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[6 + 4] and [4 + 2] Cycloaddition Reactions of Cobaloxime 1,3-Dienyl Complexes and Tropones

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1,3-Dien-2-yl(Rpyr)bis(dimethylglyoximato) cobalt(III) complexes (R = H, NMe_2) have been shown to participate in cycloaddition reactions with a variety of tropones. In general, tropones that do not contain electron-withdrawing substituents react with dienyl complexes via [6 + 4] cycloaddition and tropones that are substituted with at least one additional electron-withdrawing group react via [4 + 2] cycloaddition. Both types of metal-substituted cycloadducts ([6 + 4] and [4 + 2]) presented here have also been characterized by X-ray crystallography.

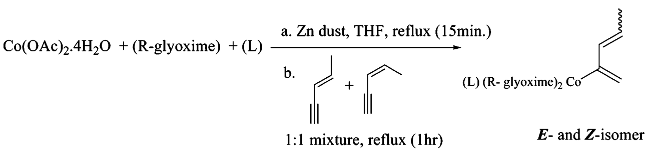
Introduction

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,[3−5] and other groups have now made use of the cycloadducts thus prepared[6] as well as the methodology.[7] We have not previously reported any higher order cycloaddition reactions of cobaloxime dienyl complexes or any reactions of these complexes with tropones. Here, we report a number of cycloaddition reactions with a variety of tropones as well as the X-ray crystallographic characterization of two of the resulting [6 +4] and [4 + 2] cycloadducts.

Results and Discussion

Tropones are unusual cycloaddition electrophiles in that they can participate as 6π or 2π electron partners in cycloadditons with organic dienes.[8] In general, free tropones participate in [6 + 4] cycloadditon reactions with organic dienes through *exo* transition states,[9−12] whereas metal-complexed tropones react with organic dienes through *endo* transition states.[13] Reactions of metal-substituted dienes with free tropones had not been investigated, hence the studies we report here to elucidate both the mode ([6 + 4] versus [4 + 2]) and stereochemical outcomes of these classes of cycloaddition reactions.

A. Cobaloxime Diene Complex Synthesis. All cobaloxime dienyl complexes used in this study (**1** and **2** as examples) were prepared using zinc-mediated hydrocobaltation of enynes, as we have reported previously.[3] We extensively studied rates of *Z*-diene to *E*-diene isomerization relative to cycloaddition rates in our earlier cobaloxime Diels−Alder chemistry.[14] Since we found that *Z* to *E* isomerization was rapid relative to cycloaddition, we have routinely used *Z*/*E*-diene mixtures and have never noted any effect on stereochemical outcomes of cycloadditon (when compared to using pure *E*- or *Z*-dienes). We, therefore, used the *E*/*Z* mixture resulting from the preparation shown here without any additional purification.



1 L = DMAP, R = DiMe
68%, 2.3:1, Z:E
2 L = pyr, R = DiPh
89%, 1.5:1, Z:E

B. Cycloaddition Reactions of Cobaloxime Dienes with Tropones. In a typical cycloaddition experiment, cobaloxime dienes were heated at various temperatures in the presence of tropones. The simplest tropone, cycloheptatrienone (**3**), reacted with a pyridine cobaloxime butadienyl complex (**4a**) and pyridine as well as DMAP-ligated cobaloxime pentadienyl complexes (**4b** and **1**). Those cycloaddition reactions proceeded via [6 + 4] cycloaddition, resulting in the formation of bicyclo-[4.4.1]undecanones (**5a**−**c**) in high yields. Cobaloxime-substituted bicycloundecanones (**5a**−**c**) were formed as single stereoisomers. NMR techniques such as ^{13}C and HMBC were used to postulate the regiochemistry [6 + 4 vs 4 + 2 cycloadduct] of the cycloadducts isolated. The [6 + 4] versus [4 + 2] regiochemistry was supported initially by C═O ^{13}C NMR

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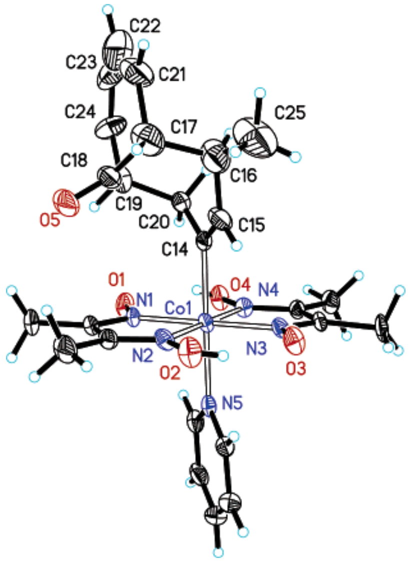
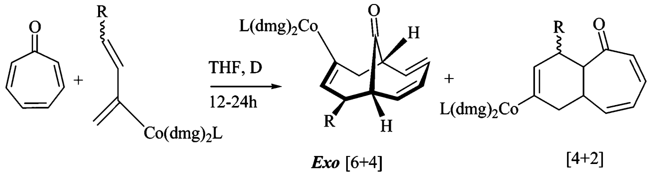


Figure 1. View of a molecule of $C_{25}H_{32}CoN_5O_5$ (**5b**) from the crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

resonances appearing in the 204−209 ppm range in all cases (**5a**−**c**) as well as HMBC cross-peaks from *both* the C*H*$_2$ and the RC*H* protons to the C═O for **5b** and **5c**. That regiochemical postulate as well as stereochemistry was subsequently confirmed by X-ray crystallography for complex **5b**.



3 **4** **5** **6**

4a R = H, L = pyr **5a**, 95%
4b R = Me, L = pyr **5b**, 93%
1 R = Me, L = DMAP **5c**, 87%

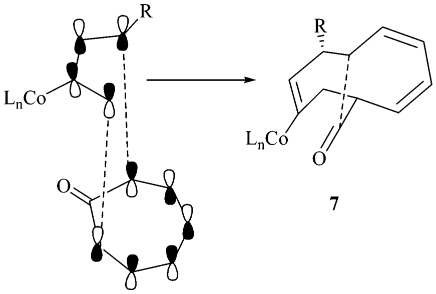
The X-ray crystallographic data for cycloadduct **5b** are presented below. The Co−carbon bond in this complex is 1.976(6) Å and is similar to most of the other cobalt−sp^2 carbon bonds we have reported in cobaloxime complexes previously.[15] The C(14)−Co−N(5) bond angle is very close to 180°, and the Co−C(14)−C(15) and Co−C(14)−C(20) bond angles are both very close to 120°, indicating that the complex has classical octahedral cobaloxime complex geometry and that there is little if any steric interaction between the cobaloxime core and the bicyclic core of the cycloadduct. The ORTEP of this complex is provided in Figure 1, and a partial listing of bond lengths and angles is provided in Table 1.

