_3^-$. Elemental analysis of **2** after initial recrystallization did not indicate a significant nitrate impurity. After adapting an alternative synthesis and crystallization, the structure of was determined as the salt of hexafluorophosphate, which is reported in the text. Because the counteranion has minimal to no observed effect on the resulting optical properties, we

proceeded with characterization. To minimize the chance of future counteranion impurities, a PF$_6^-$ counteranion exchange was performed on the *trans*-[Cr(MPC)Cl$_2$]Cl starting material before the synthesis of complex **3**.

The Cr–C bond length of 2.079(2) Å in **1** is comparable to those observed for *trans*-[Cr(cyclam)(C$_2$Ph)$_2$]$^+$ (*avg.* 2.073 Å) [12], *trans*-[Cr(HMC)(C$_2$Ph)$_2$]Cl (*avg.* 2.085 Å) [29], and *trans*-[Cr(DMC)(C$_2$Ph)$_2$]$^+$ (2.089(2) Å) [30]. This trend is expected, as there is a distinct *trans*-influence experienced by the two alkynyl ligands [12,29]. A similar trend is observed for **2** with a Cr–C bond length of 2.069(2) Å, while the average of those for *trans*-[Cr(HMC)(C$_2$Np)$_2$]Cl is 2.078 Å [31]. The Cr–C bond length of 2.059(3) Å in **3** is significantly shorter than *trans*-[Cr(HMC)(C$_2$C$_6$H$_4$^{t}Bu)$_2$]OTf (*avg.* 2.104 Å) [21], and slightly shorter than complexes **1** and **2**, despite the arylalkynyl ligand bearing an electron donating group. This is likely attributed to variation in the positions of the para-*tert*-butylphenylacetylide ligands. In **3**, the Cr1-C1-C2 bond angle is close to linearity at 177.4(3)°, while the HMC analogue has more distorted Cr-C-C angles of 172.4(5)° and 170.6(4)° [21]. Complex **3** is also more linear than **1** and **2**, with respective Cr-C-C bond angles of 173.9(2)° and 174.1(3)°.

For complexes **1 – 3**, the C≡C bonds fall within the observed range (1.150 – 1.225 Å, esd ≤ 0.010 Å) for complexes containing MC≡CR (R = C, Si) bonds [37]. The C≡C bond lengths of **1 – 3** are comparable to one another, as well as to the corresponding bis-alkynyl complexes with cyclam, DMC, and HMC macrocycles [12,21,29-31].

2.3. UV-vis spectroscopic analysis

The UV-vis absorption spectra of **1 – 3** are shown in Fig. 4. Structured *d-d* bands are observed between 350 – 450 nm for **1** and **3**, and between 400 – 560 nm for **2**. A bathochromic shift of **2** is observed due to increased aromaticity of the ethynylnapthalene ligand, which was previously noted for the analogous cyclam and HMC complexes [13,31]. The absorption has been assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}/{}^4T_{2g}$ (O_h) transition. The extinction coefficients for the *d-d* bands of complexes **1 – 3** are high in comparison to *trans*-[Cr(MPC)Cl$_2$]Cl [36], supporting the presumption of partial charge-transfer character due to dπ-π(C≡C) mixing [29]. Among the three complexes, the *t*-Bu group in **3** renders the phenylethynyl a stronger π donor than the plain phenylethynyl in **1**, and hence more intense *d-d* bands. On the other hand, the extensive π-delocalization in naphthalene makes the ethynyl in **2** less π donating than that in **1**, and thus weaker *d-d* bands.
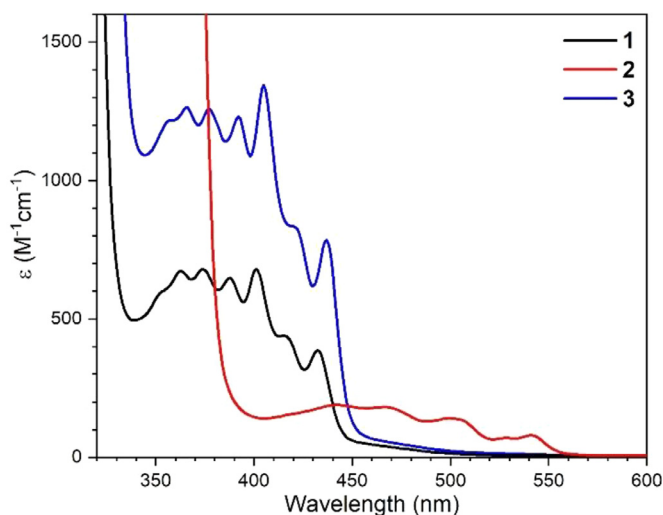
Fig. 4. UV-vis absorption spectra of **1** – **3** as CH_2Cl_2 solutions.

