

The formation and reaction chemistry of (η^5 -benzoylcyclopentadienyl) - and (η^5 -carbomethoxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene) - cobalt

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Received 24 August 1995; in revised form 29 March 1996

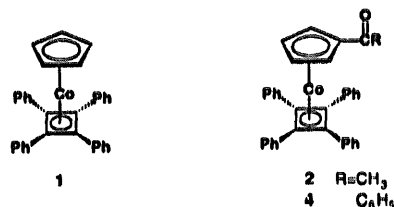
Abstract

(η^5 -Benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt, which has been synthesized from (η^5 -benzoylcyclopentadienyl)dicarbonylcobalt and 2 equivalents of diphenylacetylene, undergoes typical organic reactions, including reduction with sodium borohydride, reduction with lithium aluminum hydride/aluminum chloride, as well as the Wittig reaction. (η^5 -Carbomethoxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt has also been prepared from (η^5 -carbomethoxycyclopentadienyl)dicarbonylcobalt and diphenylacetylene. The ester can be readily converted into the corresponding carboxylic acid, and sequentially into the acid chloride, amide, and cyano derivatives. The anhydride was prepared from the acid chloride. A Friedel–Crafts acylation reaction of (η^5 -chloroformylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt, ferrocene and aluminum chloride in refluxing 1,2-dichloroethane has afforded a heterobimetallic ketone, (η^5 -ferrocenoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt.

Keywords: Cobalt; Cyclopentadienyls; Cyclobutadiene

1. Introduction

Over the years, the extensive and diverse reaction chemistry of ferrocene has stimulated investigations concerning other isoelectronic, potentially metalloaromatic systems, as well as alternative routes to functionally substituted cyclopentadienyl–metal compounds [1]. The reactivity of the mixed-ring sandwich compound (η^5 -cyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (**1**) to electrophilic aromatic substitution has been demonstrated by its ability to undergo acetoxymercuration, Vilsmeier formylation, and Mannich-type aminomethylation [2,3]. In contrast, Friedel–Crafts acylation of **1** to produce the acetyl

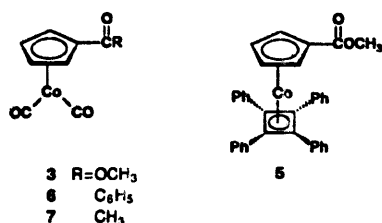


analog (**2**) has afforded less than 1% of the desired ketone, whereas attempted benzoylation of **1** gave only a minute amount of product in which electrophilic substitution had occurred exclusively on a phenyl substituent of **1** [2,3].

Carboxylic acid and related derivatives of **1** have likewise been very difficult to obtain by electrophilic substitution methods. However, we have recently demonstrated that a reaction between carbomethoxycyclopentadienylsodium, dicobalt octacarbonyl and iodine readily produces (η^5 -carbomethoxycyclopentadienyl)dicarbonylcobalt (**3**) in 41% yield [4], and the latter could

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possibly serve as a precursor for carboxylic acid derivatives of 1.



In an effort to develop new synthetic routes to functionally substituted derivatives of 1, we now report on the formation of (η^5 -benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (4) and (η^5 -carbomethoxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (5), as well as on some of their reaction chemistry.

2. Results and discussion

We have recently shown that (η^5 -cyclopentadienyl)dicarbonylcobalt readily undergoes Friedel–Crafts benzylation to produce the benzoyl derivative (6) in 49% yield [5]. In a similar manner, Friedel–Crafts acetylation afforded the acetyl analog (7) in 61% yield [5]. The ready availability of these ketones suggested that they might serve as intermediates to 2 and to 4. Reactions of 6 or 7 with 2 equivalents of diphenylacetylene in refluxing xylene resulted in displacement of both carbon monoxide ligands and the formation of 4 as well as 2 in overall yields of 18% and 5% respectively. While the yield of the acetyl analog 2 is very low by this process, it is still higher than for 2 obtained by the direct acetylation of 1, or by an alternative, lengthy procedure involving mercurated and lithiated derivatives of 1 [2,3]. The benzoyl analog 4 is a new compound, and was characterized by its IR, ¹H NMR and ¹³C NMR spectra as well as by microanalysis.

