Preparation and Reactions of Tricarbonyliron Complexes of Methyl Cycloheptadienecarboxylates and Methylcycloheptadienes

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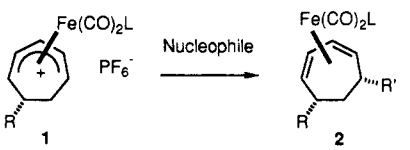
The preparation and reactions with nucleophiles of tricarbonyl[1-(methoxycarbonyl)cycloheptadienylium]iron hexafluorophosphate (7) and tricarbonyl[3-(methoxycarbonyl)cycloheptadienylium]iron hexafluorophosphate (12) were studied. Unusual regioselectivity was observed for the addition of dimethyl malonate enolate to these complexes, viz., exclusively C(2) addition to 7 and predominantly C(2) addition to 12, giving enediyl complexes. Replacement of CO ligand with triphenylphosphine does not affect this regioselectivity. Attempts to rationalize these observations using ^{13}C NMR spectroscopy and extended Huckel calculations met with limited success. The preparation and reactions of tricarbonyl(1-methylcycloheptadienylium)iron hexafluorophosphate (31) are described. Addition of malonate to 31 proceeds with exclusive formation of the substituted cycloheptadiene complex, thus confirming the marked effect of the ester substituent on the reactivity of complexes 7 and 12.

Introduction

We have previously described[1] methods for introducing substituents onto cycloheptadiene in a stereocontrolled manner, via nucleophile additions to cycloheptadienyl–$Fe(CO)_2L$ complexes of general structure 1, and this has



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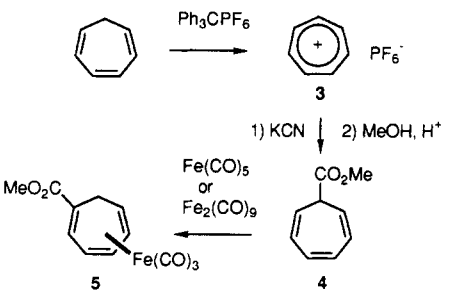
led to the construction of subunits of interest for the synthesis of macrolide antibiotics.[2] Owing to the fact that 1 (R = H) has a plane of symmetry, the products of nucleophile addition (2) are obtained in racemic form. This has been partially solved by developing methods for diastereoselective addition of chiral enolate nucleophiles,[3] but more reliable methods are required for obtaining optically pure materials. The use of substituted dienes is a promising avenue of investigation, since it has been shown that analogous cyclohexadiene–$Fe(CO)_3$ complexes can be obtained optically enriched by an asymmetric complexation procedure[4] or optically pure by resolution.[5] However, the chemistry of cycloheptadienyliron cations differs markedly from that of the cyclohexadienyl systems. Therefore, we undertook the present study to determine whether ester-substituted cycloheptadiene complexes can be prepared efficiently and whether they can be converted regioselectively to the dienyl cations. The results of nucleophile addition to the resulting ester-substituted dienyl complexes are somewhat unusual and are also discussed in this paper.

Results and Discussion

Preparation of Methoxycarbonyl-Substituted Diene and Dienyl Complexes. Our initial approach to the desired ester-substituted complexes started with the cycloheptatrienylium (tropylium) ion 3, readily prepared by



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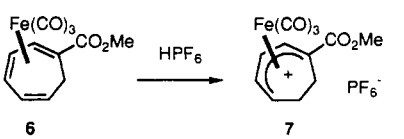
reaction of cycloheptatriene with triphenylmethyl hexafluorophosphate.[6] Addition of potassium cyanide and subsequent methanolysis gave the ester-substituted cycloheptatriene 4. Treatment of 4 with $Fe(CO)_5$ or $Fe_2(CO)_9$ gave the cycloheptatriene complex 5, where the ester is attached to the uncomplexed double bond. This complex showed spectroscopic properties identical to those reported by Deganello and co-workers,[7] for the same compound prepared by a different route. We had hoped to obtain not complex 5 but complex 6 from this sequence, since protonation of 6 is expected to give the dienyl derivative 7.



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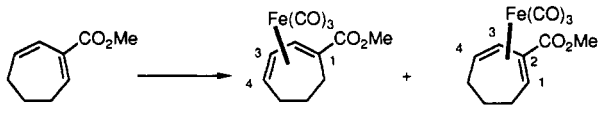
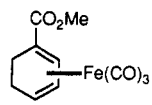
Therefore, this approach was abandoned in favor of a more reliable route via cycloheptadienecarboxylate derivative **8**, the preparation of which was recently reported.[8] Treatment of **8** with $Fe(CO)_5$ in refluxing di-*n*-butyl ether



8 **9** **10**

Method	Ratio 9 : 10	Yield
8 + $Fe(CO)_5$, Bu_2O, 140°C	3:1	75%
8 + $Fe_2(CO)_9$, acetone, 35°C	1:4	66%

afforded a 75% yield of a 3:1 mixture of complexes **9** and **10**. Birch and Williamson[9] have shown that treatment of analogous mixtures of cyclohexadiene complexes with methanolic sulfuric acid leads to complete conversion to the 1-CO_2Me complex (**11**). Isomerization of the mixture



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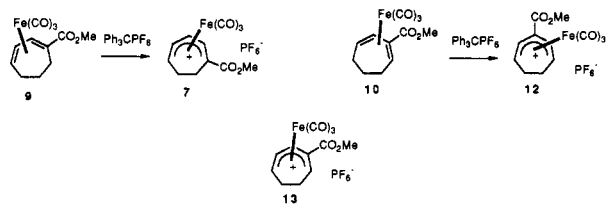
of **9** and **10** under similar conditions gave a 5:1 mixture in favor of **9**, which is apparently the thermodynamic ratio. Separation of the mixture of complexes could be effected either by fractional crystallization or, for small scale preparations, by careful flash chromatography.[10]

Treatment of **8** with $Fe_2(CO)_9$ in acetone at 35 °C, which are milder complexation conditions, gave a 1:4 mixture in favor of **10**. Thus, enriched samples of **9** or **10** could be prepared directly, according to reaction conditions, and pure complexes were readily accessible by standard separation procedures. Reaction of complexes **9** and **10** with triphenylmethyl hexafluorophosphate gave the corresponding dienyl salts **7** (95% yield) and **12** (67% yield),



respectively. In each case, no trace of the isomeric 2-CO_2Me complex **13** was present according to ^1H NMR spectroscopy, in agreement with the known powerful regiodirecting effects of the ester group observed in the cyclohexadiene series.[9]

Reactions of Dienyl Complexes with Nucleophiles. The reactions of complexes **7** and **12** with a variety of simple nucleophiles were studied. We have previously shown that "soft" nucleophiles (e.g. R_2CuLi, $NaCH(CO_2Me)_2$, PhSNa) add to the terminal dienyl carbon of simple complexes, such as **1**, to give diene products **2**, whereas "hard" nucleophiles (RLi, BH_4^-, CN^-) add to C(2) giving enediyl complexes of structure **14**.[1,11] This has been

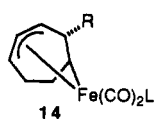


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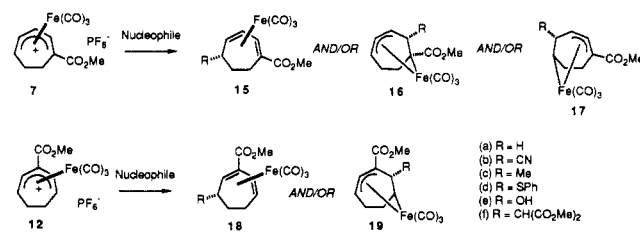
Table I. Reactions of Ester-Substituted Cycloheptadienyliron Complexes 12, 13, and 26 with Nucleophiles

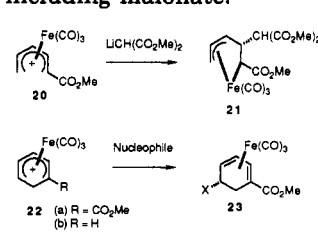
complex	nucleophile	product(s) (ratio)	yield, %
7	$NaBH_4$	**16a**	60
7	NaCN	**16b**	88
7	$Me_2CuMgCl$	**15c**	64[a]
7	NaSPh	**15d**	81
7	NaOH	**15e**	36
7	$NaCH(CO_2Me)_2$	**16f**	82
12	$NaBH_4$	**19a**	61
12	NaCN	**19b**	56
12	Me_2CuLi	**18c**	64[a]
12	NaSPh	**18d**	88
12	NaOH	**18e**	63
12	$NaCH(CO_2Me)_2$	**18f** + **19f** (1:8)	83
25	$NaBH_4$	**27a**	60
25	NaCN	**27b**	74
25	Me_2CuLi	**26c**	74[a]
25	NaSPh	**26d**	60
25	NaOH	**26e**	63
25	$NaCH(CO_2Me)_2$	**27f**	56

[a] The use of $Me_2CuMgCl$ or Me_2CuLi gave the same regiochemical outcome, but the yield of complex **16c** was lower when Me_2CuLi was used.

partially rationalized as being due to a delicate balance of orbital control, which favors addition to the terminal carbons, and charge control, which favors addition at C(2). Thus, we can expect products of general structure **15**, **16**, or **17** from complex **7** and **18** or **19** from **12**. The results of nucleophile additions are summarized in Table I.



