Experimental Section

All allyl alcohols were commercially available (Chemical Samples Co.) and were used without further purification. 1-Cyclopropyl-1-propanol[21] was prepared by the reaction of cyclopropylmagnesium bromide with propionaldehyde in THF in 28% yield (bp 80-84 °C (95 Torr)). Magic acid was prepared from triply distilled FSO_3H and doubly distilled SbF_5. The 1:1 molar ratio was used in all experiments.

Preparation of Ions. A dilute (~10%) solution of the alcohol in SO_2ClF at −78 °C was added dropwise, with efficient stirring, to an approximately 1:1 (by volume) solution of FSO_3H-SbF_5 at −78 or −120 °C. To avoid the ring opening of **15** and **17** the addition had to be carried out very slowly. The solutions were transferred to precooled NMR tubes for study.

Protonated Diisopropyl Ketone. The ^1H NMR spectrum obtained of **22** in FSO_3H-SbF_5-SO_2ClF solution did not show the nonequivalence of the methyl groups observed in SO_2 solution.[22] The ^{13}C NMR spectrum obtained after protonation of **23** with magic acid in SO_2ClF (δ_C 17.0 (q), 18.2 (q), 40.3 (d), 43.0 (d), 258.4 (s)) proved the identity of **22** as a by-product of **15** when **6** was treated with magic acid.

1-Buten-3-ylium Cation (37). ^1H NMR δ 3.53 (d, $J = 6$ Hz, CH_3), 8-9 (m, allyl H, partially overlapping with H_3O^+); ^{13}C NMR δ_C 255.1 (d, $J = 168$ Hz, C3), 201.5 (t, $J = 172$ Hz, C1), 149.8 (d, $J = 177$ Hz, C2), 36.3 (q, $J = 130$ Hz, C4).

Proton Magnetic Resonance Spectra. ^1H NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer equipped with a variable temperature probe. External Me_4Si was used as a reference.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broad band decoupler and a variable temperature probe. All shifts are from external Me_4Si.

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Annelation of Tricarbonyliron Complexes of Ortho-Disubstituted [4]Annulenes. Synthesis of Tricarbonyliron Complexes of Derivatives of Bicyclo[6.2.0]decapentaene via Wittig Cycloolefination

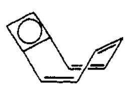
Fred A. Kaplan and Bryan W. Roberts*

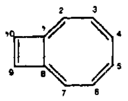
Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174. *Received February 19, 1976*

Abstract: Wittig cycloolefination of dialdehyde **4** has been studied as a route to tricarbonyliron complexes of derivatives of bicyclo[6.2.0]decapentaene. Treatment of **4** with ylides derived from bisphosphonium salts **5**, **7**, **11**, and **14** afforded benzo, furo, dihydro, and tropono derivatives **6**, **8**, **12**, and **15** in modest yields. Diels-Alder addition of *N*-phenylmaleimide to **8** led to the (syn,endo), (syn,exo), and (anti,exo) stereoisomers of **10**. All attempts to dehydrogenate **12** or to cycloolefinate **4** with the ylide derived from *cis*-2-butene-1,4-bis(triphenylphosphonium chloride) (**13**) to give parent complex **9** failed as did attempted ring expansion of tropono complex **15** with diazomethane. The enhanced intensities and bathochromic shifts observed in the electronic spectra of **6**, **8**, and stereoisomers of **10** are additional examples of the 1,2:5,6 bisannelation effect in [8]annulenes, the origin of which may be increased conjugation through flattening of the eight-membered ring. Conformational analysis of a model of the bicyclo[6.2.0]decapentaene ring system in which the four-membered ring is complexed to a tricarbonyliron group suggests a strong preference for the conformer in which the metal is on the convex face of a tub form.

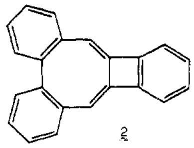
Introduction

Bicyclo[6.2.0]deca-1,3,5,7,9-pentaene, (**1**), an isomer of naphthalene and azulene, is an intriguing representative of systems comprising fused $4n$ π-electron systems. In view of the conformational flexibility of cyclooctatetraene and the contrasting conformational rigidity of cyclobutadiene, respectively, a central question concerning the nature of **1** is how ground-state geometry reflects a compromise between electronic and conformational effects. The possibilities range from tub conformer **1a**, in which [4]annulenoid antiaromatic character[1] should be maximally developed, to planar **1b**, in which some electronic stabilization associated with a peripheral complement of $4n + 2$ π-electrons[2,3] may be juxtaposed against increased bond angle strain in the eight-membered ring.[6]


