

Synthetic and Theoretical Studies of Cyclobuta[1,2:3,4]dicyclopentene.

**Organocobalt Intermediates in the Construction of the Unsaturated Carbon Skeleton
and their Transformation into Novel Cobaltacyclic Complexes by C-C Insertion.**

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General Procedures. All reactions were performed in flame-dried round-bottom or modified Schlenk (Kjeldahl shape) flasks fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Where necessary (so noted), solutions were deoxygenated by alternate evacuation and flushing with argon at $-78\text{ }^{\circ}\text{C}$ (three iterations). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25-mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at ~ 25 Torr (house vacuum). Flash column chromatography was performed as described by Still et al.,¹ employing 230–400 mesh silica gel. Alumina, deactivated with 10% water, was employed for flash column chromatography to purify certain compounds (so noted).

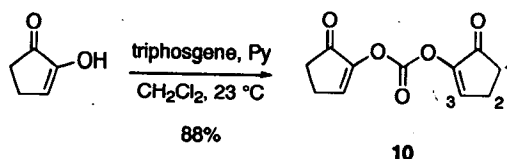
Materials. Commercial reagents were used as received with the following exceptions. Tetrahydrofuran and ethyl ether were distilled from sodium benzophenone ketyl at 760 Torr under an argon atmosphere. Methanol was distilled from magnesium methoxide at 760 Torr under a nitrogen atmosphere. Dichloromethane, *n*-hexane, pyridine, acetonitrile, and triethylamine were distilled from calcium hydride at 760 Torr under a nitrogen atmosphere. Tetrahydrofuran, ethyl ether, dichloromethane, *n*-hexane, toluene, methanol, *N,N*-dimethylformamide, pyridine, and acetonitrile were alternatively purified by the method of Pangborn et al.² Diethylamine was distilled from calcium hydride at 760 Torr under an argon atmosphere and was subsequently stored over 4-Å molecular sieves in a modified Schlenk flask. Tributyltin hydride was distilled at ~ 1 Torr and was subsequently stored in a modified Schlenk flask under an argon atmosphere at $-25\text{ }^{\circ}\text{C}$. Dichloromethane- d_2 was dried over 3-Å molecular sieves and was deoxygenated prior to use. Cesium fluoride was dried overnight under vacuum (~ 1 Torr) at $260\text{--}300\text{ }^{\circ}\text{C}$, then was cooled

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmer, F. J. *Organometallics* **1996**, *15*, 1518.

under an argon atmosphere and subsequently stored in a nitrogen-filled glove box. Lithium chloride was flame-dried under vacuum immediately prior to use. Hexamethylphosphoric triamide and 12-crown-4 were distilled from calcium hydride at ~1 Torr and were subsequently stored in modified Schlenk flasks under an argon atmosphere. Tetrahydrofuran-*d*₈ and 1,2-dimethoxyethane were vacuum transferred from sodium benzophenone ketyl at ~1 Torr. Trimethylphosphine was vacuum transferred from sodium at ~1 Torr. The molarity of *n*-butyllithium, *t*-butyllithium, and methyllithium solutions was determined by titration with a standardized toluene solution of 2-butanol using *N*-benzylidenebenzylamine as an indicator (average of three determinations).³ Solid methyllithium was prepared by careful concentration of a 1.6 M solution in ethyl ether stirring by gentle hand-swirling in a modified Schlenk flask at reduced pressure (~1 Torr, ~2–3 h). The flask was then flushed with argon, and the solid residue was stored in a nitrogen-filled glove box.

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 400 or 500 MHz. Chemical shifts for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃: δ 7.26, C₆D₅H: δ 7.15, CDHCl₂: δ 5.32, tetrahydrofuran-*d*₇: δ 3.58, CHD₂OD: δ 3.31). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125, 100, or 75 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃: δ 77.0, C₆D₆: δ 128, CD₂Cl₂: δ 53.1, tetrahydrofuran-*d*₈: δ 67.4). Data is presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad), integration, coupling constants in Hertz (Hz), and assignment. High/low resolution mass spectra were obtained at the Harvard University Mass Spectrometry Facility. X-ray crystallography was performed by Dr. Richard J. Staples at the Harvard University X-ray crystallography laboratory. Elemental analysis was performed at the California Institute of Technology Elemental Analysis Facility.



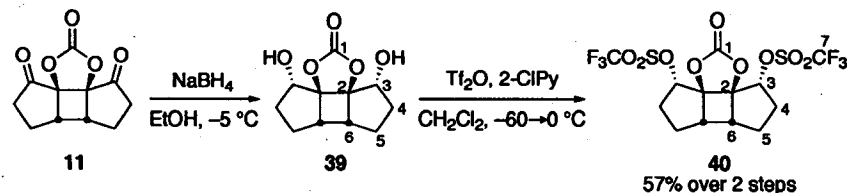
Carbonate 10. A solution of triphosgene (12 g, 40 mmol, 0.62 equiv) in dichloromethane (CH₂Cl₂, 20 mL) was transferred slowly by cannula to a stirring solution of 1,2-cyclopentanedione (6.4 g, 65 mmol, 1.0 equiv) and pyridine (7.1 mL, 88 mmol, 1.4 equiv) in CH₂Cl₂ (100 mL) at 23 °C. The addition induced a mildly exothermic process. After 12 min, the reaction mixture was placed in an ice–water bath, and any excess triphosgene that remained was then quenched by addition of aqueous sodium potassium phosphate buffer solution (pH 7, 50 mL). The resulting mixture was allowed to warm to 23 °C and then was concentrated in vacuo (to remove CH₂Cl₂). The largely aqueous layer that remained was extracted with ethyl acetate (50 mL × 5). The combined organic extracts were washed with brine (4 mL × 2) and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in minimum amount of CH₂Cl₂, and the resulting solution was filtered through a pad of Florisil® eluting with ethyl acetate. The filtrate was concentrated, furnishing the carbonate **10** (6.35 g, 88%) as a light-brown, amorphous solid. Because the carbonate **10** was unstable towards silica gel, it was used in the following step without additional purification.

¹H NMR (400 MHz, CDCl₃): δ 2.47–2.50 (m, 4H, **H2**), 2.65–2.68 (m, 4H, **H1**), 7.45 (t, 2H, *J* = 3.1 Hz, **H3**); ¹³C NMR (100 MHz, CDCl₃): δ 22.8, 32.6, 148.5, 149.6, 199.2; FTIR (neat): cm⁻¹ 1786 (s), 1725 (s), 1328 (s), 1264 (s), 1240 (s), 1062 (s), 790 (s); *R*_f 0.25 (67% ethyl acetate–hexanes).

³ Duhamel, L.; Plaquevent, J.-C.; *J. Org. Chem.* **1979**, *44*, 3404.

Tricyclic Carbonate 11. A solution of carbonate **10** (2.0 g, 9.0 mmol, 1.0 equiv) in dichloromethane (180 mL) was deoxygenated by alternate freeze-pump-thaw cycles ($\times 3$). The resulting deoxygenated solution was irradiated for 9 h using Hanovia 450-Watt medium-pressure mercury lamp with a Pyrex immersion well; the reaction vessel was water-cooled during the irradiation. After irradiation, the reaction mixture was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (40% ethyl acetate–hexanes) to afford the tricyclic carbonate **11** (0.97 g, 48%) as a white crystalline solid.

^1H NMR (400 MHz, CD_3CN): δ 2.09–2.17 (m, 4H, **H2**), 2.26–2.37 (m, 2H, **H2**), 2.50–2.58 (m, 4H, **H1**), 3.50–3.57 (m, 2H, **H3**); ^{13}C NMR (100 MHz, CDCl_3): δ 22.8, 32.6, 148.5, 149.6, 199.2; FTIR (neat): cm^{-1} 1786 (s), 1725 (s), 1328 (s), 1264 (s), 1240 (s), 1062 (s), 790 (s); R_f 0.25 (67% ethyl acetate–hexanes).



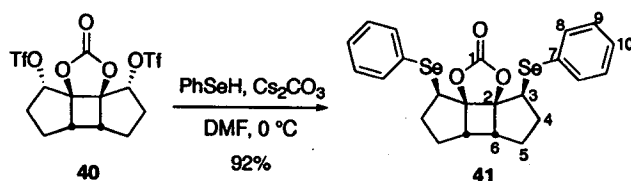
Trifluoromethanesulfonic Acid Ester 40. A suspension of sodium borohydride (3.55 g, 96.4 mmol, 2.0 equiv) in ethanol (50 mL) was transferred by cannula over 15 min to a stirring solution of dione **11** (10.7 g, 48.2 mmol, 1.0 equiv) in ethanol (150 mL) at $-5\text{ }^\circ\text{C}$. After 1.25 h, saturated aqueous ammonium chloride solution (50 mL) was added dropwise to the reaction mixture at $-5\text{ }^\circ\text{C}$ to quench any excess sodium borohydride that remained and to hydrolyze boronic esters generated during the reaction. After the evolution of hydrogen gas ceased, the resulting mixture was allowed to warm to $23\text{ }^\circ\text{C}$ and then was concentrated in vacuo (to remove ethanol). The largely aqueous layer that remained was extracted with ethyl acetate ($3 \times 50\text{ mL}$). The organic extracts were combined and were dried over anhydrous sodium sulfate, and the dried extracts were then filtered. The filtrate was concentrated in vacuo, affording the crude diol **39** (8.80 g, 81%) as an amorphous, light brown solid. Because **39** was unstable towards silica gel, the crude diol **39** was used in the following step without further purification.

Neat trifluoromethanesulfonic anhydride (10 mL, 59 mmol, 2.8 equiv) was added slowly to a stirring solution of the crude diol **39** from the previous step (4.7 g, 21 mmol, 1.0 equiv) and 2-chloropyridine (7.2 mL, 76 mmol, 3.6 equiv) in dichloromethane (200 mL) at $-60\text{ }^\circ\text{C}$.⁴ After 45 min, the reaction flask was placed in an ice bath. After 5 min, any excess trifluoromethanesulfonic anhydride that remained was quenched by the addition of aqueous sodium potassium phosphate buffer solution (pH 7, 80 mL). The aqueous and organic layers were separated, and the aqueous layer was extracted with dichloromethane ($3 \times 30\text{ mL}$). The combined organic layers were washed with brine and were dried over anhydrous sodium sulfate. The dried organic layers were then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (50% ethyl acetate–hexanes), affording the trifluoromethanesulfonic acid ester **40** (7.1 g, 69%) as an off-white, crystalline solid.

