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TRENDS IN ELECTRON-IMPACT FRAGMENTATION OF SUBSTITUTED STYRENEBIS(TRICARBONYLIRON) COMPLEXES INDUCED BY THE METAL AND SUBSTITUTION

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Summary

A study of electron-impact induced processes of thirty substituted styrene—bis(tricarbonyliron) complexes $XC_6H_4C(R^{\alpha})=CR^{\beta}[Fe(CO)_3]_2$, and of some ten corresponding styrene free ligands is described. All the mass spectra of the organoiron complexes are characterized by the consecutive losses of carbon monoxide followed by loss of one or two iron atoms:

$$[LFe_2(CO)_6]^{+\cdot} \xrightarrow{(a)} LFe_2^{+\cdot} \xrightarrow{(c)} LFe^{+\cdot} \xrightarrow{(g)} L^+$$

Depending on the nature of the substituent, X, and its position on the styrene ligand, the organic moiety in LFe^+ ruptures in four main modes: (*d*) loss of neutral methane when $X = H, CH_3, C_6H_5, CH_3O$ and F; $R^{\alpha} = CH_3$ and $R^{\beta} = H$; (*e*) loss of neutral acetylene when $X = H, CH_3O$; $R^{\alpha} = H$ and $R^{\beta} = CH_3$; (*f*) loss of HX when X = halogen, $R^{\alpha} = H, CH_3$ and $R^{\beta} = H$; (*g*) loss of iron. In the halogen-containing organoiron complexes, the ionic fragment $LFe_2^{+\cdot}$ predominates in the mass spectra. It is characterized by its tendency to lose a neutral alkyne molecule to yield the corresponding ionic fragment of diiron—halogenobenzene [mode (*b*)]. Unlike the organoiron complexes which eject neutral molecules, the corresponding free ligands tend to lose mainly radical species.

The preparation and properties of nine hitherto unreported styrene—bis(tricarbonyliron) complexes are described.

Introduction

Since 1964 extensive investigations of the relationship between the structure of organometallic compounds and their fragmentation patterns on electron impact have been described in the literature [1], and similarities have been pointed out between the behavior of these materials and that of organic compounds [2]. In addition to simple bond cleavage, neutral molecule elimination was also found, with and without new bond formation [3]. Often new bond formation was explained by rearrangement involving a cyclic transition state with the metal atom in the ring [4]. For such cases, variation in the abundances of peaks could be attributed to the distances between atoms or groups of atoms involved in the elimination, if no rearrangement occurred prior to such a process.

