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The synthesis, characterization and some reactions of cationic η^2-(α,ω-diene) complexes of iron

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Abstract

The cationic iron η^2-(α,ω-diene) complexes of the type, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$, (diene = 1,3-butadiene; 1,4-pentadiene; 1,5-hexadiene; and 1,7-octadiene) were prepared by the reaction of η^1-alkenyl compounds of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-alkenyl})]$ with the so-called trityl salt, (Ph_3CPF_6). The reactions of the η^2-diene complexes with a number of nucleophiles give a range of products resulting from nucleophillic addition to the coordinated diene and/or displacement of the diene. The reaction with triethylamine results in deprotonation leading to the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-allyl})]$ complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diene complexes; Cationic dienes; η^2-Dienes; Olefinic complexes; Iron-dienes

1. Introduction

Cationic η^2-(α,ω-diene) complexes are compounds which have a diene ligand π bonded to a cationic metal centre via only one of the C=C double bonds. The general structure for such cationic diene complexes is shown in Fig. 1.

Although cationic η^2-alkene complexes of iron [1–4] have been extensively studied, reports on the diene analogues are sparse. Only a few examples of these types of complexes are known and very little has been reported on the reactivity of these species. The reactivity of the monosubstituted η^2-alkene iron complexes of the type, $[\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$, (R = H, CH_3, Ph), has been extensively studied and reported in the literature [2,4]. Some reactions of the cationic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{butadiene})]^+$ complex with nucleophiles have been briefly reported by Rosenblum and co-workers [5]. However, no reports on the reactivity of other acyclic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-diene})]^+$ complexes have been encountered. These compounds could be implicated in organic synthesis [4,6–8] and could also serve as potential model compounds for intermediates in some catalytic reactions [7,9]. They could for example play a role in the polymerization and dimerization of dienes. It is in light of this that we have embarked on a preliminary study of some of these complexes. Consequently we have prepared a series of compounds with the general formula $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_nH_{2n-2})](PF_6)$ and we have investigated the reactivity of these with nucleophiles. Some of these results together with characterization details of the new compounds are reported in this paper.

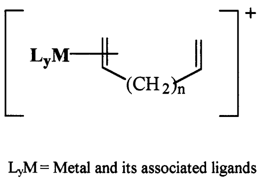

Fig. 1. General structure for η^2-diene complexes.

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2. Experimental

2.1. General procedures

All experiments, unless otherwise stated, were carried out under nitrogen using typical Schlenk line techniques. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, the *n*-bromo-1-alkenes, triphenylcarbenium hexaflourophosphate, triphenylphoshine, trimethylphospine, triethylamine and diethylmalonate were used as purchased without further purification. Tetrahydrofuran was distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane was dried by refluxing over P_2O_5 and distilling under nitrogen. All solvents were maintained over molecular sieves, and degassed prior to use. All column chromatography was performed using deactivated alumina 90 (70–230 mesh) purchased from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using either NaCl solution cells or as DRIFTS spectra in a KBr matrix. NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^{1}H NMR and 50.30 MHz for ^{13}C NMR, using tetramethylsilane as an internal standard. Elemental analyses were performed at the micro-analytical laboratory of the University of Western Cape.

The $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ compounds were prepared from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ using literature methods [10]. The η^1-alkenyl products were isolated as yellow oils and were used immediately after purification by column chromatography to prepare the η^2-(α,ω-diene) complexes.

2.1.1. General method for the preparation of the diene complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_nH_{2n-2})]PF_6$; where $n = 4$–6, 8 (**1–4**)

The preparation of the η^2-butadiene complex **1** is described below to illustrate the general procedure employed.

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CH_2CH_2\text{-}CH{=}CH_2\}]$ (0.21g, 1.03 mmol) in CH_2Cl_2 (5 ml) was added drop-wise to a solution of Ph_3CPF_6 (0.45g, 1.59 mmol) dissolved in CH_2Cl_2 (10 ml). The initial orange/yellow solution turned black with a yellow tint. The mixture was allowed to stand for 18h at room temperature. During this time a yellow crystalline material precipitated out of solution. Acetone (10 ml) was added to the mixture upon which the solid dissolved. The slow addition of diethyl ether (40 ml) afforded a yellow solid, which was collected on a Hirsch funnel and allowed to dry in air. The product was recrystallized by dissolving in a minimum amount of acetone, followed by the addition of diethyl ether. The resulting yellow solid was obtained in 49% yield.

2.1.2. Reactions of **1** and **2** with NaCl and NaI

A solution of compound **1** (0.20 g, 0.53 mmol) in dry acetone (5 ml) was added dropwise to a solution of sodium chloride (0.03 g, 0.53 mmol) dissolved in dry acetone (5 ml). The reaction mixture was allowed to stir at room temperature for 3 days. The yellow reaction mixture turned an intense orange colour during this period. The solvent was removed on a rotatory evaporator leaving an orange solid. The solid was dissolved in a minimum amount of dichloromethane and the solution was chromatographed over alumina using CH_2Cl_2 as eluent. An orange band was collected, which on the removal of the solvent gave an orange solid, identified by its IR and ^{1}H NMR spectra as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$ (86% yield). The corresponding iron-pentadiene compound, **2** undergoes a similar reaction, yielding the same product in 89% yield. Analogous results were obtained using NaI in the place of NaCl.

