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Synthesis and Reactivity of Tricarbonyl(1-ethoxy-carbonyl-2-methylpentadienyl)iron(1+) Cation

Young K. Yun

Heiko Bärmann

William Donaldson
Marquette University, william.donaldson@marquette.edu

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Young K. Yun
Department of Chemistry, Marquette University, Milwaukee, WI
Heiko Bärmann
Department of Chemistry, Marquette University, Milwaukee, WI
William A. Donaldson
Department of Chemistry, Marquette University, Milwaukee, WI

Synopsis: The title cation was prepared in two steps from the known (ethyl 3-methyl-6-oxo-2,4-hexadienoate)$Fe(CO)_3$. Reation of the cation with $NaBH_3CN$, methyl cuprate, phthalimide, water, PPh_3, or malonate anions gave predominantly the products from nucleophilic attack at the C5 pentadienyl carbon.

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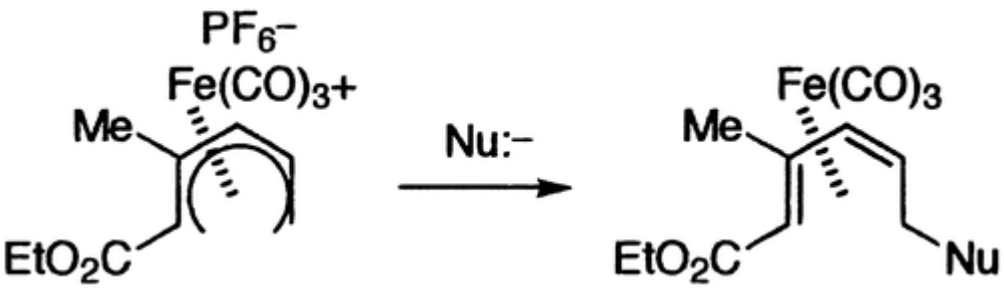
Abstract



The title cation was prepared in two steps from the known (ethyl 3-methyl-6-oxo-2,4-hexadienoate)$Fe(CO)_3$. Reation of the cation with $NaBH_3CN$, methyl cuprate, phthalimide, water, PPh_3, or malonate anions gave predominantly the products from nucleophilic attack at the C5 pentadienyl carbon.

Nucleophilic attack on coordinated polyenes is one of the paradigms of π-organometallic chemistry.[1] Where these types of reactions occur with predictable regioselectivity they can be of synthetic utility. For example, (cyclohexadienyl)iron(1+) cations (**1**) are known to undergo nuclophilic attack at the terminal dienyl carbon (eq 1).[2] While it might be anticipated that nucleophilic attack on the corresponding *acyclic* (pentadienyl)iron(1+) cations should be similar, significant differences in reactivity do exist. For instance, the reaction of a variety of soft carbon nucleophiles with (1-methoxycarbonylpentadienyl)$Fe(CO)_3^+$ (**2**) proceeds via attack at an internal carbon of the dienyl ligand (eq 2).[3] This regioselectivity has been rationalized as the result of charge control; that is, the greater partial positive charge at the C2 and C4 pentadienyl carbons directs nucleophilic attack at these sites. In contrast, for (pentadienyl)iron cations bearing a C2 methyl substituent (e.g., **3a**−**c**), attack by soft carbon nucleophiles generally occurs at the C5 pentadienyl terminus (eq 3).[4] This regioselectivity may be attributed to the ability of the C2-methyl group to direct nucleophilic attack at the more remote pentadienyl terminus due to steric hindrance. We herein report on the synthesis of a (pentadienyl)$Fe(CO)_3^+$ cation (**4**) bearing both a 2-methyl and 1-alkoxycarbonyl substituent and reactivity of **4** with carbon and heteroatom nucleophiles.