The harder nucleophiles hydride and cyanide give exclusively enediyl complexes in both series, while typically "soft" nucleophiles, $Me_2CuMgCl$ and PhSNa, give products of terminal addition, as expected. Hydroxide is somewhat anomalous, being a "hard" nucleophile[12] but giving **15e** and **18e**, exclusively. Malonate enolate, which behaved as a soft nucleophile in all of our previous studies, gives *exclusively* the C(2) adduct **16f** from **7** and an 8:1 mixture in favor of the enediyl complex **19f** from **12**. Interestingly, *none* of the nucleophiles studied gave the enediyl complex **17** on reaction with **7**. Donaldson and co-workers[13] have recently reported identical behavior for the acyclic pentadienyl complex **20**, which gives **21** on reaction with $LiCH(CO_2Me)_2$. However, the cyclohexadienyl complex **22a** gives *only* the diene product **23** on reaction with all nucleophiles, including malonate.[9,14]



(12) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.
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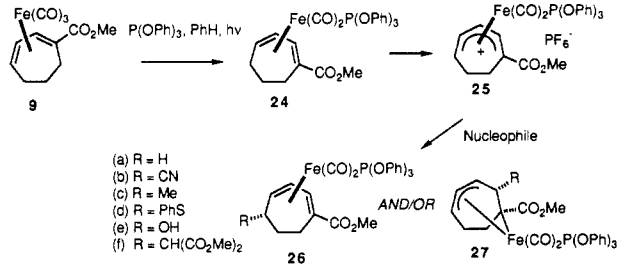
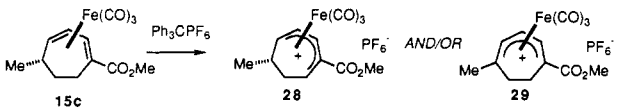
We have previously shown[1] that the regioselectivity of nucleophile additions to complexes **1** can be changed quite dramatically by ligand substitution, i.e., changing L = CO to L = PPh_3 or $P(OPh)_3$. Making a somewhat naive assumption that the regiochemistry observed during the reaction of **12** with malonate is due to electron withdrawal by CO_2Me, resulting in an electron-poor dienyl ligand, we sought to counter this by replacing a CO ligand with triphenylphosphite. Irradiation of complex **9** with $P(OPh)_3$



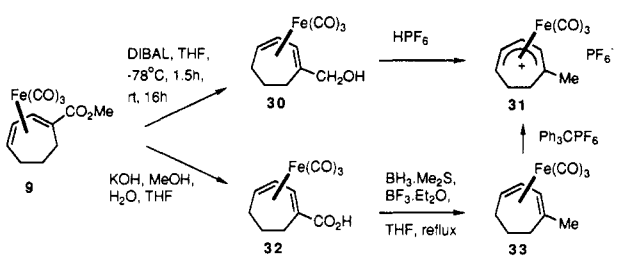
in benzene solution, using a 100-W Hanovia lamp, followed by crystallization, gave the complex **24** in 86% yield, and hydride abstraction afforded **25** in 71% yield. The reactivity of **25** toward nucleophiles is identical to that of **7** and is summarized in Table I. These results are discussed later.

Double-Functionalization Experiments. In order to use the ester-substituted complex **7**, which is unsymmetrical and can be resolved to give optically pure complexes, for synthesis in a manner analogous to that developed for complexes **1**, it is desirable to develop conditions for conversion of the substituted complexes, such as **15c**, to dienyl



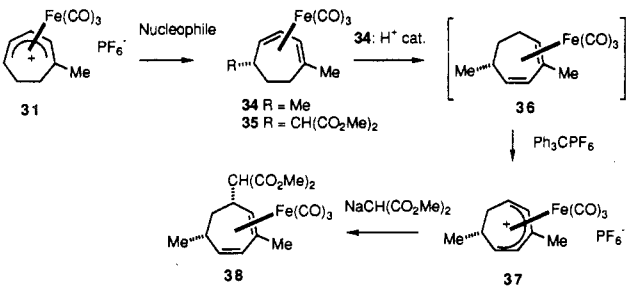
complexes, e.g., **28**. All attempts to effect the conversion of **15c** to **28** failed, starting material being recovered even after prolonged treatment with Ph_3CPF_6 in refluxing methylene chloride. This confirms the powerful regiodirecting effect noted for the ester group.[9] No dienyl complex of structure **29** is formed because only hydride anti to the metal can be removed in this process.

In an attempt to circumvent this problem, and retain the potential for using optically pure complexes, we investigated the conversion of complex **9** to the methyl-



substituted derivatives **31**. Two possible approaches to the preparation of **31** were examined. The first, based on the observations of Birch and Williamson[9] for cyclohexadiene complexes, involves reduction of **9** to the primary alcohol **30**, followed by acid treatment of **30** to give **31**. The yield for the conversion of **30** to **31** was rather low, and this reaction was not investigated further, since a better route was found. Thus, hydrolysis of **9** afforded the carboxylic acid **32** in 84% yield, and direct conversion of this to the methyl-substituted complex **33** was accomplished in 78% yield using borane–dimethyl sulfide in the presence of BF_3–etherate.[15] Hydride abstraction from **33** proceeded cleanly to give **31** as the sole product, the regioselectivity of this reaction presumably being due to steric hindrance at the alternative C(7) methylene group.

The behavior of **31** toward nucleophiles was somewhat different from that of complex **7**. Treatment with dimethylcuprate gave complex **34** in 75% yield, as expected, while treatment with $NaCH(CO_2Me)_2$ gave **35** in 83% yield, the product of addition to the dienyl terminus. The latter result parallels the behavior of complexes of type **1** and differs from complexes **7** and **12**, thereby confirming the profound effect of the ester substituent on the reactivity of these complexes. Furthermore, the reaction of **31** with dimethylcuprate proceeds more cleanly and in



better yield than the reactions of **1** (L = CO), which gives low yields of mixtures of alkylated product and dimers arising from reductive coupling. This behavior suggests that even weakly electron-donating substituents attached to the dienyl can favorably influence the outcome of nucleophile addition. Treatment of the adduct **34** with $Ph_3C^+PF_6^-$ resulted in the formation of the *unexpected* dienyl complex **37**, which is produced via acid-catalyzed rearrangement of **34** to give **36**, which then undergoes hydride abstraction.[16] Surprisingly, this rearrangement does not occur for complex **15c**, presumably due to the destabilizing effect of CO_2Me on the intermediate π-allyl–$Fe(CO)_3$ cations. The acid is produced by reaction of the trityl cation with traces of moisture during storage and use. Removal of this by prior treatment with anhydrous K_2CO_3, followed by reaction of the so-formed acid-free trityl cation with complex **34**, gave no product of hydride abstraction. We presume that steric hindrance at the 7-methylene position of **34**, which is essentially flanked by two methyls, completely suppresses the approach of the bulky trityl cation. Reaction of **37** with diethyl sodiomalonate proceeded as expected to give **38** in 85% yield.

Thus, it is possible to control the reactivity of the cycloheptadiene and cycloheptadienyl complexes and to attain stereocontrolled double functionalization of unsymmetrically substituted complexes that offer the potential for asymmetric synthesis.

Resolution of Carboxylic Acid Complexes. If the above methodology is to be useful, it is necessary to produce the (cyloheptadiene)iron complexes in optically pure form. Two approaches have been described in the literature for the resolution of methoxycarbonyl-substituted diene–$Fe(CO)_3$ complexes: (1) enantioselective hydrolysis of racemic methyl or ethyl esters using pig's liver esterase, reported to be successful when used with acyclic butadi-

(14) Pearson, A. J.; Zettler, M. W. *J. Am. Chem. Soc.* **1989**, *111*, 3908.

(15) Meyers, A. I.; Slade, J. *J. Org. Chem.* **1980**, *45*, 2785.

(16) Acid-catalyzed rearrangement of diene–$Fe(CO)_3$ complexes are well-known; see: Birch, A. J.; Haas, M. A. *J. Chem. Soc. C* **1971**, 2465. A unidirectional rearrangement as implied in the conversion **34** to **36** would preserve the chirality in complex **34**, thereby allowing the preparation of optically active complexes. This has not yet been tested in our laboratory.

ene–$Fe(CO)_3$ complex;[17] (2) classical resolution of the carboxylic acid via (1-phenylethyl)ammonium salts, as reported by Birch for the cyclohexadiene complexes.[5] All attempts to effect enzymatic hydrolysis of complex **9** or **10** failed. Therefore, the carboxylic acid **32** was treated with (*S*)-(−)-1-phenethylamine to give the desired alkylammonium salt as a mixture of diastereomers. Fractional crystallization from acetone/chloroform and subsequent treatment with dilute hydrochloric acid afforded the carboxylic acid complex (−)-**32**, which was recrystallized to constant specific rotation. The absolute stereochemistry is tentatively assigned as shown in the structure by analogy with the cyclohexadiene complex.

Regioselectivity of Nucleophile Additions to Complexes 7 and 12. The reactions of cycloheptadienyliron complexes with nucleophiles fall into three groups, with regard to the regiochemical outcome: (1) those additions that occur at the dienyl terminus to give substituted 1,3-diene complexes, (2) those additions that occur at C(2) or C(4) to give enediyl complexes, and (3) those additions that occur on a CO ligand. The latter may be followed by deinsertion and CO loss, but since it is not observed with complexes studied here, we shall not discuss this mode of addition.

It appears that acyclic pentadienyliron complexes may follow the same trends, although the available results are less extensive than for the seven-membered ring. In contrast, the cyclohexadienyliron complexes studied so far react with nucleophiles *only* at the dienyl terminal carbon, regardless of the nature of substituents or spectator ligands. At the present time, we can offer no explanation for the marked difference in behavior of the six-membered ring system, and we shall confine the present discussion to the trends observed for the cycloheptadienyl ligand.

