

# The Friedel–Crafts reactivity of ( $\eta^5$ -cyclopentadienyl) dicarbonylcobalt

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## Abstract

( $\eta^5$ -Cyclopentadienyl)dicarbonylcobalt undergoes Friedel–Crafts acylation with both organic and organometallic acid chlorides, including acetyl, benzoyl, *p*-toluoyl, *p*-anisoyl and 2-naphthoyl chlorides, and chloroformylferrocene as well as 1,1'-di(chloroformyl)ferrocene. The resulting ketones react with triphenylphosphine to afford the corresponding carbonyl–phosphine analogs. IR and NMR spectral features of the new compounds are discussed.

**Keywords:** Cobalt; Cyclopentadienyl; Ferrocene; Metallo–aromatic

## 1. Introduction

The Friedel–Crafts acylation reaction has played a very significant role in synthetic organic chemistry since its fortuitous discovery in 1877, and has laid the foundation for important modern chemical processes [1]. In 1952, Woodward and coworkers found that the organo-iron compound bis( $\eta^5$ -cyclopentadienyl)iron (ferrocene) could readily undergo Friedel–Crafts acylation to form both mono- and disubstituted acyl derivatives, depending on the number of equivalents of acylating agent used [2]. This facile electrophilic aromatic-type substitution reaction has subsequently played a key role in the extensive development of ferrocene chemistry.

Since this pioneering discovery, a small number of additional cyclopentadienyl–metal compounds have been found to exhibit metallo–aromatic properties. These include bis( $\eta^5$ -cyclopentadienyl)ruthenium (ruthenocene) [3,4], bis( $\eta^5$ -cyclopentadienyl)osmium (osmocene) [3,4], ( $\eta^5$ -cyclopentadienyl)tricarbonylmanganese (cymantrene) [5–7], ( $\eta^5$ -cyclopentadienyl)tricarbonyltechnetium [8] and -rhenium [8–10], ( $\eta^5$ -cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene) [11,12] and ( $\eta^5$ -cyclopentadienyl)tetracarbonylvandium [13–15]. In 1967, Fischer and coworkers determined the relative reactivities of many of these organometallic compounds towards Friedel–

Crafts acylation with respect to some common organic aromatic systems [16]. Ferrocene was shown to be the most reactive of all the compounds studied, with the reactivity decreasing in the following order: ferrocene > anisole > ruthenocene  $\geq$  cymantrene > osmocene > cynichrodene  $\geq$  ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>  $\approx$  benzene > ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)<sub>3</sub>.

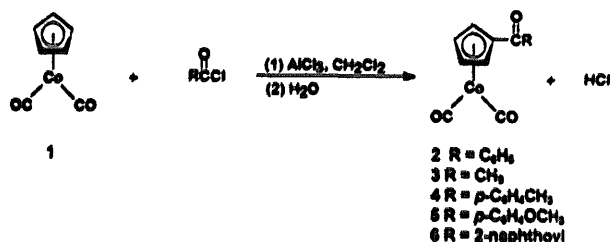
Although it was not included in the above study, ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (**1**) was reported in 1959 in the patent literature to undergo a Friedel–Crafts acylation reaction [17]. By treating a carbon disulfide solution of **1** with aluminum chloride and benzoyl chloride, Kozikowski was able to isolate ( $\eta^5$ -benzoylcyclopentadienyl)dicarbonylcobalt (**2**). It was not until 1981 that the aromatic reactivity of **1** was further investigated [18]. Hart modified the original procedure so that benzoylation occurred in a methylene chloride solution overnight at room temperature. He also formed a Perrier complex of benzoyl chloride and aluminum chloride prior to the addition of **1**. In a similar manner, Hart prepared ( $\eta^5$ -acetylcyclopentadienyl)dicarbonylcobalt (**3**). An alternative route to **3** utilizing sodium acetylcyclopentadienide, iodine and dicobalt octacarbonyl has subsequently been developed [19].

In this paper, we describe detailed synthetic procedures for a variety of new acyl derivatives of **1** obtained by the Friedel–Crafts method. Conversions of these compounds to the corresponding carbonyl–triphenylphosphine analogs are also reported, and spectral features of all new organometallic compounds are discussed.