Diol 39. ^1H NMR (400 MHz, CDCl_3): δ 1.75–2.21 (m, 8H, **H4**, **H5**), 2.94 (m, 2H, **H6**), 4.46 (t, 2H, $J = 8.4\text{ Hz}$, **H3**); ^{13}C NMR (100 MHz, CDCl_3): δ 20.7 (2C, **C4**), 32.7 (2C, **C5**), 41.8 (2C, **C6**), 74.1 (2C, **C3**), 96.5 (2C, **C2**); FTIR (neat): cm^{-1} 3346 (br), 2958 (s), 2921 (s), 2851 (s), 1798 (s), 1237, 1098, 1042; Anal.: calcd for $\text{C}_{11}\text{H}_{14}\text{O}_5$, C, 58.40; H, 6.24; found, C, 58.38; H, 6.40.

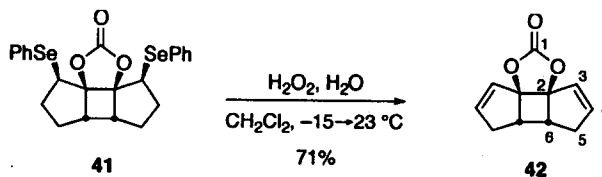
Trifluoromethanesulfonic Acid Ester 40. ^1H NMR (400 MHz, CDCl_3): δ 1.99 (dd, 2H, $J = 8.8, 15\text{ Hz}$, **H4**), 2.02 (m, 2H, **H4**), 2.42 (m, 2H, **H5**), 2.53 (m, 2H, **H5**), 3.10 (m, 2H, **H6**), 5.40 (dd, 2H, $J = 11, 8.4\text{ Hz}$, **H3**); ^{13}C NMR (100 MHz, CDCl_3): δ 20.1 (2C, **C4**), 30.1 (2C, **C5**), 40.7 (2C, **C6**), 85.0 (2C, **C3**), 92.5 (2C, **C2**), 118.4 (q, 2C, $J_{\text{C-F}} = 317\text{ Hz}$, **C7**), 151.2 (**C1**); FTIR (neat): cm^{-1} 1805 (s), 1415 (s), 1247 (s), 1206 (s), 1136 (s), 927 (s), 853 (s); R_f 0.66 (20% ethyl acetate–dichloromethane); Anal.: calcd for $\text{C}_{13}\text{H}_{12}\text{F}_6\text{O}_9\text{S}_2$, C, 31.84; H, 2.47; found, C, 32.30; H, 2.51.

⁴ Myers, A. G.; Tom, N. J.; Fraley, M. E.; Cohen, S. B.; Mader, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 6072.



Diselenide 41. Neat benzeneselenenol⁵ (3.0 mL, 29 mmol, 3.0 equiv) was added to a stirring solution of trifluoromethanesulfonic acid ester **40** (4.8 g, 9.7 mmol, 1.0 equiv) and cesium carbonate (9.5 g, 29 mmol, 3.0 equiv) in *N,N*-dimethylformamide (100 mL) at 0 °C. After 50 min, the reaction mixture was transferred to a separatory funnel containing aqueous sodium potassium phosphate buffer solution (pH 7, 100 mL), and the resulting mixture was extracted with ethyl ether–ethyl acetate (1:1, 3 × 50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, then the dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (100% hexanes→30% ethyl acetate–hexanes), affording the diselenide **41** (4.5 g, 92%) as a white, crystalline solid (mp 134 °C).

¹H NMR (400 MHz, CDCl₃): δ 1.44–1.50 (m, 2H, **H4**), 1.82–1.91 (m, 2H, **H4**), 1.94–2.03 (m, 2H, **H5**), 2.07–2.16 (m, 2H, **H5**), 3.02 (m, 2H, **H6**), 3.48 (dd, 2H, *J* = 6.6, 6.2 Hz, **H3**); ¹³C NMR (100 MHz, CDCl₃): δ 23.5 (2C, **C4**), 34.9 (2C, **C5**), 42.1 (2C, **C6**), 43.6 (2C, **C3**), 93.6 (2C, **C2**), 128.3 (2C, **C10**), 129.3 (4C, **C9**), 135.6 (4C, **C8**); FTIR (neat): cm⁻¹ 1807 (s), 1179, 1069, 741, 692; *R*_f 0.53 (40% ethyl acetate–dichloromethane); Anal.: calcd for C₂₃H₂₂O₃Se₂, C, 54.77; H, 4.40; found, C, 55.09; H, 4.45.

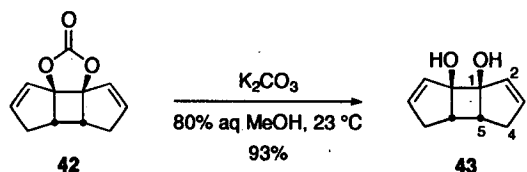


Diene 42. An aqueous solution of hydrogen peroxide (30 wt %, 3.0 mL, 29 mmol, 6.0 equiv) was added slowly to a stirring solution of diselenide **41** (2.1 g, 4.9 mmol, 1.0 equiv) in dichloromethane (80 mL) at -35 °C.⁶ The reaction mixture was then gradually warmed to 23 °C over 2 h and was maintained at that temperature for 1 h. The aqueous and organic layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were washed with brine and then were dried over anhydrous sodium sulfate. The dried organic layers were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate–hexanes), affording the diene **42** (667 mg, 71%) as a white, crystalline solid.

¹H NMR (400 MHz, CDCl₃): δ 2.31–2.38 (ddd, 2H, *J* = 18, 8.8, 2.2 Hz, **H5**), 2.53–2.63 (dddd, 2H, *J* = 19, 6.7, 4.9, 2.2 Hz, **H5**), 3.25 (m, 2H, **H6**), 5.46 (dt, 2H, *J* = 5.4, 2.2 Hz, **H4**), 6.20 (dt, 2H, *J* = 5.9, 2.2 Hz, **H3**); ¹³C NMR (100 MHz, CDCl₃): δ 31.3 (2C, **C5**), 41.6 (2C, **C6**), 100.2 (2C, **C2**), 125.1 (2C, **C4**), 125.5 (2C, **C3**), 154.9 (**C1**); FTIR (neat): cm⁻¹ 1798 (s), 1242, 1178, 1144, 1041; *R*_f 0.79 (20% ethyl acetate–dichloromethane); HRMS (CI, Ammonia) *m/z*: [M + NH₄]⁺ calcd for C₁₁H₁₄NO₃, 208.0974; found, 208.0969; Anal.: calcd for C₁₁H₁₀O₃, C, 69.47; H, 5.30; found, C, 69.32; H, 5.09.

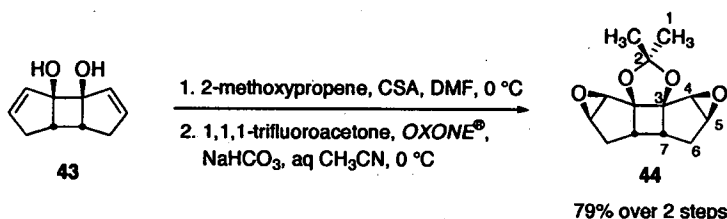
⁵ Reich, H. J.; Cohen, M. L. *J. Org. Chem.* **1979**, *44*, 3148.

⁶ Sharpless, K. B.; Lauer, R. F. A.; Teranishi, Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137.



Diol 43. An aqueous solution of potassium carbonate (1.1 M, 8.0 mL, 8.7 mmol, 2.5 equiv) was added to a stirring solution of carbonate **42** (667 mg, 3.5 mmol, 1.0 equiv) in methanol (32 mL) at 23 °C. After 2 h, aqueous sodium potassium phosphate buffer solution (pH 7, 10 mL) was added to the reaction mixture, and the resulting solution was concentrated in vacuo (to remove methanol). The largely aqueous layer that remained was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate; the dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (45% ethyl acetate–hexanes), affording the diol **43** (534 mg, 93%) as a white, crystalline solid (mp 74 °C).

¹H NMR (400 MHz, CDCl₃): δ 2.13 (dd, 2H, *J* = 18, 1.8 Hz, **H4**), 2.45 (m, 2H, **H4**), 2.77 (m, 2H, **H5**), 5.45 (ddd, 2H, *J* = 3.3, 2.6, 2.2 Hz, **H3**), 5.93 (ddd, 2H, *J* = 5.5, 2.6, 2.2 Hz, **H2**); ¹³C NMR (100 MHz, CDCl₃): δ 31.8 (2C, **C4**), 42.1 (2C, **C5**), 91.3 (2C, **C1**), 131.7 (2C, **C3**), 137.4 (2C, **C2**); FTIR (neat): cm⁻¹ 3380 (s), 3054, 3041, 2900, 1350 (s), 784; *R*_f 0.24 (20% dichloromethane–ethyl acetate); HRMS (CI, Ammonia) *m/z*: [M + NH₄]⁺ calcd for C₁₁H₁₆NO₂, 182.1181; found, 182.1175; Anal.: calcd for C₁₀H₁₂O₂, C, 73.15; H, 7.37; found, C, 72.79; H, 7.20.

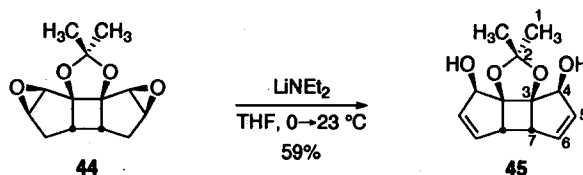


Diepoxide 44. A solution of 2-methoxypropene (500 μL, 5.2 mmol, 3.1 equiv) and 10-camphorsulfonic acid (44 mg, 0.19 mmol, 0.11 equiv) in *N,N*-dimethylformamide (2 mL) was transferred by cannula to a stirring solution of diol **43** (283 mg, 1.7 mmol, 1.0 equiv) in *N,N*-dimethylformamide (8 mL) at 0 °C. After 50 min, the reaction mixture was transferred to a separatory funnel containing aqueous sodium potassium phosphate buffer solution (pH 7.5, 10 mL), and the resulting mixture was extracted with ethyl ether (3 × 5 mL). The combined organic extracts were washed with brine (2 × 3 mL) and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo, affording the crude diene acetonide as clear oil, in quantitative yield. The crude diene acetonide was used in the following step without further purification.

