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Synthesis and Properties of Cobalt(III) Complexes of 4-Substituted Pyridine-Capped Dioxocyclams

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Cobalt(III) acetate and cyanide complexes of a series of 5,12-dioxocyclams capped across the 1,8-position by 4-substituted pyridines or pyrazine were synthesized and fully characterized. Both the spectroscopic and structural parameters for these complexes were remarkably insensitive to the electronic nature of the capping group, which ranged from the π-accepting pyrazine group to the σ-donating 4-[(dimethylamino)phenyl]pyridyl group. All of the complexes underwent an irreversible, one-electron reduction [Co(III) → Co(II)] at potentials ranging from –0.95 V vs saturated calomel electrode (SCE) for the pyrazine-capped cobalt acetate complex to –1.36 V vs SCE for the pyridine-capped cobalt cyanide complexes. Pyridine-capped cobalt(III) cyanide complex **6a** underwent reaction with $Rh_2(OAc)_4$ and ruthenium(II) phthalocyanine[bis(benzonitrile)] to form tetrametallic (**7**) and trimetallic (**8**) complexes through coordination bridging by the cyanide nitrogen lone pair. These complexes represent two quite different structural types for cyanide-bridged polymetallics. Complex **7** has a relatively long (2.192 Å) cyanide N-to-Rh bond, and the C≡N—Rh bond angle (157.6°) is strongly distorted from linear. In contrast, complex **8** has a substantially shortened cyanide N-to-Ru bond (2.017 Å) and an almost linear arrangement along the entire bridging axis of the molecule.

Introduction

Following the discovery that azapenams were readily synthesized by the photochemical reaction of chromium alkoxycarbene complexes with imidazolines and the unexpected acid-catalyzed dimerization of these to produce, after reduction, 5,12-dioxocyclams (**1**; Figure 1),[1] efforts in this research group were directed toward the development of the synthesis and complexation chemistry of functionalized members of this relatively unstudied[2] class of macrocyclic ligand. Thus, optically active dioxocyclams were available from optically active imidazolines,[3] while bis(dioxocyclams) linked through the 6 and 13 positions by alkyl chains,[4] diether linkages,[5] or polyether chains[6,7] were available from the corresponding bis(carbene) complexes. The two secondary amines in 5,12-dioxocyclams are nucleophilic and undergo

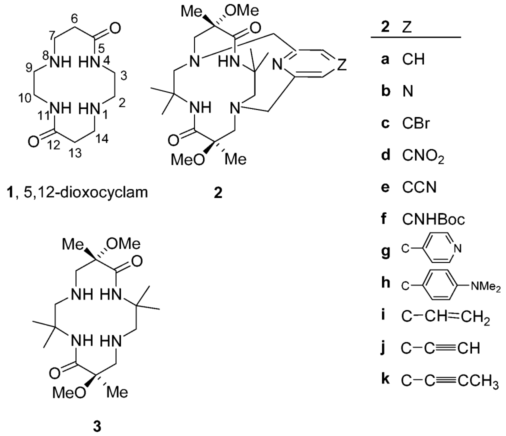

Figure 1. Cyclams.

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reaction with a range of electrophiles. Under appropriate conditions, bis(electrophiles) will “cap” these positions, producing macrobicyclic compounds having various types of metal-binding cavities.[8] Research in these laboratories has centered on the synthesis of dioxocyclams capped by 4-substituted pyridines (or pyrazine) to give macrocyclic ligands having potential metal-coordination sites both within the cavity and at the 4-substituent of the cap (**2a**−**k**; Figure 1).[9]

Although cyclams themselves readily coordinate to most transition metals, as well as some lanthanides,[10] dioxocyclams are somewhat more selective. 5,7-Dioxocyclams preferentially coordinate Ni(II), Co(II), Pd(II), Cu(II), and Pt(II),[11] while Ni(II) and Cu(II) complexes are most common for 5,12-dioxocyclams. Capped dioxocyclams **2**, being more rigid than uncapped dioxocyclams and having an additional coordination site within the macrocyclic cavity, are more difficult to coordinate to metals. Copper(II) complexes of **2a**,[9a] **2b**,[9c] and **2d**−**g**[9b] have been reported from these laboratories. In contrast to uncapped dioxocyclam complexes of copper, which undergo reversible Cu(II) → Cu(III) electrochemical oxidation,[12] the copper(II) complexes of both **2b** and pyridine-capped **1**[13] underwent irreversible, ligand-based oxidation.

A major impetus for the synthesis of ligands **2a**−**k** was to provide ligands into which redox-active metals could be incorporated and to use the external coordination site to generate extended metal−ligand arrays via coordinate linkages.[14] If the bridging ligand can transmit electronic information, the resulting coordination oligomers may have unusual electronic or magnetic properties.[15] We have already shown[9c] that the copper(II) complex of pyrazine-capped cyclam **2b** can coordinate to both metals in $Rh_2(OAc)_4$ through its remote pyrazine nitrogen to form a tetrametallic species in which the two copper(II) units are weakly antiferromagnetically coupled. However, because the copper(II) complex of **2b** is relatively redox inactive and because it can only coordinate to one metal center, complexes of redox-active, octahedral metals having an additional external coordination site were desired. The syntheses of such complexes of cobalt(III) are described below.

Experimental Section

General Procedures. Acetonitrile was distilled over calcium hydride. Methanol was distilled over calcium hydride and dried over molecular sieves. NMR spectra were recorded on a Varian JS-300 spectrometer. IR spectra were recorded on a Nicolet Magna-IR 760 spectrometer. UV−vis spectra were recorded on an Agilent G 1103 spectrometer. Electrochemical measurements were conducted with an EG&G, Princeton Applied Research, model 75 universal programmer, model 179 digital coulometer, and model 173 potentiostat/galvanostat. The complex was dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile or CH_2Cl_2. The working electrode was glassy carbon, and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE), and potentials were reported versus SCE. Cyclic voltammograms were obtained at a scan rate of 100 mV/s under an argon atmosphere at 23 °C. The glassy carbon electrode was cleaned before each run by hand polishing on a buffing pad with fine-grit alumina using deionized water. It was then rinsed repeatedly with the solvent used and dried with a Kim wipe. Data were plotted with the x axis equal to 100 mV/cm. Microwave reactions were performed in a GE countertop microwave oven, model JES1339WC, which had a capacity of 1.3 ft^3 (1.21 L) and a wattage output of 1100 W. X-ray crystallographic studies were performed on a Bruker SMART CCD diffractometer, and the intensity of the data set was integrated using Bruker SAINT software. The structures were solved using Bruker SHELXTL V6.1 software. Compounds **2a**−**g** and **2i**−**k** were synthesized by published procedures.[9]

4-[4-(*N*,*N*-Dimethylamino)phenyl]pyridine-Capped Dioxocyclam (2h). 4-Bromo-*N*,*N*-dimethylaniline (4.0 g, 20 mmol) was dissolved in distilled THF (80 mL), and the reaction was cooled to −78 °C, followed by the addition of *n*-BuLi (1.6 M in hexane, 13.8 mL, 22.0 mmol) by a syringe. After stirring for 1.5 h at −78 °C, $B(OEt)_3$ (neat, 5.2 mL, 30 mmol) was added by a syringe, and the reaction was stirred for 0.5 h at −78 °C, warmed to ambient temperature, and stirred for an additional 1.5 h. Saturated NH_4Cl (80 mL) was added in one portion, and the reaction was stirred for 2 h. The two layers were partitioned, and the aqueous layer was extracted with CH_2Cl_2 (4 × 100 mL). The organic layers were combined, and the solution was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Washing the white solid with EtOAc/hexane (10 mL/10 mL) and drying under vacuum afforded the desired 4-(*N*,*N*-dimethylamino)phenylboronic acid (2.84 g, 17.2 mmol): yield 86%; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.1 Hz, 2H), 3.07 (s, 6H).

For the preparation of **2h**, 4-bromopyridine-capped dioxocyclam **2c** (55 mg, 0.10 mmol), 4-(*N*,*N*-dimethylamino)phenylboronic acid (25 mg, 0.15 mmol), K_2CO_3 (21 mg, 0.15 mmol), and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) were added to an argon-flushed pressure tube. After dissolution in distilled MeOH (5 mL), the reaction was degassed by repeating a freeze−pump−thaw sequence three times using liquid N_2 and then purged with argon gas. The pressure tube

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was tightly sealed and placed in a 95−110 °C oil bath with stirring for 3 days. The resulting brownish reaction mixture was cooled to ambient temperature, passed through a Celite pad, washed with excess MeOH, and concentrated in vacuo. Purification by flash silica gel column chromatography (1:4 MeOH/EtOAc) afforded the light green product (54 mg, 0.09 mmol): yield 91%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.21 (s, 1H), 8.16 (s, 1H), 7.59 (d, $J = 8.8$ Hz, 2H), 7.13 (s, 1H), 7.10 (s, 1H), 6.80 (d, $J = 9.2$ Hz, 2H), 4.21−3.95 (m, 4H), 3.45 (s, 3H), 3.23 (d, $J = 13.6$ Hz, 1H), 3.05 (s, 6H), 3.00−2.95 (m, 4H), 2.89 (d, $J = 14.4$ Hz, 1H), 2.62 (d, $J = 14.0$ Hz, 1H), 2.56 (s, 3H), 2.40 (d, $J = 14.4$ Hz, 1H), 1.48 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H), 1.22 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.6, 173.0, 163.2, 158.7, 151.3, 149.6, 127.9, 125.3, 115.7, 115.67, 112.6, 82.6, 79.8, 74.6, 72.7, 69.5, 67.5, 65.8, 64.7, 56.0, 54.9, 52.0, 50.3, 40.5, 26.3, 25.7, 23.7, 23.5, 19.3; FT-IR (film) 1658 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (ϵ) 329 (22 200), 411 (8900); HRMS (FAB$^+$, *m/z*) calcd for $C_{33}H_{51}N_6O_4$ (M + H$^+$) 595.3972, found 595.3967.

Procedure for the Preparation of a Commercial Microwave Oven for Reaction Use. ***Caution!*** *All operations involving microwave techniques were carried out in a hood behind safety shields.* To prepare a commercial microwave oven for reaction conditions, the focus point of the microwave radiation must be determined. The rotation wheel was removed from under the glass plate of the microwave. The plate was then covered evenly with 4-Å molecular sieves. The microwave was then operated at high power until one area of the sieves started to glow. This spot was marked on the glass plate. This determined the focus point on the horizontal plane. For the vertical plane, a pressure tube was rotated 360° on the marked spot until maximum microwave radiation was found. This was determined by the preparation of the cobalt(III) complex **5a**. When not in the focus point, the tube would become warm but the solution would remain pink. When in the focus point, the pressure tube would become warm and the solution would turn purple. The direction the tube should point was then marked on the glass plate. This setup procedure is necessary only once to find the focus point. All reactions were performed behind a blast shield starting at a power level of 10% and a time of 30 s. The power level and time were increased until appropriate conditions were determined, and all reactions were cooled to room temperature between microwave sets. The power level and time were never increased above 20% and 3 min, respectively. To prevent explosions or bumping, all reactions were shaken prior to a microwave set. This is especially important if the reaction forms a precipitate. The precipitate must be suspended in solution prior to each microwave set. When all of these precautions were followed, our laboratories safely performed several thousand cycles with no adverse side affects such as explosions.