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## 2. Results and discussion

In agreement with earlier brief reports [17,18], **1** readily undergoes Friedel–Crafts benzylation in the presence of aluminum chloride to afford the benzoyl derivative **2** in 49% yield. In a similar manner, Friedel–Crafts acetylation produces the acetyl analog **3** in 61% yield. In order to examine further the scope of this reaction, Friedel–Crafts acylations with a variety of other acid chlorides (*p*-toluoyl, *p*-anisoyl and 2-naphthoyl chlorides) were investigated. In each case, the corresponding ketones (**4–6**) were obtained in moderate yields as low-melting, slightly air-sensitive red oils which were difficult to purify further. All acylations were conducted by adding **1** to a preformed Perrier complex of the acid chloride and aluminum chloride in methylene chloride solution.

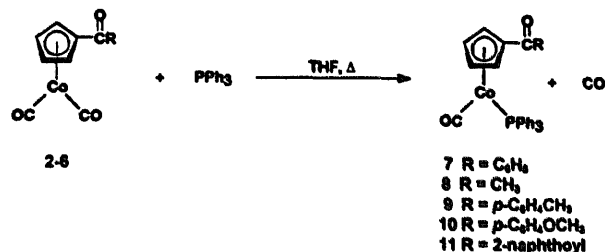


These electrophilic substitution reactions of **1** demonstrate its metallo–aromatic properties. It was therefore of interest to compare the relative reactivities of **1** and ferrocene under Friedel–Crafts conditions. Accordingly, a competition reaction was conducted between one equivalent each of **1** and ferrocene with one equivalent each of acetyl chloride and aluminum chloride. Following hydrolysis, examination of the reaction products by <sup>1</sup>H NMR demonstrated that ferrocene undergoes exclusive acylation. The <sup>1</sup>H NMR spectrum shows a singlet representative of unreacted **1** at 4.98 ppm, as well as two pseudo-triplets at 4.66 and 4.42 ppm and singlets at 4.13 and 2.25 ppm, all indicative of acetylferrocene.

The (η<sup>5</sup>-acylcyclopentadienyl)dicarbonylcobalt compounds **2–6** were converted to the corresponding cobalt–phosphine derivatives (**7–11**) by reaction with triphenylphosphine in refluxing THF [20,21]. The phosphine complexes **7–11** were obtained as air-sensitive red–black solids following purification by column chromatography and recrystallization.

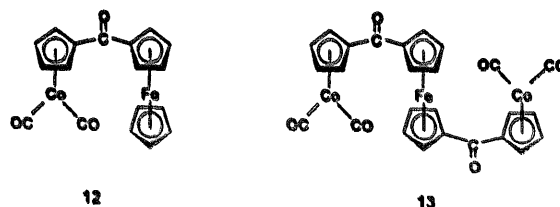
All the (η<sup>5</sup>-acylcyclopentadienyl)dicarbonylcobalt compounds **2–6** exhibit typical symmetric and antisymmetric terminal carbonyl stretches above and below 2000 cm<sup>-1</sup> in their IR spectra (2035–2000 cm<sup>-1</sup> and 1980–1950 cm<sup>-1</sup>). For the phosphine analogs **7–11**, the terminal carbonyl ligand absorbs at lower energy

(1943–1925 cm<sup>-1</sup>) than for **2–6**. This result is due to electron-donation of the phosphine ligand to the metal center, which strengthens the cobalt–carbon bond but weakens the carbon–oxygen bond in this ligand. The organic carbonyl groups in **2–6** appear between 1670 and 1590 cm<sup>-1</sup>, whereas this group is shifted to slightly lower energy (1640–1600 cm<sup>-1</sup>) in phosphine analogs **7–9** and **11**.



