Preparation of (L)(*N*,*N*′-ethylenebis(salicylideneaminato))-(1,3-butadien-2-yl)cobalt(III) Complexes and Their Utilization in Facile and Regioselective Diels−Alder Reactions

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Dark green (*N*,*N*′-ethylenebis(salicylideneaminato)cobalt(I) (Co(salen)) anions underwent smooth S_N2' reactions with allenic electrophiles in the presence of added ligands (L) to give (L)(salen)(1,3-butadien-2-yl)cobalt(III) complexes (L = pyr, DMAP, H_2O). The cobalt dienyl complexes prepared were fully characterized and then treated with a range of dienophiles to give Diels−Alder cycloaddition adducts. The cobalt−carbon bonds in Diels−Alder adducts were cleaved by utilizing straightforward chemical reactions which allowed recovery of cobalt in a reusable form as well as demetalated cycloadduct.

Introduction

Over the past 4 years, we have been preparing cobaloxime-substituted 1,3-dienes and examining the rates, regioselectivities, and stereoselectivities of their reactions with dienophiles in Diels−Alder reactions.[1] Tada et al. have also reported alternative preparations of some cobaloxime-substituted dienes as well as results of their cycloaddition reactions.[2] Several other groups have also recently reported that the alternate strategy of transition-metal substitution in dienophiles rather than dienes can have a pronounced effect on [4 + 2] cycloaddition diastereoselectivities.[3] The diastereoselectivities of the Diels−Alder reactions of these cobaloxime dienyl complexes are unusual for acyclic dienes in that products arising from *exo* transition states are the major products.

We presume that dienophile−ligand set steric interactions in metal-substituted dienes we have prepared override the normal *endo* preference seen for Diels−Alder reactions of acyclic dienes. However, we have encountered *Z*:*E* diene isomerization problems using the glyoxime ligand set which we believe are due to the presence of the moderately acidic glyoxime O−H protons. The *N*,*N*′-ethylenebis(salicylideneaminato) (salen) ligand set has no acidic protons which might cause diene isomerization, and this manuscript reports our initial progress on the synthesis and subsequent Diels−Alder chemistry of cobalt butadienyl complexes (**1**) containing equatorial salen ligands.

Synthesis of Cobalt Salen−1,3-Butadienyl Complexes

We have reported several examples of the reaction of cobaloxime anions (**2**) (L = pyr, DMAP, 3,5-dimethylpyr, 4-*tert*-butylpyr) with allenic electrophiles (**3**) (X = OTs, Cl, OAc) to produce cobalt(III) 1,3-dien-2-yl complexes (**4**)[1] (Scheme 1). The analogous (*N*,*N*′-ethylenebis(salicylideneaminato))cobalt anion (Co(salen)) was known and had been shown to react with alkyl halides.[4] The Co^{II}(salen) complex (**6**) is converted to the Co^{I}(salen) anion with no difficulty. The dark green Co^{I}(salen) anion undergoes a S_N2' reaction with 4-tosyl-1,2-butadiene (**7**)[1b] to give the desired 2-[$(H_2O)Co^{III}$(salen)]-1,3-butadienyl complex (**1a**) in high yield. If pyridine or a substituted pyridine was desired as the axial ligand (**1b** or **1c**), it was added through a ligand exchange reaction using methanol as the solvent. All dienyl complexes (**1a**−**c**) proved to be extremely stable to air and heat. The complex with the H_2O axial ligand (**1a**) is stable to 90 °C (1 mmHg) without any sign of decomposition. The complex with the axial pyridine ligand (**1b**) is stable to

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(1) (a) Smalley, T. L.; Wright, M. W.; Garmon, S. A.; Welker, M. E.; Rheingold, A. L. *Organometallics* **1993**, *12*, 998. (b) Wright, M. W.; Smalley, T. L.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777. (c) Stokes, H. L.; Richardson, B. M.; Wright, M. W.; Vaughn, S. P.; Welker, M. E.; Liable-Sands, L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5520. (d) Wright, M. W.; Welker, M. E. *J. Org. Chem.* **1996**, *61*, 133. (e) Stokes, H. L.; Welker, M. E. *Organometallics* **1996**, *15*, 2624. (f) Wright, M. W.; Stokes, H. L.; Richardson, B. M.; Adams, T. A.; Smalley, T. L.; Vaughn, S. P.; Lohr, G. J.; Welker, M. E.; Liable-Sands, L.; Rheingold, A. L.; In *Advances in Cycloaddition*; Lautens, M., Ed.; JAI Press, Greenwich, CT, 1997; Vol. 4, in press.

(2) (a) Tada, M.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1252. (b) Tada, M.; Mutoh, N.; Shimizu, T. *J. Org. Chem.* **1995**, *60*, 550.

(3) (a) For a recent review of transition-metal-mediated cycloaddition reactions see: Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (b) Sabat, M.; Reynolds, K. A.; Finn, M. G. *Organometallics* **1994**, *13*, 2084. (c) Gilbertson, S. R.; Zhao, X.; Dawson, D. P.; Marshall, K. L. *J. Am. Chem. Soc.* **1993**, *115*, 8517. (d) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784. (e) Barluenga, J.; Canteli, R.-M.; Florez, J.; Garcia-Granda, S.; Gutierrez-Rodriguez, A. *J. Am. Chem. Soc.* **1994**, *116*, 6949.

(4) (a) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *15*, 187. (b) Floriani, C.; Puppis, M.; Calderazzo, F. *J. Organomet. Chem.* **1968**, *12*, 209. (c) Bigotto, A.; Costa, G.; Mestroni, G.; Pellizer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, L.; Tauzher, G. *Inorg. Chim. Acta Rev.* **1970**, *4*, 41. (d) McAllister, R. M.; Weber, J. H. *J. Organomet. Chem.* **1974**, *77*, 91. (e) Mestroni, G.; Zassinovich, G.; Camus, A.; Costa, G. *Transition Met. Chem.* **1975**, *1*, 32.

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Scheme 1

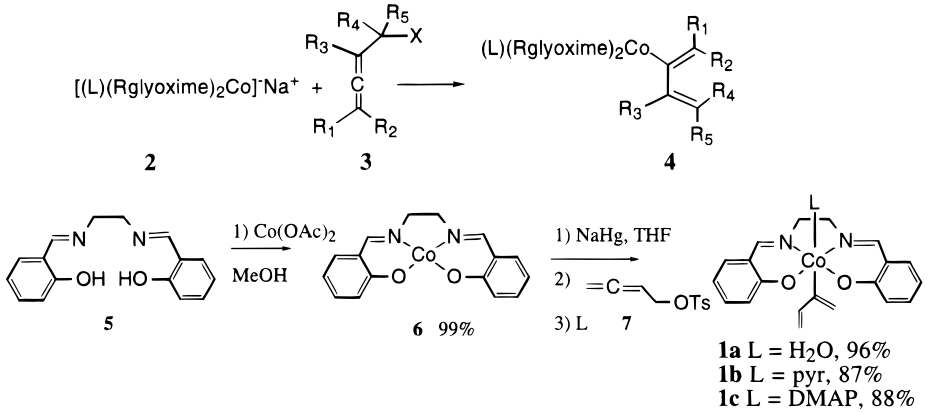


Table 1. Effect of the Axial Ligand (L) on the ^{1}H NMR Chemical Shift of the Diene Protons in 1a−c

		chem shift (ppm) ($CDCl_3$)				
entry	L	H_a	H_b	H_c	H_d	H_e
1	water (**1a**)	5.76	4.56	5.24	3.15	3.30
2	pyridine (**1b**)	6.08	4.48	5.22	3.52	3.67
3	DMAP (**1c**)	6.23	4.52	5.16	3.60	3.77

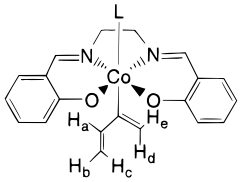


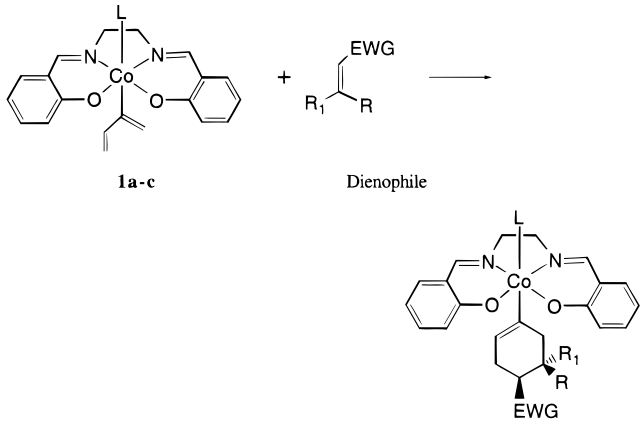
Figure 1. Labeling scheme for dienyl protons in **1a−c**.

