Inorganica Chimica Acta 380 (2012) 174–180

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Stepwise acetylide ligand substitution for the assembly of ethynylbenzene-linked Co(III) complexes

Wesley A. Hoffert[1], Md. Khayrul Kabir, Ethan A. Hill, Sara M. Mueller, Matthew P. Shores *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, USA

ARTICLE INFO

Article history:
Available online 7 September 2011

Young Investigator Award Special Issue

Keywords:
Cobalt complexes
Ethynylbenzene ligands
Synthesis
Ligand substitution
Metallodendrimer

ABSTRACT

We describe the preparation and structural characterization of a family of chloro-ethynylbenzene complexes containing $[(cyclam)Co]^{3+}$ units: $[(cyclam)CoCl(CCPh)]X$ (X = Cl (**1a**), BPh_4 (**1b**)), $[(cyclam)_2Co_2Cl_2(p\text{-DEB})]X_2$ (X = Cl (**2a**), BPh_4 (**2b**)), $[(cyclam)_3Co_3Cl_3(1,3,5\text{-TEB})]X_3$ (X = Cl (**3a**), BPh_4 (**3b**)), $[(cyclam)_2Co_2Cl_2(1,3,5\text{-TEBH})]X_2$ (X = Cl (**4a**), BPh_4 (**4b**)), where the bridging ligands *p*-DEB and TEB are the bis- and tris-deprotonated anions of 1,4-diethynylbenzene and 1,3,5-triethynylbenzene, respectively. Cyclic voltammetry of $[(cyclam)_3Co_3Cl_3(1,3,5\text{-TEB})]Cl_3$ (**3a**) suggests that electrochemical reduction of the Co(III) centers to Co(II) is accompanied by complex dissociation resulting from the increased lability of the Co(II) ions. Inclusion of the tetraphenylborate anions in **1b**–**4b** allows for the possibility of stepwise acetylide substitution by imparting complex cation solubility in tetrahydrofuran: *trans*-$[(cyclam)Co(CCPh)_2](BPh_4)$ (**5**) is prepared by mixing LiCCPh with **1b**. Isolation of **5** demonstrates the feasibility of metallodendrimer synthesis using octahedral first-row transition metal nodes, which awaits demonstration.

1. Introduction

Seeking a greater degree of synthetic control in inorganic and organometallic materials, chemists have long been concerned with being able to assemble transition metal clusters using a “building block” approach [1–3]. Small ligands such as oxide [4,5], hydroxide [6,7], and cyanide [8,9] have proven to be effective directors of multimetallic cluster self-assembly, but there is also interest in the synthesis of metal clusters bridged by a framework of larger ligands with delocalized π orbitals [10–12]. Such molecules have been suggested as components of non-linear optical devices [13], and more recently, magnetic materials [14,15]. Polyethynylbenzene bridging ligands are attractive as structural units that foster communication between nodes. Takahashi and co-workers have synthesized metallodendrimers with up to 45 square-planar Pt^{II}-containing units bridged by the triply deprotonated trianion of 1,3,5-triethynylbenzene (H_3TEB) [16]. Humphrey and co-workers later reported the preparation and properties of TEB^{3-}-based dendrimers that incorporated nine octahedral Ru^{II} ions [17]. Both types of molecules were synthesized by stepwise replacement of *trans*-chloride ligands; isolation of products with good monodispersity relied on the high inertness of the metal ions with mixed ligands at sites *trans* to each other. For this reason, Pt^{II} and Ru^{II} are ideal candidates for incorporation into metallodendrimers, as many examples of heteroleptic complexes exist for those ions.

Interesting properties are predicted for first-row transition metal analogs, especially for paramagnetic species. Considering first row transition metal complexes bridged by TEB^{3-}, this ligand engenders ferromagnetic coupling between ligated metal ions because of the mutually *meta* bridged connectivity [18], and the two-dimensional and C_3-symmetric topology imparted by the rigid ligand should enhance magnetic anisotropy [19]. Prior to attempting the synthesis of air- and moisture-sensitive paramagnetic complexes, we sought to prepare a stable structural analog of a first-row complex that could be easily studied with conventional techniques such as ^1H NMR, making Co^{III}-containing species an ideal choice. Earlier work from Giese established that Grignard reagents could be used to prepare monomeric Co^{III} chloro-acetylide complexes [20]. The syntheses of mono- and bis-acetylide Co^{III} complexes were also studied by Lewis and co-workers [21]. They discovered that trialkylstannyl acetylene precursors combined with neutral $[Co^{III}N_4Cl_2]$ complexes in the presence of catalytic amounts of CuI form monomeric metal-acetylide compounds. Depending on reaction stoichiometry, polymeric compounds could also be prepared by heating equimolar amounts of the dichloro Co^{III} precursor and ditopic *para*-bis(trimethyltin)diethynylbenzene [21]. We note that diamagnetic Fe^{II} ethynylbenzene complexes have also been the focus of considerable attention from Field and co-workers. Among several possible synthetic protocols, the dehydrohalogenation route has been shown to be a versatile method for preparing metal acetylide complexes containing $[(dmpe)_2FeCl]^-$ units (dmpe = 1,2-bis(dimethylphosphino)ethane) [22–24]. Noting

---

* Corresponding author. Tel.: +1 970 491 7235; fax: +1 970 491 1801.
E-mail address: matthew.shores@colostate.edu (M.P. Shores).

[1] Present address: Pacific Northwest National Laboratory, Richland, WA 99352, USA.

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.08.051

these precedents, our interest lies in synthetic routes that may allow for the *stepwise* preparation of multinuclear complexes. Herein, we present the preparations, X-ray structures, and spectroscopic and electrochemical characterizations of a series of diamagnetic Co^{III}(cyclam)-based chloro-acetylide complexes synthesized using a dehydrohalogenation synthetic strategy. The stepwise preparation of a di-substituted Co^{III} bis-acetylide complex is also described, which raises the possibility of using related octahedral first-row transition metal complexes as precursors for paramagnetic metallodendrimers.

2. Experimental section

2.1. Materials and methods

Unless otherwise noted, all manipulations were performed in air. The compounds [(cyclam)$CoCl_2$]Cl [25] and 1,3,5-triethynylbenzene [26] (H_3TEB) were prepared as described elsewhere. Triethylamine was freshly distilled before use. All other reagents were purchased commercially and were used without further purification. The bridging ligand *p*-DEB^{2-} is the doubly deprotonated anion of 1,4-diethynylbenzene (*p*-H_2DEB). The concentration of *n*-BuLi was verified by titration prior to the synthesis of compound **5**.