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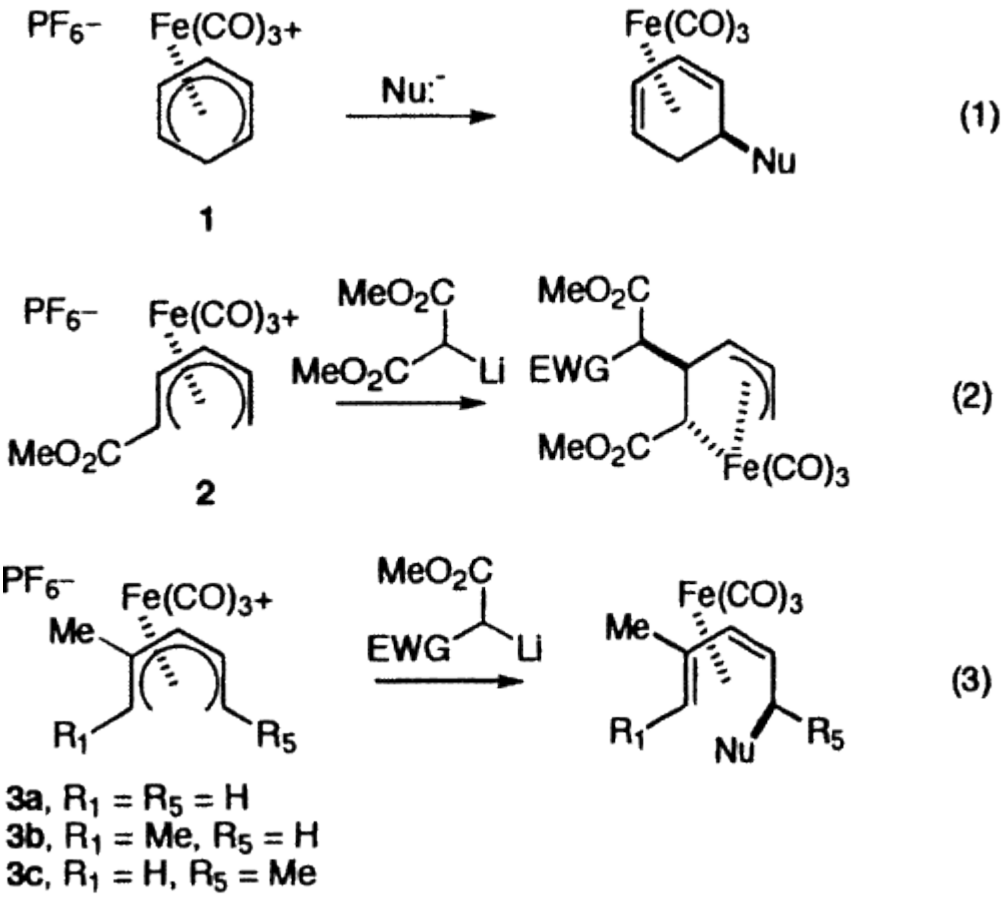


Results and Discussion

The (dienal)iron complex **5** was prepared in two steps from ethyl 3-methyl-4-oxo-2-butenoate according to the literature procedure.[5] Reduction of **5** with KBH_4 gave the dienol complex, which upon dehydration with HPF_6 afforded **4** as a stable yellow solid (eq 4). Cation **4** was assigned the cisoid structure on the basis of its ^1H NMR spectral data. In particular, the H3−H4 coupling (7 Hz) is indicative of their cis relationship. Predicted ^{13}C NMR chemical shifts (Table 1) may be calculated for **4** based of the additivity of the individual substituent effects[6] for an ester substituent at C1 (i.e., **2**) and a methyl substituent at C2 (i.e., **3a**). The observed chemical shifts for the dienyl ligand carbons of **4** are close to the predicted chemical shifts (±2.0 ppm).

