Table VII. Results of the Mass Spectrographic Analyses of the N_2 Released upon Hypobromite Oxidation of Reaction Solutions of Experiments in Table V, Expressed in mm Peak Heights. (Analysis was performed with 1-ml aliquots of a total of 4 ml)

No.	Gas phase	ATP	$^{28}N_2$	$^{29}N_2$ corr	$^{30}N_2$
1	Ar	−	10000	0.01[a]	0
2	Ar	+	11680	0.02[a]	0
3	Ar, +609 μmol of N_2	−	12000	44.4	Trace
4	Ar, +203 μmol of N_2	+	13000	49.5	3.0
5	Ar, +406 μmol of N_2	+	13650	53.0	3.5
6	Ar, +609 μmol of N_2	+	13290	220.0	10[b]
Standard			12780	119.0	2200[c]

[a] Background. [b] The yield of $^{30}N_2$ was 9 mm when a second aliquot of this solution was subjected to hypobromite oxidation after the addition of 10 μmol of $^{14}NH_4Cl$. [c] This standard corresponds to the yield of $^{30}N_2$ formed by the hypobromite oxidation of 14.4 μmol of $^{15}NH_3Cl$ of 96% isotopic purity.

However, the presence of $^{30}N_2$ in our experiments per se does not demonstrate the formation of N_2H_4 in view of the high concentration of $^{15}NH_3$. A control experiment was therefore performed in which an additional aliquot of $^{14}NH_4Cl$ was added to the reaction solutions prior to hypobromite oxidation. The results in Table VII (see experiment no. 7) show that the addition of $^{14}NH_4Cl$ did not lower the yield of $^{30}N_2$ appreciably. This is consistent with the presence of N_2H_4 containing the original $^{15}N-^{15}N$ bond of $^{30}N_2$.

Reduction of 3 with Ferredoxin Model Compounds. Solutions containing $[Fe_4S_4(SR)_4]^{4-}$ (R = n-C_3H_7) or equivalent n-propylmercaptoiron sulfide species were prepared exactly as outlined in ref 10, by combining equivalent amounts of $FeCl_2$, Li_2S, and LiS-n-C_3H_7 in anhydrous CH_3OH. The n-C_3H_7 derivatives of the ferredoxin-like species were used in the experiments due to their tendency to decompose to C_3H_6 and C_3H_8 under the reaction conditions. The C_3-hydrocarbons do not interfere with the assay for CH_4, C_2H_6, and C_2H_4. The concentrations of the systems components employed in several experiments are given in the legend to Table VI.

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Synthesis of Tricarbonyliron Complexes of Functional 1,2-Disubstituted Cyclobutadienes

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Abstract: The synthesis of a series of 1,2-disubstituted cyclobutadieneiron tricarbonyl complexes is described. The key intermediate, diester **4**, was prepared in 35-40% yield via reaction of sodium tetracarbonylferrate(-II) with tetrachlorodiester **3a**. The latter was obtained via benzophenone sensitized photochemical addition of dichloromaleic anhydride to *trans*-1,2-dichloroethylene, followed by hydrolysis and esterification. Variation of the vicinal functionality in **4** has led to tricarbonyliron complexes of 1,2-divinylcyclobutadienes, 1,2-di-*tert*-butylcyclobutadiene, "push-pull" cyclobutadienes, and a number of cyclobutadienes possessing electron-withdrawing groups. The assignment of **4** and complexes derived therefrom as authentic cyclobutadiene complexes is based on conversion of **4** to the known 1,2-dimethylcyclobutadieneiron tricarbonyl and on the consistency of a variety of data with this formulation.

The discovery in 1965 that oxidative degradation of cyclobutadieneiron tricarbonyl gave rise to free, transient cyclobutadiene[2a,3] provided new direction to organic chemists' historical quest of this elusive species.[4] Transition metal complexes have since proved to be one of the most convenient sources of cyclobutadienes for mechanistic and synthetic studies.[2]

A few years ago we became interested in utilizing cyclobutadiene transition metal complexes to generate substituted cyclobutadienes, including, in particular, systems in which the cyclobutadiene ring is fused to other polyenic rings of various sizes. As a strategy for achieving these objectives, we envisaged synthesis of transition metal derivatives of appropriate functional 1,2-disubstituted cyclobutadienes, utilization of functionality for construction of a complexed fused-ring system, and release of the cyclobutadienoid system via decomplexation procedures. We now report full details[5] of the realization of the first of these goals, namely the synthesis of tricarbonyliron complexes of a series of 1,2-disubstituted cyclobutadienes.

In more recent work, the availability of this type of complex has permitted construction of tricarbonyliron complexes of cyclobutadieno derivatives of tropone,[6a] pleiadiene,[6b] and cyclooctatetraene.[7]

Results and Discussion

At the inception of this work, general methods for constructing specifically substituted transition metal cyclobutadiene complexes[8] were limited to monosubstituted tricarbonyliron derivatives.[9] Since the feasibility of introducing vicinal substituents into a preformed complex was open to question, we examined instead the possibility of adapting to our purposes the reaction of iron carbonyls with cyclobutene 3,4-dihalides.[10] Because of the lack of methods for synthesizing the requisite dihalocyclobutene, in this instance, one bearing vicinal functional groups, we pursued the alternate approach of generating the cyclobutene in situ from an appropriate 1,2,3,4-tetrahalocyclobutane. This approach was especially attractive because of the potential accessibility of the desired cyclobutane via photochemical addition of a dihalomaleic acid derivative to an olefin.[11] Toward this end, the addition of dichloromaleic anhydride (1) to trans-1,2-dichloroethylene (2) was attempted (Scheme I).

Scheme I
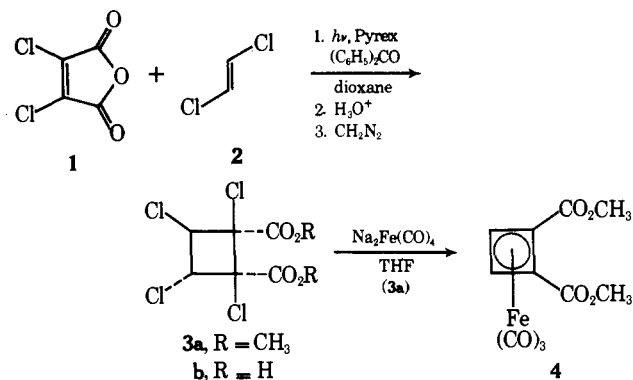
Irradiation of a dioxane solution of 1, a threefold excess of 2, and benzophenone afforded, after aqueous work-up, an isomeric mixture of acids. Because separation of the latter was capricious, the mixture was esterified with diazomethane to give a mixture of esters from which a single stereoisomer could be crystallized in up to 66% overall yield from 1. On the basis of two methyl singlets and an AB quartet in the ^{1}H NMR spectrum, this substance was identified as the cis,trans,trans isomer 3a.[12]

With 3a in hand, attempts were then made to prepare complex 4 via dehalogenation–complexation with diiron nonacarbonyl in the presence of activated zinc. In initial experiments carried out in ether, this reaction afforded, in 1% yield, a yellow, crystalline material, the spectral properties of which were entirely consistent with 4. Thus, peaks in the mass spectrum at m/e 308, 280, 252, and 224 and strong ir absorptions at 2000 and 2065 cm^{-1} were indicative of an iron tricarbonyl group, and two singlets (3:1) at δ 3.77 and 4.77 were consonant with the cyclobutadiene ligand. This assignment was then firmly established by chemical correlation (Scheme II) with the known 1,2-dimethylcyclobutadieneiron tricarbonyl (9).[13,14] It is noteworthy that, in this conversion, all attempts to reduce 4 to diol 7 directly with LiAlH$_4$ afforded only intractable product mixtures[16] and necessitated an indirect route via bis(acid chloride) (6).[17] The sequence was later refined with the discoveries that diisobutylaluminum hydride cleanly reduces 4 to 7 in high yield and that reduction of diacid 5 with B$_2$H$_6$–BF$_3$ affords 9 directly. Comparison of ir and ^{1}H NMR spectra estab-

Scheme II
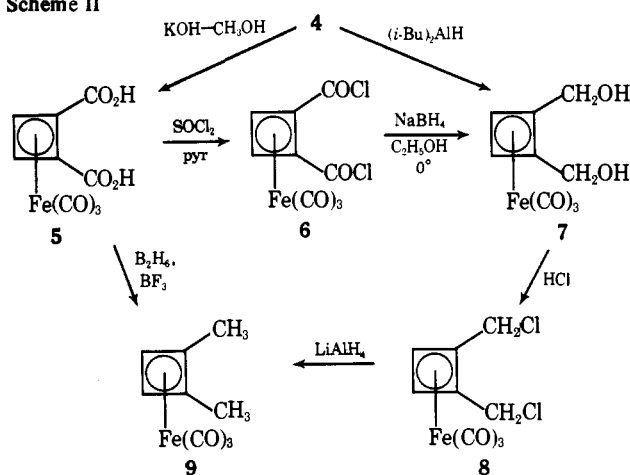
lished the identity of our material with that prepared previously.

