Synthesis and Chemistry of h^4-Cyclobutadiene(h^5-cyclopentadienyl)cobalt[1]

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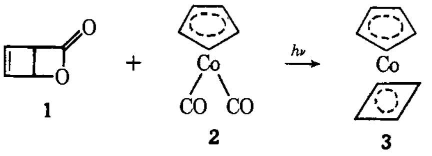
Abstract: Cyclobutadiene(cyclopentadienyl)cobalt (**3**) has been prepared by photochemical reaction of cyclopentadienylcobalt dicarbonyl with photo-α-pyrone. Two other complexes, α-pyrone(cyclopentadienyl)cobalt (**4**) and a dicobalt complex shown to have structure **5**, are formed in this photochemical reaction. The dicobalt complex exhibits fluxional behavior at elevated temperatures involving the interchange of the cobalt atoms with concurrent exchange of metal–carbon σ and π bonds. Activation parameters for this valence tautomerism for **3** and for a derived dicarboxylic acid ester (**6**) have been determined. Cyclobutadiene(cyclopentadienyl)cobalt undergoes Friedel–Crafts acetylation and metallation with *n*-butyllithium preferentially on the cyclobutadiene ring. Attempts to prepare a cation derived by oxidation of **3**, or to effect arylation of the complex with benzenediazonium chloride were unsuccessful. On controlled oxidation, **3** exhibits two anodic waves at 0.79 and 1.14 V, neither of which was reversible, the first corresponding to the transfer of two electrons. The dissociation constants for the isomeric monocarboxylic acids **9a** and **11a** and for the dicarboxylic acid (**10a**) have been determined, and these are compared with the corresponding ferrocenoic acids.

Among organotransition metal π complexes, those incorporating a cyclobutadiene ring occupy a place of particular importance, largely owing to the long held interest in the free hydrocarbon.[2] Several such complexes are now known. These have been prepared either by metal-promoted cycloaddition of acetylenes,[3] by transfer of cyclobutadiene ligands from one metal to another,[4] by demetallation of heterodienes,[5] or by reduction of 3,4-dihalocyclobutenes,[6] of 3,4-cyclobutenediol carbonates,[7] or of 1,2,3,4-tetrahalocyclobutanes[8] with metal carbonyls. For the most part these reactions have been used for the synthesis of fully substituted cyclobutadiene–metal complexes. Only the reductive method has been successfully employed in the synthesis of complexes of unsubstituted and partially substituted cyclobutadiene.

We recently described the formation of cyclobutadieneiron tricarbonyl in the reaction of iron carbonyl with photo-α-pyrone (**1**).[9] These results prompted us to examine the reaction of **1** with other transition metal carbonyls. Of these, cyclopentadienylcobalt dicarbonyl (**2**) seemed particularly attractive since, although polysubstituted cyclobutadiene(cyclopentadienyl)cobalt complexes had been prepared,[10] the parent complex **3** was unknown.

Results and Discussion

We found that, although photo-α-pyrone failed to react with cyclopentadienylcobalt dicarbonyl in refluxing toluene, photolysis of ether solutions of these substances led to the formation of **3** in moderate yield.[11]



Physical Properties of Complex 3. Cyclobutadiene(cyclopentadienyl)cobalt is a yellow, crystalline material, mp 88.5–89.0°, which sublimes readily at atmospheric pressure, is very soluble in the common organic solvents, and appears to be indefinitely stable in air. Its mass spectrum exhibits three intense peaks at *m/e* 176 (molecular ion), 150 ($C_5H_5COC_2H_2$), and 124 (C_5H_5Co), and three low-intensity peaks at *m/e* 98 (C_3H_3Co), 85 (C_2H_2Co), and 59 (Co). The presence of a low-intensity peak at *m/e* 88.5 corresponding to the doubly charged parent ion, which itself accounts for almost 40% of the total ion current, reflects the high thermodynamic stability of the complex. But the mass spectrum provides no evidence for the presence of a cyclobutadiene ring, rather than two acetylene units in the complex, since the only metastables observed are at *m/e* 127.8, 102.5, and 77.5 These correspond to the transitions 176 → 150, 150 → 124, and 124 → 98, associated with the successive loss of C_2H_2 fragments from the parent ion.[12]

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(1) Taken in part from the Ph.D. Thesis of B. North, Brandeis University, Feb 1971; NSF Trainee, 1966–1969.

(2) M. P. Cava and M. J. Mitchell in "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(3) See, for example: W. Hübel, E. H. Braye, A. Clauss, E. Weiss, D. H. Brown, G. S. D. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); W. Hübel and R. Merenyi, *J. Organometal. Chem.*, **2**, 213 (1964); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **34**, 452 (1961); P. M. Maitlis, D. Pollack, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965); F. Canziani, P. Chini, A. Quarta, and A. DiMartino, *J. Organometal. Chem.*, **26**, 285 (1971); R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **92**, 6071 (1970).

(4) P. M. Maitlis and A. Efraty, *J. Organometal. Chem.*, **4**, 172, 175 (1965); P. M. Maitlis and M. L. Games, *J. Amer. Chem. Soc.*, **85**, 1887 (1963).

(5) H. H. Freedman, *ibid.*, **83**, 2194, 2195 (1961).

(6) R. Criegee and G. Schroeder, *Justus Liebigs Ann. Chem.*, **623**, 1 (1959); G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(7) R. H. Grubbs, *ibid.*, **92**, 6693 (1970).

(8) B. W. Roberts, A. Wissner, and R. A. Rimerman, *ibid.*, **91**, 6208 (1969).

(9) M. Rosenblum and C. Gatsonis, *ibid.*, **89**, 5074 (1967).

(10) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **34**, 452 (1961); H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, P22 (1967); J. F. Helling, S. C. Rennison, and A. Merijan, *J. Amer. Chem. Soc.*, **89**, 7140 (1967); M. D. Rausch and R. A. Genetti, *ibid.*, **89**, 5502 (1967); P. M. Maitlis, A. Efraty, and M. L. Games, *ibid.*, **87**, 719 (1965).

(11) M. Rosenblum and B. North, *ibid.*, **90**, 1060 (1968). A second synthesis of this substance was reported at the same time by R. G. Amiet and R. Pettit, *ibid.*, **90**, 1059 (1968).

(12) The loss of acetylene rather than cyclobutadiene fragments from several tetraphenylcyclobutadiene–metal complexes has also been noted by R. B. King and A. Efraty, *Org. Mass. Spectrom.*, **3**, 1233 (1970). Scrambling effects in the loss of C_2 ring fragments from $(FeC_4Ar_4)^+$ ions have been discussed by M. M. Bursey, F. E. Tibbetts and W. F. Little, *J. Amer. Chem. Soc.*, **92**, 1087 (1970).

Table I. Principal Infrared Absorptions of Cyclobutadieneiron Tricarbonyl, Ferrocene, and Cyclobutadiene(cyclopentadienyl)cobalt

Complex	Absorption bands, cm^{-1}										
$C_4H_4Fe(CO)_3$[a]	3100			1320	1230			934	817		770
$(C_5H_5)_2Fe$[b]		3084	1407			1101	999		813	787	
$C_4H_4CoC_5H_5$[b]	3090	3060	1408	1308	1210	1101	997	926	815	787	775
									749	739	

[a] Determined in CS_2 solution. [b] Determined in KBr.