We note that similarly low extinction coefficients (between 100-200 M^{-1} cm^{-1}) were reported for *trans*-[Cr(cyclam)(C_2Np)_2]OTf [13] and *trans*-[Cr(HMC)(C_2Np)_2]Cl [31]. Intense absorptions below 330 nm (not shown) are associated with intraligand π-π^* and charge transfer transitions (see Figure S4.3 in SI). Hence, the *difference* in the extinction coefficients among compounds **1** – **3**, merely hundreds, is dwarfed by the intense π-π^* bands in the full spectra. The $^4T_{1g}$ term typically observed in *trans*-[Cr(cyclam')Cl_2]^+ complexes is likely hidden beneath the charge transfer bands or beyond the UV-vis window [29] because the replacement of a halide with an alkynyl ligand leads to a stronger ligand field.

The origin of the highly-structured *d-d* bands may be determined from the vibronic spacing of the absorption spectra. The calculated vibronic progressions of complexes **1** – **3** are found in Table S2. The average spacing of **1** and **3** are 872 and 841 cm^{-1}, respectively, which are consistent with aromatic out-of-plane C–H bending [14]. The irregularly spaced vibronic progressions of **2** have an average spacing of 1090 cm^{-1}, which closely aligns with phenyl ring deformations of the Np ligand or aromatic C=C stretching modes [31].

2.4. Emission studies

The emissive nature of Cr^III complexes is well established [38]. For the pseudo-octahedral Cr^III complexes **1** – **3**, phosphorescence can occur 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]. Emission spectra of **1** – **3** are displayed in Fig. 5 and relevant parameters are compiled in Table 2. The spectra exhibit fine structuring at 77 K with emission centered around 750 nm, which is red-shifted from the 650-710 nm range observed for traditional $^2E_g \rightarrow {}^4A_{2g}$ emitters [40]. The room temperature emission spectra are broad and structureless, which is indicative of $^2T_{1g}$ (O_h) emission. Based on these findings, the observed emission has been assigned as $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h). A secondary transition is observed in the spectra of **2** and **3** at 77 K, which has been previously observed for *trans*-[Cr(HMC)(C_2Np)_2]^+ and *trans*-[Cr(HMC)(C_2C_6H_4^tBu)_2]^+ and has been assigned to a $^2E_g \rightarrow {}^4A_{2g}$ (O_h) transition. The room temperature spectra do not exhibit ^2E_g (O_h) emission. Although a strong 0–0 transition should be forbidden for a centrosymmetric complex [38], it is likely that rotation of the ethynylnapthalene and para-*tert*-butylphenylacetylide ligands induce enough asymmetry to make the transition more

allowed [14,30]. The fine structuring observed in the phosphorescence spectra of **1** – **3** at 77 K is believed to be of vibronic origin [41]. Because the *trans* influence results in elongated Cr–C bonds, bis-alkynyl complexes exhibit less structured emission spectra than mono-alkynyl *trans*-[Cr(HMC)(C_2Ar)Cl]^+ type complexes due to weaker vibronic coupling [21].

At 77 K, complexes **1** – **3** exhibit phosphorescence lifetimes of 369 μs, 333 μs, and 372 μs, respectively. The lifetimes were calculated from decay curves generated by measuring the emission intensity at increasing delay times (Figs. S5 – S10). The room temperature lifetimes are significantly reduced, with lifetimes of 130 μs, 60 μs, and 56 μs for **1** – **3**, respectively. The phosphorescence lifetimes at 77 K and room temperature of complexes **1** – **3** are of similar magnitude to previously reported HMC and DMC Cr^III bis-alkynyl complexes [21,29-31].

