Preparation, Characterization, and Reactivity of (3-Methylpentadienyl)iron(1+) Cations

Subhabrata Chaudhury,[†] Shukun Li,[†] Dennis W. Bennett,[‡] Tasneem Siddiquee,[‡]
Daniel T. Haworth,[†] and William A. Donaldson*,[†]

*Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881, and
Department of Chemistry and Biochemistry, University of Wisconsin−Milwaukee,
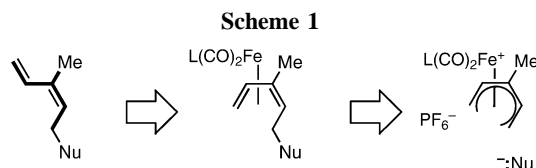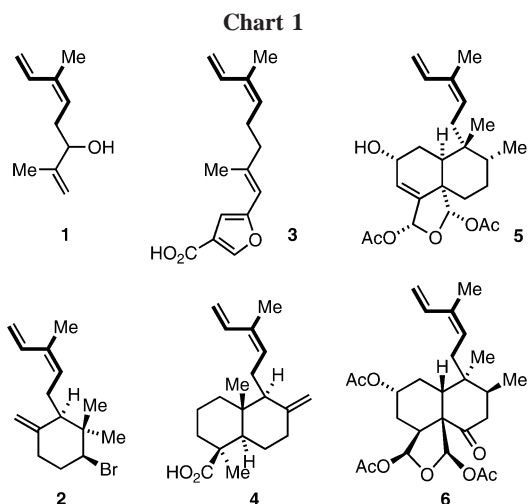Milwaukee, Wisconsin 53201-0413*

The title cations (**9** and **12**) were prepared by dehydration of (3-methyl-2,4-pentadien-1-ol)Fe(CO)$_2$L$^+$ complexes. The structure of the (CO)$_2$PPh$_3$-ligated **12** was determined by single-crystal X-ray analysis. Reaction of carbon and heteroatom nucleophiles to (3-methylpentadienyl)Fe(CO)$_3^+$ cations **9** and **12** proceeds either via attack at the dienyl terminus to give (3-methyl-1,3Z-diene)iron complexes or via attack at the internal carbon, followed by carbon monoxide insertion and reductive elimination to afford 3-methyl-4-substituted cyclohexenones. Cyclohexenone formation was found to be prevalent for addition of stabilized nucleophiles with strongly dissociated counterions to cation **9** (L = CO). Reaction of cation **9** with sodium bis[(−)-8-phenylmenthyl] malonate gave a single diastereomeric cyclohexenone.

Introduction

There are a variety of monoterpenes (e.g., *cis*-ocimenol, **1**),[1] sesquiterpenes (e.g., luzonensin, **2**),[2] and diterpenes which possess a 3-methyl-1,3-(*Z*)-pentadienyl segment (Chart 1). Certain of these compounds exhibit useful biological activity. For example, the furanoic acid **3**[3] inhibits bee venom phospholipase A2 in vitro (IC$_{50}$ = 0.5 μM) while *cis*-communic acid[4] (**4**) exhibits antibacterial activity against Gram positive bacteria. Alternatively, the clerodane caseargrewiin D[5] (**5**) demonstrates both antimalarial and antitumor activity and casearinone B[6] (**6**) has potential as an immunosuppressive agent since it inhibits binding of leukocyte function antigen-1 (LFA-1) to intercellular adhesion molecule-1 (ICAM-1). To our knowledge, there are no reported syntheses of any 3-methyl-1,3(*Z*)-pentadienyl-containing diterpenes.[7]

One potential route for the introduction of a 3-methyl-1,3-(*Z*)-pentadienyl functionality involves the addition of nucleophiles to a (3-methylpentadienyl)Fe(CO)$_2$L$^+$ cation, followed by decomplexation of the metal (Scheme 1). We here report on

Chart 1

Scheme 1

the preparation, structural characterization, and reactivity of (3-methylpentadienyl)iron(1+) cations.

Results and Discussion

Preparation and Characterization of (3-Methylpentadienyl)iron(1+) Cations. The (dienoate)iron complex **7** was prepared in two steps from ethyl 3-methyl-4-oxo-2-butenoate according to the literature procedure.[8] Reduction of **7** gave the known[8] (dienol)iron complex **8**, which upon dehydration with HPF$_6$/Ac$_2$O gave **9** as a stable pale yellow solid (Scheme 2).

* To whom correspondence should be addressed. E-mail: william.donaldson@marquette.edu.

† Marquette University.

‡ University of Wisconsin−Milwaukee.

(1) Williams, P. J.; Strauss, C. R.; Wilson, B.; Massy-Westropp, R. A. *J. Agric. Food Chem.* **1982**, *30*, 1219−1223.

(2) Kuniyoshi, M.; Marma, M. S.; Higa, T.; Bernardinelli, G.; Jefford, C. W. *J. Nat. Prod.* **2001**, *64*, 696−700.

(3) (a) Coll, J. C.; Mitchell, S. J.; Stokie, G. J. *Tetrahedron Lett.* **1977**, 1539−1542. (b) Grace, K. J. S.; Zavortink, D.; Jacobs, R. S. *Biochem. Pharmacol.* **1994**, *47*, 1427−1434.

(4) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1974**, *107*, 1416−1419. Muhammad, I.; Mossa, J. S.; Al-Yahya, M. A.; Ramadan, A. F.; El-Feraly, F. S. *Phother. Res.* **1995**, *9*, 584−588.

(5) Kanokmedhakul, S.; Kanokmedhakul, K.; Kanarsa, T.; Buayairaksa, M. *J. Nat. Prod.* **2005**, *68*, 183−188.

(6) Hunter, M. S.; Corley, D. G.; Carron, C. P.; Rowold, E.; Kilpatrick, B. F.; Durley, R. C. *J. Nat. Prod.* **1997**, *60*, 894−899.
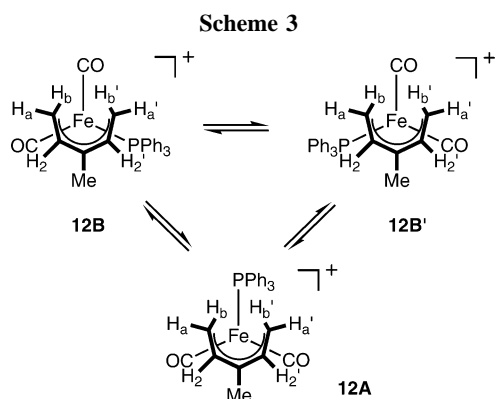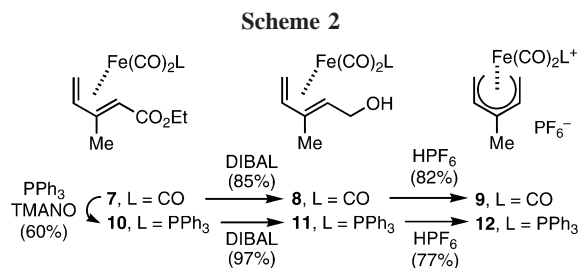
(7) There are only two syntheses reported of crotomachlin, a 3-methyl-1,3(*E*)-pentadienyl-containing labdane diterpene: (a) Harlem, D.; Khuong-Huu, F.; Kende, A. S. *Tetrahedron Lett.* **1993**, *34*, 5587. (b) Teramoto, T.; Yono, T.; Morita, H.; Katsumura, S.; Sakaguchi, K.; Isoe, S. *Synlett* **1996**, 141.

(8) Adams, C. M.; Cerioni, G.; Hafner, A.; Kalchhauser, H.; von Philipsborn, W.; Prewo, R.; Schwenk, A. *Helv. Chim. Acta* **1988**, *71*, 1116−1142.
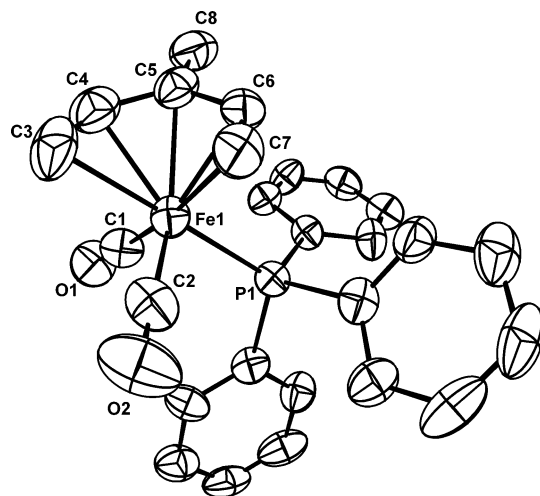
Scheme 2

Scheme 3

Figure 1. ORTEP of the cationic portion of **12** (50% elipsoids). Selected bond lengths (Å): Fe(1)−C(3), 2.180(11); Fe(1)−C(4), 2.120(11); Fe(1)−C(5), 2.188(11); Fe(1)−C(6), 2.116(8); Fe(1)−C(7), 2.132(9); C(3)−C(4), 1.336(17); C(4)−C(5), 1.422(15); C(5)−C(6), 1.440(14); C(6)−C(7), 1.390(14).

Chart 2

Cation **9** was assigned the symmetrical cisoid structure shown; the ^{1}H and ^{13}C NMR spectra of **9** consisted of four and five signals, respectively. It is well-known that replacement of CO by a phosphine ligand can affect the regioselectivity of nucleophilic addition to dienyl iron complexes.[9] Ligand substitution of **7** with triphenylphosphine in the presence of trimethylamine *N*-oxide gave **10**. Reduction of **10** gave **11**, which upon dehydration with HPF_6/Ac$_2$O gave **12** as a stable golden yellow solid.

