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Reactivity of 1-substituted (pentadienyl)iron(1 +) cations: regioselectivity for addition of malonate nucleophiles; formation of (pentenediyl)- and (diene)iron complexes

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Abstract

The reaction of six 1-substituted (pentadienyl)iron cations (**1–6**) with malonate anions was examined. The electronic nature of substituents present on the pentadienyl ligand, the steric bulk of the malonate anion, and the peripheral ligands about the iron metal were varied. (Pentenediyl)- and/or (diene)iron complexes, resulting from attack at either an internal (C2/C4) or terminal (C1/C5) pentadienyl carbon, were isolated as products. These results indicate that strongly electron withdrawing substituents direct malonate attack at the internal pentadienyl site, while strongly electron donating substituents direct malonate attack at the terminal pentadienyl site. The single crystal X-ray diffraction analysis of two (pentenediyl)iron complexes (**7a** and **7b**) are reported. © 1997 Elsevier Science S.A.

Keywords: Iron; Diene complexes

1. Introduction

Nucleophilic addition to (cyclohexadienyl)- and (cycloheptadienyl)iron(1 +) cations has been extensively studied [1] and this chemistry has gained distinction [2] as an effective tool for organic synthesis. In particular, attachment of a (tricarbonyl)iron adjunct to an acyclic diene has been shown to protect the diene against reduction, oxidation, and cycloaddition reactions [3]. In addition, the steric bulk of the $Fe(CO)_3$ group serves to effect diastereoselective bond formation at unsaturated centers adjacent to the (diene) [3]. One method for the preparation of the precursor acyclic (1,3-diene)$Fe(CO)_3$ complexes is from the reaction of substituted acyclic (pentadienyl)iron(1 +) cations with nucleophiles [4]. This methodology has been utilized in the preparation of linear polyenes, such as leukotrienes [5], terpenes [6,7] and toxins [8]. In order to exploit this type of reaction in organic synthesis, it has been necessary to explore the regioselectivity for addition of carbon and heteroatom nucleophiles with these cations [9–11]. In general, for 2-substituted systems, attack by carbon nucleophiles occurs predominantly at C5 [4,10,11]. We herein report on a detailed study of the reaction of malonate nucleophiles with substituted (pentadienyl)iron(1 +) cations **1–6** (Fig. 1) (see preliminary communications in Refs. [12,13]).

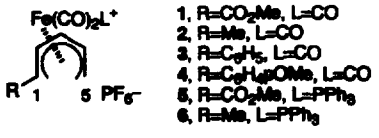

Fig. 1. Structures of substituted (pentadienyl)iron(1 +) cations **1–6**.

2. Results and discussion

2.1. Preparation of 1-substituted (pentadienyl)iron(1 +) cations

The (tricarbonyl)iron cations **1** [5], **2** [14], and **3** [15] were prepared according to literature procedures. The

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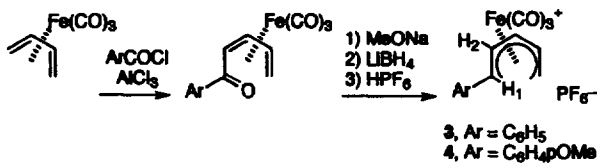
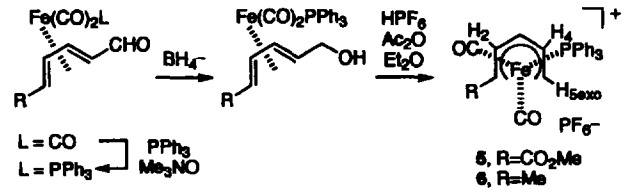


Scheme 1.



Scheme 2.

p-methoxyphenyl-substituted pentadienyl cation **4** was prepared by a modified literature procedure [15] as shown in Scheme 1. The ^{1}H NMR spectra of **3** and **4** are somewhat similar; however, the signal for H1 of **4** (δ 4.52) appears downfield of that for **3** (δ 4.2) while the signal for H2 of **4** (δ 6.53) appears upfield of that for **3** (δ 6.7). These differences may be due to the greater ability of the *p*-methoxyphenyl substituent, in **4**, to stabilize the $\delta+$ charge at C1 in comparison to the phenyl substituent in **3**.

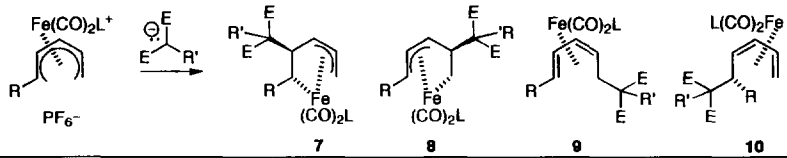
The dicarbonyl(triphenylphosphine)iron cations **5** and **6** [13,16] were prepared from the corresponding tricarbonyl(dienal)iron complex by ligand substitution [16], reduction, and protonation (Scheme 2). The tendency of phosphine ligands to occupy basal sites in (dienyl)Fe(CO)$_2$L cations has been noted [16,17]. We [13] and others [16] have reported that for **6**, bulky triphenylphosphine ligand occupies the basal position trans to the C1 substituent (see Scheme 2). Cation **5** exhibits the same tendency. It should be noted that signals for H4 and H5*exo* of **5** and **6** are ca. 1.3 and 1.0 ppm upfield of the signals for H4 and H5*exo* in the corresponding (tricarbonyl)iron cations **1** and **2**, while the signal for H2 of **5** and **6** are only ca. 0.2 ppm upfield of those of **1** and **2**. The considerably larger upfield shifts for H4 and H5*exo* are presumably due to the anisotropic effect of the triphenylphosphine ligand present along this edge of the pentadienyl ligand.

2.2. Nucleophilic attack on 1-substituted (pentadienyl)iron(1 +) cations

The reaction of **1** with lithium dimethyl malonate or dimethyl methylmalonate gave the (pentenediyl)iron complexes **7a** and **7b**. A trace of diene complex **9a** was observed in the crude product along with **7a**; however, none of the corresponding **9b** was observed (Table 1, entries 1, 2). The reaction of **1** with dimethyl methoxymalonate gave a mixture of (pentenediyl)iron complexes **7c** and **8c** (3:1) as the crude product (Table 1, entry 3). Only complex **7c** was isolated upon chromatographic purification, and thus **8c** was characterized only as part of the crude mixture.

The structures of pentenediyl complexes **7a** and **7b** were unambiguously established by single crystal X-ray

Table 1
Products from addition of malonate anion to (pentadienyl)iron(1 +) cations



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Entry	Cation	R	L	R′	Products			
1	**1**	MeO_2C	CO	H	**7a** (61%)		**9a** (< 5%)	
2	**1**	MeO_2C	CO	Me	**7b** (66%)			
3	**1**	MeO_2C	CO	OMe	**7c**	**8c** (3:1) [a]		
4	**2**	Me	CO	H			**9d**	**10d** (1:2, 28–50%) [b]
5	**2**	Me	CO	H		**8d**	**9d**	**10d** (4:1:2) [c]
6	**2**	Me	CO	H			**9d**	**10d** (1:2, 13–19%) [d]
7	**2**	Me	CO	Me		**8e**	**9e**	**10e** (2:1:1, 50%)
8	**3**	Ph	CO	H		**8f**	**9f** (2:3, 10%)	**10f** (50%)
9	**3**	Ph	CO	Me		**8g** (25%)		**10g** (55%)
10	**4**	$pMeOC_4H_6$	CO	H				**10h** (92%)
11	**5**	MeO_2C	PPh_3	H	**7i** (72%)			
12	**6**	Me	PPh_3	H				**10j** (87%)
13	**6**	Me	PPh_3	OMe			**9k** (9%)	**10k** (83%)

[a] Only **7c** isolated upon chromatographic work-up (62%).
[b] Products isolated after chromatography of reaction run for 1 h.
[c] Ratios determined by integration of ^{1}H NMR spectrum of reaction mixture at 1 h.
[d] Products isolated after chromatography of reaction run for 24 h; additionally a mixture of **11**/**12** was isolated (35%).

