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Synthesis and reactivity of tricarbonyl (1-methoxycarbonyl-5-phenylpentadienyl)iron(1+) cation [☆]

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Abstract

Tricarbonyl(1-methoxycarbonyl-5-phenylpentadienyl)iron(1+) hexafluorophosphate (**7**) was prepared in two steps from tricarbonyl(methyl 6-oxo-2,4-hexadienoate)iron. While addition of carbon and heteroatom nucleophiles to **7** generally occurs at the phenyl-substituted dienyl carbon to afford (2,4-dienoate)iron products, the addition of phthalimide proceeded at C2 to afford a (pentenediyl)iron product (**18**). Complex **18** was structurally characterized by X-ray diffraction analysis.
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Keywords: Carbonyl iron complexes; Dienyl; Nucleophilic attack; Crystal structure

1. Introduction

While (η^5-pentadienyl)iron(1+) cations were first prepared more than 40 years ago [1], the reactivity of these complexes is of continuing interest, particularly for the synthesis of conjugated polyenes [2]. The stereoselectivity and regioselectivity for nucleophilic attack on these cationic complexes is dependent on the nature of the nucleophile. For example, nucleophilic addition of triphenylphosphine to pentadienyl cation **1** proceeds at the unsubstituted terminus to generate 2*E*,4*Z*-dienoate complex **2a** [3], while addition of stabilized carbon nucleophiles such as malonate anion proceeds at the internal C2 carbon to afford primarily (pentenediyl)iron complex **3b** (Eq. 1) [4]. While the former regioselectivity is attributed to steric interactions in the transition state leading to attack at the unsubstituted carbon, the latter regioselectivity has been rationalized as the result of charge control; that is, the greater partial positive charge

at the C2 and C4 pentadienyl carbons of **1** directs nucleophilic attack at these sites.


$$(1)$$
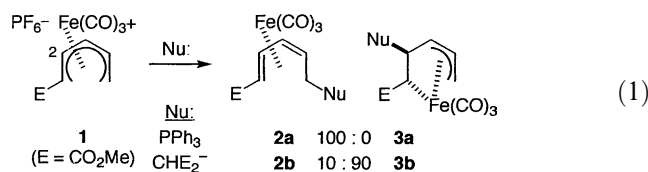
The regioselectivity of nucleophilic addition also depends upon substituents present on the pentadienyl ligand; addition of malonate anion to pentadienyl cation **4** gave predominantly the *Z*-diene product **6b** from attack at the substituted pentadienyl terminus (Eq. 2) [4a]. For this stabilized (pentadienyl)iron cation, nucleophilic attack is predominantly frontier orbital controlled (i.e., attack at the dienyl termini); superimposed on this is the greater stabilization of the partial positive charge at the phenyl substituted dienyl terminus. While there are numerous reports concerning nucleophilic attack on mono-substituted, and 1,2- and 1,4-disubstituted (pentadienyl)Fe(CO)$_3^+$ cations [5], there are few studies of nucleophilic addition to unsymmetrical 1,5-disubstituted (pentadienyl)Fe(CO)$_3^+$ cations [6,7]. We here report on
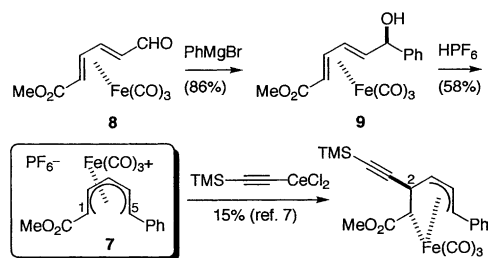
the synthesis and reactivity of a (pentadienyl)Fe(CO)$_3^+$ cation **7** bearing both 1-methoxycarbonyl and 5-phenyl substituents.
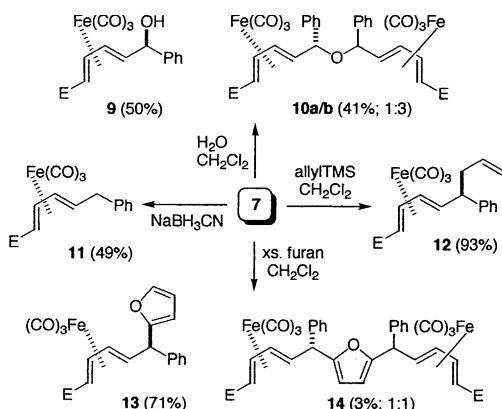
(2)
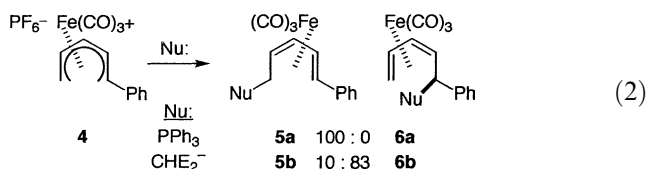
2. Results