The ^{1}H NMR spectrum of **12** at 16 °C consisted of a set of four broad signals (3:2:2:2) for the pentadienyl ligand portion. The signal for the methyl protons was observed at δ 2.37 ppm (3H) as well as three broad multiplets at δ 5.71, 2.95, and 1.94 ppm (2H each). Upon lowering of the temperature, the multiplets decoalesce and eventually at −70 °C separate into four multiplets integrating to 1H each and one multiplet integrating to 2H. This fluxional behavior is characteristic of a tetragonal pyramidal iron complex in which the phosphine ligand is rapidly exchanging between basal sites (**12B** and **12B′**; Scheme 3). At 16 °C, the "windshield-wiper" motion of the Ph$_3$P(CO)$_2$Fe moiety is sufficiently fast that only time-averaged signals appear for the pairs H$_a$/H$_{a'}$, H$_b$/H$_{b'}$, and H$_2$/H$_{2'}$. As the temperature is lowered, rotation about the Fe−dienyl ligand slows, and the phosphine occupies one of two equivalent basal sites. With the loss of the symmetry, protons H$_a$, H$_b$, and H$_2$ become nonequivalent with H$_{a'}$, H$_{b'}$, and H$_{2'}$, respectively. No additional resonances were observed in the ^{1}H NMR spectrum that might correspond to an apical isomer conformation (**12A**). This was further corroborated by a variable-temperature ^{31}P NMR study. In this case, only a single resonance (δ 62.4 ppm) was observed for the phosphine ligand in the temperature range 16 to −70 °C. Exchange of the phosphine ligand between equivalent basal sites gives rise to a single ^{31}P NMR resonance signal; if basal−apical exchange of the phosphine ligand had occurred, an additional ^{31}P NMR resonance would be expected
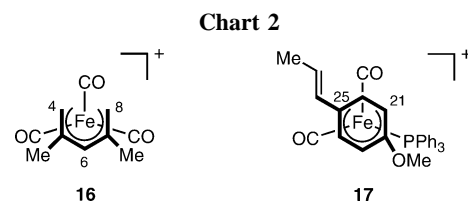
at low temperature due to the apical phosphine rotamer. The internal dienyl hydrogens H$_2$ and H$_{2'}$ coalesce at −10 °C, corresponding to k_c= 349 s^{-1} and $\Delta G^{\ddagger}$ =12.8 kcal mol^{-1}. This activation energy is comparable with that found for apical−basal phosphite exchange in (cyclohexadienyl)Fe(CO)$_2$(EPTB)$^+$ (**13**) and (cycloheptadienyl)Fe(CO)$_2$(EPTB)$^+$ (**14**) (9.8 and 11.4 kcal mol^{-1}, respectively)[10] and basal−basal phosphine exchange in (bicyclo[5.1.0]octadienyl)Fe(CO)$_2$PPh$_3$$^+$ (**15**) (13.3 kcal mol^{-1}).[11]
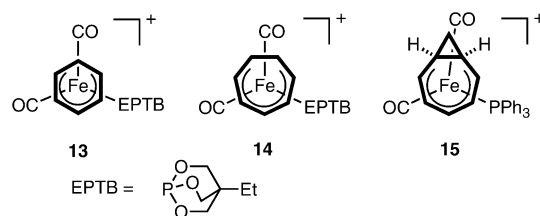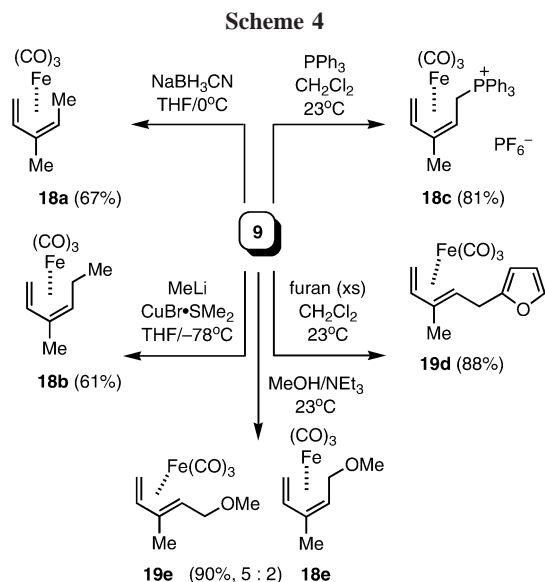

The crystal structure of **12** (Figure 1) represents the first X-ray crystal structure of an *acyclic* dicarbonyl triphenylphosphine ligated (pentadienyl)iron cation and may be compared with the structures for **16** and **17** (Chart 2).[12] The structure for **12** revealed that the triphenylphosphine ligand occupies the basal site in the solid state. For **12** the distances between iron and the pentadienyl termini (i.e., Fe−C3 and Fe−C7) are not equal; the distance for the Fe−pentadienyl terminus trans to the PPh$_3$ ligand (i.e., Fe−C3) is 0.048 Å greater than for the Fe−pentadienyl terminus cis to the PPh$_3$ ligand (i.e., Fe−C7). For cation **17**, the distance

(9) (a) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060−6074. (b) McDaniel, K. F.; Kracker, L. R.; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373−2376. (c) Millot, N.; Guillou, C.; Thal, C. *Tetrahedron Lett.* **1998**, *39*, 2325−2326. (d) Barmann, H.; Prahlad, V.; Tao, C.; Yun, Y. K.; Wang, Z.; Donaldson, W. A. *Tetrahedron* **2000**, *56*, 2283−2295.

(10) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664−676.

(11) Wallock, N. J.; Donaldson, W. A. *J. Org. Chem.* **2004**, *9*, 2997−3007.

(12) (a) Rheingold, A. L.; Haggerty, B. S.; Ma, H.; Ernst, R. D. *Acta Cryst.* **1996**, *C52*, 1110−1112. (b) Hudson, R. D. A.; Anson, C. E.; Mahon, M. F.; Stephenson, G. R. *J. Organomet. Chem.* **2001**, *630*, 88−103.

Scheme 4

Figure 2. ORTEP of phosphonium salt **18c** (50% elipsoids). Selected bond lengths (Å): Fe(1)−C(1), 2.090(7); Fe(1)−C(2), 2.061(7); Fe(1)−C(3), 2.056(7); Fe(1)−C(4), 2.106(6); P(1)−C(5), 1.810(6); C(1)−C(2), 1.398(12); C(2)−C(3), 1.417(11); C(3)−C(4), 1.435(9); C(4)−C(5), 1.535(8).

between the Fe−pentadienyl terminius trans to the PPh$_3$ ligand (Fe−C25, numbering taken from ref 12b) is also greater (by 0.127 Å) than for the Fe−pentadienyl terminus cis to the PPh$_3$ ligand (Fe−C21). While this greater Fe−C distance may be largely attributed to steric hindrance for **17**,[12b] for the 3-methylpentadienyl ligand (**12**) this greater distance is presumably due to the greater trans influence[13] of a phosphine compared to CO; the PPh$_3$ ligand weakens the Fe−C bond trans to itself. In a comparison of bond angles within the pentadienyl ligand, for cation **12** the central bond angle (C4−C5−C6 = 120.3°) is smaller than the adjacent bond angles about C4 and C6 (C3−C4−C5 = 128.7°, C5−C6-C7 = 125.1°). This is opposite for **16** where the central pentadienyl C−C−C bond angle (C5−C6-C7 = 129.1, numbering taken from ref 12a) is larger than the adjacent angles (C4−C5−C6 = 121.2°, C6−C7−C8 = 122.0°).[12] These differences in bond angle are presumably due to the differences in substitution at these carbons. The smaller bond angles are observed at the methyl-substituted pentadienyl carbons. The steric size of the methyl group is likely to increase the outside C−C−C bond angles (i.e., C4−C5−C8 in **12**) at the expense of the inner bond angle.

Reactivity of (3-Methylpentadienyl)iron(1+) Cations.[14] The reaction of **9** with hydride, methyl cuprate, and triphenylphosphine gave (3-methyl-1,3Z-pentadiene)Fe(CO)$_3$ complexes **18a−c**, while reaction with excess furan gave (3-methyl-1,3E-pentadiene)Fe(CO)$_3$ complexes **19d** (Scheme 4). Reaction of **9** with methanol gave an inseparable mixture E- and Z-diene complexes (**19e/18e**, 5:2). Structural assignments for these products were made on the basis of their NMR spectral data. In particular, the signals for H1$_{endo}$ and H4$_{exo}$ of 1,3Z-diene complexes **18** appear at ca. δ 0.9−1.3 and 2.4−2.9 ppm, respectively, while signals for H1$_{endo}$ and H4$_{endo}$ of 1,3E-diene complexes **19** appear at ca. δ 0.2−0.3 and 1.1−1.9 ppm. Furthermore, the 3-methyl-1,3Z-pentadiene complex **18a** was identified by comparison of its ^{13}C NMR spectral data with the literature values,[15] while the structural assignment for phosphonium salt **18c** was corroborated by the X-ray crystal structure
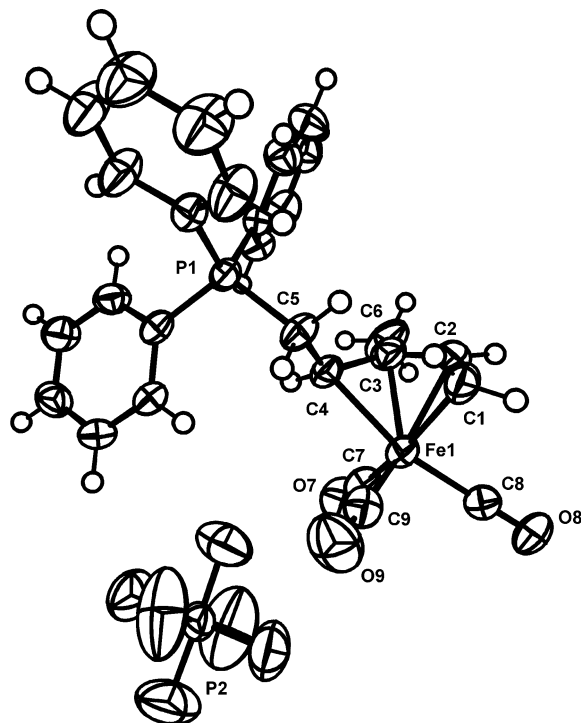
(Figure 2). The bond lengths and angles for **18c** are consistent with those of other dienylphosphonium salts.[16]

Reaction with lithium dimethyl malonate gave the 1,3Z-diene complex **18f** in good yield (Table 1, entry 1). It was thus surprising that changing the malonate counterion to sodium followed by treatment of the reaction mixture with methanolic NaHCO$_3$, gave the 4,5-disubstituted cyclohexenone **20f** (entry 2). This difference in reactivity was attributed to the association of the malonate nucleophile with the counterion: the reaction of **9** with lithium dimethyl malonate in the presence of 12-crown-4 gave only the cyclohexenone product **20f**, while reaction of **9** with sodium dimethyl malonate/ZnCl$_2$ gave only the diene complex **18f**. This difference in product formation was also dependent on the steric bulk of the carbon nucleophile. Reaction with lithium dimethyl methylmalonate anion afforded the diene complex **18g** (entry 5) and reaction with the sodium salt of this nucleophile gave a separable mixture of **18g** and cyclohexenone **20g** (entry 6), while reaction with the sodium salt of 2-(ethoxycarbonyl)cyclohexanone gave the diene complex **18h** (as a mixture of diastereomers, entry 7). In contrast, reaction of **9** with lithium methyl cyclohexanecarboxylate gave a mixture of 2- and 3-cyclohexenones **20i**. Finally, reaction with potassium phthalimide gave a mixture of diene complex **18j**, 2- and 3-cyclohexenones **20j** (entry 9).