In the <sup>1</sup>H NMR spectra of the (η<sup>5</sup>-acylcyclopentadienyl)dicarbonylcobalt compounds **2–6**, the aromatic protons are observed as multiplets between 7.80 and 6.30 ppm, the cyclopentadienyl protons as pseudo-triplets on either side of 5.00 ppm (5.05–4.76 ppm and 4.60–4.17 ppm), and the methyl protons as singlets between 2.85 and 1.70 ppm. The corresponding phosphine complexes **7–11** show slight downfield shifts in the multiplets for the aromatic protons (7.41–7.30 ppm), the pseudo-triplets of the cyclopentadienyl protons (5.18–5.04 ppm and 4.73–4.66 ppm), and the singlets of the methyl protons (3.85–2.24 ppm). The <sup>31</sup>P NMR spectra of **7–11** contain somewhat broadened signals between 63.54 and 64.58 ppm. Broadening is likely due to spin–spin interaction with cobalt, which has a nuclear spin of 5/2.

The Friedel–Crafts reactivity of **1** can also be extended to the synthesis of bi- and trimetallic ketones. Thus, (η<sup>5</sup>-ferrocenylcyclopentadienyl)dicarbonylcobalt (**12**) has been prepared in 57% yield from ferrocenoyl chloride<sup>1</sup>, aluminum chloride and **1** by preforming the Perrier complex and subsequently adding **1**.



<sup>1</sup>Knobloch and Rauscher's procedure [22] for the preparation of 1,1'-di(chloroformyl)ferrocene using oxalyl chloride as the chlorinating agent was applied to the synthesis of chloroformylferrocene. This method is superior to those employing thionyl chloride or phosphorus pentachloride, owing to the absence of tar formation.

Compound **12** has previously been obtained by us in 36% yield from ( $\eta^5$ -chloroformylcyclopentadienyl)dicarbonylcobalt, aluminum chloride and ferrocene [23], but the procedure developed here is more convenient and straightforward. The spectral data for **12** obtained in this manner correspond to the earlier literature values [23].

In an analogous manner, 1,1'-bis( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt]ferrocene diketone (**13**) has been obtained from **1** in 33% yield, using 1,1'-di(chloroformyl)ferrocene [22] as the acylating agent. The IR spectrum of **13** shows the symmetric and antisymmetric terminal carbonyl stretches at 2013 and 1950  $\text{cm}^{-1}$ . The organic carbonyl stretching frequency for **13** at 1620  $\text{cm}^{-1}$  is comparable with the carbonyl frequency for diferrocenyl ketone (1612  $\text{cm}^{-1}$ ) [4]. In the  $^1\text{H}$  NMR spectrum of **13**, the pseudo-triplets representing protons on the cyclopentadienyl-cobalt rings appear at 5.56 and 5.33 ppm, whereas resonances representing the less deshielded protons on the cyclopentadienyl-iron rings appear at 4.97 and 4.58 ppm.

We have previously demonstrated that acyl derivatives of **1**, such as ( $\eta^5$ -formylcyclopentadienyl)dicarbonylcobalt and **3**, undergo a wide variety of transformations that implicate the formation of cobalt-stabilized carbonium ions [18,19]. The availability of the corresponding aroyl analogs as reported here should considerably facilitate further studies along these lines.

### 3. Experimental section

All operations were performed under an inert atmosphere of nitrogen using standard Schlenk or glove box techniques. Nitrogen was dried via 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, hexane and benzene were likewise distilled from Na/K alloy, whereas methylene chloride was dried and distilled from calcium hydride. Deoxygenated water was prepared by bubbling nitrogen just under the surface of distilled water as it was being heated to boiling overnight. It was then cooled under a nitrogen stream. Aluminum chloride and benzoyl chloride were obtained from Fisher Scientific Co. and Eastman Kodak respectively, whereas most other reagents were obtained from Aldrich. Column chromatography was conducted under nitrogen using neutral alumina or silica gel. The adsorbents were activated by heating in an oven prior to use. After the adsorbent had cooled to room temperature, it was packed into a glass column.  $^1\text{H}$  and  $^{31}\text{P}$  NMR data were obtained on a Bruker NR-80AF spectrometer.

Infrared 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. ( $\eta^5$ -Cyclopentadienyl)dicarbonylcobalt (**1**) was prepared by the method of Rausch and Genetti [24]. Since **1**, a red oil, decomposes readily in the presence of light and slowly in air, it was stored at  $-20^\circ\text{C}$  under nitrogen in the absence of light. It can be kept for months in this manner.