Compound 4 is reactive to nucleophilic addition, as demonstrated by its ability to undergo a Wittig reaction, sodium borohydride reduction, and reduction with lithium aluminum hydride/aluminum chloride. (η^5 -1-Phenylvinylcyclopentadienyl)

riphenylphosphorane, prepared from methyltriphenylphosphonium iodide [6] and *n*-butyllithium. Alkene 8 was characterized by its ¹H NMR spectrum, which contained a phenyl multiplet at 7.24 ppm, methylene doublets at 5.03 and 4.94 ppm, and an A₂B₂ pattern of pseudo triplets at 4.81 and 4.66 ppm. The IR spectrum of 8 exhibited a strong C=C stretching band at 1600 cm⁻¹.

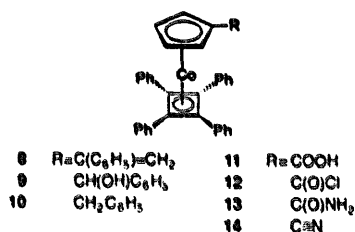
Reduction of 4 with sodium borohydride in methanol produced the corresponding alcohol (9) in 63% yield. Surprisingly, an IR spectrum of 9 exhibited only weak absorption in the OH stretching region (3600–3200 cm⁻¹), although the carbonyl stretching band for 4 at 1630 cm⁻¹ was absent. The ¹H NMR spectrum of 9 did contain a broadened singlet resonance assignable to a hydroxyl proton at 0.91 ppm, as well as a methine singlet at 1.28 ppm, pseudo triplets for the cyclopentadienyl protons at 5.34 and 4.89 ppm, and an aromatic proton multiplet at 7.24 ppm.

Using the more powerful reducing agent lithium aluminum hydride/aluminum chloride [7], 4 was readily converted to (η^5 -benzylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (10) in 98% yield. The ¹H NMR spectrum of 10 exhibited sharp singlets for the cyclopentadienyl and methylene protons at 4.52 ppm and 3.14 ppm respectively, as well as multiplets for the phenyl protons. Reductions of this type presumably proceed via stabilized carbonium ion intermediates [7], and both spectral and reactivity data have demonstrated enhanced stabilization of a carbocationic center adjacent to an (η^5 -cyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt moiety [8].

In order to synthesize carboxylic acid derivatives of 1, which are currently unknown, the ester derivative 5 was prepared by a metathesis reaction of carbomethoxycyclopentadienylsodium with dicobalt octacarbonyl and iodine [Co(CO)₈I] [4] to form 3, followed by subsequent ligand substitution with 2 equivalents of diphenylacetylene. In this manner, 5 was obtained in 54% overall yield, based on dicobalt octacarbonyl. The carbonyl group absorption of 5 exhibited a higher stretching frequency than for the ketone analogs 2 and 4, occurring at 1715 cm⁻¹. The product was further characterized by its ¹H NMR spectrum and by microanalysis.

Treatment of the ester 5 with potassium hydroxide in aqueous ethanol followed by acidification afforded (η^5 -carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (11) in 51% yield. The IR spectrum of 11 exhibited a carbonyl band (1682 cm⁻¹) at lower energy than found for 5, whereas the ¹H NMR spectrum of 5 showed an A₂B₂ pattern of pseudo triplets for the cyclopentadienyl protons at 5.23 and 4.82 ppm, as well as a phenyl proton multiplet at 7.24 ppm.

Reaction of carboxylic acid 11 with oxalyl chloride in methylene chloride solution produced (η^5 -chloroform-



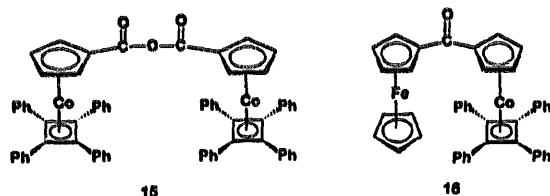
(η^4 -tetraphenylcyclobutadiene)cobalt (8) was obtained in 39% yield by the addition of ketone 4 to methylenet-

mylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (**12**) in 35% yield. An IR spectrum of **12** indicated carbonyl group absorption at 1753 and 1720 cm^{-1} , at higher energy as expected than for carbonyl absorptions for **5** or **11**. The ^1H NMR spectrum of **12** was also consistent with the assigned structure.