The diene complexes **18f,g,h,j** were identified by comparison of their NMR spectral data with that for other 3-methyl-1,3Z-diene complexes (vide supra). The 2-cyclohexenone products **20f,g,i,j** were also identified on the basis of their NMR spectroscopic data. In particular, signals for H2 and H3 appear

(13) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

(14) Preliminary communication: Chaudhury, S.; Donaldson, W. A. *J. Am. Chem. Soc.* **2006**, *128*, 5984−5985.

(15) Adams, C. M.; Cerioni, G.; Hafner, A.; Kalchhauser, H.; von Philipsborn, W.; Prewo, R.; Schwenk, A. *Helv. Chim. Acta* **1988**, *71*, 1116−1142.

(16) (a) Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2504−2506. (b) Donaldson, W. A.; Shang, L.; Rogers, R. D. *Organometallics* **1994**, *13*, 6−7. (c) Donaldson, W. A.; Shang, L.; Ramaswamy, M.; Droste, C. A.; Tao, C.; Bennett, D. W. *Organometallics* **1995**, *14*, 5119−5126.

Table 1. Addition of Stabilized Carbon and Nitrogen Nucleophiles to (3-Methylpentadienyl)Fe(CO)$_3^+$

entry	nucleophile	products (% yield)
1	LiCH(CO$_2$Me)$_2$	**18f** (80)
2	NaCH(CO$_2$Me)$_2$[a]	**20f** (91)
3	LiCH(CO$_2$Me)$_2$/12-C-4[a]	**20f** (84)
4	NaCH(CO$_2$Me)$_2$/ZnCl$_2$	**18f** (60)
5	LiC(Me)(CO$_2$Me)$_2$	**18g** (45)
6	NaC(Me)(CO$_2$Me)$_2$[a]	**18g** (34), **20g** (55)
7		**18h** (78)[b]
8		**20i** (80)[c]
9	K$^+$ $^-$NPhth[d]	**18j** (34) **20j** (27)[e]

^{a} After 2 h, the reaction mixture was diluted with CH$_2$Cl$_2$ and methanolic NaHCO$_3$ was 1added. The mixture was stirred for an additional 18 h. ^{b} The product is a mixture of diastereomers at the new chiral center (∗) and the (diene)Fe coordination. ^{c} The product is a 6:1 mixture of 2- and 3-cyclohexenones. ^{d} 23 °C. ^{e} The product is a 2.5:1 mixture of 2- and 3-cyclohexenones.
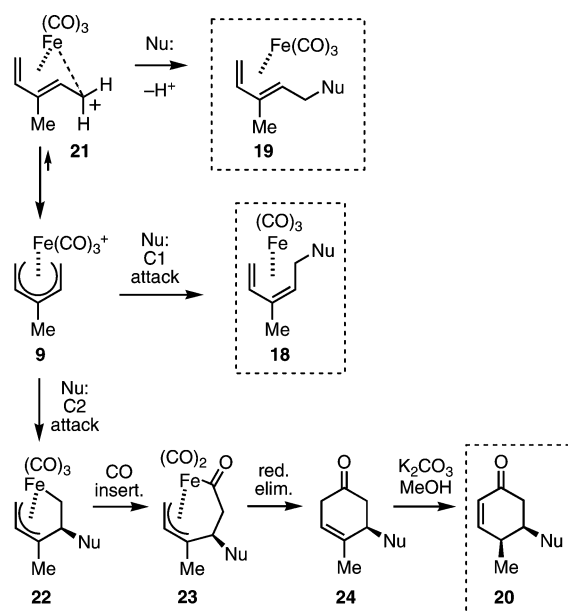
at ca. δ 5.8−5.9 (d, J = 10.1 Hz) and 6.1−6.2 (dd, J = 10.1, 6.1 Hz) ppm, respectively; the 6.1 Hz coupling (H3−H4) is consistent with a pseudoequatorial disposition for H4.

In solution, acyclic (pentadienyl)iron cations are known to exist in an equilibrium between the cisoid form (i.e., **9**) and the corresponding less stable transoid form (i.e., **21**, Scheme 5).[17] While NMR spectroscopy reveals that **9** exists predominantly in the cisoid form (vide supra), reactions of (pentadienyl)Fe-(CO)$_3^+$ cations with weak nucleophiles, such as methanol (N = 7.73)[18a] or furan (N = 1.36),[18b] proceed via the less stable but more reactive transoid form.[19] Thus, the reaction of **9** with furan or methanol gives predominantly the 3-methyl-1,3E-pentadiene products **19d,e**. In contrast, stronger nucleophiles such as hydride, methyl cuprate, and triphenylphosphine ($N \approx$ 13)[18a] attack on a terminal carbon of the cisoid form of the cation to give the 3-methyl-1,3Z-pentadiene products **18a−c**. For malonate anions, diene complexes **18f/g** or cyclohexenones **20f/g** are formed depending on the counterion of the nucleophile

Scheme 5

(Table 1). For strongly associated counterions (e.g., Li$^+$ or Zn^{2+}, entries 1, 4, 5) attack on a terminal carbon of the cisoid form of the cation gives **18**. In contrast, for more weakly associated counterions (e.g., Na$^+$ or Li$^+$/12-crown-4, entries 2, 3, 6) nucleophilic attack proceeds predominantly at the C2 internal carbon to generate a (pentenediyl)iron complex **22** (Scheme 5). Carbonyl insertion[20] into **22** affords the acyl complex **23** which upon reductive elimination gives the 3-cyclohexenone **24**.[21] Workup with methanolic NaHCO$_3$ effects conjugation to give the product **20**. On the basis of ^{13}C NMR spectroscopy[22] and DFT calculations[23c] the C2/C4 carbons of the pentadienyl ligand are believed to bear greater partial positive charge than the C1/C3/C5 positions, while molecular orbital calculations indicate that the LUMO of the (dienyl)iron cations has greater orbital contribution from C1/C5 than from C2/C4.[22a,24] Thus, for strongly dissociated malonate nucleophiles attack at C2/C4 is believed to be due to charge control, while for nucleophiles where there is greater association between the malonate anion and the counterion the decreased polarization in electron density would lead to frontier orbital controlled nucleophilic attack at C1/C5. It should be noted that the steric bulk and/or the strength of the nucleophile may play additional roles in directing nucleophilic attack. For the bulky 2-(ethoxycarbonyl)cyclohex-anone nucleophile (Na$^+$ counterion), attack occurs at the less hindered pentadienyl terminus, while for methyl cyclohexan-ecarboxylate nucleophile (Li$^+$ counterion) attack occurs at C2.

(17) Sorensen, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970**, *25*, C62−C66.

(18) Nucleophilicity parameters (N, s) for neutral nucleophiles have been assigned from correlation analysis: (a) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957. (b) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.

(19) Hossain, M. A.; Jin, M.-J.; Donaldson, W. A. *J. Organomet. Chem.* **2001**, *630*, 5−10 and references therein.
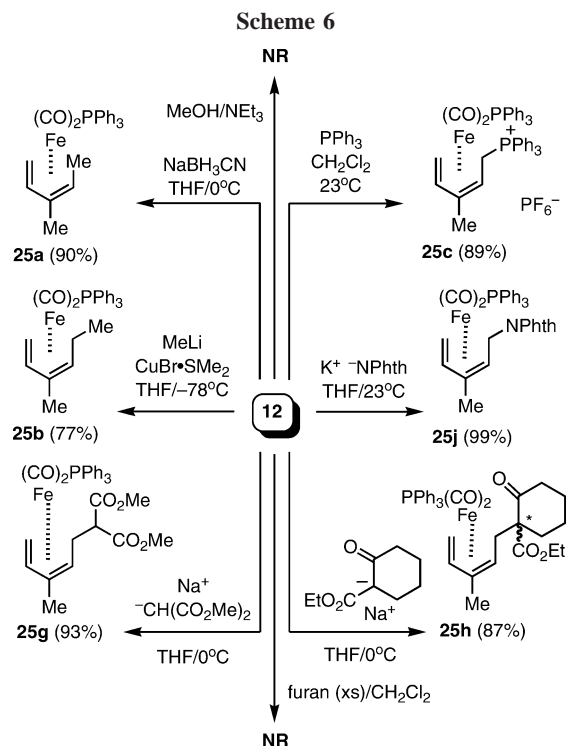
(20) Carbonyl insertion into (pentenediyl)iron complexes and reductive elimination have previously been reported: (a) Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631−2632. (b) Schulze, M. M.; Gockel, U. *J. Organomet. Chem.* **1996**, *525*, 155−158. (c) Taber, D. F.; Kanai, K.; Jiang, Q.; Bui, G. *J. Am. Chem. Soc.* **2000**, *122*, 6807−6808.

(21) A similar mechanism has been proposed to account for the formation of cyclohexenones from nucleophilic attack of organolithiums on (penta-dienyl)iron(1+) cations: McDaniel, K. F.; Kracker, L. R., II; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373−2376.

(22) (a) Dobosh, P. A.; Gresham, D. G.; Lillya, C. P.; Magyar, E. S. *Inorg. Chem.* **1978**, *17*, 1775−1781. (b) Birch, A. J.; Westerman, P. W.; Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1671−1677.

(23) (a) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *107*, C40−C42. (b) Hoffmann, R.; Hofmann, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 598−604. (c) Pfletschinger, A.; Schmalz, H.-G.; Koch, W. *Eur. J. Inorg. Chem.* **1999**, 1869−1880.

(24) (a) Eisenstein, O.; Butler, W. M.; Pearson, A. J. *Organometallics* **1984**, *3*, 1150−1157. (b) Pearson, A. J.; Burello, M. P. *Organometallics* **1992**, *11*, 448−456.