We have proposed earlier that C(1) attack is characteristic of "softer" nucleophiles, having a high-energy HOMO, because these experience a stronger interaction with the LUMO of the dienyl complex. Typically, this list has included cuprates, thiophenoxide, and the enolate from dimethyl malonate. MO calculations[18] indicate that this LUMO has larger coefficients at the terminal carbon atoms than at C(2)/C(4), suggesting that an orbital-controlled nucleophile addition would occur there. On the other hand, "harder" nucleophiles, with lower energy HOMOs, would experience a weak frontier orbital interaction, and the site of addition is more likely to be charge-controlled.[19] It has been shown, using ^{13}C NMR spectroscopy and MO calculations, that C(2) and C(4) of the complexed dienyl ligand carry the highest positive charge. A nucleophile that adds under charge control would be expected to seek the more electrophilic carbon, and this is expected to be that having the greater positive charge. The balance between orbital and charge control is expected to be related to the difference in energy between the nucleophile HOMO and dienyl complex LUMO[19] or, for an identical set of nucleophiles, the variation in LUMO energy for a series of complexes. On the basis of these suppositions, we have examined the following parameters: (1) relative charge densities as revealed by ^{13}C NMR shieldings[20] and EHT calculations;[21] (2) relative energy levels for the dienyl–$Fe(CO)_3$ LUMO; (3) coefficients at each carbon in the complexed dienyl LUMO.

Table II. Carbon-13 NMR Shieldings[a] for Dienyliron Complexes

complex	^{13}C chem shift				
	C(1)	C(2)	C(3)	C(4)	C(5)
22b	65.4	103.2	89.9	103.2	65.4
22a	52	101.7	88	99.7	68.6
cyclohexadienyl-3-CO_2Me–$Fe(CO)_3$	68.6	103	89.6	103	68.6
1 (R = H, L = CO)	94.9	104.1	100.8	104.1	94.9
1 (R = H, L = $P(OPh)_3$)	95.2	104.5	101.1	104.5	95.2
7	*b*	106.8	100.6	104.9	99.4
12	97.1	104.0	100	104.0	97.1
20[c]	64.9	106.2	98.0	105.8	68.5

[a] In ppm downfield from Me_4Si internal standard. All run in CD_3CN solution. [b] Not observed. [c] Data provided by Professor W. A. Donaldson at Marquette University.

Table III. Relative Positive Charge Densities for Pentadienyl–$Fe(CO)_3$ Complexes, Calculated by EHT Methods

complex	charge densities[a]				
	C(1)	C(2)	C(3)	C(4)	C(5)
pentadienyl–$Fe(CO)_3$	0	0.31045	0.16575	0.31045	0
pentadienyl-1-CO_2H–$Fe(CO)_3$	0.02164	0.4536	0.22839	0.45197	0
pentadienyl-3-CO_2H–$Fe(CO)_3$	0	0.30335	0.11278	0.30335	0

[a] Adjusted to give C(5) a charge density of 0.

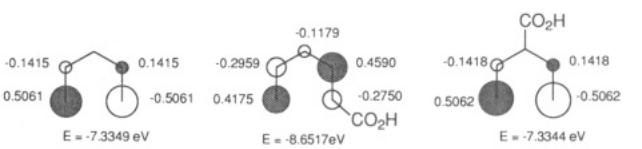


Figure 1. Coefficients and energy levels for the lowest unoccupied molecular orbital of pentadienyl–$Fe(CO)_3$ cations (metal omitted for clarity).

^{13}C NMR data for several cyclohexadienyl and cycloheptadienyl complexes, measured in our laboratory, together with data for the acyclic complex **20**, provided by Professor W. A. Donaldson,[22] are given in Table II. The *relative* charge densities calculated for *acyclic* pentadienyl complexes using EHT methods are given in Table III. These are expected to be approximate, given the limitations of EHT calculations, and in order to facilitate comparison, we have adjusted the values such that the C(5) charge density is set at zero. The calculated distribution agrees quite well with the NMR data, and it can be seen that only slight perturbations are caused by introduction of the CO_2Me group, in all cases. We conclude that the preference for addition of certain ("hard") nucleophiles at C(2) is not due to a marked difference in positive charge between C(2) and C(4).

The coefficients for the dienyl carbons in the complex LUMO are summarized diagrammatically in Figure 1. This is a much more difficult set of parameters to obtain because there is a cluster of metal orbitals in the energy range −7 to −9 eV that show dienyl character and that are very close in energy, as with earlier EHT results obtained from cyclohexadienyliron complexes.[18a] The coefficients listed are for the orbital that shows uncomplexed dienyl ψ_4 character. Also included in Figure 1 are the calculated LUMO energy levels. The unsubstituted complexed pentadienyl ligand has large coefficients at the terminal

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carbons, in agreement with previous results, supporting the notion that orbital-controlled nucleophilic addition should occur at the dienyl terminus. The 3-CO_2H dienyl also shows a larger coefficient at the termini than at C-(2)/C(4). Furthermore, there is essentially no change in LUMO energy on introducing the CO_2H group at C(3), suggesting that the interactions between nucleophile HOMO and complex LUMO should be unchanged. On this basis, no explanation can be offered for the change in regioselectivity of malonate addition in going from cycloheptadienyl-$Fe(CO)_2L$ (C(1)/C(5)) to 3-(methoxycarbonyl)cycloheptadienyl-$Fe(CO)_3$ (predominantly C-(2)/C(4)). The 1-CO_2H dienyl complex LUMO does show a marked difference in coefficients compared with the unsubstituted system. Indeed, C(2) now shows the largest coefficient, so we might expect a pronounced tendency for nucleophiles to add here, as is indeed observed in several cases. However, the fact that similar effects are not observed for the 3-CO_2H system, and the fact that not all nucleophiles add at C(2), lead to some uncertainty about the significance of these observations. Also, the LUMO energy level is *lowered* for the 1-CO_2H system relative to both the parent and 3-CO_2H, indicating that a stronger orbital interaction should occur with the HOMO for *all* nucleophiles.

The main conclusion that can be drawn from these measurements and calculations is that the observed changes in regioselectivity for malonate addition are not due to strong perturbations in charge distribution and that the predominant C(2) addition mode for complex **7** is not due to a higher charge at this carbon compared with C(4). There might be a preference for some nucleophiles to attack at C(2) because of the unusually large coefficient here, but we are unable to explain the difference observed between malonate on the one hand and cuprates or thiophenoxide on the other. It is of course possible that different nucleophiles will be subject to different controlling factors, depending on the exact position of the transition state along the reaction coordinate. Thus, reactions having early transition states might be influenced by coefficient and/or charge distribution in the dienyl complex, while those having late transition states would be more sensitive to thermodynamic effects (strength of bonds in the resulting complex). Clearly, a much more sophisticated analysis of the reaction profile is required for a full understanding of these phenomena.

Experimental Section

All reactions were carried out under a dry argon or nitrogen atmosphere. Solvents were freshly distilled under nitrogen as follows: Et_2O from $LiAlH_4$, THF and benzene from Na/benzophenone, and CH_2Cl_2 from CaH_2. Di-*n*-butyl ether was filtered through basic alumina to remove peroxides and purged with dry nitrogen prior to use. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. NMR spectra were recorded on a Varian XL-200 spectrometer, and peak assignments were made by using homonuclear ^1H-decoupling experiments. Elemental analyses were obtained from Galbraith Laboratories Inc., Knoxville Tn, and high-resolution mass spectra were obtained in house on a Kratos MS25A spectrometer.

Tricarbonyl[1–4-η-1-(methoxycarbonyl)cyclohepta-1,3-dienyl]iron (9). To a clean, dry flask under argon was added 2-(methoxycarbonyl)cyclohepta-1,3-diene (1.0 g), $Fe(CO)_5$ (1.93 g, 1.3 mL), and 50 mL of butyl ether (degassed). This solution was heated to reflux and stirred for 24 h. The solution was cooled to room temperature and filtered through Celite. (*Caution!* Pyrophoric iron is produced by thermal decomposition of iron pentacarbonyl.) The butyl ether was then removed on the rotary evaporator. The resultant oil was taken up in ethyl acetate and passed through a column of silica gel to remove impurities. The filtrate was concentrated, taken up in chloroform, and adsorbed onto flash silica gel. Flash chromatography (SiO_2, 5% ethyl acetate/pentanes) with dry loading yielded 1.13 g of complex **9** and 0.37 g of **10** (total yield 75%). Complex **9** gave the following data. Mp: 76–78 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 2050, 1980, 1700. ^1H NMR ($CDCl_3$): δ 5.99 (d, 1 H, J = 5 Hz, H-2), 5.29 (dd, 1 H, J = 8, 10 Hz, H-3), 3.67 (s, 3 H, $-OCH_3$), 3.19 (t, 1 H, J = 7 Hz, H-4), 2.00 (dt, 2 H, J = 4, 12 Hz, H-5_{exo}, H-5_{endo}), 1.9 (broad triplet, 2 H, J = 11 Hz, H-7_{exo}, H-7_{endo}), 1.47 (ddd, 1 H, J = 3, 7, 11 Hz, H-6_{exo}); 1.23–1.00 (m, 1 H, H-6_{endo}). Anal. Calcd for $C_{12}H_{12}O_5Fe$: C, 49.35; H, 4.14. Found: C, 49.42; H, 4.14.

