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Reactions of chelated η^3-pentadienyl iron complexes with nucleophiles

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Abstract

Ferracyclic (1-3-η^3)pentadienyl complexes with electronically decoupled allyl and vinyl moieties were reacted with various heteroatom and carbon nucleophiles. Primary amines selectively attacked neutral (4-6-η^3-pentadienyl)ferralactones **2** on the end of the allyl ligand to give 3-(*endo*-vinyl)-(4-6-η^3-allyl)ferralactams **4** and by a similar reaction of the latter eventually 6-(*exo*-vinyl)-(4-6-η^3-allyl)ferralactams **5**. S'_N-like attack on the conjugated coplanar vinyl residue of **2** was not observed. The cationic η^3-allyl complex **3** was attacked by nucleophiles either on the allylic terminus furnishing free (1*Z*, 3*E*)-dienes **8,** or on the vinyl residue which is part of an activated Michael system to give η^4-1,3-diene complexes **9**. η^4-1,3,5-Triene complex **10** was obtained with basic nucleophiles.

Keywords: Pentadienyl complexes; Allyl complexes; Metallacycles; Fe

1. Introduction

Regioselectivity can arise both from differences in the stereochemical accessibility and/or in the electronic attractiveness of potential reaction sites. Rigid normal and medium-sized metallacycles with π-ligands are particularly suited for studying the delicate balance between these two factors in bond forming processes. (η^3-allyl) ferralactones such as **1** can be readily obtained from reactions of diironnonacarbonyl with either vinyl epoxides [1–5], but-2-ene-1,4-diols [6] or the cyclic sulfites of but-3-ene-1,2-diols [7]. They have been exploited in regioselective reactions involving the allyl ligand, eventually leading to prominent target structures such as β-lactones and -lactams, 1,3-dienes and dihydropyranones [8,9]. For instance, Aumann found the reactions with amines, furnishing (η^3-allyl)ferralactams, to proceed by attack on the terminal C-atom C-6 of the π-ligand with inversion of configurations both at this and at carbon atom C-3 [10]. Complexes **2**, accessible from reaction of $Fe_2(CO)_9$ with the respective hexatriene monoxides or with cyclic sulfites of hexa-3,5-diene-1,2-diols [11], are the formal vinylogues of **1**. They feature a planar (4-8)-pentadienyl π-system having but a slight twist between the (4-6-η^3)-allyl moiety which is coordinated and the 7-vinyl residue which is not, as to the X-ray structure. Attack of nucleophiles on the vinyl terminus C-8 in an S'_N fashion should be sterically less hindered than attack on the more electrophilic end C-6 of the π-ligand. In complex **3**, which was obtained upon Meerwein alkylation of a 3-vinyl-(η^3-allyl)ferralactone [11,12], two equally well accessible electrophilic π-systems can compete for nucleophiles. They are also electronically decoupled with an angle 'γ' = 41.7° between the plane of the allyl ligand and the plane of the C=C bond [12,13]. The latter can be looked at as a model of a reactive Michael system activated by complexation of the carbonyl oxygen to a Lewis acidic Fe(II) centre. Typical nucleophiles were reacted with complexes **2** and **3** to gauge the influence of sterical vs. electronic factors (See Fig. 1).

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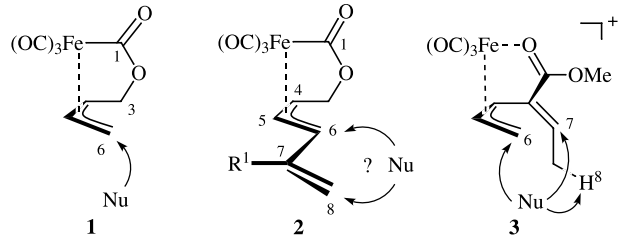
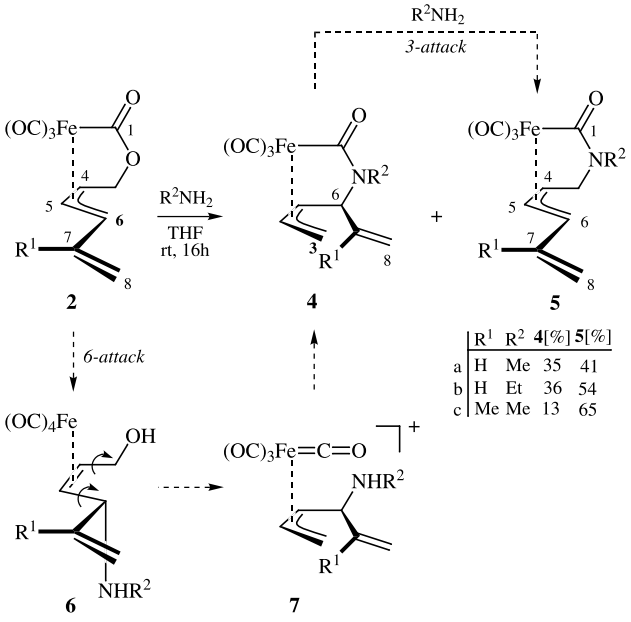


Fig. 1. (η^3-Allyl)ferralactone **1**, its vinylogues **2**, and cationic η^3-pentadienyl complex **3**.

2. Results and discussion

2.1. Reactions of (4-6-η^3-pentadienyl)ferralactone complexes 2 with primary amines

Generally, complexes **2** reacted less readily with amines than the parent compound **1**, typically requiring several hours at room temperature for complete consumption of the starting complex and formation of two product (π-allyl)ferralactam complexes **4** and **5**, the ratio of which depended on the residues R^1 in **2** and R^2 in the 1° amine (Scheme 1). In the case of reactions of **2a** ($R^1 = H$) it was unclear whether products **5a** ($R^1 = H$, $R^2 = Me$) and **5b** ($R^1 = H$, $R^2 = Et$), respectively, had arisen from attack of the amine on C-8, concurrent with formation of **4a/4b** by attack on C-6, or from a second amine attack on C-3 of the latter. Aumann's early work had shown, that (π-allyl)ferralactams can, upon prolonged exposure, indeed react with amines at their allyl terminus [10]. Treatment of complex **2b** ($R^1 = Me$) with methylamine, however, gave rise to a 1:5 mixture of product complexes **4c** and **5c** ($R^1 = R^2 = Me$). The absence of product complexes bearing the methyl group at C-4 instead of C-7 unequivocally refutes a mechanism implying S'_N-attack by the amine on C-8 of **2**. In accord with the established mechanism of the reaction of amines with **1**, one can likewise assume an exclusive attack of 1° amines on C-6 of **2**, followed by 180° rotation about the C3–C4 and the C5–C6 bonds in the intermediate η^2-alkene complexes **6** to allow for amide bond linkage and expulsion of water, and thus formation solely of *endo*-vinyl-(η^3-allyl)ferralactams **4**. Fig. 2 depicts the molecular structure of **4b** ($R^1 = H$, $R^2 = Et$) as obtained from a single crystal X-ray structure analysis, clearly showing the *endo* configuration of the vinyl residue with respect to the curvature of the π-allyl segment. The NMR spectra of **4a**–**4c** also prove the *endo* geometry. Purified complexes **4a**, **4b** were found to react with excess amine at a rate comparable to that of the reaction of **2**. Complex **4c** ($R^1 = R^2 = Me$) reacted considerably faster than **4a** and **4b**. This can be explained by a greater congestion due to the *endo*-propenyl group in **4c** and thus a more



Scheme 1. Regioselective reactions of (4-6-η^3)pentadienylferralactones **2** with primary amines (for clarity: atom numbering of **2** retained in **4**; inversion of configuration enroute **2** → **4** omitted).

