

Notes

Synthesis of Planar Chiral Cobalt Metalloenes by Microwave-Assisted Diastereoselective Complexation

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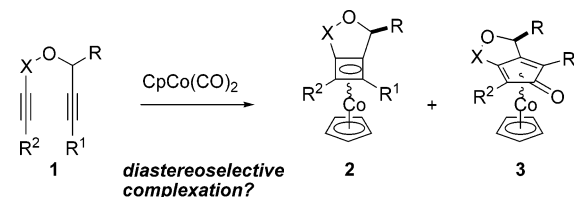
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Summary: Ether- and ester-linked diynes were readily synthesized in two steps by starting from secondary terminal propargylic alcohols. On either heat- or microwave-assisted reaction of the diynes with cyclopentadienylcobalt dicarbonyl, new planar chiral (η^5 -cyclopentadienone)(η^5 -cyclopentadienyl)cobalt metalloenes were formed with diastereomeric ratios of up to 5:1. For both the ether and ester series the identity of the major isomer was established by X-ray crystallography. The complexation method was shown to be applicable to the synthesis of scalemic planar chiral metalloenes. Preliminary investigations were carried out to transform the new complexes into other functionalized cobalt metalloenes.

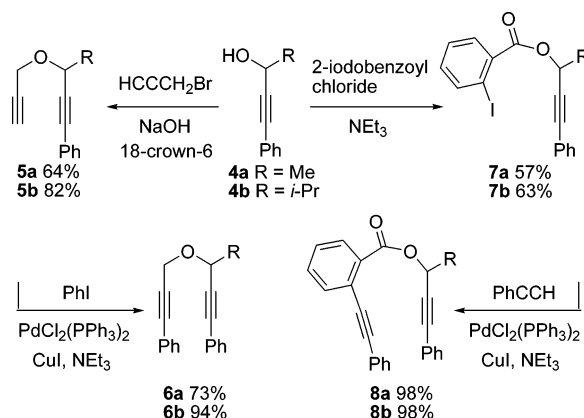
Introduction

Planar chiral metalloenes, and in particular ferrocene derivatives, have found widespread application as ligands and catalysts in asymmetric synthesis.¹ They have also been extensively employed as building blocks for the synthesis of new materials.² The vast majority of such enantiopure derivatives are generated by a three-step sequence involving (a) metallocene synthesis, (b) introduction of a chiral auxiliary or a fixed stereogenic center, and (c) diastereoselective attachment of a second substituent leading to a new element of planar chirality.³ An alternative and potentially more attractive strategy is to generate the planar chirality simultaneously with the metallocene. One way in which this has been achieved, for example for the synthesis of group 4 metalloenes, utilizes the diastereofacial complexation of auxiliary substituted cyclopentadienyl anions.⁴ In contrast, we were attracted by the potential of employing chiral diynes **1** for the stereoselective synthesis of cobalt metalloenes **2** and **3** (Scheme 1). The use of achiral diynes in such complexation reactions is well precedented,⁵ and the unwitting isolation of chiral cyclobutadiene cobalt metalloenes has also been reported.⁶ In this note we report on our initial results exploring this strategy for the stereoselective synthesis of planar chiral cyclopentadienone complexes **3**.

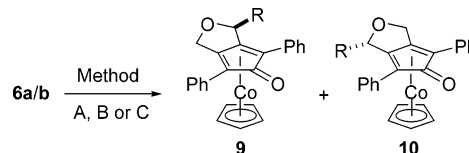
Scheme 1. General Approach to Planar Chiral Cobalt Metalloenes



Scheme 2. Synthesis of Diynes



Scheme 3. Synthesis of 5-Ring Ether Fused Metalloenes



Results and Discussion

Two different diynes of general structure **1** were employed, with X = CH₂, *o*-C₆H₄CO. The former were used to provide a new stable five-membered-ring ether and the latter to give a seven-membered-ring lactone with the potential for ring opening and further synthetic manipulation. Two examples of both classes of diene were synthesized from the propargylic alcohols **4a,b** employing a straightforward two-step procedure (Scheme 2).

