

Enantioselective Diels–Alder Reactions of Optically Active (Buta-1,3-dien-2-yl)(salen)cobalt(III) Complexes

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The syntheses of two optically active (buta-1,3-dien-2-yl)(salen)Co complexes are reported. These dienyl complexes undergo Diels–Alder reactions with high enantioselectivity with a variety of dienophiles. One of the (salen)Co-substituted Diels–Alder cycloadducts was characterized by X-ray crystallography. A highlight of this chemistry is that the

Diels–Alder cycloadduct containing cobalt complexes were cleanly cleaved at the cobalt–carbon bond with sodium borohydride in ethanol with concomitant optically active cobalt complex starting material and optically active cyclohexene cycloadduct recovery.

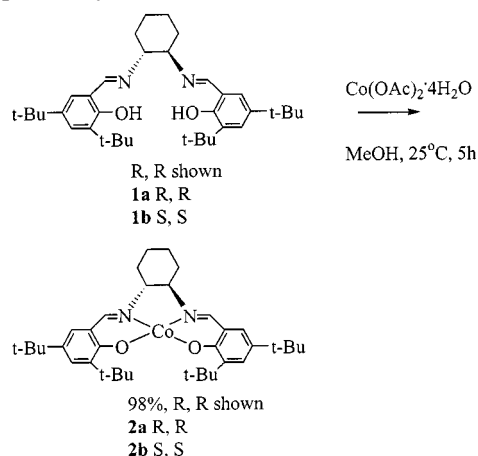
Introduction

We have been interested in the preparation and [4 + 2] cycloaddition chemistry of dienylcobalt complexes for a number of years.^[1] These dienyl complexes are of synthetic interest because they participate in Diels–Alder reactions via *exo* transition states and thereby provide access to stereoisomers normally not obtainable by standard *endo*-selective [4 + 2] cycloaddition reactions. We recently reported an efficient method for the preparation of (buta-1,3-dien-2-yl)(salen)Co^{III} complexes and demonstrated their utility as reactive buta-1,3-diene synthons in numerous Diels–Alder cycloaddition reactions.^[2] Earlier, we communicated the synthesis of optically active (buta-1,3-dien-2-yl)(salen)Co complexes which underwent Diels–Alder reactions with dimethyl fumarate with high enantioselectivity.^[3] Many examples of chiral organic dienes have been reported,^[4] but our report was the first use of optically active transition metal substituted dienyl complexes in enantioselective Diels–Alder reactions.^[5] Unactivated dienes such as buta-1,3-diene have proven to be difficult substrates for Lewis acid catalyzed enantioselective Diels–Alder reactions, hence our search for buta-1,3-diene synthons.^[6] Wulff,^[7] Barluenga,^[8] and Dötz^[9] have all independently reported the use of carbene transition metal complexes as dienophiles in enantioselective Diels–Alder reactions. Here we report additional circular dichroism data which can be used to characterize the (dienyl)(salen)Co complexes, X-ray crystallographic characterization of one of the (salen)Co-substituted Diels–Alder cycloadducts, results of enantioselective Diels–Alder reactions with a number of dienophiles, and

a model which can be used to rationalize and predict the stereochemical outcomes of these [4 + 2] cycloaddition reactions.

Results and Discussion

Our strategy for the preparation of optically active (dienyl)(salen)Co complexes is analogous to the one we originally used to prepare (dienyl)cobaloxime complexes.^[1] The cobalt(II) complex with appropriate ligands is prepared first, then it is reduced and alkylated with allenic electrophiles. In the present case, the optically active (salen)Co^{II} complexes **2a** and **2b** were prepared in quantitative yield by the condensation of cobalt acetate with the appropriate salen ligand **1a** or **1b**^[10] in methanol at 60 °C (Scheme 1). The *R,R*-(–) enantiomer of this (salen)Co complex (**2a**) was characterized by X-ray crystallography by Leung et al. in 1996 but no optical rotation was reported.^[11] Jacobsen and co-workers have reported the use of these (salen)Co complexes as catalysts for enantioselective epoxide ring opening^[12] and their use as hetero Diels–Alder catalysts has been reported by Wu et al. in 1998.^[13]



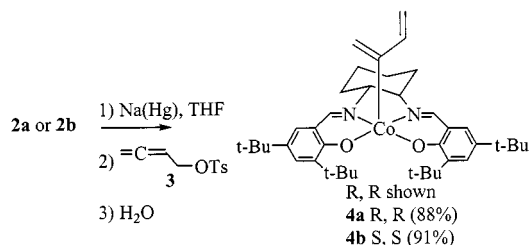
Scheme 1

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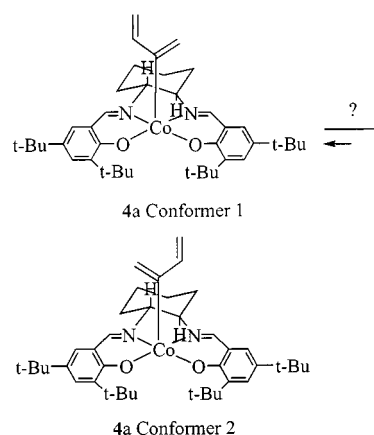
Leung et al. reported that they reduced the (salen)Co^{II} complexes **2a**, **2b** with sodium amalgam and treated the corresponding anion with unspecified alkyl halides.^[11] However, they could not isolate the presumably formed alkylation products. We found that **2a** or **2b** were easily converted into the dark green (salen)Co^I anions by Na(Hg) reduction in THF and that these anions reacted with 4-tosylbuta-1,2-diene (**3**) to give the corresponding optically active (*R,R*)-(+)- and (*S,S*)-(–)-[*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)aminato](buta-1,3-dien-2-yl)(cyclohexane-1,2-diamine)cobalt(III) complexes (**4a** and **4b**) in high yield (Scheme 2).



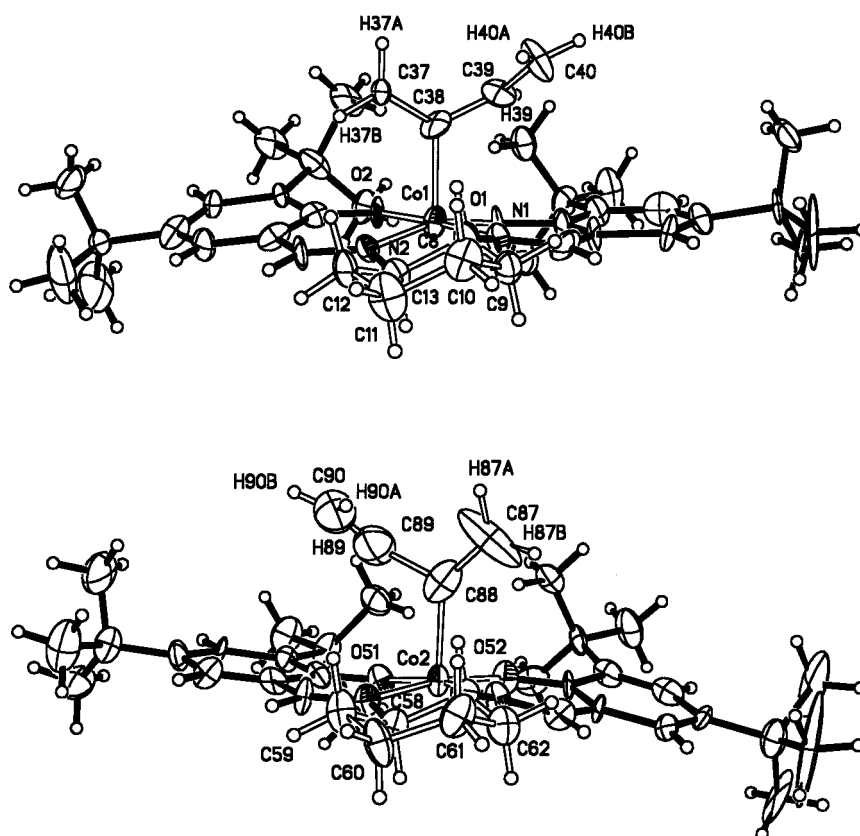
Scheme 2

The dienyI complex **4a** from the (*R,R*)-salen ligand was characterized by X-ray crystallography.^[3] The solid-state structure showed two distinct conformers (**4a** conformer 1 and **4a** conformer 2) for this complex (Scheme 3) with equal solid-state conformer populations (ORTEPs of these conformers are also provided as Figure 1, a and b). These con-

formers have dihedral (torsion) angles around the C(38)–C(39) and C(88)–C(89) bonds of 68–70°, similar to (dienyl)(glyoxime)cobalt complexes we have reported previously.^[14] The Co(1)–C(38) and Co(2)–C(88) distances of 1.962(9) Å and 2.007(13) Å are also similar to those seen in the glyoxime ligand series.^[14] In solution, we saw no ¹H NMR line broadening over a temperature range of 25 to –63 °C. This NMR-spectroscopic data indicates that conformer interconversion is facile and we see a time-averaged spectrum, or there is one dominant solution conformer over the temperature ranges we employ for cycloadditions.



