

Organometallic π Complexes. XXII. The Chemistry of π -Cyclopentadienyltetraphenylcyclobutadienecobalt and Related Compounds

M. D. RAUSCH¹ AND R. A. GENETTI

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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The reaction of π -cyclopentadienyldicarbonylcobalt and diphenylacetylene in refluxing xylene products π -cyclopentadienyltetraphenylcyclobutadienecobalt (1) and π -cyclopentadienyltetraphenylcyclopentadienonecobalt (2) in yields of 50 and 10%, respectively. This method has also been extended to the direct synthesis of the corresponding trimethylsilyl (3, 5) and phenyl (4, 6) derivatives, starting with trimethylsilyl- or phenylcyclopentadiene. The π -cyclopentadienyl ring in 1, as in ferrocene, undergoes a number of electrophilic ring substitution reactions. Acetoxymercuration with a perchloric acid catalyst, followed by treatment with lithium chloride, produces a chloromercuri derivative 7 in 65% yield, together with a 1,2-bis(chloromercuri) derivative 8. Complex 7 is readily converted into its iodo analog 9. The transmetalation of 7 with *n*-butyllithium gives a lithium intermediate 10 which on treatment with acetyl chloride affords the acetyl derivative 11. When 9 is heated with copper-bronze or with cuprous cyanide in *N*-methyl-2-pyrrolidone, the Ullmann product 12 and the cyano derivative 13 are obtained. Similar reactions with cupric acetate and cupric phthalimide produce acetate 14 and phthalimido 15 derivatives, respectively, which on hydrolysis give phenol 16 and amine 17. The relative acidity and basicity of these products have been determined. Aminomethylation and Vilsmeier formylation give dimethylaminomethyl (18) and formyl (20) derivatives in yields of 74 and 8%, respectively. The conclusion is drawn that, while 1 participates in a variety of electrophilic substitution reactions, it is in general less reactive than is ferrocene.

Although the concept of aromaticity is still not well defined, ferrocene and related organometallic compounds are generally considered "aromatic" in that they resist ring-addition reactions and undergo ring-substitution reactions. Thus, ferrocene is known to undergo various electrophilic substitution reactions such as Friedel-Crafts acylation,² alkylation,^{3,4} formylation,⁵⁻⁷ sulfonation,⁸⁻¹⁰ acetoxymercuration,^{11,12} and aminomethylation.¹³ Following these initial studies on ferrocene, various other organotransition metal compounds containing a π -cyclopentadienyl ring were found to exhibit similar chemical reactivities. Thus, ruthenocene,¹⁴ osmocene,¹⁴ cymantrene,¹⁵⁻¹⁸ and its technetium¹⁹ and rhenium^{19,20} analogs, π -cyclopentadienyltetracarboxylvanadium,^{21,22} and π -cyclopenta-

dienyldicarbonylnitrosylchromium²³ all form acyl derivatives under Friedel-Crafts conditions. In addition, cymantrene has been shown to undergo many of the other ring-substitution reactions that are characteristic of ferrocene,¹⁷ while π -cyclopentadienyltricarboxylrhenium can be mercurated and sulfonated,²⁴ and zirconocene dichloride has been reported to undergo sulfonation.²⁵ The aromatic-type reactivity of metallocenes has been the subject of several reviews.²⁶⁻²⁹

When our present program of research was undertaken, no examples of aromatic-type substitution reactions of cobalt-containing metallocenes had been described in the literature.^{30,31} It appeared to us, however, that the organocobalt compound π -cyclopentadienyltetraphenylcyclobutadienecobalt (1), first prepared in 1961 by Nakamura and Hagihara,³² and later by Wilkinson, *et al.*,³³ and by Maitlis, *et al.*,³⁴ possessed the necessary chemical stability and electronic configuration to undergo such substitution reactions without appreciable concurrent decomposition under the reaction conditions involved. Complex 1 is reported to be thermally stable to 360° under nitrogen and withstands external reagents such as hydrochloric acid, alcoholic potassium hydroxide, lithium aluminum hy-

(1) Alexander von Humboldt Research Fellow, 1969-1970. Author to whom correspondence should be addressed.

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(3) A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **109**, 543 (1956).

(4) M. Vogel, M. D. Rausch, and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957).

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(6) G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *ibid.*, 209 (1957); *J. Chem. Soc.*, 650 (1958).

(7) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957).

(8) V. Weinmayer, *J. Amer. Chem. Soc.*, **77**, 3009 (1955).

(9) A. N. Nesmeyanov, E. G. Perevalova, and S. S. Churanov, *Dokl. Akad. Nauk SSSR*, **114**, 335 (1957).

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(18) R. Riemschneider and H. G. Kassahn, *Z. Naturforsch.*, **14b**, 348 (1959); *Chem. Ber.*, **92**, 3208 (1959).

(19) E. O. Fischer and W. Fellmann, *J. Organometal. Chem.*, **1**, 191 (1963).

(20) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and L. I. Baryshnikov, *Dokl. Akad. Nauk SSSR*, **154**, 646 (1964).

(21) E. O. Fischer and K. Plesske, *Chem. Ber.*, **93**, 1006 (1960).

(22) R. Riemschneider, O. Goehring, and M. Kruger, *Monatsh. Chem.*, **91**, 305 (1960).

(23) E. O. Fischer and K. Plesske, *Chem. Ber.*, **94**, 93 (1961).

(24) A. N. Nesmeyanov, N. E. Kolobova, K. N. Anisimov, and L. T. Baryshnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1135 (1964).

(25) R. Kh. Friedlina, E. M. Brainina, M. Kh. Minacheva, and A. N. Nesmeyanov, *ibid.*, 1417 (1964).

(26) K. Plesske, *Angew. Chem., Int. Ed. Engl.*, **1**, 312, 394 (1962).

(27) M. D. Rausch, *Can. J. Chem.*, **41**, 1289 (1963).

(28) W. F. Little, *Surv. Progr. Chem.*, **1**, 133 (1963).

(29) M. Rosenblum, "Chemistry of Iron-Group Metallocenes," Part 1, Wiley, New York, N. Y., 1965.

(30) Although it is claimed [J. Kozikowski, U. S. Patent 2,916,503 (Dec 8, 1959)], that the reaction of π -cyclopentadienyldicarbonylcobalt, benzoyl chloride, and aluminum chloride produced a corresponding benzoyl derivative, no experimental details were given.

(31) It has recently been reported [J. Lewis and A. W. Parkins, *J. Chem. Soc. A*, 1150 (1967)], that π -cyclopentadienylcycloocta-1,5-dienecobalt reacts with trityl fluoroborate to give a product containing the trityl group on the π -cyclopentadienyl ring in 0.3% yield.

(32) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **34**, 452 (1961); *Nippon Kagaku Zasshi*, **84**, 339 (1963).

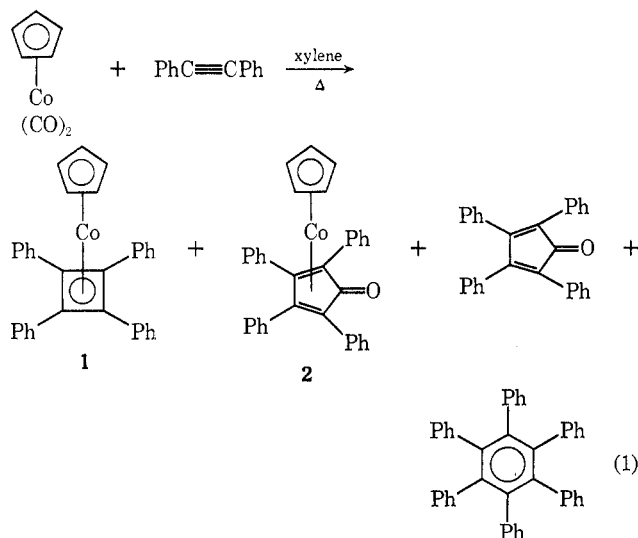
(33) J. L. Boston, D. W. Sharpe, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

(34) P. M. Maitlis and M. L. Games, *J. Amer. Chem. Soc.*, **85**, 1887 (1963); P. M. Maitlis, A. Efraty, and M. L. Games, *J. Organometal. Chem.*, **2**, 284 (1964); *J. Amer. Chem. Soc.*, **87**, 719 (1965).

dride, carbon monoxide under pressure, triphenylphosphine, dimethyl acetylenedicarboxylate, iodine, etc.³² Further, **1** is isoelectronic with ferrocene and might be expected to have somewhat similar reactivity properties.

Our present article describes the reactions of **1** with various electrophilic reagents, and some chemistry of the resulting ring-substitution products.³⁵ It should be mentioned also that **1**,³⁵ like ferrocene,³⁶ is readily metalated by *n*-butyllithium-*N,N,N',N'*-tetramethylethylenediamine, and this nucleophilic-type substitution of **1** will be more fully described in a subsequent paper. When our reactivity studies on **1** were essentially completed, two other research groups reported the formation and properties of the parent complex of **1**, *viz.*, π -cyclopentadienylcyclobutadienecobalt.^{37,38}

Direct Synthesis of π -Cyclopentadienyltetraphenylcyclobutadienecobalt Complexes.—Our studies concerning the aromatic-type reactivity of **1** have been greatly facilitated by the discovery of a new and convenient method for the synthesis of this compound. The method utilizes a reaction between diphenylacetylene and π -cyclopentadienyldicarbonylcobalt (eq 1).