Table 2
Crystallographic parameters for **7a** and **7b**

	7a	**7b**
Compound	$C_{15}H_{16}O_9Fe$	$C_{16}H_{18}O_9Fe$
Formula weight	396.13	410.15
Temperature (K)	173(2)	173(2)
Crystal size (mm^3)	0.50×0.50×0.12	0.50×0.12×0.10
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	6.2788(1)	7.1786(1)
b (Å)	13.3075(2)	13.9801(2)
c (Å)	20.1614(2)	17.8519(3)
β (deg)	96.486(1)	
V (Å^3)	1673.81(4)	1791.57(4)
D_{calc} (g cm^{-3})	1.572	1.521
Z	4	4
$F(000)$	816	848
Range of θ (deg)	1.84 to 25.01	1.85 to 25.04
Reflections collected	8695	9209
Independent reflections	2955	3170
Final R indices [$I > 2\sigma(I)$]	0.0329	0.0283
GOF	1.036	1.082

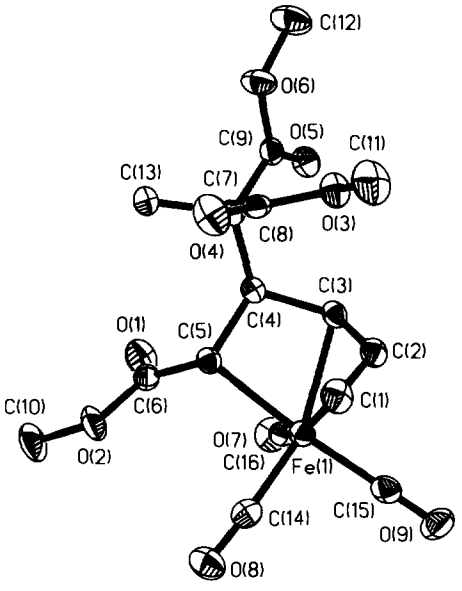


Fig. 3. Molecular structure of **7b** in the crystal.

diffraction analysis (Table 2, Figs. 2 and 3). In both cases, the malonate group is situated trans to the $Fe(CO)_3$ group, thus implying nucleophilic attack opposite to the metal adjunct. The bond distances and angles (Table 3) are in good agreement with those for other (pentenediyl)iron complexes reported in the literature [18,19]. The structure of **7c** was assigned by comparison of its NMR spectral data with that of **7a** and **7b**. Signals at δ 11.2, 14.2, and 10.4 ppm in the ^{13}C NMR spectra, and signals at δ 0.14 (d), 0.33 (d), and 0.66 (d) ppm in the ^1H NMR spectra, of **7a**, **7b**, and **7c** respectively, are

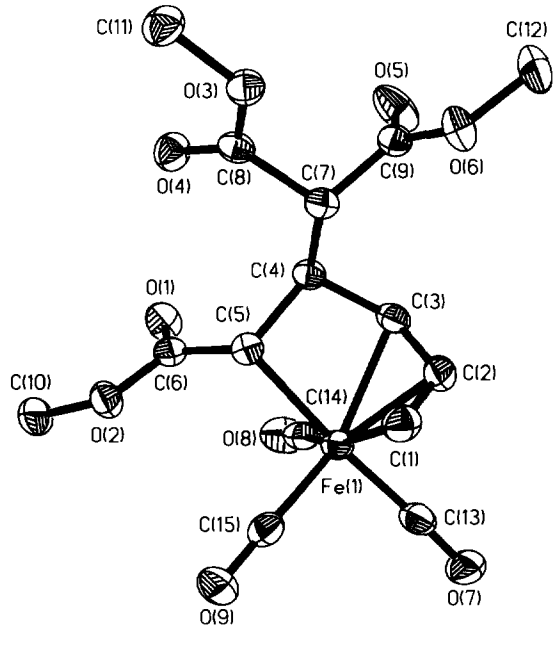


Fig. 2. Molecular structure of **7a** in the crystal.

characteristic of a carbon which is σ-bound to iron and its associated proton [18–20]. The structure of **8c** was assigned on the basis of its ^1H NMR spectral data. In particular, the signals at δ 0.35 (br t, $J = 9.1$ Hz) and −0.46 (br t, $J = 9.1$ Hz) are characteristic of a methylene group which is σ-bound to iron [19–22].

We have previously reported that the reaction of **2** with dimethyl malonate anion (THF, ca. 1–2 h), after chromatography, gives a mixture of regioisomeric (diene)iron complexes **9d** and **10d** (1:2, Table 1, entry 4) [12]. While separation of **9d** and **10d** was possible by preparative thin layer chromatography, they were most often characterized as a mixture. The structural assignments of the isomeric diene complexes **9d** and **10d** are based upon their ^1H NMR spectral data. For complex

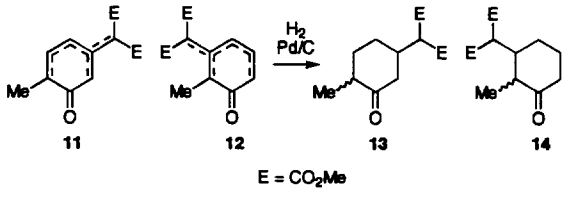
Table 3
Selected bond distances (Å) and bond angles (deg) (with e.s.d.s in parentheses)

	7a	**7b**
Fe(1)–C(1)	2.130(2)	
Fe(1)–C(2)	2.094(2)	2.092(2)
Fe(1)–C(3)	2.155(2)	2.168(2)
Fe(1)–C(5)	2.123(2)	2.109(2)
C(1)–C(2)	1.420(3)	1.413(4)
C(2)–C(3)	1.391(3)	1.397(3)
C(3)–C(4)	1.525(3)	1.520(3)
C(4)–C(5)	1.529(3)	1.533(3)
C(1)–C(2)–C(3)	123.7(2)	124.6(2)
C(2)–C(3)–C(4)	123.0(2)	126.4(2)
C(3)–C(4)–C(5)	104.2(2)	104.2(2)
C(3)–C(4)–C(7)	110.9(2)	117.5(2)
C(5)–C(4)–C(7)	114.9(2)	116.6(2)
C(4)–C(5)–Fe(1)	93.85(12)	93.25(14)
C(4)–C(3)–Fe(1)	92.69(12)	91.35(14)
C(3)–Fe(1)–C(5)	68.56(8)	68.59(9)

9d the malonate methine proton appears as a doublet of doublets (δ 3.27), indicating attachment of the malonate group adjacent to a methylene carbon. Selective double irradiation ^{1}H NMR spectra of **9d** facilitated the assignment of signals at δ 1.62 and 2.15 to the adjacent, diastereotopic methylene protons, and signals at δ 2.25, 5.04, 5.22, and 2.36 ppm to the protons of the complexed diene. For diene complex **10d** the one proton doublet (δ 3.12 ppm) is characteristic of the malonate methine proton adjacent to a secondary center and the one proton doublet of doublet of doublets (δ 5.42 ppm) is characteristic of a 1-substituted (diene)Fe(CO)$_3$ complex [21].

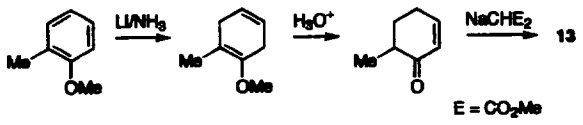
Since the mixture of **9d** and **10d** was reproducibly afforded in 29–50% yield, the reaction of **2** with dimethyl malonate anion was monitored by ^{1}H NMR spectroscopy (THF-d_8). After 50 min, the diene complexes **9d** and **10d** were observed along with a third compound tentatively identified as a (pentenediyl)iron complex **8d** (ca. 1:2:4, Table 1, entry 5). In particular, the signals appearing upfield at δ 0.25 (br t) and δ −1.10 (br t) are characteristic of a methylene group which is σ-bound to iron [19,22]. Over a period of ca. 24 h the signals for **8d** disappeared; however, it was not possible to distinguish the formation of any new products due to spectral broadening.

Attempts to isolate **8d**, by work-up of the reaction mixture after 1–2 h, followed by chromatography, were unsuccessful and led only to the isolation of a mixture of **9d/10d**. In this instance, portions of the reaction mixture visibly appear to become entrained upon silica gel chromatographic work-up. On the other hand, if the reaction was allowed to run 24–48 h before chromatographic work-up, a new organic fraction was isolated in addition to the fraction containing the known diene complexes (Table 1, entry 6). This organic fraction was tentatively identified as mixture of cyclohexenones **11/12** (Eq. (1)) on the basis of spectral analysis. Analysis of **11/12** by GC/MS indicated a multi-component mixture for which each component exhibited an ion of 240 m/z ($C_{12}H_{16}O_5$). The IR spectrum of this fraction revealed absorptions at 1736 and 1676 cm^{-1}, indicative of ester and α,β-unsaturated carbonyl groups.



