The formation and reactions of (η^5-formylcyclopentadienyl)dicarbonylcobalt and (η^5-acetylcyclopentadienyl)dicarbonylcobalt *

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Abstract

(η^5-Formylcyclopentadienyl)dicarbonylcobalt and (η^5-acetylcyclopentadienyl)dicarbonylcobalt have been prepared and the reactivity of the organic functional groups studied. These transformations include the Wittig reaction, sodium borohydride reduction, and Grignard reactions. In addition, alcohol derivatives were converted into their acrylates. Reaction pathways indicating the formation of cobalt-stabilized carbonium ions as intermediates have been implicated.

Introduction

Since its discovery in 1955 [1,2], (η^5-cyclopentadienyl)dicarbonylcobalt (**1**) has played an important role in the development of organocobalt chemistry. Considerable effort has focused on the substitution reactions that can take place at the metal center [3]. Recently, **1** has also been bound to styrenedivinylbenzene copolymers and examined as a hydrogenation [4] and Fischer–Tropsch [5] catalyst.

In contrast, relatively few studies have been reported concerning derivatives of **1** which have functional groups on the cyclopentadienyl ring [6–8]. In an earlier communication, we reported the preparation of (η^5-formylcyclopentadienyl)dicarbonylcobalt (**2**) and (η^5-acetylcyclopentadienyl)dicarbonylcobalt (**3**), and described the conversions of **2** and **3** to their corresponding vinyl (**4**) and isopropenyl (**5**) derivatives [9]. We now describe further reactions of **2** and **3** as well as the synthetic utility of their derivatives.

Results and discussion

As reported previously, sodium formylcyclopentadienide (**6**) and sodium acetyl-cyclopentadienide (**7**) can be readily prepared from reactions between sodium cyclopentadienide and ethyl formate or ethyl acetate [9]. The salts are isolable and relatively air-stable, but are moisture-sensitive white or off-white solids. The structures of the salts are undoubtedly more complex than illustrated, both in solution and in the crystal state, as indicated by our recent structural studies on **7** [10].

Transition metal derivatives of these salts can be obtained by reactions with appropriate metal halides. Thus, reactions of **6** and **7** with [Rh(CO)$_2$Cl]$_2$ afforded the corresponding substituted (η^5-cyclopentadienyl)dicarbonylrhodium complexes **8** and **9** in good yields [9].

(**6** : R = H ;

   7 : R = CH$_3$)

(**8** : R = H ;

   9 : R = CH$_3$)
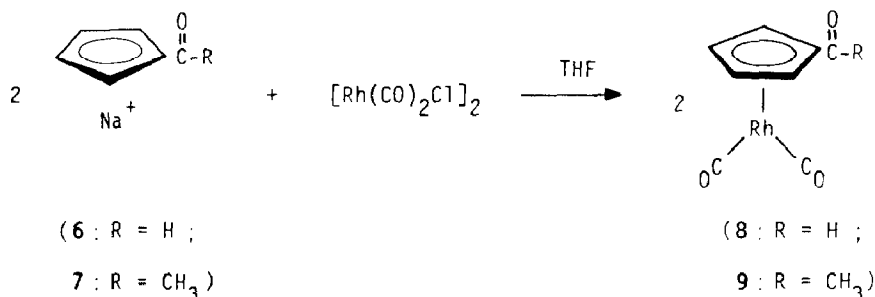
In order to synthesize the corresponding cobalt complexes, a suitable cobalt carbonyl halide was required. Several earlier studies in this area had been reported. Hieber and Schulten had described the synthesis of "CoI$_2$·CO" during a high pressure synthesis of Co$_2$(CO)$_8$ from CoI$_2$ and CO [11]. Heck reported that his efforts to prepare Co(CO)$_4$I from CHI$_3$ and HCo(CO)$_4$ at $-80°$C led to decomposition, as did a reaction of acetyltetracarbonylcobalt with an equivalent of iodine. In constrast, however, Heck noted that treatment of acetyltricarbonyl(triphenyl-phosphine)cobalt with iodine afforded Co(CO)$_3$(PPh$_3$)I in 60% yield [12]. In 1967, Bigorgne and Pankowski described the preparation of "Co(CO)$_4$I" by treatment of Co(CO)$_4$PbEt$_3$ or Hg[Co(CO)$_4$]$_2$ with iodine at $-40°$C in hexane, or by treatment of Co$_2$(CO)$_8$ with iodine in hexadecane solution at 25°C. The IR spectrum of the product in hexadecane solution was reported to exhibit carbonyl stretching bands at 2115, 2050 and 2046 cm^{-1} [13].

Our attempts to reproduce Bigorgne's results were inconclusive. We did obtain a "Co(CO)$_x$I" species when iodine and Co$_2$(CO)$_8$ were combined in either THF or Nujol. However, in THF a terminal metal carbonyl frequency was observed at 2025 cm^{-1} as a weak absorption, while another terminal carbonyl absorption at 1900 cm^{-1} was very strong. In Nujol, two carbonyl bands were also observed, one at 2060 cm^{-1} which was strong, and one at 1860 cm^{-1} which was of medium intensity. As in the case of Bigorgne's studies, we were unable to isolate a complex such as "Co(CO)$_4$I". The only recoverable materials were Co$_2$(CO)$_8$ and CoI$_2$, the latter possibly as a THF complex.

It is not clear why the discrepancy between our results and those of Bigorgne occurred. It is perhaps possible that we were examining a complex that was a subsequent reaction product derived from "Co(CO)$_4$I", as described by Bigorgne.

In any event, we were able to successfully utilize our intermediate in reactions with **6** and **7** to prepare the substituted (η^5-cyclopentadienyl)dicarbonylcobalt derivatives **2** and **3**.

(6 : R = H ;

7 : R = CH$_3$)

(2 : R = H ;

3 : R = CH$_3$)

Thus, one equivalent each of iodine and $Co_2(CO)_8$ were combined in THF at 25°C. Evolution of carbon monoxide ensued, and the reaction mixture turned green. Addition of **6** or **7** afforded the corresponding transition metal derivatives in 30–45% yield. These compounds were readily purified by column chromatography and could be obtained analytically pure by vacuum distillation. They were characterized by their ^{1}H NMR spectra which consisted of an A_2B_2 pattern of pseudo triplets for the hydrogens of the monosubstituted cyclopentadienyl ring. Their IR spectra exhibited two strong metal carbonyl stretching frequencies and one strong organic carbonyl absorption. The acetyl derivative also exhibited a molecular ion peak in the mass spectrum.

We previously reported that **2** and **3** could be converted into the corresponding vinyl **(4)** and isopropenyl **(5)** derivatives by reactions with methylene-triphenylphosphorane in ethyl ether solution at 25°C [9].

(4)

(5)

Previous attempts to prepare the above led to low yields of isolated products [14,15]. Compounds **4** and **5** were purified by column chromatography and were obtained analytically pure by vacuum distillation at 25°C. The ^{1}H NMR spectrum of each compound exhibited a complex splitting pattern. Compound **4** exhibited a doublet of doublets for the vinylic proton H_a at δ 6.05 in C_6D_6 solution. A J value of 17.5 Hz was the result of *trans* coupling between H^a and H^c, whereas a J value of 10.5 Hz was due to *cis* coupling of H^a and H^b. A doublet of doublets was also observed for H^c at δ 5.18 with J values of 17.5 Hz due to *trans* coupling with H^a and 1.5 Hz due to geminal coupling with H^b. The remaining vinylic proton (H^b) was observed at δ 4.87 with J values of 10.5 Hz due to *cis* coupling with H^a and 1.5 Hz due to geminal coupling with H^c. An A_2B_2 pattern of pseudo triplets at δ 4.77 and 4.48 were assignable to the protons of the cyclopentadienyl ring.

The ^{1}H NMR spectrum of the isopropenyl analog **5** exhibited a doublet at δ 5.10 for H^a, with a J value of 1.5 Hz due to geminal coupling with H^b. The resonance for H^b at δ 4.70 was partially obscured by the presence of the A$_2$B$_2$ pattern of pseudo triplets at δ 4.80, assignable to the H(2,5) protons of the cyclopentadienyl ring. In addition, a pseudo triplet due to the H(3,4) protons and a singlet for the methyl protons were observed at δ 4.50 and 1.75, respectively.