3. Conclusion

An advantage of MPC over previously employed tetraazamacro-cycles is that it favors the *trans* isomer upon insertion of Cr^III, resulting in higher yields of *trans*-[Cr(MPC)Cl_2]^+ starting material, and thus higher quantities of *trans*-[Cr(MPC)(C_2Ar)_2]^+ after alkynylation. Tuning the macrocyclic ligand framework afforded bis-alkynyl complexes with similar properties to the previously reported Cr^III cyclam and cyclam' analogues, but in larger quantity. The increased amount of *trans*-[Cr(MPC)(C_2Ar)^2]^+ will aid the further pursuit of a dissymmetric Cr^III bis-alkynyl complex, which will allow for further study of PET processes in 3*d* metal alkynyl complexes.

4. Experimental

4.1. Materials

Phenylacetylene was purchased from Oakwood Chemical and used without further purification. MPC [27], TMS-C_2Np [42], and TMS-C_2C_6H_4^tBu [43], were prepared according to literature procedures. An adapted literature procedure [44] was used to generate *trans*-[Cr(MPC)Cl_2]Cl [36] as further described in Appendix A. The *trans*-[Cr(MPC)Cl_2]PF_6 analogue was synthesized from *trans*-[Cr(MPC)Cl_2]Cl via anion exchange with aqueous KPF_6 followed by an extraction into CH_2Cl_2. Tetrahydrofuran was freshly distilled over Na/benzophenone. The preparation of **1** – **3** was performed under a dry N_2 atmosphere using standard Schlenk procedures and the resulting complexes were purified under ambient conditions.

4.2. Physical measurements

ESI-MS were analyzed on an Advion Mass Spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc in Norcross, GA. UV-vis spectra were obtained with a JASCO V-670 spectrophotometer as 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.