70 °C (1 mmHg) while **1c** is stable to above 80 °C (1 mmHg) before slowly deteriorating. All the 1,3-butadien-2-yl complexes (**1a−c**) have been stored under ambient conditions for 12−15 months with no decomposition noted. These dienyl complexes (**1a−c**) are very hygroscopic. For example **1a**, which contains 1 equivalent of coordinated water by ^{1}H NMR (δ 1.93, s, 2H in $CDCl_3$) and elemental analysis, turns from green to brown-orange within seconds when exposed to the atmosphere. The original color is restored when the complex is dried at 60 °C (1 mmHg) for 6−24 h. The complexes (**1a−c**) may also be dried at 25 °C (1 mmHg) over P_2O_5 for 6−48 h. The ^{1}H NMR resonances for the 1,3-dienyl protons are presented in Table 1. As noted in the glyoxime series,[1] the protons on the #1 carbon, H_d and H_e (Figure 1) (H_d, H_e assignments were made by analogy to cobaloxime dienyl complexes),[1] are strongly shielded by the adjacent low-valent cobalt. However, the effect here is even more dramatic than in the glyoxime series, since the H_d and H_e protons for the pyridine (**1b**) and DMAP (**1c**) complexes are 1 ppm upfield from their corresponding glyoxime complex values.

[4 + 2] Cycloaddition Reactions

The cobalt 1,3-butadien-2-yl complexes (**1a−c**) reacted under relatively mild conditions with a wide range of dienophiles to give the corresponding Diels−Alder adducts **8−17** (Scheme 2) (Table 2). Cycloadditions with maleic anhydride and *N*-phenylmaleimide were very rapid (Table 2, entries 1−5) with the DMAP and pyr complexes (**1b**,**c**) reacting slightly faster than the aquo

Scheme 2



complex (**1a**). However, since complexes **1b,c** offered little rate advantage and **1a** had the greatest thermal stability, we chose to survey other dienophiles using complex **1a**. We also noted that cycloadducts **9** and **10** lost their axial pyridine ligands more easily than the dienyl complexes (**1b**,**c**) upon drying at high vacuum so there was an additional practical consideration in choosing **1a** for the Diels−Alder survey presented in Table 2. Other dienophiles with two electron-withdrawing groups such as diethyl and dimethyl maleate and fumarate required refluxing in THF for a minimum of 18 h as did monosubstituted dienophiles methyl vinyl ketone and methyl acrylate. The vinyl protons in all of the [4 + 2] cycloaddition adducts were located between 3.4 and 4.5 ppm ($CDCl_3$) analogous to the upfield shifts we noted for protons β to cobalt in the diene complexes (**1a−c**).[1] To verify these unusually low vinyl proton chemical shifts, HETCOR and APT experiments were carried out on several [4 + 2] cycloaddition adducts. *Cis* ring junction stereochemistry in the maleic anhydride cycloadduct (**8**) was indicated by a $J(H_{3a}-H_{7a})$ (ring junction protons) value of 8.6 Hz, which is very similar to *cis* ring junction coupling constants (ca. 9 Hz) we[1b,c] and others[5] have noted previously in related 1,3-dioxoisobenzofurans.

The cycloaddition reaction between diethyl maleate and cobalt(III) 1,3-butadien-2-yl (**1a**) gave unexpected results from three perspectives. First, diethyl maleate reacted with **1a** to give 10−15% of the *trans*-Diels−

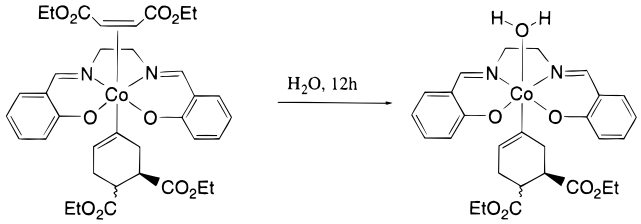
(5) Lo Cicero, B.; Weisbuch, F.; Dana, G. J. *J. Org. Chem.* **1981**, *46*, 914.

Table 2. Regioselective Diels−Alder Reactions of Complexes 1a−c

entry	diene	dienophile	temp (°C)	time (h)	solvent	regiochem	yield (%)	product	EWG[j]	R	R_1
1	**1a**	MA[a]	25	1.0	$CHCl_3$	N/A	93	**8**	−C(O)OC(O)−		H
2	**1a**	MA	60	0.5	none	N/A	99	**8**	−C(O)OC(O)−		H
3	**1b**	MA	25	0.5	$CHCl_3$	N/A	98	**9**	−C(O)OC(O)−		H
4	**1c**	MA	25	0.4	$CHCl_3$	N/A	80	**10**	−C(O)OC(O)−		H
5	**1a**	NPM[h]	25	18	$CHCl_3$	N/A	91	**11**	−C(O)NPhC(O)		H
6	**1a**	DMM[c]	reflux	64	THF	N/A	75	**12**	CO_2Me	CO_2Me	H
7	**1a**	DMF[d]	reflux	48	THF	N/A	83	**13**	CO_2Me	H	CO_2Me
8	**1a**	DEM[e]	reflux	72	THF	N/A	75[i]	**14**	CO_2Et	CO_2Et	H
9	**1a**	DEM	reflux	36	$(ClCH_2)_2$	N/A	75[i]	**14**	CO_2Et	CO_2Et	H
10	**1a**	DEM	reflux	18	1,4-dioxane	N/A	80[i]	**14**	CO_2Et	H	H
11	**1a**	DEF[f]	reflux	64	THF	N/A	92	**15**	CO_2Et	H	CO_2Et
12	**1a**	MVK[b]	reflux	48	THF	>20:1	85	**16**	C(O)Me	H	H
13	**1a**	MVK	reflux	18	none	>20:1	86	**16**	C(O)Me	H	H
14	**1a**	MVK	reflux	18	$(ClCH_2)_2$	>20:1	85	**16**	C(O)Me	H	H
15	**1a**	MAC[g]	reflux	48	THF	>20:1	95	**17**	CO_2Me	H	H

[a] MA = maleic anhydride. [b] MVK = methyl vinyl ketone. [c] DMM = dimethyl maleate. [d] DMF = dimethyl fumarate. [e] DEM = diethyl maleate. [f] DEF = diethyl fumarate. [g] MAC = methyl acrylate. [h] NPM = *N*-phenylmaleimide. [i] 10−15% of cycloadduct **15** was noted in each case; L = H_2O in **14** was obtained after stirring the initially isolated cycloadduct **18** with water. [j] EWG = electron-withdrawing group.

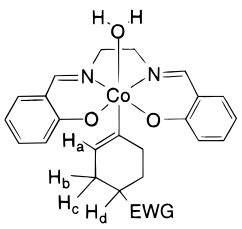
Scheme 3



18 **14**

Alder cycloaddition product (identical by spectroscopic comparison to the diethyl fumarate cycloadduct (**15**)) in addition to **14** whereas diethyl fumarate reacted with **1a** to give **15** with no trace of **14**. Second, diethyl maleate reacted much more slowly than diethyl fumarate in parallel reactions. The diethyl maleate required 73 h in refluxing THF to completely react with **1a** while diethyl fumarate reacted in 48 h. The observation that diethyl maleate underwent cycloaddition slower than diethyl fumarate is the opposite of the cycloaddition reactivity we had noted previously for cobaloxime dienyl complexes (**4**) with dimethyl fumarate and maleate.[1b] Third, ^{1}H NMR indicated that initial Diels−Alder cycloaddition product (**18**) contained 1 equiv of diethyl maleate either coordinated to the cobalt or entrained in the solid. This diethyl maleate remained even after triturating with a generous portion of diethyl ether. In comparison, coordination of diethyl fumarate was not observed in the initially isolated Co^{III}(salen) Diels−Alder adduct (**15**). Simply stirring the initially isolated diethyl maleate cycloadduct (postulated as structure **18**) in water (12 h, 25 °C) resulted in replacement of the diethyl maleate by a water molecule to yield **14** (Scheme 3). The analogous reverse reaction with **1a** does not occur; i.e. stirring **1a** with diethyl maleate (10 equiv) in THF at 25 °C for 18 h produced no axial ligand exchange or cycloadduct **14**. Initial isolation of this proposed diethyl maleate adduct is probably caused by a change in workup procedure which had to be used with diethyl maleate. In the maleic anhydride, dimethyl maleate, dimethyl fumarate, and diethyl fumarate cycloadditions reported in Table 2, the cooled solutions containing cycloadduct were poured into hexanes causing precipitation of the cycloadduct. In the case of the diethyl maleate cycloadduct (**14**), no precipitation occurred when the cycloadduct containing solution was poured into hexanes. The solvent had to be removed by rotary evaporation, and then the solid product was triturated with hexanes and diethyl ether. This workup procedure (unlike the one used for other cycloadducts) presents the cycloadduct with a large concentrated reservoir of excess dienophile which can act as a ligand. When we subsequently used this alternate workup procedure for the maleic anhydride cycloadduct (**8**), we also saw 1 equiv of unreacted maleic anhydride in the product by ^{1}H NMR. We now believe dienophile for water axial ligand exchange can occur at high temperature and this ligand exchange may also be partly responsible for the slow cycloaddition rate of diethyl maleate. Dienyl complex (**1a**) will react completely with this dienophile at 45 °C over 36 h in THF whereas reactions run under the same conditions in refluxing THF always show significant amounts of unreacted **1a** when worked up at these shorter reaction times.