Reaction of dienal complex **8** with phenylmagnesium bromide gave dienol complex **9** (Scheme 1). Dehydration of **9** with HPF$_6$ afforded **7** as a stable yellow solid. While Labassi and Grée [7] have previously used this route for the preparation of **7**, spectral data for this cation were not reported. On the basis of its ^{1}H NMR spectral data, the cation **7** exists, in solution, predominantly as the *cisoid* structure. In particular, the H2–H3 and H3–H4 couplings (7.1 and 7.3 Hz, respectively) are indicative of their *cis* relationship. Only a single example of nucleophilic addition to **7** has been reported; reaction of **7** with (trimethylsilyl)alkynyl cerium dichloride gave a (pentenediyl)iron product, albeit in low yield (Scheme 1) [7].

The reaction of **7** with water gave a separable mixture of **9** and two diastereomeric ethers **10a** and **10b** (Scheme 2). The ψ-*exo* E,E-dienol **9** was identified by comparison of its NMR spectral data with that of the

complex previously obtained by addition of phenyl Grignard to **8** (vide supra). While NMR spectra of dienyl ethers **10a/b** are similar to that for **9**, the IR spectra of ethers **10a/b** are devoid of an absorption corresponding to a hydroxyl stretch. In a similar fashion, the reaction of **7** with NaBH$_3$CN, or allyltrimethylsilane or excess furan gave *E,E*-dienoate products **11–13**, respectively (Scheme 2). The reaction of **7** with furan also afforded a small amount of the 2:1 (cation:furan) product **14** as an inseparable mixture of diastereomers. The structures of products **11–13** were assigned by comparison of their NMR spectral data with that of **9**. In particular, signals at ca. δ 0.9–1.1 (d), 5.7–5.9 (dd), and 5.3–5.5 (dd) ppm, in their ^{1}H NMR spectra, and signals at ca. δ 65–71, 85–87, and 83–84 ppm in their ^{13}C NMR spectra are characteristic for H2, H3, H4, and C2, C3, and C4 of (2*E*,4*E*-dienoate)Fe(CO)$_3$ complexes [2a].

Reaction of **7** with dimethyl malonate or dimethyl methylmalonate anion afforded *E,Z*-diene complexes **15** or **16**, respectively (Scheme 3). The structural assignments of these products are based on their NMR spectral data. In particular, signals at ca. δ 2.3–2.4 (d), 6.0 (dd), and 5.2–5.3 (dd) ppm, in their ^{1}H NMR spectra, and signals at ca. δ 94 and 84–85 ppm in their ^{13}C NMR spectra are characteristic for H2, H3, H4, and C3 and C4 of (2*E*,4*Z*-dienoate)Fe(CO)$_3$ complexes [8]. Reaction of **7** with triphenylphosphine gave the *E,Z*-dienylphosphonium salt **17** (Scheme 3). The structural assignment for **17** was made by comparison of its NMR spectral data with that for **15** and **16**.

Finally, reaction of **7** with potassium phthalimide gave a single product **18**, proceeding via attack at an internal pentadienyl carbon to afford a crystalline pentenediyl product (Scheme 3). The structural assignment of **18** was based on its NMR spectral data. In particular, the presence of three signals for the metal-carbonyls (δ 208.9, 207.8, and 202.6 ppm) is highly characteristic of (pentenediyl)Fe(CO)$_3$ complexes. Additionally, a ^{13}C NMR signal at δ 17.4 ppm and a ^{1}H NMR signal at δ 1.99 (d) ppm are characteristic of a carbon σ-bonded to iron and its attached proton [2a,4]. The attachment of the phthalimide group at C2 was tentatively assigned on the basis of the NOESY spectrum of **18**; cross-peaks

Scheme 1. (E = CO$_2$Me).
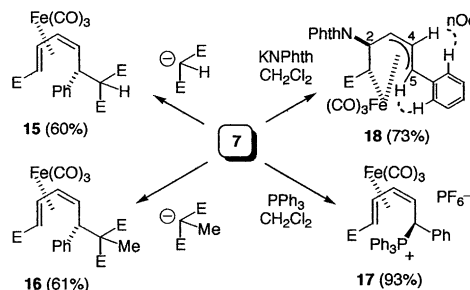
Scheme 2. (E = CO$_2$Me).

Scheme 3. (E = CO$_2$Me).

were observed between the phenyl *ortho*-protons (δ 7.38–7.25 ppm) and the signals for H4 and H5 of the η^3-fragment (δ 5.48 ppm). This tentative assignment was eventually corroborated by single crystal X-ray diffraction analysis (Table 1, Fig. 1). The phthalimide group is situated *trans* to the (tricarbonyl)iron fragment, implying nucleophilic attack opposite to the metal center. The bond distances and angles for **18** (Table 2) are in good agreement with those for other (pentenediyl)iron complexes [4,9].

