

Note

Reactivity of acyclic (pentadienyl)iron(1 +) cations with weak carbon nucleophiles

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This paper is dedicated to Professor Myron Rosenblum on the occasion of his 75th birthday

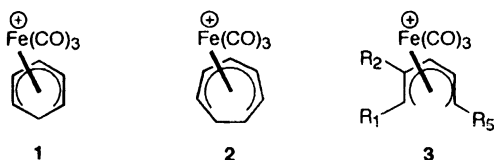
Abstract

The reaction of acyclic tricarbonyl(pentadienyl)iron(1 +) cations with allyl trimethylsilane or with excess furan leads to (*E,E*-diene)iron complexes. Attack of these weak nucleophiles on the transoid form of the pentadienyl cation is presumably faster than attack on the more stable cisoid form. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbonyl iron complexes; Dienyl; Nucleophilic attack

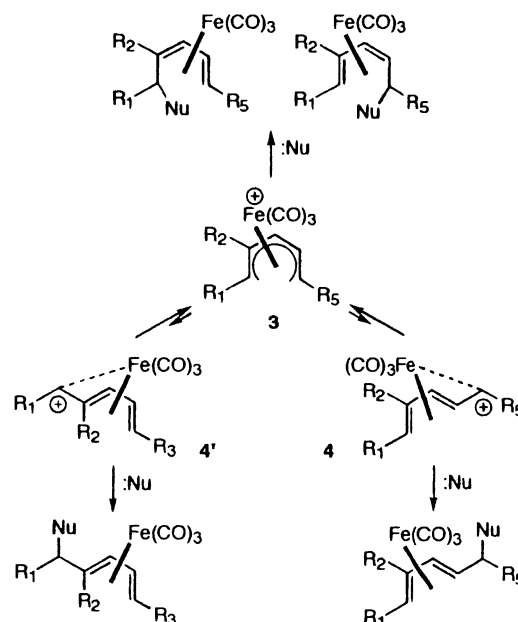
1. Introduction

The reactivity of (cyclohexadienyl)-, (cycloheptadienyl)-, and acyclic (pentadienyl)iron cations (**1–3**) with carbon and heteroatom nucleophiles has been extensively examined for the past two decades [1]. The regioselectivity for nucleophilic attack on these cations is dependent on the nature of the nucleophile, on the substituents present on the dienyl ligand, and on the peripheral ligands about the iron metal.



In solution, the acyclic (pentadienyl)iron cations **3** are known to exist in an equilibrium between the cisoid form (i.e. **3**) and the corresponding less stable transoid

form (i.e. **4** and **4'**, Scheme 1) [2]. Nucleophilic attack directly on the cisoid cation **3** generates *Z*-diene com-



Scheme 1.

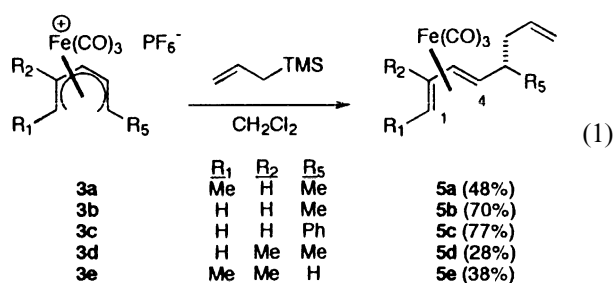
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plexes, while nucleophilic attack on the transoid cation **4** or **4'** gives *E*-diene products. Thus, reactions of cations **3** with nucleophiles are subject to inquiry concerning both regioselectivity and diene stereoselectivity. In general, the reaction of cations **3** with water and other heteroatom nucleophiles occurs via attack on the transoid form **4** to afford substituted *E*-diene products [3]. In contrast, reaction of cations **3** with carbanion nucleophiles or organometallic reagents proceeds via attack on the cisoid form to give *Z*-diene products [4]. There are only a few reports of the reaction of cations **3** with electron rich aromatics [5] or with allylsilanes [6]. The reaction of (cyclohexadienyl)Fe(CO)₃⁺ cations with allyl trimethylsilane [7] or with furan [8] has previously been reported. Herein we report on the reactivity of acyclic (pentadienyl)Fe(CO)₃⁺ cations **3a–h** with these two nucleophiles.