2.2. Preparation of compounds

2.2.1. Trans-[(cyclam)CoCl(C_2Ph)]Cl (*1a*)

Triethylamine (1.62 mL, 11.6 mmol) was added to a green methanolic (10 mL) solution of [(cyclam)$CoCl_2$]Cl (213 mg, 0.582 mmol) and phenylacetylene (61 μL, 0.55 mmol) in a 100 mL round-bottomed flask, causing the solution color to darken. The flask was fitted with a condenser tube, and the solution was heated with stirring at reflux for 24 h, during which time the solution color turned to red-orange. The solvent was removed by rotary evaporation, and the resulting red-brown residue was washed with diethyl ether (10 mL) and dried under vacuum to yield 231 mg of crude **1a** as a red-brown solid. Crystals of **1a** suitable for X-ray diffraction were grown by diffusion of diethyl ether vapor into a concentrated solution of the crude product in tetrahydrofuran.

2.2.2. Trans-[(cyclam)CoCl(C_2Ph)]BPh_4 (*1b*)

A solution of $NaBPh_4$ (184 mg, 0.536 mmol) in *ca.* 3 mL of methanol was added to a solution of compound **1a** (231 mg) in *ca.* 10 mL of methanol, causing an orange solid to precipitate. This solid was isolated by filtration, washed with methanol (3 × 3 mL) and diethyl ether (3 × 3 mL) and dried in air to afford 251 mg of the final product (0.334 mmol, 61% overall yield based on phenylacetylene used to produce **1a**). Absorption spectrum (THF): λ_{max} (ε_M) 227 (43 500), 258 (33 300), 326 (sh, 10 600), 381 (sh, 1400) 486 nm (1100 M^{-1} cm^{-1}). IR: $\nu_{C\equiv C}$ 2125 cm^{-1}. ^1H NMR (($(CD_3)_2CO$): δ 7.37–7.22 (m, 13H, B-C_6H_5, CCC_6H_5), 6.93 (t, 8H, B-C_6H_5), 6.78 (t, 4H, B-C_6H_5), 5.06 (br, 2H, N-*H*), 4.92 (br, 2H, N-*H*), 3.03–2.59 (m, 18H, CH_2), 1.74–1.64 ppm (m, 2H, exo-$CH_{(2)}$). [*Note:* the integrations of the most upfield resonances in the chloro-acetylide complexes are not consistent with there being two equivalent H atoms on the aliphatic cyclam carbon. Rather, we assign these signals to the "exo" or Cl-pointing protons only.] ESI^+-MS (acetone): *m*/*z* 395.20 ($[\mathbf{1a}^{-}BPh_4]^+$). *Anal.* Calc. for $C_{42}H_{49}BClCoN_4$: C, 70.55; H, 6.91; N, 7.84. Found: C, 70.37; H, 7.14; N, 7.79%. Crystals of **1b** suitable for X-ray structural analysis were grown by diffusion of diethyl ether vapor into a concentrated solution of **1b** in tetrahydrofuran.

2.2.3. Trans,trans-[$(cyclam)_2Co_2Cl_2$(μ-p-DEB)]Cl_2 (*2a*)

Triethylamine (1.32 mL, 9.44 mmol) was added to a green methanolic (10 mL) solution of [(cyclam)$CoCl_2$]Cl (181 mg, 0.495 mmol) and freshly sublimed *p*-H_2DEB (29.7 mg, 0.236 mmol) in a 50 mL round-bottomed flask, causing the solution to darken. The flask was fitted with a condenser tube and the solution was heated with stirring at reflux for 24 h, during which time the solution color turned to red-orange. The solvent was removed by rotary evaporation, and the resulting red-brown residue was washed with diethyl ether (10 mL) and dried under vacuum to yield 196 mg of crude **2a** as an orange solid. Crystals of **2a** suitable for X-ray diffraction were grown by diffusion of diethyl ether vapor into a concentrated solution of the crude product in MeOH.

2.2.4. Trans,trans-[$(cyclam)_2Co_2Cl_2$(μ-p-DEB)]$(BPh_4)_2$ (*2b*)

A solution of $NaBPh_4$ (256 mg, 0.748 mmol) in *ca.* 3 mL methanol was added to a solution of compound **2a** (196 mg) in *ca.* 10 mL methanol, causing **2b** to precipitate as an orange solid. This solid was isolated by filtration, washed with methanol (3 × 3 mL) and diethyl ether (3 × 3 mL). The compound was recrystallized by slow diffusion of diethyl ether into a concentrated solution of **2b** in acetone to afford 151 mg of the final product (0.112 mmol, 47% overall yield based on *p*-H_2DEB used to produce **2a**). Absorption spectrum (acetone): λ_{max} (ε_M) 327 (3720), 386 (sh) (940) 488 (440 M^{-1} cm^{-1}). IR: $\nu_{C\equiv C}$ 2133 cm^{-1}. ^1H NMR ((CD_3CN): δ 7.36 (s, 4H, CC(Ar-*H*)CC), 7.27 (br, 20H, B-C_6H_5), 6.99 (t, 16H, B-C_6H_5), 6.84 (t, 8H, B-C_6H_5), 4.48 (br, 8H, N-*H*), 2.89-2.40 (m, 36H, CH_2), 1.54–1.38 ppm (m, 4H, exo-$CH_{(2)}$). ESI^+-MS (acetone): *m*/*z* 1031.47 ($[\mathbf{2b}\text{-}BPh_4]^+$), 356.13 ($[\mathbf{2b}\text{-}2BPh_4]^{2+}$). *Anal.* Calc. for $C_{84}H_{104}B_2Cl_2Co_2N_8O_2$ ($\mathbf{2b}\cdot 2C_3H_6O$): C, 68.72; H, 7.14; N, 7.63. Found: C, 68.56; H, 7.06; N, 7.36%.

2.2.5. Trans,trans,trans-[$(cyclam)_3Co_3Cl_3$(TEB)]Cl_3 (*3a*)

Triethylamine (1.70 mL, 12.3 mmol) was added to a green methanolic (10 mL) solution of [(cyclam)$CoCl_2$]Cl (239 mg, 0.655 mmol) and freshly sublimed H_3TEB (30.7 mg, 0.205 mmol) in a 100 mL round-bottomed flask, causing the solution color to darken. The flask was fitted with a condenser tube and the solution was refluxed with stirring for 24 h, during which time the solution color turned to red-orange. The solvent was removed by rotary evaporation, and the resulting red-brown residue was washed with diethyl ether (10 mL) and dried under vacuum to yield 271 mg of crude **3a** as an orange solid. Crystals of **3a** suitable for X-ray diffraction were grown by diethyl ether vapor diffusion into a concentrated solution of the crude product in MeOH.