Scheme 3

Figure 1. Perspective drawings of the two crystallographically independent molecules present in the solid-state structure of **4a**

To gain some additional information about the conformers, the total energy of each solid-state conformer was calculated using Spartan Plus 1.3. The conformers were parameterized using the semi-empirical PM3† method. Conformer 2 (Figure 1, b) is 2.7 kcal/mol more stable than conformer 1. If valid, this energy difference would correspond to an equilibrium ratio of about 100:1 and conformer 2 would be favored at 25 °C. The results of these total energy calculations are also consistent with intramolecular close contacts between the dienyl fragment and the ligand set in each of the solid-state conformers. For conformer 1 (Figure 1, a) there are a number of close contacts that could contribute to the higher energy. H37B has close contacts to N2 (2.720 Å) and C14 (2.831 Å). The analogous contacts in conformer 2 (Figure 1, b) are considerably longer: H87B–N52 (2.907 Å), H87B–C64 (3.154 Å). Likewise, H39 in conformer 1 (Figure 1, a) has close contacts to O1 (2.702 Å), C1 (2.839 Å), and one of the *tert*-butyl group hydrogen atoms (H24B 2.537 Å). The analogous hydrogen atom, H89, in conformer 2 (Figure 1, b) has similar contacts to ligand oxygen (H89–O51, 2.758 Å) and carbon atoms (H89–C51, 2.763 Å) but is much further removed from the *tert*-butyl group: H89–H74B (2.873 Å), H89–H74C (2.767 Å). These total energy calculations and X-ray data are consistent with the conclusion that our NMR-spectroscopic data are indicative of one dominant solution conformer rather than a rapidly equilibrating mixture of two conformers. As a working hypothesis, we will therefore use conformer 2 to develop a model for the rationalization and prediction of the outcomes of Diels–Alder cycloadditions.

In addition to characterization by NMR-spectroscopy and X-ray crystallography, the circular dichroism (CD) spectra of the dienyl complexes **4a** and **4b** were also recorded (Figure 2). The (*R,R*)-(+)-(dienyl)(salen)Co complex **4a** has a positive Cotton effect for the long-wavelength transition and a negative Cotton effect for the short-wavelength transition. The short-wavelength absorption is most likely the ¹L_b band of the benzene chromophore. In the 1970s Sznatke et al. determined rules for predicting the signs of Cotton effects for chirally substituted benzene rings

and tetralins and they found that the chiral sphere nearest to the benzene chromophore generally determines the sign of the Cotton effect.^[15] For tetralins they found that the helicity of the nonaromatic ring also has a strong effect on the sign of this absorption. If we consider the benzene ring in the ligand and the adjacent six-membered ring with Co as a “metallotetralin” we find that the ring systems have almost no helicity in the solid-state structures (Figure 1, a and b). The sign of the short-wavelength Cotton effect is therefore expected to be determined by the chiral centers nearest to that chromophore. CD spectra of two tetralins with chiral centers located two and three carbon atoms removed from the benzene ring with the same relative (*trans*) and absolute configurations have been reported and they also show negative Cotton effects for the ¹L_b (≈ 250 nm) CD band.^[15b]

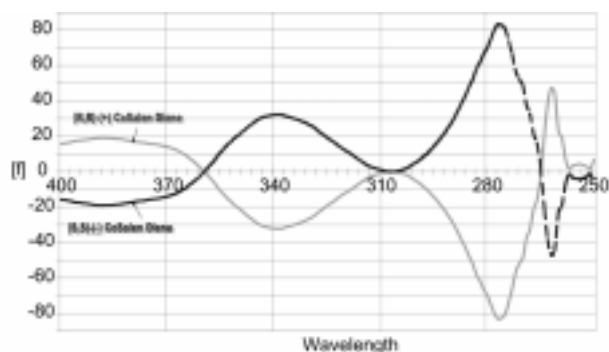


Figure 2. CD spectra of (*R,R*)-(+)-**4a** and (*S,S*)-(-)-**4b**

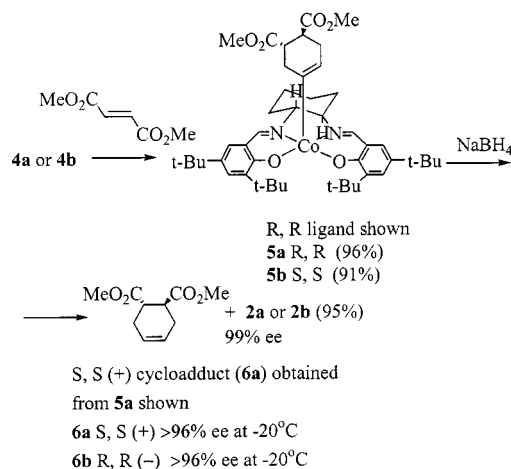
The optically active dienyl complexes **4a** and **4b** were treated with dimethyl fumarate in a series of thermal and Lewis acid catalyzed Diels–Alder reactions (Table 1) and then with a variety of dienophiles (Table 2) using reaction conditions which were optimized using dimethyl fumarate. The cobalt-containing cycloadducts **5a** and **5b** can be isolated and characterized if desired; however, for most of the

Table 1. Enantioselective synthesis of dimethyl fumarate cycloadducts

Entry	Diene	Solvent	Lewis. acid	<i>T</i> [°C]	<i>t</i> [h]	Step 2	Yield (%)	<i>ee</i> (%)	Cycloadduct
1	4a	THF	none	40	6	NaBH ₄ , EtOH	81	36	6a
2	4b	THF	none	40	6	NaBH ₄ , EtOH	86	24	6b
3	4a	THF	5-Å molecular sieves	25	24	NaBH ₄ , EtOH	84	51	6a
4	4a	CH ₂ Cl ₂	none	25	72	NaBH ₄ , MeOH	92	12	6a
5	4b	CH ₂ Cl ₂	none	25	72	NaBH ₄ , MeOH	91	15	6b
6	4a	CHCl ₃	none	25	24	LiBH ₄ , EtOH	87	29	6a
7	4a	CH ₂ Cl ₂	Et ₃ AlCl	25	0.33	NaBH ₄ , EtOH	73	46	6a
8	4a	CH ₂ Cl ₂	EtAlCl ₂	25	0.33	NaBH ₄ , EtOH	75	64	6a
9	4a	CH ₂ Cl ₂	AlCl ₃	0–25	0.67	NaBH ₄ , EtOH	89	78	6a
10	4b	CH ₂ Cl ₂	AlCl ₃	0–25	0.67	NaBH ₄ , EtOH	79	76	6b
11	4b	CH ₂ Cl ₂	AlCl ₃	0–25	0.5	Hg(OAc) ₂ , NaBH ₄ , EtOH	65	82	6b
12	4a	CH ₂ Cl ₂	AlCl ₃	–20	18	NaBH ₄ , EtOH	55	> 96	6a
13	4b	CH ₂ Cl ₂	AlCl ₃	–20	18	NaBH ₄ , EtOH	54	> 96	6b