A solution of diene **6a** and cyclopentadienylcobalt dicarbonyl in toluene was heated at reflux overnight. After filtration through a silica plug to remove paramagnetic impurities, the ratio of the two new dark red complexes was established by ¹H NMR spectroscopy as 4:1 (Scheme 3, Table 1, entry 1). Following

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(1) (a) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101. (b) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377.

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(3) See for example: (a) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835. (b) Rebière, F.; Riant, O.; Ricard, L.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 568.

(4) Schumann, H.; Stenzel, O.; Dechert, S.; Halterman, R. L. *Organometallics* **2001**, *20*, 1983.

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Table 1. Synthesis of 5-Ring Ether Cyclopentadienone Complexes

entry	substrate	R	conditions	yield, %	9:10 ^a
1	6a	Me	A ^b	61	4:1
2	6a	Me	B ^c	68	3.2:1
3	6b	<i>i</i> -Pr	A	47	5:1
4	6b	<i>i</i> -Pr	B	49	5:1
5	6b	<i>i</i> -Pr	C ^d	34	3.5:1

^a Ratio determined by ¹H NMR spectroscopy. ^b Conditions A: CpCo(CO)₂, toluene, 120 °C, N₂, 18 h. ^c Conditions B: CpCo(CO)₂, decalin, 190 °C, N₂, microwave, 10 min. ^d Conditions C: Co₂(CO)₈ (0.5 equiv) C₅H₆ (2 equiv), decalin, 5 min at 40 °C, 10 min at 190 °C.

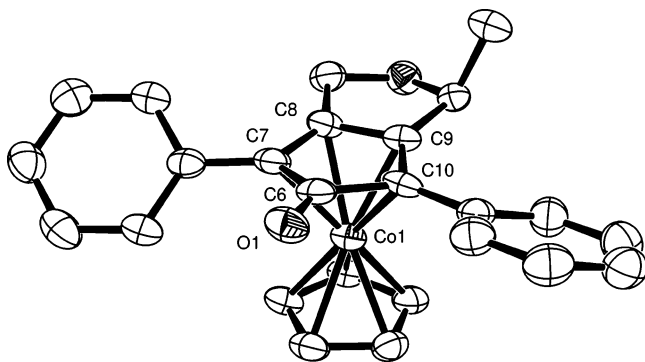


Figure 1. Representation of the X-ray crystal structure of **9a**. Selected bond lengths (Å): C(6)–O(1) = 1.247(6), C(7)–C(6) = 1.482(8), C(8)–C(7) = 1.415(7), C(9)–C(8) = 1.423(8), C(10)–C(9) = 1.438(7), C(6)–C(10) = 1.504(7).

separation by chromatography, the identity of the major product as a cyclopentadienone metallocene was established by a X-ray crystal structure determination (Figure 1).⁷

The minor product was assigned as the diastereoisomer **10a**, due to the similarity of both the color and the ¹H NMR spectrum to those of **9a** and the presence of a band at 1581 cm⁻¹ in the infrared spectrum indicative of a complexed cyclopentadienone carbonyl group. The corresponding cyclobutadiene complexes were not observed, even when the reaction was repeated while being irradiated with light, conditions which have previously been used to isolate cyclobutadiene complexes.^{6a,8}

The reaction time was shortened to only 10 min on microwave irradiation of a reaction mixture in decalin at 190 °C. Significantly, these conditions resulted in little erosion of diastereoselectivity (entry 2). In contrast, microwave irradiation of otherwise identical decalin, toluene, THF, or acetonitrile solutions up to 140 °C for 10 min resulted in yields of less than 10% and, for the last three solvents, in essentially no diastereoselectivity. Microwave irradiation has previously been employed to shorten the reaction times of the Dötz⁹ and Pauson–Khand¹⁰ annulation reactions employing Cr(CO)₆ and