Tricarbonyl[1–5-η-1-(methoxycarbonyl)cyclohepta-1,3-dienylium]iron Hexafluorophosphate (7). To a solution of the ester complex **9** (1.0 g, 3.42 mmol) in 8.0 mL of methylene chloride was added triphenylmethyl hexafluorophosphate (2.92 g, 7.52 mmol) in 7 mL of methylene chloride. After 24 h of stirring at room temperature, the red solution was concentrated under reduced pressure and the dark syrup was dissolved in a minimum of acetonitrile. This solution was added slowly and dropwise to 200 mL of wet ether. The yellow precipitate was collected by decanting the ether. The solid was rinsed several times with ether by decantation and was dried in vacuo. This yielded 1.42 g (95%) of **7** as a light yellow powder. IR (cm^{-1}, CH_3CN): ν_{max} 2110, 2065, 1715. ^1H NMR (CD_3CN): δ 7.12 (t, 1 H, J = 6 Hz, H-3), 6.86 (d, 1 H, J = 6 Hz, H-2), 5.95 (t, 1 H, J = 9 Hz, H-4), 5.33 (m, 1 H, H-5), 3.80 (s, 3 H, $-OCH_3$), 3.02 (ddt, 1 H, J = 4, 9, 17 Hz, H-6_{exo}), 2.63 (t, 1 H, J = 12 Hz, H-7_{exo}), 2.31 (m, 1 H, H-6_{endo}), 1.11 (m, 1 H, H-7_{endo}). Anal. Calcd for $C_{12}H_{11}O_5F_6FeP$: C, 33.03; H, 2.54. Found: C, 32.89; H, 2.57.

Tricarbonyl[1–4-η-1-(methoxycarbonyl)-5-methylcyclohepta-1,3-dienyl]iron (15c). Copper(I) iodide (219 mg, 1.14 mmol) was suspended in 25 mL of THF in a clean, dry flask under a nitrogen atmosphere. The stirred suspension was cooled to −10 °C, and to it was added dropwise methyl magnesium chloride (765 μL of a 3.0 M solution). This was stirred for 40 min at −10 °C and then cooled to −78 °C. The dienyl complex **7** (250 mg, 0.573 mmol) was added in one portion. The reaction mixture was stirred at −78 °C for 20 min and then allowed to warm to room temperature slowly. The solution was poured into 50 mL of saturated aqueous ammonium chloride, and the mixture was stirred for 30 min and then extracted three times with diethyl ether. The ether solution was filtered through a plug of silica gel, washed with brine, and dried over $MgSO_4$. Solvent removal under reduced pressure gave an amber oil. Flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave 130 mg (75%) of a yellow oil which crystallized on standing. Mp: 68–69 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 2045, 1965, 1700. ^1H NMR ($CDCl_3$): δ 5.99 (d, 1 H, J = 5 Hz, H-2), 5.29 (dd, 1 H, J = 5, 8 Hz, H-3), 3.69 (s, 3 H, $-OCH_3$); 2.98 (d, 1 H, J = 7 Hz, H-4), 2.12–1.96 (m, 3 H, H-5, H-7_{endo}, H-7_{exo}), 1.47–1.38 (m, 1 H, H-6_{exo}), 1.00 (e, 3 H, J = 7 Hz, $-CH_3$), 0.80 (qd, 1 H, J = 13, 5 Hz, H-6_{endo}). Anal. Calcd for $C_{13}H_{14}O_5Fe$: C, 51.10; H, 4.60. Found: C, 51.18; H, 4.50.

Tricarbonyl[1–4-η-1-(methoxycarbonyl)-5-(phenylthio)-cyclohepta-1,3-dienyl]iron (15d). A suspension of sodium thiophenoxide was formed by reacting thiophenol (142 mg, 1.29 mmol) and NaH (68 mg, 50% dispersion in mineral oil, 1.1 equiv) in 10 mL of THF. A 1.0-mL aliquot of this suspension was added to a suspension of the dienyl salt **7** (50 mg, 0.115 mmol) in a clean, dry flask under an argon atmosphere. This mixture was stirred for 10 min and then diluted with diethyl ether. The reaction mixture was washed with brine and the organic phase collected and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow oil. Purification by flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave 37 mg (81%) of a yellow crystalline material. Mp: 118–120 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 1990, 1700. 200-MHz ^1H NMR ($CDCl_3$): δ 7.43–7.26 (m, 5 H, SPh), 6.05 (d, 1 H, J = 5 Hz, H-2), 5.30 (dd, 1 H, J = 5, 7 Hz, H-3), 3.69 (s, 3 H, $-OCH_3$), 3.61 (ddd, 1 H, J = 1.4, 4, 12 Hz, H-5), 3.3 (d, 1 H, J = 7 Hz, H-4), 2.21 (dt, 1 H, J = 3, 12 Hz, H-7_{exo}), 2.11 (dt, 1 H, J = 4, 12 Hz, H-7_{endo}), 1.86–1.76 (m, 1 H, H-6_{exo}), 1.16 (dd, 1 H, J = 4, 12 Hz, H-6_{endo}). Anal. Calcd for $C_{18}H_{16}O_5FeS$: C, 54.00; H, 4.00. Found: C, 53.88; H, 3.97.

Tricarbonyl[1–4-η-1-(methoxycarbonyl)-5-hydroxycyclohepta-1,3-dienyl]iron (15e). Complex **7** (20.0 mg, 4.59×10^{-5} mol) was stirred in 2.0 mL of THF at 0 °C, and NaOH (2.2 mg, 5.5×10^{-5} mol) in 0.5 mL of water was added in one portion. The reaction mixture was stirred for 30 min and then allowed to warm

to room temperature. This was extracted with diethyl ether three times, and the combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed under reduced pressure to give an oil. Purification by flash chromatography (SiO_2, 50% ethyl acetate/hexanes) gave 5.0 mg (36%) of product **15e** as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 3600, 2050, 1985, 1715. 200-MHz ^1H NMR ($CDCl_3$): δ 6.04 (d, 1 H, J = 5 Hz, H-2), 5.44 (dd, 1 H, J = 5, 7 Hz, H-3), 4.14–4.05 (m, 1 H, H-5), 3.68 (s, 3 H, $-OCH_3$), 3.00 (d, 1 H, J = 7 Hz, H-4), 2.33–2.10 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.75–1.59 (broad m, –OH), 1.27–1.15 (m, 1 H, H-6_{exo}), 1.01 (qd, 1 H, J = 12, 5 Hz, H-6_{endo}). HRMS for $C_{13}H_{14}O_5Fe$ (M^+): calcd, m/e 307.9983; found, m/e 307.9959.

Tricarbonyl[3-5-η-1-σ-1-(methoxycarbonyl)cyclohept-3-enediyl]iron (16a). Sodium borohydride (20 mg) was stirred in a mixture of 1.0 mL of water and 2.0 mL of diethyl ether at 0 °C while the complex **7** (20 mg, 4.59×10^{-5} mol) was added in one portion. After the mixture was stirred for 30 min, the layers were separated and the aqueous phase extracted three times with diethyl ether. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed under reduced pressure to give a yellow oil. Purification by flash chromatography (SiO_2, 10% ethyl acetate/pentanes) gave 8.0 mg (60%) of the complex **16a** as a waxy solid. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 1990, 1680. 200-MHz ^{H} NMR ($CDCl_3$): δ 5.06–4.96 (m, 1 H, H-5), 4.46–4.32 (m, 2 H, H-3, H-4), 3.69 (s, 3 H, $-OCH_3$), 3.46 (dd, 1 H, J = 8, 14 Hz, H-2_{exo}), 2.48–2.38 (m, 2 H, H-6_{exo}, H-6_{endo}), 2.30 (d, 1 H, J = 14 Hz, H-2_{endo}), 2.04–1.93 (m, 1 H, H-7_{exo}), 1.32 (dt, 1 H, J = 7, 12 Hz, H-7_{endo}). HRMS for $C_{11}H_{12}O_4Fe$ (M – CO): calcd, m/e 264.0085; found, m/e 264.0073.

Tricarbonyl[3-5-η-1-σ-2-cyano-1-(methoxycarbonyl)-cyclohept-3-enediyl]iron (15b). The dienyl salt **7** (15 mg, 3.4×10^{-5} mol) was stirred in anhydrous acetonitrile (3 mL) at 0 °C, crystalline KCN (3.1 mg, 4.8×10^{-5} mol) was added, and the reaction mixture was stirred for 20 min. The reaction mixture was allowed to warm to room temperature and then was partitioned between water and diethyl ether. The layers were separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a yellow oil. Purification by flash chromatography (SiO_2, 40% ethyl acetate/hexanes) gave the complex **15b** (9.5 mg, 88%) as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 2000, 1680. 200-MHz ^1H NMR ($CDCl_3$): δ 5.19–5.09 (m, 1 H, H-5), 4.75 (d, 1 H, J = 7 Hz, H-2), 4.62 (t, 1 H, J = 8 Hz, H-4), 4.43 (t, 1 H, J = 7 Hz, H-3), 3.73 (s, 3 H, $-OCH_3$), 2.64–2.43 (m, 2 H, H-6_{exo}, H-7_{exo}), 2.34–2.15 (m, 1 H, H-6_{endo}), 1.71 (dd, 1 H, J = 7 Hz, 13 Hz, H-7_{endo}). HRMS: calcd for $C_{13}H_{10}O_5NFe$, m/e 316.9987; found, m/e 316.9992.

Tricarbonyl[3-5-η-1-σ-2-(bis(methoxycarbonyl)methyl)-1-(methoxycarbonyl)cyclohept-3-enediyl]iron (16f). A solution of dimethyl sodiomalonate in THF (2 mL) was prepared at 0 °C from dimethyl malonate (10 mg) and NaH dispersion (4.4 mg). The dienyl complex **7** (30 mg, 6.88×10^{-5} mol) was added in one portion, and the mixture was stirred for 30 min and then diluted with water. The usual ether extraction, followed by flash chromatography (SiO_2, 25% ethyl acetate/hexanes) gave 24 mg (82%) of crystalline complex. Mp: 117–119 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 2000, 1730, 1680. ^1H NMR ($CDCl_3$): δ 4.83 (broad t, 1 H, J = 7 Hz, H-5), 4.57 (t, 1 H, J = 7 Hz, H-3), 4.53 (t, 1 H, J = 8 Hz, H-4), 4.26 (dd, 1 H, J = 7, 12 Hz, H-2), 3.76 (s, 3 H, $-OCH_3$) and 3.56 (s, 6 H, $2 \times -OCH_3$), 3.00 (d, 1 H, J = 12 Hz, C*H*$(CO_2CH_3)_2$), 2.51–2.44 (m, 2 H, H-6_{exo}, H-6_{endo}), 1.88–1.83 (m, 1 H, H-7_{exo}), 1.46 (dd, 1 H, J = 7 Hz, 14 Hz, H-7_{endo}). Anal. Calcd for $C_{17}H_{18}O_9Fe$: C, 48.37; H, 4.3. Found: C, 48.63; H, 4.38.