The IR spectra for both **4** and **5** contained two strong absorptions in the terminal metal carbonyl region as well as relatively weak olefinic stretching bands between 1630–1640 cm^{-1}. The vinyl derivative **4** also exhibited a molecular ion peak in its mass spectrum.

Attempted free radical polymerizations of the two complexes have thus far not been successful [16]. It was found that **4** and **5** prepared in this manner would not homopolymerize or copolymerize with several vinyl type monomers using AIBN initiation at 50°C in benzene. Inorganic decomposition products were often ob-

(**2** : R = H ;

3 : R = CH$_3$)

(**10** : R = H ;

11 : R = CH$_3$)
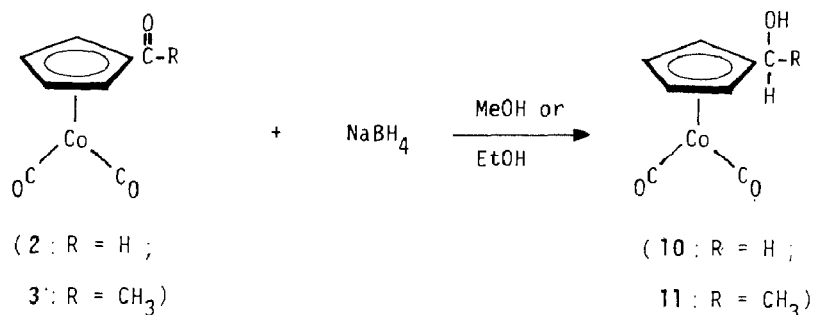
tained. In contrast, the related monomer (η^5-vinylcyclopentadienyl)dicarbonyliridium has been successfully homo- and co-polymerized, demonstrating the higher stability of the heavier metal analog [17].

We further studied the reactivity of the formyl and acetyl substituents in **2** and **3** by conducting a number of reduction experiments. Thus, both **2** and **3** were allowed to react with sodium borohydride in methanol or ethanol for several hours at 25°C. (η^5-1-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (**10**) and (η^5-1-hydroxyethylcyclopentadienyl)dicarbonylcobalt (**11**), respectively, were isolated in good yields without additional acid hydrolysis. The alcohols **10** and **11** were purified by column chromatography and were characterized by their IR and ^{1}H NMR spectra.

(**2** : R = H ;

3 : R = CH$_3$)

(**12** : R = H, R' = C$_2$H$_5$;

13 : R = CH$_3$, R' = C$_2$H$_5$;

**14** : R = CH$_3$, R' = CH$_3$)
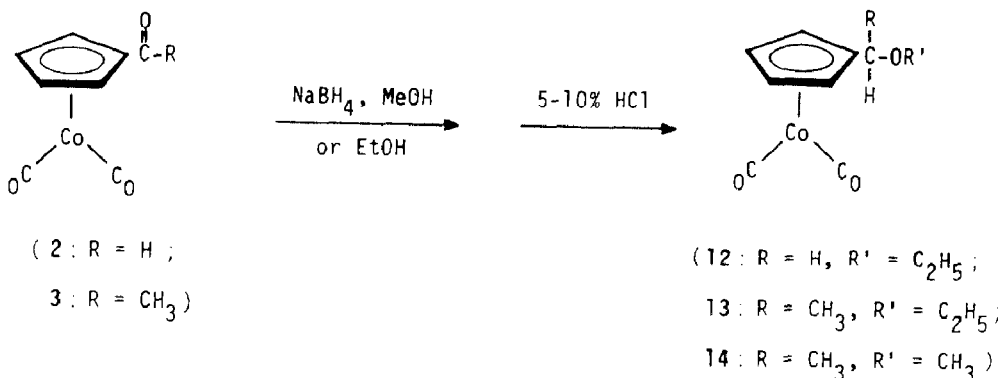
Acid hydrolysis of the intermediate borate esters was not necessary. It appeared that the intermediate was sufficiently labile to be hydrolyzed by the small amount of water present in the laboratory-grade alcohols employed as solvents.

In fact, if acid hydrolysis (5–10% HCl) was carried out subsequent to reduction, a significant quantity of the corresponding ethers (12–14) could be isolated. Further, if reduction of 2 or 3 was conducted in absolute ethanol, up to 20% of (η^5-methylcyclopentadienyl)dicarbonylcobalt (15) or (η^5-ethylcyclopentadienyl)dicarbonylcobalt (16) could be isolated, respectively. Evidently, in the absence of water in the alcohol, the intermediate borate esters can be further reduced to the

(15)   (16)
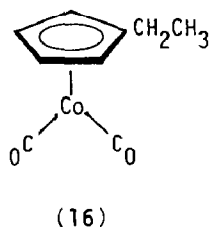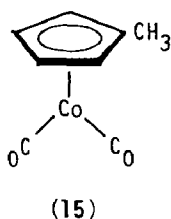
alkyl substituents. We confirmed the presence of ethers and their ease of formation by reacting 10 and 11 with methanol in the presence of a catalytic amount of p-toluenesulfonic acid.

(10 : R = H ;   (17 : R = H ;

11 : R = CH$_3$)   14 : R = CH$_3$)
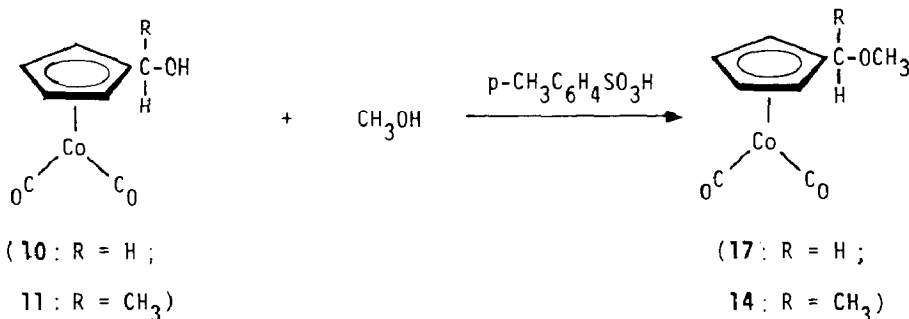
The ethers 12–14 and 17 were purified by column chromatography and were obtained analytically pure via vacuum distillation. Each was fully characterized by its IR and ^{1}H NMR spectra.

The formyl and acetyl derivatives 2 and 3 reacted readily with Grignard reagents via addition at the organic carbonyl group. Thus, addition of methylmagnesium iodide to either 2 or 3 afforded the corresponding alcohols 11 or 18 in 70–80% yield after mild acid hydrolysis.


(2 : R = H ;   (11 : R = H ;

3 : R = CH$_3$)   18 : R = CH$_3$)
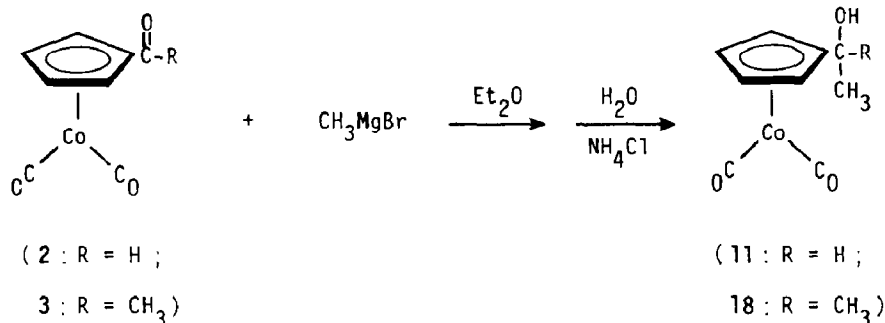
Compound **11** was characterized by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample. Compound **18** was purified by column chromatography and distilled in vacuo to yield an analytically pure product. It was also characterized by its IR and ^{1}H NMR spectra. The hydroxyl hydrogen was exchangeable with deuterium oxide as noted by a loss of the O–H resonance in the latter spectrum.

