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SYNTHETIC STUDIES WITH IRON CARBONYL COMPLEXES. VERSATILE SYNTHESIS OF OLEFINIC SIDE-CHAINS TO A TRICARBONYL(CYCLOHEXADIENE)IRON(0) RING

BRIAN F.G. JOHNSON, JACK LEWIS, DAVID G. PARKER * and G. RICHARD STEPHENSON **

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

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Summary

Tricarbonyl(cyclohexadiene)iron(0) complexes bearing olefinic side-chains at the 2- or the 5-position have been prepared by a versatile route. Terminal olefins are isomerised to internal isomers. The presence of a methoxy substituent at the 2-position prevents isomerisation of the coordinated diene into conjugation with the olefin, so locking the side-chain at the 5-*exo*-position.

Introduction

Both alkyl cadmium [1] and alkynyl borate reagents [2] have in the past been used to prepare tricarbonyl(cyclohexadiene)iron(0) complexes with olefinic side-chains. Our interest in the relative reactivity of coordinated and uncoordinated olefins led us to consider ways in which series of such complexes might be produced by a versatile synthetic route.

Results and discussion

Tricarbonyl-5-*exo*-(acetonyl)cyclohexa-1,3-dieneiron(0), (I) was prepared by the literature method [3] and treated with methyl magnesium iodide to give tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (II) in 80% yield. Treatment of this complex with *p*-toluenesulphonic acid in refluxing benzene produced a mixture of dehydration products which were readily separated from tricarbonyl-2-(2-methyl-2-hydroxypropyl)cyclohexa-

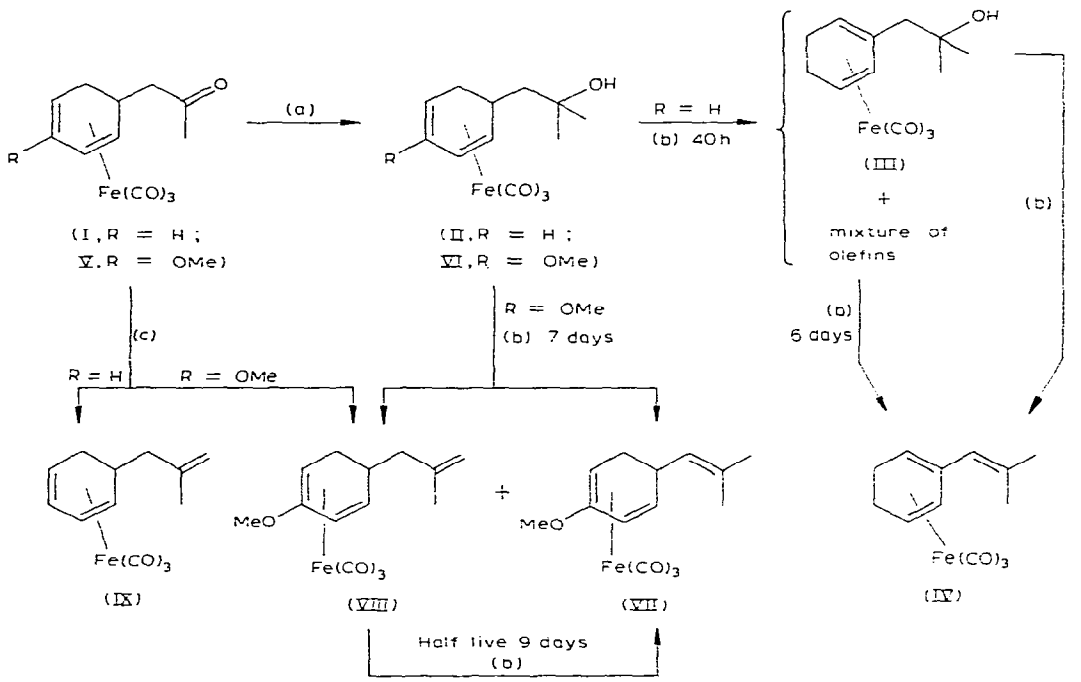
* Present address: ICI Petrochemicals Division, PO Box 90, Wilton, Middlesbrough, Cleveland 7S6 8JE (Great Britain).