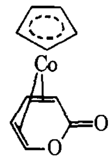
The clearest evidence for the presence of a C_4H_4 unit within the complex is provided by its infrared spectrum. This is essentially a composite of the spectrum of ferrocene and of cyclobutadieneiron tricarbonyl, excluding the carbonyl absorptions near 2000 cm^{-1} of the latter complex. These data, summarized in Table I, suggest weak coupling between the vibrational modes associated with each of the rings. As with ferrocene, the two prominant bands at 1101 and 997 cm^{-1} (9 and 10 μ), assignable to cyclopentadienyl ring breathing and C–H in-plane bending modes, are valuable in determining the location of substituents in the complex.

The nmr spectrum of **3**, taken in CCl_4 solution, exhibits two singlet peaks at τ 5.10 and 6.34 with relative intensities of 5:4, which are assignable to cyclopentadienyl and cyclobutadiene protons, respectively. The chemical shift of cyclopentadienyl protons is very close to that found in cyclopentadienylcobalt dicarbonyl (τ 5.08, $CDCl_3$), but reflects a significant deshielding compared with protons in ferrocene (τ 5.96, CCl_4). By contrast, the cyclobutadiene ring protons in **3** are significantly shielded compared to those in cyclobutadieneiron tricarbonyl (τ 5.96, CCl_4).

The electronic spectra of **3**, as well as of cobalticinium perchlorate[13] and 1,5-cyclooctadiene(cyclopentadienyl)cobalt, are shown in Figure 1. These latter compounds may be regarded as formally six- and five-coordinate metal complexes, respectively. The strikingly close correspondence in the spectra of **3** and the cobalticinium ion serves to illustrate the similarity of the electronic structures and in particular of the ligand fields associated with these two complexes.

Other Photochemical Products. The photolysis reaction which led to the formation of **3**, yielded two additional complexes, one red and the other green. The crystalline red complex, mp 152–153°, was shown to be identical with α-pyrone(cyclopentadienyl)cobalt (**4**) prepared by photolysis of **2** in the presence of α-pyrone.[14]

The green complex, a crystalline material, mp 121–122°, analyzed for $C_{14}H_{14}Co_2$. Its infrared spectrum exhibited several peaks in the olefinic C–H stretching region, and all of the absorptions indicative of the presence of a cyclopentadiene ring, but absorptions suggestive of a cyclobutadiene ring were absent. The mass spectrum exhibited a parent peak at m/e 300 but was otherwise uninformative, except for a peak at m/e 118, corresponding to a Co_2^+ fragment which suggested the presence of a metal–metal bond.[15] The nmr spectrum exhibited a two-proton triplet at τ 1.79 (J = 4 Hz), a seven-proton singlet at τ 5.04, partly obscuring a multiplet, and a five-proton singlet at τ 5.16. These data suggested the presence of two nonequivalent cyclopentadienyl rings and two pairs of nonequivalent protons constituting an AA′XX′ set. On the basis of this information structure **5** was proposed for this complex,[11] and this has subsequently been confirmed by an X-ray crystallographic study.[16]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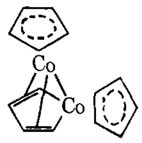
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The green complex **5** is relatively stable photochemically and is evidently a terminal product of the photolysis reaction of **1** and **2**. Thus, photolysis of **3** alone gave **5** in low yield, but in the presence of the dicarbonyl **2**, the conversion was increased to 54%. Similarly, photolysis of **4** alone gave both the cyclobutadiene complex **3** as well as **5** in low yield, while photolysis of the dicarbonyl complex **2** and α-pyrone gave principally **4** and a small amount of **5**.

The formation of **5** from **3** is most simply viewed as resulting from the insertion of a C_5H_5Co unit in the latter complex, but the question as to whether both of the C_5H_5Co groups became equivalent in the course of this reaction must, for the present, remain unanswered.

The green complex exhibits unusual fluxional behavior at elevated temperatures which involves exchange of the two structurally nonequivalent rings within the molecule. This process is evidenced in the nmr spectrum of **5** by exchange broadening of the two cyclopentadienyl resonances above 90° and their collapse to a single broad peak at 142° which continually narrows up to 160°. These changes were found to be reversible.

The rate of exchange of cyclopentadienyl rings in **5** is independent of complex concentration, thereby excluding an intermolecular exchange process. Two possible intramolecular processes, involving interchange of the two cobalt atoms with concurrent exchange of cobalt–carbon σ and π bonds, are possible. Of these, that defined by mechanism a, which requires the simultaneous exchange of cobaltacyclopentadiene protons, may be excluded, since the low-field signal due to β protons at τ 1.79 in this ring remains unchanged throughout the temperature range examined.[17]

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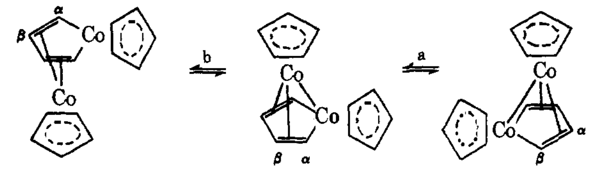
(13) G. Wilkinson, *J. Amer. Chem. Soc.*, 74, 6148 (1952).

(14) The formation of an α-pyrone complex from photo-α-pyrone is reminiscent of the formation of α-pyroneiron tricarbonyl in the reaction of 1 with iron carbonyls.[9] However, the latter reaction more clearly implicates a metal-promoted thermally forbidden electrocyclic process, since the α-pyroneiron tricarbonyl complex is formed from 1 and iron enneacarbonyl in a dark reaction, as well as photochemically.

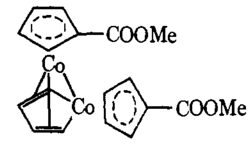
(15) R. B. King, *J. Amer. Chem. Soc.*, 88, 2075 (1966); J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, 1, 245 (1968).

(16) O. S. Mills, private communication.

(17) The α protons on this ring are largely obscured by the cyclopentadienyl resonance at τ 5.04.



Similar behavior is manifested by the dicarboxylic ester **6**, the synthesis of which will be described later.



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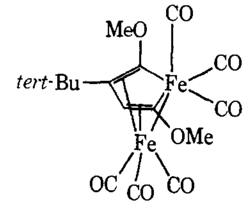
At room temperature, the nmr spectrum of this substance shows two methyl singlet signals at τ 6.12 and 6.18, a complex multiplet centered at τ 5.0 assigned to cobaltacyclopentadienyl α protons, and the two cyclopentadienyl ring β protons, a second complex multiplet at τ 4.44 due to α protons of the two cyclopentadienyl rings, and a triplet at τ 1.76 (J = 3.8 Hz) assigned to β protons of the cobaltacyclopentadienyl ring. Above 121°, the methyl group signals collapse to a singlet, while the multiplet at τ 4.44 is resolved into a triplet (J = 2 Hz) typical of monosubstituted cyclopentadienyl systems. Over the temperature range, the signal at τ 1.76 remains unchanged. These changes are shown in Figure 2.

Rates for the exchange process were determined from the nmr spectra of **5** and **6** in *o*-dichlorobenzene solution, over a 30° temperature range by a combination of line-shape functions.[18] Activation parameters, calculated from least-squares plots of the rate data, are summarized in Table II.