2.1.3. Reactions of **1–4** with tertiary phosphines

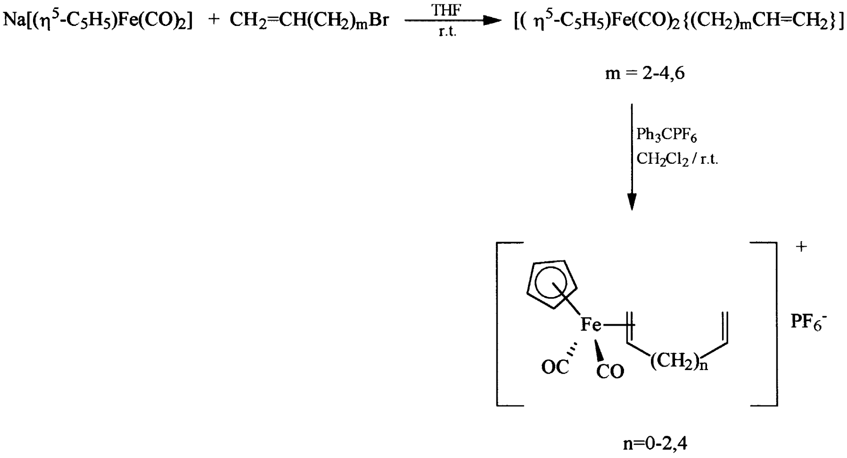
A solution of compound **1** (0.20 g, 0.53 mmol) in dry acetone (5 ml) was added dropwise to a solution of triphenylphosphine (0.14 g, 0.53 mmol) dissolved in dry acetone (5 ml). The resulting pale yellow solution was stirred under a constant flow of nitrogen for 1 h at room temperature after which the solvent was removed by rotatory evaporation. The resulting pale yellow crystalline solid obtained was recrystallized by dissolving in a minimum amount of acetone (6 ml) followed by the dropwise addition of diethyl ether (20 ml). The product was collected on a Hirsch funnel as fine pale yellow crystals and identified as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}(PPh_3)][PF_6]$ in a 92% yield. Similar reactions were carried out using compounds **2–4** as the starting material resulting in the same product in 90–95% yields. The above reactions were repeated in a sealed Schlenk tube previously flushed with nitrogen and the reaction time extended to 1 day. Compounds **2–4** yielded the same product viz. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)][PF_6]$. Compound **1** however yielded a brown oil identified as $[(\eta^5\text{-}C_5H_5)\{CH_2CH{=}CHCH_2PPh_3\}]^+$, compound **5**. With PMe_3 a complex mixture of η^1-alkenyl complexes were formed on reaction with **1**, evident by the appearance of a number of Cp resonances (σ 4.7–5.1) in the ^{1}H NMR spectrum of the reaction product.

The corresponding iron-pentadiene compound **2** undergoes a similar reaction with PMe_3, also yielding a complex mixture of products.

2.1.4. Reactions of **2–4** with triethylamine

The reaction of compound **2** with triethylamine is described here but the procedure has also been applied to compounds **3** and **4**, which gave similar results.

A suspension of compound **2** (0.20 g, 0.51 mmol) in 10 ml CH_2Cl_2 was treated dropwise with triethylamine



Compound	n	Diene
1	0	1,3-butadiene
2	1	1,4-pentadiene
3	2	1,5-butadiene
4	4	1,7-butadiene

Scheme 1.

Table 1
Yields, micro-analytical and infrared spectral data for compounds, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}CH{=}CH(CH_2)_nCH{=}CH_2\}]$ [a]

	Analysis (%) [b]						IR data [c]			
	n	Yield(%)	C	H	(C)	(H)	ν(CO) (cm^{-1})		ν(C=C) (cm^{-1})	
1	0	49	35.12	2.93	35.14	2.95	2080(s)	2049(s)	1624(m)	1517(m)
2	1	46	36.94	3.34	36.95	3.36	2080(s)	2048(s)	1639(m)	1518(m)
3	2	40	38.63	3.72	38.64	3.74	2075(s)	2043(s)	1639(m)	1519(m)
4	4	50	41.69	4.46	41.69	4.43	2077(s)	2045(s)	1640(m)	1521(m)

[a] $n = 0-2$; 4.

[b] Calculated values in parentheses.

[c] Measured as DRIFTS in a KBr matrix, s = strong; m = medium.

(0.07 ml, 0.51 mmol). The yellow solution turns brown immediately and the iron-diene complex goes into solution upon addition of Et_3N. The mixture was allowed to stir at room temperature for 45 min. The solvent was removed from the reaction mixture by rotatory evaporation, leaving a brown residue. The residue was extracted with ether, filtered and the solvent removed from the filtrate. The remaining brown oil was dissolved in a minimum amount of hexane and chromatographed on an alumina column using hexane as eluent. Only one yellow band was observed, which upon removal of the solvent yielded a yellow–brown oil identified as the product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2\text{-}CH{=}CHCH{=}CH_2)]$, (compound **6**). In a similar manner compounds **7** and **8** were isolated in 40 and 45% yield, respectively, using compounds **3** and **4** as starting materials.

*2.1.5. Reactions of **1–4** with diethylmalonate*

The reaction of compound **1** with diethylmalonate is described below. Again the procedure was also extended to compounds **2–4**.

To a solution of $Li[N(SiMe_3)_2]$ in THF at − 78°C was added diethylmalonate (0.08 ml, 0.51 mmol). After 15 min, the resultant clear solution of the diethylmalonate anion was added to a suspension of compound **1** (0.20 g, 0.51 mmol) in THF (10 ml) at − 78°C. The reaction mixture was stirred at this temperature and then allowed to warm to room temperature over a period of 3 h. The solution remains orange/yellow throughout the reaction. The solvent was removed by rotatory evaporation leaving a yellow/brown oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and the solution chromatographed on a neutral alumina column. Elution with CH_2Cl_2 gave a yellow band, which on the removal of the solvent, yielded the product as a yellow/brown oil. This was identified as an η^1-alkenyl compound, with a malonate substituent at the β position of the chain (compound **9**, 84% yield).