Scheme 6

Figure 3. Diastereomeric transition states for addition to (3-methylpentadienyl)Fe(CO)$_3^+$. The Fe(CO)$_3$ fragment, which is away from the direction of the viewer, is not shown for clarity.

Scheme 7

This regioselectivity may be due to the greater strength of this ester enolate compared to malonate (i.e., charge control).

Reaction of the Fe(CO)$_2$PPh$_3$ ligated cation **12** with a variety of nucleophiles gave only the 1,3Z-diene complexes **25** in good to excellent yields; no reaction was observed with the weak nucleophiles furan or methanol (Scheme 6). Products **25** were assigned as (3-methyl-1,3Z-pentadiene)Fe(CO)$_2$PPh$_3$ complexes on the basis of their NMR spectral data. In particular, the resonance for H$_2$ appears as a broad signal at ca. δ 4.0−4.4 ppm, while the resonances for C2 appear at ca. δ 93−95 ppm. Notably, the signal for C2 of (3-methyl-1,3E-pentadiene)Fe-(CO)$_2$PPh$_3$ complexes (cf. **10** and **11**) appears further upfield (ca. δ 86−88 ppm). Complex **25h** was formed as an inseparable mixture of diastereomers at the new chiral center and the (diene)-Fe coordination as evidenced by two sets of signals in its ^{1}H and ^{13}C NMR spectrum. Decomplexation of the mixture of diastereomers **25h** (or of **18h**) with CAN gave the "free" diene **26** as a single product (eq 1). For reactions of the Fe(CO)$_2$PPh$_3$-ligated cation **12**, the electron donating ability of the phosphine ligand increases the electron density on the pentadienyl ligand and thus all reactions are frontier orbital controlled (i.e., attack on the C1/C5 terminal carbons).
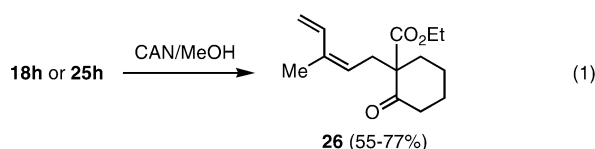
Previous efforts at the desymmetrization of achiral (cyclohexadienyl)- and (cycloheptadienyl)iron(1+) cations by the use of chiral phosphine ligands on iron[11,25a] or with chiral nucleophiles such as sulfoximinyl acetates[25b] or N-acetyl- or

N-propionyloxazolidinones[25c] resulted in enantioselectivities ranging from 11 to 60% ee. With these precedents in mind, we therefore sought the desymmetrization of achiral cation **9**. To this end, reaction **9** with sodium bis[(−)-8-phenylmenthyl] malonate[26] gave the cyclohexenone (−)-**27** as a *single diastereomer* in excellent yield (Scheme 7). Luche reduction of (−)-**27** gave the equatorial cyclohexenol **28**.[27] Assignment of the absolute stereochemistry at the carbinol carbon was based on the ^{1}H NMR chemical shifts of the alkenyl proton (H^2) of the derived (S)- and (R)-Mosher's esters **29** and **30** (δ 5.41 and 5.33 ppm, respectively). These relative chemical shifts are consistent with an (R)-stereochemical assignment at C1, and therefore C5 is assigned as (S). This stereochemical assignment was subsequently corroborated by X-ray crystal structure analysis of **27**.[28] This route to chiral nonracemic 3-substituted-4-methylcyclohexenones should be synthetically useful; notably the cyclohexenone **31** (enantiomeric with **27** about the cyclohexenone ring) was utilized in the synthesis of mevinolin and compactin.[29]

The diastereoselectivity for addition of the chiral malonate to **9** is rationalized in the following fashion. Nucleophilic attack occurs on the face of the pentadienyl ligand opposite to the Fe metal and the malonate anion is oriented such that the π-system of the nucleophile is synclinal with respect to the electrophilic π-system (i.e., the C1−C2 bond) (Figure 3). Steric interaction between the phenyl substitutent and the pentadienyl ligand

(25) (a) Howell, J. A. S.; Thomas, M. J. *J. Chem Soc., Dalton Trans.* **1983**, 1401−1409. (b) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134−144. (c) Pearson, A. J.; Khetani, V. D.; Roden, B. *J. Org. Chem.* **1989**, *54*, 5141−5147. Notably, the greatest % ee's were observed for addition to the (3-methoxycyclohexadienyl)Fe(CO)$_3^+$ cation.
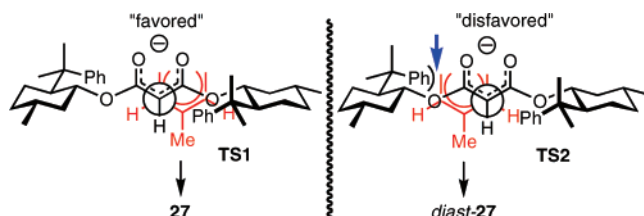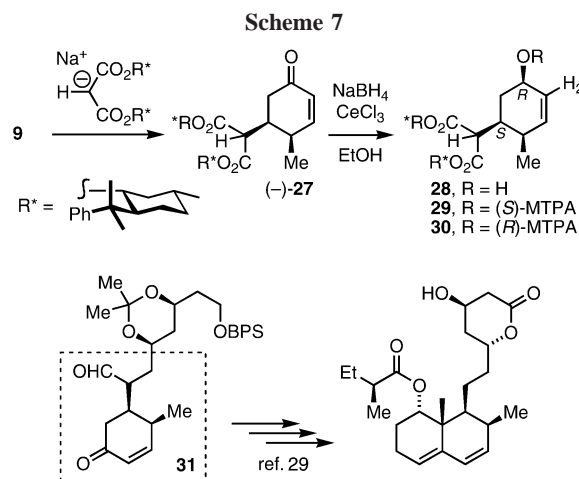
(26) Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W. D.; Adam, F.; Baier, H.; Frank, G.; Duerner, G. *Liebigs Ann. Chem.* **1982**, 1999−2040.

(27) A similar reduction of chiral 4,5-disubstituted cyclohexenones (prepared by nucleophilic addition/protonation of (arene)Cr(CO)$_3$ complexes) was previously reported: Pearson, A. J.; Gontcharov, A. V. *J. Org. Chem.* **1998**, *63*, 152−162.

(28) Bennett, D. W.; Siddiquee, T. A.; Haworth, D. T.; Chaudhury, S.; Donaldson, W. A. *J. Chem. Crystallogr.* **2006**, *36*, 777−780.

(29) Clive, D. L. J.; Murthy, K. S. K.; Wee, A. G. H.; Prasad, J. S.; da Silva, G. V. J.; Majewski, M.; Anderson, P. C.; Evans, C. F.; Haugen, R. D.; Heerze, L. D.; Barrie, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 3018−3028.

present in **TS2** (see blue arrow) is expected to raise the energy of this transition state compared to **TS1**.

In summary, nucleophilic attack on (3-methylpentadienyl)-iron(1+) cation **9** or **12** generally occurs at a terminal (C1) carbon to give (3-methyl-1,3-pentadiene)iron products. However for stabilized nucleophiles such as malonate anions, attack at either C1 or an internal (C2) carbon of the $Fe(CO)_3^+$-ligated cation (**9**) is controlled by the nature of the counterion—nucleophile association. The (pentenediyl)iron complexes formed by attack at the C2 carbon eventually afford cyclohexenone products as a result of CO insertion followed by reductive elimination. Synthesis of the optically active cyclohexenone **27** was realized using bis[(−)-8-phenylmenthyl] malonate as the nucleophile.

Experimental Section

All melting point measurements were carried out on a Mel-Temp apparatus and are uncorrected. All ^{1}H and ^{13}C NMR spectra were recorded on either a Varian 300 Mercury+ or a Varian 400 UnityInova spectrometer. Elemental analyses were preformed by Midwest Microlabs, Ltd., Indianapolix, IN. High-resolution mass spectra were performed either at the Washington University Resource for Mass Spectrometry or the Nebraska Center for Mass Spectrometry.

Tricarbonyl(3-methylpentadienyl)iron(1+) Hexafluorophosphate (9). To an ice-cold solution of tricarbonyl(3-methyl-2,4-pentadien-1-ol)iron (**8**)[8] (0.700 g, 3.33 mmol) in ether (10 mL) and acetic anhydride (1 mL) was added dropwise an ice-cold solution of acetic anhydride (3 mL) and hexafluorophosphoric acid (60% w/w solution, 1 g). The mixture was stirred for 15 min, during which time a pale yellow precipitate formed. The mixture was added dropwise to a large excess of ether (200 mL), and the resultant precipitate was collected by vacuum filtration. The solid was washed with additional ether and dried under high vacuum to afford **9** as a pale yellow amorphous solid (0.926 g, 82%): mp 130−135 °C (dec); IR (KBr) 2119, 2068 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.49 (t, $J = 11.5$ Hz, 2H), 3.81 (dd, $J = 10.1, 3.2$ Hz, 2H), 2.87 (s, 3H), 2.44 (dd, $J = 12.6, 2.9$ Hz, 2H); ^{13}C NMR (acetone-d_6, 23 °C) δ 117.9, 104.5, 64.2, 22.4 (the signal for the metal carbonyls not observed). Anal. Calcd for $C_9H_9O_3PF_6Fe$: C, 29.53; H, 2.48. Found: C, 29.32; H, 2.50.