Table 1
Crystallographic data for **18**

| Empirical formula	$C_{24}H_{17}FeNO_7$
Formula weight	487.26
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	$0.43 \times 0.43 \times 0.40$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.949(5)
b (Å)	13.645(5)
c (Å)	14.734(5)
β (deg)	97.030(5)
V (Å)	2184.7(15)
Z	4
D_{calc} (g cm^{-1})	1.481
Absorption coefficient (mm^{-1})	0.737
$F(000)$	1004
Range of θ (°)	2.04–24.99
Reflections collected/unique	4883/3831 ($R_{int} = 0.0244$)
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0375$, $wR2 = 0.0870$
R indices (all data)	$R1 = 0.0548$, $wR2 = 0.0948$
Largest difference peak and hole (e Å^{-3})	0.339 and −0.310
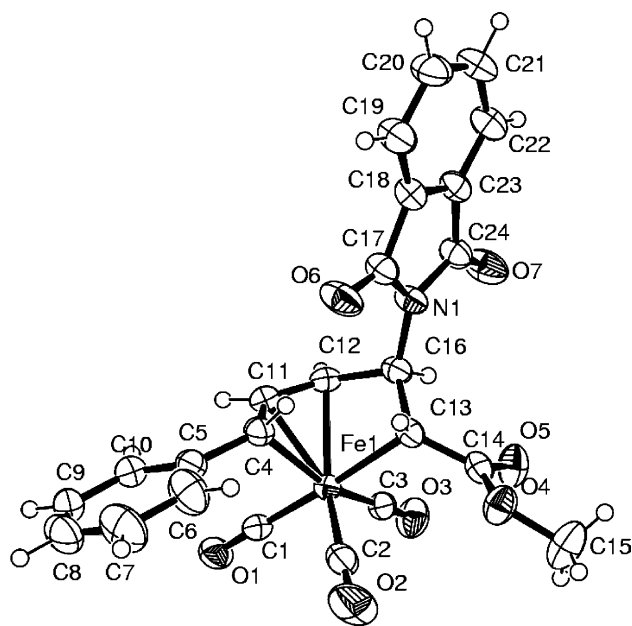
Fig. 1. ORTEP view of **18** with crystallographic numbering scheme (50% probability elipsoids).

Table 2
Selected bond distances (Å) and bond angles (°) (with e.s.d.s in parentheses)

Fe(1)–C(11)	2.095(3)	C(13)–Fe(1)–C(12)	69.09(10)
Fe(1)–C(13)	2.115(2)	N(1)–C(16)–C(12)	115.1(2)
Fe(1)–C(12)	2.150(2)	N(1)–C(16)–C(13)	116.7(2)
Fe(1)–C(4)	2.179(3)	C(12)–C(16)–C(13)	105.95(19)
C(16)–C(12)	1.511(4)	C(11)–C(12)–C(16)	127.2(2)
C(16)–C(13)	1.518(3)	C(16)–C(12)–Fe(1)	89.98(14)
C(12)–C(11)	1.406(3)	C(12)–C(11)–C(4)	125.8(2)
C(4)–C(11)	1.409(4)	C(16)–C(13)–Fe(1)	91.13(15)

3. Discussion

In solution, acyclic (pentadienyl)Fe(CO)$_3^+$ cations are known to exist in an equilibrium between the *cisoid* form and the corresponding less stable *transoid* form [10]. In general, reaction of (pentadienyl)iron cations with weak nucleophilies, such as water, proceeds via attack on the less stable, but therefore more reactive, *transoid* form [11]. Of the two possible *transoid* isomers of **7** the structure **19A**, in which the phenyl substituent is adjacent to the carbon bearing the greatest partial positive charge, is anticipated to be considerably more stabilized than **19B** where this carbon is adjacent to the ester substituent (Scheme 4). Formation of the E,E-ψ-exo dienol **9**, from the reaction of **7**, is consistent with attack by a weak nucleophile water on the *transoid* form **19A**. The ether products **10a/b** arise via reaction of the cation **7** with dienol **9** at a competitive rate to reaction with water. Since the cation **7** and therefore the dienol **9** are both racemic mixtures of enantiomers (with respect to coordination of the diene) then two diastereomeric ethers are formed [12]. In a similar fashion, the formation of single products from the addition of the weak nucleophiles allyltrimethylsilane and furan are not surprising, since the regiochemical directing effects of the two substituents present on **7** are ''matched'' [5c].

