

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

Young K. Yun, Heiko Bärmann, and William A. Donaldson*

Department of Chemistry, Marquette University, P.O. Box 1881,
Milwaukee, Wisconsin 53201-1881

Received January 16, 2001

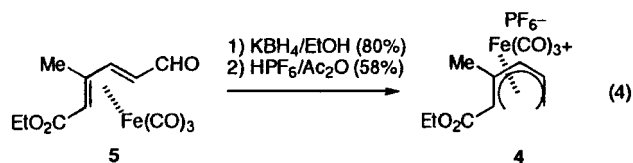
Summary: The title cation was prepared in two steps from the known (ethyl 3-methyl-6-oxo-2,4-hexadienoate)-Fe(CO)₃. Reaction of the cation with NaBH₃CN, methyl cuprate, phthalimide, water, PPh₃, or malonate anions gave predominantly the products from nucleophilic attack at the C5 pentadienyl carbon.

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 nucleophilic 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.

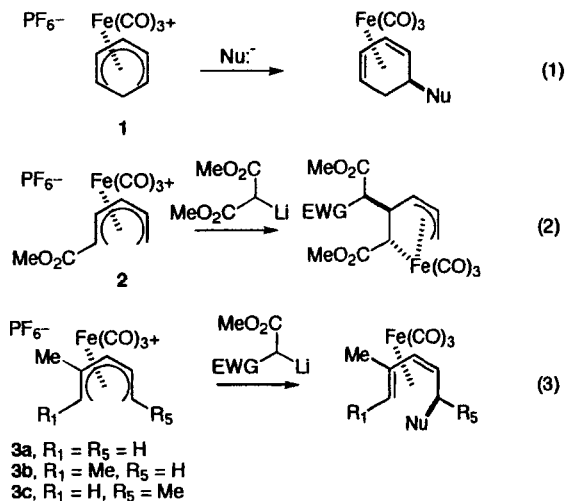
Results and Discussion

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 KBH₄ gave the dienol complex, which upon dehydration with HPF₆ 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 ¹³C NMR chemical shifts (Table 1) may be calculated for **4** based on the additivity of the individual substituent effects⁶ 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).

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



(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) McQuillen, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, UK, 1990.

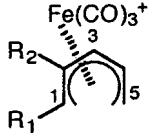
(2) (a) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463–476. (b) Knölker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151–157. (c) Ong, C. W.; Wang, J. N.; Chien, T. L. *Organometallics* **1998**, *17*, 1442–1445.

(3) (a) Donaldson, W. A.; Shang, L.; Tao, C.; Yun, Y. K.; Ramaswamy, R.; Young, V. G., Jr. *J. Organomet. Chem.* **1997**, *539*, 87–98. (b) Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134–2143.

(4) (a) Donaldson, W. A. *J. Organomet. Chem.* **1990**, *395*, 187–193. (b) Donaldson, W. A.; Jin, M.-J.; Bell, P. T. *Organometallics* **1993**, *12*, 1174–1179. (c) Donaldson, W. A.; Jin, M.-J. *Tetrahedron* **1993**, *39*, 8787–8794.

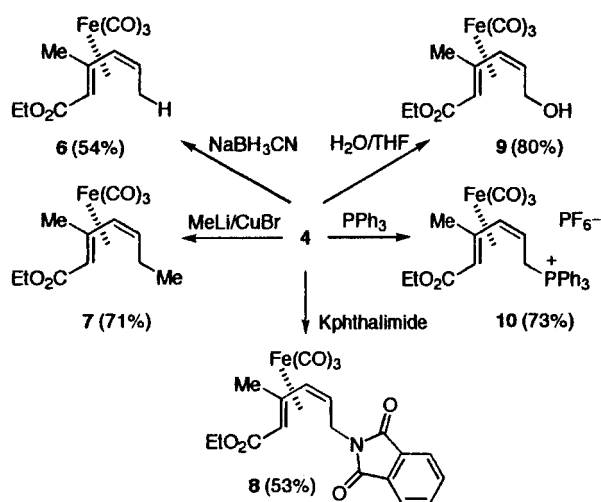
(5) Adams, C. M.; Cerioni, G.; Hafner, A.; Kalchauer, H.; von Philipsborn, W.; Prewo, R.; Schwenk, A. *Helv. Chim. Acta* **1988**, *71*, 1116–1142.

(6) Dobosh, P. A.; Gresham, D. G.; Kowalski, D. J.; Lillya, C. P.; Magyar, E. S. *Inorg. Chem.* **1978**, *17*, 1775–1781.

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

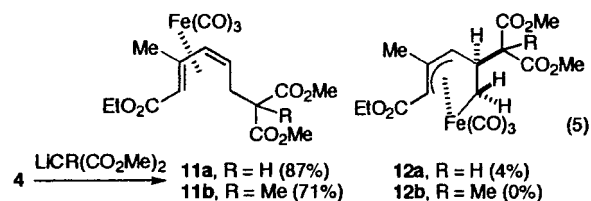
^a In ppm downfield from SiMe₄; CD₃NO₂; 75 MHz; substituent chemical shift in parentheses. ^b Ref 6, corrected for CD₃NO₂ solvent. ^c Ref 3b. ^d Ref 4a. ^e Calculated chemical shifts = parent + substituent chemical shifts.