4.3. Synthesis of trans-[Cr(MPC)(C_2Ph)_2]Cl *(1)*

A suspension of *trans*-[Cr(MPC)Cl_2]Cl (0.20 g, 0.37 mmol) in 30 mL THF was combined with 5 equivalents of LiC_2Ph (prepared from 1.9 mmol HC_2Ph in THF and 2.5 mmol *n*-BuLi). The reaction mixture was stirred for 2 h at room temperature. After quenching the reaction in air, solvent was removed via rotary evaporation. A silica gel plug was used for purification and **1** was eluted with 9:1 CH_2Cl_2:MeOH to afford 0.14 g of a yellow solid (57% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from
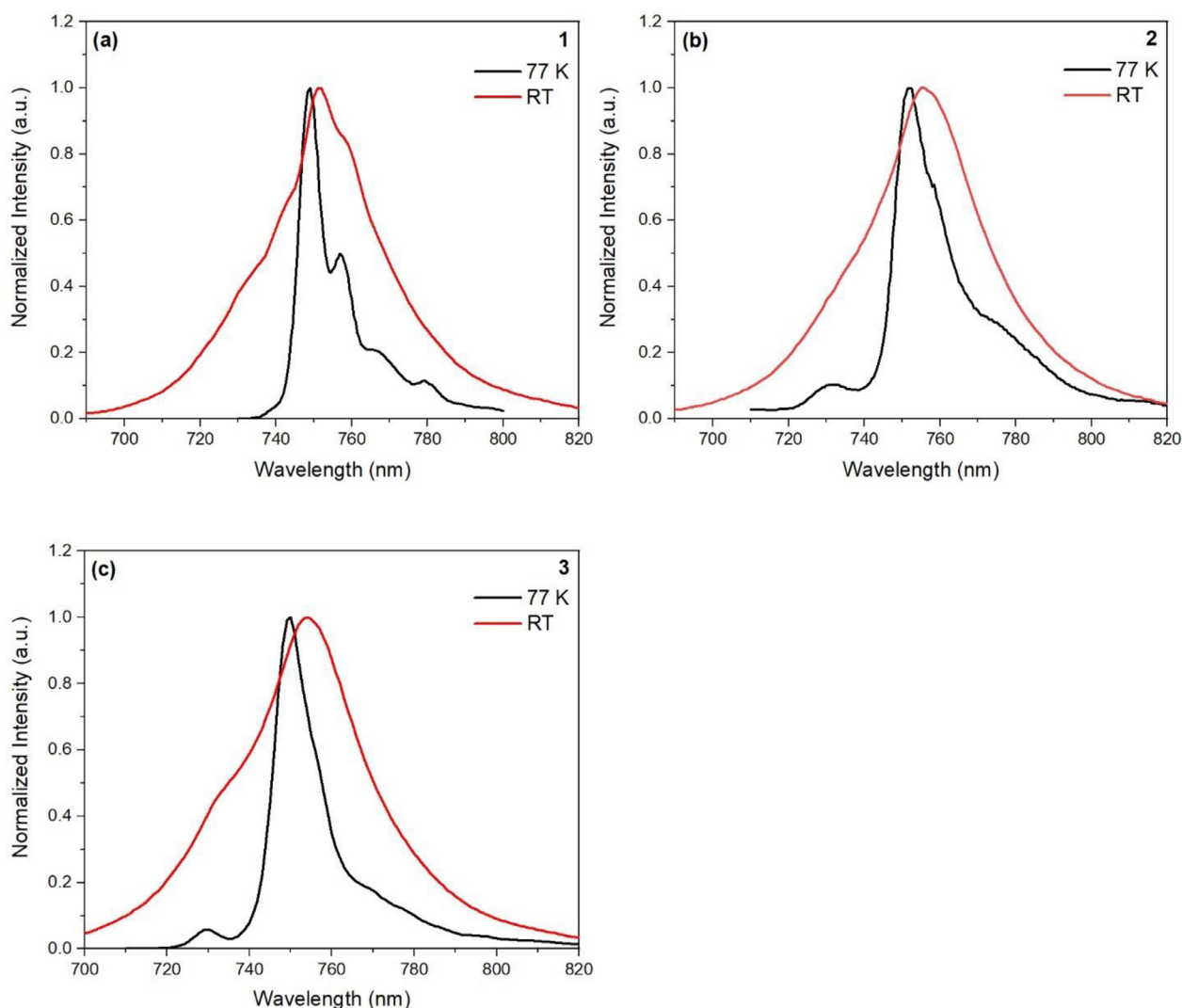
Fig. 5. Emission spectra of (a) **1**, (b) **2**, and (c) **3** at 77 K in 4:1 EtOH:MeOH and room temperature in degassed MeCN.

Table 2
Photophysical data for complexes **1** – **3**.

	Frozen Glass [a]			Room Temperature [b]		
	λ_{ex} (nm)	λ_{em} (nm)	τ (µs)	λ_{ex} (nm)	λ_{em} (nm)	τ (µs)
1	405	749	369	405	752	130
2	466	752	333	466	755	60
		732[c]	206			
3	406	750	372	406	754	56
		730[c]	316			
***trans*-[Cr(HMC)(C₂Ph)₂]Cl**	425	744	469	425	746	164
***trans*-[Cr(HMC)(C₂Np)₂]Cl**	445	747	447	445	747	218
		727[c]	362			
***trans*-[Cr(HMC)(C₂C₆H₄ᵗBu)₂]Cl**	403	745	479	403	748	117
		726[c]	345			

[a] Measured at 77 K in a 4:1 EtOH/MeOH glass

[b] Measured at room temperature in degassed MeCN

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

slow diffusion of Et$_2$O into MeOH. Elem. Anal. Found (Calcd) for *trans*-[Cr(MPC)(C$_2$Ph)$_2$]Cl•2H$_2$O (recrystallized from CH$_2$Cl$_2$/Et$_2$O): C, 67.85 (68.02); H, 6.85 (7.13); N, 7.86 (7.93). UV-vis, λ_{max} / nm (ε / M^{-1}cm^{-1}): 353 (600), 362 (670), 374 (680), 388 (650), 402 (670), 416 (440), 433 (380). FT-IR ν(C≡C) / cm^{-1}: 2082*w*. ESI-MS [M$^+$]: 634 *m/z* for the cationic species.