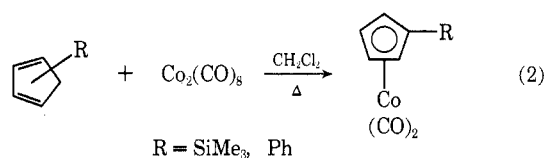


The latter has also been prepared by a new and improved method (90–95% yield) from a reaction between octacarbonyldicobalt and cyclopentadiene in methylene chloride solution at reflux. Complex **1** was thus obtained in ~50% yield compared to 15% overall yield from Nakamura's and Hagihara's method,³² which first involved the reaction of π -cyclopentadienyldicarbonylcobalt with 1,5-cyclooctadiene and then treatment of the resulting diene complex with diphenylacetylene.

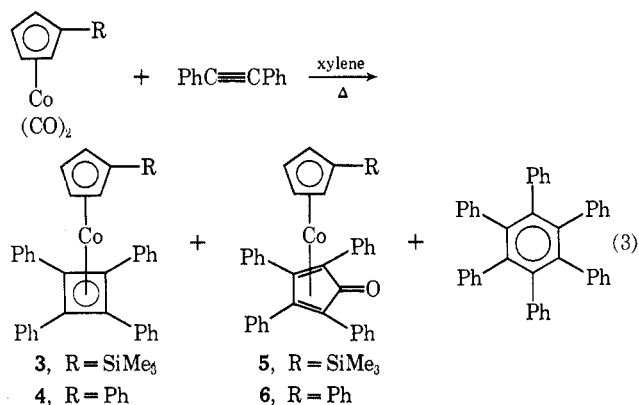
In addition to the major product **1**, a 10% yield of π -cyclopentadienyltetraphenylcyclopentadienonecobalt (**2**), a 15% yield of the cyclic trimerization product, hexaphenylbenzene, and a small amount of tetraphenylcyclopentadienone were obtained. Complex **2**

could also be prepared directly from π -cyclopentadienyldicarbonylcobalt and tetraphenylcyclopentadienone. In contrast to our heat-promoted reaction between π -cyclopentadienyldicarbonylcobalt and diphenylacetylene (eq 1), it has previously been reported that these reactants gave an 80% yield of **2** when irradiated with sunlight for 2 weeks in benzene solution.³⁹

In view of the successful synthesis of **1** as outlined in eq 1, it was of considerable interest to investigate the generality of the reaction. This has been done in two ways: (1) by utilizing substituted cyclopentadienes; (2) by utilizing acetylenes other than diphenylacetylene. The reactions of both phenyl- and trimethylsilylcyclopentadiene with octacarbonyldicobalt were successful and led to the corresponding substituted derivatives of π -cyclopentadienyldicarbonylcobalt (eq 2). Furthermore, both of the resulting carbonyls



reacted with diphenylacetylene to give trimethylsilyl and phenyl derivatives of **1** (**3** and **4**), as well as lesser amounts of the corresponding derivatives of **2** (**5** and **6**) (eq 3).



Thus, a useful and unequivocal route to π -cyclopentadienyl-substituted derivatives of **1** has been developed, and it seems probable that many other such derivatives could be prepared in an analogous manner. This route seems even more useful in view of a recent report by Altman and Wilkinson⁴⁰ that substituted π -cyclopentadienyldicarbonylcobalt complexes can be prepared from 6,6-dialkylfulvenes and octacarbonyldicobalt. The insertion of carbon monoxide to give tetraphenylcyclopentadienone complexes and the formation of hexaphenylbenzene also appear to be general reactions.

Two reactions of π -cyclopentadienyldicarbonylcobalt with acetylenes other than diphenylacetylene have been described in the literature. A reaction with 2-butyne in sunlight has been reported to give a tetramethylcyclopentadienone complex in 80% yield,³⁹

(35) A preliminary account of this work has been published: M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, **89**, 5502 (1967).

(36) M. D. Rausch and D. J. Ciappenelli, *J. Organometal. Chem.*, **10**, 127 (1967).

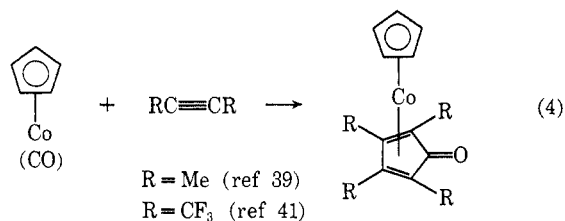
(37) R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 1059 (1968).

(38) M. Rosenblum and B. North, *ibid.*, **90**, 1060 (1968).

(39) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959).

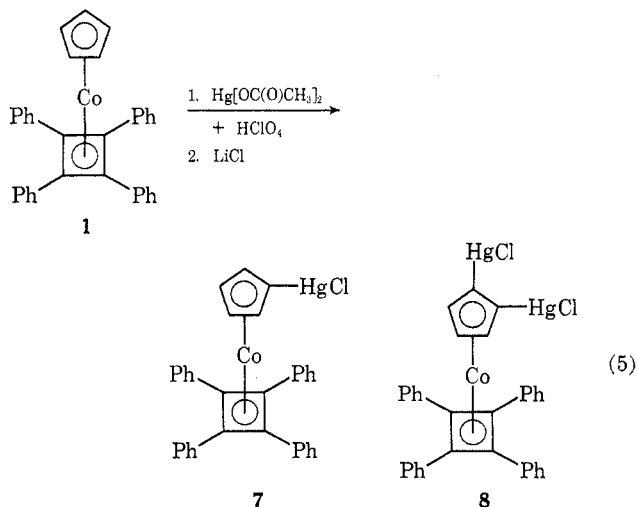
(40) J. Altman and G. Wilkinson, *J. Chem. Soc.*, 5654 (1964).

whereas a sealed tube reaction with hexafluoro-2-butyne at 110° resulted in the formation of a tetrakis-(trifluoromethyl)cyclopentadienone analog⁴¹ (eq 4).



The latter complex was originally formulated incorrectly as a cyclobutadiene complex.⁴² Neither 2-butyne nor hexafluoro-2-butyne therefore gave a cyclobutadiene complex on reaction with π -cyclopentadienyldicarbonyl cobalt, and attempts in our laboratory to prepare π -cyclopentadienyltetramethylcyclobutadienecobalt from 2-butyne have also been unsuccessful. However, the tetramethylcyclobutadiene complex has recently been prepared by Bruce and Maitlis⁴³ using an alternate procedure. Reactions of π -cyclopentadienyldicarbonyl cobalt with a variety of other mono- and diarylacetylenes have been studied in detail⁴⁴ and will be described separately in a forthcoming paper.

Ring-Substitution Reactions of π -Cyclopentadienyltetraphenylcyclobutadienecobalt (1).—Complex 1, like ferrocene, has been found to undergo a variety of electrophilic substitution reactions on the π -cyclopentadienyl ring, and may thus be classified as a new aromatic organometallic system. The most important ring-substitution reaction of 1 in terms of developing the chemistry of this system has been acetoxymercuration. Treatment of 1 with mercuric acetate in methylene chloride solution containing perchloric acid, followed by the addition of lithium chloride, resulted in the formation of mono- and bis(chloromercuri) complexes 7 and 8 (eq 5). This mercuration reaction is a modification of a procedure described by Brown and coworkers.⁴⁵



(41) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964); M. Gerlock and R. Mason, *Proc. Chem. Soc.*, 107 (1963); *Proc. Royal Soc. A*, **279**, 170 (1964).

(42) J. L. Boston, D. W. Sharpe, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

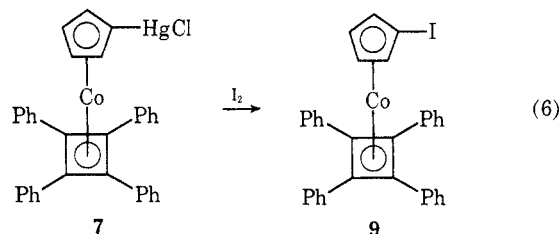
(43) R. Bruce and P. M. Maitlis, *Can. J. Chem.*, **45**, 2017 (1967).

(44) M. D. Rausch, R. A. Genetti, and F. Higbie, 157th National Meeting of the American Chemical Society, Division of Inorganic Chemistry, Minneapolis, Minn., April 1969.

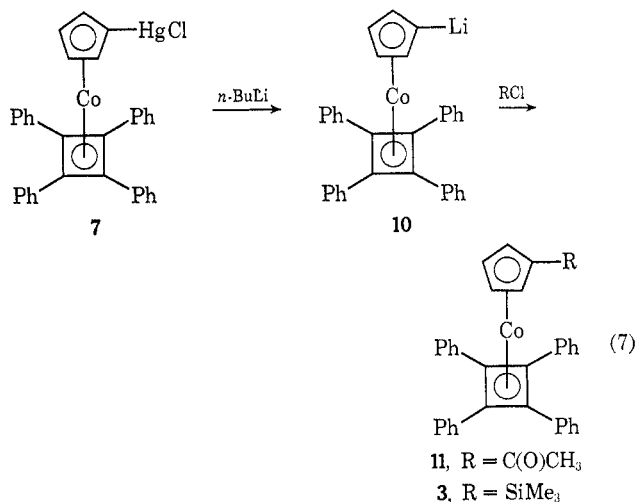
(45) A. J. Kresge, M. Dubeck, and H. C. Brown, *J. Org. Chem.*, **32**, 745, 752, 756 (1967).