The low yield of 4 was later improved to 7–9% and then 15% by employing HOAc–ether and DMF–ether solvent systems, respectively. We subsequently discovered, however, that the metalated carbonyl, Na$_2$Fe(CO)$_4$, in THF was significantly more effective, affording 4 in 35–40% yield. More recently, Schmidt has demonstrated the importance of halogen lability in an efficient (70%) preparation of 4 from a dibromo analog of 3a with Fe$_2$(CO)$_9$–DMF.[18,19]

Possible mechanisms for complexation of 3a with Zn–Fe$_2$(CO)$_9$ and Na$_2$Fe(CO)$_4$ are speculative. Presumably, in the former case, the carbonyl intercepts a cyclobutene dichloride, although we were unable to isolate such an intermediate when 3a was treated with zinc alone. In the latter case, the metal carbonyl anion could give rise via double displacement[20] of cis chlorines to an intermediate tetracarbonyliron complex of a cyclobutene dichloride or possibly to the cyclobutene dichloride itself via reductive dehalogenation.[21]

Parenthetically, we mention here an unsuccessful approach to 4 because of the possible future value of an intermediate encountered therein. We expected that photochemical addition of vinylene carbonate to dibromomaleic anhydride[22] (Scheme III) would afford, after hydrolysis and es-

Scheme III
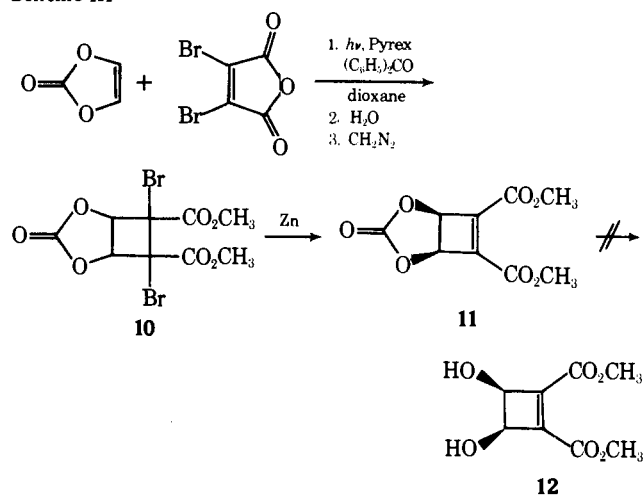
terification, a functional equivalent (10) of tetrachlorodiester 4. Subsequent debromination would then provide a cyclobutenediol derivative 11 potentially convertible into a precursor for 4. This approach succeeded up to 11, the photo-

chemical cycloaddition affording a single stereoisomer of **10**. However, numerous attempts to hydrolyze **11** to **12** or the corresponding diacid consistently afforded intractable mixtures. This behavior is most likely due to the sensitivity of **12** or the corresponding diacid to acid or base catalyzed ring cleavage of the retroaldol type. Ironically, this approach was attempted and abandoned before the appearance of the Grubbs synthesis of cyclobutadiene complexes from iron carbonyls and cyclobutenediol carbonates such as **11**.[23] While the development of tetrachloro diester **3** as a precursor to **4** obviated the need for further development of this route, the availability of **11** does provide the basis for an alternative approach.

Bis(acid chloride) **6** provided the starting point for functional group interconversions which have led to tricarbonyliron complexes of several theoretically interesting cyclobutadienes and which have also demonstrated the ability of the cyclobutadieneiron tricarbonyl unit to withstand a variety of experimental conditions. Thus **6** routinely underwent
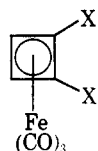
13, X = CO₂CH₂C₆H₅
14, X = CONH₂
15, X = COC₆H₅
16, X = COCH₂Cl
17, X = COCH₂I
18, X = COCH₃
19, X = CN
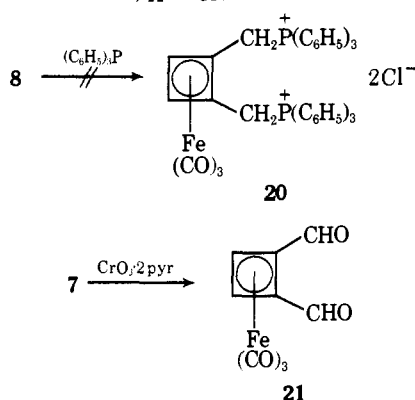
esterification to **13** ($C_6H_5CH_2OH$-pyr), amidation to **14** (NH_3-(C_2H_5)$_2O$), Friedel-Crafts acylation to **15** (C_6H_6-AlCl₃), and chloromethylation to **16** (CH_2N_2, then HCl). In turn, **14** could be dehydrated to dinitrile **19** (P_4O_{10}) and **16** reductively cleaved to bis(methyl ketone) **18** (NaI-HOAc, then $Na_2S_2O_3$), the presumed intermediate bis(iodomethyl ketone) **17** also being available independently from **16** (NaI-acetone). It was subsequently found that **18** could be obtained more conveniently and in higher overall yield by treating the intermediate bis(diazo ketone), resulting from reaction of **6** and diazomethane, with hydriodic acid.

Attention was then turned toward the elaboration of suitable substrates for application of the Wittig reaction to the synthesis of polyenic cyclobutadienoid systems. Initially, we envisaged participation of the cyclobutadiene component as either a 1,2-bis(phosphorane) derived, for example, from bis(phosphonium chloride) **20**, or as a dicarbonyl compound such as dialdehyde **21**. Attempts to effect the bis(phosphorane) approach, however, were unpromising. Reaction of **8**

with 2 equiv of triphenylphosphine led to complete consumption of the dichloride and formation of an orange oil. Most of the phosphine, however, was recovered. Consequently, attention was focused on developing the dicarbonyl route through dialdehyde **21**. Initial efforts to prepare this key intermediate via reduction of diacid chloride **6** with lithium tri-*tert*-butoxyaluminum hydride[24] or oxidation of diol **7** with activated manganese dioxide in benzene,[25] Me_2SO-DCC-pyridinium trifluoroacetate,[26] or pyridine·SO_3-Me_2SO-(C_2H_5)$_3N$[27] all failed. We were gratified to find, however, that oxidation of **7** with Collins' reagent[28a] according to the procedure of Dauben et al.[28b] afforded **21** in 60-65% yield as a stable, bright yellow, crystalline solid.

Wittig olefination of **21** with various triphenylphosphoranes (Scheme IV) proceeded unexceptionally. The parent
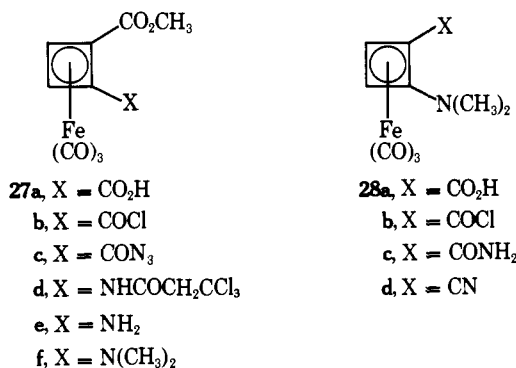
Scheme IV[a]
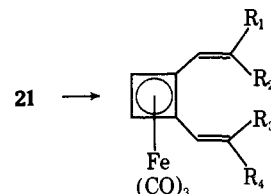
22, R₁ = R₂ = R₃ = R₄ = H
23, R₁ = R₄ = C₆H₅; R₂ = R₃ = H
24, R₁ = R₃ = C₆H₅; R₂ = R₄ = H
25, R₁ = R₄ = H; R₂ = R₃ = C₆H₅
26, R₁ = R₂ = R₃ = R₄ = C₆H₅

[a]Conditions (yield): **22**, $CH_2P(C_6H_5)_3$-THF, -10° (28%); **23, 24, 25**, $C_6H_5CHP(C_6H_5)_3$-C_2H_5OH (92%); **26**, (C_6H_5)$_2CP(C_6H_5)_3$-DMF, 130° (64%).

member of the series (**22**) was obtained as a somewhat unstable air and light sensitive yellow liquid. With benzylidenetriphenylphosphorane, **21** behaved rather indiscriminately and afforded a mixture of the three possible 1,2-distyryl derivatives, **23**, **24**, and **25**, in almost statistical 3:5:2 proportions, respectively. These isomers were separated by TLC as stable bright yellow crystalline solid (**23**) and liquids (**24**, **25**) and distinguished on the basis of molecular symmetries and the magnitudes of the vicinal olefinic coupling constants observed in their ¹H NMR spectra. Condensation of **21** with the sterically encumbered benzhydrylidenetriphenylphosphorane required forcing conditions but nevertheless produced **26** in moderate yield.

Diester **4** has also been examined as a source of chiral cyclobutadieneiron tricarbonyl complexes possessing nonidentical substituents.[18,29] Entry into a functional series of this type of compound was effected by partial saponification of **4** to half-ester **27a** (Scheme V) and subsequent elaboration of the latter to aminoester **27e** by Curtius rearrangement of acylazide **27c** as shown. **27e** was then N-methylated to **27f**, which afforded aminonitrile **28d** upon dehydration of the derived amide **28c**.

Diester **4** has also been tested as a substrate for constructing tricarbonyliron complexes of cyclobutadienes possessing bulky substituents with the objective of generating and observing the free, potentially stable cyclobutadiene. The preparation of systems of this type has recently been realized by Maier et al. in the low temperature photolysis of *tert*-butyl-substituted cyclobutene-3,4-dicarboxylic acid anhydrides,[30] and by Kimling and Krebs[31] and Masamune et al.[32] in the preparation of stable cyclobutadienes of the tetra- and tri-*tert*-butyl types, respectively. Toward this end, the 1,2-di-*tert*-butyl complex **31** was prepared (Scheme VI) by sequential conversion of **4** to diol **29** with methyllithium, thence to the unstable bis(*tert*-chloride) **30**

Scheme V[a]

27a, X = CO₂H
b, X = COCl
c, X = CON₃
d, X = NHCOCH₂CCl₃
e, X = NH₂
f, X = N(CH₃)₂

28a, X = CO₂H
b, X = COCl
c, X = CONH₂
d, X = CN

[a]Reagents: **4** → **27a**, KOH–CH₃OH; → **27b**, SOCl₂–pyr; → **27c**, NaN₃–acetone–H₂O; → **27d**, Cl₃CCH₂OH (70°); → **27e**, Zn–90% HOAc; → **27f**, CH₃I–NaH–DME; → **28a**, KOH–CH₃OH; → **28b**, ClCOCOCl–C₆H₆; → **28c**, NH₃; → **28d**, POCl₃–pyr.