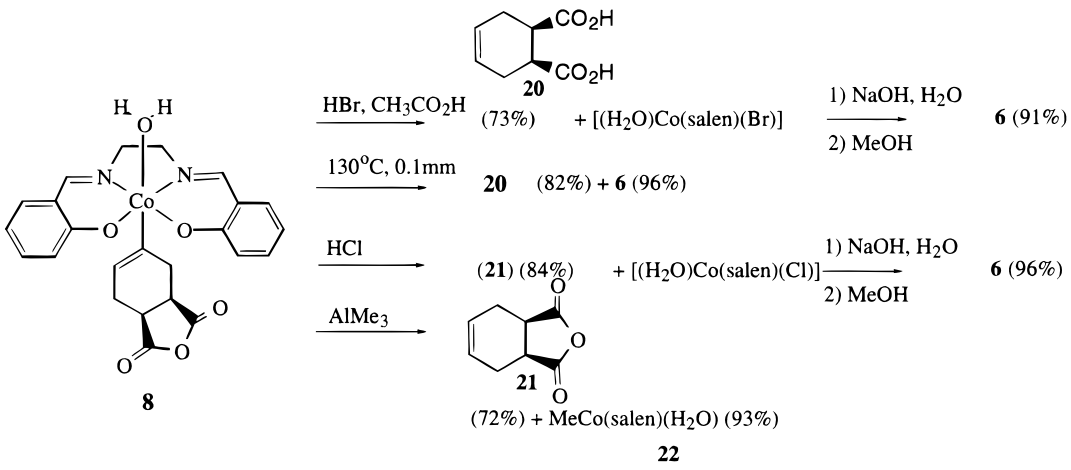
All disubstituted dienophiles reacted to give just one stereoisomer of cycloadduct consistent with the dienophile stereochemistry except diethyl maleate, where 10−15% of the *trans* cycloadduct (**15**) was always noted in the product (**14**). Cycloaddition adducts resulting from methyl vinyl ketone and methyl acrylate were para products exclusively. H,H-COSY experiments were used to establish regioselectivity for Diels−Alder adducts (**16**, **17**) prepared from these unsymmetrical dienophiles. The labeling scheme for the protons, H_a, H_b, H_c, and H_d, for the [4 + 2] cycloaddition adducts are shown in **19**. We observed in both cases (**16**, **17**)



19

that the vinyl proton (H_a) and the proton located on the carbon containing the electron-withdrawing group (EWG) (H_d) were strongly coupled to the same two diastereotopic methylene protons (H_b and H_c) indicating para regiochemistry for these cycloadducts.

Scheme 4



Demetalation

In the cobaloxime complex series,[1] we had previously demonstrated we could effect a variety of cobalt−carbon bond cleavages with cycloadducts which allowed us to recover cycloadducts as well as cobaloximes in a reusable form. We had the same criteria for measuring success in the Co(salen) series, in that we wanted to effect cobalt−carbon bond cleavage with concomitant cobalt and cycloadduct recovery. RCo(salen)(L) complexes had previously been reported to be both photo- and thermally labile generating RH and Co^{II}(salen)(L) when heated or photolyzed.[4,6] Similarly, we have noted that cycloadducts (**8**−**17**) are somewhat photolabile in methanol at 25 °C and some are thermally labile when heated above 100 °C (dioxane). For example, we found that the diethyl maleate cycloaddition (Table 2, entry 10) could be performed in refluxing dioxane and cycloadduct **14** isolated in high yield. However, when the dimethyl maleate or dimethyl fumarate cycloadditions were performed at that temperature in refluxing dioxane, a significant amount of demetalated cycloadduct was seen in addition to **12** or **13**. We also determined that the Diels−Alder cycloaddition adducts were not stable in methanol for long periods in normal room light. However, the Diels−Alder adducts reported in Table 2 appear to be stable at temperatures below 100 °C in all other nonprotic solvents examined during the course of this work.

A variety of conditions can be used to replace the cobalt with a proton in the cycloadducts. The maleic anhydride adduct (**8**) was cleanly cleaved by HBr in glacial acetic acid, thermolysis, HCl, and trimethylaluminum to give the *cis*-1,2,3,6-tetrahydrophthalic acid (**20**) or *cis*-1,2,3,6-tetrahydrophthalic anhydride (**21**) in 73, 82, 84, and 72% yields, respectively (Scheme 4). The harsher HBr/acetic acid and thermolysis cleavage caused hydrolysis of the anhydride to the diacid. All these cleavage reactions except the thermolysis and HBr/acetic acid are analogous to ones we had reported previously for cobaloxime containing cycloadducts.[1] Co^{II}(salen) (**6**) was recovered from the HBr as well as HCl cleavages via the halides using known chemistry.[4,6] The Co(salen) (**6**) recovered from the HBr cleavage sequence was then taken back through the dienyl complex synthesis procedure to yield **1a** (88%). *The Co(salen) metal and ligand set have thus been taken through three manipulations (diene sythesis, cycloaddition, cleavage), and we have arrived back at our original dienyl complex (**1a**) with 80% overall cobalt recovery in addition to excellent cycloadduct recovery.* Co^{II}(salen) (**6**) was recovered directly from the thermolysis, and MeCo(salen)(H_2O)[4b] (**22**) was recovered from the $AlMe_3$ cleavage.

Likewise, the methyl vinyl ketone adduct (**16**) was cleanly cleaved by HBr in glacial acetic acid, thermolysis, HCl, trimethylaluminum, and diethylzinc to give 1-acetyl-3-cyclohexene (**23**) in 84, 90, 88, 88, and 88% yields, respectively (Scheme 5). EtCo(salen)(H_2O)[4d] (**24**) was the cobalt-containing product from the Et_2Zn reaction. Mercuric acetate[4d,e] also reacted smoothly with adduct **16** to give 4-(mercuric acetate)-1-acetyl-3-cyclohexene (**25**, 87%).

Conclusion

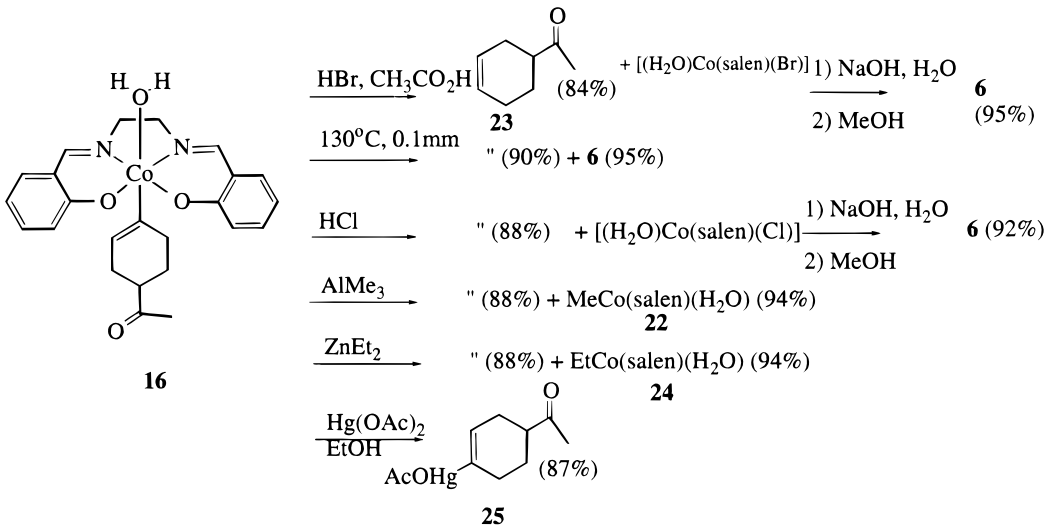
We have demonstrated that 2-[(L)Co^{III}(salen)]-1,3-butadien-2-yl complexes (**1**) are readily prepared through S_N2' reactions of Co^{I}(salen) anions with allenic electrophiles. These Co(salen)(dienyl) complexes are crystalline and hygroscopic but do not decompose in air and have high thermal stability. They are reactive toward a range of dienophiles in Diels−Alder reactions. Demetalation reactions were developed which provide organic cycloadducts as well as Co(salen) complexes which have been recycled to prepare additional 2-[(L)-Co^{III}(salen)]-1,3-butadien-2-yl. Future work will include preparation of cobalt dienyl complexes containing pentadienyl ligands as well as optically active salen ligands and the investigation of their use in regio, enantio, and *exo* selective Diels−Alder reactions. The hope here is that the salen ligand, which contains no acidic protons, will allow us to circumvent some diene stereochemistry isomerization problems we encountered with the glyoxime ligand set.[1c,e]

Experimental Section

General Methods. All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR or a Varian Gemini 300 FT NMR. All absorptions are expressed in parts per million relative to tetramethylsilane. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR or an OMINA FTIR. All elemental analyses were performed

(6) (a) Costa, G.; Mestroni, G.; Tauzher, G. *J. Chem. Soc., Dalton Trans.* **1972**, 450. (b) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *15*, 187.