4.4. Synthesis of trans-[Cr(MPC)(C$_2$Np)$_2$]Cl (*2*)

A suspension of *trans*-[Cr(MPC)Cl$_2$]Cl (0.25 g, 0.46 mmol) in 30 mL THF was combined with 5 equivalents of LiC$_2$Np (prepared from 2.32 mmol TMS-C$_2$Np in THF and 3.0 mmol *n*-BuLi). The reaction mixture was stirred for 2 h at room tem-

perature. After quenching the reaction in air, solvent was removed via rotary evaporation. A silica gel plug was used for purification and **2** was eluted with 9:1 CH_2Cl_2:MeOH to afford 0.15 g of an orange solid (41% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from vapor diffusion of Et_2O into MeOH. Complex **2** was further purified by recrystallization from minimal CH_2Cl_2 and Et_2O after the crystallographic data indicated the presence of a NO_3^- counteranion impurity. Elemental analysis of the recrystallized sample indicated the NO_3^- impurity was no longer present. Elem. Anal. Found (Calcd) for *trans*-[Cr(MPC)(C_2Np)$_2$]Cl•CH_2Cl_2•4.5H_2O (recrystallized from CH_2Cl_2/Et_2O): C, 62.82 (62.85); H, 6.56 (6.57); N, 6.42 (5.98). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 439 (190), 468 (180), 502 (140), 528 (70), 543 (80). FT-IR ν(C≡C) / cm^{-1}: 2071w. ESI-MS [M$^+$]: 734 m/z for the cationic species.

Synthesis of trans-[Cr(MPC)(C$_2$Np)$_2$](PF$_6$) ([**2**]PF$_6$).

A suspension of *trans*-[Cr(MPC)Cl$_2$]PF$_6$ (0.100 g, 0.15 mmol) in 25 ml THF was combined with 10 equivalents of LiC_2Np (prepared from 1.97 mmol HC_2Np in THF and 1.97 mmol *n*-BuLi). The reaction mixture was stirred for 2 h at room temperature before quenching the reaction in air and filtering through Celite. The solvent was removed via rotary evaporation. The complex was purified over a silica gel column and PF$_6$ was eluted using 9:1 CH_2Cl_2:MeOH mixture to afford 20.8 mg of orange solid (16% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from slow diffusion of Et_2O into CH_2Cl_2.

4.5. Synthesis of trans-[Cr(MPC)(C$_2$C$_6$H$_4$^{t}Bu)$_2$]PF$_6$ (3)

A suspension of *trans*-[Cr(MPC)Cl$_2$]PF$_6$ (0.250 g, 0.39 mmol) was generated upon the addition of 25 mL THF and 5 equivalents of HC_2C$_6$H$_4$^{t}Bu (0.34 g, 1.93 mmol). A dry ice-acetone bath was used to cool the flask, and then 1.0 mL (2.5 mmol) 2.5 M *n*-BuLi was added. The reaction mixture was stirred for 2 h at room temperature. After quenching the reaction in air, solvent was removed via rotary evaporation. A silica gel plug was used for purification and **3** was eluted with 9:1 CH_2Cl_2:MeOH to afford 0.18 g of a yellow solid (53% yield based on Cr). Single crystals suitable for X-ray diffraction were grown from slow diffusion of Et_2O into MeOH. Elem. Anal. Found (Calcd) for *trans*-[Cr(MPC)(C$_2$C$_6$H$_4$^{t}Bu)$_2$]PF$_6$•2H_2O (recrystallized from CH_2Cl_2/Et_2O): C, 62.31 (62.12); H, 7.08 (7.17); N, 5.76 (6.04). UV-vis, λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 358 (1210), 366 (1260), 377 (1260), 392 (1240), 405 (1340), 419 (830), 437 (780). FT-IR ν(C≡C) / cm^{-1}: 2082w. ESI-MS [M$^+$]: 746 m/z for the cationic species.

