Journal of Organometallic Chemistry, 282 (1985) 111–121
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE FORMATION AND REACTIONS OF (η^5-CARBOXYCYCLOPENTADIENYL)DICARBONYLCOBALT

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(Received August 6th, 1984)

Summary

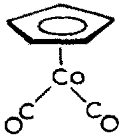
A reaction between sodium cyclopentadienide and dimethyl carbonate in THF solution produces sodium carbomethoxycyclopentadienide in high yield. The analogous carbethoxy derivative can also be readily prepared starting with diethyl carbonate. Carbomethoxycyclopentadienylthallium has been prepared by cracking carbomethoxycyclopentadiene dimer and passing the unstable monomer into an aqueous mixture of thallium(I) chloride and potassium hydroxide. Reactions of these reagents with mixtures of dicobalt octacarbonyl and iodine in THF solution afford moderate yields of the respective products (η^5-carbomethoxycyclopentadienyl)dicarbonylcobalt and (η^5-carbethoxycyclopentadienyl)dicarbonylcobalt. (η^5-Carboxycyclopentadienyl)dicarbonylcobalt is obtained in 67–74% yield by treatment of either ester with potassium hydroxide in aqueous ethanol followed by acidification. A reaction between this acid and oxalyl chloride in benzene solution produces (η^5-chloroformylcyclopentadienyl)dicarbonylcobalt in 67% yield, and the latter reacts readily with ammonia and with aniline to form the respective amide and anilide derivatives. The acid chloride also reacts with ferrocene and aluminum chloride under Friedel–Crafts conditions to afford the bimetallic product (η^5-ferrocenoylcyclopentadienyl)dicarbonylcobalt. The IR and ^{1}H NMR spectra of these new functionally-substituted derivatives of (η^5-cyclopentadienyl)dicarbonylcobalt are discussed.

Introduction

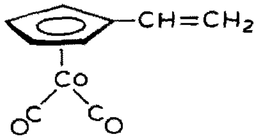
(η^5-Cyclopentadienyl)dicarbonylcobalt (I) has played an important role in the development of organocobalt chemistry since its discovery in 1955 [1,2]. In 1970, we described a convenient, high-yield synthesis of I [3], based on earlier observations by others [1,4]. Since that time, the reactivity of I with respect to substitution reactions of the carbonyl substituents has been widely investigated [5]. Recently, I and its rhodium analogue (η^5-C_5H_5)Rh(CO)$_2$ have been attached to cross-linked poly-

0022-328X/85/$03.30

styrene-divinylbenzene copolymer, and the resulting polymer-supported systems have been shown to exhibit novel properties, including their utility as hydrogenation [6], olefin isomerization [6], olefin hydroformylation [6], and Fischer–Tropsch [7] catalysts. In contrast, the formation and chemistry of derivatives of I which contain functional substituents on the cyclopentadienyl ring have received little attention [8], although we have recently described a convenient route to (η^5-vinylcyclopentadienyl)dicarbonylcobalt (II) as well as to its rhodium and iridium analogues [9].



(I)



(II)

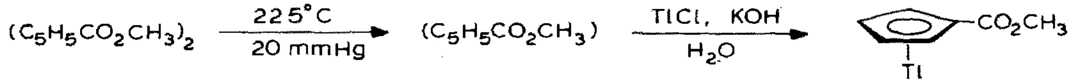
We report herein a convenient synthesis of (η^5-carboxycyclopentadienyl)dicarbonylcobalt (VIII), and describe some of its reactions which demonstrate that it is a useful intermediate in the formation of functionally-substituted derivatives of I. A portion of this research has been previously described in communication form [10].

Results and discussion

As we have briefly reported earlier [10], a reaction between sodium cyclopentadienide and dimethyl carbonate in THF solution produces sodium carbomethoxycyclopentadienide (III) in very high (92%) yield. The analogous carbethoxy derivative (IV) can likewise be readily obtained, utilizing diethyl carbonate in place of dimethyl carbonate. Organosodium reagents III and IV are formulated as sodium cyclopentadienides in the manner usually described for the parent compound, $(C_5H_5)^- Na^+$. The structures of III and IV both in solution and in the crystal state are undoubtedly more complex, however, in view of our recent structural studies on the related compound sodium acetylcyclopentadienide [11]. Both III and IV are hygroscopic but are stable in air for short periods of time, in marked contrast to sodium cyclopentadienide itself.