For phosphine nucleophiles, attack generally occurs on the more abundant *cisoid* form of the (pentadienyl)iron cation, and at the less sterically hindered terminus [3,6d,13]. Thus the regiochemical directing effects of the substituents present on **7** are ''mismatched'' for the addition of phosphines (cf. Eqs. 1 and 2). The product (**18**) from reaction of PPh$_3$ with **7** results from attack at the phenyl substituted terminus. The ester and phenyl substituents are anticipated to lie nearly coplanar with respect to the pentadienyl ligand, thus both substituents should present roughly the same steric hin-
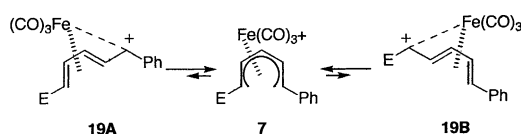
Scheme 4.

drance. Since the selectivity observed for phosphine addition cannot be attributed to steric hindrance, the selectivity may be due to the greater partial positive charge at the C5 pentadienyl carbon due to the stabilizing effect of the phenyl substituent.

Similarly, the regiochemical directing effects of the substituents present on **7** are "mismatched" for the addition of malonate nucleophiles (cf. Eqs. (1) and (2)). The products (**15** or **16**) from reaction of dimethyl malonate or dimethyl methylmalonate with **7** result from attack at the phenyl substituted terminus. The regioselectivity for malonate attack may be attributed to the greater partial positive charge at the C5 pentadienyl terminus.

To our knowledge, the formation of pentenediyl complex **18** is the only case of phthalimide nucleophilic attack at an internal position of a $(dienyl)Fe(CO)_2L^+$ cation; all of the literature reactions proceed via nucleophilic attack at the dienyl terminus [5b,14]. The reason for the divergent regioselectivity observed for the reaction of **7** with phthalimide is not apparent.

4. Experimental

4.1. General data

All m.p. measurements were carried out on a Mel-Temp apparatus and are uncorrected. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using a Varian Mercury 300+ Spectrometer. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN, or Atlantic Microlabs, Norcross, GA. High resolution mass spectra were performed at the Washington University Resource for Mass Spectrometry. Dry tetrahydrofuran (THF) and dry ether were distilled from sodium benzophenone ketyl 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. The term brine refers to a saturated aqueous solution of sodium chloride. Column chromatography was performed over silica gel 60 (230–400 mesh); column size was ca. 2 cm × 35 cm unless otherwise noted.

4.2. Tricarbonyl(methyl 6-hydroxy-6-phenyl-2,4-hexadienoate)iron (**9**)

To a solution of tricarbonyl(methyl 6-oxo-2,4-hexadienoate)iron (2.00 g, 7.14 mmol) in dry THF, cooled to −15 °C (dry ice/CH_3CN bath), was added a solution of phenylmagnesium bromide (2.4 ml, 3.0 M in ether, 7.2 mmol). After the addition was complete, the cooling bath was removed and the reaction mixture was warmed to r.t., and stirred for 5 h. Water (10 ml) was added, and the mixture was extracted several times with ethyl acetate. The combined extracts were dried ($MgSO_4$) and concen-

trated. The residue was purified by column chromatography (4 cm × 35 cm, hexanes–ethyl acetate = 5:1) to afford **9** as a yellow solid (2.20 g, 86%); m.p. 107–109 °C; IR (Nujol) 3390, 2063, 1999, 1712 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.38–7.32 (m, 4H), 5.83 (dd, $J = 5.0$, 8.2 Hz, 1H), 5.63 (dd, $J = 5.0$, 8.5 Hz, 1H), 4.55 (dd, $J = 2.3$, 7.0 Hz, 1H), 3.63 (s, 3H), 2.66 (d, $J = 2.3$ Hz, OH), 1.51 (br t, $J = 7.6$ Hz, 1H), 1.05 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.8, 143.1, 128.4, 127.8, 125.5, 85.0, 83.2, 76.3, 67.3, 52.2, 46.7. Anal. Calc. for $C_{16}H_{14}O_6Fe$: C, 53.66; H, 3.94. Found: C, 54.08; H, 3.95%.

4.3. Tricarbonyl(η^5-1-methoxycarbonyl-5-phenylpentadienyl)iron(1+) hexafluorophosphate (**7**)

To an ice-cold mixture of acetic anhydride (0.46 ml) and hexafluorophosphoric acid (0.36 g, 60% by weight) was added drop-wise an ice-cold solution of dienol **9** (0.270 mg, 0.750 mmol) and acetic anhydride (0.22 ml) in ether (3 ml). After the addition the mixture was stirred for 30 min during which time a pale yellow precipitate appeared. The mixture was added drop-wise to excess of ether (100 ml), and the resultant precipitate was collected by vacuum filtration. The precipitate was washed with ether and dried in vacuo to give cation **7** as a bright yellow solid (277 mg, 76%); IR (KBr) 2118, 2080, 1792 cm^{-1}; ^1H NMR (CD$_3$NO$_2$) δ 7.75–7.55 (m, 5H), 7.33 (t, $J = 7.2$ Hz, 1H), 6.84 (dd, $J = 7.1$, 13.5 Hz, 1H), 6.76 (dd, $J = 7.3$, 10.6 Hz, 1H), 4.69 (d, $J = 13.2$, 1H), 3.90 (s, 3H), 3.13 (d, $J = 10.6$ Hz, 1H); ^{13}C NMR (CD$_3$NO$_2$) δ 133.8, 133.1, 130.8, 129.1, 105.5, 98.5, 98.1, 94.8, 64.3, 54.7 (signals for the metal and ester carbonyls were not observed). Anal. Calc. for $C_{16}H_{13}O_5FePF_6$: C, 39.53; H, 2.70. Found: C, 39.80; H, 2.78%.

