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Preparation of an Aquocobaloxime 1,3-Dienyl Complex and Its Diels−Alder Reactions in Water and Organic Solvents

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Cobaloxime complex [(H_2O)(dimethylglyoxime)$_2$Co(I)] (generated in situ) reacts with an allenic electrophile to produce 1,3-butadien-2-yl(H_2O)bis(dimethylglyoximato)cobalt(III). This dienyl complex (which has also been characterized by X-ray crystallography) reacts with a number of dienophiles in both water and organic solvents.

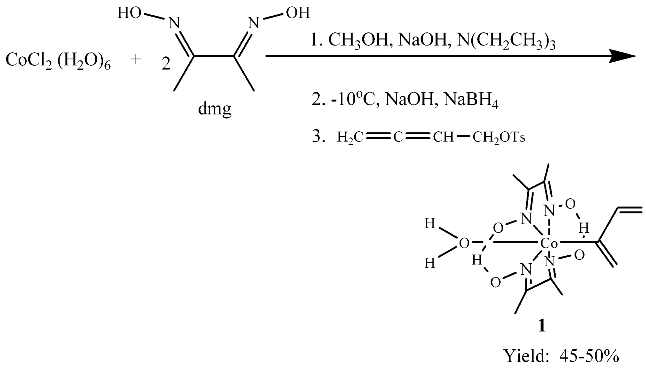
Introduction

Our group[1] and the Tada group[2] independently reported the preparation and Diels−Alder reactions of pyridine cobaloxime dienyl complexes over 10 years ago. Since that time, we have reported a number of synthetic routes to these and other related types of cobalt dienyl complexes as well as their subsequent cycloaddition and demetalation chemistry,[3,4] and other groups have now made use of the cycloadducts thus prepared[5] as well as the methodology.[6] We have not previously prepared one of these complexes that had enough water solubility to permit Diels−Alder chemistry of these complexes to be explored in that solvent. Here, we report an optimized preparation of 1,3-butadien-2-yl(H_2O)bis(dimethylglyoximato)cobalt(III) (**1**) as well as its X-ray crystallographic characterization and Diels−Alder chemistry.

Results and Discussion

Alkyl-substituted aquocobaloxime complexes were first prepared in the 1960s.[7] They were reported to have moderate water solubility, and while the methyl aquocobaloxime complex could be dehydrated without decomposition, water removal from higher alkyl homologues did not prove as facile. The water ligand in these complexes was easily replaced by phosphines, nitrogen heterocycles, and sulfides. We became interested in the preparation of an aquocobaloxime 1,3-dienyl complex for two reasons. We believed this complex might have enough water solubility to allow cobaloxime dienyl complex Diels−Alder reactions to be performed in water, and we thought the water ligand might be labile enough to allow the formation of η^3-butadienyl cobaloxime complexes or even possibly insertion chemistry. We report our investigation of both of those possibilities.

We first prepared aquocobaloxime 1,3-diene (**1**) by generating the cobaloxime anion in situ in aqueous methanol followed by treatment of that anion with 4-tosyl-1,2-butadiene.[1] The red, air-stable aquo dienyl complex (**1**) could be isolated, but the yield was disappointing (15%), and a side product (9%) resulting from the nucleophilic addition of a dimethylglyoxime hydroxyl to the allenic electrophile (with resulting displacement of the tosylate) ($CH_3C(=NOH)C(=NOCH_2CH=C=CH_2)CH_3$) was also isolated. We soon discovered that running these reactions in aqueous methanol with the addition of alkylamines resulted in much higher isolated yields of the aquo complex **1** and eliminated side product formation. Isolated yields of complex **1** were 27% and 36%, respectively, when diethyl- and diisopropylamines were used as the additives and reproducibly improved to nearly 50% when triethylamine was used. It should be pointed out that the aquo dienyl complex **1** crystallizes from the aqueous methanol upon standing at 0 °C, so the isolated yields reported require no purification other than a simple filtration.



The ^1H and ^{13}C NMR characteristics of the diene fragment of this aquo dienyl complex were similar to those of pyridine and substituted pyridine cobaloxime dienes we have reported previously.[8−12] The X-ray crystallographic data of diene **1** shows a diene torsional

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[1] Smalley, T. L.; Wright, M. W.; Garmon, S. A.; Welker, M. E.; Rheingold, A. L. *Organometallics* **1993**, *12*, 998−1000.

[2] Tada, M.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1252−1256.

[3] Pickin, K. A.; Kindy, J. M.; Day, C. S.; Welker, M. E. *J. Organomet. Chem.* **2003**, *681*, 120−133.

[4] Welker, M. E. *Curr. Org. Chem.* **2001**, *5*, 785−807.