Dicarbonyl(3-methylpentadienyl)(triphenylphosphine)iron-(1+) Hexafluorophosphate (12). To a solution of tricarbonyl(ethyl 3-methyl-2*E*,4-pentadienoate)iron (**7**)[8] (5.49 g, 19.6 mmol) in acetone (130 mL) was added triphenylphosphine (5.66 g, 21.6 mmol), followed by trimethylamine *N*-oxide dihydrate (4.35 g, 39.2 mmol). The mixture as heated at reflux for 2 h, cooled to room temperature, filtered through a pad of Celite, and concentrated. The crude residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 20:1 to 5:1 gradient) to afford **10** as a bright golden-yellow semisolid (7.22 g, 77%): IR (neat) 1987, 1930, 1701 cm^{-1}; ^{1}H NMR (CDCl$_3$, 70 °C) δ 7.58 (br t, $J = 8.6$ Hz, 6H), 7.05−7.03 (m, 9H), 4.43 (br t, $J = 7.6$ Hz, 1H), 4.00 (m, 2H), 2.61 (s, 3H), 1.29 (m, 1H), 1.02 (t, $J = 7.2$ Hz, 3H), 0.42 (s, 1H), −0.15 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 212.8 (d, $J_{CP} = 18.9$ Hz), 173.7, 135.5 (d, $J_{CP} = 40.1$ Hz), 133.2 (d, $J_{CP} = 10.9$ Hz), 129.9, 128.3 (d, $J_{CP} = 9.8$ Hz), 101.2, 88.4, 59.6, 42.8, 31.9, 18.9, 14.5. This material was used in the next step without further characterization. To a solution of **10** (5.44 g, 10.6 mmol) in CH$_2$-Cl$_2$ (160 mL), cooled in a dry ice/acetone bath, was added, via syringe, a solution of DIBAL in hexanes (1.0 M, 32.0 mL, 32.0 mmol). The reaction mixture was stirred at −78 °C for 90 min. After this time, methanol (15 mL) was added, followed by water. The layers were separated, and the aqueous layer was extracted several times with CH$_2$Cl$_2$. The combined organic extracts were dried (MgSO$_4$) and concentrated. The crude residue was purified

by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1 to 1:1 gradient) to afford **11** as a bright yellow oil (4.55 g, 91%): IR (neat) 3379, 1969, 1907 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.55−7.50 (m, 6H), 7.36 (br m, 9H), 4.20 (br m, 1H), 3.81 (br d, $J = 7.4$ Hz, 2H), 2.15 (s, 3H), 1.64 (br m, 1H), 0.91 (m, 1H), 0.53 (br t, $J = 7.3$ Hz, 1H), −0.13 (br t, $J = 8.6$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 214.5 (d, $J_{CP} = 22.3$ Hz), 136.1 (d, $J_{CP} = 38.9$ Hz), 133.1 (d, $J_{CP} = 10.8$ Hz), 129.7 (d, $J_{CP} = 2.3$ Hz), 128.2 (d, $J_{CP} = 9.2$ Hz), 99.0, 86.5, 62.8, 56.2, 40.9, 14.4. This material was used in the next step without further characterization. To an ice-cold solution of acetic anhydride (5 mL) and hexafluorophosphoric acid (60% w/w solution, 1.5 mL) was added an ice-cold solution of **11** (2.72 g, 5.76 mmol) and acetic anhydride (2.5 mL) in ether (35 mL). The mixture was stirred for 30 min, during which time a bright yellow precipitate formed. The mixture was added dropwise to a large excess of ether (300 mL), and the resultant precipitate was collected by vacuum filtration. The solid was washed with additional ether and dried under high vacuum to afford **12** as a golden yellow solid (3.23 g, 93%): mp 160−161 °C; IR (KBr) 2054, 2006 cm^{-1}; ^{1}H NMR (CDCl$_3$, 23 °C) δ 7.70−7.35 (m, 15H), 5.37 (br m, 2H), 2.37 (br s, 3H), 1.80 (br m, 2H), 1.47 (br m, 2H); ^{1}H NMR (acetone-d_6, −70 °C) δ 7.72−7.65 (m, 15H), 6.07 (br t, $J = 10.8$ Hz, 1H), 5.54 (dd, $J = 17.4, 10.3$ Hz, 1H), 3.75 (br d, $J = 10.0$ Hz, 1H), 2.52 (s, 3H), 2.45 (m, 1H), 1.63 (br m, 2H); ^{13}C NMR (acetone-d_6, 23 °C) δ 133.9 (d, $J_{CP} = 11.3$ Hz), 133.1 (d, $J_{CP} = 3.0$ Hz), 130.9, 130.4 (d, $J_{CP} = 10.6$ Hz), 116.4 (d, $J_{CP} = 1.6$ Hz), 101.5, 62.3, 22.2. Anal. Calcd for $C_{26}H_{24}O_2P_2F_6Fe$: C, 52.02; H, 4.03. Found: C, 51.80; H, 4.10.

Tricarbonyl(3-methyl-1,3Z-pentadiene)iron (18a). To a solution of iron cation **9** (0.200 g, 0.546 mmol) in dry THF (10 mL), cooled to 0 °C, was added in one portion solid sodium cyanoborohydride (0.056 g, 0.82 mmol). The reaction mixture was stirred at 0 °C for 30 min and then poured over a brine solution (10 mL). The reaction mixture was extracted several times with ethyl acetate, and the combined extracts were dried (MgSO$_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **18a** as a yellow oil (0.079 g, 67%): IR (neat) 2043, 1963 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.32 (dt, $J = 8.5, 1.8$ Hz, 1H), 2.72 (dq, $J = 7.3, 1.8$ Hz, 1H), 2.16 (s, 3H), 1.68 (dd, $J = 7.6, 2.9$ Hz, 1H), 1.30 (dd, $J = 9.4, 2.9$ Hz, 1H), 1.07 (d, $J = 7.3$ Hz 3H); ^{13}C NMR (CDCl$_3$) δ 211.5, 105.2, 89.8, 56.0, 37.4, 25.5, 13.7. The ^{13}C NMR spectral data for this product were identical with the literature values.[15]

Dicarbonyl(3-methyl-1,3Z-pentadiene)(triphenylphosphine)-iron (25a). The reaction of iron cation **12** (0.200 g, 0.333 mmol) with sodium cyanoborohydride (0.044 g, 0.698 mmol) was carried out in a fashion similar to the preparation of **18a**. The reaction mixture was quenched by the addition of water (10 mL). The resulting mixture was extracted several times with ethyl acetate, and the combined organic extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (alumina, hexane−ethyl acetate = 10:1) to afford **25a** as a yellow oil (0.135 g, 90%): IR (neat) 1967, 1907 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.54−7.39 (m, 15H), 4.19 (m, 1H), 2.44 (q, $J = 7.1$ Hz, 1H), 2.06 (s, 3H), 1.30 (m, 1H), 1.08 (br d, $J = 7.1$ Hz 3H), 0.92 (t, $J = 7.5$ Hz, 1H); ^{1}H NMR (benzene-d_6) 7.62 (m, 6H), 7.04 (m, 9H), 4.35 (m, 1H), 2.48 (dq, $J = 1.5, 7.1$ Hz, 1H), 2.01 (s, 3H), 1.33 (dt, $J = 1.3, 8.4$ Hz, 1H), 1.15 (m, 1H), 1.11 (d, $J = 3.1$ Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 214.9 (d, $J_{CP} = 22.5$ Hz) 136.5 (d, $J_{CP} = 39.0$ Hz), 133.2 (d, $J_{CP} = 12.5$ Hz), 129.5, 128.2 (d, $J_{CP} = 9.7$ Hz), 101.7, 92.8, 48.3, 39.3, 24.2, 13.9. Anal. Calcd for $C_{26}H_{25}O_2$-PFe: C, 68.44; H, 5.52. Found: C, 68.59; H, 5.83.

Tricarbonyl(3-methyl-1,3Z-hexadiene)iron (18b). To a suspension of CuBr−SMe$_2$ (0.210 g, 1.03 mmol) in THF (20 mL) at −78 °C was added a solution of methyl lithium in ether (1.6 M, 1.3 mL, 2.0 mmol), and mixture was stirred at −78 °C for 1 h. Solid cation **9** (0.300 g, 0.820 mmol) was added and the mixture

stirred at −78 °C for an additional 1 h. The mixture was warmed to room temperature, diluted with saturated aqueous NH$_4$Cl (15 mL) and water (15 mL), and extracted several times with ether. The combined organic extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **18b** as a yellow oil (0.118 g, 61%): IR (neat) 2042, 1962 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.33 (t, J = 8.2 Hz, 1H), 2.59 (t, J = 6.9 Hz, 1H), 2.17 (s, 3H), 1.69 (dd, J = 7.3, 2.3 Hz, 1H), 1.49 (pentet, J = 7.0 Hz, 1H), 1.27 (dd, J = 9.2, 2.2 Hz, 1H), 1.16 (pentet, J = 7.2 Hz, 1H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 211.5, 103.9, 90.3, 65.3, 37.4, 26.1, 22.1, 17.8. A satisfactory elemental analysis was not obtained for this compound, and purity was assessed on the basis of NMR spectroscopy.

Dicarbonyl(3-methyl-1,3*Z*-hexadiene)(triphenylphosphine)-iron (25b). The reaction of **12** (0.200 g, 0.333 mmol) with MeLi/CuBr−SMe$_2$ was carried out in a fashion similar to the preparation of **18b**. The residue was purified by column chromatography (Al$_2$O$_3$, hexane-ethyl acetate = 10:1) to afford **25b** as a waxy solid (0.120 g, 77%): IR (neat) 1967, 1907 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.51−7.37 (m, 15H), 4.09 (m, 1H), 2.25 (br t, J = 7.1 Hz, 1H), 2.03 (s, 3H), 1.99 (m, 1H), 1.51 (m, 1H), 1.26 (m, 1H), 1.11 (t, J = 7.8 Hz, 3H), 0.92 (m, 1H); ^{1}H NMR (benzene-d_6) δ 7.62 (m, 6H), 7.00 (m, 9H), 4.27 (dd, J = 7.9, 8.1 Hz, 1H), 2.42 (br t, J = 7.1 Hz, 1H), 2.02 (s, 3H), 1.70 (m, 1H), 1.36 (dt, J = 2.6, 8.4 Hz, 1H), 1.23−1.14 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 215.2, 136.5 (d, J_{CP} = 37.6 Hz), 133.2 (d, J_{CP} = 10.9 Hz), 129.5, 128.2 (d, J_{CP} = 9.3 Hz), 100.4, 93.2, 58.0 (J_{CP} = 10.1 Hz), 39.4 (d, J_{CP} = 6.3 Hz), 24.8, 22.3, 18.0 (d, J_{CP} = 2.4 Hz). Anal. Calcd for C$_{27}$H$_{27}$O$_2$PFe: C, 68.95; H, 5.78. Found: C, 69.07; H, 5.88.