The isolation of 8 indicates that mercuration of 1 occurs very readily under these conditions. It was found advantageous to employ 3 equiv of 1 per equiv of mercuric acetate, in order to obtain 7 as the major product (65% yield). Even under these conditions small amounts of polymercured products were occasionally observed; however, these were not investigated further. The assignment of 8 as the 1,2 isomer is based on nmr studies (*vide infra*). Mercuration could also be accomplished by treatment of 1 with mercuric acetate in methylene chloride-methanol in the absence of perchloric acid, as has been successfully demonstrated for the mercuration of ferrocene.^{11,12} However, the perchloric acid modification provided generally higher yields of products, and product separation was considerably easier.

Chloromercuri complex 7 has proved to be a valuable derivative of 1, since a large number of new organocobalt compounds have been derived from it. For example, iodo complex 9 is readily obtained in 83% yield from a reaction between 7 and iodine in chloroform solution (eq 6). Transmetalation of 7 with *n*-butyl-



lithium resulted in rapid formation of the lithium intermediate 10. This organolithium intermediate could be characterized by treatment with either acetyl chloride or trimethylchlorosilane to give acetyl derivative 11 or trimethylsilyl derivative 3, respectively (eq 7). The

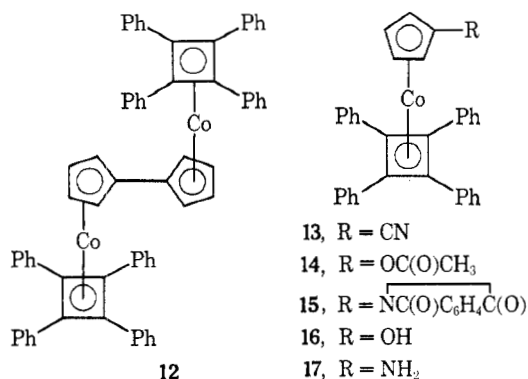


latter was shown to be identical to 3 prepared directly.

Iodo complex 9, like iodoferrocene, has led to a variety of interesting derivatives when treated with activated copper or copper salts. For example, 9 when heated with copper-bronze affords the Ullmann coupling product 12, a novel organometallic system containing both fulvalene and tetraphenylcyclobutadiene ligands coordinated to cobalt.⁴⁶ Complex 9 undergoes

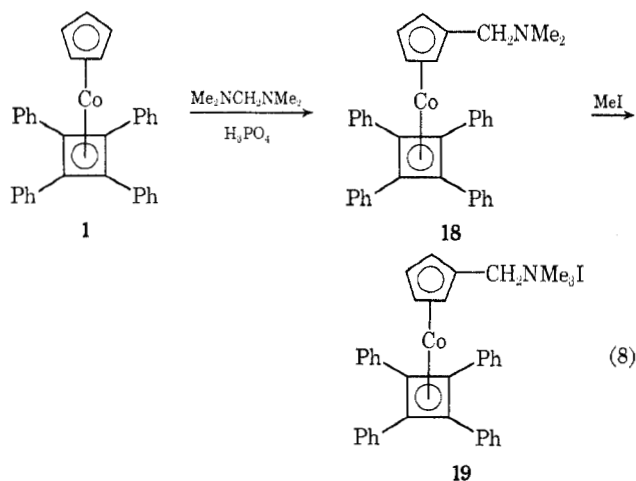
(46) Fulvalene complexes of iron and manganese have previously been described: M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **91**, 1259 (1969).

the Rosenmund-von Braun reaction with cuprous cyanide in *N*-methyl-2-pyrrolidone⁴⁷ to give the cyano derivative **13** in 40% yield. Treatment of **9** with

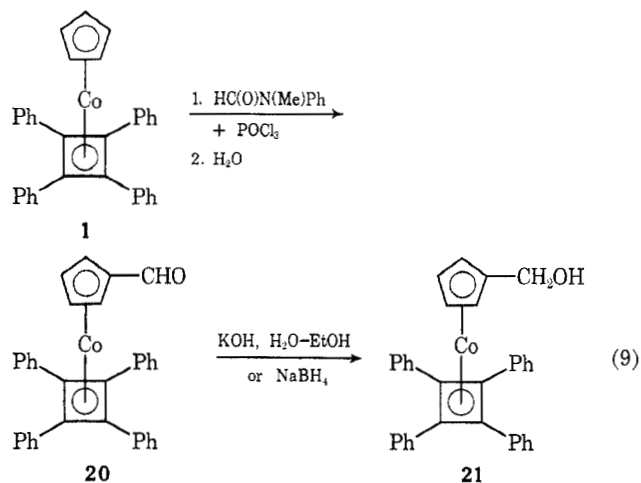


cupric acetate or cupric phthalimide afforded acetoxy and phthalimido derivatives **14** and **15**, respectively. Acetoxy derivative **14** readily gave phenol **16** upon treatment with ethanolic potassium hydroxide solution. Phthalimido derivative **15** similarly produced amine **17** when hydrolyzed with aqueous ethanolic hydrazine solution. The ferrocene analogs of **13**–**17** have been previously prepared in a similar manner.⁴⁸

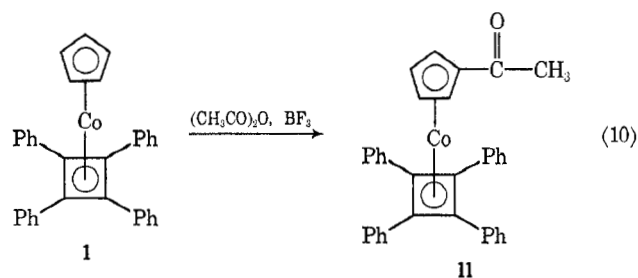
Another electrophilic substitution reaction which has been of widespread use in ferrocene chemistry is Mannich-type aminomethylation.¹³ Cobalt complex **1** likewise readily undergoes this reaction to give the dimethylaminomethyl derivative **18** in 71% yield (eq 8). Amine **18** has also been characterized as the methiodide **19**.



Vilsmeier formylation of **1** under conditions which have been used successfully for the formylation of ferrocene⁶ gave the expected aldehyde derivative **20**, however, in only 8% yield (eq 9). Small amounts of several other products were obtained from this reaction, but were not further identified. Aldehyde **20** underwent a Cannizzaro reaction upon treatment with ethanolic potassium hydroxide solution. One of the products, hydroxymethyl derivative **21**, was also prepared by sodium borohydride reduction of **1**, as well as by treatment of methiodide **19** with strong base.



Although a variety of metallocenes have been found to readily undergo Friedel-Crafts acylation, attempts to acylate cobalt complex **1** in a similar manner have been largely unsuccessful. Numerous reactions involving various acylating reagents and Lewis acid catalysts were examined, and acylated products were obtained in only a few instances, and even then in extremely low yield. Since a brown complex appears to form between Lewis acid catalysts and **1**, this complex formation may possibly deactivate the system toward electrophilic substitution. Thus, when an excess of catalyst was used, very little acylated products were produced, and most of the starting material **1** could be recovered after hydrolysis. When **1** was treated with acetic anhydride and boron trifluoride under conditions which have been successfully used to acetylate ferrocene,⁴⁹ a trace amount of the acetyl acetyl derivative **11** was obtained (eq 10). However, acetyl derivative **11** is more satisfactorily prepared by the transmetalation reaction involving **7**.



In another experiment involving benzoyl chloride and aluminum chloride in carbon disulfide solution, an acylated product was obtained in ~1% yield, in which substitution appeared to have occurred on a phenyl rather than the π -cyclopentadienyl ring. This conclusion was based on the appearance of a singlet for the π -cyclopentadienyl protons in the nmr spectrum of the product, and on the presence of a carbonyl stretching band in its infrared spectrum.

Spectra of π -Cyclopentadienyltetraphenylcyclobutadienecobalt Derivatives.—Proton nmr spectra of most of the organocobalt compounds prepared in this study are summarized in Table I. All monosubstituted derivatives of **1** in which the substituent is an electron-withdrawing group exhibit an A₂B₂ pattern, as is typical of

(47) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).

(48) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, **130**, 1030 (1960); *Chem. Ber.*, **93**, 2719 (1960).