In a similar manner, phenylmagnesium bromide was combined with **2** or **3** to afford the alcohols **19** and **20** in 60–75% yield after mild acid hydrolysis. Both
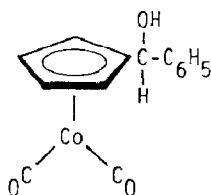
(19)
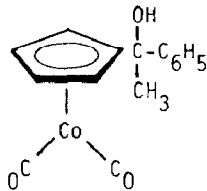
(20)

alcohols were isolated after column chromatography and purified by vacuum distillation. They were characterized by elemental analyses and by their IR and ^{1}H NMR spectra.

We elaborated on the chemistry of the alcohols by converting them into their acrylate esters. Alcohols **10** and **11** were treated with acryloyl chloride and pyridine in ethyl ether or benzene to afford the acrylates **21** and **22** in low yield.
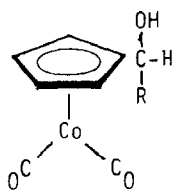
(10 : R = H ;

11 : R = CH_3)
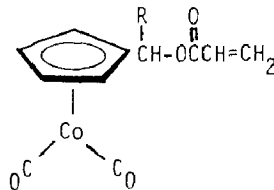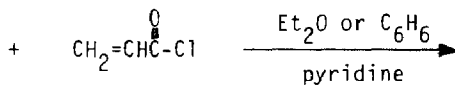
(21 : R = H ;

22 : R = CH_3)

The esters were isolated and purified via column chromatography and subsequent vacuum distillation at 25° C. They were characterized via their IR spectra by an ester carbonyl absorption at 1725 cm^{-1} and metal carbonyl bands at 2030 and 1960 cm^{-1}. The ^{1}H NMR spectrum of **21** exhibited the typical A_2B_2 pseudo triplets at δ 5.40 and δ 5.28 as well as a complex pattern of absorptions for the three vinylic hydrogens at δ 5.90–6.50. Compound **22** likewise displayed an A_2B_2 pseudo triplet pattern at δ 4.70 and δ 4.45 as well as a complex pattern of vinylic hydrogen resonances at δ 5.90–6.20. The methine hydrogen appeared as a quartet at δ 5.64 (J 6 Hz). It was coupled with the methyl hydrogens which appeared as a doublet at δ 1.25 (J 6 Hz). The acrylate **21** did not exhibit a molecular ion in the mass spectrum, although fragmentation peaks at m/e 236 and 208 due to losses of one or both metal carbonyl subsituents, respectively, were observed.

In connection with our program on vinyl-type organometallic monomers [7,17–24] we needed a more efficient synthetic route for the preparation of cobalt-containing

acrylate esters. We subsequently found that a slurry of alcohol **10** and sodium hydride when combined with acryloyl chloride afforded a 56% yield of acrylate **21** after column chromatography.

(10)   (21)
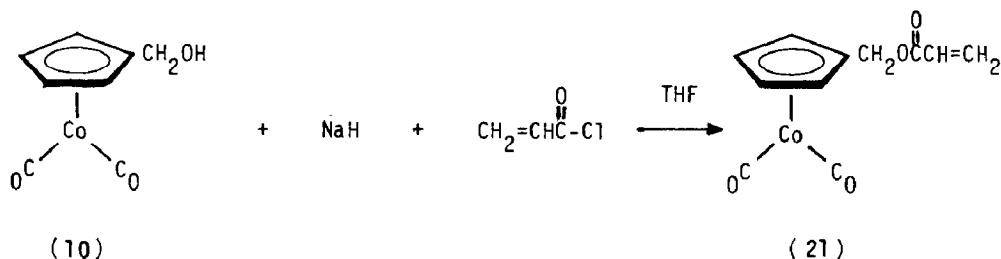
In addition, a second product (**23**) was isolated in 11% yield, resulting most likely from Michael addition of the sodium salt of **10** to acrylate **21** formed in the reaction.


(23)
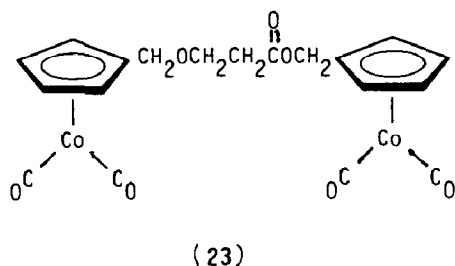
The IR spectrum of **23** revealed an ester carbonyl at 1738 cm^{-1} and terminal metal carbonyls at 2020 and 1960 cm^{-1}. The ^{1}H NMR spectrum exhibited A_2B_2 pseudo triplets at δ 4.80 and 4.60 due to the hydrogens of the cyclopentadienyl rings, a four hydrogen singlet at δ 3.80 due to the methylene groups adjacent to the rings, a two hydrogen triplet at δ 3.50 (J 6 Hz) assigned to the methylene group adjacent to the carbonyl function, and a two hydrogen triplet at δ 2.32 (J 6 Hz) attributed to the methylene group adjacent to and coupled with the other methylene unit. The mass spectrum revealed no molecular ion, but did exhibit peaks at m/e 418, 390 and 362 assignable to $(M-2CO)^+$, $(M-3CO)^+$ and $(M-4CO)^+$ fragments, respectively.

A third product isolated in very small amounts from the reaction mixture via column chromatography was characterized as (η^5-methylcyclopentadienyl)dicarbonylcobalt **15** by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample. This result was unusual since the formation of **15** would presumably involve nucleophilic attack of hydride ion on either alcohol **10** or acrylate **21**. Sodium hydride, however, is a non-nucleophilic base. In order to provide additional information on the reaction pathway, **10** was treated with sodium hydride in THF at reflux for 30 minutes. After hydrolysis and column chormatography, a 30% yield of **15** was obtained.

(10)   (15)
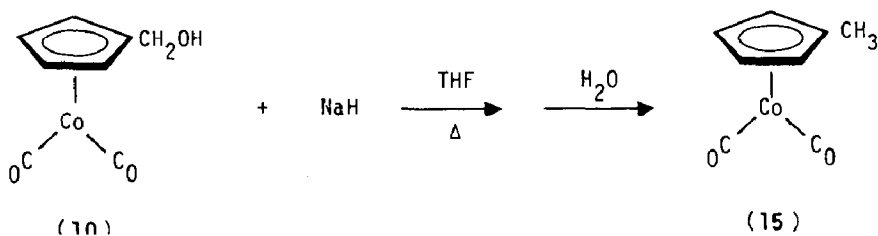
Thus, **15** was probably produced in the first part of the reaction sequence leading to acrylate **21**. While further studies on the mechanism of the reaction are necessary, it seems likely that a cobalt-assisted hydride displacement of the alcohol group and/or pre-ionization of the OH function with addition of hydride ion could have taken place.

In a final reaction sequence, we were successful in hydrogenating the organic carbonyl functions of **2** and **3** entirely to the corresponding methyl **15** and ethyl **16** derivatives using a slurry of aluminum chloride/lithium aluminum hydride. Compounds **15** and **16** were isolated in moderate yields following column chromatography, and their IR and ^{1}H NMR spectra were compared to authentic samples.

$$(2 : R = H ;$$
$$3 : R = CH_3)$$

$$(15 : R = H ;$$
$$16 : R = CH_3)$$
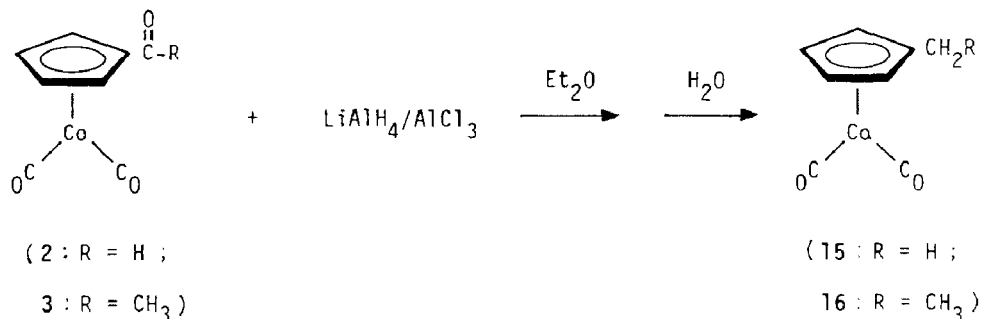
Previous investigations by Brown and White have suggested that reactions of this type proceed via a stabilized carbonium ion intermediate [25]. Our results thus point to enhanced stability of a carbocationic center adjacent to the (η^5-cyclopentadienyl)dicarbonylcobalt moiety. Indeed, a stabilized carbonium ion intermediate would tend to support the above suggestion that in the reaction of **10** and sodium hydride, a pre-ionization of the alcohol group took place.

