Regio- and Stereocontrolled Functionalization of a Seven-Membered Ring via (Cycloheptatriene)iron Tricarbonyl

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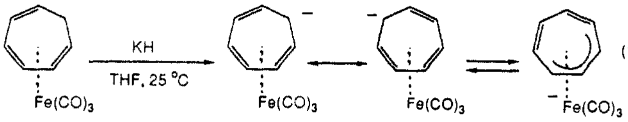
Abstract: Deprotonation of (cycloheptatriene)Fe(CO)$_3$ gives a deep red nucleophilic anion $(C_7H_7)Fe(CO)_3(K^+)$, **1**. Anion **1** reacts with acid chlorides to give (7-*exo*-acyl-C_7H_7)Fe(CO)$_3$ complexes, **2**, in high yield. The products were characterized by spectroscopic techniques and by a single-crystal X-ray diffraction study on the benzoyl derivative: **2b** crystallizes in the monoclinic space group $P2_1/c$, with unit cell constants a = 11.790 (3) Å, b = 6.643 (2) Å, c = 19.419 (8) Å, β = 99.33 (2)°, and Z = 4. Acyl complexes **2** have a propensity to rearrange to the 5- and 6-acyl-substituted derivatives. Anion **1** also reacts with BF_3-activated ketones and aldehydes to give the expected 7-exo-alkyl hydroxy compounds, **5**, in excellent yield. The acyl complexes **2** can be deprotonated very easily to give new organometallic anions that behave much like the enolates of β,γ-unsaturated ketones. Alkylation with methyl iodide, allyl bromide, or benzyl bromide gave the 7,7-disubstituted (cycloheptatriene)Fe(CO)$_3$ compounds; the 7-alkyl-5-acyl isomers are always formed as minor byproducts. In addition to spectroscopic techniques, the alkylation products were characterized by X-ray crystallography. The structure of the 7-7′-methylbenzoyl derivative reveals that alkylation occurs on the top face of the ring, away from the Fe(CO)$_3$ fragment: **6** crystallizes in the orthorhombic space group *Pcab* with cell constants a = 7.587 (3) Å, b = 16.959 (6) Å, c = 25.099 (6) Å, β = 90°, and Z = 8. The anions derived by deprotonation of **2** react with acid chlorides and silyl chlorides at the oxygen atom of the dienolate fragment. The resulting heptafulvene complexes exist in solution as a mixture of Z and E isomers about the exocyclic double bond; the Z isomer dominates in each case. The molecules crystallize exclusively in the Z form as indicated by the X-ray structure for [((*t*-BuMe$_2$Si)-O)phenylheptafulvene]Fe(CO)$_3$: **8d** crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 14.896 (3) Å, b = 6.448 (1) Å, c = 23.679 (5) Å, β = 92.47 (1)°, and Z = 4.

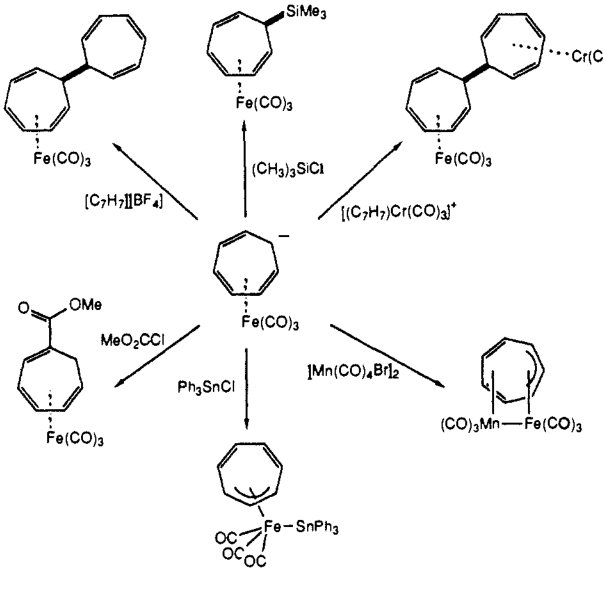
Deprotonation of (cycloheptatriene)Fe(CO)$_3$ provides a species that can be considered as the antiaromatic cycloheptatrienide anion stabilized by a transition-metal fragment (eq 1).[2] This deep red organometallic anion can be considered in terms of two limiting bonding alternatives: one of which delocalizes the negative charge in the ring as an allylic carbanion and one that places the charge density on the metal center. Molecular orbital calculations suggest a very small preference for the latter,[3] and its solid-state structure is also consistent with this formulation.[4] However, the molecule is highly fluxional, even at −160 °C,[5] and it is known to act as a mild ambident nucleophile.



(1)

The $(C_7H_7)Fe(CO)_3^-$ anion, **1**, has been known for several years, but studies of its reactivity patterns have, in the main, been restricted to inorganic or organometallic systems (Scheme I). Most notably, anion **1** has been used to prepare a number of heterobimetallic complexes linked by either a metal–metal bond or through the seven-membered ring.[6] Many of these compounds have interesting structural or fluxional properties. Several years ago, **1** was reported to react with alkyl chloroformates to give carboalkoxy derivatives of (cycloheptatriene)iron tricarbonyl.[7a]

Scheme I



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(2) (a) Maltz, H.; Kelly, B. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1390–1391. (b) Kerber, R. C. *J. Organomet. Chem.* **1983**, *354*, 131–142. (c) Moll, M.; Behrens, H.; Kellner, B.; Knockel, H.; Wurstl, P. Z. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1019–1020.

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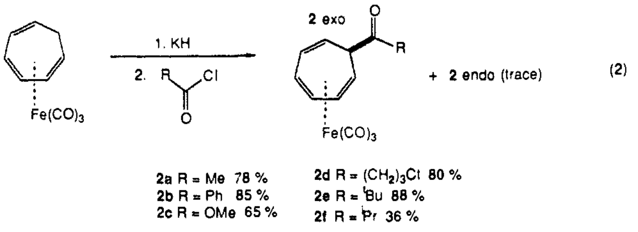
Curiously, the isolated organometallic products of these reactions had the ester functionality at the six position of the ring (see below). The same system was reinvestigated very recently, and similar results were reported.[7b] Apart from the alkyl chloroformate example, there has been no concentrated effort to develop the carbon–carbon bond-forming reactions of $(C_7H_7)Fe(CO)_3^-$. This anion is an attractive substrate for the regio- and stereocontrolled elaboration of seven-membered rings, and in this paper we present a full account of our study on the reactivity patterns of organic electrophiles with anion **1** and its derivatives.[8]

Results and Discussion

Synthesis of the (Cycloheptatrienyl)Fe(CO)$_3$ Anion. Several strong bases can be used to remove the 7-exo hydrogen atom from (cycloheptatriene)Fe(CO)$_3$, including KH,[6c] *n*BuLi,[2a] $Na[(CH_3)_3Si]_2N$,[2c] and KO-*t*-Bu.[6g] Among these, we find potassium hydride to be the most convenient and reliable when a drybox is available; however, all of the compounds described in this paper can be prepared by using standard Schlenk techniques. Addition of $C_7H_8Fe(CO)_3$ to a suspension of KH in THF gives immediate vigorous gas evolution. After 1 h, filtration to remove excess KH provides a deep red solution of anion **1**. Removal of solvent gives a red crystalline solid that can be stored under an inert atmosphere at low temperature. Sodium hydride can also be employed in this manner, but the deprotonation requires several hours. In our hands, organolithium bases are less effective, perhaps due to the interaction of these nucleophilic species with the Fe(CO)$_3$ fragment[9] or with the ring.[10]

Reaction of $(C_7H_7)Fe(CO)_3^-$ with Acid Chlorides. As our starting point for developing the carbon–carbon bond-forming reactions of anion **1**, we chose to study its reactions with acid chlorides. Dropwise addition of the anion to an excess of the electrophile provides (7-*exo*-acyl-C$_7$H$_7$)Fe(CO)$_3$, **2**, in good to excellent yield (eq 2). The iron carbonyl fragment controls the stereochemistry by directing the electrophile to the top side of the coordinated ring. In the case of acetyl chloride, addition of the anion to the electrophile at room temperature gives a 35:1 mixture of the 7-exo and 7-endo isomers. The minor endo isomer probably arises by acylation at the metal followed by intramolecular reductive coupling; there is ample precedent for the ambident character of this organometallic nucleophile.[6] For all other acid halides, the exo/endo product ratios are in excess of 50:1, and if the acylation is conducted at 0 °C, the endo product is formed only in trace quantities. Most of these substituted (cycloheptatriene)Fe(CO)$_3$ derivatives are yellow oils that are moderately stable under an inert atmosphere at 0 °C. They will tolerate exposure to air (chromatography on the bench-top is routine), but they decompose easily when they are impure. A few of the products are crystalline solids; these are much more stable.



(2)

2a R = Me 78 %
2b R = Ph 85 %
2c R = OMe 65 %
2d R = (CH$_2$)$_3$Cl 80 %
2e R = ^{t}Bu 88 %
2f R = ^{i}Pr 36 %

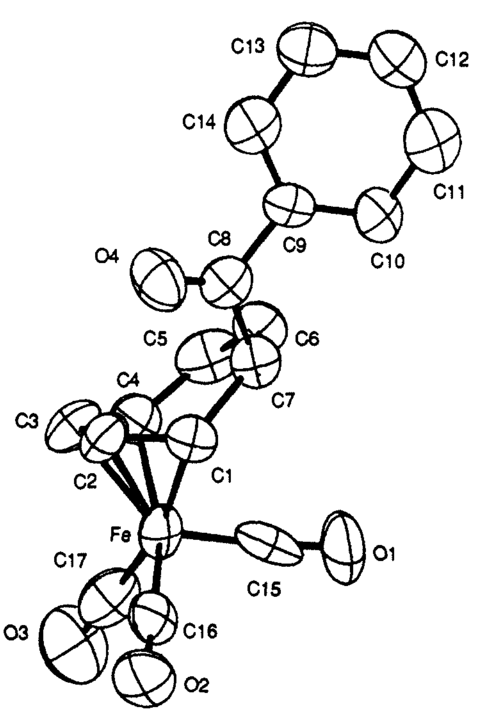


Figure 1. Molecular structure (7-*exo*-benzoyl-C$_7$H$_7$)Fe(CO)$_3$ (**2b**).

Substitution at the 7-position is made evident by the ^{13}C NMR spectra of the iron acyl complexes. The free double bond carbons, C-5 and C-6, give rise to absorptions at ca. 132 and 123 ppm. The signals for the inner two carbons of the coordinated diene, C-2 and C-3, are always found at ca. 95 and 88 ppm. Chemical shifts of the three remaining ring-carbons, C-1, C-4, and C-7, range between 50 and 60 ppm. In a few cases described below, we have isolated substituted cycloheptatriene complexes that bear substituents at either C-5 or C-6. The double-bond carbon atoms of these products show relatively small variance in their chemical shifts. However, when the 7-position is unsubstituted, the signal for that carbon atom is shifted upfield to ca. 30 ppm.

The ^{1}H NMR spectra of $(C_7H_8)Fe(CO)_3$ and its 7-substituted derivatives have been discussed extensively.[6c,d,7b,11] Each of the (7-acyl-C$_7$H$_7$)Fe(CO)$_3$ complexes listed in eq 2 shows the characteristic spectrum of an η^4-cycloheptatriene complex. The inner two hydrogens of the coordinated diene absorb at ca. δ 5.45; usually these multiplets overlap. Most revealing are the signals for the hydrogens bound to the noncomplexed double bond. In each case, the symmetrical multiplets for H-5 and H-6 appear at ca. δ 6.0 and 5.1, respectively. The outer diene hydrogens, H-1,4, and the endo hydrogen, H-7, appear as multiplets ranging between δ 3.0 and 4.5. Invariably, C-7 is the most downfield of the group, and the signals for H-1 and H-4 often overlap.

Both chemical shifts and ring coupling interactions have been used for assignment of stereochemistry in metal polyolefin complexes.[11,12] We conducted a thorough analysis of the ring hydrogen coupling interactions and the chemical shifts for both isomers of (7-acetyl-C$_7$H$_7$)Fe(CO)$_3$, **2a**. The coupling constants of the exo and endo isomers are too similar to allow assignment of stereochemistry to the major product. The chemical shift of H-7 in the major isomer is 3.48 ppm, and its coupling interactions are J_{1-7} = 4.5 Hz, J_{6-7} = 4.6 Hz, and J_{5-7} = 1.7 Hz. For the minor product, H-7 appears at δ 3.31, and the coupling interactions are essentially identical with those of its isomer: J_{1-7} = 4.5 Hz, J_{6-7} = 4.4 Hz, J_{5-7} = 1.8 Hz.

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The stereochemistry of the major isomer of these acylation reactions was determined by an X-ray crystallographic study on (7-*exo*-benzoyl-C_7H_7)iron tricarbonyl, **2b**. The molecular structure of the compound is illustrated in Figure 1. The structural study establishes exo stereochemistry for the acylation of $(C_7H_7)Fe(CO)_3^-$ anion. We suggest that for all of the acid chlorides, the $Fe(CO)_3$ fragment blocks one face of the coordinated ring from the approaching electrophile. Formally, acylation at either end of the ring's allylic carbanion gives the exo acyl complex.

One curious aspect of this chemistry concerns the reaction of $(C_7H_7)Fe(CO)_3^-$ with alkyl chloroformates. Two different groups have studied this reaction. In the initial report,[7a] Behrens and co-workers found that esterification of **1** gave a solution of (7-CO_2Me-C_7H_7)$Fe(CO)_3$, **2c**, identified by ^1H and ^{13}C NMR. However, on workup, the product rearranged to its isomer, (6-CO_2Me-C_7H_7)$Fe(CO)_3$, **3**. Recently, this system was reexamined by Deganello, and slightly different results were reported.[7b] The second group found no evidence for the 7-substituted product, **2c**. Rather, they isolated both **3** and (5-CO_2Me-C_7H_7)$Fe(CO)_3$, **4**, along with significant quantities of $(C_7H_8)Fe(CO)_3$ and small amounts of "diester-substituted (cycloheptatriene)$Fe(CO)_3$ derivatives".[13] In our hands, however, anion **1** reacts with methyl chloroformate to give (7-CO_2Me-C_7H_7)$Fe(CO)_3$, **2c**, isolated in 65% yield as a moderately stable yellow-orange oil. The NMR spectra of this material are in complete accord with our formulation of the product. In addition to the usual signals for the η^4-diene fragment, the hydrogens of the free double bond give the expected multiplets at 5.96 and 5.22 ppm, and the carbomethoxy singlet is observed at 3.71 ppm. The ^{13}C NMR spectrum confirms the assignment. Specifically, lines for the carbon atoms of the noncomplexed double bond are observed at 131.1 and 122.4 ppm, while the ester carbon gives a signal at 173.2 ppm, and the C-7 methine appears at δ 52.3. The ^{13}C NMR spectra of **3** and **4** are clearly distinguished from **2c** by the chemical shift of C-7: δ 29.6 and δ 30.7, respectively, vs 52.3 for **2c**. In addition, the ^1H NMR spectra for **2c**, **3**, and **4** are quite distinct. Figure 2 illustrates how the chemical shifts of the ring hydrogens change as the carbomethoxy group moves from C-7 to C-6 to C-5.