1a



1b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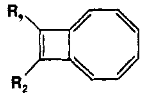


3

a, R_1 = $OC(CH_3)_3$, R_2 = Cl
b, R_1 = $OC(CH_3)_3$, R_2 = H
c) R_1 = R_2 = $OC(CH_3)_3$
d) R_1 = CH_3, R_2 = Cl
e) R_1 = CH_3, R_2 = H

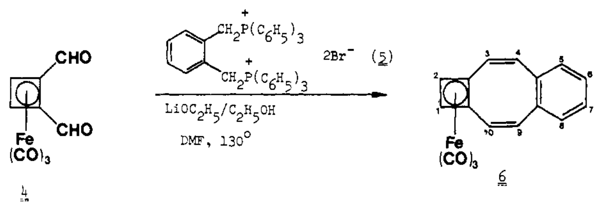
In recent years, interest in experimental study of **1** has led to syntheses of several derivatives. The first example, tribenzo derivative **2**, was prepared by Garratt et al. via Wittig cycloolefination of benzocyclobutenedione.[5] Although quite stable, the compound did not reveal either spectrally or chemically any particular stabilization deriving from $4\pi + 8\pi$ fusion and, in line with expected localization effects within a biphenyl system, appears to be nonplanar. Almost simultaneously, Schröder et al.[9] described the preparation, via annelation of cyclooctatetraene, of a series of 9- and 9,10-substituted derivatives **3a–e** which were found to be highly colored and unstable and to undergo cycloaddition with tetracyanoethylene at C(1)–C(2) and/or C(7)–C(8).[10]

Since **1** can formally be regarded as an annelated [4]annulene, we were prompted by our recent development of syntheses of a wide range of tricarbonyliron complexes of ortho-disubstituted [4]annulenes[11] to explore an alternate approach to **1**, namely fusion of an [8]annulene ring to such a complex, followed by removal of the metal carbonyl moiety. We have now completed the first stages of this program and describe in this and the following paper[12] the development of Wittig cycloolefination and ortho,ortho′ cyclobisacylation of biphenyls, respectively, as approaches to construction of tricarbonyliron complexes of derivatives of **1**.

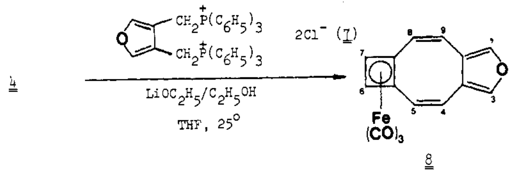
Results and Discussion

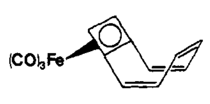
As a first approach to [8]annelation, we focused on cyclization of dialdehyde **4**[11] via Wittig cycloolefination with various 1,4-bis(phosphoranes). Earlier work had shown **4** to be an excellent substrate in the Wittig reaction for synthesis of *o*-divinyl[4]annulene complexes.[11]

When **4** was treated with *o*-xylylenebis(triphenylphosphonium bromide) (**5**) and $LiOC_2H_5$ in ethanol under mild conditions (25–80 °C), the only isolable nonpolar products were triphenylphosphine and a small amount of a mixture of at least three compounds (TLC) the mass spectra of which indicated products of 2:2 condensation.[13] However, variation of reaction parameters eventually revealed that the desired benzo complex **6**, a stable, bright-yellow crystalline material, could be obtained in 14% yield when the reaction was conducted in DMF at 130 °C with slow addition of $LiOC_2H_5$. The ^1H NMR spectrum of **6** in $CDCl_3$ exhibited a singlet at δ 3.96 for H(1) and H(2), an AB quartet at δ 5.93 and 6.51 (J_{AB} = 12.4 Hz) for H(3), H(4), H(9), and H(10), and an AA′BB′ multiplet at δ 6.92 and 7.20 ($J_{AA'}$ = 0.3, $J_{BB'}$ = 7.1, J_{AB} = 7.8, and $J_{AB'}$ = 1.4 Hz) for the four benzenoid protons. The fact that the protons in benzocyclooctatetraene corresponding to H(4), H(5), and H(6) absorb at δ 6.51, 6.91, and 7.15[15] suggests that H(4), H(9) and H(6),H(7) give rise to the low-field absorptions in each of the cited multiplets.

