Synthesis of Cobalt-Substituted 1,3-Diene Complexes with Unusual Structures and Their Exo-Selective Diels–Alder Reactions

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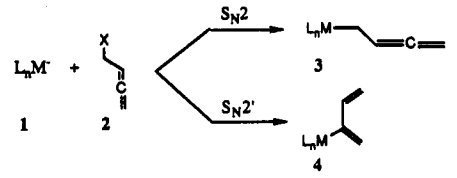
Received March 4, 1994•

Abstract: The synthesis and characterization (including crystallographic data) of several substituted-pyridine (Rpyr) cobalt bis(dimethylglyoxime) 1,3-butadiene complexes (R = H, tBu, 3,5-diMe, and *N,N*-dimethylamino) and their Diels–Alder reactions with a variety of dienophiles are reported here. The cobalt–carbon bonds in the Diels–Alder cycloadducts can be cleaved so that cobalt complexes as well as functionalized organic cycloadducts are recovered. Through these cobalt–carbon bond cleavage reactions, cobalt–diene complexes can serve as synthons for a variety of 1,3-dienes such as 1,3-butadiene, 2-(trimethylsiloxy)-1,3-butadiene, iodoprene, (*E*)-1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Danishefsky's diene), and 1,2-dichloro-1,3-butadiene. The preparation of several cobalt-substituted 1,2- and 1,3-pentadiene complexes and highly exo-selective Diels–Alder reactions of the 1,3-pentadiene complexes are then discussed followed by demetalation reactions of these more highly substituted cobalt cycloadducts. These demetalation reactions maintain the stereochemical integrity found in the metal cycloadducts and also lead to cobalt recovery.

Introduction

Over the last 15 years, several groups (following the pioneering leads of the Rosenblum[1d] and Wojcicki[1c] groups) have been investigating organic applications of cycloaddition reactions between transition-metal complexes containing σ bonds to unsaturated ligands and electrophiles.[1,2] As an outgrowth of our interest in the preparation of metal allyls and propargyls for use in 3 + 2 cycloadditions,[1a] we became interested in preparing transition-metal-substituted η^1-1,2-butadienyl (η^1-allenic) complexes (**3**) and 2-transition-metal substituted 1,3 butadienes (**4**).



Complexes of the general form **3** and **4** should be available via reactions of transition-metal anions (**1**) with 1,2-butadienyl electrophiles (**2**). There are many examples of η^1-propargyl and η^1-allyl complex synthesis through reactions analogous to the S_N2 reaction shown above,[1] and there are some examples of S_N2' attack by transition-metal anions on propargyl and pentadienyl electrophiles.[3] Recently, we communicated how pyr(glyoxime)$_2$-cobalt anions (pyr = pyridine) react with allenic electrophiles to produce cobalt-substituted 1,3-dienes via the S_N2' pathway,[4a] and Tada and Shimizu reported an alternative preparation of these same 1,3-dienes.[5] This transition-metal substitution enhanced the reactivity of 1,3-dienes in cycloaddition reactions.[4a,5] In the present paper, we first report the synthesis and characterization (including crystallographic data) of several cobalt glyoxime 1,3-butadiene complexes and their Diels–Alder reactions with a variety of dienophiles.[6] We next demonstrate how to cleave the cobalt–carbon bonds in the cycloadducts so that cobalt complexes as well as functionalized organic cycloadducts are recovered. The preparation of several cobalt-substituted 1,2- and

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• Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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1,3-pentadiene complexes and highly exo-selective Diels–Alder reactions of the 1,3-pentadiene complexes are then discussed followed by demetalation reactions which maintain the stereochemical integrity found in the metal cycloadducts and also lead to cobalt recovery.

Experimental Section

General Methods. All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR. All absorptions are expressed in parts per million relative to tetramethylsilane. Infrared (IR) spectra were obtained using a Perkin Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc., of Norcross, GA. High-resolution (HR) mass spectral analyses were performed by the Midwest 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 chloride hexahydrate was purchased from Aldrich Chemicals and used as received. 1,2-Butadien-4-ol (**7a**),[7] 4-methyl-2,3-pentadien-1-ol (**11a**),[8] 3,4-pentadien-2-ol (**7b**),[9] 5-methyl-3,4-hexadien-2-ol (**11b**),[8] and dimethyl- and diethyl methylenemalonate[10] were prepared according to literature methods.

Preparation of 4-Chloro-1,2-butadiene (12). Pyridine (8.0 mL, 98.9 mmol) in anhydrous diethyl ether (20 mL) was cooled to 0 °C. Thionyl chloride (7.5 mL, 0.103 mol) was then slowly added. 1,2-Butadien-4-ol[7] (**7a**) (5.83 g, 83.2 mmol) in anhydrous diethyl ether (50 mL) was cooled to 0 °C. The pyridine/thionyl chloride mixture was then added to **7a** at 0 °C, and the resulting mixture was stirred for 10 min and then refluxed for 2 h. After the reaction mixture was cooled to 25 °C, water (50 mL) was added and the mixture was extracted with diethyl ether (5 × 25 mL). The combined organic layers were dried ($MgSO_4$), and the ether was distilled off at 1 atm, followed by **12** (3.38 g, 38.3 mmol (46%)) (Bp: 86-90 °C) (lit.[11] 86–88 °C). ^1H NMR ($CDCl_3$): 5.34 (pentet, J = 7.3 Hz, 1H), 4.89 (dt, J = 7.3, 2.3 Hz, 2H), 4.06 (dt, J = 7.3, 2.3 Hz, 2H).[11b]

Preparation of 4-(*p*-Tolylsulfonyl)-1,2-butadiene (13). In an adaptation of a literature procedure,[12] 1,2-butadien-4-ol (**7a**) (8.935 g, 0.128mol) and *p*-toluenesulfonyl chloride (25.120 g, 0.132 mol) in anhydrous diethyl ether (250 mL) were cooled to −14 °C. Crushed potassium hydroxide (40.50 g, 0.772 mol) was added in 5-g portions over 30 min, and the resulting mixture was stirred for an additional 45 min. Ice/water (240 mL) was added, and the resulting mixture was extracted with diethyl ether (4 × 50 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was triturated with petroleum ether (80 mL) and cooled to −78 °C to cause solidification of **13**. The waxy, white solid was vacuum-dried to yield 4-(*p*-tolylsulfonyl)-1,2-butadiene (**13**) (23.0 g, 0.103 mol (80%)). Mp: 23–24 °C. ^1H NMR ($CDCl_3$): 7.76 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 5.17 (pentet, J = 7.2, 1H), 4.79 (dt, J = 7.2, 2.2 Hz, 2H), 4.53 (dt, J = 7.2, 2.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$): 209.92, 144.62, 133.04, 129.61, 127.59, 84.96, 79.94, 68.24, 21.45. IR ($CDCl_3$): 3068, 3050, 2958, 2927, 1956, 1599, 1495, 1456, 1354, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.63; H, 5.40.

Preparation of 5-(*p*-Tolylsulfonyl)-2-methyl-2,3-pentadiene (14). A procedure and workup analogous to the one reported above for **13** were performed using 4-methyl-2,3-pentadien-1-ol (**11a**)[8] (3.21g, 32.8 mmol) in diethyl ether (100 mL), *p*-toluenesulfonyl chloride (6.12 g, 32.1 mmol), and KOH (16.4 g, 292 mmol) to yield waxy, white crystals (which melt below 25 °C), which were vaccum-dried and stored under nitrogen (**14**); 5.58 g, 22.1 mmol (68%)). ^1H NMR ($CDCl_3$): 7.79 (d, J =7.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 5.0 (m, 1H), 4.49 (m, 2H), 2.42 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H). IR ($CDCl_3$): 3067, 3049, 2986, 2944, 1971, 1794, 1648, 1599, 1495, 1452 cm^{-1}. FAB HRMS calcd for $C_{13}H_{16}O_3S$ 252.0820, found 252.0831.

Synthesis of 2-Acetoxy-3,4-pentadiene (15). 3,4-Pentadien-2-ol (**7b**)[9] (4.50 g, 53.7 mmol) was dissolved in dry THF (60 mL), and the solution was cooled to −45 °C. MeLi (46.5 mL of a 1.4 M solution, 65.1 mmol) was added slowly, and the solution was stirred for 2 h. Acetic anhydride (7.08 mL, 75 mmol) was added at a rate of about 2 drops/s. The reaction mixture was allowed to warm to 25 °C and was stirred for 2 h. Saturated $NaHCO_3$ (90 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extracts were dried ($MgSO_4$), and the solvent was removed by rotary evaporation (bath set at 27 °C), yielding **15** (6.270 g, 49.7 mmol (93%)) of sufficient purity for further reactions. If desired the acetate (**15**) can be isolated analytically pure in 50–70% yield after vacuum distillation. Bp: 49–53 °C/25 mmHg. ^1H NMR ($CDCl_3$): 5.47–5.30 (m, 1H, MeC(*H*)OAc), 5.29 (apparent q, J = 6.8 Hz, 1H, =C=C(*H*)(MeCHOAc)), 4.90–4.85 (m, 2H), 2.05 (s, 3H), 1.35 (d, J = 6.8 Hz, 3H). IR (neat): 3065, 2985, 2935, 1958, 1739, 1653, 1558cm^{-1}. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.36; H, 8.08.

Synthesis of 2-(Trimethylacetoxy)-3,4-pentadiene (16). A procedure and workup analogous to the one reported above for **15** were performed using 3,4-pentadien-2-ol (**7b**)[9] (4.00 g, 47.6 mmol) in dry THF (40 mL), MeLi (40.8 mL of a 1.4 M solution, 57.1 mmol), and trimethylacetic anhydride (12.40 mL, 66.6 mmol) to yield **16** (6.010 g, 33.7 mmol (75%)) after vacuum distillation. Bp: 60–65 °C/25 mmHg. ^1H NMR ($CDCl_3$): 5.32 (m, 1H), 5.23 (apparent q, J = 7.9 Hz, 1H), 4.83 (m, 2H), 1.29 (d, J = 7.2 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR ($CDCl_3$): 207.59, 177.15, 91.92, 77.21, 67.16, 38.39, 26.88, 19.38. IR (neat): 2979, 2935, 1959, 1728, 1484 cm^{-1}. HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1151.

Synthesis of 2-Acetoxy-5-methyl-3,4-hexadiene (17). A procedure and workup analogous to the one reported above for **15** were performed using 5-methyl-3,4-hexadien-2-ol (**11b**)[9] (2.00 g, 17.9 mmol) in dry THF (40 mL), MeLi (15.3 mL of a 1.4 M solution in ether, 21.4 mmol), and acetic anhydride (2.37 mL, 25.1 mmol) to yield **17** (2.50 g, 16.2 mmol (91%)) of sufficient purity for further reactions. If desired the acetate (**17**) can be isolated analytically pure in 50–70% yield after vacuum distillation. Bp: 108–110 °C/25 mmHg (Lit.[13] 62-64 °C/20 mmHg). IR and ^1H NMR data for this acetate were identical to those reported.[13]

1,3-Butadiene-2-ylpyridinebis(dimethylglyoximato)cobalt(III) (19). In an adaptation of a literature procedure,[14] cobalt(II) chloride hexahydrate (3.56 g, 15 mmol) and dimethylglyoxime (3.44 g, 30 mmol) were dissolved in degassed methanol (40 mL). The rapidly stirred mixture was degassed for the duration of all subsequent additions of reagents. Sodium hydroxide (1.24 g, 30 mmol) dissolved in water (1 mL) and pyridine (1.24 mL, 15 mmol) were added slowly over 10 min. The mixture was allowed to stir for 20 min at 25 °C and then was cooled to −10 °C. Sodium hydroxide (0.64 g, 15 mmol) dissolved in water (1 mL) was then added very slowly. Sodium borohydride (0.132 g, 4.0 mmol) dissolved in water (1 mL) was added over 5 min to avoid heating the mixture. 4-(*p*-Toluylsulfonyl)-1,2-butadiene (**13**); 3.40 g, 15 mmol) was added rapidly, and the mixture was allowed to warm to 25 °C slowly overnight. The reaction volume was reduced to $^1/_4$th its original volume by rotary evaporation, then the reaction mixture was poured into ice/water (60 mL) containing about 1 mL of pyridine, and the precipitate was collected and vacuum-dried to yield an orange-yellow solid (**19**; 4.69 g, 11.1 mmol (75%)). (The amounts used in this procedure can be doubled, but the isolated yields of **19** drop off slightly to 50–60%.) Mp: decomposes at 180 °C. ^1H NMR ($CDCl_3$): 8.60 (d, J = 6.7 Hz, 2H), 7.70 (apparent t, J = 6.7 Hz, 1H), 7.30 (apparent t, J = 6.7 Hz, 2H), 6.44 (dd, J = 16.7, 10.4 Hz, 1H), 4.80 (dd, J = 16.7, 3.2 Hz, 1H), 4.57 (dd, J = 10.4, 3.2 Hz, 1H), 4.51 (s, 1H), 4.42 (s, 1H), 2.09 (s, 12H). ^{13}C NMR ($CDCl_3$): 149.77, 149.71, 145.27, 137.52, 125.05, 114.01, 108.03, 12.17. Several times we noted in ^{13}C data of diene complexes that the carbon ortho to the nitrogen in the complexed pyridine and the carbon of the glyoxime have overlapping resonances. IR ($CDCl_3$) 3155, 3080, 2989, 2926, 1606, 1562, 1450, 1235, 1090 cm^{-1}. Anal. Calcd for $C_{17}H_{24}CoN_5O_4$: C, 48.46; H, 5.74; N, 16.62. Found: C, 48.56; H, 5.74; N, 16.70.

Complex **19** was also synthesized from 4-chloro-1,2-butadiene (**12**) using the following procedure: cobalt(III) chloride hexahydrate (1.35 g, 5.65 mmol) and dimethylglyoxime (1.31 g, 11.3 mmol) in methanol (25 mL) were cooled to 0 °C and stirred for 20 min. Pyridine (0.460 mL,

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5.69 mmol) was degassed with nitrogen and added. Sodium hydroxide (0.481 g, 12.0 mmol) in water (1 mL) was then added. Compound **12** (0.504 g, 5.70 mmol) was added and the reaction mixture was warmed to 25 °C and stirred for 5 min. The reaction mixture was then poured into ice/water (50 mL) containing pyridine (10 drops). The solid that precipitated out was filtered, washed with water, and vacuum-dried to give **19** (0.793 g, 1.88 mmol (33%)), identical to **19** isolated above by spectroscopic comparison.

1,3-Butadien-2-yl(4-*tert*-Butylpyridine)bis(dimethylglyoximato)cobalt-(III) (20). This complex was prepared on the same scale as that for the pyr complex (**19**) above except 4-*tert*-butylpyridine (2.23 mL, 15 mmol) was used instead of pyridine to yield a yellow solid (**20**) which was then recrystallized from methanol (4.15 g, 8.70 mmol (58%)). Mp: decomposed at 176 °C. ^{1}H NMR ($CDCl_3$): 8.45 (d, J = 7.7 Hz, 2H), 7.25 (t, J = 3.9 Hz, 2H), 6.49 (dd, J = 15.4 , 11.6 Hz, 1H), 4.80 (dd, J = 15.4, 3.9 Hz, 1H), 4.58 (dd, J = 11.6, 3.9 Hz, 1H), 4.53 (s, 1H), 4.45 (s, 1H), 2.11 (s, 12H), 1.25 (s, 9H). ^{13}C NMR ($CDCl_3$): 161.72, 149.62, 149.25, 145.45, 122.28, 113.98, 107.97, 34.77, 30.15, 12.25. IR ($CDCl_3$): 2970, 2871, 1782, 1618, 1564, 1235 cm^{-1}. Anal. Calcd for $C_{21}H_{32}O_4N_5Co$: C, 52.83; H, 6.76; N, 14.67. Found: C, 52.66; H, 6.78; N, 14.64.

1,3-Butadien-2-yl[(3,5-dimethylpyridine)bis(dimethylglyoximato)cobalt-(III) (21). This complex was prepared on half the scale of the pyr complex (**19**) above, and 3,5-dimethylpyridine (0.856 mL, 7.5 mmol) was used instead of pyridine to yield a yellow solid (**21**; 2.03 g, 4.5 mmol (60%)) Mp: decomposes at 188 °C. ^{1}H NMR ($CDCl_3$): 8.22 (s, 2H), 7.26 (s,1H), 6.45 (dd, J = 16.3, 8.1 Hz, 1H), 4.79 (dd, J = 16.3, 3.3 Hz, 1H), 4.55 (dd, J = 8.1, 3.3 Hz, 1H), 4.50 (s, 1H), 4.41 (s, 1H), 2.24 (s, 6H), 2.09 (s, 12H). ^{13}C NMR ($CDCl_3$): 149.44, 146.99, 145.45, 139.00, 134.17, 113.89, 107.78, 18.48, 12.18. IR ($CDCl_3$): 3155, 3078, 2984, 2902, 1602, 1563, 1472, 1235, 1100 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_4N_5Co$: C, 50.78; H, 6.28. Found: C, 50.72; H, 6.29.

1,3-Butadien-2-yl-(4-(dimethylamino)pyridine)bis(dimethylglyoximato)-cobalt(III) (22). Cobalt–diene complex **19** (0.910 g, 2.07 mmol) was suspended in methanol (10 mL), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.278 g, 2.27 mmol) was added. The solution was refluxed for 3 h under N_2 (during which time it goes homogeneous), and then the solution was cooled to 0 °C for 20 min to precipitate the product as a yellow-orange solid (**22**; 0.881 g, 1.84 mmol (90%)) which was isolated by vacuum filtration. Mp: decomposes at 189 °C. ^{1}H NMR ($CDCl_3$): 8.10 (apparent d, J = 8.1 Hz, 2H), 6.50 (dd, J = 16.6, 10.0 Hz, 1H), 6.41 (apparent d, J = 7.8 Hz, 2H), 4.80 (dd, J = 16.6, 4.3 Hz, 1H), 4.58 (dd, J = 10.0, 4.3Hz, 1H), 4.55 (s, 1H), 4.49 (s, 1H), 2.97 (s, 6H), 2.11 (s, 12H). ^{13}C NMR ($CDCl_3$): 154.09, 149.15, 148.71, 145.83, 113.76, 107.52, 107.37, 38.98, 12.15. IR ($CDCl_3$): 3690, 2995, 2926, 2832, 1616, 1537, 1446, 1233, 1092, 1067 cm^{-1}. Anal. Calcd for $C_{19}H_{29}O_4N_6Co$: C, 49.14; H, 6.29. Found: C, 48.97; H, 6.34%.