[5] Miyaki, Y.; Onishi, T.; Ogoshi, S.; Kurosawa, H. *J. Organomet. Chem.* **2000**, *616*, 135−139.

[6] Chai, C. L. L.; Johnson, R. C.; Koh, J. *Tetrahedron* **2002**, *58*, 975−982.

[7] Windgassen, G. N. S. R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738−3743.

10.1021/om040010z CCC: $27.50

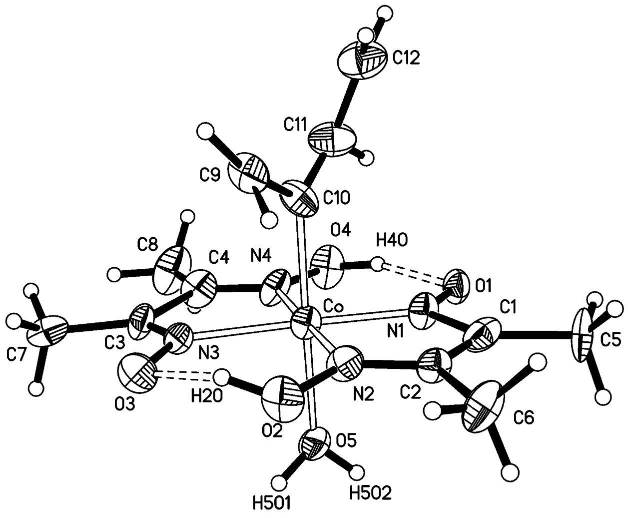

Figure 1. View of a molecule of Co[$C_4H_7N_2O_2$]$_2$(C_4H_5)(H_2O) from the crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms are displayed with an arbitrarily small radius. Hydrogen bonding interactions are represented by double dashed lines.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Co[$C_4H_7N_2O_2$]$_2$(C_4H_5)(H_2O)

Co−C10	1.962(3)	Co−O5	2.026(2)
C9−C10	1.471(10)	C10−C11	1.313(11)
C11−C12	1.325(9)	C10−Co−O5	177.7(4)
C11−C10−Co	119.2(6)	C9−C10−Co	118.9(5)
C10−C11−C12	126.4(7)	C11−C10−C9	121.7(4)

angle of 30.0° and a Co−C bond length of 1.962(3) Å. The Co−carbon bond in this complex is short compared to most of the other dienyl complexes we have reported previously,[13] and this manifests itself in a diene torsion angle smaller than any we have noted previously. The ORTEP of this complex is provided in Figure 1, and a partial listing of bond lengths and angles is provided in Table 1.

If the solid state diene torsion angle parallels the solution angle, then one would predict these dienes to be quite reactive in Diels−Alder chemistry. We found this to be true. We screened four different dienophiles, maleic anhydride, dimethyl fumarate, citraconic anhydride, and methyl vinyl ketone, in [4 + 2] cycloaddition chemistry (Table 2). All four reacted to produce high yields of cycloadduct in organic solvents, and the non-anhydride dienophiles *also cyclized well in water*. Maleic anhydride and dimethyl fumarate cyclized to produce the single diastereomers shown. Citraconic anhydride and methyl vinyl ketone cyclized to produce regioisomers, and the major regioisomer produced in each case is shown. The major citraconic anhydride regioisomer was also characterized by X-ray crystallography (Figure 2; selected bond lengths and angles, Table 3). The regiochemistry of the major cycloadduct from the reaction with methyl vinyl ketone was proven by NMR spectroscopy. The fact that the citraconic anhydride cycloaddition was somewhat regioselective (Co&Me meta:Co&Me para 1.6:1) is unusual given the fact that other electron-rich organic dienes, such as substituted furans, have been reported to react with citraconic anhydride to yield 1:1 mixtures of regioisomers.[14,15] Similary, a thermal cycloaddition between isoprene and citraconic anhydride performed in our laboratory produced a 1.05:1 mixture of meta:para regioisomers.

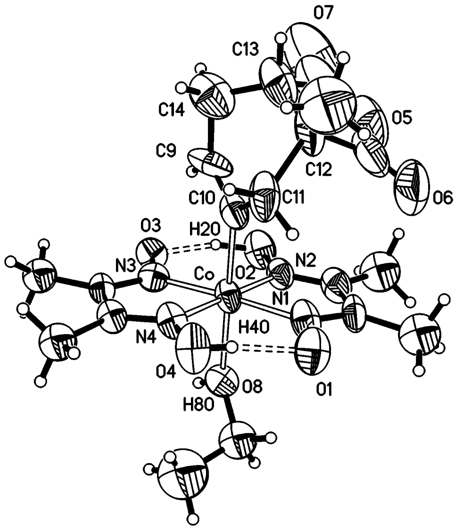

Figure 2. View of a molecule of Co[$C_4H_7N_2O_2$]$_2$($C_9H_9O_3$)(EtOH) from the crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms are displayed with an arbitrarily small radius. Hydrogen bonding interactions are represented by double dashed lines.