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(7) Crystal data for **9a**: C₂₅H₂₁CoO₂·1/6CH₃OH, *M*_r = 417.69, trigonal, *a* = 33.155(5) Å, *b* = 33.155(5) Å, *c* = 9.4226(7) Å, α = 90.00°, β = 90.00°, γ = 120.00°, *V* = 8970(2) Å³, space group *R*3 (No. 146), *Z* = 18, *D*_c = 1.392 Mg/m³, μ = 0.880 mm⁻¹, 13 654 reflections measured, 3277 unique reflections with *R*_{int} = 0.0826, *T* = 120(2) K, final *R* indices for *I* > 2σ(*I*) *R*₁ = 0.0630, *wR*₂ = 0.1483 and for all data *R*₁ = 0.1380, *wR*₂ = 0.1829.

(8) The reaction between cyclopentadienylcobalt dicarbonyl and diphenylacetylene under thermal conditions results in the formation of both the corresponding cyclobutadiene (46%) and the cyclopentadienone (10%) complexes; see: Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, 35, 3888.

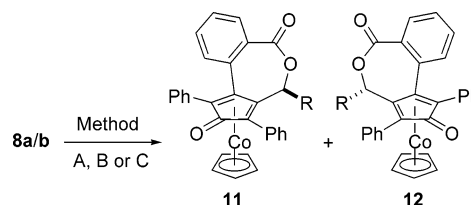
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Table 2. Synthesis of 7-Ring Lactone Cyclopentadienone Complexes

entry	substrate	R	conditions	yield, %	11:12 ^a
1	8a	Me	A ^b	21	3:1
2	8a	Me	B ^c	29	3.4:1
3	8b	<i>i</i> -Pr	A	33	4:1
4	8b	<i>i</i> -Pr	B	57	3:1
5	8b	<i>i</i> -Pr	C ^d	11	5:1

^a Ratio determined by ¹H NMR spectroscopy. ^b Conditions A: CpCo(CO)₂, toluene, 120 °C, N₂, 18 h. ^c Conditions B: CpCo(CO)₂, decalin, 190 °C, N₂, microwave, 10 min. ^d Conditions C: Co₂(CO)₈ (0.5 equiv), C₅H₆ (2 equiv), decalin, 5 min at 40 °C, 5 min at 190 °C.

Scheme 4. Synthesis of 7-Ring Lactone Fused Metallocenes

Co₂(CO)₈, respectively. However, we are not aware of any previous reports on the application of microwave conditions to the synthesis of an organometallic species from a metal carbonyl starting material.

The isopropyl-substituted diyne **6b** gave improved diastereoselectivity under both sets of conditions (entries 3 and 4), the identity of the major isomer **9b** being confirmed by the similarity of the ¹H NMR spectrum to that of **9a**. As cyclopentadienylcobalt dicarbonyl is generated from the reaction between dicobalt octacarbonyl and cyclopentadiene,⁸ combination of these last two reagents with **6b** followed by microwave irradiation also resulted in the formation of the cyclopentadienone metallocenes (entry 5). Following isolation of the minor diastereoisomer **10b** by column chromatography, microwave irradiation of a solution of this in decalin at 190 °C resulted in no change into **9b**, a result which suggests that the diastereoselectivity observed is a consequence of kinetic control of metallocene formation.

These complexation procedures were also applied to the ester-linked diynes **8a,b** (Scheme 4). With a methyl R substituent the same major diastereoisomer was obtained from both the heat- and microwave-assisted complexation reactions, albeit in rather modest yield (Table 2, entries 1 and 2). Following purification of the major product by recrystallization, its identity as the cyclopentadienone complex **11a** was established by an X-ray crystal structure determination (Figure 2).¹¹ As observed in the previous example, the preferred diastereoisomer is that with the methyl group oriented away from the cobalt–cyclopentadienyl moiety. Again the corresponding cyclobutadiene complexes were not observed. Better yields were obtained with the isopropyl-substituted derivative (entries 3 and 4), and as before, the major diastereoisomer **11b** was assigned by comparison of NMR data. This complex was also synthesized in low yield using dicobalt octacarbonyl as the starting material (entry 5).

