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Reactivity of (2-Alkenyl-3-pentene-1,5-diyl)iron Complexes: Preparation of Functionalized Vinylcyclopropanes and Cycloheptadienes

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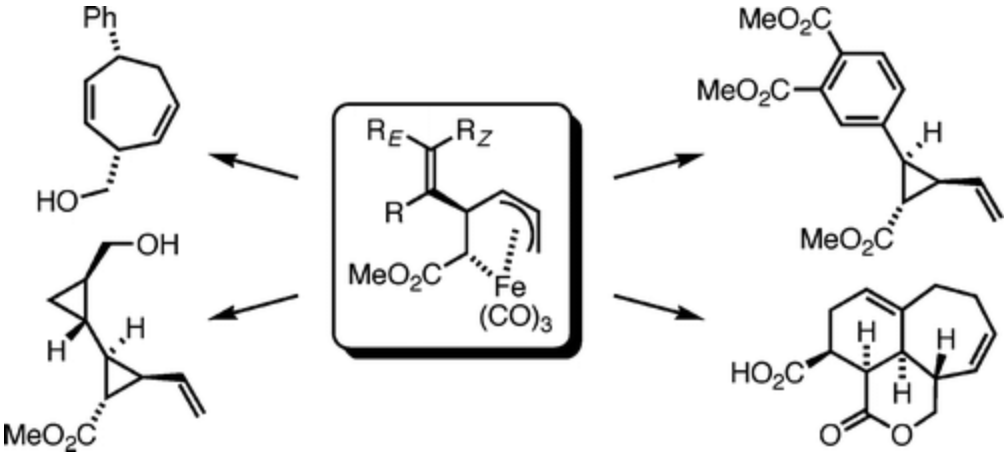
SUBJECTS:

Hydrocarbons, Addition reactions, Mixtures, Organic compounds, Oxidation

Abstract

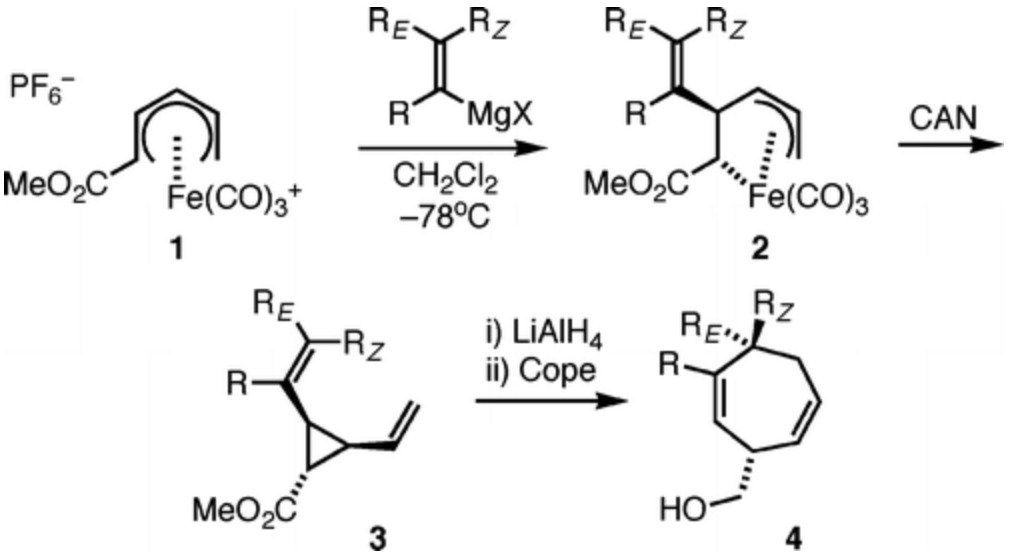


The reactivity of (2-alkenyl-3-pentene-1,5-diyl)iron complexes toward olefin metathesis, cycloaddition, and mild oxidations (MnO_2 or mCPBA) was examined. Cycloaddition reactions were observed to occur with modest diastereoselectivity (33−63% de). Decomplexation of the (3-pentenediyl) ligand may be accomplished by oxidation with either CAN or alkaline hydrogen peroxide to afford vinylcyclopropanecarboxylates or divinylcyclopropanecarboxylates. Reduction of the latter, followed by Cope rearrangement generates cycloheptadienylmethanols. These studies demonstrate that (2-alkenyl-3-pentene-1,5-diyl)iron complexes can serve as organometallic scaffolds for the preparation of a wide variety of structural motifs containing up to 5 contiguous stereocenters.

Introduction

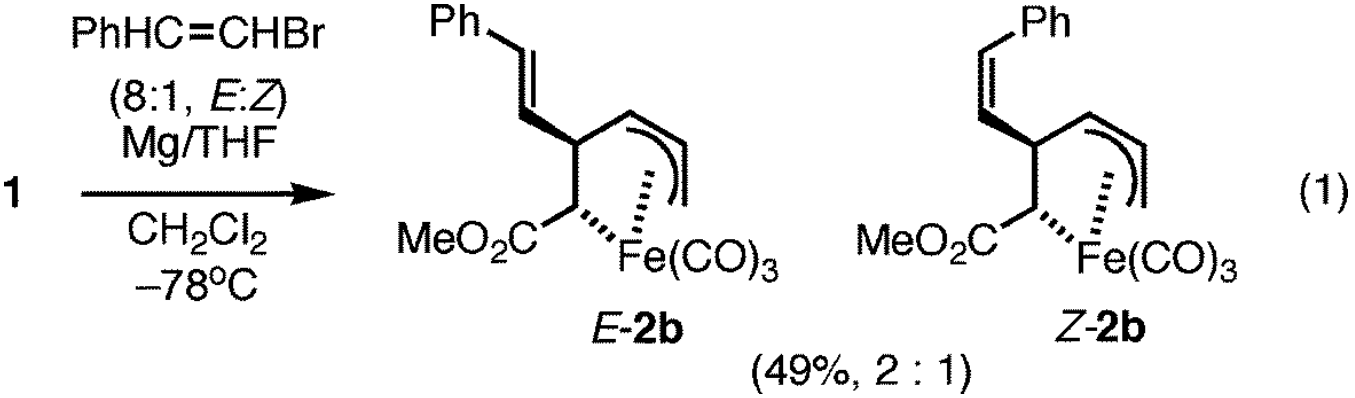
Neutral (diene)iron and cationic (dienyl)iron(1+) complexes have been utilized by numerous research groups as versatile, organometallic scaffolds for the preparation of a diverse families of natural products.(1) Liebeskind has pointed out that organometallic scaffolds "...can be viable partners in the multistep enantiocontrolled construction of complex molecules that bear multiple stereocenters if...the stoichiometric nature of the chemistry is mitigated by the use of a single metal moiety over multiple steps to impart novel reactivity...around the unsaturated ligand."(2) In particular, we and others have been interested in the reactivity of *acyclic* (pentadienyl)iron(1+) cations and have utilized these cations as stoichiometric reagents for the synthesis of polyenes,(3) cyclopropanes,(4) and cyclohexenones.(5) Recently, we have demonstrated that the addition of alkenyl Grignard reagents to (1-methoxycarbonylpentadienyl)$Fe(CO)_3^+$ (**1**) results in the formation of (2-alkenylpentenediyl)iron complexes (**2**) which upon oxidative decomplexation afford divinylcyclopropanes (**3**, Scheme 1).(6) Ester reduction and Cope rearrangement generates cycloheptadienes **(4**). In an effort to extend the utility of this organometallic scaffold, we have examined the reactivity of (2-alkenylpentenediyl)iron complexes **2** and the application of these products to the synthesis of functionalized cyclopropanes and cycloheptadienes.

Scheme 1



Results and Discussion

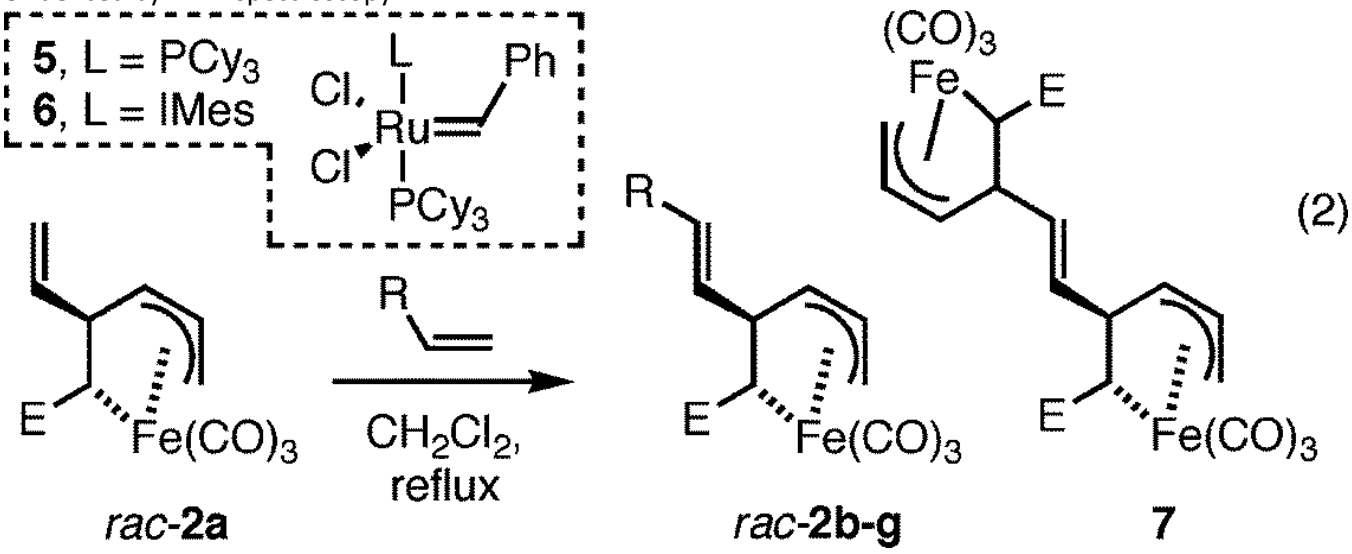
The preparation of stereodefined cycloheptadienes **4** depends on obtaining geometrically pure (2-alkenylpentenediyl)iron complexes **2**. Difficulties in attaining geometrically pure complexes **2** were encountered in certain cases, particularly for those alkenylhalides which undergo *E*/*Z* isomerization upon Grignard formation.(7) For example, reaction of the Grignard reagent generated from the commercially available β-bromostyrene (an 8:1 mixture of *E*:*Z* isomers) gave an inseparable mixture of *E*-**2b** and *Z*-**2b** (2:1, eq 1).



Olefin Metathesis of (2-Vinylpentenediyl)iron

To generate functionalized (2-alkenylpentenediyl)iron complexes with high *E*-selectivity, the cross-metathesis(8) of the parent (2-vinyl) complex *rac*-**2a** (R = R_E = R_Z = H) with a variety of olefins was examined (eq 2, Table 1.)(9) Optimization reactions conducted with styrene (entries 1−4) indicated use of 1.2−4 equiv of the olefin partner and 5 mol % of the Grubbs' first generation ruthenium carbene.(10a) Cross-metathesis of **2a** with 4-acetoxystyrene (2 equiv) afforded an inseparable mixture of *E*-**2c**, the homodimer **7**, and 4,4'-diacetoxystilbene (entry 5).(11) Cross-metathesis of **2a** with vinylcyclohexane or 6-*tert*-butyldimethylsilyloxy-1-hexene was also successful. Chromatographic separation of the product from reaction of **2a** with 6-(*tert*-butyldimethylsilyloxy)-1-hexene from the homodimer 1,10-bis(*tert*-butyldimethylsilyloxy)-5-decene was difficult; a pure sample of the corresponding alcohol **2e** could be obtained by treatment of the reaction mixture with TBAF followed by purification. Cross-metathesis of **2a** with allyltrimethylsilane could only be accomplished by using the Grubbs' second generation(10b, 10c) catalyst **6** and with longer reaction time (entry 8). The attempted cross-metathesis of **2a** with allyl alcohol or allyl acetate was unsuccessful with use of either catalysts **5** or **6**. In contrast, reaction of **2a** with 1,4-diacetoxy-2(*Z*)-butene with either **5** or **6** gave the allylic acetate complex *E*-

2g (Table 1, entries 9 and 10). While the 2-alkenylpentenediyl complex **2e** was obtained as a mixture of *E*- and *Z*-isomers (5:1), all of the other cross-metathesis products (**2b**,**c**,**d**,**f**,**g**) are only formed as the *E*-isomers as evidenced by NMR spectroscopy.