One of the original rationales for making these complexes (other than their water solubility and ability to participate in aqueous Diels−Alder chemistry) was the hope that the water ligand would prove labile enough to allow η^3-dienyl complex isolation or insertion chemistry. The isolation of the ethanol complex from the ethanol recrystallization of the citraconic anhydride adduct **4** also gave us cause to attempt dehydration of the dienyl complex **1** as well as the maleic anhydride **2** and dimethyl fumarate **3** cycloadducts. A variety of methods (heating in a variety of solvents with different dehydrating agents such as sieves of differing sizes, $MgSO_4$, $CF_3CO_2{}^iPr$) were attempted for removal of the coordinated water from **1** and attempted isolation of an η^3-dienyl complex, but none produced a new complex. The aquo dienyl complex **1** was reisolated in all cases. Likewise, heating the water coordinated cycloadducts **2** and **3** under CO or ethylene failed to yield any new complexes.

In summary, a new water-soluble cobaloxime 1,3-dienyl complex (**1**) has been prepared and characterized

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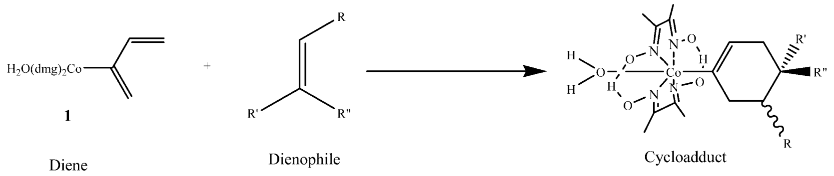
(14) Murali, R.; Rao, H. S. P.; Scheeren, H. W. *Tetrahedron* **2001**, *57*, 3165−3174.

(15) Beusker, P. H.; Aben, R. W. M.; Seerden, J. P. G.; Smits, J. M. M.; Scheeren, H. W. *Eur. J. Org. Chem.* **1998**, 2483−2492.

Table 2. Diels–Alder Chemistry of Complex 1



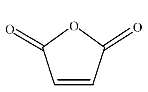
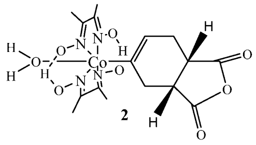
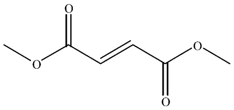
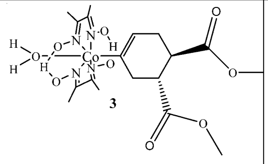
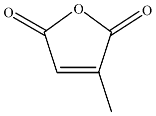
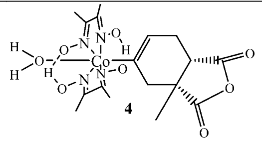
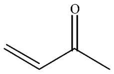
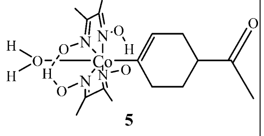
Dienophile	Structure	Condition	Cycloadduct	Yield (%)	Meta: Para
Maleic Anhydride		(**1**) THF, 67°C, 3hrs (**2**) THF, 25°C, 6hrs (**3**) THF, microwave 5 min.	 **2**	70 97 96	N/A
Dimethyl Fumarate		(**1**) THF, 100°C, 24hrs (**2**) THF, 25°C, 3 days (**3**) H_2O, microwave 15 min	 **3**	94 97 76	N/A
Citraconic Anhydride		THF, 100°C, 24hrs	 **4**	99	1.6 : 1.0
Methyl Vinyl Ketone		(**1**) THF, 100°C, 24hrs (**2**) THF, microwave 20 min. (**3**) H_2O, microwave 20 min	 **5**	89 97 89	1.0 : 5.1

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Co[C_4H_7N_2O_2]_2(C_9H_9O_3)(EtOH)$