(49) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

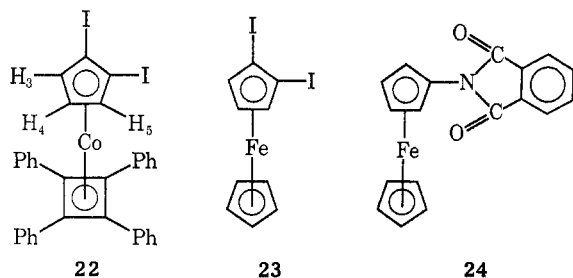
TABLE I
 PROTON NMR SPECTRA OF SOME ORGANOCOBALT COMPOUNDS

Compd	Chemical shift and multiplicity ^{a-c}			Other
	H _{2,5}	H _{3,4}	Ph	
(π -C ₅ H ₅)Co(C ₆ H ₄) (1)	... ^d	... ^d	2.32-2.83 (m)	
(π -C ₅ H ₅)Co[C ₆ H ₄ C(O)] (2)	... ^e	... ^e	2.32-2.58 (m), 2.70-3.05 (m)	
(π -C ₅ H ₄ SiMe ₃)Co(C ₆ H ₄) (3)	5.23 (t) ^f	5.33 (t) ^f	2.40-2.91 (m)	10.15 (s) (CH ₃)
(π -C ₅ H ₄ SiMe ₃)Co[C ₆ H ₄ C(O)] (5)	4.90 (t) ^f	5.43 (t) ^f	2.10-2.30 (m), 2.62-2.96 (m)	10.03 (s) (CH ₃)
(π -C ₅ H ₄ Ph)Co(C ₆ H ₄) (4)	5.00 (t)	5.31 (t)	2.52-3.18 (m)	
(π -C ₅ H ₄ Ph)Co[C ₆ H ₄ C(O)] (6)	4.95 (t)	5.05 (t)	2.45-2.68 (m), 2.72-3.05 (m)	
(π -C ₅ H ₄ HgCl)Co(C ₆ H ₄) (7)	5.15 (t)	5.32 (t)	2.25-2.90 (m)	
(π -C ₅ H ₄ I)Co(C ₆ H ₄) (9)	5.24 (t)	5.45 (t)	2.40-2.92 (m)	
(π -C ₅ H ₃ I ₂)Co(C ₆ H ₄) (22)	5.21 (d) ^g	5.49 (t) ^h	2.40-2.92 (m)	
(π -C ₅ H ₄ CHO)Co(C ₆ H ₄) (20)	4.77 (t)	5.13 (t)	2.42-2.88 (m)	0.65 (s) CHO
(π -C ₅ H ₄ CH ₂ OH)Co(C ₆ H ₄) (21)	5.25 (t) ^f	5.37 (t) ^f	2.34-2.82 (m)	5.91 (s) (CH ₂) 8.90 (s) (OH)
[π -C ₅ H ₄ C(O)CH ₃]Co(C ₆ H ₄) (11)	4.71 (t)	5.15 (t)	2.30-2.79 (m)	8.32 (s) (CH ₃)
(π -C ₅ H ₄ CH ₂ NMe ₂)Co(C ₆ H ₄) (18)	5.37 (s)	5.37 (s)	2.35-2.90 (m)	7.29 (s) (CH ₂) 7.96 (s) (CH ₃)
(π -C ₅ H ₄ CH ₂ NMe ₃ I)Co(C ₆ H ₄) (19)	5.01 (t)	5.18 (t)	2.40-2.87 (m)	6.42 (s) (CH ₂) 6.82 (s) (CH ₃)
(π -C ₅ H ₄ CN)Co(C ₆ H ₄) (13)	4.98 (t)	5.23 (t)	2.35-2.80 (m)	
[π -C ₅ H ₄ OC(O)CH ₃]Co(C ₆ H ₄) (14)	5.22 (t)	5.59 (t)	2.45-3.10 (m)	8.24 (d) (CH ₃)
[π -C ₅ H ₄ NC(O)C ₆ H ₄ C(O)]Co(C ₆ H ₄) (15)	4.22 (t)	5.29 (t)	2.31-3.04 (m)	
(π -C ₅ H ₄ NH ₂)Co(C ₆ H ₄) (17)	5.91 (t) ^f	5.66 (t) ^f	2.44-3.01 (m)	

^a Determined in dilute solutions in deuteriochloroform and given in τ , ppm, units. ^b s, singlet; d, doublet; t, triplet; m, multiplet. ^c Integrated intensities of resonances were consistent with the proposed structure. ^d Resonance for π -C₅H₅ ring protons occurs at τ 5.32 (s). ^e Resonance for π -C₅H₅ ring protons occurs at τ 5.16 (s). ^f Assignments are tentative and may be reversed. ^g Assigned to protons flanking adjacent iodine atoms (H_{3,5}). ^h Assigned to the proton β to both iodine atoms (H₄).

substituted cyclopentadienyl ring protons in many other metallocene derivatives.⁵⁰ The spectra consist of a pair of apparent triplets, and in each case the downfield triplet is assigned to the H_{2,5} protons. Such an assignment is made on the basis that these protons are nearest the electron-withdrawing group, and thus would be expected to be deshielded to a greater extent than the protons H_{3,4}. Analogous assignments for monosubstituted ferrocenes have been unequivocally determined from the nmr spectra of 2,5-dideuterated ferrocene derivatives.⁵¹ Assignment of the resonance peaks in the spectrum of amine **17** have been made in analogy to similar assignments in the spectrum of aminoferrocene.⁵²

Our conclusion that the dimercurated complex **8** has a 1,2 rather than a 1,3 configuration has been made on the basis of the corresponding diiodo complex **22**. An nmr



(50) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963); R. A. Benkeser, Y. Nagai, and J. Hooz, *Bull. Chem. Soc. Jap.*, **36**, 482 (1963); G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **160**, 1075 (1965).

(51) M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, **17**, 117 (1969).

(52) D. W. Slocum, P. S. Shenkin, and T. R. Englemann, Abstracts, 4th International Conference on Organometallic Chemistry, Bristol, England, July 27-Aug 1, 1969, p G5.

spectrum of the latter exhibits a low-field, two-proton doublet at τ 5.21, and a higher field, one-proton triplet⁵³ at τ 5.49. The protons (H_{3,5}) nearest the iodine substituents in **22** are assumed to be deshielded compared to proton H₄, by analogy to similar deshielding effects in iodobenzene and diiodobenzenes. In the iodobenzene derivatives, protons ortho to an iodine atom are substantially deshielded with respect to other ring protons.⁵⁴ Furthermore, the proton nmr spectrum of 1,2-diiodoferrocene (**23**) of known orientation exhibits a similar pattern for the ring-substituted protons.⁵⁵

The proton nmr spectrum of the phthalimido derivative **15** is worthy of special comment. The downfield triplet for **15** occurs at \sim 30 Hz lower field than the corresponding triplets in all other monosubstituted derivatives of **1** examined thus far, while the upfield triplet appears in the normal region. Molecular models indicate that the H_{2,5} protons in **15** reside in the deshielding region of the carbonyl groups, and this fact may possibly account for the enhanced deshielding of these protons. A similar enhanced deshielding is observed for the H_{2,5} protons in the nmr spectrum of phthalimidoferrocene (**24**).⁵⁵

The proton nmr spectra of derivatives of **1** are of additional interest when compared to the spectra of analogous ferrocene derivatives. The resonances of protons on exocyclic carbon atoms in the former series invariably occur at significantly higher fields than do corresponding resonances in the ferrocene series. Some

(53) This resonance peak was incorrectly designated as a singlet in our earlier communication (ref 35).

(54) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); M. Martin and B. P. Dailey, *ibid.*, **37**, 2594 (1962).

(55) P. V. Roling and M. D. Rausch, unpublished studies.

examples of this relationship are summarized in Table II. Molecular models indicate that a substantial

TABLE II
NMR COMPARISONS OF DERIVATIVES OF 1 AND
DERIVATIVES OF FERROCENE

X	Fc-X, ^{a,b} τ ppm	R-X, ^a τ ppm
CH ₂ OH	5.65	5.91
Si(CH ₃) ₃	9.79	10.15
CH ₂ N(CH ₃) ₂	6.74	7.29
CH ₂ N(CH ₃) ₂	7.89	7.96
CH ₂ N(CH ₃) ₂ I	5.00	6.42
CH ₂ N(CH ₃) ₂ I	6.65	6.82
C(O)CH ₃	7.62	8.32
CHO	0.05	0.65

^a Fc-X represents ferrocene derivatives and R-X represents π -cyclopentadienyltetraphenylcyclobutadienecobalt (1) derivatives. ^b Reference 51 and unpublished studies by M. D. Rausch.

shielding effect may be imposed by the phenyl groups attached to the cyclobutadiene ring. This effect, together possibly with metal anisotropy differences between iron and cobalt, may account for the observed chemical shifts.

The infrared spectra of 1 and its derivatives can be interpreted by direct analogy to other metallocenes. Complex 1 exhibits absorbances at 1115 and 1005 cm⁻¹; such bands are well known to be characteristic of an unsubstituted cyclopentadienyl ring.⁵⁶ Both of these absorbances are absent in all derivatives of 1 examined, as is also the case for 1,1'-disubstituted ferrocenes.⁵⁶ Complex 1 and its derivatives also exhibit absorbances characteristic of a monosubstituted phenyl group. Each complex exhibited prominent absorptions in each of the following regions: 3080-3050, 1600, 1500, 1075-1065, and 1030-1020 cm⁻¹, as well as four bands between 815 and 690 cm⁻¹. The normal absorbances for functional groups such as -CN, -CHO, etc., were also observed in the appropriate derivatives and are listed in the Experimental Section.

Relative Acidity and Basicity Studies.—It was of interest to compare acidity and basicity constants of derivatives of 1 with similar constants in the ferrocene and benzene series. This was accomplished by determining the "pK" values of phenol 16 and amine 17. It should be emphasized that the "pK" values reported are not authentic pK values, since they have been determined in nonaqueous systems. The "pK_A" values were determined in pyridine as the solvent by titrating with 0.1 N tetrabutylammonium hydroxide in benzene-methanol. The "pK_B" values were determined in acetonitrile as the solvent by titrating with 0.1 N perchloric acid in acetic acid. Both types of titrations were performed with an automatic recording titrimeter. The relative acidities and basicities presented in Tables III and IV are estimated to be accurate to within $\sim \pm 0.1$ unit.

By this procedure, it was found that 16 is a slightly stronger acid than phenol (Table III), and that 17 has essentially the same base strength as aniline (Table IV). In contrast, Nesmeyanov and coworkers have reported that hydroxyferrocene is a weaker acid than phenol,⁴⁸ and that aminoferrocene is a stronger base than aniline.⁵⁷

(56) Reference 29, p 38.