(1)

In order to corroborate these tentative assignments, further derivatization of the organic fraction was undertaken. Catalytic hydrogenation of **11/12** gave an inseparable mixture of **13** and the known methylcyclohexanone **14** [23] (53%, ca. 1:2, Eq. (1)). Cyclohexanone



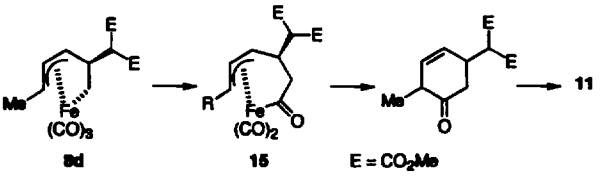
Scheme 3.

14 was identified by comparison of its GC/MS spectral data with the literature values [23], while **13** was identified by comparison (^{1}H, ^{13}C NMR, and GC/MS) with a sample prepared by independent synthesis (Scheme 3). Identification of the hydrogenation products as **13/14** implies that the initial organic fraction consists of a mixture of cyclohexenones with carbon skeletons represented by **11/12**; for each skeleton there are present a mixture of double bond positional isomers.

The disappearance of **8d** and formation of cyclohexenone products **11** are rationalized as indicated in Scheme 4. Insertion of a carbonyl ligand into the iron–carbon σ-bond of **8d** generates the π-allyl–σ-acyl complex **15**. Reductive elimination from **15** gives a cyclohexenone ring, which upon double bond migration generates the mixture **11**. Aumann has previously reported that reversible CO insertion of this type occurs for the parent unsubstituted (pentenediyl)Fe(CO)$_3$ complex, and that decomposition of the π-allyl–σ-acyl complex gives 2-cyclohexenone [24]. Similar mechanisms have been proposed to account for the formation of cyclohexenone products from (i) the reaction of (pentadienyl)Fe(CO)$_2$PPh$_3$ cations with alkyl and aryl lithium reagents [22], and (ii) the reaction of vinylcyclopropanes with Fe(CO)$_5$/CAN [25]. The isolation of cyclohexenone **12** implicates the putative formation of pentenediyl complex **7d**. Failure to spectroscopically identify **7d** in the initial mixture from the reaction of **2** with dimethyl malonate anion may be due to spectral broadening and/or the relative instability of **7d**.

The relative instability of pentenediyl complex **8d** compared to the **7a–c** is due to the relative rates of carbonyl insertion into the Fe–C σ-bond of each. It is known that an electron withdrawing substituent present on a carbon σ-bound to a transition metal slows the rate of carbonyl insertion [26]. Thus for **7a–c** carbonyl insertion into the Fe–Cl bond (bearing a methoxycarbonyl substituent) should be considerably slower than for carbonyl insertion into the corresponding bond of **8d**.

The reaction of **2** with dimethyl methylmalonate (3 h) gave a mixture of **8e**, **9e**, and **10e** (2:1:1) as the crude



Scheme 4.

product (Table 1, entry 7). Chromatography of this mixture (SiO_2) gave a mixture of **9e** and **10e**. As is the case for **8d** the pentenediyl complex **8e** could not be isolated and entrainment of material on the column was observed. The reaction of **3** with dimethyl malonate anion gave a mixture of products which could be separated into diene complex **10f** (50%) and an unstable mixture of pentenediyl complex **8f** and diene complex **9f** (10%, Table 1, entry 8). The reaction of **3** with dimethyl methylmalonate anion gave a separable mixture of pentenediyl complex **8g** (25%) and diene complex **10g** (55%, entry 9), while reaction of **4** with dimethyl malonate anion gave exclusively the diene complex **10h** (92%, entry 10).

The structures of **9e**, **10e**, **10f**, **10g**, and **10h** were assigned by comparison of their ^{1}H NMR spectral data with that of **9d** and **10d**. Of the pentenediyl complexes **8**, only **8g** was sufficiently stable to allow for isolation and complete characterization. The signal at δ −0.3 ppm in the ^{13}C NMR spectrum, and the signals at δ 0.46 (br t, J = 9.3 Hz) and −0.65 (dd, J = 8.7, 10.9 Hz) in the ^{1}H NMR spectrum of **8g** are characteristic of a methylene group which is σ-bound to iron [19,22]. The structure of complexes **8f** was assigned by comparison of its ^{1}H NMR spectral data with that of **8g**.

The differences in regioselectivity for malonate attack on cations **1–4** are qualitatively rationalized in the following fashion. For the tricarbonyl iron complexed cation **1**, the strongly electron withdrawing methoxycarbonyl substituent *lowers* the relative energy of the pentadienyl LUMO, thus allowing for a better energy match with the metal d orbitals [27]. This effects a greater transfer of electron density from the metal to the pentadienyl ligand at C1, C3, and C5. Thus formation of pentenediyl products **7a–c** from nucleophilic attack at C2 of **1** is the result of charge control (i.e. greater $\delta+$ charge at C2/C4). Extended Hückel calculations, performed by Pearson and Burello [28], on the (1-hydroxycarbonylpentadienyl)$Fe(CO)_3^+$ cation indicate greater charge density at C2 and C4 compared to the parent unsubstituted (pentadienyl)-$Fe(CO)_3^+$ cation. In addition, these calculations indicate that the LUMO for the (1-hydroxy-carbonylpentadienyl)$Fe(CO)_3^+$ cation has its largest coefficients at C2. For the tricarbonyl iron complexed cation **4**, the strongly electron donating *p*-methoxyphenyl substituent *raises* the relative energy of the pentadienyl LUMO, thus directing attack by the relatively 'soft' malonate anion at the pentadienyl terminus due to frontier orbital control. For the tricarbonyl iron complexed cations **2** and **3**, the substituents are neither strongly electron withdrawing nor strongly electron donating. Thus nucleophilic attack on these cations does not occur in a highly selective fashion (i.e. formation of both pentenediyl and diene products).

Increasing the substitution on the malonate nucleophile (e.g. R′ = H vs. R′ = Me) leads to a small decrease in the percent nucleophilic attack at the substituted pentadienyl terminus (entry 5 vs. entry 7, and entry 8 vs. entry 9). This small decrease in attack at the substituted pentadienyl terminus is attributed to an increase in the steric hindrance in the transition state for nucleophilic attack. It should be noted that the magnitude of this effect is relatively small, when compared to the electronic effect of the substituent present on the pentadienyl ligand.

It should be noted that attack of 'soft' malonate nucleophiles to the (pentadienyl)$Fe(CO)_3$ cations **2** and **3** proceeds at both the terminal and internal carbons of the pentadienyl ligand to give mixtures of pentenediyl (**7**/**8**) and diene (**9**/**10**) complexes. A similar lack of regioselectivity for attack by relatively 'hard' alkyl and aryl lithium reagents on the parent (pentadienyl)$Fe(CO)_3$ complex has been reported [22]. However, these authors also reported that reaction of the $Fe(CO)_2PPh_3$ complexed cation with alkyl and aryl lithium reagents proceeded with good regioselectivity [22]. For this reason, we were interested in examining malonate attack on the $Fe(CO)_2PPh_3$ complexed cations **5** and **6**.

The reaction of **5** with dimethyl malonate anion gave exclusively the pentenediyl product **7j** (Table 1, entry 11). This selectivity is the same as observed for **7a**. The structure of **7j** was assigned by comparison of its NMR spectral data with that of **7a**. In particular, the signals for the carbon σ-bound to the iron and its associated proton for both **7a** and **7j** are nearly identical. The signals for **7j**, however, exhibit an additional coupling (J_{P-C} = 15.7 Hz, J_{P-H} = 3.3 Hz) due to the phosphine ligand.

Reaction of **6** with lithium dimethyl malonate gave exclusively the diene complex **10j**, while reaction of **6** with lithium dimethyl methoxymalonate gave a separable mixture of diene complexes **10k** (83%) and **9k** (9%) (Table 1, entries 12 and 13). The structural assignments for **10j** and **10k** were based on the appearance of signals in their ^{13}C NMR spectra at ca. δ 43, 84, and 92 ppm which are characteristic of a 1,3*Z*-pentadiene fragment complexed to $Fe(CO)_2PPh_3$ [29]. Similarly, the structure of **9h** was based on the appearance of signals at δ 52.6, 92.0, 86.0, and 51.4 in its ^{13}C NMR spectrum which are characteristic of a 2*E*,4*Z*-hexadiene fragment complexed to $Fe(CO)_2PPh_3$ [29].