** Research School of Chemistry, Australian National University, Canberra A.C.T. 2600 (Australia).

1,3-dieneiron(0) (III) on a short column of silica gel by elution with benzene. The dehydration products were shown by ^{13}C NMR to be a mixture of several positional isomers, but equilibration could be achieved by repeated treatment with *p*-toluenesulphonic acid in refluxing benzene, yielding tricarbonyl-2-(2-methyl-prop-1-enyl)cyclohexa-1,3-dieneiron(0) (IV) in high yield. Complex III could also be converted into complex IV by prolonged similar treatment.

Treatment of tricarbonyl(2-methoxycyclohexadienyl)iron tetrafluoroborate with acetone in refluxing ethanol resulted in the formation of tricarbonyl-5-*exo*-(acetonyl)-2-methoxycyclohexa-1,3-dieneiron(0) (V) in 71% yield after purification by chromatography. Complex V was treated with methylmagnesium iodide to produce the alcohol VI, tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)2-methoxycyclohexa-1,3-dieneiron(0), which was dehydrated as above. In this case the dehydration products proved to be a mixture of only two compounds, differing solely in the position of the double bond in the olefinic side-chain. The components of this mixture could not be separated, but were easily recognised by their ^{13}C NMR spectra. Equilibration of the mixture with *p*-toluenesulphonic acid in refluxing benzene was slow, having a half life of about 9 days. However, a 5/2 mixture of VII and VIII produced by dehydration of VI over a period of 7 days, was converted into a 6/1 mixture of olefins in a further 9 days. (The ratios are derived from ^{13}C NMR peak heights of C(6)). The major component of this mixture is assigned as tricarbonyl-5-*exo*-(2-methylprop-1-enyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VII) and is the major product of the dehydration reaction. The minor component of the mixture was synthesised unambiguously by a Wittig reaction. Triphenylmethylphosphonium bromide was converted to an ylid with n-butyllithium. An ether solution of the acetonyl derivative V was added dropwise to the orange reaction mixture resulting in almost immediate precipitation of triphenylphosphine oxide and formation of tricarbonyl-5-*exo*-(2-methylallyl)2-methoxycyclohexa-1,3-dieneiron(0) (VIII), which was readily separated from a small amount of starting material by column chromatography. The ^{13}C NMR peaks of VIII are identical to those of the minor component of the mixture of dehydration products, so confirming the assignment of both compounds. Pure VIII was converted by *p*-toluenesulphonic acid in refluxing benzene to a 1/1 mixture of VII and VIII in 9 days. No products with the olefinic side-chain at the 2-position were observed either for the dehydration or equilibration reactions, in contrast to the results obtained in the absence of the methoxy substituent.

Treatment of I with the phosphonium ylide successfully produced tricarbonyl-5-*exo*-(2-methylallyl)cyclohexa-1,3-dieneiron(0) (IX) in the same way. The ^{13}C NMR peaks of this compound were found to correspond to peaks in the spectrum of the mixture of dehydration products formed from II. This observation is of some importance since it indicates that the alcoholic complex III, isolated from the reaction mixture, is not an essential intermediate in the process, but rather that, since III itself can be dehydrated to form IV, the rearrangement of the diene system and the dehydration of the alcohol are the first steps of competing pathways for the formation of tricarbonyl-2-(2-methyl-prop-1-enyl)cyclohexa-1,3-dieneiron(0). This rearrangement to the 2-position brings the olefinic substituent into conjugation with the coordinated diene. Since C(2) of the diene unit shows greater sp^2 character than does C(1), as is



SCHEME 1. (a) MeMgI/diethyl ether; (b) *p*-toluenesulphonic acid, saturated solution in benzene at reflux; (c) Ph_3PMeBr/diethyl ether/BuLi.

demonstrated by the positions of their resonances in ^{13}C NMR and proton NMR spectra, rearrangement to bring the side-chain to this position is to be expected, so maximising conjugation.