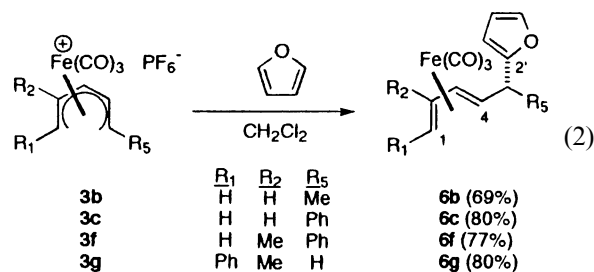
2. Results [9]

The substituted (pentadienyl)iron cations **3a–h** were prepared by literature procedures [3a–c,10]. The reaction of cations **3a–e** with allyl trimethylsilane gave the corresponding trienyl complexes **5a–e** in fair to good yields (Eq. (1)). The structure of **5a** was assigned by comparison of its ¹H-NMR spectral data with the literature values [6a]. The structures for **5b–e** were assigned on the basis of their ¹H-NMR spectral data (Table 1). The signals for the proton at C4 of **5b, d**, and **e** are similar to those for **5a**. For complexes **5b, c**, and **d**, the signals for the *endo*-methylene proton at C1 appear at ca. δ 0.24–0.30 ppm, which is characteristic of a (1,3*E*-diene)iron complex. The relative configuration of **5b–d** was assigned by analogy to **5a**.



The reaction of cations **3b, c, f**, and **g** with furan (ca. 10 equivalents) gave the corresponding 5-(2'-furyl)-1,3-diene complexes **6b, c, f**, and **g** in good yields (Eq. (2)). The structural assignments for complexes **6** are based on their ¹H- and ¹³C-NMR spectral data (Tables 1 and 2). In particular, signals at ca. δ 7.3, 6.3–6.2, and 6.1–5.9 ppm in their ¹H-NMR spectra and at ca. δ 159, 141, 110, and 104 ppm in their ¹³C-NMR spectra are characteristic of a 2-substituted furan functionality [11]. For **6b** and **6c** (and similarly for **5b** and **5c**), ¹³C-NMR

signals at ca. δ 87 and 81 ppm are characteristic for the C3 and C2 carbons of (1,3*E*-diene)iron complexes while for **6f** and **6g**, ¹³C-NMR signals at ca. δ 99 and 86 ppm are characteristic for the C2 and C3 carbons of (2-methyl-1,3*E*-diene)iron complexes [12].



The reaction of (1-methoxycarbonylpentadienyl)-Fe(CO)₃⁺ (**3h**) with allyl trimethylsilane gave a mixture of nonatrienoate complexes *E,E*-**5h** and *E,Z*-**5h** in a 1:1.6 ratio (Scheme 2). Attempts to separate this mixture were unsuccessful. The structure of *E,E*-**5h** was assigned by comparison of its ¹H- and ¹³C-NMR spectral data with the literature values [13]. In comparison, the structural assignment for *E,Z*-**5h** was based on its NMR spectral data. In particular, the ¹H-NMR signals at δ 6.03 (dd) and 5.31 (dd), and the ¹³C-NMR signals at δ 92.4 and 86.0 ppm are characteristic of a (2*E*,4*Z*-dienoate)Fe(CO)₃ complex [10b]. In a similar fashion, the reaction of **3h** with excess furan gave an inseparable mixture of *E,E*-**6h** and *E,Z*-**6h** (1.7:1 ratio). The structures of these products were assigned by comparison of their NMR spectral data with that of *E,E*-**5h** and *E,Z*-**5h**.

3. Discussion

The reaction of cations **3a–g** with the weak nucleophiles allyl trimethylsilane or furan occurs in a highly diastereoselective fashion to afford *E*-diene products. While NMR spectroscopy reveals that the cations **3** exist prevalently as the cisoid structure in solution [3a,b,10], it would appear that reaction with weak carbon nucleophiles occurs via the less stable (but more reactive) transoid form of the cation [14]. For the unsymmetrically substituted pentadienyl cations, nucleophilic attack was found to occur in a regioselective fashion. For mono-substituted cations (R₁ = R₂ = H, i.e. **3b, c**) and 2,5-disubstituted cations (R₁ = H, i.e. **3d, f**) C–C bond formation occurs via nucleophilic attack at the *substituted* pentadienyl terminus. In contrast, for the 1,2-disubstituted cations (R₅ = H, i.e. **3e, g**) nucleophilic attack occurs at the *unsubstituted* pentadienyl terminus. For cations **3b–g**, two possible transoid pentadienyl cations, **4** or **4'**, may be considered (Scheme 1). For cations **b, c, d**, and **f** the transoid form **4** should be more stable than the isomeric structure **4'** due to the