The stereoisomers we isolated (**5a**−**c**) can be rationalized by an *exo* approach of the tropone to the cobaloxime dienes (**1** and **4b**) (Scheme 1). This tropone approach would place the reactive and sterically most cumbersome triene portion of the tropone away from the cobaloxime diene substituent in the transition state. This is consistent with our stereochemical observations of Diels−Alder reactions of these dienes.[4] The [6 + 4] cycloadduct yields and stereochemistries obtained here compare favorably to those previously obtained with organic dienes such as 1,3-butadiene, *trans*-piperylene, and isoprene, which reacted with tropone in sealed tubes heated to 130 °C in xylenes to produce a 9:1 mixture of [6 + 4]:[4 + 2] products, a 60% yield of [6 + 4] product, and an 86% yield of [6 + 4] product, respectively.[9,10]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $C_{25}H_{32}CoN_5O_5$ (5b)

Co(1)−C(14)	1.976(6)
O(5)−C(18)	1.206(9)
C(14)−C(15)	1.350(8)
C(14)−C(20)	1.469(8)
C(15)−C(16)	1.467(10)
C(16)−C(17)	1.584(12)
C(16)−C(25)	1.592(13)
C(17)−C(18)	1.509(14)
C(17)−C(21)	1.535(18)
C(18)−C(19)	1.557(13)
C(19)−C(24)	1.426(13)
C(19)−C(20)	1.569(10)
C(21)−C(22)	1.40(3)
C(22)−C(23)	1.1161
C(23)−C(24)	1.47(2)
N(4)−Co(1)−C(14)	90.7(2)
N(2)−Co(1)−C(14)	89.6(2)
N(3)−Co(1)−C(14)	90.0(2)
N(1)−Co(1)−C(14)	89.6(2)
C(14)−Co(1)−N(5)	179.5(2)
C(15)−C(14)−C(20)	118.2(6)
C(15)−C(14)−Co(1)	121.6(5)
C(20)−C(14)−Co(1)	120.1(4)
C(14)−C(15)−C(16)	124.6(7)
C(15)−C(16)−C(17)	109.7(7)
C(15)−C(16)−C(25)	112.4(8)
C(17)−C(16)−C(25)	110.6(8)
C(18)−C(17)−C(21)	113.4(12)
C(18)−C(17)−C(16)	111.6(7)
C(21)−C(17)−C(16)	112.1(9)
O(5)−C(18)−C(17)	123.6(10)
O(5)−C(18)−C(19)	116.2(9)
C(17)−C(18)−C(19)	120.0(8)
C(24)−C(19)−C(18)	113.4(10)
C(24)−C(19)−C(20)	111.8(8)
C(18)−C(19)−C(20)	111.5(7)
C(14)−C(20)−C(19)	112.6(6)
C(22)−C(21)−C(17)	122.5(17)
C(23)−C(22)−C(21)	130.5(12)
C(22)−C(23)−C(24)	142.9(10)
C(19)−C(24)−C(23)	121.8(14)

Scheme 1. *exo* Approach of Tropone to a Cobalt-Substituted Diene



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We next investigated the cycloaddition chemistry of some simple monosubstituted tropones with cobaloxime dienes. Specifically, we looked at reactions of both 2-methyl and 2-phenyltropone (**8**, R_1 = Me or Ph). Substituents at the 2 and 7 positions of a tropone would be expected to sterically retard the rates of [6 + 4] cycloaddition, and that trend is what we encountered here. Whereas tropone (**3**) reacted completely with all three cobaloxime dienes we tried in 12−24 h, we found that 2-methyl- and 2-phenyltropone (**8**, R_1 = Me and Ph) produced

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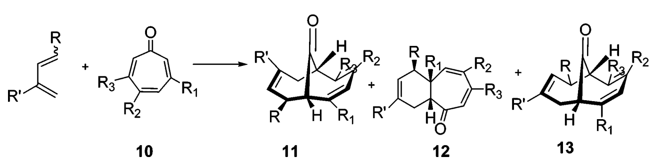
Table 2. Reactions of 2,7-Unsubstituted-3−6-Substituted Tropones

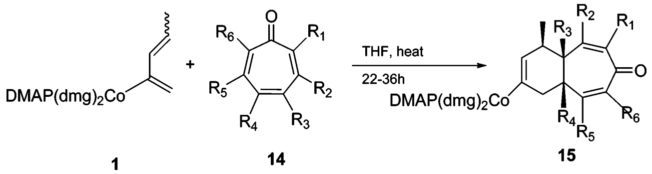


entry	R	R′	R$_1$	R$_2$	R$_3$	**11**	**12**	**13**
1 a	Me	(pyr)(dmg)$_2$Co	CO$_2$Me	Ph	OMe	(a) 13%	55%	0
2 b	H	Me	CO$_2$Et	H	H	(b) 38%	0	0
3 c	H	Me	H	CO$_2$Et	H	(c) 0	0	25%
4 d	H	Me	OMe	H	H	(d) 15%	0	15%

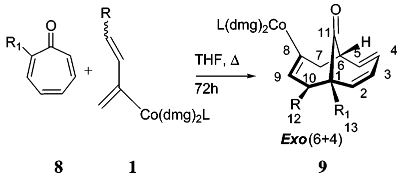
cycloadducts (**9a** and **9b**) in only 44% and 26% yields, respectively, after 72 h of heating with diene (**1**). At these long heating times significant cobaloxime diene decomposition also starts to compete with cycloaddition. Interestingly, these tropones (**8**) reacted with cobaloxime dienyl complex (**1**) to produce a single regio- and stereoisomer. The regio- and stereochemistries of these cycloadducts (**9a** and **9b**) are postulated as shown based on ^{1}H and ^{13}C NMR analogy to the cycloadduct **5b**, which we characterized by X-ray crystallography. Proton and carbon resonances in the bicycloundecatrienone core for protons and carbons other than the bridgehead carbon attached to R$_1$ are almost identical when one compares spectroscopic data for **5b** to **9a** or **9b**. The methine proton alpha to R = Me in both **9a** and **9b** shows coupling to only one alkene proton and the methyl group (R = Me), as expected for the regiochemical outcome shown. In the case of **9a**, it did not prove possible to use NOESY to gain additional stereochemical information about the relationship between R and R$_1$. In **9a**, where both R and R$_1$ are CH$_3$ groups, their chemical shifts are too close together to permit meaningful data to be gathered from NOESY. However, in the case of **9b**, where R = CH$_3$ and R$_1$ = Ph, the ortho protons on the benzene ring show NOESY cross-peaks to the protons on carbons 2, 9, and 12 but not to the methine proton on C10. The methine proton on C10 shows strong NOESY cross-peaks to both H2 and H3. This NMR data along with the general spectroscopic similarities to **5b** mentioned above led us to postulate the stereochemistry shown for **9a** and **9b**. Isolated yields of [6 + 4] cycloadducts (**9a** and **b**) were modest; however, [6 + 4] cycloadduct formation is known to be suppressed in intermolecular cycloaddition reactions between 2-substituted tropones and organic rather than organometallic 1,3 dienes.[8,16] This organometallic chemistry therefore provides access to structural types that were not previously readily available.

We also note one unusual experimental observation that we observed in performing these reactions. In the past, we had noted that we could synthesize stereochemically pure cobaloxime *E*-dienes using reactions of cobaloxime anions with allenic electrophiles[17] or prepare *E*/*Z* mixtures using the enyne hydrocobaltation procedure described earlier here. In Diels−Alder chemistry, we had noted that *Z*-diene cycloadditions were much slower than *Z*:*E* isomerization and that cycloaddition rates of *E*-dienes were fast relative to *Z*:*E* isomerization.[14] In these [6 + 4] cycloadditions with **1** (R = Me, L = DMAP) and **8a** (R$_1$ = Me), we noted a difference between using the *Z*/*E* mixture and stereochemically pure *E*. Whereas pure *E*-**1** had reacted completely with **8a** in 72 h, the *E*/*Z* **1** mixture reaction was only ~50% complete in that same time frame. The implication here is that [6 + 4] cycloaddition is slower than [4 + 2] cycloadditions were and therefore cannot be used to readily drive *Z*:*E* isomerization.