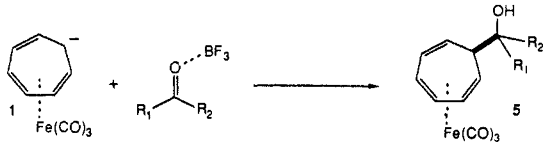
Usually, we isolate only small quantities (<10%) of **3** from the acylation reaction. In part, the difference in results can be attributed to the sensitivity of the acylated products to reaction conditions. The endo hydrogen on C-7 of these 7-exo acyl iron complexes is acidic; it is removed rapidly by anion **1**. The distribution of products reported by Deganello and co-workers reflects a competition for anion **1** between methyl chloroformate and **2c**. In all of these acylation reactions, it is important to add the anion to a solution containing several equivalents of the electrophile, and the addition should be conducted at a rate that allows dissipation of the anion's red color with each added drop.[14] Purification of the (7-acyl-C_7H_7)$Fe(CO)_3$ complexes is best accomplished by chromatography on Florisil; silica gel and alumina can cause isomerization. We find that **2c** and the acetyl complex **2a** are particularly susceptible to isomerization.

Isomerization of **2** to **3** and **4** can occur by reversible loss of a hydrogen atom from C-7, either by transfer to the ring to give an iron hydride or by dissociation of a proton to give an organoiron anion. In either case, migration of the η^3-trienyl ligand followed by return of the hydrogen atom completes the isomerization. The C-5 substituted acyl complex (e.g., **4**) is the kinetic product of isomerization. Subsequent rearrangement leaves the acyl group at C-6 (e.g., **3**), probably because conjugation of the carbonyl group in this position allows positive charge buildup at C-5, α to the coordinated diene fragment.

Compound **2c** can be converted to **4** in very good yield by isomerizing the noncomplexed double bond. For example, if **2c** is treated with KH for 15 min and then filtered and quenched with CF_3CO_2H (−78 °C), the 5-substituted material, **4**, is isolated in 83% yield. We have conducted this isomerization reaction for a number of the 7-substituted acyl complexes; good to excellent yields of (5-acyl-C_7H_7)$Fe(CO)_3$ can be isolated in each case (70–90%).

Reaction of $(C_7H_7)Fe(CO)_3^-$ with Other Electrophiles. Neither *n*-butyl bromide nor *n*-butyl tosylate react with $(C_7H_7)Fe(CO)_3^-$ at room temperature. Allyl bromide and methyl iodide react readily with the anion, but several products are formed in each case. These electrophiles are particularly prone to electron transfer, and such processes probably complicate their reactions with $(C_7H_7)Fe(CO)_3^-$. Significant quantities of the ring-coupled dimer $[(C_7H_7)Fe(CO)_3]_2$[6g] can be isolated in each case.

Ketones and aldehydes will react with $(C_7H_7)Fe(CO)_3^-$, **1**, if they are activated by precoordination of BF_3 (eq 3). The resulting



(3)

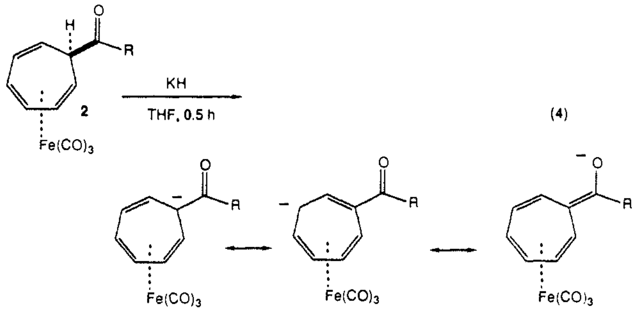
R_1, R_2 = Me = 72 %
R_1, R_2 = cyclopentyl = 70 %
R_1, R_2 = cyclohexyl = 81 %
R_1 = Et, R_2 = *n*-Bu = 76 %

R_1 = H, R_2 = Ph = 93 %
R_1 = H, R_2 = Me = 71 %
R_1 = H, R_2 = 2-furyl = 94 %
R_1 = H, R_2 = $CH(Et)_2$ = 87 %
R_1 = H, R_2 = *n*-pentyl = 94 %

alcohols, **5**, can be isolated by chromatography on silica gel in yields of 65–95%. Anion **1** is added to a solution containing 1 equiv of the activated carbonyl compound. An excess of either the electrophile or BF_3 results in a significant decrease in the yield. These reactions require approximately 12 h of stirring at room temperature, and even at this point the solutions retain much of the red color attributed to the anion. The products are typically viscous yellow-orange oils, but a few are yellow solids. The spectroscopic properties of alcohols **5** are much the same as their 7-exo acyl counterparts, **2**.

Aldehydes and unsymmetrical ketones produce diastereomers that we have not been able to separate. In general, the 200 MHz ^1H NMR spectra of the alcohol complexes fail to reveal the presence of diastereomers in any way other than a broadening of all lines. When a distinction between isomers is possible, it is usually the signal for H-6 that is resolved. In most cases, the ^{13}C NMR spectra reveal both diastereomers. When measurable, the ratio of diastereomers is seldom larger than 1.1:1.

Elaboration of (7-Acylcycloheptatriene)$Fe(CO)_3$. A second substituent can be introduced to the seven-membered ring of (7-acyl-C_7H_7)$Fe(CO)_3$ by taking advantage of the acidity of the remaining hydrogen on C-7. These compounds are readily deprotonated even though the acidic hydrogen is on the more hindered endo face of the ring. Either sodium ethoxide or potassium hydride will generate a deep red solution of the desired anion within minutes at room temperature. Although several possible resonance structures can be written for these new organometallic anions, the three forms illustrated in eq 4 appear to dominate the chemistry.



(4)

The anion of (7-benzoyl-C_7H_7)$Fe(CO)_3$, **2b**, reacts with methyl iodide at room temperature to give two products (eq 5). Alkylation occurs in 85% yield with a 6:1 preference for reactivity at the α-carbon of the dienolate fragment. Characterization of (7-

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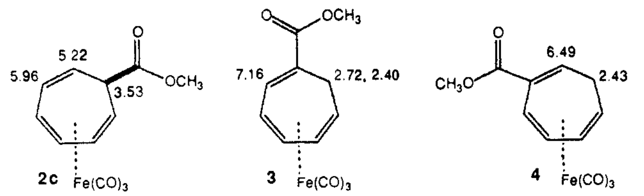
[13] No data were provided for the characterization of the presumed diester complexes, and no structural assignment was suggested.

[14] Color dissipation during anion addition is routine for the reaction between **1** and acid chlorides. For methyl chloroformate, the reaction mixture remains dark red-brown. Addition of the anion to the electrophile over a 90-min period at 0 °C minimizes competing side reactions.



2c 3 4

Figure 2. 200 MHz ^{1}H NMR data for **2c**, **3**, and **4** in CDCl$_3$.

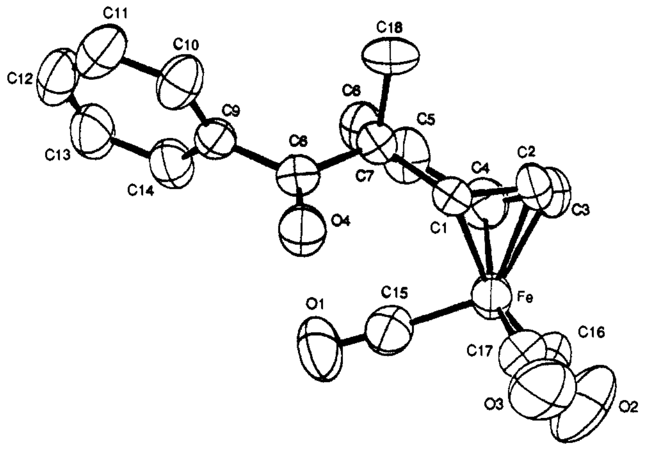
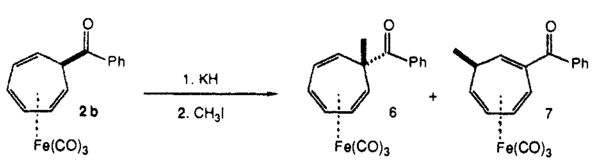


Figure 3. Molecular structure of (7-*exo*-CH$_3$-*endo*-benzoyl-C$_7$H$_7$)Fe(CO)$_3$ (**6**).

exo-methyl-7-*endo*-benzoyl-C$_7$H$_7$)Fe(CO)$_3$, **6**, rests upon both spectral properties and a single-crystal X-ray diffraction study.



(5)

The 250 MHz ^{1}H NMR spectrum of **6** is readily interpreted. The hydrogens on the noncomplexed double bond give rise to an adjacent set of multiplets that show significant deviation from first-order behavior. A doublet of doublets at δ 5.55 is assigned to H-5 (J_{5-6} = 10.8 Hz, J_{5-4} = 7.6). This signal is skewed strongly toward a doublet of multiplets (δ 5.44) that is attributed to H-6 (J_{6-1} = 2.2 Hz, J_{6-4} = 1.0 Hz). The internal diene hydrogens give a symmetrical multiplet at 4.69 ppm. The outer diene hydrogens are found at δ 3.82 and δ 2.48 (H-1 and H-4 respectively). Finally, the methyl singlet is observed at 1.32 ppm. The benzoyl group is identified in the ^{13}C NMR spectrum at 204.9 ppm and in the IR spectrum at 1683 cm^{-1}.

The stereochemistry of the methylation reaction was determined by X-ray crystallography. The molecular structure is illustrated in Figure 3. Alkylation occurs on the exo face of the ring, away from the Fe(CO)$_3$ fragment.

The minor alkylation product, **7**, arises by methylation at the γ-carbon of the dienolate fragment; it can be identified by its ^{1}H NMR spectrum. In addition to the typical η^4-diene signals, the methyl group gives a doublet at 0.67 ppm ($J_{\mathrm{Me-H7}}$ = 7.2 Hz). The benzoyl fragment is located at C-5, as indicated by the lack of a signal at ca. 6.0 (expected for H-5). All other spectra are also in accord with this assignment.

The minor product, **7**, is formed in only trace quantities if the alkylation is conducted at low temperature. If methylation of the anion derived from **2b** is carried out at −78 °C, compound **6** is isolated in 85% yield; only a trace of **7** is formed.

The methyl iodide reaction illustrated in eq 5 is representative of these organoiron enolates. Yields of C-alkylation are high for allyl bromide, benzyl bromide, and methyl iodide; the results are summarized in eq 6. Less reactive electrophiles do not interact with the anions. For example, although *n*-propyl iodide will alkylate the anion derived from **2b**, the reaction requires 15 h in refluxing THF, and the yield is only moderate (48%).

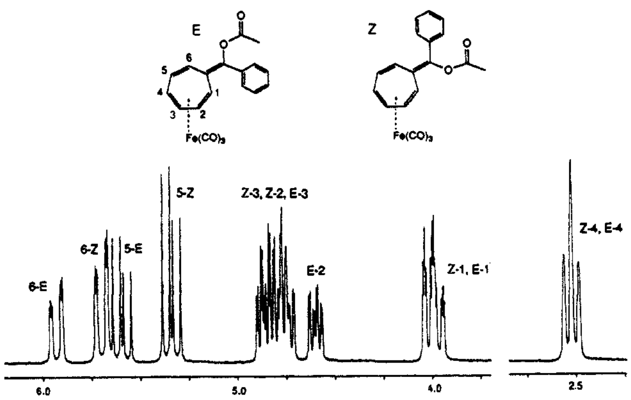
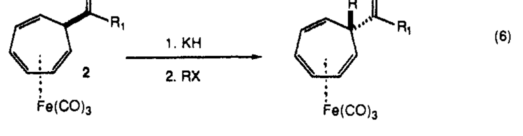


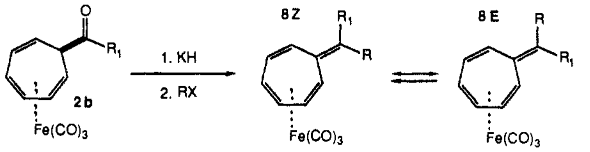
Figure 4. 200 MHz ^{1}H NMR spectrum of (8-phenyl-8-acetoxyheptafulvene)Fe(CO)$_3$ (**8a**).



(6)

R = allyl, R$_1$ = Me 70 %
R = Me, R$_1$ = OMe 63 %
R = *n*-Pr, R$_1$ = Ph 48 %
R = Me, R$_1$ = Ph 85 %
R = benzyl, R$_1$ = Ph 79 %
R = allyl, R$_1$ = Ph 64 %
R = Me, R$_1$ = Me 92 %

These 7-acyl iron anions react with acid halides and silyl chlorides to give coordinated heptafulvenes in excellent yield (eq 7). For example, acetyl chloride reacts with the 7-benzoyl anion to give the heptafulvene enol ester **8a** as a yellow oil. The chlorocomplex **2d** also cyclizes exclusively to the heptafulvene **8f**; there is no evidence for the spiro isomer.



(7)

8a R$_1$ = Ph, R = OAc 93 % Z:E = 1.6:1
8b R$_1$ = Ph, R = benzoyl 90 % Z:E = 1.6:1
8c R$_1$ = Ph, R = OSiMe$_3$ 78 % Z:E = 3:1
8d R$_1$ = Ph, R = OSi(*tert*-Bu)Me$_2$ 78 % Z:E = 3:1
8e R$_1$ = Me, R = OAc 74 % Z:E = 1.4:1
8f R$_1$, R$_2$ = -CH$_2$CH$_2$CH$_2$O- 79 % Z:E = 3.2:1

These heptafulvene complexes establish a mixture of isomers about the exocyclic double bond. This is illustrated most clearly by the ^{1}H NMR signals for the noncomplexed double bond (Figure 4); **8a** shows two distinct sets of signals in the region of H-5 (dd, J_{5-6} = 11 Hz, J_{5-4} = 8) and H-6 (dm, J_{1-6} = 2 Hz). Relative to their acyl precursors, **2**, the exocyclic substituent of **8a** and its analogues exerts a deshielding influence on H-6; the chemical shift ranges between δ 5.6 and 6.6. (Compare with δ 5.1–5.3 for **2**.) The signal for H-5 shifts upfield slightly (δ 5.3–5.6, compared with 5.9–6.1 for **2**). The outer diene hydrogen, H-1, is also deshielded by the exocyclic substituent, moving to about δ 4.0 (3.0–3.1 for **2**). The signal for H-4 is seen as a broad triplet at ca. 2.5; in all cases H-4 of the major isomer masks H-4 of the minor isomer.

