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Co(III) Phenylacetylide Complexes Supported By Tetraazamacrocyclic Ligands: Syntheses and Characterizations

Brandon L. Mash and Tong Ren [*]

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Abstract: Reported herein are the syntheses and characterization of mono- and bis- Co(III) phenylacetylide complexes *trans*-$[Co(L)(C_2Ph)Cl]^+$ (**2a/b**) and *trans*-$[Co(L)(C_2Ph)_2]^+$ (**3a/b**), where L is MPD (**a**) or MPC (**b**) (MPD = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, MPC = 5,12-dimethyl-9,14-diphenyl-1,4,8,11-tetraazacyclotetradecane). All the new complexes were characterized by UV-Vis, FT-IR spectroscopic and voltammetric techniques. Single crystal X-ray diffraction studies revealed that the MPD ligand is a stronger donor to the Co(III) center than the MPC ligand, and the enhanced Co-N interactions manifest some subtle contrast in terms of spectroscopic and voltammetric properties between Co(MPD) and Co(MPC) complexes. These experimental observations were further corroborated by DFT calculations.

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[*] To whom correspondence should be addressed. E-mail: tren@purdue.edu

Dedicated to Professor Richard J. Puddephatt on the occasion of his 75th birthday.

Keywords: Cobalt, MPC, MPD, phenylacetylene

1. Introduction

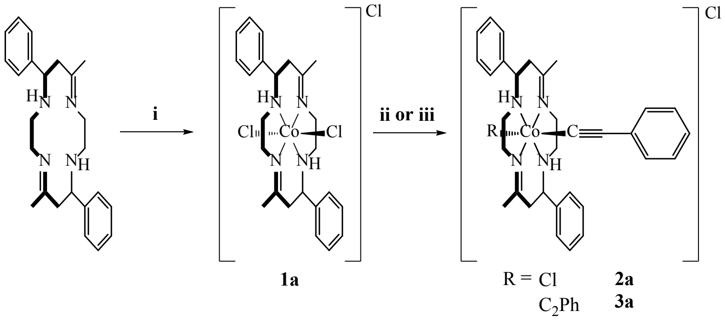
The chemistry of metal alkynyl compounds has been studied for decades since the pioneering work of Nast [1-4], and both the structural rigidity and conjugated $M–(C≡C)_nR$ backbone render these compounds ideal candidates for molecular wires [5-10]. Earlier successful examples include the work of Lapinte with C_4-bridged diiron compounds [11] and that of Gladysz with C_4-bridged dirhenium compounds [12]. Similar compounds developed in the following years include Mn [13], Ru [14], Pt [15] and Au [16]. The potential of diruthenium/triruthenium termini bridged by oligoyn-diyls as prototypical molecular wires were explored by our group [17-19], the laboratories of Lehn [20] and Peng [21-23], where both wire characteristics [24,25] and functional devices [26,27] have been demonstrated. Besides wire-like motifs, rings, double-rings and [2]-catenane supramolecules have been realized based on Au(I) acetylide building blocks [28-31].

With the exception of Fe [11] and Mn [13], the majority of the aforementioned examples are based on 4*d* and 5*d* metals. Our group is interested in expanding this class of compounds to include 3*d* metal based systems supported by tetra-azamacrocyclic ligands [32-38]. In addition to our efforts, alkynyl complexes supported by cyclam (1,4,8,11-tetraazacyclotetradecane) have been explored by other laboratories including Wagenknecht [39-42], Shores [43,44] and Nishijo [45-49], and provide a promising framework for low cost replacement for precious metal based materials. Although metal complexes of *C*- and *N*-substituted tetra-azamacrocyclic ligands have received significant attention as catalysts for oxygen activation and carbon dioxide reduction [50,51], the exploration of alkynyl complexes remains limited [36,52-55].

While the synthesis of M(cyclam) is fairly expedient with M as 3*d* metals, the cyclam ligand is costly to procure and nontrivial to synthesize. With *C*-substituted cyclam derivatives prepared from a simple route [56], the cost is significantly reduced. The synthesis of these ligands and their complexes have been discussed in depth by the laboratories of Curtis [56-58], Lloyd [59-61], and Hay [62,63]. Notable among these are MPD (MPD = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and MPC (MPC = 5,12-dimethyl-9,14-diphenyl-1,4,8,11-tetraazacyclotetradecane) [57,60,63,64]. While most of the macrocycles in diene form were produced via Schiff base condensation reaction of a singly protonated ethylenediamine and a vinyl ketone [56], MPD can be formed simply by mixing ethylenediamine and benzylideneacetone in ether over several days. Subsequent reduction of MPD using sodium borohydride yields MPC. Due to the wide availability of the reagents, both MPD and MPC can be produced on any desired scale at low cost. Herein, we report the first examples of alkynyl complexes based on the tetraazacyclotetradeca-4,11-diene framework, complexes **2a** and **3a** (Scheme 1), and provide additional examples of alkynyl complexes of *C*-substituted cyclam with complexes **2b** and **3b**.