Table II. Activation Parameters for Valence Tautomerism of Complexes **5** and **6**

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
5	25.8 ± 1.8	8.6 ± 4.5
6	24.3 ± 0.7	8.6 ± 1.8

The fluxional behavior of the dicobalt complexes **5** and **6** is closely related to the behavior of the structurally related diiron complex **7**[19] which racemizes with a half-life of about 10 min at 76°.[20]



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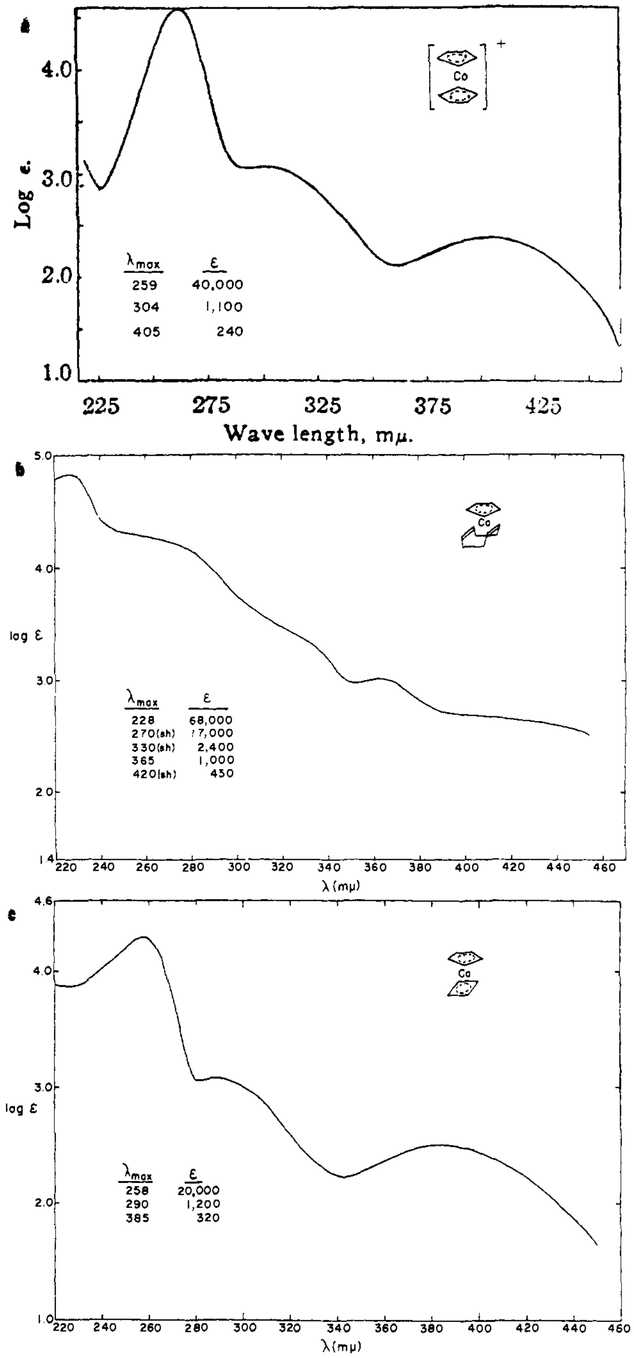

Figure 1. Electronic spectra of complex **3**, cobalticinium perchlorate and 1,5-cyclooctadiene (cyclopentadienyl)cobalt. Spectra of the neutral complexes were determined in 95% ethanol; that of the salt was determined in water (taken from ref 13).

Chemistry of Complex 3. Although cyclobutadiene-(cyclopentadienyl)cobalt is isoelectronic with ferrocene, the chemistries of these two substances differ substantially. Thus, Friedel–Crafts acetylation, which proceeds readily and in good yield with ferrocene, is less successful with **3**. Under a variety of conditions, yields of acetylated **3** were poor, the highest yield (5%) being obtained with stannic chloride and either acetyl chloride or acetic anhydride.[21]

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[18] L. M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, p 55; E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Amer. Chem. Soc.*, **84**, 4664 (1962). The precision of measurement of parameters for complex **5** is relatively low, owing to the overlap of the low-field cyclopentadienyl singlet with the triplet signal of the cobaltacyclopentadienyl ring α protons.

[19] A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).

[20] R. Case, E. R. H. Jones, N. V. Schwartz, and M. C. Whiting, *Proc. Chem. Soc.*, 256 (1962).

[21] The possibility that ring expansion had intervened in these reactions to give a methylcobalticinium cation, by processes analogous to those observed in the Friedel–Crafts acetylation of benzene(cyclopentadienyl)manganese and -chromium,[22] was examined and could be ex-

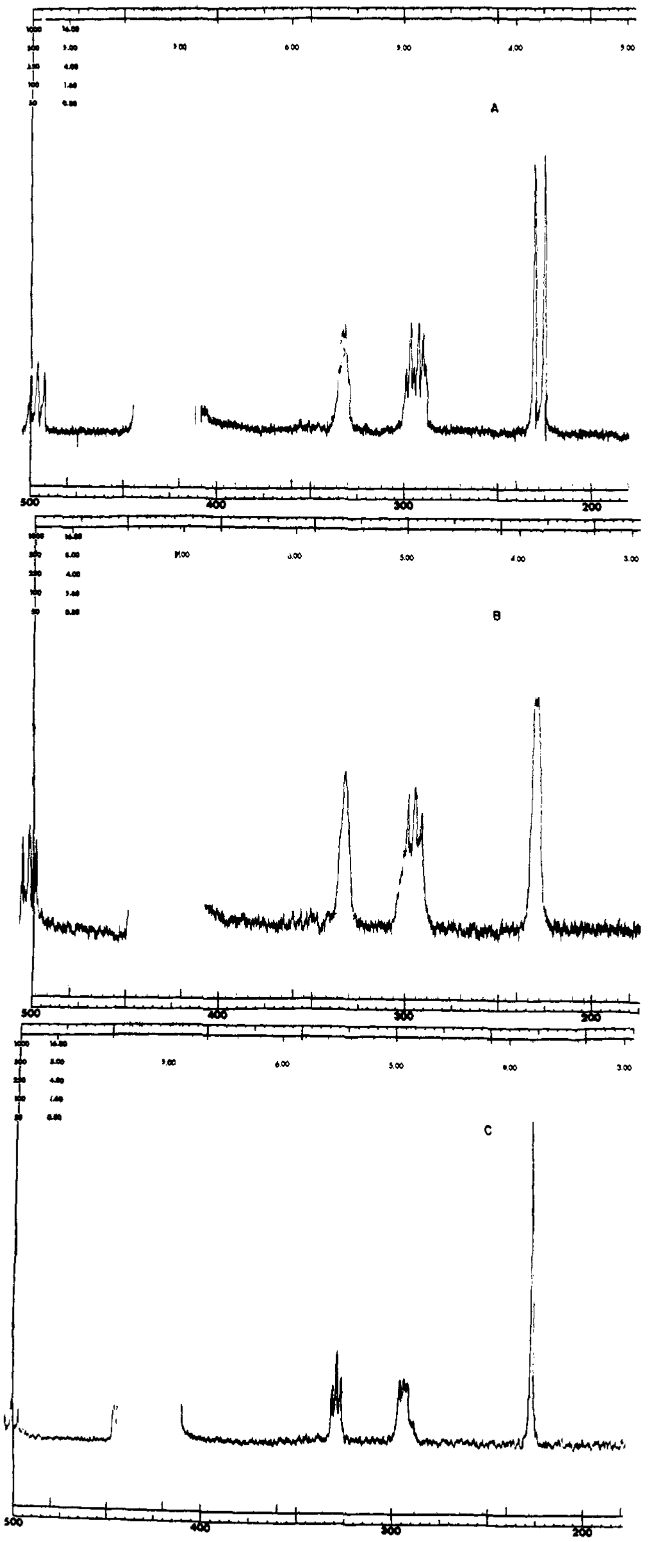
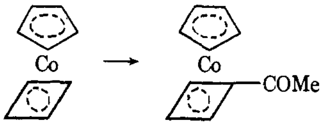


Figure 2. Nmr spectrum of complex **6**: A, at 30°; B, at 121°; C, at 163°. Taken in *o*-dichlorobenzene solution at 60 MHz.