(2)

Table 1. Olefin Cross-Metathesis of *rac*-2a (E = CO_2Me)

entry	R	olefin equiv	cat.	mol % catalyst	rxn time (h)	product(s) (%)
1	Ph	1.2	**5**	1.0	72	*E*-**2b** (25) + **2a** (25)
2	Ph	1.2	**5**	5.0	3.5	*E*-**2b** (72)
3	Ph	4.0	**5**	5.1	3	*E*-**2b** (80)
4	Ph	4.0	**6**	5.1	3	*E*-**2b** (78)
5	*p*-C_6H_4OAc	2.0	**5**	5.0	2	*E*-**2c** (64)a
6	c-C_6H_{11}	4.0	**5**	5.0	7	*E*-**2d** (66)
7	$(CH_2)_4OTBS$	3.9	**5**	5.0	3	**2e** (77)b
8	CH_2SiMe_3	4.0	**6**c	5.0	20	*E*-**2f** (53)
9	d	4.0	**5**	5 + 5e	24	*E*-**2g** (61)
10	d	3.0	**6**	2 + 0.5f	26	*E*-**2g** (73)
11	no olefin	0.0	**5**	5 + 5e	20	**7** (88)

[a]The product consisted of an inseparable mixture of *E*-**2c**, **7**, and 4,4'-diacetoxystilbene (13:2:1).

[b]The reaction mixture was treated with TBAF prior to purification; the product is a 5:1 (*E*:*Z*) mixture of alcohols [R = $(CH_2)_4OH$].

[c]Use of catalyst **5** (5.0 mol %) was unsuccessful.

[d]*Z*-1,4-Diacetoxy-2-butene used as cross-metathesis component.

[e]5 mol % was initially used, and an additional 5 mol % was added after 8 h.

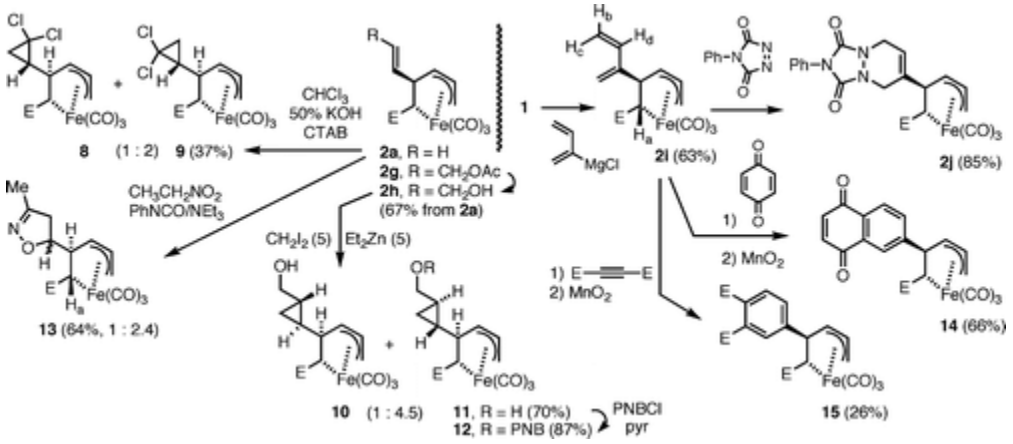
[f]2 mol % was initially used, and an additional 0.5 mol % was added after 6 h.

While the self-metathesis of **2a** was generally not observed except in the case of 4-acetoxystyrene, exposure of *rac*-**2a** to catalyst **5***in the absence of another olefin* led to the formation of homodimer **7** as a mixture of *meso*- and *dl*-diastereomers. However, to obtain good yields of the self-metathesis product, an additional 5 mol % of catalyst was required along with extended reaction time (entry 11). The *dl*-diastereomer was separable by fractional crystallization and was characterized by single-crystal X-ray diffraction analysis (see the Supporting Information). From the results outlined in Table 1, complex **2a** may be categorized as a type II olefin (slow homodimerization) in the Grubbs' model for cross-metathesis.(8c)

Cyclopropanation**(12)** and Cycloaddition Reactions of (2-Alkenylpentenediyl)iron Complexes

The attempted reaction of (2-vinylpentenediyl)iron complex **2a** with methyl diazoacetate in the presence of either $Rh_2(OAc)_4$ or $Cu(OTf)_2$ gave only recovered **2a** and a mixture of dimethyl fumarate/dimethyl maleate. In contrast, reaction of **2a** in $CHCl_3$ with 50% aqueous NaOH and cetyltrimethylammonium bromide(13) (80 h) proceeded to 83% completion to afford a separable mixture of diastereomeric complexes **8** and **9** (1:2) along with unreacted starting material **2a** (Scheme 2.) The major product **9** was separable from **8**/**2a** by column chromatography; pure **8** could be separated from **2a** by recrystallization. Base saponification of **2g** proceeded exclusively at the allylic acetate to afford the allylic alcohol **2h**. Notably, the methoxycarbonyl group of **2a** or **2g** is resistant to base hydrolysis. Simmons−Smith cyclopropanation(14) of **2h** gave a separable mixture of diastereomeric cyclopropanes **10** and **11** (1: 4.5).

Scheme 2



Scheme 2. [a]

*Scheme a*E = CO_2Me.

The relative configurations of the minor product from dichlorocyclopropanation **8** and the major product from the Simmons−Smith cyclopropanation **11** were elucidated by X-ray diffraction analysis; in the latter case this was for the *p*-nitrobenzoate ester **12** of **11**.(4b) The stereoselectivity for these cyclopropanations may be rationalized on the basis of the approach of the dichlorocarbene or Zn-carbenoid species on the less hindered face of the olefin (Figure 1.)(15) Notably, the X-ray crystal structure of the parent 2-alkenylpentenediyl complex **2a** has the vinyl group (C11−C12) aligned nearly parallel to the C6−C7 bond (dihedral angle = 0.5°).(6b)

Figure 1

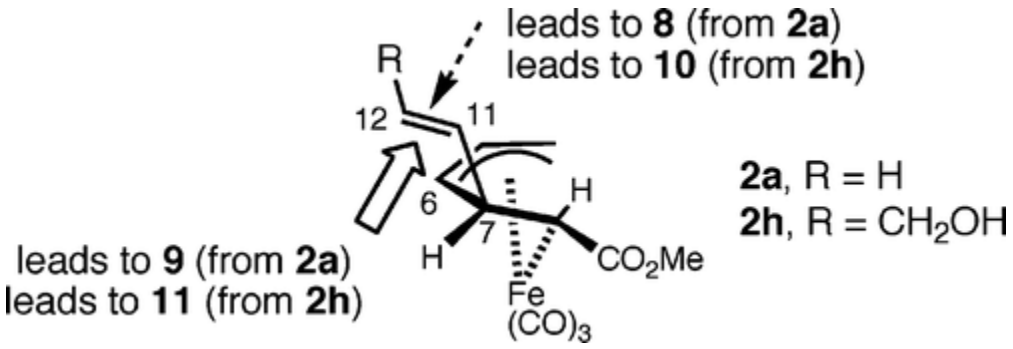


Figure 1. Structure of **2a**,**h** (E = CO_2Me).

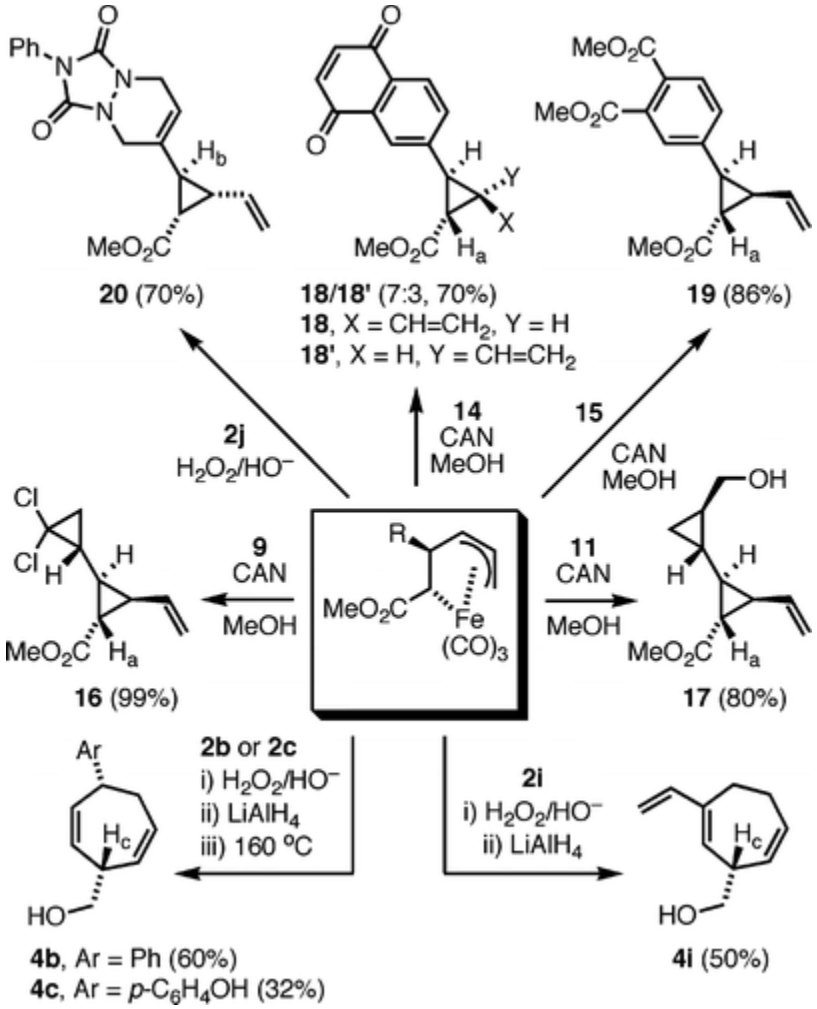
Reaction of **2a** with the nitrile oxide generated from nitroethane(16) gave an inseparable mixture of isoxazolines **13**, in a 1:2.4 ratio as determined by integration of the signals for H_a. While it was not possible to unambiguously assign the relative configuration of the major and minor isoxazolines, we note that the diastereoselectivity observed in this 1,3-dipolar cycloaddition reaction was similar to that observed for the above cyclopropanations.(17)

Reaction of the Grignard reagent derived from 2-chloro-1,3-butadiene with **1** gave the [2-(1′-methylene-2-propenyl)-3-pentene-1,5-diyl]iron complex **2i** (Scheme 2). The structural assignment for **2i** was based on its NMR spectral data. In particular, the signals at δ 0.28 (d, *J* = 8.7 Hz), 5.02 (d, *J* = 11.2 Hz), 5.29 (d, *J* = 17.9 Hz), and 6.09 (dd, *J* = 11.2, 17.9 Hz) ppm in the ^{1}H NMR spectrum correspond to H_a, H_b, H_c, and H_d, respectively, while the signals at δ 204.2, 210.3, and 210.9 ppm in the ^{13}C NMR spectrum correspond to the three iron carbonyls.(4d) Attack of the Grignard reagent on the face opposite to iron was tentatively assigned by analogy to the reaction of **1** with vinyl Grignard;(6b) this tentative assignment was eventually corroborated by the X-ray crystal structure of the cycloadduct (vide infra). Cycloaddition of **2i** with a slight excess of 4-phenyl-1,2,4-triazoline-3,5-dione [PTAD] proceeded rapidly to afford the adduct **2j**. The disappearance of 4 signals in the olefinic region of **2i** and the appearance of two 2H multiplets (δ 3.88−3.94 and 4.08−4.13 ppm) are consistent with the formation of **2j**. Reaction of **2i** with *p*-benzoquinone, at elevated temperature, gave an adduct that was labile toward air oxidation. For this reason, the crude product was treated with excess MnO_2 to yield the 7′-substituted naphthoquinone **14**, in good isolated yield (Scheme 2). In a similar fashion, reaction of **2i** with dimethyl acetylenedicarboxylate followed by oxidation with MnO_2 gave the (2-aryl-3-pentene-1,5-diyl)iron complex **15**, albeit in attenuated yield. Notably, the (pentenediyl)iron moiety present in **14** and **15** is stable under these oxidation conditions. The structures of **14** and **15** were assigned on the basis of their NMR spectral data and by single-crystal X-ray diffraction analysis in the case of **15** (see the Supporting Information).(18)