The increase in regioselectivity for nucleophilic attack on the $Fe(CO)_2PPh_3$ complexed cation **6** compared to the $Fe(CO)_3$ cation **2** is rationalized on the basis of the 'reactivity–selectivity' principle [30]. Thus, the more reactive $Fe(CO)_3$ complexed cation **2** undergoes attack by malonate anions in a relatively non-selective fashion to give both diene and pentenediyl products. In comparison, the more stable, and therefore less reactive, $Fe(CO)_2PPh_3$ complexed cation **6** displays greater regioselectivity for nucleophilic addition with malonate anion.

The regiodirecting effects examined can be summarized as follows. Nucleophilic attack by malonate anions on tricarbonyl iron complexed 1-substituted pentadienyl cations occurs with little regioselectivity unless there is either a strongly electron withdrawing or strongly electron donating substituent present at the terminal position of the ligand. Regioselectivity of nucleophilic attack on $Fe(CO)_2PPh_3$ complexed pentadienyl cations is generally improved over that of the corresponding $Fe(CO)_3$ complexed cations due to the increased stability/decreased reactivity of the $Fe(CO)_2PPh_3$ cations. Finally, the steric bulk of the malonate nucleophile has only a minor effect on the regioselectivity of nucleophilic attack on the pentadienyl ligand.

3. Experimental section

All melting point measurements were measured on a Mel-Temp apparatus and are uncorrected. Unless otherwise specified, all ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300 MHz, 75 MHz, and 120 MHz respectively using a GE Omega GN-300 Spectrometer. Infrared spectra were recorded on a Matteson 4020 FT-IR spectrophotometer. Elemental analyses were performed by Midwest Microlabs, Ltd., Indianapolis, IN. High resolution mass spectra were performed at the Nebraska Center for Mass Spectrometry, Lincoln, NE. 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. The (pentadienyl)$Fe(CO)_3$ cations **1**, **2**, **3** and **6** were prepared by literature procedures [5,14,15]. The ^1H and ^{13}C NMR data for **3** and **6** are reported here.

3: ^1H NMR (60 MHz, CD_3NO_2) δ 7.5 (br s, 5H), 7.2 (t, J = 7.0 Hz, 1H), 6.7 (dd, J = 7.0, 12.7 Hz, 1H), 6.2 (m, 1H), 4.2 (d, J = 12.0 Hz, 1H), 3.8 (dd, J = 4.0, 9.0 Hz, 1H), 2.7 (dd, J = 4.0, 12.0 Hz, 1H); ^{13}C NMR (15 MHz, CD_3NO_2) δ 133.2, 133.0, 129.5, 127.3, 103.3, 96.6, 94.0, 93.3, 63.1.

6: ^1H NMR (CD_3NO_2) δ 6.79 (br t, J = 6.6 Hz, 1H), 5.70 (dd, J = 6.6, 11.9 Hz, 1H), 5.21 (m, 1H), 3.13 (dq, J = 12.0, 6.6 Hz, 1H), 2.25 (m, 1H), 1.89 (d, J = 6.6 Hz, 3H), 1.52 (m, 1H); ^{13}C NMR (CD_3NO_2) δ 134.6 (J_{PH} = 9.7 Hz), 133.7, 132.0 (J_{PH} = 48.5 Hz), 130.8 (J_{PH} = 10.9 Hz), 105.0, 102.3, 95.6, 89.0 (J_{PH} = 2.5 Hz), 21.2, signal for C5 obscured by CD_3NO_2 (63.7–61.9).

3.1. Tricarbonyl[1-(4'-methoxyphenyl)-2Z,4-pentadienone]iron

To a suspension of $AlCl_3$ (1.61 g, 12.0 mmol) in CH_2Cl_2 (15 ml) at 0 °C was added 4-methoxybenzoylchloride (2.11 g, 12.3 mmol) and the mixture was stirred for 10 min. To this solution was added a solution of butadiene(tricarbonyl)iron (2.00 g, 10.3 mmol) in CH_2Cl_2 (10 ml) and the reaction mixture was stirred for 20 min. To the mixture was added 30% aqueous NH_4OH (30 ml) and ice (ca. 20 g). After stirring for 5 min, the mixture was extracted with CH_2Cl_2 (3 × 60 ml), and the combined organic extracts were washed with H_2O (4 × 30 ml) and dried ($MgSO_4$). The residue was purified by column chromatography (SiO_2, CH_2Cl_2) to give the *cis*-dienone complex as a yellow oil which solidified in the refrigerator (1.64 g, 49%); ^1H NMR ($CDCl_3$) δ 7.88 and 6.93 (AA'BB', J_{AB} = 8.9 Hz, 4H), 5.66–5.56 (m, 2H), 3.87 (s, 3H), 3.82 (d, J = 6.6 Hz, 1H), 2.30 (br d, J = 7.5 Hz, 1H), 1.47 (dd, J = 2.5, 9.0 Hz, 1H); Anal. Calcd. for $C_{15}H_{12}FeO_5$: C, 54.91; H, 3.66. Found: C, 54.86; H, 3.76.

3.2. Tricarbonyl[1-(4'-methoxyphenyl)pentadienyl]iron-(1 +) hexafluorophosphate (4)

To a solution of tricarbonyl[1-(4'-methoxyphenyl)-2Z,4-pentadienone]iron (1.50 g, 4.57 mmol) in methanol (40 ml) was added excess sodium methoxide (1.23 g). The mixture was stirred at room temperature for 20 h, and then diluted with H_2O (40 ml), extracted with ether (2 × 30 ml), and the combined extracts dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (5:1)) to afford tricarbonyl[1-(4'-methoxyphenyl)-2E,4-pentadienone]iron as a yellow oil: 0.75 g (50%); ^1H NMR ($CDCl_3$) δ 7.91 and 6.93 (AA'BB', J_{AB} = 9 Hz, 4H), 6.24 (tdd, J = 1.0, 5.1, 8.1 Hz, 1H), 5.54 (dddd, J = 1.0, 5.1, 6.9, 9.3 Hz, 1H), 3.87 (s, 3H), 2.10 (ddd, J = 1.0, 2.7, 6.9 Hz, 1H), 1.94 (dd, J = 1.0, 8.1 Hz, 1H), 0.87 (ddd, J = 1.0, 2.3, 9.3 Hz, 1H). To a solution of the above ketone (0.100 g, 0.305 mmol) in ether (6 ml) was added, via syringe, a solution of $LiBH_4$ (0.18 ml, 2 M in THF, 0.36 mmol). The reaction mixture was stirred for 8 h and then H_2O (5 ml) was added and the mixture extracted with CH_2Cl_2 (2 × 5 ml), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (5:1)) to afford tricarbonyl[1-(4'-methoxyphenyl)-2E,4-pentadien-1-ol]iron as a yellow oil: 0.070 g (69%); ^1H NMR ($CDCl_3$) δ 7.31 and 6.90 (AA'BB', J_{AB} = 8.5 Hz, 4H), 5.35 (tdd, J = 4.8 8.4 Hz, 1H), 5.24 (m, 1H), 4.47 (dd, J = 1.8, 7.9 Hz, 1H), 3.80 (s, 3H), 1.94 (br s, 1H), 1.78 (dd, J = 2.4, 6.8 Hz, 1H), 1.26 (t, J = 8.3 Hz, 1H), 0.34 (dd, J = 2.4, 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 211.3, 159.3, 136.9, 126.7, 114.0, 85.0, 81.9, 76.3, 69.7, 55.3, 40.2. To a solution of the alcohol (0.50 g, 1.5 mmol) in Ac_2O (0.6 ml) at 0 °C, was added a solution of HPF_6 (1.2 ml, 60% solution) in Ac_2O (1 ml). The mixture was stirred for 30 min, and then added dropwise to a large excess of ether (250 ml). The yellow precipitate obtained was dissolved in a minimal amount of CH_2Cl_2

and added dropwise to a large excess of ether (250 ml). The precipitate was collected by vacuum filtration and dried in vacuo to afford **4** as a golden yellow powder (0.26 g, 38%); ^{1}H NMR (CD_3NO_2) δ 7.65 and 7.08 (AA'BB', J_{AB} = 8.9 Hz, 4H), 7.11 (br t, J = 7.1 Hz, 1H), 6.53 (dd, J = 7.1, 13.3 Hz, 1H), 6.27 (ddd, J = 6.8, 9.7, 12.2 Hz, 1H), 3.89 (s, 3H), 3.74 (ddd, J = 1.0, 4.0, 9.8 Hz, 1H), 2.72 (dd, J = 3.9, 12.4 Hz, 1H); ^{13}C NMR (CD_3NO_2) δ 165.1, 132.0, 127.7, 117.5, 105.0, 101.3, 96.5, 95.8, 57.2. Anal. Calcd. for $C_{15}H_{13}F_6FeO_4P$: C, 39.33; H, 2.86. Found: C, 39.32; H, 2.95.