Co–C10	1.947(10)	Co–O8	2.051(7)
C9–C10	1.340(13)	C9–C14	1.493(14)
C10–C11	1.488(12)	C11–C12	1.658(15)
C12–C17	1.443(14)	C12–C13	1.506(15)
C12–C15	1.537(16)	C13–C16	1.458(17)
C13–C14	1.484(15)	O8–C18	1.413(12)
O8–H8O	0.83(8)	C10–Co–O8	178.4(4)
C16–O5–C15	111.3(11)	C10–C9–C14	123.7(10)
C9–C10–C11	116.3(9)	C9–C10–Co	122.5(7)
C11–C10–Co	121.1(8)	C10–C11–C12	109.3(8)
C17–C12–C13	117.8(11)	C17–C12–C15	109.5(10)
C13–C12–C15	106.2(11)	C17–C12–C11	105.9(10)
C13–C12–C11	111.8(8)	C15–C12–C11	104.8(9)
C16–C13–C14	110.9(11)	C16–C13–C12	104.4(12)
C14–C13–C12	117.4(10)	C13–C14–C9	105.9(10)
O6–C15–O5	120.5(16)	O6–C15–C12	133.6(19)
O5–C15–C12	105.8(13)	O7–C16–O5	121.2(16)
O7–C16–C13	127(2)	O5–C16–C13	112.2(14)

by a variety of spectroscopic techniques in addition to X-ray crystallography. This dienyl complex reacts with a variety of dienophiles in Diels–Alder reactions in organic solvents as well as in water.

Experimental Section

General Procedures. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained using a Bruker Avance 300 MHz spectrometer operating at 300.1 MHz or a Bruker 500 MHz spectrometer operating at 500.1 MHz. ^{13}C NMR spectra were obtained using a Bruker 300 MHz spectrometer operating at 75.48 MHz. All spectra were referenced to the residual proton or carbon signals of the respective deuterated solvents. Infrared (IR) spectra were obtained on a Mattson Genesis II FT IR. Melting points were recorded using a Mel-Temp apparatus and are reported uncorrected. All elemental analyses were performed by Atlantic Microlabs, Inc. in Norcross, GA. High-resolution mass spectrometry was performed at the Duke University Mass Spectrometry Facility in Durham, NC. Microwave reactions were carried out using a Discover microwave system from CEM Corporation. All reactions were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone immediately prior to use. Pentane was distilled under nitrogen from calcium hydride, prior to use. Dimethylglyoxime was purchased from Aldrich and recrystallized from 95% ethanol (12 mL/g) prior to use. Sodium borohydride, isopropyl trifluoroacetate, maleic anhydride, dimethyl fumarate, citraconic anhydride, and methyl vinyl ketone were purchased from Aldrich. Amines were purchased from Aldrich or Fisher. Cobalt acetate tetrahydrate and cobalt chloride hexahydrate were purchased from Strem. Allenic tosylate, 4-tosyl-1,2-butadiene, was prepared according to a known literature procedure.[12,16]

Synthesis of 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (1). Cobalt acetate tetrahydrate (1.56 g, 6.25 mmol) and dimethylglyoxime (dmg) (1.45 g, 12.5 mmol) were stirred under a dry nitrogen atmosphere in degassed methanol (25 mL) for 1 h. Potassium hydroxide (0.715 g, 12.75 mmol) in degassed water (2.14 mL) was added, and the

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(16) Chapman, J. J.; Welker, M. E. *Organometallics* **1997**, *16*, 747–755.

reaction mixture was cooled in an ice bath. After the contents of the flask were chilled, 4-tosyl-1,2-butadiene (1.54 g, 6.88 mmol) was added. Sodium borohydride (0.150 g, 3.96 mmol) and potassium hydroxide (0.013 g, 0.22 mmol) in degassed water (5 mL) was added dropwise over 1 h. The reaction mixture was filtered, and the filtrate volume was reduced by one-half on a rotary evaporator. The mixture was diluted back up to full volume with degassed water and stored at approximately 4 °C overnight. Filtration of the reaction mixture revealed a mixture of red crystals (**1**) and white solid. The white solid was removed via chloroform in which the red crystals were not soluble, and it proved to have NMR characteristics consistent with the product of the nucleophilic addition of a dimethylglyoxime hydroxyl to the allenic electrophile (with resulting S_N2 displacement of the tosylate) ($CH_3C(=NOH)C(=NOCH_2CH=C=CH_2)CH_3$): ^{1}H NMR ($CDCl_3$): 5.37 (p, $J = 6.8$ Hz, 1H), 4.82 (dt, $J = 6.6$, 2.4 Hz, 2H), 4.67 (dt, $J = 7.0$, 2.4 Hz, 2H), 2.08 (s, 3H), 2.02 (s, 3H). ^{13}C NMR ($CDCl_3$): 209.6, 155.6, 153.7, 87.3, 75.8, 72.2, 10.1, 9.3. The red crystals (**1**) were collected and dried under vacuum (0.328 g, 0.91 mmol, 15.0% yield). Mp: 140 °C dec. ^{1}H NMR (d_8-THF): 18.50 (bs, 2H), 6.23 (dd, $J = 16.9$, 10.5 Hz, 1H), 4.73 (dd, $J = 16.7$, 2.8 Hz, 1H), 4.39 (dd, $J = 10.5$, 3.1 Hz, 1H), 4.23 (s, 1H), 3.89 (bs, 1H), 2.54 (bs, 2H), 2.15 (s, 12H). ^{13}C NMR (d_8-THF): 151.4, 145.9, 114.7, 107.6, 11.8. IR (NaCl): 3010, 2359, 2341, 1201, 1145 cm^{-1}. Anal. Calcd for $C_{12}H_{21}CoN_4O_5$: C, 40.01; H, 5.88. Found: C, 40.22; H, 5.94.