Saturated aqueous sodium bicarbonate solution (15 mL), solid OXONE® (10.5 g, 17 mmol, 10 equiv), and neat 1,1,1-trifluoroacetone (500 μL, 5.6 mmol, 3.3 equiv) were added sequentially to a stirring solution of the crude diene acetonide from the previous step (1.7 mmol, 1.0 equiv) in water–acetonitrile (1:2, 30 mL) at 0 °C.⁷ After 1 h, saturated aqueous sodium bicarbonate solution (7 mL) was added to the reaction mixture, followed 2 h later by neat 1,1,1-trifluoroacetone (500 μL, 5.6 mmol, 3.3 equiv). After an additional stirring for 40 min at 0 °C, the reaction mixture was transferred to a separatory funnel containing water (30 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate; the dried organic layers were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (30% ethyl acetate–hexanes), affording the diepoxide **44** (317 mg, 79% from **43**), as a white, crystalline solid.

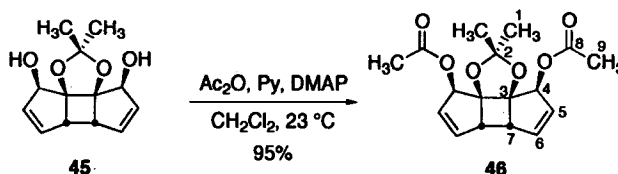
⁷ Yang, D.; Wong, M-K.; Yip, Y-C. *J. Org. Chem.* **1995**, *60*, 3887.

¹H NMR (400 MHz, CDCl₃): δ 1.54 (s, 3H, **H1**), 1.52 (s, 3H, **H1'**), 1.80 (d, 2H, *J* = 15 Hz, **H6**), 2.21 (ddd, 2H, *J* = 15, 9.2, 2.6 Hz, **H6'**), 2.43 (m, 2H, **H7**), 3.49 (d, 2H, *J* = 2.6 Hz, **H5**), 3.54 (br s, 2H, **H4**); *R*_f 0.26 (5% ethyl acetate–hexanes).



Allyl Alcohol 45. A solution of *n*-butyllithium in hexanes (1.57 M, 1.95 mL, 3.1 mmol, 10 equiv) was added to a stirring solution of diethylamine (0.32 mL, 3.1 mmol, 10 equiv) in tetrahydrofuran (1 mL) at –6 °C. After 10 min, a solution of diepoxide **44** (73 mg, 0.31 mmol, 1.0 equiv) in tetrahydrofuran (2 mL) was added to the resulting cold (–6 °C) solution of lithium diethylamide, whereupon the reaction mixture was allowed to warm to 23 °C.⁸ At this temperature, the reaction mixture was observed to form an opaque, green solution. After 12 h, saturated aqueous ammonium chloride solution (3 mL) was added dropwise to the reaction mixture, and the resulting biphasic mixture was concentrated in vacuo (to remove tetrahydrofuran and diethylamine). The largely aqueous layer that remained was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with brine (3 mL) and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (75% ethyl acetate–hexanes), affording the allyl alcohol **45** as a white, crystalline solid (44 mg, 59%).

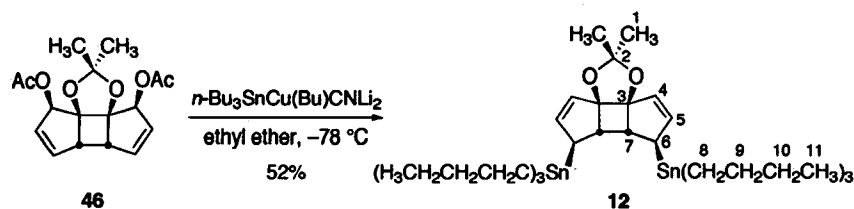
¹H NMR (400 MHz, CDCl₃): δ 1.50 (s, 3H, **H1**), 1.66 (s, 3H, **H1'**), 2.38 (br s, 2H, **H8**), 3.42 (s, 2H, **H7**), 4.46 (br s, 2H, **H4**), 5.67 (d, 2H, *J* = 6.2 Hz, **H6**), 6.00 (dd, 2H, *J* = 6.2, 2.2 Hz, **H5**); ¹³C NMR (100 MHz, CDCl₃): δ 26.7 (C1), 27.2 (C1'), 49.4 (2C, C7), 72.3 (2C, C3), 89.8 (2C, C4), 113.8 (C2), 134.0 (2C, C6), 135.6 (2C, C5); FTIR (neat): cm^{–1} 3450 (s), 1116, 1068, 971, 955, 822; *R*_f 0.37 (100% ethyl acetate); MS (CI) *m/z*: 254 ([M + NH₄]⁺).



Allyl Acetate 46. Neat acetic anhydride (100 μL, 1.1 mmol, 4.0 equiv) was added to a stirring solution of allyl alcohol **45** (63 mg, 0.27 mmol, 1.0 equiv), pyridine (200 μL, 2.5 mmol, 9.2 equiv), and 4-(dimethylamino)pyridine (6 mg, 0.047 mmol, 0.18 equiv) in dichloromethane (4 mL) at 23 °C. After 3 h, the reaction mixture was diluted with ethyl acetate (20 mL), and the diluted solution was washed sequentially with saturated aqueous sodium bicarbonate solution (3 mL), saturated aqueous ammonium chloride solution (3 mL), and brine (3 mL), and then was dried over anhydrous sodium sulfate. The dried solution was then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate–hexanes), affording the allyl acetate **46** (80 mg, 95%) as a white solid.

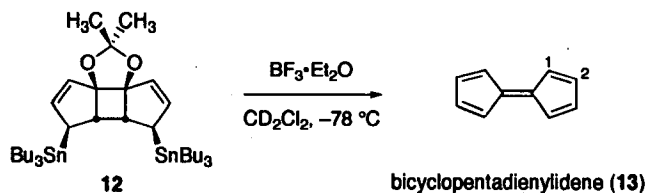
¹H NMR (500 MHz, C₆D₆): δ 1.47 (s, 3H, **H1**), 1.52 (s, 3H, **H1'**), 1.77 (s, 6H, **H9**), 3.09 (br s, 2H, **H7**), 5.28 (br d, 2H, *J* = 5.0 Hz, **H6**), 5.71 (dd, 2H, *J* = 5.0, 1.0 Hz, **H5**), 5.90 (br s, 2H, **H4**); ¹³C NMR (125 MHz, C₆D₆): δ 20.5 (2C, C9), 27.7 (C1), 28.3 (C1'), 50.5 (2C, C7), 74.2 (2C, C4), 90.0 (2C, C3), 115.1 (C2), 132.5 (2C, C6), 136.0 (2C, C5), 169.5 (2C, C8); FTIR (neat): cm^{–1} 1736 (s), 1371, 1253, 1232 (s), 1017; *R*_f 0.28 (30% ethyl acetate–hexanes).

⁸ Rickborn, B.; Thummel, R. P. *J. Org. Chem.* **1969**, *34*, 3583; *J. Am. Chem. Soc.* **1970**, *92*, 2064.



Allyl Tributylstannane 12. A solution of *n*-butyllithium in hexanes (2.62 M, 274 μL , 0.72 mmol, 7.4 equiv) was added to a stirring suspension of copper(I) cyanide (32 mg, 0.36 mmol, 3.7 equiv) in ethyl ether (Et_2O , 2 mL) at -78°C . The reaction flask was briefly removed from the dry ice–acetone bath periodically until the reaction mixture was observed to have become a homogeneous, pale yellow solution, then the resulting reaction solution was maintained at that temperature. After 20 min, neat tri-*n*-butyltin hydride (193 μL , 0.72 mmol, 7.4 equiv) was added dropwise to the resulting cold (-78°C) cuprate solution.⁹ The reaction mixture was maintained at -78°C for 25 min, and then a solution of allyl acetate **46** (31 mg, 0.097 mmol, 1.0 equiv) in Et_2O (0.8 mL) was transferred to the reaction mixture by cannula, followed by two 0.5-mL rinses (Et_2O) of the flask that contained **46**. After 30 min, aqueous sodium potassium phosphate buffer solution (pH 7, 1 mL) was added to the reaction flask, then the cooling bath was removed. After warming to $\sim 23^\circ\text{C}$, the biphasic mixture was extracted with ethyl acetate (3 mL \times 3). The combined organic extracts were washed with brine (3 mL) and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (100% pentane), affording the allyl tributylstannane **12** (39 mg, 52%) as clear oil.

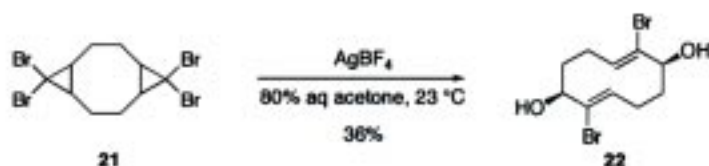
^1H NMR (500 MHz, C_6D_6): δ 0.96 (t, 18H, $J = 7.3$ Hz, **H11**), 1.08 (m, 12H, **H10**), 1.58 (m, 12H, **H9**), 1.61 (s, 3H, **H1**), 1.68 (m, 12H, **H8**), 1.71 (s, 3H, **H1'**), 2.60 (s, 2H, $J_{\text{H-Sn}} = 65$ Hz, **H6**), 3.20 (s, 2H, $J_{\text{H-Sn}} = 56$, 74 Hz, **H7**), 5.42 (dd, 2H, $J = 6.0, 2.3$ Hz, **H5**), 6.12 (dd, 2H, $J = 6.0, 2.5$ Hz, **H4**); ^{13}C NMR (125 MHz, C_6D_6): δ 10.4, 14.0, 17.8, 19.7, 28.0, 28.0, 31.2, 46.0, 102.6, 113.2, 125.7, 142.2; R_f 0.53 (10% ethyl acetate–hexanes).