Preparation of Cyclopropanes and Cycloheptadienes by Decomplexation

Oxidative decomplexation of (pentenediyl)iron complexes **9**, **11**, and **15** with cerium ammonium nitrate [CAN] in methanol gave the vinylcyclopropanecarboxylates **16**, **17**, and **19** as single products (Scheme 3), while the decomplexation of **14** gave an inseparable mixture of stereoisomeric cyclopropanes **18**/**18′** (ca. 7:3). The relative configurations about the trisubstituted cyclopropane ring in **16**−**19** were assigned on the basis of their NMR spectral data. In particular, the signal for H_a of each appears as a doublet of doublets (*J* ≈ 4.5−5.0 Hz), and the small couplings are characteristic of trans-couplings in cyclopropane rings.(19) This stereochemistry is consistent with that for an oxidatively induced reductive elimination of the (pentenediyl)iron complex (i.e., retention of configuration at the carbon atoms undergoing reductive elimination).(4d) The stereochemistry of **18′** was assigned by comparison of its ^{1}H NMR spectral data with that obtained for **20** (vide infra). While attempted oxidative decomplexation of **2j** with CAN/methanol gave a complex mixture of unidentifiable products, treatment of **2j** with alkaline hydrogen peroxide(6) successfully gave vinylcyclopropane **20** (Scheme 3). The structure of this trisubstituted cyclopropane was assigned as having a cis-relationship between the vinyl and ester substituents on the basis of its ^{1}H NMR spectral data (C_6D_6). In particular, the signal for H_b appears at δ 2.02 ppm (br t, *J* = 5.7 Hz) and the signal for the vinyl proton (H_d) is relatively downfield (δ 6.02 ppm). These chemical shifts/couplings are similar to those of a trisubstituted cyclopropane previously characterized in our laboratory.(4d) The stereochemistry of **20** represents an oxidatively induced reductive elimination of **2j** with apparent inversion of configuration at C3. Inversion at C3 in the oxidative decomplexation of (pentenediyl)iron complexes has been previously observed, and is attributed to a π−σ−π rearrangement of iron about the pentenediyl ligand under oxidative decarbonylation reaction conditions.(4d, 6)

Scheme 3



Oxidative decomplexation of **2b**, **2c**, or **2i** with alkaline hydrogen peroxide gave the corresponding divinylcyclopropanecarboxylates which upon reduction ($LiAlH_4$) and subsequent Cope rearrangement gave the substituted 2,6-cycloheptadienylmethanols **4b**, **4c**, or **4i**, respectively (Scheme 3). While **4b** and **4c** were both quite stable, concentrated solutions of **4i** were somewhat unstable leading to a complex mixture of unidentified products. The stability of **4i** could be greatly enhanced by the addition of a small amount of hydroquinone. The structural assignment for these products is based on comparison of their NMR spectral data to that of similar compounds.(6) In particular, the signals at ca. δ 3.4−3.5 (m, 1H) and 3.7 (apparent d, *J* = 6.2 Hz, 2H) ppm correspond to H_c and C*H*$_2$OH. Both **4b** and **4c** are formed as single stereoisomers as a result of the preferential preparation of the *E*-alkenyl pentenediyl in the olefin cross-metathesis reaction (vide supra).

The presence of a conjugated diene in **4i** gave rise to the possibility of further cycloaddition reactions.(20) Thus, reaction of freshly prepared **4i** with maleic anhydride or PTAD gave the tricyclic products **21** and **22** as single products, respectively (Scheme 4). The relative configuration of the 4 contiguous stereocenters present in structure of **21** was assigned on the basis of its X-ray crystal structure (Figure 2) while the stereochemistry of **22** was assigned on the basis of its spectral data. In particular an amide N−H stretch (3432 cm^{-1}) was observed in the IR spectrum of **22**, while the signal at δ 4.57 ppm (d, *J* = 9.9 Hz) in the ^{1}H NMR spectrum is assigned to H_b; the large coupling indicates a trans-relationship to H_a.

Scheme 4

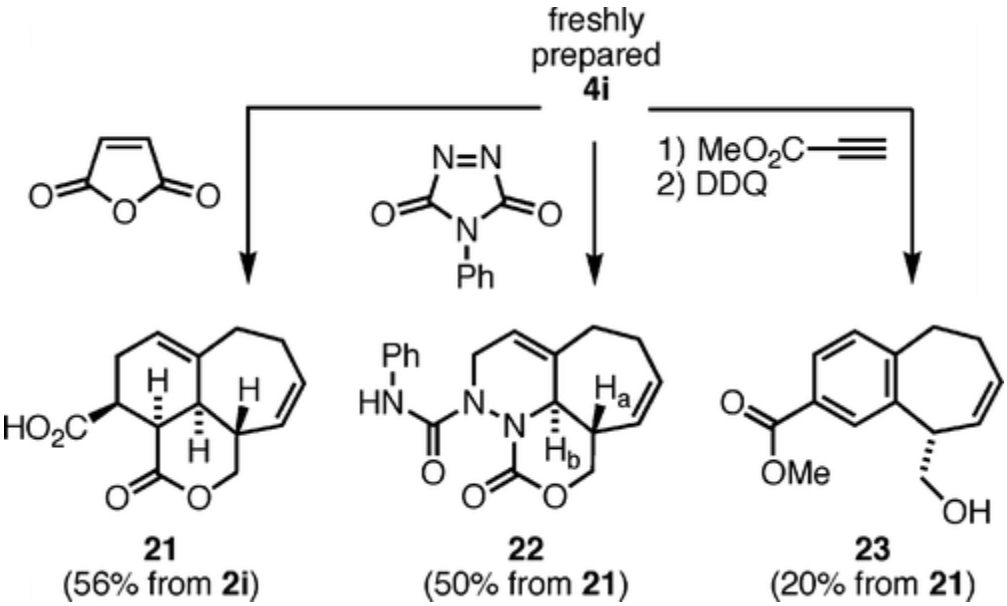


Figure 2

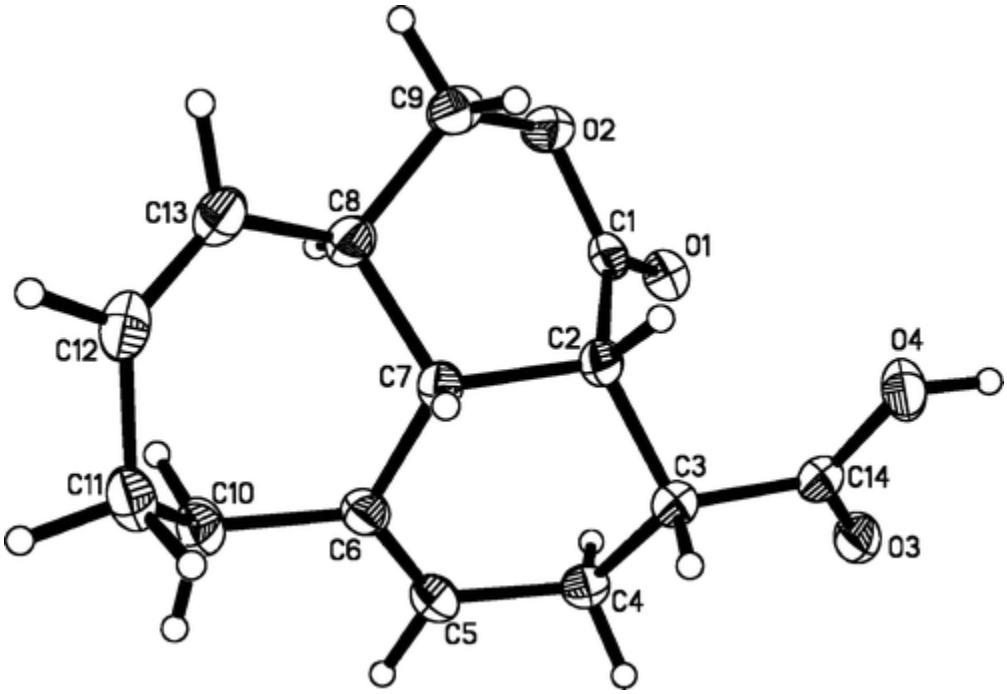


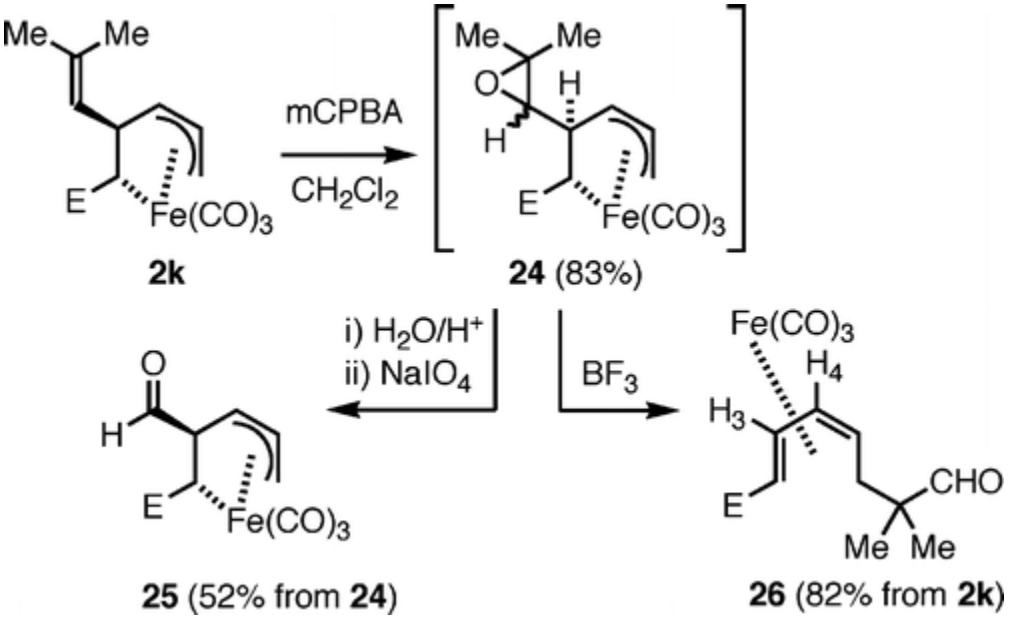
Figure 2. Molecular structure of **21**.

The cycloadduct products **21** and **22** arise via approach of the dienophile (maleic anhydride or PTAD), in an *endo* orientation, on the face of **2i** opposite to the hydroxymethylene substituent. Subsequent intramolecular reaction of the hydroxymethyl group generates the lactone ring present in **21** or the cyclic carbamate present in **22**. Reaction of **2i** with methyl propiolate, followed by oxidation of the product with DDQ, gave the aryl ester **23**; the substitution pattern about the aromatic ring was assigned on the basis of the couplings between the aromatic protons of this product.