Scheme VI
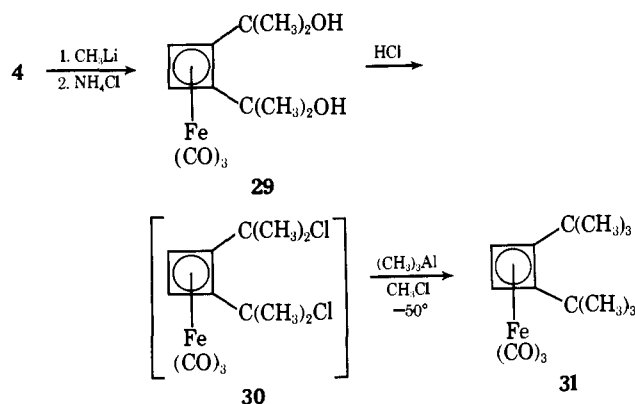
with hydrogen chloride, and, finally, coupling of **30** with trimethylaluminum in methyl chloride.[33]

As described above, diester **4** has been converted to the known dimethyl complex **9**. In addition, each of the other complexes newly reported herein exhibited spectral properties in accord with assigned structures. These included (a) appearance in ¹H NMR spectra of one or two singlets for the cyclobutadiene ring protons, depending upon molecular symmetry, with no observable coupling between chemically shifted vicinal protons,[34] (b) the diastereotopic nature of geminal protons revealed in the appearance of an ABX splitting pattern in the ¹H NMR spectrum of bis(hydroxymethyl) derivative **7** in Me₂SO-d_6 and of AB quartets in those of bis(chloromethyl) and bis(iodomethylcarbonyl) derivatives **8** and **17** (an effect which was absent, however, in **13** and **16**), and (c) the sequential loss of carbon monoxide and strong absorptions at ~2000 cm⁻¹ in mass and infrared spectra, respectively, characteristic of the Fe(CO)₃ group. In addition, ring proton chemical shifts were sensitive to substituent electronic effects and ranged from the δ 3.9 region characteristic of the parent and alkyl-substituted complexes down to δ 5.38 for bis(nitrile) **19**. Iron-coordinated carbonyl ir absorptions also exhibited slight shifts to higher frequency with increasing electron withdrawal by substituents. Such an effect accords with decreased electron density on iron available for Fe–CO backbonding.[35]

Although the utility of the complexes described herein in providing access to free cyclobutadienes has not been fully explored, certain preliminary observations are revealing. Diester **4**, for example, undergoes rapid oxidative degradation with ceric ion (but not with lead tetraacetate) to give

products formally derived through Diels–Alder reactions of the free cyclobutadiene.[36] In contrast, aminoester **27f**, while readily degraded by a number of oxidizing agents, has thus far yielded no tractable products.[37] In addition, the use of complexes possessing bulky substituents as a route to the free cyclobutadienes remains to be demonstrated in view of Ciabattoni and Feiring's intriguing discovery that oxidative degradation of tri-*tert*-butylcyclobutadieneiron tricarbonyl afforded *tert*-butyl 1,2-di-*tert*-butylcyclopropen-3-yl ketone exclusively and no tri-*tert*-butylcyclobutadiene-derived products.[38] While the chemistry of decomplexation remains to be more fully delineated, the results of the present study provide the basis for the investigation of a wide range of 1,2-disubstituted complexes.

Experimental Section

General. All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Associates A60-A and HA-100D spectrometers. Chemical shifts are reported as δ values relative to internal tetramethylsilane (Me₄Si). Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMH-2 or a Consolidated Electrodynamics Corporation Model CEC-110 spectrometer operating at an ionizing potential of 70 eV. Preparative thin-layer chromatography was performed on 2-mm silica gel plates from Analtech or Brinkmann. Alumina (Fisher A-540) was used for routine column chromatography or filtration. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Micro-Analysis, Inc., Wilmington, Del. Unless indicated otherwise, analyses of all new compounds containing C, H, Fe, halogen, and N agreed within 0.35% of theoretical values.

Materials. Anhydrous THF and DME were freshly distilled from lithium aluminum hydride. Anhydrous benzene and dioxane were obtained by distillation from sodium. Pyridine and DMF were dried over potassium hydroxide and distilled from barium oxide. Commercially available dichloromaleic anhydride (Aldrich or Columbia) was purified by sublimation until the melting point was at least 115–118°. *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide was purchased from Aldrich and iron pentacarbonyl from GAF Corp. Diisobutylaluminum hydride and trimethylaluminum were purchased as benzene solutions from Texas Alkyls. All other materials were either used as received from commercial sources or were purified by standard methods.

cis,trans,trans-1,2,3,4-Tetrachlorocyclobutane-1,2-dicarboxylic Acid (3b). A solution of dichloromaleic anhydride (187.5 g, 1.125 mol), freshly distilled *trans*-1,2-dichloroethylene (327.0 g, 3.375 mol), and benzophenone (34.2 g, 0.187 mol) in 1400 ml of anhydrous dioxane was prepared in a 1800-ml three-necked photochemical reaction vessel equipped with a magnetic stirring bar, a gas-dispersion tube, a gas-outlet adapter leading to a mercury trap, and a water-cooled quartz immersion well containing a Pyrex filter sleeve and a 450-W Hanovia high-pressure mercury lamp. The solution was irradiated until the anhydride had been consumed (~72 hr), as indicated by monitoring of ir absorption at 1612 cm⁻¹. Evaporation of dioxane and unreacted dichlorethylene left a dark-red viscous oil which was poured into 1500 ml of 0.1% hydrochloric acid preheated to 70°. The resulting mixture was stirred for 2 hr during which time a dark tarry material separated. The supernatant aqueous layer was decanted, washed with 500 ml of benzene, saturated with NaCl, and extracted with 3 × 500 ml of ether. The combined ethereal extracts were dried (MgSO₄), filtered, and evaporated to give the crude diacid as a red-orange oil. In some instances, the oil crystallized in vacuo to give an off-white semisolid product. The crude diacid, ~228 g, was routinely esterified without further purification.

A crystalline sample of diacid was obtained by dissolving the oil in a minimum volume of warm 1:2:3 (v/v) acetone-CCl₄-petroleum ether (60–110°), adding petroleum ether until the solution was saturated, and cooling to 0°. The crystals, which formed slowly over 2–3 weeks, were filtered, washed with petroleum ether, and dried in vacuo. Repeated crystallization of the solid in this manner afforded the pure diacid **3b** as colorless microcrystals: mp 189–190°; ir (KBr). 3080–3160. 1780 (sh), 1725. 1705 (sh), and 1670

cm^{-1}; NMR (CDCl$_3$), AB quartet, δ_A 4.50, δ_B 5.18 (J_{AB} = 9.3 Hz, 2 H, ring protons), 11.77 (s, 2 H, CO$_2$H).

Dimethyl *cis,trans,trans*-**1,2,3,4-Tetrachlorocyclobutane-1,2-dicarboxylate (3a).** The crude diacid (228 g) from the foregoing experiment was esterified in 28.0-g portions (0.1 mol) with an ethereal solution of diazomethane generated from 63.0-g portions (0.3 mol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to the procedure of de Boer and Backer.[39] To minimize the hazards associated with handling large quantities of diazomethane, the reagent was distilled as formed into a cooled (0°), magnetically stirred solution of diacid in 50 ml of ether. Excess diazomethane was then destroyed by adding small amounts of diacid to the reaction mixture until nitrogen evolution ceased. The reaction mixtures thus obtained were combined, dried (K$_2$CO$_3$), treated with activated charcoal, filtered, and evaporated to give an oily white solid. Recrystallization from 70% aqueous ethanol afforded 230 g (66% yield based on dichloromaleic anhydride) of **3a** as colorless needles: mp 92–93°; ir (CCl$_4$) 1765 (sh), 1755, and 1725 cm^{-1}; NMR (CDCl$_3$) δ 3.82 (s, 3 H, CO$_2$CH$_3$), 3.89 (s, 3 H, CO$_2$CH$_3$), AB quartet, δ_A 4.47, δ_B 5.17 (J_{AB} = 9.0 Hz, 2 H, ring protons).

Preparation of Disodium Tetracarbonylferrate.[40] A 2-l. three-necked flask containing a Teflon-coated magnetic stirring bar was fitted with a 125-ml pressure-equalizing addition funnel leading to a source of nitrogen, a condenser leading to a mercury trap, and a mechanical stirrer. The flask was placed under nitrogen and charged with freshly cut sodium (20.7 g, 0.90 g-atom). Distilled mercury (30.9 g, 0.154 g-atom) was placed in the addition funnel. The flask was heated gently with a flame until the sodium was molten. The mercury was then added with magnetic stirring over 0.25 hr, after which the addition funnel was recharged with iron pentacarbonyl (81 ml, 0.60 mol), the magnetic stirring bar was removed, and the amalgam was covered with 600 ml of anhydrous THF. The iron pentacarbonyl was added to the amalgam with vigorous mechanical stirring over 3 hr. The resulting suspension was stirred 1 hr longer and quickly transferred by decantation to a 2-l. separatory funnel. To complete the transfer, the reaction flask was rinsed with 3 × 50 ml of anhydrous THF. The reagent was used immediately in the preparation of complex **4** as described below.

Tricarbonyl[dimethyl 1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxylate]iron (4). A 3-l. three-necked flask equipped with a mechanical stirrer, a gas-outlet adapter leading to a mercury trap, and a condenser leading to a source of nitrogen was charged with a solution of diester **3a** (48.0 g, 0.156 mol) in 500 ml of anhydrous THF. To the stirred solution was rapidly added, via a separatory funnel, the suspension of disodium tetracarbonylferrate described in the previous experiment. A moderately exothermic reaction ensued, after which the mixture was stirred for 16 hr under nitrogen. The mixture was then filtered twice through Celite, with suction, using coarse, sintered glass funnels. The filtered solids were washed thoroughly with anhydrous ether and retained. The filtrate and washings were combined and evaporated to give a reddish-purple oil which was extracted in portions with 750 ml of anhydrous ether. After each extraction, the ether was decanted and filtered through Celite, and the filtered solids were washed with anhydrous ether and retained. The combined filtrates and washings were then passed through a 1.5 × 12 in. column of alumina with ether elution. Evaporation of solvent afforded crude **4** as a bright yellow crystalline solid.