4.6. X-ray crystallographic analysis

Single crystal X-ray data were collected at 150 K on a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded Goebel mirror for monochromatization, a Photon-II (**1** and (Cl/NO$_3$)) or Photon-III (**3**) area detector and an Oxford Cryosystems low temperature device with Cu$K\alpha$ (λ = 1.54178 Å) radiation. Single crystal X-ray data for PF$_6$ were collected a Photon II area detector and an Oxford Cryosystems low temperature device with Mo$K\alpha$ (λ = 0.71073 Å) radiation. Data for **1**, **2**, and **3** were collected and processed using APEX3 [45] and reduced using SAINT [45], space groups were assigned using XPREP within the SHELXTL [46] suite of programs and solved using ShelXS [47]. All structures were refined using Shelx2018 and the graphical interface Shelxle [48,49]. In some of the structures (**1**, PF$_6$ and **3**) only part of the solvent molecules were sufficiently resolved to model, and were included as partially occupied. Based on the XRD data it was not possible to determine whether the remaining volume remained unoccupied, or if additional highly disordered solvate molecules are present. A complete removal of the partially oc-cupied solvent molecules via the Squeeze procedure did not substantially improve the overall quality of the structure, and we thus decided to include the resolved fraction of the void content as partially occupied solvate molecules. Further refinement details and crystal data are provided in Appendix A.

Declaration of Competing Interest

The authors declare no conflicts of interest

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.122110.

References

[1] A. Haque, R.A. Al-Balushi, I.J. Al-Busaidi, Muhammad S. Khan, P.R. Raithby, Rise of Conjugated Poly-ynes and Poly(Metalla-ynes): From Design Through Synthesis to Structure–Property Relationships and Applications, Chem. Rev. 118 (2018) 8474.
[2] J.P. Launay, Mixed-Valent Compounds and their Properties - Recent Developments, Eur. J. Inorg. Chem. 2020 (2020) 329.
[3] C.-L. Ho, Z.-Q. Yu, W.-Y. Wong, Multifunctional polymetallaynes: properties, functions and applications, Chem. Soc. Rev. 45 (2016) 5264.
[4] M.R. Bryce, A review of functional linear carbon chains (oligoynes, polyynes, cumulenes) and their applications as molecular wires in molecular electronics and optoelectronics, J. Mater. Chem. C 9 (2021) in press.
[5] M. Delor, T. Keane, P.A. Scattergood, I.V. Sazanovich, G.M. Greetham, M. Towrie, A.J.H.M. Meijer, J.A. Weinstein, On the Mechanism of Vibrational Control of Light-Induced Charge Transfer in Donor-Bridge-Acceptor Assemblies, Nature Chem 7 (2015) 689.
[6] I.V. Rubtsov, STATE-SPECIFIC ELECTRON TRANSFER Shake it off, Nature Chem 7 (2015) 683.
[7] S.D. Banziger, M. Zeller, T. Ren, New Synthetic Route for Cobalt(III) Dissymmetric Bisalkynyl Complexes Based on Cobalt(III)(cyclam)(C$_2$NAP^{Mes}), Eur. J. Inorg. Chem. (2019) 4766.
[8] S.D. Banziger, X. Li, J. Valdiviezo, M. Zeller, P. Zhang, D.N. Beratan, I.V. Rubtsov, T. Ren, Unsymmetrical Bis-Alkynyl Complexes Based on Co(III)(cyclam): Synthesis, Ultrafast Charge Separation, and Analysis, Inorg. Chem. 58 (2019) 15487.
[9] R. Taube, H. Drevs, G. Marx, Über die Natur der Übergangsmetall-Kohlenstoff-s-Bindung. III. Phenyläthinyl-Metallphthalocyanine der ersten Übergangsreihe, Z. Anorg. Allg. Chem. 436 (1977) 5.
[10] L.A. Berben, J.R. Long, Synthesis and Alkali Metal Ion-Binding Properties of a Chromium(III) Triacetylide Complex, J. Am. Chem. Soc. 124 (2002) 11588.
[11] L. A. Berben Ph.D. Dissertation, University of California, Berkeley, 2005.
[12] D.L. Grisenti, W.W. Thomas, C.R. Turlington, M.D. Newsom, C.J. Priedemann, D.G. VanDerveer, P.S. Wagenknecht, Emissive Chromium(III) Complexes with Substituted Arylethynyl ligands, Inorg. Chem. 47 (2008) 11452.
[13] C. Sun, C.R. Turlington, W.W. Thomas, J.H. Wade, W.M. Stout, D.L. Grisenti, W.P. Forrest, D.G. VanDerveer, P.S. Wagenknecht, 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, Inorg. Chem. 50 (2011) 9354.
[14] L.E. Eddy, P.U. Thakker, C.D. McMillen, J.A. Pienkos, J.J. Cordoba, C.E. Edmunds, P.S. Wagenknecht, A comparison of the metal-ligand interactions of the pentafluorophenylethynyl and trifluoropropynyl ligands in transition metal cyclam complexes, Inorg. Chim. Acta. 486 (2019) 141.
[15] J. Nishijo, K. Judai, S. Numao, N. Nishi, Chromium Acetylide Complex Based Ferrimagnet and Weak Ferromagnet, Inorg. Chem. 48 (2009) 9402.
[16] J. Nishijo, M. Enomoto, A Series of Weak Ferromagnets Based on a Chromium-Acetylide-TTF Type Complex: Correlation of the Structures and Magnetic Properties and Origin of the Weak Ferromagnetism, Inorg. Chem. 52 (2013) 13263.
[17] J. Nishijo, M. Enomoto, Synthesis, structure and magnetic properties of [CrCyclam(CC-6-methoxynaphthalene)2](TCNQ)n(1,2-dichloroethane) (n = 1, 2), Inorg. Chim. Acta. 437 (2015) 59.
[18] J. Nishijo, Y. Shima, M. Enomoto, Synthesis, crystal structures and magnetic properties of new chromium(III)-acetylide-TTF type complexes, Polyhedron 136 (2017) 35.
[19] W.P. Forrest, Z. Cao, R. Hambrick, B.M. Prentice, P.E. Fanwick, P.S. Wagenknecht, T. Ren, Photoactive Cr(III)(cyclam) Complexes with Axially Bound geminal-Diethynylethenes, Eur. J. Inorg. Chem. 2012 (2012) 5616.