3.3. Dicarbonyl(methyl 6-hydroxy-2,4-hexadienoate)(triphenylphosphine)iron

To a solution of dicarbonyl(methyl 6-oxo-2,4-hexadienoate)(triphenylphosphine)iron [16] (2.12 g, 4.1 mmol) in dry ethanol (15 ml), was added KBH_4 (0.27 g, 4.9 mmol). The solution was stirred for 30 min, and then diluted with water (10 ml). The mixture was extracted with ether (3 × 30 ml), the combined extracts dried and the solvent evaporated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (3:1)) to afford the dienol complex as a yellow solid (1.45 g, 68%); m.p. 106–112 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.6–7.4 (m, 15H), 5.83 (m, 1H), 5.18 (m, 1H), 3.48 (br d, J = 6.6 Hz, 2H), 3.29 (s, 3H), −0.03 (m, 1H), −0.16 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 173.8, 135.4 (J_{PH} = 41.2 Hz), 132.7 (J_{PH} = 9.7 Hz), 129.8, 128.3 (J_{PH} = 9.7 Hz), 86.6, 85.6, 65.2, 64.3, 50.8, 49.5.

3.4. Dicarbonyl(1-methoxycarbonylpentadienyl)triphenylphosphineiron(1 +) hexafluorophosphate (5)

To a cold solution of HPF_6 (0.82 ml, 60% solution, 5.5 mmol) in Ac_2O (2 ml) was added a solution of dicarbonyl(methyl 6-hydroxy-2,4-hexadienoate)(triphenylphosphine)iron (1.45 g, 2.81 mmol) in Ac_2O (2 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 (700 ml) and the precipitate collected by vacuum filtration and dried in vacuo to afford **5** as a bright yellow powder (1.21 g, 67%); m.p. 125–135 °C (dec.); ^{1}H NMR (CD_3NO_2) δ 7.75–7.55 (m, 15H), 7.03 (br t, J = 6.3 Hz, 1H), 6.57 (dd, J = 7.2, 10.5 Hz, 1H), 5.47 (m, 1H), 3.90 (s, 3H), 2.77 (br d, J = 9.6 Hz, 1H), 2.43 (d, J = 11.1 Hz, 1H), 1.88 (br m, 1H); ^{13}C NMR (CD_3NO_2) δ 170.7, 134.5 (J_{PH} = 9.7 Hz), 134.0, 131.0 (J_{PH} = 10.9 Hz), 129.9 (J_{PH} = 49.7 Hz), 108.1, 103.7, 98.8, 67.3, 66.8, 54.1. Anal. Calcd. for $C_{27}H_{27}F_6FeO_4P_2 \cdot H_2O$: C, 48.97; H, 3.96. Found: C, 49.11; H, 3.78.

3.5. Reaction of 1 with dimethyl malonate anion

To a solution of lithium dimethyl malonate (0.58 mmol, freshly prepared from dimethylmalonate and *n*-butyl lithium) in THF (10 ml) at 0 °C was added solid cation **1** (200 mg, 0.48 mmol) in one portion. The mixture was stirred at 0 °C for 1 h and at 23 °C for 18 h. Water (10 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 **7a** as a yellow solid (110 mg, 61%). Diffusion controlled recrystallization (ethyl acetate–hexanes) gave a sample which was suitable for X-ray diffraction analysis; m.p. 85–87 °C; ^{1}H NMR ($CDCl_3$) δ 4.65–4.55 (m, 2H), 3.85–3.60 (m, 2H), 3.74, 3.67, and 3.58 (3 × s, 9H), 2.88 (d, J = 10.8 Hz, 1H), 2.46 (dd, J = 2.7, 11.4 Hz, 1H), 0.14 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.1, 209.6, 203.3, 179.5, 167.3, 166.9, 97.8, 62.2, 60.0, 54.5, 52.4, 52.3, 51.3, 38.4, 11.2. Anal. Calcd. for $C_{15}H_{16}FeO_9$: C, 45.48; H, 4.07. Found: C, 45.60; H, 4.10.

3.6. Reaction of 1 with dimethyl methylmalonate anion

To a solution of lithium dimethyl methylmalonate (2.47 mmol, freshly prepared from dimethyl methylmalonate and *n*-butyl lithium) in THF (60 ml) at 0 °C was added solid cation **1** (1.00 g, 2.43 mmol) in one portion. The mixture was stirred at 0 °C for 1 h. Water (30 ml) was added and the mixture was extracted with Et_2O (2 × 30 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (Florisil, hexanes–ethyl acetate (3:1)) to afford **7b** (0.625 g, 66%). Diffusion controlled recrystallization (ethyl acetate–hexanes) gave a sample which was suitable for X-ray diffraction analysis; m.p. 125–129 °C; ^{1}H NMR ($CDCl_3$) δ 4.71 (t, J = 7.2 Hz, 1H), 4.57 (ddd, J = 7.5, 8.7, 12.0 Hz, 1H), 3.85 (dd, J = 7.5, 10.5 Hz, 1H), 3.69, 3.64 and 3.63 (3 × s, 9H), 3.40 (br d, J = 8.4 Hz, 1H), 2.32 (dd, J = 2.6, 12.0 Hz, 1H), 1.10 (s, 3H), 0.33 (d, J = 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.2, 209.5, 203.6, 179.9, 171.0, 170.9, 99.6, 66.1, 60.2, 54.3, 53.1, 53.0, 52.0, 46.1, 18.2, 14.2. Anal. Calcd. for $C_{16}H_{18}FeO_9$: C, 46.85; H, 4.42. Found: C, 47.19; H, 4.47.

3.7. Reaction of 1 with dimethyl methoxymalonate anion

To a solution of lithium dimethyl methoxymalonate (0.58 mmol, freshly prepared from dimethyl methoxymalonate and *n*-butyl lithium) in THF (10 ml) at 0 °C was added solid cation **1** (200 mg, 0.48 mmol) in one portion. The mixture was stirred at 0 °C for 1 h and at 23 °C for 18 h. Water (10 ml) was added and the mixture was extracted with Et_2O (3 × 20 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. A ^{1}H NMR spectrum of the crude product indicated a mixture of **7c** and **8c** (3:1). The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate

(3:1)) to afford **7c** (120 g, 62%). **7c**: m.p. 107–110 °C; ^{1}H NMR ($CDCl_3$) δ 4.33 (t, J = 7.4 Hz, 1H), 4.56 (ddd, J = 7.4, 8.7, 12.3 Hz, 1H), 3.86 (dd, J = 7.5, 9.6 Hz, 1H), 3.80, 3.63, 3.60, and 3.37 (4 × s, 12H), 3.78–3.72 (m, 1H), 2.67 (br d, J = 12.0 Hz, 1H), 0.66 (d, J = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.4, 209.9, 203.8, 180.0, 168.1, 167.3, 99.4, 86.7, 60.9, 55.6, 55.3, 52.4, 52.3, 51.2, 45.6, 10.4. Anal. Calcd. for $C_{16}H_{18}FeO_{10}$: C, 45.09; H, 4.26. Found: C, 45.32; H, 4.34. **8c**: ^{1}H NMR (partial, $CDCl_3$) δ 5.19 (dd, J = 7.5, 10.8 Hz), 4.28 (t, J = 7.5 Hz), 3.79, 3.75, 3.73 and 3.40 (4 × s), 3.19 (d, J = 10.3 Hz), 0.35 (br t, J = 9.1 Hz), −0.46 (br t, J = 9.1 Hz).