Low-Temperature NMR Experiment: Formation of Bicyclopentadienylidene (13) from Distannane 12. A solution of boron fluoride ethyl etherate (5 μL , 0.04 mmol, 2.2 equiv) in dichloromethane- d_2 (CD_2Cl_2 , ca. 0.2 mL) was added to a solution of allyl tributylstannane **12** (14 mg, 0.018 mmol, 1.0 equiv) in CD_2Cl_2 (0.4 mL) in an NMR tube placed in a dry ice–acetone bath. The tube was then loaded into the pre-cooled (-78°C) probe of a 500 MHz NMR spectrometer. At -78°C , 2 new vinyl peaks assigned as proton resonances from bicyclopentadienylidene (**13**), δ 6.58 (dd, 4H, $J = 5.0, 1.5$ Hz, **H1**) and 6.68 ppm (dd, 4H, $J = 5.0, 1.5$ Hz, **H2**),¹⁰ were observed. As the probe temperature was increased from -78 to -30°C , these two peaks slowly grew, accompanied by the slow disappearance of the peaks corresponding to **12**. When the probe temperature was increased to -20°C , the emergence of a complicated pattern of peaks was observed to occur as the peaks corresponding to both **12** and **13** disappeared.

⁹ (a) Fleming, I. *Synthetic Application of Silylcuprates and Stannylcuprates*. In *Organocopper Reagents*; Taylor, R. J. K., Ed.; Oxford University Press: New York, 1994; Chapter 12. (b) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.

¹⁰ Synthesis of bicyclopentadienylidene (**13**): (a) Escher, A.; Ritsch, W.; Neuschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644. NMR spectroscopic data of **13**: (b) *Helv. Chim. Acta* **1986**, *69*, 1052.



2,7-Dibromo-*cis*-3,8-Dihydroxy-*trans,trans*-1,6-Cyclodecadiene (22). Solid 5,5,10,10-tetrabromo-1,6-cyclodecadiene (**21**) (47.8 g, 0.11 mol, 1.0 equiv) was added in portions over 10 min to a suspension of silver tetrafluoroborate (60.7 g, 0.31 mol, 3.0 equiv) in 80% aqueous acetone (320 mL) at 23 °C. The addition induced a mildly exothermic process. The reaction flask was wrapped with aluminum foil to avoid exposure to light. After 4 h, an aqueous solution of sodium carbonate (0.25 M, 500 mL) was added slowly to the reaction mixture over 5 min. After generation of carbon dioxide had ceased, the reaction mixture was filtered, and the solid was washed with ethyl acetate (100 mL). The filtrate was extracted with ethyl acetate (8 × 500 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo until to a volume of ca. 100 mL, where precipitation of white powdery solid was observed to occur. The precipitate was then collected by filtration and washed with ethyl ether. The solid collected was recrystallized from acetonitrile, affording 2,7-dibromo-*cis*-3,8-dihydroxy-*trans,trans*-1,6-cyclodecadiene (**22**) as a white, crystalline solid (12.5 g, 36%). The product **22** was further recrystallized from ethyl acetate–hexanes by the vapor-diffusion methods as follows: the recrystallized solid was dissolved in a minimum amount of ethyl acetate in a 2-mL vial, then that vial was placed in a 20-mL vial containing hexanes. Dry argon was blown into the layered vials, and the outer vial was then tightly capped and was stored at 23 °C. The single crystals obtained were subjected to X-ray crystallographic analysis (see thermal ellipsoid drawing below; CIF file submitted).

Analytical data for 2,7-dibromo-*cis*-3,8-dihydroxy-*trans,trans*-1,6-cyclodecadiene (**22**) have been previously reported.^{11a}

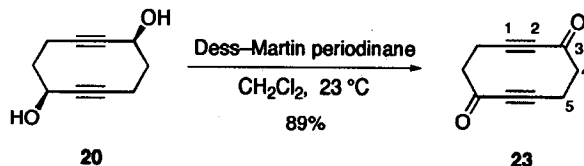


3,8-Dihydroxy-1,6-Cyclodecadiyne (20). Solid 2,7-dibromo-*cis*-3,8-dihydroxy-*trans,trans*-1,6-cyclodecadiene (**22**) (5.0 g, 0.015 mol, 1.0 equiv) was added in one portion to a suspension of sodium hydride (3.7 g, 0.15 mol, 10 equiv) in *N,N*-dimethylformamide–tetrahydrofuran (1:1, 160 mL) at 23 °C. After 9 h, the reaction mixture was cooled to 0 °C, and an aqueous solution of hydrochloric acid (1 N, ca. 15 mL) was added dropwise. The reaction mixture was diluted with ethyl acetate (100 mL), and the diluted solution was washed with an aqueous solution of hydrochloric acid (1 N, 3 × 50 mL). The aqueous layers were combined and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate solution and then were dried over anhydrous sodium sulfate.

¹¹ (a) Reese, C. B.; Shaw, A. *J. Chem. Soc., Perkins I* **1975**, 2422. (b) *J. Chem. Soc., Perkins I* **1976**, 890.

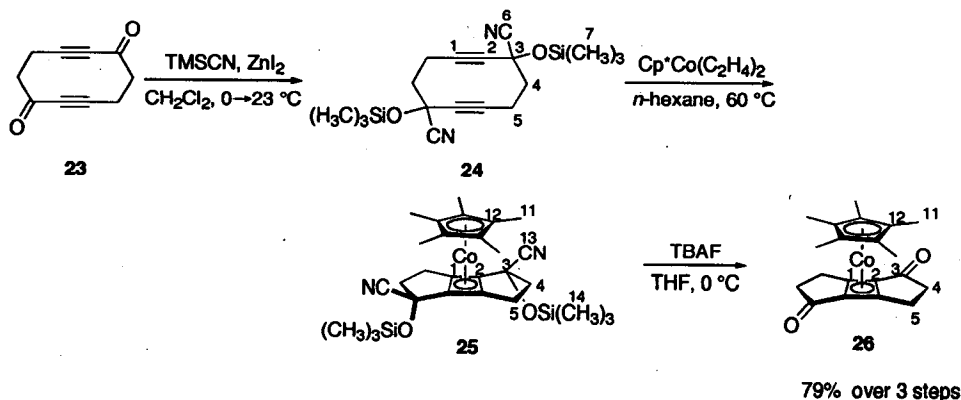
The dried extracts were filtered, and the filtrate was concentrated in vacuo for a prolonged time (to remove residual *N,N*-dimethylformamide). Purification of the residue by flash column chromatography on silica gel (50% ethyl acetate–hexanes) furnished 3,8-dihydroxy-1,6-cyclodecadiyne (**20**) (2.3 g, 90%) as a white, crystalline solid.

Analytical data for 3,8-dihydroxy-1,6-cyclodecadiyne (**20**) have been previously reported.^{11b}



3,8-Diketo-1,6-Cyclodecadiyne (23). Solid Dess–Martin periodinane (7.3 g, 17 mmol, 2.3 equiv) was added in one portion to a stirring suspension of 3,8-dihydroxy-1,6-cyclodecadiyne (**20**) (1.2 g, 7.4 mmol, 1.0 equiv) in dichloromethane (200 mL) at 23 °C. During the addition, the reaction mixture was observed to form a colorless, homogeneous solution, and so it remained throughout the reaction. After 8.5 h, the reaction mixture was cooled to 0 °C and was maintained at that temperature for 8 h. The reaction mixture was then allowed to warm to 23 °C, whereupon methanol (0.7 mL), saturated aqueous sodium bicarbonate solution (50 mL), and saturated aqueous sodium thiosulfate solution (50 mL) were added sequentially. The organic and aqueous layers were separated, and the aqueous layer was extracted with ethyl ether (3 × 50 mL). The combined organic extracts were washed sequentially with saturated aqueous sodium thiosulfate solution (10 mL) and saturated aqueous sodium bicarbonate solution (10 mL), and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (25% ethyl acetate–hexanes), affording 3,8-diketo-1,6-cyclodecadiyne (**23**) (976 mg, 82%) as a light-sensitive, white, crystalline solid (mp 125 °C).

¹H NMR (400 MHz, CDCl₃): δ 2.73 (m, 8H, **H4**, **H5**); ¹³C NMR (100 MHz, C₆D₆): δ 6.3 (2C, **C5**), 42.7 (2C, **C4**), 84.9 (2C, **C2**), 100.0 (2C, **C1**), 185.2 (2C, **C3**); FTIR (neat): cm⁻¹ 1674 (s), 1435, 1422, 1346 (w), 1264 (s), 1207 (s), 1207, 1152, 1044, 859 (s); *R*_f 0.65 (80% ethyl acetate–hexanes); HRMS (CI) *m/z*: [M + NH₄]⁺ calcd for C₁₀H₁₂NO₂, 178.0868; found, 178.0870.



(η^5 -Pentamethylcyclopentadienyl)[(1,2:6,7- η)-3,8-Diketotricyclo[5.3.0.0^{2,6}]deca-1⁷,2⁶-Diene]Cobalt

(26). Trimethylsilyl cyanide (1.0 mL, 7.5 mmol, 3.0 equiv) was added dropwise over 3 min to a stirring suspension of zinc iodide (161 mg, 0.50 mmol, 0.20 equiv) and 3,8-diketo-1,6-cyclodecadiyne (**23**) (408 mg, 2.5 mmol, 1.0 equiv) in dichloromethane (17 mL) at 0 °C. The reaction mixture was then allowed to warm to 23 °C, where it was observed to form a brown solution. After 1.25 h, the reaction mixture was carefully transferred to a separatory funnel containing saturated aqueous sodium bicarbonate solution (20 mL). The resulting biphasic mixture was extracted with hexanes (3 × 30 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution, and then were dried over anhydrous sodium sulfate. The dried extracts were filtered, and the filtrate was concentrated in vacuo,

affording the crude diastereomeric mixture (~1:1) of trimethylsilyl cyanohydrins **24**, as a brown, amorphous solid. Because the trimethylsilyl cyanohydrins **24** were unstable towards silica gel, they were used in the next step without purification.