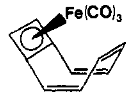


Because the efficiency of **5** as an olefination reagent suffers from a tendency to eliminate triphenylphosphine, we also examined the reaction of **4** with furan-3,4-bis(methylenetriphenylphosphonium chloride) (**7**), which has been shown to be a much more effective reagent for this type of reaction as a result of its resistance to elimination.[16] When a solution of ethanolic lithium ethoxide was slowly added to a mixture of **4** and **7** in THF at room temperature, furo derivative **8** was produced in 26% yield as a stable, yellow-orange crystalline material with no evidence of triphenylphosphine formation. The ^1H NMR spectrum of **8** in $CDCl_3$ exhibited a singlet at δ 4.35 for H(6) and H(7), an AB quartet at δ 5.37 and 6.01 for H(4), H(5), H(8), and H(9) (J_{AB} = 12.4 Hz), and a singlet at δ 7.31 for H(1) and H(3). Since the protons in other furo[8]-annulenes corresponding to H(4) and H(9) absorb at δ 6.0–6.5,[16,17] this suggests that H(4) and H(9) are the source of the low-field absorption of the AB quartet.





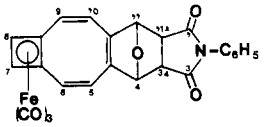
$9_{Fe\text{-}exo}$



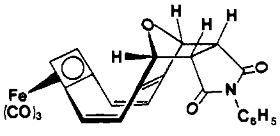
$9_{Fe\text{-}endo}$

At this point, as a prelude to further results discussed below, it is useful to consider an important probable consequence of fusing complexed [4]annulene and [8]annulene moieties. Unfortunately, definitive structural information on this type of system is not yet available, and the following qualitative analysis is necessarily tentative. Molecular models incorporating measured structural parameters of tricarbonyliron complexes of [4]annulene[18] indicate that the [8]annulene moiety exists preferentially as a tub-shaped conformer as in [8]annulene itself. However, since introduction of a tricarbonyliron group on one face of the four-membered ring of **1** destroys the degeneracy of tub forms, two distinct conformers, $9_{Fe\text{-}exo}$ and $9_{Fe\text{-}endo}$, must be considered in a conformational description of the system. The models also suggest that whereas $9_{Fe\text{-}exo}$ is sterically unexceptional, the steric interaction between iron-bound carbonyl groups and the crossring olefinic bond in $9_{Fe\text{-}endo}$ is severe. While flattening of the eight-membered ring would relieve this interaction, it can only be effected at the expense of increased bond angle strain. Consequently, we assume here as a reasonable working hypothesis a significant stereochemical bias for the exo conformer in complexes related to **9**.

The foregoing analysis was particularly useful in interpreting the course of Diels-Alder addition to **8**, which we next pursued as a method for generating formal dialkyl derivatives of **9**. When **8** was treated with *N*-phenylmaleimide in refluxing THF for 6 h, there was obtained in quantitative yield a mixture of red-orange Diels-Alder adducts which were separated by preparative TLC to give crystalline stereoisomers A (32%), B (41%), and C(27%). Spectral data fully corroborated gross structure **10** for each adduct. A partial sterochemical distinction was achieved through analysis of ^{1}H NMR spectra. The spectrum of adduct A exhibited a singlet at δ 4.57 for H(7) and H(8), atn AB quartet at δ 5.32 and 5.54 (J_{AB} = 13.9 Hz) for H(5), H(6), H(9), and H(10), a multiplet at δ 7.18–7.50 for five *N*-phenyl protons, and an AA′XX′ multiplet at δ 3.63 and 5.06 (J_{AX} = 5.4, $J_{AX'}$ = 0.20, $J_{AA'}$ = 8.1, and $J_{X'}$ = 2.2 Hz) for H(3a),H(11a) and H(4),H(11), respectively. The magnitude of J_{AX} correlates well with bridgehead-exo proton coupling measured in similar ring systems[19] and identifies A as one of the two possible endo adducts. On the basis of the aforementioned conformational argument, this must be the $\mathbf{10}_{\text{syn,endo}}$ adduct since formation of the anti,endo adduct would lead to a severe steric interaction between the concave face of the four-membered ring and the *N*-phenyl group of the incoming dienophile.