(III, $R = CH_3$; IV, $R = C_2H_5$)

A related and potentially useful intermediate is carbomethoxycyclopentadienylthallium (V). This compound has been prepared in 38% yield by cracking carbomethoxycyclopentadiene dimer and passing the unstable monomer directly into an aqueous solution of thallium(I) chloride and potassium hydroxide, following a general procedure developed by Mrowca [12]. Organothallium intermediate V is an



(V)

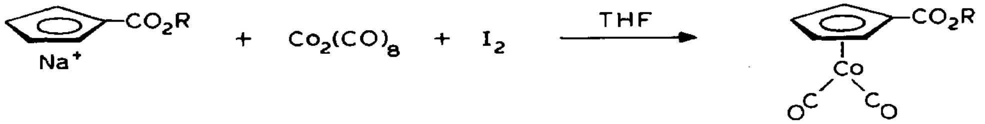
air-stable white solid whose properties closely resemble those of the parent compound, cyclopentadienylthallium.

As we have reported previously, reactions of functionally substituted cyclopentadienylsodium and -thallium reagents such as III–V with various metal halides or metal carbonyl halides provide a new, general route to functionally substituted η^5-cyclopentadienyl derivatives of the transition metals [8,10]. An initial problem confronting us, however, was the preparation of a suitable "cobalt carbonyl halide", analogous to $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_3Cl]_n$ in the rhodium and iridium series, with which to react our functionalized cyclopentadienide salts to form organocobalt analogues.

Some earlier studies in this area had been conducted. Hieber and Schulten [13] described the formation of "$CoI_2 \cdot CO$" during a high pressure synthesis of $Co_2(CO)_8$ from CoI_2 and CO. Heck [14] reported that his efforts to prepare $Co(CO)_4I$ 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 contrast, however, Heck noted that treatment of acetyltricarbonyltriphenylphosphinecobalt with iodine afforded to $Co(CO)_3(PPh_3)I$ in 60% yield. In 1967, Bigorgne and Pankowski [15] reported the preparation of $Co(CO)_4I$ by treatment of $Co(CO)_4PbEt_3$ 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}.

Efforts on our part to reproduce Bigorgne's results with $Co_2(CO)_8$ and iodine were inconclusive. However, we did obtain a "$Co(CO)_nI$" species when $Co_2(CO)_8$ and iodine were combined in either THF or Nujol. In THF, a terminal metal carbonyl frequency occurred at 2025 cm^{-1} as a weak absorption, while another 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 Heck's studies, we were unable to isolate a complex such as $Co(CO)_4I$. The only materials recovered were $Co_2(CO)_8$ and CoI_2, the latter possibly as a THF complex.

The reason for the discrepancy between our results and those of Bigorgne is not clean. It is possible that we were examining a product that was a subsequent reaction product derived from $Co(CO)_4I$. In any event, we were able to successfully utilize our intermediate in reaction schemes involving the functionally substituted metal cyclopentadienide salts described above. Thus, formation of the "$Co(CO)_nI$" intermediate from $Co_2(CO)_8$ and iodine in THF, followed by the addition of either III or IV, afforded (η^5-carbomethoxycyclopentadienyl)dicarbonylcobalt (VI) and its carbethoxy analogue (VII) in yields of 41 and 26%, respectively. The methyl ester VI could alternatively be prepared from a reaction between thallium reagent V and $Co_2(CO)_8$ plus iodine in THF solution [16].

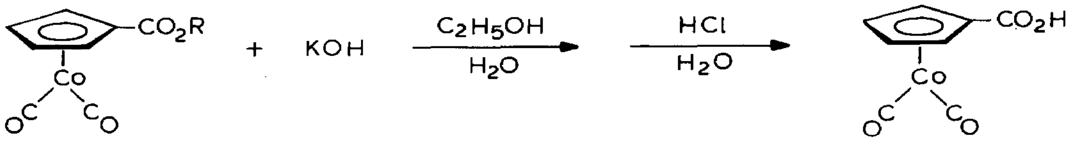


(III, R = CH_3;
IV, R = C_2H_5)

(VI, R = CH_3;
VII, R = C_2H_5)

Products VI and VII were readily purified by column chromatography, and were obtained in analytical purity via vacuum distillation at 50°C. They were characterized by their ^1H NMR spectra, which contained an A_2B_2 pattern of pseudo triplets for the hydrogens of the monosubstituted cyclopentadienyl ring, by their IR spectra, which exhibited two strong terminal metal carbonyl stretching frequencies as well as a strong organic carbonyl absorption, and by their mass spectra and elemental analyses.