Conclusions

The facile method of preparation of **2** and **3** described in this study has opened the door for further exploration of the chemistry of formyl and acyl functional groups attached to the (η^5-cyclopentadienyl)dicarbonylcobalt moiety. These functionally substituted derivatives of **1** as well as carboalkoxy [8] and halogeno [26] analogs have sufficient stability to permit many reactions to take place at the side chain. Reaction pathways suggestive of the formation of cobalt-stabilized carbonium ions as intermediates have been implicated. Additional studies along these lines are currently under way and will be reported in due course.

Experimental

All operations including chromatographic separations were carried out under a nitrogen atmosphere utilizing standard Schlenk techniques. Trace oxygen was removed from the nitrogen by passage through a column of BTS catalyst. The nitrogen was then dried via passage through successive columns of sulfuric acid and phosphorus pentoxide. Hexane and pentane were distilled under argon from calcium hydride. Tetrahydrofuran (THF) and ethyl ether were predried over potassium hydroxide, dried over sodium wire, and finally distilled under argon from sodium/

benzophenone. Column chromatography was carried out using Fisher-brand Florisil, Davison-brand silica gel (100–200 mesh) and CAMAG-brand alumina. All adsorbants were predried for 24 h in a drying oven at 150°C and then heated under vacuum (0.01 mmHg) on a rotary evaporator to remove residual water and oxygen. The alumina was subsequently deactivated with 5% (by weight) degassed water. Dicobalt octacarbonyl was obtained from Strem Chemicals. Dichlorotetra-carbonyldirhodium [27], sodium formylcyclopentadienide [9,28] and sodium acetyl-cyclopentadienide [9,10] were prepared according to literature procedures. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer. IR spectra were recorded on either a Perkin–Elmer 237-B or a Beckman IR-10 spectrometer. Mass spectra were obtained on a Perkin–Elmer Hitachi RMU 6L mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA.

(η^5-Formylcyclopentadienyl)dicarbonylcobalt (2)

Dicobalt octacarbonyl (1.00 g, 2.9 mmol) was dissolved in 75 ml of THF. Iodine crystals (0.74 g, 2.9 mmol) were then added with stirring at 25°C. Although the evolution of carbon monoxide was immediate, the solution was stirred for 1 h to insure complete reaction. Sodium formylcyclopentadienide (0.67 g, 5.8 mmol) was then added with stirring. The solution turned brown with evolution of carbon monoxide. The reaction mixture was stirred for 12 h and then concentrated to ca. 30 ml. Ethyl ether was added and the resultant slurry was filtered through alumina. Alumina was added to the filtrate and the solvent removed in vacuo. The residue was placed on an alumina-packed column. The first band eluted with pentane was not collected. The second band eluted with 1/1 ethyl ether/pentane was collected under nitrogen. Evaporation of the solvent afforded 0.44 g (37%) of (η^5-for-mylcyclopentadienyl)dicarbonylcobalt (2) as a red liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr. (Found: C, 46.28; H, 2.54. $C_{14}H_9CoO_3$ calcd.: C, 46.18; H, 2.42%). IR (liquid film): 3125(w), 2020(w), 1980(s), 1680(s), 1460(m), 1375(m), 1230(m), 1025(m), 810(m) cm^{-1}. ^{1}H NMR (C_6D_6) δ 9.32 (s, 1H, CHO), 4.83 (t, 2H, H(2,5)), 4.65 (t, 2H, H(3,4)).

(η^5-Formylcyclopentadienyl)dicarbonylrhodium (8)

To a solution of sodium formylcyclopentadienide (0.80 g, 6.9 mmol) in 75 ml of THF was added dichlorotetracarbonyldirhodium (1.34 g, 3.4 mmol) and the reaction mixture was stirred for 24 h at 25°C. The solvent was then removed in vacuo and the residue dissolved in ethyl ether. Silica gel was added, the ether evaporated, and the resulting residue was placed on a silica gel-packed column. Elution with 2/1 ethyl ether/hexane produced a single band which after evaporation of the solvent gave 0.79 g (46%) of (η^5-formylcyclopentadienyl)dicarbonylrhodium (8) as an orange liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr. (Found: C, 38.34; H, 2.18. $C_8H_5O_3Rh$ calcd.: C, 38.13; H, 2.00%). IR (CDCl$_3$): 2030(s), 1995(s), 1680(s), 1475(m), 1370(m), 1350(s), 1230(m), 1080(w) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 9.36 (s, 1H, CHO), 5.82 (m, 4H, C$_5$H$_4$).

(η^5-Acetylcyclopentadienyl)dicarbonylcobalt (3)

Dicobalt octacarbonyl (1.00 g, 2.9 mmol) was dissolved with stirring in 75 ml of THF. Iodine crystals (0.74 g, 2.9 mmol) were then added slowly, and the resulting

green solution was stirred for 1 h. Sodium acetylcyclopentadienide (0.75 g, 5.8 mmol) was added with stirring. The evolution of carbon monoxide was evident as was a color change from green to violet. The cloudy solution was then allowed to stir for an additional 12 h at 25°C. It was concentrated to 30 ml, ethyl ether was added, and the resultant slurry was filtered through alumina. Alumina was then added to the filtrate and the ether removed in vacuo. The resultant residue was placed on an alumina column. The first band, eluted with pentane, was not collected. The second band was eluted with 1/1 ethyl ether/pentane. Evaporation of the solvent afforded 0.58 g (45%) of (η^5-acetylcyclopentadienyl)dicarbonylcobalt (3) as a red liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr. (Found: C, 48.95; H, 3.36. $C_9H_7CoO_3$ calcd.: C, 48.67; H, 3.18%). IR (liquid film): 3100(w), 2020(s), 1980(s), 1670(s), 1470(s), 1380(s), 1270(s). 1110(w), 1020(w, br), 960(w), 900(w), 820(m), 610(w) cm^{-1}. ^{1}H NMR (C_6D_6) δ5.00 (t, 2H, H(2,5)), 4.68 (t, 2H, H(3,4)), 1.96 (s, 3H, CH$_3$). MS m/e 222 (M^+).

(η^5-Acetylcyclopentadienyl)dicarbonylrhodium (9)

To a solution of sodium acetylcyclopentadienide (0.87 g, 6.7 mmol) in 75 ml of THF was added dichlorotetracarbonyldirhodium (1.30 g, 3.34 mmol), and the reaction mixture was stirred for 24 h. The mixture was then filtered and the solvent removed in vacuo. Ethyl ether and silica gel were added, and the solvent was evaporated. The resulting residue was placed on a silica gel packed column and eluted with 2/1 ethyl ether/hexane. Evaporation of the solvent gave 1.15 g (65%) of (η^5-acetylcyclopentadienyl)dicarbonylrhodium as a red-orange liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr. (Found: C, 40.39; H, 2.86. $C_9H_7O_3Rh$ calcd.: C, 40.63; H, 2.66%). IR (CDCl$_3$): 2050(s), 1990(s), 1670(s), 1475(w), 1375(m), 1275(m), 1120(w), 1030(w) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ5.90 (t, 2H, H(2,5)), 5.69 (t, 2H, H(3,4)), 2.34 (s, 3H, CH$_3$).