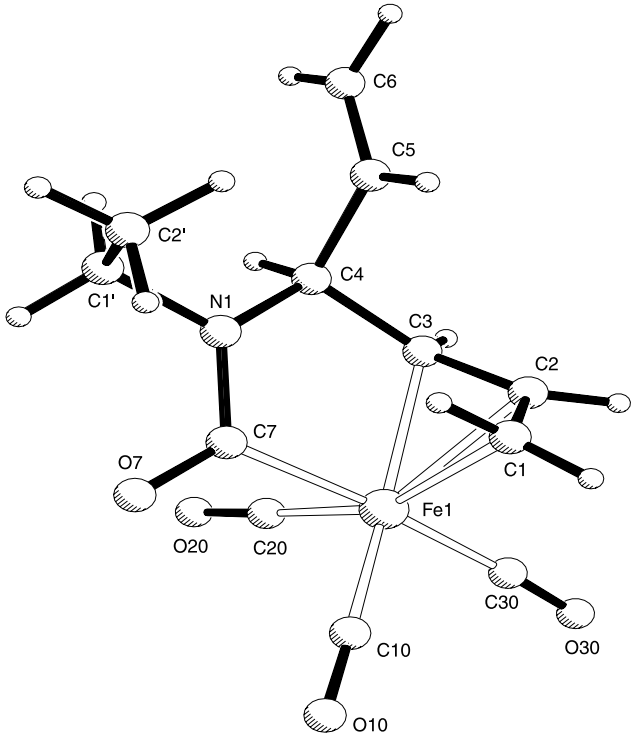
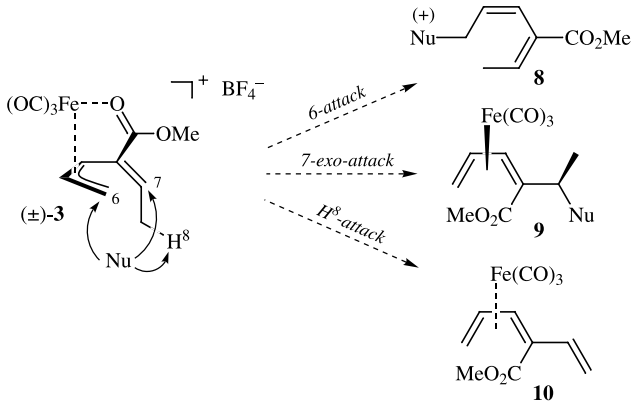


Fig. 2. Molecular structure of **4b** ($R^1 = H$, $R^2 = Et$). Selected bond lengths (Å) and angles (°): Fe1–C10 1.803(4), Fe–C20 1.775(4), Fe–C30 1.830(3), Fe–C7 2.015(3), Fe–C1 2.176(4), Fe–C2 2.067(3), Fe–C3 2.104(3), N1–C7 1.360(4), N1–C4 1.463(4), N1–C1' 1.474(4), C1–C2 1.395(5), C7–O7 1.237(4); C1–C2–C3 122.9(3), C2–C3–C4 125.5(3), N1–C4–C3 110.6(3), N1–C7–Fe1 115.4(2), C2–Fe1–C3 39.76(13), C2–Fe1–C1 38.29(13), C3–C4–C5 109.4(3), C4–C5–C6 123.4(4), N1–C4–C5 112.0(3).

pronounced tendency to release this strain by unfolding the π-ligand through uptake of a second amine and formation of the straight ligand system of **5c**. The greater ratio of products **5c**:**4c** as compared to **5a**:**4a** and **5b**:**4b** reflects these differences in the stabilities and rates.

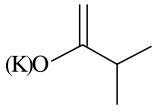
2.2. Reactions of (±)-E-[(4-6-η³)-3-methoxycarbonyl-hexa-2,5-diene-4-yl]tricarbonyl-iron(II) tetrafluoroborate **3**

Conceivable sites open to attack of nucleophiles in complex **3** are the allylic terminus C-6, the β-C of the activated Michael system, C-7, and with sufficiently basic nucleophiles the H-atoms attached to C-8 as well. To gauge intrinsic differences in the charge densities and frontier orbital coefficients of these potentially electrophilic sites we performed hybrid density functional (B3LYP) single point calculations [14] using the geometry obtained from the X-ray structure analysis of **3**. The orbital coefficients of the allylic end C-6 were calculated to be considerably larger in the LUMO and also in the nearest two unoccupied MOs, when compared to the coefficients on the vinyl carbon atoms C-3 and C-7 (Table 2). Hence orbital-controlled reactions with sufficiently soft nucleophiles possessing HOMOs not too different in energy from the LUMO of **3** ($E_{LUMO} = -9.142$ eV) should preferentially take place at C-6. Calculated Mulliken charges of C-6 (2.721) and C-7 (6.004), on the other hand, suggest hard nucleophiles to attack predominantly on C-7. However, uncertainties may arise with nucleophiles of unknown aggregation states and thus hard to predict softness and HOMO energies. Less significant differences exist in terms of sterical accessibility of C-6 vs. C-7. In reactions with various heteroatom and carbon nucleophiles we observed the formation of either uncoordinated or coordinated substituted 1,3-dienes **8**, **9** or **10**, respectively. Conveniently, mixtures of these were not found in any case (Scheme 2).



Scheme 2. Reactions of cationic η³-pentadienyl complex **3** with heteroatom and carbon nucleophiles.

The relatively soft and bulky triphenylphosphane, but also Grignard compounds and Normant cuprates with large organic residues such as phenyl attacked the allylic terminus C-6 of **3** in fair accord with the calculations. The ancillary ligation via the carbonyl oxygen apparently persists in the resulting intermediate η²-alkene complexes, therefore it does not allow the Michael system to adopt a coplanar geometry suitable for a η⁴-1,3-diene coordination (**3**: dihedral angle C7–C3–C4–C5 = 135°). They rather decomplex to yield the free difunctionalized (1-*Z*,3-*E*)-dienes **8**. Conversely and somewhat unexpected, Gillman cuprates which are not normally regarded as being harder than Grignard compounds, selectively attacked on C-7 of complex **3** shifting the double bond between carbon atoms C-3 and C-4. As the dihedral twist between this bond and the conjugated C=C bond between C-5 and C-6 is a mere 35°, coordination can easily change to η⁴. Enols of malonates also reacted in this way when pre-activated with bis(trimethylsilyl)acetamide (BSA) [19] albeit requiring more vigorous conditions. The products **9** are formed with the methoxycarbonyl residue adopting an

Nu(El)	Product	Conditions	Yield (%)
Ph_3P	**8a**: Nu = Ph_3P/BF_4^-	CH_3CN, 16 h, r.t.	70
Ph(MgBr)	**8b**: Nu = Ph	THF, −40 °C → r.t.	65
$Ph_2(CuMgI)$	**8b**	THF, −30 °C → r.t.	76
$Me_2(CuLi)$	**9a**: Nu = Me	THF, −78 °C → r.t.	68
$Bu_2(CuLi)$	**9b**: Nu = Bu	THF, −78 °C → r.t.	60
$(MeO_2C)_2CH–H$	**9c**: Nu = $CH(CO_2Me)_2$	BSA,[a] THF, 72 h, refl.	66
	10	THF, −78 °C → r.t.	74[b]
			

[a] BSA = bis(trimethylsilyl)acetamide.
[b] A series of 10 other cyclic and acyclic K- and Li-enolates all gave solely **10** in yields ranging from 60% to 75%.