2.2.6. Trans,trans,trans-[$(cyclam)_3Co_3Cl_3$(TEB)]$(BPh_4)_3$ (*3b*)

A solution of $NaBPh_4$ (326 mg, 0.953 mmol) in ca. 5 mL of methanol was added to a solution of compound **3a** (271 mg) in *ca.* 10 mL methanol, causing a salmon-colored solid to precipitate. This solid was isolated by filtration, washed with methanol (3 × 3 mL) and diethyl ether (3 × 3 mL) and dried in air to afford 234 mg of the final product (0.118 mmol, 57% overall yield based on H_3TEB used to produce **3a**). Absorption spectrum (acetone): λ_{max} (ε_M) 329 (3300), 384 (sh, 575) 485 nm (420 M^{-1} cm^{-1}). IR: $\nu_{C\equiv C}$ 2114 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.34 (m, 27H, B-C_6H_5 and Ar-*H*), 6.93 (t, 24H, B-C_6H_5), 6.78 (t, 12H, B-C_6H_5), 4.93 (br, 12H, N-*H*), 3.07-2.54 (m, 56H, CH_2), 1.74-1.58 ppm (m, 6H, exo-$CH_{(2)}$). ESI-MS^+ (acetone): *m*/*z* 1667.60 ($[\mathbf{3b}\text{-}BPh_4]^+$), 674.80 ($[\mathbf{3b}\text{-}2BPh_4]^{2+}$), 343.90 ($[\mathbf{3b}\text{-}3BPh_4]^{3+}$). *Anal.* Calc. for $C_{114}H_{135}B_3Cl_3Co_3N_{12}$: C, 68.84; H, 6.84; N, 8.45. Found: C, 68.58; H, 6.83; N, 8.19%.

2.2.7. Trans,trans-[$(cyclam)_2Co_2Cl_2$(HTEB)]Cl_2 (*4a*)

Triethylamine (0.34 mL, 2.42 mmol) was added to a green methanolic (10 mL) solution of [(cyclam)$CoCl_2$]Cl (233 mg, 0.637 mmol) and freshly sublimed H_3TEB (45.5 mg, 0.303 mmol) in a 100 mL round-bottomed flask, causing the solution color to darken. The flask was fitted with a condenser tube and the solution was refluxed with stirring for 24 h, during which time the solution turned to orange-brown. The solvent was removed by rotary evaporation, and the resulting red-brown residue was washed with 10 mL of absolute ethanol, causing an orange solid to precipitate. The solid was isolated by filtration, washed with ethanol (3 × 3 mL) and diethyl ether (3 × 3 mL) and dried in air to afford 92.1 mg of **4a**. Single crystals suitable for X-ray analysis were grown by diffusing diethyl ether vapor into a concentrated solution of **4a** in methanol.

2.2.8. *Trans,trans-[(cyclam)$_2$Co$_2$Cl$_2$(HTEB)](BPh$_4$)$_2$ (**4b**)*

A solution of $NaBPh_4$ (*ca.* 1 g, 342 mmol) in 10 mL methanol was added to a solution of compound **4a** (145 mg) in 10 mL methanol, causing an orange solid to precipitate. This solid was isolated by filtration, washed with methanol (3 × 3 mL) and diethyl ether (3 × 3 mL). The compound was recrystallized by diffusing diethyl ether vapor into a concentrated solution of **4b** in acetone. After 1 day, orange crystals were isolated by filtration, washed with diethyl ether (3 × 3 mL), and dried in air to afford 166 mg of the final product (0.121 mmol, ~67% for the step described above, 27% overall yield based on H_3TEB used to produce **4a**). Absorption spectrum (acetone): λ_{max} (ε_M) 326 (1770), 333 (2340), 380 (sh, 360), 483 nm (260 M^{-1} cm^{-1}). IR: $\nu_{C\equiv C}$ 2122 cm^{-1}, ν_{CC-H} 3311 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): 7.42 (t, 1H, Ar-*H*), 7.38 (d, 2H, Ar-*H*), 7.34 (m, 16H, BAr-*H*), 6.94 (t, 16H, BAr-*H*), 6.79 (t, 8H, BAr-*H*), 4.94 (br s, 8H, N-*H*), 3.79 (s, 1H, CC-*H*), 2.99-2.52 (br m, 36H, CH_2), 1.66 ppm (br m, 4H, exo-$CH_{(2)}$). *Anal.* Calc. for $C_{86}H_{104}B_2Cl_2Co_2N_8O_2$ (**4b**·$2C_3H_6O$): C, 69.22; H, 7.02; N, 7.51. Found: C, 68.78; H, 6.98; N, 7.71%.

2.2.9. *Trans-[(cyclam)Co(C$_2$Ph)$_2$](BPh$_4$) (**5**)*

Under an atmosphere of dinitrogen, LiC_2Ph was generated by adding *n*-BuLi (0.07 mL of a 1.6 M solution in hexanes, 0.112 mmol) to a solution of phenylacetylene (13.1 μL, 12.1 mg, 0.119 mmol) in diethyl ether (3 mL). After stirring for 5 min, the ethereal solution was added to an orange solution of **1b** (77.3 mg, 0.108 mmol) in tetrahydrofuran (5 mL). After 1 h of stirring, the solvent was removed *in vacuo* to afford a brown residue. Washing with pentane afforded a yellow-brown solid, which was isolated by filtration and washed with diethyl ether (3 × 3 mL) to yield 88 mg of crude yellow solid. The product was recrystallized by slow diffusion of diethyl ether vapor into a concentrated solution of the crude product in tetrahydrofuran. The yellow needle crystals that formed after one day were isolated by filtration, washed with diethyl ether (3 × 3 mL), and dried under dinitrogen to afford 53.8 mg of the final product (64%). Absorption spectrum (MeCN): λ_{max} (ε_M) 268 (28200), 363 (sh, 270), 463 nm (84 M^{-1} cm^{-1}). IR: $\nu_{C\equiv C}$ 2100 cm^{-1}. ^1H NMR (CD_3CN): δ 7.48 (d, 4H, Ar-*H*), 7.34-7.19 (m, 14H, B-C_6H_5 and Ar-*H*), 6.99 (t, 8H, B-C_6H_5), 6.84 (t, 4H, B-C_6H_5), 4.16 (br, 4H, N-*H*), 2.86 (m, 4H, CH_2), 2.58–2.40 (m, 12H, CH_2), 1.87 (d, 2H, CH_2), 1.32 (m, 2H, CH_2). ESI-MS$^+$ (acetone): *m/z* 461.07 (**5**-BPh_4^+). *Anal.* Calc. for $C_{56}H_{66}BCoN_4O_{1.5}$ (**5**·$1.5C_4H_8O$): C, 75.67; H, 7.48; N, 6.30. Found: C, 75.64; H, 7.26; N, 6.52%.

2.3. *X-ray structure determinations*

Structures were determined for the compounds listed in Table 1. Single crystals were coated in Paratone oil, supported on cryoloops, transferred to a Bruker Kappa Apex 2 CCD diffractometer, and cooled under a stream of dinitrogen. All data collections were performed at 100 or 120 K with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Initial lattice parameters were determined from a minimum of 190 reflections harvested from 36 frames, and data sets were collected targeting complete coverage and four-fold redundancy. Data were integrated and corrected for absorption effects with the Apex 2 software package [27]. Structures were solved by direct methods with the aid of successive Fourier difference maps and were refined against all data using the SHELXTL software package [28]. Displacement parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and were refined using a riding model where the isotropic displacement parameters were set at 1.2 times those of the attached carbon or nitrogen atoms (1.5 times for methyl protons). The final structures have been deposited (in cif format) with the Cambridge Crystallographic Data Centre (Table 1).