Acid chloride **12** was further characterized by preparing an amide derivative. Ammonia was bubbled through a THF solution of **12** at 0°C , forming (η^5 -carbamoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (**13**) in 44% yield. The amide was characterized by two bands in its IR spectrum at 3510 and 3410 cm^{-1} , indicative of an NH_2 group, and a strong, broad carbonyl band at 1660 cm^{-1} . The ^1H NMR spectrum of **13** likewise contained a broad singlet for the NH_2 protons at 3.20 ppm, as well as pseudo triplets for the cyclopentadienyl protons at 5.04 and 4.71 ppm, and phenyl proton multiplets centered at 7.4 and 7.2 ppm.

Dehydration of amide **13** in refluxing acetic anhydride readily produced (η^5 -cyanocyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (**14**) in 55% yield. Both IR and ^1H NMR spectral data obtained for this compound agreed with literature data for **14** prepared previously from a Rosenmund–von Braun reaction between (η^5 -iodocyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt and cuprous cyanide [2,3].

Since only a few bimetallic anhydrides are known, bis[(η^5 -carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt] anhydride (**15**) was synthesized by oxidation of the acid chloride **12**. The procedure was patterned after the literature preparation of ferrocenecarboxylic anhydride [9]. Anhydride **15** was isolated in 21% yield and purified by means of Soxhlet extraction using diethyl ether. Both the IR and ^1H NMR spectra of the product were consistent with the proposed structure.



It was also of interest to determine if the acid chloride **12** could be useful in the formation of hetero-bimetallic ketones such as (η^5 -ferrocenoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (**16**). After several failed attempts to form **16** from **12**, ferrocene and aluminum chloride in methylene chloride solution at room temperature, the solvent was replaced by higher boiling 1,2-dichloroethane, the catalyst was added last, and the reaction was heated at reflux for 4 days. Following hydrolysis and purification by chromatography on alumina, **16** was isolated in 16% yield. The need for a higher reaction temperature and longer reaction time

may be associated with the known enhanced stability of carbocations adjacent to the (η^5 -cyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt moiety. As discussed above, a positive charge on the acylium ion could be extensively delocalized [8] which would require more rigorous reaction conditions. Ketone **16** was characterized by its ^1H NMR spectrum, which exhibited sets of pseudo triplets for both the $\text{C}_5\text{H}_4\text{Co}$ and the $\text{C}_5\text{H}_4\text{Fe}$ protons, as well as a singlet for the C_5H_5 ring and a phenyl proton multiplet. The IR spectrum of **16** contained a strong, low-energy carbonyl stretching band at 1618 cm^{-1} .

In conclusion, reactions of readily obtainable, substituted (η^5 -cyclopentadienyl)dicarbonylcobalt compounds such as **3** and **6** with 2 equivalents of diphenylacetylene provide attractive alternative routes to functionally substituted (η^5 -cyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt compounds that are complimentary to the previously reported electrophilic substitution reactions of **1** [2,3]. Compounds such as **4** and **5**, which can only be prepared by intermediates **3** and **6**, have in turn been converted to a wide range of derivatives by standard organic reactions that are successful for ferrocene and other highly stable aromatic systems. Like the analogous ferrocene derivatives, functionally substituted derivatives of **1** are generally air-stable and crystallize readily. Thus, extensive chemistry of **1** can be anticipated.

3. Experimental section

All operations were performed under an inert atmosphere of nitrogen using standard Schlenk or glove box techniques unless otherwise specified. Nitrogen was dried by passage through two successive tubes, one containing molecular sieves and the other phosphorus pentoxide. Trace oxygen was removed by passage through a column of BTS catalyst. All solvents were dried prior to use. Diethyl ether and tetrahydrofuran (THF) were predried over sodium wire and subsequently distilled from Na–K alloy. Pentane and hexane were likewise distilled from Na–K alloy, whereas methylene chloride and 1,2-dichloroethane were dried and distilled from calcium hydride. Diphenylacetylene was prepared by a modified literature procedure [10], in which the product was purified by crystallization from methanol followed by vacuum sublimation. Dicobalt octacarbonyl and benzoyl chloride were purchased from Strem Chemicals and Eastman Kodak respectively, whereas most other reagents were obtained from Aldrich. Column chromatography was conducted under nitrogen on activated neutral grade alumina. NMR spectra were recorded on a Bruker NR-80AF spectrometer. IR spectra were acquired on a Perkin–Elmer 1310 spectrometer. All melting points were recorded on a Mel-Temp

apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

3.1. (η^5 -Benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (6)