Table 1
¹H-NMR spectral data for (diene)Fe(CO)₃ complexes ^a

Compound	H1	H2	H3	H4	H5	Other
5a	^b	1.39 (d, 3H)	^b	^b	0.81 (dd)	5.77 (m), 5.10–4.90 (m, 4H), 2.09 (t, <i>J</i> = 6.9, 2H), 1.39 (m), 1.06 (m & d, <i>J</i> = 6.8, 4H))
5b	0.24 (dd)	<i>J</i> = 6.0 1.70 (dd)	^b	^b	<i>J</i> = 7.3, 9.8 0.86 (dd)	5.79 (m), 5.20 (m, 2H), 5.00 (m, 2H), 2.12 (t, <i>J</i> = 6.8, 2H), 1.44–1.39 (m), 1.08 (d, <i>J</i> = 6.1, 3H)
5c	<i>J</i> = 2.4, 8.4 0.30 (ddd)	<i>J</i> = 2.5, 6.6 1.68 (ddd)	5.22 (m)	5.34 (ddd)	<i>J</i> = 8.1, 9.8 1.21 (ddd)	7.74–7.18 (m, 5H), 5.76–5.62 (m), 5.04–4.98 (m, 2H), 2.52 (dd, <i>J</i> = 5.1, 10.2), 2.57–2.44 (m, 2H)
5d	<i>J</i> = 1.2, 2.5, 9.1 0.30 (d)	<i>J</i> = 1.0, 2.5, 6.8 1.76 (d)	2.16 (s, 3H)	<i>J</i> = 1.0, 4.9, 8.6 5.12 (d)	<i>J</i> = 0.7, 8.8, 8.8 0.63 (dd)	5.80 (tdd, <i>J</i> = 7.2, 10.3, 16.7), 5.00 (m, 2H), 2.10 (m, 2H), 1.42 (m), 1.07 (d, <i>J</i> = 6.7, 3H)
5e	<i>J</i> = 2.1 0.86 (q)	<i>J</i> = 2.1 1.42 (d, 3H)	2.12 (s, 3H)	<i>J</i> = 8.5 4.89 (d)	<i>J</i> = 8.5, 9.7 0.98 (m)	5.80 (tdd, <i>J</i> = 6.6, 10.1, 16.8), 5.05–5.00 (m, 2H), 2.10 (m), 1.73 (m), 1.63 (m, 2H)
<i>E,E</i> - 5h	<i>J</i> = 7.3 0.97 (dd)	<i>J</i> = 7.3 3.64 (s, 3H)	^b	<i>J</i> = 9.0 5.24 (dd)	1.36 (dq)	5.86–5.73 (m, 2H), 5.07 (qd, <i>J</i> = 1.6, 17.4), 5.02 (m), 2.27–2.12 (m, 2H), 1.82 (dtd, <i>J</i> = 6.5, 7.2, 14.7), 1.70 (dtd, <i>J</i> = 6.8, 7.3, 14.7)
<i>E,Z</i> - 5h	<i>J</i> = 1.0, 8.0 2.17 (d)	3.67 (s, 3H)	6.03 (dd)	<i>J</i> = 5.3, 8.6 5.31 (dd)	<i>J</i> = 1.0, 6.9 2.70 (br dt)	5.69 (tdd, <i>J</i> = 6.6, 10.3, 17.1), 5.05 (m, 2H), 2.40 (br q, <i>J</i> = 7.6), 2.27–1.98 (m, 2H), 1.82–1.65 (m)