Tricarbonyl[1-4-η-2-(methoxycarbonyl)cyclohepta-1,3-diene]iron (10). 2-(Methoxycarbonyl)cyclohepta-1,3-diene (0.50 g, 3.29 mmol) and $Fe_2(CO)_9$ (3.20 g, 2.6 equiv) in 50 mL of anhydrous acetone were stirred under argon at 35 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting oil was dissolved in hexane and filtered through Celite to remove iron residues. The filtrate was again concentrated, taken up in chloroform, and adsorbed onto silica gel. The adsorbed product was then dry-loaded onto a silica gel column, and flash chromatography (5% ethyl acetate/pentanes) yielded 0.49 g (66%) of the diene complex **10** as an orange oil which solidified at low temperature. IR (cm^{-1}, $CHCl_3$): ν_{max} 2050, 1970, 1715. ^1H NMR ($CDCl_3$): δ 6.13 (d, 1 H, J = 8 Hz, H-3), 3.81 (s, 3 H, $-OCH_3$), 3.65 (d, 1 H, J = 7 Hz, H-1), 3.13 (t, 1 H, J = 7 Hz, H-4), 2.10–1.92 (m, 2 H, H-5_{exo}, H-5_{endo}), 1.91–1.75 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.42 (ddd, 1 H, J = 2, 6, 10 Hz, H-6_{exo}), 1.20 (qt, 1 H, J = 14, 5 Hz, H-6_{endo}). HRMS: calcd for $C_{11}H_{12}O_4Fe$ (M – CO), m/e 264.0085; found, m/e 264.0083.

Tricarbonyl[1-5-η-3-(methoxycarbonyl)cyclohepta-1,3-dienylium]iron Hexafluorophosphate (12). Treatment of the diene complex **10** (910 mg, 3.11 mmol) in 6 mL of methylene chloride with triphenylmethyl hexafluorophosphate (2.63 g, 2.2 equiv) in 6 mL of methylene chloride, as previously described, gave the complex **12** as a yellow powder (820 mg, 67%). IR (cm^{-1}, CH_3CN): ν_{max} 2120, 2070, 1965, 1740. 200-MHz ^1H NMR (CD_3CN): δ 6.53 (d, 2 H, J = 10 Hz, H-2, H-4), 5.15–5.06 (m, 2 H, H-1, H-5), 4.03 (s, 3 H, $-OCH_3$), 2.75–2.66 (m, 2 H, H-6_{exo}, H-7_{exo}), 1.89–1.78 (m, 2 H, H-6_{endo}, H-7_{endo}). Anal. Calcd for $C_{12}H_{11}O_5F_6FeP$: C, 33.04; H, 2.52. Found: C, 33.35; H, 2.63.

Tricarbonyl[1-4-η-5-methyl-3-(methoxycarbonyl)cyclohepta-1,3-diene]iron (18c). The procedure described for complex **15c** was followed, using complex **12** (20.0 mg). Purification by flash chromatography (SiO_2, 20% ethyl acetate/hexanes) gave 9.0 mg (64%) of the diene complex **18c** as a golden oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2045, 1960, 1715. 200-MHz ^1H NMR ($CDCl_3$): δ 6.12 (d, 1 H, J = 8 Hz, H-2), 3.81 (s, 3 H, $-OCH_3$), 3.47 (d, 1 H, J = 2 Hz, H-4), 3.13 (t, 1 H, J = 6 Hz, H-1), 2.11–1.83 (m, 3 H, H-5, H-7_{exo}, H-7_{endo}), 1.4–1.25 (m, 1 H, H-6_{exo}), 0.96 (d, 3 H, J = 7 Hz, $-CH_3$), 0.79 (qd, 1 H, J = 14, 5 Hz, H-6_{endo}). HRMS: calcd for $C_{12}H_{14}O_4Fe$ (M – CO), m/e 278.0241; found, m/e 278.0242.

Tricarbonyl[1-4-η-5-(phenylthio)-3-(methoxycarbonyl)-cyclohepta-1,3-diene]iron (18d). Treatment of complex **12** (20 mg) with sodium thiophenoxide, as described previously, followed by flash chromatography (SiO_2, 10% ethyl acetate/pentanes) gave 16 mg (88%) of the product as a golden oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 1985, 1720. ^1H NMR ($CDCl_3$): δ 7.46–7.23 (m, 5 H, –SPh), 6.10 (d, 1 H, J = 8 Hz, H-2), 3.81 (s, 3 H, $-OCH_3$), 3.80 (d, 1 H, J = 5 Hz, H-4), 3.52 (ddd, 1 H, J = 2 Hz, 4 Hz, 12 Hz, H-5), 3.15 (t, 1 H, J = 8 Hz, H-1), 2.15–1.93 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.80–1.71 (m, 1 H, H-6_{exo}), 1.23 (qd, 1 H, J = 12, 5 Hz, H-6_{endo}). HRMS: calcd for $C_{17}H_{16}O_4FeS$ (M – CO), m/e 372.0119; found, m/e 372.0121.

Tricarbonyl[1-4-η-5-hydroxy-3-(methoxycarbonyl)cyclohepta-1,3-diene]iron (18e). The dienyl complex **12** (74.5 mg, 1.71×10^{-4} mol) was suspended in 7.0 mL of THF under argon atmosphere and cooled to 0 °C. NaOH (12 mg, 3.0×10^{-4} mol) in 1.0 mL of water was slowly added, and the reaction mixture was stirred for 30 min and then allowed to warm to room temperature. The product was extracted with diethyl ether in the usual way. Purification by flash chromatography (SiO_2, 40% ethyl acetate/hexanes) gave 44 mg (84%) of complex **18e** as a yellow solid. Mp: 115–117 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 3600 (broad), 2050, 1985, 1715. ^1H NMR ($CDCl_3$): δ 6.17 (d, 1 H, J = 8 Hz, H-2), 4.14–4.04 (m, 1 H, H-5), 3.85 (s, 3 H, $-OCH_3$), 3.52 (d, 1 H, J = 2 Hz, H-4), 3.17 (t, 1 H, J = 7 Hz, H-1), 2.26–1.98 (m, 2 H, H-7_{exo}, H-7_{endo}), 2.04 broad singlet, 1 H, –OH), 1.81–1.63 (m, 1 H, H-6_{exo}), 1.05 (qd, 1 H, J = 13, 5 Hz, H-6_{endo}). Anal. Calcd for $C_{12}H_{12}O_6Fe$: C, 46.79; H, 3.93. Found: C, 47.00; H, 3.97.

Tricarbonyl[1-3-η-5-σ-3-(methoxycarbonyl)cyclohept-1-enediyl]iron (19a). Reduction of the complex **12** (20 mg, 4.59×10^{-5} mol) with sodium borohydride (20 mg) was carried out as described earlier. Purification by flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave 8.0 mg (60%) of **19a** as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 1985, 1705. ^1H NMR ($CDCl_3$): δ 5.30 (d, 1 H, J = 9 Hz, H-2), 5.15 (dt, 1 H, J = 2, 8 Hz, H-1), 3.75 (s, 3 H, $-OCH_3$), 3.39 (dd, 1 H, J = 10, 14 Hz, H-4_{exo}), 2.34–2.15 (m, 1 H, H-6_{exo}), 2.26 (d, 1 H, J = 14 Hz, H-4_{endo}), 2.14–1.99 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.34–1.23 (m, 2 H, H-5, H-6_{endo}). HRMS: calcd for $C_{11}H_{12}O_4Fe$ (M – CO), m/e 264.0085; found, m/e 264.0081.

Tricarbonyl[3-5-η-1-σ-2-cyano-3-(methoxycarbonyl)-cyclohept-3-enediyl]iron (19b). Complex **12** (10 mg, 2.3×10^{-5} mol) was treated with KCN (2.1 mg) as described earlier. The reaction mixture was stirred for 30 min and then allowed to warm to room temperature over about 2 h. Purification by flash chromatography (SiO_2, 40% ethyl acetate/hexanes) gave **19a** (4.0 mg, 56%) as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 2000, 1715.

^{1}H NMR ($CDCl_3$): δ 5.47 (d, 1 H, J = 11 Hz, H-4), 5.27 (td, 1 H, J = 3, 8 Hz, H-5), 4.44 (d, 1 H, J = 10 Hz, H-2), 3.82 (s, 3 H, $-OCH_3$), 2.50–2.33 (m, 1 H, H-6_{exo}), 2.29–2.22 (m, 1 H, H-6_{endo}), 2.20–1.86 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.47–1.39 (m, 1 H, H-1). HRMS: calcd for $C_{11}H_{10}O_3NFe$ (M – 2CO), m/e 261.0088; found, m/e 261.0092.