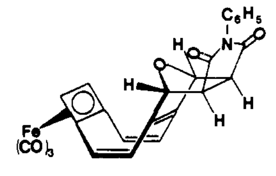


10



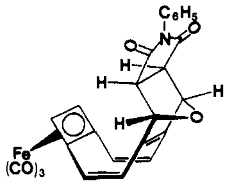
$\mathbf{10}_{\text{syn,endo}}$

(adduct A)



$\mathbf{10}_{\text{syn,exo}}$

(adduct B or C)



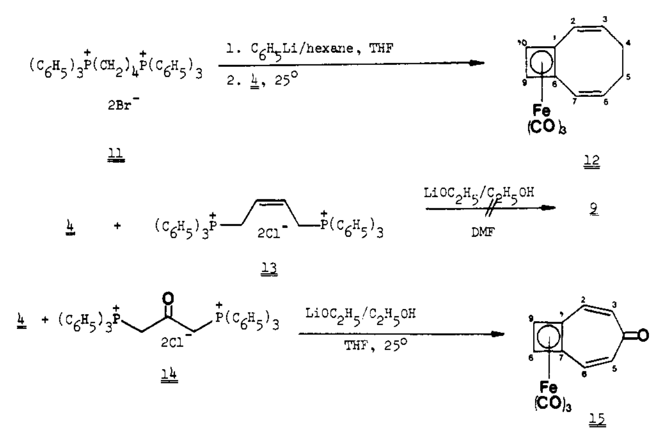
$\mathbf{10}_{\text{anti,exo}}$

(adduct C or B)

The ^{1}H NMR spectra of adducts B and C were similar to that of A except that H(3a) and H(11a) were shifted upfield ~0.5 δ and, together with H(4) and H(11), appeared as two singlets at δ ~3.1 and 5.0, respectively. The lack of observable coupling between the latter sets of protons is expected for H_{endo}–$H_{bridgehead}$ coupling and identifies B and C as adducts $\mathbf{10}_{\text{syn,exo}}$ and $\mathbf{10}_{\text{anti,exo}}$. The near identity of spectral properties, however, prevented unambiguous distinction between the two isomers.

Further experiments demonstrated the reversibility of adduct formation. When the reaction of **8** with *N*-phenylmaleimide in refluxing THF was extended to 24 h, or when adduct A was treated with an excess of *N*-phenylmaleimide in refluxing toluene for 12 h, there was complete conversion to a mixture of adducts B and C as indicated by TLC. This result is consistent with the generally lesser thermodynamic stability of endo adducts.

Attempts to prepare the unsubstituted complex **9** have thus far been unsuccessful. In one approach dihydro derivative **12** was generated in 12% yield via cycloolefination of **4** with 1,4-butanediylidenebis(triphenylphosphorane). The compound was obtained as an unstable, yellow-orange oil which exhibited, in its ^{1}H NMR spectrum ($CDCl_3$), a symmetrical multiplet at δ 2.12–2.38 for four methylene protons, a singlet at δ 4.15 for H(9) and H(10), and a multiplet at δ 5.61–6.10 for four olefinic protons. The upfield portion of the latter absorption appeared to be half of an AB quartet. This was confirmed by double irradiation experiments on the methylene protons which produced the full pattern (δ_A 5.68, δ_B 5.88, J_{AB} = 11.0 Hz). The mass spectrum of **12** was of particular interest in revealing a series of *m/e* − 2 peaks for certain fragments. Thus, in addition to peaks at *m/e* 270 (M^+), 242, 214, 186 (sequential loss of 3CO), 160 (186 − C_2H_2), 134 (160 − C_2H_2), 130 [M^+ − $Fe(CO)_3$], and 56 (Fe), prominent peaks also appeared at *m/e* 184, 158, 132, and 128. While there is the possibility that fragments at *m/e* 184 and 128 could be related to intact **1**, a more detailed labeling study would be required to establish the fate of the carbocycle during fragmentation.



Thus far, all attempts to dehydrogenate **12** with DDQ or to effect allylic bromination with NBS have failed. Evidently, allylic attack is obviated by the sensitivity of other functionality to the reaction conditions since, in every attempt, starting complex was completely consumed without concurrent formation of nonpolar reaction products.