Experimental Procedure for the Preparation of Capped Dioxocyclams in the Microwave. Dioxocyclam **3** (80.8 mg, 0.216 mmol), capping reagent (0.260 mmol), and *i*-Pr_2NEt (0.3 mL, 1.735 mmol) were combined in a screw-cap pressure tube. The mixture was dissolved in 5 mL of CH_3CN and then degassed with argon for 5 min. The reaction vessel was sealed tightly and then microwaved for periods of 2 min at a power level of 20% until no starting material was detected by thin-layer chromatography (TLC; 20−25 cycles). The tube was allowed to cool to room temperature between microwave sets. The solvent was removed in vacuo, then brought up in CH_2Cl_2, and washed with 2 × 10 mL of saturated $NaHCO_3$. The organic layer was isolated and dried over Na_2SO_4. The solvent was removed in vacuo. Purification by flash chromatography on silica gel (5% MeOH/CH_2Cl_2) afforded the product as a white solid.

Pyridine-Capped Dioxocyclam 2a. Purification by flash chromatography on silica gel (95:5 CH_2Cl_2/MeOH) afforded a white solid in 69% yield.

Pyrazine-Capped Dioxocyclam 2b. Purification by flash chromatography on silica gel (1.5:1 hexanes/THF) afforded a white solid in 40% yield.

4-Bromopyridine-Capped Dioxocyclam 2c. Purification by flash chromatography on silica gel (97:3 $CHCl_3$/MeOH) afforded a white solid in 75% yield.

4-Cyanopyridine-Capped Dioxocyclam 2e. Purification by flash chromatography on silica gel (97:3 CH_2Cl_2/MeOH) afforded a white solid in 64% yield.

Preparation of Cobalt(III) (Ring-Opened 2a) Acetate Complex (4a). Method A. 5,12-Dioxocyclam **3** (40 mg, 0.1 mmol), Co($CH_3CO_2)_2\cdot 4H_2O$ (213 mg, 0.855 mmol), and *i*-Pr_2NEt (0.15 mL, 0.86 mmol) were combined in a screw-cap pressure tube. The mixture was suspended in MeOH (4 mL) and then degassed with argon for 20 min. The reaction vessel was sealed tightly and microwaved an average of 15 times for periods of 2 min at a power level of 20%. The tube was allowed to cool to room temperature between microwave sets. The solution was initially clear pink in color. After each microwave cycle, the solution became deep purple. The resulting purple solution was passed through a Celite pad and concentrated under vacuum. Purification by flash chromatography on silica gel (10% EtOH/CH_2Cl_2) gave a purple solid **4a** in 31% yield.

Method B. 5,12-Dioxocyclam **3** (60 mg 0.16 mmol), Co($CH_3CO_2)_2\cdot 4H_2O$ (320 mg, 1.2 mmol), and *i*-Pr_2NEt (0.220 mL, 1.26 mmol) were combined in a screw-cap pressure tube. The mixture was suspended in MeOH (6 mL) and then degassed with argon for 20 min. The reaction vessel was sealed tightly and heated to reflux under argon for 5 days. The resulting purple solution was passed through a Celite pad and concentrated under vacuum. Purification by flash chromatography on silica gel (10% EtOH/CH_2Cl_2) afforded a purple solid **4** in 44% yield.

Cobalt(III) (Ring-Opened 2a) Acetate Complex (4a). X-ray-quality crystals were obtained by recrystallization from CH_2Cl_2 and hexanes: mp 185−187 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (s, 1H), 6.63−6.57 (m, 1H), 6.09 (d, $J = 10.6$ Hz, 1H), 5.57 (d, $J = 10.2$ Hz, 1H), 3.41 (d, $J = 6.2$ Hz, 1H), 3.37 (s, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.24−3.10 (m, 2H), 2.85 (dd, $J = 5.1$ Hz, 12.4, 1H), 2.63−2.51 (m, 4H), 1.76 (s, 3H), 1.71 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.0, 172.7, 171.7, 79.4, 78.3, 67.1, 64.1, 64.1, 58.8, 57.8, 54.6, 52.3, 51.4, 29.4, 28.7, 27.9, 26.9, 24.8, 21.4, 20.6; FT-IR (film) 1639, 1567 cm^{-1}; UV−vis (MeOH) λ_{max} (ϵ) 561 (110); HRMS (FAB$^+$, *m/z*) calcd for $C_{20}H_{40}CoN_4O_7$ (M + H$^+$) 507.2229, found 507.2237.

Preparation of the Cobalt(III) (3−3H) Complex (4b). Dioxocyclam **3** (100 mg, 0.228 mmol) and Co(acac)$_3$ (100 mg, 0.280 mmol) were combined in a 50-mL round-bottomed flask fitted with a reflux condenser. The mixture was suspended in EtOH (10 mL). The reaction was heated at reflux under nitrogen for 2 days. The resulting green solution was passed through a Celite pad and concentrated under vacuum. Purification by flash chromatography on silica gel (5% MeOH/$CHCl_3$) afforded 20 mg of a pink solid **4b**: yield 20%; ^{1}H NMR (CD_3OD, 400 MHz) δ 5.43 (t, 1H), 5.10 (t, 1H), 3.60 (d, $J = 4.7$ Hz, 1H), 3.23 (s, 3H), 3.19 (d, $J = 11.9$ Hz, 1H), 2.88 (m, 5H), 2.58 (m, 2H), 2.42 (dd, $J = 4.3$ and 11.5 Hz, 1H), 1.54 (s, 6H), 1.53 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 177.1, 175.1, 80.0, 79.7, 70.1, 67.0, 63.4, 63.2, 63.0, 59.8, 52.0, 51.6, 27.3, 26.5, 24.7, 23.5, 20.3, 20.0; FT-IR (film) 1550, 1445 cm^{-1}; UV−vis (MeOH) λ_{max}

(ϵ) 538 (176); LRMS (ES$^-$, *m/z*) calcd for $C_{18}H_{32}CoN_4O_4$ (M $-$ H$^+$) 427.41, found 427.17.

General Procedure for the Preparation of Cobalt(III) Complexes. The capped dioxocyclam **2** (0.287 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (35 mg, 1.436 mmol), and *i*-Pr_2NEt (0.25 mL, 1.436 mmol) were combined in a screw-cap pressure tube. The mixture was suspended in MeOH (2 mL) and then degassed with argon for 20 min. During this time, the cobalt acetate completely dissolved, resulting in a clear pink solution. The reaction vessel was sealed tightly and microwaved an average of 60 times for periods of 2 min at a power level of 20% or until no starting material was present by TLC. The tube was allowed to cool to room temperature between each microwave set. After several microwave sets, a blue precipitate began to form. Once the precipitate had formed, the precipitate was suspended in solution prior to each microwave set by shaking the tube to prevent bumping and/or explosions of the reaction mixture. The solution was initially clear and pink in color. After each microwave cycle, the solution became deep purple and would fade back to pink as the solution cooled. The resulting pink solution was passed through a Celite pad to remove precipitate and concentrated in vacuo.

Pyridine-Capped Cobalt(III) (2g$-$2H) Acetate Complex (5a). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) afforded a pink solid. X-ray-quality crystals were obtained by recrystallization from hot THF and CH_2Cl_2: yield 78%; mp 207 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (t, 1H), 7.04 (dd, *J* = 6.7 and 13.6 Hz, 2H), 5.32 (d, *J* = 17.9 Hz, 1H), 4.83 (d, *J* = 2.1 Hz, 2H), 4.78 (d, *J* = 18.0 Hz, 1H), 4.59 (d, *J* = 12.9 Hz, 1H), 4.39 (d, *J* = 13.1 Hz, 1H), 3.91 (dd, *J* = 13.6 and 26.0 Hz, 2H), 3.44 (s, 1H), 3.38 (s, 3H), 2.89 (s, 3H), 2.68 (dd, *J* = 12.8 and 19.6 Hz, 2H), 2.52 (d, *J* = 12.1 Hz, 1H), 1.96 (s, 3H), 1.65 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H), 1.55 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.5, 173.8, 173.0, 164.3, 160.6, 139.0, 117.7, 117.4, 81.0, 79.8, 79.1, 78.7, 69.6, 68.3, 68.2, 67.7, 63.7, 62.7, 52.5, 50.8, 31.2, 29.5, 28.7, 28.6, 28.2, 26.9, 22.2; FT-IR (film) 1613, 1564 cm^{-1}; UV$-$vis (MeOH) λ_{max} (ϵ) 526 (156); LRMS (ES$^-$, *m/z*) calcd for $C_{27}H_{41}CoN_5O_6$ (M $-$ H$^+$) 590.25, found 590.20.

Pyrazine-Capped Cobalt(III) (2b$-$2H) Acetate Complex (5b). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) afforded a pink solid. X-ray-quality crystals were obtained by recrystallization from hot THF and CH_2Cl_2: yield 54%; mp 155$-$160 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35 (s, 1H), 8.33 (s, 1H), 5.20 (d, *J* = 17.6 Hz, 1H), 4.86 (m, 1H), 4.62 (d, *J* = 12.8 Hz, 1H), 4.38 (d, *J* = 13.2 Hz, 1H), 3.81$-$3.75 (m, 4H), 3.38 (s, 3H), 2.85 (d, *J* = 13.5 Hz, 1H), 2.78 (s, 3H), 2.68 (d, *J* = 12.8 Hz, 2H), 2.52 (d, *J* = 12.1 Hz, 1H), 1.98 (s, 3H), 1.74 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.7, 174.2, 172.5, 143.5, 138.8, 138.1, 81.4, 79.5, 78.8, 78.1, 68.7, 68.3, 67.7, 66.5, 64.0, 63.0, 52.7, 50.6, 32.2, 30.1, 29.6, 29.0, 28.8, 28.1, 26.8, 21.7; FT-IR (film) 1616, 1559 cm^{-1}; UV$-$vis (CH_2Cl_2) λ_{max} (ϵ) 530 (160); LRMS (ES$^-$, *m/z*) calcd for $C_{26}H_{40}CoN_6O_6$ (M $-$ H$^+$) 591.23, found 591.20.