In the structure of **5**·2THF, the β-acetylenic carbon atoms in each complex exhibited abnormally small thermal ellipsoids compared to their nearest neighbors. For those atoms, the thermal parameters along the bond axis with the α-acetylenic carbon atoms were constrained to be the same as those of the α-acetylenic carbon atoms.

2.4. *Other physical measurements*

Absorption spectra were obtained in quartz cuvettes with a Hewlett-Packard 8453 spectrophotometer. Infrared spectra were measured with a Nicolet 380 FT-IR using the Smart Performer ZnSe ATR accessory. ^1H NMR spectra were recorded using a Varian INOVA instrument operating at 300 MHz. Cyclic voltammetry experiments were performed in 0.1 M solutions of $(Bu_4N)PF_6$ in tetrahydrofuran or acetonitrile. The voltammograms were recorded with either a CH Instruments 1230A or 660C potentiostat using a 0.25 mm Pt disk working electrode, Ag/Ag$^+$ reference electrode, and a Pt mesh auxiliary electrode. All voltammograms shown were measured with a scan rate of 0.1 V/s. Reported potentials are referenced to the $[Cp_2Fe]^+/[Cp_2Fe]$ redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment. Elemental analyses were performed by Robertson Microlit Laboratories in Madison, NJ.

3. Results and discussion

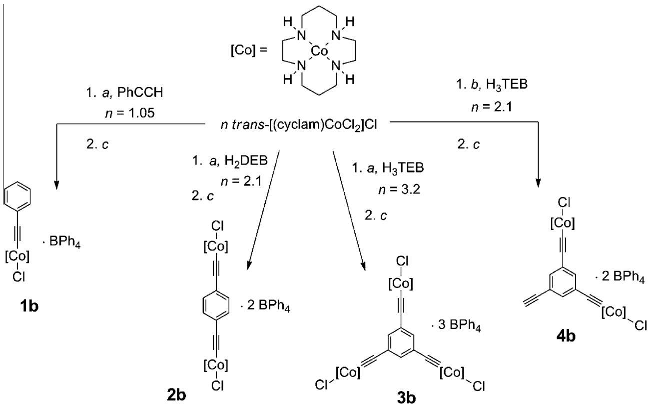
3.1. *Syntheses and characterizations of Co^{III} acetylide complexes*

Our approach to making "0th" generation metallodendrimers is based on a dehydrohalogenation strategy that has been employed in the synthesis of other Co^{III}-, Fe^{II}-, and Ru^{II}-containing metal-acetylide complexes. For Ru-containing complexes, the reaction has been shown to proceed by way of a metal–vinylidene intermediate, which reacts readily with a base to afford the metal acetylide. Shown in Scheme 1, *trans*-[Co(cyclam)Cl_2]Cl reacts directly with an arylacetylide ligand using triethylamine as the base, yielding the chloro-acetylide complexes as orange solids in acceptable yield. No changes in (visible) color or infrared spectra are observed if the reaction is carried out in the absence of Et_3N. In order to drive the ligand substitution reactions in the syntheses of **1a**, **2a**, and **3a** to completion, it was necessary to use a slight stoichiometric excess [29] of [(cyclam)CoCl_2]Cl. As evidenced by the isolation of **4a**, Co^{III}-deficient reaction mixtures lead to "incomplete" substitution of the ethynylbenzene ligands. Obtaining pure bulk samples of the chloride salts of all complexes presented herein was not possible, likely owing to the similar solubilities of the acetylide complexes, surplus [(cyclam)CoCl_2]Cl, and triethylammonium hydrochloride, which forms as the conjugate acid byproduct of dehydrohalogenation. Although recrystallization of the chloride salts could be used to obtain a few X-ray quality crystals, crystalline samples subjected to combustion analysis were not acceptably pure. Occasionally, crops of crystals of **4a** contained a green-colored side product, consistent with excess [(cyclam)CoCl_2]Cl. In order to impart differential solubility between the product and impurities, tetraphenylborate anion metathesis was performed, allowing for workup to be performed in less polar solvents like tetrahydrofuran. Slow diffusion of diethyl ether vapor into THF solutions of the tetraphenylborate salts produced microcrystalline

Table 1
Crystallographic data[a] for compounds [(cyclam)CoCl(C_2Ph)]BPh_4 (**1b**), [(cyclam)$_2Co_2Cl_2$(μ-*p*-DEB)]Cl_2·2MeOH (**2a**·2MeOH), [(cyclam)$_3Co_3Cl_3$(TEB)]Cl_3·5MeOH (**3a**·5MeOH), [(cyclam)$_2Co_2Cl_2$(HTEB)]Cl_2·2MeOH (**4a**·2MeOH), and [(cyclam)Co(C_2Ph)$_2$]BPh_4·2THF (**5**·2THF).

	1b	**2a**·2MeOH	**3a**·5MeOH	**4a**·2MeOH	**5**·2THF
Formula	$C_{42}H_{49}BClCoN_4$	$C_{32}H_{60}Cl_4Co_2O_2N_8$	$C_{47}H_{95}Cl_6Co_3\ N_{12}O_5$	$C_{36}H_{68}Cl_4Co_2N_8O_4$	$C_{58}H_{70}BCoN_4O_2$
Formula weight	715.04	848.55	1297.84	911.01	924.92
Color, habit	orange needle	orange prism	orange prism	orange prism	yellow needle
T (K)	120(2)	100(2)	120(2)	120(2)	120(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
Z	4	2	2	4	4
a (Å)	16.0376(4)	14.3852(3)	8.617(1)	18.4701(3)	15.911(1)
b (Å)	21.5470(5)	9.6749(2)	15.070(2)	9.7704(1)	18.464(1)
c (Å)	21.1968(5)	17.4624(4)	24.676(3)	28.8748(4)	17.139(1)
α (°)	90	90	72.656(3)	90	90
β (°)	92.266(1)	119.535(1)	89.289(4)	94.850(1)	97.391(2)
γ (°)	90	90	80.701(4)	90	90
V ($Å^3$)	7319.1(3)	2114.52(8)	3016.4(6)	4472.8(1)	4993.8(5)
D_{calc} (g/cm^3)	1.298	1.433	1.429	1.353	1.230
Goodness-of-fit (GOF)	0.996	1.038	1.084	1.068	1.031
R_1 (wR_2)[b], %[c]	4.58 (11.14)	3.98 (9.83)	5.21 (13.96)	5.30 (14.19)	4.63 (1128)
R_1 (wR_2)[b], %[d]	6.96 (12.83)	5.55 (10.49)	7.01 (15.15)	7.54 (15.67)	8.80 (13.27)
CCDC reference #	830633	830634	830635	830636	830637

[a] Obtained with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation.
[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{|\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]|\}^{1/2}$.
[c] For data where $I > 2\sigma(I)$.
[d] For all data.