Table 2. Reactions of other dienophiles with diene complexes **4a** and **4b** according to Scheme 5

Entry	Diene	Yield (%)	% ee	Cycloadduct configuration
1	4a	65	> 96	(<i>R</i>)-(-)- 7a
2	4b	67	> 96	(<i>S</i>)-(+)- 7b
3	4b	69	> 96	(<i>S</i>)-(+)- 8b
4	4a	70	> 96	(1 <i>S</i> ,2 <i>R</i>)-(-)- 9a
5	4b	71	> 96	(1 <i>R</i> ,2 <i>S</i>)-(+)- 9b

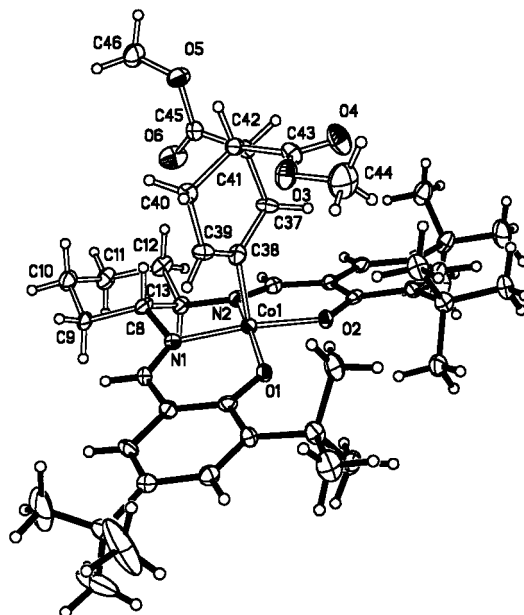
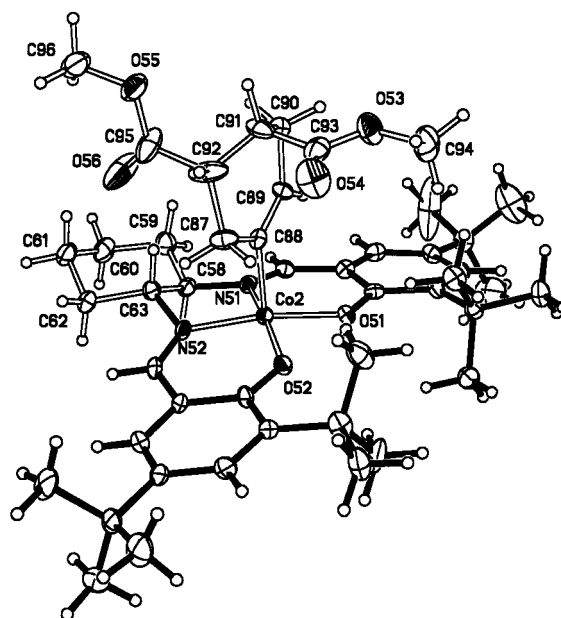


Scheme 4

runs in Table 1 and all the experiments in Table 2, the cycloaddition and subsequent demetallation were performed in the same flask (Scheme 4).

It is worthy to note that the Diels–Alder cycloadducts **5a**, **5b** were cleanly cleaved at the cobalt–carbon bond by sodium borohydride in ethanol with concomitant optically active cobalt starting material (**2a**, **2b**) and cycloadduct (**6a**, **6b**) recovery. The optical purities of the cleaved cycloadducts **6a**, **6b** were established by chiral GC analysis, and specific rotations of cleaved cycloadducts were compared with the literature values to derive the absolute stereochemistry of the cycloadducts.^[16] Corey has previously noted that the esters **6** cannot be obtained in high optical purity from the Diels–Alder reaction of buta-1,3-diene with dimethyl fumarate followed by menthyl ester transesterification.^[17] However, the chiral diene rather than chiral dienophile approach does provide compounds **6** in high enantiomeric purity.

The cycloadduct **5a** (molecule 2) and its diastereomer **5a** (molecule 1) with the (*R,R*) configuration at the cycloadduct stereocenters formed from a thermal reaction of low enantiomeric excess (Table 1, Entry 1) were also characterized by X-ray crystallography and the structure of **5a** was confirmed as shown. The diastereomers from this thermal reaction [**5a** (molecules 1 and 2)] crystallize in the noncentrosymmetric space group *P*1 with two molecules per unit cell in a pseudo-centrosymmetric manner. The solid-state structure approximates to a centrosymmetric arrangement in space group *P*1̄. The two crystallographically independ-

Figure 3. Molecular structure of complex **5a** (molecule 1) with 50% probability for thermal ellipsoidsFigure 4. Molecular structure of complex **5a** (molecule 2) with 50% probability for thermal ellipsoids

ent molecules (Figure 3, molecule 1; Figure 4, molecule 2) are labeled and translated in the unit cell to give names and fractional coordinates that are related by a pseudo-inversion center at the origin of the unit cell. The largest deviations from a rigorously centrosymmetric arrangement involve atoms near the chiral centers of the cyclohexane rings (C8/C58 0.69 Å, C10/C60 0.57 Å, C11/C61 0.72 Å, C13/C63 0.68 Å) and methyl groups for one of the *tert*-butyl groups (C26/C76 1.16 Å, C27/C77 0.47 Å, C28/C78 0.49 Å). The Co(1)–C(38) bond length of 1.937(6) Å and the Co(2)–C(88) bond length of 1.936(5) Å are similar to

Table 3. Crystal data and structure refinement for complexes **5a** (molecules 1 and 2)

Empirical formula	C ₄₆ H ₆₅ CoN ₂ O ₆
Formula mass	800.93
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$ C ₁ ¹ (No. 1)
Unit cell dimensions	$a = 11.9238(2)$ Å, $\alpha = 92.562(1)^\circ$ $b = 13.8776(2)$ Å, $\beta = 99.568(1)^\circ$ $c = 14.3141(1)$ Å, $\gamma = 110.543(1)^\circ$
Volume, Z	2173.47(5) Å ³ , 2
Density (calculated)	1.224 g/cm ^{−3}
Absorption coefficient	0.443 mm ^{−1}
$F(000)$	860
Crystal size	0.32 × 0.36 × 0.44 mm
θ range for data collection	1.45–28.21°
Limiting indices	−10 ≤ h ≤ 15, −18 ≤ k ≤ 8, −18 ≤ l ≤ 18
Reflections collected	14337
Independent reflections	11391 ($R_{\text{int}} = 0.0327$)
Absorption correction	integration
Transmission range	0.836–0.912
Refinement method	full-matrix least squares on F^2
Data/parameters	10946/1063
Goodness-of-fit on F^2	1.065
Final R indices	
[10082 $F_o > 4\sigma(F_o)$ data]	$R_1 = 0.0513$
(10946 $F_o > 0$ data)	$wR_2 = 0.1266$
(all 11391 data)	$R_1 = 0.0636$, $wR_2 = 0.1386$
Absolute structure parameter	0.03(2)
Largest diff. peak and hole	0.542 and −0.332 e/Å ³

Table 4. Selected bond lengths [Å] for **5a** (molecules 1 and 2)