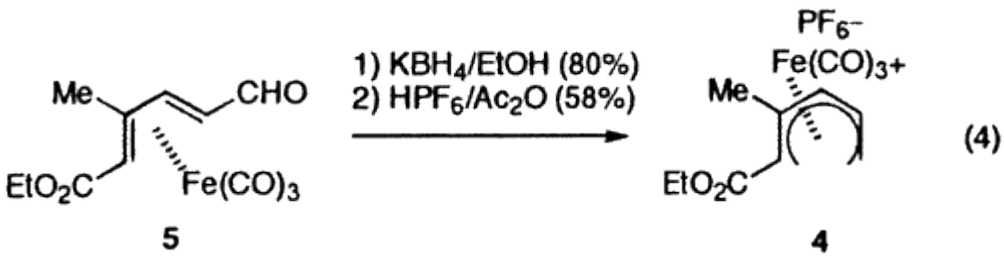
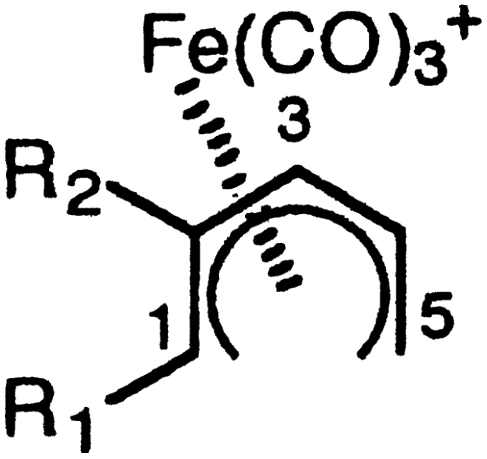


Table 1. ^{13}C NMR Spectral Data for (Pentadienyl)iron Cations[a]



	parent $R_1 = R_2 = H$[b]	**2**[c]	**3a**[d]	**4** (calc)[e]	**4** (expt)
C1	60.8	64.9 (+4.1)	60.2 (−0.6)	64.2	66.0
C2	99.9	106.2 (+6.3)	122.2 (+22.3)	128.5	127.1
C3	93.7	97.9 (+4.2)	94.6 (+0.9)	98.8	97.7
C4	99.9	105.8 (+5.9)	99.1 (−0.8)	105.0	103.0
C5	60.8	68.5 (+7.7)	62.0 (+1.2)	69.7	68.0

[a] In ppm downfield from $SiMe_4$; CD_3NO_2; 75 MHz; substituent chemical shift in parentheses.[b] Ref 6, corrected for CD_3NO_2 solvent.[c] Ref 3b.[d] Ref 4a.[e] Calculated chemical shifts = parent + substituent chemical shifts.

The results of the reactions of **4** with sodium cyanoborohydride, methylcuprate, potassium phthalimide, water, and triphenylphosphine appear in Scheme 1. In each case, the product was assigned as an *E*,*Z*-dienoate structure on the basis of its NMR spectral data (Tables 2 and 3). In particular, the singlet at ca. δ 1.9−2.2 ppm, the doublet at 4.5−5.1, and the multiplet at 2.3−2.7 in their ^1H NMR spectra are characteristic for H1, H3, and H4, while signals at ca. δ 46, 110, and 86 ppm in their ^{13}C NMR spectra are characteristic for C1, C2, and C3. The formation of single products from the addition of methylcuprate and triphenylphosphine is not surprising, since the regiochemical directing effects of the two substituents present on **4** are