Products **10**–**12** were isolated in 80–86% yields starting from the corresponding compounds **2**–**4** and using a similar procedure.

3. Results and discussion

3.1. Diene complexes

3.1.1. Preparation of diene complexes

The preparation of the complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$, was carried out by the reaction of the appropriate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ [10,11] with triphenylcarbenium–hexaflourophosphate, (Ph_3CPF_6). The overall reaction scheme for the preparation of the η^2-diene complexes is outlined in Scheme 1.

Compounds **1** and **4** have previously been reported. The authors however prepared these compounds via a different synthetic route [6,12–14], which involved a direct ligand exchange reaction of the compound, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+$ with the free diene. In addition, the yields of the compounds prepared by this route are quite low. Also complete characterisation data were not given.

All the compounds were isolated as yellow air stable solids, which show thermal decomposition in the range 150–160°C. These compounds were fully characterized, by NMR and IR spectroscopy, the data for which are presented in Tables 1–3.

The infrared spectral data for compounds **1**–**4** are summarized in Table 1. All the compounds show two strong ν(CO) bands at 2077 cm^{-1} and 2040 cm^{-1} for the terminal carbonyls. The ν(CO) bands for compounds **1**–**4** appear at higher frequencies, relative to those of the corresponding η^1-alkenyl compounds, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{(CH_2)_nCH{=}CH_2\}]$, ($n = 2$–4, 6). The latter compounds have two strong ν(CO) bands at 2000 cm^{-1} and 1940 cm^{-1}. All the compounds with the exception of compound **1** give IR spectra which exhibit two bands of medium intensity at ~1518 and ~1640 cm^{-1}. These can be assigned to ν(C=C) of the coordinated and uncoordinated C=C double bonds of the diene, respectively. In the case of compound **1** the corresponding bands are observed at 1517 and 1624 cm^{-1}. The distinctive difference in the ν(C=C) of the uncoordinated C=C double bond for compound **1** can

Table 2
^1H and ^{13}C NMR. data for the compounds **1**–**4**

	^1H NMR (δ [a]/ppm)	^{13}C NMR (δ [a]/ppm)
1	3.85 (d, 1H, $J_{3,2,trans} = 14$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	52.71 Fe(η^2-$\underline{\mathbf{C}}$H$_2$=CH)
	4.04 (d, 1H, $J_{3,1,cis} = 7.2$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	88.05 Fe(η^2-CH$_2$=$\underline{\mathbf{C}}$H)
	5.54 (m, 1H) Fe(η^2-CH$_2$=CH)-C$\underline{\mathbf{H}}$=CH$_2$	90.22 $\underline{\mathbf{C}}_5$H$_5$
	5.90 (m, 8H) Fe(η^2-CH$_2$=C$\underline{\mathbf{H}}$)-CH=C$\underline{\mathbf{H}}_2$, C$_5\underline{\mathbf{H}}_5$	124.66 Fe(η^2-CH$_2$=CH)CH=$\underline{\mathbf{C}}$H$_2$
		137.71 Fe(η^2-CH$_2$=CH)$\underline{\mathbf{C}}$H=CH$_2$
		209.33 $\underline{\mathbf{C}}$O
		211.22 $\underline{\mathbf{C}}$O
2	2.50 (m, 1H) Fe(η^2-CH$_2$=CH)-C$\underline{\mathbf{H}}_2$CH=CH$_2$	40.15 Fe(η^2-CH$_2$=CH)-$\underline{\mathbf{C}}$H$_2$CH=CH$_2$
	3.18 (m, 1H) Fe(η^2-CH$_2$=CH)-C$\underline{\mathbf{H}}_2$CH=CH$_2$	54.72 Fe(η^2-$\underline{\mathbf{C}}$H$_2$=CH)
	3.68 (d, 1H, $J_{3,2,trans} = 14.6$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	85.82 Fe(η^2-CH$_2$=$\underline{\mathbf{C}}$H)
	4.15 (d, 1H, $J_{3,1,cis} = 8.4$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	90.26 $\underline{\mathbf{C}}_5$H$_5$
	5.19 (m, 3H) Fe(η^2-CH$_2$=C$\underline{\mathbf{H}}$)-CH$_2$CH=C$\underline{\mathbf{H}}_2$	118.02 Fe(η^2-CH$_2$=CH)-CH$_2$CH=$\underline{\mathbf{C}}$H$_2$
	5.85 (m, 1H) Fe(η^2-CH$_2$=CH)-CH$_2$C$\underline{\mathbf{H}}$=CH$_2$	137.07 Fe(η^2-CH$_2$=CH)-CH$_2\underline{\mathbf{C}}$H=CH$_2$
	5.91 (s, 5H) C$_5\underline{\mathbf{H}}_5$	209.33 $\underline{\mathbf{C}}$O
		211.22 $\underline{\mathbf{C}}$O
3	1.65–2.62 (4 x m, 4H) Fe(η^2-CH$_2$=CH)-(C$\underline{\mathbf{H}}_2$)$_2$CH=CH$_2$	36.39; 36.93 Fe(η^2-CH$_2$=CH)($\underline{\mathbf{C}}$H$_2$)$_2$-CH=CH$_2$
	3.64 (d, 1H, $J_{3,2,trans} = 14.4$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	55.26 Fe(η^2-$\underline{\mathbf{C}}$H$_2$=CH)
	4.07 (d, 1H, $J_{3,1,cis} = 8.4$ Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	87.61 Fe(η^2-CH$_2$=$\underline{\mathbf{C}}$H)
	5.04 (m, 2H) Fe(η^2-CH$_2$=CH)-(CH$_2$)$_2$CH=C$\underline{\mathbf{H}}_2$	90.09 $\underline{\mathbf{C}}_5$H$_5$
	5.24 (m, 1H) Fe(η^2-CH$_2$=C$\underline{\mathbf{H}}$)-(CH$_2$)$_2$CH=CH$_2$	116.40 Fe(η^2-CH$_2$=CH)(CH$_2$)$_2$-CH=$\underline{\mathbf{C}}$H$_2$
	5.81 (m, 1H) Fe(η^2-CH$_2$=CH)-(CH$_2$)$_2$C$\underline{\mathbf{H}}$=CH$_2$	137.39 Fe(η^2-CH$_2$=CH)(CH$_2$)$_2$-$\underline{\mathbf{C}}$H=CH$_2$
	5.91 (s, 5H) C$_5\underline{\mathbf{H}}_5$	209.21 $\underline{\mathbf{C}}$O
		211.42 $\underline{\mathbf{C}}$O
4	1.50–2.70 (3 x m, 8H) Fe(η^2-CH$_2$=CH)-(C$\underline{\mathbf{H}}_2$)$_4$CH=CH$_2$	30.73–36.77 Fe(η^2-CH$_2$=CH)($\underline{\mathbf{C}}$H$_2$)$_4$-CH=CH$_2$
	3.64 (d, 1H, $J_{3,2,trans}$) = 14.6 Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	54.88 Fe(η^2-$\underline{\mathbf{C}}$H$_2$=CH)
	4.06 (d, 1H, $J_{3,1,cis}$) = 8.2 Hz) Fe(η^2-C$\underline{\mathbf{H}}_2$=CH)	88.88 Fe(η^2-CH$_2$=$\underline{\mathbf{C}}$H)
	4.95 (m, 2H) Fe(η^2-CH$_2$=CH)-(CH$_2$)$_4$CH=C$\underline{\mathbf{H}}_2$	90.07 $\underline{\mathbf{C}}_5$H$_5$
	5.31 (m, 1H) Fe(η^2-CH$_2$=C$\underline{\mathbf{H}}$)-(CH$_2$)$_4$CH=CH$_2$	114.95 Fe(η^2-CH$_2$=CH)(CH$_2$)$_4$-CH=$\underline{\mathbf{C}}$H$_2$
	5.81 (m,1H) Fe(η^2-CH$_2$=CH)-(CH$_2$)$_4$C$\underline{\mathbf{H}}$=CH$_2$	139.18 Fe(η^2-CH$_2$=CH)(CH$_2$)$_4$-$\underline{\mathbf{C}}$H=CH$_2$
	5.90 (s, 5H) C$_5\underline{\mathbf{H}}_5$	209.27 **C**O
		211.50 $\underline{\mathbf{C}}$O