3.8. Reaction of 2 with dimethyl malonate anion

Monitoring of the reaction of **2** with sodium dimethyl malonate in THF-d_8 indicated the initial (50 min) formation of **8d**, **9d**, and **10d** (4:1:2). Over a period of 22 h, the signals for **8d** disappeared. **10d**: ^{1}H NMR (THF-d_8, partial) δ 5.38 (dd, J = 5.1, 9.3 Hz, 1H), 5.16 (m, 1H), 3.31 (dd, J = 6.6, 8.4 Hz, 1H), 1.45 (d, J = 6.3 Hz, 3H); **9d**: ^{1}H NMR (THF-d_8, partial) δ 5.57 (m, 1H), 5.20 (dd, J = 5.0, 7.6 Hz, 1H), 3.14 (d, J = 7.8 Hz, 1H), 1.99 (dd, J = 2.1, 7.8 Hz, 1H), 1.12 (d, J = 6.6 Hz, 3H); **8d**: ^{1}H NMR (THF-d_8, partial) δ 4.47 (br m), 4.20 (br m), 1.82 (br d), 0.25 (br t), −1.10 (br t). On a preparative-scale, to a solution of sodium dimethylmalonate (0.88 mmol, freshly prepared from dimethylmalonate and excess NaH) in THF (20 ml) at 0 °C was added solid **3** (0.30 g, 0.82 mmol). The reaction mixture was stirred for 24 h under N_2 and then opened to the atmosphere and stirred for 4 h. Water (10 ml) was then added and the mixture extracted with ether (2 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (5:1 to 3:1 gradient)) to give a mixture of **9d/10d** (1:2) as a yellow oil (0.054 g, 19%) followed by an organic fraction tentatively identified as a mixture of cyclohexenones **11/12** (0.069 g, 35%). If the reaction was worked up after only 1 h, and the residue dissolved in CH_2Cl_2, rapid decomposition was observed. After filtration and chromatography, a mixture of **9d/10d** (1:2, 13–19%) was recovered. The mixture of **9d/10d** could be further separated by preparative thin layer chromatography (C_6H_6). **9d**: ^{1}H NMR ($CDCl_3$) δ 5.22 (dd, J = 5.2, 9.4 Hz, 1H), 5.04 (dd, J = 5.2, 7.6 Hz, 1H), 3.70 (s, 6H), 3.27 (dd, J = 6.2, 8.5 Hz, 1H), 2.36 (dq, J = 9.4, 6.2 Hz, 1H), 2.25 (ddd, J = 4.7, 7.6, 10.4 Hz, 1H), 2.15 (ddd, J = 4.7, 6.2, 14.2 Hz, 1H), 1.62 (ddd, J = 8.5, 10.4, 14.2 Hz, 1H), 1.43 (d, J = 6.5 Hz, 3H); ^{13}C NMR (15 MHz, $CDCl_3$) δ 210.3, 168.7, 95.1, 81.7, 58.0, 54.3, 54.0, 52.3, 29.7, 29.2, 20.3; Anal. Calcd. for $C_{14}H_{16}FeO_7 \cdot \frac{1}{6}C_6H_6$: C, 49.63; H, 4.69. Found: C, 49.48; H, 4.82. **10d**: ^{1}H NMR ($CDCl_3$) δ 5.42 (ddd, J = 5.0, 7.0, 11.0 Hz, 1H), 5.08 (dd, J = 5.0, 7.0 Hz, 1H), 3.70 (s, 6H), 3.12 (d, J = 7.5 Hz, 1H), 2.37 (dd, J = 7.0, 11.0 Hz, 1H), 1.94 (dd, J = 2.0, 7.0 Hz, 1H), 1.80 (ddq, J = 7.5, 11.0, 6.5 Hz, 1H), 1.41 (dd, J = 2.0, 11.0 Hz, 1H), 1.11 (d, J = 6.5 Hz, 3H); ^{13}C NMR (15 MHz, $CDCl_3$) δ 210.3, 168.2, 92.2, 85.2, 64.3, 61.0, 52.3, 41.8, 34.4, 20.2. **11/12**: IR ($CDCl_3$, cm^{-1}) 1736, 1676; ^{1}H NMR ($CDCl_3$) δ 6.87 (m) and 6.69 (m) and 6.00 (dd, J = 1.8, 9.9 Hz) and 5.94 (s) total 0.9H, 4.23 (s, 0.3H), 3.76, 3.73, 3.72 (3 × s, 6H), 3.46 (m) and 3.67 (d, J = 8.4 Hz) total 0.7H, 2.9–2.0 (m, 5.1H), 1.76 (s) and 1.18 (dd, J = 2.1, 6.9 Hz) and 1.12 (dd, J = 1.7, 6.6 Hz) total 3H; GC/MS m/z 240 ($C_{12}H_{16}O_5$), 108 (100, C_7H_8O).

3.9. Dimethyl (4-methyl-3-oxocyclohexyl)propanedioate (13) and dimethyl (2-methyl-3-oxocyclohexyl)propanedioate (14)

A solution of **11/12** (0.13 g, 0.54 mmol) and Pd on carbon (10 mg) in methanol (10 ml) under H_2 (3 atm) was shaken in a micro Parr apparatus for 6 h. The reaction mixture was filtered through filter-aid and concentrated. Purification of the residue by chromatography (SiO_2, hexanes–ethyl acetate (5:1)) gave **13** and **14** as a light yellow oil (69 mg, 53%). Product **13** was identified by comparison (NMR and GC/MS) with a sample prepared by independent synthesis (vide infra) and **14** was identified by comparison to literature [23] spectral data.

3.10. Independent synthesis of dimethyl (4-methyl-3-oxocyclohexyl)propanedioate (13)

To anhydrous methanol (2 ml) was added sodium metal (15 mg, 0.7 mmol). To this solution was added a solution of dimethyl malonate (0.30 g, 2.2 mmol) in methanol (1 ml). After stirring for a period of 5 min, a sample of 6-methyl-2-cyclohexenone [31] (0.21 g, 1.91 mmol) was added. The mixture was heated at reflux for 20 min, and then stirred at room temperature for an additional 16 h. The mixture was acidified by addition of 0.3 N HCl, diluted with water (10 ml), and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by kugelrohr distillation to afford **13** as a colorless oil (0.26 g, 57%); ^{1}H NMR ($CDCl_3$) δ 3.74, 3.73 (2 × s, 6H), 3.32 (d, J = 7.5 Hz, 1H), 2.55–2.20 (m, 4H), 2.15–2.05 (m, 1H), 1.95–1.87 (m, 1H), 1.65–1.50 (m, 1H), 1.45–1.30 (m, 1H), 1.08 and 1.01 (2 × d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 210.6 (212.5), 168.2, 168.1 (168.3), 56.8 (55.0), 52.5, 45.1, 44.6 (44.0, 42.9), 39.1 (37.4), 33.8 (30.6), 29.4 (25.5), 14.2 (15.5); GC/MS: R_t 21.5 min, m/z (relative abundance) 242 (M+, < 1), 153 (34), 132 (32), 111 (58), 110 (100), 69 (45), 55 (83), 41 (85). Anal.

Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 58.79; H, 7.38.

3.11. Reaction of 2 with dimethyl methylmalonate anion

To a solution of lithium dimethyl methylmalonate (0.27 mmol, freshly prepared from dimethyl methylmalonate and *n*-BuLi) in THF (10 ml) at 0 °C was added solid cation **2** (60 mg, 0.16 mmol). The mixture was stirred at 0 °C for 3 h, quenched with water (10 ml) and extracted with ether (2 × 50 ml). The combined extracts were dried ($MgSO_4$) and the solvent evaporated to afford an orange oil (30 mg, 50%) which was identified by ^{1}H NMR spectroscopy as a mixture of **8e**, **9e** and **10e** (ca. 2:1:1). **9e/10e**: ^{1}H NMR ($CDCl_3$) δ 5.40 (br dt, J = 5.2, 9.0 Hz, 0.5H, **10e**), 5.22 (dd, J = 5.1, 9.0 Hz, 0.5H, **9e**), 5.10 (m, 1H), 3.72, 3.69, 3.68 and 3.67 (4 × s, 6H), 2.45–2.20 (m, 2H), 1.95–1.70 (m, H), 1.52 (dd, J = 2.7, 14.1 Hz, 0.5H, **10e**), 1.40 (m, 0.5H, **?**), 1.44 (d, J = 6.3 Hz, 1.5H, **9e**), 1.36 and 1.34 (2 × s, 3H), 1.10 (d, J = 6.6 Hz, 1.5H, **10e**); ^{13}C NMR ($CDCl_3$) δ 210.9, 172.1, 171.6, 94.6, 91.6, 85.8, 82.9, 62.7, 60.0, 57.9, 55.2, 52.6, 52.5, 52.4, 52.3, 51.5, 41.5, 37.6, 35.9, 29.7, 20.3, 19.7, 18.8, 15.5. **8e**: ^{1}H NMR ($CDCl_3$) δ 4.34 (dd, J = 7.3, 11.2 Hz, 1H), 4.19 (t, J = 7.3 Hz, 1H), 3.70 and 3.68 (2 × s, 6H), 3.36 (dt, J = 6.9, 10.5 Hz, 1H), 3.04 (dq, J = 5.1, 6.0 Hz, 1H), 1.77 (d, J = 6.3 Hz, 3H), 1.17 (s, 3H), 0.35 (t, J = 9.3, 1H), −0.94 (dd, J = 8.4, 10.8, 1H).