(57) E. G. Perevalova, K. I. Grandberg, N. A. Zharikova, S. P. Gubin, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 832 (1966).

TABLE III
"pK_A" VALUES OF PHENOLS

Phenol	"pK _A " in pyridine, 23°	pK _A in water ^a
<i>p</i> -Chlorophenol	9.1	9.38
(π -C ₅ H ₄ OH)Co(C ₆ H ₅) ₄ (16)	9.4	
Phenol	10.0	9.99
<i>o</i> -Cresol	10.3	10.29
(π -C ₅ H ₄ OH)Fe(π -C ₅ H ₅)	11.2	10.20 ^b

^a L. Meites, "Handbook of Analytical Chemistry," 1st ed, McGraw-Hill, New York, N. Y., 1963, pp 1-20. ^b Obtained in 5% ethanol (ref 48).

TABLE IV
"pK_B" VALUES OF AMINES

Amine	"pK _B " in acetonitrile, 23°	pK _B in water ^{a,b}
<i>p</i> -Toluidine	8.7	8.90
(π -C ₅ H ₄ NH ₂)Co(C ₆ H ₅) ₄ (17)	9.4	
Aniline	9.4	9.40
<i>p</i> -Chloroaniline	10.5	10.01

^a L. Meites, "Handbook of Analytical Chemistry," 1st ed, McGraw-Hill, New York, N. Y., 1963, pp 1-20. ^b The pK_B of aniline = 11.95 and the pK_B of aminoferrocene = 10.33 in 80% ethanol (ref 57).

Since the success of electrophilic substitution reactions in metallocenes depends in part on the availability of π -electrons in the π -cyclopentadienyl ring, it might be expected that 1, which appears from the "pK" values to be electron-poor compared to ferrocene, would be less reactive than is ferrocene in these types of reactions. In general, this appears to be the case. However, a reliable comparison of reactivities can best be made on the basis of competition studies, and we intend to carry out such experiments in the near future.

Experimental Section

Melting points were determined using a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated with polystyrene; all samples were prepared as potassium bromide pellets. Nmr spectra were recorded on a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Mr. Charles Meade of the Microanalytical Laboratory, Office of Research Services, University of Mass. Ethyl ether and tetrahydrofuran were dried over sodium and potassium hydroxide, respectively, and distilled from lithium aluminum hydride. Methylene chloride was dried by passing it through a short column of neutral alumina. Octacarbonyldicobalt was purchased from the Strem Chemical Co., Danvers, Mass., and *N*-methyl-2-pyrrolidone was obtained from the General Aniline and Film Co., New York, N. Y.

π -Cyclopentadienyldicarbonylcobalt.—Freshly distilled cyclopentadiene (31 ml, 0.38 mol), 60 ml of dried methylene chloride, and octacarbonyldicobalt (25 g, 0.073 mol) were placed in a 200-ml flask, which was fitted with a reflux condenser and a mercury check valve. The system was flushed with nitrogen and was covered with aluminum foil to exclude light. The contents were heated to reflux on a steam bath for 2 days, after which time the methylene chloride was distilled under water aspirator pressure. Continued distillation produced 24.6 g (93%) of product as a dark red liquid, bp 75-80° (22 mm) [lit.⁵⁸ bp 75° (22 mm)]. The product was stored under nitrogen at -20° in a covered flask.

π -Cyclopentadienyltetraphenylcyclobutadienecobalt (1) and π -Cyclopentadienyltetraphenylcyclopentadienecobalt (2).—A 1-l. three-necked flask was fitted with a glass stopper, condenser, and a gas inlet tube which was used to maintain a nitrogen at-

(58) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 165 (1955).

mosphere during the reaction. A mixture of 19.7 g (0.11 mol) of diphenylacetylene, 10.0 g (0.055 mol) of π -cyclopentadienyldicarbonylcobalt, and 500 ml of *p*-xylene was placed in the flask. The latter was covered with aluminum foil and the solution heated to reflux. Soon after heating was begun, a definite but slow evolution of gas occurred. After 24 hr, the solution was allowed to cool to room temperature and the reaction mixture was filtered in air. The filtered solid was washed with cold benzene; the white residue remaining was identified as hexaphenylbenzene (2.8 g, 15%) on the basis of its melting point (454–455°) and a mixture melting point with an authentic sample.

The original xylene solution and the benzene extracts were chromatographed on separate columns of alumina, using benzene as the eluent. The orange cyclobutadiene complex 1 was eluted first as a dark orange band from both columns. A faint purple band, identified as a trace amount of tetraphenylcyclopentadienone by comparison with an authentic sample, was the second band to be eluted from the column containing the xylene solution. Finally, both columns gave the tetraphenylcyclopentadienone complex 2 as a red band when elution was made with chloroform.

The orange bands were combined and evaporated to dryness, and the product recrystallized from a mixture of benzene and heptane to give 12.0 g (46%) of 1, mp 262–264° (lit.³² mp 256°; lit.³³ mp 264°). Yields of 1 from other runs varied from 44 to 61%: ir 1115 and 1005 cm^{-1} (π -C₅H₅).

Anal. Calcd for C₃₃H₂₅Co: C, 82.49; H, 5.24; Co, 12.27; mol wt, 480. Found: C, 82.40; H, 5.31; Co, 12.31; mol wt (parent molecular ion), 480.

The red bands were combined and evaporated to dryness, and the product was recrystallized from a mixture of chloroform and heptane to give 2.65 g (9.5%) of 2, mp 323–325° (lit.³⁹ mp 327–329°). An authentic sample of 2 was prepared by the reaction of tetraphenylcyclopentadienone with π -cyclopentadienyldicarbonylcobalt in refluxing xylene: mol wt (calcd) 508, mol wt (found, parent molecular ion) 508; ir 1590 cm^{-1} (C=O stretch).

(π -Chloromercuricyclopentadienyl)tetraphenylcyclobutadiene-cobalt (7) and [π -1,2-Bis(chloromercuri)cyclopentadienyl]tetraphenylcyclobutadiene-cobalt (8).—In a 250-ml erlenmeyer flask were placed 6.0 g (0.012 mol) of π -cyclopentadienyltetraphenylcyclobutadiene-cobalt, 150 ml of methylene chloride, and a magnetic stirring bar. To this solution was added 1.32 g (0.0042 mol) of mercuric acetate. Vigorous stirring was begun and 6 to 10 drops of perchloric acid were added dropwise over a 30-min period until most of the mercuric acetate had disappeared. Stirring was continued for 15 min and 1.0 g (0.024 mol) of lithium chloride was added, followed after an additional 15-min period by the addition of 3.0 g of sodium sodium bicarbonate. Finally, 4.0 g of sodium sulfate was added and the solution was allowed to dry. The dark orange methylene chloride solution was poured directly onto a short column of basic alumina (pH 9.5). The initial dark orange band, eluted with methylene chloride, gave 3.85 g of starting material 1. The second band was eluted by adding 1–2% methanol to the methylene chloride. Upon evaporation of the solvent and recrystallization of the dark orange solid from a mixture of benzene and heptane, 1.93 g (65%) of 7, mp 234–235°, was obtained.

Anal. Calcd for C₃₃H₂₄ClCoHg: C, 55.39; H, 3.39; Cl, 4.95; Co, 8.23. Found: C, 55.83; H, 3.72; Cl, 4.68; Co, 7.98.

In several runs, a third band was eluted which produced ~0.1 g (5%) of a dark orange solid (8) that was very sparingly soluble in most organic solvents. Since this product was difficult to purify because of its insolubility, it was treated with iodine to give an identifiable product as described below.

(π -Iodocyclopentadienyl)tetraphenylcyclobutadiene-cobalt (9) and (π -1,2(Diiodocyclopentadienyl)tetraphenylcyclobutadiene-cobalt (23).—A saturated solution of iodine in chloroform was slowly added with stirring to 3.0 g (0.0042 mol) of (π -chloromercuricyclopentadienyl)tetraphenylcyclobutadiene-cobalt dissolved in 75 ml of chloroform, until a definite darkening of the solution persisted for 30 sec. The solution was then immediately washed, twice with 100-ml portions of a 0.01 *M* solution of sodium thiosulfate, and once with water. The chloroform layer was dried over sodium sulfate and the solvent was removed. The solid residue was dissolved in a small amount of benzene and chromatographed on a short column of alumina to remove a small amount of polar material. The benzene was evaporated and the resulting yellow-orange residue was recrystallized from heptane to give 2.1 g (83%) of 9, mp 191–192°.

Anal. Calcd for C₃₃H₂₄CoI: C, 65.36; H, 3.99; Co, 9.71; I, 20.93. Found: C, 65.16; H, 4.20; Co, 9.57; I, 21.19.

The bischloromercuri complex 8 was treated with iodine in the same manner to give 22, mp 201–202°.

Anal. Calcd for C₃₃H₂₅CoI₂: C, 54.12; H, 3.18; Co, 8.05; I, 34.66. Found: C, 54.02; H, 3.31; Co, 8.14; I, 34.50.