X-ray crystallography for 1,3-Butadien-2-yl(4-*tert*-butylpyridine)bis-(dimethylglyoximato)cobalt(III) (20). Crystal, data collection, and refinement parameters are collected in Table 3. An orange-brown crystal of $C_{21}H_{32}CoN_5O_4$ was mounted on a glass fiber with epoxy cement. Unit cell parameters were determined through least squares refinement of the angular settings for 25 reflections ($20° \leq 2\theta \leq 25°$). The systematic absences in the diffractometer data uniquely established the space group as $P2_1/c$. No correction for absorption was required (low μ).

The structure was solved by a Patterson synthesis which located the Co atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses and full matrix least squares refinements. All non-hydrogen atoms, except carbon, were refined anisotropically. All hydrogen atoms were calculated and fixed to ideal isotropic positions (d_{CH} = 0.96 Å, U = 0.08 Å^2). The three methyl groups of the *tert*-butyl group are disordered in two locations with occupancies of 0.65 and 0.35. All software and the sources of the scattering factors are contained in the SHELXTL PLUS[15] (v4.2) program library. Positional parameters are collected in the supplementary material, and selected bond lengths and angles are listed in Table 4. Additional crystallographic data are available as supplementary material.

X-ray crystallography for 1,3-butadien-2-yl(3,5-dimethylpyridine)bis-(dimethylglyoximato)cobalt(III) (21). Crystal, data collection, and refinement parameters are collected in Table 5. An orange-brown crystal of $C_{19}H_{28}CoN_5O_4$ was mounted on a glass fiber with epoxy cement. Unit cell parameters were determined through least squares refinement of the angular settings for 25 reflections ($20° \leq 2\theta \leq 25°$). The systematic absences in the diffractometer data uniquely established the space group as *Pbca*. No correction for absorption was required (low μ).

The structure was solved by direct methods which located the Co atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were calculated and fixed to ideal isotropic positions (d_{CH} = 0.96 Å, U = 0.08 Å^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. The lutidine (3,5-dimethylpyridine) ring was fixed as a regular hexagon. Positional parameters are in the supplementary material, and selected bond distances and angles are listed in Table 6. All software and the sources of the scattering factors are contained in the SHELXTL PLUS[15] (v4.2) program library.

Diels–Alder Adducts of 19 from Symmetrical Dienophiles. A typical procedure for Diels–Alder reactions of **19** follows: 1,3-butadien-2-ylpyridinebis(dimethylglyoximato)cobalt(III) (**19**) (0.200 g, 0.475 mmol) was dissolved in THF (5 mL). Two equivalents of the dienophile were added, and this mixture was refluxed or stirred for the specified amount of time (Table 7, entries 1–7). The solution was cooled to room temperature, and the solvent was removed under reduced pressure. The residue, containing the cycloadducts and excess dienophile, was purified by dissolving the crude material in a minimal amount of methylene chloride (1–2 mL) and slowly adding pentane until a solid precipitated out. This solution was then cooled in an ice bath for 10 min, and the precipitated solid was isolated by vacuum filtration. Alternatively, the cycloadduct could be washed with several 5-mL portions of ether to remove excess dienophile. The solid was then vacuum-dried.

Spectroscopic Data for Diels–Alder Adducts 23–27. (0.205 g, 0.345 mmol (72%)). **23**: Mp: 190 °C dec. ^{1}H NMR ($CDCl_3$): 8.61 (d, J = 6.0 Hz, 2H), 7.70 (apparent t, J = 6.0 Hz, 1H), 7.30 (apparent t, J = 6.0 Hz, 2H), 5.21 (br s, 1H), 4.22 (q, J = 7.6 Hz, 2H), 4.15 (q, J = 8.0 Hz, 2H), 2.97 (m, 4H), 2.10 (s, 12H), 1.30 (t, J = 7.6 Hz, 3H), 1.24 (t, J = 8.0 Hz, 3H). IR ($CDCl_3$): 2984, 2905, 1713, 1665, 1562, 1252, 1235, 1092, 1069 cm^{-1}. Anal. Calcd for $C_{25}H_{34}CoN_5O_8$: C, 50.76; H, 5.79; N, 11.84. Found: C, 50.57; H, 5.69; N, 11.74.

24 (0.194 g, 0.374 mmol (80%)). Mp: 190 °C dec. ^{1}H NMR ($CDCl_3$): 8.58 (d, J = 6.4 Hz, 2H), 7.70 (apparent t, J = 6.4 Hz, 1H), 7.29 (apparent t, J = 6.4 Hz, 2H), 5.66 (m, 1H), 3.17 (m, 2H), 2.88 (d, J = 15.3 Hz, 1H), 2.58 (dd, J = 15.3, 7.8 Hz, 1H), 2.20 (m, 1H), 2.09 (s, 12H), 1.92 (m, 1H). ^{13}C NMR ($CDCl_3$): 174.77, 174.13, 150.73, 150.64, 149.91, 137.74, 127.27, 125.24, 41.27, 30.50, 25.90, 12.43, 12.12. IR ($CDCl_3$): 3082, 2902, 1841, 1775, 1562, 1450, 1380, 1235, 1090 cm^{-1}. Anal. Calcd for $C_{21}H_{26}CoN_5O_7$: C, 48.56; H, 5.05. Found: C, 48.04; H, 4.98.

25 (0.669 g, 1.27 mmol (99%)). Mp: 170 °C dec. ^{1}H NMR (C_6D_6): 8.97 (d, J = 6.8 Hz, 2H), 6.62 (apparent t, J = 6.8 Hz, 1H), 6.45 (apparent t, J = 6.8 Hz, 2H), 6.03 (d, J = 9.0 Hz, 1H), 5.94 (d, J = 9.0 Hz, 1H), 5.81 (m, 1H), 3.01 (ddd, J = 15.2, 5.8, 2.3 Hz, 1H), 2.79 (dd, J = 11.4, 5.8 Hz, 1H), 2.68 (dd, J = 13.3, 7.2, 5.8 Hz, 1H), 2.54 (m, 1H), 2.49 (m, 1H), 2.15 (m, 1H), 1.97 (s, 6H), 1.90 (s, 6H). IR ($CDCl_3$): 3155, 2924, 1687, 1563, 1450, 1379, 1233, 1092 cm^{-1}. ^{13}C NMR ($CDCl_3$): 150.3, 150.2, 150.1, 139.6, 138.5, 137.5, 125.2, 121.4, 116.2, 49.0, 47.4, 30.7, 27.7, 12.2. Anal. Calcd for $C_{23}H_{28}CoN_5O_6$: C, 52.18; H, 5.33; N, 13.23. Found: C, 51.94; H, 5.37; N, 13.10.

26 (0.145 g, 0.250 mmol, from 0.128 g, 0.282 mmol, of **19** (89%)). Mp: 230 °C dec. ^{1}H NMR ($CDCl_3$): 8.65 (d, J = 7.3 Hz, 2H), 7.65 (apparent t, J = 7.3 Hz, 1H), 7.25 (apparent t, J = 7.3 Hz, 2H), 5.12 (m, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 2.65 (m, 2H), 2.51 (m, 1H), 2.42 (m, 1H), 2.31 (m, 1H), 2.17 (m, 1H), 2.10 (s, 12H). ^{13}C NMR ($CDCl_3$): 175.57, 175.34, 165.07, 149.79, 149.70, 149.58, 137.42, 133.15, 124.99, 121.94, 52.15, 51.57, 51.45, 43.73, 41.92, 34.52, 30.11, 12.06. IR ($CDCl_3$): 3156, 2926, 1729, 1562, 1450, 1438, 1380, 1175, 1090 cm^{-1}. HR FAB mass spectra calcd for $C_{23}H_{33}CoN_5O_8$ 566.1653, found 566.1661 (MH^+) (30), 486 (M^+ - pyridine) (100).

27 (0.100 g, 0.177 mmol (34%)). Mp: 200 °C dec. ^{1}H NMR ($CDCl_3$): 8.60 (d, J = 7.3 Hz, 2H), 7.68 (apparent t, J = 7.3 Hz, 1H), 7.27 (apparent t, J = 7.3 Hz, 2H), 5.08 (m, 1H), 3.59 (s, 3H), 3.54 (s, 3H), 2.97 (m, 1H), 2.66 (m, 1H), 2.53 (m, 1H), 2.40 (m, 1H), 2.25 (m, 1H), 2.16 (m, 1H), 2.08 (s, 6H), 2.07 (s, 6H). IR ($CDCl_3$): 2953, 1730, 1565, 1233, 1203 cm^{-1}. Anal. Calcd for $C_{23}H_{32}CoN_5O_8$: C, 48.85; H, 5.70; N, 12.39. Found: C, 48.20; H, 5.74; N, 12.11.

Diels–Alder Reactions of 19 and 20 with Unsymmetrical Dienophiles. Regiochemistry Studies. A representative procedure follows: cobalt substituted butadiene **19** (0.200 g, 0.475 mmol) was dissolved in freshly distilled THF (10 mL). The dienophile (2 equiv if the dienophile had two electron-withdrawing groups and 20 equiv if only one electron-withdrawing group was present) was added, and reaction was refluxed

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for the time specified in Table 7. The solvent was removed by rotary evaporation, and the residue was vacuum-dried to remove excess dienophile. Purification was accomplished by recrystallization from methanol.

Spectroscopic Data for the Major Regioisomers (unless otherwise specified) of Diels–Alder Adducts 28-35. **28** (0.246 g, 0.436 mmol (96%)). Mp: 180 °C dec. ^{1}H NMR (C_6D_6): 9.00 (d, J = 7.7 Hz, 2H), 6.68 (apparent d, J = 6.7 Hz, 1H), 6.44 (t, J = 5.6 Hz, 2H), 5.93 (m, 1H), 3.27 (s, 6H), 3.01 (s, 2H), 2.37 (m, 2H), 2.5 (t, J = 5.6 Hz, 2H), 1.89 (s, 12H). ^{13}C NMR ($CDCl_3$): 171.7, 150.1, 149.8, 137.5, 125.3, 121.4, 60.7, 53.5, 33.1, 30.2, 29.8, 14.0, 12.1. IR ($CDCl_3$): 3036, 3022, 3012, 1729, 1605, 1449 cm^{-1}. Anal. Calcd for $C_{23}H_{32}O_8N_5Co$: C,48.85; H, 5.70; N, 12.39. Found: C, 48.70; H, 5.73; N, 12.33.

29 (1.23 g, 2.07 mmol, from 0.910g, 2.17 mmol, of **19** (96%)). Mp: 198 °C dec. ^{1}H NMR (C_6D_6): 9.00 (d, J = 7.0 Hz, 2H), 6.59 (apparent t, J = 7.0 Hz, 1H), 6.45 (t, J = 7.0 Hz, 2H), 5.90 (m, 1H), 3.91 (q, J = 7.0 Hz, 4H), 3.01 (s, 2H), 2.74 (m, 2H), 2.50 (t, J = 7.0 Hz, 2H), 1.89 (s, 12H), 0.93 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): 171.46, 149.87, 149.64, 137.36, 124.99, 121.14, 60.56, 53.40, 33.07, 30.15, 29.73, 14.00, 12.01. IR ($CDCl_3$): 2984, 2934, 2903, 1793, 1724, 1561, 1250 cm^{-1}. Anal. Calcd for $C_{25}H_{36}O_8N_5Co$: C, 50.59; H, 6.11; N, 11.80. Found: C, 50 .51; H, 6.15; N, 11.73.

30 (0.376 g, 0.579 mmol, from 0.400 g, 0.838 mmol, of **20** (69%)). Mp: 180 °C dec. ^{1}H NMR (C_6D_6): 8.45 (d, J = 7.0 Hz, 2H), 7.21 (d, J = 7.0 Hz, 2H), 5.11 (m, 1H), 4.08 (q, J = 7.0 Hz, 4H), 2.53 (m, 2H), 2.10 (s, 12H), 2.09–1.91 (m, 4H), 1.26 (s, 9H), 1.18 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): C (171.33, 161.40, 149.11, 53.28), CH (149.32, 122.07, 120.84), CH_2 (60.40, 34.60, 32.94, 29.54), CH_3 (30.02, 13.89, 11.90). IR (C_6D_6): 2971, 2939, 1724, 1617, 1564, 1437, 1308, 1233 cm^{-1}. Anal. Calcd for $C_{29}H_{42}N_5O_8Co$: C, 53.78; H, 6.54; N, 10.81. Found: C, 53.56; H, 6.62; N, 10.88.

31 (0.215 g, 0.437 mmol (92%)). Mp: decomposes at 190 °C. ^{1}H NMR (C_6D_6): 8.96 (apparent d, J = 8.5 Hz, 2H), 6.60 (apparent t, J = 8.5 Hz, 1H), 6.43 (apparent t, J = 8.5 Hz, 2H), 5.84 (m, 1H), 2.80 (m, 1H), 2.48 (m, 1H), 2.28 (m, 3H), 1.90 (m, 2H), 1.81 (s, 6H), 1.79 (s, 6H), 1.62 (s, 3H). ^{13}C NMR ($CDCl_3$): 212.36, 149.84, 149.72, 149.51, 137.40, 125.05, 122.30, 48.22, 32.22, 29.85, 27.94, 27.71, 12.18. IR ($CDCl_3$): 3390, 3081, 2927, 1701, 1605, 1562, 1230, 1086 cm^{-1}. Anal. Calcd for $C_{21}H_{30}O_5N_5Co$; C, 51.33; H, 6.15. Found: C, 51.52; H, 6.25.

32 (0.126 g, 0.242 mmol (51%)). Mp: 205 °C dec. ^{1}H NMR (C_6D_6): 8.95 (d, J = 5.3 Hz, 2H), 6.55 (apparent t, J = 6.7 Hz, 1H), 6.42 (t, J = 6.7 Hz, 2H), 5.84 (m, 1H), 3.28 (s, 3H), 2.99–2.88 (d, J = 15.4 Hz, 1H), 2.75–2.60 (m, 2H), 2.20–2.10 (m, 2H), 1.83 (d, J = 2.2 Hz, 12H), 1.80–1.75 (m, 1H) 1.24 (s, 3H), 0.68 (s, 2H, OH's). ^{13}C NMR ($CDCl_3$): 178.22, 149.85, 149.50, 149.43, 137.33, 124.99, 122.11, 51.29, 41.10, 37.17, 33.90, 30.10, 22.35, 12.01. IR (C_6D_6): 3164, 3079, 2932, 1720, 1605, 1561, 1450, 1233 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_6N_5$-Co: C, 50.67; H, 6.19; N, 13.43. Found: C, 50.53; H, 6.14; N, 13.42.

33 (0.177 g, 0.332 mmol (70%)). Mp: 220 °C dec. ^{1}H NMR (C_6D_6): 8.96 (d, J = 7.4 Hz, 2H), 6.65 (apparent t, J = 8.9 Hz, 1H), 6.5 (t, J = 7.4 Hz, 2H), 5.83 (m, 1H), 3.90 (q, J = 7.4 Hz, 2H), 2.99 (d, J = 17.3 Hz, 1H), 2.75–2.60 (m, 2H), 2.30–2.15 (m, 2H), 1.85 (d, J = 2.5 Hz, 12H), 1.80–1.65 (m, 1H), 1.18 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H). IR (C_6D_6): 3080, 2979, 2932, 1716, 1604, 1232 cm^{-1}. HR FAB MS calcd for MH^+ $C_{23}H_{35}O_6N_5Co$ 536.1919, found 536.1923.

34 (0.217 g, 0.428 mmol (90%)). Mp: decomposes at 180 °C. ^{1}H NMR (C_6D_6): 8.97 (d, J = 6.5 Hz, 2H), 6.60 (apparent t, J = 6.5 Hz, 1H), 6.44 (apparent t, J = 6.5 Hz, 2H), 5.89 (m, 1H), 3.25 (s, 3H), 2.83–2.67 (m, 2H), 2.58 (m, 3H), 2.10 (m, 2H), 1.81 (s, 6H), 1.79 (s, 6H). ^{13}C NMR ($CDCl_3$): 177.71, 149.83, 149.47, 149.41, 137.34, 124.98, 122.15, 59.71, 40.92, 37.15, 33.82, 30.08, 22.28, 14.17, 11.99. IR ($CDCl_3$): 3081, 2980, 2952, 1724, 1605, 1562, 1450, 1437, 1376, 1232, 1090 cm^{-1}. HRMS calcd for $C_{21}H_{30}CoN_5O_6$: 507.1521, found 507.1519.

35 (0.191 g, 0.365 mmol (77%)). ^{1}H NMR (C_6D_6): 9.00 (d, J = 6.3 Hz, 2H), 6.72 (apparent t, J = 8.0 Hz, 1H), 6.45 (t, J = 6.3 Hz, 2H), 5.91 (m, 1H), 3.98 (q, J = 8.0 Hz, 2H, minor isomer), 3.90 (q, J = 8.0 Hz, 2H, major isomer), 2.99–2.70 (m, 2H), 2.70-2.30 (m, 3H), 2.20–2.05 (m, 2H), 1.84 (d, J = 2.2 Hz, 12H), 0.97 (t, J = 6.3 Hz, 3H, minor isomer), 0.92 (t, J = 6.3 Hz, 3H, major isomer). ^{13}C NMR ($CDCl_3$): C (176.05, 149.57, 149.34), CH (149.69, 137.33, 124.93, 122.16, 40.16), CH_2 (59.71, 32.00, 30.35, 28.18), CH_3 (14.12, 11.99). IR ($CDCl_3$): 2984, 2931, 1720, 1561, 1449, 1234 cm^{-1}. HR FAB MS calcd for MH^+ $C_{22}H_{33}O_6N_5Co$ 522.1763, found 522.1768.