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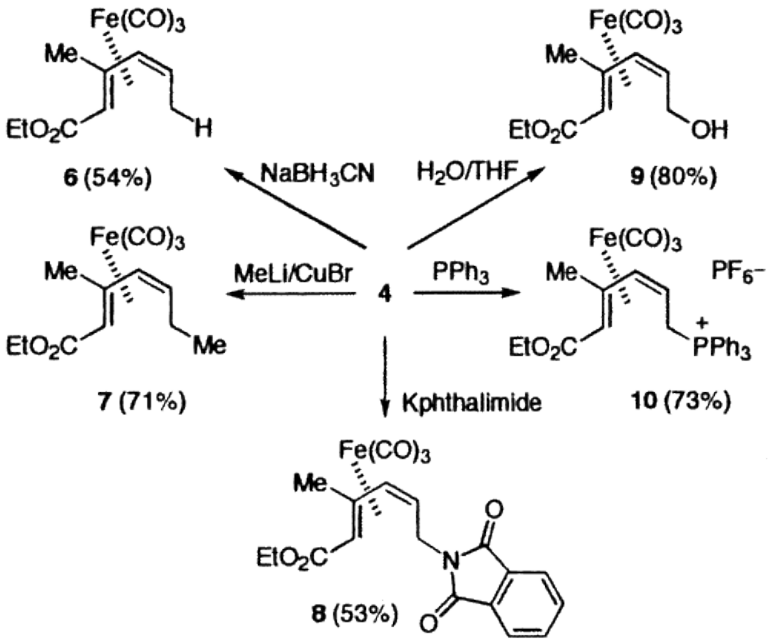
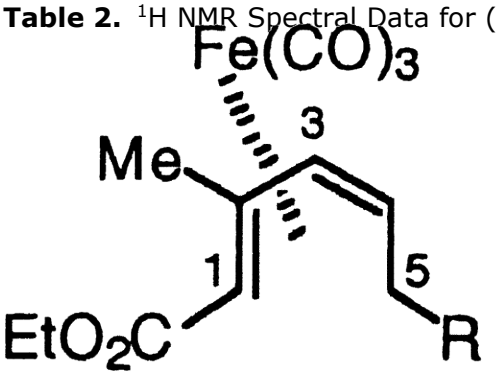
"matched".[3,4,7] While the regiochemical directing effects of the two substituents are "matched" for addition of water, it should be noted that addition of water to **2** affords an *E*,*Z*-dienol complex,[8] while addition of water to **3a** proceeds via the transoid form of the cation to give an *E*-dienol complex.[4a] The electron-withdrawing ethoxycarbonyl substituent present on **4** increases the reactivity of this cation such that even weak nucleophiles (e.g., water) react via the cisoid form.



Scheme 1

Table 2. ^{1}H NMR Spectral Data for (Dienoate)iron Complexes[a]



compd	H1	2-Me	H3	H4	other
6	1.98 (s, 1H)	2.54 (s, 3H)	5.11 (d, 1H) J = 8.1	2.70 (pent, 1H) J = 7.3	4.2−4.0 (m, 2H), 1.26 (t, J = 7.2, 3H), 1.22 (d, J = 7.2 Hz, 3H)
7	1.92 (s, 1H)	2.53 (s, 3H)	5.05 (d, 1H) J = 7.8	2.53 (m, 1H)	4.2−4.0 (m, 2H), 1.59 (m, 1H), 1.31 (m, 1H), 1.25 (t, J = 7.2, 3H), 0.99 (t, J = 7.2, 3H)
8	2.25 (s, 1H)	2.57 (s, 3H)	5.09 (d, 1H) J = 7.8	2.68 (ddd, 1H) J = 5.5, 7.6, 10.0	7.89−7.82 (m, 2H), 7.78−7.70 (m, 2H), 4.26−4.07 (m, 2H), 3.97 (dd, J = 5.4, 14.4, 1H), 3.40 (dd, J = 10.0, 14.5, 1H), 1.29 (t, J = 7.2, 3H)
9[b]	1.91 (s, 1H)	2.31 (s, 3H)	4.46 (d, 1H) J = 7.8	2.31 (m, 1H)	4.05−3.80 (m, 2H), 3.25−3.15 (m, 1H), 2.96 (br t, J = 9.0, 1H), 1.17 (br s, OH), 0.96 (t, J = 7.2, 3H)
10[c]	1.99 (s, 1H)	2.32 (s, 3H)	5.12 (d, 1H) J = 7.5	2.69 (ddt, 1H) J = 3.9, 7.5, 11.4	8.0−7.7 (m, 15H), 4.18 (dq, J = 10.8, 7.2, 1H), 4.05 (dq, J = 10.8, 7.2, 1H), 3.88 (ddd, J = 3.6, 13.8, 15.6, 1H), 3.08 (dt, J = 15.6, 12.7, 1H), 1.23 (t, J = 7.2, 3H)
11a	1.94 (s, 1H)	2.53 (s, 3H)	5.04 (d, 1H) J = 7.8	d	4.2−4.0 (m, 2H), 3.74 and 3.73 (2 × s, 6H), 3.35 (dd, J = 6.1, 8.2, 1H), 2.45−2.25 (m, 2H), 1.76 (m, 1H), 1.27 (t, J = 7.2, 3H)
11b	1.90 (s, 1H)	2.53 (s, 3H)	5.08 (d, 1H) J = 7.3	2.30 (m, 1H)	4.16 (dq, J = 10.7, 7.0, 1H), 4.07 (dq, J = 11.1, 7.1, 1H), 3.71 and 3.68 (2 × s, 6H), 2.37 (dd, J = 3.8, 13.8, 1H), 1.63 (dd, J = 10.5, 13.8, 1H), 1.38 (s, 3H), 1.25 (t, J = 7.1, 3H)