To illustrate the viability of this protocol for the synthesis of nonracemic metallocenes, we employed the propargylic alcohol (*S*)-**4b**¹² of 72% ee, obtained in three steps following the

(11) Crystal data for **11a**: C₃₁H₂₃CoO₃, *M*_r = 502.42, triclinic, *a* = 10.512(3) Å, *b* = 10.734(3) Å, *c* = 11.473(3) Å, α = 68.257(3)°, β = 71.825(3)°, γ = 81.176(4)°, *V* = 1141.4(5) Å³, space group *P*1 (No. 1), *Z* = 2, *D*_c = 1.462 Mg/m³, μ = 0.785 mm⁻¹, 8280 reflections measured, 3868 unique reflections with *R*_{int} = 0.0674, *T* = 120(2) K, final *R* indices for *I* > 2σ(*I*) *R*₁ = 0.0537, *wR*₂ = 0.1146 and for all data *R*₁ = 0.1060, *wR*₂ = 0.1375.

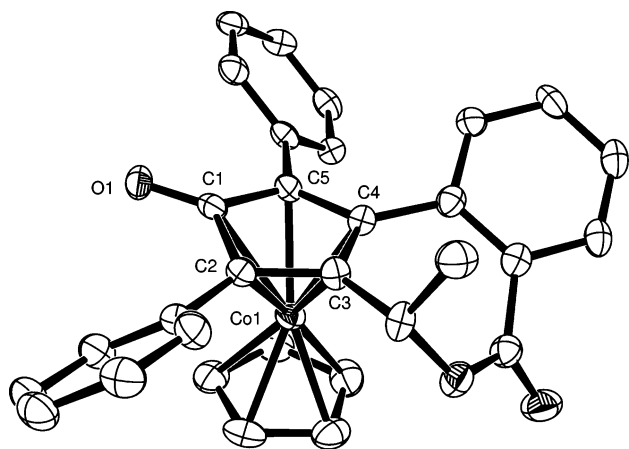
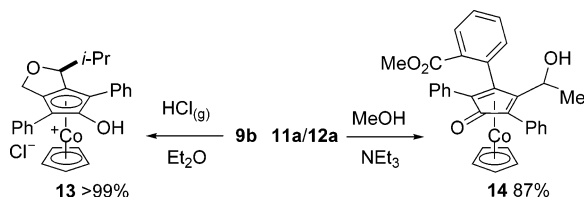


Figure 2. Representation of the X-ray crystal structure of **11a**. Selected bond lengths (Å): C(1)–O(1) = 1.233(5), C(1)–C(2) = 1.486(6), C(2)–C(3) = 1.431(6), C(3)–C(4) = 1.437(6), C(4)–C(5) = 1.434(6), C(5)–C(1) = 1.476(6).

Scheme 5. Representative Transformations of the Cyclopentadienone Complexes **9b and **11a****



enantioselective addition of 2-methyl-3-buten-2-ol to isobutyraldehyde.¹³ Following conversion into (*S*)-**8b**, as summarized in Scheme 2, microwave-assisted complexation with CpCo(CO)₂ gave a 3.8:1 ratio of diastereoisomers in 38% yield. The major and minor isomers were shown by HPLC to have enantiomeric excesses of 74% and 72%, respectively. This proves that no erosion of absolute stereochemistry occurs during conversion to the metallocene, making this procedure suitable for the synthesis of scalemic complexes containing both central and planar elements of chirality.

Finally, two aspects of the chemistry of these new cyclopentadienone complexes were explored in the context of making new metallocene derivatives. First, addition of gaseous HCl to **9b** dissolved in ether resulted in precipitation of **13** (Scheme 5). As far as we are aware, this is the first example of a planar chiral hydroxycobaltocenium salt, which in contrast to most isoelectronic hydroxyferrocene derivatives is stable on exposure to atmospheric oxygen. Second, reaction of a 3:1 mixture of **11a** and **12a** with methanol gave the ring-opened ester **14**, unchanged as a 3:1 mixture of diastereoisomers. Related motifs containing a hydroxy-substituted stereogenic center α to a metallocene have proven very valuable in ferrocene chemistry for the synthesis of a wide variety of ligands.