[a] Acetone-d_6 as solvent.

Table 3
Yields, melting points and spectral data for products obtained from reactions of η^2-diene compounds

Starting complex	Reagent	Product	Yield (%)	Melting point (°C)	ν(CO)/cm^{-1} [a]		1H NMR δ (ppm) [b]
1, **2**	Cl^-	$Cp(CO)_2Fe–Cl$	86–89	110–112	2040(s)	2000(s)	5.25 (s, 5H, $C_5\underline{\mathbf{H}}_5$)
1, **2**	I^-	$Cp(CO)_2Fe–I$	56–60	117–121	2037(s)	1991(s)	5.28 (s, 5H) $C_5\underline{\mathbf{H}}_5$
1–**4**	$:PPh_3$	$[CpFe(CO)_2PPh_3)]^+PF_6^-$	90–95	115–117	2057(s)	2013(s)	5.65 (s, 5H) $C_5\underline{\mathbf{H}}_5$
1	PPh_3	$[CpFe(CO)_2^-CH_2CH$ $=CHCH_2PPh_3^+]\ PF_6^-$ **5**	71	OIL	2007(s)	1950(s)	1.0–2.0 (m, 2H) $FpC\underline{\mathbf{H}}_2CH=CHCH_2PPh_3^+$ 4.0 (dd, 2H) $FpCH_2CH=CHC\underline{\mathbf{H}}_2PPh_3^+$ 4.7 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 5.0 (m, 1H) $FpCH_2CH=C\underline{\mathbf{H}}CH_2PPh_3^+$ 6.2 (m, 1H) $FpCH_2C\underline{\mathbf{H}}=CHCH_2PPh_3^+$ 7.0–7.8 (m, 15) $P(\mathbf{C}_5\underline{\mathbf{H}}_5)_3$
2	Et_3N:	Fp-$CH_2CH=CHCH$ $=CH_2$ **6**	40.26	OIL	2005(s)	1950(s)	2.12 (m, 2H) Fp-$C\underline{\mathbf{H}}_2CH=CHCH=CH_2$ 4.97 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}CH=CH_2$ 4.97 (m, 2H) Fp-$CH_2CH=CHCH=C\underline{\mathbf{H}}_2$ 5.30 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}CH=CH_2$ 5.70 (m, 1H) Fp-$CH_2C\underline{\mathbf{H}}=CHCH=CH_2$ 5.70 (m, 1H) Fp-$CH_2CH=CHC\underline{\mathbf{H}}=CH_2$ 4.67 (s, 5H, $C_5\underline{\mathbf{H}}_5$) 4.73 (s, 5H, $C_5\underline{\mathbf{H}}_5$)
3	Et_3N	Fp-$CH_2CH=CHCH_2$ $CH=CH_2$ **7**	46.66	OIL	2005(s)	1950(s)	2.12 (m, 2H) Fp-$C\underline{\mathbf{H}}_2CH=CHCH_2CH=CH_2$ 2.67 (t, 1H) Fp-$CH_2CH=CHC\underline{\mathbf{H}}_2CH=CH_2$ 2.80 (t, 1H) Fp-$CH_2CH=CHC\underline{\mathbf{H}}_2CH=CH_2$ 4.97 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}CH_2CH=CH_2$ 4.97 (m, 2H) Fp-$CH_2CH=CHCH_2CH=C\underline{\mathbf{H}}_2$ 5.30 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}CH_2CH=CH_2$ 5.70 (m, 1H) Fp-$CH_2C\underline{\mathbf{H}}=CHCH_2CH=CH_2$ 5.70 (m, 1H) Fp-$CH_2CH=CHCH_2C\underline{\mathbf{H}}=CH_2$ 4.67 (s, 5H, $C_5\underline{\mathbf{H}}_5$) 4.73 (s, 5H, $C_5\underline{\mathbf{H}}_5$)
4	Et_3N	Fp-$CH_2CH=CH$ $(CH_2)_3CH=CH_2$ **8**	43.10	OIL	2005(s)	1950(s)	1.0–2.4 (2 x m, 6H) Fp-$CH_2CH=CH(C\underline{\mathbf{H}}_2)_3CH=CH_2$ 2.12 (m, 2H) Fp-$C\underline{\mathbf{H}}_2CH=CH(CH_2)_3CH=CH_2$ 4.97 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}(CH_2)_3CH=CH_2$ 4.97 (m, 2H) Fp-$CH_2CH=CH(CH_2)_3CH=C\underline{\mathbf{H}}_2$ 5.30 (m, 1H) Fp-$CH_2CH=C\underline{\mathbf{H}}(CH_2)_3CH=CH_2$ 5.70 (m, 1H) Fp-$CH_2C\underline{\mathbf{H}}=CH(CH_2)_3CH=CH_2$ 5.70 (m, 1H) Fp-$CH_2CH=CH(CH_2)_3C\underline{\mathbf{H}}=CH_2$ 4.67 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 4.73 (s, 5H) $C_5\underline{\mathbf{H}}_5$