Table 3. Reactions of Highly Substituted Tropones



entry	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	**15** (% yields)	#
1 **14a**	CO$_2$Et	H	CO$_2$Et	H	H	OMe	67	**15a**
2 **14b**	Ph	H	CO$_2$Me	H	OMe	H	38	**15b**
3 **14c**	Me	H	CO$_2$Me	H	OMe	H	46	**15c**
4 **14d**	SEt	H	CO$_2$Me	H	OMe	H	87	**15d**
5 **14e**	Ph	H	CO$_2$Me	H	H	OMe	29	**15e**



9a R$_1$ = Me, 44%
9b R$_1$ = Ph, 26% (37% based on recovered starting material)

Last, we examined the cycloaddition chemistry of a number of tropones that were polysubstituted and contained at least one electron-withdrawing substituent in order to see what effect this would have on the regio- and stereochemical outcome of these cycloaddition reactions. In previously reported thermal intermolecular cycloaddition reactions of unsymmetrical 1,3-dienes with 3- or 4-substituted tropones, electron-withdrawing substituents provided slightly higher yields of [6 + 4] products than electron-donating substituents, but product yields and regioisomer outcomes were modest (10−20%) in both cases.[10] Tropone (**10a**), which was unsubstituted at the second and seventh positions, but which also had an electron-withdrawing group led to the formation of two types of cycloadducts. In both cases a single stereo/regioisomer was isolated. Higher-order [6 + 4] cycloaddition produced the minor isomer (**11a**) in this case, whereas [4 + 2] cycloaddition led to the major isomer (**12a**) in 1.0:4.2 ratio (13%:55% isolated yields of **11a**:**12a**). Once again this reaction of a cobaloxime-substituted diene with a tropone compared favorably with a reaction of an organic diene like isoprene with similar tropones (Table 2, entries 2−4).[10]

Tropones **14** that have substituents at the second or seventh positions and EWGs inhibited the higher-order pathway. They reacted in [4 + 2] reaction pathways to yield bicyclo[5.4.0]-undecanones (**15**) (Table 3). It should also be noted here that tricarbonyl(tropone)iron has also previously been shown to contain a tropone core, which reacted with dienes in [4 + 2]

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(16) Ito, S. S., K.; Fujise, Y. *Tetrahedron Lett.* **1969**, *10*, 775−778.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Co(C_4H_7N_2O_2)_2(C_7H_{10}N_2)(C_{19}H_{23}O_6)$ (15a)

Co(1)−N(4)	1.864(6)
Co(1)−N(2)	1.869(5)
Co(1)−N(3)	1.872(5)
Co(1)−N(1)	1.890(5)
Co(1)−C(16)	1.987(6)
Co(1)−N(5)	2.058(6)
O(5)−C(28)	1.192(9)
O(6)−C(28)	1.335(9)
O(6)−C(29)	1.468(16)
O(7)−C(31)	1.164(14)
O(8)−C(31)	1.180(12)
O(8)−C(32)	1.479(12)
O(9)−C(24)	1.228(9)
O(10)−C(25)	1.403(8)
O(10)−C(34)	1.409(11)
C(16)−C(17)	1.321(9)
C(16)−C(21)	1.523(9)
C(17)−C(18)	1.502(9)
C(18)−C(27)	1.514(10)
C(18)−C(19)	1.583(9)
C(19)−C(22)	1.515(10)
C(19)−C(28)	1.513(9)
C(19)−C(20)	1.521(10)
C(20)−C(26)	1.495(9)
C(20)−C(21)	1.547(9)
C(22)−C(23)	1.325(9)
C(23)−C(24)	1.529(11)
C(23)−C(31)	1.553(16)
C(24)−C(25)	1.448(10)
C(25)−C(26)	1.331(9)
C(29)−C(30)	1.35(2)
C(32)−C(33)	1.377(15)
N(4)−Co(1)−N(2)	177.0(3)
N(4)−Co(1)−N(3)	81.2(3)
N(2)−Co(1)−N(3)	99.3(3)
N(4)−Co(1)−N(1)	98.5(3)
N(2)−Co(1)−N(1)	81.1(3)
N(3)−Co(1)−N(1)	178.3(2)
N(4)−Co(1)−C(16)	87.9(2)
N(2)−Co(1)−C(16)	89.1(2)
N(3)−Co(1)−C(16)	91.0(2)
N(1)−Co(1)−C(16)	90.6(2)
N(4)−Co(1)−N(5)	90.8(2)
N(2)−Co(1)−N(5)	92.2(2)
N(3)−Co(1)−N(5)	88.8(2)
N(1)−Co(1)−N(5)	89.6(2)
C(16)−Co(1)−N(5)	178.7(2)
C(17)−C(16)−C(21)	120.6(6)
C(17)−C(16)−Co(1)	122.8(5)
C(21)−C(16)−Co(1)	116.5(4)
C(16)−C(17)−C(18)	126.6(6)

rather than [6 + 4] cycloaddition reactions.[18] Presumably, in that case, the $Fe(CO)_3$ acts as an electron-withdrawing group on two of the three alkene groups in the tropone, leaving one of the alkene functional groups to react as a typical enone in Diels−Alder chemistry.

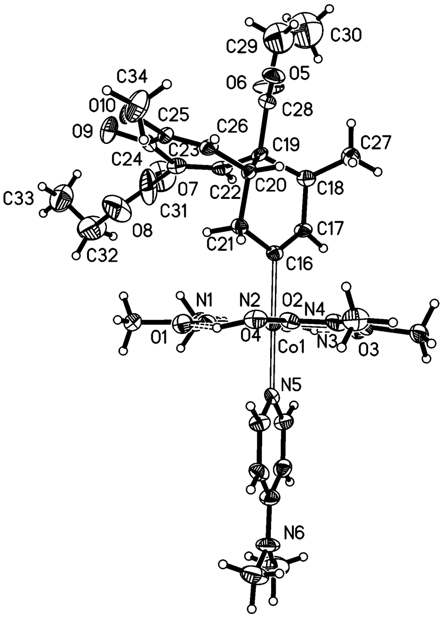
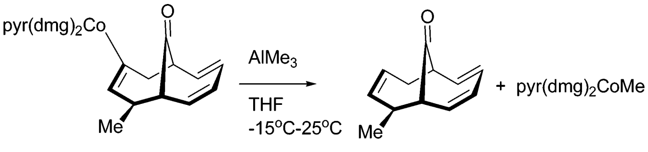


Figure 2. View of a molecule of $Co(C_4H_7N_2O_2)_2(C_7H_{10}N_2)$-$(C_{19}H_{23}O_6)$ (**15a**) from the crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms are displayed with an arbitrarily small radius. Hydrogen-bonding interactions are represented by double dashed lines.

The structure of cycloadduct **15a** was confirmed by X-ray crystallography. The X-ray crystallographic data of cycloadduct **15a** revealed a Co−carbon bond length of 1.987(6) Å in this complex. This and other cobalt coordination sphere bond lengths and angles are similar to those that have have observed previously for complexes containing cobalt−sp^2 carbon bonds.[5] The ORTEP of this complex is provided in Figure 2, and a partial listing of bond lengths and angles is provided in Table 4. The structures of cycloadducts **15b**−**e** were inferred by analogy with the spectroscopic data of **15a** and additional NMR data. With respect to the regiochemistry of cycloaddition in the case of cycloadduct **15b**, HMBC confirmed that the conjugated carbonyl carbon absorbing at 190 ppm contained cross-peaks *only* to the alkenyl proton R_2 = H. Stereochemistry was inferred by the strong NOESY cross-peak between the ring junction proton (R_4 = H) and the methyl group. Likewise, for **15e**, HMBC also confirmed that the conjugated carbonyl in that case showed cross-peaks only to the alkenyl protons R_2 = R_5 = H.

C. Demetalation of Tropone Cycloadducts. We have previously reported numerous examples of the cleavage of cobaloxime−sp^2 carbon bonds that yield demetalated organic cycloadducts and a reusable cobaloxime complex.[4] These cobaloxime tropone cycloadducts also fall into this reaction category. When [6 + 4] adduct **5b** was treated with trimethylaluminum, cycloadduct **16** was isolated in almost quantitative yield along with $pyr(dmg)_2CoMe$ (**17**).