6b	<i>J</i> = 8.3 0.34 (dd)	1.77 (dd)	<i>J</i> = 5.4, 8.2 5.26 (m)	<i>J</i> = 5.4, 7.6 5.43 (m)	<i>J</i> = 4.6, 8.3 1.04 (dd)	7.32 (dd, <i>J</i> = 0.7, 1.9), 6.31 (dd, <i>J</i> = 1.9, 3.2), 6.01 (dd, <i>J</i> = 0.7, 3.2), 2.70 (m), 1.45 (d, <i>J</i> = 6.8, 3H)
6c	<i>J</i> = 2.2, 9.3 0.44 (dd)	<i>J</i> = 2.2, 7.1 1.68 (dd)	5.30 (m)	5.59 (dd)	<i>J</i> = 8.5, 8.5 1.46 (br t)	7.3–7.2 (m, 6H), 6.22 (dd, <i>J</i> = 1.9, 3.2), 5.94 (dd, <i>J</i> = 1.0, 3.2), 3.88 (d, 10.3), 1.68 (dt, <i>J</i> = 1.2, 6.9)
6f	<i>J</i> = 1.2, 9.3 0.41 (d)	<i>J</i> = 1.2, 6.9 1.76 (d)	2.13 (s, 3H)	<i>J</i> = 4.8, 8.3 5.43 (d)	<i>J</i> = 9.3 1.13 (dd)	7.3–7.2 (m, 6H), 6.24 (dd, <i>J</i> = 1.9, 3.2), 5.95 (d, <i>J</i> = 3.2), 3.75 (d, <i>J</i> = 10.3)
6g	<i>J</i> = 2.1 1.88 (s)	<i>J</i> = 2.1 7.3–7.1 (m)	2.37 (s, 3H)	<i>J</i> = 10.3 5.19 (d)	<i>J</i> = 8.1, 10.3 1.30 (m)	7.34 (dd, <i>J</i> = 0.7, 1.9), 6.31 (dd, <i>J</i> = 1.9, 3.2), 6.07 (dd, <i>J</i> = 0.7, 3.2), 2.96 (d, <i>J</i> = 7.3), 2.95 (d, <i>J</i> = 6.8)
<i>E,E</i> - 6h	1.02 (d)	3.64 (s, 3H)	5.81 (dd)	<i>J</i> = 8.3 5.36 (dd)	1.51 (ddd)	7.35 (dd, <i>J</i> = 0.7, 1.9), 6.30 (dd, <i>J</i> = 1.9, 3.2), 6.00 (dd, <i>J</i> = 0.7, 3.2), 3.05 (dd, <i>J</i> = 6.7, 15.7), 2.85 (m)
<i>E,Z</i> - 6h	<i>J</i> = 8.3 2.24 (d)	3.69 (s, 3H)	<i>J</i> = 5.1, 8.1 6.09 (m)	<i>J</i> = 5.1, 8.8 5.36 (dd)	<i>J</i> = 6.6, 7.6, 8.3 2.96 (m)	7.30 (dd, <i>J</i> = 0.7, 1.9), 6.27 (dd, <i>J</i> = 1.9, 3.2), 6.00 (dd, <i>J</i> = 0.7, 3.2), 2.85 (m), 2.41 (dd, <i>J</i> = 9.3, 15.7)
	<i>J</i> = 8.8			<i>J</i> = 5.1, 8.1		