The sole product of the acetylation reaction is the monosubstituted complex **8**. No evidence could be obtained for the formation of the isomeric monoacetyl derivative.[23]



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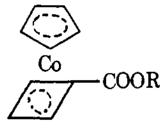
The higher reactivity of the cyclobutadiene ring toward electrophilic reagents, reflecting its higher π-electron density, may be inferred from the more pronounced magnetic shielding of protons on this ring compared with those of the cyclopentadienyl ring.[24,25]

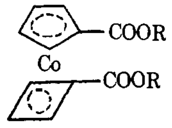
The cation, derived from **3** by electron transfer, and isoelectronic with the ferricinium ion, is evidently unstable. Thus, attempts to effect arylation of **3** by treatment with benzenediazonium chloride resulted in extensive decomposition of the complex and the formation of azobenzene.[26] Similarly, attempts to generate the cation by treatment of **3** with silver tetrafluoroborate, bromine, or BF_3 etherate in the presence of oxygen led uniformly to rapid decomposition of the complex.

A study of the controlled oxidation of **3** by cyclic voltammetry served to confirm this conclusion.[27] Whereas ferrocene in acetonitrile solution exhibited a well-behaved reversible one-electron wave on the anodic scan at 0.37 V relative to the saturated calomel electrode, the cobalt complex exhibited two waves on the anodic scan at 0.79 and 1.14 V, the first of which corresponded to the transfer of two electrons, and neither of which was reversible.[28]

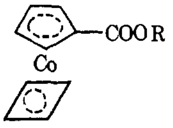
Metallation of **3** with *n*-butyllithium in the presence of tetramethylethylenediamine, followed by carboxylation, gave the mono- and dicarboxylic acids **9a** and **10a** in 30 and 18% yields, respectively. No evidence for the presence of the isomeric monocarboxylic acid **11a** could be obtained.



9a, R = H
b, R = Me



10a, R = H
b, R = Me



11a, R = H
b, R = Me

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cluded. It was subsequently found that the complex **3** is sensitive to Lewis acids and is decomposed by these reagents rapidly even at low temperatures.

(22) E. O. Fischer and S. Breitschaft, *Chem. Ber.*, **99**, 2213 (1966). A similar ring expansion has been reported in the solvolysis of 5-(α-haloalkyl)cyclopentadiene(cyclopentadienyl)cobalt by G. E. Herberich, G. Greiss, and H. F. Heil, *J. Organometal. Chem.*, **22**, 723 (1970).

(23) Very similar results have been reported by Amiet and Pettit,[11] who also found that acetoxymercuration of **3** proceeded in high yield to give substitution of the cyclobutadiene ring only.

(24) A similar correlation of reactivity in Friedel–Crafts acetylation with proton chemical shifts (τ in brackets) is manifested in the iron group metallocenes [Cp_2Fe (5.82) > Cp_2Ru (5.42) > Cp_2Os (5.26)] and within a group of cyclopentadienylmetal carbonyls [$CpMn(CO)_3$ (5.25) > $CpCr(CO)_2NO$ (4.92) $\sim$ $CpV(CO)_4$ (4.92) > $CpRe(CO)_3$ (4.63)]: E. O. Fischer, M. V. Foerster, C. G. Kreiter, and K. W. Schwarzhanz, *J. Organometal. Chem.*, 7, 113 (1967).

(25) For correlations of proton chemical shifts with π-electron densities in aromatic systems, see B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, **34**, 18 (1962); T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2208 (1961); G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

(26) By contrast, ferrocene is readily arylated under these conditions in a reaction involving initial electron transfer, followed by coupling of the resulting ferricinium ion with an aryl radical: W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1970); W. F. Little, K. N. Lynn, and R. Williams, *J. Amer. Chem. Soc.*, **85**, 3055 (1963); A. L. J. Beckwith and R. J. Leydon, *Tetrahedron Lett.*, 6, 385 (1963).

(27) We are indebted to Drs. James Butler and Lloyd Jones, Tyco Laboratories, for assistance in carrying out these experiments.

(28) When the cycle is scanned several times between zero and 1.0 V, in benzonitrile solution, a species with a half-wave potential of 0.17 V appears to build up.

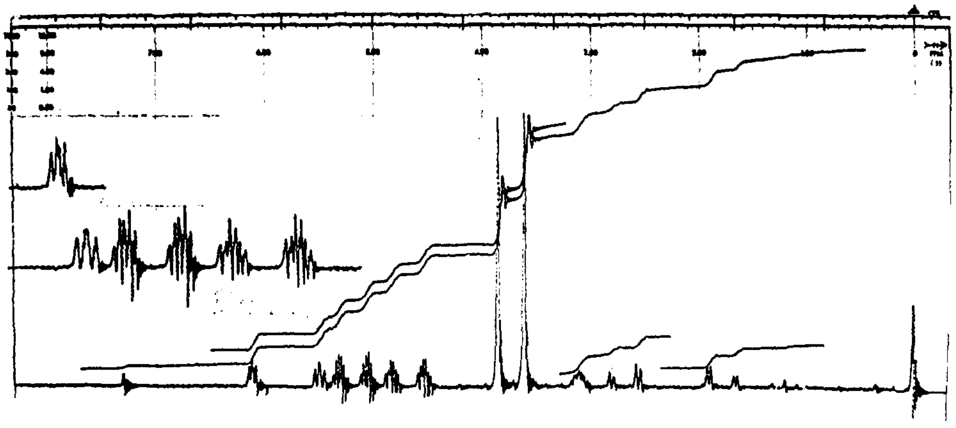
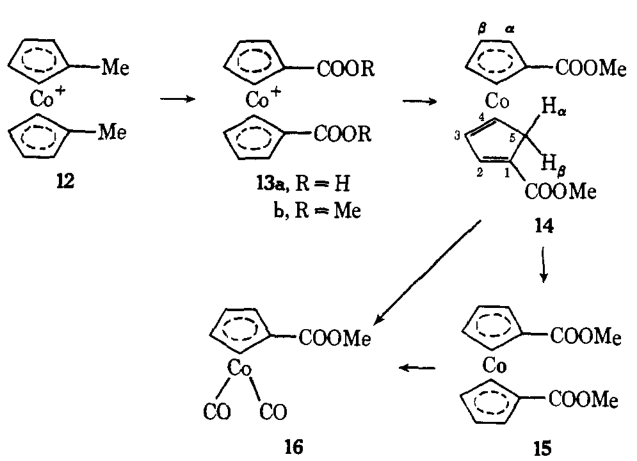


Figure 3. Nmr spectrum of complex **14**. Taken at $CDCl_3$ in 60 MHz.