[20] A. López-Hernández, K. Venkatesan, H.W. Schmalle, H. Berke, Chemistry of Chromium Bis-Acetylide Complexes, Monatsh Chem. 140 (2009) 845.

[21] A.J. Schuman, S.F.T. Robey, E.C. Judkins, M. Zeller, T. Ren, A unique series of chromium(III) mono-alkynyl complexes supported by tetraazamacrocycles, Dalton Trans 50 (2021) 4936.

[22] S. F. T. Robey Ph.D. Dissertation, Purdue University, 2017.

[23] N.F. Curtis, R.W. Hay, A novel heterocycle synthesis. Formation of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate by reaction of diaminoethane monohydroperchlorate with mesityl oxide or acetone, Chem. Commun. (1966) 524.

[24] N. F. Curtis In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Springer US: Boston, MA, 1979; pp 219-344.

[25] N.F. Curtis, Compounds formed by Mannich reaction of a coordinated amine with an alpha-methylene nitro compound and formaldehyde - Syntheses and structures, Coord. Chem. Rev. 366 (2018) 109.

[26] K. Hideg, D. Lloyd, The reaction between aß-unsaturated ketones and ethylenediamine, J. Chem. Soc. D (1970) 929.

[27] K. Hideg, D. Lloyd, Reaction products from aß-unsaturated ketones and aliphatic diamines or dithiols, J. Chem. Soc. C. (1971) 3441.

[28] R.W. Hay, N.F. Curtis, G.A. Lawrance, A Convenient Synthesis of the Tetra-aza-macrocyclic Ligands trans-[14]-diene, tet a, and tet b, J. Chem. Soc., Perkin Trans. I. (1975) 591.

[29] S.F. Tyler, E.C. Judkins, Y. Song, F. Cao, D.R. McMillin, P.E. Fanwick, T. Ren, Cr(III)-HMC (HMC = 5,5,7,12,14-Hexamethyl-1-4-8-11-tetraazacyclotetradecane) Alkynyl Complexes: Preparation and Emission Properties, Inorg. Chem. 55 (2016) 8736.

[30] E.C. Judkins, S.F. Tyler, M. Zeller, P.E. Fanwick, T. Ren, Synthesis and Investigation of Macrocyclic CrIII Bis(alkynyl) Complexes: Structural and Spectroscopic Properties, Eur. J. Inorg. Chem. 2017 (2017) 4068.