(η^5-Vinylcyclopentadienyl)dicarbonylcobalt (4)

To a solution of n-butyllithium (1.4 mmol) in 80 ml of ethyl ether was added methyltriphenylphosphonium iodide (0.56 g, 1.4 mmol), and the resulting cloudy yellow solution was stirred for 4 h at 25°C. Then (η^5-formylcyclopentadienyl)dicarbonylcobalt (0.29 g, 1.4 mmol) was added and the cloudy red solution was stirred at 25°C for 12 h. The reaction mixture was subsequently filtered, the filtrate evaporated on alumina, and the resulting residue placed on an alumina-packed column. Elution with pentane afforded an orange band which when collected and the solvent evaporated gave 0.09 g (30%) of (η^5-vinylcyclopentadienyl)dicarbonylcobalt as a red liquid. An analytical sample was obtained by vacuum distillation at 25°C/10^{-3} Torr. (Found: C, 52.32; H, 3.58. $C_9H_7CoO_2$ calcd.: C, 52.45; H, 3.43%). IR (liquid film): 2910(s), 2850(m), 2010(s), 1950(s), 1630(w), 1450(m), 1370(w), 1300(w), 1255(w), 1030(w, br), 980(m), 910(m), 815(s), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ6.05 (dd (J 17.5, 10.5 Hz), 1H), 5.18 (dd (J 17.5 Hz, 1.5 Hz), 1H), 4.87 (dd (J 10.5, 1.5 Hz), 1H), 4.77 (t, 2H, H(2,5), 4.48 (t, 2H, H(3,4)). MS m/e 206 (M^+).

(η^5-Isopropenylcyclopentadienyl)dicarbonylcobalt (5)

Methyltriphenylphosphonium iodide (1.41 g, 3.5 mmol) was dissolved with stirring in a solution of n-butyllithium (3.5 mmol) in 80 ml of ethyl ether at 25°C.

The cloudy yellow solution was stirred at 25°C for 4 h. (η^5-Acetylcyclopenta-dienyl)dicarbonylcobalt (0.78 g, 3.5 mmol) was then added and stirring was continued for 12 h. The mixture was filtered, the filtrate concentrated over alumina, and the resulting residue was placed on an alumina-packed column. Elution with pentane afforded a single orange band which when collected and the solvent removed gave 0.24 g (30%) of (η^5-isopropenylcyclopentadienyl)dicarbonylcobalt as a red liquid. An analytical sample was obtained by distillation at 25°C/10^{-3} Torr. (Found: C, 54.57; H, 4.28. $C_{10}H_9CoO_2$ calcd.: C, 54.57; H, 4.12%). IR (liquid film): 2980(s), 2940(s), 2020(s), 1965(s), 1640(m), 1460(m), 1310(w), 1265(w), 1150(w), 1050(m), 890(m), 815(m), 765(m), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ5.10 (d, 1H, J 1.5 Hz, =CH), 4.80 (t, 2H, H(2,5)), 4.70 (d, 1H, =CH), 4.50 (t, 2H, H(3,4)), 1.75 (s, 3H, CH$_3$).

(η^5-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (10)

(η^5-Formylcyclopentadienyl)dicarbonylcobalt (3.05 g, 14.6 mmol) was dissolved in 75 ml of methanol and the solution was stirred with sodium borohydride (0.56 g, 14.6 mmol) at 25°C for 2.5 h. The solvent was then evaporated in vacuo. Ethyl ether and alumina were added and solvent again evaporated. The resultant residue was placed on an alumina-packed column and eluted with 1/1 pentane/ethyl ether. A red-orange band was collected and the solvent was removed in vacuo. (η^5-Hy-droxymethylcyclopentadienyl)dicarbonylcobalt remained as a red liquid (2.6 g) in 84% yield. Distillation at 50°C/10^{-3} Torr afforded an anlaytically pure sample. (Found: C, 45.81; H, 3.19. $C_8H_7CoO_3$ calcd.: C, 45.74; H, 3.36%). IR (liquid film): 3600–3100(s, br), 2935(w), 2890(w), 2005(s), 1950(s), 1620(w), 1460–1350(m, br), 1240(w, br), 1180(w, br), 1040(m), 1010(m). 930(w), 890(w), 820(w), 730(w), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ 4.65 (t, 2H, H(2,5)), 4.45 (t, 2H, H(3,4)), 3.88 (s, 2H, CH$_2$), 1.70 (s, 1H, OH); D$_2$O exchange, loss of 1.70 resonance. MS m/e 210 (M^+).

(η^5-1-Hydroxyethylcyclopentadienyl)dicarbonylcobalt (11)

(η^5-Acetylcyclopentadienyl)dicarbonylcobalt (0.88 g, 4.0 mmol) was dissolved in 25 ml of methanol and stirred at 25°C with sodium borohydride (0.15 g, 3.9 mmol) for 3 h. The solvent was removed, ethyl ether and alumina were added, and the solvent was evaporated in vacuo. The resulting residue was placed on a column of alumina and eluted with 1/1 ethyl ether/pentane. A single band was eluted which after removal of the solvent yielded 0.82 g (82%) of (η^5-1-hydroxyethylcyclopenta-dienyl)dicarbonylcobalt. (Found: C, 48.37; H, 4.09. $C_9H_9CoO_3$ calcd.: C, 48.24; H, 4.05%). IR (liquid film): 3600–3200(s, br), 2990(m), 2030(s), 1955(s), 1450(w), 1375(m), 1100(m), 1015(w), 875(m), 815(m), 620(s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ5.25 (t, 2H, H(2,5)), 5.10 (t, 2H, H(3,4)), 4.50 (q, J 6 Hz, 1H, CH), 4.00 (d, J 5 Hz, 1H, OH), 1.40 (d, J 6 Hz, 3H, CH$_3$); D$_2$O exchange, loss of 4.00 resonance. MS m/e 224 (M^+).

Sodium borohydride reduction of 2 with acid hydrolysis. Preparation of (η^5-etho-xymethylcyclopentadienyl)dicarbonylcobalt (12)

(η^5-Formylcyclopentadienyl)dicarbonylcobalt (1.09 g, 0.09 mmol) was dissolved in 60 ml of absolute ethanol and stirred with sodium borohydride (0.31 g, 8.1 mmol) for 3.5 h at 25°C. The solution was concentrated to two-thirds of its original volume and 42 ml of a 10% hydrochloric acid solution was slowly added with

stirring until gas evolution had ceased. The solution was then extracted with ethyl ether (2 × 25 ml). The ether extracts were washed with water, dried over magnesium sulfate, filtered and the solvent was removed on alumina. The resulting residue was placed on an alumina-packed column. Pentane elution afforded 0.15 g (10%) of (η^5-methylcyclopentadienyl)dicarbonylcobalt (15), identified by comparison with an authentic sample. Elution with 10/1 pentane/ethyl ether afforded 0.33 g (17%) of (η^5-ethoxymethylcyclopentadienyl)dicarbonylcobalt (12). An analytical sample was obtained by distillation at 25°C/10^{-3} Torr. (Found: C, 50.23; H, 4.82. $C_{10}H_{11}CoO_3$ calcd.: C, 50.44; H, 4.66%). IR (liquid film): 2990(m), 2885(m), 2030(s), 1955(s), 1450(w), 1380(m), 1110(s), 1015(w), 900(w), 820(w), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ4.82 (t, 2H, H(2,5)), 4.50 (t, 2H, H(3,4)), 3.80 (s, 2H, CH_2O), 3.29 (q, J 6 Hz, 2H, CH_2), 1.08 (t, J 6 Hz, 3H, CH_3). Finally, elution with 1:1 ethyl ether/pentane afforded 0.45 g (20%) of (η^5-hydroxymethylcyclopentadienyl)dicarbonylcobalt (10).