Treatment of esters VI or VII with potassium hydroxide in aqueous ethanol solution followed by acidification afforded (η^5-carboxycyclopentadienyl)dicarbonylcobalt (VIII) as an orange-red solid in 67–74% yield. Subsequent studies demonstrated that for preparing VIII, it was not necessary to isolate the ester in pure form, since the overall yield of VIII based on III was almost the same as for the 2-step method.

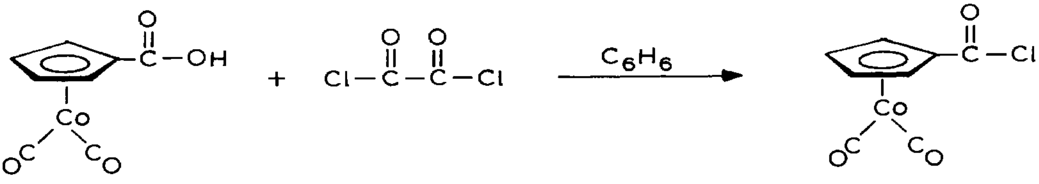


(VI, R = CH_3 ;
VII, R = C_2H_5)

(VIII)

VIII was characterized in its IR spectrum by the presence of an organic carbonyl band at 1670 cm^{-1} as well as a broad O–H absorption from 3200–2400 cm^{-1}. In addition, terminal metal carbonyl bands were observed at 2035 and 1970 cm^{-1}. The ^1H NMR spectrum of VIII contained a broad singlet at δ 8.94 ppm assignable to the hydroxyl proton, and a set of A_2B_2 pseudo triplets at δ 5.64 and 5.52 ppm attributable to the ring protons. Acid VIII exhibited a molecular ion at m/e 224 in the mass spectrum. A pK_a value of 5.8 for VIII was also determined in 66% ethanol/water solution using 0.70 M NaOH solution as the titrant.

Realizing the potential utility of VIII as a synthetic intermediate, we next attempted to prepare the corresponding acid chloride. Reactions of VIII with either phosphorus pentachloride or thionyl chloride led to the formation of a green colored solution. Based upon similar reactions involving the parent compound I, a probable product was one in which a carbonyl ligand on the metal had been replaced by two chloro ligands [1,19]. A milder source of halide ion was thus required, one that would not lead to oxidation of the metal. Fortunately, a reaction between VIII and oxalyl chloride in benzene solution gave the desired product (η^5-chloroformylcyclopentadienyl)dicarbonylcobalt (IX) as a red liquid in 67% yield, and only a small amount of oxidation products was observed.

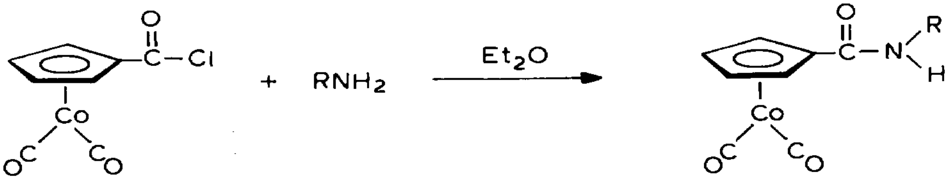


(VIII)

(IX)

Compound IX was purified by pentane extraction of the crude reaction mixture, and was obtained analytically pure by vacuum distillation at 50°C. The IR spectrum of IX exhibited a characteristic carbonyl band at 1750 cm^{-1} as well as terminal carbonyl absorptions at 2035 and 1980 cm^{-1}. Its ^1H NMR spectrum displayed A_2B_2 pseudo triplets at δ 4.60 and 4.28 ppm for the ring protons.