^a In ppm downfield from SiMe₄ (multiplicities: d = doublet, t = triplet, q = quartet, br = broad); coupling in Hz; integration equals 1H unless otherwise indicated; CDCl₃ solution; 300 MHz.

^b Peak is obscured by other multiplets (listed in 'other').

stabilizing effect of a methyl or phenyl group present on the carbon bearing the greatest partial positive charge. For the cations **e** and **g**, the transoid cation **4** should be more stable than the isomeric form **4'**, due to

the unfavorable steric interactions present where R₂ is the more bulky methyl group (compared to hydrogen). Thus, in all cases the concentration of transoid cation **4'** should be less than that of transoid cation **4**.

Table 2

¹³C-NMR spectral data for (diene)Fe(CO)₃ complexes^a

Compound	C1	C2	C3	C4	Other
5a	57.3	84.3 ^b	83.0 ^b	70.9 ^b	136.3 (C=C), 116.5 (C=CH ₂), 44.3, 38.9, 22.4, 19.2
5b	39.7	80.9	87.4	72.0	212.1 (M-CO), 136.3 (C=C), 116.5 (C=CH ₂), 44.2, 38.9, 22.4
5c	39.5	81.0	87.3	69.8	211.4 (M-CO), 136.0 (C=C), 116.7 (C=CH ₂), 144.7, 128.5, 126.9, 126.5 (4 × Ar), 51.5, 44.7
<i>E,E</i> - 5h	45.9	87.5	83.4	64.8	173.3 (CO ₂ R), 137.3 (C=C), 116.0 (C=CH ₂), 51.8 (OMe), 36.0, 33.6
<i>E,Z</i> - 5h	45.6	92.4	86.0	60.6	173.2 (CO ₂ R), 136.1 (C=C), 115.4 (C=CH ₂), 51.5 (OMe), 36.7, 28.9
6b	40.0	81.7	87.5	67.9	212 (M-CO), 159.1, 141.2, 110.0, 103.5 (4 × furan), 37.8, 20.7
6c	39.8	81.8	87.6	65.8	212 (M-CO), 157.6, 141.7 ^b , 110.0, 105.8 (4 × furan), 141.9 ^b , 128.6, 127.5, 127.0 (4 × Ar), 49.8
6f	43.2	99.7	87.7	63.2	212 (M-CO), 158.0 ^c , 141.7, 110.0, 105.6 (4 × furan), 142.0 ^c , 128.5, 127.5, 127.0 (4 × Ar), 49.8, 22.7
6g	65.1	98.2	85.5	55.9	212 (M-CO), 154.7 ^c , 141.2, 110.2, 105.2 (4 × furan), 139.4 ^c , 129.4, 128.2, 126.3 (4 × Ar), 32.4, 19.8
<i>E,E</i> - 6h	45.8	86.8	83.5	60.8	172.4 (CO ₂ R), 154.7, 141.4, 110.1, 105.5 (4 × furan), 51.5 (OMe), 32.2
<i>E,Z</i> - 6h	46.0	93.2	85.4	56.7	173.0 (CO ₂ R), 154.6, 141.3, 110.2, 105.4 (4 × furan), 51.6 (OMe), 27.3

^a In ppm downfield from SiMe₄; CDCl₃ solution; 75 MHz.^b The assignments for these peaks may be interchanged.^c Quarternary carbon as assigned by APT.

For the methoxycarbonyl substituted pentadienyl cation **3h**, reaction with allyl trimethylsilane or furan occurs via nucleophilic attack on *both* the cisoid form **3h** and the transoid form **4h** (Scheme 3). No reaction occurs via the transoid form **4h'** since this is greatly destabilized due to the proximity of the ester substituent to the carbon bearing the greatest partial positive charge. The electron withdrawing ester substituent increases the electrophilicity of the cisoid form of the pentadienyl cation **3h** such that it is more nearly equal in reactivity to the transoid cation **4h**. Nucleophilic attack on **3h** occurs at the unsubstituted pentadienyl terminus since this site is better able to stabilize the partial positive charge. Notably, the reaction of cation **3h** with water results in the formation of (methyl 6-hydroxy-2*E*,4*Z*-hexadienoate)Fe(CO)₃, via attack on the cisoid form of the cation at the unsubstituted dienyl terminus [16].

In general, reaction of weak carbon nucleophiles with acyclic (pentadienyl)Fe(CO)₃⁺ cations occurs via the more reactive transoid form of the cation. The regioselectivity for this reaction is dictated by the more stable of the two possible transoid forms, **4** or **4'**.