In another approach, all attempts to cycloolefinate **4** directly to **9** with *cis*-2-butene-1,4-bis(triphenylphosphonium chloride) (**13**) under conditions used to prepare benzo derivative **6** failed completely and produced high yields of triphenylphosphine. This result is consistent with the reported behavior of a dibromide in the same series (stereochemistry unspecified),[20] but contrary to that of the *cis*-dibromide which was successfully used as a Wittig component with aldehydes.[21]

In view of the failure of direct approach to **9** via [8]annelation, we have also developed the first stage of a strategy involving [7]annelation of **4** followed by ring expansion. Toward this end, **4** was cycloolefinated with the ylide derived from 2-propanone-1,3-bis(triphenylphosphonium chloride)[20,22] (**14**) to give tropono complex **15** in 24% yield as a golden-yellow crystalline material. The ^{1}H NMR spectrum of **15** in $CDCl_3$ exhibited a singlet at δ 4.54 for H(8) and H(9) and what at first glance appeared to be an AB quartet for four protons centered at δ 6.44. Closer examination of the multiplet, however, revealed secondary splitting arising from cross-ring coupling. Full analysis as an AA′BB′ multiplet yielded parameters [δ_A 6.23 (H(2), H(6)), δ_B 6.64 (H(3), H(5)), $J_{AA'}$ ~ 0 Hz, $J_{BB'}$ = 1.9, J_{AB} = 11.8 $J_{AB'}$ ~ 0 Hz] in acceptable agreement with those of tropone itself.[23] In the only attempt thus far to expand the seven-membered ring of **15**, the compound proved inert to diazomethane and boron trifluoride etherate. However, the chemistry of **15**, has yet to be fully explored, and alternate methods may be more successful.

An interesting aspect of the annelated [8]annulenes encountered in this work is the progression of bathochromic shifts and increases in absorption intensity observed in the electronic spectra of **6**, **8**, and the stereoisomers of **10** (see Table I). This phenomenon was first observed by Sondheimer et al.[16] who noted its association with 1,2:5,6 bisannelation in [8]annulene. The present examples provide additional substantiation for the reality of the effect. Moreover, a survey of known examples reveals that the magnitude of the effect seems to be related to increasing ring contraction effects in passing from benzo

Table I. Electronic Absorption of [1,2:5,6]Bisannulated [8]Annulenes in EtOH

Compd	λ_{max}	ϵ
6	274	17 400
	304 (sh)	7 080
8	268	25 700
	319	11 000
$\mathbf{10}_{syn,exo}$	287	14 100
	316	13 500
	402 (sh)	1 740
Adduct B[a]	285	19 100
	316	17 000
	402 (sh)	1 860
Adduct C[a]	287	19 500
	315	17 400
	405 (sh)	1 780

[a] $\mathbf{10}_{syn,exo}$ or $\mathbf{10}_{anti,exo}$. See text.

through furo and bridged dihydrofuro derivatives to cyclobuteno and complexed [4]annuleno derivatives. In our view, the simplest explanation for these observations is generally increased conjugation attributable to flattening of the eight-membered ring in response to extra-annular bond angle contraction. X-ray diffraction studies should clarify this question and provide insight into the general conformational effects of annelation of [8]annulene.

Experimental Section

General. All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. Only the most characteristic and prominent peaks are cited. Nuclear magnetic resonance spectra were recorded on a Varian HA-100D spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane used as an internal standard. Complex spin-spin splitting patterns were analyzed, wherever possible, by computer simulation with the aid of LAOCN 3.[24] 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. Only the molecular ion and base peaks are cited. All tricarbonyliron complexes exhibited peaks corresponding to sequential loss of three CO units. Electronic spectra were recorded on a Cary 14 recording spectrophotometer or a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Preparative thin layer chromatography (TLC) was carried out on 20 × 20 × 0.2 cm precoated silica gel GF plates from Analtech. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Materials. THF was freshly distilled from lithium aluminum hydride. DMF was dried over potassium hydroxide and freshly distilled from barium oxide. All other materials were either used as received from commercial sources or were purified by standard methods.