However, the presence of a methoxy-group at C(2) of the cyclohexadiene ring allows rearranged complexes to be formed with the side-chain remaining in the 5-*exo*-position. Interaction of the methoxy oxygen with the coordinated π-system of the tricarbonyl(diene)iron complex is most thermodynamically advantageous at the 2-position [4]. This effect proves more powerful than movement into conjugation with the olefinic side-chain. The methoxy group serves to lock the side-chain in the 5-*exo*-position, allowing the formation of both terminal and internal positional isomers of the olefin. No evidence exists for rearrangement under these conditions to form complexes with an exocyclic double bond at C(5), even though this would be adjacent to the coordinated diene. Thus it is possible to prepare selectively by this method complexes which differ in the position of both the side chain and the double bond.

Experimental

Tricarbonyl-5-exo-(acetonyl)cyclohexa-1,3-dieneiron(0) (I)

This compound was prepared by the method of Birch [3].

Tricarbonyl-5-exo-(2-methyl-1-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (II)

Methyl iodide (2.5 g, 0.018 mol) in dry diethyl ether (15 ml) was added to

magnesium turnings (0.4 g, 0.017 mol) in dry ether (15 ml). After stirring under nitrogen for 1 h, tricarbonyl-5-*exo*-(acetonyl)cyclohexa-1,3-dieneiron(0) (I, 2.9 g, 0.01 mol) in ether (20 ml) was added slowly to the cloudy suspension of the Grignard reagent. Stirring was continued for 20 minutes. The mixture was poured into distilled water (200 ml) and extracted with ether (3 × 50 ml). The extracts were washed twice with water and dried over magnesium sulphate. After filtration, the yellow solution was reduced in volume and purified by chromatography on a short silica column. The product (II), a yellow oil (2.4 g, 0.008 mol, 80%), was obtained by elution with 2/1 petroleum (30—40)/diethyl ether. The oil solidified to form a yellow crystalline mass when the last of the solvent was removed under vacuum. Analysis: Found: C, 53.7; H, 5.74. $C_{13}H_{16}FeO_4$ calcd.: C, 53.5; H, 5.52%. Mass spectrum, *m/e*: 292 — 3 CO, —H_2, —H_2O.

Tricarbonyl-2-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (III)

Tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)cyclohexa-1,3-dieneiron(0) (II, 0.303 g, 1.04 mmol) was dissolved in a saturated solution of *p*-toluenesulphonic acid in dry benzene (50 ml), and heated under reflux for 40 h. The reaction mixture was filtered, when cool, through a 7 cm column of silica. The dehydration products were eluted with benzene, and a mixture of isomers was obtained as a yellow oil (0.132 g, 0.46 mmol, 46%) on removal of the solvent.

Further elution of the column, this time with diethyl ether, yielded (III) as a second yellow oil (0.146 g, 0.50 mmol, 48%). No further purification was required. Analysis: Found: C, 53.7; H, 5.72. $C_{13}H_{16}FeO_4$ calcd.: C, 53.5; H, 5.52%. Mass spectrum *m/e*: 292 — 3 CO, —H_2, —H_2O.

Tricarbonyl-2-(2-methylprop-1-enyl)cyclohexa-1,3-dieneiron(0) (IV)

The mixture of olefinic products from the above reaction (0.212 g, 0.77 mmol) were heated under reflux for 140 h in a saturated solution of *p*-toluenesulphonic acid in benzene (40 ml). When cool, the mixture was filtered under suction through a 5 cm column of silica; eluting with benzene, to yield (IV) (0.199 g, 0.73 mmol, 94%) as a mobile yellow oil on removal of solvent. Analysis: Found: C, 58.1; H, 5.65. $C_{13}H_{14}FeO_3$ calcd.: C, 57.0; H, 5.15%. Mass spectrum *m/e*: 274 — 3 CO, —H_2.