The identity of the major isomer of **8a** was established by an NOE ^{1}H NMR experiment. Irradiation of H-6 of the major isomer gives NOE enhancements in the signals for H-5 and the ortho hydrogens of the phenyl group. Irradiation of H-6 in the minor isomer of **8a** gives an enhancement in H-5, but there is no effect on the signals for the phenyl ring. On the basis of these data we suggest that the major heptafulvene isomer for **8a** places the ester group in closest proximity to the Fe(diene) fragment; we designate this as the *Z* isomer (Figure 4). Trends in chemical shift data for the ring hydrogens in closest proximity to the exocyclic double bond suggest that the *Z* isomer predominates in

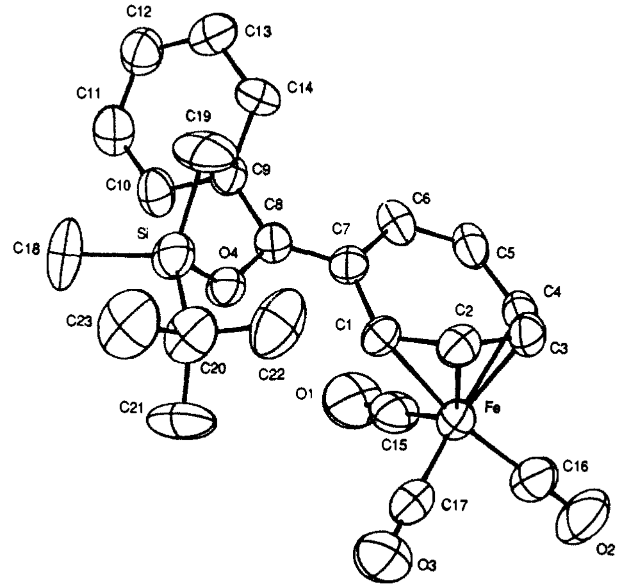
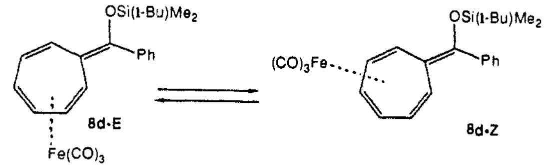


Figure 5. Molecular structure of [8-((t-BuMe$_2$Si)O)-8-phenylheptafulvene]Fe(CO)$_3$ (**8d**).

all of the heptafulvene complexes examined to date. Figure 4 shows that the H-5 and H-6 of the minor isomer, **8a-E**, resonate further downfield than do the corresponding hydrogens of the Z isomer. These observations extend to all of the heptafulvene complexes prepared here, and we suggest that the Z isomer predominates in each case.

A single-crystal X-ray diffraction study of [8-((*tert*-butyldimethylsilyl)oxy)-8-phenylheptafulvene]Fe(CO)$_3$, **8d**, confirms the structural assignment of these heptafulvene complexes. The molecular structure of **8d** is illustrated in Figure 5. Although **8d** establishes a mixture of Z and E isomers in solution, the molecule crystallizes exclusively in the Z form. If a crystalline sample of **8d** is dissolved in C_6D_6, a 4:1 equilibrium mixture of the two isomers is established in the time required to obtain a ^{1}H NMR spectrum. Most likely, equilibration occurs by a 1,3-shift as the Fe(CO)$_3$ fragment shuttles between the two possible sites for η^4-coordination (eq 8). This mechanism was established in



(8)

a previous study of (8-phenylheptafulvene)Fe(CO)$_3$; the free energy of activation for Z/E isomerization was determined to be 20.0 kcal/mol.[15] The ratio of Z to E isomers depends upon the substituents on the exocyclic double bond and, to a small extent, on the solvent. The enol esters range between 1.2 and 1.6:1, while the silyl enol ethers are in excess of 3:1.

There are scattered reports in the literature of metal-stabilized heptafulvene complexes.[16-23] The parent compound, heptafulveneFe(CO)$_3$, has been isolated in two forms. One of the isomers is a crystalline solid in which the metal is bound to the ligand in a trimethylenemethane interaction;[16] the mode of bonding was verified by X-ray crystallography.[17] The second isomer is an unstable oil whose ^{1}H NMR spectrum supports an η^4-diene formulation similar to the complexes reported here.[18] Lewis and co-workers have prepared a number of methyl- and aryl-substituted heptafulvene derivatives of both Fe and Cr,[19,20] and Goldschmidt has synthesized a series of (8-alkoxyheptafulvene)Fe(CO)$_3$ complexes.[21] The syntheses reported in this work complement existing routes to metal-stabilized heptafulvenes. The chemistry provides ready access to a range of substituted heptafulvene complexes and should facilitate reactivity studies of this class of compound.

Scheme II

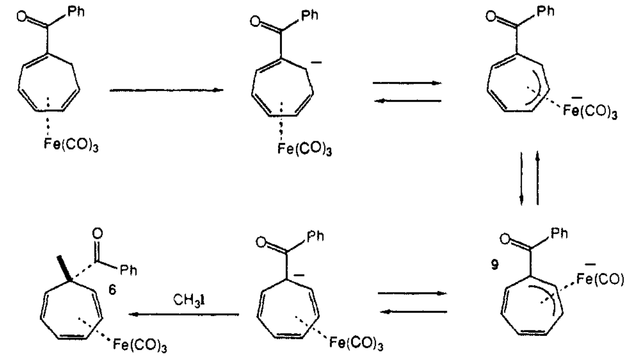


Table I. Bond Distances and Bond Angles for (η^4-7-*exo*-Benzoyl-C_7H_7)Fe(CO)$_3$, **2b**

Bond Distances (Å)			
Fe–C(15)	1.780 (3)	C(15)–O(1)	1.142 (4)
Fe–C(17)	1.792 (3)	C(16)–O(2)	1.127 (4)
Fe–C(16)	1.791 (3)	C(17)–O(3)	1.140 (4)
Fe–C(1)	2.109 (3)	C(1)–C(2)	1.417 (4)
Fe–C(2)	2.058 (3)	C(2)–C(3)	1.392 (5)
Fe–C(3)	2.053 (3)	C(3)–C(4)	1.429 (5)
Fe–C(4)	2.130 (3)	C(4)–C(5)	1.459 (5)
C(7)–C(8)	1.544 (4)	C(5)–C(6)	1.326 (5)
C(8)–O(4)	1.212 (4)	C(6)–C(7)	1.499 (4)
C(8)–C(9)	1.498 (4)	C(7)–C(1)	1.518 (4)
C(9)–C(10)	1.394 (4)	C(10)–C(11)	1.370 (5)
C(11)–C(12)	1.384 (5)	C(12)–C(13)	1.376 (5)
C(13)–C(14)	1.389 (4)	C(14)–C(9)	1.383 (4)
Bond Angles (deg)			
O(1)–C(15)–Fe	177.7 (4)	C(1)–C(2)–C(3)	119.1 (3)
O(2)–C(16)–Fe	177.5 (3)	C(2)–C(3)–C(4)	120.0 (3)
O(3)–C(17)–Fe	177.4 (3)	C(3)–C(4)–C(5)	127.5 (3)
C(6)–C(7)–C(8)	106.6 (2)	C(4)–C(5)–C(6)	128.9 (3)
C(1)–C(7)–C(8)	108.7 (2)	C(5)–C(6)–C(7)	124.2 (3)
C(7)–C(8)–C(9)	119.5 (3)	C(6)–C(7)–C(1)	118.0 (2)
O(4)–C(8)–C(7)	120.9 (3)	C(7)–C(1)–C(2)	125.6 (3)
O(4)–C(11)–C(12)	119.6 (3)	C(11)–C(10)–C(9)	120.6 (3)
C(10)–C(9)–C(8)	117.8 (3)	C(10)–C(11)–C(12)	120.2 (3)
C(14)–C(9)–C(8)	123.1 (3)	C(13)–C(12)–C(11)	119.8 (3)
C(14)–C(9)–C(10)	119.0 (3)	C(12)–C(13)–C(14)	120.2 (3)
C(13)–C(14)–C(9)	120.2 (3)	C(15)–Fe–C(17)	89.5 (2)
C(15)–Fe–C(16)	101.6 (2)	C(17)–Fe–(C16)	101.0 (1)

Similar to anion **1**, these acyl-$C_7H_6Fe(CO)_3^-$ anions can be discussed in terms of two limiting structures: one which localizes charge on the metal and one that distributes the charge through the ring. The reactivity patterns, particularly the strong preference for α-alkylation, suggest that deprotonation gives an anion that acts much like the enolate of a β,γ-unsaturated ketone.[23] The

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Table II. Bond Distances and Angles for (7-*exo*-Methyl-7-*endo*-benzoylC_7H_6)Fe$(CO)_3$, **6**

Bond Distances (Å)			
Fe–C(15)	1.759 (9)	C(15)–O(1)	1.164 (9)
Fe–C(16)	1.780 (9)	C(16)–O(2)	1.143 (9)
Fe–C(17)	1.790 (10)	C(17)–O(3)	1.135 (9)
Fe–C(1)	2.118 (7)	C(1)–C(2)	1.431 (10)
Fe–C(2)	2.044 (7)	C(2)–C(3)	1.395 (11)
Fe–C(3)	2.038 (8)	C(3)–C(4)	1.413 (11)
Fe–C(4)	2.139 (8)	C(4)–C(5)	1.467 (11)
C(7)–C(8)	1.547 (10)	C(5)–C(6)	1.297 (10)
C(8)–O(4)	1.208 (7)	C(6)–C(7)	1.490 (10)
C(8)–C(9)	1.492 (9)	C(7)–C(1)	1.525 (10)
C(9)–C(10)	1.379 (10)	C(10)–C(11)	1.394 (10)
C(11)–C(12)	1.382 (10)	C(12)–C(13)	1.352 (12)
C(13)–C(14)	1.394 (12)	C(14)–C(9)	1.382 (10)
C(7)–C(18)	1.600 (10)		

Bond Angles (deg)			
O(1)–C(15)–Fe	176.7 (7)	C(1)–C(2)–C(3)	120.6 (7)
O(2)–C(16)–Fe	179.4 (8)	C(2)–C(3)–C(4)	119.1 (7)
O(3)–C(17)–Fe	178.9 (9)	C(3)–C(4)–C(5)	126.6(8)
C(6)–C(7)–C(8)	110.9 (6)	C(4)–C(5)–C(6)	129.1 (7)
C(1)–C(7)–C(8)	110.4 (6)	C(5)–C(6)–C(7)	125.8 (7)
C(7)–C(8)–C(9)	119.7 (6)	C(6)–C(7)–C(1)	117.8 (6)
O(4)–C(8)–C(7)	120.7 (7)	C(7)–C(1)–C(2)	125.4 (6)
O(4)–C(8)–C(9)	119.6 (6)	C(9)–C(10)–C(11)	120.6 (3)
C(8)–C(9)–C(10)	118.6 (7)	C(10)–C(11)–C(12)	119.2 (8)
C(8)–C(9)–C(14)	121.9 (7)	C(11)–C(12)–C(13)	120.5 (9)
C(14)–C(9)–C(10)	119.4 (7)	C(12)–C(13)–C(14)	120.7 (9)
C(13)–C(14)–C(9)	119.7 (8)	C(18)–C(7)–C(6)	108.3 (6)
C(18)–C(7)–C(1)	105.4 (6)	C(18)–C(7)–C(8)	102.9 (6)
C(15)–Fe–(C16)	102.6 (4)	C(15)–Fe–C(17)	101.0 (4)
		C(16)–Fe–(C17)	93.8 (4)

iron carbonyl fragment removes the other two double bonds from the reactivity manifold and directs the stereochemistry of alkylation. The metal also attenuates the reactivity of the dienolate, but it does not appear to play a *direct* role in the anions' reactions with organic electrophiles. However, this view of the acyl anions is certainly oversimplified. The alternative formulation, a metal-centered η^3-trienyl system must also be important. The analogous η^3-bonding mode for anion **1** is well established in terms of both physical properties and chemical reactivity. The reaction illustrated in Scheme II suggests that the η^3-trienyl form is indeed important.[24] Deprotonation of (6-benzoyl-C_7H_7)Fe$(CO)_3$ followed by alkylation with CH_3I at -78 °C gives **6** in 78% yield. The organometallic anion can rearrange via a metal-centered trienyl species such as **9** to an anion identical with the one derived from the 7-benzoyl isomer **2b**.

Molecular Structures of (η^4-7-*exo*-Benzoyl-C_7H_7)Fe$(CO)_3$, 2b, (η^4-7,7′-*exo*-Me-*endo*-benzoyl-C_7H_7)Fe$(CO)_3$, 6, and [η^4-8-((*t*-BuMe$_2$Si)O)-8-phenylheptafulvene]Fe$(CO)_3$, 8d. Perspective drawings and the atomic numbering schemes for these molecules are shown in Figures 1, 2, and 3, respectively. Important bond distances and angles are given in Table I for **2b**, Table II for **6**, and Table III for **8d**. Crystal and collection data are presented in Table IV. The overall features of all three compounds are similar to the three previously published structures of simple 7-substituted (cycloheptatriene)Fe$(CO)_3$ complexes.[6c,25,26] In each case, the metal adopts approximately square-pyramidal geometry; the CO oriented toward C-6 occupies the apical position of the pyramid, while the remaining two CO's and the midpoints of the two coordinated double bonds constitute the basal plane.