4-Bromopyridine-Capped Cobalt(III) (2b$-$2H) Hydroxide Complex (6c). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) and a second and third column by flash chromatography on alumina neutral (2% MeOH/CH_2Cl_2) to yield a brown solid: yield 20%; mp 105$-$110 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (s, 2H), 6.32 (d, *J* = 18.7 Hz, 1H), 5.15 (d, *J* = 19.4 Hz, 1H), 4.75 (d, *J* = 19.4 Hz, 1H), 4.42 (d, *J* = 18.3 Hz, 1H), 4.37 (d, *J* = 12.9 Hz, 1H) 4.17$-$4.11 (m, 2H), 4.02 (d, *J* = 12.1 Hz, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.83 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 12.1 Hz, 1H), 2.58 (d, *J* = 12.1 Hz, 1H), 1.69 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.1, 172.7, 164.1, 161.3, 136.7, 122.2, 121.9, 81.3, 80.8, 79.9, 78.8, 77.6, 67.8, 67.4, 67.3, 67.1, 63.8, 63.1, 52.9, 51.7, 31.2, 29.3, 28.7, 28.2, 23.6; FT-IR (film) 1597, 1560 cm^{-1}; UV$-$vis (CH_2Cl_2) λ_{max} (ϵ) 556 (160); LRMS (ES$^-$, *m/z*) calcd for $C_{25}H_{38}CoBrN_5O_5$ (M $-$ H$^+$) 626.14, found 626.13.

4-Nitropyridine-Capped Cobalt(III) (2d$-$2H) Methoxide Complex (6d). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) afforded a pink solid: yield 10%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.65 (d, *J* = 10.0 Hz, 1H), 5.11 (d, *J* = 17.7 Hz, 1H), 4.63$-$4.54 (m, 3H), 4.26 (d, *J* = 13.6 Hz, 1H), 3.91 (s, 3H), 3.68 (dd, *J* = 12.8 and 35.7 Hz, 2H), 3.45 (d, *J* = 20.4 Hz, 1H), 3.42 (s, 3H), 3.28 (s, 1H), 2.93 (s, 3H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.56 (dd, *J* = 13.2 and 29.0 Hz, 2H), 2.38 (d, *J* = 12.6 Hz, 1H), 1.58 (s, 3H), 1.50 (s, 3H), 1.49 (s, 3H), 1.48 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 172.8, 168.8, 163.2, 159.6, 104.6, 104.0, 81.1, 80.0, 79.3, 78.6, 71.0, 70.3, 68.1, 67.9, 64.2, 63.4, 56.6, 52.5, 51.0, 30.9, 29.4, 28.1, 28.0, 27.8, 22.3; FT-IR (film) 1570, 1379, 1323 cm^{-1}; LRMS (ES$^-$, *m/z*) calcd for $C_{26}H_{40}CoN_6O_7$ (M $-$ H$^+$) 607.24, found 607.07.

Procedure for the Acetate/Cyanide Ligand Exchange of Cobalt Complexes 5a, 5b, and 6c. The cobalt acetate complex (0.217 mmol) was dissolved in absolute MeOH (2 mL), giving a dark pink solution. NaCN (10.6 mg, 0.217 mmol) was added to the stirring solution. The mixture was stirred at room temperature for 48 h, over which time the solution changed from dark pink to orange. The solvent was removed under an air stream in the hood. The orange solid was brought up in CH_2Cl_2, the remaining white solid was removed by filtration, and the solvent was removed in vacuo.

Pyridine-Capped Cobalt(III) (2a$-$2H) Cyanide Complex (6a). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) to yield an orange solid. X-ray-quality crystals were obtained from a mixture of CH_2Cl_2 and Et_2O: mp 226 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (t, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 5.90 (d, *J* = 18.4 Hz, 1H), 4.96 (d, *J* = 19.0 Hz, 1H), 4.66 (d, *J* = 18.9 Hz, 1H), 4.43 (d, *J* = 18.3 Hz, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.80$-$3.65 (m, 3H), 3.48 (s, 3H), 3.47 (s, 1H), 3.20 (s, 3H), 3.06 (d, *J* = 13.6 Hz, 1H), 2.88 (d, *J* = 13.0 Hz, 1H), 2.67 (d, *J* = 12.2 Hz, 1H), 2.55 (d, *J* = 12.4 Hz, 1H), 1.70 (s, 3H), 1.66 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.0, 172.5, 162.2, 159.3, 139.5, 129.6, 118.9, 118.5, 82.5, 81.8, 79.7, 78.4, 69.5, 69.2, 68.6, 67.8, 63.6, 62.7, 52.7, 51.4, 50.9, 30.2, 28.8, 28.7, 27.7, 27.2, 22.9; FT-IR (film) 2123, 1566 cm^{-1}; UV$-$vis (MeOH) λ_{max} (ϵ) 463 (313); LRMS (ES$^-$, *m/z*) calcd for $C_{26}H_{38}CoN_6O_4$ (M $-$ H$^+$) 557.24, found 557.18.

Pyrazine-Capped Cobalt(III) (2b$-$2H) Cyanide Complex (6b). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) to yield an orange solid: yield 93%. X-ray-quality crystals were obtained from a mixture of acetone and THF: mp <260 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (s, 1H), 8.60 (s, 1H), 5.77 (d, *J* = 18.3 Hz, 1H), 4.98 (d, *J* = 19.4 Hz, 1H), 4.77 (d, *J* = 19.4 Hz, 1H), 4.60 (d, *J* = 18.3 Hz, 1H), 3.89 (d, *J* = 13.2 Hz, 1H), 3.77 (d, *J* = 12.5 Hz, 1H), 3.66 (d, *J* = 12.3 Hz, 2H), 3.60 (d, *J* = 14.1 Hz, 1H), 3.41 (s, 3H), 3.07 (s, 3H), 3.03 (d, *J* = 13.9 Hz, 1H), 2.88 (d, *J* = 13.18 Hz, 1H), 2.72 (d, *J* = 12.27 Hz, 1H), 2.58 (d, *J* = 12.27 Hz, 1H), 1.71 (s, 3H), 1.68 (s, 3H), 1.52 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.9, 172.5, 157.3, 154.4, 140.3, 139.8, 127.9 82.5, 81.4, 79.9, 78.3, 69.7, 69.1, 67.4, 66.4, 64.0, 63.1, 52.7, 51.4, 29.9, 29.7, 29.3, 27.7, 27.4, 22.4; FT-IR (film) 2128, 1558 cm^{-1}; UV$-$

vis (CH_2Cl_2) λ_{max} (ϵ) 454 (475); LRMS (ES^+, m/z) calcd for $C_{25}H_{39}CoN_7O_4$ ($M + H^+$) 560.55, found 560.13.

4-Methoxypyridine-Capped Cobalt(III) (2c−2H) Cyanide Complex (6c′). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) to yield an orange solid: yield 53%; mp <260 °C (dec); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.72 (s, 1H), 6.71 (s, 1H), 5.89 (d, J = 18.3 Hz, 1H), 4.87 (d, J = 18.7 Hz, 1H), 4.58 (d, J = 19.0 Hz, 1H), 4.28 (d, J = 18.3 Hz, 1H), 3.96 (d, J = 13.1 Hz, 1H), 3.91 (s, 3H) 3.78−3.62 (m, 3H), 3.47 (s, 3H), 3.27 (s, 3H), 3.04 (d, J = 13.9 Hz, 1H), 2.86 (d, J = 13.2 Hz, 1H), 2.64 (d, J = 12.45 Hz, 1H), 2.53 (d, J = 12.45 Hz, 1H), 1.69 (s, 3H), 1.64 (s, 3H), 1.52 (s, 3H), 1.48 (s, 3H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.3, 172.4, 168.8, 163.0, 160.3, 105.5, 104.9, 82.6, 82.0, 79.6, 78.5, 69.3, 69.2, 68.5, 67.8, 63.4, 62.7, 56.7, 52.7, 51.6, 30.5, 28.7, 28.5, 27.7, 27.2, 23.2; FT-IR (film) 2123, 1560 cm^{-1}; UV−vis (MeOH) λ_{max} (ϵ) 462 (317); LRMS (ES^+, m/z) calcd for $C_{27}H_{42}CoN_6O_5$ ($M + H^+$) 589.25, found 589.13.

4-Nitrosopyridine-Capped Cobalt Cyanide Complex (6d′). Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) to yield an orange solid: yield 6%; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.77 (d, J = 23.6 Hz, 2H), 5.88 (d, J = 18.2 Hz, 1H), 4.91 (d, J = 18.5 Hz, 1H), 4.60 (d, J = 19.0 Hz, 1H), 4.31 (d, J = 18.3 Hz, 1H), 4.19 (s, 1H), 3.95 (s, 1H), 3.92 (s, 3H), 3.77−3.63 (m, 4H), 3.46 (s, 2H), 3.35 (s, 2H), 3.25 (s, 3H), 3.05 (d, J = 13.6 Hz, 1H), 2.89 (d, J = 13.4 Hz, 1H), 2.67 (d, J = 12.3 Hz, 1H), 2.55 (d, J = 12.4 Hz, 1H), 1.69 (s, 3H), 1.64 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.2, 172.3, 168.7, 162.9, 160.2, 130.2, 105.4, 104.9, 82.5, 81.8, 79.5, 78.5, 69.4, 69.1, 68.4, 67.7, 63.4, 62.7, 56.7, 53.6, 52.7, 51.5, 50.3, 30.3, 29.9, 28.6, 28.4, 27.6, 27.1, 23.1; FT-IR (film) 2125, 1560, 1448, 1360 cm^{-1}; LRMS (ES^-, m/z) calcd for $C_{26}H_{38}CoN_7O_5$ ($M - H^+$) 586.22, found 587.30.

Procedure for the Ligand Exchange of Cobalt Complex 6c. Complex **6c** (14 mg, 0.02 mmol) was dissolved in acetonitrile (3 mL), giving a dark pink solution. KCN (4.0 mg, 0.06 mmol) and 18-crown-6 (2 mg, 0.0075 mmol) were added to the stirring solution. The mixture was stirred at reflux for 7 h, over which time the solution changed from dark pink to orange. The solvent was removed by air stream in the hood. The orange solid was brought up in CH_2Cl_2, and the resulting white solid was filtered off through Celite. Solvent was removed in vacuo. Purification by flash chromatography on silica gel (10% MeOH/CH_2Cl_2) afforded an orange solid in 86% yield.