Kinetic Experiments. General Methods. All kinetic experiments were carried out in THF-d_8 or $CDCl_3$ with a 5–10-fold excess of dienophile present, and rate constants were determined from the first-order decay of DMG or TMS methyl proton signals monitored by ^{1}H NMR correcting the observed integral value if necessary for any changes due to variations in instrument tuning using the integration of the signal from the methyl protons of the internal standard *tert*-butanol. The first order rate constant was determined by one of two methods. For the cobalt–dienes, analysis of the decay of the DMG methyl signals was carried out for several half-lives. Analyses were carried out by graphic means —a linear plot on semilogarithmic paper of methyl peak integrals against time yielded the half time $t_{1/2}$, and the rate constant was obtained from the equation $k_{obs} = 0.693/t_{1/2}$. The second method for determining k_{obs}, used for the slower reacting (trimethylsiloxy)butadiene in THF-d_8, was that of initial rates, monitoring the first 10% of the reaction.

(a) Diethylmethylene malonate (0.0124 g, 0.072 mmol, containing 260 ppm MEHQ (4-methoxyphenol) to inhibit polymerization) and *tert*-BuOH (1 μL, 0.016 mmol) were dissolved in THF-d_8 (800 μL) in an NMR tube. Cobalt–diene (**19**) (0.0053 g, 0.013 mmol) was added to the NMR tube, and a total of 18 sets of FIDs were collected (data collected every 4 min) starting 4 min after mixing. The temperature was 24.1 °C. $k = 1.25 \times 10^{-3}$ s^{-1} +/- 2.0%. $t_{1/2}$ = 9.2 min.

(b) Diethylmethylene malonate (0.0127 g, 0.074 mmol, containing 260 ppm MEHQ (4-methoxyphenol) to inhibit polymerization) and *tert*-BuOH (1 μL, 0.016 mmol) were dissolved in THF-d_8 (800 μL) in an NMR tube. Cobalt–diene **21** (0.0060 g, 0.013 mmol) was added to the NMR tube, and a total of 18 sets of FIDs were collected (data collected every 3 min) starting 4 min after mixing. The temperature was 24.1 °C. $k = 1.21 \times 10^{-3}$ s^{-1} +/- 2.4% $t_{1/2}$= 9.5 min.

(c) Diethylmethylene malonate (0.0124 g, 0.072 mmol, containing 260 ppm MEHQ (4-methoxyphenol) to inhibit polymerization) and *tert*-BuOH (1 μL, 0.016 mmol) were dissolved in THF-d_8 (800μL) in an NMR tube. (Trimethylsiloxy)butadiene (0.0018 g, 0.013 mmol) was added to the NMR tube, and a total of 18 sets of FIDs were collected (data collected every 8 min) starting 6 min after mixing. The temperature was 23.8 °C. $k = 2.54 \times 10^{-5}$ s^{-1}. $t_{1/2}$= 471.4 min.

(d) Cobalt–diene **19** (0.024 g, 0.0564 mmol) was dissolved in $CDCl_3$ (700 μL) in an NMR tube and pre-cooled to –20 °C. Diethylmethylene malonate (also precooled to -20 °C) (0.098 g, 0.569 mmol) with 260 ppm MEHQ (4-methoxyphenol to inhibit polymerization) was added to the NMR tube and rapidly shaken. Eighteen sets of FIDs were then obtained at a probe temperature of –20 °C. Nine points were taken every 3 min, and then nine more points were taken every 9 min. The reaction was monitored for 4.8 half-lives. $k = 5.22 \times 10^{-4}$ s^{-1} +/- 1.7%. $t_{1/2}$= 22.1 min

(e) Cobalt–diene **22** (0.025 g, 0.0559 mmol) was dissolved in $CDCl_3$ (700 μL) in an NMR tube and pre-cooled to –20 °C. Diethylmethylene malonate (also precooled to -20 °C) (0.0962 g, 0.559 mmol) with 260 ppm MEHQ (4-methoxyphenol to inhibit polymerization) was added to the NMR tube and rapidly shaken. Eighteen sets of FIDs were obtained at –20 °C. Nine points were taken every 2 min, and then nine more points were taken every 7 min. The reaction was monitored for 4 half-lives. $k = 9.42 \times 10^{-4}$ s^{-1} +/- 6.2%. $t_{1/2}$ = 12.3 min.

(f) 2-(Trimethylsiloxy)-1,3-butadiene (0.026 g, 0.0621 mmol) was dissolved in $CDCl_3$ (700 μL) in an NMR tube and precooled to –20 °C. Diethylmethylene malonate (precooled to –20 °C) (0.097 g, 0.563 mmol) with 260 ppm MEHQ (4-methoxyphenol to inhibit polymerization) was added to the NMR tube and rapidly shaken. Twenty sets of FIDs were obtained at –20 °C. Eighteen points were taken every 15 min, and then two more points were taken every 4 h. The reaction was monitored for 2.5 half-lives. $k = 1.82 \times 10^{-5}$ sec^{-1} +/- 8%. $t_{1/2}$= 631.7min

Synthesis of 1,1-Dicarboethoxycyclohex-3-ene (40) and 4,4-Dicarboethoxycyclohexanone (41) via Acidic Cobalt–Carbon Bond Cleavages. (1) Aqueous Acid. Cycloadduct **29** (0.200 g, 0.337 mmol) was dissolved in degassed methylene chloride (40 mL) and cooled to 0 °C. Five equivalents of 12 M HCl (140 μL) was then added as degassing continued. After the addition of the HCl, the solution was allowed to stir overnight under nitrogen. Water (50 mL) was added and extracted with two additional portions of CH_2Cl_2 (25 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was chromatographed on silica gel (pentane/ether, 4:1) to yield alkene **40** followed by ketone **41**. A reaction run on the same scale under identical conditions except run in the presence of air also produced alkene **40** (39%) and ketone **41** (51%).

Spectroscopic data for **40** and **41** are as follows. **40** (32 mg, 0.141 mmol (42%)). R_f = 0.49 (pentane/ether, 4:1). ^{1}H NMR ($CDCl_3$) (previous characterization without NMR data[10]): 5.51 (s, 2H), 4.18 (q, J = 7.5 Hz, 4H), 2.55 (m, 2H), 2.12 (m, 4H), 1.25 (t, J = 7.5 Hz, 6H).

IR ($CDCl_3$): 3033, 2983, 2932, 1741, 1655, 1474 cm^{-1}. EI MS M^+ 226 (19), 181 (13), 152 (59), 123 (35), 107 (11), 79 (100).

41 (28 mg, 0.115 mmol, (34%)). R_f = 0.21 (pentane/ether, 4:1). ^1H NMR ($CDCl_3$) (lit.[16]): 4.25 (q, J = 7.5 Hz, 4H), 2.40 (m, 8H), 1.28 (t, J = 7.5 Hz, 6H). IR ($CDCl_3$): 2963, 2930, 2873, 1730, 1602, 1466, 1458 cm^{-1}. EI MS M^+ 242 (51), 214 (8), 197 (36), 168 (100), 150 (24), 140 (61), 112 (31), 99 (44), 71 (34).

(2) Anhydrous HCl. Cycloadduct **29** (0.200 g, 0.337 mmol) was dissolved in methylene chloride (40 mL) and cooled to 0 °C. Anhydrous HCl was bubbled through the solution for 1 min, and then the solution was allowed to warm to 25 °C and stir for 3 h. The solvent was removed under reduced pressure, and the green residue was extracted with ether (40 mL) . The ether extract was dried ($MgSO_4$) and concentrated by rotary evaporation. The crude product was then chromatographed on silica gel (pentane/ether, 4:1) to yield **40** (7.2 mg, 0.032 mmol (9%)) and **41** (61.4 mg, 0.25 mmol, (75%)).

A portion of the green residue remaining after ether trituration (believed to be pyridiniumbis(dimethylglyoximato)cobalt(III) dichloride[17] (**49**) Mp: 185 °C dec. ^1H NMR (D_2O): 8.1 (apparent t, J = 5.0 Hz, 2H), 7.92 (d, J = 8.3 Hz, 1H), 7.41 (t, J = 6.7 Hz, 2H), 2.88 (br s, 12H).) (0.075 g, 0.170 mmol) was dissolved in methanol (30 mL). Pyridine (200 μL, 2.47 mmol) and water (150 μL) were added, and the solution was allowed to stir for 1 h. The methanol was removed under reduced pressure, and the residue was triturated with ether (15 mL) to remove excess pyridine. The residue was then extracted with CH_2Cl_2 (40 mL) and dried ($MgSO_4$), and the solvent was removed by rotary evaporation to yield pyr$(dmg)_2$CoCl (**42**; 0.0609 g, 0.151 mmol, (89%)). The product was identical by TLC (R_f = 0.25, ethyl acetate) and ^1H NMR comparison to an authentic sample.[14]

(3) Aqueous HCl/H_2O_2. Cycloadduct **29** (0.200 g, 0.337 mmol) was dissolved in CH_2Cl_2 as described above. HCl (12 M, 140 μL, 1.68 mmol) was added at 0 °C followed by H_2O_2 (225 μL, 0.67 mmol (30%)), and the solution was allowed to warm to 25 °C overnight. Extraction and chromatography as described above yielded **40** (1.5 mg, 0.006 mmol, (2%)) and **41** (39.5 mg, 0.163 mmol, (48%)).

(4) *hν*. Cycloadduct **29** (0.200 g, 0.337 mmol) was dissolved in CH_2Cl_2 as described above. The solution was cooled to 0 °C and photolyzed for 3 h (Hanovia 450W immersion well, quartz filter) while air was bubbled through the solution. The solvent was removed by rotary evaporation to yield a green residue which was triturated with Et_2O (5 × 2 mL). The ether extracts were chromatographed as described above to yield **40** (2.5 mg, 0.011 mmol, 3%) and **41** (50.0 mg, 0.207 mmol, 61%). A portion of the green residue resulting after ether trituration (believed to be pyridiniumbis(dimethylglyoximato)cobalt(III) dichloride[17] (**49**)) (0.064 g, 0.1454 mmol) was treated as described above to yield pyr$(dmg)_2$CoCl (**42**; 0.041 g, 0.1008 mmol (69%)).

Synthesis of 1,1-Dicarboethoxy-4-iodocyclohex-3-ene (43). Cycloadduct **29** (0.200 g, 0.337 mmol) was dissolved in CH_2Cl_2 (40 mL) and cooled to 0 °C. To this mixture, iodine (0.094 g, 0.371 mmol) was added and allowed to warm to 25 °C and stir for 2 h. The solvent was removed under reduced pressure and the residue triturated with diethyl ether (3 × 5 mL). The ether-insoluble residue was determined to be >95% pure Co$(dmg)_2$PyrI (**44**; 0.144 g, 0.312 mmol, (92%)) by spectroscopic comparison to an authentic sample.[18] The ether extracts were washed with aqueous saturated $NaHSO_3$ (10 mL) and dried ($MgSO_4$). The ether was removed by rotary evaporation, and the resulting oil was purified by radial chromatography on silica (pentane/ether, 4:1), yielding **43** (R_f = 0.56, 0.0932 g, 0.264 mmol (78%)) as a light-yellow oil. ^1H NMR ($CDCl_3$): 6.25 (m, 1H), 4.17 (q, J = 7.0 Hz, 4H), 2.62 (m, 2H), 2.55 (m, 2H), 2.16 (t, J = 6.4 Hz, 2H), 1.2 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): 170.70, 133.89, 94.18, 61.57, 51.67, 36.30, 33.95, 30.05, 14.05. IR ($CDCl_3$): 2980, 2935, 1644, 1558, 1295, 1215 cm^{-1}. Anal. Calcd for $C_{12}H_{17}O_4I$: C, 40.93; H, 4.87; I, 36.04. Found: C, 41.01; H, 4.90; I, 36.11.

Synthesis of Alkene 40 Using Diethylzinc. Cycloadduct **29** (0.100 g, 0.168 mmol) was dissolved in THF (20 mL) and cooled to -78 °C under a nitrogen atmosphere. Diethyl zinc (0.202 mmol, 202 μL of a 1 M solution in ether) was added. The mixture was allowed to warm to 25 °C and stir (2 h). The solvent was removed by rotary evaporation to yield a red oil. Water (15 mL) was added, and a yellow solid precipitated, which dissolved during extraction with CH_2Cl_2 (3 × 5 mL). Subsequent evaporation of the solvent yields a mixture of alkene **40** and Co$(dmg)_2$(pyr)Et (**45**). This crude product was dissolved in CH_2Cl_2 (2 mL) and chromatographed on flash silica. Elution with CH_2Cl_2 yielded alkene **40** (0.0315 g, 0.139 mmol, 83%), identical by spectroscopic comparison to material isolated from the HCl cleavage reported above. Elution with ethyl acetate yielded Co$(dmg)_2$(pyr)Et (**45**; (0.0585 g, 0.147 mmol, 88%) as a yellow solid, identical by spectroscopic comparison to an authentic sample.[14]

Synthesis of Alkene 40 using $Al(CH_2CH_3)_3$. Cycloadduct **29** (0.100 g, 0.168 mmol) was dissolved in dry THF (10 mL) and cooled to 0 °C under a nitrogen atmosphere. $Al(CH_2CH_3)_3$ (0.202 mL of a 1 M solution in ether, 0.202 mmol) was added. The mixture was allowed to warm to 25 °C and stir for 1.5 h. The solvent was removed by rotary evaporation, yielding a red oil. Water (15 mL) was added, and a yellow precipitate was immediately noted, which dissolved upon extraction with CH_2Cl_2 (3 × 10 mL). Subsequent drying with $MgSO_4$ and evaporation of the solvent yields a mixture of alkene **40** and Co$(dmg)_2$(pyr)Et (**45**). Alkene **40** was isolated by triturating with 5:1 ether/pentane (3 × 3 mL) and passing through a short plug of silica (0.034 g, 0.148 mmol, (88%)) and proved to be identical by spectroscopic comparison to the material isolated above. Co$(dmg)_2$(pyr)Et (**45**) was purified by flash silica gel chromatography using EtOAc as the eluent (0.0557 g, 0.140 mmol (83%)) and was identical by spectroscopic comparison to an authentic sample.[14]

Synthesis of 4,4-Dicarboethoxy-2-cyclohexenone (46) using Br_2. Cycloadduct **29** (0.255 g, 0.429 mmol) was dissolved in CH_2Cl_2 (80 mL) and cooled to 0 °C under a nitrogen atmosphere. Br_2 (0.140 mL, 0.472 mmol of a 3.37 M solution in CH_2Cl_2) was added. The mixture was allowed to warm to 25 °C and stir for 8 h. Saturated $NaHCO_3$ (20 mL) was added, and the mixture was vigorously stirred for 5 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), and the solvent was removed by rotary evaporation to yield a mixture of α,β-unsaturated ketone **46** and Co$(dmg)_2$(pyr)Br (**47**). Crude α,β unsaturated ketone **46** was isolated by triturating with ether (3 × 3 mL) and removing the solvent under reduced pressure to produce a brown oil. The brown oil was chromatographed on silica (ether/pentane, 4:1) to elute α,β-unsaturated ketone **46** (R_f = 0.36) (0.0515 g, 0.2144 mmol, (50%)). ^1H NMR (lit. CCl_4)[19] ($CDCl_3$): 7.05 (d, J = 10.0 Hz, 1H), 6.09 (d, J = 10.0 Hz, 1H), 4.22 (q, J = 6.7 Hz, 4H), 2.62–2.45 (m, 4H), 1.26 (t, J = 6.7 Hz, 6H). IR ($CDCl_3$): 2986, 2939, 1733, 1632, 1232, 1206, 1065 cm^{-1}. EI MS: 65 (32), 95 (34), 112 (21), 140 (110), 168 (61), 194 (37), 212 (54), 240 (90, M^+). HRMS calcd for $C_{12}H_{16}O_5$ 240.0997, found 240.0997. The solid remaining after the ether trituration was identified as Co$(dmg)_2$(pyr)Br (**47**; 0.244 g, 0.289 mmol (67%)), on the basis of spectroscopic comparison to an authentic sample.[14]

Synthesis of 1,1-Dicarboethoxy-4,5-dichlorocyclohex-3-ene (48). Cycloadduct **29** (0.167 g, 0.281 mmol) was dissolved in CH_2Cl_2 (50 mL) and cooled to -78 °C. Anhydrous HCl was bubbled through the solution for 1 min, and H_2O_2 (0.035 mL, 0.309 mmol of a 30% aqueous solution) was added. The solution was allowed to warm (turning red at 0 °C) to 25 °C and stir for 6 h. The solvent was removed under reduced pressure, and the residue was extracted with ether (3 × 15 mL). The ether extracts were dried ($MgSO_4$) and concentrated by rotary evaporation. The resulting oil was then chromatographed on silica gel (pentane/ether, 3:1, R_f = 0.58) to yield **48** as a colorless oil (0.073 g, 0.218 mmol (88%)). IR (neat): 2975, 2930, 2875, 1720, 1690, 1245, 1175, 1050, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): 6.00 (t, J = 4.2 Hz, 1H), 4.63 (t, J = 6.2 Hz, 1H, H_5), 4.31–4.05 (m, 4H), 2.92 (dd, J = 18.5, 4.2 Hz, 1H, H_2), 2.85 (dd, J = 14.4, 6.2 Hz, 1H, H_6), 2.65 (dd, J = 14.4, 6.2 Hz, 1H, H_6'), 2.49 (dd, J = 18.5, 4.2 Hz, 1H, H_2'), 1.34–1.16 (m, 6H). ^{13}C NMR ($CDCl_3$): 170.1, 160.6, 130.5, 126.6, 62.0, 56.1, 51.3, 37.8, 31.2, 25.0, 13.9, 13.8. CI MS: 51 (12), 77 (50), 113 (50), 157 (47), 113 (3), 141 (5), 185 (8), 215 (1), 259 (100), 260 (14), 261 (34), 262 (5), 263 (1), 294 (0.6), 295 (12, M^+ + 1 for $Cl^{35}Cl^{35}$ isotope), 296 (2), 297 (8, M + 1 for $Cl^{35}Cl^{37}$ isotope), 298 (1), 299 (1.7). EI MS: 55 (11), 57 (17), 113 (50), 157 (47), 185 (100), 220 (9), 294 (1, M^+). The green residue remaining after ether trituration proved to be bis(dimethylglyoximato)cobalt(III) dichloride$^-$ pyridinium$^+$ (**49**;[17] (0.101 g, 0.229 mmol, (82%)) identical by spectroscopic comparison to the material reported above.