The filtered solids retained during the foregoing procedure were combined and extracted with anhydrous ether in a Soxhlet apparatus. Chromatography of the ethereal extract on alumina as before yielded additional product. All product fractions were then combined and recrystallized from hexane to give 16.8–20.2 g (35–42%) of pure **4** as yellow needles: mp 105–106°; ir (CHCl$_3$) 2065, 2000, 1727 (sh), 1708, and 1700 cm^{-1}; NMR (CDCl$_3$) δ 3.77 (s, 6 H, OCH$_3$), 4.77 (s, 2 H, ring protons); *m/e* 308.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxylic acid]iron (5). To a swirled solution of 85% potassium hydroxide (19.8 g, 0.30 mol) in 20 ml of water and 300 ml of methanol was gradually added diester **4** (18.5 g, 0.060 mol). After standing in the dark for 3 hr, the solution was concentrated at room temperature under aspirator pressure on a rotary evaporator until crystals formed. The resulting mixture was diluted with 500 ml of water, washed with 250 ml of CH$_2$Cl$_2$, acidified with concentrated HCl, and extracted with 3 × 375 ml of ether. The combined ethereal extracts were then dried (MgSO$_4$), filtered, and evaporated in vacuo to give 15.2

g (90%) of crude **5** as a pale yellow powder. Recrystallization from ethyl acetate afforded an analytical sample as yellow-orange monoclinic prisms: dec >200°; ir (KBr) 3000–2350 (br), 2080, 1995, 1695 (sh), and 1680 cm^{-1}; NMR (Me$_2$SO-*d$_6$*) δ 5.18 (s, 2 H, ring protons) and 12.64 (br s, 2 H, -CO$_2$H); *m/e* 280.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarbonyl chloride]iron (6). To a swirled suspension of diacid **5** (14.0 g, 0.050 mol) in 180 ml of thionyl chloride was slowly added 12.1 ml (11.8 g, 0.15 mol) of anhydrous pyridine. The mixture was then sealed and stored for 2 hr in the dark. Excess thionyl chloride and pyridine were removed in vacuo, and the residue was extracted with 3 × 250 ml of hot benzene. The combined benzene extracts were filtered while hot and evaporated to give crude **6**. Recrystallization from CCl$_4$ afforded 14.6 g (92%) of pure material as yellow-orange needles: mp 153–156°; ir (CHCl$_3$) 2082, 2030, 2018, 1772, and 1720 cm^{-1}; NMR (CDCl$_3$) δ 5.10 (s, ring protons); *m/e* 316.

Tricarbonyl[1,2,3,4-η-1,2-bis(hydroxymethyl)-1,3-cyclobutadiene]iron (7). A. From Bis(acid chloride) 6. To a cooled (−10°), magnetically stirred suspension of sodium borohydride (1.92 g, 50.8 mmol) in 25 ml of ethanol was added bis(acid chloride) **6** (2.00 g, 6.32 mmol) over 0.25 hr. The reaction mixture was maintained at −10° for 0.5 hr, then warmed slowly to 0°, and poured into 25 ml of cold saturated aqueous NH$_4$Cl. After stirring for 1 hr, the resulting mixture was extracted with 4 × 100 ml of chloroform. The combined extracts were dried (MgSO$_4$), filtered, and evaporated to give crude **7** as an oily yellow-orange solid. Sublimation of the crude solid [bath temp 80–100° (0.05–0.10 mmHg)] afforded 1.06 g (68%) of the diol as a pale yellow powder, mp 64–67°.

B. From Diester 4. A solution of diester **4** (9.24 g, 0.030 mol) in 60 ml of anhydrous benzene was placed in a 250-ml three-necked flask fitted with a 125-ml pressure-equalizing addition funnel capped with a rubber septum, a gas-inlet adapter leading to a source of dry nitrogen, a gas-outlet adapter leading to a mercury trap, and a magnetic stirring bar. The system was placed under an atmosphere of dry nitrogen, and the addition funnel was charged, via syringe, with 90 ml of a 1.5 *M* solution of diisobutylaluminum hydride in benzene. The flask was cooled to 0°, and the hydride solution was added, with stirring, over a period of 1.25 hr. After stirring an additional 1.5 hr at room temperature, excess hydride was destroyed by slow addition of a solution of 5.7 ml of methanol in benzene and then a solution of 7.6 ml of water in 25 ml of methanol. The resulting suspension was stirred for 0.5 hr and then filtered with suction through a sintered glass funnel. The filtered, gelatinous solid was washed thoroughly, in portions, with benzene, ether, and methanol, respectively, dried in air, finely ground, stirred overnight in methanol, and filtered again. The combined filtrate and washings were evaporated in vacuo to give 6.94 g (92%) of relatively pure diol, mp 64–67°. Recrystallization from hexane afforded an analytical sample as pale yellow, feathery needles: mp 66–67°; ir (CHCl$_3$) 3595, 3380, 2040, and 1968 cm^{-1}; NMR (CDCl$_3$) δ 3.42 (br s, 2 H, OH), 4.08 (s, 4 H, -CH$_2$-), and 4.20 (s, 2 H, ring protons); NMR (Me$_2$SO-*d$_6$*) ABX multiplet, δ_A 3.83, δ_B 3.94, δ_X 5.05 (J_{AB} = 13.3 Hz, J_{AX} = 5.6 Hz, J_{BX} = 5.2 Hz, -CH$_2$OH); *m/e* 252.

Tricarbonyl[1,2,3,4-η-1,2-bis(chloromethyl)-1,3-cyclobutadiene]iron (8). A solution of diol **7** (352 mg, 1.40 mmol) in 5 ml of methylene chloride was shaken for 3–5 min. in a separatory funnel with two 5-ml portions of concentrated hydrochloric acid. The organic layer was then dried (Na$_2$SO$_4$), filtered, and evaporated under aspirator pressure at 20–25° to afford 330 mg (82%) of crude **8** as a pale yellow crystalline solid, mp 72–77° dec (gas evolution). Recrystallization from hexane at −20° gave an analytical sample as pale yellow needles: mp 76–78° dec; ir (CHCl$_3$) 2042 and 1962 cm^{-1}; NMR (CDCl$_3$) AB quartet, δ_A 4.01, δ_B 4.11 (J_{AB} = 12.6 Hz, 4 H, CH$_2$Cl), and 4.35 (s, 2 H, ring protons); *m/e* 288.

Tricarbonyl[1,2,3,4-η-1,2-dimethyl-1,3-cyclobutadiene]iron (9). A. From Dichloride 8. A solution of dichloride **8** (300 mg, 1.04 mmol) in 2.5 ml of ether was added dropwise to a stirred suspension of 65 mg (1.8 mmol) of lithium aluminum hydride in 3 ml of ether. The resulting mixture was stirred for 45 min and then cooled to 0°. Excess hydride was destroyed by cautious addition of water. Ether (40 ml) was added, and the organic phase was washed sequentially with dilute hydrochloric acid and water, dried (CaCl$_2$), and evaporated. The residue was evaporatively distilled [bath temp 45° (0.1 mmHg)] and collected at −78° to give 75 mg (33%) of **9**

as a light yellow liquid.

B. From Diacid 5. To a suspension of diacid **5** (500 mg, 1.79 mmol) in 4.7 ml of boron trifluoride etherate was added dropwise 9.5 ml of a 1.0 M solution of borane in THF. The mixture was refluxed for 0.6 hr, poured over cracked ice, and extracted with ether. The extract was dried ($CaCl_2$) and evaporated, and the residue was purified as described in part A to give 220 mg (56%) of **9**.

The ir and NMR spectra of this material were identical with those of material prepared by Brune et al.[13]

Photochemical Cycloaddition of Vinylene Carbonate and Dibromomaleic Anhydride. Preparation of Diester 10. A solution of vinylene carbonate (9.00 g, 0.104 mol), dibromomaleic anhydride (23.3 g, 0.091 mol), and benzophenone (2.7 g) in 200 ml of anhydrous dioxane was irradiated under nitrogen in a Pyrex tube with a 450-W Hanovia high-pressure mercury lamp placed in an adjacent water-cooled quartz immersion well. The tube and lamp assembly were cooled initially to 0° in an ice water bath. During the irradiation, ice was continually added to the bath such that its temperature never exceeded 35°. The reaction was followed by monitoring the disappearance of the ir absorption of dibromomaleic anhydride at 1595 cm^{-1}. After 46 hr of irradiation, the tube was cooled to 0°, and a colorless solid (4.55 g, fraction A) was collected by filtration and washed with cold, anhydrous dioxane. The filtrate and dioxane washings were evaporated, and the residue was triturated with cold chloroform to give, after filtration and washing with cold chloroform, a colorless solid (13.2 g, fraction B). NMR spectroscopy indicated that fractions A and B were 17:3 and 3:2 mixtures, respectively, of the [2 + 2] adduct of vinylene carbonate and dibromomaleic anhydride and the corresponding diacid (56% total yield based on dibromomaleic anhydride), the latter apparently arising from adventitious water.

To 4.00 g of the combined anhydride-diacid mixtures A and B was added 30 ml of water containing a few drops of concentrated hydrochloric acid. The resulting mixture was heated on a steam bath until homogeneous, cooled to room temperature, saturated with sodium chloride, and extracted, in portions, with 100 ml of ether. The combined extracts were dried ($MgSO_4$), filtered, and evaporated, and the residue was recrystallized from cold chloroform to give 2.80 g of crude diacid which was converted directly to the dimethyl ester.

To a solution of the aforementioned diacid (2.49 g, 64 mmol) in ether was added an ethereal solution of diazomethane[39] until a yellow color persisted in the reaction mixture. Excess diazomethane was destroyed by addition of a few drops of acetic acid. Upon cooling the mixture to 0°, a colorless solid crystallized and was collected by filtration to give 1.82 g of **10**. Slow evaporation of the filtrate afforded two more crops of product and raised the total yield of **10** to 2.12 g (47% based on the 4.00 g of anhydride-diacid mixture): mp 145-149°; ir ($CHCl_3$) 1840, 1740, and 1710 cm^{-1}; NMR ($CDCl_3$) 3.86 (s, 6 H, -OCH_3) and 5.45 (s, 2 H, ring protons).