5b **16** (96%) **17** (73%)

D. Summary. Cobaloxime dienyl complexes reacted with tropone and 2-methyl as well as 2-phenyltropone to produce [6 + 4] cycloadducts through *exo* transition states. When cobaloxime dienyl complexes are treated with tropones that contain electron-withdrawing substituents, then they participated in [4 + 2] cycloaddition reactions with the alkene in the tropone that contained the electron-withdrawing group. The [6 + 4] cycloadduct produced in one case was removed from the cobaloxime core and recovered along with a cobaloxime methyl complex, which can be recycled back into the synthesis of the original dienyl complex.

Experimental Section

General Procedures. The ^1H NMR spectra were recorded by using a Bruker Avance 300 MHz spectrometer and Bruker Avance

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500 MHz spectrometer operating at 300.13 and 500.13 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer operating at 75.48 MHz. Chemical shifts were reported in parts per million (δ) relative to the residual peaks of either tetramethylsilane (TMS) or chloroform (CDCl$_3$). Coupling constants (J values) were reported in hertz (Hz), and spin multiplicities were indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and p (pentet).

All elemental analyses were carried out by Atlantic Microlabs Inc., GA. High-resolution mass spectrometric (HRMS) analysis was carried out at the Duke Mass Spectrometric Facility, Durham, NC. Flash chromatography was performed using thick-walled glass chromatography columns and "Ultrapure" silica gel (Silicycle Ind., Canada, 40−63 μm).

All reactions were carried out under an inert atmosphere unless otherwise noted. Diethyl ether, pentane, tetrahydrofuran, hexanes, and methylene chloride were purchased from Fischer Scientific. Tetrahydrofuran, pentane, and diethyl ether were distilled from sodium/benzophenone ketyl; methylene chloride was distilled from CaH$_2$. Deuterated solvents were purchased from Cambridge Isotopes and used as received. All other chemicals were purchased from Sigma-Aldrich and used as received. 2-Methyltropone (**8**, R$_1$ = Me),[19] 2-phenyltropone (**8**, R$_1$ = Ph),[20] (3*E*)- and (3*Z*)-1,3-pentadien-2-yl-(pyridine)bis(dimethylglyoximato)cobalt(III) (**4b**),[3] and 1,3-butadiene-2-yl-(pyridine)bis(dimethylglyoximato)cobalt(III) (**4a**)[2] were prepared according to the reported literature. Other tropones were kindly donated by Dr. Huw M. L. Davies and his research group at SUNY−Buffalo.

(3*E*)- and (3*Z*)-1,3-Pentadien-2-yl-(4-(dimethylamino)pyridine)bis(dimethylglyoximatio)cobalt(III) (1). A modification of a literature procedure was used to synthesize cobaloxime diene **1**.[3] Cobalt(II) acetate tetrahydrate (2.452 g, 9.844 mmol) and dimethylglyoxime (2.275 g, 19.59 mmol) were dissolved in degassed THF (100 mL). To this was added successively 4-(dimethylamino)pyridine (1.808 g, 14.80 mmol), predissolved in 5.00 mL of degassed THF, and Zn dust (3.194 g, 48.86 mmol). This mixture was refluxed for 15 min. The reaction mixture was cooled enough to cease the reflux, then 3-penten-1-yne[21] (0.972 g, 14.70 mmol) was added and the reflux was resumed for 1 h. The reaction pot was cooled to room temperature and filtered using a Celite pad (10 mm) to remove any insoluble materials. The Celite pad was washed with THF (3 × 10 mL), and the solvent removal resulted in cobaloxime complex deposition as a yellowish-orange solid. The solid was vacuum-dried and passed through a column (100 mm, EtOAc) to remove polar impurities, affording 3.210 g (6.709 mmol, 68%) of the cobaloxime diene **1** as an orange-yellow fluffy powder. The isomeric ratio (1.0:2.3 *E* to *Z*) was determined by ^{1}H NMR, and the spectral data were identical to those reported earlier by our group.[17]

(3*E*)- and (3*Z*)-1,3-Pentadien-2-yl-(pyridine)bis(diphenylglyoximato)cobalt(III) (2). Cobaloxime diene **2** was prepared according to the procedure mentioned above except using pyridine and diphenylglyoxime in place of 4-(dimethylamino)pyridine and dimethylglyoxime. Cobalt(II) acetate tetrahydrate (1.250 g, 5.018 mmol), diphenylglyoxime (2.403 g, 10.0 mmol), freshly distilled pyridine (1.170 g, 14.79 mmol), Zn dust (3.194 g, 48.86 mmol), and 3-penten-1-yne (0.500 g, 7.560 mmol) were used. The resulting crude product was purified by column chromatography (silica gel, 14.5 mm × 250 mm; 10 mm; EtOAc), which provided 3.386 g (4.953 mmol, 89%) of the title compound (**2**) as a brown-yellow amorphous solid. The isomeric ratio (1.0:1.5 *E* to *Z*) was calculated on the basis of ^{1}H NMR, and the spectral data were identical to those reported earlier by our group.[17]

General Procedure for the Cycloaddition Reactions. A representative procedure follows: In a sealed tube, cobalt-substituted diene was dissolved in freshly distilled THF (7.0 mL) and purged with nitrogen for few minutes. Tropone was added to the tube and heated in an oil bath at 110 °C over a period of time. After completion of the reaction, the sealed tube was cooled to room temperature and solvent was removed by rotary evaporation. Purification of the crude compound by flash column chromatography using silica gel afforded the cycloadduct in good to moderate yields.

Higher-Order [6π + 4π] Cycloaddition Reactions. Synthesis of ((1Hβ,6Hβ)-Bicyclo[4.4.1]undeca-2,4,8-trien-11-one-8-yl)-pyridinebis(dimethylglyoximato)cobalt (5a). Diene **4a** (0.2 g, 0.475 mmol) and tropone **3** (0.075 g, 0.712 mmol) were heated for 24 h according to the general procedure stated above. Removal of solvent and purification of the product by flash chromatography afforded cycloadduct **5a** (0.238 g, 4.52 mmol, 95%) as a yellow amorphous powder: mp (neat) 194 °C dec; R_f 0.044 (pentane/ethyl acetate, 2:1); IR (CHCl$_3$) ν 1562, 1449, 1089, 904, 703, 647 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 8.63 (ad, J = 5.0 Hz, 2H), 7.70 (tt, J = 7.7, 1.3 Hz, 1H), 7.30 (t, J = 6.9 Hz, 2H), 5.72−5.78 (m, 2H, H-3, 4), 5.54−5.66 (m, 2H, H-9, 2/5), 5.43−5.52 (m, 1H, H-2/5), 3.05−3.21 (m, 2H, H-1, 6), 2.80 (dd, J = 14.9, 8.9 Hz, 1H, H-10), 2.41−2.52 (m, 1H, H-7), 2.24−2.33 (m, 1H, H-7), 2.15 (s, 6H), 2.04 (s, 6H), 2.08−2.03 (m, 1H, H-10); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 208.8 (C-11), 149.9 (CH), 137.3 (CH), 130.0 (C-9), 129.0 (C-2), 128.5 (C-5), 125.0 (CH), 123.9 (C-3/4), 121.8 (C-3/4), 56.6 (C-6), 55.8 (C-1), 36.2 (C-10), 30.4 (C-7), 12.1 (CH$_3$), 11.9 (CH$_3$). Anal. Calcd for C$_{24}$H$_{30}$CoN$_5$O$_5$: C, 54.65; H, 5.73. Found: C, 54.42; H, 5.75.