[a] In ppm downfield from $SiMe_4$; J couplings in Hz; $CDCl_3$ solution unless otherwise noted; 300 MHz. [b] C_6D_6 solution. [c] CH_3NO_2 solution. [d] This signal is overlapped with that for one of the H5 protons (reported in other).

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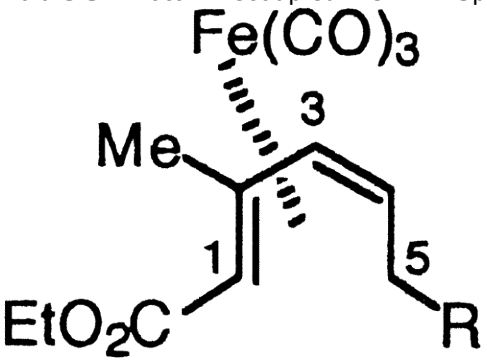
Table 3. Proton-Decoupled ^{13}C NMR Spectral Data for (Dienoate)iron Complexes[a]



compd	$CH_3CH_2OC(O)$					C1	C2	C3	C4	C5	2-Me	other
6	14.2	59.9	172.3	46.6	109.4	88.3	50.6	14.3	19.2			
7	14.1	60.3	172.3	46.7	109.9	86.9	59.9	22.6	19.0	17.5		
8	14.9	60.9	172.4	47.3	112.7	86.7	51.5	38.0	20.1	168.4, 134.8, 132.8, 124.1		
9[b]	14.2	60.6[c]	172.0	45.9	111.1	86.5	57.7	60.1[c]	19.0			
10[d]	11.8	58.7	170.1	46.4	110.9	84.8 (dd) J_{PH} = 3.6	39.2 (d) J_{PH} = 10.9	23.2 (d) J_{PH} = 42.4	16.4	133.9, 132.4 (d, J_{PH} = 9.7), 128.8 (d, J_{PH} = 12.1), 116.3 (d, J_{PH} = 84.8)		
11a	14.0	59.9	171.8	46.6	110.6	86.6	53.9	28.9	19.0	168.7, 168.5, 52.3, 51.7, 40.8		
11b	14.1	60.1	172.0[c]	46.6	110.2	87.6	55.1	35.9	19.2[c]	171.9[c], 171.8, 52.6, 52.5, 49.6, 19.8[c]		

[a] In ppm downfield from $SiMe_4$; ^{31}P couplings in Hz; $CDCl_3$ solution unless otherwise noted; 75 MHz. [b] C_6D_6 solution. [c] Assignments for these signals may be interchanged. [d] CH_3NO_2 solution.