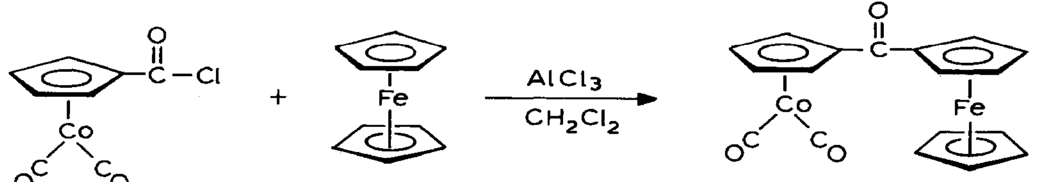
Acid chloride IX reacted readily with aniline and with ammonia to form the corresponding carboxamide derivatives of I. Thus, when IX was combined with aniline in ethyl ether solution, a 63% yield of (η^5-*N*-phenylcarbamoylcyclopentadienyl)dicarbonylcobalt (X) was produced. The IR spectrum of X contained terminal metal carbonyl bands at 2050 and 1975 cm^{-1}, as well as an amide I band at 1670 and an amide II band at 1620 cm^{-1}. The ^1H NMR spectrum of X exhibited a broad singlet due to the N–H proton at δ 9.40 and an A_2B_2 pattern of pseudo triplets at 6.20 and 5.80 ppm for the protons on the substituted cyclopentadienyl ring. Likewise, treatment of IX with dry ammonia in ethyl ether at room temperature rapidly generated (η^5-carbamoylcyclopentadienyl)dicarbonylcobalt (XI) in 65% yield. Amide XI exhibited characteristic amide bands in its IR spectrum at 1685 and 1620 cm^{-1}, as well as terminal carbonyl absorptions at 2025 and 1960 cm^{-1}. The ^1H NMR spectrum of XI contained a broad singlet at δ 2.82 due to the NH_2 protons, and pseudo triplets at 5.16 and 5.49 ppm due to the substituted cyclopentadienyl ring protons.



(IX)

(X, R = C_6H_5;
XI, R = H)

The ability of IX to undergo reactions typical of an aromatic acid chloride suggested that it might be a useful intermediate in Friedel–Crafts reactions. We subsequently found that a Perrier-type complex between IX and aluminum chloride could readily be formed, and would react with ferrocene in methylene chloride solution to afford, after hydrolysis, a 36% yield of (η^5-ferrocenoylcyclopentadienyl)dicarbonylcobalt (XII) as an orange solid.



(IX)

(XII)

Ketone XII was characterized in its IR spectrum by an organic carbonyl band at 1630 cm^{-1} and terminal metal carbonyl absorptions at 2040 and 1980 cm^{-1}. The organic carbonyl band occurred at lower energy than for other carbonyl derivatives of I prepared, due probably to the added conjugation supplied by the ferrocenyl substituent. The ^1H NMR spectrum of XII exhibited A_2B_2 pseudo triplets at δ 5.84 and 5.52 ppm due to the protons on the substituted cyclopentadienyl ring bound to cobalt, and another set at δ 4.97 and 4.62 ppm, due to the protons of the substituted cyclopentadienyl ring bound to iron. In addition, a singlet at δ 4.32 ppm was assigned to the protons of the unsubstituted cyclopentadienyl ring. Ketone XII also exhibited a molecular ion at *m/e* 392 in its mass spectrum.

In conclusion, the availability of carboxylic acid VIII in good yield has opened up a potentially large area of research involving functionally substituted derivatives of I. The effects that these substituents will have in modifying the reactivity and catalytic properties of the parent compound I are of special interest, as are reactions of new bimetallic compounds such as XII. Studies in these areas are currently under investigation in our laboratory.

Experimental

All operations were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques. Trace oxygen was removed by passage through a column of BTS catalyst. The gas was then dried via passage through successive columns of sulfuric acid and phosphorus pentoxide. Pentane, hexane and methylene chloride were distilled from calcium hydride under argon. Diethyl ether was predried over sodium wire and distilled from sodium-benzophenone under argon. Tetrahydrofuran (THF) was predried over potassium hydroxide, then sodium wire, and finally distilled under argon from sodium-benzophenone. Column chromatography was carried out using Fisher brand Florisil or Alfa-Ventron neutral CAMAG alumina. The Florisil and alumina adsorbents were heated under vacuum (0.01 Torr) on a rotary evaporator by means of a heat gun for 2 h to remove water and oxygen. The alumina was subsequently deactivated with 5% (by weight) argon-saturated water. Dimethyl and diethyl carbonate were obtained from Aldrich Chemical Co., while dicobalt octacarbonyl was obtained from Strem Chemical Co.

^{1}H NMR spectra were recorded on a Varian A-60 spectrometer. IR spectra were obtained 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. Melting points were obtained on a Mel-Temp apparatus in sealed tubes under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA.