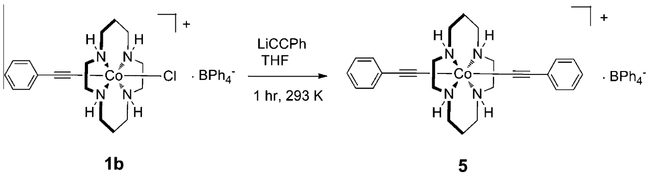
Scheme 1. Synthetic conditions used for the preparation of Co^{3+} acetylide complexes **1b**, **2b**, **3b**, and **4b**. Reaction conditions: *a* = MeOH, excess Et_3N, reflux 24 h; *b* = MeOH, 4 eq. Et_3N per Co^{3+}, reflux 24 h; *c* = excess $NaBPh_4$, MeOH.

samples that were found to be analytically pure. In most cases, the BPh_4-containing crystals were not suitable for X-ray analysis, although a structure of the mononuclear complex **1b** was obtained (Section 2.2.2), and we recently reported a structure of the mixed bridging ligand salt [1,3-{(cyclam)$_2Co_2Cl_2C_2$}-5-(C_2H)$_{0.88}$(Br)$_{0.12}$-benzene](BPh_4)$_2$ [30].

The use of dehydrohalogenation conditions allows for the retention of one chloride ligand *trans* to the acetylide in this family of complexes. Attempts to prepare the bis-alkynyl complex **5** directly from *trans*-[(cyclam)CoCl$_2$]Cl and excess phenylacetylene only afford the mono-substituted **1a**, as evidenced from mass spectra obtained on the reaction mixtures. Based on the tetradentate chelating ligand environment and the propensity for Co^{III} to undergo dissociative-type ligand substitution reactions [31], and noting Field's observation of monosolvento species in related isoelectronic Fe^{II} complexes [22], it seems reasonable that the substitution of acetylide for chloride proceeds through a methanol complex. In that case, we suspect bis-alkynyl complexes are not observed under dehydrohalogenation conditions because the *trans*-[(cyclam)Co(C_2R)Cl]$^+$ species is less electron-rich compared to *trans*-[(cyclam)CoCl$_2$]$^+$; the dissociation equilibrium to form the putative *trans*-[(cyclam)Co(C_2R)(MeOH)]$^{2+}$ species is disfavored due to a trans influence of the acetylide. Notwithstanding, isolation of half-substituted complexes is important for the controlled, rational preparation of larger assemblies, especially considering the propensity for polymeric metal acetylide compounds to form via other synthetic methods [21].

The increased solubility of the tetraphenylborate salts **1b**–**4b** in nonpolar solvents like tetrahydrofuran allows for the application of additional ligand substitution methods beyond dehydrohalogenation. A common way to exchange halide ligands for acetylides proceeds via salt metathesis involving alkali metal acetylides [10], which are only stable in ethereal solvents. Thus, the synthesis of **5** was achieved by combining a slight excess of lithium phenylacetylide with **1b** in THF (Scheme 2). The product was isolated from the lithium chloride byproduct by recrystallization. The isolation of **5** is the first known example of stepwise acetylide ligand substitution in a Co^{III} system. Related to stepwise acetylide substitution, Field previously demonstrated differential reactivity at a low-spin Fe^{II} center by using sequential dehydrohalogenation and photochemical reactions starting with [(dmpe)$_2$FeCl(CH_3)] (dmpe = 1,2-bis(dimethylphosphino)ethane) [24].

The synthesis of dinuclear **4a** was achieved by mixing 2.1 equivalents of [(cyclam)CoCl$_2$]Cl with H_3TEB and four equivalents of triethylamine per Co in methanol solution. Attempts to synthesize **4a** using less triethylamine resulted in greatly diminished yields, whereas a larger excess of base appears to favor the formation of **3a**. Unlike trinuclear **3a**, **4a** is sparingly soluble in ethanol; rinsing the product with ethanol essentially removes all triethylammonium hydrochloride and undesired mono- and tri-nuclear Co^{3+} acetylide species. Presumably, mono-, di- and trinuclear complexes are all formed during the reaction, but the reaction stoichiometry favors the formation of **4a**. The wedge-like topology of **4b** would



Scheme 2. Synthesis of bis-acetylide complex **5** from the chloro acetylide complex **1b**. The tetraphenylborate anion allows the complex in **1b** to be soluble in tetrahydrofuran.

at first appear to be useful in the schematic assembly of metallodendrimers, for example when combined with one-third of an equivalent of trinuclear **3b**. However, attempts to lithiate the acetylene moiety of **4b** were thwarted by the presence of the amine hydrogens on the cyclam ligands, which appear to be more reactive toward *n*-BuLi than the acetylene hydrogen. Although a direct comparison of the pK_a values for the relevant protons is not available, a measured amine pK_a for $[(\text{cyclam})\text{Co}(\text{CO}_3)]^+$ in H_2O (10.76) is significantly lower than that for phenylacetylene in dimethylsulfoxide (28.7) [32,33].

The IR spectra of **1b**, **2b**, and **3b** each contain a single absorbance between 2114 and 2133 cm^{-1} that corresponds to the stretching frequency of the acetylide ligand when coordinated to the Co^{III} ion. In **4b**, two separate absorbances should be visible due to the different acetylene environments; however a single broad peak centered at 2122 cm^{-1} masks the contribution from the non-bridging acetylene, which absorbs at 2109 cm^{-1} for H_3TEB. However, IR evidence for the non-bridging acetylene in **4b** is found in the sharp acetylenic C–H stretch that is observed at 3313 cm^{-1}. For the bis-acetylide complex **5**, the acetylide stretching frequency moves to lower energies and is found at 2100 cm^{-1}.

3.2. X-ray crystal structures of Co^{III} acetylide complexes

Crystals of mononuclear **1b** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether vapor into a concentrated solution of **1b** in tetrahydrofuran. The compound crystallizes in the $P2_1/c$ space group with two molecules in the unit cell. The coordination geometry about each Co^{3+} center is essentially octahedral, with the equatorial positions occupied by the nitrogen atoms from the cyclam ligand (Fig. 1). The chloride and acetylide ligands are apically coordinated with metal-ligand distances of *ca.* 2.3 and 1.9 Å, respectively (Table 2).

Similar local coordination geometries are observed for the di- and tri-nuclear complexes **2a**, **4a**, and **3a** as for mononuclear **1b** (Figs. 1 and 2). Bond distances and angles measured for the complex cation in the structure of **4a** (Table 2) are statistically identical to those measured for $[1,3\text{-}\{(\text{cyclam})_2\text{Co}_2\text{Cl}_2\text{C}_2\}\text{-}5\text{-}(\text{C}_2\text{H})_{0.88}(\text{Br})_{0.12}\text{-benzene}]^{2+}$ [30].