Scheme 5



by Atlantic Microlab, Inc., of Norcross, GA. High-resolution mass spectral analyses were performed by the Nebraska Center for Mass Spectrometry, University of Nebraska—Lincoln. Low-resolution EI mass spectra were obtained on a Hewlett Packard 5989 GC/MS system. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Alumina adsorption (80−200 mesh) for column chromatography was purchased from Fisher Scientific and deactivated with an acetone/water mixture (90/10) immediately prior to use. Flash silica gel (40 μm) was purchased from Universal Scientific Inc. Cobalt(II) acetate and 2-butyne-1,4-diol were obtained from Aldrich Chemical Co. and used as received.

4-Chloro-2-butyne-1-ol from Propargyl Chloride. This alkyne was prepared on a 600 mmol scale in 70.4% yield by a previously reported procedure.[1b,7] IR and ^{1}H NMR data (δ) are not reported for this compound in ref 7. IR ($CDCl_3$): 3390 br, 2125, 1660, 1060, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.30 (t, J = 2.3 Hz, 2H), 4.14 (t, J = 2.3 Hz, 2H), 1.90 (s, 1H).

1,2-Butadiene-4-ol. A previously reported procedure[1b,7] was modified to improve product recovery. 4-Chloro-2-butyne-1-ol (20.9 g, 199.94 mmol) was dissolved in diethyl ether (400 mL) as described previously.[7] A solid's addition funnel was charged with lithium aluminum hydride (8.0 g, 210.8 mmol) which was added slowly. After the addition was completed, a portion of ice water (8 mL) was carefully added, followed by 15% aqueous NaOH solution (8 mL) and finally additional ice water (24 mL). The white aluminum salts were removed by vacuum filtration and washed with additional diethyl ether. The product (10.1 g, 144.3 mmol, 72%) was distilled at 46−47 °C (18 mmHg).

4-(p-Tolylsulfonyl)-1,2-butadiene (7). A previously reported procedure[1b,8] was modified in that THF (200 mL) was used instead of diethyl ether to yield tosylate (79%) from 1,2-butadien-4-ol (97 mmol).

***N,N′*-Ethylenebis(salicylidenamine) (5).** A 300 mmol reaction was carried out according to the method of Pfeiffer[9] and Tsumaki,[10] and the imine was isolated in 99% yield. Mp: 127.5−128 °C (lit. mp: 123−125 °C).[11] The following characterization data were not previously reported. ^{1}H-NMR ($CDCl_3$): 8.31 (s, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.20 (d, J = 7.3 Hz, 2H), 7.03 (d, J = 7.3 Hz, 2H), 6.94 (t, J = 7.3 Hz, 2H), 4.03 (s, 4H). ^{13}C NMR ($CDCl_3$): 167.5, 162.04, 133.45, 132.54, 119.74, 119.69, 118.00, 60.81. IR ($CDCl_3$): 3702, 1683, 1510, 1475, 1370, 1285, 1225, 1155 cm^{-1}.

***(N,N′*-Ethylenebis(salicylideneaminato))cobalt(II) (6).** A modified procedure of Pfeiffer[9] et al. was used to prepare the Co^{II}(salen) complex (**6**). Salen (**5**) (67.1 g, 250.9 mmol) was dissolved in degassed methanol (500 mL) in a 3 L flask equipped with a mechanical stirrer. The flask contents were heated to 60 °C, and cobalt acetate tetrahydrate (62.5 g, 250.9 mmol) in methanol (1000 mL) was added with stirring under an atmosphere of nitrogen. The reactants were maintained at 60 °C for an additional 45 min and then cooled to 25 °C, and the dark red product was collected by vacuum filtration. The red crystals were stirred in 1 N NaOH (500 mL) for 30 min and again collected by vacuum filtration, washed with distilled water until neutral, and dried in a vacuum oven at 80 °C (0.1 mmHg) for 24 h. Dark red crystals (80.5 g, 247.7 mmol, 99%) of **6** were collected and stored under argon at 25 °C. Mp: 250 °C dec. IR ($CDCl_3$): 3853, 3744, 3676, 3090, 3050, 2360, 2336, 1616, 1606, 1594, 1558, 1540, 1527, 1527, 1522, 1447, 1429, 1419, 1308, 1204, 1154, 1129, 1085, 988, 932, 908, 761 cm^{-1}.

(1,3-Butadien-2-yl)(aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (1a). Under argon, Co^{II}(salen) (**6**) (6.0 g, 18.45 mmol) was added to freshly distilled, degassed THF (375 mL). Sodium amalgam (5.0 g, 41% Na, 89.52 mmol) was added and the reactants stirred rapidly at 25 °C for 3 h. The dark green solution of the Co^{I}(salen) anion was transferred by cannula into a THF solution (100 mL) containing 4-tosyl-1,2-butadiene (**7**) (4.3 g, 19.168 mmol) at −75 °C. The reactants were stirred at −75 °C for 2 h, then allowed to warm to 25 °C, and stirred for 18 h. The solution was then filtered into 0.3 N aqueous NaOH (500 mL) at 0 °C and stirred 1 h under argon. The resulting orange crystals isolated by vacuum filtration were washed with water (∼100 mL) until the washings were essentially neutral. The product was then washed with diethyl ether (∼25 mL) and dried in a vacuum oven at 75 °C (1 mmHg) for 18 h to yield **1a** as a bright green solid (6.8 g, 17.2 mmol, 93%). Mp: 135 °C dec. ^{1}H NMR ($CDCl_3$): 7.96 (s, 2H), 7.43 (m, 2H), 7.34 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.65 (t, J = 7.9 Hz, 2H), 5.76 (dd, J = 16.5, 10.8 Hz, 2H), 5.24 (dd, J = 16.5, 2.2 Hz, 1H), 4.56 (dd, J = 10.8, 2.2 Hz, 1H), 4.05 (br s, 2H), 3.75 (br s, 2H), 3.30 (d, J = 4.4 Hz, 1H), 3.15 (d, J = 4.4 Hz, 1H), 1.93 (br s, 2H, exchanges w/D_2O). ^{13}C NMR ($CDCl_3$): 166.01, 164.63, 143.62, 134.55, 133.37, 125.33, 119.79, 117.60, 116.36, 109.98, 59.42. As noted previously in the glyoxime series, we normally do not see the carbon directly attached to Co in ^{13}C NMR, presumably because it is coupling with the neighboring ^{59}Co with a spin of $^7/_2$ to such an extent that it is not visible above the baseline

(7) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier Publishing Co.: New York, 1981; pp 65, 171, 188.
(8) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier Publishing Co.: New York, 1971; p 256.
(9) Pfeiffer, P. *Annu. Chem.* **1933**, *84*, 503.
(10) Tsumaki, T. *Bull. Jpn. Chem. Soc.* **1938,** *13*, 252.
(11) Fieser, L. F.; Novello, L. F. *J. Am. Chem. Soc.* **1942,** *64*, 802.

noise or it is broadened by the Co quadrupole. IR ($CDCl_3$): 3852, 3743, 3054, 2359, 2337, 1629, 1635, 1614, 1601, 1468, 1451, 1345, 1329, 1317, 1201, 1150, 905, 896, 827, 808, 760 cm^{-1}. Anal. Calcd for $CoC_{20}H_{21}N_2O_3$: C, 60.61; H, 5.34. Found: C, 60.84; H, 5.29.