#### 3.1. ( $\eta^5$ -Acetylcyclopentadienyl)dicarbonylcobalt (**3**)

Acetyl chloride (0.53 ml, 7.4 mmol) and aluminum chloride (1.019 g, 7.64 mmol) were combined with 125 ml of dry methylene chloride in a 250 ml Schlenk flask equipped with a magnetic stirring bar and a nitrogen outlet leading to an oil bubbler. The solution was stirred at room temperature for 1.75 h. ( $\eta^5$ -Cyclopentadienyl)dicarbonylcobalt (1.35 g, 7.50 mmol) was then added and the red solution stirred at room temperature overnight in the absence of light. The solution was hydrolyzed by the slow addition of 50 ml of deoxygenated water containing ten drops of concentrated hydrochloric acid. The layers were separated and the aqueous layer extracted with methylene chloride. The combined organic layer was washed with water and dried over magnesium sulfate. The solution was filtered through Celite and the solvent removed to give 1.01 g (61%) of ( $\eta^5$ -acetylcyclopentadienyl)dicarbonylcobalt as a red oil. IR and  $^1\text{H}$  NMR spectra of the product were identical to literature data [18,19].

#### 3.2. ( $\eta^5$ -Acetylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt (**8**)

Following the above procedure, ( $\eta^5$ -acetylcyclopentadienyl)dicarbonylcobalt was synthesized from 1.346 g (10.1 mmol) of aluminum chloride, 0.90 ml (13 mmol) of acetyl chloride, and 1.543 g (8.57 mmol) of ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt. About 120 ml of dry THF and 2.45 g (9.35 mmol) of triphenylphosphine was added to the crude red oil in a 250 ml Schlenk flask equipped with a magnetic stirring bar, condenser, and nitrogen outlet attached to an oil bubbler. The red solution, which became brown instantly, was stirred at reflux overnight in the absence of light. The reaction mixture was allowed to cool to room temperature under a gentle flow of nitrogen. The solvent was removed in vacuo and the residue dissolved in dry methylene chloride. Alumina was added and the solvent removed. The material was loaded onto an alumina column ( $2 \times 21.5 \text{ cm}^2$ ) under nitrogen and the column eluted with diethyl ether to yield an orange-brown band. Removal of the solvent produced 0.76 g

(19% based on **1**) of ( $\eta^5$ -acetylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt, which was recrystallized from diethyl ether/hexane to give red-black crystals, m.p. 110–113 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.41 (m, 15H, phenyl), 5.04 (t, 2H,  $\text{H}_{2,5}$ ), 4.66 (t, 2H,  $\text{H}_{3,4}$ ), 2.24 (s, 3H,  $\text{CH}_3$ ).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  64.58. IR ( $\text{CH}_2\text{Cl}_2$ ): 1928 (s), 1648 (m), 1460 (w), 1425 (w), 1375 (w), 1087 (m)  $\text{cm}^{-1}$ . Anal. Found: C, 68.63; H, 4.91.  $\text{C}_{26}\text{H}_{22}\text{CoO}_2\text{P}$  Calc.: C, 68.43; H, 4.86%.

### 3.3. ( $\eta^5$ -Benzoylcyclopentadienyl)dicarbonylcobalt (**2**)

Benzoyl chloride (1.05 ml, 9.05 mmol) and aluminum chloride (1.207 g, 9.05 mmol) were combined with 100 ml of dry methylene chloride in a 250 ml Schlenk flask equipped with a magnetic stirring bar and a nitrogen outlet attached to an oil bubbler. The resulting yellow solution was stirred at room temperature under nitrogen for 2 h. Subsequently, ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.63 g, 9.05 mmol) was added and the red solution stirred overnight in the absence of light. The reaction mixture was hydrolyzed by the addition of 43 ml of deoxygenated water containing six drops of concentrated hydrochloric acid. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted twice with methylene chloride. The combined organic layer was washed twice with water, dried over magnesium sulfate, and filtered through a frit containing a small amount of Celite. Removal of the solvent in vacuo produced 1.25 g (49%) of ( $\eta^5$ -benzoylcyclopentadienyl)dicarbonylcobalt as a red oil. The product can be further purified by column chromatography on alumina, eluting with 2:1 pentane/diethyl ether and distillation at 50–60 °C/0.02 Torr. Storage of the distillate at –20 °C led to the formation of a red solid, which upon recrystallization from pentane at –78 °C afforded **3** as an orange solid, m.p. 41–42 °C.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (m, 2H, *o*-phenyl), 7.20 (m, 3H, *m*- and *p*-phenyl), 5.05 (t, 2H,  $\text{H}_{2,5}$ ), 4.58 (t, 2H,  $\text{H}_{3,4}$ ). IR ( $\text{C}_6\text{H}_6$ ): 3020 (br, w), 2040 (s), 1975 (s), 1650 (s), 1375 (m), 1275 (m), 1165 (w), 1020 (w), 880 (w), 720 (w)  $\text{cm}^{-1}$ . MS: *m/e* 284 ( $\text{M}^+$ ). Anal. Found: C, 58.91; H, 3.02.  $\text{C}_{14}\text{H}_9\text{CoO}_3$  Calc.: C, 59.17; H, 3.19%.