Table 3 (*Continued*)

Starting complex	Reagent	Product	Yield (%)	Melting point (°C)	ν(CO)/cm^{-1} [a]		^{1}H NMR δ (ppm) [b]
1	$CH(COOCH_2CH_3)_2^-$	$Fp\text{-}CH_2CH\{(CH$ $(COOEt)_2)\}CH{=}CH_2$ **9**	81.34	OIL	2004(s)	1944(s)	0.98 (t, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}CH{=}CH_2$ 1.25(m, 6) $CH(COOCH_2C\underline{\mathbf{H}}_3)_2$ 1.74 (dd, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}CH{=}CH_2$ 2.71 (m, 1H) $FpCH_2C\underline{\mathbf{H}}\{(CH(COOEt)_2)\}CH{=}CH_2$ 3.32 (d, 1H) $C\underline{\mathbf{H}}(COOCH_2CH_3)_2$ 4.15 (m, 4) $CH(COOC\underline{\mathbf{H}}_2CH_3)_2$ 4.79 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 5.05 (m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH{=}C\underline{\mathbf{H}}_2$ 5.60 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{\mathbf{H}}{=}CH_2$
2	$CH(COOCH_2CH_3)_2^-$	$Fp\text{-}CH_2CH\{(CH(CO$ $OEt)_2)\}CH_2CH{=}CH_2$ **10**	87.26	OIL	2004(s)	1944(s)	1.1 (t, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}CH_2CH{=}CH_2$ 1.26(m, 6) $CH(COOCH_2C\underline{\mathbf{H}}_3)_2$ 1.65 (dd, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}CH_2CH{=}CH_2$ 2.20 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{\mathbf{H}}_2CH{=}CH_2$ 2.30 (m, 1H) $FpCH_2C\underline{\mathbf{H}}\{(CH(COOEt)_2)\}CH_2CH{=}CH_2$ 3.0 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}C\underline{\mathbf{H}}_2CH{=}CH_2$ 3.50 (d, 1H) $C\underline{\mathbf{H}}(COOCH_2CH_3)_2$ 4.19 (m, 4) $CH(COOC\underline{\mathbf{H}}_2CH_3)_2$ 4.83 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 5.05 (m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2CH{=}C\underline{\mathbf{H}}_2$ 5.80 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2C\underline{\mathbf{H}}{=}CH_2$
3	$CH(COOCH_2CH_3)_2^-$	$Fp\text{-}CH_2CH\{(CH(CO$ $OEt)_2)\}(CH_2)_2CH{=}CH_2$ **11**	80.95	OIL	2004(s)	1944(s)	1.1 (t, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH$ 1.27 (m, 6) $CH(COOCH_2C\underline{\mathbf{H}}_3)_2$ 1.60 (dd, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$ 1.4–2.4 (m, 4H) $FpCH_2CH\{(CH(COOEt)_2)\}(C\underline{\mathbf{H}}_2)_2CH{=}CH_2$ 2.10 (m, 1H) $FpCH_2C\underline{\mathbf{H}}\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$ 3.50 (d, 1H) $C\underline{\mathbf{H}}(COOCH_2CH_3)_2$ 4.19 (m, 4) $CH(COOC\underline{\mathbf{H}}_2CH_3)_2$ 4.79 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 4.82 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 5.0 (m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}(CH_2)_2CH{=}C\underline{\mathbf{H}}_2$ 5.80 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}(CH_2)_2C\underline{\mathbf{H}}{=}CH_2$
4	$CH(COOCH_2CH_3)_2^-$	$Fp\text{-}CH_2CH\{(CH(CO$ $OEt)_2)\}(CH_2)_4CH{=}CH_2$ **12**	85.00	OIL	2004(s)	1944(s)	1.1 (t, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}(CH_2)_4CH{=}CH_2$ 1.27 (m, 6) $CH(COOCH_2C\underline{\mathbf{H}}_3)_2$ 1.50 (dd, 1H) $FpC\underline{\mathbf{H}}_2CH\{(CH(COOEt)_2)\}(CH_2)_4CH{=}CH_2$ 1.4–2.4 (m, 8H) $FpCH_2CH\{(CH(COOEt)_2)\}(C\underline{\mathbf{H}}_2)_4CH{=}CH_2$ 2.0 (m, 1H) $FpCH_2C\underline{\mathbf{H}}\{(CH(COOEt)_2)\}(CH_2)_2CH{=}CH_2$ 3.50 (d, 1H) $C\underline{\mathbf{H}}(COOCH_2CH_3)_2$ 4.20 (m, 4) $CH(COOC\underline{\mathbf{H}}_2CH_3)_2$ 4.77 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 4.81 (s, 5H) $C_5\underline{\mathbf{H}}_5$ 5.0 (m, 2H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2CH{=}C\underline{\mathbf{H}}_2$ 5.80 (m, 1H) $FpCH_2CH\{(CH(COOEt)_2)\}CH_2C\underline{\mathbf{H}}{=}CH_2$