Sodium borohydride reduction of 3 with acid hydrolysis. Preparation of (η^5-1-ethoxyethylcyclopentadienyl)dicarbonylcobalt (13)

(η^5-Acetylcyclopentadienyl)dicarbonylcobalt (1.11 g, 5.0 mmol) was dissolved in 30 ml of absolute ethanol. To this red orange solution was added sodium borohydride (0.19 g, 5.0 mmol) with stirring at 25°C. The resultant dark red solution was stirred for 3 h, then 42 ml of 10% hydrochloric acid solution was added slowly. The solution was diluted with additional water and extracted with ethyl ether (2 × 25 ml). The combined ether extracts were washed with water (3 × 25 ml), dried over magnesium sulfate, filtered, alumina added, and the solvent was removed in vacuo. The resultant residue was placed on an alumina-packed column. Elution with pentane afforded 0.24 g (23%) of (η^5-ethylcyclopentadienyl)dicarbonylcobalt (16) as a red liquid, identified by comparison with an authentic sample. A second band eluted with pentane afforded 0.16 g (13%) of (η^5-1-ethoxyethylcyclopentadienyl)dicarbonylcobalt (13). An analytical sample was obtained by distillation at 25°C/10^{-3} Torr. (Found: C, 52.65; H, 5.26. $C_{11}H_{13}CoO_3$ calcd.: C, 52.40; H, 5.20%). IR (liquid film): 2990(m), 2950(w), 2890(w), 2030(s), 1970(s), 1450(m), 1375(m), 1320(m), 1230(w), 1105(w), 940(w), 900(m), 820(m), 620(m) cm^{-1}. ^{1}H NMR (C_6D_6) δ4.80 (t, 2H, H(2,5)), 4.55 (t, 2H, H(3,4)), 3.82 (q, J 5 Hz, 1H, CH), 3.35 (q, J 6 Hz, 2H, CH_2), 1.25 (d, 3H, CH_3), 1.10 (t, 3H, CH_3).

Sodium borohydride reduction of 3 with acid hydrolysis. Preparation of (η^5-1-methoxyethylcyclopentadienyl)dicarbonylcobalt (14)

(η^5-Acetylcyclopentadienyl)dicarbonylcobalt (1.21 g, 5.5 mmol) was dissolved in 50 ml of methanol together with sodium borohydride (0.21 g, 5.5 mmol) and the solution was stirred for 3 h at 25°C. The reaction mixture was then hydrolyzed with 30 ml of 5% hydrochloric acid solution and diluted with an additional 50 ml of water. The solution was extracted with ethyl ether, the ether extracts washed with water, dried over magnesium sulfate, filtered, and the solvent was removed on alumina. Elution with 5/1 pentane/ethyl ether afforded an orange band which when collected and the solvent evaporated afforded 0.85 g (65%) of (η^5-1-methoxyethylcyclopentadienyl)dicarbonylcobalt (14), identified by comparison with an authentic sample. Elution with 1/1 ethyl ether/pentane afforded 0.09 g (7%) of (η^5-1-hydroxyethylcyclopentadienyl)dicarbonylcobalt (11).

(η⁵-Methoxymethylcylopentadienyl)dicarbonylcobalt (17)

(η^5-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (0.54 g, 2.6 mmol) was dissolved in 50 ml of methanol followed by the addition of p-toluenesulfonic acid (0.04 g, 0.26 mmol). The reaction mixture was stirred at reflux for 2 h. The solvent was removed over alumina and the resulting residue was placed on an alumina column. Elution with pentane afforded a trace of an orange band which was not collected. Further elution with pentane developed an orange band which when collected and the solvent evaporated in vacuo produced 0.24 g (42%) of (η^5-methoxymethylcyclo-pentadienyl)dicarbonylcobalt (**17**). An analytical sample was obtained by distillation at 25°C/10⁻³ Torr. (Found: C, 48.42; H, 4.19. $C_9H_9CoO_3$ calcd.: C, 48.24; H, 4.05%). IR (liquid film): 2940(w), 2030(s), 1960(s), 1450(w), 1390(w), 1190(w), 1120(s), 960(w), 920(m), 615(s) cm⁻¹. ¹H NMR (C_6D_6) δ4.80 (t, 2H, H(2,5)), 4.50 (t, 2H, $H_{3,4}$), 3.70 (s, 2H, CH_2), 3.10 (s, 3H, CH_3).

(η⁵-1-Methoxyethylcyclopentadienyl)dicarbonylcobalt (14)

(η^5-1-Hydroxyethylcyclopentadienyl)dicarbonylcobalt (0.30 g, 1.3 mmol) was dissolved in 20 ml of methanol with p-toluenesulfonic acid (0.02 g, 0.13 mmol) and the solution was refluxed for 2 h. The solvent was then evaporated on alumina and the resulting residue was placed on an alumina-packed column. Elution with pentane afforded a trace amount of an orange band followed by a second orange band. The latter when collected and the solvent removed gave 0.23 g (72%) of (η^5-1-methoxyethylcyclopentadienyl)dicarbonylcobalt (**14**) as a red liquid. An analytical sample was obtained by distillation at 25°C/10⁻³ Torr. (Found: C, 50.60; H, 4.66. $C_{10}H_{11}CoO_3$ calcd.: C, 50.44; H, 4.66%). IR (liquid film): 2990(m), 2920(m), 2030(s), 1960(s), 1450(br), 1375(m), 1190(w), 1110(s), 1090(w), 810(m), 610(s) cm⁻¹. ¹H NMR (C_6D_6) δ4.80 (t, 2H, H(2,5)), 4.60 (t, 2H, H(3,4)), 3.75 (q, J 6 Hz, 4H, CH) 3.12 (s, 3H, OCH_3), 1.20 (d, J 6 Hz, 3H, CH_3).

(η⁵-1-Hydroxyethylcyclopentadienyl)dicarbonylcobalt (11)

(Iodomethane (0.53 g, 0.23 ml, 3.75 mmol) was combined with magnesium turnings (0.09 g, 3.75 mmol) at 25°C in 50 ml of ethyl ether, and the mixture was stirred until the magnesium had reacted. To this solution, (η^5-formylcyclopentadienyl)dicarbonylcobalt (0.78 g, 3.75 mmol) was added with stirring. After stirring for 5 h, the reaction mixture was quenched with an aqueous solution of ammonium chloride (ca. 25 ml) and extracted with ethyl ether. The combined ether extracts were washed with water, dried over manesium sulfate, filtered, and the solvent was removed on alumina. The residue was placed on an alumina-packed column. Elution with 1/1 ethyl ether/pentane afforded 0.74 g (80%) of (η^5-1-hydroxyethyl-cyclopentadienyl)dicarbonylcobalt (**11**) identical to **11** described above.

(η⁵-1-Hydroxy-1-methylethylcyclopentadienyl)dicarbonylcobalt (18)

Iodomethane (0.41 g, 0.18 ml, 2.9 mmol) was added to 50 ml of ethyl ether, followed by magnesium turnings (0.70 g, 2.9 mmol) with stirring at 25°C. When the magnesium had reacted, (η^5-acetylcyclopentadienyl)dicarbonylcobalt (0.64 g, 2.9 mmol) was added. After 3.5 h, the reaction mixture was quenched with 40 ml of an aqueous ammonium chloride solution. The ether layer was separated, washed with water, dried over magnesium sulfate, filtered, and the solvent removed on alumina. The resulting residue was placed on an alumina column. Elution with pentane gave

a faint orange band which was not collected. Elution with 2/1 ethyl ether/pentane produced an orange band which when collected and the solvent removed gave 0.46 g (69%) of (η^5-1-hydroxy-1-methylethylcyclopentadienyl)dicarbonylcobalt (18) as a red liquid. An analytical sample was prepared by distillation at $50°C/10^{-3}$ Torr. (Found: C, 50.37; H, 4.73. $C_{10}H_{11}CoO_3$ calcd.: C, 50.44; H, 4.66%). IR (liquid film): 3600–3200(s, br), 2950(m), 2910(m), 2850(w), 2010(s), 1960(s), 1510(w), 1375(m), 1325(m), 1260(m), 1225(w), 1165(m), 1110(m), 1040(w), 1020(w), 950(m), 820(m), 800(m), 610(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ5.22 (t, 2H, H(2,5)), 5.08 (t, 2H, H(3,4)), 3.78 (s, 1H, OH), 1.48 (s, 6H, CH_3); D_2O exchange, loss of 3.78 resonance.