Tricarbonyl[1,2,2a,10a-η-benzo[*a*]cyclobuta[*e*]cyclooctene]iron (6). A 100-ml three-necked flask equipped with a rubber septum, a magnetic stirring bar, a condenser, a 10-ml pressure-equalizing addition funnel, and a source of dry nitrogen was charged with dialdehyde **4** (250 mg, 1.0 mmol), *o*-xylylenebis(triphenylphosphonium bromide)[25] (828 mg, 1.10 mmol), and 50 ml of anhydrous DMF. The flask was placed under nitrogen, and the addition funnel was charged with 10 ml of a 0.25 M solution of ethanolic lithium ethoxide (prepared under nitrogen from 17.5 mg of freshly cut lithium). After the flask was heated to 130 °C, the lithium ethoxide solution was added slowly, with stirring, over 9 h. The reaction mixture was maintained at 130 °C 16 h longer, and then cooled to room temperature, poured into 300 ml of water, and extracted with 3 × 100 ml of hexane. The combined extracts were washed with 3 × 300 ml of water and 300 ml of saturated aqueous sodium chloride, dried ($MgSO_4$), filtered, and evaporated under aspirator pressure. The residue was chromatographed with hexane on a preparative silica gel TLC plate. Extraction of the least polar band with chloroform and evaporation of the extract in vacuo afforded 46 mg (14%) of **6** as a bright-yellow crystalline solid. Sublimation [60-65 °C (0.15 mm Hg)] and recrystallization from methanol at −20 °C provided an analytical sample: mp 78-80 °C; IR ($CHCl_3$) 3060 (w), 3005 (w), 2040 (vs), 1960 (vs, br), 1625 (w), 1488 (m), and 720 cm^{-1} (s, br); NMR, see text; electronic spectrum, see Table I; *m/e* 318 (20%), 234 (100%).

Anal. Calcd for $C_{17}H_{10}FeO_3$: C, 64.18; H, 3.17; Fe, 17.56. Found: C, 63.96; H, 3.07; Fe, 17.73.

Tricarbonyl[5a,6,7,7a-η-cyclobuta[5,6]cycloocta[1,2-*c*]furan]iron (8). A 100-ml three-necked flask equipped as described in the preceding experiment (25-ml addition funnel) was charged with dialdehyde **4** (500 mg, 2.0 mmol) and furan-3,4-bis(methylenetriphenylphosphonium chloride)[16] (1.48 g, 2.1 mmol) and placed under nitrogen. After addition of 40 ml of THF, 20 ml of a 0.25 M solution of ethanolic lithium ethoxide (prepared under nitrogen from 35 mg of freshly cut lithium) was added over 5 h. The reaction mixture was then refluxed for 3 h, cooled to room temperature, poured into 600 ml of water, and extracted with 4 × 100 ml of hexane. The combined extracts were washed with 3 × 400 ml of water and 400 ml of saturated aqueous NaCl, dried ($MgSO_4$), filtered, and evaporated under aspirator pressure. Chromatography of the residue with hexane on a ¾ × 18 in. column of silica gel afforded 160 mg (26%) of **8** as a yellow-orange crystalline solid. Recrystallization from hexane provided an analytical sample as yellow rectangular prisms: mp 130-132 °C dec; IR (CCl_4) 3015 (w), 2038 (vs), 1982 (vs, br), 1968 (vs, br), 1937 (sh), 1640 (w), and 1528 cm^{-1} (m); NMR, see text; electronic spectrum, see Table I; *m/e* 308 (41%), 224 (100%).

Anal. Calcd for $C_{15}H_8FeO_4$: C, 58.48; H, 2.62; Fe, 18.13. Found: C, 58.56; H, 2.69; Fe, 18.14.

Diels-Alder Adducts from Complex 8 and *N*-Phenylmaleimide. A solution of complex **8** (124 mg, 0.40 mmol) and *N*-phenylmaleimide (138 mg, 0.80 mmol) in 3.5 ml of anhydrous THF was prepared in a 10-ml flask fitted with a condenser and a drying tube ($CaSO_4$). The mixture was refluxed for 6 h with stirring, cooled to room temperature, and evaporated under aspirator pressure. The residue, a mixture of three adducts and unreacted *N*-phenylmaleimide, was chromatographed with benzene on four preparative silica gel TLC plates. After 8-12 developments, only the most polar band was completely resolved. Extraction of the latter with methylene chloride and evaporation of the extract in vacuo afforded 63 mg (32%) of adduct A as a red-orange crystalline solid. The two remaining product bands were resolved by careful sectioning of the TLC plates and repeated chromatography of appropriately combined bands until a satisfactory separation was achieved. Isolation of the bands of intermediate and least polarity afforded 52 mg (27%) and 80 mg (41%) of adducts B and C, respectively, both as red-orange crystalline solids.