[a] Measured in acetone in NaCl solution cells.

[b] Measured in acetone-d_6.

be ascribed to the fact that the two double bonds are conjugated. The band assigned to ν(C=C) at 1518 cm^{-1} is absent in the IR spectra of the parent alkenyl complexes and we propose that this peak is due to the double bond of the diene ligand, which is bonded to the metal in an η^2-fashion.

The ^1H NMR spectra for all the compounds show signals, which are characteristic of species containing a vinylic functionality. The assignments of the vinylic protons for compounds **1**–**4** are based on the structure in Fig. 2 and are listed in Table 2.

The spectra of all the compounds show two doublets in the region δ3.6–3.9 ppm and δ4.0–4.2 ppm. These signals were assigned to the coordinated vinylic protons, H^1 and H^2, respectively. These protons have *trans* ($J_{3,2}$) and *cis* ($J_{3,1}$) coupling constants of ~14 and 8 Hz, respectively. The chemical shift difference between protons H^1 and H^2 are ~0.4 ppm in all the compounds except compound **1**. The butadiene compound shows a lower chemical shift difference of 0.2 ppm for the coordinated vinylic protons. Similar results for other π-coordinated α-olefins were reported previously. Rosenblum et al. ascribed the large chemical shift differences to the anisotropic effects associated with the cyclopentadienyl ring currents. However effects of the CO ligands may also be significant [15]. The signals in the region δ4.9–6.0 ppm, with the exception of the sharp broad peak around δ5.9 ppm, were assigned to the protons H^5 and H^6 of the uncoordinated vinylic protons. The sharp broad peak around δ5.9 ppm observed in all the spectra were assigned to the cyclopentadienyl protons. The corresponding peak for the cyclopentadienyl protons of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^1\text{-alkenyl}\}]$ compounds appears around δ4.7 ppm. This downfield chemical shift is again due to the influence of the cationic metal centre, which draws electrons from the neighboring Cp ring, hence leading to the deshielding of the Cp protons.

The ^{13}C NMR spectra for the series of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{\eta^2\text{-}(\alpha,\omega\text{-diene})\}]PF_6$ complexes, (**1**–**4**), were all recorded in acetone and are briefly discussed here. The assignment of the carbonyls and vinylic carbons are based on the structure in Fig. 3.

Two carbonyl resonances are observed at δ209 ppm and 201 ppm. It has previously been reported that monosubstituted olefin complexes exhibit two CO resonances due to steric interactions between the carbonyl group and the olefin ligand resulting from a conformation in which the olefin is near the $CpFe(CO)_2$ moiety. This causes the CO to have different chemical environments [15].

The π-coordinated vinylic carbons C_a and C_b were assigned to the peaks in the region δ52–56 ppm and δ85–89 ppm, respectively. The uncoordinated vinylic carbons were assigned to the peaks in the region of δ114–125 ppm and δ137–139 ppm, respectively. The intense peak at δ ~ 90 ppm observed in all the spectra is due to the cyclopentadienyl resonance.

3.2. Reactivity of diene complexes

The reactions of cationic dicarbonyl η^5-cyclopentadienyl(olefin) complexes with nucleophiles have previously been reported to proceed via one of the following pathways: (a) addition to the olefin double bond; (b) addition to the carbonyl carbon; and (c) displacement of the olefin. In addition to these reactions, allylic deprotonation with tertiary amines (d) is another possible reaction. This leads to the formation of η^1-allyl complexes [1,2,16]. The displacement of the coordinating olefin and the formation of the iron dimer, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were found to compete effectively with the desired addition reaction. Treatment of the cationic diene complexes **1**–**4**, with various nucleophiles were found to proceed via pathways (a), (c) or (d). The analytical and spectral data of the products of these reactions are summarized in Table 3 and are discussed below.