Tricarbonyl-5-exo-(acetonyl)-2-methoxycyclohexa-1,3-dieneiron(0) (V)

Tricarbonyl(2-methoxycyclohexadienyl)iron tetrafluoroborate (1.55 g, 4.6 mmol) was added to A.R. acetone (35 ml) in A.R. ethanol (55 ml). The mixture was heated under reflux with vigorous stirring for 5 h, allowed to cool, and poured into distilled water (200 ml) and extracted with diethyl ether (3 × 50 ml). The combined extracts were washed twice with distilled water, once with saturated brine, and then dried over magnesium sulphate. Careful chromatography on a 30 cm silica column yielded V (1.00 g, 3.3 mmol, 71%) as a rich buttercup yellow solid on removal of solvent. Analysis: Found: C, 51.3; H, 4.80. $C_{13}H_{14}FeO_5$ calcd.: C, 51.0; H, 4.61%. Mass spectrum *m/e*: 306 — 3 CO, —H_2, base peak at 164.

Tricarbonyl-5-exo-(2-methyl-2-hydroxypropyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VI)

Magnesium turnings (0.08 g, 3.3 mmol) were stirred with methyl iodide

(0.5 g, 3.5 mmol) in dry diethyl ether (20 ml) for 20 minutes. Tricarbonyl-5-*exo*-(acetonyl)-2-methoxycyclohexa-1,3-dieneiron(0) (V, 0.27 g, 0.88 mmol) in ether (20 ml), was added dropwise with an almost instantaneous reaction. The mixture was stirred for a further 20 minutes and then poured into 1 *N* hydrochloric acid (100 ml) and extracted with ether (3 × 50 ml). The combined extracts were washed twice with distilled water and dried over magnesium sulphate. The solution was reduced in volume and filtered through a short column of alumina (UG_1) and the solvent was removed in vacuo to yield VI (0.25 g, 0.78 mmol, 88%), as a golden yellow oil. Analysis: Found: C, 52.9; H, 5.86. $C_{14}H_{18}FeO_5$ calcd.: C, 52.2; H, 5.63%. Mass spectrum *m/e*: 322 — 3 CO, $-H_2O$, $-H_2$.

Reaction of tricarbonyl-5-exo-(2-methyl-2-hydroxypropyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VI) with p-toluenesulphonic acid in benzene

Tricarbonyl-5-*exo*-(2-methyl-2-hydroxypropyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VI, 0.439 g, 1.36 mmol) was dissolved in a saturated solution of *p*-toluenesulphonic acid in benzene (150 ml) and heated under reflux for 7 days. The volume was reduced to 40 ml, and the solution was filtered through an 8 cm column of silica, eluting with benzene to yield dehydration products (0.20 g, 0.66 mmol, 48%) which were shown by ^{13}C NMR to be a 5/2 mixture of tricarbonyl-5-*exo*-(2-methylprop-1-enyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VII) and tricarbonyl-5-*exo*-(2-methylallyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VIII). Further elution with ether gave unreacted starting material (0.19 g, 0.59 mmol, 43%), accounting for the low yield of dehydration products.

Tricarbonyl-5-exo-(2-methylprop-1-enyl)2-methoxycyclohexa-1,3-dieneiron(0) (VII)

The mixture of isomers obtained in the above reaction was heated under reflux in a saturated solution of *p*-toluenesulphonic acid in benzene (150 ml) for 9 days. The mixture when cool was filtered through silica and the solvent removed in vacuo. The ratio of the desired product was increased to 6/1. Repetition yielded an almost pure sample of VII with 60% recovery. Analysis: Found: C, 56.4; H, 6.09. $C_{14}H_{16}FeO_4$ calcd.: C, 55.3; H, 5.30%. Mass spectrum *m/e*: 304 — 3 CO, $-H_2$ base peak at 164.