4.4. Reaction of **7** with water

To a solution of cation **7** (200 mg, 0.412 mmol) in CH_2Cl_2 (5 ml) was added water (15 ml). The reaction mixture was stirred at r.t. for 2 h, and then extracted several times with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (hexanes–ethyl acetate = 5:1) to afford ether **10a** (15 mg, 10%), followed by ether **10b** (44 mg, 31%) and finally dienol **9** (74 mg, 50%) all as yellow oils. The spectral data for dienol **9** was identical to that previously obtained.

10a: IR (neat) 2060, 1995, 1712 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.35–7.20 (m, 5H), 5.80 (dd, $J = 5.0$, 8.1 Hz, 1H), 5.47 (dd, $J = 5.0$, 8.5 Hz, 1H), 4.23 (d, $J = 7.9$ Hz, 1H), 3.63 (s, 3H), 1.46 (br t, $J = 8.1$ Hz, 1H), 1.04 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 172.4, 141.2, 128.9, 128.5, 126.7, 85.5, 83.9, 80.7, 65.5, 52.0, 46.6.

10b: IR (KBr) 2066, 2008, 1709 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.47–7.28 (m, 5H), 5.47 (dd, $J = 5.0$, 8.2 Hz, 1H), 5.24 (dd, $J = 5.0$, 9.1 Hz, 1H), 3.68 (d, $J = 8.8$ Hz,

1H), 3.61 (s, 3H), 1.45 (br t, $J = 8.5$ Hz, 1H), 1.05 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 172.5, 140.3, 129.1, 128.8, 126.8, 86.4, 84.6, 80.8, 65.4, 52.0, 46.5. Anal. Calc. for C$_{32}$H$_{26}$O$_{11}$Fe$_2$: C, 55.05; H, 3.75. Found: C, 54.77; H, 3.87%.

4.5. Tricarbonyl(methyl 6-phenyl-2E,4E-hexadienoate)-iron (11)

To a suspension of cation 7 (100 mg, 0.203 mmol) in dry THF (10 ml), cooled to 0 °C, was added solid sodium cyanoborohydride (14 mg, 0.22 mmol) in one portion. The reaction mixture turned from brown to pale yellow in color. The reaction mixture was stirred at 0 °C for 1 h, warmed to r.t. and stirred for an additional 1 h. The mixture was poured into water (10 ml) and extracted with ethyl acetate. The combined extracts were dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (hexanes–ethyl acetate = 3:1) to afford 11 as a yellow oil (33.2 mg, 49%). The reaction of 7 with either potassium borohydride or K-selectride gave 11 (51% and 70%, respectively); IR (neat) 2057, 1992, 1701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.28–7.11 (m. 5H), 5.70 (dd, $J = 5.0$, 8.2 Hz, 1H), 5.28 (dd, $J = 5.0$, 8.7 Hz, 1H), 3.58 (s, 3H), 2.96 (dd, $J = 7.4$, 14.7 Hz, 1H), 2.80 (dd, $J = 6.6$, 14.7 Hz, 1H), 1.43 (br q, $J = 7.4$ Hz, 1H), 0.94 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.9, 140.4, 128.5, 127.7, 126.4, 87.1, 83.5, 65.1, 52.1, 46.3, 40.6. FAB-HRMS m/z 350.0336 (Calc. for C$_{16}$H$_{14}$O$_5$FeLi (M + Li) m/z 350.0385).

4.6. Tricarbonyl(methyl 6-phenyl-2E,4E,8-nonatrienoate)iron (12)

To a solution of 7 (150 mg, 0.309 mmol) in degassed CH$_2$Cl$_2$ (15 ml) was added allyltrimethylsilane (0.5 ml, 0.3 mmol). 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 (hexanes–ethyl acetate = 3:1) to afford 12 as a golden yellow oil (110 mg, 93%) which solidified upon standing in the refrigerator; mp 49–51 °C; IR (neat) 2058, 1996, 1713 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38–7.25 (m, 3H), 7.19–7.16 (m, 2H), 5.79 (dd, $J = 5.0$, 8.1 Hz, 1H), 5.84–5.70 (m, 1H), 5.37 (dd, $J = 5.0$, 8.8 Hz, 1H), 5.15–5.06 (m, 2H), 3.64 (s, 3H), 2.55–2.49 (m, 3H), 1.55–1.49 (m, 1H), 1.03 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.9, 143.7, 135.3, 128.4, 126.5 (two signals), 116.9, 86.6, 82.9, 71.0, 52.1, 51.7, 46.1, 45.1. Anal. Calc. for C$_{19}$H$_{18}$O$_5$Fe: C, 59.70; H, 4.76. Found: C, 59.96; H, 4.79%.