The metal-ligand interactions are typical of (η^4-diene)Fe complexes; each shows the characteristic short–long–short patterns for the lengths of the three C–C bonds of the coordinated diene. However, there are significant variations in the lengths of the

Table III. Bond Distances and Angles for [(8-(*t*-BuMe$_2$Si)O)-8-C_6H_5heptafulvene]Fe$(CO)_3$, **8d**

Bond Distances (Å)			
Fe–C(15)	1.765 (7)	C(15)–O(1)	1.156 (7)
Fe–C(16)	1.778 (7)	C(16)–O(2)	1.144 (7)
Fe–C(17)	1.767 (8)	C(17)–O(3)	1.156 (7)
Fe–C(1)	2.157 (5)	C(1)–C(2)	1.429 (7)
Fe–C(2)	2.053 (6)	C(2)–C(3)	1.412 (8)
Fe–C(3)	2.049 (6)	C(3)–C(4)	1.423 (8)
Fe–C(4)	2.144 (6)	C(4)–C(5)	1.482 (8)
C(7)–C(8)	1.332 (7)	C(5)–C(6)	1.342 (7)
C(8)–O(4)	1.379 (6)	C(6)–C(7)	1.474 (7)
C(8)–C(9)	1.481 (7)	C(7)–C(1)	1.496 (7)
C(9)–C(10)	1.397 (7)	C(10)–C(11)	1.408 (8)
C(11)–C(2)	1.388 (9)	C(12)–C(13)	1.370 (9)
C(13)–C(14)	1.420 (8)	C(14)–C(9)	1.397 (7)
Si–C(18)	1.892 (6)	C(20)–C(21)	1.57 (1)
Si–C(19)	1.872 (7)	C(20)–C(22)	1.57 (1)
Si–C(20)	1.860 (7)	C(20)–C(23)	1.558 (9)

Bond Angles (deg)			
O(1)–C(15)–Fe	173.9 (6)	C(1)–C(2)–C(3)	120.4 (5)
O(2)–C(16)–Fe	178.5 (7)	C(2)–C(3)–C(4)	120.2 (5)
O(3)–C(17)–Fe	179.0 (7)	C(3)–C(4)–C(5)	127.1 (5)
C(6)–C(7)–C(8)	119.3 (5)	C(4)–C(5)–C(6)	128.9 (5)
C(1)–C(7)–C(8)	118.4 (5)	C(5)–C(6)–C(7)	123.2 (5)
C(7)–C(8)–C(9)	127.4 (5)	C(6)–C(7)–C(1)	122.2 (5)
O(4)–C(8)–C(7)	119.1 (5)	C(7)–C(1)–C(2)	128.1 (5)
O(4)–C(8)–C(9)	113.4 (4)	C(9)–C(10)–C(11)	119.7 (6)
C(8)–C(9)–C(10)	118.1 (5)	C(10)–C(11)–C(12)	120.6 (6)
C(8)–C(9)–C(14)	122.1 (5)	C(11)–C(12)–C(13)	119.7 (6)
C(14)–C(9)–C(10)	119.7 (5)	C(12)–C(13)–C(14)	120.6 (6)
C(13)–C(14)–C(9)	119.3 (6)	C(15)–C(16)	100.6 (3)
Si–O(4)–C(8)	129.9 (8)	C(15)–Fe–(C17)	101.2 (3)
Si–C(20)–C(21)	109.4 (5)	C(16)–Fe-(17)	92.8 (3)
Si–C(20)–C(22)	108.1 (5)	O(4)–Si–C(18)	108.8 (3)
Si–C(20)–C(23)	110.4 (5)	O(4)–Si–C(19)	110.4 (3)
C(18)–Si–C(19)	109.5 (4)	O(4)–Si–C(20)	105.1 (3)
C(18)–Si–C(20)	109.5 (4)	C(19)–Si–C(20)	113.4 (4)

individual C–C and Fe–C bonds. The exact position of the Fe$(CO)_3$ fragment under the coordinated diene is influenced by the inductive effect of the substituent in the 7-position. This has been expressed as the difference in bond length, Δ, between (Fe–C4) and (Fe–C1).[25a] For an electron-withdrawing substituent, the value of Δ is positive: the metal fragment is skewed toward C-1. The value of Δ is +0.021 Å for both **2b** and **6**. For the heptafulvene complex **9** the value of Δ is -0.013. Displacement of the Fe$(CO)_3$ fragment toward C-4 implies that the exocyclic double bond acts as an electron-donating group. This notation is supported by a computational study which suggests that a π-donor at C-7 is slightly antibonding with respect to the metal 2e$_a$ orbital.[15] Displacement of the Fe$(CO)_3$ group minimizes this destabilizing interaction.

The cycloheptatriene ligands of these three complexes form two planes that are folded about the C1–C4 axis. The tip angles of C(1)–C(2)–C(3)–C(4) away from C(4)–C(5)–C(6)–C(7)–C(1) are 38.5° for **9**, 41.1° for **2b**, and 42.0° for **6**. These values are typical of (cycloheptatriene)Fe$(CO)_3$ derivatives.

Conclusions

Metal–polyolefin complexes have played a prominent role in the development of organometallic reagents for organic synthesis. In most cases, the ligand undergoes substitution by addition of a nucleophile to a neutral or cationic organometallic electrophile.[27]

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(24) The position of the acyl group in the putative η^3 intermediate is unknown. All of these anions are certain to be fluxional at room temperature. Variable temperature NMR studies on **1**[5] and the anion of [(EtCO$_2$)C_7H_6]-Fe$(CO)_3$[7b] failed to give definitive evidence for the low-temperature limiting structures. Efforts to crystallize one of these anions for X-ray analysis are underway.

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This wide collection of reactions has been developed extensively; there are many applications to total synthesis.

In this study we have developed an organoiron nucleophile for the introduction of two functional groups to a seven-membered ring. The reactions occur in high yield with excellent control of regio- and stereochemistry. At this point, it is possible to remove the metal fragment. For example, oxidation of **6** with pyridinium chlorochromate gives the expected ketone in 92% yield.[28] However, the retention of the $Fe(CO)_3$ fragment in the disubstituted products is significant. These compounds should be amenable to further elaboration. We are developing new procedures to expand the functionality of these substituted seven-membered rings using the iron fragment as a fulcrum for the control of regio- and stereochemistry.

Experimental Section

General Considerations. All reactions were conducted in the absence of water and oxygen with use of either Schlenk techniques or a Vacuum Atmospheres drybox. All of the chemistry described in this paper can be done without a drybox with use of standard Schlenk-cannular techniques.[29] Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Cycloheptatriene (Aldrich) and iron pentacarbonyl (Pressure Chemical) were used as obtained to prepare (cycloheptatriene)iron tricarbonyl by a literature method.[30] All other reagents and solvents were distilled from calcium hydride under a nitrogen atmosphere. Potassium hydride was stored in the drybox as a solid after removing the oil by hexane extraction. Reaction mixtures were separated and purified by flash chromatography[31] using Florisil (100–200 mesh) or silica (240–400 mesh) under aerobic conditions with reagent grade anhydrous diethyl ether and 30–60 petroleum ether; these solvents were used as obtained. Most yields are unoptimized. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. Magnetic resonance spectra were recorded on either a Bruker WM250 (250 MHz ^1H; 62.9 MHz ^{13}C), General Electric QE300 (300 MHz ^1H; 75.5 MHz ^{13}C), General Electric GN500 (500 MHz ^1H; 125.8 MHz ^{13}C) or Bruker AC200 (200 MHz ^1H; 50.3 MHz ^{13}C) spectrometer as specified. Chemical shifts are given in parts per million downfield of tetramethylsilane, and coupling constants are all recorded in Hz. Mass spectra were recorded on a Finnagan 9610 spectrometer at the University of California, Irvine or at the Mass Spectrometry Laboratory at the University of California, Riverside. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation and Reactions of (Potassium cycloheptatrienide)iron Tricarbonyl (1). In a drybox under nitrogen, (cycloheptatriene)$Fe(CO)_3$ (1.0 g, 4.3 mmol) was added to a slurry of KH (0.35 g, 8.6 mmol) in 40 mL of THF. The reaction was stirred for 2 h and then filtered through Celite to give a deep red solution of **1**. The anion was transferred to a dropping funnel, which was fitted above a Schlenk flask. The apparatus was removed from the drybox and placed on an inert atmosphere manifold.

(1–4-η-7-*exo*-Acetylcycloheptatriene)iron Tricarbonyl (2a). THF (10 mL) and acetyl chloride (0.90 mL, 13.2 mmol) were transferred by syringe to the Schlenk flask. Anion **1** was added dropwise at 0 °C slowly enough to allow dissipation of the deep red color with each added drop. The resulting murky yellow-brown solution was stirred at room temperature for 12 h. Filtration through Celite and removal of solvent left a brown oil. Purification on Florisil using 15:1 petroleum ether/Et_2O gave 0.92 g (78%) of **2a** as a yellow oil: ^1H NMR (250 MHz, $CDCl_3$) 6.02 (m, 1 H, H-5, $J_{5-6} = 10.6$, $J_{5-7} = 1.7$, $J_{5-4} = 8.0$), 5.45 (m, 2 H, H-2, 3), 5.21 (ddd, 1 H, H-6, $J_{6-7} = 4.6$), 3.48 (td, 1 H, H-7, $J_{7-1} = 4.5$), 3.11 (m, 2 H, H-1, 4), 2.12 (s, 3 H, Me); ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.2 (Fe–CO), 207.5 (C=O), 131.6, 122.7 (C-5, 6), 94.9, 88.3 (C-2, 3), 58.5, 58.3, 55.3 (C-1, 4, 7); IR ($CHCl_3$) 2050, 1989, 1708 cm^{-1}; HRMS $C_{12}H_{10}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{11}H_{10}O_3Fe$ (M^+ – CO) 245.9979, found 245.9988; *m/e* calcd for $C_{10}H_{10}Fe$(M^+ – 2CO) 218.0030, found 218.0012. LRMS 246.0 (9.2), 218.0 (9.6), 190.0 (12.6), 147.0 (84.1), 91.0 (100).

When the reaction was conducted at room temperature a second product was formed. In addition to **2a** (0.86 g, 73%), the isomer (1–4-η-7-*endo*-acetylcycloheptatriene)iron tricarbonyl was isolated as a yellow oil (0.030 g, 2%): ^1H NMR (250 MHz, $CDCl_3$) 5.91 (m, 1 H, H-5, $J_{5-6} = 10.8$, $J_{5-7} = 1.8$, $H_{5-4} = 7.9$), 5.41 (m, 2 H, H-2, 3), 5.14 (ddd, 1 H, H-6, $J_{6-7} = 4.4$, $J_{6-1} = 1.7$), 3.31 (td, 1 H, H-7, $J_{7-1} = 4.5$), 3.28 (m, 1 H, H-1), 3.01 (m, 1 H, H-4), 2.18 (s, 3 H, Me; ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.0 (Fe–CO), 143.7, 135.8 (C-5, 6), 94.1, 89.0 (C-2, 3), 60.5, 53.5 (C-1, 4), 28.6 (C-7), 24.9 (Me); IR ($CHCl_3$) 2050, 1989, 1708 cm^{-1}; HRMS $C_{12}H_{10}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{11}H_{10}O_3Fe$ (M^+ – CO) 245.9979, found 245.9983; *m/e* calcd for $C_{10}H_{10}O_2Fe$ (M^+ – 2CO) 218.0030, found 218.0019.

(1–4-η-7-*exo*-Benzoylcycloheptatriene)iron Tricarbonyl (2b). Chromatography on Florisil with 8:1 petroleum ether/Et_2O gave a yellow solid (85%): ^1H NMR (250 MHz, $CDCl_3$) 7.96 (m, 2 H, o-Ph), 7.55 (m, 3 H, *m,p*-Ph), 6.03 (m, 1 H, H-5, $J_{5-6} = 10.7$, $J_{5-7} = 1.9$, $H_{5-4} = 7.9$), 5.57 (m, 1 H, H-3), 5.47 (m, 1 H, H-2), 5.27 (ddd, 1 H, H-6, $J_{6-7} = 4.4$), 4.55 (td, 1 H, H-7, $J_{7-1} = 4.3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.5 (Fe–CO), 199.3 (C=O), 136.1, 133.2, 131.7, 128.8, 128.5, 123.2 (phenyl, C-5, 6), 95.0, 89.2 (C-2, 3), 57.8, 55.1, 52.2 (C-1, 4, 7); IR (cyclohexane) 2050, 1989, 1980, 1692 cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_4Fe$: C, 60.75; H, 3.60. Found: C, 60.90; H, 3.55.

The same reaction was conducted at room temperature. The solvent was removed from an aliquot of the reaction mixture, and the crude material was examined by ^1H NMR. In addition to **2b**, a second product was observed whose spectral characteristics were consistent with the 7-*endo*-benzoyl isomer. The integrated ratio of these two materials was ca. 70:1. The minor component was not isolated.

(1–4-η-7-*exo*-Carbomethoxycycloheptatriene)iron Tricarbonyl (2c). Chromatography on Florisil with 20:1 petroleum ether/Et_2O gave an orange oil (65%): ^1H NMR (250 MHz, $CDCl_3$) 5.96 (m, 1 H, H-5, $J_{5-6} = 10.6$, $J_{5-7} = 2.0$, $H_{5-4} = 7.9$), 5.48 (m, 2 H, H-2, 3), 5.22 (ddd, 1 H, H-6, $J_{6-7} = 4.6$, $J_{6-1} = 1.7$), 3.71 (s, 3 H, OMe), 3.53 (td, 1 H, H-7, $J_{7-1} = 4.2$), 3.21 (m, 1 H, H-1, $J_{1-2} = 7.3$), 3.03 (t, 1 H, H-4); ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.2 (Fe–CO), 173.2 (C=O), 131.1, 122.4 (C-5, 6), 95.6, 88.7 (C-2, 3), 57.2, 54.6, 52.5, 48.7 (C-1, 4, 7, OMe); IR (cyclohexane) 2052, 1995, 1984, 1779 cm^{-1}; HRMS $C_{12}H_{10}O_5Fe$ (M^+) not observed; *m/e* calcd for $C_{11}H_{10}O_4Fe$(M^+ – CO) 261.9929, found 245.9918; *m/e* calcd for $C_{10}H_{10}O_3Fe$ (M^+ – 2CO) 233.9979, found 233.9994; LRMS (EI) 262.0 (27.8), 234.0 (17.5), 206.0 (46.0), 148.0 (70.7), 91.0 (100).