3.12. Reaction of 3 with dimethyl malonate anion

To a solution of lithium dimethylmalonate (0.47 mmol, freshly prepared from dimethylmalonate and *n*-butyl lithium) in THF (4 ml) at 0 °C was added solid cation **3** (200 mg, 0.46 mmol) in one portion. The mixture was stirred at 0–5 °C for 30 min. Water (2 ml) was added and the mixture was extracted with Et_2O (2 × 5 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (hexanes–ethyl acetate (5:1)) to afford a mixture of **8f** and **9f** (1.5:1, 20 mg, 10%) as an unstable yellow oil followed by **10f** as a yellow oil (97 mg, 50%). **8f/9f**: R_f 0.39 (pentane–ether (5:2); ^{1}H NMR ($CDCl_3$), **8f**: δ 7.4–7.1 (m, 5H), 5.93 (ddd, J = 5.1, 9.6, 11.0 Hz, 1H), 5.18 (br t, J = 6.3 Hz, 1H), 3.69 and 3.64 (2 × s, 6H), 3.29 (br t, J = 7.5 Hz, 1H), 3.26 (d, J = 9.8 Hz, 1H), 2.37 (m, 2H), 1.80 (m, 1H); **9f**: δ 7.4–7.1 (m, 5H), 5.11 (dd, J = 7.5, 12.3 Hz, 1H), 4.24 (t, J = 7.5 Hz, 1H), 4.14 (d, J = 12.3 Hz, 1H), 3.67 (s, 6H), 3.38 (m, 1H), 0.45 (t, J = 9.5 Hz, 1H), −0.89 (t, J = 9.3 Hz, 1H). **10f**: R_f 0.23 (pentane–ether (5:2)); IR (neat, cm^{-1}) 2051, 1985, 1752, 1728; ^{1}H NMR ($CDCl_3$) δ 7.35–7.25 (m, 3H), 7.15–7.10 (m, 2H), 5.45 (ddd, J = 5.4, 7.8, 9.6 Hz, 1H), 5.25 (br t, J = 5.4 Hz, 1H), 3.79 and 3.38 (2 × s, 6H), 3.63 (d, J = 9.6 Hz, 1H), 2.77 (m, 2H), 1.93 (dd, J = 3.0, 7.8 Hz, 1H), 1.71 (dd, J = 3.0, 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 209.6, 168.0, 167.1, 141.6, 128.4, 127.6, 127.4, 92.3, 84.9, 62.1, 60.1, 52.4, 52.1, 44.0, 41.1. Anal. Calcd. for $C_{19}H_{18}FeO_7$: C, 55.10; H, 4.38. Found: C, 56.50; H, 4.75.

3.13. Reaction of 3 with dimethyl methylmalonate anion

To a solution of lithium dimethyl methylmalonate (0.56 mmol, freshly prepared from dimethylmalonate and *n*-butyl lithium) in THF (4 ml) at 0 °C was added solid cation **3** (200 mg, 0.46 mmol) in one portion. The mixture was stirred at 0–5 °C for 1 h. Water (2 ml) was added and the mixture was extracted with Et_2O (2 × 5 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (20:1)) to afford **8g** (50 mg, 25%) followed by **10g** (110 mg, 55%) both as yellow oils. **8g**: R_f 0.51 (pentane–ether (5:2)); IR (neat, cm^{-1}) 2052, 1983, 1728; ^{1}H NMR ($CDCl_3$) δ 7.30–7.14 (m, 5H), 5.14 (dd, J = 7.7, 12.1 Hz, 1H), 4.36 (t, J = 7.5 Hz, 1H), 3.92 (d, J = 12.3 Hz, 1H), 3.64 and 3.59 (2 × s, 6H), 3.43 (dt, J = 7.2, 10.5 Hz, 1H), 1.19 (s, 3H), 0.46 (t, J = 9.3 Hz, 1H), −0.65 (dd, J = 8.7, 10.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 213.5, 211.9, 203.5, 171.3, 171.2, 140.6, 129.0, 126.9, 125.4, 95.7, 75.4, 59.9, 58.7, 52.3, 46.5, 17.8, −0.3; EI-HRMS m/z 372.0651 [$C_{18}H_{20}O_5Fe$ (M − 2CO) calcd. 372.0663]. **10g**: R_f 0.35 (pentane–ether (5:2)); IR (neat, cm^{-1}) 2048, 1979, 1736; ^{1}H NMR ($CDCl_3$) δ 7.32–7.25 (m, 3H), 7.15–7.10 (m, 2H), 5.46 (dddd, J = 1.0, 5.0, 7.8, 9.9 Hz, 1H), 5.30 (dd, J = 5.0, 7.7 Hz, 1H), 3.73 and 3.59 (2 × s, 6H), 3.16 (dd, J = 7.7, 12.3 Hz, 1H), 2.93 (d, J = 12.4 Hz, 1H), 1.92 (ddd, J = 1.0, 3.0, 7.7 Hz, 1H), 1.68 (ddd, J = 1.0, 3.0, 9.9 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.7, 171.0, 170.9, 140.4, 129.3, 127.8, 127.3, 92.0, 85.9, 60.7, 58.8, 52.2, 47.7, 41.1, 17.6; EI-HRMS m/z 372.0673 [$C_{18}H_{20}O_5Fe$ (M − 2CO) calcd. 372.0663].

3.14. Reaction of 4 with dimethyl malonate anion

To a solution of lithium dimethyl malonate (0.13 mmol, freshly prepared from dimethylmalonate and *n*-butyl lithium) in THF (2 ml) at 0 °C was added solid cation **4** (50 mg, 0.11 mmol) in one portion. The mixture was stirred at 0–5 °C for 30 min. Water (2 ml) was added and the mixture was extracted with ether (2 × 5 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (5:1)) to afford **10h** as a yellow oil (45 mg, 92%): ^{1}H NMR ($CDCl_3$) δ 7.05 and 6.84 (AA'BB', J_{AB} = 8.8 Hz, 4H), 5.45 (ddd, J = 4.9, 7.9 Hz, 1H), 5.24 (m, 1H),

3.80, 3.79 and 3.41 (3 × s, 9H), 3.59 (d, $J = 9.7$ Hz, 1H), 2.75 (m, 2H), 1.93 (ddd, $J = 1.0$, 3.0, 7.7 Hz, 1H), 1.67 (ddd, $J = 1.0$, 3.0, 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 209.7, 168.0, 167.2, 158.8, 133.9, 128.6, 113.8, 92.2, 85.0, 62.2, 60.6, 55.2, 52.4, 52.1, 43.3, 41.1; EI-HRMS m/z 360.0675 [$C_{17}H_{20}O_5Fe$ (M − 3CO) calcd. 360.0663].

3.15. Reaction of 5 with dimethyl malonate anion

To a solution of lithium dimethyl malonate (0.58 mmol, freshly prepared from dimethylmalonate and *n*-butyl lithium) in THF (10 ml) at 0 °C was added solid cation **5** (200 mg, 0.48 mmol) in one portion. The mixture was stirred at 0 °C for 1 h and at 23 °C for 18 h. Water (10 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 **7i** as a yellow foam (180 mg, 72%); m.p. 125–130 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (m, 15H), 4.38 (br t, $J = 6.9$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 1H), 3.86 (m, 1H), 3.72, 3.68, and 3.57 (3 × s and m, 10H), 2.85 (d, $J = 10.5$ Hz, 1H), 0.13 (dd, $J = 3.3$, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 217.3, 181.0, 167.8, 167.3, 97.1, 60.2, 59.8 ($J =$ 6.1 Hz), 57.0, 52.2, 52.1, 51.0, 39.4, 9.6 ($J = 15.7$ Hz). Anal. Calcd. for $C_{32}H_{31}FeO_8P$: C, 60.97; H, 4.96. Found: C, 60.66; H, 5.03.