(1,3-Butadien-2-yl)(pyridine)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (1b). Complex **1a** (0.1 g, 0.252 mmol) was dispersed in degassed methanol (5 mL) containing pyridine (1 mL). The mixture was stirred at 25 °C for 2 h and the orange product then precipitated with diethyl ether (50 mL). The pyridine complex (**1b**) was collected by vacuum filtration and washed with diethyl ether (15 mL). The complex was dried at 65 °C and 1 mmHg for 18 h to yield red-orange **1b** (0.1 g, 0.219 mmol, 87%). Mp: 135 °C dec. ^{1}H NMR ($CDCl_3$): 8.67 (d, J = 8.5 Hz, 2H), 7.97 (s, 2H), 7.65 (m, 2H), 7.37 (m, 5H), 7.18 (d, J = 8.5 Hz, 2H), 6.62 (t, J = 8.5 Hz, 2H), 6.08 (dd, J = 16.9, 10.5 Hz, 1H), 5.22 (dd, J = 16.9, 2.7 Hz, 1H), 4.48 (dd, J = 10.5, 2.7 Hz, 1H), 3.76 (m, 4H), 3.67 (d, J = 2.9 Hz, 1H), 3.52 (d, J = 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): 166.99, 165.34, 150.89, 145.41, 137.22, 134.59, 133.92, 125.43, 125.12, 120.73, 117.55, 115.98, 109.62, 59.49. IR ($CDCl_3$): 3157, 2955, 2259, 1614, 1533, 1453, 1384, 1358, 1335, 1311, 1247, 1210, 1155, 1132, 1094, 986, 963, 938, 897, 876, 772, 756, 742, 712 cm^{-1}. Anal. Calcd for $CoC_{25}H_{24}N_3O_2$: C, 65.64; H, 5.29. Found: C, 65.39; H, 5.54.

(1,3-Butadien-2-yl)[4-(dimethylamino)pyridine](*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (1c). The DMAP complex (**1c**) was prepared using the procedure outlined above for **1b** on a 2.1 mmol scale (0.84 g of **1a**), and **1c** was obtained as a red orange solid (0.934 g, 1.85 mmol, 88%). Mp: 160 °C dec. ^{1}H NMR ($CDCl_3$): 8.18 (d, J = 6.3 Hz, 2H), 7.91 (s, 2H), 7.26 (m, 4H), 7.05 (d, J = 8.2 Hz, 2H), 6.54 (t, J = 8.2 Hz, 2H), 6.43 (d, J = 8.2 Hz, 2H), 6.23 (dd, J = 17.2, 10.6 Hz, 1H), 5.16 (dd, J = 17.2, 2.7 Hz, 1H), 4.52 (dd, J = 10.6, 2.7 Hz, 1H), 3.77 (s, 1H), 3.70 (m, 4H), 3.60 (s, 1H), 2.97 (s, 6H). ^{13}C NMR ($CDCl_3$): 167.19, 164.99, 150.63, 146.24, 134.47, 133.95, 125.38, 120.77, 117.30, 115.52, 114.45, 109.14, 107.95, 59.25, 40.09. IR ($CDCl_3$): 3853, 3744, 2364, 2340, 1623, 1616, 1602, 1539, 1456, 1385, 1353, 1319, 1279, 1261, 1228, 1201, 1160, 1140, 1081, 1016, 988, 827, 808, 758 cm^{-1}. Anal. Calcd for $CoC_{27}H_{29}N_4O_2$: C, 64.79; H, 5.84. Found: C, 64.33; H, 5.40.

(*cis*-4,4,7,7,8,9-Hexahydro-1,3-dioxoisobenzofuran-6-yl)(aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt-(III) (8). Under argon, maleic anhydride (0.250 g, 2.549 mmol) and **1a** (0.500 g, 1.261 mmol) were dispersed in $CHCl_3$ (20 mL). After the mixture was stirred for 5 min, the color changed from orange-red to dark green and the reactants dissolved. Stirring was continued for 60 min at 25 °C and hexanes (100 mL) was added. The grass green product (0.60 g, 1.21 mmol, 96%) was collected by vacuum filtration and dried at 55 °C (0.1 mmHg) for 24 h. Mp: 130 °C dec. ^{1}H NMR ($CDCl_3$): 8.11 (s, 1H), 8.03 (s, 1H), 7.37 (m, 2H), 7.33 (m, 2H), 7.21 (d, J = 7.3 Hz, 2H), 6.75 (t, J = 7.3 Hz, 2H), 4.26 (m, 1H), 3.70 (m, 4H), 3.19 (m, 2H), 2.65 (m, 1H), 2.51 (ddd, J = 14.3, 6.5, 2.0 Hz, 1H), 2.18 (dddd, J = 16.6, 5.7, 2.8, 2.8 Hz, 1H), 1.68 (s, 2H), 1.53 (d, J = 16.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 176.02, 167.55, 166.23, 165.92, 165.62, 135.29, 135.16, 134.39, 134.04, 131.45, 125.65, 125.09, 120.72, 120.02, 117.21, 117.12, 60.65, 60.09, 42.38, 42.29, 31.56, 27.66. IR ($CDCl_3$): 3694, 3060, 2931, 2275, 2245, 1839.32, 1776.73, 1731.81, 1611.02, 1534.63, 1453.11, 1311.42, 1240.23, 1198, 1155, 1091, 987, 925, 913, 895, 874, 794, 771, 756, 740, 726, 711, 627 cm^{-1}. Anal. Calcd for $CoC_{24}H_{23}N_2O_6$: C, 58.31; H, 4.69. Found: C, 58.29; H, 4.73.

Neat Synthesis of (*cis*-4,4,7,7,8,9-Hexahydro-1,3-dioxoisobenzofuran-6-yl)(aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (8). Complex **1a** (0.06 g, 0.151 mmol) and maleic anhydride (0.25 g, 2.55 mmol) were heated to 58−60 °C for 4 h under argon. The heat was increased to 70−75 °C, the argon flow was increased, and excess maleic anhydride was removed by sublimation. The flask contents were cooled to 25 °C and the product dispersed in hexanes (20 mL). The product (identical by spectroscopic comparison to **8** reported above) (0.074 g, 0.150 mmol, 99%) was collected by vacuum filtration and dried at 55 °C (0.1 mmHg) for 18 h.

(*cis*-4,4,7,7,8,9-Hexahydro-1,3-dioxoisobenzofuran-6-yl)(pyridine)(*N,N′*-ethylenebis(salicylideneaminato))-cobalt(III) (9). Complex **1b** (0.50 g, 1.093 mmol) and maleic anhydride (0.25 g, 2.549 mmol) were dispersed in chloroform (20 mL), and the originally heterogeneous mixture became homogeneous after 5 min. Stirring was continued at 25 °C for 0.5 h, and then hexanes (100 mL) was added to precipitate the product (0.60 g, 1.08 mmol, 99%) which was collected by vacuum filtration and dried at 55−60 °C (0.1 mmHg) for 24 h. Mp: 130 °C dec. ^{1}H NMR ($CDCl_3$): 8.70 (d, J = 6.4 Hz, 2H), 8.01 (s, 1H), 7.94 (s, 1H), 7.51 (m, 2H), 7.35−7.22 (m, 5H), 7.17 (d, J = 7.6 Hz, 2H), 6.65 (t, J = 7.6 Hz, 2H), 4.38 (s, 1H), 3.95−3.55 (m, 4H), 3.20 (m, 2H), 2.58 (m, 2H), 2.18 (dd, J = 16.9, 2.82 Hz, 1H), 1.71 (d, J = 16.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): 176.17, 171.01, 167.55, 165.42, 153.47, 151.19, 140.32, 137.29, 136.01, 135.23, 134.38, 134.04, 131.08, 126.39, 125.57, 125.11, 124.8, 117.9, 116.80, 116.67, 60.42, 59.72, 42.38, 42.33, 31.70, 27.58. IR ($CDCl_3$): 3080, 2550, 1843, 1774, 1714, 1628, 1603, 1535, 1461, 1382, 1344, 1204, 1154, 1128, 1087, 988, 933, 908, 761 cm^{-1}. Anal. Calcd for $CoC_{29}H_{26}N_3O_5$: C, 62.70; H, 4.70. Found: C, 60.50; H, 4.81. This analytical data (obtained on many different samples) is very close to what we would expect for the hydrated complex $CoC_{29}H_{26}N_3O_5 \cdot H_2O$: C, 60.77; H, 4.92. LRFABMS (m/z): found for M^+ − pyr, 476.1.