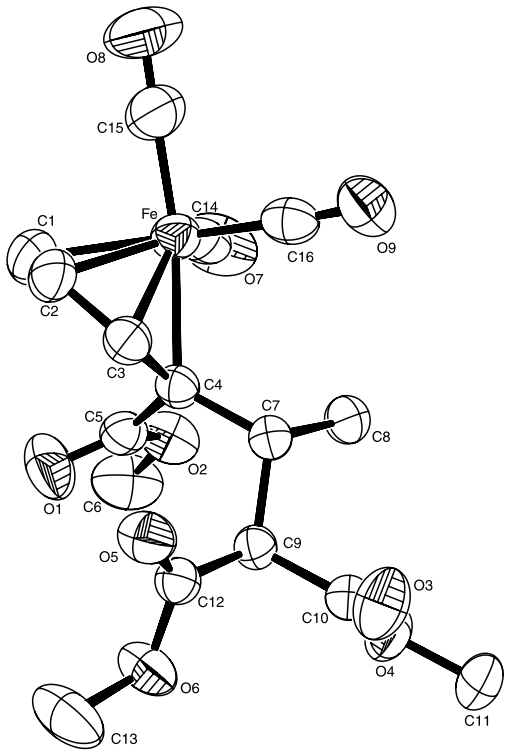


Fig. 3. Molecular structure of **9c**. Selected bond lengths (Å) and angles (°): Fe–C16 1.787(4), Fe–C14 1.788(4), Fe–C15 1.796(4), Fe–C3 2.060(2), Fe–C2 2.064(3), Fe–C1 2.122(3), Fe–C4 2.154(3), C1–C2 1.402(5), C2–C3 1.407(4), C3–C4 1.430(4), C4–C5 1.495(4), C4–C7 1.541(3), C7–C8 1.541(4), C7–C9 1.561(4), C9– C12 1.514(4), C9–C10 1.524(4); C1–C2–C3 121.0(3), C2–C3–C4 120.7(3), C1–Fe–C4 83.97(12), C3–C4–C7–C8–136.5(3), C5–C4–C7–C8 79.5(3), C8–C7–C9–C12 178.2(2).

endo position due to its *endo* pre-orientation in the starting complex **3**. When Nu≠Me, compounds **9** are formed selectively as a single racemic diastereoisomer. Fig. 3 depicts the molecular structure of **9c** as obtained from a single crystal X-ray structure analysis. It reveals a configuration of the new stereogenic centre next to the diene system stemming from attack of the nucleophile from the *exo*-face. The terminal CO ligand of the $Fe(CO)_3$ moiety sticking out into the *exo* half space is obviously less of an obstacle than the CH_2 terminus of the concave allyl ligand which shields the *endo* face of the C3–C7 double bond. Noticeably 'harder' nucleophiles such as lithium and potassium enolates did not react with C–C bond formation at all, but acted as bases and gave rise to the formation of η^4-1,3,5-triene **10** by abstracting a proton H^8, regardless of the bulkiness of the enolate. Surprisingly and in stark contrast to the chemistry of (η^3-allyl)ferralactones such as **1** and **2**, reaction of **3** with various amines only gave unidentifiable decomposition products, presumably due to an irreversible attack on the terminal CO ligands. The same was observed with softer carbon nucleophiles like silyl enol ethers and potassium enoxyborates which undergo clean C–C bond formation with cationic carbene complexes derived from lactones **1** [20–22].

2.3. Conclusion

The vinyl residue in the neutral complexes **2**, though coplanar with the η^3-allyl ligand, is not activated towards nucleophilic attack which therefore takes place exclusively on the latter. S'_N-type reactions were not observed. The *endo*-3-vinyl residue in complexes **4** is neither coordinated nor even formally conjugated to the η^3-allyl ligand. Hence even in sterically congested derivatives such as **4c** strain relief is achieved not by attack on the vinyl but on the allyl terminus. In complex **3** both electronically decoupled π-systems are activated towards nucleophilic attack – the allyl ligand by η^3-coordination and the vinyl residue by being part of a Michael system the carbonyl oxygen of which is ligated to a Lewis acidic Fe(II) centre. Only with downright hard and soft reagents the site of attack can be predicted with certainty whereas in other cases factors such as aggregation, solvent polarity, counter ions, and bulkiness of residues etc. can dip the scales in favour of the allyl or the vinyl residue.

3. Experimental

3.1. General information

All reactions were carried out under an atmosphere of argon. All solvents were dried according to literature procedures and freshly distilled under argon prior to use. The starting complexes **2** and **3** were prepared as published [11,12]. Melting points are uncorrected. IR: Perkin–Elmer 1420. NMR: Jeol GNM GX 400 FT and Bruker Avance 300; TMS as internal standard. MS: Varian MAT-CH-4B (EFO-4B-source; 70 eV). MA: Heraeus Mikromat C–H–N.

3.2. Aminolysis of (±)-[(4-6-η^3)-7-alkyl-2-oxa-1-oxo-octa-5,7-diene-1,4-diyl]tricarbonyliron(II) (2) to give mixtures of ferralactams (4) and (5): general procedure

A solution of ferralactone complex **2** (1.00 mmol) in dry THF (10 mL) was chilled to −20 °C and treated with liquid methylamine (45 μL, 1.00 mmol) or ethylamine (66 μL, 1.00 mmol), respectively. The mixture was allowed to warm to room temperature and stirred for another 16 h. All volatile components were removed on a rotary evaporator and the remainder purified by column chromatography with diethyl ether on silica gel 60 or preferably by preparative HPLC on Nucleosil.

*3.2.1. [(4-6-η³)-2-aza-2-methyl-1-oxo-3-(endo-vinyl)-hex-5-ene-1,4-diyl]tricarbonyliron(II) (**4a**) and [(4-6-η³)-2-aza-2-methyl-1-oxo-octa-5,7-diene-1,4-diyl]tricarbonyliron (II) (**5a**)*

97 mg (35%) **4a** and 114 mg (41%) **5a** from **2a** (264 mg). Separation by HPLC (pentane/diethyl ether 3:2, v:v; 18 mL/min).

4a: $t_R = 24.35$ min, $R_f = 0.83$ (diethyl ether), yellow crystals of m.p. 105 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.30$ [s, 3H, NMe], 2.55 [d, ^3J(6-H^{en}/5-H) = 12.9 Hz, 1H, 6-H^{en}], 2.84 [d, ^3J(6-H^{ex}/5-H) = 8.3 Hz, 1H, 6-H^{ex}], 3.26 [dd, ^3J(3-H/4-H) = 6 Hz, ^3J(3-H/7-H) = 9 Hz, 1H, 3-H], 3.67 [dd, ^3J(4-H/5-H) = 7 Hz, ^3J (3-H/4-H) = 6 Hz, 1H, 4-H], 3.80 [ddd, ^3J (6-H^{ex}/5-H) = 8.3 Hz, ^3J (5-H/4-H) = 7 Hz, ^3J(6-H^{en}/5-H) = 12.9 Hz, 1H, 5-H], 4.71–4.75 [two d superimposed, ^3J(7-H/8-H) = 16.8 Hz, ^3J(7-H/8-H′) = 9 Hz, 2H, 8-H, 8-H′], 5.00 [ddd, ^3J(7-H/8-H) = 16.8 Hz, ^3J(7-H/8-H′) = 9 Hz, ^3J(3-H/7-H) = 9 Hz, 1H, 7-H]. ^{13}C NMR (100.5 MHz, C_6D_6): δ = 31.0 (Me), 59.5 (C-6), 64.4 (C-3), 74.8 (C-4), 90.2 (C-5), 116.7 (C-7), 140.5 (C-8), 199.3, 204.1, 209.0, 211.6 (FeCO). IR (film): $\nu = 2950$ cm^{-1}, 2922, 2870, 2066, 2003, 1590. MS (FAB): m/z (%) = 278 (100) [MH$^+$], 265 (19), 250 (25), 222 (67), 210 (25), 194 (64), 193 (77). Anal. Calc. for $C_{11}H_{11}FeNO_4$ (277.1): C, 47.69; H, 4.00; N, 5.06. Found: C, 47.55; H, 3.91; N, 4.99.