### 3.4. ( $\eta^5$ -Benzoylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt (**7**)

( $\eta^5$ -Benzoylcyclopentadienyl)dicarbonylcobalt was synthesized as described above using 1.15 ml (9.92 mmol) of benzoyl chloride, 1.324 g (9.93 mmol) of aluminum chloride, and 1.623 g (9.01 mmol) of ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt. Dry THF (125 ml) was added to the red oil in a 250 ml Schlenk flask which was equipped with a magnetic stirring bar,

condenser, and a nitrogen inlet attached to an oil bubbler. Triphenylphosphine (2.246 g, 8.56 mmol) was added and the resultant red solution heated at reflux for 36 h in the absence of light. Foaming and gas evolution were initially observed. The solution was allowed to cool to room temperature and the solvent removed in vacuo. The residue was dissolved in methylene chloride, and alumina was added. The solvent was removed and the material loaded onto an alumina column ( $2 \times 20 \text{ cm}^2$ ). Two bands were observed upon elution with diethyl ether, a faint yellow band and a red-brown band. Removal of the solvent from the second band yielded 1.14 g (24% based on **1**) of ( $\eta^5$ -benzoylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt, which was recrystallized from diethyl ether/hexane to give red-brown needles, m.p. 136–138 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.37 (m, 20H, phenyl), 5.17 (t, 2H,  $\text{H}_{2,5}$ ), 4.68 (t, 2H,  $\text{H}_{3,4}$ ).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  63.94. IR ( $\text{CH}_2\text{Cl}_2$ ): 1935 (s), 1615 (m), 1370 (m), 1275–1245 (m), 1085 (m)  $\text{cm}^{-1}$ . Anal. Found: C, 71.53; H, 4.72.  $\text{C}_{31}\text{H}_{24}\text{CoO}_2\text{P}$  Calc.: C, 71.82; H, 4.67%.

### 3.5. ( $\eta^5$ -*p*-Toluoylcyclopentadienyl)dicarbonylcobalt (**4**)

The reaction procedure was analogous to that described for **3**, using *p*-toluoyl chloride (1.05 ml, 7.94 mmol), aluminum chloride (1.126 g, 8.45 mmol), methylene chloride (130 ml) and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.43 g, 7.94 mmol). Following hydrolysis, extraction, drying and removal of the solvent, 1.783 g (75%) of ( $\eta^5$ -*p*-toluoylcyclopentadienyl)dicarbonylcobalt was obtained as a red oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.53 (d, 2H, phenyl), 6.62 (d, 2H, phenyl), 4.76 (t, 2H,  $\text{H}_{2,5}$ ), 4.17 (t, 2H,  $\text{H}_{3,4}$ ), 1.70 (s, 3H,  $\text{CH}_3$ ). IR (pentane): 2930–2825 (s), 2000 (s), 1953 (s), 1710 (w), 1623 (m), 1593 (m), 1550 (w), 1450–1437 (m), 1365 (m), 1337 (m), 1295 (w), 1265 (m), 1165 (m), 1150 (w), 1105 (w), 1073 (w), 1025 (w), 1005 (w), 847 (w), 827–803 (w), 770 (m), 727 (w)  $\text{cm}^{-1}$ .