(*cis*-4,4,7,7,8,9-Hexahydro-1,3-dioxoisobenzofuran-6-yl)[4-(dimethylamino)pyridine](*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (10). Complex **1c** (0.08 g, 0.159 mmol) and maleic anhydride (0.03 g, 0.305 mmol) were reacted as described for **9** above to produce **10** (0.088 g, 0.147 mmol, 92%). Mp: 138 °C dec. ^{1}H NMR ($CDCl_3$): 8.13 (s, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.35−7.22 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 6.69 (t, J = 8.4 Hz, 2H), 6.27 (d, J = 7.8 Hz, 2H), 4.19 (s, 1H), 3.93−3.62 (m, 4H), 3.20 (m, 2H), 2.88 (s, 6H), 2.65 (m, 2H), 2.30 (dd, J = 16.4, 2.8 Hz, 1H), 1.80 (d, J = 16.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): 176.13, 169.42, 167.08, 166.7, 165.2, 151.19, 148.2, 135.14, 134.39, 134.04, 130.84, 125.53, 125.10, 121.0, 120.03, 116.53, 108.83, 107.67, 60.32, 59.54, 42.37, 40.34, 40.20, 31.75, 27.56. IR ($CDCl_3$): 3054, 2982, 2368, 2342, 1869, 1844, 1779, 1728, 1659, 1629, 1603, 1578, 1567, 1450, 1351, 1271, 1266, 1227, 1203, 1174, 1129, 1087, 989, 936, 911, 762 cm^{-1}. Anal. Calcd for $CoC_{31}H_{31}N_4O_5$: C, 62.21; H, 5.22. Found: C, 60.73; H, 5.19. As with complex **9** above these analytical data (obtained on many different samples) are very close to what we would expect for the hydrated complex $CoC_{31}H_{31}N_4O_5 \cdot H_2O$: C, 60.42; H, 5.39. LRFABMS (m/z): calcd for $CoC_{31}H_{32}N_4O_5$ (M + H), 599.2; found, 599.2.

(*cis*-4,4,7,7,8,9-Hexahydro-*N*-phenyl-1,3-dioxoisobenzopyrrol-6-yl)(aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (11). Complex **1a** (0.300 g, 0.756 mmol) and *N*-phenylmaleimide (0.259 g, 1.5 mmol) were dispersed in degassed chloroform (20 mL). After the mixture was stirred for 5 min, the color changed from orange-red to dark green and the reactants dissolved. Stirring was continued for 18 h at 25 °C, and hexanes (100 mL) was added. The grass green product (0.39 g, 0.685 mmol, 91%) was collected by vacuum filtration and dried at 55 °C (1 mmHg) for 24 h. Mp: 155 °C dec. ^{1}H NMR ($CDCl_3$): 8.05 (s, 2H), 7.56−7.10 (m, 9H), 6.72 (m, 4H), 4.14 (m, 1H), 3.95 (m, 4H), 3.06 (m, 2H), 2.68 (m, 1H), 2.60 (dd, J = 15.4, 6.1 Hz, 1H), 2.15 (m, 1H), 1.68 (s, 2H), 1.56 (d, J = 16.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): 166.96, 166.3, 164.95, 135.25, 134.99, 134.93, 134.07, 133.70, 130.69, 129.53, 127.12, 126.88, 125.71, 125.07, 116.92, 116.7, 60.39, 59.8, 42.02, 41.61, 31.56, 27.92. IR ($CDCl_3$): 3681, 3054, 2940, 1771, 1719, 1649, 1639, 1604, 1535, 1501, 1468, 1450, 1421, 1384, 1352, 1333, 1318, 1270, 1200, 1173, 1163, 1151, 1109, 1081, 989, 935, 907, 761 cm^{-1}. Anal. Calcd for $CoC_{30}H_{28}N_3O_5$: C, 63.27; H, 4.96. Found: C, 63.36; H, 4.93.

(*cis*-1,2-Dicarbomethoxy-4-cyclohexen-4-yl)(aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (12). Under argon, **1a** (0.2 g, 0.504 mmol), a crystal of hydroquinone, and dimethyl maleate (0.75 g, 5.203 mmol) were dispersed in THF (30 mL). The flask contents were refluxed (84 h), cooled to 25 °C, and vacuum filtered into hexanes (100 mL). A 0.12 g portion of product was collected from the initial filtration, and an additional 0.11 g portion precipitated from the hexanes and was collected by vacuum filtration. The combined filtered products were dried at 55 °C (0.1 mmHg) for 18 h to yield **12** (0.20 g, 0.370 mmol, 74%). Mp: 135 °C dec. ^{1}H NMR ($CDCl_3$): 8.10 (s, 1H), 7.98 (s, 1H), 7.42 (m, 2H), 7.33 (m, 2H), 7.17 (d, J = 6.8 Hz, 2H), 6.68 (t, J = 6.8 Hz, 2H), 4.10−3.71 (m, 4H), 3.62 (s, 3H), 3.57 (s, 3H), 3.54 (br s, 1H), 3.04 (m, 1H), 2.97 (m, 1H), 2.53 (bs, 2H), 2.21 (m, 1H), 1.95 (br s, 2H), 1.77 (d, J = 17.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): 174.55, 174.43, 166.9, 166.34, 165.66, 164.90, 134.74, 133.85, 127.06, 125.57, 125.12, 120.69, 120.13, 116.76, 60.08, 60.42, 52.69, 43.04, 41.55, 34.19, 28.45. IR ($CDCl_3$): 3055, 1734, 1680, 1655, 1613, 1534, 1450, 1352, 1333, 1271, 1261, 1202, 1151, 1133, 1109, 1028, 932, 908, 758, 733, 733, 724 cm^{-1}. Anal. Calcd for $CoC_{26}H_{29}N_2O_7$: C, 57.78; H, 5.41. Found: C, 58.39; H, 5.23.

[*trans*-1,2-Dicarbomethoxy-4-cyclohexen-4-yl](aquo)-(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (13). Under argon, **1a** (0.2 g, 0.504 mmol), a crystal of hydroquinone, and dimethyl fumarate (0.75 g, 5.203 mmol) were dispersed in THF (30 mL). The flask contents were refluxed (48 h), cooled to 25 °C, and vacuum filtered into hexanes (100 mL). A 0.14 g portion of product was collected initially, and an additional 0.09 g portion precipitated from the hexanes and was collected by vacuum filtration. After drying at 55 °C (0.1 mmHg) for 18 h, **13** (0.23 g, 0.426 mmol, 85%) was obtained. Mp: 135 °C dec. ^{1}H NMR ($CDCl_3$): 7.96 (s, 2H), 7.34 (m, 2H), 7.27 (m, 2H), 7.09 (d, J = 7.4 Hz, 2H), 6.62 (t, J = 7.4 Hz, 2H), 3.96 (br s, 2H), 3.79(br s, 2H), 3.58 (s, 3H), 3.59 (br s, 1H), 3.44 (s, 3H), 3.00 (m, 1H), 2.83 (m, 1H), 2.41 (m, 2H), 1.90 (m, 1H), 1.78 (dd, J = 16.6, 2.6 Hz, 1H), 1.68 (s, 2H, H_2O). ^{13}C NMR ($CDCl_3$): 174.90, 174.49, 165.09, 163.98, 163.57, 133.74, 132.58, 125.91, 124.24, 123.97, 118.80, 115.38, 115.30, 59.92, 51.63, 51.49, 43.53, 42.56, 34.99, 29.71. IR ($CDCl_3$): 3056, 3056, 2958, 1736, 1731, 1641, 1616, 1535, 1468, 1421, 1385, 1352, 1344, 1333, 1225, 1201, 1174, 1151, 1132, 1028, 932, 908, 732, 721 cm^{-1}. Anal. Calcd for $CoC_{26}H_{29}N_2O_7$: C, 57.78; H, 5.41. Found: C, 57.95; H, 4.75.

[*cis*-1,2-Dicarbethoxy-4-cyclohexen-4-yl](aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (14). Under argon, **1a** (0.13 g, 0.328 mmol), a crystal of hydroquinone, and diethyl maleate (0.91 g, 5.285 mmol) were dispersed in THF (30 mL). The flask contents were refluxed (96 h) and cooled to 25 °C, and the solvent was removed with the aid of a rotary evaporator. A 0.14 g portion of product was collected. A 1 equiv amount of diethyl maleate, coordinated to or entrained with, the product was observed by ^{1}H NMR (alkene protons at δ 6.2, $CDCl_3$). The crude product was stirred in degassed water (3 mL) (24 h) and recovered by vacuum filtration. The product (**14**) (0.13 g, 0.229 mmol, 70%) (contaminated by 10−15% of diastereomer **15**) was dried at 55 °C (0.1 mm Hg). Mp: 130 °C dec. ^{1}H NMR ($CDCl_3$) (major): 8.05 (br s, 1H), 7.93 (br s, 1H), 7.45 (m, 2H), 7.28 (m, 2H), 7.12 (d, J = 7.3 Hz, 2H), 6.65 (t, J = 7.3 Hz, 2H), 4.15−3.60 (m, 8H), 3.58 (br s, 1H), 3.00 (m, 2H), 2.55 (m, 2H), 2.20 (m, 1H), 1.85 (br s, 2H), 1.62 (dd, J = 17.8, 5.4 Hz, 1H), 1.22 (t, J = 7.3 Hz, 3H), 1.11 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) (major): 175.65, 174.30, 165.37, 164.35, 163.79, 134.40, 132.85, 130.78, 126.51, 125.46, 125.01, 124.75, 116.70, 115.99, 61.13, 60.93, 43.06, 41.32, 35.34, 33.70, 27.99, 15.00, 14.86. IR ($CDCl_3$): 3695, 3062, 2985, 2941, 2337, 2247, 1725, 1612, 1533, 1453, 1381, 1310, 1241, 1197, 1158, 1092, 1033, 980, 926, 898, 880, 858, 794, 764, 744, 725, 710 cm^{-1}. Anal. Calcd for $CoC_{28}H_{33}N_2O_7$: C, 59.16; H, 5.85. Found C, 59.05; H, 5.61.