To a 250 ml Schlenk flask under nitrogen was added 100 ml of dry methylene chloride, aluminum chloride (1.603 g, 12.0 mmol), benzoyl chloride (1.50 ml, 12.9 mmol), and a magnetic stirring bar. The yellow solution was stirred for 1 h before adding (η^5 -cyclopentadienyl)dicarbonylcobalt [2,3] (1.809 g, 10.0 mmol) dissolved in 2 ml of methylene chloride. The resultant red solution was stirred at room temperature overnight. The solution was slowly hydrolyzed with 50 ml each of deoxygenated water and 10% hydrochloric acid. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layer was then dried over magnesium sulfate and filtered through a small amount of Celite. The solvent was removed in vacuo to give a red oil.

About 15 ml of xylene was added to the red oil and the solution was transferred to a 25 ml Schlenk flask. Diphenylacetylene (4.286 g, 24.0 mmol) was added and a condenser and gas outlet were attached. The red solution was heated at reflux overnight in the absence of light, and then allowed to cool to room temperature under a gentle flow of nitrogen. Alumina was added and the material was loaded onto an alumina column (2 × 24 cm). A single yellow band was eluted with 1:4 THF–diethyl ether. Removal of the solvent gave 1.04 g (18%) of (η^5 -benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt. Recrystallization of the product first from hot heptane followed by benzene–heptane afforded yellow crystals, m.p. 231–234°C. Anal. Found: C, 82.13; H, 5.13. $C_{40}H_{29}CoO$. Calc.: C, 82.18; H, 5.00%. 1H NMR ($CDCl_3$): δ 7.12 (m, 25H, phenyl), 5.22 (t, 2H, $H_{2,3}$), 4.77 (t, 2H, $H_{3,4}$). ^{13}C NMR ($CDCl_3$): δ 192.77 (C=O), 139.77 (benzoyl C_1), 134.84 (benzoyl $C_{3,5}$), 130.92 (benzoyl C_4), 128.80 (phenyl $C_{2,6}$), 128.36 (phenyl C_4), 128.06 (phenyl $C_{3,5}$), 127.67 (phenyl C_1), 126.76 (benzoyl $C_{2,6}$), 93.15 (Cp C_1), 87.70 (Cp $C_{3,4}$), 85.16 (Cp $C_{2,3}$), 76.67 (C_4 ring). IR ($CDCl_3$): 3080–3030 (m), 1630 (s), 1600 (m), 1495 (m), 1445 (s), 1360 (s), 1290 (s), 1275 (s), 1023 (m), 925–880 (m), 853 (m), 778 (m), 687 (s) cm^{-1} .

3.2. (η^5 -Acetylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (2)

The Perrier complex derived from aluminum chloride (1.615 g, 12.1 mmol) and 0.90 ml (12 mmol) of acetyl chloride in 100 ml of methylene chloride was stirred at room temperature for 85 min in a 250 ml Schlenk flask equipped with a magnetic stirring bar, gas outlet and oil

bubbler. (η^5 -Cyclopentadienyl)dicarbonylcobalt (1.436 g, 7.98 mmol) was added and the red solution was stirred overnight under nitrogen. The reaction mixture was hydrolyzed with 50 ml of deoxygenated water followed by the addition of 50 ml of 10% hydrochloric acid. The mixture was separated and the aqueous layer was extracted with methylene chloride. The combined organic layer was washed with water, dried over magnesium sulfate, and filtered through a small amount of Celite. The solvent was removed to give a red oil.

Xylene (15 ml) was added to the red oil and the solution was transferred to a 25 ml Schlenk flask. Diphenylacetylene (2.923 g, 16.4 mmol) was added and a condenser and gas inlet were attached. The solution was heated at reflux overnight in the absence of light. Under nitrogen, the reaction mixture was cooled to room temperature. Alumina was added until all the solvent had been adsorbed. The material was subsequently loaded onto a dry-packed alumina column (2 × 24 cm). A minute yellow band was eluted with pentane followed by a second yellow band eluted with diethyl ether. The latter band gave 0.200 g (5%) of (η^5 -acetylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt. The spectral data for the product corresponded to literature values for this compound [2,3].