In contrast to the above results, the regiochemical directing effects of the substituents present on **4** are "mismatched" for the addition of malonate nucleophiles (cf. eqs 2 and 3). Thus it was of interest to note that reaction of **4** with dimethyl malonate anion afforded predominantly **11a** (87%) along with a minor amount of **12a** (4%) (eq 5). The structural assignments for both products are based on their NMR spectral data. Notably, the ^1H and ^{13}C NMR spectra of **11a** (Tables 2 and 3) exhibit signals characteristic of an *E,Z*-dienoate complex. Complex **12a** was assigned a pentenediyl structure; in particular, the signal at δ −2.2 ppm in its ^{13}C NMR spectrum and the signals at δ 0.53 (dd) and −0.74 (dd) ppm in its ^1H NMR spectrum are characteristic of a *methylene* carbon which is σ-bound to iron.[3] In a

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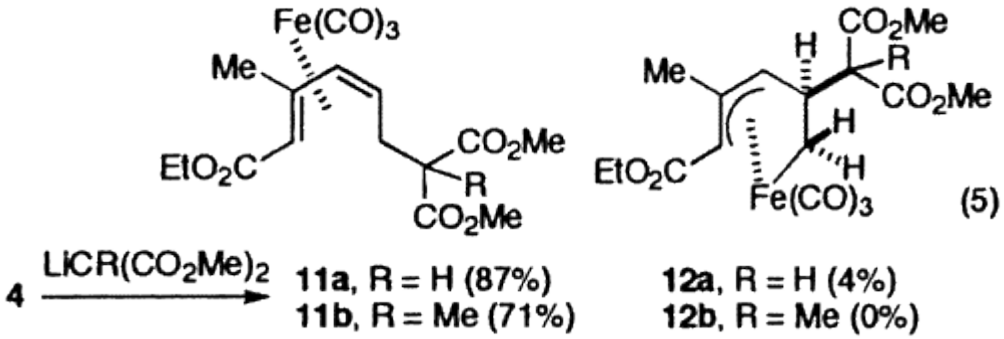
similar fashion, the reaction of **4** with dimethyl methylmalonate anion gave the *E*,*Z*-diene complex **11b**; no pentenediyl complex was observed in this reaction. The structure of **11b** was assigned by comparison of its NMR spectral data with that obtained for **11a**. In these cases, the directing nature of the 2-methyl substituent dominates that of the 1-alkoxycarbonyl substituent. This is presumably due to the steric hindrance for nucleophilic attack at C2.



In summary, the reaction of (1-ethoxycarbonyl-2-methylpentadienyl)$Fe(CO)_3^+$ cation (**4**) with carbon and heteroatom nucleophiles proceeds in a highly regioselective fashion to afford (2*E*,4*Z*-dienoate)$Fe(CO)_3$ products.

Experimental Section

All melting point measurements were carried out on a Mel-Temp apparatus and are uncorrected. Unless otherwise specified all ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using a GE Omega GN-300 spectrometer. Elemental analyses were performed by Midwest Microlabs, Ltd., Indianapolis, IN. High-resolution mass spectra were performed at the Washington University Resource for Mass Spectrometry. Dry tetrahydrofuran (THF) and dry ether were distilled from potassium and sodium benzophenone ketyl, respectively, and dry CH_2Cl_2 was distilled from P_2O_5 prior to use. All other solvents were spectral grade and were used without further purification.

Tricarbonyl)(1-ethoxycarbonyl-2-methylpentadienyl)iron(1+) Hexafluorophosphate (4). To a solution of tricarbonyl(ethyl 3-methyl-6-oxo-2,4-hexadienoate)iron[5] (6.22 g, 20.2 mmol) in dry ethanol (75 mL) was added KBH_4 (1.31 g,