5a: $t_R = 25.23$ min, $R_f = 0.56$ (diethyl ether/pentane 1:1, v:v), yellow crystals of m.p. 110 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.61$ [s, 3H, NMe], 3.24 [dd, ^2J(3-H^{en}/3-H^{ex}) = 12.70 Hz, ^3J(3-H^{en}/4-H) = 1.5 Hz, 1H, 3-H^{en}], 3.40 [dd, ^2J(3-H^{en}/3-H^{ex}) = 12.70 Hz, ^3J(3-H^{ex}/4-H) = 7 Hz, 1H, 3-H^{ex}], 4.30 [ddd, ^3J(4-H/3-H^{ex}) = 7 Hz, ^3J(3-H^{en}/4-H) = 1.5 Hz, ^3J(5-H/4-H) = 8.55 Hz, 1H, 4-H], 4.39 [dd, ^3J(6-H/5-H) = 11 Hz, ^3J(7-H/6-H) = 11 Hz, 1H, 6-H], 4.87 [dd, ^3J(5-H/4-H) = 8.55 Hz, ^3J(5-H/6-H) = 11 Hz, 1H, 5-H], 5.23 [d, ^3J(7-H/8-H^{trans}) = 10.0 Hz, 1H, 8-H^{trans}], 5.55 [d, ^3J (7-H/8-H^{cis}) = 16.85 Hz, 1H, 8-H^{cis}], 6.0 [ddd, ^3J (7-H/8-H^{cis}) = 16.85 Hz, ^3J (6-H/7-H) = 11 Hz, ^3J (8-H^{trans}/7-H) = 10.0 Hz, 1H, 7-H]. ^{13}C NMR (100.5 MHz, C_6D_6): δ = 31.0 (Me), 49.8 (C-3), 63.3 (C-6), 81.5 (C-4), 92.7 (C-5), 118.2 (C-8), 137.1 (C-7), 201.2, 204.2, 206.7, 210.6 (FeCO). IR (film): $\nu = 2950$ cm^{-1}, 2922, 2870, 2066, 2003, 1590. MS (FAB): m/z (%) = 278 (100) [MH$^+$], 265 (11), 250 (36), 222 (74), 210 (36), 194 (52), 193 (68). Anal. Calc. for $C_{11}H_{11}FeNO_4$ (277.1): C, 47.69; H, 4.00; N, 5.06. Found: C, 47.51; H, 3.89; N, 4.98.

*3.2.2. [(4-6-η³)-2-aza-2-ethyl-1-oxo-3-(endo-vinyl)-hex-5-ene-1,4-diyl]tricarbonyliron(II) (**4b**) and [(4-6-η³)-2-aza-2-ethyl-1-oxo-octa-5,7-diene-1,4-diyl]tricarbonyliron (II) (**5b**)*

105 mg (36%) **4b** and 157 mg (54%) **5b** from **2a** (264 mg). Separation by HPLC (pentane/diethyl ether 1:1, v:v; 18 mL/min).

4b: $t_R = 12.01$ min, $R_f = 0.75$ (diethyl ether), yellow crystals of mp 107 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.77$ [t, $^3J = 6.6$ Hz, 3H, Me], 2.60 [m, 2H, MeC*H*,6-H^{en}], 2.90 [d, ^3J(6-H^{ex}/5-H) = 8 Hz, 1H, 6-H^{ex}], 3.17 [m, 1H, MeC*H*′], 3.50 [dd, ^3J(3-H/4-H) = 6.8 Hz, ^3J(3-H/7-H) = 7 Hz, 1H, 3-H], 3.67 [dd, ^3J(4-H/5-H) = 8 Hz, ^3J(3-H/4-H) = 6.8 Hz, 1H, 4-H], 3.81 [ddd superimposed, ^3J(6-H^{en}/5-H) = 12.7 Hz, ^3J(5-H/4-H) = 8 Hz, ^3J(6-H^{ex}/5-H) = 8 Hz, 1H, 5-H], 4.71–4.75 [two d superimposed, ^3J(7-H/8-H) = 17.1 Hz, ^3J(7-H/8-H′) = 9.7 Hz, 2H, 8-H, 8-H′], 5.02 [ddd, ^3J(7-H/8-H) = 17.1 Hz, ^3J(7-H/8-H′) = 9.7 Hz, ^3J(3-H/7-H) = 7 Hz, 1H, 7-H]. ^{13}C NMR (100.5 MHz, C_6D_6): δ = 12.3 (Me), 38.2 (Me*C*), 59.9 (C-6), 62.4 (C-3), 74.5 (C-4), 90.1 (C-5), 116.5 (C-7), 140.5 (C-8), 199.2, 204.1, 208.4, 211.8 (FeCO). IR (film): $\nu = 2973$ cm^{-1}, 2930, 2862, 2064, 2001, 1998, 1587, 1191. MS (FAB): m/z (%) = 292 (68) [MH$^+$], 280 (27), 264 (63), 252 (45), 236 (100), 224 (54), 223 (48). Anal. Calc. for $C_{12}H_{13}FeNO_4$ (291.1): C, 49.51; H, 4.50; N, 4.81. Found: C, 49.47; H, 4.43; N, 4.79.

5b: $t_R = 16.44$ min, $R_f = 0.64$ (diethyl ether), yellow crystals of mp 108 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.69 [t, $^3J = 6.8$ Hz, 3H, Me], 2.55 [d, ^2J(3-H^{en}/3-H^{ex}) = 12 Hz, 1H, 3-H^{en}], 2.87 [q and d superimposed, $^3J = 6.8$ Hz, ^2J(3-H^{en}/3-H^{ex}) = 12 Hz, 3H, MeC*H*$_2$, 3-H^{ex}], 3.42 (m, 1H, 4-H), 4.13 [dd, ^3J(5-H/4-H) = 6.9 Hz, ^3J(5-H/6-H) = 11 Hz, 1H, 5-H], 4.26 [dd, ^3J(5-H/6-H) = 11 Hz, ^3J(6-H/7-H) = 10 Hz, 1H, 6-H], 4.85 [d, ^3J(7-H/8-H^{trans}) = 10 Hz, 1H, 8-H^{trans}], 5.15 [d, ^3J(7-H/8-H^{cis}) = 17.1 Hz, 1H, 8-H^{cis}], 5.50 [ddd, ^3J(7-H/8-H^{trans}) = 10 Hz, ^3J(8-H^{cis}/7-H) = 17.1 Hz, ^3J(6-H/7-H) = 10 Hz, 1H, 7-H]. ^{13}C NMR (100.5 MHz, C_6D_6): δ = 12.4 (Me), 38.5 (Me*C*), 46.6 (C-3), 63.5 (C-6), 82.1 (C-4), 92.5 (C-5), 117.5 (C-8), 138.2 (C-7), 197.6, 204.8, 207.5, 212.1 (FeCO). IR (film): $\nu = 2974$ cm^{-1}, 2930, 2862, 2065, 2003, 1999, 1587, 1191. MS (FAB): m/z (%) = 292 (100) [MH$^+$], 264 (18), 236 (38), 223 (18), 208 (30). Anal. Calc. for $C_{12}H_{13}FeNO_4$ (291.1): C, 49.51; H, 4.50; N, 4.81. Found: C, 49.48; H, 4.31; N, 4.68.