### 3.6. ( $\eta^5$ -*p*-Toluoylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt (**9**)

The reaction procedure was analogous to that described for **8**, using *p*-toluoyl chloride (1.50 ml, 11.3 mmol), aluminum chloride (1.303 g, 9.77 mmol), methylene chloride (130 ml), and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.500 g, 8.33 mmol). Subsequent reaction of the resulting red oil (**4**) with triphenylphosphine (2.283 g, 8.70 mmol) in 150 ml of THF in a 250 ml Schlenk flask at reflux for 3 days, removal of the solvent and column chromatography on alumina gave a dark brown band (pentane), a light yellow band (1:1 pentane/diethyl ether), and a red band (diethyl ether). Removal of the solvent from the third band yielded 0.673 g (15% based on **1**) of ( $\eta^5$ -*p*-toluoyl-

cyclopentadienyl)carbonyl(triphenylphosphine)cobalt, which was recrystallized from diethyl ether/hexane to give red–black needles, m.p. 131–134°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.36 (m, 19H, phenyl), 5.15 (t, 2H,  $\text{H}_{2,5}$ ), 4.66 (t, 2H,  $\text{H}_{3,4}$ ), 2.40 (s, 3H,  $\text{CH}_3$ ).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  63.67. IR ( $\text{CH}_2\text{Cl}_2$ ): 1938 (s), 1620 (m), 1370 (m), 1275–1245 (m), 1090 (m)  $\text{cm}^{-1}$ . Anal. Found: C, 72.23; H, 4.99.  $\text{C}_{22}\text{H}_{26}\text{CoO}_2\text{P}$  Calc.: C, 72.18; H, 4.92%.

### 3.7. ( $\eta^5$ -*p*-Anisoylcyclopentadienyl)dicarbonylcobalt (5)

Following the reaction procedure described for 3, *p*-anisoyl chloride (1.97 ml, 14.5 mmol), aluminum chloride (2.012 g, 15.1 mmol), 130 ml of methylene chloride and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (2.62 g, 14.5 mmol) produced 2.16 g (47%) of (*p*-anisoylcyclopentadienyl)dicarbonylcobalt as a red oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.80 (d, 2H, phenyl), 6.30 (d, 2H, phenyl), 4.80 (t, 2H,  $\text{H}_{2,5}$ ), 4.20 (t, 2H,  $\text{H}_{3,4}$ ), 2.85 (s, 3H,  $\text{CH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 2015 (s), 1950 (s), 1590 (m)  $\text{cm}^{-1}$ .

### 3.8. ( $\eta^5$ -*p*-Anisoylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt (10)

Following the procedure described for 8, using *p*-anisoyl chloride (1.40 ml, 12.9 mmol), aluminum chloride (1.337 g, 10.0 mmol), methylene chloride (130 ml) and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.599 g, 8.88 mmol), 5 was obtained as a red oil. Subsequent reaction of the red oil with triphenylphosphine (2.254 g, 8.59 mmol) in 120 ml of THF at reflux overnight followed by column chromatography ( $2 \times 20 \text{ cm}^2$ ) on alumina gave two bands: a brown band (1:1 pentane/diethyl ether) and a red–brown band (diethyl ether). The latter afforded 0.57 g (12% based on 1) of ( $\eta^5$ -*p*-anisoylcyclopentadienyl)carbonyl(triphenylphosphine)cobalt. The product was recrystallized from methylene chloride/hexane to give red–brown crystals, m.p. 139–141°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.37 (m, 19H, phenyl), 5.13 (t, 2H,  $\text{H}_{2,5}$ ), 4.68 (t, 2H,  $\text{H}_{3,4}$ ), 3.85 (s, 3H,  $\text{CH}_3$ ).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  63.74. IR ( $\text{CH}_2\text{Cl}_2$ ): 1930 (s), 1595 (m), 1455 (m), 1370 (m), 1280–1245 (m), 1160 (m), 1090 (m), 1025 (m), 860 (w), 840 (w), 810 (w)  $\text{cm}^{-1}$ . Anal. Found: C, 70.03; H, 4.80; P, 5.98.  $\text{C}_{32}\text{H}_{26}\text{CO}_3\text{P}$  Calc.: C, 70.08; H, 4.78; P, 5.65%.