3.3. (η^5 -1-Phenylvinylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (8)

Methyltriphenylphosphonium iodide (0.32 g, 0.79 mmol) [6] was weighed into a 250 ml Schlenk flask containing a magnetic stirring bar. Dry diethyl ether (120 ml) was added to the flask and a rubber septum was inserted. To the white suspension was added 0.60 ml of *n*-butyllithium (1.6 M, 0.96 mmol) via a syringe. The resulting yellow solution was stirred at room temperature for 80 min. (η^5 -Benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (0.330 g, 0.56 mmol) was added, and the solution was stirred for 50 min at room temperature and heated at reflux for 100 min. The solution was cooled to room temperature and the solvent was removed to give 0.130 g (39%) of (η^5 -1-phenylvinylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt. The solid was recrystallized from hexane to yield red-brown crystals, m.p. 122–124°C. Anal. Found: C, 84.36; H, 5.48. $C_{41}H_{31}Co$. Calc.: C, 84.52; H, 5.36%. 1H NMR ($CDCl_3$): δ 7.24 (m, 25H, phenyl), 5.03 and 4.94 (d, 2H, CH_2), 4.81 (t, 2H, $H_{2,3}$), 4.66 (t, 2H, $H_{3,4}$). IR ($CDCl_3$): 3105–3030 (m), 1600 (s), 1498 (s), 1443 (m), 1073 (m), 1025 (s), 820 (s), 778 (s), 693 (s) cm^{-1} .

3.4. (η^5 -Hydroxybenzylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (9)

Under nitrogen, (η^5 -benzoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (1.85 g, 3.16 mmol) dis-

solved in 10 ml of methylene chloride was transferred to a 25 ml Schlenk flask equipped with a magnetic stirring bar. Methanol (10 ml) was added followed by 0.131 g (3.46 mmol) of sodium borohydride. The solution was stirred at room temperature for 2 days. During this time the brown solution became red with the formation of a tan solid. Water (50 ml) was added to the reaction mixture followed by 50 ml of 10% hydrochloric acid. The layers were then separated and the aqueous layer was extracted with methylene chloride. The combined organic layer was washed with aqueous calcium chloride, and was subsequently dried over calcium chloride and filtered. The solvent was removed to give 1.17 g (63%) of $(\eta^5\text{-hydroxybenzylcyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ as an orange solid. The product was recrystallized from toluene–heptane to give orange-brown crystals, m.p. 222.5–224°C. Anal. Found: C, 82.35; H, 5.04. $\text{C}_{40}\text{H}_{31}\text{CoO}$. Calc.: C, 81.90; H, 5.33%. ^1H NMR (C_6D_6): δ 7.24 (m, 25H, phenyl), 5.34 (t, 2H, $\text{H}_{2,5}$), 4.89 (t, 2H, $\text{H}_{3,4}$), 1.28 (s, 1H, CH), 0.91 (s, 1H, OH). IR (C_6D_6): 3555 (w), 3225 (m), 3065 (w), 3045 (m), 3020 (w), 2950 (m), 2915 (m), 2860 (m), 2840 (m), 2375 (m), 2270 (m), 2235 (m), 1605 (m), 1590 (w), 1540 (w), 1490 (s), 1440 (s), 1383 (m), 1315 (m), 1155 (m), 1100 (w), 1065 (w), 1057–1045 (w), 1020 (w), 1005 (w), 860 (w), 810–795 (s), 775 (m), 740 (m), 697 (s), 655 (w) cm^{-1} .

3.5. $(\eta^5\text{-Benzylcyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (10)

Into a 25 ml Schlenk flask was added 15 ml of dry diethyl ether and 0.05 g (1.3 mmol) of lithium aluminum hydride under nitrogen. A magnetic stirring bar was placed in the flask and an oil bubbler was attached. Aluminum chloride (0.175 g, 1.31 mmol) was slowly added and the mixture was stirred for 25 min under nitrogen at room temperature. $(\eta^5\text{-Benzoylcyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (0.189 g, 0.323 mmol) was then added and the light yellow solution was stirred at room temperature for 30 min. The reaction mixture was hydrolyzed with 50 ml of water followed by 50 ml of 10% hydrochloric acid. The layers were separated, the aqueous layer was extracted with diethyl ether, and the combined organic layer was washed with water. The solution was dried over magnesium sulfate and filtered through Celite. The solvent was removed to give 0.180 g (98%) of $(\eta^5\text{-benzylcyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$. Golden-brown crystals were obtained by Soxhlet extraction with heptane, m.p. 195–197°C. Anal. Found: C, 83.75; H, 5.65. $\text{C}_{40}\text{H}_{31}\text{Co}$. Calc.: C, 84.20; H, 5.48%. ^1H NMR (CDCl_3): δ 7.51–7.08 and 6.97–6.80 (m, 25H, phenyl), 4.52 (s, 4H, C_5H_4), 3.14 (s, 2H, CH_2). IR (CDCl_3): 3110–3035 (m), 1600 (s), 1500 (s), 1450

(m), 1078 (m), 1030 (m), 920–890 (m), 823 (m), 785 (s), 765 (s), 700 (s) cm^{-1} .