*3.2.3. X-ray crystal structure determination of [(4-6-η³)-2-aza-2-ethyl-1-oxo-3-(endo-vinyl)-hex-5-ene-1,4-diyl] tricarbonyliron(II) (**4b**)*

Formula $C_{12}H_{13}FeNO_4$, molar mass 291.08 g mol^{-1}, crystal size 0.30 × 0.10 × 0.10 mm, $a = 8.5810(17)$, $b = 11.581(2)$, $c = 12.981(3)$ Å, $\alpha = 90°$, $\beta = 93.33(3)°$, $\gamma = 90°$, $V = 1287.9(4)$ Å^3, $T = 173(2)$ K, $d_{calc} = 1.501$ g cm^{-3}, $\mu = 1.176$ mm^{-1}, $Z = 4$, monoclinic, space group P2(1)/c, Nonius Mach 3 diffractometer, $\lambda = 0.71073$ Å, Θ-range 2.36–25.02°; $\omega\Theta$-scans, index ranges $-10 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$, 4128 collected reflections, 2268 independent reflections [$1 > 2\sigma(1)$], 215 refined parameters, absorption correction by ψ-scans. Structure solution: direct methods (SHELXS 97), structure refinement: full-matrix least-squares on F^2 (SHELXL 97), H atoms calculated and not included into least-squares refinement, $R_1 = 0.0389[w = 1/\sigma^2(F_0)]$,

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **4b**

Atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	7148(1)	2053(1)	4365(1)	25(1)
N(1)	4185(3)	2182(2)	3220(2)	26(1)
O(7)	5525(3)	582(2)	2845(2)	39(1)
O(10)	8364(3)	−321(2)	4302(2)	51(1)
O(20)	8300(3)	3114(2)	2516(2)	47(1)
O(30)	9875(3)	2854(2)	5692(2)	42(1)
C(1′)	2887(4)	1879(3)	2476(3)	34(1)
C(1)	5430(4)	1599(3)	5466(3)	34(1)
C(2′)	1703(5)	1099(4)	2952(3)	43(1)
C(2)	5730(4)	2781(3)	5423(3)	29(1)
C(3)	5569(4)	3428(3)	4495(3)	27(1)
C(4)	4225(4)	3332(3)	3688(3)	26(1)
C(5)	2718(4)	3619(3)	4172(3)	30(1)
C(6)	1792(5)	4474(4)	3855(4)	44(1)
C(7)	5465(4)	1493(3)	3338(2)	28(1)
C(10)	7905(4)	601(3)	4336(3)	34(1)
C(20)	7884(4)	2689(3)	3248(3)	29(1)
C(30)	8793(4)	2545(3)	5213(3)	31(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U*ij* tensor.

$wR_2 = 0.0774$, largest diff. peak and hole 0.325 and −0.304 e Å^{-3} (see Table 1).

3.2.4. [(4-6-η³)-2-aza-2-methyl-1-oxo-3-(endo-isopropenyl)-hex-5-ene-1,4-diyl]tricarbonyliron(II) (**4c**) and [(4-6-η³)-2-aza-2,7-dimethyl-1-oxo-octa-5,7-diene-1,4-diyl]tricarbonyliron(II) (**5c**)

38 mg (13%) **4c** and 189 mg (65%) **5c** from **2b** (278 mg). Separation by HPLC (hexane/diethyl ether 1:1, v:v; 18 mL/min).

4c: $t_R = 28.25$ min, $R_f = 0.89$ (diethyl ether), yellow solid, decomposition >45 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.60$ (s, 3H, 7-Me), 2.40 (s, 3H, NMe), 2.99 [d, ^3J(6-H^{en}/5-H) = 13 Hz, 1H, 6-H^{en}], 3.70 [d, ^3J(6-H^{ex}/5-H) = 8.5 Hz, 1H, 6-H^{ex}], 4.05 [m, 1H, 3-H], 4.46 [m, 1H, 4-H], 4.68 [dd, ^3J(6-H^{ex}/5-H) = 8.5 Hz, ^3J(6-H^{en}/5-H) = 13 Hz, 1H, 5-H], 4.95 (s, 1H, 8-H), 5.03 (s, 1H, 8-H′). IR (film): $\nu = 2920$ cm^{-1}, 2062, 1990, 1981, 1582. MS (EI, 70 eV): *m*/*z* (%) = 291 (3) [M$^+$], 263 (20), 237 (62), 207 (100), 191 (40), 167 (43), 148 (38). Anal. Calc. for $C_{12}H_{13}FeNO_4$ (291.1): C, 49.51; H, 4.50; N, 4.81. Found: C, 49.11; H, 4.33; N, 5.04.

5c: $t_R = 30.02$ min, $R_f = 0.64$ (diethyl ether), yellow solid of m.p. 111 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.81$ (s, 3H, 7-Me), 2.65 (s, 3H, NMe), 3.25 [d, ^2J(3-H^{en}/3-H^{ex}) = 12.45 Hz, 1H, 3-H^{en}], 3.44 [dd, ^3J(3-H^{ex}/4-H) = 6.8 Hz, ^2J(3-H^{en}/3-H^{exo}) = 12.45 Hz, 1H, 3-H^{ex}], 4.25 [dd, ^3J(4-H/3-H^{ex}) = 6.8 Hz, ^3J(5-H/4-H) = 7.8 Hz, 1H, 4-H], 4.48 [d, ^3J(5-H/6-H) = 12.7 Hz, 1H, 6-H], 4.93 [dd, ^3J(5-H/6-H) = 12.7 Hz, ^3J(5-H/4-H) = 7.8 Hz, 1H, 5-H], 5.14 [d, ^2J(8-H/8-H′) = 1.47 Hz, 1H, 8-H], 5.36 [d, ^2J(8-H/8-H′) = 1.47 Hz, 1H, 8-H′]. ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 17.5$ (7-Me), 30.9 (NMe), 49.9 (C-3), 61.3 (C-4), 86.3 (C-6), 89.1 (C-5), 118.2 (C-8), 141.4 (C-7), 201.5, 205.1, 206.7, 210.8 (FeCO). IR (film): $\nu = 2923$ cm^{-1}, 2062, 1986, 1980, 1582. MS (EI, 70 eV): *m*/*z* (%) = 291 (4) [M$^+$], 263 (23), 235 (62), 207 (100), 191 (53), 167 (50). Anal. Calc. for $C_{12}H_{13}FeNO_4$ (291.1): C, 49.51; H, 4.50; N, 4.81. Found: C, 49.46; H, 4.41; N, 4.71.

3.3. Reactions of (±)-E-[(4-6-η³)-3-methoxycarbonyl-hexa-2,5-diene-4-yl]tricarbonyl-iron(II) tetrafluoroborate (**3**) with nucleophiles

3.3.1. DFT calculations

The density functional single point calculations were performed with the Gamess 2001 suite of programs [14] using the geometry as obtained from the X-ray single crystal structural analysis and the B3LYP [15,16] density functional and a split valence basis set [17], augmented with standard polarization functions on the non-hydrogen atoms [18]. Table 2 lists the most significant Mulliken charges and orbital coefficients (in the LUMO and the nearest unoccupied MO) at the allyl ligand and vinyl residue. $E_{HOMO} = -9.333$ eV, $E_{LUMO} = -9.142$ eV, $E_{LUMO+1} = -8.992$ eV, $E_{LUMO+2} = -8.975$ eV.