Epoxidation of a (2-Alkenylpentenediyl)iron

Reaction of [2-(2′-methyl-1-propenyl)-3-pentene-1,5-diyl]iron (**2k**) (prepared from the reaction of **1** with 2-methyl-1-propenyl Grignard)(6) with *m*-CPBA/CH_2Cl_2 gave a crude mixture of diastereomeric epoxides **24** that was not fully characterized (Scheme 5). Acidic hydrolysis of this crude mixture followed by periodate cleavage gave the 2-formylpentenediyl complex **25**. Alternatively, treatment of the crude mixture of epoxides **24** with boron trifluoride-etherate led to the rearranged 8-oxo-2*E*,4*Z*-octadienoate complex **26**. The structure of **26** was assigned on the basis of its NMR spectral data. In particular singlets at δ 0.51 (6H), 3.34 (3H), and 8.88 (1H) ppm correspond to the geminal dimethyls, the methyl ester, and the neopentyl aldehyde, while the signals at δ 4.49 (ddd, *J* = 0.6, 5.4, 7.8 Hz) and 5.72 (ddd, *J* = 1.2, 5.1, 8.4 Hz) ppm are characteristic of H3 and H4 of a 2*E*,4*Z*-dienoate complex.(21)

Scheme 5

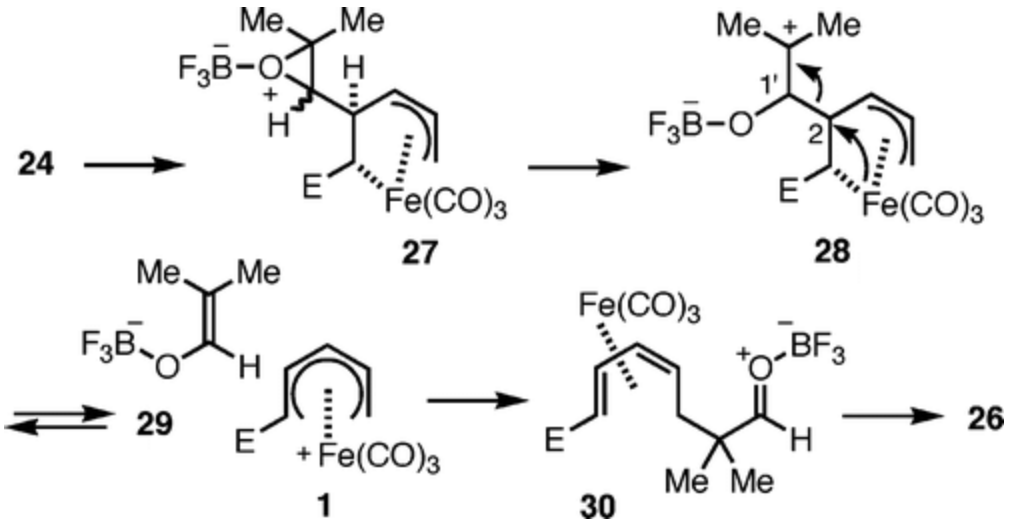


Scheme 5. [a]

Scheme aE = CO_2Me.

The rearrangement of **24** to **26** is rationalized in the following fashion: Coordination of the BF_3 to the oxirane, as in **27**, leads to activation of the C−O bond to generate **28** (Scheme 6). Electron donation from iron influences ionization of the C2−C1′ bond in **28** to generate the BF_3-enolate **29** and the (pentadienyl)iron cation **1**. These can recombine either by attack at C2 to give **28** or by attack at C5 of cation **1** to generate the BF_3-aldehyde complex **30**. Disengagement of the Lewis acid gives **26**. This Lewis acid catalyzed equilibration between **24** and **26** proceeds to the thermodynamically more stable diene complex **26**. We have previously observed reversible nucleophilic attack on (pentadienyl)iron cations.(17d, 22)

Scheme 6



Scheme 6. [a]

*Scheme a*E = CO_2Me.

In summary, the (3-pentene-1,5-diyl)iron moiety is stable toward a variety of reaction conditions including olefin metathesis, strong hydroxide, Simmons−Smith cyclopropanation, nitrile oxide generation, cycloaddition, and mild oxidations (MnO_2 or mCPBA). Cycloadditions proceed with modest diastereoselectivity (33−63% de). Decomplexation of the (pentenediyl) ligand may be accomplished by oxidation with either CAN or alkaline hydrogen peroxide to afford vinylcyclopropanecarboxylates or divinylcyclopropanecarboxylates. Reduction of the latter, followed by Cope rearrangement generates cycloheptadienylmethanols. These studies demonstrate that (2-alkenyl-3-pentene-1,5-diyl)iron complexes can serve as organometallic scaffolds for the preparation of a wide variety of structural motifs containing up to 5 contiguous stereocenters (cf. **17**).

Experimental Section

Reaction of 1 with Grignard Prepared from *trans*-1-Bromopropene (*E*-2b/*Z*-2b)

To a solution of **1** (820 mg, 2.00 mmol) in anhydrous CH_2Cl_2 (20 mL) at −70 °C was added a solution of the Grignard reagent freshly prepared from β-bromopropene and Mg ribbon in THF. After being stirred at −70 °C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl and warmed to room temperature. The mixture was poured onto water, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered through a short bed of SiO_2, and concentrated. Immediate column chromatography (SiO_2, hexanes−ethyl acetate = 40:1 → 30:1 gradient) afforded a yellow-orange semisolid (362 mg, 49%). This was determined to be a mixture of *E*-**2b** and *Z*-**2b** (2:1) by ^{1}H NMR spectroscopy; *E*-**2b** was identified by comparison to its NMR spectral data with that of an independently prepared sample (vide infra). *Z*-**2b**: ^{1}H NMR (300 MHz, $CDCl_3$, partial) δ 0.18 (d, *J* = 7.5 Hz, 1H), 2.56 (dd, *J* = 2.4, 11.4 Hz, 1H), 3.66 (s, 3H), 4.22 (q, *J* = 8.1 Hz, 1H), 4.42−4.53 (m, 2H), 5.06 (dd, *J* = 9.2, 11.4 Hz, 1H), 6.10 (d, *J* = 11.4 Hz, 1H), 7.15−7.29 (m, 5H); ^{13}C NMR (partial, 75 MHz, $CDCl_3$) δ 12.6, 37.3, 51.5, 54.3, 64.5, 96.8.

Cross-Metathesis of 2a with Styrene (*E*-2b)

To a stirring solution of **2a**(6) (0.659 g, 2.26 mmol) and styrene (1.05 mL, 99%, 9.07 mmol) in CH_2Cl_2 (6.0 mL, passed through a plug of SiO_2) in a flame-dried reflux apparatus was added Grubbs' second generation catalyst (0.097 g, 0.11 mmol, 5.1 mol %). The solution was heated to reflux under static nitrogen. After the 3 h, the solution was cooled and concentrated. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 30:1) gave *E*-**2b** as an orange crystalline solid (0.648 g, 78%). Use of Grubbs' first

generation catalyst (5.1 mol %) also gave *E*-**2b** (80%). *E*-**2b**: mp 76−80 °C; IR (KBr) 3022, 2955, 2069, 2010, 1976, 1687, 1439, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.31 (d, *J* = 8.6 Hz, 1H), 2.48 (ddd, *J* = 0.9, 2.3, 12.0 Hz, 1H), 3.60 (ddd, *J* = 1.4, 2.5, 8.4 Hz, 1H), 3.71 (s, 3H), 3.89−3.98 (m, 1H), 4.52−4.60 (m, 1H), 4.71 (dddd, *J* = 0.6, 6.7, 8.4, 12.3 Hz, 1H), 5.72 (dd, *J* = 6.2, 15.8 Hz, 1H), 6.16 (dd, *J* = 1.8, 15.8 Hz, 1H), 7.15−7.29 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 41.5, 51.7, 54.6, 63.9, 98.2, 126.2, 127.4, 128.0, 128.6, 133.2, 136.9, 180.5, 203.7, 210.3, 210.6. Anal. Calcd for $C_{18}H_{16}FeO_5$: C, 58.72; H, 4.38. Found: C, 59.06; H, 4.67.

Cross-Metathesis of 2a with 4-Acetoxystyrene (*E*-2c)

To a stirring solution of **2a** (1.35 g, 4.62 mmol) and 4-acetoxystyrene (1.42 mL, 9.25 mmol) in CH_2Cl_2 (20 mL, passed through a plug of SiO_2) in a flame-dried reflux apparatus was added Grubbs' first generation catalyst (190 mg, 0.23 mmol, 5 mol %). The solution was heated to reflux under static nitrogen. After 3 h, the solution was cooled and concentrated. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 4:1) gave an orange solid (1.64 g). Analysis by ^1H NMR spectroscopy indicated this to be a mixture of *E*-**2c**, **7**, and 4,4′-diacetoxystilbene (13:2:1 ratio, ca. 64% yield of *E*-**2c**). The self-metathesis dimer **7** was identified by comparison of its spectral data with an independently prepared sample (vide infra), and 4,4′-diacetoxystilbene was identified by comparison to the literature spectral data.(11)*E*-**2c**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (d, *J* = 8.4 Hz, 1H), 2.25 (s, 3H), 2.42 (dd, *J* = 2.1, 12.3 Hz, 1H), 3.56 (br d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 3.89 (br q, *J* = 7.5 Hz, 1H), 4.51 (br t, *J* = 7.5 Hz, 1H), 4.62−4.74 (m, 1H), 5.64 (dd, *J* = 6.0, 16.2 Hz, 1H), 6.10 (d, *J* = 16.2 Hz, 1H), 6.95 and 7.22 (AA′BB′, J_{AB} = 8.7 Hz, 4H total). FAB-HRMS *m*/*z* 427.0473 (calcd for $C_{20}H_{19}O_7Fe$ ($M + H^+$) *m*/*z* 427.0480).

Cross-Metathesis of 2a with *cis*-1,4-Diacetoxy-2-butene (*E*-2g)

To a stirring solution of **2a** (3.20 g, 11.0 mmol) and *cis*-1,4-diacetoxy-2-butene (5.23 mL, 33.0 mmol) in CH_2Cl_2 (32 mL, passed through a plug of SiO_2) in a flame-dried reflux apparatus was added Grubbs' second generation catalyst (232 mg, 0.273 mmol, 2 mol %). The solution was heated to reflux under static nitrogen. After 6 h, the solution was cooled and additional Grubbs' second generation catalyst (46 mg, 0.5 mol %) was added. The solution was heated to reflux under static nitrogen for an additional 20 h. The solution was cooled and concentrated. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 92:8) gave *E*-**2g** as an orange syrup (2.92 g, 73%). *E*-**2g**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, *J* = 8.4 Hz, 1H), 2.01 (s, 3H), 2.36 (dd, *J* = 1.8, 12.3 Hz, 1H), 3.54 (br d, *J* = 8.4 Hz, 1H), 3.65 (s, 3H), 3.71−3.80 (m, 1H), 4.38 (d, *J* = 4.2 Hz, 2H), 4.43 (t, *J* = 7.2 Hz, 1H), 4.63 (td, *J* = 7.6, 11.7 Hz, 1H), 5.25 (dd, *J* = 4.8, 15.6 Hz, 1H), 5.31 (td, *J* = 5.4, 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6, 21.2, 40.8, 51.7, 54.4, 63.3, 64.6, 98.3, 122.5, 138.2, 170.9, 180.5, 203.9, 210.4, 210.8. Anal. Calcd for $C_{15}H_{16}O_7Fe$: C, 49.48; H, 4.43. Found: C, 49.63; H, 4.40.

General Procedure for Small-Scale Cross-Metathesis

A Schlenk tube fitted with a Teflon vacuum stopcock and microstirbar was flame heated under vacuum and refilled with nitrogen. Complex **2a** (100−200 mg), olefin (1−4 equiv with respect to complex **2a**, see Table 1), and dry CH_2Cl_2 (3 mL) were added followed by Grubb's first generation catalyst (5 mol % relative to complex **2a**). Three-fold evacuation−N_2 refills were carried out and the solution was heated at reflux. The reaction progress was monitored by TLC or ^1H NMR, using periodic aliquots.