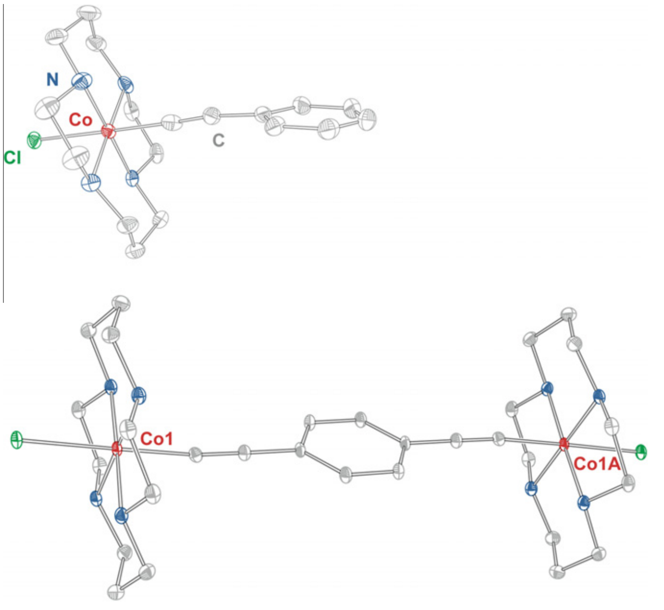


Fig. 1. X-ray structures of the complex cations in **1b** (top) and **2a**·2MeOH (bottom), with thermal ellipsoids rendered at 40% probability. Hydrogen atoms have been omitted for clarity. The complex in **2a**·2MeOH resides on an inversion center. Red, blue green, and gray ellipsoids represent cobalt, nitrogen, chloride, and carbon atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The structure of the mononuclear bis-acetylide complex **5** was also determined by X-ray crystallography (Fig. 3). The coordination geometry of the Co^{3+} center is similar to the chloro-acetylide complex **1b** with the exception of the second phenylacetylide ligand in place of the chloride. Only minor differences in bond lengths and angles are observed among the series of chloro-acetylide complexes (Table 2). When compared to the X-ray structure of $[\text{Co}(\text{cyclam})\text{Cl}_2]\text{Cl}$ [34], the Co–Cl bond in all of the chloro-acetylide complexes studied herein is slightly elongated, which is likely due to the trans influence of the acetylide ligand. Substitution of the second chloride ligand for another acetylide in **5** causes a significant elongation in the Co–C bond length compared to **1a**, along with a concomitant contraction in the carbon–carbon triple bond distance. Here, a decrease in the Co–C bonding interaction would be expected to lead to a reduction in M–L π-backbonding, thereby giving a shorter C–C bond [35,36].

3.3. Cyclic voltammetry

Although the Co^{III} complexes reported here are meant to serve as structural models for future paramagnetic dendritic building blocks, we note that there are several reported examples of Co^{II}-based single-molecule magnets [37–39]. Thus, we undertook a study of the compounds' electrochemical behaviors to probe the possibility of reducing the Co^{III} salts to neutral, paramagnetic Co^{II}-containing analogs. To our knowledge, there are no reports of electrochemical characterization of cobalt acetylide complexes in the literature.

In acetonitrile solution, crystals of trinuclear **3a** display an irreversible reduction during an initial cathodic scan at −1.52 V. During subsequent scans, a quasi-reversible wave grows in at $E_{1/2} = -0.74$ V while the wave at −1.52 is diminished (Fig. 4). We

Table 2
Selected measured interatomic distances (Å) and angles (°) for the X-ray structures of $[(\text{cyclam})\text{CoCl}_2]\text{Cl}$ [34], $[(\text{cyclam})\text{CoCl}(\text{C}_2\text{Ph})]\text{BPh}_4$ (**1b**), $[(\text{cyclam})_2\text{Co}_2\text{Cl}_2(\mu\text{-}p\text{-DEB})]\text{Cl}_2\cdot 2\text{MeOH}$ (**2a**·2MeOH), $[(\text{cyclam})_3\text{Co}_3\text{Cl}_3(\text{TEB})]\text{Cl}_3\cdot 5\text{MeOH}$ (**3a**·5MeOH), $[(\text{cyclam})_2\text{Co}_2\text{Cl}_2(\text{HTEB})]\text{Cl}_2\cdot 1.8\text{MeOH}$ (**4a**·2MeOH), and $[(\text{cyclam})\text{Co}(\text{C}_2\text{Ph})_2]\text{-BPh}_4\cdot 2\text{THF}$ (**5**·2THF).

	$[\text{Co}(\text{cyclam})\text{Cl}_2]\text{Cl}$ [34]	**1b**[a]	**2a**·2MeOH	**3a**·5MeOH	**4a**·2MeOH	**5**·2THF[a]
Co–N	1.974[4][b]	1.975[2]	1.979[7]	1.979[6]	1.978[3]	1.983[2]
Co–Cl	2.253(3)	2.3089[5]	2.3123(4)	2.320[5]	2.3149(7)	–
Co–C	–	1.898[2]	1.885(2)	1.881[4]	1.878(3)	2.001[3]
C≡C	–	1.160[3]	1.210(2)	1.193[5]	1.195(4)	1.113[4]
C≡CH	–	–	–	–	1.189(7)	–
Co–C≡C	–	174.5[5]	173.4(1)	174.7[3]	174.6(3)	175.5[2]
C–Co–Cl	–	179.0[3]	179.17(5)	178.6[1]	178.52(9)	–

[a] These structures each have two complex residues in the asymmetric unit; bond lengths and angles are averaged from both residues.

[b] Square brackets [ ] represent standard uncertainties for averaged metric parameters and round brackets represent standard uncertainties obtained from a single interatomic distance or angle.