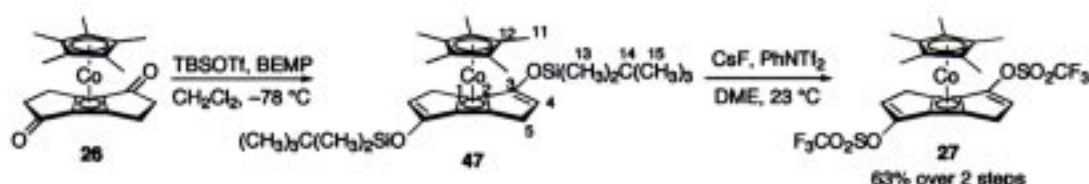
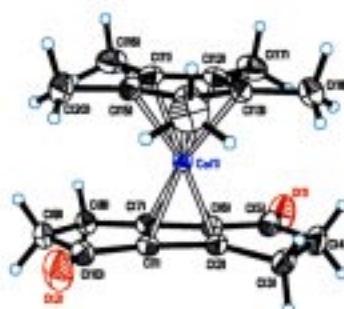
A solution of the crude diastereomeric mixture of trimethylsilyl cyanohydrins **24** from the previous step in *n*-hexane (20 mL) in a 100-mL modified Schlenk flask was deoxygenated by alternately evacuating the reaction vessel and flushing it with dry argon at -78 °C (3 ×). The deoxygenated solution was brought into a nitrogen-filled glove box, where solid bis(ethylene)(η^5 -pentamethylcyclopentadienyl)-cobalt (626 mg, 2.5 mmol, 1.0 equiv) was added to the reaction flask in one portion. The reaction mixture was removed from the glove box and was placed in an oil bath heated to 60 °C under a positive pressure of dry argon. After 1 h, the reaction mixture was removed from the oil bath. After cooling to ~23 °C, the reaction solution was filtered through a pad of Celite (eluent: 50% hexanes–ethyl acetate). Concentration of the filtrate afforded the crude trimethylsilyl cyanohydrin cobalt-cyclobutadiene complex **25** as a dark brown, amorphous solid. Because the trimethylsilyl cyanohydrin cobalt-cyclobutadiene complex **25** was also unstable towards silica gel, it was used in the next step without further purification.

A solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (THF, 1.0 M, 6.0 mL, 6.0 mmol, 2.4 equiv) was added dropwise to a stirring solution of the crude trimethylsilyl cyanohydrin cobalt complex **25** from the previous step in THF (20 mL) at 0 °C. During the addition, a bright orange solid precipitated from the dark reaction mixture. After 30 min, the reaction mixture was directly loaded onto an alumina column and (η^5 -pentamethylcyclopentadienyl)[(1,2:6,7- η)-3,8-diketotricyclo[5.3.0.0^{2,6}]deca-1⁷,2⁶-diene]cobalt (**26**) was eluted with 50% ethyl acetate–hexanes. The high crystallinity of **26** required a polar solvent system (50% ethyl acetate–hexanes) to dissolve and elute **26** from the alumina column, which made isolation of **26** difficult. Therefore repeated alumina column purification (25% → 50% ethyl acetate–hexanes) was necessary to obtain pure **26**, a bright orange, crystalline solid (700 mg, 79% from **23**, mp 198 °C dec). The product **26** was recrystallized from the THF–*n*-hexane by the vapor-diffusion methods at -25 °C as follows: the chromatographed solid was dissolved in a minimum amount of THF in a 2-mL vial, and that vial was placed in a 20-mL vial containing *n*-hexane. Dry argon was blown into the layered vials, and the outer vial was then tightly capped and was stored in a freezer (-25 °C). The single crystals obtained were subjected to X-ray crystallographic analysis (see thermal ellipsoid drawing below; CIF file submitted).

Trimethylsilyl Cyanohydrins 24. ¹H NMR (400 MHz, CDCl₃): δ 0.26 (s, 9H, **H7**), 0.28 (s, 9H, **H7'**), 1.70 (m, 4H, **H4**), 1.72–2.05 (m, 4H, **H5**); ¹³C NMR (100 MHz, C₆D₆): δ 0.9 (6C, **C7**), 13.7 (2C, **C5**), 39.9 (2C, **C4**), 63.5 (2C, **C3**), 79.2 (2C, **C1**), 89.8 (2C, **C2**), 118.8 (2C, **C6**); FTIR (neat): cm⁻¹ 2961 (w), 1254, 1164 (w), 1098 (s), 989 (w), 846 (s); *R*_f 0.63 (30% ethyl acetate–hexanes); HRMS (CI) *m/z*: [M + NH₄]⁺ calcd for C₁₈H₃₀N₃O₂Si₂, 376.1877; found, 376.1883.

Trimethylsilyl Cyanohydrin Cobalt-Cyclobutadiene Complex 25. ¹H NMR (400 MHz, C₆D₆): δ 0.19 (s, 18H, **H14**), 1.63 (ddd, 2H, *J* = 14, 4.8, 3.2 Hz, **H4**, syn to cobalt), 1.74 (s, 15H, **H11**), 1.94 (ddd, 2H, *J* = 14, 8.0, 8.0 Hz, **H4**, anti to cobalt), 2.21 (m, 4H, **H5**); ¹³C NMR (100 MHz, C₆D₆): δ 0.9 (6C, **C14**), 9.5 (5C, **C11**), 22.6 (2C, **C5**), 47.1 (2C, **C4**), 72.1 (2C, **C3**), 72.6 (2C, **C1**), 74.3 (2C, **C2**), 90.1 (5C, **C12**), 120.4 (2C, **C13**); FTIR (neat): cm⁻¹ 2955 (w), 1253 (s), 1074 (s), 98.14 (w), 844 (m); *R*_f 0.69 (30% ethyl acetate–hexanes); HRMS (FAB) *m/z*: [M]⁺ calcd for C₂₈H₄₁CoN₂O₂Si₂, 552.2039; found, 552.2026.

(η^5 -Pentamethylcyclopentadienyl)[(1,2:6,7- η)-3,8-Diketotricyclo[5.3.0.0^{2,6}]deca-1⁷,2⁶-Diene]Cobalt (26**).** ¹H NMR (400 MHz, C₆D₆): δ 1.36 (s, 15H, **H11**), 1.93 (m, 4H, **H5**), 2.14 (m, 4H, **H4**); ¹³C NMR (100 MHz, C₆D₆): δ 7.9 (5C, **C11**), 21.2 (2C, **C5**), 42.3 (2C, **C4**), 68.8 (2C, **C2**), 89.1 (2C, **C1**), 89.9 (5C, **C12**), 199.1 (2C, **C3**); FTIR (neat): cm⁻¹ 2920, 1674 (s), 1381, 1302, 1270, 1056, 880; *R*_f 0.25 (80% ethyl acetate–hexanes); HRMS (ES) *m/z*: [M + H]⁺ calcd for C₂₀H₂₄CoO₂, 355.1108; found, 355.1111.

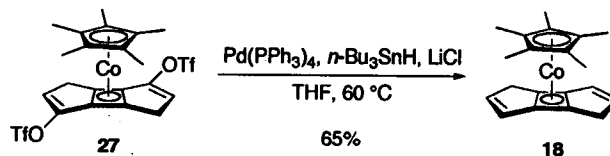


Trifluoromethanesulfonic Acid Ester Cobalt-Cyclobutadiene Complex 27. Neat 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza-phosphorine (1.3 mL, 4.5 mmol, 3.0 equiv) was added dropwise to a stirring solution of diketone cobalt-cyclobutadiene complex **26** (539 mg, 1.5 mmol, 1.0 equiv) in dichloromethane (30 mL) at $-78\text{ }^{\circ}\text{C}$, followed by the slow addition of neat *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 840 μL , 3.7 mmol, 2.4 equiv). During the addition of TBSOTf, the bright orange reaction mixture was observed to form a dark red solution, immediately returning to the original color upon completion of the reaction. After 15 min, any excess TBSOTf that remained was quenched by the addition of methanol (1 mL) to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was then allowed to warm to $23\text{ }^{\circ}\text{C}$ and was diluted with hexanes (30 mL), and the diluted solution was filtered through a pad of silica gel (pretreated with 10% triethylamine–hexanes; eluent: 10% triethylamine–hexanes). Concentration of the filtrate in vacuo furnished the crude *tert*-butyldimethylsilyl enol ether cobalt-cyclobutadiene complex **47** as thick, brown oil. Because the *tert*-butyldimethylsilyl enol ether cobalt-cyclobutadiene complex **47** was unstable towards both silica gel and alumina, it was used in the next step without additional purification.

The crude *tert*-butyldimethylsilyl enol ether cobalt-cyclobutadiene complex **47** from the previous step was azeotropically dried from toluene in a 10-mL round-bottom flask, and the flask containing the dried complex was then brought into a nitrogen-filled glove box, where solid cesium fluoride (1.85 g, 12 mmol, 8.0 equiv, based on **26**), solid *N*-phenyltrifluoromethanesulfonimide (1.85 g, 5.2 mmol, 3.4 equiv, based on **26**), and 1,2-dimethoxyethane (2.5 mL) were added sequentially, and the flask was then tightly capped. The reaction mixture was removed from the glove box and was rigorously stirred for 8 h at $23\text{ }^{\circ}\text{C}$, then was directly loaded onto a pad of silica gel (pretreated with 5% triethylamine–hexanes) and was flashed with 5% triethylamine–hexanes. Concentration of the filtrate afforded the trifluoromethanesulfonic acid ester cobalt-cyclobutadiene complex **27** as an orange, crystalline solid (592 mg, 63% from **26**).

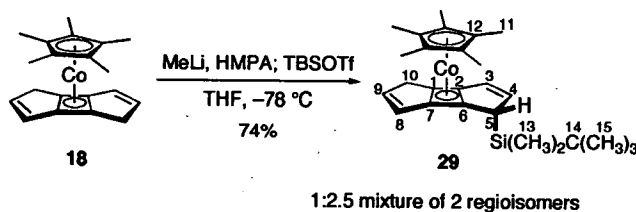
***tert*-Butyldimethylsilyl Enol Ether Cobalt-Cyclobutadiene Complex 47.** ^1H NMR (400 MHz, C_6D_6): δ 0.13 (s, 6H, **H13**), 0.16 (s, 6H, **H13'**), 0.98 (s, 18H, **H15**), 1.86 (s, 15H, **H11**), 2.33 (dd, 2H, $J = 22, 2.4\text{ Hz}$, **H5**, syn to cobalt), 2.42 (dd, 2H, $J = 22, 2.0\text{ Hz}$, **H5**, anti to cobalt), 4.91 (dd, 2H, $J = 2.4, 2.0\text{ Hz}$, **H4**); ^{13}C NMR (100 MHz, C_6D_6): δ -4.7 (2C, **C13**), -4.6 (2C, **C13'**), 9.1 (5C, **C11**), 18.3 (2C, **C14**), 25.8 (6C, **C15**), 29.6 (2C, **C5**), 70.3 (2C, **C1**), 73.8 (2C, **C2**), 88.3 (5C, **C12**), 104.2 (2C, **C4**), 154.2 (2C, **C3**); FTIR (neat): cm^{-1} 2956, 2929, 2886, 2858, 1560, 1303, 1222, 1169, 978, 865, 840, 782; R_f 0.77 (50% ethyl acetate–hexanes; a triethylamine-pretreated TLC plate was used); HRMS (ES) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{32}\text{CoO}_2\text{Si}_2$, 583.2838; found, 583.2841.