Co(1), molecule 1		Co(2), molecule 2	
Co(1)–O(1)	1.861(4)	Co(2)–O(51)	1.886(5)
Co(1)–O(2)	1.869(5)	Co(2)–O(52)	1.869(5)
Co(1)–N(1)	1.868(6)	Co(2)–N(51)	1.885(6)
Co(1)–N(2)	1.892(6)	Co(2)–N(52)	1.868(5)
Co(1)–C(38)	1.937(6)	Co(2)–C(88)	1.936(5)
O(1)–C(1)	1.317(8)	O(51)–C(51)	1.306(8)
O(2)–C(20)	1.313(8)	O(52)–C(70)	1.318(8)
O(3)–C(43)	1.325(9)	O(53)–C(93)	1.281(11)
O(5)–C(45)	1.346(7)	O(55)–C(95)	1.343(10)
O(3)–C(44)	1.450(11)	O(53)–C(94)	1.475(11)
O(5)–C(46)	1.440(9)	O(55)–C(96)	1.431(11)
O(4)–C(43)	1.230(10)	O(54)–C(93)	1.194(12)
O(6)–C(45)	1.188(8)	O(56)–C(95)	1.180(10)
N(1)–C(7)	1.304(9)	N(51)–C(57)	1.292(9)
N(2)–C(14)	1.291(9)	N(52)–C(64)	1.305(9)
N(1)–C(8)	1.486(7)	N(51)–C(58)	1.484(7)
N(2)–C(13)	1.494(7)	N(52)–C(63)	1.471(7)
C(6)–C(7)	1.439(9)	C(56)–C(57)	1.445(9)
C(14)–C(15)	1.447(9)	C(64)–C(65)	1.417(11)
C(38)–C(39)	1.320(10)	C(88)–C(89)	1.328(9)
C(37)–C(38)	1.495(9)	C(87)–C(88)	1.513(9)
C(37)–C(42)	1.521(8)	C(87)–C(92)	1.566(9)
C(39)–C(40)	1.527(8)	C(89)–C(90)	1.522(9)
C(40)–C(41)	1.550(10)	C(90)–C(91)	1.536(12)
C(41)–C(43)	1.506(9)	C(91)–C(92)	1.465(12)
C(41)–C(42)	1.540(8)	C(91)–C(93)	1.589(12)

those we have observed previously for cobalt–sp²–carbon bonds.^[2,3,14] Crystal data and structure refinement parameters are provided in Table 3. Selected bond lengths for

Table 5. Selected bond angles [°] for **5a** (molecules 1 and 2)

Co(1), molecule 1		Co(2), molecule 2	
O(1)–Co(1)–N(1)	94.3(2)	N(52)–Co(2)–O(52)	93.5(2)
O(1)–Co(1)–O(2)	84.9(2)	N(52)–Co(2)–N(51)	85.7(3)
N(1)–Co(1)–N(2)	85.2(3)	O(52)–Co(2)–O(51)	85.2(2)
O(2)–Co(1)–N(2)	93.7(2)	N(51)–Co(2)–O(51)	93.3(2)
O(1)–Co(1)–C(38)	99.4(2)	N(52)–Co(2)–C(88)	92.2(2)
N(1)–Co(1)–C(38)	91.5(3)	O(52)–Co(2)–C(88)	98.0(2)
O(2)–Co(1)–C(38)	96.0(3)	N(51)–Co(2)–C(88)	94.5(2)
N(2)–Co(1)–C(38)	96.2(3)	O(51)–Co(2)–C(88)	98.2(2)
N(1)–Co(1)–O(2)	172.5(2)	O(52)–Co(2)–N(51)	167.5(2)
O(1)–Co(1)–N(2)	164.4(2)	N(52)–Co(2)–O(51)	169.6(2)
C(1)–O(1)–Co(1)	128.6(4)	C(51)–O(51)–Co(2)	129.4(4)
C(20)–O(2)–Co(1)	129.9(4)	C(70)–O(52)–Co(2)	129.3(4)
C(43)–O(3)–C(44)	115.0(8)	C(93)–O(53)–C(94)	113.8(9)
C(45)–O(5)–C(46)	117.5(6)	C(95)–O(55)–C(96)	113.5(7)
C(7)–N(1)–C(8)	120.7(5)	C(57)–N(51)–C(58)	119.7(6)
C(7)–N(1)–Co(1)	126.9(5)	C(57)–N(51)–Co(2)	126.2(5)
C(8)–N(1)–Co(1)	112.1(4)	C(58)–N(51)–Co(2)	113.4(4)
C(14)–N(2)–C(13)	119.4(5)	C(64)–N(52)–C(63)	122.5(5)
C(14)–N(2)–Co(1)	126.1(5)	C(64)–N(52)–Co(2)	126.5(5)
C(13)–N(2)–Co(1)	113.4(4)	C(63)–N(52)–Co(2)	110.8(4)
O(1)–C(1)–C(6)	122.9(6)	O(51)–C(51)–C(56)	122.5(6)
O(1)–C(1)–C(2)	119.3(6)	O(51)–C(51)–C(52)	119.9(6)
C(6)–C(1)–C(2)	117.7(6)	C(56)–C(51)–C(52)	117.6(6)
C(1)–C(6)–C(7)	121.8(6)	C(55)–C(56)–C(51)	120.7(6)
C(7)–C(6)–C(5)	116.7(6)	C(51)–C(56)–C(57)	121.5(7)
N(1)–C(7)–C(6)	125.0(6)	N(51)–C(57)–C(56)	126.4(6)
N(2)–C(14)–C(15)	125.0(6)	N(52)–C(64)–C(65)	127.2(6)
C(2)–C(15)–C(14)	123.5(6)	C(66)–C(65)–C(70)	120.1(7)
C(16)–C(15)–C(14)	116.5(6)	C(64)–C(65)–C(70)	120.0(7)
O(2)–C(20)–C(15)	121.0(6)	O(52)–C(70)–C(69)	120.8(6)
O(2)–C(20)–C(19)	120.4(5)	O(52)–C(70)–C(65)	122.5(6)
N(1)–C(8)–C(13)	104.5(4)	N(51)–C(58)–C(59)	117.9(5)
N(1)–C(8)–C(9)	117.5(5)	N(51)–C(58)–C(63)	106.8(4)
N(2)–C(13)–C(12)	117.2(5)	N(52)–C(63)–C(58)	107.2(4)
N(2)–C(13)–C(8)	106.5(4)	N(52)–C(63)–C(62)	118.5(5)
C(19)–C(33)–C(35)	109.5(6)	C(69)–C(83)–C(86)	111.5(6)
C(38)–C(37)–C(42)	112.1(6)	C(88)–C(87)–C(92)	113.0(6)
C(39)–C(40)–C(41)	111.1(6)	C(89)–C(90)–C(91)	110.7(6)
C(43)–C(41)–C(42)	110.3(6)	C(92)–C(91)–C(90)	115.9(7)
C(43)–C(41)–C(40)	114.2(5)	C(92)–C(91)–C(93)	105.1(8)
C(42)–C(41)–C(40)	108.3(5)	C(90)–C(91)–C(93)	112.0(7)
C(45)–C(42)–C(37)	112.3(5)	C(91)–C(92)–C(87)	110.7(7)
C(45)–C(42)–C(41)	112.3(5)	C(91)–C(92)–C(95)	107.3(8)
C(37)–C(42)–C(41)	112.3(5)	C(87)–C(92)–C(95)	111.0(7)
C(39)–C(38)–Co(1)	119.5(6)	C(89)–C(88)–Co(2)	120.5(5)
C(37)–C(38)–Co(1)	116.0(5)	C(87)–C(88)–Co(2)	115.4(5)
C(39)–C(38)–C(37)	124.5(6)	C(89)–C(88)–C(87)	124.1(5)
C(38)–C(39)–C(40)	122.6(6)	C(88)–C(89)–C(90)	123.0(6)
O(4)–C(43)–O(3)	123.2(8)	O(54)–C(93)–O(53)	121.8(9)
O(4)–C(43)–C(41)	123.4(7)	O(54)–C(93)–C(91)	126.3(9)
O(3)–C(43)–C(41)	113.4(7)	O(53)–C(93)–C(91)	111.7(9)
O(6)–C(45)–O(5)	121.8(6)	O(56)–C(95)–O(55)	123.4(8)
O(6)–C(45)–C(42)	125.8(6)	O(56)–C(95)–C(92)	127.1(8)
O(5)–C(45)–C(42)	112.4(5)	O(55)–C(95)–C(92)	109.4(7)

these complexes are provided in Table 4 and selected bond angles are provided in Table 5.