The preferential reaction of the four-membered ring in these reactions is most plausibly attributed to the greater acidity of the protons in this ring due to the increased s character of its C–H bonds.[29]

In order to further examine the question of charge separation within the molecule, the synthesis of the carboxylic acid **11a** was undertaken. Initial attempts to prepare the requisite starting material **16** by metallation and carboxylation of **2** or through Friedel–Crafts acetylation[33] of this substance failed. The synthesis of carbomethoxycyclopentadienylcobalt dicarbonyl (**16**) was ultimately achieved as outlined below. Dimethylcobalticinium hexafluorophosphate (**12**) was oxidized to the corresponding dicarboxylic acid **13a**[34] with aqueous permanganate and then esterified with methanolic HCl. Reduction of the diester **13b** with sodium borohydride in tetrahydrofuran and subsequent sublimation of this product gave 1,1′-dicarbomethoxycobaltocene (**15**) which was then converted to **16** by high-pressure carbonylation. The intermediate in the reduction reaction, as in the hydride reduction of the unsubstituted cobalticinium cation, is a cyclopentadiene(cyclopentadienyl)cobalt complex.[35] This substance, **14**, may be isolated from the borohydride reduction and converted directly to **16** by high-pressure carbonylation, thus providing a more expeditious route to the dicarbonyl complex.

The structure of the product of borohydride reduction follows from its ir spectrum which exhibits low-frequency C–H absorption at 2762 cm^{-1} characteristic of an exo C–H bond,[36] and from its nmr spectrum which is reproduced in Figure 3.



The two three-proton singlets at τ 6.14 and 6.38 are due to the two methyl ester protons, while the pair of quartets centered at τ 7.32 and 8.22 is assigned to H_α and H_β, respectively, of the cyclopentadiene ring.[37] The splitting of these protons,[38] and the presence of two low-field one-proton triplet peaks at τ 3.88 and 4.50 as well as one high-field multiplet at τ 6.90, assignable to H_2, H_3, and H_4, respectively, require the placement of the carbomethoxy group in the cyclopentadiene ring at C_1.

One further feature of this spectrum deserves comment. The two pairs of α and β protons of the substituted cyclopentadienyl ring would normally be isochronous and each would appear as an apparent triplet. In the present circumstances, the intrinsic asymmetry of the cyclopentadiene ring renders each of these pairs diastereotopic, and they appear separately as four multiplet absorptions between τ 4.67 and 5.47.[39] The temperature-dependent component of the observed magnetic inequivalence is probably small, since the rotational barrier of the rings in **14** is not likely to be very different from that in the closely related metallocenes (*ca.* 1 kcal/mol).[40]

Photolysis of **16** in the presence of photo-α-pyrone (**1**) gave cyclobutadiene(carbomethoxycyclopentadi-

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(29) The relationship between kinetic acidities as measured by rates of metallation of strained hydrocarbons with methyllithium,[30] or by tritium exchange of cycloalkanes with cesium cyclohexylamide,[31] and ^{13}C–H coupling constants has been noted, and the qualitative correlation of J_{C-H} with s character of the C–H bond and with ring size is well accepted.[32]

(30) G. L. Closs and R. B. Larrabee, *Tetrahedron Lett.*, 287 (1965).

(31) A. Streitwieser, R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969).

(32) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 345.

(33) Benzoylation of **2** has been claimed in a patent: J. Kosikowski, *Chem. Abstr.*, **54**, 5693 (1960).

(34) E. O. Fischer and G. Herberich, *Chem. Ber.*, **94**, 1517 (1961).

(35) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961); J. M. Birmingham, E. O. Fischer, and G. Wilkinson, *Naturwissenschaften*, **42**, 96 (1955).

(36) See M. L. H. Green, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen and Co., London, 1968, p 80, for a brief discussion of this problem.

(37) The chemical shift of methylene protons in cyclopentadiene(cyclopentadienyl)cobalt is given as τ 7.32, 7.99: M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

(38) $J_{\alpha,\beta}$ = 15 Hz, $J_{\alpha 4}$ = 2.4 Hz, $J_{\beta 4}$ = 1.9 Hz.

(39) A closely related nonequivalence of these protons has been observed by A. Davison and J. C. Smart (*J. Organometal. Chem.*, **19**, 7 (1969)) and J. J. Bishop and A. Davison (*Inorg. Chem.*, **10**, 826 (1971)) in certain ferrocenophanes having appreciable torsional barrier associated with the bridging element.

(40) A. Haaland and J. Nilsson, *Chem. Commun.*, 88 (1968).

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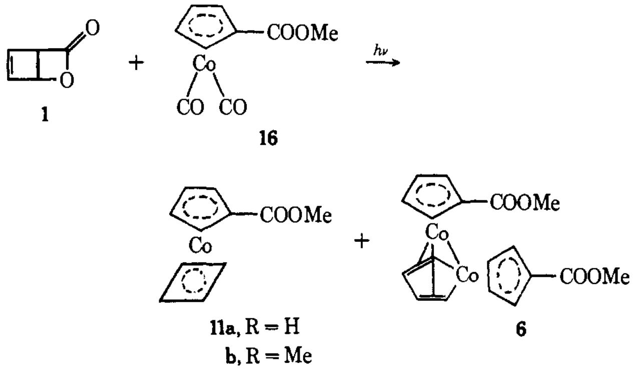
enyl)cobalt (**11b**) in addition to the green complex **6**. Saponification of **11b** gave the desired acid **11a**.



The acidity constants for the isomeric monocarboxylic acids **9a** and **11a**, and the dicarboxylic acid **10a** were determined by potentiometric titration in 2:1 (v/v) ethanol–water, at low ionic strength. These data, together with the acidity constants for benzoic acid and ferrocene mono- and dicarboxylic acids, similarly determined, are summarized in Table III.

Table III. Acid Dissociation Constants

Acid	$K_1 \times 10^7$	$K_2 \times 10^7$	K_1/K_2
Benzoic	6.5		
Ferrocenemonocarboxylic	1.6		
1,1′-Ferrocenedicarboxylic	6.1	0.41	14.7
9a	2.8		
11a	1.9		
10a	13	0.60	21.7

The near identity in the dissociation constants for ferrocenoic acid and **11a** suggests a very similar π-electron density in the cyclopentadienyl ring of each complex. While metal to cyclopentadienyl ring bonding in the cobalt complex is essentially covalent as in ferrocene, the decreased acidities of these acids compared with benzoic acid reflect somewhat higher π-electron densities in the cyclopentadienyl rings of these complexes.

The higher acidity of **9a** compared to its isomer **11a** is to be expected in view of the increased electronegativity of carbon atoms in the four-membered ring, but the difference between their acidities is somewhat smaller than might be anticipated by a comparison of the dissociation constants for cyclobutene- and cyclopentene-1-carboxylic acids which differ by an order of magnitude.[41] This is probably due to the comparatively higher π-electron density in the cyclobutadiene ring of this complex, which is similarly manifested in the relative magnetic shielding of protons in the four- and five-membered rings. A good correlation between π-electron densities and acid dissociation constants has previously been noted for several isomeric azulenecarboxylic acids.[42]

Finally, a comparison of the dissociation constants for 1,1′-ferrocenedicarboxylic acid and **10**, and especially of K_1/K_2, suggests that interactions of the two carboxyl groups in these acids are very similar, as would be anticipated from the similarity in their molecular dimensions.