Cross-Metathesis of 2a with Vinylcyclohexane (*E*-2d)

The reaction of **2a** (200 mg, 0.685 mmol) and vinylcyclohexane (375 µL, 2.74 mmol) was carried out by the general procedure above. After heating at reflux for 3 h, the solution was cooled and concentrated. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 97:3) gave *E*-**2d** as a crystalline orange solid (168 mg, 66%). A sample for elemental analysis was purified by vacuum sublimation: 60 °C/0.2 mmHg. *E*-**2d**: mp 68−70 °C; IR (film) 2066, 2002, 1691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.20 (d, *J* = 8.4 Hz, 1H), 0.88−1.03 (m, 2H), 1.06−1.29 (m, 3H), 1.55−1.85 (m, 6H), 2.40 (dd, *J* = 2.1, 12.3 Hz, 1H), 3.53 (br d, *J* = 8.4 Hz, 1H),

3.63−3.71 (s and m, 4H total), 4.48 (br t, *J* = 7.1 Hz, 1H), 4.61 (td, *J* = 7.5, 12.0 Hz, 1H), 4.90 (dd, *J* = 6.0, 15.6 Hz, 1H), 5.16 (ddd, *J* = 1.2, 6.7, 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5, 26.2, 26.3, 33.1, 40.4, 41.2, 51.6, 54.2, 65.0, 97.8, 131.2, 135.2, 180.8, 204.2, 210.8, 211.2. Anal. Calcd for $C_{18}H_{22}O_5Fe$: C, 57.77; H, 5.92. Found: C, 57.82; H, 6.00.

Cross-Metathesis of 2a with 6-*tert*-Butyldimethylsilyloxy-1-hexene Followed by Deprotection (*E*-2e)

The reaction of **2a** (100 mg, 0.342 mmol) and 6-*tert*-butyldimethylsilyloxy-1-hexene (294 mg, 1.34 mmol) was carried out by the general procedure above. After 3 h, the solution was cooled and concentrated. Column chromatography (SiO_2, hexanes−ethyl acetate = 97:3) of the residue gave an orange oil (148 mg) that was contaminated with 1,10-bis(*tert*-butyldimethylsilyloxy)-5-decene. The oil was dissolved in dry THF and a solution of TBAF in THF (1.76 mL, 1.0 M, 1.76 mmol) was added. The solution was stirred at room temperature for 30 min, and then water (5 mL) was added and the mixture was extracted several times with CH_2Cl_2. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification of residue by column chromatography (SiO_2, petroleum ether−ethyl acetate = 7:3) gave **2e** as a yellow oil (96.0 mg, 77%). This was determined to be mixture of *E*- and *Z*-isomers (5:1) on the basis of ^{1}H NMR integration. Anal. Calcd for $C_{16}H_{20}O_6Fe$: C, 52.77; H, 5.54. Found: C, 52.86; H, 5.68. ***E*-2e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (d, *J* = 8.7 Hz, 1H), 1.25−1.60 (m, 7H), 1.88 (q, *J* = 6.9 Hz, 2H), 2.37 (dd, *J* = 1.8, 12.0 Hz, 1H), 3.51 (br d, *J* = 8.4 Hz, 1H), 3.58−3.69 (s and m, 4H total), 4.44 (br t, *J* = 7.2 Hz, 1H), 4.58 (td, *J* = 7.6, 12.0 Hz, 1H), 4.93 (dd, *J* = 6.3, 15.6 Hz, 1H), 5.18 (td, *J* = 6.9, 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5, 25.5, 32.0, 41.3, 51.6, 54.3, 64.8, 98.0, 128.8, 134.2, 204.1, 210.7, 211.1. ***Z*-2e**: ^{1}H NMR (partial, 300 MHz, $CDCl_3$) δ 0.06 (d, *J* = 8.1 Hz, 1H), 2.49 (dd, *J* = 2.2, 11.8 Hz, 1H), 4.86 (br t, *J* = 9.6 Hz, 1H).

Cross- Metathesis of 2a with Allyl Trimethylsilane (*E*-2f)

The reaction of **2a** (50 mg, 0.17 mmol) and allyl trimethysilane (109 µL, 0.68 mmol) was carried out by the general procedure above, using Grubbs' second generation catalyst. After being heated at reflux for 20 h, the solution was cooled and concentrated, and the residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 97:3) to give ***E*-2f** as an orange oil (34 mg, 53%). ***E*-2f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.04 (s, 9H), 0.17 (d, *J* = 8.4 Hz, 1H), 1.30 (d, *J* = 8.1 Hz, 2H), 2.40 (dd, *J* = 1.8, 12.0 Hz, 1H), 3.54 (td, *J* = 1.8, 8.1 Hz, 1H), 3.68 (s and m, 4H total), 4.49 (t, *J* = 7.2 Hz, 1H), 4.62 (td, *J* = 7.6, 11.7 Hz, 1H), 4.83 (dd, *J* = 6.5, 15.1 Hz, 1H), 5.21 (dtd, *J* = 1.4, 8.1, 15.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.75, 13.2, 22.5, 41.6, 51.6, 54.2, 65.4, 97.8, 125.5, 132.5, 180.8, 204.2, 210.8, 211.2. FAB-HRMS *m*/*z* 379.0668 (calcd for $C_{16}H_{23}O_5SiFe$ ($M + H^+$) *m*/*z* 379.0664).

Self-Metathesis of *rac*-2a (7)

A Schlenk tube fitted with a Teflon vacuum stopcock and microstirbar was flame heated under vacuum and refilled with nitrogen. Complex **2a** (100 mg, 0.342 mmol) and dry CH_2Cl_2 (3.0 mL) were added followed by Grubbs' first generation catalyst (14 mg, 0.017 mmol, 5 mol%). The solution was heated to reflux under static nitrogen. After 8 h, the solution was cooled and additional Grubbs' first generation catalyst (14 mg) was added. The solution was heated to reflux under static nitrogen for an additional 12 h. The solution was cooled and concentrated. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 9:1) gave **7** as an orange solid (84 mg, 0.30 mmol, 88%). Recrystallization from CH_2Cl_2 gave ***dl*-7**·CH_2Cl_2 as orange crystals, which were suitable for X-ray diffraction analysis. **7**: mp 150−155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (d, *J* = 8.4 Hz, 2H), 2.45 (dd, *J* = 2.0, 12.4 Hz, 2H), 3.48 (td, *J* = 1.7, 8.4 Hz, 2H), 3.57 (br t, *J* = 7.4 Hz, 2H), 3.64 (s, 6H), 4.36 (t, *J* = 7.2 Hz, 2H), 4.56 (td, *J* = 7.6, 12.3 Hz, 2H), 4.73 (d, *J* = 2.4 Hz, 2H). Anal. Calcd for $C_{22}H_{20}O_{10}Fe_2$: C, 47.52; H, 3.68. Found: C, 47.72; H, 3.69.

Dichlorocyclopropanation of 2a (8/9)

To a solution of **2a** (1.83 g, 6.27 mmol) and cetyltrimethylammonium bromide (27.6 mg, 0.076 mmol) in $CHCl_3$ (40 mL) was added 50% aqueous NaOH. The biphasic mixture was vigorously stirred at room temperature for 80 h. After this time, the mixture was diluted with water (50 mL) then extracted several times with CH_2Cl_2, and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Analysis of the crude product by ^{1}H NMR spectroscopy indicated this to be a mixture of **8**, **9**, and unreacted **2a** (ca. 3:6:2 by integration). Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 24:1) gave a mixture of **8** and **2a** as an orange solid, followed by **9** as a yellow solid (863 mg, 2.30 mmol, 37%). Recrystallization of the mixture of **8** and **2a** from CH_2Cl_2/pentane gave crystals of **8** which were suitable for X-ray diffraction analysis.

8: mp 130−132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, *J* = 9.0 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 1H), 1.18 (dt, *J* = 7.5, 10.2 Hz, 1H), 1.37 (dd, *J* = 6.3, 9.9 Hz, 1H), 2.50−2.61 (m, 1H), 2.89−2.99 (m, 1H), 3.65−3.72 (m and s, 4H total), 4.65−4.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 26.3, 38.8, 40.8, 51.7, 54.9, 59.7, 64.6, 98.3, 180.4, 203.6, 210.3, 210.6. Anal. Calcd for $C_{13}H_{12}O_5Cl_2Fe$: C, 41.64; H, 3.22. Found: C, 41.69; H, 3.23.

9: mp 66−68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (d, *J* = 6.0 Hz, 1H), 1.08−1.21 (m, 2H), 1.47 (dd, *J* = 5.4, 7.5 Hz, 1H), 2.49 (dd, *J* = 1.9, 9.1 Hz, 1H), 3.03 (q, *J* = 6.0 Hz, 1H), 3.60 (br d, *J* = 6.6 Hz, 1H), 3.67 (s, 3H), 4.36 (br t, *J* = 5.7 Hz, 1H), 4.62 (ddd, *J* = 5.7, 6.6, 9.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 26.4, 38.6, 39.8, 51.6, 53.3, 54.2, 61.5, 97.9, 180.0, 203.9, 210.1, 210.6.

Pentenediyl Allylic Alcohol (*E*-2h)

To asolution of **2a** (3.50 g, 12.0 mmol) and (*Z*)-1,4-diacetoxy-2-butene (7.6 mL, 47 mmol) in anhydrous CH_2Cl_2 (35 mL) was added Grubbs' second generation catalyst (0.20 g; 2 mol%). The reaction vessel was evacuated and refilled with nitrogen three times and then heated at reflux for 16 h under nitrogen atmosphere. After this time additional Grubbs' second generation catalyst (0.054 g; 0.05 mol%) was added and the reaction mixture was heated at reflux for an additional 8 h. After this time, the solution was cooled to room temperature and the solvent and excess (*Z*)-1,4-diacetoxy-2-butene were evaporated in vacuo. The crude residue was dissolved in methanol (77 mL) and an aqueous solution of LiOH (1.51 g, 62.9 mmol, in 77 mL of water) was added. The reaction was stirred at room temperature. After 30 min, the saponification was judged to be complete by TLC and the solvents were evaporated. The residue was dissolved in CH_2Cl_2 (100 mL) and neutralized by the addition of 10% aqueous HCl. The organic layer was separated and the aqueous layer was extracted several times with CH_2Cl_2. The combined organic layers were washed with water, followed by brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 3:2) provided **2h** as an orange gum (2.58 g, 67%). *E*-**2h**: IR (CH_2Cl_2) 3449, 2065, 2002, 1698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (d, *J* = 8.7 Hz, 1H), 2.41 (dd, *J* = 2.2, 12.1 Hz, 1H), 3.57 (td, *J* = 1.5, 8.4 Hz, 1H), 3.68 (s, 3H), 3.76 (br q, *J* = 7.1 Hz, 1H), 4.01 (d, *J* = 5.7 Hz, 2H), 4.48 (t, *J* = 7.5 Hz, 1H), 4.65 (ddd, *J* = 7.1, 8.1, 12.1 Hz, 1H), 5.24 (dd, *J* = 5.7, 15.6 Hz, 1H), 5.31 (dtd, *J* = 1.5, 5.5, 15.5 Hz, 1H), the signal for OH was not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.9, 40.8, 51.6, 54.4, 63.0, 63.8, 98.2, 127.6, 135.1, 180.7, 203.9, 210.5, 210.8. FAB-HRMS *m*/*z* 323.0217 (calcd for $C_{13}H_{15}O_6Fe$ (M + H$^+$) *m*/*z* 323.0218).

Simmons−Smith Cyclopropanation of 2h (10/11)

To a solution of **2h** (4.31 g, 13.4 mmol) in anhydrous CH_2Cl_2 at −20 °C was added dropwise a solution of diethylzinc in hexanes (68.4 mL, 1.0 M, 68.4 mmol) followed by diiodomethane (5.4 mL, 67 mmol). The reaction mixture was gradually warmed to room temperature over a 4 h period. Saturated aqueous NH_4Cl (70 mL) was added and the mixture was diluted with ether (400 mL) and 10% aqueous HCl (70 mL). The layers were separated and the organic layer was washed with saturated aqueous Na_2SO_3, followed by saturated aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated under reduced pressure. Analysis of the crude product

by ^{1}H NMR spectroscopy indicated this to be a mixture of **10** and **11** (1:4.5 by integration of the signals for H_a). Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 13:7) gave **10** as an orange oil followed by **11** as a red syrup (3.15 g, 70%).