[1–4-η-7-*exo*-(4-Chlorobutyryl)cycloheptatriene]iron Tricarbonyl (2d). Chromatography on Florisil with 10:1 petroleum ether/Et_2O gave an orange oil (80%). ^1H NMR (250 MHz, $CDCl_3$) 6.04 (m, 1 H, H-5, $J_{5-6} = 10.7$, $J_{5-7} = 1.7$, $H_{5-4} = 8.1$), 5.46 (m, 2 H, H-2, 3), 5.18 (ddd, 1 H, H-6), 3.57 (t, 2 H, H-10), 3.51 (m, 1 H, H-7), 3.09 (m, 2 H, H-1, 4), 2.77, 2.52 (m, 1 H, H-9, 9′), 2.03 (m, 2 H, H-8); ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.1 (Fe–CO), 208.6 (C=O), 131.9, 122.4 (C-5, 6), 95.0, 88.2 (C-2, 3), 57.9, 57.8, 55.2 (C-1, 4, 7), 44.3 (C-8), 37.0 (C-10), 26.5 (C-9); IR ($CHCl_3$) 2053, 1989, 1990, 1711 cm^{-1}; HRMS $C_{14}H_{13}O_4ClFe$ (M^+) not observed; *m/e* calcd for $C_{13}H_{13}O_3ClFe$ (M^+ – CO) 307.9903 + 309.9872, found 307.9875 + 309.98685; *m/e* calcd for $C_{12}H_{13}O_2ClFe$ (M^+ – 2CO) 279.9954 + 281.9923, found 279.99147 + 281.98826; *m/e* calcd for $C_{11}H_{13}OClFe$ (M^+ – 3CO) 252.0005 + 253.9974, found 251.99731 + 253.99415; LRMS 280.0 (15), 252.0 (17.9), 182.0 (34.8), 147.0 (79.2), 91.0 (100).

[1–4-η-7-*exo*-(Trimethylacetyl)cycloheptatriene]iron Tricarbonyl (2e). Chromatography on Florisil with 100:1 petroleum ether/Et_2O gave a yellow solid (88%): ^1H NMR (250 MHz, $CDCl_3$) 5.97 (m, 1 H, H-5, $J_{5-6} = 10.7$, $J_{5-7} = 1.5$, $H_{5-4} = 8.2$), 5.43 (m, 2 H, H-2, 3), 5.07 (ddd, 1 H, H-6, $J_{6-7} = 4.8$, $J_{6-1} = 1.7$), 4.12 (td, 1 H, H-7, $J_{7-1} = 4.7$), 3.10 (m, 1 H, H-4), 2.95 (m, 1 H, H-1), 1.20 (s, 9 H, Me's); ^{13}C NMR (62.9 MHz, $CDCl_3$) 214.9 (Fe–CO), 210.7 (C=O), 131.4, 123.8 (C-5, 6), 94.9, 88.7 (C-2, 3), 58.7, 55.5, 52.2 (C-1, 4, 7), 45.7 (C-), 25.8 (Me's); IR ($CHCl_3$) 2051, 1986, 1712 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_4Fe$: C, 56.98; H, 5.10. Found: C, 56.80; H, 5.21.

Examination of the crude reaction mixture revealed the presence of a minor byproduct whose ^1H NMR spectrum was consistent with the *endo*-trimethylacetyl compound. The exo/endo ratio was >70:1.

(1–4-η-7-*exo*-Isobutyrylcycloheptatriene)iron Tricarbonyl (2f). Chromatography on Florisil with 10:1 petroleum ether/Et_2O gave a yellow oil (36%): ^1H NMR (250 MHz, $CDCl_3$) 6.01 (m, 1 H, H-5, $J_{5-6} = 10.7$, $J_{5-7} = 1.7$, $J_{5-4} = 8.0$), 5.45 (m, 2 H, H-2, 3), 5.19 (ddd, 1 H, H-6), 3.63 (td, 1 H, H-7), 3.08 (m, 2 H, H-1, 4), 2.81 (m, 1 H, H-8, J_{8-9} and $J_{8-10} = 9.3$, 9.4 Hz), 1.10 and 1.06 (d, 3 H, H-9, 10); ^{13}C NMR (62.9 MHz, $CDCl_3$) 213.7 (Fe–CO), 210.4 (C=O), 131.7, 122.4 (C-5, 6), 94.7, 88.5 (C-2, 3), 58.0, 56.8, 55.2 (C-1, 4, 7), 38.1 (C-8), 19.3, 18.8 (C-9, 10); IR ($CHCl_3$) 2051, 1992, 1710, 1678 cm^{-1}; HRMS $C_{13}H_{14}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{12}H_{14}O_3Fe$ (M^+ – CO) 274.0292, found 274.0291; *m/e* calcd for $C_{11}H_{14}O_2Fe$ (M^+ – 2CO) 246.0343, found 246.0334; LRMS 274.0 (13.5), 246 (11.0), 218.0 (14.2), 147.0 (100), 91.0 (97.7).

Reactions of Anion 1 with Activated Carbonyl Compounds: [1–4-η-7-*exo*-(1-Hydroxy-1-methylethyl)cycloheptatriene]iron Tricarbonyl. In a general procedure, a solution of anion **1** was prepared from 2.0 g (8.6

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[27] (a) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982; Chapters 3 and 4 and references therein. (b) Hegedus, L. S. *J. Organomet. Chem.* **1988**, *343*, 147–398 and **1989**, *360*, 409–655.

[28] Williams, G. M.; Barmore, R. M. Unpublished data.

mmol) of $(C_7H_8)Fe(CO)_3$ as described above. The solution was placed in a dropping funnel above a clean dry Schlenk flask. The flask was charged with 30 mL of THF to which was added the ketone or aldehyde (acetone, 0.63 mL, 8.6 mol) and $BF_3\cdot Et_2O$ (0.79 mL, 8.6 mmol). The anion was added dropwise to the electrophile at −78 °C, and the mixture was slowly warmed to room temperature and allowed to stir for 12 h. The resulting dark red-brown solution was poured into 25 mL of H_2O and extracted with Et_2O (2 × 25 mL). The organic fractions were dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The resulting oil was purified by chromatography on silica gel (4:1 petroleum ether/Et_2O) to give 1.88 g (75%) of a pale yellow solid: ^1H NMR (200 MHz, $CDCl_3$) 5.91 (m, 1 H, H-5, $J_{5-6} = 10.9$, $J_{5-7} = 1.5$, $H_{5-4} = 7.8$), 5.51 (m, 1 H, H-2, $J_{2-1} = 7.4$, $J_{2-3} = 4.8$), 5.34 (m, 1 H, H-3, $J_{3-4} = 6.7$), 5.25 (m, 1 H, H-6, $J_{6-7} = 4.5$, $J_{6-1} = 1.3$), 3.22 (m, 1 H, H-1, $J_{1-7} = 4.5$), 2.94 (t, 1 H, H-4, $J_{4-2} = 1.5$), 2.59 (m, 1 H, H-7), 1.23 (s, 6 H, Me's); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.9 (Fe–CO), 131.1, 125.6 (C-5, 6), 94.3, 89.1 (C-2, 3), 74.2 (C-8), 60.1, 55.5, 54.3 (C-1, 4, 7), 28.0, 27.9 (Me's); IR (cyclohexane) 3410, 2064, 1980, 1949 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_4Fe$: C, 53.82; H, 4.87. Found: C, 53.74; H, 5.00.

[1–4-η-7-*exo*-(1-Hydroxyethyl)cycloheptatriene]iron tricarbonyl was prepared from acetaldehyde and purified on silica (20:1 petroleum ether/Et_2O). Recrystallization gave a pale yellow solid as a 1.6:1 mixture of diastereomers (71%); ^1H NMR (250 MHz, $CDCl_3$) 5.96 (m, 1 H, H-5), 5.52 (m, 1 H, H-2), 5.39 (m, 1 H, H-3), 5.17 (dm, 1 H, H-6), 3.89 (m, 1 H, H-8), 3.14 (m, 1 H, H-1), 2.97 (t, 1 H, H-4), 2.73 (m, 1 H, H-7), 1.22 (d, 3 H, H-9); ^{13}C NMR (62.9 MHz, $CDCl_3$) 211.4 (Fe–CO), 132.0, 125.1 (C-5, 6), 94.6, 89.7 (C-2, 3), 72.1, 71.6 (C-8), 761.4, 60.2, 55.7, 55.6, 50.8, 50.6 (C-1, 4, 7), 28.0, 27.9 (Me's); IR (KBr) 3310 cm^{-1} (cyclohexane) 2040, 1990, 1980 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4Fe$: C, 52.21; H, 4.38. Found: C, 51.27; H, 4.44.

[1–4-η-7-*exo*-(1-Hydroxy-1-phenylmethyl)cycloheptatriene]iron tricarbonyl was prepared from benzaldehyde and purified on silica (20:1 petroleum ether/Et_2O). Recrystallization gave a pale yellow solid as a 1.5:1 mixture of diastereomers (93%): ^1H NMR (250 MHz, $CDCl_3$) 7.35 (br s, 5 H, Ph), 5.98 (br t, 1 H, H-5), 5.46 (m, 1 H, H-2), 5.38 (m, 1 H, H-3), 5.09 (tt, 1 H, H-6), 4.69 (m, 1 H, H-8), 2.98 (m, 3 H, H-1, 4, 7); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.7 (Fe–CO), 142.4, 142.3, 131.9, 128.2, 127.4, 126.7, 126.2, 124.2 (C-5, 6, Ph), 94.2, 89.2, 88.6 (C-2, 3), 78.1, 77.5 (C-8), 61.7, 59.6, 55.0, 54.7, 51.0 (C-1, 4, 7); IR (neat) 3415 cm^{-1} (cyclohexane) 2045, 1990, 1985 cm^{-1}; HRMS (EI, 20 eV) *m/e* calcd for $C_{17}H_{14}O_4Fe$ (M^+) 338.0241, found 338.0725; *m/e* calcd for $C_{16}H_{14}O_3Fe$ ($M^+ - CO$) 310.0292, found 310.0287; *m/e* calcd for $C_{15}H_{14}O_2Fe$ ($M^+ - 2CO$) 282.0343, found 282.0332; LRMS (EI) 310 (11), 282 (15), 254 (39), 176 (16), 147 (57), 105 (23), 91 (100). Anal. Calcd for $C_{17}H_{14}O_4Fe$: C, 60.38; H, 4.18. Found: C, 60.51; H, 4.22.

[1–4-η-7-*exo*-(1-Hydroxy-1-cyclopentyl)cycloheptatriene]iron tricarbonyl was prepared from cyclopentanone and purified on silica (10:1 petroleum ether/Et_2O). Recrystallization gave a yellow-orange solid (70%): ^1H NMR (200 MHz, $CDCl_3$) 5.95 (m, 1 H, H-5, $J_{5-6} = 10.9$, $J_{5-7} = 1.1$, $J_{5-4} = 8.1$), 5.56 (m, 1 H, H-2, $J_{2-1} = 7.7$, $J_{2-3} = 4.7$), 5.30 (m, 2 H, H-3, 6), 3.20 (m, 1 H, H-1, $J_{1-7} = 4.9$, $J_{1-6} = 1.2$), 2.94 (t, 1 H, H-4), 2.61 (m, 1 H, H-7, $J_{7-6} = 4.5$), 1.8–1.4 (m, 8 H, cyclopentyl); ^{13}C NMR (50.3 MHz, $CDCl_3$) 211.0 (Fe–CO), 131.8, 125.1 (C-5, 6), 94.4, 89.1 (C-2, 3), 74.6 (C-8), 60.14, 55.62, 53.4 (C-1, 4, 7), 36.0, 35.2 (C-8, 8′), 25.7, 22.0 (C-9, 9′). Anal. Calcd for $C_{15}H_{16}O_4Fe$: C, 56.98; H, 5.10. Found: C, 56.92; H, 5.04.

[1–4-η-7-*exo*-(1-Hydroxy-2-ethylbutyl)cycloheptatriene]iron tricarbonyl was prepared from 2-ethylbutanal and purified on silica with 25:1 petroleum ether/Et_2O. The yellow-orange oil was isolated as a mixture of diastereomers (87%): ^1H NMR (200 MHz, $CDCl_3$) 5.94 (br q, 1 H, H-5), 5.45, 5.30 (m, 1 H, H-2, 3), 5.03 (m, 1 H, H-6), 3.38 (m, 1 H, H-8), 3.1–2.7 (3 H, H-1, 4, 7), 1.7–1.1 (5 H, H-9, 10, 12), 0.82 (m, 6 H, Me's); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.5 (Fe–CO), 132.3, 131.6, 127.0, 123.5 (C-5, 6), 93.8, 93.7, 89.1, 88.4 (C-2, 3), 76.0, 75.5 (C-8), 62.6, 58.7, 54.8, 54.7, 45.7, 43.9, 42.4 (C-1, 4, 7, 9), 21.2, 20.9, 20.6, 20.1 (C-10, 12) 10.2 (C-11, 13); IR (neat) 3470, 2040, 1965 cm^{-1}; HRMS (EI, 20 eV) $C_{16}H_{20}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{15}H_{20}O_3Fe$ ($M^+ - CO$) 304.0762, found 304.0775; LRMS (EI) 248 (16), 164 (20), 148 (32), 147 (59), 145 (19), 92 (26), 91 (100).

[1–4-η-7-*exo*-(1-Hydroxyhexyl)cycloheptatriene]iron tricarbonyl was prepared from hexanal and purified on silica with 25:1 petroleum ether/Et_2O. An orange oil was isolated as a mixture of diastereomers (76%): ^1H NMR (200 MHz, $CDCl_3$) 5.89 (br t, 1 H, H-5), 5.46 (m, 1 H, H-2), 5.32 (m, 1 H, H-3), 5.08 (m, 1 H, H-6), 3.60 (m, 1 H, H-8), 3.05 (m, 1 H, H-1), 2.89 (t, 1 H, H-4), 2.65 (m, 1 H, H-7), 1.64 (br s, 1 H, OH), 1.6–1.1 (8 H, H-9, 10, 11, 12), 0.86 (q, 3 H, H-13); ^{13}C NMR (50.3 MHz. $CDCl_3$) 210.8 (Fe–CO), 131.7, 131.4, 126.6, 124.2 (C-5, 6), 93.9, 89.3, 89.1 (C-2, 3), 75.5, 74.6 (C-8), 61.5, 58.1, 55.0, 49.2, 48.8 (C-1, 4, 7), 34.9, 33.7 (C-9), 31.7 (C-11), 26.0, 25.9 (C-10), 22.5 (C-12), 13.9 (C-13); IR (neat) 3385 (cyclohexane) 2060, 1988, 1975 cm^{-1}; HRMS (EI, 20 eV) $C_{16}H_{20}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{15}H_{20}O_3Fe$ ($M^+ - CO$) 304.0762, found 304.0754; LRMS (EI) 304 (24), 276 (18), 248 (55), 174 (20), 164 (42), 148 (36), 147 (73), 92 (18), 91 (100).