The reactions between dimethyl fumarate and both enantiomers of (buta-1,3-diene)(salen)Co^{III} (**4a** and **4b**) were carried out in polar and nonpolar solvents between −78 and 68 °C as described in Table 1. The fact that all reaction components were highly soluble in CH₂Cl₂ and the ability to screen a variety of Lewis acids in CH₂Cl₂ led us to invest-

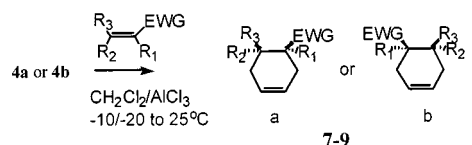
igate catalyzed Diels–Alder reactions in this solvent. $\text{BF}_3 \cdot \text{Et}_2\text{O}$, SnCl_4 , and TiCl_4 all appeared to destroy the dienes **4a**, **4b** when employed as catalyst. Alkylaluminum chlorides reacted under mild conditions but resulted in lower *ee* values than aluminum chloride (Table 1, Entries 7, 8). Aluminum chloride catalyzed reactions gave *ee* values > 75% at 0–25 °C (Table 1, Entries 9–11) and *ee* values close to 100% at –20 °C (Table 1, Entries 12, 13). Reactions attempted with aluminum chloride were too slow to monitor below –20 °C.

After optimization of the cycloaddition conditions using dimethyl fumarate, we examined Diels–Alder reactions of the dienyl complexes **4a** and **4b** with methyl methacrylate, methacrolein, and citraconic anhydride (Table 2). (*R,R*)-(+)-Dienyl complex **4a** and (*S,S*)-(–)-dienyl complex **4b** reacted with methyl methacrylate to provide *R*-(–)-**7a** and *S*-(+)-**7b** cycloadducts, respectively (Table 2, Entries 1, 2). Only one product enantiomer was detected by chiral GC analysis in each case. Likewise, the (*S,S*)-(–)-dienyl complex **4b** reacted with methacrolein to give the *S*-(+) cycloadduct **8b** in similar yield. After investigating these disubstituted dienophiles, we proceeded to citraconic anhydride as an example of a trisubstituted dienophile. Citraconic anhydride also reacted with both **4a** and **4b** to provide cyclo-

adducts **9a** and **9b** in high yield and enantioselectivity (Scheme 5). The absolute stereochemistries of the cycloadducts produced (**7a**, **7b**, **8b**^[18] and **9a**, **9b**^[19]) were determined by comparison of their optical rotations with those previously reported. In the reactions reported in Table 2, the solution was allowed to warm to 25 °C in the presence of Lewis acid to effect demetalation. This demetalation, rather than the reductive method used for the reactions reported in Table 1, also yielded a green solid which is presumably (*salen*)Co^{III} chloride as the cobalt by-product. However, with these demetalation reactions reported in Table 2, we made no attempt to recover the cobalt as we had done for the examples in Table 1.

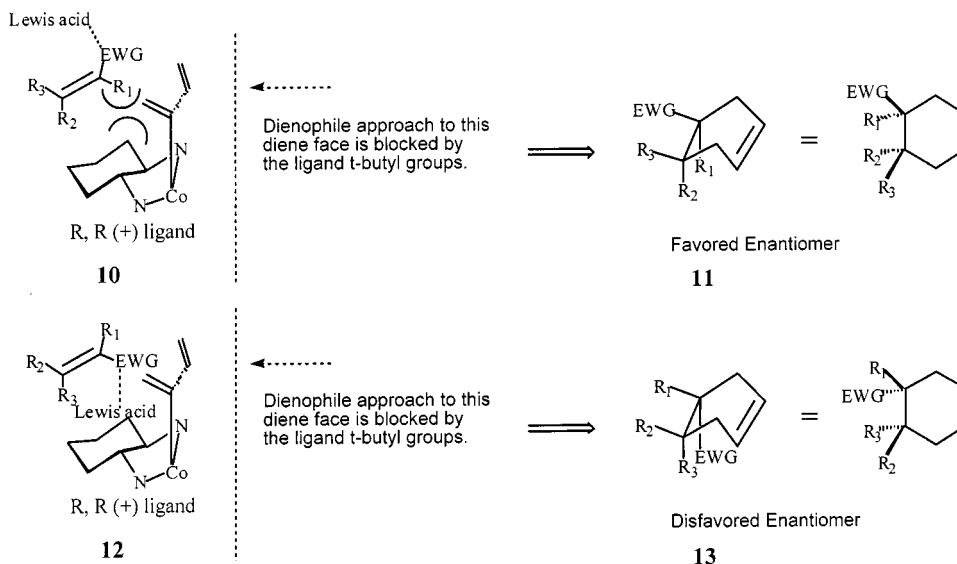
Model for the Rationalization and the Prediction of the Regioselectivity and Enantioselectivity of Cycloaddition

To develop a model to understand and to predict the [4 + 2] cycloaddition reactions, we have made several assumptions based on our past experience with related (dienyl)(*salen*)Co and (dienyl)cobaloxime complex Diels–Alder chemistry. The protons in the CH_2 group of C-1 of the 1,3-dienyl unit in **4** absorb at $\delta = 3.27$ and 3.00 (CDCl_3). This large upfield shift of the alkene protons is similar to what we had noted previously for achiral (*salen*)Co complexes and (glyoxime)cobalt complexes.^[2,14] Therefore, we will assume the low-valent Co in **4a** and **4b** to be a strong “*para*”-directing group for the prediction of the regiochemical outcomes of the dienyl complex Diels–Alder reactions. Similarly, in (*salen*)Co and cobaloxime chemistry, we have seen that dienophiles react with metal-substituted dienes preferentially via *exo* transition states, therefore, we have assumed that the Lewis acid complexed carbonyl group of the dienophile will be oriented away from the metal substituent on the dienes. Lastly, we have developed a model for these reactions, and this uses the conformer of the diene (**4a**, conformer 2) which is predicted to be the lowest energy conformer present. We will assume that dienophiles approach



	R ₁	R ₂	R ₃	EWG
7	CH ₃	H	H	CO ₂ Me
8	CH ₃	H	H	CHO
9	CH ₃	H	-C(O)O-EWG	C(O)

Scheme 5



Scheme 6

this conformer from the diene face which is not blocked by the *tert*-butyl groups in the ligand.

Given these constraints, which seemed reasonable from our experience with related Diels–Alder chemistry^[2,14] and Jacobsen's experience with this ligand,^[10,12] we wanted to be able to rationalize the enantioselective outcome for a variety of dienophiles. We will only use the (*R,R*)-(+)-enantiomer of the ligand in the dienyl complex **4a**; however, similar arguments could be made for **4b**. Recall (Table 1, Entry 12) that the (*R,R*)-(+)-dienyl complex **4a** led to the (*S,S*)-(+)-cycloadduct **6a** using AlCl₃ as the Lewis acid at low temperature. Our model for understanding this reaction would place the Lewis acid complexed electron-withdrawing group (EWG) “*para*” to the Co and *exo* to the ligand (Scheme 6; **10**). This dienophile approach to the diene face closest to the cyclohexanediamine portion of the ligand forces the R₁ substituent on the dienophile to interact with the indicated CH₂ of the cyclohexane. Reaction from the other dienophile face would suffer from steric problems if the *endo* EWG with the correct regiochemical orientation was complexed to the Lewis acid (**12**).

This model also correctly rationalizes that the (*R,R*)-(+)-ligand dienyl complex **4a** will favor the formation of (*R*) cycloadduct stereocenters (**7a**) from dienophiles that contain a methyl substituent on the alkene α to the electron-withdrawing group (EWG) and R₁ = Me; R₂ = R₃ = H (Table 2, Entry 1) and (*S*) stereocenters when R₁ = Me and R₃ = –OC(O)– (Table 2, Entry 4). Likewise, the (*S,S*)-(–)-ligand in dienyl complex **4b** favors the formation of (*S*) cycloadduct stereocenters at the methyl-substituted carbon atom from dienophiles that contain a methyl substituent on the alkene α to the electron-withdrawing group (EWG) and R₁ = Me; R₂ = R₃ = H (Table 2, Entries 2, 3) and (*R*) stereocenters when R₁ = Me and R₃ = –OC(O)– (Table 2, Entry 5).