Experimental Section

All reactions were carried out under nitrogen in a flame-dried apparatus. Solvents were, as a rule, distilled before use under nitrogen from appropriate drying agents. Melting points were determined in nitrogen-filled sealed tubes using a Thomas-Hoover melting point apparatus. Infrared spectra were recorded with a Perkin-Elmer spectrophotometer, Model 137, 472, or 457. Nuclear magnetic resonance spectra were recorded on a Model A 60-A spectrometer purchased through NIH Grant No. GM-13183-01. Mass spectra were taken on an AEI MS-12 spectrometer purchased through NSF Grant No. 3644. Ultraviolet spectra were recorded with the use of a Cary 14 spectrophotometer purchased through NSF Grant No. GP-1745. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., by Stephen M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Photolysis of α-Pyrone. Formation of Photopyrone in Ether and Benzene. The photolysis of α-pyrone was carried out with a medium-pressure quartz mercury-vapor lamp (Hanovia Type L, 450 W) with a Corex filter.

The apparatus was filled with a solution of α-pyrone[43] (1.0 g, 10.4 mmol) in 250 ml of anhydrous ether (or benzene), and a slow stream of nitrogen was bubbled through during the course of irradiation which was normally complete in 6 hr. The photopyrone is stable in solution at room temperature so that the solution may be left overnight without appreciable decomposition.

Reaction of Photopyrone with Cyclopentadienylcobalt Dicarbonyl. Isolation of Cyclobutadiene(cyclopentadienyl)cobalt (3). Photopyrone was prepared by irradiation of 5.9 g (61.5 mmol) of α-pyrone in 1300 ml of anhydrous benzene for 35 hr. The irradiation was continued, while cyclopentadienylcobalt dicarbonyl (5.7 g, 31.6 mmol) was added in 1.0-ml quantities over a period of 83 hr. The reaction was monitored periodically by ir, and cyclopentadienylcobalt dicarbonyl was added only when its concentration in the reaction mixture became low. Photolysis may be accelerated by periodic cleaning of the lamp immersion well with aqua regia. At the end of the reaction period, more than 80% of the photopyrone had been consumed.

Solvent was removed from the reaction mixture under vacuum, below room temperature, leaving a viscous sludge which was extracted with ether. The ether mixture was filtered under nitrogen, and the residue was washed well with ether. The filtrate was concentrated and chromatographed under nitrogen with degassed solvents on an alumina column (Camag neutral alumina, activity 1, 125 g). Elution with Skellysolve B gave a yellow band consisting of cyclopentadienylcobalt dicarbonyl and cyclobutadiene(cyclopentadienyl)cobalt. The weight of this fraction, after removing the solvent, was 1.00 g. On standing in air in a stoppered flask for several days, the liquid cyclopentadienylcobalt dicarbonyl decomposed to a green solid. The crude product was rechromatographed on an alumina column under the same conditions and the single yellow band eluted with ether was carefully evaporated under vacuum at room temperature to give 0.92 g of **3**, mp 88.5–89.0° (17% based on $CpCo(CO)_2$).

Anal. Calcd for C_9H_9Co: C, 61.36; H, 5.11. Found: C, 61.25; H, 5.20.

Dicobalt Complex 5. Chromatography of the reaction mixture yielded, in addition to the yellow band, a green band followed by a red band which were each eluted with ether. Removal of the solvent from the first fraction gave 1.67 g of dark green crystals, mp 121–122°.

Anal. Calcd for $C_{14}H_{14}Co_2$: C, 56.21; H, 4.73. Found: C, 56.00; H, 4.67.

The compound is soluble in most common organic solvents, but solutions decompose rapidly in air. It can be recrystallized from petroleum ether (bp 20–40°) at −70°.

α-Pyrone Complex 4. Removal of the solvent from the last chromatographic fraction afforded 0.36 g of a red, air-stable solid, mp 140–153°. Recrystallization from ether–petroleum ether (bp 20–40°) gave bright red needles, mp 152–153°.

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(41) O. H. Wheeler and I. Lerner, *J. Amer. Chem. Soc.*, **78**, 63 (1956). Determined in 50% aqueous ethanol at 25°.

(42) P. A. Leermakers and W. A. Bauman, *J. Org. Chem.*, **29**, 3708 (1964).

(43) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 2330 (1969).

Anal. Calcd for $C_{10}H_9CoO_2$: C, 54.55; H, 4.09. Found: C, 54.37; H, 4.01.

This substance was also obtained by irradiation of 1.1 g of α-pyrone and 1.3 g of cyclopentadienylcobalt dicarbonyl in 250 ml of benzene for 17 hr. Removal of solvent followed by ether extraction of the red-brown solid remaining, and subsequent chromatography of the ether solution, gave 0.11 g of **5** and 0.71 g of the α-pyrone complex **4**.

Acetylation of Cyclobutadiene(cyclopentadienyl)cobalt. A solution of cyclobutadiene(cyclopentadienyl)cobalt (0.310 g, 1.78 mmol) in 40 ml of methylene chloride was cooled in a Dry Ice–acetone bath and stirred in a nitrogen atmosphere. A solution of acetic anhydride (3.7 ml, 40 mmol) and stannic chloride (0.37 ml, 3.2 mmol) in 10 ml of methylene chloride was added to this from a dropping funnel over a 5-min period. After 1 hr the reaction mixture was poured into 50 ml of ice-cold 2 *N* hydrochloric acid solution, and the aqueous phase was extracted twice with methylene chloride. The combined organic phase was extracted with 0.01 *N* sodium hydroxide solution and then washed with water to neutrality. After drying the solution over magnesium sulfate, the solvent was removed and the resulting yellow oil was chromatographed on an alumina column (Camag activity 3). Elution with Skellysolve B–ether (1:1) produced two yellow bands. The first gave 5 mg of material identified as starting material. Removal of solvent from the second band gave 20 mg (5%) of yellow crystals of acetylcyclobutadiene(cyclopentadienyl)cobalt: mp 89.0°; ir (KBr) 9.0 and 10.0 μ (Cp); nmr ($CDCl_3$) τ 5.0 (5), 5.5 (2), 6.0 (1), 7.9 (3).

Anal. Calcd for $C_{11}H_{11}OCo$: C, 60.55; H, 5.05. Found: C, 60.56; H, 4.83.

Carboxylation of Cyclobutadiene(cyclopentadienyl)cobalt. A solution of 4.0 mmol of *n*-butyllithium and 0.6 ml (4.0 mmol) of *N,N,N′,N′*-tetramethylethylenediamine in 30 ml of dry hexane was cooled in an ice bath. After stirring for 15 min, a solution of 0.420 g (2.4 mmol) of cyclobutadiene(cyclopentadienyl)cobalt in 10 ml of hexane was added rapidly to the stirred solution. After 5 hr of stirring at 0°, the solution, which had turned dark brown, was rapidly transferred to a suction flask containing Dry Ice and anhydrous ether protected by a stream of nitrogen. The mixture was allowed to warm to room temperature, and was worked up. The neutral fraction, after chromatography on alumina, gave 0.086 g (0.45 mmol) of unreacted cyclobutadienyl(cyclopentadienyl)-cobalt.

The acidic product was suspended in anhydrous ether and treated with diazomethane in ether at 0°. Solvent was removed and the orange oil was chromatographed on an alumina column (Camag, Activity 3, 125 g). Elution with Skellysolve B–ether (1:1) gave, after removal of the solvent, yellow crystals of carbomethoxycyclobutadiene(cyclopentadienyl)cobalt (**9b**), mp 55–57° (0.138 g, 30% based on consumed $(C_4H_4)(C_5H_5)Co$. Further elution of the column with ether produced a second band which afforded yellow crystals of $(C_4H_4CO_2CH_3)(C_5H_5CO_2CH_3)Co$ (**10b**): mp 77–78° (0.048 g); 18% based on consumed $(C_4H_4)(C_5H_5)Co$; nmr ($CDCl_3$) τ 4.51 (t, 2, cp-α), 4.89 (t, 2, cp-β), 5.52 (s, 2, cb-α), 6.05 (s, 1, cb-β), 6.20 (s, 3, CO_2CH_3), 6.33 (s, 3, CO_2CH_3).