Adduct A: Recrystallization from ether afforded an analytical sample as rectangular plates: mp 147-150 °C dec; IR ($CHCl_3$) 2050 (vs), 1970 (vs, br), 1770 (m), and 1708 cm^{-1} (vs); NMR, see text; electronic spectrum, see Table I; *m/e* 483 (0.4%), 224 (100%).

Anal. Calcd for $C_{25}H_{15}FeNO_6$: C, 62.39; H, 3.14; Fe, 2.91; N, 11.61. Found: C, 62.48; H, 3.28; Fe, 2.88; N, 11.48.

By virtue of its ^1H NMR spectrum, adduct A was assigned structure $\mathbf{10}_{syn,endo}$.

Adduct B: Recrystallization from ether afforded an analytical sample as dark-red, rectangular plates: mp 239-240 °C; IR ($CHCl_3$) 2048 (vs), 1990 (vs, br), 1972 (vs, br), 1772 (m), and 1705 cm^{-1} (s); NMR spectrum ($CDCl_3$), δ 3.06 (s, 2 H, H(3a) and H(11a)), 4.63 (s, 2 H, H(7) and H(8)), 5.01 (s, 2 H, H(4) and H(11)), 5.52 (AB quartet, 4 H, δ_A 5.42, δ_B 5.62, J_{AB} = 12.2 Hz, H(5), H(6), H(9), and H(10)), and 7.15-7.44 (m, 5 H, $-C_6H_5$); electronic spectrum, see Table I; *m/e*, same as for adduct A.

Anal. Found: C, 62.29; H, 3.08; Fe, 2.89; N, 11.45.

Adduct C: Recrystallization from ether afforded an analytical sample as dark-red, columnar prisms: mp 212-214 °C dec; IR ($CHCl_3$) 2045 (vs), 1982 (vs, br), 1770 (m), and 1708 cm^{-1} (s); NMR ($CDCl_3$) δ 3.10 (s, 2 H, H(3a) and H(11a)), 4.66 (s, 2 H, H(7) and H(8)), 5.00 (s, 2 H, H(4) and H(11)), 5.48 (AB quartet, 4 H, δ_A 5.38, δ_B 5.58, J_{AB} = 12.1 Hz, H(5), H(6), H(9), and H(10)), and 7.11-7.44 (m, 5 H, $-C_6H_5$); electronic spectrum, see Table I; *m/e*, same as for adduct A.

Anal. Found: C, 62.28; H, 3.08; Fe, 2.93; N, 11.76.

On the basis of their ^1H NMR spectra, adducts B and C were assigned structures $\mathbf{10}_{syn,exo}$ and $\mathbf{10}_{anti,exo}$ but further distinction between the two was not established.

Tricarbonyl[1,8,9,10-η-bicyclo[6.2.0]deca-1(8),2,6,9-tetraene]iron (12). A 100-ml three-necked flask equipped as described in the preparation of **8** was charged with 1,4-bis(triphenylphosphonium)butane dibromide[26] (1.48 g, 2.0 mmol) and placed under nitrogen, after which

3 ml of THF and 1.71 ml of a 2.34 M solution of *n*-butyllithium in hexane were added successively. The resulting bright-red suspension was stirred for 1 h and diluted with 50 ml of THF. A solution of dialdehyde **4** (500 mg, 2.0 mmol) in 25 ml of THF was then slowly added over 4 h. The mixture was heated at reflux for 24 h, cooled to room temperature, poured into 500 ml of water, and extracted with 4 × 100 ml of hexane. The combined extracts were washed with 3 × 500 ml of water, dried ($MgSO_4$), filtered, and evaporated under aspirator pressure at 25 °C. The residue was chromatographed with pentane on two preparative silica gel TLC plates. Extraction of the least polar band with methylene chloride and evaporation of the extract in vacuo afforded 65 mg (12%) of **12** as a yellow-orange liquid which decomposed on prolonged exposure to heat or light. An analytical sample was prepared by evaporative distillation [bath temperature 55-58 °C (0.03 mm Hg)]; IR ($CHCl_3$) 3020 (w), 2995 (w), 2940 (m), 2920 (m), 2855 (m), 2035 (vs), 1968 (vs, br), and 1632 cm^{-1} (w); NMR, see text; electronic spectrum (EtOH), max (ϵ), 226 (15 800) and 252 nm (11 500), sh (ϵ), 300 nm (2690); m/e 270 (52%), 186 (100%).

Anal. Calcd for $C_{13}H_{10}FeO_3$: C, 57.81; H, 3.73; Fe, 20.68. Found: C, 57.94; H, 3.66; Fe, 20.38.