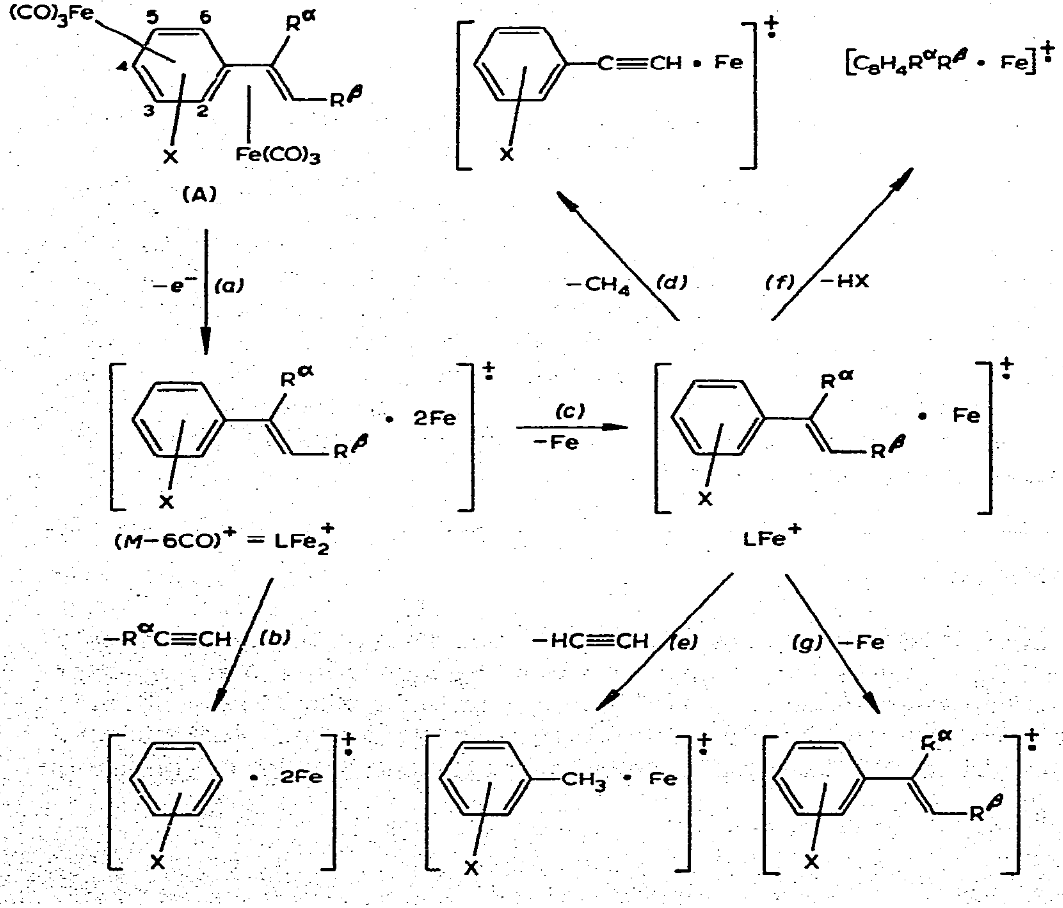
We report here the results of the mass spectral study of a series of styrene—bis(tricarbonyliron) complexes [(A), (I)—(XXX) in the Tables]. The preparation and description of most of the complexes have been given in an earlier publication [5]. Previously unreported complexes [(VII), (IX), (XI), (XIV), (XXVI)—(XXX)] and deuterium-labelled analogs of the complexes of α-methylstyrene and *p*-chloro-α-methylstyrene, all of which have been prepared by photochemical reaction of the styrene with $Fe(CO)_5$, are described in the Experimental Section.

Results and discussion

A few of the fragmentation trends that evolved in which iron remains on the organic skeleton are summarized in Scheme 1. In most cases the molecular

SCHEME 1

(*a*) Stepwise loss of 6 CO. (*b*) Where X = hal, $R^{\alpha} = CH_3$, H; R^{β} = H. (*c*) For all substitution. (*d*) Where $R^{\alpha} = CH_3$; R^{β} = H; X = H, CH_3, C_6H_5, CH_3O, F. (*e*) R^{α} = H; $R^{\beta} = CH_3$; X = H, CH_3O. (*f*) $R^{\alpha} = CH_3$, H; R^{β} = H; X = hal. (*g*) For all substitution.

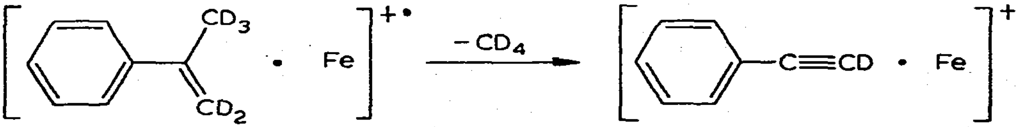


ion peak is apparent, but only in very low abundance. All mass spectra are characterized by the consecutive loss of neutral CO and the metal atoms [modes (*a*), (*c*) and (*g*)], a fragmentation sequence well-documented for metal carbonyl complexes [1c]. A dominant peak in most of the spectra studied was that in which one iron remains on the intact ligand. This ion will be referred to as $LFe^{+\cdot}$ (ligand—iron) and will assume the role of the base peak in reference to relative abundances. In none of the cases studied where iron remains in the ionic fragment was there observed loss of carbon from the original six-membered ring of the ligand. Rather the rupture of the organic moiety involves elimination from ring positions and from the sidechain, and both the relative intensities of fragments and the type of fragmentation are affected seriously by the nature of the substituent and its position on the styrene ligand. Whereas in the fragmentation of the organoiron complexes neutral species are generally extruded (e.g.; H_2, CH_4, halH), in the corresponding free ligands, loss is mainly of radical species (e.g.; H, CH_3, hal). Such comparisons on a more quantitative basis are given in Table 1. Modes of fragmentation in the complexes as a function of substitution are discussed below and compared with general trends observed in the free ligand.