Tricarbonyl[3-5-η-1-σ-2-(bis(methoxycarbonyl)methyl)-3-(methoxycarbonyl)cyclohept-3-enediyl]iron (19f). The dienyl complex **12** (30 mg) was treated with dimethyl sodiomalonate (1.1 equiv), as described earlier, to give **19f** (24 mg, 82%) as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2060, 1990, 1730 (broad). ^{1}H NMR ($CDCl_3$): δ 5.50 (d, 1 H, J = 9 Hz, H-4), 5.03 (t, 1 H, J = 8 Hz, H-5), 4.08 (t, 1 H, J = 10 Hz, H-2), 3.72 (s, 3 H, $-OCH_3$), 3.68 (s, 3 H, $-OCH_3$), 3.62 (s, 3 H, $-OCH_3$), 2.90 (d, 1 H, J = 12 Hz, CH(CO_2CH_3)$_2$), 2.48–2.35 (m, 1 H, H-6_{exo}), 2.05–1.85 (m, 2 H, H-6_{endo}, H-7_{exo}), 1.70–1.63 (m, 1 H, H-1), 1.42–1.30 (m, 1 H, H-7_{endo}). HRMS: calcd for $C_{15}H_{18}O_7Fe$ (M – 2CO), m/e 366.0402; found, m/e 366.0409. The minor product **18f** was identified as being present in the product mixture (NMR) but was not isolated and fully characterized.

Dicarbonyl[1-4-η-1-(methoxycarbonyl)cyclohepta-1,3-dienyl](triphenyl phosphite)iron (24). The ester complex **9** (600 mg, 2.05 mmol) and triphenyl phosphite (636 mg, 1.0, 2.05 mmol) were taken up in 15 mL of dry, degassed benzene. This solution was placed in an argon-filled quartz tube and externally irradiated with a 100-W Hanovia lamp for 20 h. The solution was allowed to cool to room temperature and then filtered through a column of activity I neutral alumina. The amber-colored solution was concentrated under reduced pressure, and the resulting viscous syrup was placed under high-vacuum for several hours. Trituration with pentane gave a yellow solid, which was recrystallized from pentane to give 760 mg (65%; 86% yield based on recovered starting material) of complex **24**. Mp: 121–122 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 2005, 1950, 1695. ^{1}H NMR ($CDCl_3$): δ 7.42–7.12 (m, 15 H, 3 × –OPh, 5.28 (dd, 1 H, J = 1 Hz, 5 Hz, H-2) (dt, 1 H, J = 5 Hz, H-3), 3.60 (s, 3 H, $-OCH_3$), 3.10 (dt, 1 H, J = 7 Hz, 13 Hz, H-4), 2.02–1.70 (m, 4 H, H-5_{exo}, H-5_{endo}, H-7_{exo}, H-7_{endo}), 1.34–1.26 (m, 1 H, H-6_{exo}), 0.93 (qt, 1 H, J = 13, 5 Hz, H-6_{endo}). Anal. Calcd for $C_{29}H_{27}O_7FeP$: C, 60.65; H, 4.73. Found: C, 60.45; H, 4.63.

Dicarbonyl[1-5-η-1-(methoxycarbonyl)cyclohepta-1,3-dienylium](triphenyl phosphite)iron Hexafluorophosphate (25). The complex **24** (816 mg, 1.42 mmol) was taken up in 8 mL of dry methylene chloride and treated with triphenylmethyl hexafluorophosphate (1.1 g, 2 equiv). The reaction mixture was stirred for 22 h at room temperature, and then the solvent was removed under reduced pressure. The resulting syrup was dissolved in a minimum amount of acetonitrile, and the solution was added dropwise to 300 mL of wet diethyl ether. The ether was decanted to leave a yellow gum, which was washed several times with ether. The gum was then placed under high vacuum for 36 h to produce 710 mg (71%) of complex **25** as a yellow solid. IR (cm^{-1}, CH_3CN): ν_{max} 2070, 2040, 1720. ^{1}H NMR (CD_3CN): δ 7.50–7.15 (m, 15 H, 3 × –OPh), 6.45 (d, 1 H, J = 6 Hz, H-2), 6.19–6.11 (m, 1 H, H-3), 5.90 (broad quartet, 1 H, J = 8 Hz, H-4), 5.01–4.93 (m, 1 H, H-5), 3.72 (s, 3 H, $-OCH_3$), 2.98–2.83 (m, 1 H, H-6_{exo}), 2.64–2.52 (m, 1 H, H-7_{exo}), 2.09–2.02 (m, 1 H, H-6_{endo}), 1.11–0.97 (m, 1 H, H-7_{endo}). Anal. Calcd for $C_{29}H_{26}O_7F_6FeP_2$: C, 48.49; H, 3.65. Found: C, 48.69; H, 3.64.

Dicarbonyl[1-4-η-1-(methoxycarbonyl)-5-methylcyclohepta-1,3-dienyl](triphenyl phosphite)iron (26c). Treatment of complex **25** (25 mg) with dimethylcopperlithium (1.1 equiv), as described earlier, followed by purification using flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave 15.3 mg (74%) of complex **26c** as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2005, 1950, 1690. ^{1}H NMR ($CDCl_3$): δ 7.41–7.17 (m, 15 H, 3 × –OPh), 5.28 (d, 1 H, J = 5 Hz, H-2), 4.68–4.60 (m, 1 H, H-3), 3.61 (s, 3 H, $-OCH_3$), 2.80 (dd, 1 H, J = 9, 14 Hz, H-4), 2.05–1.68 (m, 3 H, H-5, H-7_{exo}, H-7_{endo}), 1.31–1.21 (m, 1 H, H-6_{exo}), 0.80 (d, 3 H, J = 7 Hz, $-CH_3$), 0.54 (qd, 1 H, J = 13, 4 Hz, H-6_{endo}). HRMS: calcd for $C_{28}H_{29}O_5FeP$ (M – 2CO), m/e 532.1135; found, m/e 532.1144.

Tricarbonyl(1-4-η-cyclohepta-1,3-dienoic acid)iron (32). The ester complex **9** (500 mg, 1.71 mmol) was dissolved in 10 mL of methanol under an argon atmosphere, 10 mL of 30% KOH solution and 10 mL of THF were added, and the reaction mixture was stirred for 20 h. Acidification with a 10% HCl solution, with external cooling, to a pH of about 2, and ether extraction in the usual way afforded the product as a yellow solid. The product was purified by dissolving it in a 30% NaOH solution, washing several times with ether, and then acidifying with a 10% HCl solution. Extraction with ether, followed by solvent removal, gave 400 mg (84%) of the product as a yellow crystalline solid. IR (cm^{-1}, $CHCl_3$): ν_{max} 3300–2500 (broad), 2050, 1980, 1670. ^{1}H NMR ($CDCl_3$): δ 5.96 (dd, 1 H, J = 1, 5 Hz, H-2), 5.28 (ddd, 1 H, J = 1, 5, 8 Hz, H-3), 3.23 (t, 1 H, J = 7 Hz, H-4), 2.15–1.75 (m, 4 H, H-5_{exo}, H-5_{endo}, H-7_{exo}, H-7_{endo}), 1.49 (dt, 1 H, J = 3, 15 Hz, H-6_{exo}), 1.23–0.96 (m, 1 H, H-6_{endo}). Anal. Calcd for $C_{11}H_{10}O_5Fe$: C, 47.52; H, 3.63. Found: C, 47.50; H, 3.61.

Tricarbonyl[1-4-η-1-(hydroxymethyl)cyclohepta-1,3-diene]iron (30). The ester complex **9** (50 mg, 1.71×10^{-4} mol) was suspended in 5 mL of THF, and the suspension was cooled to –78 °C in a dry ice/acetone bath. Dibal-H (2.74 mL of a 1.0 M solution in THF, 2.74 mmol) was added, and the reaction mixture was stirred for 1.5 h. The solution was warmed to room temperature and stirred overnight. The reaction mixture was diluted with water, stirred for 10 min, and then diluted with ethyl acetate. The mixture was then filtered through Celite, the filtrate was extracted three times with ethyl acetate, the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The resulting solid was dissolved in ethyl acetate, and the solution was passed through a column of silica gel to remove iron residues. Flash chromatography (SiO_2, 20% ethyl acetate/hexanes) gave 34 mg (76%) of the product as yellow crystals. Mp: 92–93 °C. IR (cm^{-1}, $CHCl_3$): ν_{max} 3600 (broad) 2040, 1960. ^{1}H NMR ($CDCl_3$): δ 5.21 (d, 1 H, J = 5 Hz, H-2), 5.14 (dd, 1 H, J = 6, 8 Hz, H-3), 3.63 (s, 3 H, $-CH_2OH$), 3.06 (dt, 1 H, J = 2, 6 Hz, H-4), 2.20–1.70 (m, 4 H, H-5_{exo}, H-5_{endo}, H-7_{exo}, H-7_{endo}), 1.48 (dddt, 1 H, J = 1 Hz, 1 Hz, 4 Hz, 7 Hz, 13 Hz, H-6_{exo}), 1.15 (qt, 1 H, J = 13, 4 Hz, H-6_{endo}). Anal. Calcd for $C_{11}H_{12}O_4Fe$: C, 50.03; H, 4.58. Found: C, 50.54; H, 4.68.

Dicarbonyl[1-4-η-1-(methoxycarbonyl)-5-(phenylthio)-cyclohepta-1,3-dienyl](triphenyl phosphite)iron (26d). Treatment of the complex **25** (25 mg) with PhSNa (1.1 equiv), as described earlier, followed by purification by flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave 14 mg (60%) of complex **26d** as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 2000, 1955, 1695. ^{1}H NMR ($CDCl_3$): δ 7.41–7.04 (m, 20 H, 3 × –OPh and 1 × SPh), 5.30 (d, 1 H, J = 4 Hz, H-2), 4.75–4.67 (m, 1 H, H-3), 3.60 (s, 3 H, $-OCH_3$), 3.60–3.53 (m, 1 H, H-5), 3.30 (dd, 1 H, J = 7, 14 Hz, H-4), 2.13–1.94 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.75–1.61 (m, 1 H, H-6_{exo}), 102 (qd, 1 H, J = 13 4 Hz, H-6_{endo}). A molecular ion was not observed in the mass spectrum of this compound, owing to very facile fragmentation.