Synthesis of (7β-Methyl-(1Hβ,6Hβ)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one-9-yl)pyridinebis(dimethylglyoximato)cobalt (5b). Diene **4b** (0.100 g, 0.230 mmol) and tropone **3** (0.037 g, 0.344 mmol) were heated for 16 h according to the general procedure. After heating, the solvent was reduced and the compound was purified by flash chromatography to yield cycloadduct **5b** (0.115 g, 0.212 mmol, 93%) as a yellowish-brown powder: mp (neat) 210 °C dec; R_f 0.195 (pentane/ethyl acetate, 2:3); IR (CHCl$_3$) ν 1562, 1449, 1089, 902, 726, 703, 648 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 8.63 (dt, J = 5.0, 1.3 Hz, 2H), 7.70 (tt, J = 7.7, 1.3 Hz, 1H), 7.30 (at, J = 6.9 Hz, 2H), 5.75−5.83 (m, 2H, H-3, 4), 5.67−5.75 (m, 1H, H-5), 5.39−5.47 (m, 1H, H-2), 5.31 (bs, 1H, H-8), 3.05−3.15 (m, 1H, H-1), 2.88 (dd, J = 14.8, 9.3 Hz, 1H, H-10), 2.64−2.77 (m, 2H, H-6, 7), 2.15 (s, 6H), 2.09 (s, 6H), 1.97 (ddd, J = 15.4, 9.3, 2.4 Hz, 1H, H-10), 1.07 (d, J = 6.1 Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 208.7 (C-11), 150.9 (C), 150.5 (C), 150.2 (CH), 138.9 (C-8), 137.5 (CH), 129.3 (C-2), 127.8 (C-5), 125.2 (CH), 124.5 (C-4), 121.7 (C-3), 64.5 (C-6), 55.4 (C-1), 37.1 (C-10), 36.8 (C-7), 19.3 (C-12), 12.3 (CH$_3$), 12.1 (CH$_3$); HRMS calcd for C$_{25}$H$_{32}$CoN$_5$O$_5$ (M$^+$) 541.1735, found 541.1727. Anal. Calcd for C$_{25}$H$_{32}$CoN$_5$O$_5$: C, 55.44; H, 5.96. Found: C, 55.04; H, 5.99.

Synthesis of (7β-Methyl-(1Hβ,6Hβ)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis-(dimethylglyoximato)cobalt (5c). Diene **1** (0.200 g, 0.418 mmol) and tropone **3** (0.067 g, 0.631 mmol) were heated for 12 h according to the general procedure. The solvent was removed and the compound was crystallized using a dual solvent technique, where the product was first dissolved in hot dichloroethane followed by the addition of cyclohexane at room temperature, which afforded cycloadduct **5c** (0.212 g, 0.363 mmol, 87%) as brown crystalline material: mp (neat) 240 °C dec; IR (CHCl$_3$) ν 1620, 1388, 1089, 905, 760, 739, 705, 649 cm^{-1}; ^{1}H NMR (300 MHz, TMS) δ 8.09 (d, J = 6.9 Hz, 2H), 6.40 (t, J = 6.9 Hz, 2H), 5.73−5.83 (m, 2H, H-3, 4), 5.65−5.73 (m, 1H, H-5), 5.42 (dd, J = 12.4, 6.2 Hz, 1H, H-2), 5.33 (bs, 1H, H-8), 3.04−3.17 (m, 1H, H-1), 2.96 (s, 6H), 2.84−2.93 (m, 1H, H-10), 2.62−2.75 (m, 2H,

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H-6, 7), 2.14 (s, 6H), 2.09 (s, 6H), 1.91−2.03 (m, 1H, H-10), 1.06 (d, $J = 5.7$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 208.8 (C-11), 154.2 (C), 150.2 (C), 149.8 (C), 149.0 (CH), 138.7 (C-8), 129.5 (C-2), 127.9 (C-5), 124.4 (C-4), 121.5 (C-3), 107.5 (CH), 64.6 (C-6), 55.6 (C-1), 39.0 (CH_3), 37.1 (C-10), 36.7 (C-7), 19.4 (C-12), 12.2 (CH_3), 12.0 (CH_3); Anal. Calcd for $C_{27}H_{37}CoN_6O_5$: C, 55.46; H, 6.38. Found: C, 55.76; H, 6.42.

Synthesis of (10*β*-Methyl-(1*β*-methyl,6H*β*)-bicyclo[4.4.1]-undeca-2,4,8-trien-11-one-8-yl)(4′-*N*,*N*-dimethylamino)pyridinebis-(dimethylglyoximato)cobalt (9a). Diene **1** (0.100 g, 0.209 mmol) and tropone (**8**, R_1 = Me) (0.050 g, 0.418 mmol) were heated for 72 h according to the general procedure. Purification of the compound by column chromatography yielded cycloadduct **9a** (0.055 g, 0.092 mmol, 44%) as a yellow amorphous material: mp (neat) 154 °C dec; R_f 0.189 (diethyl ether/hexane, 3:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, $J = 7.2$ Hz, 2H), 6.39 (d, $J = 7.2$ Hz, 2H), 5.77 (dd, $J = 11.7$, 7.2 Hz, 1H, H-4), 5.71 (dd, $J = 11.7$, 7.2 Hz, 1H, H-3), 5.25−5.39 (m, 3H, H-2, 5, 9), 3.30−3.42 (m, 1H, H-6), 2.91−3.09 (m, 2H, H-7, 10), 2.96 (s, 6H), 2.14 (s, 6H), 2.08 (s, 6H), 1.91−2.01 (m, 1H, H-7), 1.01 (s, 3H, H-13), 0.96 (d, $J = 6.8$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 209.2 (C-11), 154.2 (C), 150.2 (C), 149.8 (C), 149.1 (CH), 138.5 (C-9), 135.1 (C-2), 130.8 (C-5), 123.7 (C-3), 120.7 (C-4), 107.5 (CH), 60.8 (C-1), 54.9 (C-6), 39.0 (CH), 37.1 (C-10), 37.0 (C-7), 18.5 (C-13), 15.3 (C-12), 12.1 (CH_3), 11.9 (CH_3); HRMS calcd for $C_{28}H_{40}CoN_6O_5$ $(M + H)^+$ 599.2392, found 599.2399.

Synthesis of (10*β*-Methyl-(1*β*-phenyl,6H*β*)-bicyclo[4.4.1]-undeca-2,4,8-trien-11-one-8-yl)(4′-*N*,*N*-dimethylamino)pyridinebis-(dimethylglyoximato)cobalt (9b). Diene **1** (0.200 g, 0.418 mmol) and tropone (**8**, R_1 = Ph) (0.138 g, 0.758 mmol) were heated for 72 h according to the general procedure. Initial chromatographic separation of the crude product yielded excess tropone (**8**, R_1 = Ph) (0.084 g, 0.462 mmol, 61%) followed by the cycloadduct **9b** and unreacted diene **1** as a dark yellow mixture (0.119 g): R_f 0.64 (100% diethyl ether). Further purification of the cobaloxime mixture by another column chromatography yielded the pure cycloadduct **9b** (0.073 g, 0.111 mmol, 26%) as a yellow powder: mp (neat) 156−159 °C; R_f 0.16 (hexanes/diethyl ether, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, $J = 6.6$ Hz, 2H), 7.29−7.36 (m, 2H, H-15), 7.18−7.24 (m, 3H, H-14, 16), 6.42 (d, $J = 6.6$ Hz, 2H), 6.05 (d, $J = 12.1$ Hz, 1H, H-2), 5.90 (dd, $J = 12.1$, 7.6 Hz, 1H, H-3), 5.81 (dd, $J = 11.3$, 7.6 Hz, 1H, H-4), 5.68 (dd, $J = 11.3$, 7.1 Hz, 1H, H-5), 5.63 (d, $J = 7.6$ Hz, 1H, H-9), 3.40 (p, $J = 7.1$ Hz, 1H, H-10), 3.13−3.25 (m, 1H, H-6), 2.90−3.06 (m, 1H, H-7), 2.98 (s, 6H), 2.13−2.20 (m, 1H, H-7), 2.11 (s, 6H), 2.02 (s, 6H), 0.81 (d, $J = 7.1$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 207.9 (C-11), 154.2 (C), 150.2 (C), 149.9 (C), 149.0 (CH) 141.2 (C-13), 132.1 (C-2), 131.2 (C-5), 130.2 (C-15), 127.4 (C-14), 126.1 (C-16), 122.3 (C-3), 121.3 (C-4), 107.5 (CH), 71.5 (C-1), 55.2 (C-6), 42.6 (C-10), 39.0 (CH_3), 37.5 (C-7), 16.2 (C-12), 12.2 (CH_3), 12.0 (CH_3); HRMS calcd for $C_{33}H_{42}CoN_6O_5$ $(M + H)^+$ 661.2548, found 661.2542.