3.2.1. Reactions with halides

*3.2.1.1. Reactions of **1** and **2** with NaCl and NaI.* The reaction of **1** and **2** with NaCl in an acetone solution leads to the exclusive formation of $CpFe(CO)_2Cl$ (**5**). The product was isolated as a red, air stable crystalline solid. The reaction was easily monitored by IR spectroscopy by following the replacement of the carbonyl bands for the Fp-η^2-(α,ω-diene) complexes, **1** and **2** at 2045 and 2080cm^{-1} with two strong carbonyl stretching frequencies at 2040 and 2000 cm^{-1} for the product. Using this method, it was found that the reaction was complete after 3 days. The ^1H NMR of the product exhibits a single strong peak at δ5.25 ppm, which is assigned to the cyclopentadienyl protons. This correlates well with data obtained from an authentic sample of $CpFe(CO)_2Cl$. Analogous results were obtained with sodium iodide in the place of the chloride, with $CpFe(CO)_2I$ being formed in good yields.

3.2.2. Reactions with phosphines

*3.2.2.1. Reaction of **1**–**4** with triphenylphosphine.* For the reactions of compounds **1**–**4** with PPh_3 under a constant flow of nitrogen, the displacement product, $[CpFe(CO)_2(PPh_3)][PF_6]$, was isolated in all cases. These reactions take place rapidly at room temperature and the product was isolated as a pale yellow, air stable crystalline solid after a reaction time of 2 h.

Repeating the above reactions using a sealed system, gave a different result for compound **1**, the reactions of compounds **2**–**4** giving the same results as obtained previously. In the case of compound **1**, the reaction

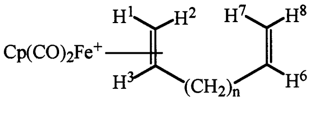


Fig. 2. Labelling of protons to assist ^{1}H NMR assignments for the complexes **1**–**4**.

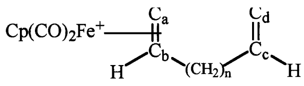
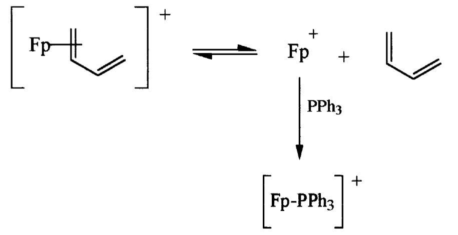


Fig. 3. Labelling of the carbon atoms to assist ^{13}C NMR assignments for the complexes **1**–**4**.

proceeds via an addition mechanism resulting in the formation of the cationic species, $\text{Fp-CH}_2\text{CH=CHCH}_2 - {}^{+}\text{PPh}_3$, (compound **5**), which was isolated as an unstable yellow/brown oil. The ^{1}H NMR spectrum of this yellow brown oil shows two distinct signals in the vinylic region, at δ5.0 ppm and δ6.2 ppm, respectively. The signals resonate for one proton each. Of the possible products of addition of triphenylphosphine to **1**, compound **5** is the only one which has an internal C=C functionality with each carbon having a single proton. The above reaction was also followed in a sealed NMR tube and this yielded similar results. Monitoring the reaction using ^{1}H NMR revealed that the addition product was formed via a rearrangement process as shown in Scheme 2. Unfortunately compound **5** was found to be highly unstable with the result that we were unable to isolate it in a pure state. We were thus not able to fully characterise it.

We are also not entirely sure why a different reaction product is obtained when the reaction is carried out in a sealed system as opposed to doing the reaction under a constant flow of nitrogen. It is however speculated that the butadiene complex undergoes some dissociation in solution to produce the free diene ligand (some NMR evidence for this). Butadiene being volatile is then removed in the nitrogen stream aiding further dissociation of the starting diene complex. This leads to a lowering of the possibility of the addition product being formed. In the sealed system the equilibrium in Scheme 3 is more to the left leading to the addition reaction being favoured.

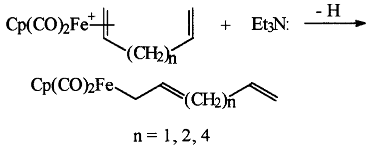


Scheme 3.

*3.2.2.2. Reactions of **1** and **2** with PMe$_3$.* The reactions of **1** and **2** with PMe$_3$ take place rapidly at room temperature resulting in a complex mixture of η^1-alkenyl species, evident by the appearance of a number of Cp resonances (σ 4.7–5.1ppm) in the ^{1}H NMR spectra of the reaction products. The appearance of vinylic protons suggests that the reactions proceed via the addition of the nucleophile to the coordinated diene. Our observations are in agreement with reports in the literature, where it was found that the Cp signals for the products of addition reactions appear in the range between δ4.9–5.1 ppm [2]. Due to the complex nature of the ^{1}H NMR spectra, it was not possible to identify unequivocally any of the products.

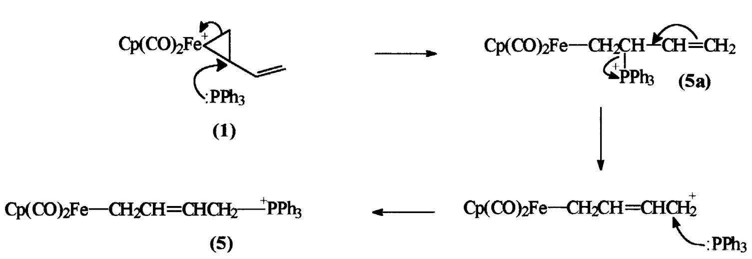
3.2.3. Reactions with triethylamine

The treatment of the diene compounds (**2**–**4**) with triethylamine results in the deprotonation of the diene ligand producing Fp-(η^1-allyl) complexes as shown in Equation (1). The reactions proceed fairly rapidly at room temperature in dichloromethane and are complete within 45 min. The progress of the reaction was easily monitored by following the replacement of the carbonyl bands for the Fp-η^2-(α,ω-dienes) (**2**–**4**) at ~2045 and 2080 cm^{-1} and comparing it with those of the neutral Fp-η^1-(α,ω-allyl) products at ~1950 and 2005 cm^{-1}. The products were isolated as relatively unstable yellow/brown oils.