2. Results and discussion

2.1 Synthesis



Scheme 1. Synthesis of Co(MPD) complexes **1a-3a**. (i) 1 equiv $CoCl_2•6H_2O$, MeOH, O_2, excess HCl; (ii) 7 equiv. HC_2Ph, Et_3N, MeOH, reflux, 24 h; (iii) excess LiC_2Ph, dry THF, 24 h. Co(MPC)-based complexes **1b-3b** were similarly prepared.

The complexes *trans*-[Co(MPD)Cl_2]Cl (**1a)** and *trans*-[Co(MPC)Cl_2]Cl (**1b)** were synthesized using a procedure modified from the preparation of [Co(cyclam)Cl_2]Cl [65]. Specifically, a methanolic solution of the desired macrocyclic ligand with $CoCl_2•6H_2O$ was sparged with oxygen followed by the addition of HCl to yield the desired cobalt(III) complex. Complex **1b** is insoluble in water, allowing for the removal of residual cobalt chloride with a water rinse to provide **1b** in 89% yield. Due to its solubility in water, complex **1a** was extracted using dichloromethane from the crude reaction mixture, and then recrystallized with ether for a yield of *ca.* 70%.

From complexes **1a** and **1b** were prepared the mono-phenylacetylide complexes, *trans*-[Co(MPD)(C_2Ph)Cl]Cl (**2a**) and *trans*-[Co(MPC)(C_2Ph)Cl]Cl (**2b**) under weak base conditions in ambient atmosphere, similar to the method developed by Shores [43,44]. Specifically, complex **1a** was reacted with excess phenylacetylene in the presence of triethylamine under reflux for 24 h. The crude reaction mixture was purified on silica to afford **2a** in a yield of *ca.* 20%. Complex **2b** was similarly prepared from **1b** and purified in a yield of 54%. The low yield of **2a** is likely due to the hydrolysis of the imino bonds of MPD under basic conditions [66], as well as the lability of the chloro ligand. It was noted in the synthesis of **2b** that the use of 5 equiv or more of phenylacetylene led to the formation of the bis-phenylacetylide complex as a minor product, and the yield of the *bis*-byproduct increases with equivalency of phenylacetylide. The bis-phenylacetylide complexes, *trans*-[Co(MPD)$(C_2Ph)_2$]Cl (**3a**) and *trans*-[Co(MPC)$(C_2Ph)_2$]Cl (**3b**), were prepared from the reaction between a large excess of LiC_2Ph and complexes **1a** or **1b**, and purified over silica with a gradient of dichloromethane and methanol in yields of 64% and 56%, respectively. All complexes are diamagnetic, which is consistent with a low spin Co(III) center.

2.2 Molecular Structures

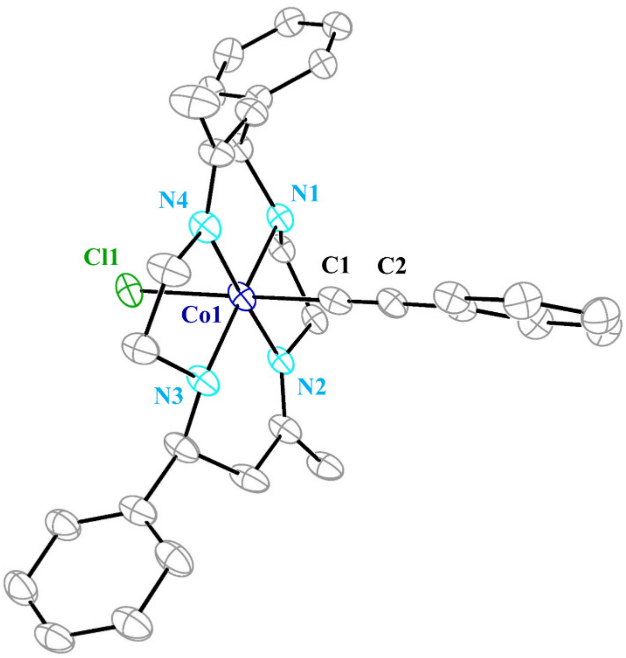


Fig. 1. ORTEP plot of [**2a**]$^+$ at the 30% probability level. Hydrogen atoms, solvent molecules, and Cl$^-$ counter ion were omitted for clarity.