10: IR (CH_2Cl_2) 3447, 2062, 1997, 1698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, *J* = 8.7 Hz, 1H), 0.21−0.35 (m, 2H), 0.38−0.46 (m, 1H), 0.80 (m, 1H), 1.70 (br s, OH), 2.40−2.55 (m, 2H), 3.29 (d, *J* = 6.3, 2H), 3.60 (d, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 4.40−4.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 13.9, 19.2, 26.0, 43.0, 51.6, 54.5, 65.8, 66.4, 97.9, 181.0, 204.1, 210.7, 211.0. FAB-HRMS *m/z* 337.0363 (calcd for $C_{14}H_{17}O_6Fe$ (M + ^{H}+) *m/z* 337.0375).

11: IR (CH_2Cl_2) 3447, 2067, 2002, 1698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, *J* = 9.0 Hz, 1H), 0.19−0.30 (m, 3H), 0.90−1.00 (m, 1H), 1.60 (br s, OH), 2.49 (m and dd, *J* = 2.4, 11.4 Hz, 2H total), 3.30 (dd, *J* = 7.2, 11.2 Hz, 1H), 3.41 (dd, *J* = 6.6, 11.1 Hz, 1H), 3.61 (d, *J* = 8.7 Hz, 1H), 3.67 (s, 3H), 4.50 (t, *J* = 7.2 Hz, 1H), 4.59 (td, *J* = 7.7, 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 14.0, 20.4, 26.2, 42.9, 51.6, 54.6, 65.8, 66.6, 97.9, 181.0, 204.0, 210.6. FAB-HRMS *m/z* 337.0380 (calcd for $C_{14}H_{17}O_6Fe$ (M + H^+) *m/z* 337.0375).

p-Nitrobenzoate Ester (12)

A solution of *p*-nitrobenzoic acid (30 mg, 0.18 mmol) in $SOCl_2$ (0.5 mL) was heated at reflux for 1 h and then the excess $SOCl_2$ was removed under reduced pressure. The resulting *p*-nitrobenzoyl chloride was dissolved in pyridine (0.5 mL) and added to a solution of **11** (20 mg, 0.059 mmol) in pyridine (0.5 mL). The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with water (1 mL) and extracted several times with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification of the residue by column chromatography (SiO_2, hexanes−ethyl acetate = 9:1) gave an orange gum (25 mg, 87%). Recrystallization from CH_2Cl_2 gave **12** as an orange solid. **12**: mp 139−145 °C; ^{1}H NMR ($CDCl_3$) δ 0.19 (d, *J* = 9.0 Hz, 1H), 0.39−0.47 (m, 2H), 0.85−0.95 (m, 1H), 1.08−1.17 (m, 1H), 2.49 (m and dd, *J* = 2.2, 10.9 Hz, 2H total), 3.59 (dd, *J* = 2.4, 10.2 Hz, 1H), 3.68 (s, 3H), 4.06 (dd, *J* = 7.8, 11.4 Hz, 1H), 4.20 (dd, *J* = 7.1, 11.4 Hz, 1H), 4.42−4.55 (m, 2H), 8.25 and 8.32 (AA'BB', J_{AB} = 9.3 Hz, 4H total); ^{13}C NMR ($CDCl_3$) δ 9.2, 13.8, 16.5, 26.6, 31.2, 42.8, 51.7, 54.5, 65.2, 69.6, 97.8, 123.8, 130.9, 164.9, 180.9, 203.9, 207.2, 210.6, 210.9. FAB-HRMS *m/z* 486.0508 (calcd for $C_{21}H_{20}NO_9Fe$ (M + H^+) *m/z* 486.0487).

Tricarbonyl[4,5-dihydro-3-methyl-2-[(1,3,4,5-η)-3-pentene-1,5-diyl]isoxazole]iron (13)

To a solution of **2a** (292 mg, 1.00 mmol), nitroethane (143 µL, 1.99 mmol), and phenylisocyanate (218 µL) in benzene (2 mL) at room temperature was added triethylamine (278 µL, 2.00 mmol). The reaction mixture was stirred for 48 h, diluted with water, and extracted several times with ether. The combined extracts were washed with water, followed by brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 3:1) to afford **13** as a yellow oil (224 mg, 64%). This was determined to be a mixture of two diastereomers (2.4:1) by integration of the signals at δ 0.08 and 0.34 ppm. **13**: ^{1}H NMR ($CDCl_3$) δ 0.08 (d, *J* = 9.0 Hz, 0.7H), 0.34 (d, *J* = 9.3 Hz, 0.3H), 1.87 (s, 0.9H), 1.94 (s, 2.1 H), 2.30−2.42 (m, 1H), 2.59−2.81 (m, 2H), 3.23 (q, *J* = 8.4 Hz) and 3.23−3.30 (m, 1H total), 3.60−3.70 (m and s, 4H total), 3.87 (ddd, *J* = 6.8, 8.7, 10.0 Hz, 0.7 H), 4.06−4.16 (m, 0.3H), 4.35 (br t, *J* = 7.2 Hz, 0.3H), 4.51 (br t, *J* = 7.2 Hz, 0.7 H), 4.59−4.70 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 8.6 [8.7], 13.3 [13.2], 40.5 [40.8], 43.4 [43.9], 51.7, 55.3 [55.9], 63.0 [62.5], 84.6 [83.0], 99.0 [99.6], 180.6, 203.7, 210.2, 210.5 (diastereomeric signals in square brackets).

Tricarbonyl[2-(1'-methylene-2-propenyl)-3-pentene-1,5-diyl]iron (2i)

In a round-bottomed flask, under N_2, was added magnesium turnings (1.15 g, 47.3 mmol), 1,2-dibromoethane (0.4 mL), and THF (0.7 mL), followed by a solution of $ZnCl_2$ (0.21 g 1.5 mmol) in THF (17 mL). To this mixture was added dropwise, over a 40 min period, a solution of 2-chloro-1,3-butadiene (5.68 g, 50% in toluene, 32.1 mmol) and 1,2-dibromoethane (0.7 mL) in THF (10 mL), during which time the reaction temperature was kept between

25 and 35 °C. After the addition, the reaction mixture was heated at reflux for 1 h and then cooled to room temperature. To a solution of **1** (6.56 g, 16.0 mmol) in anhydrous CH_2Cl_2, at −70 °C under N_2, was added the above prepared solution of 2-(1,3-butadienyl)magnesium chloride in THF. The reaction mixture was stirred for 1 h, and then quenched with saturated aqueous NH_4Cl (240 mL) and warmed to room temperature. The layers were separated and the aqueous layer extracted several times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered through a short bed of SiO_2, and concentrated. Immediate column chromatography (SiO_2, hexane−ethyl acetate = 35:1) afforded **2i** as an orange oil that crystallizes upon cooling (3.20 g, 63%). **2i**: mp 51−53 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (d, *J* = 8.7 Hz, 1H), 2.34 (dd, *J* = 1.9, 12.3 Hz, 1H), 3.50 (br d, *J* = 6.9 Hz, 1H), 3.72 (s, 3H), 4.03 (br t, *J* = 8.1 Hz, 1H), 4.50 (t, *J* = 7.2 Hz, 1H), 4.78 (ddd, *J* = 6.9, 7.8, 11.7 Hz, 1H), 4.89 (s, 1H), 4.98 (s, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 5.29 (d, *J* = 17.9 Hz, 1H), 6.09 (dd, *J* = 11.2, 17.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.1, 40.5, 51.6, 54.1, 63.3, 98.1, 114.4, 115.3, 136.1, 148.7, 181.0, 204.2, 210.3, 210.9. Anal. Calcd for $C_{14}H_{14}FeO_5 \cdot {}^2/_3H_2O$: C, 51.89; H, 4.56 Found: C, 51.96; H, 4.45.

Cycloaddition of 2i with PTAD (2j)

To a solution of **2i** (160 mg, 0.503 mmol) dissolved in a minimal amount of ethyl acetate/hexane (1:1, ca. 0.3 mL) was added dropwise a solution of 4-phenyl-1,2,4-triazoline-3,5-dione [PTAD] dissolved in a minimal amount of ethyl acetate/hexane until the red color of the PTAD persisted. The mixture was stirred for an additional 30 min. Gaseous 1,3-butadiene was bubbled through the reaction mixture to react with the excess PTAD. The reaction mixture was evaporated and the residue was purified by column chromatography (SiO_2, hexane−ethyl acetate = 1:1) to give **2j** as a light yellow solid (210 mg, 85%). **2j**: mp 170−172 °C; IR (KBr) 2925, 2064, 1990, 1772, 1712, 1503, 1418, 1169, 766, 611 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.32 (d, *J* = 8.4 Hz, 1H), 2.35 (dd, *J* = 2.3, 12.1 Hz, 1H), 3.62 (br d, *J* = 8.1 Hz, 1H), 3.73 (s, 3H), 3.88−3.94 (m, 2H), 4.08−4.13 (m, 3H), 4.43 (t, *J* = 7.2 Hz, 1H), 4.83 (ddd, *J* = 7.1, 8.1, 12.0 Hz, 1H), 5.52 (br s, 1H), 7.36−7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 42.3, 43.4, 52.0, 54.8, 60.9, 99.2, 114.0, 125.6, 128.4, 129.4, 131.3, 135.9, 152.4, 152.6, 180.3, 203.6, 209.9, 210.2. FAB-HRMS *m*/*z* 500.0723 (calcd for $C_{22}H_{19}N_3O_7FeLi$ (M + Li$^+$) *m*/*z* 500.0732).

Cycloaddition of 2i with *p*-Benzoquinone and Oxidation (14)

A solution of **2i** (0.96 g, 3.0 mmol) and *p*-benzoquinone (648 mg, 6.00 mmol) in CH_2Cl_2 (5 mL) was heated at reflux, under N_2, for 4 h. The reaction mixture evaporated and the residue was purified by column chromatography (SiO_2, hexane−ethyl acetate = 3:1). The unstable product was dissolved in dioxane (30 mL) and activated manganese dioxide (4.0 g, 46 mmol) was added. The mixture was stirred under nitrogen for 3 h. The reaction mixture was filtered, the filtrate was evaporated, and the residue was purified by flash chromatography (SiO_2, hexane−ethyl acetate = 5:1) to afford **14** as a yellow solid (0.84 g, 66%). **14**: mp 125−129 °C; IR (KBr) 2925, 2069, 2005, 1994, 1686, 1668, 1596, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.50 (d, *J* = 8.8 Hz, 1H), 2.23 (br d, *J* = 11.6 Hz, 1H), 3.60 (br d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 4.61 (t, *J* = 7.6 Hz, 1H), 4.75 (t, *J* = 7.0 Hz, 1H), 4.90−4.98 (m, 1H), 6.95 (s, 2H), 7.40 (br d, *J* = 7.6 Hz, 1H), 7.78 (br s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.7, 43.2, 52.0, 55.0, 62.3, 99.1, 123.1, 127.1, 130.2, 131.3, 132.0, 138.7, 138.9, 152.2, 180.5, 184.9, 185.2, 203.6, 210.0, 210.3. Anal. Calcd for $C_{20}H_{14}O_7Fe$: C, 56.90; H, 3.31. Found: C, 57.00; H, 3.53.