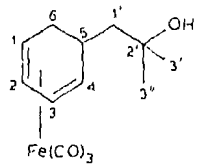
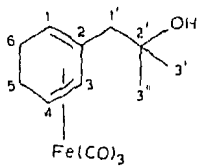
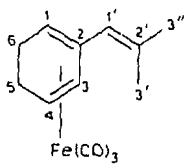
Tricarbonyl-5-exo-(2-methylallyl)2-methoxycyclohexa-1,3-dieneiron(0) (VIII)

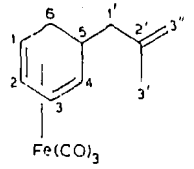
Methyltriphenylphosphonium bromide (1.1 g, 3.08 mmol) was suspended in diethyl ether (40 ml) and n-butyllithium (2.4 ml ether solution, 3.1 mmol) was added dropwise from a syringe. The mixture was heated gently under reflux for 30 minutes, by which time the phosphonium salt had been taken up to form a deep orange solution. Portions of this solution, when cool, were transferred by syringe to a second flask containing tricarbonyl-5-*exo*-(acetonyl)-2-methoxycyclohexa-1,3-dieneiron(0) (V, 0.289 g, 0.944 mmol) producing an immediate reaction marked by precipitation of triphenylphosphine oxide. Addition of the Wittig reagent was continued until no further change could be discerned, monitoring by TLC (at this point a small spot corresponding to the starting material still remained). The mixture was chilled in ice and filtered twice, washed three

(Continued on p. 75)

TABLE 1

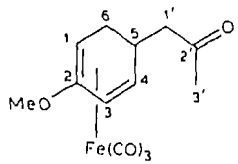
^{1}H AND ^{13}C NMR (in $CDCl_3$) AND INFRARED DATA FOR COMPOUNDS II–IX

Complex	Proton	Chemical shift τ(ppm)	Intensity	Multiplicity J(CH) (HZ)	Carbon	Chemical shift τ(ppm)	Multiplicity J(CH) (HZ)	IR (cm^{-1})
 (II)	H(2), H(3)	4.68	2	m	C(1)	60.0	d	cyclo-hexane
	H(1), H(4)	6.90	2	m	C(2)	84.1	d	2043
	HO	7.6		s	C(3)	85.6	d	1976
	H(5′)	7.8		m	C(4)	68.6	d	1972
	H(6′)	8.0	4	m	C(5)	34.4	d	
	H(6)	8.3		m	C(6)	32.5	t	liquid film
	H(1′)	8.58	2	m	C(1′)	54.0	t	3620
	H(3′), H(3″)	8.9	6	s	C(2′)	71.2	s	3420
					C(3′)	30.3	q	(br)
					C(3″)	29.8	q	
					C=O	211.9	s	
 (III)	H(3)	4.77	1	dd 6.2	C(1)	66.2	d	cyclo-hexane
	H(1), H(4)	6.85	2	m	C(2)	102.3	s	2042
	H(1′)	7.78	2	dd AB system [14]	C(3)	87.1	d	1973
		7.54			C(4)	59.6	d	1967
	H(5), H(6)	8.4	4	m	C(5)	23.7	t	assignment by
	HO	8.5	1	s	C(6)	24.3	t	off-resonance
	H(3′), H(3″)	8.68	6	s	C(1′)	52.1	t	decoupling
					C(2′)	71.3	t	3610
					C(3′)	29.2	q	3380
					C(3″)	29.8	q	(br)
					C=O	211.7	s	
 (IV)	H(1′)	4.26	1	m	C(1)	64.3	d	cyclo-hexane
	H(3′)	4.74	1	dd 7, 2	C(2)	102.5	s	2042
	H(1)	6.60	1	m	C(3)	85.5	d	assignment by 1974
	H(4)	6.91	1	d 7	C(4)	59.6	d	off resonance 1970
	H(3′)	8.09	3	d	C(5)	20.0	t	decoupling
	H(3″)	8.19	3	d	C(6)	26.4	t	liquid film
	H(5), H(6)	8.30	2	m	C(1′)	124.1	d	1655
					C(2′)	131.2	s	840
					C(3′)	24.2	q	
					C(3″)	24.0	q	
					C=O	211.8	s	