Preparation of sodium carbomethoxycyclopentadienide (III)

To a slurry of sodium sand (3.22 g, 137 mmol) in 120 ml of THF at 0°C in a Schlenk flask was added freshly cracked cyclopentadiene (28.0 ml, 338 mmol). The flask was fitted with a gas outlet tube connected to a mercury overpressure valve to allow for the evolution of hydrogen. The mixture was magnetically stirred until the sodium had reacted. Additional cyclopentadiene was added as necessary in order to completely consume the sodium. To the resulting pink solution of sodium cyclopentadienide, dimethyl carbonate (36.5 ml, 425 mmol) was added. The reaction mixture was stirred at room temperature for 10 min, subsequently refluxed for 4 h, and then the solvent was removed in vacuo. The resulting solid was washed with diethyl ether until the filtrate was clear, and dried to afford 18.43 g (92%) of sodium carbomethoxycyclopentadienide as a hygroscopic, slightly air-sensitive solid. ^{1}H NMR (D_2O, ext. TMS) δ 3.75 (s, 3H, CH_3), 6.06 (m, 2H, H(3,4)), 6.56 ppm (M, 2H, H(2,5)).

Preparation of sodium carbethoxycyclopentadienide (IV)

A solution of 100 mmol of sodium cyclopentadienide was prepared in 75 ml of THF as described above. To this pink solution, 50.6 ml (300 mmol) of diethyl carbonate was added. The reaction mixture was stirred for 10 min at room temperature and for 2 h at reflux. The solution was then cooled, the solvent removed, and the resulting residue washed with diethyl ether and dried to give 11.0 g (71%) of sodium carbethoxycyclopentadienide as a hygroscopic white solid. ^{1}H NMR (D_2O, ext. TMS) δ 1.60 (t, 3H, CH_3), 4.30 (q, 2H, CH_2), 6.60 (m, 2H, H(3,4)), 7.20 ppm (m, 2H, H(2,5)).

Preparation of carbomethoxycyclopentadiene dimer

This synthesis has been adapted from a procedure by Peters [20]. A solution of 1.0 mol of sodium cyclopentadienide in ca. 600 ml of THF was prepared from 24.0 g (1.0 mol) of sodium sand and 70.0 g (1.1 mol) of cyclopentadiene. To the resulting red solution, methyl chloroformate (94.0 g, 1.0 mol) was added at 0°C and the reaction mixture was stirred for 4 h at 25°C. The solvent was then removed and the resulting pink solution was extracted with ca. 100 ml of dry diethyl ether. The extracts were filtered and concentrated, and the resulting red oil was distilled at 80–90°C/20 Torr. The distillate was a yellow liquid which slowly crystallized. Addition of pentane increased the rate of crystallization. Filtration and drying afforded 1.5 g (10%) of carbomethoxycyclopentadiene dimer as a white crystalline solid, m.p. 78–80°C (lit. m.p. 82–83°C) [20].

Preparation of carbomethoxycyclopentadienylthallium (V)

Carbomethoxycyclopentadiene dimer (3.2 g, 12.8 mmol) was cracked at 225°C/20 Torr and the distillate was passed directly into a solution of 6.23 g (25.9 mmol) of thallium(I) chloride and 100 g of potassium hydroxide in 250 ml of water. The resulting white precipitate was collected, washed with water, and dried under vacuum (10^{-2} Torr) to afford 3.2 g (38%) of carbomethoxycyclopentadienylthallium as an air-stable white solid, m.p. 136–140°C dec. (Found: C, 48.95; H, 3.36. $C_9H_7CoO_3$ calcd.: C, 48.67; H, 3.18%).

Preparation of (η^5-carbomethoxycyclopentadienyl)dicarbonylcobalt (VI)

Method A. To a solution of dicobalt octacarbonyl (3.53 g, 10.3 mmol) in 200 ml of THF was slowly added iodine crystals (2.60 g, 10.3 mmol) and the reaction mixture was stirred for 2 h. Sodium carbomethoxycyclopentadienide (3.04 g, 20.1 mmol) was subsequently added to the green solution and stirring was continued for 24 h. The red solution was concentrated to ca. 30 ml, diethyl ether was added, and the resultant slurry was filtered through alumina. Alumina (15 g) was then added to the filtrate and the solvent removed in vacuo. The residue was placed on an alumina-packed column (2 × 15 cm) and eluted with pentane and diethyl ether. The product band was eluted with 1/1 pentane/ether. Evaporation of the solvent afforded 1.42 g (41%) of (η^5-carbomethoxycyclopentadienyl)dicarbonylcobalt as a red liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr (Found: C, 45.41; H, 3.22. $C_9H_7CoO_4$ calcd.: 45.40; H, 2.96%). ^{1}H NMR (acetone-d_6) δ 3.80 (s, 3H, CH_3), 5.50 (t, 2H, H(3,4)), 5.65 ppm (t, 2H, H(2,5)). IR (neat) 3105w, 2970w, 2015s, 1970s, 1720s, 1485s, 1435s, 1385s, 1275s, 1185m, 1135s, 1065w, 1015s, 970m, 890w, 815m, 785w, 765m, 615s cm^{-1}. MS *m/e* 238 (M^+), 210

($M-CO^+$), 182 ($M-2CO^+$), 124 ($C_5H_5Co^+$), 92 ($C_5H_4CO^+$), 64 ($C_5H_4{}^+$).