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24.2 mmol). The solution was stirred for 30 min and then diluted with water (75 mL). The mixture was extracted with ether (3 × 50 mL), the combined extracts were dried, and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 2:1) to afford the dienol complex as a yellow solid (5.03 g, 80%): ^{1}H NMR ($CDCl_3$) δ 5.23 (d, *J* = 8.4 Hz, 1H), 4.2−4.0 (m, 2H), 3.84 (dd, *J* = 5.4, 11.9 Hz, 1H), 3.70 (dd, *J* = 7.2, 11.9 Hz, 1H), 2.53 (s, 3H), 1.7−1.64 (br m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.83 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 171.8, 101.3, 87.4, 63.9, 60.1, 59.1, 48.0, 18.4, 13.9. To a cold solution of HPF_6 (4.7 mL, 60% solution) in Ac_2O (14 mL) was added a solution of tricarbonyl(ethyl 3-methyl-6-hydroxy-2,4-hexadienoate)iron (5.03 g, mmol) in Ac_2O (5 mL) at 0 °C. The mixture was stirred for 30 min, during which time a bright yellow precipitate formed. The mixture was added to a large excess of ether and the precipitate collected by vacuum filtration and dried in vacuo to afford **4** as a yellow powder (4.16 g, 58%): ^{1}H NMR (CD_3NO_2) δ 7.03 (d, *J* = 6.9 Hz, 1H), 6.23 (ddd, *J* = 7.2, 10.2 12.9 Hz, 1H), 4.06 (dd, *J* = 3.6, 10.2 Hz, 1H), 2.93 (dd, *J* = 3.6, 12.9 Hz, 1H), 2.76 (s, 3H), 2.02 (s, 1H), 1.34 (t, *J* = 7.2 Hz, 3H) (signals for ester CH_2 obscured by the signal for residual CD_2HNO_3 ca. 4.3 ppm); ^{13}C NMR (CD_3NO_2) δ 204.3, 197.4, 194.7, 166.6, 127.1, 103.0 (CH), 97.7 (CH), 68.0 (CH_2), 66.6 (CH), 61.8 (CH_2), 19.0 (CH_3), 12.1 (CH_3). Anal. Calcd for $C_{12}H_{13}O_5FePF_6$: C, 32.90; H, 2.99. Found: C, 32.84; H, 2.94.

Tricarbonyl(ethyl 3-methyl-2*E*,4*Z*-hexadienoate)iron (6). To a solution/suspension of cation **4** (250 mg, 0.569 mmol) in THF (15 mL) at 0 °C was added solid $NaBH_3CN$ (40 mg, 0.63 mmol) in one portion. The mixture was stirred at 0 °C for 1 h, warmed to room temperature, and stirred at 23 °C for 1 h. Water (15 mL) was added, and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 3:1) to afford **6** as a yellow oil (90 mg, 54%): R_f 0.62 (hexanes−ethyl acetate = 3:1); see Tables 1 and 2 for NMR spectral data.

Tricarbonyl(ethyl 3-methyl-2*E*,4*Z*-heptadienoate)iron (7). To a solution of methyllithium (2.4 mL, 1.4 M in ether, 3.4 mmol) in THF (15 mL) and ether (5 mL) at −78 °C was added CuBr·Me_2S (233

mg, 1.14 mmol). The mixture was stirred for 45 min, and then solid cation **4** (250 mg, 0.569 mmol) was added in one portion. The mixture was stirred for an additional 2 h at −78 °C, then quenched with saturated aqueous NH_4Cl (20 mL). The resultant mixture was extracted with ethyl acetate, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate (3:1)) to afford **7** as a yellow oil (110 mg, 63%): R_f 0.61 (hexanes−ethyl acetate = 3:1); EI−HRMS *m*/*z* 308.0337 (calcd for $C_{13}H_{16}O_5Fe$ *m*/*z* 308.0347); see Tables 1 and 2 for NMR spectral data.

Reaction of 4 with Potassium Phthalimide. To a solution of cation **4** (60 mg, 0.14 mmol) in THF (5 mL) was added potassium phthalimide (51 mg, 0.27 mmol). The reaction mixture was stirred for 1.5 h, poured into water, and extracted several times with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 10:1) to afford **8** as a yellow oil, which solidified upon standing in the refrigerator (32 mg, 53%): mp 106−110 °C; FAB-HRMS *m*/*z* 440.0430 (calcd for $C_{20}H_{18}NO_7Fe$ *m*/*z* 440.0433); see Tables 1 and 2 for NMR spectral data.