Trifluoromethanesulfonic Acid Ester Cobalt-Cyclobutadiene Complex 27. ^1H NMR (400 MHz, C_6D_6): δ 1.58 (s, 15H, H11), 1.98 (dd, 2H, $J = 23, 2.4$ Hz, H5, syn to cobalt), 2.12 (dd, 2H, $J = 23, 2.4$ Hz, H5, anti to cobalt), 4.98 (dd, 2H, $J = 2.4, 2.4$ Hz, H4); ^{13}C NMR (100 MHz, C_6D_6): δ 8.6 (5C, C11), 29.1 (2C, C5), 69.2 (2C, C1), 69.9 (2C, C2), 89.6 (5C, C12), 114.6 (2C, C4), 119.0 (q, 2C, $J_{\text{C-F}} = 320$ Hz, C13), 148.5 (2C, C3); FTIR (neat): cm^{-1} 2924, 1560, 1427 (s), 1214 (s), 1105, 961, 918, 854; R_f 0.77 (50% ethyl acetate–hexanes); HRMS (ES) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{22}\text{CoF}_6\text{O}_6\text{S}_2$, 616.9937; found, 616.9938.



(η^5 -Pentamethylcyclopentadienyl)[(1,2:6,7- η)Tricyclo[5.3.0.0^{2,6}]deca-1⁷,2⁶,3,8-Tetraene]Cobalt (18). A mixture of trifluoromethanesulfonic acid ester cobalt-cyclobutadiene complex 27 (151 mg, 0.24 mmol, 1.0 equiv), tri-*n*-butyltin hydride (132 μL , 0.49 mmol, 2.0 equiv), and lithium chloride (108 mg, 2.5 mmol, 10 equiv) in tetrahydrofuran (40 mL) in a 100-mL modified Schlenk flask was deoxygenated by alternately evacuating the reaction vessel and flushing it with dry argon at -78 $^\circ\text{C}$ (3 \times). To the cold (-78 $^\circ\text{C}$) deoxygenated mixture, under a gentle flow of dry argon, solid tetrakis(triphenylphosphine)palladium(0) (111 mg, 0.096 mmol, 0.40 equiv) was added in one portion, and the resulting mixture was promptly deoxygenated by the same procedure described above. The deoxygenated reaction mixture was placed in an oil bath heated to 60 $^\circ\text{C}$ and was maintained at that temperature for 30 min. The reaction mixture was then removed from the oil bath. After cooling to ~ 23 $^\circ\text{C}$, the reaction mixture was diluted with hexanes (40 mL), and the diluted solution was filtered through a pad of alumina (eluent: hexanes). The filtrate was concentrated in vacuo. The residue was purified by repeated flash column chromatography on alumina (100% *n*-pentane), affording (η^5 -pentamethylcyclopentadienyl)[(1,2:6,7- η)tricyclo[5.3.0.0^{2,6}]deca-1⁷,2⁶,3,8-tetraene]cobalt (18) (51 mg, 65%) as an acid- and oxygen-sensitive, brown-orange, crystalline solid (mp 130 $^\circ\text{C}$ dec).

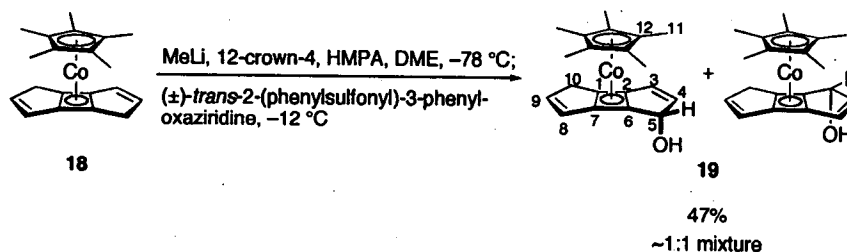
^1H NMR (500 MHz, C_6D_6): δ 1.73 (s, 15H, H11), 2.19 (dd, 4H, $J = 2.5, 2.5$ Hz, H5), 5.70 (dt, 2H, $J = 5.0, 2.5$ Hz, H4), 6.08 (dt, 2H, $J = 5.0, 2.5$ Hz, H3); ^{13}C NMR (100 MHz, C_6D_6): δ 9.2 (5C, C11), 32.9 (2C, C5), 70.8 (2C, C1), 79.7 (2C, C2), 87.9 (5C, C12), 129.3 (2C, C4), 130.4 (2C, C3); FTIR (neat): cm^{-1} 2885 (w), 1148; R_f 0.69 (30% ethyl acetate–hexanes; a triethylamine-pre-treated TLC plate was used.); HRMS (EI) m/z : $[\text{M} - \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{Co}$, 321.1053; found, 321.1054.



***tert*-Butyldimethylsilane Cobalt-Cyclobutadiene Complex 29.** A solution of methyllithium in ethyl ether (1.54 M, 14 μL , 0.022 mmol, 1.1 equiv) was added dropwise to a stirring solution of diene cobalt-cyclobutadiene complex 18 (6 mg, 0.020 mmol, 1.0 equiv) and hexamethylphosphoric triamide (18 μL , 0.10 mmol, 5.0 equiv) in tetrahydrofuran (0.5 mL) at -78 $^\circ\text{C}$. During the addition, the pale yellow reaction mixture was observed to form a deep red solution. After 30 min, neat *tert*-butyldimethylsilyl trifluoromethanesulfonate (8 μL , 0.33 mmol, 1.7 equiv) was added to the reaction mixture at -78 $^\circ\text{C}$, causing the deep red color of the reaction mixture to become black. After additional stirring for 15 min at -78 $^\circ\text{C}$, triethylamine (50 μL) was added to the reaction mixture and any excess *tert*-butyldimethylsilyl trifluoromethanesulfonate that remained was quenched by the addition of methanol (50 μL) at -78 $^\circ\text{C}$. The resulting mixture was allowed to warm to 23 $^\circ\text{C}$ and then was diluted with hexanes (3 mL), and the diluted solution was filtered through a pad of silica gel (pretreated with 4% triethylamine–hexanes; eluent: 4%

triethylamine–hexanes). Concentration of the filtrate furnished a regioisomeric mixture (1:2.5) of *tert*-butyldimethylsilane cobalt-cyclobutadiene complexes **29** as yellow oil (8 mg, 74%).

^1H NMR (500 MHz, C_6D_6 , 1:2.5 mixture of regioisomers, major isomer noted by *): δ –0.22 (s, 3H, **H13**), –0.20 (s, 3H, **H13***), –0.06 (s, 3H, **H13***), –0.04 (s, 3H, **H13***), 0.96 (s, 9H, **H15**), 0.98 (s, 9H, **H15***), 1.73 (s, 15H, **H11**), 1.77 (s, 15H, **H11***), 2.14–2.24 (m, 3H, **H5**, **H10**, **H5***, **H10***), 5.67 (m, 1H, **H4**), 5.70 (m, 1H, **H4***), 5.84 (m, 1H, **H9**), 5.88 (m, 1H, **H9***), 6.10 (m, 2H, **H8***, **H3***), 6.17 (m, 2H, **H8**, **H3**); ^{13}C NMR (125 MHz, C_6D_6): δ –8.4, –6.3, 9.2, 17.7, 27.1, 32.9, 34.7, 69.5, 74.4, 77.4, 81.8, 87.6, 126.3, 129.4, 130.0, 132.5; FTIR (neat): cm^{-1} 3077 (s), 2952 (s), 2926 (s), 2897 (s), 2854, 1480, 1469 (s), 1443, 1379, 1282, 1248 (s), 1152 (s), 1060, 927 (s), 834 (s), 723, 701 (s); R_f 0.73 (100% pentane; a triethylamine-pretreated TLC plate was used.); HRMS (ES) m/z : $[\text{M}]^+$ calcd for $\text{C}_{26}\text{H}_{37}\text{CoSi}$, 436.1997; found, 436.2005.

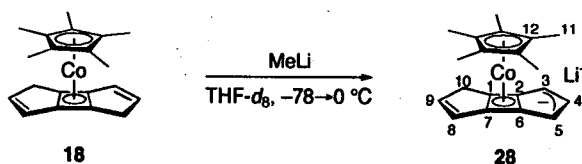


Diene Alcohol Cobalt-Cyclobutadiene Complex 19. A solution of methyllithium in ethyl ether (1.42 M, 245 μL , 0.35 mmol, 1.1 equiv) was added dropwise to a stirring solution of diene cobalt-cyclobutadiene complex **18** (103 mg, 0.32 mmol, 1.0 equiv), hexamethylphosphoric triamide (600 μL , 3.4 mmol, 11 equiv), and 12-crown-4 (75 μL , 0.46 mmol, 1.4 equiv) in 1,2-dimethoxyethane (DME, 20 mL) at –78 °C. During the addition, the yellow-brown reaction mixture was observed to become a dark red solution. After 30 min, the reaction flask was transferred to an ice–salt bath. After 5 min, a precooled (–12 °C) solution of (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine (126 mg, 0.48 mmol, 1.5 equiv) in DME (0.5 mL) was transferred rapidly by cannula to the reaction mixture, followed by two 0.5-mL rinses (DME) of the flask that contained (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine, whereupon the dark red color of the reaction mixture was observed to become yellow-brown. After an additional stirring for 15 min at –12 °C, saturated aqueous ammonium chloride solution (300 μL) was added to the reaction mixture, and then the reaction flask was removed from the cooling bath. After warming up to ~23 °C, the reaction mixture was diluted with 1:4:20 triethylamine–ethyl acetate–hexanes (30 mL), and the diluted solution was filtered through a pad of silica gel (pretreated with 1:4:20 triethylamine–ethyl acetate–hexanes; eluent: 1:4:20 triethylamine–ethyl acetate–hexanes). The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (1:2:47 triethylamine–ethyl acetate–hexanes), affording a regioisomeric mixture (ca. 1:1) of the diene alcohol cobalt-cyclobutadiene complexes **19** (47 mg, 44%) as a yellow-brown, amorphous solid. Repeated column chromatography purification on silica gel (1:2:47 triethylamine–ethyl acetate–hexanes) of the regioisomeric mixture of **19** eventually afforded each isomer in pure form.