Method B. To a THF solution of dicobalt octacarbonyl (1.00 g, 2.90 mmol) and iodine crystals (0.74 g, 2.90 mmol) prepared as above was added carbomethoxycyclopentadienylthallium (1.38 g, 5.80 mmol), and the reaction mixture was stirred for 12 h. The mixture was then filtered through a frit and the solvent was evaporated on alumina. The resulting residue was placed on an alumina column and eluted as before. Evaporation of the solvent gave 0.26 g (19%) of (η^5-carbomethoxycyclopentadienyl)dicarbonylcobalt as a red liquid.

Preparation of (η^5-carbethoxycyclopentadienyl)dicarbonylcobalt (VII)

A THF solution of dicobalt octacarbonyl (1.00 g, 2.90 mmol) and iodine crystals (0.74 g, 2.90 mmol) was stirred for 1 h at 25°C. To the green solution was added sodium carbethoxycyclopentadienide (0.93 g, 5.8 mmol) and the deep red solution was stirred for 12 h. The reaction mixture was concentrated to ca. 30 ml, diethyl ether was added, and the slurry was filtered through an alumina plug. Alumina was added to the filtrate and the solvent was removed in vacuo. The resulting residue was placed on an alumina-packed column, and eluted with pentane and diethyl ether. A forerun of (η^5-cyclopentadienyl)dicarbonylcobalt was initially eluted, followed by a second orange band which eluted with 5/1 pentane/ether. The latter when collected and the solvent removed produced 0.24 g (26%) of (η^5-carbethoxycyclopentadienyl)dicarbonylcobalt as a red liquid. An analytical sample was obtained by distillation at 50°C/10^{-3} Torr (Found: C, 47.72; H, 3.51. $C_{10}H_9CoO_4$ calcd.: C. 47.64; H, 3.60%). ^{1}H NMR (acetone-d_6) δ 1.25 (t, 3H, CH_3), 4.25 (q, 2H, CH_2), 5.50 (t, 2H, H(3,4)), 5.60 ppm (t, 2H, H(2,5)). IR (neat) 3000s, 2020s, 1965s, 1720s, 1485m, 1385m, 1275s, 1135m, 1090m, 1025w, 905w, 855m, 815 w cm^{-1}.

Preparation of (η^5-carboxycyclopentadienyl)dicarbonylcobalt (VIII)

Method A. (η^5-Carbomethoxycyclopentadienyl)dicarbonylcobalt (2.06 g, 8.66 mmol) was dissolved in 75 ml of 95% ethanol, followed by the addition of a solution of potassium hydroxide (0.98 g, 17.3 mmol) in 30 ml of water. The dard red mixture was stirred at room temperature for 12 h. To the solution was then added 400 ml of deoxygenated water, followed by the dropwise addition of concentrated hydrochloric acid until the solution was acidic. The resulting precipitate was filtered, washed with deoxygenated water until the filtrate was neutral, and dried. In addition, the aqueous layer was extracted with ether, the extracts were washed with water, and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was evaporated. The combined precipitate and residue amounted to 1.44 g (74%) of (η^5-carboxycyclopentadienyl)dicarbonylcobalt. An analytical sample, m.p. 135–137°C, was obtained by two recrystallizations from diethyl ether/hexane solution (Found: C, 42.75; H, 2.20. $C_8H_5CoO_4$ calcd.: C, 42.88; H, 2.25%). ^{1}H NMR (acetone-d_6) δ 5.52 (t, 2H, H(3,4)), 5.64 (t, 2H, H(2,5)), 8.94 ppm (s, 1H, COOH), IR (KBr) 3100–2400br, 2035s, 1970s, 1670s & br, 1490s, 1415m, 1290s, 1155m, 1050w, 1030w, 1010w, 910w, 815m, 740m, 615m cm^{-1}. MS m/e 224 (M^+), 196 ($M-CO^+$), 168 ($M-2CO^+$), 124 ($C_5H_5Co^+$), 92 ($C_5H_4CO^+$).