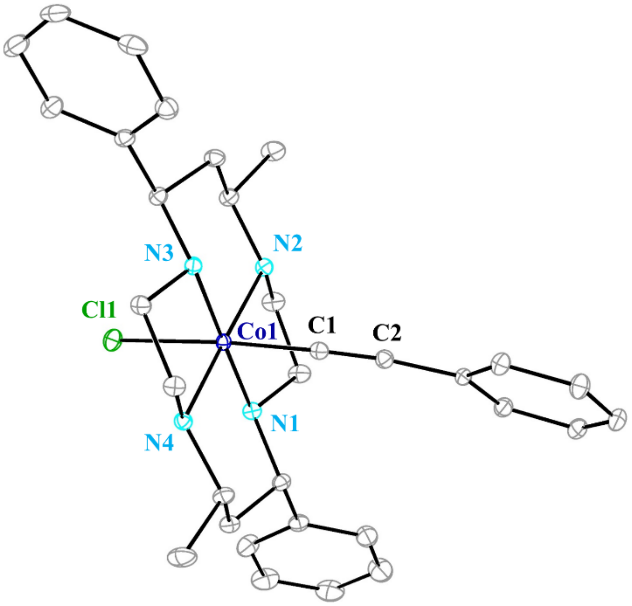


Fig. 2. ORTEP plot of [**2b**]$^+$ at the 30% probability level. Hydrogen atoms, solvent molecules, and Cl$^-$ counter ion were omitted for clarity.

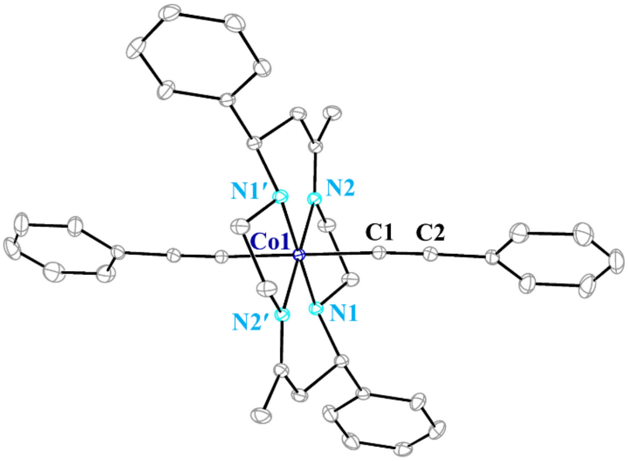


Fig. 3. ORTEP plot of [**3a**]$^+$ at the 30% probability level. Hydrogen atoms, solvent molecules, and Cl$^-$ counter ion were omitted for clarity.

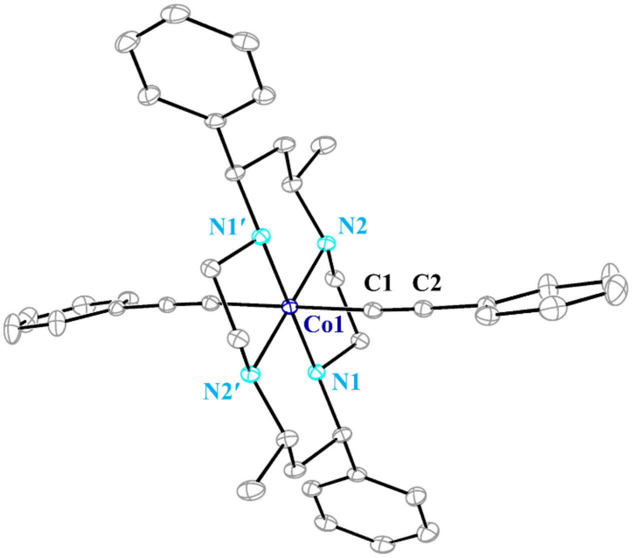


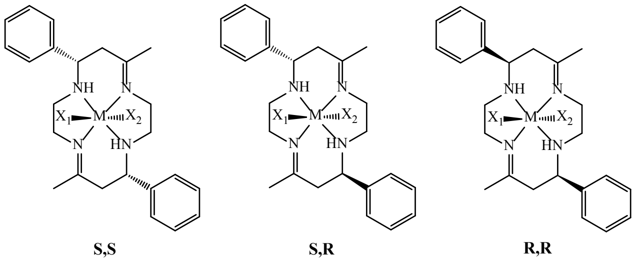
Fig. 4. ORTEP plot of [**3b**]$^+$ at the 30% probability level. Hydrogen atoms, solvent molecules, and Cl$^-$ counter ion were omitted for clarity.

Table 1

Selected bond lengths and angles for [**2a**]$^+$, [**2b**]$^+$, [**3a**]$^+$ and [**3b**]$^+$.