### 3.9. ( $\eta^5$ -2-Naphthoylecyclopentadienyl)dicarbonylcobalt (6)

The reaction procedure was analogous to that described for 3, using 2-naphthoyl chloride (1.96 g, 10.3 mmol), aluminum chloride (1.37 g, 10.3 mmol), methylene chloride (100 ml) and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.85 g, 10.3 mmol). Following

hydrolysis, extraction, drying and removal of the solvent, 1.249 g (36%) of ( $\eta^5$ -2-naphthoylecyclopentadienyl)dicarbonylcobalt was obtained as a red oil. IR ( $\text{CH}_2\text{Cl}_2$ ): 3045 (w), 2975 (m), 2933 (w), 2035 (s), 1970 (s), 1683 (s), 1623 (w), 1590 (w), 1507 (m), 1433 (m), 1370 (w), 1320 (w), 1270–1230 (w), 1207 (w), 1193 (m), 1090 (w), 825 (m), 787–690 (m)  $\text{cm}^{-1}$ .

### 3.10. ( $\eta^5$ -2-Naphthoylecyclopentadienyl)carbonyl(triphenylphosphine)cobalt (11)

The reaction procedure was analogous to that described for 8, using 2-naphthoyl chloride (1.426 g, 7.48 mmol), aluminum chloride (1.001 g, 7.51 mmol), methylene chloride (100 ml) and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.307 g, 7.26 mmol). Reaction of the resulting red oil (6) with triphenylphosphine (1.999 g, 7.62 mmol) in 130 ml of THF at reflux overnight, removal of the solvent, and column chromatography on alumina gave several small bands on elution with pentane/ethyl ether as well as the product band on elution with diethyl ether. Removal of the solvent from the latter band yielded 0.83 g (20% based on 1) of ( $\eta^5$ -2-naphthoylecyclopentadienyl)carbonyl(triphenylphosphine)cobalt, which was recrystallized from diethyl ether/hexane to give a red–black solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.30 (m, 22H, aromatic), 5.18 (t, 2H,  $\text{H}_{2,5}$ ), 4.73 (t, 2H,  $\text{H}_{3,4}$ ).  $^{31}\text{P}$  NMR( $\text{H}$ ) ( $\text{CDCl}_3$ ):  $\delta$  63.55. IR ( $\text{CDCl}_3$ ): 1943 (s), 1610 (m), 1435 (m), 1380 (m), 1290 (m)  $\text{cm}^{-1}$ . Anal. Found: C, 74.26; H, 4.63.  $\text{C}_{35}\text{H}_{26}\text{CoO}_2\text{P}$  Calc.: C, 73.95; H, 4.61%.

### 3.11. Chloroformylferrocene

Ferrocenecarboxylic acid [25] (4.96 g, 21.6 mmol) was weighed into a 250 ml Schlenk flask equipped with a magnetic stirring bar. The flask was evacuated and filled with nitrogen several times. To the flask was added 100 ml of dry methylene chloride, 4.0 ml (47 mmol) of oxalyl chloride, and four drops of pyridine. A mercury bubbler was attached via a gas outlet and the flask was wrapped with aluminum foil in order to exclude light. The reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue extracted repeatedly with hexane. The solvent was removed from the combined hexane extracts to give 1.984 g (37%) of chloroformyl ferrocene as a red solid. The IR and  $^1\text{H}$  NMR spectra of the product corresponded to literature values [26].

### 3.12. ( $\eta^5$ -Ferrocenoylcyclopentadienyl)dicarbonylcobalt (12)

Under nitrogen, 100 ml of dry methylene chloride was added to chloroformylferrocene (1.984 g, 7.98 mmol) contained in a 250 ml Schlenk flask equipped

with a magnetic stirring bar and a gas outlet. Aluminum chloride (1.073 g, 8.05 mmol) was added to the red solution, which turned blue as it was stirred at room temperature. After 2 h, ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (1.340 g, 7.44 mmol) dissolved in 15 ml of methylene chloride was added to the flask, and the solution immediately turned purple. The reaction mixture was stirred at room temperature overnight, hydrolyzed with 50 ml of water followed by 50 ml of 10% hydrochloric acid, and the layers were separated. The aqueous layer was extracted with methylene chloride and the combined organic layer washed with water. The organic layer was dried over magnesium sulfate and filtered through Celite. The solvent was removed on silica gel. The coated material was loaded onto a silica gel column ( $2 \times 20.5$  cm) under nitrogen. Elution with pentane removed a yellow band, whereas diethyl ether eluted a red band. After removal of the solvent from the latter band, 1.65 g (57%) of ( $\eta^5$ -ferrocenylcyclopentadienyl)dicarbonylcobalt was obtained. Both the IR and  $^1\text{H}$  NMR spectra were identical to those previously reported [23].