Conclusion

We have demonstrated that the reaction between ether- or ester-linked chiral diynes and cyclopentadienylcobalt dicarbonyl results in a one-pot diastereoselective synthesis of planar chiral

cobalt metallocenes. Furthermore, the method is applicable to the synthesis of nonracemic complexes. In view of the variety of methods now available for the enantioselective synthesis of propyglycic alcohols,¹⁴ and the potential modularity of subsequent diyne syntheses, this methodology is applicable to the synthesis of a variety of scalemic planar chiral metallocenes for application in asymmetric catalysis and materials chemistry.

Experimental Section

Petroleum ether refers to that fraction boiling in the range 40–60 °C. THF was distilled from sodium benzophenone ketyl and toluene from sodium wire. Silica gel (40–63 μ m) was used for chromatography. Butyllithium was used as a 2.5 M solution in hexanes. Microwave reactions were carried with a CEM Discover instrument (300 W). Thin-layer chromatography was performed on silica gel 60 F₂₅₄ plates (Merck).

General Procedure for the Synthesis of **9–12 via Thermal Complexation using CoCp(CO)₂: Conditions A.** To a stirred solution of the required ether (**6a** or **6b**) or ester (**8a** or **8b**) (1.2 equiv) in dry toluene (5 mL/mmol of **6a,b**) under nitrogen was added CoCp(CO)₂ (1 equiv) via syringe, and the mixture was then heated at reflux for 18 h. After it was cooled, the reaction mixture was filtered through a plug of silica gel, washing through with 30% EtOAc/70% petroleum ether. The solvent was removed in vacuo and the ratio of diastereoisomers determined by ¹H NMR spectroscopy.

General Procedure for the Synthesis of **9–12 via Microwave Complexation using CoCp(CO)₂: Conditions B.** To a dry microwave tube containing a magnetic bean was added CoCp(CO)₂ (1 equiv), the required ether (**6a** or **6b**) or ester (**8a** or **8b**) (1.2 equiv), and decalin (5 mL/mmol of **6a,b**). The tube was sealed and the reaction mixture microwaved for 10 min at 190 °C (ramp time ca. 5 min, hold time 10 min). The reaction mixture was then filtered through a short plug of silica gel, first with petroleum ether as eluent, followed by 5–10% MeOH/90–95% ethyl acetate. The solvent was removed in vacuo and the ratio of diastereoisomers determined by ¹H NMR spectroscopy.

General Procedure for the Synthesis of **9–12 via Microwave Complexation using Co₂(CO)₈ and Cyclopentadiene: Conditions C.** In a dry microwave tube containing a magnetic bean was added Co₂(CO)₈ (1 equiv), freshly cracked cyclopentadiene (4 equiv), and decalin (2.5 mL/mmol of Co₂(CO)₈). The tube was sealed and the reaction mixture microwaved for 5 min at 40 °C. The required ether (**6a** or **6b**) or ester (**8a** or **8b**) (2.4 equiv) was placed into the reaction mixture, which was then microwaved for a further 10 min at 190 °C. The reaction mixture was then filtered through a short plug of silica gel, first with petroleum ether as eluent, followed by 5–10% MeOH/90–95% ethyl acetate. The solvent was removed in vacuo and the ratio of diastereoisomers determined by ¹H NMR spectroscopy.

9a/10a: conditions A, use of **6a** (0.160 g, 0.61 mmol) gave a 4:1 ratio of **9a** and **10a** isolated as a red crystalline solid (0.155 g, 61%); conditions B, use of **6a** (0.160 g, 0.61 mmol) gave a 3.2:1 ratio of **9a** and **10a** (0.173 g, 68%). Subsequent chromatography (30% EtOAc/70% petroleum ether; *R_f*(major isomer) = 0.32, *R_f*(minor isomer) = 0.26) resulted in separation of the two diastereoisomers.