Cycloaddition of 2i with DMAD and Oxidation (15)

A solution of **2i** (322 mg, 1.01 mmol) in dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol) was stirred at room temperature for 24 h. After evaporation of the DMAD, the residue was purified by column chromatography (SiO_2, hexane−ethyl acetate = 5:1) to give a yellow solid. The solid (345 mg, 0.75 mmol) thus obtained was dissolved in dioxane (20 mL) and activated manganese dioxide (1.30 g, 14.9 mmol) was added. The mixture was stirred at room temperature for 3 h and filtered, tehn the filtrate was evaporated. The residue was purified by flash chromatography (SiO_2, hexane−ethyl acetate = 3:1) to give **15** as a light yellow solid (120 mg, 26%). **15**: mp 102−104 °C; IR (KBr) 2925, 2068, 2005, 1988, 1738, 1722, 1686, 1436, 1289, 1165 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 0.46 (d, *J* = 9.2 Hz, 1H), 2.24 (dd, *J* = 2.0, 12.4 Hz, 1H), 3.58 (ddd, *J* = 1.4, 2.6, 8.6 Hz, 1H), 3.76, 3.88 and 3.90 (3 × s, 9H total), 4.53 (t, *J* = 8.0 Hz, 1H), 4.70 (t, *J* = 7.2 Hz, 1H), 4.88 (ddd, *J* = 6.8, 8.4, 12.0 Hz, 1H), 7.19 (d, *J* = 1.2, 7.6 Hz, 1H), 7.32 (d, *J* = 1.2 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.8, 42.9, 51.9, 52.8, 52.9, 55.0, 62.5, 99.0, 125.7, 128.1, 129.1, 129.6, 133.0, 149.5, 167.6, 168.7, 180.6, 203.7, 210.1, 210.4. Anal. Calcd for $C_{20}H_{18}O_9Fe$: C, 52.42; H, 3.96. Found: C, 52.42; H, 4.02.

(1*S**,2*R**,3*R**,4*R**)-5,5-Dichloro-1-methoxycarbonyl-2-vinylbicyclopropane (16)

To a solution of **9** (400 mg, 1.07 mmol) in methanol (13 mL) at room temperature was added portionwise ceric ammonium nitrate (4.1 g, 7.5 mmol) over a period of 10 min. The mixture was stirred for an additional 10 min and then poured into brine and extracted several times with ethyl acetate. The combined organic extracts were washed with water, followed by saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated under reduced pressure to give **16** as a colorless syrup (250 mg, 1.06 mmol, 99%). **16**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28−1.42 (m, 2H), 1.52 (td, *J* = 4.5, 8,1 Hz, 1H), 1.70 (dd, *J* = 6.1, 9.4 Hz, 1H), 1.90 (t, *J* = 4.8 Hz, 1H), 2.26 (br dt, *J* = 4.8, 8.1 Hz, 1H), 3.74 (s, 3H), 5.19 (br d, *J* = 10.2 Hz, 1H), 5.29 (br d, *J* = 17.1 Hz, 1H), 5.63 (ddd, *J* = 8.1, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 27.5, 28.3, 29.0, 29.8, 52.2, 60.7, 118.4, 133.6, 173.0. Anal. Calcd for $C_{10}H_{12}O_2Cl_2 \cdot 0.3H_2O$: C, 49.94; H, 5.28. Found: C, 49.90; H, 5.16.

(1*S**,2*R**,3*R**,4*S**,6*R**)-6-Hydroxymethyl-1-methyloxycarbonyl-2-vinylbicyclopropane (17)

The decomplexation of **11** (690 mg, 2.05 mmol) with CAN (12.8 mmol) in methanol (24 mL) was carried out in a fashion similar to the decomplexation of **9**, to give **17** as a colorless syrup (324 mg, 1.65 mmol, 80%). **17**: IR (CH_2Cl_2) 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.49−0.62 (m, 3H), 1.03−1.14 (m, 1H), 1.45 (td, *J* = 4.8, 9.3 Hz, 1H), 1.58 (br s, OH), 1.61 (t, *J* = 4.5 Hz, 1H), 2.18 (dt, *J* = 4.4, 9.0 Hz, 1H), 3.40 (dd, *J* = 6.9, 11.1 Hz, 1H), 3.50 (dd, *J* = 6.6, 11.4 Hz, 1H), 3.67 (s, 3H), 5.15 (br d, *J* = 10.5 Hz, 1H), 5.27 (br d, *J* = 17.4 Hz, 1H), 5.65 (ddd, *J* = 9.0, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.6, 14.8, 21.0, 27.0, 30.8, 31.5, 52.1, 66.6, 117.4, 134.7, 173.7. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.21. Found: C, 66.94; H, 8.22.

6-[(2′-Methoxycarbonyl-3′-ethenyl)cyclopropyl]-1,4-naphthalenedione (18)

The decomplexation of **14** (18 mg, 0.043 mmol) with CAN (0.3 mmol) in absolute methanol (8 mL) and CH_2Cl_2 (2 mL) was carried out in a fashion similar to the decomplexation of **9**. Purification of the product by column chromatography (SiO_2, hexane−ethyl acetate = 5:1) gave an inseparable mixture of cis-/trans-diastereomers **18/18′** as a yellow solid (8.0 mg, 66%). **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (dd, *J* = 4.8, 5.2 Hz, 1H), 2.56−2.60 (m, 1H), 3.04 (dd, *J* = 5.6, 9.6 Hz, 1H), 3.78 (s, 3H), 5.05 (dd, *J* = 2.0, 10.4 Hz, 1H), 5.13 (dd, *J* = 8.4, 10.0 Hz, 1H), 5.26−5.32 (m, 1H), 6.98 (s, 2H), 7.39 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 32.0, 32.8, 52.5, 118.7, 126.6, 126.8, 130.7, 131.9, 133.0, 134.7, 138.7, 139.0, 143.2, 172.8, 184.9, 185.4. FAB-HRMS *m*/*z* 282.0880 (calcd for $C_{17}H_{14}O_4$ *m*/*z* 282.0892).

Methyl 3-[3′,4′-Bis(methoxycarbonyl)phenyl]-2-vinylcyclopropanecarboxylate (19)

The decomplexation of **15** (20 mg, 0.044 mmol) with CAN (0.41 mmol) in absolute methanol (2 mL) was carried out in a fashion similar to the decomplexation of **9**, to give **19** as a volatile yellow oil (12 mg, 86%). ^{1}H NMR ($CDCl_3$) δ 2.27 (t, *J* = 5.0 Hz, 1H), 2.47−2.54 (m, 1H), 2.97 (dd, *J* = 5.4, 9.4 Hz, 1H), 3.76, 3.90 and 3.92 (3 × s, 9H total), 5.02−5.13 (m, 2H), 5.23−5.29 (m, 1H), 7.37 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.9, 31.5, 32.6, 52.4, 52.9, 53.0, 118.3, 129.3, 129.4, 130.2, 131.8, 132.6, 133.4, 140.1, 167.9, 168.3, 172.9. FAB-HRMS *m*/*z* 319.1193 (calcd for $C_{17}H_{19}O_6$ (M + H$^+$) *m*/*z* 319.1181).

Decomplexation of 2j (20)

To a stirring solution of pentadienediyl iron complex **2j** (100 mg, 0.203 mmol) in absolute methanol (5 mL) and 30% aqueous H_2O_2 (1.5 mL) at −78 °C under nitrogen was added a methanolic solution of NaOH (50 mg, 1.2 mmol, dissolved in a minimal volume of methanol). The mixture was stirred at −78 °C for 30 min, the cold bath was removed, and the mixture was stirred for an additional 30 min while warming to room temperature. The brown mixture was diluted with water (10 mL) and extracted several times with ether. The combined extracts were washed with water, followed by brine, dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (SiO_2, hexane−ethyl acetate = 1:1) gave **20** as light yellow solid (35 mg, 70%). **20**: ^{1}H NMR (300 MHz, $CDCl_3$ δ 2.10−2.16 (m, 2H), 2.32 (br t, *J* = 5.7 Hz, 1H), 3.73 (s, 3H), 4.08−4.11 (m, 2H), 4.15−4.19 (m, 2H), 5.15 (dd, *J* = 1.5, 10.8 Hz, 1H), 5.31 (dd, *J* = 1.5, 17.4 Hz, 1H), 5.71−5.76 (m, 1H), 5.77−5.90 (m, 1H), 7.35−7.56 (m, 5H); ^{1}H NMR (300 MHz, C_6D_6) δ 1.55 (dt, *J* = 6.6, 9.3 Hz, 1H), 1.75 (dd, *J* = 6.0, 9.0 Hz, 1H), 2.02 (br t, *J* = 5.7 Hz, 1H), 3.34 (s, 3H), 3.34−3.38 (m, 2H), 3.48−3.52 (m, 2H), 4.58−4.64 (m, 1H), 5.05 (dd, *J* = 1.5, 10.2 Hz, 1H), 5.12 (dd, *J* = 1.5, 17.4 Hz, 1H), 6.02 (ddd, *J* = 9.3, 10.2, 17.1 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 2H) [one signal at ca. δ 7.16 was obscured by the signal for solvent]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1, 30.5, 31.3, 43.4, 45.2, 52.3, 116.1, 117.9, 125.6, 128.4, 129.4, 130.8, 131.2, 133.4, 152.5, 152.6, 170.9. FAB-HRMS *m*/*z* 354.1461 (calcd for $C_{19}H_{20}N_3O_4$ (M + H^+) *m*/*z* 354.1454).

cis-(4-Phenylcyclohepta-2,6-dienyl)methanol (4b)

To a stirring solution of complex *E*-**2b** (0.621 g, 1.69 mmol) in absolute methanol (34 mL) and 30% aqueous H_2O_2 (10.1 mL) at −78 °C under nitrogen was added a methanolic solution of NaOH (0.41 g, 10 mmol NaOH dissolved in a minimal volume of methanol). The mixture was stirred at −78 °C for 30 min, the cold bath was removed, and the mixture was stirred for an additional 30 min while warming to room temperature. During this period, the reaction bubbled and became brown. The muddy mixture was diluted with water (50 mL) and extracted with ether (4 × 50 mL). The combined extracts were washed with water (3 × 50 mL) followed by brine (50 mL). The organic phase was dried ($MgSO_4$) and concentrated to give an amorphous solid. The crude mixture was dissolved in ether (2 mL) and added dropwise to a stirring solution of $LiAlH_4$ in ether (2.9 mL, 1.0 M, 2.9 mmol) in a flame-dried round-bottomed flask at 0 °C. Additional ether (2 mL) was used to ensure a quantitative transfer. The solution was stirred at 0 °C for 3 h, then quenched with saturated aqueous sodium bicarbonate (5 mL). After warming to room temperature and being diluted with 2 M NaOH (10 mL), the mixture was extracted with ether (4 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated to a turbid oil. The oil was dissolved in mesitylene (8.5 mL) and heated under nitrogen in a sealed reaction tube at 160−165 °C for 1 h. After cooling to ambient temperature, purification by column chromatography (SiO_2, hexanes−ethyl acetate gradient = 10:1 → 5:1) provided **4b** as a pale yellow oil (0.203 g, 1.01 mmol, 60%). **4b**: IR (neat) 3344 (br), 3060, 3025, 2931, 2883, 1653, 1602, 1492, 1452, 1066, 1030, 882, 797, 757, 700, 668 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (br s, 1H), 2.40−2.60 (m, 2H), 3.42−3.53 (m, 1H), 3.75 (app d, *J* = 6.2 Hz, 2H), 3.79−3.89 (m, 1H), 5.59−5.81 (m, 3H), 5.89 (ddd, *J* = 2.5, 4.7, 11.2 Hz, 1H), 7.18−7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.3, 41.4, 43.6, 67.0, 126.3, 127.6, 128.5, 130.2, 130.39, 130.45, 136.1, 145.6; GC/MS *m*/*z* 200. Anal. Calcd for $C_{14}H_{16}O·0.25H_2O$: C, 82.11; H, 8.12. Found: C, 81.93; H, 8.01.

cis-[4-((4′-Hydroxyphenyl)cyclohepta-2,6-dienyl)methanol (4c)

The decomplexation, reduction, and Cope rearrangement of **2c** (1.00 g, 2.33 mmol) was carried out in a fashion similar to that for **2b**. Purification by column chromatography (SiO_2, hexanes−ethyl acetate = 7:3) provided **4c** as a colorless solid (0.16 g, 32%). **4c**: mp 90−94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (br s, 1H), 2.35−2.55 (m, 2H), 3.40−3.50 (m, 1H), 3.70−3.80 (m, 3H), 5.56−5.86 (m, 4H), 6.74 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), the signal for the phenol OH was not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.4, 41.5, 42.7, 67.1, 115.4, 128.9, 130.0, 130.6, 130.7, 136.6, 154.1; FAB-HRMS *m*/*z* 216.1157 (calcd for $C_{14}H_{16}O_2$ (M^+) *m*/*z* 216.1150).