Dicarbonyl[1-4-η-1-(methoxycarbonyl)-5-hydroxycyclohepta-1,3-diene](triphenyl phosphite)iron (26e). The dienyl complex **25** (25 mg) was treated with NaOH (1.7 mg), as described earlier, to give **26e** (13 mg, 63%) as a yellow oil. IR (cm^{-1}, $CHCl_3$): ν_{max} 3580, 2020, 1960, 1695. NMR ($CDCl_3$): δ 7.41–7.18 (m, 15 H), 5.39 (d, 1 H, J = 4 Hz, H-2), 4.78–4.69 (m, 1 H, H-3), 3.83–3.77 (m, 1 H, H-5), 3.62 (s, 3 H), 2.83 (dd, 1 H, J = 7, 14 Hz, H-4), 2.2–1.86 (m, 2 H), 1.53–1.40 (m, 1 H), 1.33 (d, 1 H, J = 5 Hz, exch D_2O, OH), 0.80 (qd, 1 H, J = 13, 4 Hz). This compound was not characterized further. Mass spectrometry reveals facile loss of $P(OPh)_3$ and CO ligands with no molecular ion.

Dicarbonyl[3-5-η-1-σ-1-(methoxycarbonyl)cyclohept-3-enediyl](triphenyl phosphite)iron (27a). Reduction of complex **25** (25 mg) with sodium borohydride, as described earlier, gave complex **27a** as a yellow oil (12 mg, 60%). IR (cm^{-1}, $CHCl_3$): ν_{max} 2000, 1960, 1670. 200-MHz ^{1}H NMR ($CDCl_3$): δ 7.40–7.09 (m, 15 H, 3 × –OPh), 4.62–4.53 (m, 1 H, H-4); 4.37–4.26 (m, 1 H, H-3), 3.65 (s, 3 H, $-OCH_3$), 3.27–3.22 (m, 2 H, H-2_{exo}, H-5), 2.43–2.30 (m, 1 H, H-6_{exo}), 2.28–2.05 (m, 2 H, H-2_{endo}, H-7_{exo}), 1.91–1.75 (m, 1 H, H-6_{endo}), 1.29–1.15 (m, 1 H, H-7_{endo}). HRMS: calcd for $C_{27}H_{27}O_5FeP$ (M – 2CO), m/e 518.0945; found, m/e 518.0921. R_f (SiO_2, 20% ethyl acetate/hexanes) = 0.38.

Dicarbonyl[3-5-η-1-σ-2-cyano-1-(methoxycarbonyl)cyclohept-3-enediyl](triphenyl phosphite)iron (27b). The dienyl complex **25** was treated with KCN (3.2 mg), as described earlier, giving **27b** as a yellow oil (16 mg, 74%). IR (cm^{-1}, $CHCl_3$): ν_{max} 2010, 1970, 1680. NMR ($CDCl_3$): δ 7.5–7.08 (m, 15 H), 4.7–4.63 (m, 1 H, H-3), 4.59–4.44 (m, 2 H, H-2, H-5), 3.67 (s, 3 H), 3.12 (t, 1 H, J = 6 Hz, H-4), 2.56–2.2 (m, 2 H), 2.12–1.96 (m, 1 H),

1.64–1.45 (m, 1 H). R_f (SiO_2, 30% EtOAc/hexanes) = 0.32. No further characterization was attempted.

Dicarbonyl[3-5-η-1-σ-2-(bis(methoxycarbonyl)methyl)-1-(methoxycarbonyl)cyclohept-3-enediyl](triphenyl phosphite)iron (27f). Treatment of complex **25** (50 mg) with dimethyl sodiomalonate (1.1 equiv), as described earlier, followed by flash chromatography (SiO_2, 40% ethyl acetate/hexanes) gave complex **27f** as a yellow oil (27.4 mg, 56%). IR (cm^{-1}, $CHCl_3$): ν_{max} 2010, 1970, 1730, 1670. 200-MHz ^1H NMR ($CDCl_3$): δ 7.37–7.07 (m, 15 H, 3 × –OPh), 4.57–4.40 (m, 2 H, H-4, H-5), 4.17–4.03 (m, 1 H, H-2), 3.69 (s, 3 H, $-OCH_3$), 3.64 (s, 3 H, $-OCH_3$), 3.53 (s, 3 H, $-OCH_3$), 3.43–3.34 (m, 1 H, H-3), 2.97 (d, 1 H, J = 14 Hz, $-CH(CO_2CH_3)_2$), 2.50–2.17 (m, 2 H, H-6_{exo}, H-6_{endo}), 1.54–1.23 (m, 2 H, H-7_{exo}, H-7_{endo}). R_f (SiO_2, 40% ethyl acetate/hexanes) = 0.35.

Tricarbonyl(1-4-η-1-methylcyclohepta-1,3-diene)iron (33). The acid complex **32** (600 mg, 2.15 mmol) was dissolved in THF (50 mL) in a clean, dry three-neck flask fitted with a reflux condenser and argon bubbler. To this was added $BF_3{\cdot}Et_2O$ (300 μL, 2.6 mmol), and the mixture was heated to reflux for 20 min and then cooled to room temperature. $BH_3{\cdot}Me_2S$ (1.3 mL of a 2.0 M solution in THF) was added dropwise over 5 min, and the mixture was refluxed for 3.5 h. To the cooled mixture was added 20 mL of 1:1 THF–water and then 50 mL of a 6 N NaOH solution. This was then heated at reflux for 4 h, the reaction mixture was cooled to room temperature, and the organic layer was separated. The aqueous layer was extracted three times with ethyl acetate, the organic layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave the complex **33** as a golden oil (370 mg, 78%) IR (cm^{-1}, $CHCl_3$): ν_{max} 2025, 1955. ^1H NMR ($CDCl_3$): δ 5.10–5.01 (m, 2 H, H-2, H-3), 2.94 (t, 1 H, J = 5 Hz, H-4), 2.19–2.02 (m, 1 H, H-6_{exo}), 1.98–1.73 (m, 2 H, H-5_{exo}, H-7_{exo}), 1.55 (s, 3 H, $-CH_3$), 1.51–1.35 (m, 1 H, H-5_{endo}), 1.34–1.05 (m, 2 H, H-6_{endo}, H-7_{endo}). Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.26; H, 4.87. Found: 53.34; H, 5.02.

Tricarbonyl(1-5-η-1-methylcyclohepta-1,3-dienylium)iron Hexafluorophosphate (31). The methyl-substituted complex **33** (368 mg, 1.48 mmol) was dissolved in methylene chloride (5 mL), and the solution was treated with triphenylmethyl hexafluorophosphate (602 mg, 1.05 equivalents) for 2 h at –78 °C. The reaction mixture was warmed to room temperature and concentrated under reduced pressure to give a viscous oil, which was dissolved in 1 mL of acetonitrile. This solution was added dropwise to 20 mL of wet ether. The product precipitated as a yellow powder. The ether was decanted, and the product was washed again by decantation with ether and dried under high vacuum overnight to give **31** (380 mg, 65%) as a bright yellow powder. IR (cm^{-1}, CH_3CN): ν_{max} 2110, 2050. ^1H NMR (CD_3CN): δ 6.90 (t, 1 H, J = 4 Hz, H-3), 6.00–5.85 (m, 2 H, H-2, H-4), 4.90–4.73 (m, 1 H, H-5), 2.95–2.70 (m, 1 H, H-6_{exo}), 2.65–2.30 (m, 1 H, H-6_{endo}), 2.38 (s, 3 H, $-CH_3$), 2.13–1.77 (m, 2 H, H-7_{exo}, H-7_{endo}). Anal. Calcd for $C_{11}H_{11}FeO_3PF_6$: C, 33.70; H, 2.83. Found: C, 33.89; H, 2.68.

Tricarbonyl(1-4-η-1,5-dimethylcyclohepta-1,3-diene)iron (34). Treatment of the dienyl complex **31** (158 mg) with $Me_2CuMgCl$ (2 equiv), as described for the earlier cuprate additions, followed by flash chromatography (SiO_2, 10% ethyl acetate/hexanes) gave complex **34** as a yellow oil (79 mg, 75%). IR (cm^{-1}, $CHCl_3$): ν_{max} 2030, 1950. 200-MHz ^1H NMR ($CDCl_3$): δ 5.33–5.01 (m, 2 H, H-2, H-3), 2.73 (d, 1 H, J = 6 Hz, H-4), 2.26–2.10 (m, 1 H, H-6_{exo}), 2.08–1.75 (m, 2 H, H-5, H-6_{endo}), 1.52 (s, 3 H, CH_3), 1.41–1.20 (m, 1 H, H-7_{exo}), 0.95 (d, 3 H, J = 4 Hz, CH_3), 0.90–0.80 (m, 1 H, H-7_{endo}). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 54.99; H, 5.38. Found: C, 54.72; H, 5.51.

Tricarbonyl[1-4-η-5-(bis(methoxycarbonyl)methyl)-1-methylcyclohepta-1,3-diene]iron (35). Treatment of the complex **31** (25 mg) with dimethyl sodiomalonate (1.5 equiv) in THF at 0 °C, as described earlier, followed by flash chromatography (SiO_2, 30% ethyl acetate/hexanes) gave the diester **35** as a yellow oil (20 mg, 83%) IR (cm^{-1}, $CHCl_3$): ν_{max} 2040, 1975, 1750, 1725. ^1H NMR ($CDCl_3$): δ 5.22–5.04 (m, 2 H, H-2, H-4), 3.70 (s, 6 H, 2 × $-OCH_3$), 3.21 (s, 1 H, $-CH(CO_2CH_3)_2$), 3.13–3.06 (m, 1 H, H-5), 2.98 (d, 1 H, J = 7 Hz, H-3), 2.09–1.80 (m, 2 H, H-6_{exo}, H-6_{endo}), 1.60–1.45 (m, 2 H, H-7_{exo}, H-7_{endo}), 1.19 (s, 3 H, $-CH_3$).