Conclusions

In summary, we report the synthesis and X-ray crystallographic characterization of the first chiral transition metal substituted 1,3-dienes with σ bonds from the transition metal to the dienyl fragment. The dienyl complexes react with a variety of dienophiles to produce (salen)Co-substituted cycloadducts, one of which has been characterized by X-ray crystallography. The (salen)Co can then be removed from the optically active cyclohexene cycloadducts and recovered in high enantiomeric purity. A model for the rationalization and the prediction of the absolute stereochemistries of cyclohexenyl cycloadducts has also been developed.

Experimental Section

General: NMR spectra were obtained with a Bruker AVANCE 300 FT NMR or a Varian Gemini-300 Broad Band FT NMR. All absorptions are expressed in ppm using TMS as the reference. – IR spectra were obtained using a Perkin–Elmer 1620 FTIR or an OMINA FTIR. – Elemental analyses were performed by Atlantic

MicroLab Inc. of Norcross, Georgia. – Melting Points were obtained with a Mel Temp apparatus and are reported uncorrected. – Alumina (80–200 mesh) was purchased from Fisher Scientific and deactivated with a 90:10 by volume acetone/water mixture. Flash silica gel was purchased from Universal Scientific Inc. Cobalt acetate and but-2-yne-1,4-diol were obtained from Aldrich Chemical Company and used as purchased. (*R,R*)-(–)- and (*S,S*)-(+)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (**1a** and **1b**) were prepared according to a literature method^[10a] with the exception of the use of a slightly modified method for obtaining the diamines reported below. Authentic samples of racemic *trans*-1,2-dimethoxycarbonylcyclohex-4-ene (**6a** and **6b**) were prepared according to a literature procedure^[20] as was 4-methoxycarbonyl-4-methylcyclohex-1-ene (**7a** and **7b**)^[18] and *cis*-1-methyl-1,2,3,6-tetrahydrophthalic anhydride (**9a** and **9b**).^[19] The enantiomers were separated and *ee* values determined using a 30-m trifluoroacetyl- γ -cyclodextrin column (Advanced Separation Technologies) with helium carrier gas with a split-ratio of 1:50.

Buta-1,2-dien-4-ol: A previously reported procedure^[21] was modified to improve product recovery. A 1-L round-bottomed flask was charged with diethyl ether (400 mL) and 4-chlorobut-2-yn-1-ol (20.9 g, 199.9 mmol). An addition funnel for solids was charged with lithium aluminum hydride (8.0 g, 210.8 mmol) which was added slowly. Then a portion of iced water (8 mL) was carefully added, followed by aqueous sodium hydroxide solution (8 mL, 15% solution) and finally additional iced water (24 mL). The white aluminum salts were removed by suction filtration. The product was distilled at 46–47 °C and 18 Torr to give colorless buta-1,2-dien-4-ol (10.1 g, 144.3 mmol, 72%). The allene was determined to be one component (98+%) by GC.

4-(*p*-Tolylsulfonyl)buta-1,2-diene (3): A previously reported procedure^[14a] was modified to improve the consistency of preparation and enhance the yield. A portion of buta-1,2-dien-4-ol (6.8 g, 97.0 mmol) was dissolved in dry THF (200 mL) instead of ether. Crushed potassium hydroxide (24.2 g, 431.4 mmol) was added in one portion at 0 °C; after which, *p*-toluenesulfonyl chloride (19.1 g, 100.2 mmol) was added. The product (17.2 g, 76.8 mmol, 79%) was isolated and stored as described previously.

(*R,R*)-(+)- and (*S,S*)-(–)-Cyclohexane-1,2-diammonium Monotartrate from *cis/trans*-Cyclohexane-1,2-diamine: This procedure is a modification of earlier methods^[10a] and allows the isolation of monotartrate salts of the (*R,R*)- and (*S,S*)-diamines from a single batch of the *cis/trans* mixture. A 3-L three-necked round-bottomed flask was equipped with a mechanical stirrer, a reflux condenser, and a constant-pressure addition funnel. A mixture of 60% *trans*- and 40% *cis*-cyclohexane-1,2-diamine (Aldrich) (152.7 g, 1337.0 mmol) was dissolved in absolute ethanol (1.0 L) and heated to a gentle reflux. Hot absolute ethanol (460 mL) with L-(+)-tartaric acid (60.2 g, 401.0 mmol) was added to the refluxing solution of diamine over 5 min. A white precipitate formed immediately but remained slightly emulsified. The reaction mixture was refluxed for 1 h and allowed to cool to 25 °C. The mixture was cooled with an ice/water bath to 0 °C, diluted with an acetone/water mixture (95:5, 200 mL), then allowed to stand for 2 h. White crystals were recovered by suction filtration. The product was washed with an acetone/water mixture (95:5, 100 mL) and dried at 45 °C/0.1 Torr to constant weight. A quantitative yield of (*R,R*)-(+)-cyclohexane-1,2-diammonium monotartrate (106.0 g, 401.0 mmol) was obtained. The filtrate from the above reaction was then concentrated at 25 °C (11 Torr) and the product mixture was dispersed in water (100 mL) and cooled to 0 °C. Aqueous sodium hydroxide (50%, 80 mL) was added over 10 min. Dichloromethane (225 mL) was ad-

ded and the mixture stirred for 20 min. The phases were separated and the aqueous phase extracted with dichloromethane (60 mL). The organic phases were combined, washed with saturated aqueous brine (50 mL), and concentrated in a rotary evaporator. The concentrated CH_2Cl_2 extracts were dissolved in absolute ethanol (800 mL), heated to a gentle reflux, and treated with D-(–)-tartaric acid (60.2 g, 401.0 mmol) in hot ethanol (460 mL). Following a procedure analogous to the one outlined above for the (*R,R*) enantiomer, (*S,S*)-(–)-cyclohexane-1,2-diammonium monotartrate (98.6 g, 373.0 mmol, 93%) was obtained.

(*R,R*)-(–)-Cobalt(II) Complex 2a: A 2-L three-necked round-bottomed flask was equipped with a mechanical stirrer and a reflux condenser. Under nitrogen, (*R,R*)-(–)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (**1a**) (31.0 g, 56.7 mmol) was dissolved in methanol (250 mL). Cobalt acetate tetrahydrate (14.2 g, 57.0 mmol) was dispersed in methanol (250 mL) and heated to 65 °C and the mixture was purged with nitrogen. The cobalt acetate dispersion was added to the yellow ligand solution over 2–3 min, with thorough mixing. The reaction mixture was heated at a gentle reflux for 1 h, cooled to room temperature, and the crystallized product collected by suction filtration. The red-orange crystals were washed with ice-cold methanol (25 mL, 2 ×). Red-orange crystals (33.8 g, 56.1 mmol, 99%) were collected and dried under high vacuum. – $[\alpha]_{\text{D}}^{20} = -1145.1$ ($c = 0.0324$, CHCl_3). – M.p. > 290 °C. – $\text{C}_{36}\text{H}_{52}\text{CoN}_2\text{O}_2$ (603.761): calcd. C 71.62, H 8.68; found C 71.48, H 8.55. – IR and MS data have been reported previously.^[13]

(*S,S*)-(+)-Cobalt(II) Complex 2b: The reaction described above was repeated with (*S,S*)-(+)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine **1b**, and **2b** (33.2 g, 55.1 mmol, 97%) was isolated. – $[\alpha]_{\text{D}}^{20} = +1147.3$ ($c = 0.0319$, CHCl_3). – Other physical constants and spectra are identical to those reported for **2a** above.