4. Experimental

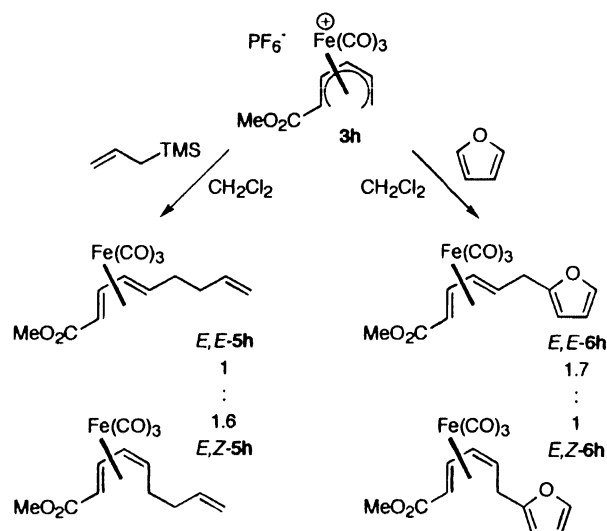
4.1. General data

All ¹H- and ¹³C-NMR spectra were recorded at 300 and 75 MHz respectively using a GE Omega GN-300 spectrometer. All IR spectra were recorded on either a Mattson 4020 FT-IR or a Nicolet 560 Magna-IR spectrophotometer. High resolution mass spectra were performed at the Nebraska Center for Mass Spectrometry. Methylene chloride was distilled from P₂O₅ followed by

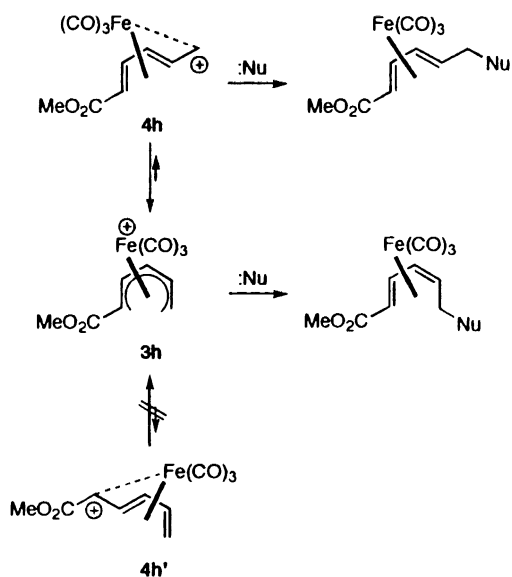
storing over activated molecular sieves. The substituted (pentadienyl)iron cations **3a–h** were prepared by literature procedures [3a–c,10].

4.2. General procedure for reaction of cations **3** with allyl trimethylsilane

To a suspension of **3** (0.2–0.5 mmol) in CH₂Cl₂ (ca. 5–20 ml) was added allyl trimethylsilane (1.5–2.0 mole equivalents). The reaction mixture was stirred at room temperature for 8–24 h and then treated with water and extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄) and concentrated. The residue was purified by column chromatography (SiO₂). The following compounds were prepared by the above procedure.



Scheme 2.



Scheme 3.

4.2.1. Tricarbonyl(6-methyl-2,4,8-nonatriene)iron (**5a**)

The reaction of **3a** (80 mg, 0.21 mmol) with allyl trimethylsilane (0.05 ml, 0.3 mmol) gave **5a** as a yellow oil (28 mg, 48%). The ¹H-NMR spectral data for this product were similar to the literature values [6a].

4.2.2. Tricarbonyl(5-methyl-1,3,7-octatriene)iron (**5b**)

The reaction of **3b** (185 mg, 0.500 mmol) with allyl trimethylsilane (0.15 ml, 0.95 mmol) gave **5b** as a yellow oil (100 mg, 70%). EI-HRMS *m/z* 262.0284 [calc. for C₁₂H₁₄O₃Fe *m/z* 262.0291]. IR (cm⁻¹, hexanes): 2047, 1978.

4.2.3. Tricarbonyl(5-phenyl-1,3,7-octatriene)iron (**5c**)

The reaction of **3c** (215 mg, 0.500 mmol) with allyl trimethylsilane (0.15 ml, 0.95 mmol) gave **5c** as a golden yellow oil (135 mg, 77%). EI-HRMS *m/z* 324.0457 [calc. for C₁₇H₁₆O₃Fe *m/z* 324.0447]. IR (cm⁻¹, hexanes): 2047, 1973.

4.2.4. Tricarbonyl(2,5-dimethyl-1,3,7-octatriene)iron (**5d**)

The reaction of **3d** (200 mg, 0.526 mmol) with allyl trimethylsilane (0.16 ml, 1.0 mmol) gave **5d** as a yellow oil (40 mg, 28%). IR (cm⁻¹, hexanes): 2045, 1970.