In a similar manner, alkaline hydrolysis of (η^5-carbethoxycyclopentadienyl)dicarbonylcobalt afforded (η^5-carboxycyclopentadienyl)dicarbonylcobalt as a red-orange solid in 67% yield.

Method B. A solution of dicobalt octacarbonyl (3.53 g, 10.3 mmol) dissolved in

200 ml of THF was stirred with iodine crystals (2.60 g, 10.3 mmol) for 2 h. To the resulting green solution was added sodium carbomethoxycyclopentadienide (3.04 g, 20.1 mmol) and stirring was continued for 24 h. The solution was concentrated to ca. 30 ml in vacuo and diethyl ether was added. The resultant slurry was filtered through alumina. The solvent was removed in vacuo, and 90 ml of 95% ethanol was then added, followed by the addition of 10% aqueous potassium hydroxide (25 ml). The red solution was stirred at room temperature for 15 h. To the mixture was added 400 ml of deoxygenated ice-water followed by the dropwise addition of concentrated hydrochloric acid until the solution was acidic (pH = 4). The resulting precipitate was filtered, washed with deoxygenated water, washed with pentane, and dried to afford 1.41 g (30%) of (η^5-carboxycyclopentadienyl)dicarbonylcobalt as an orange solid, m.p. 133–135°C.

Preparation of (η^5-chloroformylcyclopentadienyl)dicarbonylcobalt (IX)

To a solution of (η^5-carboxycyclopentadienyl)dicarbonylcobalt (0.25 g, 1.12 mmol) in 30 ml of benzene, freshly distilled oxalyl chloride (0.20 ml, 2.29 mmol) was added via a syringe. The reaction mixture was stirred at room temperature for 18 h with the outlet interfaced to a mercury overpressure valve. The cloudy red brown solution was filtered and the solvent was removed in vacuo. The red residue was extracted with pentane and the extracts were transferred to a Schlenk tube using a cannula. Removal of the solvent in vacuo afforded 0.18 g (67%) of (η^5-chloroformylcyclopentadienyl)dicarbonylcobalt as a red liquid. An analytical sample was prepared by distillation at 25°C/10^{-3} Torr (Found: C, 39.43; H, 1.66. $C_8H_4ClCoO_3$ calcd.: C, 39.62; H, 1.66%). ^1H NMR (C_6D_6) δ 4.28 (t, 2H, H(3,4)) 4.60 ppm (t, 2H, H(2,5)). IR (neat) 3110w, 2035s, 1980s, 1750br & s, 1455m, 1235m, 1040m, 940m, 820w, 778s, 610w cm^{-1}.

Preparation of (η^5-carbamoylcyclopentadienyl)dicarbonylcobalt (XI)

To a solution of (η^5-carboxycyclopentadienyl)dicarbonylcobalt (0.72 g, 3.2 mmol) in 70 ml of benzene, oxalyl chloride (0.70 ml, 8.0 mmol) was added. The reaction mixture was stirred at room temperature for 18 h with the outlet interfaced to a mercury overpressure valve. The dark solution was filtered, the solvent was removed in vacuo, and the red residue was extracted with pentane. Removal of the solvent in vacuo afforded 0.52 g (67%) of (η^5-chloroformylcyclopentadienyl)cobalt. Without further purification, the dark red liquid was dissolved in 60 ml of diethyl ether and dry ammonia was passed through the solution for 1 h, resulting in an immediate precipitation of yellow crystals. After removal of the solvent, 60 ml of methylene chloride was added and the solution was washed with deoxygenated water until the washings were neutral. After the solution was dried over anhydrous magnesium sulfate for 1 h, it was filtered through an alumina plug (2 × 2.5 cm) and was chromatographed on an alumina column using THF as the eluent. Removal of the solvent in vacuo produced 0.31 g (65%) of (η^5-carbamoylcyclopentadienyl)dicarbonylcobalt as an orange solid, m.p. 128–130°C. An analytical sample was obtained by vacuum sublimation at 68°C/10^{-3} Torr (Found: C, 42.77; H, 2.74; N, 6.24. $C_8H_6CoNO_3$ calcd.: C, 43.07; H, 2.71; N, 6.28%). ^1H NMR (acetone-d_6) 2.82 (br s, 2H, NH_2), 5.16 (t, 2H, H(3,4)), 5.49 ppm (t, 2H, H(2,5)). IR (THF) 2025s, 1960s, 1685s, 1620m, 1480m, 1440m, 1400m, 1230w, 1150m cm^{-1}.