Scheme 1

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 “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.

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 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 (*2E,4Z*-dienoate)Fe(CO)₃ products.

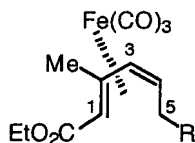
Experimental Section

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 CH₂Cl₂ was distilled from P₂O₅ 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)iron⁵ (6.22 g, 20.2 mmol) in dry ethanol (75 mL) was added KBH₄ (1.31 g, 24.2 mmol). The solution was stirred for 30 min and then diluted with water (75 mL). The mixture was extracted with ether (3 \times 50 mL), the combined extracts were dried, and the solvent was evaporated. The residue was purified by column chromatography (SiO₂, hexanes–ethyl acetate = 2:1) to afford the dienol complex as a yellow solid (5.03 g, 80%): ^1H NMR (CDCl₃) 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 (CDCl₃) δ 171.8, 101.3, 87.4, 63.9, 60.1, 59.1, 48.0, 18.4, 13.9. To a cold solution of HPF₆ (4.7 mL, 60% solution) in Ac₂O (14 mL) was added a solution of tricarbonyl(ethyl 3-methyl-6-hydroxy-2,4-hexadienoate)iron (5.03 g, mmol) in Ac₂O (5 mL) at 0 $^\circ\text{C}$. The mixture was stirred for 30 min, during which time a bright yellow precipitate formed. The

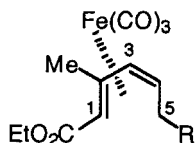
(7) Donaldson, W. A.; Shang, L.; Ramaswamy, M.; Droste, C. A.; Tao, C.; Bennett, D. W. *Organometallics* **1995**, *14*, 5119–5126.

(8) Morey, J.; Grée, D.; Mosset, P.; Toupet, L.; Grée, R. *Tetrahedron Lett.* **1987**, *28*, 2959–2962.

Table 2. ¹H 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 SiMe₄; J couplings in Hz; CDCl₃ solution unless otherwise noted; 300 MHz. ^b C₆D₆ solution. ^c CH₃NO₂ solution. ^d This signal is overlapped with that for one of the H5 protons (reported in other).

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

compd	CH ₃ CH ₂ OC(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 (d) $J_{PH} = 3.6$	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 SiMe₄; ³¹P couplings in Hz; CDCl₃ solution unless otherwise noted; 75 MHz. ^b C₆D₆ solution. ^c Assignments for these signals may be interchanged. ^d CH₃NO₂ solution.

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%): ¹H NMR (CD₃NO₂) 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 CH₂ obscured by the signal for residual CD₂HNO₃ ca. 4.3 ppm); ¹³C NMR (CD₃NO₂) δ 204.3, 197.4, 194.7, 166.6, 127.1, 103.0 (CH), 97.7 (CH), 68.0 (CH₂), 66.6 (CH), 61.8 (CH₂), 19.0 (CH₃), 12.1 (CH₃). Anal. Calcd for C₁₂H₁₃O₅FePF₆: C, 32.90; H, 2.99. Found: C, 32.84; H, 2.94.

Tricarbonyl(ethyl 3-methyl-2E,4Z-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 NaBH₃CN (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 Et₂O (3 × 20 mL). The combined organic extracts were dried (MgSO₄) and concentrated. The residue was purified by column chromatography (SiO₂, 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-2E,4Z-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·Me₂S (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 NH₄Cl (20 mL). The resultant mixture was extracted with ethyl acetate, and the combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by column chromatography (SiO₂, 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 C₁₃H₁₆O₅Fe 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 (MgSO₄) and concentrated. The residue was purified by column chromatography (SiO₂, 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 C₂₀H₁₈NO₇Fe *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–H₂O (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 (MgSO₄) 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 C₁₂H₁₃O₅Fe (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 CH₂Cl₂ (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 CH₂Cl₂ 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 C₃₀H₂₈O₅FeP₂F₆: 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 (MgSO₄) and concentrated. The

residue was purified by column chromatography (SiO₂, 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 C₁₇H₂₀O₉Fe: C, 48.14; H, 4.75. Found: C, 47.83; H, 4.69. See Tables 1 and 2 for NMR spectral data.

12a: ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 (MgSO₄), and concentrated. The residue was purified by column chromatography (SiO₂, 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 C₁₅H₂₂O₆Fe (M – 3CO) *m/z* 354.0766); see Tables 1 and 2 for NMR spectral data.

Acknowledgment. Financial support for this work was provided by the National Institutes of Health (GM-42641). Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954).

Supporting Information Available: Copies of the ¹H and ¹³C NMR spectra of compounds **6–9**, **11b**, and **12a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0100333