Cyclic Carbonate of Dimethyl *cis*-3,4-Dihydroxycyclobutene-1,2-dicarboxylate (11). To a solution of diester **10** (2.28 g, 5.88 mmol) in 30 ml of anhydrous THF was added freshly activated zinc dust (0.393 g, 60 g-atoms). The reaction mixture was stirred for 1 hr, and solvent was then evaporated. The residue was taken up in methylene chloride, filtered, and evaporated to give crude **11**. Recrystallization from ethanol-water (3:2 v/v) afforded 0.77 g (58%) of pure **11** as colorless plates: mp 120-123°; ir ($CHCl_3$) 1825, 1744, and 1645 cm^{-1}; NMR ($CDCl_3$) 3.88 (s, 6 H, -OCH_3) and 5.57 (s, 2 H, ring protons).

Attempts to cleave **11** with aqueous sodium hydroxide, potassium hydroxide in methanol, and boron trifluoride in methanol gave complex intractable mixtures.

Tricarbonyl[dibenzyl 1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxylate]iron (13). Benzyl alcohol (0.36 ml) was added to a solution of bis(acid chloride) **6** (100 mg, 0.315 mmol) in 2 ml of dry pyridine. After standing for 15 min, the reaction mixture was heated 10 min at 50°, poured into water, and extracted with ether. The extract was then dried ($MgSO_4$), filtered, and evaporated in vacuo, and the residue was chromatographed on a ⅜ × 6 in. column of alumina. The product was eluted as a yellow band with benzene and benzene-ether mixtures. After evaporation of solvent, the residue was sublimed [bath temp 110-125° (0.15 mmHg)] to give 0.40 g (30%) of **13** as yellow needles: mp 70.0-71.5°; ir (KBr) 2065, 1998, 1977, and 1730 cm^{-1}; NMR ($CDCl_3$) 4.77 (s, 2 H, cyclobutadiene ring protons), 5.17 (s, 4 H, -CH_2-), and 7.32 (s, 10 H,

-C_6H_5); m/e 460.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxamide]iron (14). Gaseous ammonia was passed over a stirred solution of bis(acid chloride) **6** (100 mg, 0.315 mmol) in 20 ml of anhydrous benzene for 3 min. The precipitate was collected by filtration and recrystallized from water to give 65 mg (76%) of diamide **14** as light yellow plates: mp 297-298°; ir (KBr) 3360, 3170, 2080, 2000, 1674, 1660, 1625, and 1606 cm^{-1}; NMR (Me_2SO-d_6) δ 5.08 (s, 2 H, ring protons), 7.40 (br s, 2 H, -NH-), and 8.12 (br s, 2 H, -NH-).

Tricarbonyl[1,2,3,4-η-1,2-dibenzoyl-1,3-cyclobutadiene]iron (15). A solution of bis(acid chloride) **6** (100 mg, 0.315 mmol) and anhydrous aluminum chloride (100 mg, 0.766 mmol) in 10 ml of dry benzene was stirred under nitrogen for 15 hr. The reaction was quenched with 25 ml of water and extracted with ether. The ethereal extract was then dried ($MgSO_4$), filtered, and evaporated. Recrystallization of the residue from carbon tetrachloride-hexane (4:1 v/v) gave 90 mg (71%) of diketone **15** as yellow plates: mp 171-173°; ir (KBr) 2062, 1995, and 1635 cm^{-1}; NMR ($CDCl_3$) δ 5.00 (s, 2 H, cyclobutadiene ring protons), 7.23-7.65 (m, 6 H, meta and para protons), and 7.65-8.00 (m, 4 H, ortho protons); m/e 400.

Tricarbonyl[1,2,3,4-η-1,2-bis(2-chloroacetyl)-1,3-cyclobutadiene]iron (16). To a solution of bis(acid chloride) **6** (700 mg, 2.21 mmol) in 100 ml of anhydrous ether was slowly added, with stirring, a solution containing ~10 mmol of dry, alcohol-free diazomethane[39] in ether. The flask was placed in a water bath at 40°, and ether and excess diazomethane were removed in a stream of dry nitrogen. The residue was dissolved in chloroform, and gaseous HCl was bubbled through the resulting solution for 5 min. Solvent was removed by evaporation, and the residue was extracted with several portions of boiling hexane. The combined extracts were filtered while hot, concentrated, and cooled to give, after filtration, 445 mg (58%) of **16** as yellow needles: mp 115.5-117.5°; ir ($CHCl_3$) 2075, 2015, and 1676 cm^{-1}; NMR ($CDCl_3$) δ 4.26 (s, 4 H, -CH_2Cl), and 5.10 (s, 2 H, ring protons).

Tricarbonyl[1,2,3,4-η-1,2-bis(2-iodoacetyl)-1,3-cyclobutadiene]iron (17). Mixing of a solution of sodium iodide (129 mg, 0.854 mmol) in 3 ml of acetone with a solution of bis(chloro ketone) **16** (100 mg, 0.290 mmol) in 3 ml of acetone produced an immediate precipitate. After standing for 10 min, the reaction mixture was poured into 25 ml of water and extracted with ether. The ethereal extract was then washed with water, dried ($MgSO_4$), and evaporated to give, after recrystallization of the residue from hexane, 85 mg (56%) of **17** as small orange crystals: mp 97-99°; ir ($CHCl_3$), 2075, 2010, and 1667 cm^{-1}; NMR ($CDCl_3$) AB quartet, δ_A 3.91, δ_B 4.13 (J_{AB} = 10.0 Hz, 4 H, -CH_2I), and 5.02 (s, 2 H, ring protons).

Tricarbonyl[1,2,3,4-η-1,2-bis(acetyl)-1,3-cyclobutadiene]iron (18). A. From Bis(chloro ketone) 17. A solution of bis(chloro ketone) **17** (150 mg, 0.435 mmol) and sodium iodide (1.20 g, 8.0 mmol) in 7.0 ml of glacial acetic acid was stirred at 65° for 1.25 hr. The solution was cooled to room temperature, and a solution of saturated aqueous sodium thiosulfate was added until the iodine color discharged. The mixture was poured into 25 ml of water and extracted with ether. The combined ethereal extracts were then washed with water and saturated aqueous $NaHCO_3$, respectively, dried ($MgSO_4$), and evaporated. The residue was recrystallized from hexane to give 98 mg (82%) of diketone **18** as small yellow crystals, mp 122.5-124.0°.

B. From Bis(acid chloride) 6. A dried (K_2CO_3), alcohol-free solution of diazomethane (~0.12 mol) in ether[39] was slowly poured into a solution of bis(acid chloride) **6** (9.10 g, 0.033 mol) in 900 ml of ether. The reaction mixture was stirred for 1.25 hr at room temperature, and to it was then slowly added 250 ml of 47% hydriodic acid. The resulting mixture was stirred an additional 0.5 hr and then shaken with saturated aqueous sodium thiosulfate solution until the iodine color discharged. After the aqueous phase had been separated, it was extracted several times with ether. The combined ethereal extracts were washed with saturated aqueous $NaHCO_3$ and water, respectively, dried, ($MgSO_4$), and evaporated. The residue was recrystallized from hexane to give 6.52 g (83%) of small, yellow crystals: mp 122.5-124.0°; ir (KBr) 2060, 1990, 1960, 1675, and 1658 cm^{-1}; NMR ($CDCl_3$) δ 2.25 (s, 6 H, -CH_3) and 4.89 (s, 2 H, ring protons).

Tricarbonyl[1,2,3,4-η-1,2-dicyano-1,3-cyclobutadiene]iron (19).

Bis(amide) **14** (100 mg, 3.59 mmol) was mixed with phosphorus pentoxide (1.80 g) in a 50-ml round-bottomed flask fitted with a drying tube (CaCl₂). The flask was then heated in an oil bath at 150-170° for 1 hr with occasional shaking. The mixture was cooled to 0°, treated with 25 ml of ice water, and extracted several times with ether. The combined extracts were washed with water, dried (MgSO₄), and evaporated, and the residue was recrystallized from benzene to give 30 mg (35%) of **19** as yellow needles. An analytical sample was obtained by sublimation [bath temp 120-140° (1.5 mmHg)] followed by recrystallization from ethyl acetate-CCl₄: mp 205-216° dec (sealed tube); ir (KBr) 2225, 2085, and 2005 cm⁻¹; NMR (acetone-d_6) δ 5.38 (s).

Attempted Preparation of Bis(triphenylphosphonium chloride) 20. A solution of dichloride **8** (58 mg, 0.020 mmol) and triphenylphosphine (105 mg, 0.040 mmol) in 1.5 ml of anhydrous benzene was stirred for 48 hr at room temp in a flask fitted with a condenser and a drying tube (CaSO₄). During this time, a water-insoluble, red-orange oil separated. Analytical TLC examination indicated the presence of large amounts of unreacted **8** and triphenylphosphine. When the mixture was heated to reflux, **8** was completely consumed, and an intractable, polymer-like material coated the walls of the flask.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxaldehyde]-iron (21). A 3-l. three-necked flask equipped with a pressure-equalizing addition funnel, a mechanical stirrer, and a drying tube (CaSO₄) was charged with chromium trioxide–pyridine complex (106.4 g, 0.412 mol)²⁸ᵇ and 1200 ml of anhydrous methylene chloride. To the vigorously stirred solution of the complex was rapidly added a solution of diol **7** (6.86 g, 0.0272 mol) in 25 ml of anhydrous methylene chloride. The resulting mixture was stirred for 0.5 hr and filtered, with suction, through a sintered glass funnel. The reaction flask and chromium salts were thoroughly washed, in portions, with 500 ml of ether. The combined ethereal and methylene chloride filtrates were washed with 3 × 500 ml of saturated aqueous NaHCO₃, 3 × 500 ml of 5% hydrochloric acid, 500 ml of 5% aqueous NaHCO₃, and 500 ml of saturated aqueous NaCl, respectively, dried (MgSO₄), filtered, and evaporated to give the crude dialdehyde as a yellow-orange solid. Recrystallization from hexane afforded 4.18 g (62%) of pure **21** as golden yellow flakes (mp 127-130°): ir (CHCl₃) 3020, 3005, 2840, 2815, 2792 (sh), 2075, 2010, 1680, 1670, and 1648 (sh) cm⁻¹; NMR (CDCl₃) δ 5.05 (s, 2 H, ring protons) and 9.66 (s, 2 H, -CHO); m/e 248.