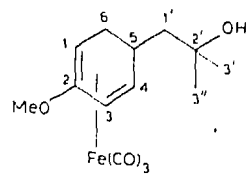
(IX)

H(2), H(3)	4.74	2	m	C(1)	59.9		cyclo-hexane
H(3″)	5.40	2	m	C(1)	84.2		2041
H(1), H(4)	6.95	2	m	C(3)	85.6		1974
H(5′)	7.85	1	m	C(4)	66.8		1970
H(1′)	8.10	2	s (br)	C(5)	35.8		
H(6′)	8.20	1	m	C(6)	30.6		liquid film
H(3′)	8.39	3	s (br)	C(1′)	48.7		1655
H(6)	8.50	1	m	C(2′)	144.3		895
				C(3′)	22.3		
				C(3″)	111.3		
				C=O	211.9		



(V)

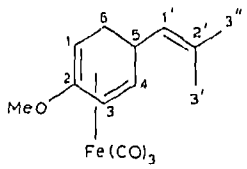
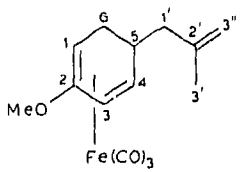
H(3)	5.00	1	dd 7, 2	C(1)	52.5	d 157	cyclo-hexane
MeO	6.41	3	s	C(2)	139.8	s —	2045
H(1)	6.75	1	m	C(3)	66.0	d 172	1975
H(4)	7.38	1	d 7	C(4)	54.1	d 156	1969
H(1′)	7.70	2	s	C(5)	33.0	d 142	
H(3′)	7.98	3	s	C(6)	31.9	t 131	liquid film
H(5′), H(6′)	8.63	2	m	C(1′)	53.5	t 127	1718
H(6)	8.85	1	m	C(2′)	207.1	s —	
				C(3′)	30.0	q 127 [a]	
				MeO	54.2	q 144 [a]	
				C=O	210.7	s —	



(VI)

H(3)	4.98	1	dd 2.2, 6.5	C(1)	52.8	d 156	cyclo-hexane
MeO	6.43	3	s	C(2)	139.4	s —	2043
H(1)	6.71	1	m	C(3)	66.1	d 172	1970
H(4)	7.27	1	dd 3, 6.5	C(4)	57.3	d 158	(br)
HO	7.75		s (br)	C(5)	33.9	d 130	
H(6′)	7.85		d	C(6)	33.4	t 132	liquid film
H(5′)	7.79	4	d 3	C(1′)	53.8	t 120	3620
H(6)	8.25		dd	C(2′)	71.1	s —	3420
H(1′)	8.5	2	m	C(3′)	30.3	q 137	(br)
H(3′), H(3″)	8.81	6	s	C(3″)	29.6	q 127	3620
				MeO	54.2	q 144 [a]	3420
				C=O	212.3	s —	(br)
							1231
							1030

TABLE 1 (continued)