3.6. $(\eta^5\text{-Carbomethoxycyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (5)

Sodium metal (3.392 g, 147.5 mmol) was added to a nitrogen-filled 250 ml three-necked round-bottom flask equipped with a magnetic stirring bar and nitrogen inlet. An addition funnel and gas outlet were attached and 125 ml of dry THF was added. Freshly distilled cyclopentadiene (13.0 ml, 158 mmol) dissolved in 25 ml of THF was added dropwise to the mixture with stirring via an addition funnel. After the addition was complete, the reaction was heated at reflux until all of the sodium had been consumed. The reaction mixture was then cooled to room temperature under a gentle flow of nitrogen and 14.0 ml (166 mmol) of dimethyl carbonate dissolved in 25 ml of THF was added dropwise. The reaction was heated to reflux overnight, allowed to cool to room temperature, and the solvent was removed to produce 18.23 g (57%) of carbomethoxycyclopentadienylsodium as a brown solid.

The brown solid was added to a previously prepared THF solution of dicobalt octacarbonyl and iodine. Iodine (10.648 g, 41.95 mmol) had been added over 20 min to dicobalt octacarbonyl (14.350 g, 41.97 mmol) dissolved in 120 ml of THF in a 250 ml Schlenk flask equipped with a magnetic stirring bar. The green iodocobalt complex became red upon addition of the sodium salt. The resultant solution was stirred at room temperature overnight.

The solvent was removed and replaced with 20 ml of xylene. Diphenylacetylene (29.85 g, 167.6 mmol) was added and the solution was stirred at reflux for 2 days. The solvent was removed and the resulting crude product was recrystallized from methylene chloride–hexane to give 24.24 g of $(\eta^5\text{-carbomethoxycyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (54% based on $\text{Co}_2(\text{CO})_8$) as orange-brown needles, m.p. 219–221°C. Anal. Found: C, 78.16; H, 5.26. $\text{C}_{35}\text{H}_{27}\text{CoO}_2$. Calc.: C, 78.06; H, 5.06%. ^1H NMR (CDCl_3): δ 7.24 (m, 20H, phenyl), 5.18 (t, 2H, $\text{H}_{2,5}$), 4.74 (t, 2H, $\text{H}_{3,4}$), 3.21 (s, 3H, CH_3). IR (CDCl_3): 3020–3010 (w), 1715 (s), 1600 (s), 1585 (s), 1498 (m), 1470 (m), 1443 (m), 1430 (w), 1413 (w), 1400–1370 (m), 1283 (s), 1195 (m), 1147 (s), 1073 (w), 1027 (w), 967 (w), 930–880 (m), 847 (w), 835 (w), 800 (w), 680 (s), 640 (m) cm^{-1} .

3.7. $(\eta^5\text{-Carboxycyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (11)

$(\eta^5\text{-Carbomethoxycyclopentadienyl})(\eta^4\text{-tetraphenylcyclobutadiene})\text{cobalt}$ (3.87 g, 7.19 mmol) was added to a 250 ml round-bottom flask followed by 150 ml of 100% ethanol. Potassium hydroxide (1.016 g, 18.11

mmol) dissolved in sufficient distilled water was added to the slurry and the mixture was heated at reflux overnight. The orange-red solution containing fine particulates was poured into a beaker containing 200 ml of distilled water. Concentrated hydrochloric acid was added until the solution was acidic. A bright yellow precipitate formed immediately. The mixture was filtered and the solid was rinsed with water. The solid was dissolved in methylene chloride, dried over magnesium sulfate, and filtered to give 3.037 g (81%) of (η^5 -carboxycyclopentadienyl)(η^5 -tetraphenylcyclobutadiene)cobalt as a yellow solid. The solid was recrystallized from methylene chloride–hexane to form orange-brown crystals, m.p. 246–248°C. Anal. Found: C, 77.70; H, 4.84. $C_{34}H_{25}CO_2$. Calc.: C, 77.86; H, 4.80%. 1H NMR ($CDCl_3$): δ 7.24 (m, 20H, phenyl), 5.23 (t, 2H, $H_{2,3}$), 4.82 (t, 2H, $H_{3,4}$), 1.26 (s, 1H, OH). IR (CH_2Cl_2): 3300–2800 (br m), 1682 (s), 1600 (w), 1500 (m), 1475 (m), 1420 (m), 1295–1275 (s), 1245 (m), 1170 (w), 1110 (w), 1027 (w), 898 (m), 775 (m), 675 (w) cm^{-1} .