4-Bromopyridine-capped cobalt(III) (2c−2H) cyanide complex (6c″): mp <260 °C (dec); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44 (s, 1H), 7.42 (s, 1H), 5.86 (d, J = 18.3 Hz, 1H), 4.92 (d, J = 19.4 Hz, 1H), 4.66 (d, J = 19.4 Hz, 1 H), 4.42 (d, J = 18.3 Hz, 1 H), 3.94 (d, J = 13.2 Hz, 1 H), 3.94 (d, J = 12.4 Hz, 1H) 3.71−3.70 (m, 2H), 3.45 (s, 3H), 3.22 (s, 3H), 3.03 (d, J = 13.5 Hz, 1H), 2.87 (d, J = 13.2 Hz, 1H), 2.68 (d, J = 12.45 Hz, 1H), 2.55 (d, J = 12.45 Hz, 1H), 1.71 (s, 3H), 1.68 (s, 3H), 1.50 (s, 3H), 1.49 (s, 6H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 172.6, 163.1, 160.2, 136.7, 122.4, 122.1, 82.5, 81.7, 79.7, 78.3, 77.5, 69.7, 69.2, 68.4, 67.5, 63.6, 62.8, 52.7, 51.6, 30.2, 29.2, 29.1, 27.6, 27.3, 22.9; FT-IR (film) 2124, 1567 cm^{-1}; UV−vis (MeOH) λ_{max} (ϵ) 462 (238); LRMS (ES^+, m/z) calcd for $C_{26}H_{39}CoBrN_6O_4$ ($M + H^+$) 637.15, found 637.07.

Preparation of 4-Pyridylpyridine-Capped Cobalt(III) (2g−2H) Cyanide Complex (6g). 4-Pyridylpyridine-capped dioxocyclam **2g** (95 mg, 0.17 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (428 mg, 1.72 mmol), and i-Pr_2NEt (222 mg, 1.72 mmol) were placed in a screw-cap pressure tube, and the mixture was dissolved in distilled MeOH (4 mL). The reaction vessel was sealed tightly and microwaved an average of 24 times for periods of 2 min at a power level of 20%. The resulting red solution with blue precipitate was filtered through a Celite pad and washed with excess MeOH. Air was bubbled through the red solution and purified by column chromatography on neutral alumina, eluting the uncapped starting cyclam with EtOAc and complex **6g** with 5% MeOH/EtOAc. The reddish cobalt complex solution was concentrated under vacuum and dissolved in MeOH (3 mL), followed by the addition of NaCN (84 mg, 1.72 mmol). After the reaction was stirred overnight, the solvent was removed under reduced pressure and purified on neutral alumina column chromatography (5% MeOH/CH_2Cl_2). The orange solid was dissolved in CH_2Cl_2 (2 mL) and precipitated by the diffusion of hexane (5 mL). The solid was filtered through a cotton pad and washed with excess EtOAc. The orange precipitate was washed from the cotton pad using excess MeOH. Concentration under reduced pressure afforded the desired product (58 mg, 0.091 mmol): yield 53%; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.82 (bs, 2H), 7.51 (bs, 2H), 7.46 (bs, 2H), 6.05 (d, J = 13.5 Hz, 1H), 5.09 (d, J = 16 Hz, 1H), 4.74 (d, J = 16.8 Hz, 1H), 4.48 (d, J = 18 Hz, 1H), 3.99 (d, J = 13.2 Hz, 1H), 3.80 (d, J = 12.4 Hz, 1H), 3.76 (d, J = 13.6 Hz, 1H), 3.69 (d, J = 12.4 Hz, 1H), 3.48 (s, 3H), 3.26 (s, 3H), 3.11 (d, J = 13.6 Hz, 1H), 2.94 (d, J = 12.8 Hz, 1H), 2.73 (d, J = 12.4 Hz, 1H), 2.61 (d, J = 12.0 Hz, 1H), 1.71 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 172.5, 162.8, 160.2, 151.3, 150.3, 143.4, 129.3, 121.6, 117.0, 116.8, 82.6, 81.8, 79.6, 78.5, 69.4, 69.2, 68.6, 68.0, 63.7, 62.9, 52.7, 51.5, 30.4, 28.9, 28.7, 27.7, 27.2, 23.1; FT-IR (film) 2126, 1566 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (ϵ) 268 (15 700), 460 (430); HRMS (FAB^+, m/z) calcd for $C_{31}H_{43}CoN_7O_4$ ($M + H^+$) 636.2709, found 636.2725.

Preparation of the 4-[4-(*N*,*N*-Dimethylamino)phenyl]pyridine-Capped Cobalt(III) (2h−2H) Cyanide Complex (6h). 4-[4-(*N*,*N*-Dimethylamino)phenyl]pyridine-capped dioxocyclam **2h** (87 mg, 0.15 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (364 mg, 1.46 mmol), and i-Pr_2NEt (189 mg, 1.46 mmol) were used for the reaction. The above procedure afforded the desired product (0.067 g, 0.099 mmol): yield 68%; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, J = 12.0 Hz, 2H), 7.32 (bs, 2H), 6.75 (d, J = 11.6 Hz, 2H), 5.97 (d, J = 24.0 Hz, 1H), 4.96 (d, J = 24.8 Hz, 1H), 4.61 (d, J = 25.2 Hz, 1H), 4.33 (d, J = 24.4 Hz, 1H), 3.99 (d, J = 17.6 Hz, 1H), 3.78 (d, J = 16.0 Hz, 1H), 3.76 (d, J = 18.0 Hz, 1H), 3.66 (d, J = 16.4 Hz, 1H), 3.49 (s, 3H), 3.28 (s, 3H), 3.07 (d, J = 17.2 Hz, 1H), 3.05 (s, 6H), 2.89 (d, J = 17.6 Hz, 1H), 2.67 (d, J = 16.4 Hz, 1H), 2.55 (d, J = 16.4 Hz, 1H), 1.70 (s, 3H), 1.65 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H), 1.46 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 172.3, 161.3, 158.7, 152.5, 152.2, 131.1, 128.3, 121.9, 114.8, 114.5, 112.5, 82.6, 82.0, 79.5, 78.5, 69.3, 69.2, 68.3, 67.7, 63.5, 62.7, 52.7, 51.5, 40.3, 30.6, 28.5, 28.3, 27.6, 27.1, 23.2; FT-IR (film) 1568 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (ϵ) 380 (29 500), 460 (426); HRMS (FAB^+, m/z) calcd for $C_{34}H_{49}N_7O_4Co$ ($M + H^+$) 678.3178, found 678.3163.

Synthesis of the Rhodium Acetate Bridged Cobalt Cyanide Pyridine Complex (7). A solution of cobalt complex **6a** (32.8 mg, 0.059 mmol) and rhodium(II) acetate (13 mg, 0.029 mmol) in 6 mL of absolute MeOH was stirred at reflux for 3 h. The color of the solution turned from orange to a greenish brown. The solution was filtered through a cotton plug. Evaporation of the solvent gave a brown solid. Recrystallization by vapor diffusion of MeOH and Et_2O gave red plate crystals: yield 95%; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (t, 1H), 7.26 (d, J = 7.9 Hz, 2H), 5.89 (d, J = 18.1 Hz, 1H), 5.02 (d, J = 18.8 Hz, 1H), 4.72 (d, J = 18.7 Hz, 1H), 4.54 (d, J = 18.1 Hz, 1H), 3.48 (s, 3H), 3.20 (s, 3H), 3.12 (d, J = 14.7 Hz, 1H), 2.88 (d, J = 13.4 Hz, 1H), 2.65 (dd, J = 11.4, 23.5 Hz, 2H), 1.83 (s, 12H), 1.70 (s, 6H), 1.53 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 191.1, 173.1, 172.8, 162.4, 159.5, 139.4, 118.8, 118.3, 82.4, 81.9, 79.8, 78.5, 77.4, 69.1, 68.2, 63.8, 63.0, 53.0, 51.4, 30.6, 29.2, 28.8, 27.8, 27.0, 23.7, 22.8; FT-IR (film) 2228, 2200, 2142, 1595, 1566 cm^{-1}; UV−vis (MeOH) λ_{max} (ϵ) 455 (744), 574 (246); LRMS (FAB$^+$, *m/z*) calcd for $C_{60}H_{90}Co_2N_{12}O_{16}Rh_2$ (M + H$^+$) 1559.34, found 1559.40.

Synthesis of the Ruthenium Phthalocyanine Bridged Cobalt Cyanide Pyridine Complex (8). A solution of bis(benzonitrile)-phthalocyaninate ruthenium(II)[28] (10 mg, 0.012 mmol) and 18 mg (0.032 mmol) of cobalt cyanide complex **6a** in 5 mL dry CH_2Cl_2 was heated at 65 °C under nitrogen in a sealed tube for 24 h. Evaporation of solvent gave a blue product. Purification by flash chromatography on silica gel (10% MeOH/CHCl$_3$) afforded a blue solid. X-ray quality crystals were obtained by recrystallization via vapor diffusion of MeOH and Et$_2$O giving blue crystals: yield 71%, mp $<$260 °C dec; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.94 (s, 8H), 7.70 (s, 8H), 7.38 (t, $J = 7.8$ Hz, 2H), 6.68 (d, $J = 7.8$ Hz 2H), 6.67 (d, $J = 7.8$ Hz, 2H), 5.23 (d, $J = 19.2$ Hz, 2H), 3.98 (d, $J = 20.2$ Hz, 2H), 3.89 (d, $J = 19.2$ Hz, 2H), 3.64 (m, 8H), 3.45 (d, $J = 12.4$ Hz, 2H), 2.77 (s, 6H), 1.73 (s, 6H), 1.65 (d, $J = 14.8$ Hz, 2H), 1.58 (d, $J = 12.6$ Hz, 2H), 1.47 (d, $J = 14.8$ Hz, 2H), 1.38 (d, $J = 12.6$ Hz, 2H), 0.81 (s, 6H), 0.77(s, 6H), 0.73 (s, 6H), 0.61 (s, 6H), −0.03 (s, 6H), −0.19 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 171.5, 171.1, 161.3, 158.2, 140.2, 139.3, 130.0, 127.3, 121.4, 118.7, 118.2, 117.9, 81.2, 79.5, 78.3, 76.5, 70.5, 66.9, 66.8, 66.2, 61.5, 60.8, 50.8, 50.6, 29.6, 29.1, 28.3, 26.0, 25.0, 21.7; FT-IR (film) 2920, 2125, 1562 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}(ϵ) 320 (42201), 412 (2500), 571 (sh), 628 (26871); LRMS (FAB$^+$, *m/z*) calcd for $C_{84}H_{94}Co_2RuN_{20}O_8$ (M$^+$) 1730.5, found 1730.7.