Complex	Proton	Chemical shift τ(ppm)	Intensity	Multiplicity J(CH) (HZ)	Carbon	Chemical shift τ(ppm)	Multiplicity J(CH) (HZ)	IR (cm^{-1})
 (VII)	H(3)	5.00	1	dd	C(1)	53.3	d 155	cyclo-hexane
	H(1′)	5.38	1	d 8.5	C(2)	139.8	s —	2044
	MeO	6.43	3	s	C(3)	66.3	d 173	1973
	H(1)	6.72	1	m	C(4)	55.9	d 156	1970
	H(4)	7.45	1	m	C(5)	36.5	d 162	
	H(5′)	7.70	1	m	C(6)	32.9	t 125	liquid film
	H(6′)	8.15		m	C(1′)	131.5	d 162	1655
	H(3′)	8.39		d	C(2′)	130.3	s —	850
	H(3″)	8.45	10	d	C(3′)	25.5	q 131	
	H(6)	8.55		m	C(3″)	17.8	q 131	
					MeO	54.1	q 143 [a]	
					C=O	211.1	q —	
 (VIII)	H(3)	5.08	1	dd 2, 6.5	C(1)	52.8		cyclo-hexane
	H(3″)	5.45	2	m 2	C(2)	139.7	s	2043
	MeO	6.51	3	s	C(3)	66.3		1972
	H(1)	6.73	1	m	C(4)	55.5		1969
	H(4)	7.40	1	dd	C(5)	35.5		
	H(5′)	7.85	1	m	C(6)	31.4		liquid film
	H(1′)	8.15	2	s (br)	C(1′)	48.6	t 131 [b]	1650
	H(6′)	8.20	1		C(2′)	144.4	s —	895
	H(3′)	8.42	3	s (br)	C(3′)	22.3		
	H(6)	8.60	1	m	C(3″)	111.3	t 155 [b]	
					MeO	54.2		
					C=O	211.1		

[a] Sharp singlets. [b] From GG spectrum of mixture of VII and VIII.

times with saturated brine and dried over magnesium sulphate. Column chromatography, eluting with a 1/1 mixture of petroleum (30—40) and diethyl ether separated VIII (0.204 g, 0.669 mmol, 71%) from unchanged starting material (0.054 g, 0.176 mmol, 19%). Analysis: Found: C, 56.7; H, 5.60. $C_{13}H_{16}FeO_4$ calcd.: C, 55.3; H, 5.30%. Mass spectrum *m/e*: 304 — 3 CO, $-H_2$, base peak at 164.

Equilibration reaction starting with tricarbonyl-5-exo-(2-methylallyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VIII)

Tricarbonyl-5-*exo*-(2-methylallyl)-2-methoxycyclohexa-1,3-dieneiron(0) (VIII, 0.314 g, 1.03 mmol) was heated under reflux with a saturated solution of *p*-toluenesulphonic acid in benzene (150 ml) for 9 days. Filtration when cool through a short silica column, and removal of the solvent in vacuo left a 1/1 mixture of the (2-methylallyl) and (2-methylprop-1-enyl) complexes (0.187 g, 0.615 mmol, 60%).

Tricarbonyl-5-exo-(2-methylallyl)cyclohexa-1,3-dieneiron(0) (IX)

Methyltriphenylphosphonium bromide (0.7 g, 1.96 mmol) was suspended in dry diethyl ether (40 ml) and n-butyllithium (1.6 ml ether solution, 2.0 mmol) was added dropwise from a syringe. The reaction mixture was stirred at reflux for 15 minutes, and the resulting orange solution was allowed to cool. Tricarbonyl-5-*exo*-(acetonyl)cyclohexa-1,3-dieneiron(0) (I, 0.34 g, 1.23 mmol) was added slowly in ether solution (10 ml), with the immediate formation of a white precipitate. The mixture was heated under reflux for 40 minutes, chilled, and filtered twice. The filtrate was then washed with 3 portions of saturated brine and dried over magnesium sulphate. After reduction in volume IX (0.26 g, 0.94 mmol, 76%) was separated from a small quantity of unreacted starting material by chromatography on silica, eluting with 3/2 petroleum (30—40)/diethyl ether. Analysis: Found: C, 56.4; H, 5.60. $C_{13}H_{14}FeO_3$ calcd.: C, 57.0; H, 5.15%. Mass spectrum *m/e*: 274 — 3 CO, $-H_2$.

The ^1H and ^{13}C NMR and infrared data are gathered together in Table 1.

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