	[**2a**]$^+$	[**2b**]$^+$	[**3a**]$^+$	[**3b**]$^+$
Co—N1	1.978(4)	2.005(2)	1.980(1)	2.019(2)
Co—N2	1.945(3)	2.012(2)	1.947(1)	1.990(2)
Co—N3	1.971(4)	2.007(2)	-	-
Co—N4	1.932(3)	2.002(2)	-	-
Co—Cl	2.329(1)	2.3115(6)	-	-
Co—C	1.876(5)	1.870(2)	1.943(1)	1.924(3)
C1—C2	1.202(7)	1.200(4)	1.212(2)	1.201(4)
Cl-Co-C1	177.3(1)	175.19(7)	-	-
Co-C1-C2	172.5(4)	171.8(2)	176.6(1)	172.0(2)
C1-C2-C3	176.7(5)	174.6(3)	178.6(1)	178.8(3)

Single crystals of X-ray quality were grown by slow diffusion of diethyl ether into either a 1:1 mixture of acetonitrile and water (**2a**, **2b**) or methanol (**3a**, **3b**). The ORTEP plots for the complex cations are shown in Figs. 1-4, and the selected geometric parameters are listed in Table 1. Each unit cell contains one crystallographically independent formula unit. All cations display a nearly linear Cl—Co—C or C—Co—C linkage, which lies normal to the plane of the coordinated nitrogen atoms, conforming to a pseudo-octahedral geometry. The bis-alkynyl cations, [**3a**]$^+$ and [**3b**]$^+$, are centrosymmetric at the cobalt center, while the mono-alkynyl cations, [**2a**]$^+$ and [**2b**]$^+$, possess no crystallographic symmetry. Both cyclam-based complexes, **2b** and **3b**, hold the *trans*-III conformation [67] that is ubiquitous in this class of compounds with no chiral variation at the methyl or phenyl sites (Figs. 2 and 4) [65]. Depending on the orientation of phenyl groups, the Co(III)(MPD) complexes **1a**, **2a** and **3a** may exist as one of three possible stereo-isomers, namely (*R,R*), (*S,S*) and (*R,S*) forms, as shown in Scheme 2. The ring conformation differs among stereo-isomers, with both (*R,R*) and (*S,S*) adopting a boat conformation (Fig. 1) and (*R,S*) a chair conformation (Fig. 3). It is possible that the (*R,R*), (*S,S*) isomers were lost in the purification of the reduced form, MPC, hence those isomers are not seen in the Co(III)(MPC) complexes.[Donald F. Cook, Neil F. Curtis *, Olga P. Gladkikh, David C. Weatherburn. A further source of isomerism is introduced in mono-acetylide complexes, depending on which chloride is displaced. Since the stereo-isomerism has minimal impact on the electronic structures of the resultant cobalt(III) complexes, isolation of each of possible isomers was not pursued in this work.



Scheme 2. Stereo-isomers of M(MPD). X_1, X_2 = axial ligands. (*R,S*) and (*S,R*) are meso when $X_1 = X_2$

X-ray structures of both the mono- and bis-phenyacetylide complexes of Co(III)(cyclam), $[Co(cyclam)(C_2Ph)Cl]^+$ and $[Co(cyclam)(C_2Ph)_2]^+$, were reported by Shores [43]. Compared with these structures, the addition of methyl and phenyl groups in compound **2b** causes an increase in averaged Co—N bond length to 2.006 [2] Å from the 1.975 [2] Å in $[Co(cyclam)(C_2Ph)Cl]^+$ [43]. Intuitively, the σ-donation of the nitrogen atoms should be increased with the addition of electron rich substituents. Clearly, the lengthening of the Co—N bonds in **2b** is attributed to the steric effects of the added *C*-substitutents. The Co—C bond (1.870 (2) Å) is shortened while the Co—Cl bond (2.3115 (6) Å) is lengthened compared to those of Co(III)(cyclam) (Co—C 1.898 [2] Å, Co—Cl 23089 [5] Å). Similar lengthening of Co—N (2.004 [2] Å) and shortening of Co—C (1.924(3) Å) bond are observed for **3b** from $[Co(cyclam)(C_2Ph)_2]^+$ (Co—N 1.983 [2] Å, Co—C 2.001 [3] Å) [43]. The strengthening of Co—C bond has a pronounced effect on the electrochemical properties as discussed later. Structures of the diene-based complexes, namely **2a** and **3a**, display substantial differences in bond lengths from those of cyclam-based complexes, **2b** and **3b**. As shown in Table 1, the π-accepting capability and structurally smaller ring of MPD shortens the Co—N bonds significantly, which also results in the lengthening of the Co—C and Co—Cl bonds. The C1—C2 alkynyl bond lengths exhibit little variation among the complexes studied, ranging from 1.200 (4) Å for **2b** to 1.212 (2) Å for **3a**. These bonds are longer than those reported for the unsubstituted cyclam variant [43], however they are consistent with other Co(III)(cyclam) complexes reported from our laboratory [34,35,68,69].

2.3 Voltammetric Studies

Fig. 5. Cyclic voltammograms of 1.0 mM **2a**, **2b**, **3a**, and **3b** recorded in 0.1 M solution of Bu_4NPF_6 in MeCN at a scan rate of 0.10 V/s.

Table 2

Reduction potentials for **2a**, **2b**, **3a**, and **3b**.