Reaction of 9 with Triphenylphosphine (18c). To a solution/suspension of **9** (0.114 g, 0.311 mmol) in CH$_2$Cl$_2$ (10 mL) was added triphenylphosphine (0.086 g, 0.328 mmol). The suspension rapidly dissolved, and the golden yellow solution was stirred for 30 min. The reaction mixture was concentrated. The golden yellow sticky residue was triturated with ether which made the solution cloudy. After standing overnight in the refrigerator, **18c** was collected as golden yellow crystalline solid (0.159 g, 81%): mp 175−177 °C; IR (KBr) 2059, 1975 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.97−7.83 (m, 15 H), 5.62 (t, J = 8.8 Hz, 1H), 4.00 (dt, J = 14.6, 3.2 Hz, 1H), 3.40 (m, 1H), 2.90 (br d, J = 10.1 Hz, 1H), 2.67 (br t, J = 12.6 Hz, 1H), 1.85 (dd, J = 9.8, 3.6 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (acetone-d_6) δ 210.9, 136.4 (d, J_{CP} =3.1 Hz), 135.2 (d, J_{CP} = 10.2 Hz), 131.6 (d, J_{CP} = 12.7 Hz), 119.6 (d, J_{CP} = 83.8 Hz), 105.3, 93.9, 47.6 (d, J_{CP} = 10.1 Hz), 40.4 (d, J_{CP} = 1.8 Hz), 25.5, 25.4 (d, J_{CP} = 41.7 Hz). Anal. Calcd for C$_{27}$H$_{24}$O$_3$P$_2$F$_6$Fe: C, 51.61; H, 3.86. Found: C, 51.49; H, 3.86.

Reaction of 12 with Triphenylphosphine (25c). The reaction of **12** (0.100 g, 0.167 mmol) in CH$_2$Cl$_2$ (6 mL) with triphenylphosphine was carried out in a fashion similar to the preparation of **18c**. After stirring of the solution for 20 h, the solvent was evaporated and the residue was taken up in a minimal amount of CH$_2$Cl$_2$ (1 mL) and triturated with ether until the solution became cloudy. After standing for 1 h, **25c** was collected as golden yellow crystalline solid (128 mg, 89%): mp 120−123 °C; ^{1}H NMR (CDCl$_3$) δ 7.81 (dt, J = 1.8, 7.8 Hz, 3H), 7.70 (dt, J = 3.3, 7.8 Hz, 6H), 7.57 (dd, J = 7.5, 12.3 Hz, 6H), 7.48−7.34 (m, 15H), 4.34−4.05 (br s, 1H), 3.30−3.08 (br s, 1H), 2.78−2.60 (br m, 1H), 1.92−1.79 (m, 1H), 1.76−1.66 (br s, 1H), 1.48 (s, 3H), 1.48−1.36 (br m, 1H); ^{13}C NMR (CDCl$_3$) δ 135.0 (d, J_{CP} = 2.9 Hz), 134.4 (d, J_{CP} = 39.4 Hz), 133.0 (d, J_{CP} = 9.1 Hz), 129.8 (d, J_{CP} = 1.7 Hz), 128.2 (d, J_{CP} = 9.7 Hz), 117.6 (d, J_{CP} = 82.9 Hz), 99.7, 95.5 (br), 66.1, 41.6, 24.0, 16.0. Anal. Calcd for C$_{44}$H$_{39}$O$_2$P$_3$F$_6$Fe·2/3H$_2$O: C, 60.43; H, 4.65. Found: C, 60.46; H, 4.62.

Tricarbonyl[5-(2′-furyl)-3-methyl-1,3*E*-pentadiene]iron (19d). To a solution of **9** (100 mg, 0.273 mmol) in CH$_2$Cl$_2$ (10 mL) was added excess furan (0.372 g, 5.46 mmol). The reaction mixture

was stirred at room temperature for 1 h. After this time, water (10 mL) was added and the mixture was extracted several times with CH$_2$Cl$_2$. The combined extracts were washed with brine, dried (MgSO$_4$), and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 5: 1) to afford **19d** as a golden yellow liquid (70 mg, 88%): IR (neat) 2043, 1960 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.34 (m, 1H), 6.31 (dd, J = 3.2, 1.9 Hz, 1H), 6.05 (d, J = 3.2 Hz, 1H), 5.17 (t, J = 8.2 Hz, 1H), 3.10 (dd, J = 16.1, 6.8 Hz, 1H), 2.96 (dd, J = 16.1, 7.3 Hz, 1H), 2.23 (s, 3H), 1.60 (dd, J = 6.9, 2.6 Hz, 1H), 1.08 (t, J = 7.3 Hz, 1H), 0.18 (dd, J = 9.0, 2.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 211.6, 154.7, 141.2, 110.3, 105.4, 102.7, 82.9, 60.8, 37.1, 29.7, 18.8; FAB-HRMS m/z 288.0091 (calcd for C$_{13}$H$_{12}$O$_4$Fe m/z 288.0085).

Tricarbonyl(5-methoxy-3-methyl-1,3*Z*-pentadiene)iron (18e) and tricarbonyl(5-methoxy-3-methyl-1,3*E*-pentadiene)iron (19e). To methanol (10 mL) was added solid cation **9** (100 mg, 0.273 mmol) followed by three drops of triethylamine. The reaction mixture was stirred at room temperature for 90 min. Saturated aqueous ammonium chloride (15 mL) and water (10 mL) were added, and the resulting mixture was extracted several times with CH$_2$Cl$_2$. The combined organic extracts were dried (MgSO$_4$) and concentrated. Purification of the residue by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) gave a brown oil (0.193 g, 90%), which was determined to be a mixture of *Z*-**18e** and *E*-**19e** (2:5) by ^{1}H NMR spectroscopy: IR (neat) 2045, 1962 cm^{-1}. Anal. Calcd for C$_{10}$H$_{12}$O$_4$Fe: C, 47.65; H, 4.80. Found: C, 48.00; H, 4.79.

Z-**18e:** ^{1}H NMR (CDCl$_3$) 5.40 (t, J = 8.5 Hz, 1H), 3.48 (m, 2H), 3.22 (s, 3H), 2.89 (t, J = 10.1 Hz, 1H), 2.67 (dd, J = 5.4, 9.4 Hz, 1H) 2.22 (s, 3H), 1.17 (dd, J = 7.4, 15.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) 104.5, 71.3, 58.8, 58.7, 58.3, 36.4, 25.5.

E-**19e:** ^{1}H NMR (CDCl$_3$) δ 5.14 (t, J = 7.9 Hz, 1H), 3.56 (dd, J = 10.1, 5.6 Hz, 1H), 3.49 (dd, J = 10.1, 8.4 Hz, 1H), 3.34 (s, 3H), 2.17 (s, 3H), 1.64 (dd, J = dd, 7.0, 2.7 Hz, 1H), 0.92 (dd, J = 8.4, 6.2 Hz, 1H), 0.26 (dd, J = 9.3, 2.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 211.2, 103.3, 83.6, 71.4, 58.5, 37.6, 18.3.

Reaction of 9 with Lithium Dimethyl Malonate (18f). To an ice cold stirring solution of dimethyl malonate (0.326 g, 2.47 mmol) in THF (10 mL) was added a solution of *n*-butyllithium in hexanes (2.5 M, 1.0 mL, 2.5 mmol), and the mixture was stirred for 30 min. The generated dimethyl malonate anion was then transferred to an ice-cold solution of cation **9** (0.500 g, 1.37 mmol) in THF (25 mL). The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was warmed to room temperature, and then water (20 mL) was added. The mixture was extracted several times with ether, and the combined extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **18f** as a golden yellow liquid (0.380 g, 80%): IR (neat) 2046, 1966, 1736 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.33 (br t, J = 8.4 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.29 (dd, J = 8.8, 6.1 Hz, 1H), 2.40 (ddd, J = 10.5, 4.2, 1.5 Hz, 1H), 2.17 (m, 1H), 2.09 (s, 3H), 1.73 (dd, J = 7.6, 3.3 Hz, 1H), 1.61 (ddd, J = 14.3, 10.4, 8.9 Hz, 1H), 1.28 (dd, J = 9.2, 3.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 210.6, 169.1, 168.9, 104.2, 90.8, 57.1, 54.3, 52.8, 52.7, 37.7, 29.0, 25.7. Anal. Calcd for C$_{14}$H$_{16}$O$_7$Fe: C, 47.75; H, 4.59. Found: C, 48.01; H, 4.78.

Reaction of 9 with Sodium Dimethyl Malonate (20f). To an ice cold stirring suspension of NaH (0.037 g, 0.923 mmol) in dry THF (10 mL) was added dimethyl malonate (0.081 g, 0.615 mmol). The mixture was stirred at 0 °C for 10 min, and then solid cation **9** (0.150 g, 0.410 mmol) was added in one portion and the reaction mixture was stirred for 2 h at room temperature. During this time a yellow-brown turbidity began to appear. The reaction mixture was diluted with CH$_2$Cl$_2$, a saturated solution of methanolic NaHCO$_3$ (20 mL) was added, and this mixture was stirred overnight at room temperature. Water (20 mL) was added, and the mixture was extracted several times with CH$_2$Cl$_2$. The combined extracts

were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) to afford **20f** as a light yellow liquid (0.090 g, 91%): IR (neat) 1734, 1676 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 6.11 (dd, J = 10.1, 6.1 Hz, 1H), 5.81 (d, J = 10.1 Hz, 1H), 3.31 (d, J = 10.9 Hz, 1H), 3.23 (s, 3H), 3.20 (s, 3H), 3.03 (m, 1H), 2.47 (dd, J = 16.7, 3.8 Hz, 1H), 2.31 (m, 1H), 2.10 (dd, J = 16.7, 13.5 Hz, 1H), 0.55 (d, J = 7.4 Hz, 3H); ^{13}C NMR (C$_6$D$_6$) δ 195.6, 167.9, 167.8, 153.5, 127.9, 54.6, 52.2, 52.1, 37.5, 37.3, 31.6, 12.2; FAB-HRMS *m/z* 247.1148 (calcd for C$_{12}$H$_{16}$O$_5$Li *m/z* 247.1158).

Reaction of 9 with Lithium Dimethyl Malonate/12-Crown-4 (20f). To a solution lithium dimethyl malonate in THF [freshly prepared from dimethyl malonate (0.216 g, 1.64 mmol) and butyllithium] was added 12-crown-4 (0.440 g, 2.50 mmol), and the resultant solution stirred for 15 min. To this solution was added solid cation **9** (0.300 g, 0.820 mmol). The reaction mixture was worked up in a fashion similar to that for the reaction of **9** with sodium dimethyl malonate. Purification by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) gave **20f** (0.165 g, 84%), which was identified by comparison of its ^{1}H NMR spectral data with those previously obtained.