[*trans*-1,2-Dicarbethoxy-4-cyclohexen-4-yl](aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (15). Under argon, **1a** (0.19 g, 0.479 mmol), a crystal of hydroquinone, and diethyl fumarate (0.50 g, 2.903 mmol) were dispersed in THF (30 mL). The flask contents were refluxed (64 h), cooled to 25 °C, and vacuum filtered into hexanes (100 mL). A 0.11 g portion of product was collected from the vacuum funnel, and an additional 0.14 g portion precipitated from the hexanes after cooling at 0 °C for 1 h. Cycloadduct **15** (0.25 g, 0.440 mmol, 92%) was dried at 55 °C (1 mmHg) for 18 h. Mp: 155 °C dec. ^{1}H NMR ($CDCl_3$): 7.83 (br s, 2H), 7.42 (m, 2H), 7.27 (m, 2H), 6.99 (m, 2H), 6.58 (t, J = 7.3 Hz, 2H), 4.15−3.60 (m, 8H), 3.53 (br s, 1H), 3.00 (m, 1H), 2.76 (m, 1H), 2.39 (m, 2H), 1.85 (dd, J= 17.8, 5.4 Hz, 1H), 1.62 (dd, J = 17.8, 2.5 Hz, 1H), 1.17 (t, J = 7.3Hz, 3H), 0.89 (t, J = 7.3Hz, 3H). ^{13}C NMR ($CDCl_3$): 175.55, 174.97, 166.00, 165.35, 165.79, 134.78, 133.69, 127.07, 125.48, 120.23, 116.75, 61.56, 61.13, 60.18, 44.42, 43.32, 36.02, 30.74, 15.13, 14.85. IR ($CDCl_3$): 3681, 3054, 1719, 1639, 1604, 1535, 1501, 1468, 1450, 1421, 1384, 1352, 1318, 1270, 1200, 1172, 1163, 1151, 1109, 1087, 1014, 988, 933, 907, 761 cm^{-1}. Anal. Calcd for $CoC_{28}H_{33}N_2O_7$: C, 59.16; H, 5.85. Found: C, 59.47; H, 5.66.

[1-(1-Oxoethyl)-3-cyclohexen-4-yl](aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (16). Under argon, **1a** (0.40 g, 1.01 mmol), a crystal of hydroquinone, and methyl vinyl ketone (0.5 g, 7.13 mmol) were dispersed in dry THF (20 mL) and then refluxed 48 h. The flask contents were cooled to 25 °C and vacuum filtered into hexanes (100 mL). The product was dried at 50 °C (1 mmHg) for 18 h to yield green crystals of **16** (0.37 g, 0.793 mmol, 79%). Mp: 140 °C dec. ^{1}H NMR ($CDCl_3$): 8.00 (br s, 2H), 7.31 (m, 4H), 7.19 (m, 2H), 6.63 (m, 2H), 3.75 (m, 4H), 3.62 (m, 1H), 2.55 (m, 1H), 2.40 (m, 2H), 2.09 (s, 3H), 1.75 (m, 3H), 1.50 (m, H_2O + 1H). ^{13}C NMR and DEPT ($CDCl_3$): 212.53, 166.62, 166.26, 165.57, 165.26, 134.60, 133.72, 127.34, 125.63, 125.39, 120.52, 120.35, 116.57, 60.31 CH_2, 60.24 CH_2, 49.17 CH, 33.44 CH_2, 30.21 CH_2, 28.98 CH_3, 28.31 CH_2. IR ($CDCl_3$): 3690, 3605, 3404, 3081, 2360, 2338, 2255, 1702,1602, 1535, 1468, 1449, 1384, 1352, 1345, 1332, 1313, 1291, 1265, 1205, 1152, 1132, 1091, 993, 936, 913, 761 cm^{-1}. Anal. Calcd for $CoC_{24}H_{27}N_2O_4$: C, 61.80; H, 5.83. Found: C, 61.42; H, 5.37.

[1-Carbomethoxy-3-cyclohexen-4-yl](aquo)(*N,N′*-ethylenebis(salicylideneaminato))cobalt(III) (17). Under argon, **1a** (0.13 g, 0.328 mmol), a crystal of hydroquinone, and methyl acrylate (0.91 g, 10.57 mmol) were dispersed in dry THF (20 mL) and refluxed (48 h). The flask contents were cooled to 25 °C and vacuum filtered into hexanes (100 mL). The product was dried at 65 °C (1 mmHg) for 18 h to yield **17** as a green solid (0.15 g, 0.311 mmol, 95%). Mp: 135 °C dec. ^{1}H NMR ($CDCl_3$): 7.74 (br s, 2H), 7.48 (m, 2H), 7.29 (m, 2H), 6.90 (m, 2H), 6.52 (m, 2H), 3.70 (m, 4H), 3.58 (s, 3H), 3.38 (br s, 1H), 2.49 (m, 1H), 2.36 (m, 1H), 2.30 (m, 1H), 2.00 (m, 1H), 1.75 (m, H_2O + 2H), 1.69 (m, 1H). ^{13}C NMR and DEPT ($CDCl_3$): 177.33, 166.31, 166.04, 184.85, 134.48, 133.40, 127.35, 125.74, 120.08, 116.22, 60.21 CH_2, 52.31 CH_3, 41.88 CH, 33.82 CH_2, 30.85 CH_2, 28.91 CH_2. IR ($CDCl_3$): 3680, 3054, 2948, 1728, 1647, 1639, 1534, 1450, 1431, 1333, 1203, 1151, 1203, 1169, 1151, 1132, 1087, 987, 933, 908, 763, 730 cm^{-1}. Anal. Calcd for $CoC_{24}H_{27}N_2O_5$: C, 59.75; H, 5.64. Found: C, 60.06; H, 5.28.

Preparation of *cis*-1,2,3,6-Tetrahydrophthalic acid (20) via HBr Cleavage of 8. Under argon, cycloadduct **8** (0.20 g, 0.404 mmol) was dissolved in a 8% HBr in glacial acetic acid solution (5 g, 4.94 mmol HBr) at 0 °C. The solution was allowed to warm to 25 °C and stir for 18 h and then extracted with hexane (20 mL). The hexane extract was washed with saturated aqueous $NaHCO_3$ (10 mL) and saturated aqueous NaCl (10 mL), dried ($MgSO_4$), and then the hexane was removed by rotary evaporation and high vacuum. A slightly off white solid was recovered and chromatographed on silica (1:1 ethyl acetate/pentane) to obtain *cis*-1,2,3,6-tetrahydrophthalic acid (**20**) (0.050 g, 0.294 mmol, 73%) identical by ^{1}H NMR comparison to an authentic sample (TCI America). The aqueous layer remaining after the hexane extraction was

poured into 0.1 N NaOH (10 mL). After being stirred for 30 min, the solution was extracted with CH_2Cl_2 (2 × 25 mL). Diethyl ether (20 mL) was added to precipitate a brown product presumed to be [(aqua)(Co^{III})sal_2en))]hydroxide[4a,c] (0.138 g, 0.383 mmol, 95%), which was collected by vacuum filtration and dried under vacuum over P_2O_5. This brown precipitate (0.138 g, 0.383 mmol) was then dispersed in methanol (2 mL) and stirred at 25 °C for 1 h. The product was precipitated with diethyl ether, collected by vacuum filtration, and dried at 100 °C for 18 h[12] to yield Co^{II}(salen) (**6**) (0.118 g, 0.363 mmol, 96%) identical by IR comparison to **6** prepared independently above.