(π -Formylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt (20).—A three-necked 50-ml flask was fitted with a condenser, nitrogen inlet and syringe cap, and was flushed with nitrogen. To the flask was added 0.2 ml (0.002 mol) of phosphorus oxychloride, 0.3 ml (0.002 mol) of *N*-methylformanilide, and 1.0 g (0.002 mol) of π -cyclopentadienyltetraphenylcyclobutadiene-cobalt. The mixture was heated for 4 hr at 80° with occasional addition *via* a syringe of additional 0.1-ml portions of phosphorus oxychloride (0.5 ml extra added). The mixture turned from orange to red and finally to black during the reaction period. Hydrolysis was effected by stirring the reaction mixture with excess sodium acetate solution at room temperature. It was necessary to add a few ml of benzene to dissolve the tarry residue so that complete hydrolysis could occur. After 3 hr, additional benzene was added and the resulting solution was washed with 100 ml of water. The benzene layer was separated, dried over sodium sulfate, and chromatographed on Florisil using benzene as the eluent. The first band from the column contained 0.7 g of starting material 1. The second band was collected, the solvent evaporated, and the solid residue was recrystallized from hexane to give 0.08 g (8%) of 20, mp 189–190°, ir 1685 cm^{-1} (C=O stretch).

Anal. Calcd for C₃₄H₂₅CoO: C, 80.30; H, 4.96; Co, 11.58; O, 3.15. Found: C, 80.35; H, 4.90; Co, 11.46; O, 3.24.

When the benzene solution of the reaction mixture, shown to contain the desired aldehyde by tlc, was chromatographed on alumina rather than Florisil, an unidentified red compound, mp 203–204° (parent molecular ion 548), was obtained, and none of the aldehyde could be isolated. On the other hand, if a benzene solution of the purified aldehyde 20 was chromatographed on alumina, it was recovered unchanged.

(π -Hydroxymethylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt (21).—A methanol solution of 0.1 g (0.2 mmol) of (π -formylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt was prepared by warming the compound on a steam bath with 30 ml of methanol. After the solution had been allowed to cool slightly, 0.3 g (0.008 mol) of sodium borohydride in 4 ml of water was added. The color of the solution immediately changed from orange to yellow, however; the reaction mixture was allowed to stand overnight. The methanol solution was poured into 150 ml of water which was then extracted with methylene chloride. The organic layer was separated, washed with 100 ml of water, and was dried with sodium sulfate. Removal of the solvent left a solid residue which was recrystallized from a mixture of hexane and ethyl ether to give 0.08 g (80%) of 21 as fine light yellow crystals, mp 179–180°.

Anal. Calcd for C₃₄H₂₇CoO: C, 80.00; H, 5.33; Co, 11.54. Found: C, 80.15; H, 5.43; Co, 11.16.

Cannizzaro Reaction of (π -Formylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt (20).—A suspension of 0.10 g (0.2 mmol) of (π -formylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt in 20 ml of 50% potassium hydroxide in ethanol was refluxed for 4 hr. The reaction mixture was allowed to cool and water was added. The basic solution was extracted with chloroform and then acidified. The acidic portion was extracted with chloroform, and evaporation of the solvent produced several mg of a yellow acid. This was not characterized further due to the small amount available. The original chloroform extract of the basic solution was washed with water, dried with sodium sulfate, and evaporated. The solid residue was dissolved in benzene and chromatographed on alumina to give several poorly resolved bands. The major band (band 2) was subsequently further purified by preparative tlc to afford 0.014 g (28%) of 21. The product was shown by tlc and nmr to be identical with 21 obtained from the sodium borohydride reduction of 20.

(π -Dimethylaminomethylcyclopentadienyl)tetraphenylcyclobutadiene-cobalt (18).—To a 250-ml three-necked flask were added 100 ml of glacial acetic acid and 0.50 g (0.0010 mol) of π -cyclopentadienyltetraphenylcyclobutadiene-cobalt. The flask was equipped with a condenser, a nitrogen inlet, and a magnetic stirring bar. A heating mantle was used to heat the suspension, under nitrogen and with stirring, until reflux began. To the hot solution was added 0.90 ml (0.013 mol) of phosphoric acid followed by 4.5 ml (0.036 mol) of bis(dimethylamino)methane.

Refluxing and stirring were continued, and the solution became dark orange in color.

After 5 hr, the reaction mixture was cooled, 400 ml of water was added, and the resulting aqueous suspension was extracted several times with 75 ml portions of benzene. The combined extracts were washed twice with sodium bicarbonate solution, once with water, and were dried with sodium sulfate. After reducing the volume of the solution to 30 ml with an aspirator, the solution was chromatographed on basic alumina (pH 9.5) to produce, after evaporation, 0.38 g (71%) of **18** as the third (and major) band, when eluted with a 60:40 benzene-chloroform mixture. The first band gave 0.1 g of starting material. The amine **18** was recrystallized from a methanol-methylene chloride mixture, resulting in dark orange crystals, mp 189–190°.

Anal. Calcd for $C_{38}H_{32}CoN$: C, 80.43; H, 6.00; Co, 10.96; N, 2.61. Found: C, 80.36; H, 6.11; Co, 10.86; N, 2.61.

Amine **18** was insoluble in concentrated hydrochloric acid, but dissolved with decomposition in concentrated sulfuric acid.

The methiodide of **18** was prepared by heating a solution of 0.10 g (0.18 mmol) of the amine and 4.6 ml (80 mmol) of methyl iodide in 20 ml of methanol on a steam bath for 10 min. The solvent and excess methyl iodide were removed with an aspirator and the product was recrystallized from a mixture of benzene and methanol to give 0.11 g (89%) of **19**, mp 250°. The product was characterized by its nmr spectrum (Table I).

Treatment of 0.05 g (0.07 mmol) of the methiodide **19** with 10 g of potassium hydroxide and 30 ml of 95% ethanol at reflux for 44 hr, followed by the addition of water, extraction with benzene and chromatography of the extracts on alumina, produced four bands. The third band produced 8 mg (22%) of **21**; the latter was shown to be identical with carbinol **21** obtained from the sodium borohydride reduction of aldehyde **20**. The first two bands were present in only minor amount; these and the fourth band (26 mg) were not further identified.

Friedel-Crafts Acylation of π -Cyclopentadienyltetraphenylcyclobutadienecobalt (1).—Numerous attempts were made to carry out Friedel-Crafts reactions on **1**, using various combinations of acetic anhydride, benzoyl chloride, acetyl chloride, and methyl chlorothioformate as acylating agent, aluminum chloride, phosphoric acid, tin tetrachloride, etc., as catalyst, and either methylene chloride or carbon disulfide as the reaction medium. All reactions were conducted under nitrogen and with dry solvents.

Of all the combinations, the procedure of Hauser and Lindsay⁴⁹ proved to be the most successful, employing acetic anhydride, a boron trifluoride solution in ethyl acetate, methylene chloride, and stirring for 30 min at 25°. The reaction mixture was hydrolyzed, the organic phase washed with sodium bicarbonate solution and with water, and was dried. Evaporation of the solvent and chromatography of the residue in benzene on alumina produced unreacted **1** followed by a very small second band which was not identified. Examination of the third band indicated that it contained **11**, on the basis of comparison with an authentic sample of **11** prepared from the chloromercuri complex **7**, as described below. The yield of **11**, however, was less than 1%.

Reaction of (π -Chloromercuricyclopentadienyl)tetraphenylcyclobutadienecobalt with *n*-Butyllithium.—To a 250-ml, three-necked flask, equipped with a nitrogen inlet tube, syringe cap, and condenser, were added under nitrogen 100 ml of dry hexane and 0.5 g (6.7 mmol) of (π -chloromercuricyclopentadienyl)tetraphenylcyclobutadienecobalt. The latter did not dissolve until 3 ml (7 mmol) of *n*-BuLi in hexane was added through the syringe cap. After stirring for 10 min, the clear orange solution of (π -lithiocyclopentadienyl)tetraphenylcyclobutadienecobalt (**10**) was poured into a cooled, stirred solution of 10 ml of acetyl chloride in dry hexane. A precipitate formed, and stirring was continued for 1 hr after which time the suspension was carefully poured over ice. After the ice had melted, the layers were separated, the organic layer was washed with sodium bicarbonate solution and with water, dried with sodium sulfate, and was chromatographed on alumina. The first band contained **1**; a very small second band was not collected. The third band contained starting material (**7**), while the fourth band produced 0.025 g (7%) of (π -acetylcyclopentadienyl)tetraphenylcyclobutadienecobalt (**11**), mp 175–176°, after recrystallization from heptane: ir, 1665 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{35}H_{27}CoO$: C, 80.45; H, 5.21; Co, 11.28. Found: C, 80.40; H, 5.05; Co, 11.26.

The lithium intermediate **10** could also be characterized by reaction with trimethylchlorosilane in a similar manner. The

compound was purified by preparative tlc and was shown to be identical by tlc and nmr with **3** prepared from trimethylsilylcyclopentadiene and octacarbonyldicobalt, as described below.

Fulvalene-bis(tetraphenylcyclobutadiene)dicobalt (12).—In a 50-ml Schlenk tube were combined under nitrogen 0.1 g (0.2 mmol) of (π -iodocyclopentadienyl)tetraphenylcyclobutadiene and 3.0 g of activated copper-bronze. A nitrogen atmosphere was maintained while the tube was heated at 250° for 14 hr in a bath of Wood's metal. The tube was cooled and the contents were extracted repeatedly with hot chloroform until the extracts were colorless. After filtration and concentration of the solvent, the products were separated by preparative tlc. The first band gave 0.05 g of **1**; no starting material **9** could be detected. The second band gave 0.020 g (21%) of **12**, mp 350–352° (sealed tube under nitrogen).