9a: mp 126–127 °C; IR (CH₂Cl₂) ν_{\max} 1581 cm⁻¹; ¹H NMR (δ , 270 MHz, CDCl₃) 1.36 (3 H, d, *J* = 6.2 Hz), 4.58 (5 H, s), 4.86 (1 H, d, *J* = 12.4 Hz), 5.14 (1 H, d, *J* = 12.4 Hz), 5.68 (1 H,

(12) Addition of 2-methyl-3-buten-2-ol to isobutyraldehyde in the presence of Zn(OTf)₂, NEt₃, and (–)-*N*-methylephedrine (lit.¹³ ee = 98%), was followed by benzylation, fragmentation to the primary acetylene, and Sonagashira cross-coupling with iodobenzene. See the Supporting Information.

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q, $J = 6.7$ Hz), 7.36–7.39 (6 H, m), 8.05 (2 H, d, $J = 8.2$ Hz), 8.17 (2 H, d, $J = 7.9$ Hz); ^{13}C NMR (δ , 100 MHz, CDCl_3) 19.7, 67.1, 70.7, 72.5, 76.4, 84.4, 91.7, 96.3, 127.4, 127.4, 127.7, 127.8, 128.8, 128.9, 134.5, 134.5, 159.0; high-resolution MS (m/z , FAB) found for MH^+ 413.0949, calcd for $\text{C}_{25}\text{H}_{22}\text{CoO}_2$ 413.0946.

10a: IR (CH_2Cl_2) ν_{max} 1581 cm^{-1} ; ^1H NMR (δ , 270 MHz, CDCl_3) 1.75 (3 H, d, $J = 6.2$ Hz), 4.68 (1 H, d, $J = 12.9$ Hz), 4.73 (5 H, s), 4.94 (1 H, q, $J = 6.2$ Hz), 5.13 (1 H, d, $J = 12.6$ Hz), 7.31–7.42 (6 H, m), 7.77 (2 H, dd, $J = 7.4, 1.5$ Hz), 8.09 (2 H, dd, $J = 7.9, 1.7$ Hz).

9b/10b: conditions A, use of **6b** (0.350 g, 1.21 mmol) gave a 5:1 ratio of **9b** and **10b** isolated as a red crystalline solid (0.252 g, 47%); conditions B, use of **6b** (0.160 g, 0.55 mmol) gave a 5:1 ratio of **9b** and **10b** (0.120 g, 49%); conditions C, use of **6b** (0.160 g, 0.55 mmol) gave a 3.5:1 ratio of **9b** and **10b** (0.082, 34%). Subsequent chromatography (30% EtOAc/70% petroleum ether; R_f (major isomer) = 0.55, R_f (minor isomer) = 0.49) resulted in separation of the two diastereoisomers.

9b: mp 65–67 °C; IR (CH_2Cl_2) ν_{max} 1581 cm^{-1} ; ^1H NMR (δ , 270 MHz, CDCl_3) 0.65 (3 H, d, $J = 6.7$ Hz), 0.97 (3 H, d, $J = 6.7$ Hz), 1.86–1.93 (1 H, m), 4.59 (5 H, s), 4.83 (1 H, d, $J = 12.3$ Hz), 5.20 (1 H, d, $J = 12.6$ Hz), 5.42 (1 H, d, $J = 3.0$ Hz), 7.24–7.39 (6 H, m), 8.05–8.07 (4 H, m); ^{13}C NMR (δ , 100 MHz, CDCl_3) 16.5, 19.8, 33.0, 60.4, 69.6, 84.7, 85.4, 92.2, 95.2, 127.4, 127.7, 127.8, 127.9, 128.1, 128.6, 128.9, 134.5, 171.2 (1 signal coincident); high-resolution MS (m/z , EI) found for MH^+ 441.1261, calcd for $\text{C}_{27}\text{H}_{26}\text{CoO}_2$ 441.1259.