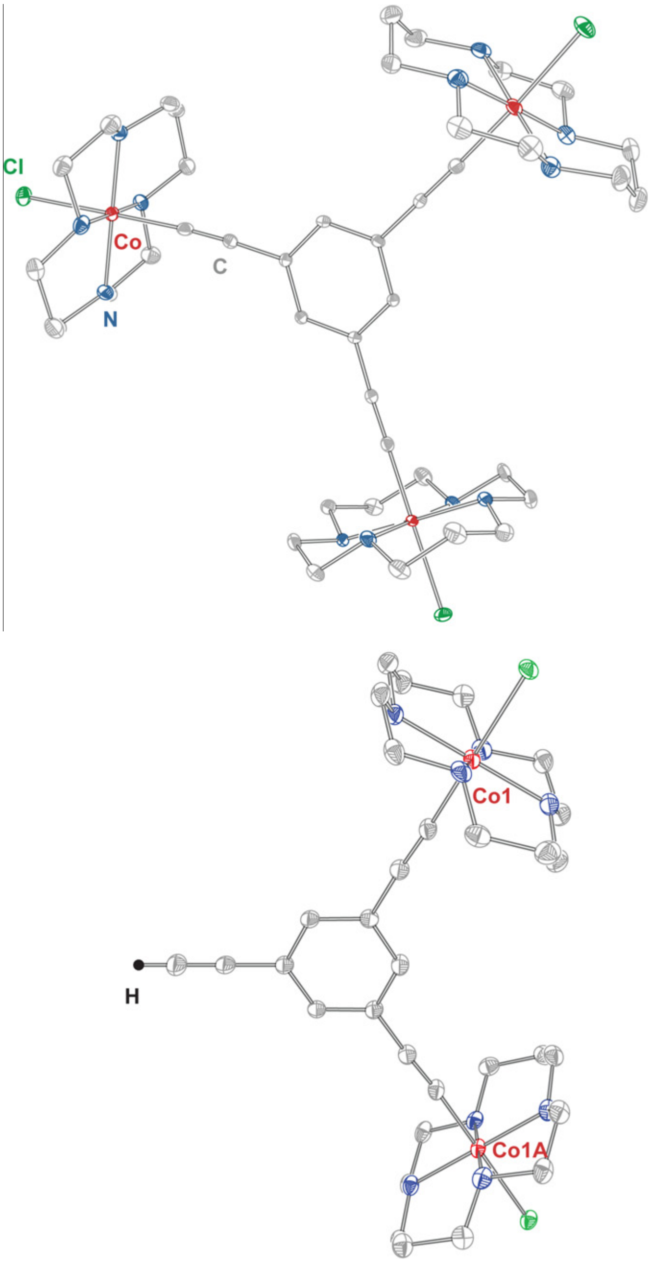


Fig. 2. X-ray structures of the complex cations in **3a**·5MeOH (top) and **4a**·2MeOH (bottom), with thermal ellipsoids rendered at 40% probability. With the exception of the acetylenic H, hydrogen atoms have been omitted for clarity. The complex in **3a**·5MeOH resides on a general position, while the complex in **4a**·2MeOH resides on a twofold rotation axis. The color scheme is the same as Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

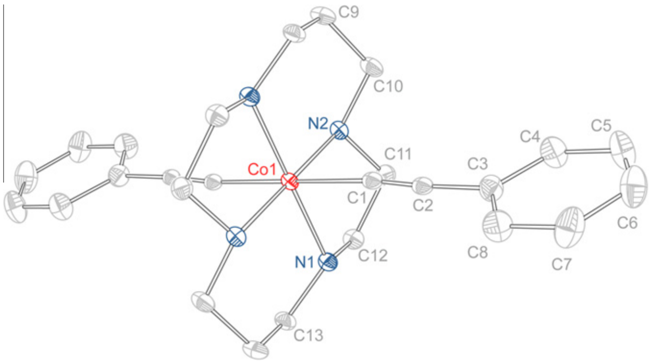


Fig. 3. X-ray structure of the complex cation in **5**·2THF, with thermal ellipsoids rendered at 40% probability. Hydrogen atoms have been omitted for clarity. The complex resides on an inversion center and unique atoms are labeled (online). The color scheme is the same as Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

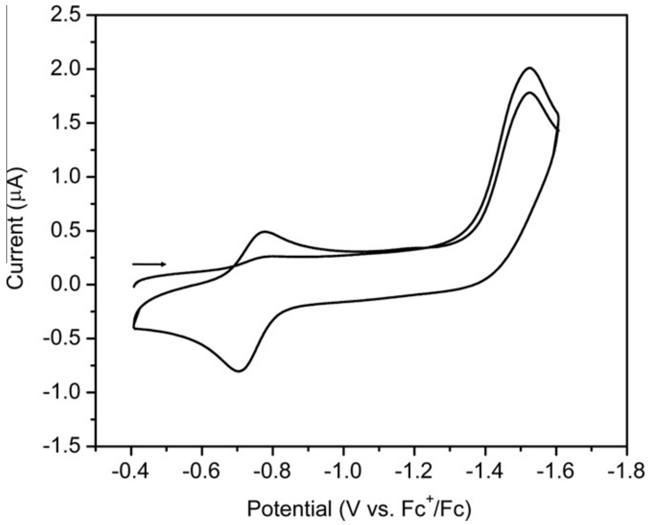


Fig. 4. Cyclic voltammogram obtained for **3a** in acetonitrile. The arrow indicates the starting point and direction of the first scan. The slight increase in current at −0.75 V during the initial scan is likely due to a [(cyclam)CoCl$_2$]Cl impurity. See text for further explanation of the electrochemical behavior.

note that a small amount of this wave is detectable even in the first scan. This redox behavior is consistent with a three electron reduction of tri-nuclear **3a** at highly negative potentials, followed by dissociation of the [(cyclam)CoCl]$^{2+}$ units from the TEB^{3-} ligand. Increased lability of Co^{2+} ions relative to Co^{3+} is the probable reason for this dissociation. In acetonitrile, the resulting vacant coordination site at the Co^{2+} center is likely occupied by a solvent molecule. This monomeric complex can then be reversibly oxidized, accounting for the quasi-reversible wave at −0.74 V. Supporting this proposed electrochemical reaction, a cyclic voltammogram of [(cyclam)CoCl$_2$]Cl in acetonitrile exhibits a single reversible Co^{3+}/Co^{2+} redox couple at −0.73 V. To investigate whether a less coordinating solvent would prevent ligand dissociation upon reduction, cyclic voltammograms of **1** and **2b** in tetrahydrofuran were also recorded. However, irreversible reduction peaks were also observed for these salts. The bis-acetylide complex **5** also exhibits non-reversible reduction behavior, indicating that replacement of a good leaving group (chloride) with phenylacetylide does not promote reversible reduction behavior on even electrochemical timescales.

As stated above, no electrochemically-characterized cobalt acetylide complexes have been reported. The closest literature comparison is Bianchini and co-workers' study of the redox behavior of trigonal bipyramidal Rh^{I} complexes with a NP$_3$(σ-C$_2$R) first coordination sphere (NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$) [40]. Starting with the Rh^{I} congener, electrochemical measurements indicate that the one- and two-electron oxidized complexes are electrochemically accessible, but the Rh^{III}–containing species could only be observed with fast electrochemical scan rates. Comparing the complexes, the Rh species enjoys better metal-ligand overlap (through lower coordination number and softer ligands) and is less labile as a divalent species. In that regard, the lack of reversible electrochemical behaviors for the Co^{III} acetylide complexes reported here is not surprising.

4. Conclusions and outlook

We have described the syntheses and structural characterizations of mono-, di-, and tri-nuclear Co^{III}(cyclam) complexes bearing a mixture of ethynylbenzene and chloride ligands at the axial coordination sites. The product nuclearity is dependent on reaction stoichiometry: isolation of dinuclear **4a** illustrates that partially substituted species can be obtained by adjusting the amounts of metal precursor complex and organic base. Importantly, the feasibility of stepwise ligand substitution has been demonstrated in the synthesis of the bis(acetylide) complex **5** by using lithium phenylacetylide to react with **1b** in tetrahydrofuran.