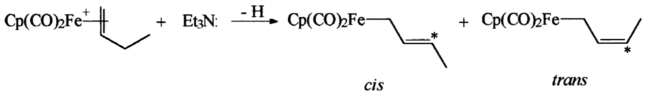
(1)

The reactions of the Fp-η^2-(α,ω-dienes) (**2**–**4**) with triethylamine are in agreement with those reported for the related alkene complexes. [(η^5-C$_5$H$_5$)Fe(CO)$_2$(η^2-



Scheme 2.

alkene)]$^+$ complexes were reported to undergo deprotonation in the presence of a tertiary amine base, yielding *cis* and *trans* (η^1-allyl) complexes. The deprotonation reaction is highly regiospecific and proceeds via preferential removal of an allylic proton *trans* to the metal-olefin bond to give mixtures of *cis* and *trans* isomers [1,4,8,16]. This is best illustrated by the reaction of [(η^5-C_5H_5)Fe(CO)$_2$(η^2-butenyl)] with triethylamine as shown in Equation (2).

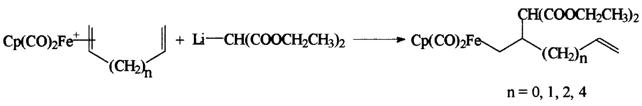


(2)

The cyclopentadienyl signals for the *cis* and *trans* [(η^5-C_5H_5)Fe(CO)$_2$(η^1-butenyl)] isomers in the above reaction were reported to appear at δ4.65 and δ4.58 ppm, respectively. Also, two protons in the region δ4.8–5.9 ppm were observed for the *cis* and *trans* methylene protons at C_* [16]. A similar pattern was found in the ^{1}H NMR spectra of compounds **6**–**8**. The two distinct singlets in the region at δ4.65–4.75 ppm, assigned to the cyclopentadienyl protons for the η^1-(α,ω-diene)iron complexes **6**–**8** are suspected to be due to the *cis* and *trans* isomers. The two resonances at δ5.0 ppm and δ5.3 ppm could possibly be assigned to the *cis* and *trans* methylene protons. A single multiplet at ~ δ2.12 ppm was observed for the FpCH$_2$ protons in the Fp-η^1-(α,ω-diene) complexes. A multiplet at ~ δ5.7 ppm, obscured by the proton for C_d, was assigned to the proton at C_b. The terminal vinylic protons at C_d and C_e remain unaffected, as expected (Fig. 4).

3.2.4. Reactions with lithium diethylmalonate

The diethylmalonate anion, generated by treatment of diethylmalonate with lithium bis(trimethylsilyl)amide Li[N(SiMe$_3$)$_2$], reacts readily with a suspension of the cationic dienyl complexes **1**–**4** in THF at −78°C. The products were isolated in high yields as amber oils and identified as products **9**–**12**. The compounds are obtained from direct addition at C_b as shown in Equation (3). They exhibit two strong ν(CO) bands for the terminal carbonyls at 2004 and 1944 cm^{-1}.



(3)

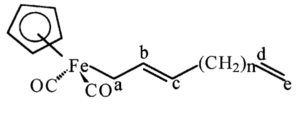


Fig. 4. Labelling of proton atoms to assist ^{1}H NMR assignments for the η^1-(α,ω-diene)iron complexes **6**–**8**.

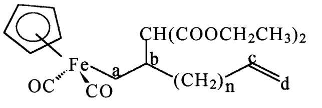


Fig. 5. Labelling of proton atoms to assist ^{1}H NMR assignments for complexes **9**–**12**.

The assignments of the signals in the NMR spectra of compounds **9**–**12** are based on the structure in Fig. 5.

The ^{1}H NMR spectra of all the products exhibit signals for the three vinylic protons of C_c and C_d in the region between δ5.0–6.0 ppm. These are typical of what is observed for the η^1-alkenyl compounds and also correspond to the position of the uncoordinated vinylic protons for the cationic Fp-η^2-(α,ω-diene) compounds **1**–**4**. The two single proton multiplets at δ1.0 and δ1.7 ppm are due to the to Fp-CH$_2$ protons at C_a. The intense peak at δ4.7 ppm, observed in all the spectra was assigned to the cyclopentadienyl protons.

The addition of enolates to Fp-(olefin) cations has been reported to be facile with uncomplicated side reactions. Nucleophillic addition to the butadiene complex **1** was reported to take place either by direct or conjugate addition to the coordinated double bond. With lithium dimethylmalonate, a single product was formed in 86% yield derived from direct addition at C_2 [6]. In our hands similar results were obtained for the reactions of the cationic diene complexes **1**–**4** with diethylmalonate.

4. Conclusion

A series of cationic iron η^2-(α,ω-diene) complexes of the type, [(η^5-C_5H_5)Fe(CO)$_2${η^2-(α,ω-diene)}]PF$_6$ have been successfully prepared. These compounds were isolated as yellow air stable solids, which decompose in the range 150–160°C. Treatment of these cationic species **1**–**4**, with nucleophiles were found to proceed via two general routes: (a) addition to the coordinated diene and (b) ligand substitution (displacement) of the diene. Reactions with triethylamine lead to the deprotonation of the diene. Microanalyses, FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy were employed to characterize all new compounds.

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