3.3.2. (4-Methoxycarbonyl-hexa-2Z,4E-dienyl)-triphenylphosphonium tetrafluoroborate (**8a**)

To a suspension of **3** (300 mg, 0.82 mmol) in CH_3CN (30 mL) was dropped a solution of Ph_3P (215 mg, 0.82 mmol) in CH_3CN (10 mL) at r.t. via a cannula. The mixture was stirred at r.t. for 16 h. All volatile components were removed on a rotary evaporator and the remainder purified by column chromatography on silica gel 60. Impurities were first washed off with diethyl ether, then with CH_2Cl_2/CH_3CN (5:1, v:v). The product was finally eluted with CH_2Cl_2/CH_3CN (1:1, v:v) and obtained as colourless crystals upon evaporation. Yield: 280 mg (70%); m.p. 166 °C (decomp.); $R_f = 0.82$ (CH_2Cl_2/

Table 2
Calculated Mulliken charges and frontier orbital coefficients on the allyl and vinyl moieties of **3**

	C-4	C-5	C-6	C-3	C-7
Mulliken charge	4.989	1.176	2.721	5.922	6.004
LUMO; s-coefficients	0.005	−0.031	−0.005	0.000	0.000
	0.015	−0.045	−0.015	−0.001	−0.000
	−0.052	−0.010	0.038	0.001	0.002
	0.091	0.413	−0.036	0.037	−0.005
	1.872	0.272	−0.142	0.037	−0.174
LUMO; p_x-coefficients	0.004	−0.142	0.170	−0.010	0.002
	−0.339	−0.218	−0.155	0.097	0.011
	−0.686	−0.547	0.775	0.160	0.065
LUMO; p_y-coefficients	0.002	0.091	−0.103	−0.002	0.001
	0.134	0.229	0.013	0.077	−0.044
	0.244	0.097	0.619	−0.587	−0.017
LUMO; p_z-coefficients	0.005	0.009	0.006	−0.004	0.002
	−0.150	−0.135	0.089	0.021	−0.023
	0.414	0.561	−0.606	−0.096	−0.006
LUMO + 1; s-coefficients	0.000	0.008	−0.007	0.000	0.000
	0.000	0.013	−0.009	−0.002	−0.000
	0.001	−0.008	−0.010	0.007	0.001
	−0.027	−0.061	0.129	−0.011	−0.003
	0.036	−0.214	0.075	0.006	−0.034
LUMO + 1; p_x-coefficients	0.002	0.030	−0.033	−0.002	−0.000
	0.006	0.005	−0.007	0.037	0.012
	0.088	0.006	0.047	0.064	0.020
LUMO + 1; p_y-coefficients	0.001	−0.019	−0.023	0.000	0.000
	−0.020	−0.020	0.036	0.001	−0.013
	0.020	−0.067	0.008	0.082	−0.086
LUMO + 1; p_z-coefficients	0.003	0.017	−0.025	0.001	0.000
	−0.004	0.071	−0.065	−0.008	−0.004
	−0.066	0.027	0.003	−0.005	−0.010

CH_3CN 1:1, v:v). ^{1}H NMR (270 MHz, acetone-D_6): $\delta = 1.83$ [d, ^3J(6-H/5H) = 7.29 Hz, 3H, 6-H], 3.63 [s, 3H, OMe], 4.30 [ddd, ^2J(1-H/P) = 16.05 Hz, ^3J(1-H/2-H) = 7.50 Hz, ^4J(1-H/3-H) = 1.50 Hz, 2H, 1-H], 5.78 [dt, ^3J(2-H/1-H) = 7.50 Hz, ^3J(2-H/3-H) = 11.15 Hz, 1H, 2-H], 6.40 [dt, ^3J (3-H/2-H) = 11.15 Hz, ^4J(1-H/3-H) = 1.50 Hz, 1H, 3-H], 7.00 [q, ^3J(5-H/6-H) = 7.29 Hz, 1H, 5-H], 7.72–8.04 [m, 15H, Ph]. ^{13}C NMR (125 MHz, acetone-D_6): $\delta = 14.4$ (C-6), 24.6 [d, ^1J(C/P) = 52.2 Hz, C-1], 53.1 (OMe), 119.0 [d, ^1J(C-*ipso*/P) = 86.2 Hz, C-*ipso*], 120.2 (C-2), 128. 9 (C-4), 131.2 (C-*ar*), 131.9 (C-5), 134.9, 136.1 (C-*ar*), 142.4 (C-3), 166.6 (C═O). ^{31}P NMR (121.4 MHz, acetone-D_6): $\delta = 22.4$. IR (film): $\nu = 3064$ cm^{-1}, 2953, 1768, 1713, 1440, 1253, 1170, 1113, 1059, 997. MS (EI): m/z (%) = 401 (1) [M^+], 368 (17), 262 (100), 183 (54), 108 (18). Anal. Calc. for $C_{26}H_{26}O_2BF_4P$ (488.27): C, 63.96; H, 5.37. Found: C, 64.12; H, 5.44.

3.3.3. Methyl (2E,3Z)-2-ethylidene-5-phenylpent-3-enoate (**8b**)

3.3.3.1. From PhMgBr. To a suspension of **3** (250 mg; 0.68 mmol) in THF (30 mL) a solution of PhMgBr (680 μl, 1.0 M in THF; 0.68 mmol) in THF (10 mL) was slowly added at −40 °C via a cannula. The mixture was allowed to warm to r.t. and stirred for another 16 h. All volatile components were removed in vacuo and the residue was purified by column chromatography (silica gel 60; pentane/diethyl ether 10:1, v:v). 96 mg (65%), $R_f = 0.57$ (pentane/diethyl ether 10:1, v:v), pale yellow oil.

3.3.3.2. From Ph_2CuMgI. A solution of PhMgBr (1.0 M in THF, 1.80 mL; 1.80 mmol) was dropped to a suspension of CuI (171 mg; 0.90 mmol) in THF (10 mL) at −10 °C. The reaction mixture was stirred at −10 °C until all CuI got dissolved and the color changed from colourless to grey. It was cooled to −30 °C and transferred to a suspension of **3** (293 mg; 0.80 mmol) in THF (10 mL) via a cannula. The mixture was allowed to warm to r.t. and stirred for another 16 h. Work-up as described above yielded 131 mg (76%).

^{1}H NMR (270 MHz, C_6D_6): $\delta = 1.42$ [d, ^3J(1′-H/2′-H) = 7.29 Hz, 3H, 2′-H], 3.11 [d, ^3J(5-H/4-H) = 7.29 Hz, 2H, 5-H], 3.42 [s, 3H, OMe], 5.73 [dt, ^3J(4-H/5-H) = 7.29 Hz, ^3J(4-H/3-H) = 11.15 Hz, 1H, 4-H], 6.09 [d, ^3J(3-H/

4-H) = 11.15 Hz, 1H, 3-H], 6.98 [q, ^3J(1′-H/2′-H) = 7.29 Hz, 1H, 1′-H], 6.93–7.22 [m, 5H, Ph]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.8 (C-2′), 36.0 (C-5), 51.7 (OMe), 123.8 (C-3), 126.7, 126.9, 129.1, (C-*ar*), 130.8 (C-2), 133.6 (C-1′), 140.0 (C-4), 140.8 (C-*ipso*), 166.8 (C-1). IR (film): ν = 3024 cm^{-1}, 2948, 1717, 1436, 1250, 1129, 1049. MS (EI): *m*/*z* (%) = 216 (80) [M$^+$], 201 (10), 184 (70), 157 (70), 141 (100), 129 (42), 115 (30), 104 (18), 91 (48). Anal. Calc. for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 77.58; H, 7.52.