Tricarbonyl[1,2,3,4-η-1,2-divinyl-1,3-cyclobutadiene]iron (22). A 15-ml three-necked flask was fitted with an addition funnel, a source of dry nitrogen, and a rubber septum. The flask was charged with triphenylmethylphosphonium bromide (392 mg, 1.10 mmol) and placed under nitrogen. Next, 2.0 ml of anhydrous THF and 0.43 ml (1.0 mmol) of a 2.34 M solution of n-butyllithium in hexane were added successively via syringe. The resulting yellow-orange suspension was stirred magnetically for 1 hr. The flask was cooled to −10°, and to it was then added a solution of dialdehyde **21** (125 mg, 0.50 mmol) in 3.0 ml of anhydrous THF over a period of 5 min. The resulting mixture was stirred at 0-5° for 0.5 hr, poured into 150 ml of cold water, and extracted with 3 × 50 ml of methylene chloride. The combined extracts were washed with 100 ml of saturated aqueous NaCl and evaporated under aspirator pressure at 20-25°. The product was purified by preparative TLC on silica gel-pentane. Extraction of the least polar band with methylene chloride and evaporation of solvent afforded 34 mg (28%) of **22** as a bright yellow liquid with a sweet odor which decomposed on prolonged exposure to heat or light. A portion of the product was evaporatively distilled [ambient temp (0.15 mmHg)] and collected at −78°: ir (CCl₄) 2035, 1972, 1942 (sh), 1920, 1625 (sh), and 1618 cm⁻¹; NMR (CDCl₃) δ 4.30 (s, 2 H, ring protons), ABC multiplet, δ_A 5.15, δ_B 5.31, δ_C 6.12 (J_{AB} = −1.0 Hz, J_{BC} = 17.4 Hz, J_{AC} = 10.8 Hz, 6 H, vinyl protons); m/e 244.

Because of the instability of this compound, a satisfactory compositional analysis could not be obtained.

***trans,trans-* (23), *cis,trans-* (24), and *cis,cis-*Tricarbonyl[1,2,3,4-η-1,2-distyryl-1,3-cyclobutadiene]iron (25).** A 50-ml three-necked flask equipped with a pressure-equalizing addition funnel, a source of dry nitrogen, and a rubber septum was charged with triphenylbenzylphosphonium chloride (975 mg, 2.50 mmol)⁴¹ and 7.5 ml of ethanol. The flask contents were placed under dry nitrogen, and 5.0 ml of a 0.50 M solution of lithium ethoxide in ethanol (prepared under nitrogen from 17.5 mg of freshly cut lithium) was

added via syringe. The mixture was stirred for 1 hr, and a solution of dialdehyde **21** (125 mg, 0.50 mmol) in 5.0 ml of ethanol was then added through the addition funnel over 0.5 hr. The mixture was stirred 2 hr more, poured into 150 ml of water, and extracted with 3 × 50 ml of hexane. The combined extracts were washed with 2 × 100 ml of water and 100 ml of saturated aqueous NaCl, respectively, dried (MgSO₄), filtered, and evaporated. The residue was dissolved in a minimum volume of carbon tetrachloride and passed through a 1 × 3 in. column of alumina with carbon tetrachloride. Evaporation of the eluate gave 182 mg (92%) of a viscous, yellow oil consisting of the three distyryl isomers. The oil, dissolved in a minimum volume of methylene chloride, was chromatographed on two preparative silica gel TLC plates. Each of the plates was developed three times with hexane and sectioned carefully to separate isomers. Appropriate sections were combined and rechromatographed with repeated solvent development until acceptable separations were achieved. Isolation of the three bands afforded, in order of decreasing polarity, 54 (27%), 79 (40%), and 33 mg (17%) of **23, 24,** and **25,** respectively.

The trans,trans isomer **23,** initially obtained as a bright yellow solid, mp 127-132°, was recrystallized from methanol to give bright yellow needles: mp 132-134°; ir (CCl₄) 2040, 1970, 1942 (sh), 1625, 1595, and 1492 cm⁻¹; NMR (CCl₄) δ 4.39 (s, 2 H, cyclobutadiene ring protons), AB quartet, δ_A 6.48, δ_B 6.60 (J_{AB} = 16.0 Hz, 4 H, vinyl protons), and 7.16-7.25 (m, 10 H, -C₆H₅); m/e 396.

The cis,trans isomer **24,** initially obtained as a bright yellow oil, was purified by evaporative distillation [bath temp, 150-155° (0.05 mmHg)]: ir (CCl₄) 2042, 1972, 1940 (sh), 1625, 1598, 1492, 1462, 1448, and 1440 cm⁻¹; NMR (CCl₄) δ 3.86 (s, 1 H, cyclobutadiene ring proton), 4.24 (s, 1 H, cyclobutadiene ring proton), AB quartet, δ_A 6.01, δ_B 6.55 (J_{AB} = 11.7 Hz, 2 H, cis vinyl protons), AB quartet, δ_A 6.20, δ_B 6.52 (J_{AB} = 16.2 Hz, 2H, trans vinyl protons), 7.19 (m, 10 H, -C₆H₅); m/e 396.

The cis,cis isomer **25,** initially obtained as a bright yellow oil, was purified by evaporative distillation [bath temp 90-95° 0.03-0.05 mmHg)]: ir (CCl₄) 2045, 1972, 1940 (sh), 1620, 1600, 1495, 1465, 1455 (sh), 1440, and 1435 (sh) cm⁻¹; NMR (CCl₄) δ 3.71 (s, 2 H, cyclobutadiene ring protons), AB quartet, δ_A 5.84, δ_B 6.46 (J_{AB} = 11.7 Hz, 4 H, vinyl protons) and 7.17 (m, 10 H, -C₆H₅); m/e 396.

Tricarbonyl[1,2,3,4-η-1,2-bis(2,2-diphenylvinyl)-1,3-cyclobutadiene]iron (26). A 25-ml three-necked flask equipped with a pressure-equalizing addition funnel, a source of dry nitrogen, and a rubber septum was charged with triphenylbenzhydrylphosphonium bromide (765 mg, 1.50 mmol)⁴² and 6.0 ml of anhydrous THF. The flask contents was placed under dry nitrogen and 0.59 ml (1.25 mmol) of a 2.13 M ethereal solution of methyllithium was added via syringe. The resulting solution was stirred for 1 hr, diluted with 8.0 ml of anhydrous DMF, and heated at 130° while a solution of dialdehyde **21** (125 mg, 0.50 mmol) in 5.0 ml of anhydrous DMF was added over 1.25 hr. The reaction mixture was maintained at 130° for 3 hr, cooled to room temperature, poured into 150 ml of water, and extracted with 3 × 75 ml of hexane. The combined extracts were then washed with 3 × 200 ml of water and 200 ml of saturated aqueous NaCl, respectively, dried (MgSO₄), filtered, and evaporated. The residue was dissolved in a minimum volume of methylene chloride and chromatographed twice with hexane on a preparative silica gel TLC plate. Extraction of the least polar band with chloroform and evaporation of solvent afforded 175 mg (64%) of a viscous, bright yellow oil which was then evaporatively distilled [bath temp 175-180° (0.05 mmHg)] and crystallized from methanol at −20° to give 118 mg (43%) of pure **26** as bright yellow needles: mp 135-136°; ir (CHCl₃) 2032, 1955, 1595, 1570, 1488, and 1450 (sh) cm⁻¹; NMR (CDCl₃) δ 2.89 (s, 2 H, cyclobutadiene ring protons), 6.64 (s, 2 H, vinyl protons), and 7.10-7.36 (m, 20 H, -C₆H₅); m/e 548.

Tricarbonyl[methyl hydrogen 1,2,3,4-η-1,3-cyclobutadiene-1,2-dicarboxylate]iron (27a). With 48.6 ml of a 0.4 M solution of KOH (85%) in methanol was mixed diester **4** (6.00 g, 0.0195 mol) in a 100-ml round-bottomed flask. The flask was stoppered and stored in the dark for 24 hr. The solution was then evaporated under aspirator pressure (<40°) to one-fourth the original volume, diluted to 150 ml with water, and extracted with 20 ml of methylene chloride. The extract was dried (MgSO₄), filtered, and evaporated to give 450 mg (7.5%) of unreacted **4.** The aqueous phase was acidi-

fied to pH ~3 by dropwise addition of concentrated hydrochloric acid, and the resulting yellow suspension was extracted with 4 × 25 ml of ether. The combined extracts were washed with 25 ml of saturated aqueous NaCl, dried (MgSO$_4$), filtered, and evaporated. Sublimation of the residue [bath temp 120–145° (0.04 mmHg)] afforded 4.80 g (90% based upon the amount of 4 consumed) of 27a as yellow needles: mp 130–137°; ir (CHCl$_3$) 2500–3400, 2075, 2010, 1735, and 1610 cm^{-1}; NMR (CDCl$_3$) δ 3.86 (s, 3 H, –OCH$_3$), 4.78 (s, 1 H, ring proton), 4.94 (s, 1 H, ring proton), and 10.06 (br s, 1 H, –CO$_2$H).