	2a	**2b**	**3a**	**3b**
E_{pc} $Co^{3+/2+}$	-1.44	-1.39	-1.83	-1.81
E_{pc} $Co^{2+/1+}$	-1.89	-1.74	-	-

Cyclic voltammograms of complexes **2a**, **2b**, **3a** and **3b** are shown in Fig. 5, and the electrode potentials are listed in Table 2. The overall characteristics are similar to those observed for related Co(III)(cyclam) based complexes [43,70]. Irreversible $Co^{3+/2+}$ (**A**) and $Co^{2+/1+}$ (**B**) couples were observed for both mono complexes. The cathodic shifts in potential from Co(III)(MPC) to Co(III)(MPD) complexes are likely due to a stronger σ-donation from MPD, consistent with the trend noted from structural studies. The presence of a second phenylacetylide in the bis complexes further shifts the reductions cathodically, so that only the $Co^{3+/2+}$ couple can be observed within the solvent window. An irreversible reduction for **3a** is present at -1.83 V, as noted previously for $[Co(cyclam)(C_2Ph)_2]^+$ [43]. Interestingly, **3b** undergoes a quasi-reversible reduction at -1.81 V (ΔE_p = 63 mV, $i_{p,a}/i_{p,c}$ = 0.70). Though not observed in the cyclam analogue reported by Shores [43], a reversible couple was detected for Co(III)(cyclam) bearing both trifluoropropynyl [40] and pentafluorophenylacetylide ligands [35]. The irreversibility in Co(III)(cyclam) complexes is generally associated with the dissociation of labile axial ligands from the reduced Co(II) center [35,40,70]. Sun and coworkers attributed the reversibility of complexes with electron withdrawing ligands to the π-accepting nature of the alkyne rather than the electron density on the metal. These results indicate it is in fact the electron density on the metal, or at least a combination of the two factors, which leads to the reversible couple. Notably, the Co—C bond length of **3b** is comparable to the aforementioned complexes ($[Co(cyclam)(C_2C_6F_5)_2]^+$ (1.926(3) Å) [35]; $[Co(cyclam)(C_2CF_3)_2]^+$ (1.917(4) Å) [40]) without the use of electron withdrawing alkynyls. It is apparent that the reduced σ-donation from the macrocycle to the metal allows for a stronger axial ligand bond in both the Co(III) and Co(II) states. This improved stability is promising for the possible future application of Co(III)(MPC) to molecular wire type devices and opens the possibility of stable Co(II) complexes with sufficiently electron withdrawing cyclam derivatives.

2.3 Electronic Absorption Spectra

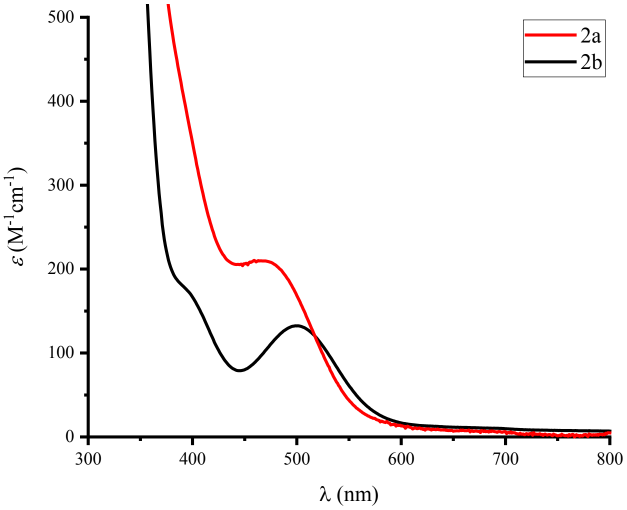


Fig 6. UV-vis spectra for **2a** (red) and **2b** (black) in MeCN.

Studies of electronic absorption spectra corroborate the findings in previous sections. As shown in Fig 6, the tighter binding of MPD results in a greater HOMO-LUMO energy gap and a hypsochromic shift in the absorption spectra. Consequently, the *d-d* transition located at 463 nm for **2a** is shifted to 499 nm for **2b**. For comparison, the *d-d* transition for $[Co(cyclam)(C_2Ph)Cl]^+$ lies between these compounds with its absorption band located at 486 nm (in THF) [43]. The bis-phenylacetylide complexes show similar results with a bathochromic shift from MPD to cyclam and then MPC (453 nm in **3a**, 475 nm in **3b** and 463 nm in $[Co(cyclam)(C_2Ph)_2]^+$; spectra in Fig. S1).