[1–4-η-7-*exo*-(1-Hydroxy-1-(2-furyl)methyl)cycloheptatriene]iron tricarbonyl was prepared from 2-furaldehyde and purified on silica with 25:1 petroleum ether/Et_2O. A yellow-orange oil was isolated as a mixture of diastereomers (94%); ^1H NMR (200 MHz, $CDCl_3$) 5.94 (br q, 1 H, H-5), 5.45, 5.30 (m, 1 H, H-2, 3), 5.03 (m, 1 H, H-6), 3.38 (m, 1 H, H-8), 3.1–2.7 (3 H, H-1, 4, 7), 1.7–1.1 (5 H, H-9, 10, 12), 0.82 (m, 6 H, Me's); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.5 (Fe–CO), 132.3, 131.6, 127.0, 123.5 (C-5, 6), 93.8, 93.7, 89.1, 88.4 (C-2, 3), 76.0, 75.5 (C-8), 62.6, 58.7, 54.8, 54.7, 45.7, 43.9, 42.4 (C-1, 4, 7, 9), 21.2, 20.9, 20.6, 20.1 (C-10, 12), 10.2 (C-11, 13); IR (neat) 3470, 2040, 1965 cm^{-1}; HRMS (EI, 20 eV) $C_{16}H_{20}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{15}H_{20}O_3Fe$ ($M^+ - CO$) 304.0762, found 304.0775; LRMS (EI) 248 (16), 164 (20), 148 (32), 147 (59), 145 (19), 92 (26), 91 (100).

[1–4-η-7-*exo*-(1-Hydroxy-1-cyclohexyl)cycloheptatriene]iron tricarbonyl was prepared from cyclohexanone. Purification on silica with 20:1 petroleum ether/Et_2O gave a pale yellow solid (81%): ^1H NMR (200 MHz, $CDCl_3$) 5.85 (m, 1 H, H-5), 5.46 (m, 1 H, H-2), 5.20 (m, 2 H, H-3, 6), 3.10 (m, 1 H, H-1), 2.84 (t, 1 H, H-4), 2.51 (td, 1 H, H-7), 1.5–1.4 (10 H, H-9, 10, 11); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.9 (Fe–CO), 131.8, 125.1 (C-5, 6), 94.3, 89.1 (C-2, 3), 74.6 (C-8), 60.1, 55.6, 53.5 (C-1, 4, 7), 35.2, 25.7, 22.0 (C-9, 10, 11); IR (KBr) 3380 (cyclohexane) 2060, 1987, 1978 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_4Fe$: C, 70.04; H, 6.63. Found: C, 70.11; H, 6.57.

[1–4-η-7-*exo*-(1-Hydroxy-1-ethylpentyl)cycloheptatriene]iron tricarbonyl was prepared from 3-heptanone and purified on silica with 20:1 petroleum ether/Et_2O. The yellow-orange oil was isolated as a mixture of diastereomers (76%): ^1H NMR (200 MHz, $CDCl_3$) 5.89 (br t, 1 H, H-5), 5.52 (m, 1 H, H-2), 5.29 (m, 1 H, H-3), 5.17 (dm, 1 H, H-6), 3.11 (m, 1 H, H-1), 2.91 (t, 1 H, H-4), 2.72 (m, 1 H, H-7), 1.7–1.1 and 1.0–0.7 (m, 14 H, H-9–14), 1.7–1.1; ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.9 (Fe–CO), 131.1, 124.9 (C-5, 6), 93.8, 89.1 (C-2, 3), 76.1 (C-8), 59.9, 55.3, 49.9 (C-1, 4, 7), 37.0, 35.7 (C-13), 30.1, 28.9 (C-9), 25.2, 25.0 (C-10), 23.0 (C-11), 13.2 (C-12), 7.5, 7.3 (C-14); IR (neat) 3490 (cyclohexane) 2063, 1989, 1974 cm^{-1}; HRMS (EI, 20 eV) $C_{17}H_{22}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{16}H_{22}O_3Fe$ ($M^+ - CO$) 318.0918, found 318.0915; LRMS (EI) 318 (17), 290 (13), 262 (30), 204 (22), 176 (20), 164 (72), 148 (100), 91 (97).

[1–4-η-7-*exo*-Methyl-7-*endo*-benzoylcycloheptratriene)iron Tricarbonyl (6). In a drybox, **2b** (0.40 g, 1.2 mmol) was dissolved in a 20-mL slurry of THF and KH (0.05 g, 1.5 mmol). The mixture was stirred for 1 h and then filtered through Celite into a clean Schlenk flask. A 5-mL solution of methyl iodide (0.10 mL, 1.5 mmol) in THF was added by syringe to the deep red anion at 25 °C. The reaction was stirred for 15 h, and then it was filtered through Celite to give a clear yellow-brown solution. The solvent was removed by rotary evaporation, and the resulting oil was purified by chromatography on silica gel (25:1 petroleum ether/Et_2O). The first compound to elute from the column gave 0.31 g (74%) of a yellow crystalline solid, **6**: ^1H NMR (250 MHz, $CDCl_3$) 7.57 (m, 2 H, *o*-Ph), 7.06 (m, 3 H, *m,p*-Ph), 5.55 (dd, 1 H, H-5, $J_{5-6} = 10.8$, $J_{5-4} = 7.6$), 5.44 (dm, 1 H, H-6, $J_{6-1} = 2.2$, $J_{6-4} = 1.0$), 4.69 (m, 2 H, H-2, 3), 3.82 (dt, 1 H, H-1, $J_{1-2} = 7.9$, $J_{1-3} = 1.4$), 2.48 (t, 1 H, H-4, $J_{4-3} = 7.3$, $J_{4-2} = 1.4$), 1.32 (s, 3 H, Me); ^{13}C NMR (62.9 MHz, $CDCl_3$) 210.2 (Fe–CO), 204.9 (C=O), 144.6, 139.0, 130.4, 128.9, 128.0, 127.5 (phenyl, C-5, 6), 94.8, 85.1 (C-2, 3), 66.7, 53.7, 53.6 (C-1, 4, 7), 31.5 (Me); IR ($CHCl_3$) 2051, 1989, 1981, 1683 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_4Fe$: C, 61.74; H, 4.03. Found: C, 61.82; H, 4.54.

The second compound to elute from the column was (1–4-η-5-benzoyl-7-*exo*-methylcycloheptatriene)iron tricarbonyl, **7**, isolated as a yellow solid in 12% yield (0.030 g): ^1H NMR (500 MHz, C_6D_6) 7.70 (m, 2 H, *o*-Ph), 7.04 (m, 3 H, *m,p*-Ph), 5.60 (m, 1 H, H-6, $J_{6-7} = 4.5$, $J_{6-4} = 1.3$, $J_{6-1} = 1.7$), 4.76 (m, 1 H, H-3, $J_{3-2} = 4.5$, $J_{3-4} = 7.6$), 4.48 (m, 1 H, H-2, $J_{2-4} = 1.2$, $J_{2-1} = 7.8$), 3.81 (dt, 1 H, H-4), 2.52 (m, 1 H, H-1), 2.17 (m, 1 H, H-7, $J_{7-Me} = 7.2$), 0.67 (d, 3 H, Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) 210.5 (Fe–CO), 197.3 (C=O), 143.6, 139.5, 138.0, 131.7, 129.4, 128.1 (phenyl, C-5, 6), 94.6, 88.3 (C-2, 3), 65.4, 52.8 (C-1, 4), 37.1 (C-7), 23.9 (Me); IR ($CHCl_3$) 2051, 1982, 1642 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_4Fe$: C, 61.74; H, 4.03. Found: C, 61.92; H, 4.18.

If the same reaction is conducted at −78 °C, 6 is isolated in 85% yield; only a trace amount (>5%) of 7 is formed. Compound **6** is also formed in very high yield from either $(5\text{-}CO_2PhC_7H_7)Fe(CO)_3$ or $(6\text{-}CO_2PhC_7H_7)Fe(CO)_3$.

(1–4-η-7-*exo*-Allyl-7-*endo*-benzoylcycloheptatriene)iron tricarbonyl was prepared from **2b** and allyl bromide and purified on silica gel (20:1 petroleum ether/Et_2O). The first compound to elute from the column gave an orange oil (64%): ^1H NMR (250 MHz, C_6D_6) 7.48 (m, 2 H, *o*-Ph), 7.07 (m, 3 H, *m,p*-Ph), 5.62 (dd, 1 H, H-5, $J_{5-6} = 11.0$, $J_{5-4} = 7.8$), 5.57 (m, 1 H, H-9), 5.40 (dd, 1 H, H-6, $J_{6-1} = 2.3$), 4.96 (m, 2 H, H-10), 4.86 (m, 1 H, H-2, $J_{2-1} = 8.0$, $J_{2-3} = 4.6$), 4.72 (m, 1 H, H-3, $J_{3-4} = 7.3$), 3.74 (br d, 1 H, H-1), 2.46 (m, 3 H, H-4, 8); ^{13}C NMR (75.5 MHz, $CDCl_3$) 211.0 (Fe–CO), 204.5 ($C{=}O$), 140.0, 133.8, 131.1, 130.9, 128.6, 128.2, 119.7 (phenyl, C-5, 6, 9, 10), 94.3, 86.9 (C-2, 3), 64.8, 59.2, 54.2 (C-1, 4, 7), 48.4 (C-8); IR ($CHCl_3$) 2050, 1983, 1683 cm^{-1}; HRMS (EI, 20 eV) $C_{20}H_{16}O_4Fe$ (M^+), $C_{19}H_{16}O_3Fe$ ($M^+ - CO$) not observed; *m/e* calcd for $C_{18}H_{16}O_2Fe$ ($M^+ - 2CO$) 350.0500, found 350.0479; *m/e* calcd for $C_{17}H_{16}OFe$ ($M^+ - 3CO$) 292.0551, found 292.0548; LRMS (EI) 320 (27), 292 (82), 251 (32), 214 (100), 105 (78).

The second compound to elute from the column was (1–4-η-5-benzoyl-7-*exo*-allylcycloheptatriene)iron tricarbonyl (yellow oil, 10%): ^{1}H NMR (300 MHz, C_6D_6) 7.73 (m, 2 H, *o*-Ph), 7.08 (m, 3 H, *m,p*-Ph), 5.71 (m, 1 H, H-6), 5.39 (m, 1 H, H-9), 4.88 (m, 1 H, H-10), 4.81 (m, 1 H, H-2), 4.68 (m, 1 H, H-3), 3.89 (dd, 1 H, H-4), 2.58, 2.31 (m, 1 H, H-1, 7), 1.85 (m, 2 H, H-8); ^{13}C NMR (75.5 MHz, $CDCl_3$) 210.4 (Fe–CO), 197.0 ($C{=}O$), 141.7, 140.5, 137.8, 135.4, 131.8, 129.4, 128.0, 117.7 (phenyl, C-5, 6, 9, 10), 94.0, 88.9 (C-2, 3), 62.8, 52.7 (C-1, 4), 42.7, 42.3 (C-7, 8); IR ($CHCl_3$) 2051, 1986, 1652 cm^{-1}; HRMS (EI, 20 eV) $C_{20}H_{16}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{19}H_{16}O_3Fe$ ($M^+ - CO$) 348.0449, found 348.0456; *m/e* calcd for $C_{17}H_{16}OFe$ ($M^+ - 3CO$) 292.0551, found 292.0539; LRMS (EI) 292 (78), 251 (42), 238 (19), 195 (39), 165 (27), 105 (100).

The final product to elute from the column was (1–4-η-6-benzoylcycloheptatriene)iron tricarbonyl (13%).

(1–4-η-7-*exo*-Methyl-7-*endo*-acetylcycloheptatriene)iron tricarbonyl was prepared from **2a** and methyl iodide and purified on silica gel (15:1 petroleum ether/Et_2O). The product was isolated as a yellow oil in 92% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 5.85 (dd, 1 H, H-5), 5.32 (m, 3 H, H-2, 3, 6), 3.47 (dt, 1 H, H-1), 2.44 (t, 1 H, H-4), 2.13 (s, 3 H, C(O)Me), 1.25 (s, 3 H, Me); ^{13}C NMR (50.3 MHz, $CDCl_3$) 211.5 (Fe–CO), 208.2 ($C{=}O$), 129.9, 128.6 (C-5, 6), 94.6, 85.3 (C-2, 3), 65.8, 53.7, 53.5 (C-1, 4, 7), 30.2 (acyl Me), 25.8 (Me); IR (cyclohexane) 2065, 1995, 1980, 1715 cm^{-1}; HRMS (EI, 20 eV) $C_{13}H_{12}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{12}H_{12}O_3Fe$ ($M^+ - CO$) 260.0136, found 260.0129; LRMS (EI, 20 eV) 260 (14), 232 (53), 204 (74), 161 (39), 134 (100), 126 (27), 105 (37).

(1–4-η-7-*exo*-Allyl-7-*endo*-acetylcycloheptatriene)iron tricarbonyl was prepared from **2a** and allyl bromide and purified on silica gel (30:1 petroleum ether/Et_2O). The first compound to elute from the column gave a yellow oil (70): ^{1}H NMR (200 MHz, $CDCl_3$) 5.89 (dd, 1 H, H-5), 5.50 (m, 1 H, H-9), 5.30 (m, 3 H, H-2, 3, 6), 4.98 (m, 2 H, H-10), 3.33 (br d, 1 H, H-1), 2.86 (m, 1 H, H-4), 2.26 (qd, 2 H, H-8), 2.09 (s, 3 H, Me); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.1 (Fe–CO), 207.5 ($C{=}O$), 133.1 (C-9), 130.4, 126.8 (C-5, 6), 118.7 (C-10), 93.4, 86.1 (C-2, 3), 63.28 58.0, 53.3 (C-1, 4, 7), 47.0 (C-8), 26.8 (Me); IR (cyclohexane) 2065, 1991, 1981, 1768 cm^{-1}; HRMS (EI, 20 eV) $C_{15}H_{14}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{14}H_{14}O_3Fe$ ($M^+ - CO$) 286.0292, found 286.0279; LRMS (EI, 20 eV) 258 (63), 230 (95), 189 (53), 187 (25), 152 (100), 133 (16), 105 (17), 91 (15).