4.2.5. Tricarbonyl(7-methyl-1,5,7-nonatriene)iron (**5e**)

The reaction of **3e** (200 mg, 0.526 mmol) with allyl trimethylsilane (0.16 ml, 1.0 mmol) gave **5e** as a yellow oil (55 mg, 38%). EI-HRMS *m/z* 192.0596 [calc. for C₁₀H₁₆Fe (M⁺ - 3CO) *m/z* 192.0603]. IR (cm⁻¹, hexanes): 2040, 1970.

4.2.6. Tricarbonyl(methyl 2,4-8-nonatrienoate)iron (**5h**)

The reaction of **3h** (200 mg, 0.487 mmol) with allyl trimethylsilane (0.11 ml, 0.68 mmol) gave a golden yellow oil (130 mg, 88%). Examination of the ¹H-NMR spectrum of this product indicated that it consisted of a mixture of the known *E,E*-**5h** [13] and *E,Z*-**5h**. Integration of the signals at δ 5.24 and 5.31 ppm indicated that the ratio of stereoisomers *E,E*-**5h** and *E,Z*-**5h** was 1:1.6. FAB-HRMS *m/z* 306.0190 [calc. for C₁₃H₁₄O₅Fe *m/z* 306.0190]. IR (cm⁻¹, hexanes): 2059, 1990, 1720.

4.3. General procedure for reaction of cations **3** with excess furan

To a suspension of **3** (0.25–0.5 mmol) in CH₂Cl₂ (ca. 8–15 ml) was added excess furan (5.5 mmol). The reaction mixture was stirred at room temperature for 3–12 h and then treated with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄) and concentrated. The residue was purified by column chromatography (SiO₂). The following compounds were prepared by the above procedure

4.3.1. Tricarbonyl[5-(2'-furyl)-1,3-hexadiene]iron (**6b**)

The reaction of **3b** (185 mg, 0.500 mmol) with furan gave **6b** as a dark yellow oil (100 mg, 69%). EI-HRMS *m/z* 288.0084 [calc. for C₁₃H₁₂O₄Fe *m/z* 288.0085]. IR (cm⁻¹, neat): 2044, 1973.

4.3.2. Tricarbonyl[5-(2'-furyl)-5-phenyl-1,3-pentadiene]iron (**6c**)

The reaction of **3c** (215 mg, 0.500 mmol) with furan gave **6c** as a dark yellow oil (140 mg, 80%). EI-HRMS *m/z* 350.0246 [calc. for C₁₈H₁₄O₄Fe *m/z* 350.0240]. IR (cm⁻¹, neat): 2048, 1977.

4.3.3. Tricarbonyl[5-(2'-furyl)-2-methyl-5-phenyl-1,3-pentadiene]iron (**6f**)

The reaction of **3f** (110 mg, 0.250 mmol) with furan gave **6f** as a dark yellow oil (70 mg, 77%). EI-HRMS *m/z* 364.0399 [calc. for C₁₉H₁₆O₄Fe *m/z* 364.0396]. IR (cm⁻¹, neat): 2048, 1977.

4.3.4. Tricarbonyl[5-(2'-furyl)-2-methyl-1-phenyl-1,3-pentadiene]iron (**6g**)

The reaction of **3g** (220 mg, 0.500 mmol) with furan gave **6g** as a dark yellow oil (145 mg, 80%). EI-HRMS *m/z* 364.0398 [calc. for C₁₉H₁₆O₄Fe *m/z* 364.0396]. IR (cm⁻¹, neat): 2050, 1979.

4.3.5. Tricarbonyl[methyl 6-(2'-furyl)-2,4-hexadienoate]iron (**6h**)

The reaction of **3h** (250 mg, 0.500 mmol) with furan gave **6h** a dark yellow oil (140 mg, 86%). Integration of the signals at δ 5.81 and 6.09 ppm indicated that the ratio of stereoisomers *E,E*-**6h** and *E,Z*-**6h** was 1.7:1. EI-HRMS m/z 276.0079 [calc. for $C_{12}H_{12}O_4Fe$ ($M^+ - 2CO$) m/z 276.0084]. IR (cm^{-1} , neat): 2052, 1984, 1710.