Diene Alcohol Cobalt-Cyclobutadiene Complex (less polar isomer) 19. ^1H NMR (500 MHz, C_6D_6): δ 1.64 (s, 15H, **H11**), 2.18 (ddd, 1H, $J = 23, 2.5, 2.0$ Hz, **H10**, syn to cobalt), 2.26 (ddd, 1H, $J = 23, 2.5, 2.0$ Hz, **H10**, anti to cobalt), 4.56 (br s, 1H, **H5**), 5.71 (dd, 1H, $J = 5.0, 2.0$ Hz, **H3**), 5.73 (ddd, 1H, $J = 5.5, 2.0, 2.0$ Hz, **H9**), 5.97 (dd, 1H, $J = 5.0, 1.0$ Hz, **H4**), 6.09 (ddd, 1H, $J = 5.5, 2.5, 2.5$ Hz, **H8**); ^{13}C NMR (125 MHz, C_6D_6): δ 9.2, 33.0, 74.6, 88.5, 129.2, 131.4, 131.4, 134.1; FTIR (neat): cm^{-1} 3369 (br), 2942, 2902 (s), 1379, 1280, 1152, 1096, 1027, 1012; R_f 0.36 (30% ethyl acetate–hexanes; a triethylamine-pretreated TLC plate was used.); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{CoO}$, 338.1081; found, 338.1077.

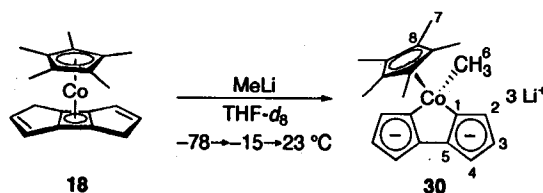
Diene Alcohol Cobalt-Cyclobutadiene Complex (polar isomer) 19. ^1H NMR (500 MHz, C_6D_6): δ 1.63 (s, 15H, **H11**), 2.15 (d, 1H, $J = 23$ Hz, **H10**, syn to cobalt), 2.33 (d, 1H, $J = 23$ Hz, **H10**, anti to cobalt), 4.50 (br s, 1H, **H5**), 5.69 (dd, 1H, $J = 5.5, 1.8$ Hz, **H3**), 5.71 (ddd, 1H, $J = 4.5, 2.0, 2.0$ Hz, **H9**), 6.00 (dd, 1H, $J = 5.5, 1.0$ Hz, **H4**), 6.05 (d, 1H, $J = 4.5$ Hz, **H8**); ^{13}C NMR (125 MHz, C_6D_6): δ 9.2, 33.2, 74.6, 74.7, 75.2, 76.9, 80.3, 88.5, 128.6, 131.2, 131.6, 133.8; FTIR (neat): cm^{-1} 3528 (br), 3387 (br), 3080 (s), 2897

(s), 1509, 1473, 1402, 1376, 1284, 1024 (s), 922, 702; R_f 0.33 (30% ethyl acetate-hexanes; a triethylamine-pretreated TLC plate was used.); HRMS (EI) m/z : $[M]^+$ calcd for $C_{20}H_{23}CoO$, 338.1081; found, 338.1077.



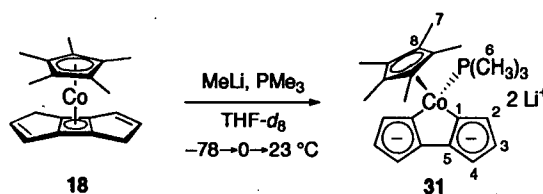
Low-Temperature NMR experiment: Formation of Monoanionic Cobalt-Cyclobutadiene Complex 28. Volatiles were removed from a solution of methyllithium in ethyl ether (1.39 M, 200 μ L, 0.28 mmol, 10 equiv) in a flame-dried NMR tube by careful concentration at ca. 1 Torr for 1 h. The NMR tube was then flushed with dry argon and was placed in a dry ice-acetone bath. Tetrahydrofuran- d_8 (THF- d_8 , 0.2 mL) and a solution of diene cobalt-cyclobutadiene complex **18** (9 mg, 0.028 mmol, 1.0 equiv) in THF- d_8 (0.45 mL) were added to the NMR tube sequentially, whereupon the NMR tube was transferred to an ice bath, causing the pale-yellow reaction mixture to darken, eventually forming a black solution. After 30 min, the sample was loaded into the probe of a 500 MHz NMR spectrometer (precooled to -30 $^{\circ}$ C), and a series of spectra of the product monolithiated cobalt-cyclobutadiene complex **28** were obtained, while maintaining the probe temperature at -30 $^{\circ}$ C, and are tabulated below. When the probe temperature was increased to 22 $^{\circ}$ C, a slow emergence of peaks corresponding to the trianionic cobaltacyclic complex **30** was observed, as further detailed in the subsequent experimental procedure.

1H NMR (500 MHz, THF- d_8 , -30 $^{\circ}$ C): δ 1.53 (d, 1H, J = 22 Hz, **H10**, syn to cobalt), 1.54 (s, 15H, **H11**), 1.96 (d, 1H, J = 22 Hz, **H10**, anti to cobalt), 4.60 (d, 1H, J = 3.0 Hz, **H3**), 4.67 (d, 1H, J = 3.0 Hz, **H5**), 5.16 (dt, 1H, J = 5.0, 2.5 Hz, **H8**), 6.17 (dt, 1H, J = 5.0, 2.5 Hz, **H9**), 6.60 (dd, 1H, J = 3.0, 3.0 Hz, **H4**); ^{13}C NMR (125 MHz, THF- d_8 , -30 $^{\circ}$ C): δ 9.5 (5C, **C11**), 34.0 (**C10**), 57.1 (**C2**), 64.6 (**C6**), 81.3 (**C3**), 81.9 (**C5**), 83.1 (5C, **C12**), 87.0 (**C1**), 89.6 (**C7**), 121.6 (**C8**), 124.0 (**C4**), 135.3 (**C9**).



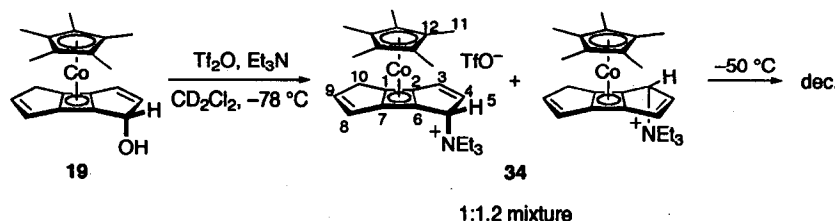
NMR Experiment: Trianionic Cobaltacyclic Complex 30. Tetrahydrofuran- d_8 (ca. 1 mL) was vacuum transferred from sodium benzophenone ketyl to a liquid-nitrogen cooled resealable pressure flask containing solid diene cobalt-cyclobutadiene complex **18** (24 mg, 0.074 mmol, 1.0 equiv) and solid methyllithium (11 mg, 0.50 mmol, 6.8 equiv). The reaction flask was flushed with dry argon, then was sealed and placed in a dry ice-acetone bath. After 8 min, the reaction vessel was transferred to an ice-salt bath, causing the pale-yellow reaction mixture to darken, eventually forming a black solution. After 1 h, the reaction mixture was removed from the cooling bath and was allowed to warm to 23 $^{\circ}$ C. At this temperature, the reaction mixture was observed to gradually form a clear, deep burgundy solution. After 7 h at 23 $^{\circ}$ C, the reaction flask was brought into a nitrogen-filled glove box, and the reaction solution was transferred by pipette to a flame-dried NMR tube. The tube was tightly capped, removed from the glove box, and then was loaded into the probe of a 500 MHz NMR spectrometer. Subsequently, a series of NMR spectra of the product trianionic cobaltacyclic complex **30** were measured at 22 $^{\circ}$ C and are tabulated below.

1H NMR (500 MHz, THF- d_8 , 22 $^{\circ}$ C): δ -1.22 (br s, 3H, **H6**), 1.54 (s, 15H, **H7**), 5.55 (br s, 2H, **H4**), 5.61 (br s, 2H, **H3**), 5.79 (br s, 2H, **H2**); ^{13}C NMR (125MHz, THF- d_8 , 22 $^{\circ}$ C): δ -5.7 (**C6**), 10.7 (5C, **C7**), 88.0 (5C, **C8**), 92.9 (2C, **C3**), 97.2 (2C, **C4**), 109.0 (2C, **C2**), 134.3 (2C, **C5**), 143.2 (2C, **C1**); NOE: **H7** \rightarrow **H2** (7.3%); **H7** \rightarrow **H6** (9.3%).



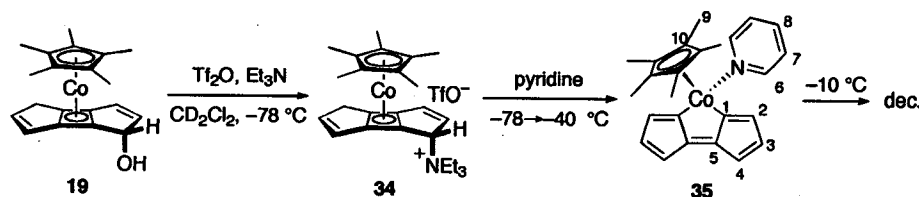
NMR Experiment: Formation of Dianionic Trimethylphosphine Cobaltacyclic Complex 31. Tetrahydrofuran- d_8 (THF- d_8 , ca. 1 mL) from sodium benzophenone ketyl and trimethylphosphine (ca. 50 μ L) from sodium were vacuum transferred sequentially to a liquid-nitrogen cooled resealable pressure flask containing solid diene cobalt-cyclobutadiene complex **18** (10 mg, 0.031 mmol, 1.0 equiv) and solid methyllithium (7 mg, 0.32 mmol, 10 equiv). The reaction vessel was flushed with dry argon, then was sealed and placed in a dry ice–acetone bath. After 15 min, the reaction flask was transferred to an ice bath, causing the pale-yellow reaction mixture to darken, eventually forming a black solution. After 45 min, the reaction mixture was removed from the cooling bath and was allowed to warm to 23 °C. At this temperature, the reaction mixture was observed to gradually form a clear, burgundy solution. After 7 h, the reaction mixture was carefully concentrated at ca. 1 Torr for 1 h (to remove any excess trimethylphosphine that remained). The reaction flask was then flushed with dry argon and was brought into a nitrogen-filled glove box, where the residue was dissolved in THF- d_8 (ca. 0.65 mL), and the resulting solution was transferred by pipette to a flame-dried NMR tube. The tube was tightly capped, removed from the glove box, and was loaded into the probe of a 500 MHz NMR spectrometer. Subsequently, a series of NMR spectra of the product dianionic trimethylphosphine cobaltacyclic complex **31** were measured at 22 °C and are tabulated below.