(*R,R*)-(+)-(Buta-1,3-dien-2-yl)cobalt(III) Complex 4a: Complex **2a** (5.4 g, 8.9 mmol) was dispersed in dry, freshly distilled, degassed THF (200 mL) under argon. Sodium amalgam (40% Na, 4.0 g, 69.6 mmol) was added in one portion and the dispersion stirred at 25 °C for 40 min. The resulting solution of dark green cobalt(I) anion was transferred into a second flame-dried air-free flask (previously cooled to –78 °C) by a cannula. 4-Tosylbuta-1,2-diene (**3**) (5.4 g, 24.1 mmol) in freshly distilled THF (10 mL) was added over 5 min, and the mixture was stirred at –78 °C for 2 h, allowed to warm to 25 °C, and stirred for an additional 18 h. The reaction mixture was vacuum-filtered through a coarse fritted funnel into degassed ice-cold aqueous sodium hydroxide solution (500 mL, 0.25 N) and stirred for 2 h. The dark green product was collected by vacuum filtration. The product was washed with cold water until the washings were neutral, allowed to air-dry in the fritted funnel, and washed with low boiling petroleum ether (25 mL, 5 ×) until the washings were clear. The product was dried to give **4a** (5.32 g, 7.88 mmol, 88.1%). – M.p. > 290 °C, turned orange-red between 210–215 °C. – $[\alpha]_{\text{D}}^{20} = +3333.3$ ($c = 0.0105$, CHCl_3). – ^1H NMR (CDCl_3): $\delta = 7.97$ (s, 1 H), 7.91 (s, 1 H), 7.38 (apparent t, $J = 2.9$ Hz, 2 H), 7.00 (d, $J = 2.8$ Hz, 1 H), 6.95 (d, $J = 2.4$ Hz, 1 H), 5.77 (dd, $J = 17.1$ Hz, 10.5 Hz, 1 H), 5.14 (dd, $J = 17.1$, 2.9 Hz, 1 H), 4.44 (dd, $J = 10.5$, 2.9 Hz, 1 H), 3.47 (m, 1 H), 3.21 (d, $J = 3.0$ Hz, 1 H), 3.13 (m, 1 H), 3.05 (d, $J = 3.0$ Hz, 1 H), 2.78 (m, 1 H), 2.66 (m, 1 H), 2.03 (m, 2 H), 1.75–1.40 (m, 4 H), 1.53 (s, 9 H), 1.49 (s, 9 H), 1.29 (s, 18 H). – ^{13}C NMR (CDCl_3): $\delta = 163.81$, 163.12, 161.73, 160.15, 143.62, 142.72, 142.28, 136.50, 136.13, 128.73, 128.51, 127.20, 126.75, 119.54, 118.86, 115.34, 108.14, 72.57, 69.44, 36.08, 34.01, 31.43, 30.00, 29.76, 29.62, 29.54, 29.47, 29.32, 29.21, 24.87, 24.62. – IR (CDCl_3): $\tilde{\nu} = 2960.7$, 2869.6,

1609.1, 1560.2, 1530.9, 1428.2, 1255.2, 1172.7, 833.9 cm^{-1} . – $\text{C}_{40}\text{H}_{57}\text{CoN}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (674.82): calcd. C 71.19, H 8.81; found C 71.61, H 8.65.

(*S,S*)-(–)-(Buta-1,3-dien-2-yl)cobalt(III) Complex 4b: Complex **4b** was prepared (using **2b**) on a 3-g scale in a manner analogous to that reported for **4a** above to give **4b** (2.96 to 3.15 g, 88.3 to 94.0%). – $[\alpha]_{\text{D}}^{20} = -3325.0$ ($c = 0.0120$, CHCl_3). – All other physical data and spectra are identical to those reported for **4a** above.

(*R,R*)-Cobalt(III) Complex 5a (Thermal Cycloaddition): Under argon, THF (3 mL), a crystal of hydroquinone, dimethyl fumarate (0.032 g, 0.222 mmol), and **4a** (0.10 g, 0.15 mmol) were added to a 5-mL thick-walled reaction vial. The mixture was purged with argon for 3–5 min, and the vial was tightly closed. The mixture was heated with stirring at 50 °C for 18 h. The solvent was then removed at 25 °C/20 Torr. Excess dimethyl fumarate was then removed from the product by heating the dark green solid to 60 °C/0.5 Torr for 3 h. Dark green cycloadduct (0.116 g, 0.142 mmol, 96%) was obtained. – M.p. > 290 °C. – $[\alpha]_{\text{D}}^{20} = +3876.9$ ($c = 0.0130$, CHCl_3). – ^1H NMR (CDCl_3): $\delta = 8.01$ (s, 1 H), 7.92 (s, 1 H), 7.37 (m, 2 H), 7.01 (m, 1 H), 6.93 (m, 1 H), 3.59 (s, 3 H), 3.44 (s, 3 H), 3.42 (m, 1 H), 3.20 (m, 1 H), 2.93–2.71 (m, 3 H), 2.39 (m, 2 H), 2.03 (m, 2 H), 1.70–1.20 (m, 8 H), 1.55 (s, 9 H), 1.49 (s, 9 H), 1.30 (s, 18 H). – ^{13}C NMR (CDCl_3): $\delta = 175.32$, 174.72, 163.69, 163.09, 161.66, 160.45, 142.69, 136.19, 128.72, 127.20, 126.20, 126.56, 123.92, 119.66, 118.58, 72.65, 72.52, 70.00, 69.67, 51.74, 51.48, 43.47, 43.06, 42.33, 37.03, 36.02, 35.16, 34.53, 34.04, 31.39, 31.15, 30.05, 29.86, 29.54, 29.47, 29.28, 28.98, 24.84, 24.59. – $\text{C}_{46}\text{H}_{65}\text{CoN}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (818.95): calcd. C 67.46, H 8.25; found C 66.29, H 7.93. – FAB HRMS: m/z calcd. for $\text{CoC}_{46}\text{H}_{65}\text{N}_2\text{O}_7$: 800.4175; found 800.4171.

(*S,S*)-Cobalt(III) Complex 5b: The reaction was performed and the mixture worked up as described above using dienyl complex **4b** to give yields ranging between 0.106–0.1171 g (88–96%) of **5b**. – $[\alpha]_{\text{D}}^{20} = -3880.0$ ($c = 0.0125$, CHCl_3). – The other physical and spectroscopic data obtained are identical to those reported for **5a** above. – FAB HRMS: m/z calcd. for $\text{C}_{46}\text{H}_{65}\text{CoN}_2\text{O}_7$: 800.4175; found 800.4136.

(*S,S*)-Cobalt(III) Complex 5b (Lewis Acid Catalyzed Cycloaddition and in situ Demetallation with NaBH_4): Under argon, CH_2Cl_2 (10 mL), a crystal of hydroquinone, aluminum chloride (0.030 g, 0.225 mmol), and dimethyl fumarate (0.032 g, 0.222 mmol) were dispersed in a dry one-necked bantum flask and stirred until a solution was obtained. **4b** (0.10 g, 0.15 mmol) was added in one portion. The reactants were stirred and the mixture was warmed from 0 to 25 °C over 20 min and then stirred at 25 °C for an additional 20 min. Then the solvent was removed at 25 °C/20 Torr. The crude product mixture (0.12 g, 100%) was used in the next step described below without further purification.