Reaction of 9 with Sodium Dimethyl Malonate/ZnCl$_2$ (18f). A solution sodium dimethyl malonate in THF [freshly prepared from dimethyl malonate (0.072 g, 0.55 mmol) and sodium hydride] was transferred by cannula to a flask containing anhydrous ZnCl$_2$ (0.148 g, 1.09 mmol). A white turbidity immediately appeared. The reaction mixture was stirred at 0 °C for 30 min, and then solid cation **9** (100 mg, 0.272 mmol) was added in one portion. The reaction mixture was stirred for 2 h at room temperature and worked up in a fashion similar to that for the reaction of **9** with lithium dimethyl malonate. Purification by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) gave **18f** (70 mg, 63%), which was identified by comparison of its ^{1}H NMR spectral data with those previously obtained.

Reaction of 9 with Lithium Dimethyl Methylmalonate (18g). The reaction of cation **9** (0.200 g, 0.546 mmol) with lithium dimethyl methylmalonate was carried out in a fashion similar to the reaction of **9** with lithium dimethyl malonate. Purification of the residue by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) gave **18g** as a golden yellow liquid (0.090 g, 45%): IR (neat) 2046, 1969, 1734 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.32 (br t, J = 8.6 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 2.28 (dd, J = 14.2, 3.7 Hz, 1H), 2.13 (m, 1H), 1.72 (dd, J = 7.7, 3.5 Hz, 1H), 1.53 (dd, J = 14.1, 11.4 Hz, 1H), 1.37 (s, 3H), 1.29 (dd, J = 9.4, 3.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 210.9, 172.4, 172.3, 105.2, 90.5, 55.4, 55.1, 52.8, 52.6, 37.8, 36.0, 25.8, 20.0. A satisfactory elemental analysis was not obtained for this compound, and purity was assessed on the basis of NMR spectroscopy.

Reaction of 9 with Sodium Dimethyl Methylmalonate (18g, 20g). The reaction of cation **9** (0.200 g, 0.546 mmol) with sodium dimethyl methylmalonate was carried out in a fashion similar to the reaction of **9** with sodium dimethyl malonate. Purification of the residue by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) gave **18g** (0.070 g, 34%) as an oil followed by **20g** (0.076 g, 55%) as a light yellow liquid. The diene complex **18g** was identified by comparison of its ^{1}H NMR spectral data with that previously obtained. **20g**: IR (neat) 2956, 1731, 1681 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 6.20 (dd, J = 10.1, 6.1 Hz, 1H), 5.86 (d, J = 10.1 Hz, 1H), 3.26 (s, 3H), 3.21 (s, 3H), 3.00 (dt, J = 14.1, 4.1 Hz, 1H), 2.72 (dd, J = 16.3, 4.1 Hz, 1H), 2.57 (dd, J = 16.3, 14.4 Hz, 1H), 2.12 (m, 1H), 1.32 (s, 3H), 0.68 (d, J = 7.1 Hz, 3H); ^{13}C NMR (C$_6$D$_6$) δ 197.6, 171.6, 171.5, 153.8, 127.6, 56.0, 52.0, 51.9, 41.3, 37.1, 31.8, 18.9, 12.0; FAB-HRMS *m/z* 261.1313 (calcd for C$_{13}$H$_{18}$O$_5$Li *m/z* 261.1314).

Reaction of 12 with Sodium Dimethyl Malonate (25f). To an ice cold stirring suspension of NaH (0.030 g, 0.748 mmol) in dry THF (10 mL) was added dimethyl malonate (0.089 g, 0.680 mmol).

The mixture was stirred at 0 °C for 10 min. Solid cation **12** (0.200 g, 0.333 mmol) was added to the malonate anion solution in one portion, and the reaction mixture was stirred at room temperature for 1 h. Water (20 mL) was added, and the reaction mixture was stirred for an additional 10 min and then extracted several times with ethyl acetate. The combined extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **25f** as a golden yellow liquid (0.181 g, 93%): IR (neat) 1973, 1912 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 50 °C) δ 7.56−7.49 (m, 6H), 6.05−6.93 (m, 9H), 4.27 (dt, J = 8.1, 4.5 Hz, 1H), 3.38 (dd, J = 8.1, 6.1 Hz, 1H), 3.33 (s, 3H), 3.31 (s, 3H), 2.49 (m, 1H), 2.35 (dd, J = 10.0, 2.3 Hz, 1H), 2.03 (s, 3H), 1.92 (m, 1H), 1.32 (dt, J = 8.5, 3.2 Hz, 1H), 1.13 (m, 1H); ^{13}C NMR (C$_6$D$_6$) δ 211.5 (d, J_{CP} = 6 Hz), 214.8 (d, J_{CP} = 22.5), 169.3, 169.1, 137.6 (d, J_{CP} = 37.5 Hz), 133.4 (d, J_{CP} = 15.0 Hz), 129.7, 128.5, 101.0, 94.4, 55.0, 52.0, 51.9, 50.7, 39.8, 29.9, 24.6. Anal. Calcd for C$_{31}$H$_{31}$O$_6$PFe: C, 63.49; H, 5.34. Found: C, 63.78; H, 5.64.

Reaction of 12 Cation with Sodium Ethyl 2-Oxocyclohexan-ecarboxylate (25h). To an stirring suspension of NaH (0.030 g, 0.75 mmol) in dry THF (20 mL) under N$_2$ at 0 °C was added ethyl 2-cyclohexanonecarboxylate (0.100 g, 0.592 mmol). The mixture was stirred at 0 °C for 1 h, and then solid cation (0.535 g, 0.888 mmol) was added in one portion. The mixture was stirred for 3 h at 23 °C and then diluted with water (20 mL). The mixture was extracted several times with ethyl acetate, and the combined extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **25h** as a golden yellow waxy solid (0.321 g, 87%). This was determined to be a mixture of diastereomers (1:1.6 by ^{1}H NMR spectroscopy): mp 124−126 °C; IR (neat) 1969, 1905, 1708 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 50 °C) δ 7.67−7.57 (m, 6H), 7.06−6.99 (m, 9H), 4.27 (m, 1H), 3.94 (m, 2H), 2.50 (m, 3H), 2.27 (m, 2H), 2.18 and 2.14 (2 × s, 3H total), 2.03 (m, 2H), 1.50 (m, 4H), 1.20 (m, 2H), 0.98 and 0.91 (2 × t, J = 7.1 Hz, 3H total); ^{13}C NMR (C$_6$D$_6$) δ 206.0 [205.7], 171.8 [171.4], 136.6 (J_{CP} = 38.5 Hz), 133.3 (d, J_{CP} = 11.3 Hz), 129.6 (J_{CP} = 2.0 Hz), 128.3 (J_{CP} = 9.0 Hz), 102.3 [102.2], 94.2 [93.9], 62.9 [62.8], 61.0 [60.9], 48.6 [48.4], 41.5 [41.3], 39.8, 36.0 [35.9], 35.8 [35.3], 27.8 [27.7], 25.1 [24.7], 22.7 [22.6], 14.2 [14.1], diastereomeric signals in brackets. Anal. Calcd for C$_{35}$H$_{37}$O$_5$PFe: C, 67.32; H, 5.97. Found: C, 67.34; H, 6.01.

Reaction of 9 with Sodium Ethyl 2-Oxocyclohexanecarboxy-late (18h). The reaction of **9** (0.240 g, 0.710 mmol) with sodium 2-cyclohexanonecarboxylate was carried out in a fashion similar to the reaction of **12** with this nucleophile. After the usual workup, the residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **18h** as a brown oil (0.179 g, 78%). This was determined to be a mixture of diastereomers (1:1.2 by ^{1}H NMR spectroscopy): IR (neat) 2044, 1966, 1713 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 50 °C) δ 4.76 (t, J = 8.3 Hz, 1H), 3.84 (m, 2H), 2.45 (m, 3H), 2.08 (m, 2H), 1.92 and 1.85 (2 × s, 3H total), 1.80 (m, 3H), 1.47 (m, 1H), 1.35 (m, 2H), 1.22 (m, 1H), 1.13 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (d$_6$-acetone) δ 211.8, 206.1 [206.0], 171.8 [171.4], 106.0 [105.8], 90.6 62.9 [62.8], 61.5 [61.4], 57.2 [56.7], 41.6 [41.5], 38.2 [38.0], 36.7, 35.9 [35.7], 28.0 [27.9], 26.0 [25.8], 23.1 [22.9], 14.4 [14.3], diastereomeric signals in brackets. Anal. Calcd for C$_{18}$H$_{22}$O$_4$Fe: C, 55.39; H, 5.69. Found: C, 55.70; H, 5.70.

Ethyl 1-(3-Methyl-2Z,4-pentadienyl)cyclohexanecarboxylate (26). To a solution of **18h** (0.179 g, 0.460 mmol) in methanol (10 mL) was added cerium(IV) ammonium nitrate (0.126 g, 2.3 mmol) in small portions. Monitoring of the reaction by TLC indicated the reaction to be complete after 30 min. Water (10 mL) was added, the resulting mixture was extracted several times with ether, and the combined extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 10:1) to afford **26** as a colorless oil (0.060 g, 55%).

Decomplexation of **25h** (0.310 g, 0.451 mmol) under similar reaction conditions gave, after chromatographic purification, **26** (83 mg, 77%): IR (neat) 3055, 1712, 1266 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.73 (dd, J = 10.8, 17.1 Hz, 1H), 5.35 (t, J = 8.3 Hz, 1H), 5.22 (d, J = 17.0 Hz), 5.10 (d, J = 10.7 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.75 (dd, J = 7.8, 14.7 Hz, 1H), 2.56−2.43 (m, 3H), 2.04 (m, 3H), 1.82 (s, 3H), 1.80−1.40 (m, 6H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 206.7, 170.7, 134.8, 132.9, 124.4, 114.1, 61.6, 61.5, 41.7, 36.4, 32.9, 28.2, 23.2, 20.8, 14.9. The purity of this compound was assessed on the basis of NMR spectroscopy.