Synthesis of (7*β*-Methyl-(1H*β*,6H*β*)-5-carbomethoxy-2-methoxy-3-phenyl-bicyclo[4.4.1]undeca-2,4,8-trien-11-one-9-yl)pyridinebis(dimethylglyoximato)cobalt (11a) and (1*β*-Carbomethoxy, 7H*β*,11*β*-methyl)-4-methoxy-3-phenylbicyclo[5.4.0]-undeca-2,4,9-trien-6-one-9-yl)pyridinebis(dimethylglyoximato)-cobalt (12a). Diene **4b** (0.033 g, 0.078 mmol) and tropone **10a** (0.021 g, 0.078 mmol) were heated for 25 h according to the general procedure mentioned above. The compound was purified by flash chromatography, which afforded cycloadducts **11a** and **12a** (0.036 g, 0.051 mmol, 68%). Cycloadduct **11a**: amorphous blackish-green solid (0.008 g, 0.011 mmol, 15%); R_f 0.234 (diethyl ether/pentane, 3:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, $J = 5.1$ Hz, 2H), 7.71 (at, $J = 7.6$ Hz, 1H), 7.27−7.34 (m, 4H), 7.15−7.24 (m, 4H), 5.34 (ad, $J = 6.2$ Hz, 1H, H-8), 3.79 (s, 3H, H-15), 3.57 (at, $J = 9.0$ Hz, 1H, H-1), 3.39 (s, 3H, H-14), 3.15−3.25 (m, 1H, H-10), 2.97−3.10 (m, 2H, H-6,7), 2.18 (s, 6H), 2.12 (s, 6H), 1.94−1.99 (m, 1H, H-10), 1.19 (d, $J = 6.2$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 206.4 (C-11), 166.9 (C-2), 158.7 (C-13), 150.8 (C), 150.3 (C), 150.2 (CH), 141.0 (C), 137.9 (C-8), 137.5 (CH), 135.4 (C-4), 129.1 (CH), 128.1 (CH), 126.6 (CH), 125.2 (CH), 125.1 (C-2), 119.5 (C-5), 63.9 (C-6), 52.1 (C-1), 37.3 (C-10), 36.3 (C-7), 19.4 (C-12), 12.3 (CH_3), 12.1 (CH_3); HRMS calcd for $C_{34}H_{40}CoN_5O_8$ $(M)^+$ 705.2209, found 705.2202. Cycloadduct **12a**: amorphous yellow-brown solid (0.028 g, 0.04 mmol, 53%); mp (neat) ± 210 °C dec; R_f 0.328 (diethyl ether/pentane, 3:2); ^{1}H NMR (500 MHz, TMS) δ 8.47 (d, $J = 5.2$ Hz, 2H), 7.59 (at, $J = 7.6$ Hz, 1H), 7.03−7.32 (m, 7H), 5.79 (s, 1H, H-2), 5.52 (s, 1H, H-5), 5.15 (d, $J = 5.5$ Hz, 1H, H-10), 3.54 (s, 3H, H-14), 3.48 (s, 3H, H-15), 3.03 (dd, $J = 12.3$, 5.5 Hz, 1H, H-7), 2.51 (p, $J = 6.3$ Hz, 1H, H-11), 2.27−2.36 (m, 1H, H-8), 1.85−1.95 (m, 1H, H-8), 1.72 (s, 6H), 1. 70 (s, 6H), 0.72 (d, $J = 6.8$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.8 (C-6), 173.8 (C-13), 163.3 (C-4), 150.0 (CH), 149.7 (C), 140.4 (C-2), 139.6 (C), 137.7 (C-3), 137.5 (CH), 128.0 (CH), 127.9 (CH), 127.5 (C-10), 127.3 (CH), 125.1 (CH), 106.9 (C-5), 55.4 (C-15), 51.8 (C-14), 51.2 (C-7), 50.5 (C-1), 43.0 (C-11), 32.9 (C-8), 17.7 (C-12), 11.8 (CH_3); HRMS calcd for $C_{34}H_{41}CoN_5O_8$ $(M + H)^+$ 706.2287, found 706.2283.

Diels−Alder [4 + 2] Cycloaddition Reactions. Synthesis of (1*β*,3-Dicarboethoxy-7H*β*,11*β*-methyl)-5-methoxy-bicyclo[5.4.0]-undeca-2,5,9-trien-4-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis-(dimethylglyoximato)cobalt (15a). Diene **1** (0.074 g, 0.155 mmol) and tropone **14a** (0.064 g, 0.228 mmol) were heated for 36 h according to the general procedure mentioned above. The compound was purified by flash chromatography to afford cycloadduct **15a** (0.078 g, 0.103 mmol, 67%) as a yellowish-brown powder. The product was further purified by dual solvent recrystallization using ethyl acetate to dissolve the compound and the cyclohexane for slow diffusion: mp (neat) ± 135 °C; R_f 0.133 (ethyl acetate/hexane, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, $J = 7.1$ Hz, 2H), 6.64 (bs, 1H, H-2), 6.38 (d, $J = 7.1$ Hz, 2H), 5.87 (d, $J = 8.7$ Hz, 1H, H-6), 5.32 (bd, $J = 5.5$ Hz, 1H, H-10), 4.17−4.25 (m, 1H, H-17), 4.09−4.17 (m, 1H, H-17), 3.94−4.06 (m, 2H, H-14), 3.56 (s, 3H, H-19), 2.95 (s, 6H), 2.85−2.92 (m, 1H, H-7), 2.47−2.60 (m, 2H, H-8, 11), 2.08 (s, 6H), 2.03 (s, 6H), 1.62−1.72 (dd, $J = 18.5$, 11.2 Hz, 1H, H-8), 1.27 (t, $J = 7.1$ Hz, 3H, H-18), 1.11 (t, $J = 7.1$ Hz, 3H, H-15), 0.76 (d, $J = 6.8$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.7 (C-4), 171.8 (C-13), 165.8 (C-16), 154.2 (C), 150.9 (C-5), 149.7 (C-9), 149.1 (C-1), 148.9 (CH), 148.7 (C-2), 135.3 (C-3), 127.0 (C-10), 119.1 (C-6), 107.5 (CH), 61.2 (C-17), 60.9 (C-14), 55.4 (C-19), 53.3 (C), 42.4 (C-11), 39.0 (CH_3), 37.0 (C-8), 33.9 (C-7), 18.0 (C-12), 14.06 & 14.00 (C-15, 18), 11.92, and 11.89 (dmg CH_3's); HRMS calcd for $C_{34}H_{47}CoN_6O_{10}$ $(M + H)^+$ 759.2764, found 759.2762.