Tricarbonyl(ethyl 6-hydroxy-3-methyl-2*E*,4*Z*-hexadienoate)iron (9). Solid cation **4** (200 mg, 0.455 mmol) was added to a solution of THF−H_2O (1:1, 20 mL). The reaction mixture was vigorously stirred for 1 h and extracted several times with ethyl acetate. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (Florisil, hexanes−ethyl acetate = 3:1) to afford **9** as a yellow oil (120 mg, 85%). The ^1H NMR spectrum of this product indicated that it may contain <7% of the *E*,*E*-diene isomer: EI-HRMS *m*/*z* 292.9882 (calcd for $C_{12}H_{13}O_5Fe$ (M^+ − OH) *m*/*z* 293.0112); see Tables 1 and 2 for NMR spectral data.

Reaction of 4 with Triphenylphosphine. To a solution/suspension of **4** (250 mg, 0.569 mmol) in CH_2Cl_2 (20 mL) was added solid triphenylphosphine (163 mg, 0.577 mmol). The reaction mixture rapidly became clear and was stirred for 16 h. The reaction mixture was concentrated under reduced pressure, and the resultant

oil was dissolved in a minimal amount of CH_2Cl_2 and triturated with ether until cloudy. After standing for 1 h, the resultant crystals were collected by filtration to afford **10** as a yellow solid (300 mg, 73%): mp 88−90 °C. Anal. Calcd for $C_{30}H_{28}O_5FeP_2F_6$: C, 51.45; H, 4.03. Found: C, 51.38; H, 4.09. See Tables 1 and 2 for NMR spectral data.

Reaction of 4 with Dimethyl Malonate Anion. To a solution of lithium dimethyl malonate (0.693 mmol, freshly prepared from dimethylmalonate and *n*-butyllithium) in THF (10 mL) at 0 °C was added solid cation **4** (250 mg, 0.569 mmol) in one portion. The mixture was stirred at 0 °C for 1 h and at 23 °C for 1 h. Water (10 mL) was added, and the mixture was extracted with ethyl acetate (2 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 3:1) to afford **12a** as a yellow oil (4 mg, 4%) followed by **11a** as a yellow solid (210 mg, 87%).
11a: mp 58−61 °C. Anal. Calcd for $C_{17}H_{20}O_9Fe$: C, 48.14; H, 4.75. Found: C, 47.83; H, 4.69. See Tables 1 and 2 for NMR spectral data.
12a: ^{1}H NMR ($CDCl_3$) δ 4.29 (dq, *J* = 10.6, 7.0 Hz, 1H), 4.20 (d, *J* = 7.3 Hz) and 4.18 (m) total 2 H, 3.73 and 3.68 (2 × s, 6H), 3.42 (dddd, *J* = 7.3, 8.7, 10.5, 11.6 Hz, 1H), 3.03 (d, *J* = 11.6 Hz, 1H), 2.92 (s, 1H), 2.23 (s, 3H), 1.32 (t, *J* = 7.2, 3H), 0.53 (dd, *J* = 8.7, 10.5 Hz), −0.74 (d, *J* = 8.7, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 221.5, 211.3, 201.4, 172.3, 167.2, 167.1, 116.9, 62.2, 60.7, 60.6, 52.5, 38.6, 20.1, 14.3, −2.2.

Reaction of 1 with Dimethyl Methylmalonate Anion. To a solution of lithium dimethyl methylmalonate (2.2 mmol, freshly prepared from dimethylmalonate and *n*-butyllithium) in THF (25 mL) at 0 °C was added solid cation **4** (906 mg, 2.06 mmol) in small portions. The mixture was stirred at 0 °C for 1 h and at 23 °C for 2 h. Water (25 mL) was added, and the mixture was extracted with ethyl acetate (2 × 30 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, hexanes−ethyl acetate = 10:1) to afford **11b** as a golden yellow oil (640 mg, 71%): R_f 0.19 (hexanes−ethyl acetate = 10:1); EI-HRMS *m*/*z* 354.0765 (calcd for $C_{15}H_{22}O_6Fe$ (M − 3CO) *m*/*z* 354.0766); see Tables 1 and 2 for NMR spectral data.

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Supporting Information Available