2.4 Electronic Structures via DFT

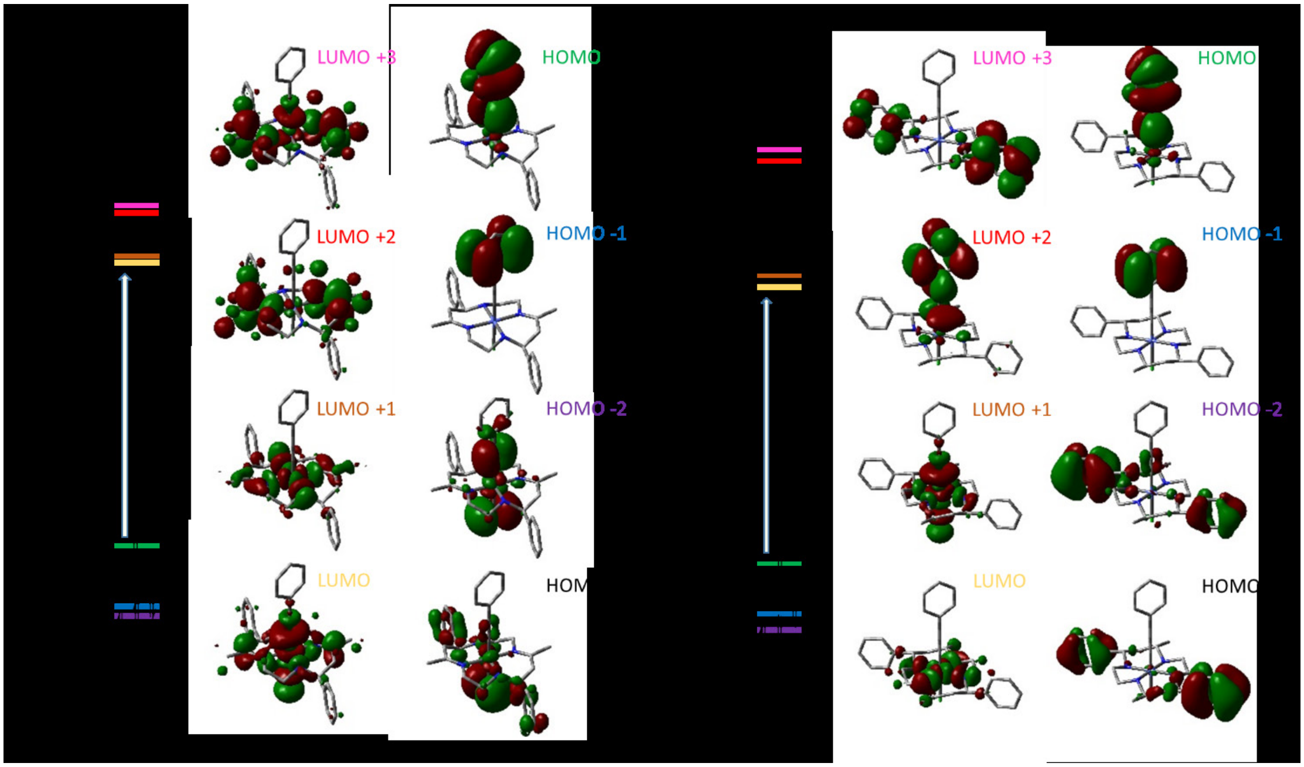


Fig. 7. Molecular orbital diagrams and energy levels for **2a** and **2b.** Plotted molecular orbitals for **3a** and **3b** are given in SI.

In order to understand the electronic structures of Co(III)(MPD) alkynyl species and rationalize the geometric differences between Co(III)(MPD) and Co(III)(MPC) species, density functional theory (DFT) calculations were performed at the B3LYP/LANL2DZ level (for all atoms) using the Gaussian16 suite [71]. All calculations were performed on gas phase cations without solvent interactions. Calculated bond lengths and angles are in agreement with the crystallographically determined parameters (Table S2). The computed contour plots and energy levels for the frontier molecular orbitals are given in Fig. 7. Expanded plots are given in Figs. S2-S5.

In complexes **2a** and **3a**, the X and Y axes approximately coincide with the Co—N bonds. In such a setting, interactions between the d_{xz} orbitals and the π orbitals of the imino groups are clearly displayed (Figs. S2, S4). For **2a** the d_{yz}, d_{z2}, and d_{xy} orbitals reside in the HOMO, LUMO, and LUMO+1, respectively (Fig. S2). For **3a** the d_{z2} lies in the LUMO+3, while the d_{yz} and d_{xy} lie in the HOMO and LUMO, respectively (Fig. S4). Both complexes **2b** and **3b** have the d_{yz}, $d_{x2\text{-}y2}$, and d_{z2} orbitals as the HOMO, LUMO, and LUMO+1, respectively (Figs. S3, S5). It can be seen that the d_{xz} and d_{yz} orbitals form planes bisecting Co—N bonds, which conforms to the computational analysis in previous studies of related Co(III)(cyclam) species [33-35,68-70]. The axial phenylacetylide groups are major contributors to the frontier molecular orbitals, with antibonding interactions to the d_{yz} orbital in the HOMO of each compound (Figs. S2-S5). The orbitals for the MPD compounds are also higher in energy than MPC, as noted in voltammetric studies.