[31] E.C. Judkins, M. Zeller, R. T, Synthesis and Characterizations of Macrocyclic Cr(III) and Co(III) 1-Ethynyl Naphthalene and 9-Ethynyl Anthracene Complexes: An Investigation of Structural and Spectroscopic Properties, Inorg. Chem. 57 (2018) 2249.

[32] R.W. Hay, M.P. Pujari, R. Bembi, B. Jeragh, P.R. Norman, The Preparation and characterization of chromium(III) complexes of C-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (Lm). Aquation and base hydrolysis kinetics of *cis*- and *trans*-[CrLmCl2]+, Trans. Met. Chem. 14 (1989) 393.

[33] T.D. Cook, S.F. Tyler, C.M. McGuire, M. Zeller, P.E. Fanwick, D.H. Evans, D.G. Peters, T. Ren, Nickel Complexes of C-Substituted Cyclams and Their Activity for CO2 and H+ Reduction, ACS Omega 2 (2017) 3966.

[34] B.L. Mash, T. Ren, Co(III) phenylacetylide complexes supported by tetraazamacrocyclic ligands: Syntheses and characterizations, J. Organomet. Chem 880 (2019) 143.

[35] B.L. Mash, Y. Yang, T. Ren, Improving Redox Reversibility and Intermetallic Coupling of Co(III) Alkynyls through Tuning of Frontier Orbitals, Organometallics 39 (2020) 2019.

[36] P.-J. Huang, J.V. Garcia, A. Fenwick, G. Wu, P.C. Ford, Nitric Oxide Uncaging from a Hydrophobic Chromium(III) PhotoNORM: Visible and Near-Infrared Photochemistry in Biocompatible Polymer Disks, ACS Omega 4 (2019) 9181.

[37] J. Manna, K.D. John, M.D. Hopkins, The Bonding of Metal-Alkynyl Complexes, Adv. Organomet. Chem. 38 (1995) 79.

[38] L.S. Forster, The Photophysics of Chromium(III) Complexes, Chem. Rev. 90 (1990) 331.

[39] N. A. P. Kane-Maguire In *Photochemistry and Photophysics of Coordination Compounds I*; Balzani, V., Campagna, S., Eds.; Springer, Berlin, Heidelberg, 2007; Vol. 280; pp 37-67.

[40] A.F. Fucaloro, L.S. Forster, S.G. Glover, A.D. Kirk, Solvent influence on emitting states in quadrate chromium(III) complexes, Inorg. Chem. 24 (1985) 4242.

[41] R.B. Lessard, M.J. Heeg, T. Buranda, M.W. Perkovic, C.L. Schwarz, R. Yang, J.F. Endicott, Stereochemical alterations of 2E chromium(III) excited-state behavior in dicyanotetraazacyclotetradecane complexes. Ground-state x-ray crystal structures, photophysical behavior, and molecular mechanics simulations of stereochemical effects, Inorg. Chem. 31 (1992) 3091.

[42] N.-H. Chang, H. Mori, X.-C. Chen, Y. Okuda, T. Okamoto, Y. Nishihara, Synthesis of Substituted [6]Phenacenes through Suzuki–Miyaura Coupling of Polyhalobenzene with Alkenylboronates and Sequential Intramolecular Cyclization via C–H Bond Activation, Chem. Lett. 42 (2013) 1257.

[43] G. Brizius, U.H.F. Bunz, Increased Activity of in Situ Catalysts for Alkyne Metathesis, Org. Lett. 4 (2002) 2829.

[44] D.A. House, R.W. Hay, M.A. Ali, The Preparation and Characterisation of Chromium(III) Complexes of C-*meso*- and C-*racemic*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *a* and tet *b*), Inorg. Chim. Acta. 72 (1983) 239.

[45] Bruker (2016), Apex3 v2018.7-2, v2019.1-0, Saint V8.38A, 2013/2014, Bruker AXS Inc., Madison (WI), USA, 2016.

[46] SHELXTL suite of programs, Bruker AXS Inc., 2003.

[47] G.M. Sheldrick, A short history of SHELX, Acta Cryst. A 64 (2008) 112.

[48] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, J. Appl. Crystallogr. (2011) 1281–1284.

[49] G.M. Sheldrick, Crystal structure refinement with SHELXL, Crystallogr Sect C Struct Chem. 71 (2015) 3.