(η^5-α-Hydroxybenzylcyclopentadienyl)dicarbonylcobalt (19)

Bromobenzene (0.77 g, 0.51 ml, 5.3 mmol) was dissolved in 25 ml of ethyl ether. Magnesium turnings (0.05 g, 2.2 mmol) were then added with stirring at 25°C. After the magnesium had reacted, (η^5-formylcyclopentadienyl)dicarbonylcobalt (0.42 g, 2.2 mmol) was added and the resultant solution was stirred at 25°C for 8 h. The reaction mixture was then hydrolyzed with 20 ml of an aqueous ammonium chloride solution. The layers were separated and the ether layer washed with water. The ether layer was dried over magnesium sulfate, filtered, and the solvent removed on alumina. The residue was placed on an alumina-packed column. Elution with pentane produced a trace amount of an orange band that was not collected. Elution with 10/1 pentane/ethyl ether gave a small amount of 2. A third band was eluted with 1/1 pentane/ethyl ether. Collection of this band and evaporation of the solvent afforded 0.47 g (75%) of (η^5-α-hydroxybenzylcyclopentadienyl)dicarbonylcobalt (19) as a red-orange liquid. An analytical sample was obtained by distillation at $40°C/10^{-3}$ Torr. (Found: C, 58.69; H, 4.12. $C_{14}H_{11}CoO_3$ calcd.: C, 58.76; H, 3.87%). IR (liquid film): 3700–3200(s,br), 3060(w), 2020(s), 1950(s), 1605(w), 1490(m), 1455(m), 1390(br), 1190(m), 1080(w), 1040(m), 1015(m), 925(w), 890(s), 825(m), 730(m), 700(s), 610(s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ7.40 (m, 5H, C_6H_5), 5.55 (d, J 4 Hz, 1H, CH), 5.18 (t, 2H, H(2,5)), 5.08 (t, 2H, H(3,4)), 4.75 (d, J 4 Hz, 1H, OH); deuterium exchange, loss of 4.75 resonance and no observed coupling of methine proton.

(η^5-α-methyl-α-hydroxybenzylcyclopentadienyl)dicarbonylcobalt (20)

Bromobenzene (0.48 ml, 0.72 g, 4.6 mmol) was dissolved in 50 ml of ethyl ether. Magnesium turnings (0.06 g, 2.3 mmol) were then added with stirring at 25°C. When all of the magnesium had reacted, (η^5-acetylcyclopentadienyl)dicarbonylcobalt (0.51 g, 2.3 mmol) was added. After stirring for 8 h, 25 ml of an aqueous ammonium chloride solution was added and stirring was continued for several min. The ether layer was separated, washed with water (2×25 ml), dried over magnesium sulfate, filtered, and the solvent removed on alumina. The resulting residue was placed on an alumina-packed column. Elution with 10/1 pentane/ethyl ether afforded a small amount of unreacted 3. Elution with 1/1 ethyl ether/pentane gave 0.42 g (61%) of (η^5-α-methyl-α-hydroxybenzylcyclopentadienyl)dicarbonylcobalt (20) as a red liquid. An analytical sample was obtained by distillation at $60°C/10^{-3}$ Torr. (Found: C, 60.14; H, 4.61. $C_{15}H_{13}CoO_3$ calcd.: C, 60.02; H, 4.36%). IR (liquid film): 3600–3300(m, br), 3000(m) 2040(s), 1965(s), 1600(w), 1490(m), 1440(m), 1370(m), 1330(m), 1230(m), 1170(m), 1070(m), 1030(m), 930(w), 900(m), 800(m),

755(s), 700(s), 640(m) cm^{-1}. ^{1}H NMR (acetone-d_6) δ7.30 (m, 5H, C_6H_5), 5.25 (t, 2H, H(2,5)), 5.10 (t, 2H, H(3,4)), 4.50 (s, 1H, OH), 1.88 (s, 3H, CH$_3$).

(η^5-Acryloxymethylcyclopentadienyl)dicarbonylcobalt (21)

Method A. (η^5-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (0.75 g, 3.6 mmol) was dissolved in 50 ml of benzene with pyridine (0.56 g, 7.1 mmol). Acryloyl chloride (0.59 ml, 0.65 g, 7.1 mmol) was subsequently added and the reaction mixture was stirred for 8 h. A white precipitate formed during the course of the reaction. The reaction was quenched with 25 ml of water and the layers were separated. The benzene layer was washed with 50 ml of a 10% sodium bicarbonate solution in two 25 ml portions and dried over magnesium sulfate. The solution was then filtered and the solvent was removed on alumina. Transfer to an alumina column and elution with pentane produced two faint orange bands that were not collected. Elution of a third band with 5 : 1 pentane/ethyl ether gave after removal of the solvent 0.33 g (35%) of (η^5-acryloxymethylcyclopentadienyl)dicarbonylcobalt (21). An analytical sample was obtained by distillation at 25°C/10^{-3} Torr. (Found: C, 50,11; H, 3.43. $C_{11}H_9CoO_4$ calcd.: C, 50.02; H, 3.43%). IR (liquid film): 2970(w), 2030(s), 1960(s), 1725(s), 1625(m), 1450(w), 1410(m), 1310(m), 1270(m), 1200(s), 1050(m), 1000(m), 810(m), 620(s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 6.5–5.9 (m, 3H, CH=CH$_2$), 5.40 (t, 2H, H(2,5)), 5.28 (t, 3H, H(3,4)), 4.92 (s, 2H, CH$_2$). MS m/e 236 $(M - CO)^+$, 208 $(M - 2CO)^+$.

Method B. (η^5-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (1.85 g, 8.77 mmol) was added to a slurry of sodium hydride (0.25 g, 10.5 mmol) in THF at −78°C. To this slurry, acryloyl chloride (0.88 ml, 0.96 g, 10.5 mmol) was added and the reaction mixture was stirred as the solution warmed to room temperature. The mixture was then refluxed for 1 h and finally cooled and stirred at 25°C for 11 h. The solvent was evaporated on alumina and the resulting residue was placed on an alumina-packed column. Elution with pentane gave trace amounts of 15 as well as 1.30 g (56%) of acrylate 21, identical to that formed via Method A. Elution with 3/1 pentane/ethyl ether produced 0.44 g (11%) of a product (23) derived from Michael addition of the alkoxide ion to the formed acrylate. Satisfactory analytical data could not be obtained after two distillations at 80°C/10^{-3} Torr. (Found: C, 48.53; H, 5.30. $C_{19}H_{16}Co_2O_7$ calcd.: C, 48.12; H, 3.40%). IR (liquid film): 2950(br), 2020(s), 1960(s,br) 1738(s), 1460(w), 1370(br), 1255(w), 1180(s), 1100(br), 830(m), 620(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ 4.80 (t, 4H, H(2,5)), 4.60 (t, 4H, H(3,4)), 3.80 (s, 4H, CH$_2$), 3.50 (t, J 6 Hz, 2H, C(O)CH$_2$), 2.32 (t, J 6 Hz, 2H, O–CH$_2$). MS m/e 418 $(M - CO)^+$, 390 $(M - 3CO)^+$, 362 $(M - 4CO)^+$. Elution with 1/1 ethyl ether/ pentane gave 0.87 g of alcohol 10.

(η^5-1-Acryloxyethylcyclopentadienyl)dicarbonylcobalt (22)

To a solution of (η^5-1-hydroxyethylcyclopentadienyl)dicarbonylcobalt (0.27 g, 1.2 mmol) in 20 ml of ethyl ether, pyridine (0.19 g, 0.19 ml, 2.4 mmol) was added with stirring, followed by the addition of acryloyl chloride (0.20 ml. 0.22 g, 2.4 mmol) in 50 ml of ethyl ether. Immediate formation of a white precipitate occurred. The slurry was stirred for 17 h and then 20 ml of water was added to dissolve the pyridine hydrochloride. The ether layer was separated, washed with 5% sodium bicarbonate solution, washed with water, and then dried over magnesium sulfate. The solution was filtered and the solvent evaporated over alumina. The resulting

residue was placed on an alumina-packed column. Elution with pentane gave 0.09 g (26%) of (η^5-acryloxyethylcyclopentadienyl)dicarbonylcobalt (22) as a red liquid. Elution with 2/1 pentane/ethyl ether led to recovery of 0.17 g (63%) of the alcohol 11. An analytical sample of the acrylate was obtained by distillation at $25\,^\circ C/10^{-3}$ Torr. (Found: C, 52.03; H, 4.28. $C_{12}H_{11}CoO_4$ calcd.: 51.82; H, 3.99%). IR (liquid film): 2990(w), 2030(s), 1960(s), 1725(s), 1625(w), 1449(w), 1405(w), 1290(w), 1265(m), 1185(s), 1040(m,br), 980(w), 900(w), 805(m), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ 6.20–5.90, 5.40–5.20 (m, 3H, CH=CH$_2$), 5.64 (q, J 6 Hz, 1H, CH), 4.70 (m, 2H, H(2,5)), 4.45 (t, 2H, H(3,4)), 1.25 (d, J 6 Hz, 3H, CH$_3$).