Cyclic voltammograms of all complexes in either acetonitrile or tetrahydrofuran demonstrate that isolation of the paramagnetic Co^{II} analogs is impeded by a secondary chemical reaction (rapid ligand exchange) upon reduction. The electrochemical data is consistent with the Co-acetylide bond breaking at negative potentials and that the appearance of a subsequent reversible redox couple is due to a mononuclear $Co^{III/II}$ species. Attempts to prepare larger complexes by combining a lithiated analog of **4b** with one third of an equivalent of **3b** were not successful. This is likely due to the presence of amine hydrogen atoms in all complexes which seem to preferentially react with *n*-BuLi over acetylene hydrogen atoms. The use of protected equatorial ligands such as 1,2-bis(dimethylphosphino)ethane (dmpe) for future metallodendritic building blocks, which would prevent such undesirable side reactions, is being explored. Alternatively, replacement of the acetylene moiety in **4b** with a trialkyltin substituent may allow for the formation of a first-generation dendrimer when combined with three equivalents of **3b** under CuI-catalyzed conditions.[21] The utility of this and related routes are currently being investigated, toward the synthesis of higher nuclearity species.

Acknowledgements

This research was supported by Colorado State University and the ACS Petroleum Research Fund (44691-G3). We thank NSF–REU (CHE-1004924) for partial support of EAH and SMM. We thank Prof. C.M. Elliott for assistance with the cyclic voltammetry measurements and interpretations.

Appendix A. Supplementary material

CCDC 830633–830637 contain the supplementary crystallographic data for compounds **1**–**5**, respectively. Color versions of Figs. 1–3 (pdf). ^1H NMR spectra of compounds **1b**, **2b**, **3b**, **4b**, and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.051.

References

[1] J.-M. Lehn, Supramolecular Chemistry, VCH Publishers, Weinheim, 1995.
[2] K.J. Nelson, A.G. DiPasquale, A.L. Rheingold, M.C. Daniels, J.S. Miller, Inorg. Chem. 47 (2008) 7768.
[3] P. Angaridis, J.F. Berry, F.A. Cotton, C.A. Murillo, X. Wang, J. Am. Chem. Soc. 125 (2003) 10327.
[4] S.C. Lee, R.H. Holm, Chem. Rev. 104 (2003) 1135.
[5] A. Müller, F. Peters, M.T. Pope, D. Gatteschi, Chem. Rev. 98 (1998) 239.
[6] C. Cañada-Vilalta, T.A. O'Brien, E.K. Brechin, M. Pink, E.R. Davidson, G. Christou, Inorg. Chem. 43 (2004) 5505.
[7] T.C. Stamatatos, A.G. Christou, S. Mukherjee, K.M. Poole, C. Lampropoulos, K.A. Abboud, T.A. O'Brien, G. Christou, Inorg. Chem. 47 (2008) 9021.
[8] L.M.C. Beltran, J.R. Long, Acc. Chem. Res. 38 (2005) 325.
[9] Z.H. Ni, H.Z. Kou, L.F. Zhang, C.H. Ge, A.L. Cui, R.J. Wang, Y.D. Li, O. Sato, Angew. Chem., Int. Ed. 44 (2005) 7742.
[10] N. Long, C.K. Williams, Angew. Chem., Int. Ed. 42 (2003) 2586.
[11] K. Onitsuka, S. Takahashi, Top. Curr. Chem. 228 (2003) 39.
[12] T. Ren, Organometallics 24 (2005) 4854.
[13] A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, Organometallics 18 (1999) 5195.
[14] T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, Organometallics 19 (2000) 5235.
[15] F. Paul, A. Bondon, G. da Costa, F. Malvolti, S. Sinbandhit, O. Cador, K. Costuas, L. Toupet, M.-L. Boillot, Inorg. Chem. 48 (2009) 10608.
[16] K. Onitsuka, M. Fujimoto, N. Ohshiro, S. Takahashi, Angew. Chem., Int. Ed. 38 (1999) 689.
[17] A.M. McDonagh, C.E. Powell, J.P. Morrall, M.P. Cifuentes, M.G. Humphrey, Organometallics 22 (2003) 1402.
[18] T. Weyland, K. Costuas, A. Mari, J.-F. Halet, C. Lapinte, Organometallics 17 (1998) 5569.
[19] H. Oshio, M. Nakano, Chem. Eur. J. 11 (2005) 5178.
[20] B. Giese, M. Zehnder, M. Neuburger, F. Trach, J. Organomet. Chem. 412 (1991) 415.
[21] M.S. Khan, N.A. Pasha, A.K. Kakkar, P.R. Raithby, J. Lewis, K. Fuhrmann, R.H. Friend, J. Mater. Chem. 2 (1992) 759.
[22] L.D. Field, A.V. George, T.W. Hambley, Inorg. Chem. 29 (1990) 4565.
[23] L.D. Field, A.V. George, F. Laschi, E.Y. Malouf, P. Zanello, J. Organomet. Chem. 435 (1992) 347.
[24] L.D. Field, A.J. Turnbull, P. Turner, J. Am. Chem. Soc. 124 (2002) 3692.
[25] B. Bosnich, C.K. Poon, M.L. Tobe, Inorg. Chem. 4 (1965) 1102.
[26] E. Weber, M. Hecker, E. Koepp, W. Orlia, M. Czugler, I. Csöregh, J. Chem. Soc., Perkin Trans. 2 (1988) 1251.
[27] Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2008.
[28] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2004) 112.
[29] T. Weyland, C. Lapinte, G. Frapper, M.J. Calhorda, J.-F. Halet, L. Toupet, Organometallics 16 (1997) 2024.
[30] W.A. Hoffert, M.P. Shores, Acta Crystallogr., Sect. E 67 (2011) m853.
[31] C.H. Langford, H.B. Gray, Ligand Substitution Processes, W.A. Benjamin, 1966.
[32] T.P. Dasgupta, Inorg. Chim. Acta 20 (1976) 33.
[33] F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456.
[34] R. Ivanikova, I. Svoboda, H. Fuess, A. Maslejova, Acta Crystallogr., Sect. E 62 (2006) m1553.
[35] C.-Y. Wong, C.-M. Che, M.C.W. Chan, J. Han, K.-H. Leung, D.L. Phillips, K.-Y. Wong, N. Zhu, J. Am. Chem. Soc. 127 (2005) 13997.
[36] W.Y. Wong, C.L. Ho, Coord. Chem. Rev. 250 (2006) 2627.
[37] K.W. Galloway, A.M. Whyte, W. Wernsdorfer, J. Sanchez-Benitez, K.V. Kamenev, A. Parkin, R.D. Peacock, M. Murrie, Inorg. Chem. 47 (2008) 7438.
[38] D. Wu, D. Guo, Y. Song, W. Huang, C. Duan, Q. Meng, O. Sato, Inorg. Chem. 48 (2009) 854.
[39] D. Yoshihara, S. Karasawa, N. Koga, J. Am. Chem. Soc. 130 (2008) 10460.
[40] C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, F. Laschi, P. Zanello, F.M. Ottaviani, Organometallics 9 (1990) 360.