Anal. Calcd for $C_{66}H_{48}Co_2$: C, 82.66; H, 5.05; Co, 12.29; mol wt, 958. Found: C, 82.81; H, 5.08; Co, 12.07; mol wt (parent molecular ion), 958.

(π -Cyanocyclopentadienyl)tetraphenylcyclobutadienecobalt (13).—To a 50-ml flask equipped with a condenser and flushed with nitrogen were added 0.5 g (0.8 mmol) of (π -iodocyclopentadienyl)tetraphenylcyclobutadienecobalt, 1.0 g (0.011 mol) of cuprous cyanide, and 20 ml of *N*-methyl-2-pyrrolidone. The flask was heated in an oil bath at 210° for 2 hr. After cooling to room temperature, the reaction mixture was poured into a mixture of water and methylene chloride. The dark orange organic layer was separated, washed five times with 100-ml portions of water (to remove *N*-methyl-2-pyrrolidone), and dried over sodium sulfate. Removal of the methylene chloride left a solid which was dissolved in benzene and chromatographed on alumina. Elution with benzene produced a band containing **1**. Elution with 50% benzene-ethyl ether produced a second band, which after removal of the solvent gave an orange solid. Recrystallization of the latter from methylene chloride-heptane gave 0.16 g (~40%) of **13**, mp 198–199°, ir 2220 cm^{-1} (C≡N stretch).

Anal. Calcd for $C_{34}H_{24}CoN$: C, 80.78; H, 4.79; Co, 11.66. Found: C, 80.58; H, 4.81; Co, 11.56.

(π -Acetoxycyclopentadienyl)tetraphenylcyclobutadienecobalt (14).—(π -Iodocyclopentadienyl)tetraphenylcyclobutadienecobalt (0.5 g, 0.8 mmol), cupric acetate (0.3 g, 0.016 mol), and 10 ml of *N*-methyl-2-pyrrolidone were combined in a 50-ml flask which had been flushed with nitrogen. The cupric acetate had previously been dried by refluxing it in acetic anhydride for 24 hr, filtration, washing the solid with dry ethyl ether, and removal of the ether *in vacuo*. A condenser was added, and the reaction mixture was heated on an oil bath at 135–140° for 24 hr and then transferred to a separatory funnel where water and chloroform were added. Following separation of the layers, the chloroform layer was washed five times with 100-ml portions of water, dried with sodium sulfate, and was evaporated to give an orange residue. This solid was dissolved in benzene and chromatographed on a 2 by 22 cm column of Florisil using benzene as eluent. The first band gave a mixture containing 75% **9** and 25% **1**, as determined by nmr integration. The second band gave 0.070 g (16%) of **14** as an orange solid. Recrystallization of the product from methylene chloride-hexane produced orange-brown crystals: mp 192–193°; ir 1760 cm^{-1} (C=O stretch); 1210 cm^{-1} (C—O stretch).

Anal. Calcd for $C_{35}H_{27}CoO_2$: C, 78.07; H, 5.05; Co, 10.94; O, 5.94. Found: C, 78.40; H, 5.16; Co, 11.32; O, 5.12.

(π -Phthalimidocyclopentadienyl)tetraphenylcyclobutadienecobalt (15).—Cupric phthalimide was prepared in the following manner. To a solution of 9.08 g (0.05 mol) of cupric acetate, dissolved in 300 ml of water and stirred by means of a mechanical stirrer, was slowly added 18.5 g (0.01 mol) of potassium phthalimide dissolved in 125 ml of water. Cupric phthalimide precipitated as a light blue powder and was collected by suction filtration. The precipitate was washed thoroughly with three 300-ml portions of water, and was then dried overnight at 65° (22 mm).

In a 50-ml flask equipped with a condenser and flushed with nitrogen were combined 0.3 g (0.5 mmol) of (π -iodocyclopentadienyl)tetraphenylcyclobutadienecobalt, 0.4 g (0.001 mol) of cupric phthalimide, and 10 ml of *N*-methyl-2-pyrrolidone. The flask was heated under nitrogen in an oil bath at 160°. During the first 2-hr period, 0.4 g of additional cupric phthalimide was added (0.1 g every 0.5 hr). After heating for a total of 24 hr, the reaction mixture was allowed to cool and was poured into 150 ml of water contained in a separatory funnel. Chloroform (40 ml) was added and the funnel was shaken. After filtration

through Filter-Cel, the orange chloroform layer was separated, washed five times with 100-ml portions of water, and was dried over sodium sulfate. The chloroform solution was concentrated to 5 ml, and an equal volume of benzene was added to give a solution which was chromatographed on a 4 × 13 cm column of Florisil. Elution with benzene gave 0.17 g of 1. Further elution with benzene and then with 10:1 benzene-chloroform produced a second band which on evaporation yielded 0.05 g (16%) of 15. Recrystallization of the product from benzene-heptane resulted in orange-brown crystals, mp 183–185°; ν 1720 cm^{-1} (C=O stretch), 1480, 1360 cm^{-1} .

Anal. Calcd for $\text{C}_{41}\text{H}_{28}\text{CoNO}_2$: C, 78.72; H, 4.51; N, 2.24. Found: C, 78.30; H, 4.43; N, 2.12.

(π -Hydroxycyclopentadienyl)tetraphenylcyclobutadienecobalt (16).—In a 50-ml flask equipped with a condenser were combined under nitrogen 0.05 g (0.1 mmol) of (π -acetoxy-cyclopentadienyl)-tetraphenylcyclobutadienecobalt, 0.6 g of potassium hydroxide in 5 ml of water, and 9 ml of 95% ethanol. The reaction mixture was heated for 45 min on a steam bath. The resulting orange solution was transferred to a separatory funnel containing water and ethyl ether. The transfer and the following purification procedure were conducted completely under nitrogen. The ether layer was separated, washed twice with 150-ml portions of water, dried over magnesium sulfate, and filtered. The filtrate was concentrated *via* a nitrogen stream and gentle heating to 15 ml, and was transferred to a tared glass vial. Hexane was added and the evaporation was continued until crystallization occurred. The shiny orange plates were dried with a nitrogen stream to give 0.04 g (78%) of 16, mp 204–206° under nitrogen after softening at $\sim 178^\circ$. The crystals were stable for only about 1 hr in air at room temperature, but for several days under nitrogen.

(π -Aminocyclopentadienyl)tetraphenylcyclobutadienecobalt (17).—(π -Phthalimidocyclopentadienyl)tetraphenylcyclobutadienecobalt (0.02 g, 0.03 mmol), 3 ml of 95% hydrazine in 1 ml of water, and 5 ml of ethanol were combined in a 50-ml flask equipped with a condenser. The suspension was refluxed until all the solid was dissolved and then poured into cold water. The resulting suspension was extracted with ethyl ether to give a yellow organic portion which was washed five times with 100-ml portions of water and dried with sodium sulfate. After the volume of solvent had been reduced to several milliliters *via* a stream of nitrogen, hexane was added and evaporation continued until orange crystals of 17 were obtained. The R_f of the amine 17 on tlc was 0.15 compared to 0.33 for 15 (elution with benzene).

Anal. Calcd for $\text{C}_{39}\text{H}_{26}\text{CoN}$: N, 2.83. Found: N, 3.00.

(π -Trimethylsilylcyclopentadienyl)tetraphenylcyclobutadienecobalt (3) and (π -Trimethylsilylcyclopentadienyl)tetraphenylcyclopentadienecobalt (5).—In a 50-ml flask equipped with a condenser and flushed with nitrogen were combined 35 ml of dried methylene chloride, 20 g (0.15 mol) of trimethylsilylcyclopentadiene,⁵⁹ and 9.5 g (0.03 mol) of octacarbonyldicobalt. The flask was covered with aluminum foil to exclude light and was heated gently on a steam bath for 48 hr. Attempts at distillation succeeded in removing the starting material, trimethylsilylcyclopentadiene, but seemed to cause decomposition of the product. Therefore, the dark red liquid product (8.0 g, 53%), π -trimethylsilylcyclopentadienyldicarbonylcobalt, was used in the next step without additional purification.

To a 200-ml flask equipped with a condenser and flushed with nitrogen were added 6.8 g (0.038 mol) of diphenylacetylene, 4.7 g (0.019 mol) of π -trimethylsilylcyclopentadienyldicarbonylcobalt, and 75 ml of *p*-xylene. The reaction mixture was heated in an oil bath at 160° for 24 hr, cooled to room temperature, and allowed to stand for 1 hr. Filtration of the resulting precipitate gave 0.7 g of hexaphenylbenzene. The red filtrate was chromatographed on a 4 × 14 cm column of alumina. Elution with benzene removed a broad orange-red band which contained starting material, as well as the desired product. After removal of the solvent, the residue was recrystallized from heptane to give 2.5 g (25%) of 3 as orange-red crystals, mp 178–179°.

Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{CoSi}$: C, 78.24; H, 6.02; Co, 10.66; mol wt, 552. Found: C, 78.00; H, 5.98; Co, 10.70; mol wt (parent molecular ion), 552.

A very small purple band was identified as tetraphenylcyclopentadienone.

A red third band, eluted with chloroform, gave 1.0 g (14%) of 5 as a brick red solid. After recrystallization of the product

from heptane-carbon tetrachloride, the mp was 200–201° (softening at $\sim 175^\circ$).