Dimethyl (*R,R*)-(–)-*trans*-1,2-Cyclohex-4-ene-1,2-dicarboxylate (6b): Ethanol (10 mL) and sodium borohydride pellets (0.060 g, 1.59 mmol) were added and the mixture purged well with argon. The dispersion was then stirred at 25 °C for 4 h. The solvent ethanol was removed with the aid of a rotary evaporator and the solid residue triturated with low-boiling petroleum ether (5 mL). The red-brown (*salen*)Co^{II} residue that remained in the flask was saved for characterization. The low-boiling petroleum ether solubles were passed through a mini column (5 mm diameter × 30 mm long) with a small plug of cotton, a 10 mm thick layer of Celite-545, and a 10 mm thick layer of carbon black. The eluent was allowed to concentrate to give **6b** (23.0 mg, 0.116 mmol, 79%). The product was dissolved in diethyl ether (0.5 mL). A 0.25- μL portion was passed

through a 30-m trifluoroacetyl- γ -cyclodextrin column at 135 °C with a helium carrier gas with a split-ratio of 1:50. The enantiomers (*R,R*)-(-)-**6b** and (*S,S*)-(+)-**6a** eluted after ca. 9.0 and 9.2 min, respectively. The GC enantiomer ratio of **6a/6b** was 12:88 or 76% *ee* and the specific rotation was $[\alpha]_D^{25} = -121.60$ ($c = 0.81$, CHCl_3) {ref.^[16] dimethyl (*R,R*)-(-)-*trans*-cyclohex-4-ene-1,2-dicarboxylate: $[\alpha]_D^{25} = -145.3 \pm 0.8$ ($c = 5.9$, CHCl_3); this literature rotation was probably of optically impure material since extrapolation of our 76% GC *ee* sample predicts a rotation of 160.0 for optically pure material; the literature rotation is of a sample that was subjected to a conc. HCl workup and this may have epimerized some of the sample.} The brown-red (salen)Co^{II} residue from the previous step, which was not soluble in petroleum ether, was added to aqueous saturated sodium carbonate solution and stirred for 15 min. The product mixture was extracted with CH_2Cl_2 (25 mL, 2 $\times$). After drying with MgSO_4 , the solution was filtered, concentrated in the rotary evaporator and dried, and the product **2b** (84.6 mg, 0.140 mmol, 94.6%) was recovered. – $[\alpha]_D^{25} = +1143.6$ ($c = 0.0188$, CHCl_3). – This reaction was carried out in a manner identical to that described above except for holding the cycloaddition step at –20 °C for 18 h prior to cycloadduct cleavage, and compound **6b** was obtained (15.9 mg, 0.08 mmol, 54%). – $[\alpha]_D^{25} = -157.9$ ($c = 0.012$, CHCl_3). – The red (salen)Co complex **2b** was also recovered as described above (85.1 mg, 0.141 mmol, 95%). – $[\alpha]_D^{25} = +1136.8$ ($c = 0.010$, CHCl_3).

Dimethyl (*S,S*)-(+)-*trans*-Cyclohex-4-ene-1,2-dicarboxylate (6a**):** The reaction was carried out starting from **4a** at 0 °C and the mixture worked up as described above to give **6a** as the major enantiomer (25.8 mg, 0.126 mmol, 89%, 78% *ee*). – This reaction was performed in a manner identical to that described above for **6b** except for holding the cycloaddition step at –20 °C for 18 h prior to cycloadduct cleavage to yield **6a** (16.2 mg, 0.09 mmol, 55%). – $[\alpha]_D^{25} = +160.2$ ($c = 0.010$, CHCl_3). – To test the *ee* detection limits of our GC system we added authentic racemic **6a/6b** back to this sample in order to obtain a 98:2 ratio of **6a/6b** and at this level **6b** could clearly be detected by GC. Our claim of *ee* values > 96% is a conservative estimate based on this experiment.

Methyl (*S*)-(+)-4-Methylcyclohex-1-ene-4-carboxylate (7b**) via (*S,S*)-Cobalt(III) Complex **4b**:** Under argon, CH_2Cl_2 (10 mL), a crystal of dihydroquinone, aluminum chloride (0.038 g, 0.285 mmol), and methyl methacrylate (0.029 g, 0.289 mmol) were dispersed in a dry one-necked bantum flask and stirred until a solution was obtained. The temperature of the flask contents was lowered to –20 °C and **4b** (0.100 g, 0.148 mmol) was added in one portion. The temperature of the cycloaddition step was held at –20 °C for 18 h then allowed to warm to 25 °C. The solvent was removed under reduced pressure and the residue triturated with low-boiling petroleum ether (4 $\times$ 10 mL). The petroleum ether extracts were dried with MgSO_4 and NaHCO_3 then the solvent was removed under reduced pressure and high vacuum to yield **7b** (15.3 mg, 0.099 mmol, 67%). – $[\alpha]_D^{25} = +63.3$ ($c = 0.014$, CHCl_3). – The (*S*)-(+)-cycloadduct was present at > 96% *ee*. The absolute configuration of this (+) enantiomer (**7b**) was assigned as (*S*) by comparison with literature rotation data^[18] of (1*R*)-1,3,4-trimethylcyclohex-3-ene-1-carbaldehyde (prepared from reaction of 2,3-dimethylbuta-1,3-diene with methacrolein) where the (–) cycloadduct has (*R*) configuration: $[\alpha]_D^{25} = -64.1$ ($c = 1.0$, CHCl_3).

Methyl (*R*)-(-)-4-Methylcyclohex-3-ene-4-carboxylate (7a**) via (*R,R*)-Cobalt(III) Complex **4a**:** The cycloaddition was carried out at –10 °C for 18 h using methyl methacrylate (29.0 mg, 0.289 mmol) and diene **4a** (0.100 g, 0.148 mmol) as above. After workup as above, **7a** (14.8 mg, 0.096 mmol, 0.099 mmol, 65%) was

obtained. – $[\alpha]_D^{25} = -60.3$ ($c = 0.012$, CHCl_3). – The (*R*)-(-) cycloadduct was present at > 96% *ee*. The absolute configuration of this enantiomer (**7a**) was assigned as (*R*) by comparison with data described above for **7b**.^[18]

(*S*)-(+)-1-Methylcyclohex-3-ene-1-carbaldehyde (8b**) via (*S,S*)-Cobalt(III) Complex **4b**:** The cycloaddition was carried out at –10 °C for 18 h using methacrolein (0.200 g, 2.85 mmol) and diene **4b** (0.230 g, 0.34 mmol) and the mixture worked up as above to give **8b** (29.2 mg, 0.235 mmol, 69%). – $[\alpha]_D^{25} = +57.8$ ($c = 0.16$, CHCl_3). – The (*S*)-(+)-cycloadduct was present at > 96% *ee*. The absolute configuration of this (+) enantiomer (**8b**) was assigned as (*S*) by comparison with literature data as described above for **7**.^[18]

***cis*-(1*S*,2*R*)-(-)-1-Methyl-1,2,3,6-tetrahydrophthalic Anhydride (**9a**) via (*R,R*)-Cobalt(III) Complex **4a**:** The cycloaddition was carried out at –20 °C for 18 h using citraconic anhydride (33.0 mg, 0.294 mmol) and diene **4a** (0.1 g, 0.148 mmol) as above. After workup as above, **9a** (17.2 mg, 0.104 mmol, 70%) was obtained. – $[\alpha]_D^{25} = -19.4$ ($c = 0.155$, CHCl_3). – The *cis*-(1*S*,2*R*)-(-) cycloadduct was present at > 96% *ee*. Paquette et al. previously determined crystallographically that the (–) enantiomer from the reaction of citraconic anhydride with buta-1,3-diene had (1*S*,2*R*) absolute configuration.^[19]

***cis*-(1*R*,2*S*)-(+)-1-Methyl-1,2,3,6-tetrahydrophthalic Anhydride (**9b**) via (*S,S*)-Cobalt(III) Complex **4b**:** The cycloaddition was carried out at –20 °C for 18 h using citraconic anhydride (35.0 mg, 0.312 mmol) and diene **4b** (0.100 g, 0.148 mmol) as above. After workup as before, **9b** (17.5 mg, 0.105 mmol, 71%) was obtained. – $[\alpha]_D^{25} = +21.4$ ($c = 0.17$, CHCl_3). – The *cis*-(1*R*,2*S*)-(+) cycloadduct was present at > 96% *ee*. The absolute stereochemistry of this (+) enantiomer was assigned as (1*R*,2*S*) as described above for **9a**.^[19]

X-ray Crystallography: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-157888 (**5a**) and -157889 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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