10b: ^1H NMR (δ , 270 MHz, CDCl_3) 0.74 (3 H, d, $J = 6.9$ Hz), 1.24 (3 H, d, $J = 6.4$ Hz), 1.99–2.10 (1 H, m), 4.54 (1 H, d, $J = 8.2$ Hz), 4.70 (1 H, d, $J = 12.9$ Hz), 4.80 (5 H, s), 5.19 (1 H, d, $J = 12.9$ Hz), 7.24–7.36 (6 H, m), 7.64–7.67 (2 H, m), 8.07–8.10 (2 H, m).

11a/12a: conditions A, use of **8a** (0.190 g, 0.54 mmol) gave a 3:1 ratio of **11a** and **12a** isolated as a red crystalline solid (0.056 g, 21%); conditions B, use of **8a** (0.190 g, 0.54 mmol) gave **11a** and **12a** as a 3.4:1 ratio of diastereoisomers (0.079 g, 29%); TLC (30% EtOAc/70% petroleum ether) $R_f = 0.25$.

11a: mp 137–138 °C; IR (CH_2Cl_2) ν_{max} 1705, 1595 cm^{-1} ; ^1H NMR (δ , 400 MHz, CDCl_3) 1.42 (3 H, d, $J = 6.9$ Hz), 4.93 (5 H, s), 5.60 (1 H, q, $J = 6.9$ Hz), 7.22–7.91 (14 H, m); ^{13}C NMR (δ , 100 MHz, CDCl_3) 21.0, 71.1, 85.5, 127.8, 128.2, 128.6, 129.0, 129.1, 130.5, 131.2, 131.3, 131.7, 131.9, 132.1, 132.3, 169.9 (7 signals coincident); m/z (ES) found for MH^+ 503.1053, calcd for $\text{C}_{31}\text{H}_{24}\text{CoO}_3$ 503.1052.

12a: ^1H NMR (δ , 400 MHz, CDCl_3) 0.92 (3 H, d, $J = 6.9$ Hz), 4.98 (6 H, brs) 7.22–7.91 (16 H, m). The ratio **11a** to **12a** may also be determined by ^{13}C NMR (**11a** δ 85.50 (C_5H_5), **12a** δ 85.25 (C_5H_5)).

11b/12b: conditions A, use of **8b** (0.200 g, 0.53 mmol) gave a 4:1 ratio of **11b** and **12b** isolated as a red crystalline solid (0.093 g, 33%); conditions B, use of **8b** (0.200 g, 0.53 mmol) gave a 3:1 ratio of **11b** and **12b** (0.16 g, 57%); conditions C, use of **8b** (0.200 g, 0.53 mmol) gave a 5:1 ratio of **11b** and **12b** (0.03, 11%); TLC (30% EtOAc/70% petroleum ether) R_f (major isomer) = 0.24, R_f (minor isomer) = 0.20).

11b: mp 214–216 °C; IR (CH_2Cl_2) 1705, 1595 cm^{-1} ; ^1H NMR (δ , 270 MHz, CDCl_3) 0.21 (3 H, d, $J = 6.7$ Hz), 0.85 (3 H, d, $J = 6.7$ Hz), 1.50–1.65 (1 H, m), 4.86 (1 H, d, $J = 11.1$ Hz), 4.90 (5 H, s), 6.93 (1 H, d, $J = 7.4$ Hz), 7.18 (1 H, td, $J = 7.4, 1.5$ Hz),

7.31–7.47 (7 H, m), 7.80–7.94 (5 H, m); ^{13}C NMR (δ , 100 MHz, CDCl_3) 18.0, 20.9, 29.3, 74.8, 80.7, 81.7, 84.6, 85.3, 92.6, 128.1, 128.2, 128.6, 128.8, 129.0, 130.0, 130.1, 130.4, 131.3, 131.6, 131.7, 131.9, 132.7, 134.0, 157.9, 170.2; high-resolution MS (m/z , EI) found for MH^+ 531.1365, calcd for $\text{C}_{35}\text{H}_{28}\text{CoO}_3$ 531.1365.