Improved Synthesis of 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (1). A flame-dried round-bottom flask and stir bar were cooled, and methanol (6 mL) was added and degassed with dry nitrogen. Cobalt chloride hexahydrate (0.531 g, 2.23 mmol) was added and was allowed to stir for several minutes. Dimethylglyoxime (0.518 g, 4.46 mmol) was added, and the mixture was again allowed to stir for several minutes. Sodium hydroxide (0.178 g, 4.46 mmol) in degassed water (297 μL) was added dropwise over 5 min. Triethylamine (1.55 mL, 11.15 mmol) was also added dropwise, over 5 min. The reaction mixture was allowed to stir for 20 min at room temperature and was then cooled to −10 °C in an ethylene glycol/dry ice bath. Sodium hydroxide (0.089 g, 2.23 mmol) in degassed water (297 μL) was added very slowly, followed by sodium borohydride (0.023 g, 0.595 mmol) in degassed water (297 μl), which was added slowly over 5 min to avoid heating the mixture. The reaction mixture turned green, indicating the presence of the cobalt anion. 4-Tosyl-1,2-butadiene (0.500 g, 2.23 mmol) was added rapidly, and the mixture was allowed to warm to room temperature slowly, overnight. The reaction volume was reduced to a fourth of the original volume via rotary evaporation. Triethylamine (0.257 mL, 1.85 mmol) in degassed water (8.82 mL) was chilled in an ice-bath and then added to the reaction mixture, which was also being chilled in an ice-bath. After approximately 30 min to 1 h, the reaction mixture was filtered and the bright red-orange solid was collected and dried under vacuum (0.375 g, 1.04 mmol, 47% yield), identical by spectroscopic comparison to the material reported above.

Diels−Alder Adduct of 1 from Maleic Anhydride Dienophile: Adduct 2. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.050 g, 0.139 mmol) was added to distilled, degassed tetrahydrofuran (THF) (4 mL). Maleic anhydride (0.027 g, 0.277 mmol) was added, and the reaction mixture was refluxed for 3 h under an atmosphere of dry nitrogen. The solution was allowed to cool to room temperature, and the solvent was removed via rotary evaporation. The remaining orange solid was purified by dissolving in a minimal amount of methylene chloride and slowly adding pentane until precipitation was complete. The solution was chilled in an ice-bath for approximately 10 min, and the product was collected by vacuum filtration and dried under vacuum (0.046 g, 0.100 mmol, 70% yield). Mp: 165 °C dec. ^{1}H NMR (d_8-THF): 5.27 (m, 1H), 3.10 (td, $J = 9.4$, 1.9 Hz, 1H), 3.07 (td, $J = 9.3$, 1.5 Hz, 1H), 2.50 (d, $J = 16.5$ Hz, 1H), 2.38 (ddd, $J = 14.7$, 7.5, 1.6 Hz, 1H), 2.15 (s, 6H), 2.12 (s, 6H), 2.10 (m, 1H), 1.69 (m, 1H). ^{13}C NMR (d_8-THF): 175.4, 174.8, 152.1, 151.8, 138.9, 128.6, 42.2, 42.2, 31.0, 26.5, 12.0, 11.7. IR (NaCl): 3405, 1776, 1681, 1193 cm^{-1}. Anal. Calcd for $C_{16}H_{23}CoN_4O_8$: C, 41.93; H, 5.06. Found: C, 41.27; H, 5.21. FAB HRMS (*m*/*z*) calcd for $C_{16}H_{22}CoN_4O_7$ ($M - H_2O + H^+$), 441.0820, found ($M - H_2O + H^+$), 441.0824.

Synthesis of Diels−Alder Adduct 2 at Room Temperature. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.300 g, 0.833 mmol) was added to distilled, degassed THF (9 mL) and allowed to stir for several minutes. Maleic anhydride (0.109 g, 1.110 mmol) was added, and the reaction mixture was allowed to stir for 6 h at room temperature, under an atmosphere of dry nitrogen. Solvent was removed using a rotary evaporator, and the orange solid was washed with several portions of pentane/anhydrous diethyl ether (50:50) to remove excess, unreacted maleic anhydride. The solid was dried under vacuum (0.371 g, 0.809 mmol, 97% yield) and was identical by spectroscopic comparison to the material isolated above.