3.8. (η^5 -Chloroformylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (12)

(η^5 -Carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (1.976 g, 3.77 mmol) was weighed into a 300 ml Schlenk flask equipped with a magnetic stirring bar. The flask was evacuated and filled with nitrogen before adding 150 ml of dry methylene chloride and 1.2 ml (14 mmol) of oxalyl chloride. The reaction mixture was heated at reflux overnight in the absence of light. The solution was cooled to room temperature under nitrogen and the solvent was removed in vacuo to give 0.71 g (35%) of (η^5 -chloroformylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt. The solid was recrystallized from hexane to yield brown crystals, m.p. 153–155°C. Anal. Found: C, 76.06; H, 4.77. $C_{34}H_{24}ClCoO$. Calc.: C, 75.21; H, 4.46%. 1H NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 5.25 (t, 2H, $H_{2,3}$), 4.83 (t, 2H, $H_{3,4}$). IR ($CDCl_3$): 3110–3033 (m), 1753 (s), 1720 (s), 1600 (m), 1580 (w), 1500 (s), 1445 (s), 1410–1383 (m), 1360 (s), 1343 (m), 1288 (w), 1260 (s), 1218 (w), 1078 (m), 1045 (s), 1035 (m), 940–850 (m), 828 (s), 788 (s), 698 (s), 623 (w) cm^{-1} .

3.9. (η^5 -Carbamoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (13)

(η^5 -Chloroformylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (1.36 g, 2.50 mmol) was weighed into a 250 ml Schlenk flask equipped with a magnetic stirring bar. THF (130 ml) was added to the flask, a rubber septum was inserted into the neck of the flask, and the solution was cooled to 0°C. With stirring, ammonia was bubbled just under the surface of the liquid via a cannula for 10 min. The red solution

became an orange-brown slurry. The reaction mixture was stirred at 0°C for 2 h and then allowed to warm to room temperature. The solvent was removed to give 0.582 g (44%) of (η^5 -carbamoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt. Red-brown crystals, m.p. 198–199°C, were obtained from diethyl ether–heptane. Anal. Found: C, 77.33; H, 5.22; N, 2.31. $C_{34}H_{26}CoNO$. Calc.: C, 78.01; H, 5.01; N, 2.68%. 1H NMR ($CDCl_3$): δ 7.48–7.43 and 7.25–7.18 (m, 20H, phenyl), 5.04 (t, 2H, $H_{2,3}$), 4.71 (t, 2H, $H_{3,4}$), 3.20 (br, 2H, NH_2). IR ($CDCl_3$): 3510 (m), 3410 (m), 3085–3030 (m), 2980–2960 (m), 1660 (s), 1600 (s), 1587 (s), 1500 (s), 1470 (s), 1447 (m), 1385 (s), 1350 (m), 1337 (m), 1287 (m), 1253 (s), 1180 (w), 1100 (m), 1077 (m), 1055 (m), 1027 (s), 930–895 (m), 827 (s), 808 (s), 785 (s), 697 (s), 667–647 (m), 623 (m) cm^{-1} .

3.10. (η^5 -Cyanocyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (14)

(η^5 -Carbamoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (0.530 g, 1.01 mmol) was placed in a 25 ml Schlenk flask equipped with a magnetic stirring bar. The flask was then evacuated and filled with nitrogen. Acetic anhydride (15 ml) was added to the flask and the solution was heated at reflux with stirring for 3 h. The reaction mixture was cooled to room temperature under nitrogen and hydrolyzed with 50 ml of water followed by 50 ml of 10% hydrochloric acid. Diethyl ether was added and the layers were separated. The aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water, dilute aqueous sodium bicarbonate, and water. The organic layer was dried over magnesium sulfate and filtered. The solvent was removed to give a dark golden solid (0.283 g, 55%). The IR and 1H NMR spectra of the product corresponded to literature values for (η^5 -cyanocyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt [2,3].