12b: ^1H NMR (δ , 270 MHz, CDCl_3) 0.32 (3 H, d, $J = 6.2$ Hz), 0.92 (3 H, d, $J = 6.2$ Hz), 2.38–2.50 (1 H, m), 4.05 (1 H, d, $J = 9.7$ Hz), 4.92 (5 H, s), 6.97 (1 H, d, $J = 7$ Hz), 7.15–7.95 (13 H, m).

Synthesis of 13. Hydrogen chloride gas was bubbled through a red solution of **9b** (0.050 g, 0.11 mmol) in ether, resulting in the immediate precipitation of a yellow solid that was filtered, washed, and dried to give **13** (0.054 g, >99%): mp 160–164 °C; IR (Nujol) ν_{max} 3425 cm^{-1} ; ^1H NMR (δ , 400 MHz, DMSO) 0.60 (3 H, d, $J = 6.7$ Hz), 0.81 (3 H, d, $J = 6.9$ Hz), 1.65–1.78 (1 H, m), 4.80 (1 H, d, $J = 12.9$ Hz), 5.05 (5 H, s), 5.32 (1 H, d, $J = 13.4$ Hz), 5.56 (1 H, d, $J = 3.9$ Hz), 7.41–7.51 (6 H, m), 7.99–8.20 (4 H, m); ^{13}C NMR (δ , 100 MHz, DMSO) 16.5, 19.1, 32.2, 67.4, 82.6, 85.0, 85.8, 94.0, 95.9, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 131.9, 132.0 (2 signals coincident); high-resolution MS (m/z , EI) found for $\text{M} - \text{Cl}^+$ 441.1259, calcd for $\text{C}_{27}\text{H}_{26}\text{CoO}_2$ 441.1259.

Synthesis of 14. A solution of **11a** and **12a** (3:1 ratio, 0.054 g, 0.11 mmol) in methanol (15 mL) containing triethylamine (0.10 mL) was stirred at 50 °C for 96 h; the solution was cooled to room temperature and poured into ether (15 mL) and dilute HCl(aq) (15 mL). The yellow aqueous layer was separated and made basic with the addition of small portions of sodium hydrogen carbonate until effervescence subsided. Upon addition of sodium hydrogen carbonate there was a color change from yellow back to red. The basic solution was then extracted with dichloromethane (10 mL), dried (MgSO_4), filtered, and evaporated to give **14** as a red-orange solid as a 3:1 ratio of diastereoisomers (0.050 g, 87%): ν_{max} 3369, 1595 cm^{-1} ; ^1H NMR (δ , 270 MHz, CDCl_3) 1.28 (3 H, d, $J = 6.7$ Hz), 1.31* (3 H, d, $J = 6.7$ Hz), 2.43* (1 H, brd, $J = 8$ Hz), 2.54 (1 H, brs), 3.47 (3 H, s), 3.48* (3 H, s), 4.76–4.90 (1 H, m), 5.01 (5 H, s), 7.05–7.20 (3 H, m), 7.33–7.51 (6 H, m), 7.60–7.68 (2 H, m), 7.96–8.01 (2 H, m), 8.18* (1 H, d, $J = 8.4$ Hz), 8.22 (1 H, d, $J = 7.7$ Hz) (asterisks denote distinct signals for minor diastereoisomer); ^{13}C NMR (δ , 100 MHz, CDCl_3) 22.3, 52.3, 64.9, 77.7, 81.4, 84.5, 94.0, 95.4, 127.1–135.5, 158.1, 167.5 (major diastereoisomer only); high-resolution MS (m/z , EI) found for MH^+ 535.1318; calcd for $\text{C}_{32}\text{H}_{28}\text{CoO}_4$ 535.1314.

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Supporting Information Available: Text giving details of the synthesis of **4a,b**–**8a,b**, (*S*)-**4b**, and (*S*)-**8b** and the subsequent reaction of the last species with $\text{CpCo}(\text{CO})_2$, together with text and figures giving details of the X-ray crystal structure determinations of **9a** and **11a**; crystallographic data for **9a** and **11a** are given as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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