3. Conclusion

Cobalt(III) complexes supported by a diene-macrocycle (MPD, **1a-3a)** and its cyclam derivative (MPC, **1b-3b**) have been prepared in yields ranging from 20 to 90%. Complexes **2a** and **3a** are the first examples of metal acetylide complexes based on a 1,4,7,11-tetra-azacyclotetradeca-4,11-diene type ligand. In comparison with cobalt(III) cyclam complexes, complexes **2a** and **3a** display enhanced Co(III)-N bonding, which increases the HOMO-LUMO energy gap and decreases axial ligand bond strength. On the other hand, complexes **2b** and **3b** exhibit weaker Co—N bonding, resulting in enhanced axial ligand strength. With stronger axial ligand binding, pseudo-reversibility of the $Co^{3+/2+}$ couple was observed for **3b**. The pseudo-reversible reduction observed in **3b** and Co(III)(cyclam) complexes bearing electron-deficient axial ligands highlights the profound effect of changes in the macrocycle on axial ligation. The ability of the *C*-substituted macrocycles to support cobalt acetylide complexes encourages further exploration of similar chemistry based on other 3*d* metals, such as Cr, Fe and Ni, an ongoing effort in our laboratory.

4. Experimental

4.1 Materials.

Phenylacetylene was purchased from GFS chemicals. $CoCl_2{\cdot}6H_2O$ and *n*-BuLi were purchased from Aldrich. MPD [58] and MPC [60] were prepared according to literature procedures. Tetrahydrofuran was freshly distilled over sodium/benzophenone. All lithiation reactions were carried out under N_2 using standard Schlenk techniques.

4.2 Physical measurements.

UV-vis spectra were obtained with a JASCO V-670 spectrophotometer. FT-IR spectra were measured as neat samples using a JASCO FT/IR-6300 spectrometer equipped with an ATR accessory. ESI-MS were analyzed on an Advion Expression Compact Mass Spectrometer. Elemental Analysis was carried out by Atlantic Micro Labs in Norcross, GA. Electrochemical analysis was done on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The analyte concentration is 1.0 mM in 4 mL dry acetonitrile with a 0.1 M Bu_4NPF_6 electrolyte concentration.

*4.3 Synthesis of [Co(MPD)Cl_2]Cl **1a**.*

A methanolic solution of $CoCl_2$•$6H_2O$ (2.20 g, 9.24 mmol) with MPD (3.00 g, 7.97 mmol) was sparged with O_2 for 1h before addition of 7 mL of 12 M HCl. Upon addition of HCl, the solution changed from brown to green. The solution was allowed to sparge for 1 hour before being transferred to a petri dish and heated at 45° C until dry. The residue was taken up in CH_2Cl_2 and filtered to give an emerald green solution, which was recrystallized with ether. Yield: 3.03 g (70%, based on MPD).

4.4 Synthesis of [Co(MPC)Cl₂]Cl ***1b.***

A methanolic solution of $CoCl_2$•$6H_2O$ (0.640 g, 2.69 mmol) with MPC (1.00 g, 2.63 mmol) was sparged with O_2 for 1 hour before addition of 4 mL of 12 M HCl. Upon addition of HCl, the solution changed from red to green with precipitate forming. The solution was allowed to sparge for 1h before the solvent was removed *in vacuo*. The crude solid was sonicated in H_2O before being filtered and washed with H_2O, THF, and ether. The collected green powder was dried under vacuum for 1.00 g. The combined filtrate was boiled down and allowed to cool producing an additional 0.28 g green crystals. Yield: 1.28 g (89% based on MPC).

4.5 Synthesis of [Co(MPD)(C₂Ph)Cl]Cl ***2a.***

To a methanolic solution of **1a** (0.500 g, 0.923 mmol) was added triethylamine (2.0 mL, 14 mmol), followed by phenylacetylene (1.01 mL, 9.23 mmol). The solution was allowed to reflux 24h. The solvent was removed via rotary evaporation and the residue was purified on silica gel with a gradient of CH_2Cl_2-MeOH. The collected orange product was recrystallized in CH_2Cl_2-Et_2O. Yield: 0.107 g, (20% based on Co). Data for **2a**: ESI-MS: (MeCN) 571 $[Co(MPD)(C_2Ph)Cl]^+$. Elem. Anal. Found (Calcd) for $C_{32.5}H_{40}N_4CoCl_3O_1$ ([**2a**]•H_2O•$0.5CH_2Cl_2$) C, 58.47 (58.44); H, 6.05 (6.04); N, 8.58 (8.39). IR (cm^{-1}) 2124 (C≡C). UV-vis absorption spectrum (MeCN) λ_{max} nm (ε_{max}, L mol^{-1} cm^{-1}): 257 (38100), 463 (210).