Synthesis of Diels−Alder Adduct 2 by Microwave. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.050 g, 0.139 mmol) was dissolved in distilled, degassed THF (3 mL) in a microwavable tube. Maleic anhydride (0.027 g, 0.277 mmol) was added, and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was run in the microwave at 75 °C for 5 min. Solvent was removed by rotary evaporation, and the remaining red-orange solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The product was placed under high vacuum to dry (0.060 g, 0.131 mmol, 96% yield) and was identical by spectroscopic comparison to the material isolated above.

Diels−Alder Adduct of 1 from Dimethyl Fumarate Dienophile: Adduct 3. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.100 g, 0.278 mmol) was added to distilled, degassed THF (5 mL) in a thick walled pressure tube. Dimethyl fumarate (0.080 g, 0.555 mmol) was added, and the pressure tube was sealed with the reaction mixture under an atmosphere of dry nitrogen. The tube was heated to 100 °C for 24 h in a silicon oil bath. The solvent was removed via rotary evaporation, and the remaining red-orange solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The product was dried under vacuum (0.133 g, 0.264 mmol, 94% yield). Mp: 205 °C dec. ^{1}H NMR (d_8-THF): 18.44 (bs, 2H), 4.83 (bs, 1H), 3.54 (s, 3H), 3.51 (s, 3H), 2.56 (td, $J = 10.8$, 5.1 Hz, 1H), 2.48 (td, $J = 10.9$, 5.8 Hz, 1H), 2.25 (m, 1H), 2.23 (m, 1H), 2.17 (s, 12H), 2.07 (m, 1H), 1.74 (m, 1H). ^{13}C NMR (d_8-THF): 175.4, 175.1, 151.6, 151.5, 123.3, 51.4, 51.4, 44.5, 42.9, 35.5, 30.7, 11.8. IR (NaCl): 3732, 2359, 2341, 1684, 1204 cm^{-1}. Anal. Calcd for $C_{18}H_{29}CoN_4O_9$: C, 42.86; H, 5.80. Found: C, 42.84; H, 5.89.

Synthesis of Diels−Alder Adduct 3. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.100 g, 0.278 mmol) was added to distilled, degassed THF (5 mL) in a thick walled pressure tube. Dimethyl fumarate (0.080 g, 0.555 mmol) was added, and the tube was sealed. The reaction was allowed to stir under a dry nitrogen atmosphere for 3 days. The solvent was removed by rotary evaporation, and the solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The red-orange product was dried under vacuum (0.139 g, 0.276 mmol, 97% yield) and was identical by spectroscopic comparison to the material reported above.

Synthesis of Diels−Alder Adduct 3 Using Water as Solvent. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.050 g, 0.139 mmol) was added to distilled, degassed H_2O (2 mL) in a microwavable tube. Dimethyl fumarate (0.042 g, 0.291 mmol) was added, and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was run in the microwave at 100 °C for 15 min. Solvent was removed by lyophilization. The remaining solid was washed with a pentane/anhydrous diethyl ether solution (50:50). The product was placed under high vacuum to dry (0.053 g, 0.105 mmol, 76% yield) and was identical by spectroscopic comparison to the material reported above.

Diels−Alder Adduct of 1 from Citraconic Anhydride Dienophile: Adduct 4. 1,3-Butadien-2-ylwaterbis(dimethylglyoximato)cobalt(III) (**1**) (0.100 g, 0.278 mmol) was added to distilled, degassed THF (5 mL) in a thick walled pressure tube. Citraconic anhydride (0.062 g, 0.555 mmol) was added, and the pressure tube was sealed with the reaction mixture under an atmosphere of dry nitrogen. The tube was heated to 100 °C for 24 h in a silicon oil bath. The solvent was removed via rotary evaporation, and the remaining rust-red solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The product was dried under vacuum (0.131 g, 0.277 mmol, 99% yield) and was found to have a ratio of 1.6:1.0, meta to para. Mp: 145 °C dec. ^{1}H NMR (d_8-THF): Major isomer: 5.30 (m, 1H), 2.78 (m, 1H), 2.46 (m, 1H), 2.42 (m, 1H), 2.12 (s, 12H), 2.12 (m, 1H), 1.49 (d, $J = 16.5$ Hz, 1H), 1.18 (s, 3H). Minor isomer: 5.25 (m, 1H), 2.72 (m, 1H), 2.50 (m, 1H), 2.34 (m, 1H), 2.14 (s, 12H), 1.91 (m, 1H), 1.78 (m, 1H), 1.21 (s, 3H). ^{13}C NMR (d_8-THF): Major isomer: 178.1, 177.5, 152.1, 151.8, 130.0, 128.8, 49.2, 47.6, 23.0, 12.0, 11.7. Major/minor CH$_2$'s: 40.4, 35.6, 31.2, 26.3. Minor isomer: 174.0, 173.8, 152.1, 151.8, 130.0, 128.8, 49.2, 47.6, 23.4, 12.0, 11.7. IR (NaCl): 3331, 1778, 1680, 1202 cm^{-1}. Anal. Calcd for $C_{17}H_{25}CoN_4O_8$: C, 43.23; H, 5.33. Found: C, 42.82; H, 5.21.