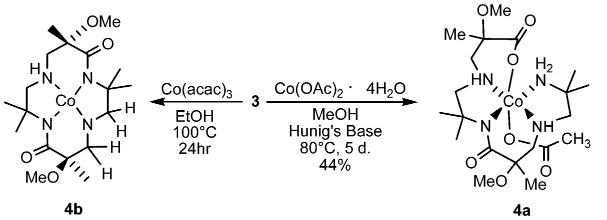
Results and Discussion

Synthesis. For the parent uncapped dioxocyclam used in these studies (**3**), nickel(II) incorporated rapidly simply by heating the ligand and nickel(II) acetate in methanol for a few minutes.[16] In contrast, introduction of copper(II) required the use of copper(II) tetrafluoroborate and heating at reflux in methanol in the presence of sodium carbonate for 1 day.[9c] Capping of this dioxocyclam greatly reduces the flexibility of the 140-membered macrocycle and further limits the range of metals that can be introduced into the cavity. For the parent pyridine-capped dioxocyclam **2a**, introduction of copper required heating at reflux in methanol in the presence of a base for 5 days,[9b] while nickel(II) remained uncomplexed under a range of conditions.

Cobalt(III) complexes of capped dioxocyclams **2a−h** were of interest because of both their anticipated redox activity and their preference to form octahedral complexes. Because cobalt(III) is relatively substitution inert, introduction via a more labile cobalt(II) precursor followed by oxidation was the planned approach.

Treatment of uncapped dioxocyclam **3** with cobalt(II) acetate under conditions sufficient to introduce nickel(II) and copper(II) into **3** resulted in no reaction. Treatment of **3** with cobalt(II) acetate in methanol in the presence of Hunig's base in a sealed tube for 5 days at 80 °C produced not the expected complex but rather the cobalt(III) complex **4a** of the ring-opened cyclam (Scheme 1), as determined by single-crystal X-ray diffraction. [Both cobalt(II)[17] and cobalt(III) complexes[18] catalyze the hydrolysis of amides.] In contrast, treatment of **3** with cobalt(III) acetylacetonate in ethanol at 100 °C for 24 h produced neutral cobalt(III) complex **4b**, in which both amide protons *and one amine* proton have been lost (Scheme 1).

Scheme 1



The structural assignment for **4b** is based on spectroscopic data. The IR spectrum has a single, intense carbonyl band at $\nu_{CO} = 1552$ cm^{-1}, indicating that both amide groups are coordinated and deprotonated and that the acetylacetone group is absent from the complex. The major peak in the (−) electrospray mass spectrum appears at $m/z = 427$, corresponding to **4b**−H, rather than at $m/z = 428$ for the expected complex in which both amines would be protonated. The ^{1}H NMR spectrum of **4b** was considerably more complex than that of similar metal(II) complexes of **3**, indicating a less-symmetrical structure for **4b**. Most telling was the appearance of a pair of two proton apparent triplets at δ 5.11 ($J = 13.8$ Hz) and δ 5.46 ($J = 11.7$ Hz). These are assigned to the two methylene groups flanking the deprotonated amine, with their downfield shift being attributed to the deshielding effect of the deprotonated amine. The protons are diastereotopic and have typical geminal coupling constant values. The ^{13}C NMR spectrum confirms this. This is best illustrated by comparison of the ^{13}C NMR spectrum of **4b** with that of the neutral nickel(II) complex of centrosymmetric dioxocyclam **3**, in which both amides are deprotonated and both amines remain protonated.[5] Because of the symmetry of the nickel(II) complex, there are nine sets of magnetically equivalent carbons: three for the three different types of methyl groups at δ 19.6, 23.0, and 25.0 ppm, one at δ 52.0 ppm for the methoxy groups, one at δ 57.2 ppm for the quaternary carbons bearing *gem*-dimethyl groups, two at δ 58.6 and 65.9 ppm for the two different types of CH$_2$N groups, one at δ 77.3 ppm for the quaternary carbons bearing methyl and methoxy groups, and one at δ 172.7 ppm for the carbonyl carbons. By deprotonation of one of the secondary amino groups, the symmetry is broken, and the ^{13}C NMR spectrum of **4b** has 18 peaks: six methyl peaks at δ 20.0, 20.3, 23.5, 24.7, 26.5, and 27.3 ppm, two methoxy peaks at δ 51.6 and 52.0 ppm, six peaks at δ 59.8, 63.0, 63.2, 63.4, 67.1, and 70.1 ppm for the four different CH$_2$N groups and the two quaternary carbons bearing *gem*-dimethyl groups, two quaternary (methoxy)(methyl)-bearing carbon peaks at δ 79.7 and 80.0 ppm, and two carbonyl peaks at δ 175.1 and 177.1 ppm.

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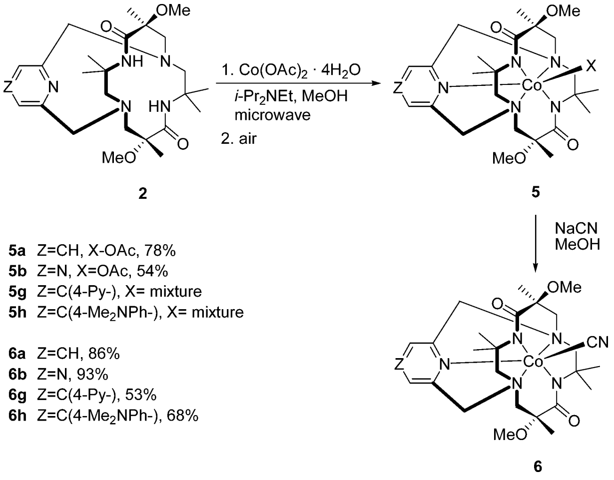
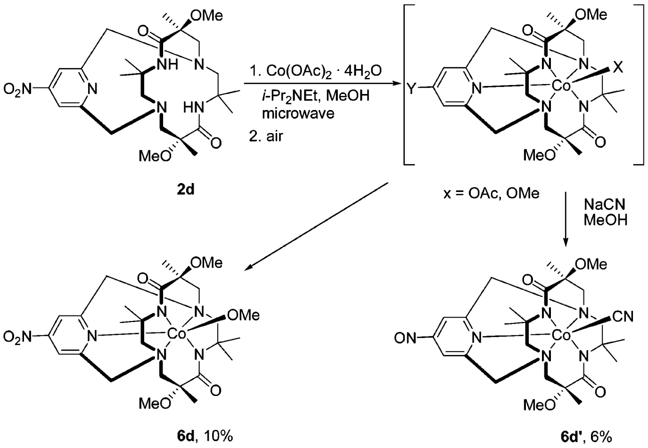
Scheme 2



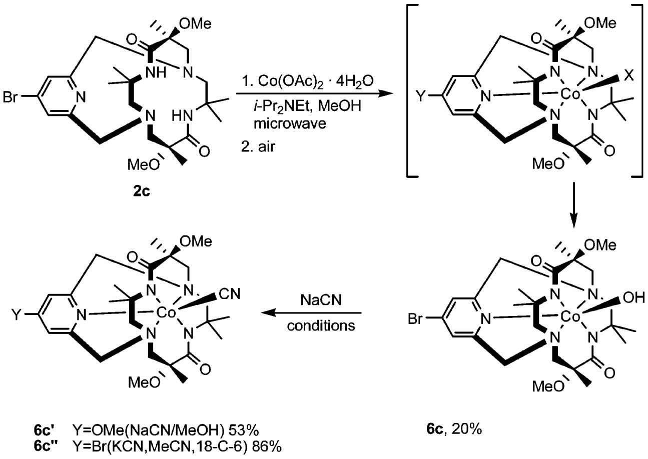
5a Z=CH, X-OAc, 78%
5b Z=N, X=OAc, 54%
5g Z=C(4-Py-), X= mixture
5h Z=C(4-Me$_2$NPh-), X= mixture

6a Z=CH, 86%
6b Z=N, 93%
6g Z=C(4-Py-), 53%
6h Z=C(4-Me$_2$NPh-), 68%

Scheme 3



Scheme 4



6c' Y=OMe(NaCN/MeOH) 53%
6c" Y=Br(KCN,MeCN,18-C-6) 86%

Formation of **4b** requires deprotonation of one of the initially formed Co(III)-complexed amines. Coordinated amines can have acidities $10^{16}-10^{25}$ higher than free amines,[19,20] and the final acetylacetonate ligand lost in the formation of **4b** could be sufficiently basic to effect the final deprotonation step.

Treatment of pyridine-capped dioxocyclam **2a** under the above conditions even with heating at 80 °C for 2 weeks resulted in complete recovery of the starting dioxocyclam, with no evidence of complex formation. Successful complexation of cobalt was achieved by resorting to microwave radiation (Scheme 2).[21] Under these conditions, ligands **2a** and **2b** cleanly formed the corresponding cobalt(III) acetate complexes **5a** and **5b**. In contrast, ligands **5g** and **5h** complexed cobalt in good yield, but inseparable mixtures of the acetate, methoxide, and hydroxide complexes were obtained. Treatment with sodium cyanide in methanol converted these cleanly to the cyanide complexes **6**.

Dioxocyclams capped with electron-poor pyridines proved problematic. Introduction of cobalt into 4-cyanopyridine-capped dioxocyclam **2e** failed under all conditions tried. Under the conditions of Scheme 1, hydrolysis of the nitrile to the amide, *without* complexation of cobalt, resulted.[22] With anhydrous cobalt salts, no reaction occurred. Introduction of cobalt into 4-nitropyridine-capped dioxocyclam **2d** produced a mixture of products that by mass spectroscopic analysis of the crude reaction mixture were found to contain the 4-nitropyridine cobalt acetate complex, the 4-nitropyridine cobalt methoxide complex, and the *4-nitroso*pyridine[9b] cobalt complex lacking a sixth ligand.[23] A low yield of the 4-nitropyridine cobalt methoxide product **6d** was obtained by chromatographic purification of the mixture, while treatment of the crude reaction mixture with sodium cyanide allowed isolation of a low yield of the 4-nitrosopyridine cobalt cyanide product **6d′** (Scheme 3).

Introduction of cobalt into the 4-bromopyridine-capped dioxocyclam **2c** was also complex and low-yielding (Scheme 4). A mass spectrum of the crude reaction mixture indicated the presence of the 4-bromopyridine cobalt acetate complex and the *4-methoxy*pyridine cobalt hydroxide complex. Chromatographic separation, first on silica gel to remove unreacted ligand and then on neutral alumina, gave an inseparable mixture of the 4-bromopyridine cobalt acetate and hydroxide complexes (from hydrolysis of the acetate during purification). A second pass through neutral alumina gave the pure 4-bromopyridine cobalt(III) hydroxide complex **6c** in 20% yield (Scheme 4). Attempts to convert **6c** to the corresponding cyanide complex (NaCN and MeOH) instead produced the 4-methoxypyridine cobalt cyanide complex **6c′**, resulting from nucleophilic substitution on the complexed 4-bromopyridine. Cyanation in acetonitrile with 18-crown-6 produced the desired complex **6c″** in excellent yield. Thus, although dioxocyclams capped with electron-rich pyridines or pyrazine readily complex cobalt, those capped with electron-poor pyridines give complex mixtures from which only low yields of desired products can be isolated.