Preparation of 5,6-Dihydro-1,4-naphthoquinone (50). Complex **25** (0.202 g, 0.382 mmol), manganese(III) acetate dihydrate[20] (0.212 g, 0.791 mmol), and sodium acetate (0.190 g, 2.32 mmol) in glacial acetic acid (10 mL) were refluxed for 1 h. This solution was then cooled to 25

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°C. Titanium(III) chloride[21] (0.193 g, 1.25 mmol) in water (1 mL) was added. This mixture was stirred at 25 °C for 90 min. Water (25 mL) was added, and this mixture was extracted with diethyl ether (4 × 25 mL). The combined organic extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was chromatographed on a 2-mm silica gel prep plate and eluted with 2:1 petroleum ether/diethyl ether. A light-ellow band with an R_f value of 0.5 was collected, and the solvent was removed under reduced pressure to yield a yellow gum (**50**; 0.0110 g, 0.0683 mmol (18%)). ^{1}H NMR ($CDCl_3$): 6.71 (dt, J = 10.0, 2.0 Hz, 1H), 6.54 (d, J = 8.7 Hz, 1H), 6.48 (d, J = 8.7 Hz, 1H), 6.05 (dt, J = 10.0, 4.9 Hz, 1H), 2.70 (t, J = 7.1 Hz, 2H), 2.29 (m, 2H). IR ($CDCl_3$): 3156, 2928, 1654, 1563, 1483, 1379, 1296, 1269, 1232, 1093 cm^{-1}. EI MS: 160 (90), 131 (100), 105 (70), 54 (40), 52 (35). HRMS calcd for $C_{10}H_8O_2$ 160.0522, found 160.0526.

(3E)-1,3-Pentadien-2-ylpyridinebis(dimethylglyoximato) cobalt (III)-(3E) (51). This complex was prepared in a manner analogous that that reported for **19** using cobalt(II) chloride hexahydrate (2.831 g, 11.9 mmol) and dimethylglyoxime (2.764 g, 23.8 mmol) for cobalt anion generation and 2-acetoxy-3,4-pentadiene (**15**) (1.50 g, 11.9 mmol) as the electrophile to produce **51** as a orange-yellow precipitate which was collected by vacuum filtration and vacuum-dried. (**51**): (3.04 g, 6.98 mmol, 59%). Using 1/3 scale of the above procedure and 2-trimethylacetoxy-3,4-pentadiene (**16**) (0.667 g, 3.97 mmol) in place of 2-acetoxy-3,4-pentadiene (**15**) also produced (**51**): (0.968 g, 2.22 mmol, 56%). The solid can be recrystallized from methanol. Mp decomposes at 210 °C. ^{1}H NMR ($CDCl_3$): 8.64 (d, J = 6.3 Hz, 2H), 7.72 (apparent t, J = 6.2 Hz, 1H), 7.33 (d, J = 6.2 Hz, 2H), 6.15 (dq, J = 15.2, 2.5 Hz, 1H), 5.29 (dq, J = 15.2, 7.6 Hz, 1H), 4.46 (s, 1H), 4.32 (s, 1H), 2.08 (s, 12H), 1.50 (dd, J = 7.6, 2.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): 149.86, 149.54, 138.47, 137.34, 124.98, 119.74, 112.82, 18.15, 12.07. IR ($CDCl_3$) 3608, 3081, 1605, 1563, 1494, 1450, 1235 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_4N_5Co$: C, 49.66%; H, 6.02%; N, 16.09%. Found: C, 49.70%; H, 6.05%; N, 16.14%.

(3E)-1,3-Pentadien-2-yl(4′-(N,N-dimethylamino)pyridine)bis(dimethylglyoximato)cobalt(III) (52). This complex (**52**) was prepared on a somewhat reduced scale compared to that of the pyr complex (**51**) above using cobalt(II) chloride hexahydrate (0.445 g, 1.88 mmol), dimethylglyoxime (0.435 g, 3.75 mmol), 4-(*N,N*-dimethylamino)pyridine (0.122 g, 1.88 mmol), and 2-acetoxy-3,4-pentadiene (**15**; (0.250 g, 1.90 mmol). All other reagents were scaled down accordingly, and the analogous workup yielded a yellow solid (**52**; 0.409 g, 0.853 mmol, (45%)). The solid can be recrystallized from methanol. Mp decomposes at 195 °C. ^{1}H NMR ($CDCl_3$): 8.20 (d, J = 6.8 Hz, 2H), 6.40 (d, J = 6.8 Hz, 2H), 6.18 (dq, J = 14.8, 1.3 Hz, 1H), 5.21 (dq, J = 14.8, 6.5 Hz, 1H), 4.44 (s, 1H), 4.39 (s, 1H), 2.97 (s, 6H), 2.19 (s, 12H), 1.50 (dd, J = 6.8, 1.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): 154.11, 149.01, 148.81, 138.95, 119.15, 112.25, 107.41, 39.04, 18.26, 12.10. IR ($CDCl_3$) 3155, 3096, 2927, 2814, 1616, 1540, 1446, 1240, 1069 cm^{-1}. Anal. Calcd for $C_{20}H_{31}O_4N_6Co$: C, 50.21; H, 6.53. Found: C, 50.22; H, 6.52.

DMAP–diene complex **52** can also be prepared via ligand exchange from pyr–diene complex **51** by the following procedure. Pyr cobalt–diene complex **51** (0.100 g, 0.230 mmol) and DMAP (0.028 g, 0.230 mmol) were dissolved in degassed methanol (5 mL) and refluxed for 2 h. The solvent was removed by rotary evaporation, and the remaining orange solid was triturated with diethyl ether (3 × 5 mL) to remove pyridine. Vacuum drying produced an orange solid (0.105 g, 0.211 mmol (95%)) identical by spectroscopic comparison to the DMAP–diene complex **52** reported above.

(4-Methyl-2,3-pentadien-1-yl)pyridinebis(dimethylglyoximato)cobalt (III)] (53). This complex was prepared on a somewhat reduced scale compared to that of the pyr complex **51** above using cobalt(II) chloride hexahydrate (1.78 g, 7.5 mmol), dimethylglyoxime (1.72 g, 15 mmol), pyridine (0.620 mL, 7.5 mmol), and 5-(*p*-tolylsulfonyl)-2-methyl-2,3-pentadiene (**14**; 1.89 g, 7.5 mmol). All other reagents were scaled down accordingly, and the analogous workup yielded a yellow solid (**53**; 2.08 g, 4.63 mmol, (62%)). Mp: decomposes at 140 °C. ^{1}H NMR ($CDCl_3$): 8.55 (d, J = 5.6 Hz, 2H), 7.68 (apparent t, J = 7.4 Hz, 1H), 7.28 (d, J = 5.6 Hz, 2H), 4.78 (m, 1H), 2.19 (d, J = 8.8 Hz, 2H), 2.12 (s, 12H), 1.59 (d, J = 2.3 Hz, 6H, terminal allene methyls absorbing at same ν). IR ($CDCl_3$): 3406, 3155, 2985, 1816, 1794, 1642, 1471 cm^{-1}. ^{13}C NMR: 201.0, 149.9, 149.1, 137.3, 125.1, 95.7, 94.0, 19.6, 12.3, 12.0. ^{13}C NMR DEPT: CH 149.9, 137.3, 125.1, 95.7; CH_3 19.6, 12.3. Anal. Calcd for $C_{19}H_{28}O_4N_5Co$: C, 50.78; H, 6.28. Found: C, 50.52; H, 6.44.

((4*Z*/*E*)-2-Methyl-2,4-hexadien-3-yl)pyridinebis(dimethylglyoximato)-cobalt(III)] (54). This complex (**54**) was prepared on a somewhat reduced scale compared to that of the pyr complex **51** above using cobalt(II) chloride hexahydrate (0.303 g, 1.28 mmol), dimethylglyoxime (0.296 g, 2.55 mmol), pyridine (0.103 mL, 1.28 mmol), and 2-acetoxy-5-methyl-3,4-hexadiene (**17**; 0.197 g, 1.28 mmol). All other reagents were scaled down accordingly, and the analogous workup yielded a brown solid, which was chromatographed on silica and eluted with EtOAc (R_f = 0.63) as a single yellow-orange band to yield **54** as a 2.5:1 mixture of *cis*/trans (Z/E) isomers (0.173 g, 0.373 mmol (29%)). ^{1}H NMR ($CDCl_3$): 8.62 (d, J = 6.0 Hz, 2H), 7.67 (apparent t, J = 7.2 Hz, 1H), 7.26 (apparent t, J = 7.2 Hz, 2H), 6.02–5.89 (m, 1H, major), 5.98–5.80 (m, 1H, minor), 5.22 (dq, J = 11.7, 6.9 Hz, 1H, =C(*H*)Me of major (*Z*) isomer), 4.80 (dq, J = 16.4, 6.6 Hz, 1H, =C(*H*)Me of minor (*E*) isomer), 2.31 (s, 3H, minor), 2.28 (s, 3H, major), 2.12 (s, 12H, major isomer), 2.04 (s, 12H, minor isomer), 1.86 (s, 3H, minor), 1.70 (s, 3H, major), 1.45 (d, J = 6.6 Hz, 3H, minor isomer), 1.09 (d, J = 6.9 Hz, 3H, major isomer). IR ($CDCl_3$): 3185, 3128, 2914, 1607, 1553, 1462, 1215, 1110 cm^{-1}. Anal. Calcd for $C_{20}H_{30}O_4N_5Co$: C, 51.84; H, 6.52. Found: C, 51.25; H, 6.55.

Synthesis of (*trans*-5-Methyl-5,8,9,10-tetrahydro-*cis*-1,4-naphthoquinon-7-yl)pyridinebis(dimethylglyoximato)cobalt (55). Diene **51** (0.100 g, 0.223 mmol) was dissolved in degassed THF (8 mL). Benzoquinone (0.024.1 g, 0.223 mmol) was added, and the mixture was stirred under nitrogen for 6 h. The solvent was removed under reduced pressure and the crude product triturated with diethyl ether (3 × 5 mL) to remove any unreacted benzoquinone. The remaining yellow-orange solid was vacuum-dried to yield **55** (0.111 g, 0.204 mmol, (92%)) as the only observable diastereomer by 200-MHz ^{1}H NMR. Refluxing diene **51** (0.300 g, 0.689 mmol) with benzoquinone (0.097 g, 0.896 mmol) in THF (10 mL) for 1 h produced a 13:1 mixture of the exo diastereomer **55** and the 9,10-dehydrogenated cycloadduct **56** (see $ZnEt_2$ cleavage reaction data below) (0.325 g, 0.598 mmol, (87%)) after chromatography on silica (EtOAc). The crude product also contained these two products in a 13:1 ratio, so we know that chromatography does not cause this dehydrogenation. Tetrahydronaphthoquinones are known to be oxidation sensitive.[22] **55:** Mp: decomposes at 200 °C. ^{1}H NMR (C_6D_6): 8.95 (d, J = 8.7 Hz, 2H), 6.58 (d, J = 8.7 Hz, 1H), 6.40 (apparent t, J = 8.7 Hz, 2H), 6.00 (d, J = 12.9 Hz, 1H), 5.91 (d, J = 12.9 Hz, 1H), 5.57 (m, 1H, major), 5.50 (m, 1H, minor, **56**), 3.09 (apparent d, J = 17.6 Hz, 1H), 2.70–2.59 (m, 1H), 2.58–2.20 (m, 3H), 2.00 (s, 6H), 1.87 (s, 6H), 1.04 (d, J = 10.8 Hz, 3H minor, **56**), 0.95 (d, J = 8.6 Hz, 3H, major). IR ($CDCl_3$): 3347(b), 3064, 2963, 1710, 1605, 1133, 1071 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6N_5Co$; C, 53.04; H, 5.56. Found C, 52.78; H, 5.65.

Synthesis of (*trans*- and *cis*-1,3,3a,4,7,7a-hexahydro-7-methyl-1,3-dioxoisobenzofuran-5-yl)pyridinebis(dimethylglyoximato)cobalt (57 and 58). Diene **51** (0.200 g, 0.459 mmol) was dissolved in degassed THF (8 mL). Maleic anhydride (0.090 g, 0.919 mmol) was added, and the mixture was stirred under nitrogen for 1 h. The solvent was removed under reduced pressure, and the crude solid was triturated with ether (3 × 5 mL) to remove excess dienophile and then vacuum-dried to yield a yellow solid (**57/58**; 2.3:1 exo/endo, 0.189 g, 0.349 mmol (76%)). The reactions run in other solvents were on similar scales at similar concentrations. ^{1}H NMR ($CDCl_3$): 8.59 (apparent d, J = 6.2 Hz, 2H), 7.72 (apparent t, J = 8.2 Hz, 1H), 7.33 (apparent t, J = 6.2 Hz, 2H), 5.56 (dd, J = 7.6, 2.4 Hz, 1H, major), 5.43 (apparent t, J = 3.2 Hz, 1H, minor), 3.23–3.10 (m, 1H), 3.05–2.91 (m, 1H, minor), 2.90–2.81 (m, 1H, major), 2.79-2.64 (m, 1H, minor), 2.68–2.58 (m, 1H, major), 2.44–2.13 (m, 2H), 2.08 (s, 12H), 1.37 (d, J = 7.3 Hz, 3H, major), 0.99 (d, J = 7.3 Hz, 3H, minor). IR ($CDCl_3$): 3051, 2965, 2877, 1717, 1605, 1558, 1236, 1060 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_7N_5Co$; C, 49.54; H, 5.29. Found C, 49.42; H, 5.29.

Synthesis of (*cis*- and *trans*-1-Acetyl-2-methyl-3-cyclohexen-4-yl)-pyridinebis(dimethylglyoximato)cobalt (59 and 60). A representative experimental for a reaction run in THF is provided here. All other reactions run in different solvents were done on the same scale with a similar amount of solvent with the exception of the reactions run in $CHCl_3$, which were performed in 1 mL of solvent. Diene **51** (0.200 g, 0.475 mmol) was dissolved in degassed THF (10 mL). Methyl vinyl ketone (0.745 mL, 0.919 mmol) was added, and the solution was refluxed under nitrogen for 8 h. The solvent was removed under reduced pressure, and the crude product was triturated with pentane (3 × 10 mL) to remove excess MVK and vacuum-dried to yield a yellow solid as a 5.0:1 mixture of endo/exo diastereomers (**60/59**; 0.221 g, 0.437 mmol, (95%)). ^{1}H NMR (C_6D_6): 8.95 (apparent d, J = 6.5 Hz, 2H), 6.60 (apparent t, J = 8.6 Hz, 1H), 6.42 (apparent t, J = 6.5 Hz, 2H), 5.72 (d, J = 6.5 Hz, 1H, major), 5.62 (m, 1H, minor), 2.81 (m, 1H), 2.60 (m, 1H), 2.50–2.20

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(m, 2H), 2.03–1.86 (m, 2H), 1.84 (s, 6H), 1.80 (s, 6H), 1.69 (s, 3H, minor), 1.61 (s, 3H, major), 1.00 (d, J = 8.6 Hz, 3H, minor), 0.81 (d, J = 8.6 Hz, 3H, major). IR ($CDCl_3$): 3386, 3116, 3081, 2960, 1699, 1605, 1561, 1450, 1233, 1088 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_5N_5Co$: C, 52.28; H, 6.38; N, 13.86. Found: C, 52.34; H, 6.42; N, 13.85.

Cleavage of 55 with $AlMe_3$. Preparation of *trans*-5-methyl-5,8,9,10-tetrahydro-*cis*-1,4-naphthoquinone (61). Adducts **55** and **56** (as a 13:1 mixture of the exo diastereomer **55** and dehydrogenated product **56**) (0.200 g, 0.368 mmol) were dissolved in dry THF (20 mL) and cooled to 0 °C under nitrogen. $AlMe_3$ (0.203 mL of a 2.0 M solution in hexanes, 0.405 mmol) was added and stirred for 20 min. Ice (10 g) and then ice/water (10 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The orange organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The remaining orange oil was chromatographed on silica using CH_2Cl_2 to yield **61** and **63** as a gum; (0.052 g, 0.295 mmol, (80%)), the major component of which was identical by ^1H NMR, capillary GC retention time, and EIMS with an authentic sample prepared from *cis*-piperylene and benzoquinone described below and the minor component of which was identical to the dehydrogenated product **63** reported below. ^1H NMR ($CDCl_3$): 6.70 (s, 2H, minor), 6.65 (s, 2H, major), 5.79-5.48 (m, 2H), 3.24 (apparent q, J = 5.3 Hz, 1H), 2.79 (dd, J = 7.5, 5.3 Hz, 1H), 2.65–2.48 (m, 2H), 2.18–2.01 (m, 1H), 1.17 (d, J = 6.5 Hz, 1H, minor), 1.01 (d, J = 6.5 Hz, 3H, major). EIMS: 55 (84), 65 (40), 77 (100), 91 (67), 105 (42), 119 (38), 133 (70), 148 (56), 161 (62), 176 (37) M^+. Elution of the cobalt complex ($pyr(dmg)_2CoCH_3$) with ethyl acetate yielded **62** (0.125 g, 0.326 mmol, (88%)), identical by spectroscopic comparison to an authentic sample.[14]

Cleavage of 55 with $ZnEt_2$. Preparation of 5-Methyl-5,8-dihydro-1,4-naphthoquinone (63). Adduct **55** (0.998 g, 1.84 mmol) was dissolved in dry THF (60 mL) and cooled to −10 °C under nitrogen. $ZnEt_2$ (2.00 mL of a 1.0 M solution in hexanes, 2.00 mmol) was added, and the solution was allowed to warm to 25 °C and stir for 4 h. Water (60 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The orange organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation. The orange oil was chromatographed on silica (CH_2Cl_2) to elute **61** and **63** as a light yellow oil (R_f = 0.40, 0.224 g, 1.29 mmol (70%)). ^1H NMR ($CDCl_3$) revealed a 6:1 mixture of dehydrated **63**/nondehydrated **61**. ^1H NMR ($CDCl_3$) [lit.[23] ^1H NMR (C_3D_6O)] for the dehydrated product (**63**): 6.78 (s, 2H), 5.74 (m, 2H), 3.42–3.26 (m, 1H), 3.05 (m, 1H), 2.93 (m, 1H), 1.12 (d, J = 7.1 Hz, 3H). EIMS: 51 (85), 54 (95), 62 (24), 63 (71), 65 (52), 77 (100), 79 (34), 82 (25), 89 (44), 91 (65), 103 (34), 105 (45), 115 (85), 116 (42), 118 (23), 131 (87), 133 (23), 159 (20), 172 (41), 174 (29, M^+). CIMS: 55 (12), 147 (88), 175 (100, M + 1).