The second compound to elute from the column was (1,4-η-5-acetyl-7-*exo*-allylcycloheptatriene)iron tricarbonyl (yellow oil, 10%): ^{1}H NMR (200 MHz, $CDCl_3$) 6.28 (br d, 1 H, H-6), 5.64 (m, 1 H, H-9), 5.36 (m, 2 H, H-2, 3), 5.08 (m, 2 H, H-10), 3.79 (dt, 1 H, H-4), 3.05 (m, 1 H, H-1), 2.79 (m, 1 H, H-7), 2.31 (m, 2 H, H-8), 2.23 (s, 3 H, Me); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.4 (Fe–CO), 197.6 ($C{=}O$), 141.0, 139.6, 135.4 (C-5, 6, 9), 117.7 (C-10), 93.7, 88.8 (C-2, 3), 62.4, 50.3 (C-1, 4), 42.6, 42.4 (C-7, 8), 25.5 (Me); IR (cyclohexane) 2040, 1991, 1979, 1670 cm^{-1}; HRMS (EI, 50 eV) $C_{15}H_{14}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{14}H_{14}O_3Fe$ ($M^+ - CO$) 286.0292, found 286.0298; LRMS (EI, 50 eV) 258 (41), 230 (64), 189 (41), 187 (22), 152 (100), 105 (21).

(1–4-η-7-*exo*-*n*-Propyl-7-*endo*-benzoylcycloheptatriene)iron tricarbonyl was prepared from the anion of **2b** and 1-iodopropane in refluxing THF (8 h) and purified on silica gel (20:1 petroleum ether/Et_2O). The major product, (7-*exo*-propyl-7-*endo*-benzoylcycloheptatriene)Fe$(CO)_3$, was isolated as a yellow crystalline solid (48%): ^{1}H NMR (300 MHz, $CDCl_3$) 7.48 (m, 5 H, Ph), 5.93 (dd, 1 H, H-5), 5.44 (m, 3 H, H-2, 3, 6), 3.72 (dt, 1 H, H-1), 2.98 (t, 1 H, H-4), 1.72 (t, 2 H, H-8), 1.38 (m, 2 H, H-9), 0.90 (t, 3 H, H-10); ^{13}C NMR (675.5 MHz, $CDCl_3$) 210.4 (Fe–CO), 204.5 ($C{=}O$), 139.6, 130.3, 129.7, 128.2, 128.0, 127.4 (phenyl, C-5, 6), 93.7, 86.0 (C-2, 3), 64.4, 58.4, 53.6 (C-1, 4, 7), 45.5, 18.3, 14.3 (*n*-Pr); IR ($CHCl_3$) 2051, 1989, 1684 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_4Fe$: C, 63.52; H, 4.80. Found: C, 63.44; H, 4.95.

Alkylation at oxygen gave a minor product, (1–4-η-8-phenyl-8-*n*-propoxyheptafulvene)Fe$(CO)_3$ (3%). In solution, this compound exists as a 2.5:1 mixture of *E* and *Z* isomers: ^{1}H NMR (500 MHz, C_6D_6) major isomer 7.10, 7.30 (m, Ph), 5.58 (d, 1 H, H-6, $J_{6-5} = 10.9$), 5.28 (dd, 1 H, H-5, $J_{5-4} = 7.9$), 4.90 (d, 1 H, H-1, $J_{1-2} = 8.2$), 4.86 (m, 1 H), 4.77 (m, 1 H) (H-2, 3), 3.36 (t, 2 H, OCH_2–), 2.74 (t, H-4), 1.42 (m, 2 H, CH_2), 0.78 (t, 3 H, Me); minor isomer 7.10, 7.30 (m, Ph), 6.55 (d, 1 H, H-6, $J_{6-5} = 11.2$), 5.59 (dd, 1 H, H-5), 4.74 (m, 1 H), 4.50 (m, 1 H) (H-2, 3), 4.02 (d, 1 H, H-1, $J_{1-2} = 8.1$), 3.24 (t, 2 H, OCH_2–), 2.74 (t, H-4), 1.32 (m, 2 H, CH_2), 0.67 (t, 3 H, Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) 211.8, 211.6 (Fe–CO), 14 signals from 153–119 (C-5, 6, 7, 8, Ph), 91.8, 91.0, 86.8, 86.2 (C-2, 3), 71.8, 71.7 (C-9), 62.9, 58.9, 57.5, 57.2 (C-1, 4), 23.1, 22.9 (C-10), 10.5, 10.4 (C-11); IR ($CHCl_3$) 2044, 1987 cm^{-1}; HRMS $C_{20}H_{18}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{19}H_{18}O_3Fe$ ($M^+ - CO$) 350.0605, found 350.0605; *m/e* calcd for $C_{18}H_{18}O_2Fe$ ($M^+ - 2CO$) 322.0656, found 322.0657; LRMS (EI) 378 (19.5), 336 (31.8), 294 (87.2), 251 (100), 165 (28.5), 105 (28.8).

(1–4-η-7-*exo*-Benzyl-7-*endo*-benzoylcycloheptatriene)iron tricarbonyl was prepared from **2b** and purified on silica gel (20:1 petroleum ether/Et_2O). The product was isolated as a yellow crystalline solid (0.50 g, 79%): ^{1}H NMR (200 MHz, $CDCl_3$) 7.6–7.0 (m, 10 H, Ph's), 5.96 (dd, 1 H, H-5, $J_{5-6} = 11.0$, $J_{5-4} = 7.5$), 5.58 (dd, 1 H, H-6, $J_{6-1} = 2.1$), 5.27 (m, 1 H, H-2, $J_{2-1} = 7.5$, $J_{2-3} = 4.6$), 5.14 (m, 1 H, H-3, $J_{3-4} = 7.4$), 3.68 (dm, 1 H, H-1), 3.31, 3.01 (AB q, 2 H, benzylic, $J_{gem} = 12.9$), 2.87 (t, 1 H, H-4); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.3 (Fe–CO), 204.4 ($C{=}O$), 139.6, 136.5, 130.8, 130.7, 130.5, 127.9, 127.7, 126.9 (phenyls, C-5, 6), 93.0, 86.3 (C-2, 3), 64.5, 60.5, 53.6 (C-1, 4, 7), 49.7 (CH_2Ph). Anal. Calcd for $C_{24}H_{18}O_4Fe$: C, 67.62; H, 4.27. Found: C, 67.41; H, 4.38.

(1–4-η-7-*exo*-Methyl-7-*endo*-carbomethoxycycloheptatriene)iron tricarbonyl was prepared from **2c** and methyl iodide and purified on silica gel (30:1 petroleum ether/Et_2O) to give an orange oil (63%): ^{1}H NMR (200 MHz, $CDCl_3$) 5.80 (dd, 1 H, H-5), 5.32 (m, 3 H, H-2, 3, 6), 3.70 (s, 3 H, OMe), 3.54 (br d, 1 H, H-1), 2.98 (t, 1 H, H-4), 1.39 (s, 3 H, Me); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.0 (Fe–CO), 174.2 (CO_2Me), 129.1, 128.0 (C-5, 6), 94.9, 85.1 (C-2, 3), 66.5, 53.9, 52.1, 47.8 (C-1, 4, 7, OMe), 30.8 (Me), HRMS (EI, 20 eV) $C_{15}H_{14}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{14}H_{14}O_3Fe$ ($M^+ - CO$) 286.0292, found 286.0298; LRMS (EI, 20 eV) 276 (22), 248 (67), 220 (96), 165 (52), 164 (53), 162 (84), 148 (100), 164 (63), 105 (82), 91 (37).

(1–4-η-8-Phenyl-8-acetoxyheptafulvene)iron tricarbonyl (8a) was prepared from **2b** and acetyl chloride. Purification on silica gel (5:1 petroleum ether/Et_2O) gave a yellow crystalline solid (72%): ^{1}H NMR (250 MHz, C_6D_6) 1.6:1 mixture of *Z* and *E* isomers, *Z* isomer, 7.45 (m, 2 H, *o*-Ph), 7.10 (m, *m,p*-Ph), 5.75 (dd, 1 H, H-6, $J_{6-1} = 1.9$, $J_{6-5} = 10.9$), 5.39 (dd, 1 H, H-5, $J_{5-4} = 8.0$), 4.92 (m, 1 H) and 4.83 (m) (H-2, 3), 4.08 (dt, 1 H, H-1, $J_{1-2} = 6.8$), 2.58 (t, H-4), 1.65 (s, 3 H, Me); *E* isomer, 7.64 (m, 2 H, *o*-Ph), 7.10 (m, *m,p*-Ph), 5.98 (dd, 1 H, H-6, $J_{6-1} = 1.9$, $J_{6-5} = 10.9$), 5.64 (dd, 1 H, H-5, $J_{5-4} = 8.0$), 4.83 (m, 1 H) and 4.68 (m) (H-2, 3), 4.02 (dt, 1 H, H-1, $J_{1-2} = 7.8$), 2.58 (t, H-4), 1.56 (s, 3 H, Me); ^{13}C NMR (62.9 MHz, $CDCl_3$) 211.3, 211.2 (Fe–CO), 168.9, 168.7 ($C{=}O$), 145.0–118.0 (13 signals from C-5, 6, 7, 8, Ph's), 94.1, 93.6, 88.4, 88.3 (C-2, 3), 59.5, 56.8, 56.6, 56.5 (C-1, 4), 21.6, 21.5 (Me's); IR ($CHCl_3$) 2050, 1996, 1767, 1736 cm^{-1}; HRMS $C_{19}H_{14}O_5Fe$ (M^+) not observed; *m/e* calcd for $C_{18}H_{14}O_4Fe$ ($M^+ - CO$) 350.02411, found 350.0220; *m/e* calcd for $C_{17}H_{14}O_3Fe$ ($M^+ - 2CO$) 322.02922, found 322.0292; *m/e* calcd for $C_{16}H_{14}O_2Fe$ ($M^+ - 3CO$) 294.03431, found 294.0334; LRMS (EI) 350 (1.3), 322 (14.3), 294 (35.7), 234 (23.3), 216 (100).

Alternatively, the same product was synthesized in 93% yield starting with (1–4-η-5-benzoylcycloheptatriene)iron tricarbonyl. Deprotonation with KH and workup by chromatography on Florisil (15:1 petroleum ether/Et_2O).

[1–4-η-8-Phenyl-8-benzoylheptafulvene)iron Tricarbonyl (8b). A solution containing 0.50 g (1.5 mmol) of **2b** in 10 mL of THF was added dropwise to a slurry of KH (0.20 g, 3.0 mmol, 10 mL of THF). After 2 h, the anion was filtered through Celite and added to a THF solution of benzoyl chloride (0.35 mL, 3.1 mmol in 10 mL). The mixture was stirred for 2 h and filtered through Celite. After the solvent was removed by rotary evaporation, the product was purified by chromatography on silica gel with 15:1 petroleum ether/Et_2O. Recrystallization gave 0.59 g (90%) of a yellow crystalline solid. In solution this compound exists as a 1.6:1 mixture of *Z* and *E* isomers: ^{1}H NMR (250 MHz, C_6D_6) *Z* isomer, 8.17 (m, 2 H, *o*-Ph), 7.59 (m, 2 H, *o*-Ph), 7.04 (m, *m,p*-Ph), 5.89 (dd, 1 H, H-6, $J_{6-1} = 10.9$), 5.44 (dd, 1 H, H-5, $J_{5-4} = 8.0$), 4.82 (m, H-2, 3), 4.16 (dt, 1 H, H-1), 2.58 (m, 1 H, H-4); *E* isomer, 8.05 (m, 2 H, *o*-Ph), 7.74 (m, 2 H, *o*-Ph), 7.04 (m, 6 H, *m,p*-Ph), 6.10 (dd, 1 H, H-6, $J_{6-1} = 2.0$, $J_{6-5} = 10.9$), 5.56 (dd, 1 H, H-5, $J_{5-4} = 8.0$), 4.82, 4.68 (m, H-2, 3), 4.12 (dt, 1 H, H-1, $J_{1-2} = 7.8$), 2.58 (m, H-4); ^{13}C NMR (75.5 MHz, $CDCl_3$) 210.6 (Fe–CO), 164.3, 163.9 ($C{=}O$), 144.0–118.0 (20 signals from C-5, 6, 7, 8, Ph's), 93.4, 93.0, 87.9, 87.7 (C-2, 3), 58.8, 56.3, 55.9, 55.8 (C-1, 4); IR ($CHCl_3$) 2050, 1986, 1742, 1736 cm^{-1}; HRMS $C_{24}H_{16}O_5Fe$ (M^+) and $C_{23}H_{16}O_4Fe$ ($M^+ - CO$) not observed; *m/e* calcd for $C_{12}H_{16}O_3Fe$ ($M^+ - 2CO$) 384.04488, found 384.0453; *m/e* calcd for $C_{11}H_{16}O_2Fe$ ($M^+ - 3CO$) 356.04997, found 356.0503; LRMS (EI) 384 (7), 356 (35), 278 (100), 234 (40), 178 (43), 165 (44), 105 (68).

[1–4-η-8-Phenyl-8-(trimethylsiloxy)heptafulvene]iron tricarbonyl (8c) was prepared from **2b** and Me_3SiCl and purified on silica gel with 10:1 petroleum ether/Et_2O to give a yellow crystalline solid (78%): ^{1}H NMR

(250 MHz, C_6D_6) 3:1 mixture of *Z* and *E* isomers, *Z* isomer, 7.30 (s, Ph), 5.79 (dm, 1 H, H-6, J_{6-1} = 1.8, J_{6-5} = 10.9), 5.34 (dd, 1 H, H-5, J_{5-4} = 7.8), 5.83 (m, 2 H, H-2, 3), 4.71 (dt, 1 H, H-1, J_{1-2} = 7.7), 2.81 (m, H-4), 0.08 (s, 9 H, $SiMe_3$); *E* isomer, 7.30 (s, Ph), 6.43 (dm, 1 H, H-6, J_{6-1} = 1.7, J_{6-5} = 11.0), 5.64 (dd, 1 H, H-5), 4.80 (m, 1 H, H-3), 4.48 (m, 1 H, H-2, J_{1-2} = 8.5), 4.22 (dt, H-4), –0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) 211.9, 211.8 (Fe–CO), 168.9, 168.7 (C=O), 150.0–118.0 (13 signals from C-5, 6, 7, 8, Ph's), 91.7, 91.0, 86.6, 86.0 (C-2, 3), 63.6, 59.4, 57.4, 57.3 (C-1, 4), 0.63, 0.32 (Me's); IR ($CHCl_3$) 2042, 1984, 1210 cm^{-1}; HRMS $C_{20}H_{20}O_4SiFe$ (M^+) not observed; *m/e* calcd for $C_{19}H_{20}O_3SiFe$ (M^+ – CO) 380.0531, found 380.0515; *m/e* calcd for $C_{18}H_{20}O_2SiFe$ (M^+ – 2CO) 352.0582, found 352.0571; *m/e* calcd for $C_{17}H_{20}OSiFe$ (M^+ – 3CO) 324.0633, found 324.0628; LRMS (EI) 380 (14.8), 352 (23.0), 324 (100), 231 (19.5), 130 (31.8).