4.7. Reaction of 7 with excess furan

To a solution of 7 (150 mg, 0.309 mmol) in degassed CH$_2$Cl$_2$ (20 ml) was added excess furan (0.50 ml, 6.8

mmol). The mixture was stirred for 15 min during which time the yellow solution turned brown in color. 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 (hexanes–ethyl acetate = 3:1) to afford 13 as a golden yellow oil (90 mg, 71%) followed by 14 (2:1) as a golden yellow oil (30 mg, 3%).

13: IR (neat) 2059, 1998, 1712 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.40–7.25 (m, 6H), 6.26 (dd, $J = 1.9$, 3.1 Hz, 1H), 5.95 (d, $J = 3.2$ Hz, 1H), 5.83 (dd, $J = 5.0$, 8.2 Hz, 1H), 5.53 (dd, $J = 5.0$, 8.5 Hz, 1H), 3.80 (d, $J = 10.3$ Hz, 1H), 3.64 (s, 3H), 1.68 (dd, $J = 8.4$, 10.3 Hz, 1H), 1.10 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.8, 156.4, 141.6, 141.0, 128.5, 127.2 (two signals), 110.1, 106.0, 87.0, 83.8, 67.0, 52.2, 50.1, 46.5. FAB-HRMS m/z 415.0440 (Calc. for C$_{20}$H$_{16}$O$_6$FeLi (M + Li) m/z 415.0456).

14: IR (neat) 2059, 1998, 1712 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38–7.21 (m, 10H), 5.86–5.78 (m, 2H), 5.81 and 5.73 (2s, 2H), 5.58 and 5.52 (2dd, $J = 5.1$, 8.5 Hz, 1H), 3.75 and 3.73 (2d, $J = 9.9$ Hz, 2H), 3.65 (s, 6H), 1.68–1.56 (m, 2H), 1.10 (br d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 171.8, 155.8, 140.8, 140.6, 128.5, 127.3, 109.7, 106.6 [106.5], 86.9, 83.8, 66.9, 52.2, 50.2 [50.1], 46.5; diastereotopic signals in brackets.

4.8. Reaction of 7 with dimethyl malonate anion

To a solution of dimethyl malonate (50 μL, 0.64 mmol) in dry THF (10 ml) at 0 °C was added, in one portion, a solution of n-BuLi (0.40 ml, 1.6 M in hexanes, 0.64 mmol). The mixture was stirred for 10 min, and then solid cation 7 (259 mg, 0.532 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 1 h, and 23 °C for 18 h. Water (10 ml) was added and the mixture was extracted several times with ethyl acetate. The combined extracts were dried (MgSO$_4$) and concentrated, and the residue was purified by column chromatography (hexanes–ethyl acetate = 3:1) to afford 15 as a golden yellow oil (151 mg, 60%); IR (neat) 2061, 1996, 1737 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.37–7.15 (m, 5H), 6.05 (dd, $J = 5.3$, 8.8 Hz, 1H), 5.25 (dd, $J = 5.4$, 7.3 Hz, 1H), 3.79, 3.68, and 3.41 (3s and m, 10H total), 2.93 (dd, $J = 7.3$, 11.7 Hz, 1H), 2.79 (dd, $J = 10.2$, 11.7 Hz, 1H), 2.40 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 172.3, 167.3, 166.3, 140.8, 128.5, 127.5, 127.2, 94.2, 84.2, 62.2, 61.7, 53.2, 52.8, 52.3, 46.5, 45.1. FAB-HRMS m/z 479.0594 (Calc. for C$_{21}$H$_{20}$O$_9$FeLi (M + Li) m/z 479.0617).

4.9. Reaction of 7 with dimethyl methylmalonate anion

To a solution of sodium dimethyl methylmalonate (0.331 mmol, freshly prepared from dimethyl malonate

and excess sodium hydride) in dry THF (15 ml) was added, in one portion, solid cation **7** (150 mg, 0.309 mmol). The reaction mixture was stirred at 0 °C for 1 h, and then poured into brine. 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 (hexanes–ethyl acetate = 3:1) to afford **16** as a golden yellow oil (91 mg, 61%); IR (neat) 2061, 1999, 1716 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.33–7.16 (m, 5H), 6.05 (dd, $J = 5.2$, 8.4 Hz, 1H), 5.28 (dd, $J = 5.2$, 7.7 Hz, 1H), 3.72, 3.66, and 3.59 (3s, 9H total), 3.34 (dd, $J = 7.7$, 12.4 Hz, 1H), 2.90 (d, $J = 12.4$ Hz, 1H), 2.36 (d, $J = 8.4$ Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 172.4, 170.3, 170.2, 139.7, 128.9, 128.0, 127.4, 93.9, 85.3, 61.1, 60.7, 52.9, 52.8, 52.2, 49.1, 46.4, 18.7. FAB-HRMS m/z 493.0762 (Calc. for C$_{22}$H$_{22}$O$_9$FeLi (M + Li) m/z 493.0773).