Properties. The spectroscopic and electrochemical properties of complexes **5** and **6** (along with free ligand **2a**) are displayed in Table 1. As previously observed with Ni(II)[3−6]

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[20] Kimura, E.; Kurogi, Y.; Takahashi, T. *Inorg. Chem.* **1991**, *30*, 4117−4121.

[21] For the use of microwave irradiation to promote complexation, see: (a) Kubrakova, I. V. *Russ. Chem. Rev.* **2002**, *71*, 283−294. (b) Van Eldik, R.; Hubbard, C. D. *New J. Chem.* **1997**, *21*, 825−838.

[22] Similar hydrolysis of this ligand by copper(II) under the conditions of Scheme 1 had previously been observed. See ref 9b.

[23] This is likely to be a cobalt(II) complex from incomplete oxidation.

Table 1. Spectroscopic and Electrochemical Data

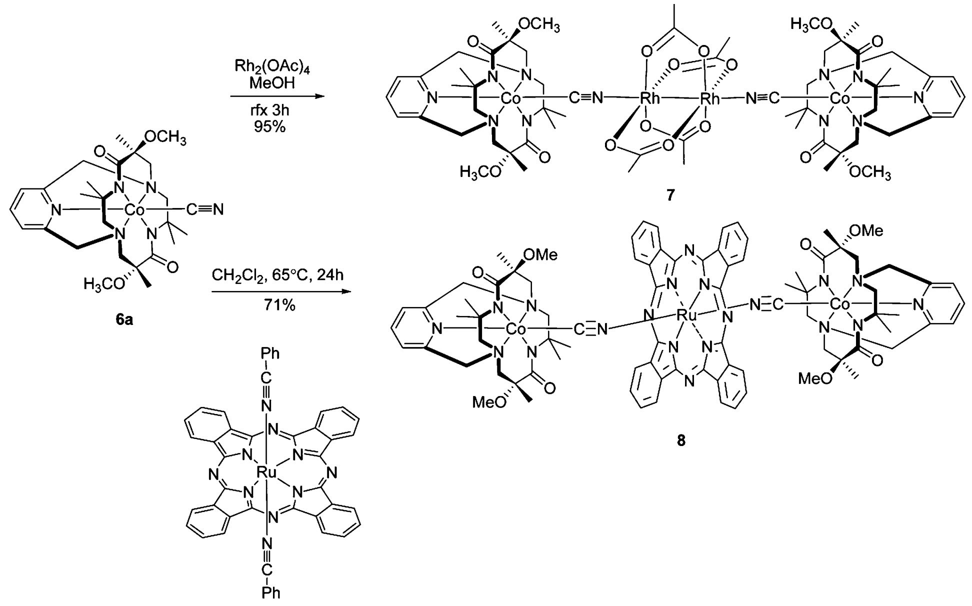
	IR, ν (cm^{-1})	UV, λ_{max} (nm)	δ ^{13}C	CV, CH_2Cl_2 vs SCE (CH_3CN)
2a	1659, amide		173.7, amide 173.3, amide	
5a	1613, acetate 1564, amide	MeOH $\epsilon[526] = 156$	173.8, amide 173.0, amide 178.5, acetate	$E_p = -1.19$ V (-1.28)
5b	1616, acetate 1559, amide	CH_2Cl_2 $\epsilon[530] = 160$	174.2, amide 172.5, amide 178.7, acetate	$E_p = -0.95$ V
6a	2123, CN 1566, amide	MeOH $\epsilon[463] = 313$	173.0, amide 172.5, amide 129.6, CN	$E_p = -1.36$ V
6b	2128, CN 1558, amide	CH_2Cl_2 $\epsilon[454] = 475$	172.9, amide 172.5, amide 139.8, CN	$E_p = -1.17$ V
6g 4-py-py-Co−CN	2125, CN 1566, amide	$CHCl_3$ $\epsilon[242] = 27176$ $\epsilon[460] = 433$	173.4, amide 172.5, amide 129.2, CN	$E_p = -1.34$ V
6h 4-Me_2NPh−Py	2120, CN 1599 1567, amide	$CHCl_3$ $\epsilon[383] = 29492$	173.4, amide 172.3, amide 131.0, CN	$E_p = -1.36$ V (-1.35)
6d	1570, amide 1379, NO_2 1323, NO_2		173.4, amide 172.8, amide	
6d′	1560, amide 1448, NO 1360, NO		174.2, amide 172.3, amide 132.2, CN	
6c	1561, amide	CH_2Cl_2 $\epsilon[556] = 160$	174.1, amide 172.7, amide	
6c′	2123, CN 1560, amide	MeOH $\epsilon[462] = 317$	173.3, amide 172.4, amide	
6c″	1560, amide	MeOH $\epsilon[462] = 238$	173.1, amide 172.6, amide 136.7, CN	
7	2228, CN 2200, CN 2142, CN 1595, acetate 1566, amide	MeOH $\epsilon[455] = 744$ $\epsilon[574] = 246$	191.1, acetate 173.1, amide 172.8, amide do not see CN	$E_p = -1.39$ V (2e) $E_p = +1.07$ V
8	2125, CN 1562, amide	CH_2Cl_2 $\epsilon[320] = 4220$ [372 (sh)] $\epsilon[412] = 2500$ [571 (sh)] $\epsilon[628] = 26900$	171.5, amide 171.1, amide do not see CN	

and Cu(II),[9] complexation of the free dioxocyclams to Co(III) resulted in a shift of the IR band for the amide carbonyl group from ≈1660 cm^{-1} in the free ligand to 1560−1570 cm^{-1} in the complex, with little variation between complexes with electron- and electron-withdrawing capping groups. Similarly, the acetate group and the cyanide group absorptions appear insensitive to the nature of the capping group appearing at ≈1615 and 2120−2130 cm^{-1}, respectively.

Most surprising is the ^{13}C NMR chemical shift of the amide carbonyl carbons. In *all* free ligands as well as the cobalt(III) complexes reported here and the nickel(II) complexes previously reported,[3−6] two amide carbonyl ^{13}C NMR peaks between δ 172−174 ppm were observed. There was virtually *no change* in chemical shift upon complexation to a metal, regardless of the metal, its oxidation state [Ni(II) and Co(III)], or its attendant ancilliary ligands (OAc, CN, OMe, OH, and electron-rich, electron-poor capping groups). The signals for the cobalt-bound acetate groups appear at ≈δ 178 ppm, for both the electron-donating pyridine-capped and the electron-accepting pyrazine-capped complexes **5a** and **5b**. The ^{13}C NMR chemical shift of the cyanide group showed slightly more sensitivity to the nature of the capping agent, ranging from δ 129.2 ppm for the electron-rich [4-(dimethylamino)phenyl]pyridine group to δ 139.7 ppm for the electron-poor pyrazine group.

The visible spectra also show remarkable homogeneity among classes of complexes. Those with acetate or hydroxides as the sixth ligand absorb weakly ($\epsilon = 160$) between

Scheme 5



526 and 556 nm, while the cyanide complexes absorb at $\approx$460 nm, with slightly greater intensity ($\epsilon = 200-475$). The two complexes with extended conjugation in the capping group, **6g** and **6h**, have an intense ligand-based absorption at shorter wavelength, 265 and 383 nm, respectively. This is in contrast to the free ligands, which have intense absorption at 320 nm for **2g** and 329 and 411 nm for **2h**.

The three pyridine-capped cobalt(III) cyanide complexes **6a**, **6g**, and **6h** underwent irreversible reduction at ≈ -1.36 V and reoxidation between -0.03 and $+0.15$ V (CH_2Cl_2 vs SCE), demonstrating an insensitivity to the 4-substituent on the capping pyridine. The pyridine-capped acetate complex **5a** was slightly easier to reduce (-1.19 V), while both the pyrazine-capped cyanide complex **6b** and the corresponding pyrazine-capped acetate complex **5b** underwent irreversible reduction at -1.17 and -0.95 V, respectively, perhaps a reflection of the strong π-accepting nature of the pyrazine group contrasting with the σ-donor nature of the pyridines.

Two complexes had additional electrochemistry associated with the ligand. The [4-(dimethylamino)phenyl]pyridine-capped complex **6h** had an irreversible oxidation at $+1.00$ V vs SCE, assigned to oxidation of the (dimethylamino)phenyl moiety. The 4-pyridylpyridine-capped complex **6g** had a reversible, one-electron reduction at $E_{1/2} = -1.52$ V vs SCE and $\Delta E = 60$ MV and a quasi-reversible one-electron reduction at $E_{1/2} = -2.00$ V vs SCE and $\Delta E = 200$ MV, assigned to stepwise reduction of the bipyridine system.[24]

Cyanide Coordination Chemistry. A major impetus for the synthesis of cobalt(III) *cyanide* complexes was the fact that metal-bound cyanides are efficient ligands for complexation of metals through the nitrogen lone pair of electrons and permit efficient electronic communication between the two metals bridged by the complexed cyanide.[25] With this in mind, pyridine-capped cobalt(III) cyanide complex **6a** was treated with $Rh_2(OAc)_4$ and with ruthenium(II) phthalocyanine to form the cyanide-bridged tetra- and trimetallic complexes **7** and **8**, respectively (Scheme 5).