Thermal Diels–Alder reaction of *cis*-Piperylene with Benzoquinone. Preparation of an Authentic Sample of *trans*-5-Methyl-5,8,9,10-tetrahydro-*cis*-1,4-naphthoquinone (61). In an adaptation of a literature procedure,[24] benzoquinone (0.040 g, 0.367 mmol) and CuCl–NH_4 (2.29:1 mixture) (0.0183 g) were added to a sealed tube along with degassed benzene (0.5 mL) and 0.145 mL (1.468 mmol) of *cis*-piperylene. The tube was quickly capped and heated for 12 h at 120 °C in the dark. The solvent was removed by rotary evaporation to yield a crude yellow oil that was dissolved in ether and cooled to 0 °C. The white solid which precipitated was collected by suction filtration and vacuum-dried to yield a 1:1 mixture of endo and exo cycloadducts (see below for the spectroscopic data on the exo cycloadduct) by ^1H NMR. The mixture was dissolved in ether and chromatographed on a 2-mm silica gel plate with 3:2 ether/pentane. The band with R_f = 0.71 was removed and eluted with ether (3 × 15 mL) and the solvent was removed by rotary evaporation to yield **61** (0.0162 g, 0.092 mmol (25%)), identical by ^1H NMR, capillary GC retention time, and EIMS with the diastereomer **61** isolated above.

Thermal Diels–Alder reaction between *Trans*-Piperylene and Benzoquinone. Preparation of *cis*-5-methyl-5,8,9,10-tetrahydro-*cis*-1,4-naphthoquinone. In an adaptation of a literature procedure,[24] benzoquinone (0.143 g, 1.321 mmol) was added to a sealed tube along with degassed benzene (0.5 mL) and 0.145 mL (1.468 mmol) of *trans*-piperylene. The tube was quickly capped and heated for 12 h at 65 °C in the dark. The solvent was removed by rotary evaporation to yield a crude yellow oil that was dissolved in ether and cooled to 0 °C. The white solid which precipitated was collected by suction filtration and vacuum-dried (0.200 g, 1.136 mmol (86%)). ^1H NMR ($CDCl_3$): 6.75 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 5.64 (m, 2H), 3.32 (dd, J = 12.9, 5.1 Hz, 1H), 3.22 (m, 1H), 2.79–2.63 (m, 1H), 2.67–2.48 (m, 1H), 2.21–2.03 (m, 1H), 0.94 (d, J = 8.5 Hz, 3H). EIMS 54 (100), 65 (21), 77 (67), 91 (41), 105 (24), 115 (26), 138 (74), 148 (99), 161 (69), 176 (44, M^+).

Cleavage of 57 and 58. Preparation of *trans*- and *cis*-3-Methylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride (64 and 65). Adducts **57** and **58** (0.490 g, 0.936 mmol) as a 2.3:1 mixture of unknown diastereomeric composition were dissolved in dry THF (20 mL) and cooled to −15 °C under nitrogen. $AlMe_3$ (802 μL of a 2.0 M solution in hexanes, 0.161 mmol) was added, and the solution was warmed to 25 °C and stirred for 2 h. Ice/water (20 mL) was then added. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL). The orange organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation. The orange oil was chromatographed on silica (ethyl acetate/pentane, 1:1) to yield a 2.3:1 mixture of *trans*/*cis*-3-methylcyclohex-4-ene-*cis*-1,2-dicarboxylic anhydride (**64**/**65**; 0.053 g, 0.378 mmol (82%)). ^1H NMR ($CDCl_3$) 6.00–5.74 (m, 2H), 3.46–3.20 (m, 2H), 2.93–2.82 (dd, J = 9.8, 5.6 Hz, 1H, major), 2.77–2.62 (ddd, J = 16.1, 6.3, 2.8 Hz, 1H, minor), 2.61–2.40 (m, 3H), 2.30–2.09 (m, 1H), 1.35 (d, J = 8.2 Hz, 3H, minor), 1.26 (d, J = 7.6 Hz, 3H, major). The major and minor products (10:1) of an authentic sample[24] prepared via reaction of *trans*-piperylene and maleic anhydride correspond to the minor and major products isolated from the cleavage reaction above. The cobalt complex $pyr(dmg)_2CoCH_3$ (**62**) was subsequently eluted with EtOAc (0.123 g, 0.321 mmol (84%)) and proved to be identical to a authentic sample by spectroscopic comparison.[14]

Cleavage of 59 and 60. Preparation of *cis*- and *trans*-1-Acetyl-2-methyl-3-cyclohexene (67 and 66). Adducts **59** and **60** as a 5:1 mixture of unknown diastereomeric composition (0.420 g, 0.831 mmol) were dissolved in dry THF (20 mL) and cooled to −10 °C under nitrogen. $AlMe_3$ (0.457 mL of a 2.0 M solution in hexanes, 0.914 mmol) was added via syringe, and the solution was allowed to warm to 25 °C and stir for 30 min. Ice/water (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL). The orange organic layer was dried ($MgSO_4$) and the solvent removed by rotary evaporation (water bath temperature 24 °C). The orange oil was chromatographed on silica using 1:1 ether/pentane to elute the cleavage products (**66** and **67**) as an oil (0.086 g, 0.622 mmol, (76%)) as a 5:1 mixture (endo/exo; **67**/**66**). The major (*cis*-1-acetyl-2-methyl-3-cyclohexene; **67**) and minor (*trans*; **66**) isomers here were identical by ^{13}C NMR comparison to literature data[25] for each diastereomer. ^1H NMR ($CDCl_3$): 5.70-5.42 (m, 2H), 2.74–2.62 (m, 2H), 2.15 (s, 3H, minor), 2.13 (s, 3H, major), 2.09–1.95 (m, 2H), 1.73–1.53 (m, 2H), 0.90 (d, J = 7.5 Hz, 3H, minor), 0.80 (d, J = 7.5 Hz, 3H, major). EIMS: *minor product, exo* 55 (2), 67 (52), 79 (22), 95 (100), 96 (12), 105 (4), 123 (6), 138 (10, M^+); *Major product, endo* 55 (31), 67 (80), 79 (27), 95 (100), 96 (11), 109 (5), 123 (7), 138 (18, M^+). Elution of the cobalt complex $pyr(dmg)_2CoCH_3$ with ethyl acetate provided **62** (0.287 g, 0.749 mmol, (90%)), identical by spectroscopic comparison to an authentic sample.[14]

Preparation of (3E)-1,3-pentadien-2-ylpyridinebis(diphenylglyoximato)-cobalt(III) (69). in MeOH. This complex was prepared on a reduced scale but in a manner analogous to that used to prepare **19** using cobalt(II) chloride hexahydrate (0.445 g, 1.88 mmol) and diphenylglyoxime (0.900 g, 3.75 mmol), for anion generation and 2-acetoxy-3,4-pentadiene (**15**) (0.250 g, 1.98 mmol) as the electrophile. The previously described workup yielded a brown solid, which was chromatographed on flash silica (R_f = 0.80) with CH_2Cl_2 as eluent to yield a yellow-orange solid (**69**; 0.431 g, 0.662 mmol (35%)). Using the same procedure except four times the scale and 2-(trimethylacetoxy)-3,4-pentadiene (**16**; 1.332 g, 7.92 mmol) as the electrophile instead of 2-acetoxy-3,4-pentadiene (**15**) yielded after chromatography 3.02 g (3.02 mmol (40%)) of **69**. Spectroscopic details for the diene complex **69** are presented below.

Synthesis of 69 in DMF. Using a modified procedure,[26] cobalt(II) chloride hexahydrate (1.78 g, 7.52 mmol) and diphenylglyoxime (3.60 g, 15.0 mmol) were dissolved in degassed DMF (75 mL) and cooled to 0 °C. The rapidly stirred mixture was degassed for the duration of all additions. Sodium hydroxide (1.20 g, 15.0 mmol) as a 50% aqueous solution and pyridine (0.608 mL, 7.52 mmol) were added slowly. After 1 h, the solution was cooled to −10 °C. Sodium hydroxide (0.620 g, 7.52 mmol) as a 50% aqueous solution was added very slowly to avoid heating the mixture. Sodium borohydride (0.040 g, 1.066 mmol) dissolved in water (0.5 mL) was added over 2 min. After the mixture was stirred for 45 min, 2-acetoxy-3,4-pentadiene (**15**; 1.00 g, 7.93 mmol) was added

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rapidly and the mixture was allowed to warm slowly over 6 h to 25 °C. Water was added (750 mL) and extracted with CH_2Cl_2 (5 × 50 mL). The combined organic layers were washed with water (10 × 700 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the remaining solid was chromatographed on silica (R_f = 0.80), eluted with CH_2Cl_2, to yield a yellow-orange solid (**69**; 3.55 g, 5.46 mmol, (73%)). Using the same procedure except 2-(trimethylacetoxy)-3,4-pentadiene (**16**) yielded 3.24 g (4.98 mmol (66%)) of **69**. The solid can be recrystallized from methanol. Mp: decomposes at 198 °C. ^{1}H NMR ($CDCl_3$): 8.95 (apparent d, J = 6.1 Hz, 2H), 7.52 (apparent t, J = 6.1 Hz, 1H), 7.45 (apparent t, J = 6.1 Hz, 2H), 7.30–7.15 (m, 12H), 7.10–7.00 (m, 8H), 6.52 (dq, J = 14.8, 2 Hz, 1H), 5.59 (dq, J = 14.8, 6.7 Hz, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 1.60 (dd, J = 6.7, 2 Hz, 3H). ^{13}C NMR ($CDCl_3$): 151.20, 149.91, 138.58, 137.95, 129.92, 129.79, 129.38, 128.80, 127.65, 125.44, 120.82, 113.72, 18.42. IR ($CDCl_3$) 3402, 3064, 2932, 2912, 2850, 1626, 1605, 1579, 1490, 1444, 1287, 1133, 1071 cm^{-1}. Anal. Calcd for $C_{38}H_{34}O_4N_5Co$: C, 66.76; H, 5.01; N, 10.24. Found: C, 66.51; H, 5.08; N, 10.17.

Synthesis of (*trans*- and *cis*-1,3,3a,4,7,7a-Hexahydro-7-methyl-1,3-dioxoisobenzofuran-5-yl)pyridinebis(diphenylglyoximato)cobalt (70 and 71). (1) $CHCl_3$/THF Solvent. Diene **69** (0.200 g, 0.307 mmol) was dissolved in degassed $CHCl_3$ (1 mL) and cooled to -22 °C. Maleic anhydride (0.060 g, 0.615 mmol) was dissolved in THF (5 mL), cooled to −22 °C, and slowly added to the diene solution. After 7 days the solvent was removed under reduced pressure. The crude solid was dissolved in CH_2Cl_2 (3 mL), and pentane (3 mL) was then added, and the solution was cooled to −22 °C for 20 min. The orange-yellow solid which precipitated was collected and vacuum-dried to yield **70** and **71** (0.221 g, 0.295 mmol, 8.4:1 exo/endo (96%)). Performing this reaction on the same scale but at 25 °C with a reaction time of 3 h produced **70** and **71** (0.175 g, 0.234 mmol, 4.9:1 exo/endo (76%)).

(2) THF/Reflux. Diene **69** (0.050 g, 0.0768 mmol) was dissolved in degassed THF (3 mL). Maleic anhydride (0.015 g, 0.156 mmol) was dissolved in THF (1 mL) and slowly added. The reaction was refluxed for 2 h. The solvent was removed under reduced pressure and the crude solid triturated with ether/pentane (1:1, 3 × 10 mL) and vacuum-dried to yield **70** and **71** (0.050 g, 0.0667 mmol, 6.0:1 exo/endo (87%)). Mp: decomposes at 189 °C. ^{1}H NMR ($CDCl_3$): 8.92 (apparent d, J = 6.4 Hz, 2H), 7.77 (apparent t, J = 6.4 Hz, 1H), 7.45 (apparent t, J = 6.4 Hz, 2H), 7.31–7.13 (m, 12H), 7.12–7.00 (m, 8H), 5.91 (dd, J = 8.4, 3.4 Hz, 1H, major), 5.80 (apparent t, J = 3.5 Hz, 1H, minor), 3.42–3.10 (m, 2H), 3.00–2.81 (m, 2H), 2.80–2.63 (m, 1H), 1.41 (d, J = 8.6 Hz, 3H, minor), 1.17 (d, J = 7.3 Hz, 3H, major). IR ($CDCl_3$): 3562, 3064, 2964, 1692, 1605, 1523, 1488, 1444, 1070 cm^{-1}. Anal. Calcd for $C_{42}H_{36}O_7N_5Co$: C, 64.53; H, 4.64. Found C, 64.53; H, 4.68.

Synthesis of (*cis*- and *trans*-1-Acetyl-2-methyl-3-cyclohexen-4-yl)-pyridinebis(diphenylglyoximato)cobalt (73 and 72). Diene **69** (0.100 g, 0.154 mmol) was dissolved in degassed $CDCl_3$ (1 mL). Methyl vinyl ketone (0.064 mL, 0.842 mmol) was added and the solution stirred for 48 h. The solvent was removed under reduced pressure, and the crude solid was triturated with pentane (3 × 10 mL) to remove excess dienophile and vacuum-dried to yield **73** and **72** as a yellow solid (1:1 endo/exo) (0.090 g, 0.125 mmol (82%)). ^{1}H NMR ($CDCl_3$): 8.97 (apparent d, J = 5.2 Hz, 2H), 7.83 (apparent t, J = 6.5 Hz, 1H), 7.45 (apparent t, J = 6.5 Hz, 2H), 7.21 (m, 12H), 7.15 (m, 8H), 5.48 (m, 1H, vinyl H endo), 5.40 (m, 1H, vinyl H exo), 2.90–2.61 (m, 2H), 2.43–2.15 (m, 2H), 2.12 (s, 3H, exo methyl), 2.09 (s, 3H, endo methyl), 1.85–1.62 (m, 2H), 1.96 (d, J = 6.5 Hz, 3H, exo), 1.78 (d, J = 6.9 Hz, 3H, endo). (Exo and endo assignments are on the basis of analogy to trends observed in the dmg series.) IR ($CDCl_3$): 3662, 3064, 3030, 2931, 1627, 1597, 1536, 1241, 1133, 1014 cm^{-1}. Anal. Calcd for $C_{42}H_{40}O_5N_5Co$: C, 66.93; H, 5.35. Found C, 66.27; H, 5.37.

Synthesis of (*cis*- and *trans*-1-Acetyl-2-methyl--3-cyclohexen-4-yl(4′-(*N*,*N*-dimethylamino)pyridine)bis(diphenylglyoximato)cobalt (75 and 74). Diene **52** (0.200 g, 0.459 mmol) was dissolved in degasssed methanol (5 mL), and 4-(*N*,*N*-dimethylamino)pyridine (0.056 g, 0.459 mmol) and methyl vinyl ketone (0.192 mL, 2.095 mmol) were added to the stirred solution, which was refluxed for 6 h. The reaction was allowed to cool slowly to 25 °C and then was cooled to 0 °C for 20 min. The orange solid was collected by filtration, washed with ether (4 × 10 mL), and vacuum-dried to yield **74** and **75** as a 7.2:1 mixture of endo/exo products (0.189 g, 0.344 mmol (75%)). ^{1}H NMR ($CDCl_3$): 8.06 (d, J = 7.8 Hz, 2H), 6.46 (d, J = 7.8 Hz, 2H), 5.08 (d, J = 5.9 Hz, 1H, major), 4.91 (m, 1H, minor), 2.94 (s, 6H), 2.70–2.47 (m, 2H), 2.31–2.14 (m, 1H), 2.07 (s, 6H), 2.05 (s, 6H), 2.00 (s, 3H), 1.85–1.62 (m, 2H), 1.56–1.42 (m, 1H), 0.75 (d, J = 7.8 Hz, 3H, minor), 0.59 (d, J = 7.8 Hz, 3H, major). IR ($CDCl_3$): 3384, 2929, 2870, 2835, 1699, 1616, 1538, 1446, 1235, 1014 cm^{-1}. Anal. Calcd for $C_{24}H_{37}O_5N_7Co$: C, 52.55; H, 6.80. Found: C, 52.29; H, 6.83.