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References

- [1] A.J. Pearson, Acc. Chem. Res. 13 (1980) 463. G.R. Stephenson, S.T. Astley, I.M. Palotai, P.W. Howard, D.A. Owen, S. Williams, in: K.H. Dötz, R.W. Hoffmann (Eds.), Organic Synthesis via Transition Metals, Vieweg, Braunschweig, 1991, p. 169. H.-J. Knölker, Synlett (1992) 371. W.A. Donaldson, Aldrichim. Acta, 30 (1997) 17.
- [2] T.S. Sorenson, C.R. Jablonski, J. Organomet. Chem. 25 (1970) C62.
- [3] (a) J.E. Mahler, R. Pettit, J. Am. Chem. Soc. 85 (1963) 3955; (b) J.E. Mahler, D.H. Gibson, R. Pettit, J. Am. Chem. Soc. 85 (1963) 3959; (c) R.S. Bayoud, E.R. Biehl, P.C. Reeves, J. Organomet. Chem. 150 (1978) 75; (d) G. Maglio, A. Musco, R. Palumbo, J. Organomet. Chem. 32 (1971) 127; (e) M.-C.P. Yeh, L.-W. Chuang, C.-C. Hwu, J.M. Sheu, L.C. Row, Organometallics 14 (1995) 3396; (f) H.-J. Bentele, K. Sunkel, W. Beck, J. Organomet. Chem. 549 (1997) 245.
- [4] (a) W.A. Donaldson, M. Ramaswamy, Tetrahedron Lett. 30 (1989) 1339; (b) W.A. Donaldson, P.T. Bell, M.-J. Jin, J. Organomet. Chem. 441 (1992) 449; (c) W.A. Donaldson, M.-J. Jin, Tetrahedron 49 (1993) 8787; (d) M.-C.P. Yeh, B.-A. Sheu, H.-W. Fu, S.-I. Tau, L.-W. Chuang, J. Am. Chem. Soc. 115 (1993) 5941.
- [5] T.G. Bonner, K.A. Holder, P. Powell, J. Organomet. Chem. 77 (1974) C37.
- [6] (a) M. Uemura, T. Minami, Y. Yamashita, K. Hiyoshi, Y. Hayashi, Tetrahedron Lett. 28 (1987) 641; (b) W.A. Donaldson, J. Organomet. Chem. 395 (1990) 187; (c) W.A. Donaldson, M.-J. Jin, Bull. Soc. Chim. Belg. 102 (1993) 297.
- [7] L.F. Kelly, A.S. Narula, A.J. Birch, Tetrahedron Lett. 21 (1980) 871.
- [8] L.A.P. Kane-Maguire, C.A. Mansfield, J. Chem. Soc. Chem. Commun. (1973) 540. C.A. Mansfield, K.M. Al-Kathumi, L.A.P. Kane-Maguire, J. Organomet. Chem. 71 (1974) C11.
- [9] All compounds shown are racemic mixture of enantiomers. Only one enantiomer has been diagrammed for clarity.
- [10] (a) W.A. Donaldson, M.-J. Jin, P.T. Bell, Organometallics 12 (1993) 1174; (b) C. Tao, W.A. Donaldson, J. Org. Chem. 58 (1993) 2134.
- [11] P. Crews, J. Rodriguez, M. Jaspars, Organic Structure Analysis, Oxford University Press, New York, 1998. R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, 5th edn., 1991.
- [12] B.E. Mann, B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, New York, 1981.
- [13] V. Prahlad, A.S. El-Ahl, W.A. Donaldson, Tetrahedron: Asymm. 11 (2000) 3091.
- [14] The alternative possibility, nucleophilic attack on the cisoid form of the pentadienyl ligand followed by an 'envelope-flip' isomerization [15], seems unlikely. In this mechanism, the *exo-endo* exchange occurs simultaneously at *both* ends of the diene ligand. For the products from **3a**, **3d**, and **3g**, this would require that the R_1 substituents possess the *Z*-configuration, instead of the observed *E*-configuration.
- [15] An 'envelope-flip' isomerization has been observed for (diene)CoCp complexes. B. Eaton, J.A. King Jr., K.P.C. Vollhardt, J. Am. Chem. Soc. 108 (1986) 1359.
- [16] J. Morey, D. Grée, P. Mosset, L. Toupet, R. Grée, Tetrahedron Lett. 28 (1987) 2959.