Thermal Diels−Alder Reaction between Isoprene and Citraconic Anhydride. Isoprene (2.00 g, 29.36 mmol) and citraconic anhydride (0.165 g, 1.47 mmol) were added to degassed, distilled THF (7 mL) in a sealable pressure tube. The reaction mixture was placed under dry nitrogen and heated to 100 °C for 24 h. Once cooled, the solvent was removed via rotary evaporation, and the thick, milky liquid left behind was triturated with pentane (2 × 5 mL) and dried via high vacuum (0.223 g, 1.24 mmol, 84.2%) (meta:para 1.05: 1). ^{1}H NMR (CDCl$_3$): Major isomer (meta): 5.58 (m, 1H), 2.99 (dd, $J = 7.0$, 2.3 Hz, 1H), 2.56 (app dd, $J = 16.0$, 2.1 Hz, 1H), 2.46 (d, $J = 16.2$ Hz, 1H), 2.28 (m, 1H), 1.97 (d, $J = 16.2$ Hz, 1H), 1.77 (s, 3H), 1.45 (s, 3H). Minor isomer (para): 5.61 (m, 1H), 2.93 (dd, $J = 7.4$, 2.1 Hz, 1H), 2.64 (dd, $J = 6.2$, 1.4 Hz, 1H), 2.53 (app d, $J = 16.0$ Hz, 1H), 2.25 (m, 1H), 2.00 (m, 1H), 1.74 (s, 3H), 1.45 (s, 3H). EI HRMS (m/z) calcd for $C_{10}H_{12}O_3$, (M$^+$), 180.0786; found, 180.0788.

Diels−Alder Adduct of 1 from Methyl Vinyl Ketone Dienophile: Adduct 5. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.100 g, 0.278 mmol) was added to distilled, degassed THF (5 mL) in a thick walled pressure tube. Methyl vinyl ketone (0.039 g, 0.555 mmol) was added, and the pressure tube was sealed with the reaction mixture under an atmosphere of dry nitrogen. The tube was heated to 100 °C for 24 h in a silicon oil bath. Solid was removed via rotary evaporation, and the remaining orange-brown solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The product was dried under vacuum (0.107 g, 0.248 mmol, 89% yield) and was found to have a ratio of 5.1:1.0, para to meta. Mp: 150 °C dec. ^{1}H NMR (d_8-THF): Major isomer: 18.43 (bs, 2H), 4.78 (m, 1H), 2.59 (bs, 2H), 2.28 (m, 1H), 2.15 (s, 6H), 2.14 (s, 6H), 2.10 (m, 1H), 1.99 (m, 1H), 1.95 (s, 3H), 1.75 (m, 1H), 1.75 (m, 1H), 1.58 (m, 1H), 1.37 (ddd, $J = 24.3$, 11.7, 5.3 Hz, 1H). Minor isomer (ketone methyl protons): 1.94 (s, 3H). ^{13}C NMR (d_8-THF): 209.7, 151.2, 123.7, 48.7, 33.1, 30.2, 28.4, 27.5, 11.7. IR (NaCl): 3393, 2360, 2341, 1686, 1203 cm^{-1}. Anal. Calcd for $C_{16}H_{27}CoN_4O_6$: C, 44.66; H, 6.32. Found: C, 44.73; H, 6.20.

Synthesis of Diels−Alder Adduct 5 by Microwave. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.050 g, 0.139 mmol) was dissolved in distilled, degassed THF (2 mL) in a microwavable tube. The tube was sealed under an atmosphere of dry nitrogen, and methyl vinyl ketone (0.020 g, 0.278 mmol) was added via syringe. The reaction mixture was run in the microwave at 125 °C for 20 min. Solvent was removed by rotary evaporation, and the remaining orange-brown solid was washed with several portions of a pentane/anhydrous diethyl ether solution (50:50). The product was placed under high vacuum to dry (0.059 g, 0.137 mmol, 97% yield) and was identical by spectroscopic comparison to the material reported above.