The mass spectrum of **7** confirmed its constitution, with a parent ion at $m/z = 1559$ and the calculated isotope ratios for $C_{60}H_{90}Co_2N_{12}O_{16}Rh_2$. In addition to the 1566-cm^{-1} amide band in the IR spectrum, a band at 1595 cm^{-1} for the bridging acetates was observed. The bridging cyanides absorbed at 2228, 2200, and 2142 cm^{-1}, in comparison to the terminal cyanide of **6a** at 2123 cm^{-1}. This increase in ν is likely due to the "kinematic" effect ("the constraint of the C−N vibration due to metal attachment at both C and N"[25e]), which is not compensated for by π^*-back-donation from the metal.[25b,c] The UV−vis spectrum is little different from the two component parts, with absorptions at λ_{max} 455 nm ($\epsilon = 744$) and 574 nm ($\epsilon = 246$) vs 463 nm ($\epsilon = 313$) for the cyclam portion and 446 and 588 nm for $Rh_2(OAc)_4$. The ^1H and ^{13}C NMR spectra of **7** are very little changed from those of the precursors. In the ^1H NMR spectrum, all peaks for the pyridine cap are unchanged and most of those from the dioxocyclam are unaltered. Only the signals due to the dioxocyclam ring methylenes α to the quaternary center are altered, changing from four doublets between δ 3.8 and 4.0 ppm to a series of three broad peaks at δ ~4.0, 4.18, and 4.20 ppm. (The acetate methyl groups appear at δ 1.83 ppm.) The ^{13}C NMR spectrum similarly showed virtually no change from that of the component parts, except the signal for the CN carbon, which appears as a weak, broad peak at δ 129.6 ppm in the dioxocyclam complex **6a** and was not detectable in the spectrum of **7**. Finally, complex **7** underwent irreversible Co(III) → Co(II) reduction at $E_p = -1.39$ V vs SCE (compared to $E_p = -1.36$ V vs SEC for **6a**) and an

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Table 2. Crystallographic Data

	5a	**5b**	**6a**	**6b**	**7**	**8**
emperical formula	$C_{31}H_{50}CoN_5O_7$	$C_{30}H_{41}CoN_6O_7$	$C_{29.5}H_{53}CoN_6O_{7.5}$	$C_{25}H_{40}CoN_7O_5$	$C_{62}H_{106}Co_2N_{12}O_{22}Rh_2$	$C_{88}H_{110}Co_2N_{20}O_{12}Ru$
fw	663.69	664.68	670.70	577.56	1695.25	1858.88
T (K)	173(2)	298(2)	173(2)	173(2)	173(3)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	trigonal	monoclinic
space group	*Cc*	*Cc*	*Pbca*	$P2_1/c$	$R\bar{3}$	$P2_1/n$
unit cell dimens						
a (Å)	10.5774(16)	10.6644(19)	14.7441(13)	16.167(4)	39.468(8)	12.0984(12)
b (Å)	20.901(3)	21.732(4)	13.4 537(12)	11.435(3)	39.468(8)	11.8549(12)
c (Å)	14.663(2)	14.189(3)	32.905(3)	15.670(4)	14.566(4)	29.740(3)
α (deg)	90	90	90	90	90	90
β (deg)	104.217	102.815(5)	90	102.626(5)	90	99.127(2)
γ (deg)	90	90	90	90	120	90
V (Å^3), Z	3142.2(8), 4	3206.5(11), 4	6527.1(10), 4	2826.9(12), 4	19650(8), 9	4211.5(7), 2
D_{calcd} (Mg/mm^{-1})	1.403	1.360	1.353	1.352	1.277	1.463
abs coeff (mm^{-1})	0.601	0.590	0.581	0.654	0.812	0.642
GOF of F^2	1.028	0.951	1.042	1.038	1.082	1.131
final R indices[a] [$I > 2\sigma(I)$]						
R1	0.0462	0.0672	0.0588	0.0659	0.0741	0.0814
wR2	0.1102	0.1069	0.1287	0.1562	0.1961	0.1869
R indices (all data)						
R1	0.0526	0.1655	0.0997	0.1235	0.1288	0.1186
wR2	0.1132	0.1323	0.1492	0.1997	0.2248	0.2059

[a] $R = ||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [[w(F_o - F_c^2)^2]/[w(F_o^2)]]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$.

irreversible oxidation due to the rhodium acetate group at $E_p = +1.07$ V vs SCE. These data indicate that there is little interaction between the cobalt moieties and the dirhodium tetraacetate.

The situation is rather different with the corresponding ruthenium(II) phthalocyanine complex **8**. Again, the mass spectrum (electrospray ionization) confirms the constitution, having a parent peak at $m/z = 1729$ and the calculated isotope ratios for $C_{84}H_{94}Co_2N_{20}O_8Ru$. In contrast to **7**, the CN absorption in the IR spectrum is *very* weak but still appears at $\nu = 2125$ cm^{-1}, virtually unchanged from that of **6a**. Because the kinematic effect of appending a group to the cyanide nitrogen should cause an increase in ν_{CN}, this lack of shift of the absorption must be due to compensating π^*-back-donation from the metal to the cyanide group.[25b] The UV−vis spectrum [λ_{max} 320 ($\epsilon = 42\,200$), 372 (sh), 412 (2500), 571 (sh), 628 nm ($\epsilon = 26\,900$)] closely resembles that of the ruthenium(II) phthalocyaninebis(benzonitrile) complex, whose intense absorptions [λ_{max} 315 ($\epsilon = 29\,900$), 372 (sh), 581 (ϵ 6000), 642 nm (ϵ 26 900)] overwhelm that of the dioxocyclam portion. The ^{1}H NMR spectrum of **8** indicates that the pyridine-capped dioxocyclam portion of the molecule is substantially affected by coordination to the ruthenium phthalocyanine portion. *All* of the proton signals from the dioxocyclam portion are strongly shielded and shifted upfield substantially. Even the most remote proton on the 4 position of the pyridine cap is shifted upfield by 0.5 ppm, from δ 7.9 to 7.4 ppm. The methoxy peaks move from δ 3.5 and 3.2 ppm in **6a** to δ 2.8 and 1.7 ppm in **8**, and two of the methyl groups are shifted to δ −0.03 and 0.20 ppm. In contrast, the phthalocyanine peaks are only slightly shifted upfield, from δ 9.28 and 7.95 ppm in the starting ruthenium phthalocyanine complex to δ 8.94 and 7.70 ppm in **8**. Except for the presence of peaks due to the phthalocyanine group, the ^{13}C NMR spectrum is virtually identical with that of the starting complex **6a**, with all major peaks being within 2−3 ppm. In this case, even the CN signal at δ 130 ppm is present. Finally, complex **8** underwent an apparent two-electron, irreversible reduction [Co(III) → Co(II)] at $E_p = -1.40$ V vs SCE, a quasi-reversible, phthalocyanine-based reduction at $E_{1/2} = -1.67$ V vs SCE ($\Delta E = 180$ MV), a quasi-reversible oxidation at $E_{1/2} = +0.41$ V vs SCE ($\Delta E = 120$ MV), and an irreversible oxidation at $E_p = +1.25$ V vs SCE. In contrast, the bis(benzonitrile)ruthenium(II) phthalocyanine precursor underwent an irreversible reduction at $E_p = -1.48$ V vs SCE, a quasi-reversible oxidation at $E_{1/2} = +0.51$ V vs SCE ($\Delta E = 100$ MV), and an irreversible oxidation at $E_p = +1.4$ V vs SCE. Thus, by cyclic voltammetric measurements, coordination of the pyridine-capped cobalt cyanide complex **6a** to ruthenium(II) phthalocyanine has virtually no detectable effect on the electrochemistry of the cobalt portion of **8** ($E_p = -1.39$ V vs SCE compared to $E_p = -1.36$ V vs SCE for **6a**) but results in a reversible reduction wave for the phthalocyanine portion of the complex. Vahrenkamp and co-workers[26] studied the electrochemistry of a related Cp(dppe)Fe−CN−FePc−NCFe(dppe)Cp system. By cyclic voltammetry, no difference in the redox waves for the two external metal cyanide units was observed. However, square-wave voltammograms revealed a splitting of the redox waves by 0.08−0.20 V, indicating weak interaction between the two external metal sites across the cyanide bridges. Thus, if communication between the two cobalts in **8** does occur, it must be very weak.

Structural Studies. X-ray crystal structures of **4a** (Supporting Information), **5a**, **5b**, **6a**, **6b**, **7**, and **8** were obtained. The crystallographic data are compiled in Table 2, the ORTEP diagrams are displayed in Figure 2, and selected

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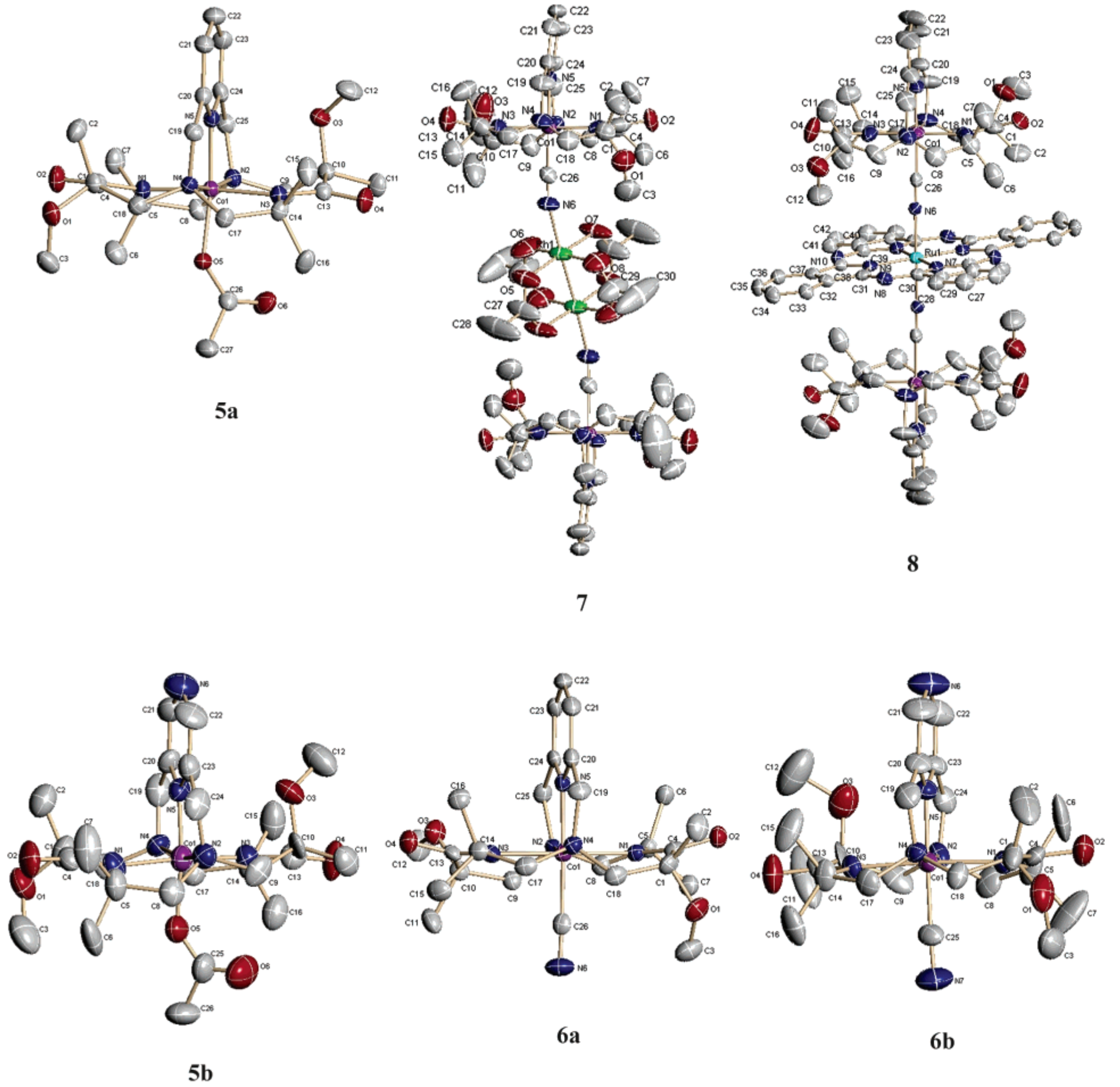
(26) Geiss, A.; Kolm, M. J.; Janiak, C.; Vahrenkamp, H. *Inorg. Chem.* **2000**, *39*, 4037−4043.