Reaction of (η^5-hydroxymethylcyclopentadienyl)dicarbonylcobalt (10) with sodium hydride

(η^5-Hydroxymethylcyclopentadienyl)dicarbonylcobalt (0.34 g, 1.6 mmol) was added to a slurry of sodium hydride (0.04 g, 1.8 mmol) in THF. The reaction mixture was stirred for 10 min at 25°C and subsequently at reflux for 30 min. The dark green cloudy solution was cooled and hydrolyzed with 30 ml of water. Ethyl ether was added and the layers were separated. The ether layer was washed with 20 ml of 10% hydrochloric acid and 20 ml of water, dried over magnesium sulfate, filtered, and the solvent evaporated on alumina. Elution of the alumina dry pack column with pentane gave 0.10 g (31%) of (η^5-methylcyclopentadienyl)dicarbonylcobalt (15), identified by comparison with an authentic sample prepared below. Elution with ethyl ether gave a second orange band which after solvent removal produced 0.15 g (45%) of recovered alcohol 10.

(η^5-Methylcyclopentadienyl)dicarbonylcobalt (15)

A slurry of aluminum chloride/lithium aluminum hydride was made by stirring aluminum chloride (0.34 g, 3.16 mmol) and lithium aluminum hydride (0.12 g, 3.2 mmol) together in ethyl ether for 5 min at 25°C. (η^5-Formylcyclopentadienyl)dicarbonylcobalt (0.66 g, 3.16 mmol) was subsequently added and the reaction mixture was stirred for 20 min. The solution was then hydrolyzed with 10 ml of water followed by 40 ml of a 10% hdyrochloric acid solution. The ether layer was separated, washed with water, dried over magnesium sulfate, filtered, and the solvent was removed on alumina. Elution of the alumina dry packed column with pentane gave 0.22 g (35%) of (η^5-methylcyclopentadienyl)dicarbonylcobalt (15) as a red liquid. An analytical sample was obtained by distillation at $25\,^\circ C/10^{-3}$ Torr. (Found: C, 49.25; H, 3.57. $C_8H_7CoO_2$ calcd.: C, 49.51; H, 3.64%). IR (liquid film): 2940(w), 2010(s), 1950(s), 1450(w), 1380(w), 1360(w), 1035(w), 910(w), 815(m), 620(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ 4.70 (t, 2H, H(2,5)), 4.50 (t, 2H, H(3,4)), 1.60 (s, 3H, CH$_3$).

(η^5-Ethylcyclopentadienyl)dicarbonylcobalt (16)

(η^5-Acetylcyclopentadienyl)dicarbonylcobalt (1.44 g, 6.5 mmol) was added to a slurry of aluminum chloride (0.70 g, 6.5 mmol) and lithium aluminum hydride (0.35 g, 6.5 mmol) in 30 ml of ethyl ether. The reaction mixture was stirred for 10 min and then hydrolyzed with 10 ml of water followed by 40 ml of 10% hydrochloric acid solution. The ether layer was separated, washed with water, dried over magnesium sulfate, filtered, and the solvent removed on alumina. The resulting residue was placed on an alumina-packed column and eluted with pentane. A single orange

band was collected which after solvent removal gave 0.58 g (43%) of (η^5-ethylcyclo-pentadienyl)dicarbonylcobalt (16) as a red liquid. An analytical sample was obtained by distillation at $25°C/10^{-3}$ Torr. (Found: C, 51.78; H, 4.58. $C_9H_9CoO_2$ calcd.: C, 51.95; H, 4.36%). IR (liquid film): 2980(m), 2020(s), 1960(s), 1455(w), 1370(w), 1310(w), 1260(w), 1030(br), 815(m), 615(s) cm^{-1}. ^{1}H NMR (C_6D_6) δ4.60 (t, 2H, H(2,5)), 4.50 (t, 2H, H(3,4)), 1.90 (q, J 6 Hz, 2H, CH_2), 0.90 (t, J 6 Hz, 3H, CH_3).

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References

1 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.
2 E.O. Fischer and R. Jira, Z. Naturforsch. B, 10 (1955) 355.
3 R.D.W. Kemmitt and D.R. Russell in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982, Vol. 5, p. 248.
4 B.H. Chang, R.H. Grubbs and C.H. Brubaker, J. Organomet. Chem., 172 (1979) 81.
5 P. Perkins and K.P.C. Vollhardt, J. Am. Chem. Soc., 101 (1979) 3985.
6 D.W. Macomber, W.P. Hart and M.D. Rausch, Adv. Organomet. Chem., 21 (1982) 1.
7 D.W. Macomber, W.C. Spink and M.D. Rausch, J. Organomet. Chem., 250 (1983) 311.
8 W.P. Hart, D. Shihua and M.D. Rausch, J. Organomet. Chem., 282 (1985) 111.
9 W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.
10 R.D. Rogers, J.L. Atwood, M.D. Rausch, D.W. Macomber and W.P. Hart, J. Organomet. Chem., 238 (1982) 79.
11 W. Hieber and H. Schulten, Z. Anorg. Allgem. Chem., 232 (1937) 17; 243 (1939) 145.
12 R.R. Heck, J. Am. Chem. Soc., 86 (1964) 5138.
13 M. Pankowski and M. Bigorgne, Compt. Rend. Sér. C, 264 (1967) 1383.
14 J. Altman and G. Wilkinson, J. Chem. Soc., (1965) 5654.
15 P Eilbracht, P. Dahler and G. Tiedke, J. Organomet. Chem., 185 (1980) C25.
16 C.U. Pittman, Jr., W.P. Hart and M.D. Rausch, unpublished studies.
17 D.W. Macomber, W.P. Hart, M.D. Rausch, C.U. Pittman, Jr., and R.D. Priester, Jr., J. Am. Chem. Soc., 104 (1982) 884.
18 M.D. Rausch and A. Siegel, J. Organomet. Chem., 11 (1968) 317.
19 E.A. Mintz, M.D. Rausch, T.D. Rounsefell, C.U. Pittman, Jr., B.H. Edwards and J.E. Sheats, J. Organomet. Chem., 137 (1977) 199.
20 C.U. Pittman, Jr., T.D. Rounsefell, J.E. Sheats, B.H. Edwards, M.D. Rausch and E.A. Mintz in C.E. Carraher, J.E. Sheats and C.U. Pittman, Jr. (Eds.), Organometallic Polymers, Academic Press, New York, 1978, p. 6.
21 D.W. Macomber, M.D. Rausch, T.V. Jayaraman, R.D. Priester, and C.U. Pittman, Jr., J. Organomet. Chem., 205 (1981) 353.
22 C.U. Pittman, Jr., T.V. Jayaraman, R.D. Priester, S. Spencer, M.D. Rausch and D.W. Macomber, Macromolecules, 14 (1982) 884.
23 M.D. Rausch, D.W. Macomber, K. Gonsalves, F.G. Fang, Z.R. Lin and C.U. Pittman, Jr., in J.E. Sheats, C.E. Carraher, and C.U. Pittman, Jr. (Eds.), Metal-Containing Polymeric Systems, Plenum Press, New York, 1985, p. 43.
24 M.D. Rausch, D.W. Macomber, F.G. Fang, C.U. Pittman, Jr., and R.D. Priester in B.M. Culbertson and C.U. Pittman, Jr. (Eds.), New Monomers and Polymers, Plenum Press, New York, 1984, p. 243.
25 B.R. Brown and A.M.S. White, J. Chem. Soc., (1957) 3755.
26 B.G. Conway and M.D. Rausch, Organometallics, 4 (1985) 688.
27 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.
28 K. Hafner, G. Schultz and K. Wagner, Justus Liebigs Ann. Chem., 678 (1964) 39.