3.16. Reaction of 6 with dimethyl malonate anion

To a solution of cation **6** (0.30 g, 0.50 mmol) in THF (25 ml) at −78 °C was added a solution of sodium dimethylmalonate (0.59 mmol, freshly prepared from dimethylmalonate and excess NaH) in THF (6.5 ml). The solution was warmed to 0 °C and stirred for 2 h, and then poured into H_2O (10 ml). The solution was extracted with ether (2 × 50 ml) and the combined extracts dried ($MgSO_4$) and the solvent evaporated. The residue was twice purified by column chromatography (SiO_2, hexanes–ether (7:3) and C_6H_6–ethyl acetate (10:3)) to afford **10j** as an orange oil (0.25 g, 87%); IR (KBr, cm^{-1}) 1973, 1915, 1734; ^{1}H NMR ($CDCl_3$) δ 7.5–7.3 (m, 15H), 4.7–4.8 (m, 2H), 3.65 (s, 6H), 3.08 (d, $J = 8.4$ Hz, 1H), 1.96 (m, 1H), 1.84 (m, 1H), 1.32 (d, $J = 6.0$ Hz, 3H), 0.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 168.7, 168.5, 135.2 ($J_{PH} = 37.6$ Hz), 133.1 ($J_{PH} =$ 10.9 Hz), 129.7, 128.2 ($J_{PH} = 8.5$ Hz), 92.3, 83.4, 61.4, 60.6, 52.0, 42.7, 34.8, 20.1; FAB-HRMS m/z 609.1081 [$C_{31}H_{31}O_6PFeNa$ (M + Na^+) calcd. 609.1105].

3.17. Reaction of 6 with dimethyl methoxymalonate anion

To a solution of lithium dimethyl methoxymalonate (3.13 mmol, freshly prepared from dimethyl methoxymalonate and LDA) in THF (40 ml) at −78 °C was added solid cation **6** (1.60 g, 2.67 mmol). The solution was warmed to 0 °C and stirred for 2.5 h, and then diluted with H_2O (20 ml). The solution was extracted with ether (3 × 50 ml) and the combined extracts dried ($MgSO_4$) and the solvent evaporated. The residue was purified by column chromatography (SiO_2, hexanes–ethyl acetate (15:1)) to give **10k** as a yellow solid (1.36 g, 83%) followed by **9k** as an orange gum (0.14 g, 9%). **10k**: ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 15H), 4.88 (m, 1H), 4.70 (m, 1H), 3.71, 3.70, and 3.41 (3 × s, 9H), 2.14 (dd, $J = 11.0$, 7.7 Hz, 1H), 1.78 (td, $J = 11.4$, 6.6 Hz, 1H), 1.13 (d, $J = 6.6$ Hz, 3H), 1.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.7, 135.1 ($J_{PH} = 38.8$ Hz), 133.1 ($J_{PH} = 19.1$ Hz), 129.7, 128.2 ($J_{PH} = 9.7$ Hz), 91.9, 90.1 ($J_{PH} = 2.4$ Hz), 84.3, 56.8 ($J_{PH} = 10.9$ Hz), 55.7 ($J_{PH} = 2.4$ Hz), 52.0, 42.6 ($J_{PH} = 2.5$ Hz), 41.2, 17.4. Anal. Calcd. for $C_{13}H_{33}FeO_7P \cdot 0.25H_2O$: C, 61.89; H, 5.43. Found: C, 61.59; H, 5.43. **9k**: ^{1}H NMR ($CDCl_3$) δ 7.5–7.3 (m, 15H), 5.00 (dd, $J = 4.8$, 8.4 Hz, 1H), 4.13 (m, 1H), 3.65, 3.61, and 2.99 (3 × s, 9H), 2.38 (m, 1H), 2.12 (m, 1H), 1.62 (dd, $J = 11.4$, 15.0 Hz, 1H), 1.46 (dd, $J = 2.1$, 6.0 Hz, 1H), 1.39 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 168.6, 135.5 ($J_{PH} = 37.6$ Hz), 133.1 ($J_{PH} = 9.7$ Hz), 129.7 ($J_{PH} = 12.2$ Hz), 128.2 ($J_{PH} =$ 9.7 Hz), 92.0, 85.9, 85.0, 52.6 ($J_{PH} = 4.9$ Hz), 52.4, 51.4 ($J_{PH} = 6.1$ Hz), 50.0 ($J_{PH} = 6.1$ Hz), 31.8, 20.4; EI-HRMS m/z 560.1313 [$C_{31}H_{33}O_6PFe$ (M − CO) calcd. 560.1413].

3.18. Crystal structure determinations of (7a) and (7b)

A crystal of **7a** was attached to a glass fiber and mounted on a Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20–30 frames based on 195 reflections. Final cell constants are calculated from a set that does not exceed a number equal to 8192 of strong reflections from the actual data collection. The experimental crystallographic data is given in Table 2. The space group $P2_1/n$ was determined based on systematic absences and intensity statistics [32].

A crystal of **7b** was attached to a glass fiber and mounted on a Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames based on 170 reflections. Final cell constants are calculated from a set of 6953 strong reflections from the actual data collection. The experimental crystallographic data is given in Table 2. The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics [32].

Both structures were solved using the SHELXTL V5.0 suite of programs. Direct-methods solutions were calculated which provided most non-hydrogen atoms from

Table 4
Final atomic coordinates (Å × 10^4) for (**7a**) and equivalent isotropic displacement parameters (Å × 10^3)

Atom	x	y	z	U_{eq}
Fe(1)	93(1)	9271(1)	3586(1)	25(1)
O(1)	658(2)	11977(1)	3346(1)	36(1)
O(2)	3935(2)	11280(1)	3332(1)	31(1)
O(3)	46(2)	10772(1)	744(1)	29(1)
O(4)	368(3)	11831(1)	1623(1)	34(1)
O(5)	−4911(3)	10625(1)	1462(1)	48(1)
O(6)	−3683(2)	9220(1)	1024(1)	34(1)
O(7)	−1346(3)	7726(1)	4485(1)	46(1)
O(8)	−1357(3)	10815(1)	4476(1)	46(1)
O(9)	4588(3)	9125(1)	4157(1)	44(1)
C(1)	373(4)	8209(2)	2810(1)	33(1)
C(2)	−1788(3)	8520(2)	2817(1)	31(1)
C(3)	−2440(3)	9520(2)	2788(1)	28(1)
C(4)	−1193(3)	10346(2)	2478(1)	24(1)
C(5)	1020(3)	10324(2)	2881(1)	24(1)
C(6)	1757(3)	11280(2)	3196(1)	27(1)
C(7)	−1191(3)	10176(2)	1722(1)	24(1)
C(8)	−161(3)	11037(2)	1378(1)	25(1)
C(9)	−3474(3)	10051(2)	1391(1)	27(1)
C(10)	4855(4)	12112(2)	3722(1)	39(1)
C(11)	1064(4)	11509(2)	356(1)	36(1)
C(12)	−5820(4)	9007(2)	693(1)	43(1)
C(13)	−830(3)	8320(2)	4132(1)	33(1)
C(14)	−790(4)	10248(2)	4106(1)	32(1)
C(15)	2834(4)	9171(2)	3933(1)	31(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Final atomic coordinates (Å × 10^4) for (**7b**) and equivalent isotropic displacement parameters (Å^2 × 10^3)

Atom	x	y	z	U_{eq}
Fe(1)	9599(1)	6823(1)	2148(1)	21(1)
O(1)	7094(3)	8902(1)	1348(1)	36(1)
O(2)	5541(3)	7575(1)	1005(1)	32(1)
O(3)	6476(2)	7297(1)	4406(1)	28(1)
O(4)	3935(3)	7045(1)	3702(1)	35(1)
O(5)	8146(3)	9523(1)	3948(1)	28(1)
O(6)	5352(3)	9312(1)	4490(1)	32(1)
O(7)	11293(3)	8436(1)	1340(1)	37(1)
O(8)	8072(3)	5613(1)	950(1)	36(1)
O(9)	13283(3)	5883(1)	2219(1)	39(1)
C(1)	8360(4)	5954(2)	2999(1)	29(1)
C(2)	9478(4)	6682(2)	3313(1)	25(1)
C(3)	9273(3)	7657(2)	3163(1)	22(1)
C(4)	7545(3)	8144(2)	2852(1)	21(1)
C(5)	7012(3)	7537(2)	2169(1)	20(1)
C(6)	6582(3)	8099(2)	1491(1)	25(1)
C(7)	5949(3)	8386(2)	3414(1)	20(1)
C(8)	5298(3)	7502(2)	3850(1)	22(1
C(9)	6654(4)	9131(2)	3974(1)	23(1)
C(10)	5061(4)	8056(3)	314(1)	42(1)
C(11)	6002(5)	6463(2)	4852(2)	41(1)
C(12)	5829(5)	10029(2)	5045(2)	44(1)
C(13)	4282(3)	8805(2)	2982(1)	26(1)
C(14)	8710(4)	6073(2)	1411(2)	25(1)
C(15)	11856(4)	6234(2)	2200(2)	28(1)
C(16)	10603(4)	7811(2)	1648(2)	25(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the *E*-map (Tables 4 and 5). Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters.

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