Synthesis of (*trans*-1,3,3a,4,7,7a-Hexahydro-7,7a-dimethyl-1,3-dioxoisobenzofuran-5-yl)pyridinebis(diphenylglyoximato)cobalt (76). Diene **69** (0.200 g 0.307 mmol) was dissolved in degassed THF (1 mL). Citraconic anhydride (0.110 mL, 1.229 mmol) was added, and the mixture was stored at −20 °C for 6 days. The solvent was removed under reduced pressure, and the crude solid was triturated with ether (3 × 5 mL) and vacuum-dried to yield **76** (0.230 g, 0.289 mmol (94%)). Mp: decomposes at 230 °C. The reaction can also be run on a multi gram scale at 25 °C with only a trace amount of the endo diastereomer seen with yields of 88–97%. ^{1}H NMR ($CDCl_3$): 8.94 (apparent d, J = 6.3 Hz, 2H), 7.88 (apparent t, J = 6.3 Hz, 1H), 7.45 (apparent t, J = 6.3 Hz, 2H), 7.31–7.13 (m, 12H), 7.12–6.99 (m, 8H), 5.75 (d, J = 6.3 Hz, 1H), 2.88 (m, 3H), 2.78–2.60 (m, 1H), 1.24 (s, 3H), 1.09 (d, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): C 176.69, 173.36, 138.29, 129.61, 127.94, 48.59; CH 151.76, 150.07, 132.02, 129.49, 129.42, 129.21, 127.90, 125.69, 48.82, 36.40; CH_2 28.93; CH_3 18.91, 15.075. IR ($CDCl_3$): 3064, 3031, 2936, 2876, 1691, 1605, 1230, 1177 cm^{-1}. Anal. Calcd for $C_{43}H_{38}O_7N_5Co$: C, 64.90; H, 4.81. Found: C, 64.70; H, 4.80.

Synthesis of *trans*-2,3-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic Anhydride (79). Cycloadduct **76** (1.00 g, 1.29 mmol) was dissolved in degassed CH_2Cl_2 (300 mL) and cooled to 0 °C in a Hanovia 450W photolysis reactor equipped with a quartz filter. The solution was photolyzed for 2.5 h. The solvent was removed by rotary evaporation to yield a greenish-brown powder. The residue was triturated with 1:1 pentane/ether (3 × 15 mL). The solvent was removed by rotary evaporation, without heating, to yield a reddish powder of about 90% pure anhydride **79** (0.263 g), which could not be separated from an aromatic impurity under a variety of chromatographic conditions. ^{1}H NMR ($CDCl_3$): 5.70–5.82 (m, 1H), 5.50–5.65 (m, 1H), 2.99 (dd, J = 8.9, 3.6 Hz, 1H), 2.72–2.56 (m, 1H), 2.61–2.45 (m, 1H), 2.50–2.32 (m, 2H), 1.28 (s, 3H), 1.11 (d, J = 7.5 Hz, 3H). IR($CDCl_3$): 2980, 2940, 1848, 1781, 1653, 1457, 1236 cm^{-1}. HRMS calculated for $C_{10}H_{12}O_3$: 180.0786, Found: 180.0790. The residual green powder (0.698 g, 1.09 mmol) (believed to be pyridinium(dpg)$_2$C·Cl_2 (**77**) on the basis of analogy to the chemistry described above for dmg complexes), which was insoluble in pentane/ether, was suspended in methanol (20 mL). NaOH (0.087 g, 1.09 mmol) was added as a 50% aqueous solution, after which the solution became homogenous. Pyridine (0.088 mL, 1.09 mmol) was added, and the solution was allowed to stir for 2 h. The solvent was removed by rotary evaporation, and the dark-brown residue was dissolved in CH_2Cl_2 (10 mL). The solution was filtered, and pentane was added until precipitate was seen. The solution was then cooled to −78 °C and after 20 min filtered to yield Pyr(dpg)$_2$CoCl (**78**; 0.615 g, 0.998 mmol (92%, 84% based on cycloadduct). Mp: 180 °C dec. ^{1}H NMR ($CDCl_3$): 8.59 (apparent d, J = 5.5 Hz, 2H), 7.81 (apparent t, J = 7.5 Hz, 1H), 7.35 (app t, J = 7.5 Hz, 2H), 7.25 (m, 20H). IR ($CDCl_3$): 3124, 3064, 3021, 1532, 1492, 1141 cm^{-1}. Anal. Calcd for $C_{33}H_{27}O_4N_5C$ °Cl: C, 60.79; H, 4.17. Found: C, 60.35; H, 4.06.

Synthesis of *trans*-2,3-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic Acid (80). The red powder (0.263 g) from the *hv* cleavage above was refluxed for 1 h in water (3 mL).[27] The water was removed from the residual brown oil, which was triturated with boiling water (4 × 2 mL). The aqueous solutions were combined, and the volume was reduced to 1 mL. The aqueous layer was extracted with ether (10 mL), and the ether extracts were dried (Na_2SO_4). Removal of solvent by rotary evaporation without heating yielded beige crystals, which were recrystallized from ether/pentane to yield white crystals (**80**); (0.129 g, 0.651 mmol (52%)). Mp: 137–139 °C. ^{1}H NMR ($CDCl_3$): 5.59 (m, 1H), 5.47 (m, 1H), 3.08 (dd, J = 6.3, 2.3 Hz, 1H), 3.07–2.95 (m, 1H, allylic CH), 2.62–2.28 (m, 2H), 1.18 (s, 3H), 1.10 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): 183.88, 180.38, 132.10, 121.54, 46.76, 44.56, 31.62, 24.06, 18.56, 16.54. IR ($CDCl_3$): 3150–2638 (v br OH), 1715, 1417, 1284, 1217 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.42; H, 7.09.

Synthesis of *trans*-2,3-Dimethylcyclohex-4-ene-*cis*-1,2-dicarboxylic Acid Dimethyl Ester (81). Using an Aldrich diazomethane generator, diacid **80** (0.026 g, 0.1311 mmol) was placed in the outer vessel and dissolved in dry ether (3 mL). With extreme precautions,[28] *N*-methyl *N*′-nitro nitrosoguanidene (MNNG) (0.133 g, 1.00 mmol) was loaded

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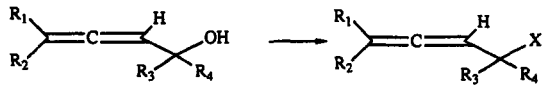
Table 1. Preparation of Allenic Electrophiles from Allenic Alcohols

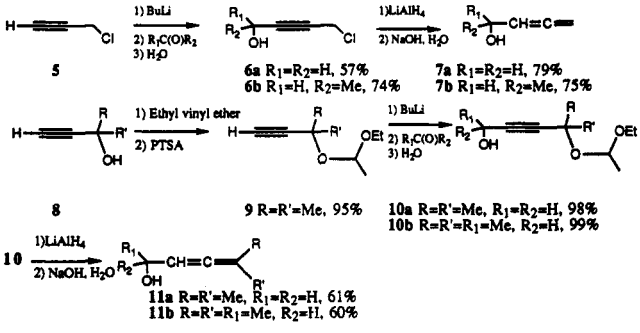


allenic alcohol				cmpd		allenic	yield	pro-
R_1	R_2	R_3	R_4	no.	conditions	electrophile	(%)	duct
H	H	H	H	**7a**	$SOCl_2$/pyr/Et_2O	X = Cl	46	**12**
H	H	H	H	**7a**	tosylCl/KOH/Et_2O	X = OTs	80	**13**
Me	Me	H	H	**11a**	tosylCl/KOH/Et_2O	X = OTs	68	**14**
H	H	Me	H	**7b**	MeLi/THF/Ac_2O	X = OAc	93	**15**
H	H	Me	H	**7b**	MeLi/THF/$(Me_3Ac)_2O$	X = OPiv	75	**16**
Me	Me	Me	H	**11b**	MeLi/THF/Ac_2O	X = OAc	91	**17**

into the center reactor, and the reactor was tightly closed. Water (0.5 mL) was added by pipet to the MNNG, taking care not to allow water to enter the ether solution. The reactor was cooled to 0 °C. NaOH (0.6 mL of a 5.0 M solution) was added via syringe (first three drops at 1 drop per second and then the remainder was added at 1 drop every five seconds). The reaction was allowed to warm to 25 °C for 1 h. Nitrogen was blown across the solution until it was evaporated to dryness. TLC (silica, 3:1 pentane/ether) indicated the presence of two compounds ($KMnO_4$ stain, R_f = 0.20 (minor) and 0.32 (major)). The crude product was purified by preparative TLC (silica, 3:1 pentane/ether) to yield pure dimethyl ester **81** (0.022 g, 0.0972 mmol (73%)), identical by ^1H NMR ($CDCl_3$) comparison to literature data for this diastereomer,[24] and the minor component (6.5 mg, 0.031 mmol, 23%) believed to be a half acid half ester precursor to **81**. ^1H NMR ($CDCl_3$): 5.68–5.54 (m, 1H), 5.53–5.51 (m, 1H), 3.71 (s, 3H), 3.10–2.84 (m, 2H), 2.61–2.22 (m, 2H), 1.20 (s, 3H), 1.06 (d, J = 7.1 Hz, 3H).

Results and Discussion

The preparation of the allenic electrophiles required to test the S_N2 and S_N2' reactions presented in the Introduction has been straightforward. All of the simple allenic alcohol precursors to the allenic electrophiles were known, so these are literature preparations or adaptations of them in most cases.[7-9] All reported yields are of isolated, purified materials which have been prepared on a multigram scale. All allenic electrophiles appear to be indefinitely stable at –20 °C. Terminally unsubstituted allenic electrophiles are prepared from propargyl chloride (**5**) whereas terminally substituted allenes are prepared from substituted propargyl alcohols (**8**). Table 1 summarizes the conditions used to prepare the allenic chlorides, tosylates, acetates, and pivalates used in the preparation of diene complexes.



Reactions of pyr(glyoxime)$_2$cobalt anions **18** with allenic electrophiles were investigated initially, since these anions are easily prepared from cobalt chloride and related alkyl cobaloximes had been heavily studied in vitamin B_{12} analog work.[14,18,26,29] When 4-chloro-1,2-butadiene (**12**) or 4-tosyl-1,2-butadiene (**13**) was treated with pyr(dmg)$_2$Co$^-$Na$^+$,[14] 4-*tert*-butyl(pyr)(dmg)$_2$Co$^-$Na$^+$, or 3,5-dimethyl(pyr)(dmg)$_2$Co$^-$Na$^+$, clean S_N2' replacement of the leaving group by the transition metal occurred

(29) For reviews of cobaloxime chemistry, see: (a) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105. (b) Schrauzer, G. N. *Pure Appl. Chem.* **1973**, *33*, 545. (c) Brown, D. G. *Prog. Inorg. Chem.* **1973**, *18*, 177.

Table 2. Reactions of Cobalt Anions with Unsubstituted Allenic Electrophiles

cobalt anion	allenic electrophile	diene complex yield (%)	product
L = pyr	**12**	33	**19**
L = pyr	**13**	75	**19**
L = 4-*tert*-butyl(pyr)	**13**	58	**20**
L = 3,5-diMe(pyr)	**13**	60	**21**
L = DMAP		90[a]	**22**

[a] The DMAP–diene complex **22** was prepared via ligand exchange from the pyridine complex **19**.

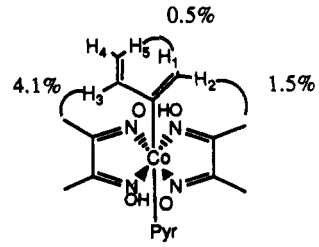


Figure 1.

(Table 2). S_N2' attack by the pyr(dmg)$_2$cobalt anion on propargyl bromide has been reported previously,[3d] so this outcome was not totally unexpected here. The DMAP– (DMAP = 4-(*N*,*N*-dimethylamino)pyridine) diene complex **22** was prepared via a ligand exchange reaction from the pyridine complex **19**.[14] All these cobalt-substituted diene complexes (**19–22**) are air-stable orange solids which have high thermal stability and can be prepared on a multigram scale from inexpensive starting materials. They precipitate from the methanol solvent used in their preparation and are easily purified by recrystallization from methanol or chromatography on silica. The 1,3- (**4**) rather than the 1,2-diene structure (**3**) was originally postulated for these complexes on the basis of their ^1H NMR spectra and was subsequently confirmed by X-ray crystallography.

On the basis of the fact that related pyr(dmg)$_2$Co-isopropyl[30] and -neopentyl[31] complexes have large Co–C–C bond angles (114° and 130°, respectively), we suspected that steric interactions between the diene and dmg ligands in the cobalt–diene complexes **19–22** might make the s-cis conformation of the diene more thermodynamically favorable than would normally be expected for 1,3-dienes. A solution diene conformation approaching s-cis was implicated for diene complex **19** by NOE experiments (Figure 1). Diene proton H_3 rather than H_5 showed an NOE to the dmg methyls. Diene proton H_5 had a small NOE to one of the protons on the other side of the diene, which we assign as H_1.

Solid-state structures for two of these diene complexes (**20** and **21**) have now been determined by X-ray crystallography, and the C(1)–C(2)–C(3)–C(4) torsion angle in **20** and C(17)–C(16)–C(18)–C(19) torsion angle in **21** were 54° and 63° respectively (Figure 2). Data collection and refinement parameters and selected bond lengths and angles for **20** are collected in Tables 3 and 4, and the analogous data for **21** is presented in Tables 5 and 6. These torsion angles are quite large when compared to reported torsion angles for s-cis dienes or trienes (5–30°)[32] but agree with Wiberg's calculations on rotational barriers in

(30) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

(31) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347.

(32) For some examples see: (a) Brouwer, A. M.; Bezemer, L.; Jacobs, H. J. C. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 138. (b) Saltiel, J.; Sears, D. F.; Sun, Y.-P.; Choi, J.-O. *J. Am. Chem. Soc.* **1992**, *114*, 3607. (c) Brouwer, A. M.; Conrelisse, J.; Jacobs, H.J.C. *Tetrahedron* **1987**, *43*, 435. (d) Squillacote,

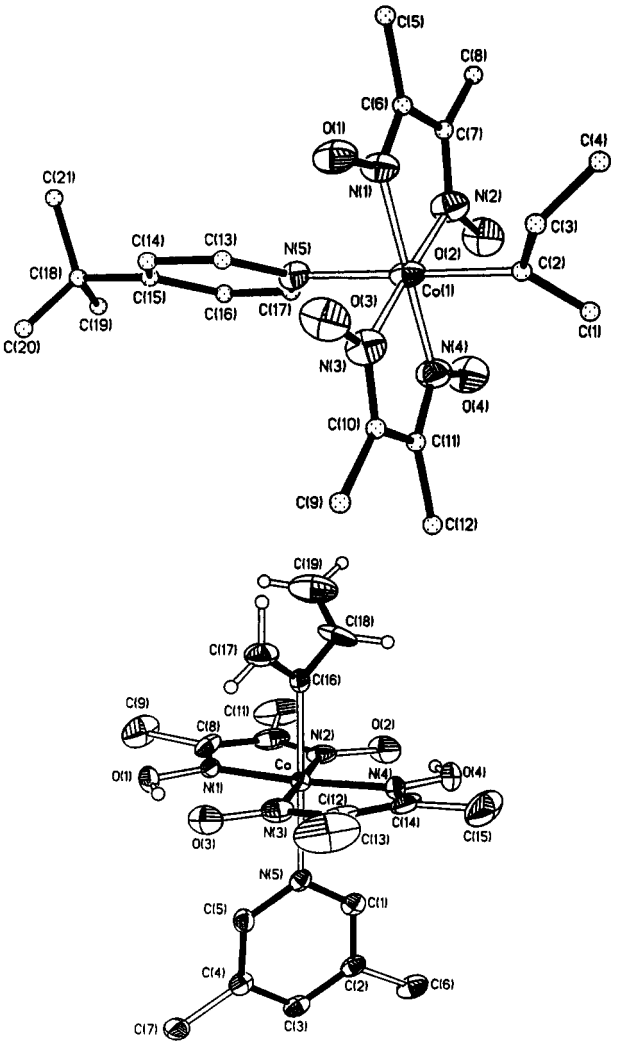


Figure 2. Molecular Structures of **20** (top) and **21** (bottom).

butadiene and heterobutadienes, which predict minimum-energy conformations with typical torsion angles of 25–55°.[32f] We initially postulated that the unusual twist angle for the diene in complex **20** might arise primarily from steric origins manifested in a displacement of C(1) resulting from very short intramolecular interactions with O(4) and N(4).[4] The H(1α) contact distances of 2.46 and 2.44 Å to O(4) and N(4), respectively, are in a range normally associated with hydrogen bonding. However, we could not rule out the possibility that the diene distortion was primarily due to intermolecular contacts of the pyridyl *tert*-butyl groups which pack head to tail with the diene, e.g., the H(3)···C(20) distance is 2.92 Å (see supplementary material for a unit cell diagram of **20**). The C=C bond lengths in **20** are within experimental error of a normal C=C bond length (1.337(6) Å)[33] and the cobalt–carbon bond (1.954(15) Å) is not particularly short when compared to cobalt–carbon bonds in related complexes (1.93–2.09A).[29-31,34]

Table 3. Crystallographic Data for Co[(dmg)$_2$(4-*t*-Bu(py))(σ-C$_4$H$_5$)]

(a) Crystal Parameters

formula	$C_{21}H_{32}CoN_5O_4$
formula weight	477.4
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	9.376(4)
b (Å)	22.260(9)
c (Å)	11.485(4)
β (deg)	94.95(3)
V (Å^3)	2388.2(18)
Z	4
cryst dimens (mm)	0.06 × 0.14 × 0.38
cryst color	orange-brown
D(calc) (g cm^{-3})	1.328
μ(Mo Kα) (cm^{-1})	7.49
temp (K)	299

(b) Data Collection

diffractometer	Siemens P4
monochromator	graphite
radiation	Mo Kα (λ = 0.710 73 Å)
2θ scan range (deg)	4–45
data collected (h, k, l)	±10, +23, +12
rflns collected	3304
indpt rflns	3123
R(merg) (%)	1.86
indpt obsvd rflns ($F_o \geq 4\sigma(F_o)$)	1428
std rflns	3 std/197 rflns
var in stds (%)	1

(c) Refinement

$R(F)$ (%)	8.08
$R_w(F)$ (%)	8.10
Δ/σ(max)	0.236
$\Delta(\rho)$ (eÅ^{-3})	0.59
N_o/N_v	7.64
GOF	1.38

Table 4. Selected Bond Lengths (Å) and Bond Angles for Co[(dmg)$_2$(4-*t*-Bu(py))(σ-C$_4$H$_5$)]

Bond Lengths (Å)

Co(1)–N(1)	1.907(9)	Co(1)–N(2)	1.895(9)
Co(1)–N(3)	1.888(10)	Co(1)–N(4)	1.881(10)
Co(1)–N(5)	2.044(9)	Co(1)–C(2)	1.954(15)
N(1)–O(1)	1.331(12)	N(1)–C(6)	1.274(17)
N(2)–O(2)	1.359(13)	N(2)–C(7)	1.302(17)
N(3)–O(3)	1.335(12)	N(3)–C(10)	1.283(18)
N(4)–O(4)	1.329(13)	N(4)–C(11)	1.307(17)
C(1)–C(2)	1.341(23)	C(2)–C(3)	1.454(22)
C(3)–C(4)	1.304(29)		

Bond Angles (deg)

N(1)–Co(1)–N(2)	80.7(4)	N(1)–Co(1)–N(3)	98.8(4)
N(2)–Co(1)–N(3)	177.4(6)	N(1)–Co(1)–N(4)	178.8(4)
N(2)–Co(1)–N(4)	98.1(4)	N(3)–Co(1)–N(4)	82.3(4)
N(1)–Co(1)–N(5)	89.6(5)	N(2)–Co(1)–N(5)	91.0(5)
N(3)–Co(1)–N(5)	91.6(5)	N(4)–Co(1)–N(5)	90.1(5)
N(1)–Co(1)–C(2)	89.6(6)	N(2)–Co(1)–C(2)	88.9(6)
N(3)–Co(1)–C(2)	88.5(6)	N(4)–Co(1)–C(2)	90.6(6)
Co(1)–C(2)–C(1)	122.9(12)	Co(1)–C(2)–C(3)	118.6(11)
C(1)–C(2)–C(3)	118.4(15)	C(2)–C(3)–C(4)	124.3(17)

In order to gain some more insight into the origin of the diene distortion, we prepared the 3,5-lutidine substituted diene complex **21** for crystallographic characterization. The diene torsion angle increased to 63° and the cobalt–carbon bond length (Co–C(16)) increased to 2.002(10) Å. The unit cell diagram (supplementary material) showed an absence of intermolecular interactions which might account for this diene twist. In **21**, the better σ-donating dialkyl pyridine has caused a lengthening of the cobalt–carbon bond, allowing the diene to twist more toward the s-trans conformation. It would now appear that these unusual diene torsion angles are due primarily to a balancing of C(1)–C(4) and

M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (e) Devaquet, A. J. P.; Townshend, R. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 4068. (f) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654.