3.3.4. Tricarbonyl[methyl(2-4-η^4)-2-isopropyl-penta-2Z,4-dienoate]iron(0) (**9a**)

To a suspension of CuI (162 mg, 0.85 mmol) in diethyl ether (10 mL) a solution of MeLi (0.91 M in hexane, 1.876 mL; 1.70 mmol) was dropwise added at −10 °C. The resulting mixture was stirred at this temperature until it had turned clear and greyish. It was cooled to −78 °C and transferred to a suspension of 3 (366 mg, 1.00 mmol) in THF (50 mL) via a cannula. This mixture was then allowed to warm to r.t. and stirred for another 16 h. All volatile components were removed in vacuo and the crude purified by column chromatography (silica gel 60; pentane/diethyl ether 10:1, v:v) to leave 170 mg (68 %) of pure **9a** as a yellow oil; R_f = 0.47 (pentane/diethyl ether 10:1, v:v). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.94 [dd, ^2J(5-H^{en}/5-H^{ex}) = 3.64 Hz, ^3J(5-H^{en}/4-H) = 9.43 Hz, 1H, 5-H^{en}], 1.06 [d, ^3J(7-H/6-H) = 6.86 Hz, 3H, 7-H], 1.25 [d, ^3J(7-H′/6-H) = 6.86 Hz, 3H, 7-H′], 1.59–1.74 [sep, ^3J(6-H/7-H) = 6.86 Hz, 1H, 6-H], 1.89 [dd, ^2J(5-H^{ex}/5-H^{en}) = 3.64 Hz, ^3J(5-H^{ex}/4-H) = 7.51 Hz, 1H, 5-H^{ex}], 3.54 [s, 3H, OMe], 5.16 [d, ^3J(3-H/4-H) = 5.15 Hz, 1H, 3-H], 5.31 [ddd, ^3J(4-H/3-H) = 5.15 Hz, ^3J(4-H/5-H^{en}) = 9.43 Hz, ^3J(4-H/5-H^{ex}) = 7.51 Hz, 1H, 4-H]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.2 (C-7), 23.7 (C-7'), 39.6 (C-6), 40.6 (C-5), 51.3 (OMe), 77.9 (C-2), 87.8 (C-4), 88.4 (C-3), 171.5 (C-1), 210 (FeCO). IR (film): ν = 2960 cm^{-1}, 2056, 1986, 1708, 1457, 1357, 1262, 1194, 1155, 1022. MS (EI): *m*/*z* (%) = 293 (30) [M$^+$-1], 238 (10), 210 (30), 167 (13), 149 (100). Anal. Calc. for $C_{12}H_{14}O_5Fe$ (294.09): C, 49.01; H, 4.80. Found: C, 48.86; H, 4.82.

3.3.5. Tricarbonyl[methyl(2-4-η^4)-2-(1′-methyl)pentyl-penta-2Z,4-dienoate]iron(0) (**9b**)

151 mg (60 %) from **3** (293 mg) and a reagent obtained from BuLi (1.12 M in hexane, 1.34 mL; 1.50 mmol) and CuI (143 mg, 0.75 mmol) as described above. Yellow oil, R_f = 0.41 (pentane/diethyl ether 10:1, v:v). ^{1}H NMR (270 MHz, C_6D_6): δ = 0.93 [t, ^3J(11-H/10-H) = 7.08 Hz, 3H, 11-H], 0.99 [d, ^3J(7-H/6-H) = 6.86 Hz, 3H, 7-H], 1.12–1.44 (m, 6H, 10-H, 9-H, 8-H), 1.50 [dd, ^2J(5-H^{ex}/5-H^{en}) = 3.00 Hz, ^3J(5-H^{ex}/4-H) = 7.50 Hz, 1H, 5-H^{ex}], 1.76–1.89 (m, 2H, 5-H^{en}, 6-H), 3.15 (s, 3H, OMe), 4.51 [d, ^3J(3-H/4-H) = 5.15 Hz, 1H, 3-H], 4.63 [ddd, ^3J(4-H/3-H) = 5.15 Hz, ^3J(4-H/5-H^{en}) = 9.43 Hz, ^3J(4-H/5-H^{ex}) = 7.50 Hz, 1H, 4-H]. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.5 (C-11), 21.3 (C-7), 23.6 (C-10), 31.8 (C-9), 38.6 (C-8), 41.4 (C-5), 45.8 (C-6), 51.4 (OMe), 80.8 (C-2), 89.2 (C-4), 89.9 (C-3), 172.0 (C-1), 210.4 (FeCO). IR (film): ν = 3025 cm^{-1}, 2949, 2361, 2049, 1980, 1717, 1437, 1250, 1195, 1130, 1049. MS (EI): *m*/*z* (%) = 334 (5) [M$^+$ − 2], 308 (4), 280 (25), 252 (100), 220 (10), 192 (16), 152 (16), 138 (25), 110 (13). Anal. Calc. for $C_{15}H_{20}O_5Fe$ (336.17): C, 53.59; H, 6.00. Found: C, 53.68; H, 6.07.

3.3.6. Tricarbonyl[methyl(4-6-η^4)-2,4-dimethoxycarbonyl-3-methyl-hepta-4Z,6-dienoate]iron(0) (**9c**)

A suspension of **3** (366 mg, 1.00 mmol) in THF (100 mL) was treated with dimethyl malonate (112 mg, 0.85 mmol) and BSA (0.865 mL, 3.50 mmol) and the resulting mixture was gently refluxed for 72 h. After removal of all volatile components in vacuo the crude product was purified by column chromatography (silica 60; pentane/diethyl ether 1:1, v:v; R_f = 0.51). Yield: 271 mg (66%), yellow oil. ^{1}H NMR (270 MHz, C_6D_6): δ = 0.97 [dd, ^2J(7-H^{en}/7-H^{ex}) = 2.79 Hz, ^3J(7-H^{en}/6-H) = 9.65 Hz, 1H, 7-H^{en}], 1.46 [dd, ^2J(7-H^{ex}/7-H^{en}) = 2.79 Hz, ^3J(7-H^{ex}/6-H) = 7.72 Hz, 1H, 7-H^{ex}], 1.63 [d, ^3J(3-H/3-Me) = 6.86 Hz, 3H, 3-Me], 2.67 [dq, ^3J(3-H/3-Me) = 6.86 Hz, ^3J(2-H/3-H) = 10.29 Hz, 1H, 3-H], 3.10 (s, 3H, OMe), 3.21 (s, 3H, OMe), 3.31 (s, 3H, OMe), 3.51 [d, ^3J(2-H/3-H) = 10.29 Hz, 1H, 2-H], 4.49 [ddd, ^3J(5-H/6-H) = 5.36 Hz, ^3J(6-H/7-H^{en}) = 9.65 Hz, ^3J (6-H/7-H^{ex}) = 7.72 Hz, 1H, 6-H], 5.44 [d, ^3J(5-H/6-H) = 5.36 Hz, 1H, 5-H]. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 21.7 (3-Me), 41.5 (C-7), 43.7 (C-3), 50.9 (C-2), 52.0 (OMe), 52.1 (OMe), 58.4 (OMe), 73.5 (C-4), 87.1 (C-6), 91.0 (C-5), 168.0, 168.1, 170.7 (COO), 210.1 (FeCO). IR (film): ν = 2953 cm^{-1}, 2056, 1976, 1736, 1711, 1435, 1249, 1146, 1021. MS (EI): *m*/*z* (%) = 354 (3) [M$^+$ − 2 CO], 326 (80), 295 (12), 226 (40), 196 (100), 157 (8), 138 (9). Anal. Calc. for $C_{16}H_{18}O_9Fe$ (410.16): C, 46.85; H, 4.42. Found: C, 46.94; H, 4.36.