***cis*-2-Butene-1,4-bis(triphenylphosphonium Chloride) (13).** A mixture of *cis*-1,4-dichloro-2-butene[27] (2.5 g, 0.020 mol) and triphenylphosphine (13.1 g, 0.050 mol) in 15 ml of DMF was stirred 48 h at room temperature in a 100-ml flask protected with a drying tube ($CaSO_4$). The resulting solid was filtered with suction, washed with ether, recrystallized from ether-methanol, and dried in vacuo at 100 °C to give 10.4 g (80%) of **13** as colorless crystals: mp 256-259 °C dec; NMR ($CDCl_3$) δ 4.70-4.99 (m, br, 4 H, $-CH_2-$, $J_{PH} \sim 14$ Hz), 6.26-6.44 (m, br, 2 H, $-CH{=}CH-$), and 7.61-7.90 (m, 30 H, $-C_6H_5$).

Anal. Calcd for $C_{40}H_{36}Cl_2P_2$: C, 73.96; H, 5.59; Cl, 10.92; P, 9.54. Found: C, 73.74; H, 5.70; Cl, 10.97; P, 9.36.

Attempted Preparation of Complex 9. A. From Dialdehyde 4. Cycloolefination of **4** with **13** was attempted by a procedure similar to that used in the preparation of **6**. Thus to a mixture of **4** (125 mg, 0.500 mmol) and **13** (341 mg, 0.525 mmol) in 10 ml of DMF was added 5 ml of a 0.5 M solution of ethanolic lithium ethoxide over 1 h at room temperature. The mixture was stirred 1 h longer and then heated at 125 °C for 24 h. During this period, analytical TLC indicated formation of substantial amounts of triphenylphosphine but no other nonpolar products. Workup as described for **6** and preparative TLC on silica gel afforded only triphenylphosphine.

B. From Complex 12. A mixture of complex **12** (48 mg, 0.18 mmol) and DDQ (122 mg, 0.84 mmol) in 2 ml of benzene was stirred at room temperature under nitrogen for 24 h. Monitoring of the reaction by TLC showed that **12** was gradually consumed without the coincident formation of nonpolar reaction products. Preparative TLC of the reaction mixture on silica gel with benzene afforded only dark, polar, intractable solids.

A similar result was obtained when **12** was heated with NBS and dibenzoyl peroxide in CCl_4.

Tricarbonyl[1,7,8,9-η-bicyclo[5.2.0]nona-1(7),2,5,8-tetraen-4-one]iron (15). A 100-ml three-necked flask equipped as described in the preparation of **8** was charged with dialdehyde **4** (0.500 g, 2.4 mmol), 2-propanone-1,3-bis(triphenylphosphonium chloride)[22] (1.55 g, 2.4 mmol), and 50 ml of THF and placed under nitrogen. To the flask was then added 20 ml of a 0.25 M solution of ethanolic lithium ethoxide (prepared under nitrogen from 35 mg of freshly cut lithium), with stirring, over 5 h. The resulting mixture was kept overnight at room temperature, then heated for 3 h at reflux, cooled, poured into 500 ml of water, and extracted with 3 × 100 ml of hexane. The combined extracts were washed with 3 × 300 ml of water and 300 ml of saturated aqueous NaCl, and then dried ($MgSO_4$), filtered, and evaporated under aspirator pressure. Chromatography of the residue with benzene on a ¾ × 18 in. column of silica gel afforded 162 mg of crude **15** as a yellow-orange solid, which on recrystallization from hexane gave 130 mg of golden-yellow rectangular plates, mp 149-153 °C. An analytical sample was obtained by repeated recrystallization from hexane: mp 154.5-155 °C; IR ($CHCl_3$) 3025 (w), 3000 (m), 2050 (vs), 1980 (vs, br), 1600 (vs), and 1585 cm^{-1} (s); NMR, see text; electronic spectrum (EtOH), max (ϵ), 261 (12 000) and 307 nm (6760); m/e 270 (45%), 132 (100%).

Anal. Calcd for $C_{12}H_6FeO_4$: C, 53.37; H, 2.24; Fe, 20.68. Found: C, 53.47; H, 2.15; Fe, 20.41.

When a solution of **15** in chloroform was treated with boron trifluoride etherate and excess ethereal diazomethane[28] for 2 h at 0 °C, only starting material was recovered (92%).

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