[1–4-η-8-Phenyl-8-((*tert*-butyldimethylsilyl)oxy)heptafulvene]iron tricarbonyl (8d) was prepared from **2b** and (*tert*-butyl)dimethylsilyl chloride. Purification on silica gel with 10:1 petroleum ether/Et_2O gave an orange crystalline solid (93%): ^1H NMR (200 MHz, C_6D_6) 4:1 mixture of *Z* and *E* isomers, *Z* isomer, 7.4–6.9 (Ph), 5.68 (br d, 1 H, H-6), 5.28 (dd, 1 H, H-5), 4.9–4.4 (m, H-2, 3, 1), 2.78 (br t, H-4), 1.00 (s, 9 H, Si-*t*-Bu), 0.05 and –0.26 (s, 3 H, $SiMe_2$); *E* isomer, 7.4–6.9 (Ph), 6.43 (br d), 5.56 (dd, H-5), 4.51 (m, 1 H, H-3), 4.12 (br d, 1 H, H-1), 2.78 (br t, H-4), 0.89 (s, 9 H, Si-*t*-Bu), –0.05 and –0.32 (s, 3 H, $SiMe_2$); H-2 is masked by (H-1, 2) of the *Z* isomer; ^{13}C NMR (50.3 MHz, $CDCl_3$) 212.0 (Fe–CO), 119–150 (11 signals from C-5, 6, 7, 8, Ph's), 91.6, 90.8, 86.4, 85.9 (C-2, 3), 63.8, 59.3, 57.4 (C-1, 4), 25.7 ($SiC\mathit{Me}_3$), 18.2 ($Si\mathit{C}Me_3$), –0.10 $Si\mathit{Me}_2$. Anal. calcd for $C_{23}H_{26}O_4SiFe$: C, 61.13; H, 5.83. Found: C, 61.07; H, 5.82.

(1–4-η-8-Methyl-8-acetoxyheptafulvene)iron tricarbonyl (8e) was prepared from **2a** and acetyl chloride. Purification on silica gel with 30:1 petroleum ether/Et_2O gave a moderately stable orange oil (74%): ^1H NMR (200 MHz, $CDCl_3$) 1.2:1 mixture of *Z*:*E* isomers 5.3–5.8 (m, H-2, 3, 5, 6, *E* and *Z*), 3.83 (br d, H-1 *Z*), 3.71 (br d, H-1 *E*), 3.06 (br t, H-4 *E* and *Z*), 2.20 (s, 3 H, OAc *Z*), 2.10 (s, 3 H, OAc *E*), 1.97 (s, 3 H, Me *E*), 1.85 (s, 3 H, Me *Z*); (200 MHz, C_6D_6) 1.4:1 mixture of *Z*:*E* isomers 6.0 (d, 1 H, H-6 *E*), 5.66 (m, H-6 *Z*, H-5 *E* and *Z*), 5.0 (m, H-2, 3 *E* and *Z*), 4.13 (br d, 1 H, H-1 *Z*), 3.76 (dt, 1 H, H-1 *E*), 2.81 (br t, H-4 *E* and *Z*), 1.89 (s 3 H, OAc *E*), 1.86 (s, 3 H, OAc *Z*), 1.84 (s, 3 H, Me *Z*), 1.78 (s, 3 H, Me, *E*); ^{13}C NMR (50.3 MHz, $CDCl_3$) 210.7 (Fe–CO), 168.4, 168.1 (C=O), 143.2 (C-8), 130.1, 129.5, 119.0, 117.6 (C-5, 6), 125.0 (C-7), 92.8, 92.5, 87.1, 86.8 (C-2, 3), 57.7, 56.1, 55.8, 55.5 (C-1, 4), 20.8, 20.7 (OAc), 17.5 (Me); IR ($CHCl_3$) 2050, 1996, 1767, 1736 cm^{-1}; HRMS $C_{14}H_{12}O_5Fe$ (M^+) not observed; *m/e* calcd for $C_{13}H_{12}O_4Fe$ (M^+ – CO) 288.0085, found 288.0076; LRMS (EI, 50 eV) 288 (5), 260 (47), 232 (80), 189 (51), 172 (76), 154 (100).

Cyclization of [1–4-η-7-*exo*-(4-Chlorobutyryl)cycloheptatriene]iron Tricarbonyl. The parent 7-acyl complex was added to a slurry of KH in THF. The mixture turned deep red, but the color quickly dissipated, leaving a golden-yellow solution. Purification by chromatography on silica gel (15:1 petroleum ether/Et_2O) gave **8f** as a golden solid (79%): ^1H NMR (250 MHz, $CDCl_3$) 3.2:1 mixture of isomers 6.22 (br d, 1 H, H-6 minor), 5.51 (m, 4 H- H-6 major, H-5 both), 5.23 (m, 2 H), 5.14 (m, 2 H, H-2, 3 both), 4.43 (dt, 1 H, H-1 major), 4.2–4.4 (m, 4 H, H-11 both), 3.86 (dt, 1 H, H-1 minor), 3.28 (m, 2 H, H-4 both), 2.66 (t, 1 H, H-9 minor), 2.57 (t, 1 H, H-9 major), 2.09 (m, 4 H, H-10 both); ^{13}C NMR (75.5 MHz, $CDCl_3$) major isomer 212.3 (Fe–CO), 157.5 (C-9), 123.5, 122.9, 121.6 (C-5, 6, 7), 89.7, 84.7 (C-2, 3), 71.6, 60.1 (C-1, 4), 59.0 (C-11), 28.2, 24.4 (C-9, 10); IR ($CHCl_3$) 2083, 1980, 1625, 1600; HRMS $C_{14}H_{12}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{13}H_{12}O_3Fe$ (M^+ – CO) 272.0135, found 372.0119; *m/e* calcd for $C_{12}H_{12}O_2Fe$ (M^+ – 2CO) 244.0186, found 244.0141; *m/e* calcd for $C_{11}H_{12}OFe$ (M^+ – 3CO) 216.0237, found 216.0233.

X-ray Crystallographic Studies of ($η^4$-7-*exo*-Benzoylcycloheptatriene)Fe(CO)$_3$, 2b, ($η^4$-7-*exo*-Methyl-7-*endo*-benzoylcycloheptatriene)Fe(CO)$_3$, 6, and [$η^4$-8-(*tert*-Butyldimethylsiloxy)-8-phenylheptafulvene]Fe(CO)$_3$, 8d. Table IV lists crystal and collection data for all three compounds examined in this study. For **2b** and **6**, yellow needles, obtained from mixtures of diethyl ether/petroleum ether, were sealed under N_2 in glass capillaries. Data were collected on an automated Syntex $P2_1$ diffractometer by using standard techniques[32] and $\theta/2\theta$ scans. In the case of **6**, a correction was made for a slight (3%) intensity decay. No such correction was required for **2b**. No absorption corrections were undertaken for either compound. For each, systematic absences uniquely defined the space group.

Table IV. Crystal Data and Experimental Parameters for **2b**, **6**, and **8d**

compound	**2b**	**6**	**8d**
formula	$C_{17}H_{12}O_4Fe$	$C_{18}H_{14}O_4Fe$	$C_{23}H_{26}O_4SiFe$
fw	336.13	350.16	450.39
system	monoclinic	orthorhombic	monoclinic
a (Å)	11.790 (3)	7.587 (3)	14.896 (3)
b (Å)	6.643 (2)	16.959 (6)	6.448 (1)
c (Å)	19.419 (8)	25.099 (6)	23.679 (5)
β (deg)	99.33 (2)	90	92.47 (1)
V (Å^3)	1501	3230	2272
Z	4	8	4
ρ (calc) g cm^{-3}	1.49	1.44	1.28
space group	P_21/c	P_{cab}	P_21/c
radiation	Mo Kα	Mo Kα	Mo Kα
λ (Å)	0.70930	0.7107	0.71073
temp (°C)	25 (1)	22 (1)	25 (1)
scan rate (deg min^{-1})	2–12	3–12	2–7
2θ max (deg)	50	45	50
reflections collected	2989	2480	4497
unique reflections	2619	2376	4385
reflections with $F_o > 3.0\sigma(F_o)$	2117		2369
reflections with $I > 3\sigma(I)$		1110	
largest Δ/σ	0.38	0.10	0.00
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.031	0.043	0.076
$R_w = [\sum_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum_w\lvert F_o\rvert^2]^{1/2}$	0.051	0.053	0.086

For both **2b** and **6**, the iron atom was located by Patterson techniques. Refinement was achieved via full-matrix least-squares methods on observed reflections. Calculations were performed on a U.C. Irvine modified version of the UCLA Crystallographic Computing Package.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 ± 0.01 Å) with fixed isotropic thermal parameters.

A yellow prism of **8d** having approximate dimensions of 0.30 × 0.15 × 0.08 mm^3, grown in diethyl ether/petroleum ether, was mounted on a glass fiber with its long axis roughly parallel to the Φ axis of the goniometer. Preliminary examination and data collection were performed at California State University Northridge on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, by using the setting angles of 25 reflections in the range 5 < θ < 13°. From space group required extinctions and from subsequent least-squares refinement, the space group was determined to be *P*21/*c* (no. 14).

A total of 4497 reflections were collected, of which 4385 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 120 min. A linear decay correction was applied to the data. Lorentz and polarization corrections were applied; no absorption correction was made. A secondary extinction correction was also applied.[34]

The structure was solved with SHELXS-86[35] by using the Patterson heavy-atom method which revealed the positions of 29 atoms. Hydrogen atoms were not included in the calculations. The structure was refined by full-matrix least-squares methods with all atoms anisotropic. Scattering factors were taken from Cromer and Waber.[36] Anomalous dispersion effects were included in F_c;[36] the values for Δ*f*′ and Δ*f*″ were those of Cromer.[38] Only the 2369 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 263 variable parameters. The standard deviation of an observation of unit weight was 2.17. There were no correction coefficients greater than zero. The largest peak in the final

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difference Fourier had a height of 0.38 e/Å^3 with an estimated error based on ΔF[39] of 0.10. Plots of $\sum w(|F_o| - |F_c|)^2$ versus F_o, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. All calculations were performed on a Micro Vax II computer by using SDP/VAX.[40]

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for **2b**, **6**, and **8d** (6 pages); a listing of observed and calculated structure factors for **2b**, **6**, and **8d** (39 pages). Ordering information is given on any current masthead page.

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Oxidation of *N*-Alkylamides to Novel Hydroperoxides by Dioxygen

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Abstract: We report the facile, uncatalyzed, oxidation of 1-methyl-2-pyrrolidinone by O_2 at 75 °C and 3 atm pressure. Approximately 2 M concentrations of an oxidizing agent are formed in the neat solvent. DEPT and APT ^{13}C NMR as well as mass spectral analysis indicate that 5-hydroperoxo-1-methyl-2-pyrrolidinone is formed. The hydroperoxide is converted to 1-methylsuccinimide by peroxide decomposition catalysts.

In the course of studying solvent variation for metal-catalyzed oxidations of alkenes, we observed that the solvent 1-methyl-2-pyrrolidinone exhibited high selectivity for formation of epoxides. Cobalt(II)-catalyzed oxidation of 1-hexene with O_2 in this solvent produced 80 turnovers of 1,2-epoxyhexane in 24 h as the main product while a comparable reaction in acetonitrile produced 1-hexen-3-ol and 1-hexen-3-one almost exclusively. The selectivity to epoxide is expected for oxygen atom transfer reactions, and this suggested involvement of the solvent by chemical reaction. The mild conditions (75 °C and 50 psig of O_2) for a reaction involving this solvent prompted a study of the direct reaction of 1-methyl-2-pyrrolidinone with dioxygen.

It is well-known that the oxidation of *tert*-alkylamines to amine oxides occurs.[1-4] Metal-catalyzed oxygen atom transfer from *N*-oxides to alkenes leads to epoxides[5,6] and diols.[7,8] Amides have a very weakly basic nitrogen donor site, and conversion of this nitrogen to an *N*-oxide would be surprising. On the other hand, the stoichiometric oxidation of amides with ruthenium tetroxide[9] or persulfate[10] produces imides. Only low yields of imides are reported for the metal-catalyzed air oxidation of amides.[11,12] The metal-catalyzed (Co(II), Mn(II), Mn(III)) oxidation of amides with *tert*-butyl hydroperoxide or peracetic acid produces the corresponding imides in high yield.[13] The oxidation of straight-chain alkylamides is characterized by the autoxidation of the *N*-alkyl, CH, or CH_2 carbon. In 5- and 6-membered lactams, oxidation occurs at positions 5 and 6, respectively. *N*-Oxides are not obtained in these oxidations.

The selective epoxidation of alkenes by O_2 in this system parallels the activity of P-450. Furthermore, the amino acid proline or a proline segment in a polypeptide or protein chain has the same (O)CNCH$_2$R functionality as 1-methyl-2-pyrrolidinone and could react in a similar fashion. These parallels to the P-450 system motivated us to try to understand the selectivity imparted to catalyzed oxidations by 1-methyl-2-pyrrolidinone. The findings may have relevance to the general understanding of the selectivity of monooxygenases and mixed-function oxidases.

Experimental Section

Materials. The 1-methyl-2-pyrrolidinone was HPLC grade from Aldrich and was used as received. The 1,5-dimethyl-2-pyrrolidinone, also from Aldrich, was vacuum distilled prior to use. The 2-pyrrolidinone and L-prolinamide were purchased from Aldrich and used as received. The Co(octoate)$_2$ (octoate = 2-ethylhexanoate) catalyst was an oil solution that was 12% cobalt(II) by weight. This catalyst was purchased from Mooney and used as received.

Methods. Proton and ^{13}C NMR spectra were run on a Varian XL-300 instrument in deuterated benzene or chloroform with TMS as an internal standard in all samples. ^{13}C NMR assignments were made using the attached proton test (APT)[14-16] and the distortionless enhancement by polarization transfer (DEPT)[17] programs available on the Varian XL-300.

GC-MS were performed on a Finnigan 700 ion trap detection system (ITDS) with a Varian 3400 GC containing a 15-m SPB-1 capillary column and by the University of Florida Microanalytical Laboratories on a Finnigan single quadrupole mass spectrometer connected to a Hewlett-Packard 5890A GC containing a direct on-column injector into a 30-m DB-1 column. Chemical ionization with methane was used to detect the parent ion of the peroxide because the molecular ion of the

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