5a **7** **8** **5b** **6a** **6b**

Figure 2. ORTEP diagrams of **5a**, **5b**, **6a**, **6b**, **7**, and **8**.

bond lengths and angles are compiled in Table 3. The most remarkable structural feature of complexes **5a**, **5b**, **6a**, and **6b** is the similarity in the bond lengths and bond angles among them. Although the pyridine cap is a strong σ donor and the pyrazine cap in **5b** and **6b** is a strong π acceptor, this has no effect on the trans cobalt acetate oxygen (1.935 and 1.930 Å) or cyanide carbon (1.892 and 1.879 Å) bond lengths. The geometry about the cobalt atom is approximately octahedral, with a slight out-of-plane displacement of the amine nitrogens. The acetate is slightly displaced from linearity with the capping nitrogen−cobalt bond (>O5−Co−N5 = 172°), while the cyanide is linear [>C26($\overline{25}$)−Co−N5 = 178°; Co−C26($\overline{25}$)−N6(7) = 178°].

Complexes **7** and **8** present two rather different structural types for cyanide-bridged polymetallics (Figure 3). The bridging metals are bound quite differently. In complex **7**, the cyanide N-to-Rh bond is relatively long, 2.192 Å (supporting the IR data suggesting little π^* back-donation),[25a,b] the C≡N−Rh bond angle is 157.6°, strongly distorted from linear, and the Co−C≡N bond angle is almost linear at 175.3°. The Rh−Rh bond length is 2.388 Å, virtually identical with that in the bis(acetonitrile) adduct of $Rh_2(OAc)_4$.[27,28] These structural features are very similar to those found in the related complex having the pyridine-capped cobalt groups replaced by Cp*Ir(CN)$_2$ groups:[25d] CN−Rh bond length = 2.232 Å; C≡N−Rh bond angle = 151.9°, Rh−Rh bond length = 2.402 Å, and Ir−C≡N bond angle = 175.8°. In contrast, complex **8** has a substantially shortened cyanide N-to-Ru bond, 2.017 Å (supporting IR

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(27) Cotton, F. A.; Thompson, J. L. *Acta Crystallogr.* **1981**, *B37*, 2235−2236. The Rh−Rh bond length in aryl isocyanide adducts of $Rh_2(OAc)_4$ was insensitive to the electronic nature of the aryl substituent: Eagle, C. T.; Farrar, D. G.; Pfaff, C. U.; Davies, J. A.; Kluwe, C.; Miller, L. *Organometallics* **1998**, *17*, 4523−4526.

(28) Bossard, G. E.; Abrams, M. J.; Darkes, M. C.; Vollano, J. F.; Brooks, R. C. *Inorg. Chem.* **1995**, *34*, 1524−1527.

Table 3. Bond Lengths and Bond Angles for **5a**, **5b**, **6a**, **6b**, **7**, and **8**

	5a	**5b**	**6a**	**6b**	**7**	**8**
			Bond Lengths (Å)			
Co−N5	1.868(3)	1.845(6)	1.888(3)	1.869(6)	1.896(7)	1.893(6)
Co−O5	1.935(2)	1.930(6)				
(Co−C26)[a]			1.892(4)	1.879(8)	1.887(9)	1.895(7)
Co−N3	1.963(2)	1.951(6)	1.958(3)	1.964(6)	1.980(8)	1.930(7)
Co−N1	1.974(2)	1.980(7)	1.971(3)	1.971(6)	1.960(8)	1.986(8)
Co−N2	1.973(3)	1.965(6)	1.967(3)	1.959(6)	1.958(8)	1.957(7)
Co−N4	1.978(2)	1.981(6)	1.963(3)	1.975(6)	1.962(7)	1.961(7)
O2−C4	1.257(4)	1.232(9)	1.264(4)	1.263(9)	1.287(12)	1.221(11)
O4−C13	1.248(4)	1.224(8)	1.257(4)	1.222(9)	1.246(12)	1.271(12)
O6−C26[a]	1.233(4)	1.215(9)				
(N6−C26)[a]			1.150(5)	1.147(10)	1.140(10)	1.178(8)
N1−C4	1.318(4)	1.331(9)	1.328(5)	1.326(10)	1.234(13)	1.246(12)
N3−C13	1.331(4)	1.339(9)	1.329(5)	1.354(10)	1.265(13)	1.261(12)
−CN6−M					2.192(8)	2.017(5)
M−M					2.3879(15)	
			Bond Angles (deg)			
N5−Co−N3	93.10(1)	92.9(2)	90.09(12)	92.9(3)	90.1(3)	92.1(3)
N5−Co−N1	91.95(11)	92.3(3)	90.09(12)	91.5(2)	92.0(3)	90.1(3)
N5−Co−N4	84.19(I1)	83.8(3)	84.56(13)	83.9(3)	84.9(3)	85.1(3)
N5−Co−N2	84.65(I1)	84.4(3)	84.29(12)	83.7(3)	84.8(3)	83.6(3)
O5−Co−N3	90.09 (10)	89.8(2)				
C26−Co−N3[a]			88.47(14)	88.2(3)	89.5(3)	86.4(3)
O5−Co−N1	84.98(10)	85.1(2)				
C26−Co−N1[a]			91.35(14)	87.4(3)	88.3(4)	91.4(3)
O5−Co−N2	102.49(1)	102.5(2)				
C26−Co−N2[a]			95.41(13)	95.2(3)	97.0(3)	97.1(3)
O5−Co−N4	88.66(10)	89.3(2)				
C26−Co−N4[a]			95.73(14)	97.2(3)	93.4(3)	94.3(3)
O5−Co−N5	171.80(10)	172.3(3)				
C26−Co−N5[a]			178.51(15)	178.3(3)	178.2(3)	178.4(3)
N3−Co−N2	96.63(10)	96.7(3)	92.86(12)	95.9(2)	93.7(4)	95.2(3)
N3−Co−N4	83.82(10)	83.6(3)	87.05(13)	84.8(2)	86.7(3)	86.3(4)
N3−Co−N1	174.92(11)	174.8(3)	179.61(14)	175.6(3)	177.6(3)	177.7(3)
N4−Co−N1	97.27(10)	97.2(2)	92.62(12)	95.4(2)	92.5(4)	93.6(4)
N2−Co−N1	83.27(10)	83.6(3)	87.50(12)	84.8(3)	87.5(4)	85.4(3)
N2−Co−N4	168.83(11)	168.2(3)	168.85(12)	167.6(2)	169.7(3)	168.6(3)
C26−N6−M[a]					157.6(7)	176.3(6)
N6−Ru−N6′						180.00(3)
N6−C26−Co[a]			178.0(4)	177.1(8)	175.3(8)	176.4(6)

[a] $C_{25}N_7$ in compounds **5b** and **6b**.

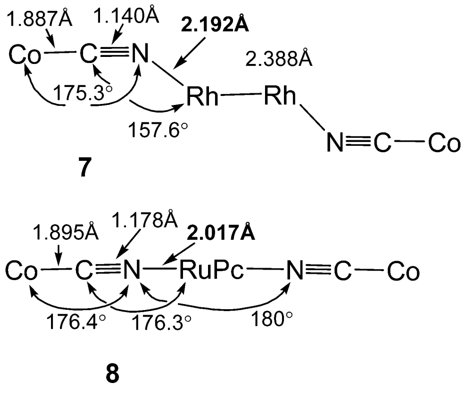

Figure 3. Key structural features of complexes **7** and **8**.

data suggesting at least modest π^* back-donation)[25a,b] and an almost linear arrangement along the entire bridging axis of the molecule. These structural features are very similar to those found in $[(NC)_5Fe-C{\equiv}N-Ru(Py)_4-N{\equiv}C-Fe(CN)_5]^{4-}$, having a short C≡N−Ru bond length of 2.02 Å and an almost linear arrangement along the bridging axis of the molecule.[25a]

Remarkably, only minor changes are observed in the cobalt dioxocyclam portion upon formation of complexes **7** and **8**. The cobalt to cyanide−carbon bond length is unchanged upon formation of **7** and **8**. One of the amide C═O bonds shortens modestly (1.264 Å → 1.246 and 1.221 Å) upon complexation to Rh and Ru, respectively, while the other lengthens (1.257 Å → 1.287 and 1.271 Å, respectively). In contrast, both amide N−CO bonds shorten substantially upon complexation (1.328 Å → 1.234 and 1.246 Å and 1.329 Å → 1.265 and 1.261 Å). It is not at all clear how these structural changes relate to the electronic changes that occur upon formation of **7** and **8** from **6a**.

Summary

Procedures for the introduction of cobalt(III) into 5,12-dioxocyclams were developed. With uncapped dioxocyclams, ring-opening hydrolysis of one of the amide groups or incorporation into dioxocyclam with deprotonation of both of the amides and one of the amines, to give a neutral cobalt(III) dioxocyclam complex, occurred depending on conditions. Introduction of cobalt(III) into 5,12-dioxocyclams capped across the amine nitrogens by 4-substituted pyridines failed under a wide range of thermal conditions but was achieved under microwave radiation. Electron-donating groups on the 4 position of the capping pyridine enhanced complexation, while electron-withdrawing groups suppressed it. These complexes were fully characterized, and the nature of the 4-substituient had little effect in the spectroscopic properties of the complexes. All of them underwent an irreversible Co(III) → Co(II) electrochemical reduction between −0.95 V and −1.36 V vs SCE. Pyridine-capped cobalt(III) cyanide complex **6a** complexed through the cyano group nitrogen to $Rh_2(OAc)_4$ and ruthenium(II) phthalocyanine to form tetra- and trimetallic coordination complexes with bridging cyanides. Cyclic voltammetry suggests little if any electronic communication among metals through the bridging cyanides.

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Supporting Information Available: Tables of crystal data, structure solutions and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4a**, **5a**, **5b**, **6a**, **6b**, **7**, and **8**, and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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