Reaction of 9 with Lithium Methyl Cyclohexanecarboxylate (20i). To a cold (−78 °C), magnetically stirring solution of diisopropylamine (0.070 g, 0.69 mmol) in dry THF (3 mL) under N$_2$ was slowly added a solution of *n*-butyl lithium (2.5 M in hexanes, 0.3 mL 0.7 mmol) and stirred for 10 min. To the LDA solution was added methyl cyclohexanecarboxylate (0.071 g, 0.50 mmol), and the mixture was stirred for an additional 30 min at −78 °C. Solid cation **9** (0.183 g, 0.500 mmol) was added to the anion solution in one portion, and the reaction mixture was stirred for 1 h at −78 °C and then 1 h at room temperature. During this time a yellow turbidity began to appear. The reaction mixture was quenched with 1 M HCl solution (10 mL) and then extracted several times with ether. The combined organic extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (SiO$_2$, hexanes−ethyl acetate = 10:1) to afford an inseparable mixture (6:1 ratio) of 2- and 3-cyclohexenones **20i**/ **20i′** (0.100 g, 80%): IR (neat) 2941, 2858, 1724, 1678 cm^{-1}. **20i** (2-cyclohexenone): ^{1}H NMR (CDCl$_3$) δ 6.91 (dd, J = 10.1, 6.4 Hz, 1H), 5.86 (d, J = 10.1 Hz, 1H), 3.68 (s, 3H), 2.59 (m, 1H), 2.50 (m, 1H), 2.20 (m, 1H), 2.11 (m, 1H), 1.59 (m, 3H), 1.24 (m, 5H), 1.01 (d, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 200.8, 176.0, 156.8, 127.3, 51.8, 42.9, 46.0, 35.6, 33.0, 32.7, 32.4, 25.8, 23.6, 23.3, 12.3. **20i′**: ^{1}H NMR (CDCl$_3$, partial) δ 5.62 (m, 1H), 3.60 (s, 3H), 2.70 (m, 1H), 1.78 (br s, 3H); ^{13}C NMR (CDCl$_3$, partial) δ 211.1, 135.5, 123.2, 52.7, 51.7, 49.3, 41.8, 39.5, 32.5, 32.3, 25.6, 25.5, 23.8, 23.6; FAB-HRMS *m/z* 257.1735 (calcd for C$_{15}$H$_{22}$O$_3$Li *m/z* 257.1729).

Reaction of 9 Cation with Potassium Phthalimide (**18j, 20j**). To a stirring solution of cation **9** (0.300 g, 0.820 mmol) in THF (20 mL) under N$_2$ at 0 °C was added solid potassium phthalimide (0.228 g, 1.23 mmol) in one portion. The reaction mixture was stirred at room temperature for 30 min and then poured into a saturated solution of ammonium chloride (15 mL) and water (10 mL). The mixture was extracted several times with ethyl acetate, and combined organic extracts were washed with water, dried (MgSO$_4$), and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) to afford **18j** as a yellow oil (81 mg, 27%) followed by an inseparable mixture (2.5:1 ratio) of 2- and 3-cyclohexenones **20j** as an oil (72 mg, 34%).

18j: IR (neat) 3057, 2360, 2340, 2049, 1976, 1716 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.84 (dd, J = 3.0, 5.4 Hz, 2H), 7.72 (dd, J = 3.0, 5.6 Hz, 2H), 5.43 (t, J = 8.5 Hz, 1H), 3.76 (dd, J = 6.0, 14.4 Hz, 1H), 3.26 (dd, J = 9.6, 14.4 Hz, 1H), 2.75 (ddd, J = 1.6, 6.1, 9.6 Hz, 1H), 2.14 (s, 3H), 1.83 (dd, J = 3.8, 7.8, Hz, 1H), 1.69 (dd, J = 3.7, 9.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) 168.2, 134.2, 132.2, 123.5, 103.7, 91.8, 55.6, 37.2, 36.7, 25.3; FAB-HRMS *m/z* 368.0234 (calcd for C$_{17}$H$_{14}$NO$_5$Fe (M + H$^+$) *m/z* 368.0221).

20j/20j′: IR (neat) 2969, 1772, 1709 cm^{-1}. Anal. Calcd for C$_{15}$H$_{13}$NO$_3$·1/2H$_2$O: C, 68.17; H, 5.34; N, 5.30. Found: C, 68.33; H, 5.28; N, 5.07. **20j** (2-cyclohexenone): ^{1}H NMR (CDCl$_3$) δ 7.77 (m, 2H), 7.67 (m, 2H), 6.92 (dd, J = 10.1, 5.3 Hz, 1H), 6.10 (d, J = 10.1 Hz, 1H), 4.90 (dt, J = 12.8, 5.1 Hz, 1H), 3.80 (dd, J = 17.0, 12.8 Hz, 1H), 2.88−2.78 (m, 1H), 2.63 (dd, J = 17.0, 4.8 Hz, 1H), 1.17 (d, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 197.4, 168.8, 153.0, 134.5, 131.9, 129.1, 123.7, 50.0, 37.5, 35.0, 14.3. **20j′** (3-cyclohexenone): ^{1}H NMR (CDCl$_3$, partial) δ 5.70 (br m, 1H), 5.06 (br t, J = 6.5 Hz, 1H), 2.92 (m, 1H), 2.84 (m, 1H), 1.65

(m & s, 4H); ^{13}C NMR (CDCl$_3$, partial) δ 206.0, 168.1, 131.8, 130.2, 49.8, 43.6, 39.4, 20.5.

Reaction of 12 with Potassium Phthalimide (25j). The reaction of **12** (0.100 g, 0.167 mmol) with potassium phthalimide was carried out in a fashion similar to the reaction of **9** with potassium phthalimide. Purified by column chromatography (SiO$_2$, hexane− ethyl acetate = 10:1) gave **25j** as a golden yellow waxy solid (0.100 g, 99%): IR (neat) 1975, 1916 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 50 °C) δ 7.57−7.49 (m, 8H), 6.96−6.94 (m, 7H), 6.89−6.86 (m, 4H), 4.33 (brm, 1H), 3.94 (dd, J = 14.2, 6.4 Hz, 1H), 3.31 (dd, J = 14.2, 9.2 Hz, 1H), 2.87 (t, J = 7.1 Hz, 1H), 1.94 (s, 3H), 1.79 (m, 1H), 1.28 (m, 1H); ^{13}C NMR (C$_6$D$_6$) δ 168.4, 136.7 (d, J_{CP} = 40 Hz), 133.8 (d, J_{CP} = 10.5 Hz), 133.6, 133.3, 130.1, 128.8, 123.3, 100.5, 95.3, 37.7, 32.2, 24.2, 14.7. Anal. Calcd for C$_{34}$H$_{28}$NO$_4$PFe: C, 67.89; H, 4.70; N, 2.33. Found: C, 67.74; H, 5.00; N, 2.45.

Reaction of 9 with Sodium Bis[(−)-8-phenylmenthyl] Malonate (27). The reaction of cation **9** (0.200 g, 0.546 mmol) with sodium bis[(−)-8-phenylmenthyl] malonate was carried out in a fashion similar to the reaction of **9** with sodium dimethyl malonate. Purification of the residue by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) gave **27** (0.190 g, 95%) as an off-white foam. Recrystallization from CH$_3$CN/H$_2$O gave a crystalline solid: mp 52−55 °C; $[\alpha]^{20}_{365}$ = −12 (*c* 0.20, hexanes); $[\alpha]^{20}_{589}$ = −25 (*c* 0.20, hexanes); IR (neat) 3055, 1742, 1676 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.31 (m, 4H), 7.25 (m, 4H), 7.16 (m, 2H), 6.95 (dd, J = 10.1, 6.0 Hz, 1H), 5.95 (d, J = 10.1 Hz, 1H), 4.91 (dt, J = 10.8, 4.4 Hz, 1H), 4.82 (dt, J = 8.3, 4.3 Hz, 1H), 2.87 (d, J = 11.3 Hz, 1H), 2.72 (m, 2H), 2.15 (d, J = 9.1 Hz, 2H), 2.04−1.50 (m, 10H), 1.43 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H), 1.23−0.93 (m, 9H), 0.97 (d, J = 7.4 Hz, 3H), 0.89 (d, J = 6.7 Hz, 3H), 0.88 d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 197.9, 168.1, 166.9, 155.6, 151.2, 150.6, 128.3, 128.2, 125.8, 54.7, 50.4, 41.5, 41.4, 40.3, 40.2, 36.8, 35.9, 34.8, 25.4, 24.7, 22.8, 22.0, 14.3, 12.6. Anal. Calcd for C$_{42}$H$_{56}$O$_5$: C, 78.70; H, 8.82. Found: C, 78.67; H, 8.91.

Reduction of Chiral Cyclohexenone (28). To a solution of **27** (150 mg, 0.234 mmol) in methanol (10 mL) was added cerium-(III) chloride (87 mg, 0.23 mmol) and sodium borohydride (28 mg, 0.74 mmol). The reaction mixture was stirred for 30 min at room temperature and then quenched with water. The resultant mixture was extracted several times with CH$_2$Cl$_2$, and the combined extracts were washed with saturated aqueous NaHCO$_3$, dried (MgSO$_4$), and concentrated. The residue was purified by column chromatography (SiO$_2$, hexane−ethyl acetate = 5:1) to afford **28** as a light yellow oil (103 mg, 69%): ^{1}H NMR (CDCl$_3$) δ 7.33 (m, 4H), 7.31 (m, 4H), 7.17 (m, 2H), 5.72 (ddd, J = 10.1, 5.9, 1.7 Hz, 1H), 5.60 (d, J = 10.1 Hz, 1H), 4.88 (m, 2H), 4.27 (br t, J = 8.0 Hz, 1H), 2.98 (d, J = 10.6 Hz, 1H), 2.53 (m, 2H), 2.09−1.83 (m, 10H), 1.74 (m, 2H), 1.48 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.23− 0.93 (m, 6H), 0.89 (m, 9H); ^{13}C NMR (CDCl$_3$) δ 168.9, 167.2, 150.9, 150.6, 134.8, 129.6, 128.3, 128.2, 125.9, 125.8, 125.6, 125.5, 68.2, 55.6, 50.7, 50.5, 41.7, 41.4, 40.6, 40.4, 35.3, 34.6 (two signals), 31.8, 31.6, 31.5, 30.9, 30.7, 30.6, 29.9, 27.6, 27.4, 24.1, 23.8, 22.9, 22.0, 15.0, 14.3; FAB-HRMS *m/z* 649.4443 (calcd for C$_{42}$H$_{58}$O$_5$Li *m/z* 649.4444).

Supporting Information Available: Copies of the NMR spectral data for **18b,g,j**, **19d**, **20f,g,i,j**, **26**, and **28** and CIF files for the X-ray crystal structures for **12** and **18c**. This material is available free of charge via the Internet at http://pubs.acs.org.