4.10. Reaction of 7 with triphenylphosphine

To a solution of cation **7** (150 mg, 0.309 mmol) in CH$_2$Cl$_2$ (20 ml) was added solid triphenylphosphine (81 mg, 0.31 mmol). The reaction mixture was stirred for 20 min, during which time the bright yellow color became a pale yellow. The reaction mixture was concentrated and triturated with ether just until it becomes cloudy. After standing, a precipitate formed which was collected by vacuum filtration, and the crystals washed with additional ether and dried in vacuo to afford **17** as a golden yellow solid (215 mg, 93%); m.p. 163–165 °C (dec.); IR (KBr) 2067, 2012, 1716 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 7.90 (br t, $J = 6.6$ Hz, 3H), 7.72–7.66 (m, 6H), 7.54–7.43 (m, 7H), 7.37 (t, $J = 7.6$ Hz, 2H), 6.90 (br d, $J = 7.2$ Hz, 2H), 6.04 (dd, $J = 5.3$, 8.8 Hz, 1H), 5.37 (br t, $J = 5.9$ Hz, 1H), 4.03 (dd, $J = 12.9$, 15.2 Hz, 1H), 3.68 (s, 3H total), 3.09 (dt, $J = 7.1$, 12.9 Hz, 1H), 2.57 (d, $J = 9.1$ Hz, 1H); ^{13}C NMR (CD$_3$CN) δ 172.9, 135.0 (d, $J_{PC} = 3.0$ Hz), 134.9 (d, $J_{PC} = 9.8$ Hz), 133.5 (d, $J_{PC} = 4.0$ Hz), 129.9, 129.7, 129.6, 129.1 (d, $J_{PC} = 2.3$ Hz), 117.5 (d, $J_{PC} = 79.6$ Hz), 96.5, 86.2, 54.2 (d, $J_{PC} = 7.4$ Hz), 53.3, 48.5, 44.4 (d, $J_{PC} = 33.2$ Hz). Anal. Calc. for C$_{34}$H$_{28}$O$_5$FeP$_2$F$_6$·0.5H$_2$O: C, 53.91; H, 3.86. Found: C, 53.85; H, 3.78%.

4.11. Reaction of 7 with potassium phthalimide

To a solution of cation **7** (150 mg, 0.309 mmol) in degassed CH$_2$Cl$_2$ (15 ml) was added solid potassium phthalimide (86 mg, 0.46 mmol). The mixture was stirred for 30 min and then water (10 ml) was added and the mixture was stirred an additional 5 min. The mixture was extracted several times with CH$_2$Cl$_2$, the combined extracts were washed with brine followed by water, dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography (hexanes–ethyl acetate = 5:1 → 3:1 gradient) to afford **18** as a bright yellow

crystalline solid (110 mg, 73%); m.p. 100–102 °C; IR (KBr) 2065, 1994, 1772, 1713 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.76–7.73 (m, 2H), 7.67–7.64 (m, 2H), 7.53–7.50 (m, 2H), 7.38–7.25 (m, 3H), 5.62 (dd, $J = 7.3$, 9.9 Hz, 1H), 5.52–5.41 (m, 2H), 4.58 (dd, $J = 6.2$, 7.3 Hz, 1H), 3.69 (s, 3H), 1.99 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 208.9, 207.8, 202.6, 178.1, 167.1, 138.7, 133.8, 131.2, 128.9, 127.6, 125.8, 123.1, 96.4, 58.0, 52.1, 48.3, 17.4 (signal for C5 obscured by CDCl$_3$ signals). Anal. Calc. for C$_{24}$H$_{17}$NO$_7$Fe: C, 59.16; H, 3.52; N, 2.87. Found: C, 59.85; H, 3.61; N, 2.75%.

4.12. X-ray structural determination of 18

Golden yellow crystals of **18** were grown from CH$_2$Cl$_2$/hexanes. A crystal (0.43 × 0.43 × 0.40 mm^3) was attached to a glass fiber and mounted on a Brucker P4 diffractometer. The data were collected at 298 K using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and the $\Theta/2\Theta$ mode in the Θ range 2.04 to 24.99°. No absorption correction was used. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 [15]. A total of 4883 reflections were collected (3831 independent reflections, $R_{int} = 0.0244$).