1-Ethenyl-3-hydroxymethyl-1,4-cycloheptadiene (4i)

To a stirring solution of complex **2i** (544 mg, 1.71 mmol) in absolute methanol (17 mL) was added, in portions over a period of 14 min, CAN (580 mg, 1.00 mmol). Shortly after the last addition and cessation of effervescence, the red reaction mixture was pour into brine (20 mL) and extracted several times with ethyl acetate. The combined extracts were washed sequentially with water, saturated aqueous sodium bicarbonate, and brine, dried ($MgSO_4$), and carefully concentrated at 20 °C to give a volatile yellow oil. The oil was dissolved in ether (2 mL) and added dropwise to a stirring solution of $LiAlH_4$ in ether (3.0 mL, 1.0 M, 3.0 mmol) at 0 °C. Additional ether (2 mL) was used to ensure a quantitative transfer of the crude. The solution was stirred at 0 °C for 3 h, and then quenched with saturated sodium bicarbonate (5 mL). After warming to room temperature and being diluted with 2 M NaOH (10 mL), the mixture was extracted several times with ether. The combined extracts were dried ($MgSO_4$) and concentrated to give **4i** as an pale oil (130 mg, 50%). A few crystals of 1,4-hydroquinone was added to stabilize this compound. **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (br s, OH), 2.10−2.21 (m, 1H), 2.28−2.38 (m, 1H), 2.38−2.46 (m, 1H), 2.54−2.63 (m, 1H), 3.45−3.53 (br s, 1H), 3.71 (d, *J* = 6.5 Hz, 2H), 4.98 (dd, *J* = 0.7, 10.5 Hz, 1H), 5.16 (dd, *J* = 0.7, 17.3 Hz, 1H), 5.51 (br d, *J* = 11.2 Hz, 1H), 5.73 (d, *J* = 4.5 Hz, 1H), 5.77−5.84 (m, 1H), 6.34 (dd, *J* = 11.2, 17.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 26.1, 40.8, 67.0, 111.0, 128.9, 132.0, 133.2, 140.2, 141.6. A satisfactory elemental analysis could not be obtained for this product.

Reaction of 4i with Maleic Anhydride (21)

To a solution of **4i** (freshly prepared from **2i**, 0.816 g, 2.57 mmol) in toluene (5 mL) was added maleic anhydride (0.5 g, 0.5 mmol). The reaction mixture was heated to reflux for 30 min, cooled to room temperature, and concentrated. Water (30 mL) was added and the mixture was extracted several times with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and concentrated. Recrystallization from acetone and diethyl ether gave **21** as colorless crystals (0.36 g, 56% from **2i**). **21**: mp 80−82 °C; IR (KBr) 3600−2400 (broad), 1734, 1698, 1397, 1196 cm^{-1}; ^{1}H NMR (300 MHz, d_6-acetone) δ 2.2−2.35 (m, 4H), 2.42−2.70 (m, 4H), 3.16 (br t, *J* = 10.2 Hz, 1H), 3.66 (dd, *J* = 3.9, 9.9 Hz, 1H), 4.18 (dd, *J* = 3.9, 10.8 Hz, 1H), 4.36 (dd, *J* = 10.8, 12.0 Hz, 1H), 5.49−5.54 (m, 1H), 5.60 (tdd, *J* = 1.5, 3.3, 10.8 Hz, 1H), 5.84−5.92 (m, 1H), signal for COOH not observed; ^{13}C NMR (75 MHz, d_6-acetone) δ 23.6, 28.3, 34.5, 39.0, 41.3, 42.1, 69.0, 120.5, 129.9, 133.7, 140.0, 173.1, 174.2 (one signal for an sp^3 hybridized carbon obscured by d_6-acetone). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.62; H, 6.44.

Reaction of 4i with PTAD (22)

The reaction of **4i** (freshly prepared from **2i**, 0.544 g, 1.71 mmol) with 4-phenyl-1,2,4-triazoline-3,5-dione was carried out in the same fashion as for the preparation of **2j**. The product was purified by flash chromatography (SiO_2, hexane−ethyl acetate = 1:1) to give **22** as a light yellow solid (280 mg, 50%). **22**: mp 60−63 °C; IR (KBr) 3432, 1761, 1681, 1506, 1443^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97−2.10 (m, 1H), 2.21 (br t, *J* = 10.8 Hz, 1H), 2.40−2.51 (m, 1H), 2.53−2.62 (m, 2H), 3.53 (dd, *J* = 2.1, 12.7 Hz, 1H), 3.66 (dd, *J* = 2.1, 12.9 Hz, 1H), 4.12 (qd, *J* = 2.4, 16.5 Hz, 1H), 4.35 (br d, *J* = 16.5 Hz, 1H), 4.57 (d, *J* = 9.9 Hz, 1H), 5.67 (t, *J* = 3.3 Hz, 1H), 5.84 (ddd, *J* = 2.1, 3.9, 11.7 Hz, 1H), 6.08 (dddd, *J* = 2.7, 5.1, 7.2, 11.7 Hz, 1H), 7.35−7.55 (m, 5H), the signal for the amide proton was not observed; ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 36.0, 45.4, 47.5, 54.4, 62.7, 115.0, 125.6, 128.5, 129.3, 130.8, 131.1, 132.8, 139.7, 150.7, 154.0. Anal. Calcd for $C_{18}H_{19}N_3O_3{\cdot}H_2O$: C, 64.08; H, 6.07. Found: C, 63.98; H, 5.60.

Reaction of 4i with Methylpropiolate (23)

A solution of the freshly prepared **4i** (129 mg, 0.860 mmol) and methyl propiolate (72 mg, 0.86 mmol) in toluene (2 mL) was heated to 110 °C under nitrogen for 20 h. The reaction mixture was cooled and evaporated and the residue was dissolved in CH_2Cl_2 (2 mL). Solid DDQ (0.20 g, 0.88 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated and the residue was passed through a bed of silica gel, using CH_2Cl_2 to rinse the filter pad. The combined washings were concentrated and the residue was purified by flash chromatography (SiO_2, hexane−ethyl acetate = 3:1) afford **23** as a light yellow solid

(40 mg, 20%). **23**: mp 62−63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30−2.40 (m, 2H), 3.03 (ddd, *J* = 4.4, 7.2, 14.0 Hz, 1H), 3.12 (ddd, *J* = 4.8, 8.4, 14.0 Hz, 1H), 3.83−3.89 (m, 1H), 3.90 (s, 3H), 3.98 (dd, *J* = 6.2, 10.8 Hz, 1H), 4.04 (dd, *J* = 8.0, 10.8 Hz, 1H), 5.61−5.67 (m, 1H), 5.68−5.74 (m, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.86 (dd, *J* = 2.2, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.9, 33.4, 47.3, 52.3, 65.8, 126.9, 128.1, 128.6, 129.0, 129.8, 131.3, 141.6, 147.3, 167.4.

Tricarbonyl(2-formyl-3-pentene-1,5-diyl)iron (25)

To a solution of tricarbonyl[2-(2′-methyl-1-propenyl)-3-pentene-1,5-diyl]iron (**2k**)(6) (322 mg, 1.01 mmol) in CH_2Cl_2 (5 mL) at room temperature was added, in a single portion, *m*-chloroperoxybenzoic acid (0.45 g, ∼75%, ∼2 mmol). The solution immediately became a darker shade of orange and warmed. Monitoring of the reaction by TLC (hexanes−ethyl acetate = 4:1) indicated disappearance of the staring material after several minutes. The mixture was quenched with saturated aqueous $Na_2S_2O_3{\cdot}5H_2O$ (2 mL). After 5 min, the solution was partioned between water and ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$, followed by water and brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 2:1) to afford **24** as an unstable yellow semisolid (283 mg, 83%). This material was used in the next step without further characterization. To a solution of the above diastereomeric epoxides (115 mg, 0.342 mmol) in dioxane (2 mL) and water (1 mL) was added three drops of concentrated H_2SO_4. The solution gradually changed from orange to yellow and monitoring of the reaction by TLC (hexanes−ethyl acetate = 4:1) indicated disappearance of the staring material after 45 min. Saturated aqueous $NaHCO_3$ was added and the mixture was extracted several times with ethyl acetate. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was dissolved in THF (1.7 mL) and water (1.7 mL) and solid $NaIO_4$ (0.11 g, 0.51 mmol) was added with stirring. The mixture began to thicken over a 20 min period. The mixture was diluted with brine and extracted several times with CH_2Cl_2, and the combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 1:1) to afford **25** as a light yellow solid (53 mg, 52%). **25**: mp 89−93 °C; IR (KBr) 2807, 2713, 2072, 2012, 1983, 1722, 1688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.59 (d, *J* = 8.1 Hz, 1H), 2.11 (dd, *J* = 2.4, 12.3 Hz, 1H), 3.58 (d, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 4.12 (t, *J* = 8.0 Hz, 1H), 4.35 (t, *J* = 7.4 Hz, 1H), 4.80 (ddd, *J* = 7.2, 8.4, 12.3 Hz, 1H), 9.08 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 3.1, 50.3, 52.1, 54.3, 55.9, 99.4, 180.0, 196.4, 203.2, 209.5, 209.7. A satisfactory elemental analysis could not be obtained for this compound.

Tricarbonyl[methyl 7,7-dimethyl-8-oxo-2*E*,4*Z*-octadienoate]iron (26)

To a solution of **2k** (361 mg, 1.13 mmol) in CH_2Cl_2 (5.6 mL) at 0 °C was added *m*-chloroperoxybenzoic acid (ca. 75%, 520 mg, ca. 2.2 mmol). The solution darkened and after 10 min TLC monitoring (SiO_2, hexanes−ethyl acetate = 4:1) indicated complete disappearance of the starting material. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (2 mL). After 5 min, the mixture was diluted with water and extracted several times with ethyl acetate. The combined extracts were washed with saturated $NaHCO_3$, followed by water and finally brine, dried ($MgSO_4$), and concentrated. The residue was dissolved in dry CH_2Cl_2 (5 mL) and stirred at room temperature. To this solution was added $BF_3{\cdot}Et_2O$ (72 µL, 0.57 mmol). The mixture was stirred for 15 min, and then quenched with saturated aqueous $NaHCO_3$. The layers were separated, the aqueous layer was extracted twice with CH_2Cl_2, and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 4:1) to afford **26** as a yellow crystalline solid (312 mg, 82%). **26**: mp 93−95 °C; IR (KBr) 2809, 2714, 2058, 1992, 1968, 1716 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.51 (s, 6H), 0.69 (dd, *J* = 11.4, 14.1 Hz, 1H), 1.61 (dd, *J* = 3.6, 14.1 Hz, 1H), 2.10−2.20 (m, 2H), 3.34 (s, 3H), 4.49 (ddd, *J* = 0.6, 5.4, 7.8 Hz, 1H), 5.72 (ddd, *J* = 1.2, 5.1, 8.4 Hz, 1H), 8.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.6, 37.4, 46.2, 47.8, 52.0, 54.6, 86.9, 92.7, 173.0, 205.1, a signal for the metal carbonyls was not observed. Anal. Calcd for $C_{14}H_{16}FeO_6$: C, 50.03; H, 4.80 Found: C, 50.84; H, 4.85.

Supporting Information

Copies of the NMR spectral data for all compounds reported and the ORTEP and CIF files for the X-ray crystal structures of *dl*-**7**, **15**, and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

Terms & Conditions

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