Synthesis of (1*β*-Carbomethoxy,7H*β*,11*β*-methyl)-6-methoxy-3-phenyl-bicyclo[5.4.0]undeca-2,5,9-trien-4-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis(dimethylglyoximato)cobalt (15b). Diene **1** (0.060 g, 0.125 mmol) and tropone **14b** (0.050 g, 0.185 mmol) were heated for 22 h according to the general procedure mentioned above. The compound was purified by flash chromatography to yield cycloadduct **15b** (0.035 g, 0.047 mmol, 38%) as an amorphous brown powder: mp (neat) ± 206 °C dec; R_f 0.326 (ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, $J = 7.0$ Hz, 2H), 7.34−7.11 (m, 5H), 6.35 (d, $J = 7.0$ Hz, 2H), 6.00 (s, 1H, H-2), 5.45 (s, 1H, H-5), 5.27 (d, $J = 5.5$ Hz, 1H, H-10), 3.70 (s, 3H, H-15), 3.58 (s, 3H, H-14), 2.93 (s, 6H), 2.83 (dd, $J = 8.6$, 5.2 Hz, 1H, H-7), 2.59 (dd, $J = 11.9$, 5.5 Hz, 1H, H-8), 2.48−2.56 (m, 1H, H-11), 1.93−2.03 (m, 1H, H-8), 1.86 (s, 6H), 1.79 (s, 6H), 0.76 (d, $J = 7.0$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 189.1 (C-4), 179.0 (C-6), 173.5 (C-13), 154.1 (C), 149.3 (C), 149.1 (C), 148.8 (CH), 142.5 (C-3), 140.3 (C-2), 140.2 (C), 128.5 (CH), 127.8 (CH), 127.1 (CH), 126.9 (C-10), 107.4 (CH), 104.2 (C-5), 56.0 (C-15), 51.9 (C-14), 51.6 (C-1), 43.3 (C-11), 41.9 (C-7), 38.9

(CH_3), 35.5 (C-8), 17.9 (C-12), 11.9 (CH_3), 11.6 (CH_3); HRMS calcd for $C_{36}H_{45}CoN_6O_8$ $(M + H)^+$ 749.2709, found 749.2709.

Synthesis of (1*β*-Carbomethoxy,7H*β*,11*β*-methyl)-3-methyl-6-methoxy-bicyclo[5.4.0]undeca-2,5,9-trien-4-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis(dimethylglyoximato)cobalt (15c). Diene **1** (0.015 g, 0.032 mmol) and tropone **14c** (0.008 g, 0.038 mmol) were heated for 23 h according to the general procedure mentioned above. The compound was purified by flash chromatography to afford cycloadduct **15c** (0.010 g, 0.015 mmol, 46%) as a brown powdery material: mp (neat) 149 °C dec; R_f 0.310 (ethyl acetate/hexane, 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, $J = 7.2$ Hz, 2H), 6.39 (d, $J = 7.2$ Hz, 2H), 5.75 (s, 1H, H-2), 5.30 (s, 1H, H-5), 5.27 (d, $J = 5.4$ Hz, 1H, H-10), 3.66 (s, 3H, H-16), 3.57 (s, 3H, H-14), 2.96 (s, 6H), 2.73 (add, $J = 11.4$, 5.4 Hz, 1H, H-7), 2.51 (dd, $J = 18.0$, 5.4 Hz, 1H, H-8), 2.39−2.46 (m, 1H, H-11), 2.09 (s, 6H), 2.04 (s, 6H), 1.86 (dd, $J = 18.0$, 11.4 Hz, 1H, H-8), 1.78 (s, 3H, H-15), 0.72 (d, $J = 6.9$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 189.4 (C-4), 178.5 (C-6), 173.6 (C-13), 154.2 (C), 149.3 (C), 148.9 (CH), 148.8 (C), 139.7 (C-2), 127.0 (C-10), 107.5 (CH), 103.3 (C-5), 55.9 (C-16), 51.8 (C-14), 43.6 (C-11), 41.5 (C-7), 39.0 (CH_3), 36.1 (C-8), 20.7 (C-15), 18.0 (C-12), 12.0 (CH_3); HRMS calcd for $C_{31}H_{43}CoN_6O_8$ $(M + H)^+$ 687.2552, found 687.2556.

Synthesis of (1*β*-Carbomethoxy,7H*β*,11*β*-methyl)-6-methoxy-3-thioethyl-bicyclo[5.4.0]undeca-2,5,9-trien-4-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis(dimethylglyoximato)cobalt (15d). Diene **1** (0.066 g, 0.138 mmol) and tropone **14d** (0.070 g, 0.275 mmol) were heated for 40 h according to the general procedure mentioned above. The compound was purified by flash chromatography, which afforded cycloadduct **15d** (0.087 g, 0.119 mmol, 87%) as a yellowish-brown powdery material: mp (neat) 183 °C dec; R_f 0.367 (diethyl ether); ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, $J = 6.0$ Hz, 2H), 6.39 (d, $J = 6.0$ Hz, 2H), 5.59 (s, 1H, H-2), 5.37 (s, 1H, H-5), 5.24 (d, $J = 5.7$ Hz, 1H, H-10), 3.68 (s, 3H, H-17), 3.57 (d, $J = 1.3$ Hz, 3H, H-14), 2.96 (d, $J = 1.1$ Hz, 6H), 2.75 (dd, $J = 11.7$, 5.4 Hz, 1H, H-7), 2.54−2.63 (m, 2H, H-8, 15), 2.42−2.63 (m, 2H, H-11, 15), 2.09 (d, $J = 1.1$ Hz, 6H), 2.06 (d, $J = 1.1$ Hz, 6H), 1.86 (dd, $J = 18.0$, 11.7 Hz, 1H, H-8), 1.26 (t, $J = 7.4$ Hz, 3H, H-16), 0.73 (d, $J = 6.8$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.7 (C-4), 179.1 (C-6), 173.1 (C-13), 154.2 (C), 149.8 (C), 148.9 (CH), 148.8 (C), 138.2 (C-3), 136.0 (C-2), 127.0 (C-10), 107.5 (CH), 102.5 (C-5), 56.2 (C-17), 52.2 (C-1), 51.9 (C-14), 43.8 (C-11), 41.7 (C-7), 39.0 (CH_3), 36.0 (C-8), 25.9 (C-15), 18.2 (C-12), 12.9 (C-16), 12.1 (CH_3), 12.0 (CH_3). Anal. Calcd for $C_{32}H_{45}CoN_6O_8S$: C, 52.44; H, 6.19. Found: C, 52.48; H, 6.52.

Synthesis of (1*β*-Carbomethoxy,7H*β*,11*β*-methyl)-5-methoxy-3-phenyl-bicyclo[5.4.0]undeca-2,5,9-trien-4-one-9-yl)(4′-*N*,*N*-dimethylamino)pyridinebis(dimethylglyoximato)cobalt (15e). Diene **1** (0.047 g, 0.01 mmol) and tropone **14e** (0.032 g, 0.118 mmol) were heated for 36 h according to the general procedure mentioned above. The compound was purified by flash chromatography to yield cycloadduct **15e** (0.019 g, 0.024 mmol, 29%) as an amorphous yellow powder: mp (neat) 156 °C dec; R_f 0.204 (diethyl ether/hexane, 4:1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, $J = 6.3$ Hz, 2H), 7.05−7.32 (m, 5H), 6.37 (d, $J = 6.3$ Hz, 2H), 6.11 (s, 1H, H-2), 5.96 (d, $J = 8.6$ Hz, 1H, H-6), 5.28 (ad, $J = 5.5$ Hz, 1H, H-10), 3.61 (s, 3H, H-15), 3.57 (s, 3H, H-14), 2.94 (s, 6H), 2.86−3.01 (m, 1H, H-7), 2.50−2.63 (m, 2H, H-8,11), 1.89 (s, 6H), 1.87 (s, 6H), 1.75 (dd, $J = 17.3$, 11.4 Hz, 1H, H-8), 0.77 (d, $J = 6.7$ Hz, 3H, H-12); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 188.1 (C-4), 173.4 (C), 154.2 (C), 151.7 (C), 149.6 (C), 148.9 (CH), 142.4 (C-2), 142.0 (C), 140.0 (C), 128.6 (CH), 127.9 (CH), 127.4 (CH), 127.1 (C-10), 119.3 (C-6), 107.5 (CH), 55.5 (C-15), 53.7 (C-1), 51.9 (C-14), 43.3 (C-11), 39.0 (CH_3), 37.2 (C-8), 33.8 (C-7), 18.3 (C-12), 11.9 (CH_3), 11.7 (CH_3); HRMS calcd for $C_{36}H_{45}CoN_6O_8$ $(M + H)^+$ 749.2709, found 749.2709.