Preparation of *cis*-1,2,3,6-Tetrahydrophthalic Anhydride (21) via HCl Cleavage of 8. Cycloadduct **8** (0.10 g, 0.202 mmol) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled to 0 °C, and anhydrous HCl was bubbled into the reaction mixture (5 min). The mixture was allowed to warm to 25 °C and stir (18 h). The solvent was removed under reduced pressure. The anhydride was extracted into hexane and worked up as in the previous example to give *cis*-1,2,3,6-tetrahydrophthalic anhydride (**21**) (0.026 g, 0.171 mmol, 84%) (identical to an authentic sample (Aldrich) by ^{1}H NMR comparison[13]). Co^{II}(salen) (**6**) (0.062 g, 0.191 mmol, 95%) was obtained by first treating the initially hexane-insoluble material with aqueous NaOH followed by the procedure outlined above.

Preparation of *cis*-1,2,3,6-Tetrahydrophthalic Acid (20) via Thermolysis of 8. Cycloadduct **8** (0.10 g, 0.202 mmol) was briefly exposed to the atmosphere to pick up excess water of hydration and then placed into a micro sublimation apparatus. The cycloadduct was heated to 130 °C (0.1 mmHg) for 30 min, and then *cis*-1,2,3,6-tetrahydrophthalic acid (**20**) (0.028 g, 0.184 mmol, 91%) was collected from the cold finger. The acid (**20**) was identical by spectroscopic comparison to material reported above. Co^{II}(salen) (**6**) (0.063 g, 0.194 mmol, 96%) was collected from the micro sublimation apparatus and proved to be identical by IR comparison to **6** prepared independently above.

Preparation of *cis*-1,2,3,6-Tetrahydrophthalic Anhydride (21) via Trimethylaluminum Cleavage of 8. Cycloadduct **8** (0.10 g, 0.202 mmol) was dissolved in dry THF (10 mL) under argon. The solution was cooled to 0 °C, and trimethylaluminum in ether (0.2 mL, 1 M, 0.200 mmol) was added via syringe. The mixture was allowed to warm to 25 °C and stir 18 h. Water (10 mL) was added and extracted with diethyl ether (2 × 10 mL). The reaction mixture was filtered, and a brown solid was collected which proved to be [(aqua)-Co^{III}(salen)] methyl (**22**) (0.064 g, 0.179 mmol, 88%) via ^{1}H NMR comparison to an independently prepared authentic sample.[4d] The filtrate was concentrated by rotary evaporation and then diluted with pentane (2 mL) and passed through silica. *cis*-1,2,3,6-tetrahydrophthalic anhydride (**21**) (0.022 g, 0.145 mmol, 72%) (identical to an authentic sample (Aldrich) by ^{1}H NMR comparison[13]) was collected after solvent removal under vacuum.

1-Acetyl-3-cyclohexene (23) via HBr Cleavage of 16. Under argon, cycloadduct **16** (0.20 g, 0.428 mmol) was dispersed in 8% HBr in glacial acetic acid (5.0 g) at 0 °C. The mixture was allowed to warm to 25 °C and stir (16 h). The acid was extracted with hexane (20 mL) then the hexane was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL) before drying over $MgSO_4$. Solvent was removed by rotary evaporation, and then the crude product was chromatographed on silica (1:1 EtOAc/pentane) to yield cyclohexen-3-yl methyl ketone (**23**; 0.046 g, 0.371 mmol, 87%) following solvent removal under vacuum. This material (**23**) had a ^{1}H NMR spectrum identical to literature data.[14] The aqueous (acid) layer was worked up as described above to yield a brown solid, which was collected by suction filtration, stirred in methanol, and finally heated at 100 °C and 0.1 mmHg to give Co^{II}(salen) (**6**) (0.132 g, 0.406 mmol, 95%) identical by IR comparison to material reported above.

1-Acetyl-3-cyclohexene (23) via HCl Cleavage of 16. Under argon, cycloadduct **16** (0.2 g, 0.428 mmol) was treated with anhydrous HCl as described for **21**. Following a work up analogous to the one reported above, **23** (0.048 g, 0.387 mmol, 90%) was recovered. A brown solid was collected by vacuum filtration and treated as above in the HBr cleavage to yield Co^{II}(salen) (**6**) (0.128 g, 0.393 mmol, 92%).

1-Acetyl-4-(acetoxymercurio)-3-cyclohexene (25) via Transmetalation of 16. Cycloadduct **16** (0.0987 g, 0.2116 mmol) was dispersed in absolute ethanol (10 mL). The dispersion was purged with argon, and mercury(II) acetate (0.0709 g, 0.2224 mmol) was added in one portion. The reaction mixture was stirred under argon for 18 h and concentrated to 3 mL, and hexane (20 mL) was added to precipitate the cobalt byproduct. The reaction mixture was vacuum filtered, the filtrate was dried ($MgSO_4$), and the solvent was removed with a rotary evaporator and high vacuum. A slightly off-white solid (**25**) (0.070 g, 0.191 mmol, 90%) was recovered. ^{1}H NMR ($CDCl_3$): 5.69 (br s, 1H), 2.63 (dd, J = 8.64, 2.86 Hz, 1H), 2.37 (m, 3H), 2.25 (m, 1H), 2.13 (s, 3H), 2.05 (s, 3H), 1.63 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm): 210.6, 177.0, 139.0, 137.8, 47.9, 34.3, 29.9, 27.0, 24.0. Anal. Calcd for $C_{10}H_{14}O_3Hg$ C: 31.38; H: 3.69. Found: C, 35.08; H, 3.79. The poor analytical data may be due to reported thermal instability of RHgOAc compounds.[15] EI HRMS (m/z): calcd for $C_{10}H_{14}O_3Hg$, 384.0649; calcd for $C_8H_{11}OHg$ ($M^+ - OAc$), 325.0516; found, 325.0505.

1-Acetyl-3-cyclohexene (23) via Reaction of Trimethylaluminum with 16. Cycloadduct **16** (0.05 g, 0.107 mmol) was dissolved in dry THF (10 mL) under argon. The solution was cooled to 0 °C, and trimethylaluminum in hexanes (0.055 mL, 2 M, 0.11 mmol) was added via syringe. The reaction was carried out as described previously above.[1b] Adduct **23** (0.0117 g, 0.094 mmol, 88%) was obtained and determined to be identical by spectroscopic comparison to the material reported above. A brown solid residue was recovered as reported above, and after the material was dried, it was determined to be methyl[(H_2O)(Co^{III}(salen)] (**22**) (0.036 g, 0.100 mmol, 94%) by ^{1}H NMR comparison to an independently prepared authentic sample.[4d]

1-Acetyl-3-cyclohexene (23) via Reaction of Diethylzinc with 16. Cycloadduct **16** (0.10 g, 0.214 mmol) was dissolved in dry THF (10 mL) under argon. The solution was cooled to 0 °C, and diethylzinc in hexanes (0.22 mL, 1 M, 0.22 mmol) was added via syringe. The reaction was carried out as previously described in the trimethylaluminum reaction and according to the literature.[1b] Adduct **23** (0.0234 g, 0.189 mmol, 88%) was determined to be identical to material obtained above by spectroscopic comparison. A brown solid residue was also recovered from the above reaction. After drying of the material as described above, it was determined to be **24** (0.0749 g, 0.201 mmol, 94%) by ^{1}H NMR comparison to an independently prepared authentic sample.[4d]

1-Acetyl-3-cyclohexene (23) via Thermolysis of 16. Cycloadduct **16** (0.10 g, 0.214 mmol) was placed into a micro sublimation apparatus. The cycloadduct was briefly exposed to the atmosphere to pick up excess water of hydration. The cold finger was filled with dry ice, and cycloadduct **16** was heated as outlined in the thermolysis above. The product **23** collected on the cold finger and was removed by rinsing with

(12) For references to the thermal decomposition of RCo^{III}(salen)-(H_2O) complexes to Co^{II}(salen), see ref 4d and: Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *11*, 333.

(13) Werner, H.; Kleinpeter, E.; Zschunke, A.; Mann, G. *Org. Magn. Reson.* **1973**, *5*, 179.

(14) (a) For bp and refractive index data for this compound, see: Johnson, W. K. *J. Org. Chem.* **1959**, *24*, 864. (b) For IR and ^{1}H NMR data for this compound, see: Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4873.

(15) (a) Brown, H. C.; Larock, R. C.; Gupta, S. K.; Rajagopalan, S.; Bhat, N. G. *J. Org. Chem.* **1989**, *54*, 6079. (b) Larock, R. C.; Brown, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 2467.

$CDCl_3$ (0.75 mL). After a ^1H NMR spectrum was obtained, the solvent was removed under vacuum to yield cyclohexen-3-yl methyl ketone (**23**; 0.024 g, 90.2%) identical by ^1H NMR comparison to literature data.[14] Co^{II}(salen) (**6**; 0.066 g, 95% of theory) was also recovered from the micro sublimation apparatus and identified by IR comparison with authentic material.

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