Tricarbonyl[methyl 1,2,3,4-η-1,3-cyclobutadiene-2-carbonyl chloride-1-carboxylate]iron (27b). Thionyl chloride (16.8 ml) was cautiously mixed with half-ester 27a (4.80 g, 0.0163 mol) in a round-bottomed flask, and then dry pyridine (1.2 ml) was added dropwise with stirring. The flask was protected with a drying tube and stored in the dark for 2 hr. After excess thionyl chloride had been removed under aspirator pressure with a warm water bath, the solid residue was heated with 15 ml of benzene. The mixture was cooled to 0°, and the supernatant solution was decanted. This procedure was repeated seven times with 8-ml portions of benzene. Solvent was evaporated from the combined extracts, and the residue was recrystallized from hexane to give 4.20 g (82.5%) of 27b as orange-yellow crystals: mp 116–117°; ir (KBr), 2077, 1999, 1753, and 1719 cm^{-1}; NMR (CDCl$_3$) δ 3.77 (s, 3 H, –OCH$_3$), 4.89 (s, 1 H, ring proton), and 4.97 (s, 1 H, ring proton).

Tricarbonyl[methyl 1,2,3,4-η-1,3-cyclobutadiene-2-carbonylazide-1-carboxylate]iron (27c). To a cooled (0°) solution of sodium azide (1.09 g, 0.0167 mol) in 2.8 ml of water contained in a 50-ml flask fitted with a pressure-equalizing addition funnel was added, with magnetic stirring, a solution of acid chloride 27b (4.20 g, 0.0134 mol) in 17.5 ml of anhydrous acetone over a period of 20 min. The funnel was rinsed with 0.5 ml of acetone, and the reaction mixture was stirred at 0° for 4 hr. Water (10 ml) was added, and acetone was then removed from the mixture with a rotary evaporator at <40°. More water (5 ml) was added, and the resulting precipitate was collected by filtration, washed with water, and dried in vacuo overnight to give 4.14 g (97%) of 27c as pale yellow crystals which exploded on heating: ir (KBr), 2170, 2075, 1995, 1710, and 1690 cm^{-1}; NMR (CDCl$_3$) δ 3.78 (s, 3 H, –OCH$_3$), 4.79 (s, 1 H, ring proton), and 4.87 (s, 1 H, ring proton).

Tricarbonyl[methyl 1,2,3,4-η-amino-1,3-cyclobutadiene-1-carboxylate]iron (27e). Azide 27c (4.00 g, 0.0126 mol) and 7 ml of freshly distilled 2,2,2-trichloroethanol were stirred magnetically for 0.5 hr in a 50-ml flask protected with a drying tube (CaCl$_2$). The flask was placed in an oil bath and the temperature was raised to 60° over 0.5 hr. (CAUTION: in some instances, the azide has exploded if warmed too rapidly.) The flask was maintained at that temperature for 4 hr, then cooled to room temperature, and fitted with a Dewar condenser cooled to −78°. Excess 2,2,2-trichloroethanol was removed in vacuo. The residue was heated again at 60° for 2 hr and then chromatographed on a 2 × 30 cm column of alumina. Elution with solvent mixtures gradually changed from 100% carbon tetrachloride to 60% (v/v) chloroform in carbon tetrachloride afforded, after evaporation in vacuo, 3.95 g (85%) of urethane 27d as a yellow oil which was homogeneous as indicated by TLC (silica gel–chloroform): ir (CHCl$_3$) 3440, 2060, 1989, 1749, 1725, and 1695 cm^{-1}; NMR (CDCl$_3$) δ 3.76 (s, 3 H, –OCH$_3$), 4.16 (s, 1 H, ring proton), 4.57 (s, 1 H, ring proton), 4.79 (s, 2 H, –CH$_2$–), and 6.82 (br s, 1 H, NH).

To a magnetically stirred solution of urethane 29d (3.60 g, 9.76 mmol) in 14 ml of 90% aqueous acetic acid cooled to 5° was added 4 g of activated zinc (prepared by swirling granular 80-mesh zinc metal in 10% aqueous hydrochloric acid, rinsing with water to neutrality and, finally, washing with acetone and ether, respectively). The resulting slurry was stirred at 5° for 4.5 hr, diluted with 30 ml of ether, and filtered. The filtrate was washed with 4 × 20 ml of water, 2 × 10 ml of saturated aqueous NaHCO$_3$, and 10 ml of saturated aqueous NaCl, respectively, dried (MgSO$_4$), filtered, and evaporated to give 2.19 g (85%) of crude amine. Recrystallization from ether–petroleum ether (30–60°) afforded an analytical sample as yellow needles: mp 115–116°; ir (KBr) 3468, 3309, 3225, 2036, 1960, 1940, and 1695 cm^{-1}; NMR (acetone-d_6) δ 2.88 [br s, 1.6 H, –NH$_2$ (possible D exchange with solvent)], 3.70 (s, 3 H, –OCH$_3$), 3.89 (s, 1 H, ring proton), and 4.22 (s, 1 H, ring proton). Addition of a drop of D$_2$O reduced the –NH$_2$ peak to 0.5 H: m/e 265.

Tricarbonyl[methyl 1,2,3,4-η-2-(N,N-dimethyl)amino-1,3-cyclobutadiene-1-carboxylate]iron (27f). To a cooled (0°), magnetically stirred solution of amino ester 27e (2.00 g, 7.55 mmol) and methyl iodide (10.2 g, 72.2 mmol) in 25 ml of anhydrous DME was added sodium hydride (3.0 g, 125 mmol, obtained by thoroughly washing 6.0 g of a 50% dispersion of NaH in mineral oil with hexane) under nitrogen. The resulting mixture was stirred under nitrogen for 3 hr at 0°. The reaction was then quenched by addition over 20 min of 25 ml of 10% acetic acid in ether via a pressure-equalizing addition funnel. After most of the solvent had been removed at room temperature under aspirator pressure, the residue was dissolved in 40 ml of ether. The ethereal solution was washed with 3 × 20 ml of water, 20 ml of saturated aqueous NaHCO$_3$, and saturated aqueous NaCl, respectively, dried (MgSO$_4$), filtered, and evaporated to give 1.68 g of a waxy solid. Chromatography of the latter on a 50 × 2 cm column of silica gel afforded crude 27f as a yellow solid on elution with 10% chloroform in carbon tetrachloride. Recrystallization from hexane at −78° yielded 1.57 g (71%) of pure 27f as orange crystals: mp 61–62°; ir (KBr) 2020, 1960, and 1694 cm^{-1}; NMR (CDCl$_3$) δ 2.79 [s, 6 H, –N(CH$_3$)$_2$], 3.65 (s, 1 H, ring proton), 3.69 (s, 3 H, –OCH$_3$), and 4.15 (s, 1 H, ring proton).

Tricarbonyl[1,2,3,4-η-2-(N,N-dimethyl)amino-1,3-cyclobutadiene-1-carboxylic acid]iron (28a). A mixture of aminoester 27f (200 mg, 0.683 mmol) and 6 ml of a methanolic solution of potassium hydroxide (~12 mmol, prepared by dissolving 2 g of 85% KOH in 2 ml of water and diluting with 20 ml of methanol) was heated at 40° for 4 hr. Water (10 ml) was added, and the methanol was evaporated under reduced pressure at <40°. The residual solution was acidified with concentrated hydrochloric acid and extracted with 3 × 20 ml of ether. The combined extracts were washed with water and saturated aqueous NaCl, respectively, dried (Na$_2$SO$_4$), filtered, and evaporated to give 188 mg (96%) of crude 28a as light yellow crystals. Recrystallization from chloroform afforded an analytical sample as yellow needles: mp 166–168°; ir (KBr), 2960, 2880, 2710, 2640, 2560, 2030, 1960, and 1658 cm^{-1}; NMR (acetone-d_6) δ 2.80 [s, 6 H, –N(CH$_3$)$_2$], 4.02 (s, 1 H, ring proton), 4.27 (s, 1 H, ring proton), and 6.64 (br s, 1 H, –CO$_2$H).

Tricarbonyl[1,2,3,4-η-2-(N,N-dimethyl)amino-1,3-cyclobutadiene-1-carbonyl chloride]iron (30b). A solution of aminoacid 28a (183 mg, 0.656 mmol) and 1 ml of oxalyl chloride in 5 ml of dry benzene was kept in the dark under nitrogen for 2.5 hr. Solvent and excess oxalyl chloride were evaporated under reduced pressure, and the brown, partly crystalline residue was extracted in portions, with hot hexane until the extract was colorless. The combined extracts were filtered and evaporated, and the residual solid was recrystallized from hexane to give 165 mg (84%) of 28b as reddish-orange crystals: mp 92–93°; ir (CHCl$_3$) 2055, 1968, and 1750 cm^{-1}; NMR (CDCl$_3$) δ 2.80 [s, 6 H, –N(CH$_3$)$_2$], 3.76 (s, 1 H, ring proton), and 4.34 (s, 1 H, ring proton); m/e 297.

Tricarbonyl[1,2,3,4-η-2-(N,N-dimethyl)amino-1,3-cyclobutadiene-1-carboxamide]iron (28c). A gentle stream of ammonia was passed over a vigorously stirred solution of acid chloride 28b (160 mg, 0.539 mmol) in 20 ml of anhydrous ether over a period of 5 min. The resulting suspension was stirred for 0.5 hr, and solvent was then evaporated with a stream of nitrogen. The residue was recrystallized from ethanol–water to give 119 mg (79%) of amide 28c as a yellow solid: mp 144–147°; ir (CHCl$_3$) 3520, 3400, 2025, 1955, 1664, 1599, and 1580 cm^{-1}; NMR (acetone-d_6/CDCl$_3$) δ 2.33 (br s, 2 H, –NH$_2$), 2.83 [s, 6 H, –N(CH$_3$)$_2$], 3.70 (s, 1 H, ring proton), and 4.14 (s, 1 H, ring proton); m/e 278.