Tricarbonyl(1-5-η-3,6-dimethylcyclohepta-1,3-dienylium)iron Hexafluorophosphate (37). The dimethyl-substituted complex **34** (80 mg, 3.05×10^{-4} mol) was stirred in methylene chloride (3 mL) with triphenylmethyl hexafluorophosphate (124 mg, 1.05 equiv) at room temperature for 4 h. Workup as described earlier afforded complex **37** as a pale yellow powder (90 mg, 70%). IR (cm^{-1}, CH_3CN): ν_{max} 2100, 2055. ^1H NMR (CD_3CN): δ 6.07 (d, 1 H, J = 9 Hz, H-2), 5.68 (d, 1 H, J = 10 Hz, H-4), 4.70 (dd, 1 H, J = 5 Hz, 14 Hz, H-5), 4.62 (dt, 1 H, J = 4 Hz, 9 Hz, H-1), 3.36–3.21 (m, 1 H, H-6), 2.65 (s, 3 H, $-CH_3$), 2.38–2.20 (m, 1 H, H-7_{exo}), 0.93 (d, 3 H, J = 7 Hz, CH_3), 0.93–0.80 (m, 1 H, H-7_{endo}). Anal. Calcd for $C_{12}H_{13}FeO_3PF_6$: C, 35.49; H, 3.23. Found: C, 35.76; H, 3.41.

Tricarbonyl[2-5-η-1-(bis(methoxycarbonyl)methyl)-3,6-dimethylcyclohepta-2,4-dienyl]iron (38). The dienyl complex **37** (25 mg, 0.07 mmol) was treated with dimethyl sodiomalonate (1.1 equiv), as described for the preparation of **16f**, followed by flash chromatography (silica gel, 10% EtOAc in hexanes) to give the diene complex **38** (20 mg, 85% yield) as a yellow low-melting solid. IR (cm^{-1}, $CHCl_3$): ν_{max} 2045, 1980, 1750, 1730. ^1H NMR ($CDCl_3$): δ 5.13 (d, 1 H, J = 7 Hz), 3.72 (s, 6 H), 3.28 (d, 1 H, J = 6 Hz), 2.75 (d, 1 H, J = 1 Hz), 2.71–2.65 (m, 2 H), 2.1 (s, 3 H), 2.03–1.96 (m, 1 H), 1.26 (br d, 1 H, J = 12 Hz), 0.93 (d, 3 H, J = 7 Hz), 0.77 (q, 1 H, J = 12 Hz). Anal. Calcd for $C_{17}H_{20}FeO_7$: C, 52.06; H, 5.14. Found: C, 52.42; H, 5.26.

Optical Resolution of the Carboxylic Acid Complex 32. The racemic acid complex (1.0 g, freshly recrystallized) was added to hot acetone. Separately, 1-(–)-α-phenylethylamine (0.487 mL, 0.457 g, 1.05 equiv) was added to acetone, and the solution was heated to boiling. The two hot solutions were combined and were boiled on a steam bath in the fume hood until some solid formation was evident (volume had been reduced from 50 mL to ca. 25 mL). The heating was then immediately stopped, and the solution was allowed to cool slowly to room temperature. The solution was allowed to stand overnight, and the solid was separated from the mother liquors and then recrystallized from acetone to constant optical rotation. The amine salt thus obtained was suspended in diethyl ether, and to this was added 10% HCl solution. The mixture was stirred until the yellow solid had disappeared, and then the aqueous layer was extracted three times with ether. The organic fractions were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow crystalline solid (225 mg, 24% recovery). $[\alpha]_D$ = –104° (acetone c = 0.5). The spectral data were identical to that of the racemic acid.

EHT Calculations. The model systems chosen for study in the extended Huckel calculations were the pentadienyl and hydroxycarbonyl-substituted pentadienyl systems. The program used was ASED, and the calculations were performed on a VAX 11/785 main-frame computer. When the positional coordinates for these systems were determined, some geometric assumptions and simplifications were made, as follows: (i) the dienyl system is planar; (ii) the C–C–C bond angle in the dienyl system was assumed to be 120°; (iii) all C–C bond lengths are equal. As a simplification, the dienyl system was centered on the xyz coordinate system such that the molecule was symmetrical about the origin and that the iron was positioned on the z axis.

The angle formed between the z axis and Fe–CO vector is 135°. This implies that the angle formed between CO–Fe and a plane perpendicular to the xz plane passing through iron is 45°, which allows calculation of the positions for the CO fragments.

The coordinates, in angstroms, used for the calculations for the $Fe(CO)_3$ moieties as well as the pentadienyl fragments were calculated using bond lengths and angles based on X-ray crystallographic data.[18] For a description of parameters used for EHT calculations, see refs 18 and 21.

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51-8; **15d**, 126796-50-7; **15e**, 126796-52-9; **16a**, 126796-54-1; **16f**, 126796-56-3; **18c**, 137203-90-8; **18d**, 137203-87-3; **18e**, 126796-39-2; **19a**, 126796-41-6; **19b**, 126796-42-7; **19f**, 126796-44-9; **24**, 137203-92-0; **25**, 137203-94-2; **26c**, 137203-95-3; **26d**, 137203-97-5; **26e**, 137203-86-2; **27a**, 137203-96-4; **27b**, 137203-89-5; **27f**, 137203-91-9; **30**, 137203-98-6; **31**, 137203-99-7; **32**, 137204-00-3; **33**, 137204-01-4; **34**, 137204-02-5; **35**, 137204-03-6; **37**, 137259-47-3; **38**, 137204-04-7.

Notes

Preparation of Electron-Rich Cationic Complexes of the Type $[(\eta^5\text{-}C_5Me_5)Ru(bipyridine)L]^+$

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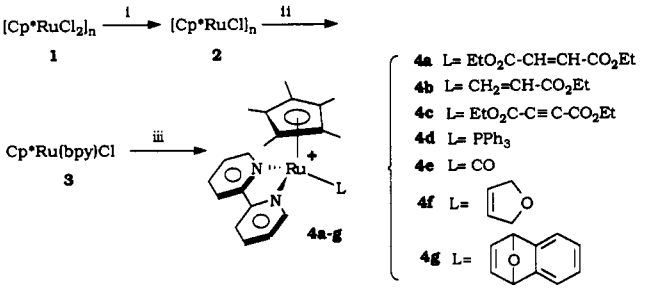
Summary: Reaction of Cp*Ru(bpy)Cl (Cp* = C_5Me_5, bpy = 2,2′-bipyridine) with various monodentate two-electron donor ligands (L) in the presence of NH_4PF_6 gives $[Cp^*Ru(bpy)L]^+PF_6^-$ (L = $EtO_2C—CH=CH—CO_2Et$; $CH_2=CH—CO_2Et$; $EtO_2C—C\equiv C—CO_2Et$; 1,4-epoxy-1,4-dihydronaphthalene; 2,5-dihydrofuran; CO; PPh_3). The molecular structure of the ethyl maleate complex determined by X-ray diffraction studies is described.

Transition-metal complexes containing electron-rich ligands have been the focus of recent studies in the field of organometallic chemistry of group VIII metals. These metal complexes are known to be stable in high formal oxidation states, which, in some cases, has proven valuable to promote C–H activation reactions.

The very strong σ-donor ligands phenanthroline and bipyridine have been extensively used in the coordination chemistry of ruthenium where they play a key role.[1] However, the development of the organometallic chemistry of ruthenium complexes containing such ligands is still rather limited. Singleton et al.[2] recently reported the synthesis of several cyclopentadienylruthenium complexes including $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$ where diamine = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy).

Pentamethylcyclopentadiene (Cp*), another electron-rich ligand, was used by Bercaw et al.[3] for the synthesis of $[Cp^*RuCl_2]_n$. This compound is a precursor for a number of complexes containing the (Cp*Ru) unit.[4]

Scheme I



[a] Key: (i) Zn, THF, room temperature; (ii) bpy (1 equiv), THF, room temperature; (iii) NH_4PF_6, L (5 equiv or 1 atm (CO)), MeOH.

So far, Cp*Ru(bpy)X (X = halide, OCH_3)[5] are the only known examples of ruthenium complexes where both electron-rich ligands, C_5Me_5 and bipyridine, are simultaneously coordinated to ruthenium. To the best of our knowledge, no X-ray structure for any of these compounds has been previously reported in the literature.

Here we describe the synthesis of various $[Cp^*Ru(bpy)L]^+PF_6^-$ complexes (Scheme I) and the molecular structure determination of the ethyl maleate complex [L = $EtO_2C—CH=CH—CO_2Et$] by X-ray diffraction.

Results and Discussion

The chloride $[(\eta^5\text{-}C_5Me_5)Ru(bpy)Cl]$ (**3**) was prepared in 91% yield by modified published procedures[5,6] using THF as solvent. Treatment of the chloride **3** with an excess (5 equiv) of a ligand L (L = diethyl maleate, ethyl acrylate, diethyl acetylenedicarboxylate, PPh_3, or CO) in methanol in the presence of ammonium hexafluorophosphate, results in the rapid displacement of the chloride ion and affords the cationic $[Cp^*Ru(bpy)L]^+PF_6^-$ complexes **4a–e**.

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