3.11. Bis[(η^5 -carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt] anhydride (15)

(η^5 -Chloroformylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (1.19 g, 2.19 mmol) was placed in a 25 ml Schlenk flask equipped with a magnetic stirring bar. Dry diethyl ether (20 ml) was added to the flask and sodium peroxide (0.597 g, 7.65 mmol) was added slowly. The resultant solution was stirred at room temperature for 2 h and subsequently at reflux for 3 days. The reaction mixture was cooled to room temperature and hydrolyzed with 50 ml of water followed by 50 ml of 10% hydrochloric acid. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layer was washed with water and aqueous calcium chloride. The organic layer

was dried over magnesium sulfate and filtered. The solvent was removed to produce 0.47 g (21%) of bis[(η^5 -carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt] anhydride. The product was recrystallized via Soxhlet extraction using diethyl ether to give a yellow solid, m.p. 202–203°C. Anal. Found: C, 78.79; H, 5.09. $C_{68}H_{48}Co_2O_3$. Calc.: C, 79.22; H, 4.69%. 1H NMR ($CDCl_3$): δ 7.24 (m, 40H, phenyl), 5.17 (t, 4H, $H_{2,5}$), 4.74 (t, 4H, $H_{3,4}$). IR ($CDCl_3$): 3085–3030 (w), 1775 (w), 1705 (s), 1600 (m), 1500 (m), 1468 (m), 1448 (w), 1400 (w), 1383 (w), 1368 (w), 1288 (s), 1250 (w), 1198 (w), 1148 (m), 1110 (w), 1100 (w), 1070 (w), 1045 (w), 1028 (w), 1015 (w), 975 (w), 930–888 (m), 828 (m), 780 (s), 698 (s), 648 (w), 623 (w) cm^{-1} .

3.12. (η^5 -Ferrocenoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (16)

(η^5 -Carboxycyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt (1.47 g, 2.80 mmol) was weighed into a 250 ml Schlenk flask equipped with a magnetic stirring bar. The flask was evacuated and filled with nitrogen before adding 1.0 ml (12 mmol) of oxalyl chloride and 125 ml of methylene chloride. The reaction mixture was heated at reflux for 3 days. The solvent was removed and replaced by 125 ml of dry 1,2-dichloroethane. Ferrocene (0.537 g, 2.89 mmol) and aluminum chloride (0.408 g, 3.06 mmol) were added and the reaction was heated at reflux in the dark. After 4 days, the blue solution with a green hue was hydrolyzed with 50 ml of water followed by 50 ml of 10% hydrochloric acid. The layers were separated, the aqueous layer was extracted with methylene chloride, and the combined organic layer was washed with water. The red organic layer was dried over magnesium sulfate and filtered through Celite. The solvent was removed on

alumina and the material was loaded onto an alumina column (2 × 26 cm). A pale yellow band was eluted with 3:2 heptane–diethyl ether, followed by an intense yellow band with 4:1 diethyl ether–THF. The orange product band was subsequently eluted with 1:1 diethyl ether–THF to give 0.307 g (16%) of (η^5 -ferrocenoylcyclopentadienyl)(η^4 -tetraphenylcyclobutadiene)cobalt as an orange solid, m.p. 210–211.5°C. Anal. Found: C, 76.61; H, 5.17. $C_{44}H_{33}CoFeO$. Calc.: C, 76.31; H, 4.80%. 1H NMR ($CDCl_3$): δ 7.25 (m, 2H, phenyl), 5.44 (t, 2H, $H_{2,5}(Co)$), 4.86 (t, 2H, $H_{3,4}(Co)$), 4.52 (t, 2H, $H_{2,5}(Fe)$), 4.31 (t, 2H, $H_{3,4}(Fe)$), 4.10 (s, 5H, $C_5H_5(Fe)$). IR ($CDCl_3$): 3080–3030 (w), 2983 (w), 1618 (s), 1600 (s), 1500 (s), 1460 (s), 1380 (m), 1365 (m), 1285 (s), 1263 (s), 1105 (s), 1063 (s), 1048 (s), 1028 (s), 930–878 (in), 828 (s), 808 (s), 698 (s), 648 (m), 618 (w) cm^{-1} .

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