Tricarbonyl[1,2,3,4-η-2-(N,N-dimethyl)amino-1,3-cyclobutadiene-1-carbonitrile]iron (28d). Phosphorus oxychloride (25 drops) was slowly added to a solution of carboxamide 28c in 5 ml of dry pyridine. The flask was protected with a drying tube (CaCl$_2$) and allowed to stand at room temperature for 4 hr. The mixture was then poured over 25 g of cracked ice and extracted with 5 × 10 ml of ether. The combined extracts were washed with water and saturated aqueous NaCl, respectively, dried (MgSO$_4$), and evaporated. The residue was sublimed [bath temp 50° (0.1 mmHg)], and the collected bright yellow solid was recrystallized from hexane at −20° to give 81 mg (75%) of nitrile 30d as yellow crystals: mp 68.0–68.3°; ir (KBr) 2200, 2034, and 1955 cm^{-1}; NMR (CDCl$_3$) δ 2.64 [s, 6 H, –N(CH$_3$)$_2$], 3.50 (s, 1 H, ring proton), and 4.17 (s, 1 H, ring proton); m/e 260.

Tricarbonyl[1,2,3,4-η-1,2-bis(1-hydroxy-1-methylethyl)-1,3-cy-

clobutadiene]iron (29). A 500-ml three-necked flask was equipped with a large magnetic stirring bar, a pressure-equalizing addition funnel, a gas-inlet adapter leading to a source of dry nitrogen, and a gas-outlet adapter attached to a mercury trap. All components of the apparatus were thoroughly dried before use. The flask was charged under nitrogen with 50 ml of anhydrous ether and 35 ml (74.6 mmol) of a 2.13 M solution of methyllithium in ether. The mixture was cooled to $-78°$, and a solution of diester 4 (5.00 g, 16.5 mmol) in 70 ml of anhydrous ether was added dropwise, with stirring, over 1 hr. After the mixture had stirred at $-78°$ 1 hr longer, the reaction was quenched by addition of 20 ml of saturated aqueous NH₄Cl, and the flask was then warmed to room temperature. The organic phase was separated and washed twice with water and once with saturated aqueous NaCl. The aqueous phase obtained after quenching the reaction was extracted twice with ether. All ethereal extracts were combined, dried (MgSO₄), filtered, and evaporated in vacuo to give 4.12 g (80%) of crude diol 29. Sublimation of the solid [bath temp 71° (0.03 mmHg)] and recrystallization of the sublimate from benzene afforded an analytical sample of 29 as fine white needles which decomposed on heating: mp 158-159°; ir (KBr), 3220, 2040, 1990, and 1940 cm⁻¹; NMR (acetone-d_6) δ 1.21 (s, 6 H, -CH₃), 1.62 (s, 6 H, -CH₃), 4.46 (s, 2 H, ring protons), and 4.90 (s, 2 H, -OH).

Tricarbonyl[1,2,3,4-η-1,2-di-tert-butyl-1,3-cyclobutadiene]iron (31). A 100-ml three-necked flask was fitted with a gas-inlet tube reaching to the bottom of the flask, a gas-outlet adapter attached to a drying tube (CaCl₂), and a magnetic stirring bar. All components of the apparatus were dried before use. The flask was then charged with diol 29 (1.55 g, 5.04 mmol), 4.2 g of MgSO₄, 15 ml of anhydrous benzene, and 37 ml of anhydrous pentane. The resulting suspension was placed under dry nitrogen and cooled to $-20°$. Hydrogen chloride was bubbled into the flask, with stirring, for 5 min, while the temperature was maintained at $-20°$. Stirring was continued for 10 min at $-20°$, then dry nitrogen was bubbled through the flask for 15 min, and 15 ml of dry pentane was added. The flask was attached, via a curved adapter, to a sintered glass funnel leading to a 100-ml three-necked flask equipped with a gas-outlet adapter and a magnetic stirring bar. After removal of the cooling bath, the reaction mixture was filtered into the receiving flask under a positive nitrogen pressure, the reaction flask and filtered material being rinsed with several small portions of pentane in the process. The receiving flask was then disconnected from the filtration apparatus and cooled to $-20°$. The gas-outlet adapter was connected through a drying tube to a water aspirator, and solvents were removed under reduced pressure at $-20°$. The residual light green, waxy solid was cooled to $-50°$, and the system was swept with helium while a rubber septum was placed on one neck of the flask and a Dewar condenser leading to a mercury trap was placed on another. The Dewar condenser was cooled to $-78°$, and 10-15 ml of methyl chloride was condensed in the flask with stirring. The system was placed under a static helium atmosphere, and 12 ml of a 15% solution of trimethylaluminum in benzene was added to the reaction mixture, under dry nitrogen, over 15 min. (CAUTION: trimethylaluminum reacts violently with moisture.) The reaction mixture was stirred at $-50°$ for 0.5 hr and at $-10°$ for 0.5 hr, then cooled back to $-50°$. The reaction was quenched by slow addition of 20 ml of 20% (v/v) methanol in benzene. The resulting mixture was swept with nitrogen, slowly warmed to room temperature (CAUTION: frothing), and mixed with 75 ml of water and 50 ml of ether. The aqueous phase was extracted with 15 ml of ether, and the combined ethereal extracts were washed with 3 × 35 ml of water and saturated aqueous NaCl, respectively, dried (MgSO₄), filtered, and evaporated to give 1.25 g of an orange oil which was then chromatographed on a 2 × 20 cm column of alumina. Di-tert-butyl complex 31 was eluted early with hexane as an orange, relatively nonpolar band. Evaporation afforded 1.15 g (75%) of 31 as an orange oil which turned brown on standing in light. An analytical sample was obtained by evaporative distillation [bath temp 45° (0.3 mmHg)]: ir (CCl₄) 2038 and 1960 cm⁻¹; NMR (CDCl₃) δ 1.11 [s, 18 H, -C(CH₃)₃] and 4.12 (s, 2 H, ring protons); m/e 304.

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$(HC≡CCO_2CH_3)_2Fe(CO)_3$

i

ii

iii

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Chemistry of the Sulfur–Nitrogen Bond. IX.[1] Transmission of Electronic Effects in N-Alkylidenearenesulfenamides, -sulfinamides, -sulfonamides, and Arenesulfenanilides

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Abstract: Transmission of electronic effects through the sulfur–nitrogen bond has been investigated by observing the ^{1}H NMR chemical shifts of the imidoyl and hydroxyl protons in sulfenamide derivatives 3–6 and the amino proton in arenesulfenanilides, 7. The measure of transmission of electronic effects is the Hammett ρ value. Substituent effects on the imidoyl protons were observed only in 3 and 6, suggesting that there is conjugation between the two aryl groups mediated by the S–N bond. A mechanism for transmission involving both the p and d orbitals on sulfur was suggested. In 4 and 5, transmission of electronic effects to the imidoyl protons and conjugation between the two aryl groups are destroyed. The ρ value obtained for the hydroxyl protons, which is a measure of transmission of substituent effects to the nitrogen lone pair of electrons, suggests that the nitrogen lone pair is not directly conjugated with the N-phenyl group. These results suggest that sulfur is a better transmitter of electronic effect when attached to a nitrogen which is sp^2 rather than sp^3 hybridized. The large solvent-induced modifications observed in the uv spectra of 4 and 5 were explained in terms of a shift in the phenolimine-quinoneamine equilibrium toward the quinoneamine form (16). The stability of 16 was in the order SO$_2$ > SO $\gg$ S and was attributed not to the presence of a strong intramolecular hydrogen bond, but rather to conjugation between the two aryl groups which stabilize the phenolimine form (16).

The ability of sulfur to utilize its d orbitals has been the subject of considerable controversy and discussion.[4] Studies aimed at elucidating the mechanism of transmission of electronic effects through sulfur have been used to investigate d orbital participation. Techniques used to measure transmission through sulfur include Hammett studies using NMR[5] and pK_a measurements,[6] ultraviolet spectroscopic techniques,[7] and polaragraphic methods.[8]

Studies of transmission using NMR[5b-e] and pK_a measurements[6b,e,f] all found evidence for transmission of electronic effects through sulfur with the order of transmission being S > SO$_2$ > SO. Enhanced transmission through sulfur, as measured by proton chemical shifts, was observed when sulfur was part of a conjugated system, i.e., phenyl vinyl sulfides.[5g] Investigation of the ultraviolet spectra of substituted diphenyl sulfides found evidence for[7b] and against[7a] transmission through sulfur. For the most part, the mechanism of transmission was ascribed to sulfur d orbital participation. However, Pasto et al. preferred to explain their results in terms of inductive effects.[6f]

A variety of studies have been aimed at elucidating the mechanism of transmission of electronic effects through the sulfur–nitrogen bond.[9] Raban and coworkers observed large barriers to rotation or stereomutation about the S–N bond in sulfenamides of type 1.[10] The barriers in these compounds were attributed either to p–d π bonding in which one sulfur d orbital overlaps with both the aromatic π system and the nitrogen lone pair in the ground state but not the transition state for stereomutation or to σ–π conjugation (negative hyperconjugation) in which the nitrogen lone

pair overlaps with the orbital that sulfur utilizes to bond to the aromatic π system. Both these effects are expected to increase the stability of the ground state as electronegative groups are attached to sulfur, and this is observed experimentally.[10]
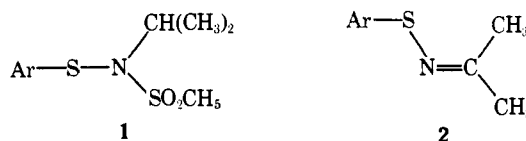
The ^{15}N–H coupling constants[11] and an X-ray structure[12] of sulfenamides suggested that nitrogen in these compounds was sp^2 hybridized. The hybridization of nitrogen in the former case was attributed to electronegativity effects and not to p–d π bonding.[11]

Rotational barriers have been observed only for sulfinamides with very electronegative groups attached to sulfur.[13-15] Directionally dependent p–d π bonds are believed to be responsible for rotational barriers in sulfonamides when electronegative groups are attached to sulfur.[16]

Although electronegative groups attached to sulfur have measurable effects on S–N torsional barriers, they have little or no effect on inversion barriers. Barriers to stereomutation in N-sulfenyl,[17,18] sulfinyl, and sulfonyl[18] aziridines are insensitive to the substituent electronic effects of groups attached to sulfur. The lower barriers in trichloromethane and trifluoromethanesulfenyl aziridines were ascribed to σ–π conjugation.[19]

Stereomutation barriers in N-isopropylidenearenesulfen-