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 221734. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk).

References

[1] J.E. Mahler, D.H. Gibson, R. Pettit, J. Am. Chem. Soc. 85 (1963) 3959.
[2] (a) L. Motiei, I. Marek, H.E. Gottlieb, V. Marks, J.-P. Lellouche, Tetrahedron Lett. 44 (2003) 5909;
    (b) S. Li, W.A. Donaldson, Synthesis (2003) 2064.
[3] W.A. Donaldson, L. Shang, M. Ramaswamy, C.A. Droste, C. Tao, D.W. Bennett, Organometallics 14 (1995) 5119.

[4] (a) W.A. Donaldson, L. Shang, C. Tao, Y.K. Yun, M. Ramaswamy, V.G. Young Jr., J. Organomet. Chem. 539 (1997) 87;
(b) Y.K. Yun, K. Godula, Y. Cao, W.A. Donaldson, J. Org. Chem. 68 (2003) 901.

[5] For a compilation of references up to 1997 see (a) W.A. Donaldson, Aldrichim. Acta 30 (1997) 17;
(b) Y.K. Yun, H. Bärmann, W.A. Donaldson, Organometallics 20 (2001) 2409;
(c) M.A. Hossain, M.J. Jin, W.A. Donaldson, J. Organomet. Chem. 630 (2001) 5.

[6] (a) J.A.S. Howell, A.G. Bell, P.J. O'Leary, G.R. Stephenson, M. Hastings, P.W. Howard, D.A. Owen, A.J. Whitehead, P. McArdle, D. Cunningham, Organometallics 15 (1996) 4247;
(b) D. Enders, B. Jandeleit, S. von Berg, J. Organomet. Chem. 533 (1997) 219–236;
(c) G.M. Williams, D.E. Rudisill, Inorg. Chem. 28 (1989) 797;
(d) P. McArdle, H. Sherlock, J. Chem. Soc., Dalton Trans. (1978) 1678;
(e) T.G. Bonner, K.A. Holder, P. Powell, E. Styles, J. Organomet. Chem. 131 (1977) 105.

[7] M. Labassi, R. Grée, Bull. Soc. Chim. Fr. 129 (1992) 151.

[8] C. Tao, W.A. Donaldson, J. Org. Chem. 58 (1993) 2134.

[9] (a) P. Pinsard, J.-P. Lellouche, J.-P. Beaucourt, L. Toupet, L. Schio, R. Grée, J. Organomet. Chem. 371 (1989) 219;
(b) J.A.S. Howell, A.G. Bell, P.J. O'Leary, G.R. Stephenson, M. Hastings, P.W. Howard, D.A. Owen, A.J. Whitehead, P. McArdle, D. Cunningham, Organometallics 15 (1996) 4247;
(c) J.R. Bleeke, M.K. Hays, Organometallics 6 (1987) 1367;

(d) J.R. Bleeke, R.J. Wittenbrink, T.W. Clayton Jr., M.Y. Chiang, J. Am. Chem. Soc. 112 (1990) 6539;
(e) S.P. Saber, A.M. Slawin, S.E. Thomas, D.J. Williams, M.F. Ward, P.A. Worthington, J. Chem. Soc., Chem. Commun. (1994) 2169;
(f) S.E. Gibson, S.P. Saberi, A.M.Z. Slawin, P.D. Stanley, M.F. Ward, D.J. Williams, P. Worthington, J. Chem. Soc., Perkin Trans. 1 (1995) 2147.

[10] T.S. Sorenson, C.R. Jablonski, J. Organomet. Chem. 25 (1970) C62.

[11] R.S. Bayoud, E.R. Biehl, P.C. Reeves, J. Organomet. Chem. 150 (1978) 75.

[12] Formation of ethers from the reaction of other (pentadienyl)iron cations with water has previously been observed W.A. Donaldson, P.T. Bell, M.-J. Jin, J. Organomet. Chem. 441 (1992) 449.

[13] (a) A. Salzer, A. Hafner, Helv. Chim. Acta 66 (1983) 1174;
(b) U. Englert, B. Ganter, M. Kaser, E. Klinkhammer, T. Wagner, A. Salzer, Chem. Eur. J. 2 (1996) 143.

[14] (a) A.J. Birch, A.J. Liepa, G.R. Stephenson, Tetrahedron Lett. (1979) 3565;
(b) A.J. Birch, A.J. Liepa, G.R. Stephenson, J. Chem. Soc., Perkin Trans. 1 (1982) 713;
(c) A.J. Pearson, M.P. Burello, J. Chem. Soc., Chem. Commun. (1989) 1332;
(d) N. Wallock, W.A. Donaldson, Tetrahedron Lett. 43 (2002) 4541.

[15] G.M. Sheldrick, SHELX 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.