Synthesis of Diels−Alder Adduct 5 Using Water as Solvent. 1,3-Butadien-2-yl(water)bis(dimethylglyoximato)cobalt(III) (**1**) (0.051 g, 0.142 mmol) was added to distilled, degassed H$_2$O (1.5 mL) in a microwavable tube. Methyl vinyl ketone (0.020 g, 0.285 mmol) was added, and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was run in the microwave at 125 °C for 20 min. Solvent was removed by lyophilization. The remaining solid was washed with a pentane/anhydrous diethyl ether solution (50:50). The product was placed under high vacuum to dry (0.054 g, 0.125 mmol, 89% yield) and was identical by spectroscopic comparison to the material above.

X-ray Experimental Information for $Co[C_4H_7N_2O_2]_2(C_4H_5)(H_2O)$ (1). An orange-red parallelepiped-shaped crystal of $C_{12}H_{21}CoN_4O_5$, approximate dimensions 0.09 mm × 0.10 mm × 0.20 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 193(2) K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1.75 kW power (50 kV, 35 mA). The detector was placed at a distance of 6.00 cm from the crystal. A total of 1800 frames were collected with a scan width of 0.30° in ω and an exposure time of 25 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic cell yielded a total of 7829 reflections to a maximum θ angle of 30.51° (0.70 Å resolution), of which 4347 were independent, completeness = 97.2%, $R_{\text{int}} = 4.65\%$, $R_{\text{sig}} = 8.07\%$ and 3424 were greater than $>2\sigma(I)\sigma(F^2)$. The final cell constants of $a = 11.657(2)$ Å, $b = 14.044(3)$ Å, $c = 9.6042(19)$ Å, $\beta = 92.228(3)°$, volume = 1571.1(5) Å^3 are based upon the refinement of the XYZ-centroids of 1800 reflections above $20\sigma(I)$ with $8.494° < 2\theta < 54.430°$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.8459. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Cc, with $Z = 4$ for the formula unit, $Co[C_4H_7N_2O_2]_2(C_4H_5)(H_2O)$. Successful refinement of the structure required the application of a racemic twinning model in which the twinning ratio refined to a value of 0.44(3). The final anisotropic full-matrix least-squares refinement on F^2 with 221 variables converged at $R_1 = 5.59\%$ for the 3424 observed data and $wR_2 = 13.92\%$ for all 4347 data. The goodness-of-fit was 1.058. The largest peak on the final difference electron density synthesis was 1.026 e$^-$/Å^3, and the largest hole was −0.394 e$^-$/Å^3 with an rms deviation of 0.106 e$^-$/Å^3. The top six peaks in the final difference Fourier map were within 0.90 Å of the cobalt atom. On the basis of the final model, the calculated density was 1.523 g/cm^3 and $F(000)$, 752 e$^-$.

X-ray Experimental Information for $Co[C_4H_7N_2O_2]_2(C_9H_9O_3)(EtOH)$ (4, L = EtOH). An orange ellipsoidal-shaped crystal of $C_{19}H_{29}CoN_4O_8$, approximate dimensions 0.01 mm × 0.06 mm × 0.22 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 193(2) K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1.75 kW power (50 kV, 35 mA). The detector was placed at a distance of 6.00 cm from the crystal. A total of 1256 frames were collected with a scan width of 0.30° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic cell yielded a total of 8360 reflections to a maximum θ angle of 21.97° (0.90 Å resolution), of which 2783 were independent, completeness = 99.6%, $R_{\mathrm{int}} = 9.95\%$, $R_{\mathrm{sig}} = 15.28\%$ and 1478 were greater than $>2\sigma(\mathrm{I})\sigma(F^2)$. The final cell constants of $a = 14.40(4)$ Å, $b = 10.82(3)$ Å, $c = 14.95(4)$ Å, $\beta = 101.78(6)°$, volume = 2280(10) Å^3 are based upon the refinement of the *XYZ*-centroids of 487 reflections above $20\sigma(I)$ with $4.41° < 2\theta < 31.73°$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group $P2_1/n$, with $Z = 4$ for the formula unit, $C_{19}H_{29}CoN_4O_8$. The final anisotropic full-matrix least-squares refinement on F^2 with 269 variables converged at $R_1 = 6.97\%$ for the observed data and $wR_2 = 18.45\%$ for all data. The goodness-of-fit was 1.007. The largest peak on the final difference electron density synthesis was 0.457 e$^-$/Å^3, and the largest hole was −0.349 e$^-$/Å^3 with an rms deviation of 0.078 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.458 g/cm^3 and *F*(000), 1048 e$^-$.

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Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic displacement parameters for **1** and **4** (L = EtOH). This material is available free of charge via the Internet at http://pubs.acs.org.

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