3.3.7. X-ray crystal structure determination of (**9c**)

Formula $C_{16}H_{18}FeO_9$, molar mass 410.15 g mol^{-1}, crystal size 0.25 × 0.22 × 0.18 mm, a = 8.7302(17), b = 9.909(2), c = 11.878(2) Å, α = 78.35(3)°, β = 81.27(3)°, γ = 69.47(3)°, V = 938.9(3) Å^3, T = 293(2) K, d_{calc} = 1.451 g cm^{-3}, μ = 0.847 mm^{-1}, Z = 2, triclinic, space group P1, STOE IPDS I diffractometer, λ = 0.71073 Å, Θ-range 2.22–25.92°; $\omega\Phi$-scans, index ranges $-10 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 11$, $-14 \leqslant l \leqslant 14$, 3371 collected reflections, 2394 independent reflections [$1 > 2\sigma(1)$], 235 refined parameters, absorption correction by ψ-scans. Structure solution: direct methods (SHELXS 97), structure refinement: full-matrix least-squares on F^2 (SHELXL 97), H atoms calculated and not included into least-squares refinement, $R1 = 0.0455[w = 1/\sigma^2(F_0)]$,

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **9c**

Atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	0.04142(5)	0.14998(5)	0.15065(3)	0.0513(2)
O(1)	−0.1054(3)	0.4816(3)	0.3131(2)	0.0823(10)
O(2)	−0.2853(3)	0.4794(2)	0.19948(18)	0.0667(8)
O(3)	−0.4452(3)	0.0993(3)	0.5815(2)	0.0744(9)
O(4)	−0.6285(2)	0.2896(2)	0.48718(19)	0.0624(8)
O(5)	−0.1120(3)	0.1866(2)	0.55840(16)	0.0557(7)
O(6)	−0.3190(3)	0.3848(2)	0.59859(18)	0.0617(8)
O(7)	−0.1568(4)	0.3441(3)	−0.0335(2)	0.1028(13)
O(8)	0.3253(4)	−0.0255(4)	0.0175(3)	0.1192(13)
O(9)	−0.0778(3)	−0.0996(3)	0.1927(2)	0.0735(9)
C(1)	0.1690(4)	0.2950(4)	0.1570(3)	0.0711(14)
C(2)	0.1835(4)	0.1887(4)	0.2562(3)	0.0593(10)
C(3)	0.0436(3)	0.1649(3)	0.3209(2)	0.0476(9)
C(4)	−0.1175(3)	0.2520(3)	0.2889(2)	0.0422(9)
C(5)	−0.1634(4)	0.4146(3)	0.2684(2)	0.0496(10)
C(6)	−0.3427(6)	0.6371(4)	0.1803(3)	0.0914(16)
C(7)	−0.2585(3)	0.1960(3)	0.3483(2)	0.0422(9)
C(8)	−0.3850(4)	0.2045(4)	0.2674(3)	0.0571(10)
C(9)	−0.3522(3)	0.2784(3)	0.4504(2)	0.0408(8)
C(10)	−0.4789(4)	0.2104(3)	0.5148(2)	0.0473(10)
C(11)	−0.7611(4)	0.2346(4)	0.5408(3)	0.0752(16)
C(12)	−0.2433(4)	0.2752(3)	0.5393(2)	0.0427(9)
C(13)	−0.2303(5)	0.3969(5)	0.6880(3)	0.0884(17)
C(14)	−0.0792(5)	0.2670(4)	0.0377(3)	0.0656(11)
C(15)	0.2160(5)	0.0429(5)	0.0688(3)	0.0755(14)
C(16)	−0.0334(4)	−0.0010(4)	0.1792(2)	0.0560(10)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U*ij* tensor.

*wR*2 = 0.1015, largest diff. peak and hole 0.525 and −0.196 e Å^{-3} (see Table 3).

3.3.8. Tricarbonyl[methyl(2-5-η^4)-2-vinyl-penta-2Z,4-dienoate]iron(0) (**10**)

3.3.8.1. General procedure. A suspension of KH (37 mg, 0.92 mmol) in THF (10 mL) was dropwise treated with the carbonyl compound (0.95 mmol) at r.t. and the resulting mixture was stirred until a clear solution was obtained (approx. 30 min). This solution was cooled to −78 °C and transferred through a cannula to a suspension of **3** (366 mg, 1.00 mmol) in THF (30 mL). The mixture was allowed to warm to room temperature and stirred for another 16 h. The crude product was purified on silica gel 60 with pentane/diethyl ether (5:1, v:v), $R_f = 0.58$. 189 mg (74%), yellow oil. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 1.14$ [dd, ^2J(5-H^{en}/5-H^{ex}) = 3.43 Hz, ^3J(5-H^{en}/4-H) = 9.65 Hz, 1H, 5-H^{en}], 1.56 [dd, ^2J(5-H^{ex}/5-H^{en}) = 3.43 Hz, ^3J(5-H^{ex}/4-H) = 7.72 Hz, 1H, 5-H^{ex}], 3.18 (s, 3H, OMe), 4.62 [ddd, ^3J(4-H/3-H) = 5.36 Hz, ^3J(4-H/5-H^{en}) = 9.65 Hz, ^3J(4-H/5-H^{ex}) = 7.72 Hz, 1H, 4-H], 4.77 [d, ^3J(3-H/4-H) = 5.36 Hz, 1H, 3-H], 4.86 [d, ^3J(2′-H^{ex}/1′-H) = 11.15 Hz, 1H, 2′-H^{ex}], 5.17 [d, ^3J(2′-H^{en}/1′-H) = 17.58 Hz, 1H, 2′-H^{en}], 5.87 [dd, ^3J(1′-H/2′-H^{ex}) = 11.15 Hz, ^3J(1′-H/2′-H^{en}) = 17.58 Hz, 1H, 1′-H]. ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 41.6$ (C-5), 51.7 (OMe), 67.7 (C-2), 85.8 (C-4), 89.3 (C-3), 112.0 (C-2′), 140.1 (C-1′), 170.2 (C-1), 210.3 (FeCO). IR (film): $\nu = 2952$ cm^{-1}, 2058, 1990, 1712, 1436, 1325, 1288, 1188, 1155. MS (EI): *m*/*z* (%) = 278 (1) [M$^+$ − 2], 250 (20), 222 (63), 194 (100), 184 (33), 164 (29), 156 (35), 141 (68), 136 (82), 115 (20). Anal. Calc. for $C_{11}H_{10}O_5Fe$ (280.06): C, 47.18; H, 3.60. Found: C, 47.09; H, 3.52.

4. Supplementary material

Crystallographic data for the structures of **4b** and **9c** have been deposited with the Cambridge Crystallographic Data Centre [CCDC Nos. 222040 (**4b**), 222041 (**9c**)]. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code+(1223) 336-033, e-mail: teched@chemcrys.cam.ac.uk).

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