Preparation of (η^5-N-phenylcarbamoylcyclopentadienyl)dicarbonylcobalt (X)

A solution composed of (η^5-chloroformylcyclopentadienyl)dicarbonylcobalt (0.31 g, 1.70 mmol) in diethyl ether and an excess of aniline (0.62 ml, 0.63 g, 6.80 mmol) was stirred at 25°C. The solution became cloudy and a fine white precipitate was formed: After stirring for 3.5 h, 20 ml of deoxygenated water was added to dissolve the anilinium chloride. The ether layer was separated, washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on alumina. Elution of an alumina column with 3/1 diethyl ether/pentane gave an orange band which when collected and the solvent was removed afforded 0.26 g (63%) of (η^5-*N*-phenylcarbamoylcyclopentadienyl)dicarbonylcobalt as an orange solid. An analytical sample, m.p. 142–144°C, was obtained by sublimation at 80°C/10^{-3} Torr (Found: C, 56.20; H, 3.40; N, 4.58. $C_{14}H_{10}CoNO_3$ calcd.: C, 56.20; H, 3.37; N, 4.68%). ^{1}H NMR (acetone-d_6) δ 5.80 (t, 2H, H(3,4)), 6.20 (t, 2H, H(2,5)), 7.30–8.20 (m, 5H, C_6H_5), 9.40 ppm (br s, 1H, NH). IR ($CHCl_3$) 2050s, 1975s, 1670s, 1600m, 1520m, 1430m, 1380w, 1305m cm^{-1}.

Preparation of (η^5-ferrocenoylcyclopentadienyl)dicarbonylcobalt (XII)

(η^5-Chloroformylcyclopentadienyl)dicarbonylcobalt (0.26 g, 1.07 mmol) was dissolved in 25 ml of methylene chloride. To this solution, 0.14 g (1.07 mmol) of anhydrous, reagent-grade aluminum chloride was added. The aluminum chloride dissolved with shaking, causing the solution to turn deep pink. This solution was then added dropwise to a solution of 0.20 g (1.07 mmol) of ferrocene in 25 ml of methylene chloride at 25°C. The solution, which turned violet and cloudy, was allowed to stir for 2 h at 25°C, followed by hydrolysis with 50 ml of deoxygenated water. The red organic layer was separated and washed with water (2 × 25 ml), dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated on alumina. Elution of the alumina dry-packed column with pentane gave a forerun of ferrocene. Elution with 3/1 diethyl ether/pentane gave after collection and evaporation of the solvent 0.18 g (36%) of (η^5-ferrocenoylcyclopentadienyl)dicarbonylcobalt as an orange solid. An analytical sample, m.p. 153–154°C, was obtained by recrystallization from a diethyl ether/hexane solution (Found: C, 55.01; H, 3.08. $C_{18}H_{13}CoFeO_3$ calcd.: C, 55.14; H, 3.34%). ^{1}H NMR (acetone-d_6) δ 4.32 (s, 5H, C_5H_5), 4.62 (t, 2H, H(3,4)Fe), 4.97 (t, 2H, H(2,5)Fe), 5.52 (t, 2H, H(3,4)Co), 5.84 ppm (t, 2H, H(2,5)Co). IR (CH_2Cl_2) 2040s, 1980s, 1630m, 1430w, 1375w, 1250w, 1100w, 1030w cm^{-1}. MS *m/e* 392 (M^+), 364 ($M-CO^+$), 336 ($M-2CO^+$), 308 ($C_5H_4CoC_5H_4FeC_5H_5^+$).

pK_a-Determination of (η^5-carboxycyclopentadienyl)dicarbonylcobalt (VIII)

The titration was conducted using a Radiometer Titrigraph Type SDR2c Copenhagen (U.S. distributor: The London Company, West Lake, Ohio) coupled with a Radiometer Titrator II and pH Meter 25 with a combination glass electrode. An analogue data collection was performed using an *X*-*Y* recorder. The titrating base was 0.70 *M* NaOH solution. The concentration of the acid in 66% ethanol/water was 0.01 *M*. The pK_a was observed as the pH value at one-half the volume of titrant necessary to achieve the neutralization point. The pK_a was determined to be 5.8.

Acknowledgement

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research program. We also wish to thank Dr. J.J. Mrowca for helpful information.

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