Demetalation Reaction of the Cycloadduct 5b Using Trimethyl Aluminum.[17,22] Cycloadduct **5b** (0.300 g, 0.554 mmol) was dissolved in distilled THF (10 mL) in a flame-dried two-neck round-bottom flask fitted with a nitrogen inlet. This contents were cooled to −15° C using an ethylene/glycol ice bath. Trimethylaluminum (850 μL of a 2.0 M solution in hexanes, 1.66 mmol) was added in ca. 5 min. The solution was warmed to room temperature over 0.5 h, and stirring continued for 2.0 h. Ice water (10 mL) was added, and the mixture was extracted with dichloromethane (4 × 10 mL). The organics were combined and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The demetalated cycloadduct was purified by column chromatography to yield cycloadduct **16** (0.092 g, 0.528 mmol, 96%) as a colorless oil: R_f 0.86 (ethyl acetate/pentane, 1:1). The spectral data of the product were correlated with the reported literature values.[9] Further elution also yielded cobalt complex **17** (0.155 g, 0.405 mmol, 73%).

X-ray Experimental Information for C_{25} $H_{32}CoN_5O_5$ (5b). Several weakly diffracting crystals of **5b** were examined before selecting an orange-brown parallelepiped-shaped crystal of approximate dimensions 0.46 mm × 0.26 mm × 0.10 mm for the X-ray crystallographic analysis. A full hemisphere of diffracted intensities (omega scan width of 0.30°) was measured using graphite-monochromated Mo K$\bar{\alpha}$ radiation on a Bruker SMART APEX CCD single-crystal diffraction system. X-rays were provided by a fine-focus sealed X-ray tube operated at 50 kV and 30 mA.

The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Integration of the data set used a monoclinic unit cell and yielded a total of 16 838 reflections to a maximum 2θ angle of 48.3° (4067 were independent, $R_{int} = 0.112$). The final cell constants of $a = 8.173(3)$ Å, $b = 22.819(8)$ Å, $c = 13.929(5)$ Å, $\beta = 99.147(5)°$, and $V = 2565(2)$ Å^3 are based upon the refinement of the XYZ-centroids of 1575 reflections with $8.23° < 2\theta < 36.32°$. Analysis of the data showed negligible decay during data collection.

The structure was solved using "direct methods" techniques with the Bruker AXS SHELXTL (vers 6.12) software package. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data. The structure was initially solved and refined in the centrosymmetric space group $P2_1/n$ since the statistics and systematically absent reflections for the intensity data indicated this was the correct choice. When the resulting structural model contained anomalous metrical parameters, the structure was solved and refined again in the noncentrosymmetric space groups $P2_1$ and Pn. These refinements also considered the possibility of merohedral twinning. Neither of the models from these noncentrosymmetric refinements resulted in metrical parameters superior to those obtained from the initial centrosymmetric refinement; furthermore, the anisotropic thermal parameters for several non-hydrogen atoms also refined to non-positive-definite values. The final structure refinement was therefore performed in the centrosymmetric $P2_1/n$ description. This refinement converged to R_1 (unweighted, based on F) = 0.068 for 2208 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 48.3° and $F^2 > 2\sigma(F^2)$; R_1 (unweighted, based on F) = 0.124 and wR_2 (weighted, based on F^2) = 0.159 for all 4067 reflections. The goodness-of-fit was 0.901. The largest peak in the final difference Fourier map was 0.83 e$^-$/Å^3, and the largest hole was −0.45 e$^-$/Å^3.

The final structural model incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydroxyl hydrogen atoms of the DMG ligands were located from a difference Fourier map and refined as independent isotropic atoms. The methyl groups were refined as rigid rotors (using idealized sp^3-hybridized geometry and a C−H bond length of 0.98 Å). The remaining hydrogen atoms were included in the structural model as fixed atoms (using idealized

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(22) Richardson, B. M.; Welker, M. E. *J. Org. Chem.* **1997**, *62*, 1299−1304.

sp^2- or sp^3-hybridized geometry and C−H bond lengths of 0.95−1.00 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for hydroxyl hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameter of the oxygen atom to which they are covalently bonded. The isotropic thermal parameter of each remaining hydrogen atom was fixed at a value 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. On the basis of the final model, the calculated density was 1.402 g/cm^3 and F(000), 1136 e$^-$.

All calculations were performed using the SHELXTL (version 6.12) interactive software package (Bruker. SHELXTL-NT (version 6.12); Bruker AXS Inc.: Madison, WI, 2001).

X-ray Experimental Information for $Co(C_4H_7N_2O_2)_2(C_7H_{10}N_2)(C_{19}H_{23}O_6)$ (15a). Single crystals of **15a** are, at 193(2) K, orthorhombic, space group $Pna2_1 - C_{2v}^9$ (No. 33) with $a = 9.199(1)$ Å, $b = 29.552(4)$ Å, $c = 14.318(2)$ Å, $V = 3892.5(9)$ Å^3, and $Z = 4$ formula units {$d_{calcd} = 1.295$ g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 0.501 mm^{-1}}. A yellow crystal of approximate dimensions 0.22 × 0.19 × 0.04 mm was used for the X-ray crystallographic analysis. A full hemisphere of diffracted intensities (omega scan width of 0.30°) was measured using graphite-monochromated Mo K$\bar{\alpha}$ radiation on a Bruker SMART APEX CCD single-crystal diffraction system. X-rays were provided by a fine-focus sealed X-ray tube operated at 50 kV and 30 mA.

Lattice constants were determined with the Bruker SMART software package (SMART version 5.628 and SAINT version 6.36a, Bruker AXS Inc.: Madison, WI) using peak centers for 2693 reflections with $7.63° < 2\theta < 35.65°$. A total of 24 196 integrated intensities were produced using the Bruker program SAINT, of which 6189 were independent and gave $R_{int} = 0.082$. 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 using "direct methods" techniques with the Bruker AXS SHELXTL (vers 6.12) software package. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data and converged to give R_1 (unweighted, based on F) = 0.079 for 5162 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 48.3° and $F^2 > 2\sigma(F^2)$ {R_1 (unweighted, based on F) = 0.095 and wR_2 (weighted, based on F^2) = 0.180 for all 6189 reflections}. The goodness-of-fit was 1.204. The largest peak in the final difference Fourier map was 0.68 e$^-$/Å^3, and the largest hole was −0.54 e$^-$/Å^3. The Flack parameter refined to a final value of 0.03(3).

The structural model incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydroxyl hydrogen atoms of the DMG ligands were located from a difference Fourier map and refined as independent isotropic atoms. The methyl groups were refined as rigid rotors (using idealized sp^3-hybridized geometry and a C−H bond length of 0.98 Å). The remaining hydrogen atoms were included in the structural model as fixed atoms (using idealized sp^2- or sp^3-hybridized geometry and C−H bond lengths of 0.95−1.00 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for hydroxyl hydrogen atoms refined to final values of 0.04(2) Å^2. The isotropic thermal parameter of each remaining hydrogen atom was fixed at a value 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

All calculations were performed using the SHELXTL (version 6.12) interactive software package (Bruker. SHELXTL-NT (version 6.12); Bruker AXS Inc.: Madison, WI, 2001).

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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 **5b** and **15a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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