(33) Mitchell, A. D., Cross, L. C., Eds. *Tables of Interatomic Distances and Angles*; The Chemical Society: London, 1958.

(34) (a) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (b) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 2722. (c) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7373. (d) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754. (e) Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96. (f) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1972**, 1433.

Table 5. Crystallographic Data for 1,3-Butadien-2-yl-3,5-lutidinebis(dimethylglyoximato)cobalt(III)

(a) Crystal Parameters	
formula	$C_{19}H_{28}CoN_5O_4$
formula weight	449.4
crystal system	orthorhombic
space group	*Pbca*
a (Å)	19.568(3)
b (Å)	13.628(3)
c (Å)	16.118(3)
V (Å^3)	4298.2(12)
Z	8
cryst dimens (mm)	0.10 × 0.25 × 0.40
cryst color	orange
D(calc) (g cm^3)	1.383
μ(Mo Kα) (cm^{-1})	8.28
temp (K)	233
(b) Data Collection	
diffractometer	Siemens *P4*
monochromator	graphite
radiation	Mo Kα (λ = 0.710 73 Å)
2θ scan range (deg)	4.0–53.0
data collected (*h*, *k*, *l*)	+17, +24, –20
rflns collected	5037
indpt rflns	4445
indpt obsvd rflns ($F_o \geq 4\sigma(F_o)$)	2309
std rflns	3/197
var in stds (%)	11.0
(c) Refinement	
$R(F)$ (%)	7.99
$R_w(F)$ (%)	8.43
Δ/σ(max)	0.090
$\Delta(\rho)$ (eÅ^{-3})	0.68
N_o/N_v	8.8
GOF	1.73

Table 6. Selected Bond Distances and Angles for 1,3-Butadien-2-yl-3,5-lutidinebis(dimethylglyoximato)cobalt(III)

Bond Lengths (Å)			
Co–N(1)	1.871(7)	Co–C(16)	2.002(10)
Co–N(2)	1.879(7)	C(16)–C(17)	1.330(16)
Co–N(3)	1.889(9)	C(16)–C(18)	1.415(17)
Co–N(4)	1.877(9)	C(18)–C(19)	1.292(23)
Co–N(5)	2.048(8)		
Bond Angles (deg)			
N(1)–Co–N(2)	81.3(4)	N(3)–Co–N(5)	91.1(3)
N(1)–Co–N(3)	98.3(4)	N(3)–Co–C(16)	90.2(4)
N(1)–Co–N(4)	175.5(3)	N(4)–Co–N(5)	92.8(3)
N(1)–Co–N(5)	91.6(3)	N(4)–Co–C(16)	88.4(4)
N(1)–Co–C(16)	87.1(4)	N(5)–Co–C(16)	178.3(4)
N(2)–Co–N(3)	179.3(4)	Co–C(16)–C(17)	122.2(8)
N(2)–Co–N(4)	98.4(5)	Co–C(16)–C(18)	117.1(8)
N(2)–Co–N(5)	89.5(4)	C(17)–C(16)–C(18)	120.6(10)
N(2)–Co–C(16)	89.1(4)	C(16)–C(18)–C(19)	128.7(15)
N(3)–Co–N(4)	81.9(5)		

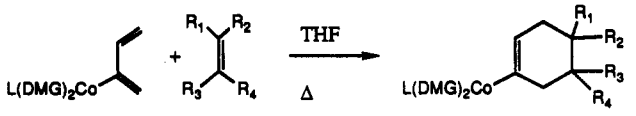
C(4)–ligand steric interactions in **20** and the analogous C(17)–C(19) and C(17)–ligand interactions in **21** rather than intermolecular packing interactions.

If complexes **19–22** exist predominantly in conformations close to s-cis in solution, then one would expect them to participate in Diels–Alder reactions under very mild conditions.[35,36] Cobalt–diene complexes **19** and **20** react with a variety of dienophiles to produce air-stable cobalt-substituted cyclohexenes in good yield (Table 7). All cycloadditions were carried out initially in

(35) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; John Wiley: New York, 1990; Chapter 1.

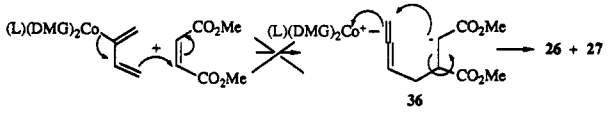
(36) For reviews of the regio- and stereochemistry of Diels–Alder reactions, see: (a) Titov, Y. A. *Russ. Chem. Rev.* **1962**, *31*, 267. (b) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537. (c) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211. (d) Oppolzer, W. In *Comprehensive Organic Synthesis;* Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 5, pp 315–399.

Table 7. Diels–Alder Reactions of Cobalt Complexes **19** and **20**



entry	diene	dienophile	Δ (h)	yield (%)	regiochem (para/meta)	product
1	**19**	diethylacetylene dicarboxylate	3	72		**23**
2	**19**	maleic anhydride	3	80		**24**
3	**19**	maleic anhydride	1 (25 °C)	76		**24**
4	**19**	benzoquinone	3	99		**25**
5	**19**	benzoquinone	6 (25 °C)	92		**25**
6	**19**	dimethyl fumarate	26	62		**26**
7	**19**	dimethyl maleate	64	34		**27**
8	**19**	dimethylmethylene malonate	2	96	>20:1 para	**28**
9	**19**	diethylmethylene malonate	2	96	>20:1 para	**29**
10	**19**	diethylmethylene malonate	1 (25 °C)	94	>20:1 para	**29**
11	**20**	diethylmethylene malonate	2	69	>20:1 para	**30**
12	**19**	methyl vinyl ketone	9	92	>20:1 para	**31**
13	**19**	methyl methacrylate	72	70	>20:1 para	**32**
14	**19**	ethyl methacrylate	72	51	>20:1 para	**33**
15	**19**	methyl acrylate	48	90	5.0:1	**34**
16	**19**	ethyl acrylate	48	77	5.0:1	**35**

tetrahydrofuran with a slight excess of the dienophile present (maleic anhydride, benzoquinone, and diethylmethylene malonate will react without heating). All the symmetrical dienophiles reacted to produce a single adduct. The benzoquinone cycloadduct **25** has the expected *cis* ring junction (J_{H9-H10} = 5.8 Hz),[37] so we conclude that epimerization α to a carbonyl does not appear to occur under these reaction conditions. The reactions of dimethyl fumarate and dimethyl maleate provided us with the first indications of how the steric bulk of the complex may influence the reactions, and they also shed light on whether these reactions are stepwise or concerted. The reaction was markedly slower with dimethyl fumarate than with the cyclic dienophiles, and dimethyl maleate produced only a 34% yield of cycloadduct (balance was unreacted diene **19**) after 64 h at reflux. Since transition-metal allyl complexes are known to react stepwise with electron-deficient alkenes in 3 + 2 cycloadditions,[1] we considered that these cycloadditions might also occur in a stepwise manner via a zwitterionic intermediate (**36**). However, if they occur



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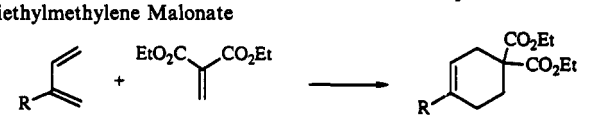
stepwise, two diastereomeric cycloadducts would be expected from the reactions of dimethyl fumarate and maleate with **19**. Instead we see only one cycloadduct from each, and they are not identical. Since bond rotation is faster than ring closure in related allyl and propargyl systems,[1] we conclude that the appearance of only one cycloadduct from these reactions is consistent with a concerted not stepwise cycloaddition reaction.

Reactions of **19** and **20** with unsymmetrical dienophiles (Table 7, entries 8–16) produced mainly para products in reasonable isolated yields with good to excellent regioselectivity. The para orientation of cobalt and the dienophile substituent was originally postulated for the major regioisomers on the basis of ^{1}H NMR homonuclear decoupling and COSY experiments and was subsequently confirmed by a study of cleavage reactions of the cobalt–carbon bond in the cycloadducts to be discussed below. Disubstituted dienophiles and methyl vinyl ketone gave very high

(37) Dasto, D. J.; Johnson, C. R. *Laboratory Text for Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1979; p 203.

Table 8. Rates of Reactions of Cobalt–Diene Complexes with Diethylmethylene Malonate



37 38 39

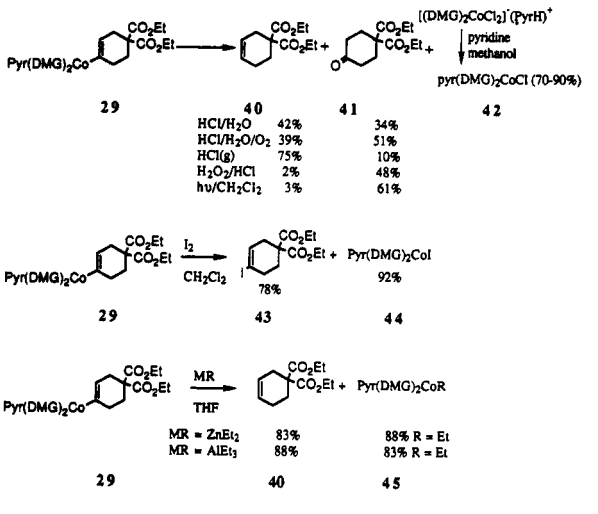
entry	R	solvent	temp (°C)	k_{obs} (s^{-1})	$t_{1/2}$ (min)
1	(pyr)(dmg)$_2$Co	THF-d_8	24	1.25×10^{-3}	9.2
2	(3,5-dimethyl(pyr)-(dmg)$_2$Co	THF-d_8	24	1.21×10^{-3}	9.5
3	TMSO	THF-d_8	24	2.45×10^{-5}	471.4
4	(pyr)(dmg)$_2$Co	$CDCl_3$	−20	5.22×10^{-4}	22.1
5	(DMAP)(dmg)$_2$Co	$CDCl_3$	−20	9.42×10^{-4}	12.3
6	TMSO	$CDCl_3$	−20	1.82×10^{-5}	631.7

selectivity for para products but regioselectivity falls off a bit to 5:1 for the monosubstituted dienophiles which are esters, ethyl and methyl acrylate. Diels–Alder reactions with dienophiles which contain only one ester substituent were considerably slower. These regiochemical results compare quite favorably with those of other thermal Diels–Alder reactions for dienes substituted with electron-donating groups in the 2-position.[36]

Cobalt-substituted butadiene **19** reacted with diethylmethylene malonate almost 50 times faster than 2-(trimethylsiloxy)-butadiene[38] in THF-d_8 at 24 °C (Table 8). An iron–diene complex prepared by us[4] and Giering[2a] has also previously shown similarly enhanced reactivity with dimethyl acetylene dicarboxylate. Cobalt complexes **19** and **21** react with diethylmethylene malonate in THF under pseudo-first-order conditions at almost identical rates, indicating that any electronic acceleration of a cycloaddition expected for this electron-donating dialkyl pyridine substituted complex (**21**) would appear to be offset by the increased diene torsion angle. The rates of these cycloadditions are significantly faster in $CDCl_3$ than in THF, a solvent effect first reported by Tada[5] for diene complex **19** and an effect noted by others previously for Diels–Alder reactions.[39] The strongly electron-donating DMAP ligand in complex **22** almost doubles the rate of cycloaddition compared to that of the pyridine complex **19**. The rate accelerations noted for the diene complexes at −20 °C are similar to those noted at 24 °C, with the pyridine complex **19** being 29 times faster than the TMSO–diene and the DMAP complex **22** being 52 times faster.

The development of methods for cleavage of the cobalt–carbon bonds in the cycloadducts which would yield organic products as well as a cobalt complex which could be recycled into the synthesis of the starting diene complexes **19–22** was our next priority. When cobalt complex **29** was treated with aqueous HCl[40] we isolated 4,4-dicarboethoxycyclohexene (**40**) (38%) and 4,4-dicarboethoxycyclohexanone (**41**) (42%). Performing the aqueous HCl cleavage in the presence of air lead to an increase in ketone **41** (51%). Anhydrous HCl produces alkene **40** (75%) along with a small amount of ketone **41**(10%). Acidic hydrogen peroxide produces ketone **41** (48%) along with a trace of alkene **40** (2%). Photolysis of **29** in CH_2Cl_2 in the presence of oxygen produced ketone **41** in even better yield (61%). Whether these cleavage products arise via cationic cobalt carbene complex intermediates or cobalt peroxo species[41] has not yet been determined. Oxidative cleavage with iodine yields vinyl iodide **43** (79%) as well as the cobalt iodide **44**.

Cleavage reactions mediated by dialkylzincs or trialkylaluminums deserve more comment because they represent a significant amount of effort to determine reaction conditions whereby a carbon–carbon bond could be formed in the cleavage reaction. Initially, **29** was treated with benzyl bromide to see if these complexes were nucleophilic enough to react with reactive alkyl halides. However, **29** was recovered unreacted after being refluxed with benzyl bromide for 24 h in THF. Complex **29** was treated with nucleophiles such as excess BuLi, MeMgBr, and Bu_2CuLi in attempts to form an ate complex[42] which might be more reactive toward electrophiles; however, aqueous workup of these reactions produced unreacted complex **29** rather than **40**. Transmetalation reactions with diethylzinc and -triethylaluminum[43] were attempted in hopes that we could recover recyclable cobalt alkyls as well as form vinylalane or zinc complexes which might be alkylated by treatment with alkyl halides.[44] We were encouraged when treatment of complex **29** with diethylzinc or triethylaluminum followed by aqueous workup produced alkene **40** (83% and 88%) as well as the cobalt ethyl complex **45** (88% and 83%). Since some dialkylvinylalanes were known to transfer their vinyl groups selectively when treated with reactive alkyl halides,[44b] we treated complex **29** with diethylzinc or triethylaluminum followed by MeI or EtBr. These reactions after aqueous workup produced the cobalt ethyl complex **45** as expected, but the organic product was again the alkene **40** rather than an alkylated cyclohexene. Since the corresponding ate complexes are known to be more reactive toward alkylation,[42] **29** was treated with triethylaluminum, followed by butyllithium and methyl iodide. To date this reaction has produced only complex mixtures of organic products from which small amounts of **40** can be isolated. Attempts at CO and alkene insertion with **29** (reflux of **29** in THF under 1 atm of CO, and reflux of **29** in THF with ethyl vinyl ether) yielded only recovered **29** in good mass balance.