Anal. Calcd for $\text{C}_{37}\text{H}_{32}\text{CoOSi}$: C, 76.53; H, 5.73; O, 2.76; Co, 10.15; mol wt, 580. Found: C, 76.30; H, 5.72; O, 2.79; Co, 9.95; mol wt (parent molecular ion), 580.

(π -Phenylcyclopentadienyl)tetraphenylcyclobutadienecobalt (4) and (π -Phenylcyclopentadienyl)tetraphenylcyclopentadienecobalt (6).—In a nitrogen-flushed Schlenk tube were combined 3.0 g (0.02 mol) of phenylcyclopentadiene (prepared from phenyllithium and 2-cyclopentenone-1 according to a literature method),⁶⁰ 1.7 g (0.005 mol) of octacarbonyldicobalt, and 10 ml of dried methylene chloride. The tube was covered with aluminum foil and was heated on a steam bath for 20 hr. The solvent was removed *via* an aspirator and the residue dissolved in hexane and chromatographed on alumina. The first band consisted of a small amount of octacarbonyldicobalt, while a second band produced, after removal of the solvent, 1.6 g (62%) of π -phenylcyclopentadienyldicarbonylcobalt as a dark red liquid.

In a 50-ml flask equipped with a condenser were combined under nitrogen 1.0 g (0.004 mol) of π -phenylcyclopentadienyldicarbonylcobalt, 1.4 g (0.008 mol) of diphenylacetylene, and 25 ml of *p*-xylene. After heating for 24 hr in an oil bath maintained at 155°, the flask was cooled and allowed to stand at room temperature for 2 hr. Filtration gave 0.06 g of hexaphenylbenzene. The xylene filtrate was chromatographed on a 4 × 13 cm column of alumina. Elution with benzene produced an orange band which when evaporated gave 0.80 g (37%) of 4. Recrystallization of the product from benzene-heptane gave orange-brown crystals, mp 209–210°.

Anal. Calcd for $\text{C}_{39}\text{H}_{26}\text{Co}$: C, 84.16; H, 5.25; Co, 10.59; mol wt, 556. Found: C, 83.80; H, 5.17; Co, 10.82; mol wt (parent molecular ion), 556.

A small red second band, eluted with chloroform, gave 0.10 g (4.5%) of 6. The product had mp 250–251° when recrystallized from chloroform-heptane.

Anal. Calcd for $\text{C}_{40}\text{H}_{28}\text{CoO}$: C, 82.18; H, 5.00; Co, 10.08; O, 2.74; mol wt, 584. Found: C, 82.00; H, 4.97; Co, 9.94; O, 3.08; mol wt (parent molecular ion), 584.

Relative Acidity and Basicity Studies.—The most convenient way of measuring the relative acidities of phenol and basicities of amines is by obtaining an acid-base titration curve. The pK value can then be determined directly from the curve by calculating the pH at half-neutralization, since at this point $pH = pK$.^{61a} For weak acids such as 16 and weak bases such as 17 it is necessary to use nonaqueous solvents to obtain a meaningful titration curve. In nonaqueous systems a true pK is not obtained, but the half-neutralization potential is proportional to pK .^{61b}

The acidity and basicity values obtained experimentally from the half-neutralization potentials for phenol 16 and amine 17 were not conveniently comparable to literature pK values obtained under aqueous conditions. To make them comparable, it was necessary to adjust the values on the basis of a standard phenol (phenol was chosen) and a standard amine (aniline was chosen) which were run under analogous conditions. Each time that titrations of phenols or amines were run, the appropriate standards were also run. A fixed number was then added to the numerical value obtained at half-neutralization for each phenol or amine so that the new " pK " value for the standard corresponded to the literature pK value for the standard in aqueous solution. Titrations of each series of phenols or amines were made consecutively and under identical conditions. Duplicate series of runs made on different days showed that the relative values reported in Tables III and IV were completely reproducible.

In the acidity studies, 10- to 11-ml samples of 0.003 *M* solutions of 16 and various phenols in pyridine were used in each run; the temperature was 23°. Tetrabutylammonium hydroxide (0.1 *N*) in benzene-methanol, prepared as described in the literature,^{62a} was used as the titrant in each case. Titrations were made on a Radiometer Titrigraph, Type SBR2c, Copenhagen, Denmark (U. S. Distributor, The London Co., Westlake, Ohio), coupled with a Radiometer Titrator 11 and pH meter 25 with a combination glass electrode. It was necessary to connect a ground wire from the chassis of the Titrigraph to that of the

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Titration 11. The Titrigraph was coupled by its flexible drive shaft to a 0.5-ml syringe which delivered the titrant into the stirred sample.

Relative basicity studies were conducted in a similar manner, using 10- to 11-ml samples of 0.003 *M* solutions of 17 and various amines in acetonitrile; the temperature was 23°. The acetonitrile was purified by treatment with sulfuric acid and benzene (to azeotrope any water), and then distillation through a column of packed helices; the fraction of bp 82° was collected and used. Perchloric acid (0.1 *N*) in glacial acetic acid was prepared as described in the literature,^{22b} and was used as the titrant. Titrations were made on the instrument described above. Titration curves and calculations were made in a similar manner, except that values obtained were subtracted from 14 to give "p*K*_B" values.

Registry No.—1, 1278-02-0; 2, 12119-11-8; 3, 12427-83-7; 4, 12427-86-0; 5, 12427-84-8; 6, 12427-87-1; 7,

12427-73-5; 9, 12427-74-6; 11, 12427-80-4; 12, 12427-89-3; 13, 12427-77-9; 14, 12427-81-5; 15, 12427-88-2; 16, 12427-75-7; 17, 12427-76-8; 18, 12427-82-6; 19, 12427-85-9; 20, 12427-78-0; 21, 12427-79-1; 22, 12427-72-4.

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The Bis Adducts of Dimethyl Acetylenedicarboxylate and Certain Furans

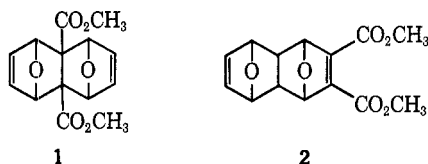
J. D. SLEE^{1a} AND E. LEGOFF^{1b}

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

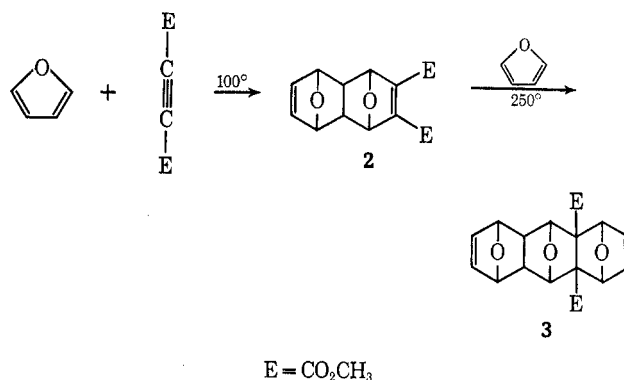
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The structures of certain furan–dimethyl acetylenedicarboxylate bis-Diels–Alder adducts were determined by nmr spectroscopy. The reaction of furan with the acetylenic ester at room temperature led to the (exo–endo) bis adduct 4, whereas 2,5-dimethylfuran did not form a bis adduct. At 100° furan reacted with the acetylenic ester to give (exo–exo) bis adduct 7, (exo–endo) bis adduct 8, and tris adduct 9. Under similar conditions 2,5-dimethylfuran reacted with the acetylenic ester to give the (exo–endo) bis adduct 11. The parent cyclic ether 17 of 11 was prepared and shown to have the (exo–endo) configuration. Selective hydrogenation of 11 led to dihydro adduct 22. Acid treatment of 22 gave dimethyl 2,5-dimethylfuran-2,3-dicarboxylate and *p*-xylene while pyrolysis of 22 led to dimethyl 2,5-dimethylfuran-2,3-dicarboxylate, 2,5-dimethylfuran, and ethylene. The two (exo–endo) trimethyl bis adducts 19 and 21 were also prepared.

In 1931 Diels and Alder² isolated a furan–dimethyl acetylenedicarboxylate adduct with a mol ratio of 2:1. They suggested that adduct 1 was the product of this reaction; however they also noted that catalytic hydrogenation could be terminated after 1 equiv of hydrogen had reacted.



Later Diels and Olsen characterized 1 by forming its dilactone.³ This adduct was synthesized at relatively low temperature, whereas the previous adduct was prepared at elevated temperatures. This suggested that the first compound reported which was thought to be 1 may have been adduct 2. In the same paper they reported the isolation of the tris adduct, 3. Dimethyl acetylenedicarboxylate was allowed to react with excess furan for 17 hr at 100° and then allowed to react further at room temperature for 2 days. The isolation of 3 suggested that bis adduct 2 was formed at elevated temperatures, and then 2 reacted at room temperature to give 3.



At the time these adducts were prepared it was difficult to make stereochemical assignments. Due to the development of nmr spectroscopy the configurations of these and other adducts could be investigated.

Results

When furan was allowed to react with acetylenic ester at room temperature (exo–endo) adduct 4 was formed along with approximately 6% of (exo–exo) adduct 5.⁴ The nmr spectrum of 4 revealed that the less symmetrical (exo–endo) adduct was the major product because the chemical shifts of the two pairs of vinyl hydrogens were different. They appeared as apparent triplets at δ 6.6 and 6.4.⁵ The olefinic hydrogens of the symmet-

(1) (a) Taken from part of the Ph.D. Thesis of J. D. Slee, 1969. (b) To whom inquiries should be addressed.

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