^1H NMR (500 MHz, THF- d_8): δ 1.21 (d, 9H, $J_{\text{P-H}} = 8.0$ Hz, **H6**), 1.65 (s, 15H, **H7**), 5.70 (br s, 4H, **H3**, **H4**), 5.84 (br s, 2H, **H2**); ^{13}C NMR: (125MHz, THF- d_8): δ 11.1 (5C, **C7**), 23.8 (d, 3C, $J_{\text{P-C}} = 16$ Hz, **C6**), 91.9 (5C, **C8**), 92.3, 99.7 (2C each, **C3**, **C4**), 109.4 (2C, **C2**), 132.5 (determined by HMBC, 2C, **C1**), 136.7 (2C, **C5**); NOE: **H7**→**H2** (4.3%); **H7**→**H6** (9.0%).



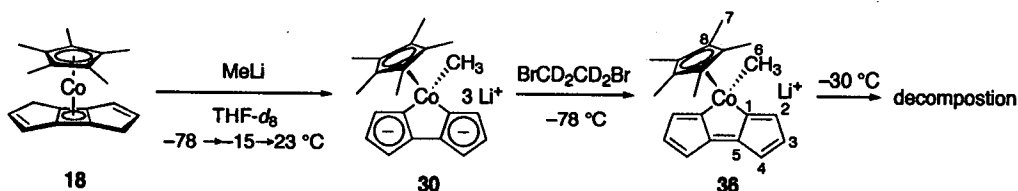
Low-Temperature NMR Experiment: Formation of Triethylammonium Salt 34. A solution of trifluoromethanesulfonic anhydride (10 μ L, 0.061 mmol, 2.5 equiv) in dichloromethane- d_2 (CD_2Cl_2 , ca. 0.2 mL) was added to a solution of diene alcohol cobalt complex **19** (8.2 mg, 0.024 mmol, 1.0 equiv) and triethylamine- d_{15} (14 μ L, 0.10 mmol, 4.2 equiv) in CD_2Cl_2 (ca. 0.4 mL) in a flame-dried NMR tube placed in a dry ice–acetone bath. During the addition, the brown reaction mixture was observed to darken, eventually forming a black solution. The tube was loaded into the precooled (–78 °C) probe of a 500 MHz NMR spectrometer, and ^1H NMR was subsequently measured. The spectrum showed a clean formation of a regioisomeric mixture (1:1.2) of the triethylammonium salts **34**. When the probe temperature was increased to –50 °C, decomposition of **34** was observed to occur.

^1H NMR (500 MHz, CD_2Cl_2 , –78 °C, 1:1.2 mixture of regioisomers, major isomer noted by *): δ 1.60 (s, 30H, **H11**, **H11***), 2.39–2.57 (m, 4H, **H10**, **H10***), 3.96 (s, 1H, **H5***), 4.00 (s, 1H, **H5**), 5.52 (br s, 1H, **H4**, **H4***), 6.07 (d, 1H, $J = 5.5$ Hz, **H8**), 6.11 (d, 1H, $J = 6.0$ Hz, **H8***), 6.13 (d, 1H, $J = 6.0$ Hz, **H9***), 6.17 (d, 1H, $J = 5.5$ Hz, **H9**), 6.61 (d, 1H, $J = 5.0$ Hz, **H3**), 6.64 (d, 1H, $J = 5.5$ Hz, **H3***); NOE (–78 °C): **H11**→**H3** (2.9%); **H11**→**H4** (2.0%); **H11**→**H5** (5.6%). Although there are equally significant NOEs between **H11**→**H8**, **H11**→**H9**, and **H11**→**H10**, due to peak overlap, the actual NOE values could not be accurately evaluated.



Low-Temperature NMR Experiment: Formation of Pyridine Cobaltacyclic Complex 35. A solution of trifluoromethanesulfonic anhydride (12 μ L, 0.068 mmol, 2.0 equiv) in dichloromethane- d_2 (CD_2Cl_2 , ca. 0.2 mL) was added to a solution of diene alcohol cobalt-cyclobutadiene complex **19** (12 mg, 0.035 mmol, 1.0 equiv) and triethylamine- d_{15} (20 μ L, 0.14 mmol, 4.0 equiv) in CD_2Cl_2 (ca. 0.4 mL) in an NMR tube placed in a dry ice-acetone bath. During the addition, the brown reaction mixture was observed to form a black solution. After 15 min, a solution of pyridine (10 μ L, 0.12 mmol, 3.5 equiv) was added to the reaction mixture at $-78^\circ C$, and the resulting reaction mixture was warmed to $-48^\circ C$ and was maintained at that temperature for 30 min. The sample was then loaded into the precooled ($-50^\circ C$) probe of a 500 MHz NMR spectrometer. By 1H NMR, it was observed that diene alcohol cobalt-cyclobutadiene complex **19** had been completely consumed, and a regioisomeric mixture of the triethylammonium salts **34** and the pyridine cobaltacyclic complex **35** had been generated. After obtaining preliminary spectra at $-50^\circ C$, the probe temperature was increased to $-40^\circ C$ and was maintained at that temperature for 20 min. It was then observed by 1H NMR that the conversion of **34** to **35** had been completed. Subsequently, the probe temperature was decreased to $-78^\circ C$, and then a series of NMR spectra of **35** were measured and are tabulated below. When the probe temperature was increased to $-10^\circ C$, decomposition of **35** was observed to occur.

1H NMR (500 MHz, CD_2Cl_2 , $-78^\circ C$): δ 1.25 (s, 15H, **H9**), 6.16 (d, 2H, $J = 5.0$ Hz, **H4**), 6.80 (br s, 2H, **H2**), 6.86 (d, 2H, $J = 5.0$ Hz, **H3**), 6.99 (dd, 2H, $J = 8.0, 5.0$ Hz, **H7**), 7.47 (t, 1H, $J = 8.0$ Hz, **H8**), 8.59 (d, 2H, $J = 5.0$ Hz, **H6**); ^{13}C NMR (125 MHz, CD_2Cl_2 , $-78^\circ C$): δ 9.2 (5C, **C9**), 91.8 (5C, **C10**), 115.1 (2C, **C4**), 124.0 (2C, **C7**), 130.5 (2C, **C2**), 136.0 (**C8**), 144.2 (2C, **C3**), 154.9 (2C, **C6**), 160.7 (2C, **C5**), 183.0 (2C, **C1**); NOE ($-78^\circ C$): **H3** \rightarrow **H2** (2.1%); **H3** \rightarrow **H4** (2.3%); **H4** \rightarrow **H3** (0.73%); **H7** \rightarrow **H6** (1.2%); **H7** \rightarrow **H8** (1.1%); **H9** \rightarrow **H2** (3.4%); **H9** \rightarrow **H6** (2.8%).



Low-Temperature NMR Experiment: Formation of Cobaltacyclic Complex 36. Tetrahydrofuran- d_8 (THF- d_8 , ca. 1 mL) was vacuum transferred from sodium benzophenone ketyl at ca. 1 Torr to a liquid-nitrogen cooled resealable pressure flask containing solid diene cobalt-cyclobutadiene complex **18** (24 mg, 0.074 mmol, 1.0 equiv) and solid methyllithium (11 mg, 0.50 mmol, 6.8 equiv). The reaction vessel was flushed with dry argon, then was sealed and placed in a dry ice-acetone bath. After 8 min, the reaction flask was transferred to an ice-salt bath, causing the pale-yellow reaction mixture to darken, eventually forming a black solution. After 1 h, the reaction mixture was removed from the cooling bath and was allowed to warm to $23^\circ C$. At this temperature, the reaction mixture was observed to gradually form a clear, deep burgundy solution. After 7 h, the reaction flask was brought into a nitrogen-filled glove box, and the reaction mixture was transferred by pipette to a flame-dried NMR tube. The tube was tightly capped and was removed from the glove box. After confirming complete generation of the trianionic cobaltacyclic compound **30** by 1H NMR, the reaction mixture was placed in a dry ice-acetone bath under a positive pressure of dry argon. A solution of 1,2-dibromoethane- d_4 (55 μ L, 0.63 mmol, 8.5 equiv) in THF- d_8 (0.1 mL) was added to the resulting cold ($-78^\circ C$) solution of **30** and methyllithium. The sample was then loaded into the probe (precooled to $-70^\circ C$) of a 500 MHz NMR spectrometer. 1H NMR analysis showed slow disappearance of **30** at $-70^\circ C$, with concomitant appearance of the cobaltacyclic complex **36**. Upon complete consumption of **30**, the NMR probe temperature was decreased to $-78^\circ C$, and a series of

NMR spectra of the product **36** were measured and are tabulated below. When the probe temperature was increased to $-30\text{ }^{\circ}\text{C}$, decomposition of **36** was observed to occur.

^1H NMR (500 MHz, $\text{THF-}d_8$, $-78\text{ }^{\circ}\text{C}$): δ 0.05 (s, 3H, **H6**), 1.43 (s, 15H, **H7**), 5.51 (d, 2H, $J = 2.5\text{ Hz}$, **H4**), 5.61 (s, 2H, **H2**), 6.25 (d, 2H, $J = 2.5\text{ Hz}$, **H3**); ^{13}C NMR (125 MHz, $\text{THF-}d_8$, $-78\text{ }^{\circ}\text{C}$): δ -2.2 (**C6**), 10.1 (**5C**, **C7**), 90.6 (**5C**, **C8**), 111.6 (**2C**, **C4**), 126.7 (**2C**, **C2**), 143.0 (**2C**, **C3**), 159.7 (**2C**, **C5**), 198.7 (**2C**, **C1**); NOE ($-78\text{ }^{\circ}\text{C}$): **H2** \rightarrow **H3** (1.8%); **H2** \rightarrow **H4** (0.86%); **H2** \rightarrow **H6** (0.15%); **H3** \rightarrow **H2** (5.4%); **H3** \rightarrow **H4** (5.4%); **H4** \rightarrow **H3** (0.73%); **H6** \rightarrow **H7** (0.27%); **H7** \rightarrow **H2** (2.3%); **H7** \rightarrow **H6** (2.3%).