29 40 41 42

29 43 44

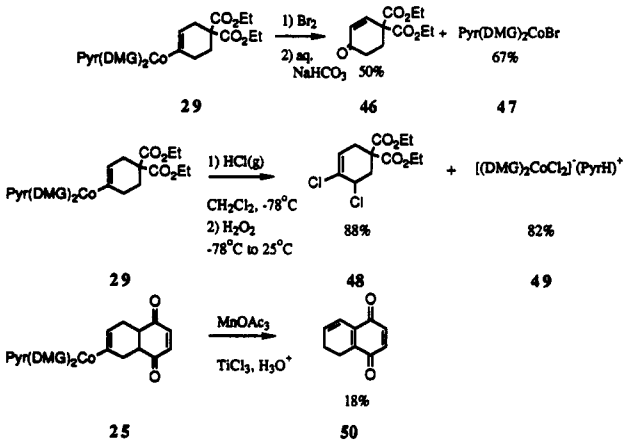
29 40 45

Cobalt recovery is exceptionally easy from all cleavage reactions discussed above. The crude products from the HCl and photolysis reactions are triturated with diethyl ether to remove the organic cleavage products **40** or **41**. The green water-soluble residue, which we believe is the pyridinium salt of $(dmg)_2CoCl_2$,[17] is simply dissolved in methanol and treated with pyridine to produce pyr-$(dmg)_2CoCl$[14] (**42**) (89% from the HCl cleavage, 69% from the photolysis), from which the cobalt anion **18**, (L = pyr) used to synthesize diene complex **6** can be regenerated.[18] The iodine cleavage yields pyr$(dmg)_2CoI$[14,45] (**44**) (92%) after trituration to

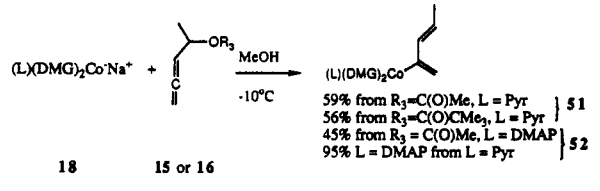
(38) Jung, M. E.; McCombs, C. A. *Tetrahedron Lett.* **1976**, 2935.
(39) For a review on mechanistic aspects of the Diels–Alder reaction, see: Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807.
(40) (a) Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295. (b) Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 301 and references therein.
(41) Branchaud, B. P.; Meier, M. S.; Malekzadeh, M. N. *J. Org. Chem.* **1987**, *52*, 212 and references therein.
(42) (a) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754. (b) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 5085. (c) Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927.
(43) Babu, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.
(44) (a) Lynd, R. A.; Zweifel, G. *Synthesis* **1974**, 658. (b) Zweifel, G.; Lynd, R. A. *Synthesis* **1976**, 816.
(45) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166.

remove **43**, and the diethylzinc or triethylaluminum cleavages yield pyr(dmg)$_2$CoEt[14] (**45**) after trituration. This cobalt recovery will become particularly important when we use optically active ligands[46] on the cobalt–diene complexes.

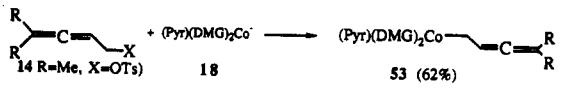
When complex **29** was treated with a slight excess of bromine followed by an aqueous base workup, cyclohexenone **46** was isolated as well as the cobalt bromide **47**. Similarly, when **29** was treated with HCl(g) followed by H_2O_2 at low temperature and no aqueous workup was performed, we isolated dichlorocyclohexene **48** and the pyridinium salt of (dmg)$_2$CoCl$_2$ (**49**) mentioned above. We suspect that both of these reactions proceed by initial halogen-induced oxidative cleavage of the cobalt–carbon bond in **29** to produce a vinyl halide which is subsequently oxidized by allylic halogenation. Aqueous-base-induced hydrolysis/elimination of the dibromo analog of **48** would account for the formation of **46** from treatment of **29** with Br_2. To explore the possibility of finding another route to ketones like **41**, cycloadduct **25** was treated with manganese acetate followed by titanium trichloride. Manganese acetate was known to oxidatvely cleave cobalt–carbon bonds[20] in related complexes to yield glyoxime ethers of the group bound to cobalt, and we suspected that the N–O bonds in these ethers could be cleaved using $TiCl_3$.[21] However, the only organic product isolated from this reaction was the dihydronapthoquinone **50**. These cleavage reactions demonstrate that cobalt–diene complexes **19–22** can serve as synthons for a variety of 1,3-dienes such as 1,3-butadiene, 2-(trimethylsiloxy)-1,3-butadiene, isoprene, (*E*)-1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Danishefsky's diene),[47] and 1,2-dichloro-1,3-butadiene.



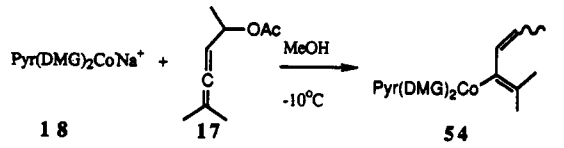
The synthesis of the allenic electrophiles required to prepare more highly substituted diene complexes was also presented in Table 1. Reaction of cobalt anion **18**, (L = pyr or DMAP) with pentadienyl acetate **15** or pivalate **16** yields exclusively the pentadienyl complexes of *E* geometry (**51** and **52**). This result



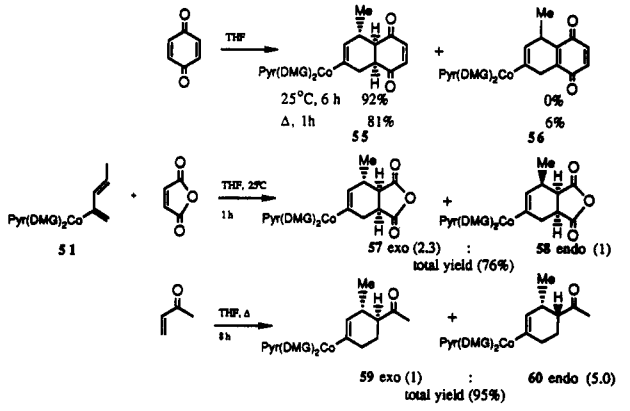
was expected on the basis of analogy to reactions of non-transition-metal nucleophiles with the acetate **15**.[13] The yields reported for these air-stable orange-yellow complexes (**51** and **52**) are after recrystallization from methanol. Reaction of this same cobalt anion (**18**, L = pyr) with the terminally disubstituted allenic tosylate **14** produced the S_N2 product **53** whereas when **18** reacts with allenic pivalate **17**, the S_N2' product **54** was again isolated



albeit as a 2.5:1 mixture of Z/E isomers (29%). Steric hindrance near the sp carbon in **14** would appear to determine the outcome of that reaction, and production of **54** indicates that substitution goes back to S_N2' for more highly substituted allenes.



There are many instances where acyclic *Z*-dienes do not react cleanly endo in Diels–Alder reactions; therefore, *E*-dienes which react cleanly exo could solve some long-standing relative stereochemistry problems.[22,24,48] Cobalt complex **51** was first treated with three dienophiles of differing sizes (benzoquinone, maleic anhydride, and methyl vinyl ketone) in THF. Benzoquinone cyclized at 25 °C in high yield to exclusively provide the cobalt substituted adduct **55** *resulting from an exo Diels–Alder reaction. This E-diene/exo Diels–Alder reaction provides mild access to the relative stereochemistry which cannot be obtained cleanly via standard thermal or Lewis acid catalyzed reactions of (Z)-piperylene with benzoquinone.*[24] Proof of relative stereochemistry in **55** was done by spectroscopic comparison to an authentic sample after cobalt–carbon bond cleavage and will be discussed below. When **51** was heated with benzoquinone in THF, **55** was again the major product but a small amount of the dehydrogenated dihydronapthoquinone **56** was isolated as well. This dehydrogenation is known to be a problem for thermal and Lewis acid-catalyzed Diels–Alder reactions of quinones.[22,24,36d] Likewise, maleic anhydride reacted with **51** to produce mainly (2.3:1, 76%) but not exclusively the exo product **57** and the smaller methyl vinyl ketone reacted with clean regiochemistry but switched to the classical endo preference (**60**) (5:1, 95%).



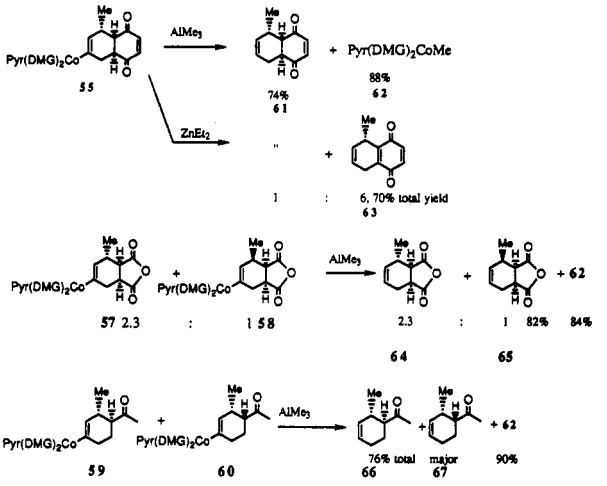
Treatment of cobalt complex **55** with $AlMe_3$ yielded tetrahydronapthoquinone **61** and cobalt methyl **62**. We prepared an authentic sample of **61** in low yield from (*Z*)-piperylene and benzoquinone using the copper catalyst (CuCl–NH_4).[24] We as well as others have noted that these tetrahydronapthoquinones are extremely sensitive to dehydrogenation to produce dihy-

(46) (a) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443. (b) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449.

(47) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

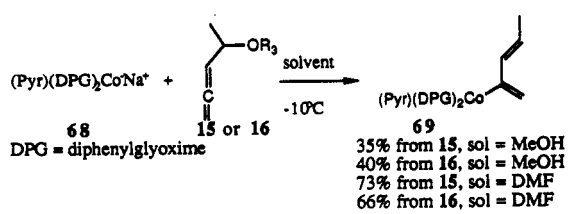
(48) For some examples of thermal and Lewis-acid catalyzed reactions of *Z*-dienes and 1,1-disubstituted 1,3-dienes, see refs 22 and 24 above as well as: (a) Craig, D. *J. Am. Chem. Soc.* **1943**, *65*, 1006. (b) Craig, D. *J. Am. Chem. Soc.* **1950**, *72*, 1678. (c) Grummitt, O.; Christoph, F. J. *J. Am. Chem. Soc.* **1951**, *73*, 3479. (d) Bachman, G.B.; Goebel, C. G. *J. Am. Chem. Soc.* **1942**, *64*, 787. (e) Goldman, N. L. *Chem. and Ind.* **1963**, 1036. (f) Ichikizaki, I.; Arai, A. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 432. (g) Arai, A.; Ichikizaki, I. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 45. (h) Engler, T. A.; Sampath, U.; Vander Velde, D.; Takusagawa, F. *Synth. Commun.* **1992**, *22*, 2031–2042. (i) Engler, T. A.; Sampath, U.; Naganathan, S.; Vander Velde, D.; Takusagawa, F.; Yohannes, D. *J. Org. Chem.* **1989**, *54*, 5712.

dronaphthoquinones when in the presence of Lewis or Bronsted acids.[22, 23, 36d] It is important from a synthetic standpoint that none of the dehydrogenated product is seen in this cobalt-mediated chemistry when the cycloaddition is run at 25 °C. It is also interesting to note that no isomerization of the stereocenters α to the carbonyl occurred in these cleavages. In our cleavage reactions of cycloadducts of the butadiene complex **19**, trialkyl aluminum and diethylzinc were interchangeable; however, here we found that if complex **55** was treated with diethylzinc followed by aqueous workup, a mixture of the di- and tetrahydronaphthoquinones **63** and **61** was isolated with the undesired dihydronapthoquinone **63** being the major product. Maleic anhydride adducts (**57** and **58**) cleave when treated with $AlMe_3$ to yield **64**[24] as the major organic product and **65** as the minor product (82%) as well as cobalt complex **62** (84%). Complexes **59** and **60** cleave to yield **66** and **67** (major),[25] proving that the selectivity has switched back to endo for this small dienophile.



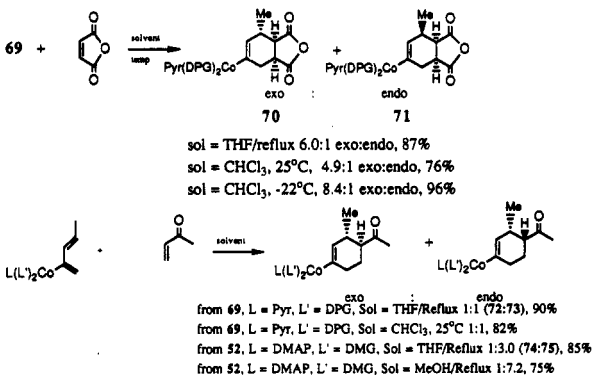
In an effort to improve the stereoselectivities of the Diels–Alder reactions of **55** with maleic anhydride and methyl vinyl ketone, we first looked at solvent and temperature effects, since many Diels–Alder reactions do show solvent effects on rates and selectivities.[39] Reaction of **55** with maleic anhydride in THF gave almost identical selectivities for **57** and **58** at reflux, 25 °C, or −78 °C. Running this reaction in xylene or chloroform produced **57** and **58** in essentially a 1:1 ratio. Solvent and temperature changes had a similarly negligible effect on the stereoselectivities of reaction of **55** with methyl vinyl ketone (MVK). Refluxing **55** with MVK in toluene produced **67**:**66** (4.8:1), in acetone (2.2:1). Treatment of **55** with MVK in EtOH at 25 °C and in $CHCl_3$ at 25 °C and −22 °C produced **67**:**66** in 4.2:1, 2.7:1, and 3.8:1 ratios, respectively. Isolated yields of **67** and **66** from all these reactions were in the range 85–95%.

Larger glyoxime ligands should favor exo selectivity to a greater extent so the complex **69** containing commercially available diphenylglyoxime ligands was prepared. Isolated yields of **69** are considerably higher from reactions performed in DMF, presumably due to increased nucleophilicity of anion **68** in this solvent compared to methanol.[26]

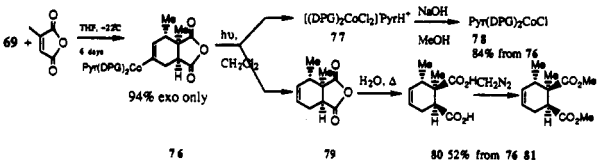


Complex **69** reacted with maleic anhydride in refluxing THF to produce **70**:**71** (87%) with an improved 6:1 exo/endo selectivity, and **69** reacted with maleic anhydride in $CHCl_3$ at −22 °C with an even greater 8.4:1 exo/endo selectivity (**70**:**71**, 96%). Complex **69** reacted with methyl vinyl ketone to produce a 1:1 mixture of exo (**72**) and endo (**73**) products in THF at reflux or $CHCl_3$ at 25 °C. Complex **69** proved unreactive toward MVK in $CHCl_3$ at −22 °C over a period of several days. Clearly we have improved exo selectivities by going to the more bulky diphenylglyoxime ligand, but additional glyoxime modifications are needed in the future to produce high exo selectivities for monosubstituted dienophiles such as MVK.

Recall from the crystallographic data presented above that electron donating pyridines increase the length of the cobalt–carbon bond in the diene; therefore, these dienes might be expected to show higher endo selectivities. Diene complex **52** reacted with MVK in THF and methanol to give crude products which were 3.0:1 mixtures of endo/exo products (**75**/**74**). The isolated cycloadducts from the methanol reaction after crystallization from methanol were a much improved 7.2:1 ratio of endo/exo (75%) (**75**/**74**) products, so a significant amount of the minor isomer can be removed via crystallization.



Piperylenes react with citraconic anhydride under thermal[27] and Lewis-acid-catalyzed[24] conditions to produce mixtures of regio- and stereoisomers, so we thought this dienophile would prove a good test of the utility of both the regio- and stereodirecting power of (pyr)(glyoxime)$_2$cobalt substitution in acyclic dienes. Under the optimum low-temperature conditions determined above, cobalt–diene **69** reacted with citraconic anhydride to produce a single regio- and stereoadduct (**76**) in 94% isolated yield. The regio chemistry as well as relative stereochemistry of this cycloadduct (**76**) was determined by cleavage to the anhydride **79** followed by hydrolysis to diacid **80** and conversion to the known dimethyl ester **81**.[24] Cobalt was also recovered from this cleavage as the chloride complex (**78**).[14]



We are not aware of any other report of such high exo selectivities for reactions of an unactivated diene synthon. Wulff et al.[6e] and Finn et al.[6j] have reported high exo selectivities for reactions of carbene complex dienophiles with activated dienes, and Gilbertson and co-workers have also reported high exo selectivities for Diels–Alder reactions of diiron-complexed dienophiles with activated dienes,[6a] so our work is complementary to their observations of transition-metal substitution in dienophiles also leading to a preference for exo products.

Summary

We have demonstrated that (pyr)(glyoxime)$_2$cobalt substituted dienes are readily prepared from S_N2' reactions of cobalt anions with allenic electrophiles. These cobalt-substituted dienes are

air-stable, crystalline complexes which also have high thermal stability. The diene moiety in these complexes exists in an unusual conformation with diene torsion angles of 50–60°. These diene complexes are very reactive toward a range of dienophiles in Diels–Alder reactions. A single diene complex can serve as a synthon for a host of dienes by virtue of the variety of metal–carbon bond cleavages one has access to after cycloaddition. These cleavage reactions are unique in organic/organometallic chemistry in that the transition metal is also routinely recovered in a reuseable form. Pyr(glyoxime)$_2$cobalt substitution in the 2-position of a 1,3-diene also leads to a high preference for exo selective Diels–Alder reactions, so we can provide clean access to relative stereochemistries in Diels–Alder cycloadducts which have been previously difficult to obtain via thermal or Lewis-acid-catalyzed reactions. We will continue to look at diene diversity in this reaction in the future and prepare bridged bicyclic glyoxime ligands which should further improve the exo selectivities noted here. Ultimately, through the use of optically active glyoxime or salen ligands, we hope to develop acyclic dienes which will react with dienophiles in exo selective and enantioselective Diels–Alder reactions.

Acknowledgment. We thank the Wake Forest University Research and Creative Activities Fund, the Donors of the Petroleum Research Fund administered by the American Chemical Society, the National Science Foundation (Grant CHE-9321454), the Exxon Education Foundation, and the Camille and Henry Dreyfus Foundation (Henry Dreyfus Teacher–Scholar Award to M. E. W., 1994–99) for their support. Low-resolution mass spectra were obtained on an instrument purchased with the partial support of the NSF (Grant CHE-9007366). The Midwest Center for Mass Spectrometry (NSF DIR9017262) performed high-resolution mass spectral analyses. M. W. W. acknowledges Sigma Xi for a student grant-in-aid of research.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, positional parameters, bond distances, and bond angles and unit cell diagrams for **20** and **21** (23 pages); tables of structure factors for **20** and **21** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.