### 3.13. 1,1'-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt]ferrocene diketone (13)

Under nitrogen, aluminum chloride (1.49 g, 11.2 mmol) was added to 1,1'-di(chloroformyl)ferrocene [22] (1.722 g, 5.54 mmol) dissolved in 120 ml of dry methylene chloride in a 250 ml Schlenk flask equipped with a magnetic stirring bar and a gas outlet. The resulting violet solution was stirred for 3 h before slowly adding ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (2.160 g, 12.0 mmol) dissolved in 15 ml of methylene chloride. The resultant blue solution was subsequently stirred at room temperature overnight. The reaction mixture was hydrolyzed with 50 ml of deoxygenated water and the layers were separated. The aqueous layer was extracted with methylene chloride, and the combined organic layer was washed with water. The organic layer was dried over magnesium sulfate and filtered through Celite. Silica gel was added and the solvent removed in vacuo. The red material was loaded onto a silica gel column ( $2 \times 21.5$  cm) under nitrogen. A light orange band was eluted with 4:1 pentane/diethyl ether followed by a red band which was eluted with diethyl ether. The solvent was removed from the second band to yield 1.11 g (33%) of 1,1'-bis[( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt]ferrocene diketone. Recrystallization of the product from methylene chloride/hexane gave red crystals, m.p. above  $260^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.56 (t, 2H,  $\text{H}_{2,5}(\text{Co})$ ), 5.33 (t, 2H,  $\text{H}_{3,4}(\text{Co})$ ), 4.97 (t, 2H,  $\text{H}_{2,5}(\text{Fe})$ ), 4.58 (t, 2H,  $\text{H}_{3,4}(\text{Fe})$ ). IR ( $\text{CDCl}_3$ ): 2013 (s), 1970 (s), 1620 (m), 1443 (m), 1380 (m), 1283 (m), 1050 (w), 805 (w), 613 (w)  $\text{cm}^{-1}$ . Anal. Found: C, 52.43; H, 3.02.  $\text{C}_{26}\text{H}_{16}\text{Co}_2\text{FeO}_6$  Calc.: C, 52.21; H, 2.70%.

### 3.14. Competition study of ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt with ferrocene towards Friedel–Crafts acylation

In a glove box, aluminum chloride (0.340 g, 2.55 mmol) was weighed into a 25 ml Schlenk flask and a magnetic stirring bar was added. After removal of the flask from the box, 10 ml of dry methylene chloride and 0.19 ml (2.7 mmol) of acetyl chloride were added to the flask, and the mixture was subsequently stirred at room temperature for 100 min. The solution was then added to a 25 ml Schlenk flask containing ferrocene (0.518 g, 2.78 mmol) and ( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt (0.500 g, 2.78 mmol) dissolved in 10 ml of dry methylene chloride. The solution immediately became purple. The reaction was then stirred for 23 h in the absence of light, and hydrolyzed with 15 ml of deoxygenated water followed by 10 ml of 10% hydrochloric acid. The layers were separated, the aqueous layer extracted with methylene chloride, and the combined organic layer washed with water. The organic layer was then dried over magnesium sulfate and filtered. The solvent was removed to give a dark red solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.98 (s, 5H,  $\text{C}_5\text{H}_5(\text{Co})$ ), 4.66 (t, 2H,  $\text{H}_{2,5}(\text{Fe})$ ), 4.42 (t, 2H,  $\text{H}_{3,4}(\text{Fe})$ ), 4.13 (s, 5H,  $\text{C}_5\text{H}_5(\text{Fe})$ ), 2.25 (s, 3H,  $\text{CH}_3$ ).

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