4.6 *Synthesis of [Co(MPC)(C_2Ph)Cl]Cl **2b.***

To a methanolic solution of **1b** (0.200 g, 0.366 mmol) was added triethylamine (1.5 mL, 11 mmol), followed by phenylacetylene (0.20 mL, 1.8 mmol). The solution was allowed to reflux 4 hours. The solvent was removed via rotary evaporation and the residue was purified on silica gel with a gradient of CH_2Cl_2-MeOH. The collected red product was recrystallized in CH_2Cl_2-Et_2O. Yield: 0.120 g, (54% based on Co). Data for **2b**: ESI-MS (MeCN): 575 $[Co(MPC)(C_2Ph)Cl]^+$. Elem. Anal. Found (Calcd) for $C_{33}H_{46}N_4CoCl_4O_{1.5}$ ([**2b**]$\cdot 1.5H_2O\cdot CH_2Cl_2$) C, 54.62 (54.79); H, 6.37 (6.41); N, 7.85 (7.74). IR (cm^{-1}) 2124 (C≡C). UV-vis absorption spectrum (MeCN) λ_{max} nm (ε_{max}, L mol^{-1} cm^{-1}): 256 (32900), 499 (132).

4.7 *Synthesis of [Co(MPD)(C_2Ph)$_2$]Cl **3a.***

A suspension of **1a** (0.250 g, 0.461 mmol) in THF was combined with a solution of LiC_2Ph (prepared from 4.6 mmol PhC_2H and 4.8 mmol *n*-BuLi) in THF and allowed to stir 24 h. The flask was opened to air and solvent was removed via rotary evaporation. The residue was purified on silica gel with a CH_2Cl_2-MeOH gradient. The solvent was removed and the remaining orange residue was recrystallized with CH_2Cl_2-Et_2O. Yield: 0.200 g (64% based on Co). Data for **3a**: ESI-MS (MeCN): 637 $[Co(MPD)(C_2Ph)_2]^+$. Elem. Anal. Found (Calcd) for $C_{41}H_{48}N_4CoCl_3O_2$ ([**3a**]$\cdot 2H_2O\cdot CH_2Cl_2$) C, 61.83 (62.01); H, 6.19 (6.09); N, 7.31 (7.06). IR (cm^{-1}) 2100 (C≡C). UV-vis absorption spectrum (MeCN) λ_{max} nm (ε_{max}, L mol^{-1} cm^{-1}): 263 (39700), 453 (191).

4.8 *Synthesis of [Co(MPC)(C_2Ph)$_2$]Cl **3b.***

A suspension of **1b** (130 mg, 0.238 mmol) in THF was combined with a solution of LiC_2Ph (prepared from 4.6 mmol PhC_2H and 4.8 mmol *n*-BuLi) in THF and allowed to stir 24h. The flask was opened to air and solvent was removed via rotary evaporation. The residue was purified on silica gel with a CH_2Cl_2-MeOH gradient. The solvent was removed and the remaining orange residue was recrystallized with CH_2Cl_2-Et_2O. Yield: 0.090 g (56% based on Co). Data for **3b**: ESI-MS (MeCN): 641 $[Co(MPC)(C_2Ph)_2]^+$. Elem. Anal. Found (Calcd) for $C_{40.5}H_{48}N_4CoCl_2O_{0.5}$ ([**3b**]$\cdot 0.5H_2O\cdot 0.5CH_2Cl_2$) C, 66.24 (66.76); H, 6.70 (6.64); N, 7.74 (7.69). IR (cm^{-1}) 2111 (C≡C). UV-vis absorption spectrum (MeCN) λ_{max} nm (ε_{max}, L mol^{-1} cm^{-1}): 269 (50500), 475 (148).

4.9 Computational Details.

The geometries of **2a**, **2b**, **3a**, and **3b** in the ground state were fully optimized from the crystal structures reported in this work using the density functional method B3LYP (Beck's three-parameter hybrid functional using the Lee−Yang−Parr correlation functional) and employing the LanL2DZ basis sets. The calculation was accomplished by using the Gaussian03 program package [71].

4.10 X-ray Crystallographic Analysis.

Single crystal X-ray data was collected on a Bruker AXS D8 Quest CMOS diffractometer using MoKα (λ = 0.71073 Å) radiation with Apex3 software. Data was reduced using SAINT and structures were solved with SHELXTL [72]. Refinement was performed with SHELXL. ORTEP plots were produced using SHELXTL [72].

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary Data

Crystal data for **2a**, **2b**, **3a** and **3b**; electronic absorption spectra for **3a** and **3b**; Relevant density functional theory calculation bond length/angle data and surface images for **2a**, **2b**, **3a** and **3b**; ^{1}HNMR spectra for **2a**, **2b**, **3a** and **3b**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 1872102, 1872101, 1872103, and 1872100 for compounds **2a**, **2b**, **3a** and **3b**, respectively. Copies of this information may be obtained free of charge from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: þ44-1233-336033; email: deposit@ccdc.cam.ac.uk or www: http://ccdc.
cam.ac.uk).

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.xxxxxxxx.

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