Carboxycyclobutadiene(cyclopentadienyl)cobalt (9a). A suspension of 59 mg of the monoester in 25 ml of 25% sodium hydroxide was refluxed for 1 hr. At the end of the reaction, the solution was cooled and acidified with concentrated hydrochloric acid, and the precipitate was collected and washed with a small amount of water. Since the carboxylic acid is somewhat soluble in water, the combined filtrate and wash was extracted with ether. After drying the ethereal phase with magnesium sulfate and removing the solvent, the yellow crystalline material thus obtained was combined with the precipitated material, recrystallized from ether–petroleum ether (bp 20–40°), and dried, yielding large orange needles: mp 162–163° (22 mg, 40%); ir (KBr) 6.0 (C=O), 9.0, 9.95 (cp); nmr (acetone-d_6) τ 4.97 (s, 5), 5.62 (s, 2), 6.07 (s, 1).

Anal. Calcd for $C_{10}H_9O_2Co$: C, 54.55; H, 4.09. Found: C, 54.62; H, 4.10.

Carboxycyclobutadiene(carboxycyclopentadienyl)cobalt (10a). A suspension of 63 mg of the diester in 20 ml of 25% sodium hydroxide was refluxed for *ca.* 1 hr. The product was obtained from the cooled, acidified reaction mixture by collecting the precipitate and extracting the aqueous filtrate with ether, as above. Recrystallization from ether gave golden-yellow needles, dec 232–236° (31 mg, 57%).

Anal. Calcd for $C_{11}H_9O_4Co$: C, 50.00; H, 3.41. Found: C, 49.76; H, 2.92.

1,1′-Dicarbomethoxycobalticinium Hexafluorophosphate (13b). 1,1′-Dicarboxycobalticinium hexafluorophosphate (20.2 g), prepared by permanganate oxidation of 1,1′-dimethylcobaltocene, was esterified by stirring overnight in 500 ml of anhydrous methanol (freshly distilled from activated magnesium) saturated with hydrogen chloride. Solvent was then removed under vacuum, leaving a cloudy oil which was dissolved in 200 ml of water, filtered, and then heated on a steam bath. A solution of *ca.* 25 g of ammonium hexafluorophosphate was added slowly to the highly acidic solution, and the yellow crystals were collected and washed with cold water, then ethanol, and finally ether. The product was dried at 100° under vacuum.

Anal. Calcd for $C_{15}H_{14}O_4PF_6Co$: C, 37.35; H, 3.13. Found: C, 37.53; H, 2.99.

1,1′-Dicarbomethoxycobaltocene (15). To a stirred suspension of 3.0 g (6.7 mmol) of 1,1′-dicarbomethoxycobalticinium hexafluorophosphate in 60 ml of dry THF was added an excess amount (0.75 g, 20 mmol) of sodium borohydride in small portions. The mixture rapidly turned blood red. After 1 hr the solution was filtered under nitrogen, and the volume of the solution was reduced under vacuum. The residue was transferred to a large sublimation apparatus, and the product was sublimed. Sublimation was continued for 5 days but was interrupted every 24 hr to collect the product and to grind up the residue. The total yield of 1,1′-dicarbomethoxycobaltocene was 0.957 g (47%).

The product is a dark red-brown solid, dec 118–120°, and is soluble in common organic solvents. In solid form it can be handled in air for short periods of time, but its solutions decompose rapidly: ir (KBr) 5.90, 6.80, 7.0, 7.25, 7.35, 7.40, 7.88, 8.40, 8.80, 9.45, 9.80, 10.30, 11.20, 12.0, 12.5, 13.25 μ.

Isolation of the Intermediate Reduction Product 14. 1,1′-Dicarbomethoxycobalticinium hexafluorophosphate (1.0 g) was reduced with sodium borohydride (0.2 g) in 40 ml of dry THF by stirring for 30 min. The solution was then filtered and the solvent removed under vacuum. The residue was extracted with ether, and the extracts were combined, concentrated, and chromatographed on an alumina column (Camag, activity 2, 50 g) to give 0.435 g of black crystals, **14**, recrystallized from ether–petroleum ether, mp 87–88.5°.

Anal. Calcd for $C_{14}H_{15}O_4Co$: C, 54.90; H, 4.90. Found: C, 54.87; H, 5.00.

Carbomethoxycyclopentadienylcobalt Dicarbonyl (16). A. The carbonylation of 1,1′-dicarbomethoxycobaltocene was carried out in a high-pressure bomb fitted with a glass liner. The bomb was charged with a solution of 0.400 g of dicarbomethoxycobaltocene in 25 ml of anhydrous benzene. The bomb was flushed twice with nitrogen, then pressurized to 1300 psi with carbon monoxide, and heated to 125–130° for 16 hr. After cooling for 6 hr, excess carbon monoxide was released, the reaction mixture was filtered under nitrogen, and the residue was washed with benzene. The combined filtrate was placed on an alumina column (Camag, activity 2, 125 g) and eluted with Skellysolve B and then ether. The second, red band was collected and yielded 0.234 g of carbomethoxycyclopentadienylcobalt dicarbonyl as red oil (yield 76%). Its ir spectrum exhibits two strong terminal CO stretching frequencies at 4.90 and 5.00 μ.

B. Reduction of 3.0 g of dicarbomethoxycobalticinium hexafluorophosphate with 1.0 g of sodium borohydride in 60 ml of dry THF was carried out as before. The reaction mixture was filtered and then transferred to the bomb, which was flushed with nitrogen, and pressurized to 1400 psi with carbon monoxide. The bomb was heated to 120° for 13 hr and then allowed to cool, after which the reaction mixture was removed and filtered. After removing the solvent, the residue was chromatographed on an alumina column (Camag, activity 2, 125 g). Skellysolve B eluted a minor band which was discarded. Ether eluted a second band which, on removal of the solvent, afforded 0.937 g of carbomethoxycyclopentadienylcobalt dicarbonyl (59%). (The ir spectrum of this product was identical with that of the product obtained in reaction A above.)

Cyclobutadiene(carbomethoxycyclopentadienyl)cobalt (11b). Carbomethoxycyclopentadienylcobalt dicarbonyl (2.6 mmol) was added to a solution of photo-α-pyrone (6.6 mmol) in 250 ml of benzene which was then irradiated for 3.5 hr.

At the end of the irradiation period, solvent was removed under vacuum, and the residue was chromatographed on an alumina column (Camag, activity 2, 125 g). Skellysolve B–ether (1:2) eluted a yellow-orange band which afforded 71 mg (12%) of yellow crystalline cyclobutadiene(carbomethoxycyclopentadienyl). A second green band eluted with ether afforded 139 mg (26%) of the green dicobalt complex **6**, mp 68.7–70°.

Anal. Calcd for $C_{18}H_{18}O_4Co_2$: C, 51.92; H, 4.33. Found: C, 51.77; H, 4.43.

Cyclobutadiene(carboxycyclopentadienyl)cobalt (11a). Cyclobutadiene(carbomethoxycyclopentadienyl)cobalt (47 mg) was dissolved in 7 ml of methanol and 6 ml of 2 *N* sodium hydroxide (thoroughly degassed). The solution was stirred for 5 hr at room temperature, methanol was then removed, and the aqueous solution was extracted twice with ether. Work-up gave 38 mg (86%) of yellow crystals. Recrystallization from ether–petroleum ether (bp 20–40°) yielded 27 mg of fine yellow crystals: dec 186–188°; nmr ($CDCl_3$) τ 2.72 (s, 1, COOH), 4.35 (m, 2, Cp-α), 4.79 (m, 2, Cp-β), 6.60 (s, 4, Cb).

Anal. Calcd for $C_{10}H_9O_2Co$: C, 54.55; H, 4.09. Found: C, 54.72; H, 4.45.

Acid Dissociation Constants. The dissociation constants were determined by potentiometric titration in 2:1 ethanol–water solution. For the monocarboxylic acids, the pK_a was taken as the pH of the solution of half-equivalence point, and duplicate titrations were run. The method used to calculate K_1 and K_2 for the dicarboxylic acids from the titration data is that of Britton.[44] The acids were dissolved in a mixture of 100 ml of absolute ethanol and 50 ml of distilled water. Titrations were carried out at 25° with Wervy standard 0.1 *N* sodium hydroxide solution, using a 10-ml buret graduated in 0.05-ml units. The pH measurements were made using a Corning Model 12 pH meter with expanding scale. In every case the concentration of the acid in the solution being titrated was such that the ionic strength was less than 0.01 *M*.

Photochemical Interconversions. Irradiation of Cyclobutadiene(cyclopentadienyl)cobalt in Benzene. A solution of 0.40 g of cyclobutadiene(cyclopentadienyl)cobalt in 250 ml of anhydrous benzene was irradiated for 23 hr. Solvent was then removed under vacuum, and the remaining dark brown oil was chromatographed on an alumina (Camag, activity 1) column. Elution with Skellysolve B–ether (1:1) produced three bands. The first yellow band (0.26 g) was identified as unreacted cyclobutadiene(cyclopentadienyl)cobalt. The second band was a red oil (weight 0.015 g) which decomposed to a green solid when stored overnight at −30°. The third band gave 0.034 g of **5**.

Irradiation of Cyclobutadiene(cyclopentadienyl)cobalt in the Presence of Cyclopentadienylcobalt Dicarbonyl. A solution of 0.41 g (2.3 mmol) of cyclobutadiene(cyclopentadienyl)cobalt and 0.41 g (2.3 mmol) of cyclopentadienylcobalt dicarbonyl in 300 ml of anhydrous benzene was irradiated for 10.5 hr under the conditions already described for the preparation of the cyclobutadiene complex. Solvent was then removed under vacuum and the residue was chromatographed on an alumina (Camag, activity 1) column. Skellysolve B–ether (3:1) eluted a yellow-orange band, which on removal of the solvent gave 0.025 g of an orange oil identified as cyclopentadienylcobalt dicarbonyl. A green band was eluted with Skellysolve B–ether (1:1) to give 0.37 g of **5** (54% yield).

Irradiation of 5 in Benzene. A solution of 0.46 g of **5** (chromatographed immediately before use) in 250 ml of anhydrous benzene was irradiated for 59 hr under the same conditions used for the synthesis of this compound. At the end of the irradiation period, the solvent was removed under vacuum, and the dark green residue was chromatographed on an alumina column (Camag, activity 1). Benzene–ether (2:1) eluted a single green band, leaving a considerable amount of insoluble residue at the top of the column. The solvent was removed from the eluted fraction, yielding 0.34 g of unchanged starting material.

Irradiation of Cyclopentadienyl(α-pyrone)cobalt. A solution of 0.174 g of cyclopentadienyl(α-pyrone)cobalt in 250 ml of anhydrous ether was irradiated for 7 hr under the same conditions used for the formation of this compound. The solution turned green after several hours.

At the end of the reaction period, solvent was removed under vacuum, and the residue was extracted with hexane and filtered, leaving a brown residue. The filtrate was concentrated and chromatographed on an alumina column (Camag, activity 1). Hexane eluted a yellow band identified as cyclobutadiene(cyclopentadienyl)cobalt (18 mg). With ether, a green band identified as **5** (weight, 7 mg) was eluted. This was followed by a diffuse light red band of cyclopentadienyl(α-pyrone)cobalt which eluted slowly and was not collected completely.

The brown residue which was filtered off before chromatography was extracted with ether and filtered. From the red-orange filtrate, 10 mg of cyclopentadienyl(α-pyrone)cobalt was obtained by precipitation with petroleum ether.

Attempts to Produce a Stable Cationic Salt of Cyclobutadiene(cyclopentadienyl)cobalt. Attempted Preparation of $[(C_4H_4)(C_5H_5)Co]^+BF_4^-$. A solution of 0.1 g (0.6 mmol) of cyclobutadiene(cyclopentadienyl)cobalt in 50 ml of anhydrous ether was treated with 0.15 ml (1.2 mmol) of boron trifluoride etherate. A stream of oxygen was bubbled into the stirred solution for 5 hr. The solution turned green, and a black precipitate formed. After standing overnight, the precipitate was collected, but it proved to be a gummy tar, insoluble in water, chloroform, or methylene chloride.

Reaction of Cyclobutadiene(cyclopentadienyl)cobalt with Bromine. A solution of 15 mg of cyclobutadiene(cyclopentadienyl)cobalt in carbon tetrachloride was treated with a solution of bromine in carbon tetrachloride. A green precipitate formed. Bromine was added until no further precipitation occurred and the bromine color persisted. The precipitate was collected and washed with carbon tetrachloride. The precipitate dissolved in water to give a violet solution and a yellow-brown residue. The solution gave a positive test for Co^{2+} ions. The ir spectrum of the precipitate showed no bands typical of the cyclobutadiene or cyclopentadienyl groups.

Treatment of Cyclobutadiene(cyclopentadienyl)cobalt with Silver Tetrafluoroborate. An ethereal solution of cyclobutadiene(cyclopentadienyl)cobalt was treated with an ethereal solution of $AgBF_4$, resulting in formation of a green-brown residue and a silver mirror. The ether was removed and replaced by acetone. After centrifuging, the solution was decanted and solvent was removed. The green-brown residue was treated with an aqueous solution of ascorbic acid. No change was observed.

Cyclic Voltammetry. Preparation of Samples. Solutions (10^{-3} *M*) of freshly sublimed ferrocene and cyclobutadiene(cyclopentadienyl)cobalt were prepared in specially purified acetonitrile, benzonitrile, methylene chloride, and dimethyl sulfoxide, all containing 0.1 *M* tetrabutylammonium perchlorate as the electrolyte. The solutions were transferred to the electrolysis cell and purged with argon gas before recording the voltammogram.

Instrumentation. The cyclic voltammetry was carried out with a Wenking potentiostate, a function generator, and a Houston Instrument Co. X–Y Recorder. The electrode was a Beckman platinum button electrode, used in conjunction with a saturated calomel electrode and a platinum counter electrode. Provisions for current amplification were made by conventional electronic amplifiers.

Acknowledgments. This work was supported in part by the National Science Foundation (GP 8714) and by the National Institutes of Health (GM 16395).

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[44] H. T. S. Britton, *J. Chem. Soc.*, **127**, 1904 (1925).