Methyl substitution

When methyl was substituted at the α-position of the original styrene ($R^\alpha = CH_3$, $R^\beta = H$), a significant mode observed was that of elimination of a molecule of methane from the ion $LFe^{+\cdot}$ to yield the corresponding ionic fragment of iron—arylacetylene [mode (*d*), Scheme 1 and (I)—(XI), Table 2]. Thus, the complex of α-methylstyrene-d_5 with all deuterium in the sidechain gave exclusive elimination of a CD_4 molecule (Scheme 2)*.

SCHEME 2



The presence of a second methyl group at a ring position does not affect the CH_4 elimination (Table 2), nor is part of the methane derived from the ring methyl group since in the absence of the α-methyl group [(XXIV), Table 2] no such elimination is observed. In the α-methyl-substituted free ligands the cleavage of methyl becomes a major mode of fragmentation comparable in importance to methane elimination from the corresponding complexes (Table 1).

When, on the other hand, methyl is present at the β-position, elimination of a molecule of acetylene from $LFe^{+\cdot}$ is a dominant mode of fragmentation [mode (*e*), Scheme 1 and (XII) and (XIII), Table 2], and no methane loss is observed. Similarly in the free ligand loss of the methyl radical is suppressed, and here the major fragmentation processes are derived from cleavage of hydrogen atoms and C_2 and C_3 units (Table 1).

The mass spectra of three methylstyrene complexes where methyl is at the

(continued on p. 71)

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* Methane elimination from 5,5-dimethylcyclohexadienetricarbonyliron to give the aromatized ligand has been previously reported [6].

TABLE 1. RELATIVE ABUNDANCES OF MOST PROMINENT PEAKS IN THE MASS SPECTRA OF SOME FREE STYRENE LIGANDS (L) AND THEIR IRON CARBONYL COMPLEXES

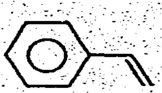
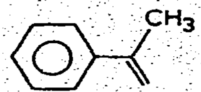
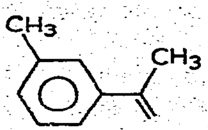
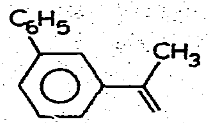
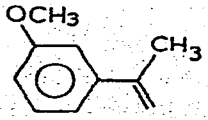
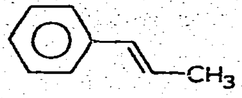
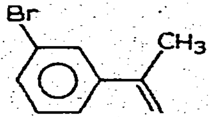
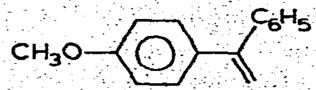
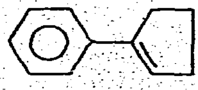
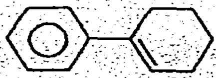
Styrene	No.	L^+ (%)	LFe^+ (%)	$[L—(\ \ )]^+$ (%)	$[LFe—(\ \ )]^+$ (%)	Other (%)
	(I)	100	100	47(—H) 57(—C_2H_2) 26(—C_2H_3)		
	(II)	100	100	88(—H) 53(—CH_3) 22(—C_2H_3) 35(—C_3H_4) 28(—C_3H_5)	48(—CH_4)	
	(III), (V)	100	100	86(—CH_3) 58(—CH_3, H_2) 41(—C_3H_4) 44(—C_3H_5)	55,59(—CH_4)	
	(VII), (IX)	100	100	36(—CH_2) 44(—CH_3) 103(—C_3H_4)	33,41(—CH_4)	
	(XI)	100	100	20(—CH_3) 20(—C_2H_5) 50(—C_3H_4)	22(—CH_4) 8(—CH_2O)	
	(XII)	100	100	150(—H) 88(—3H) 13(—CH_3) 58(—C_2H_3) 17(—C_3H_4) 20(—C_3H_5)	80(—C_2H_2)	
	(XVIII), (XIX)	100	100	9(—CH_3) 12(—C_3H_4) 64(—Br) 45(—Br, H_2) 29(—Br, CH_3)	69,92(—HBr)	396 LFe_2^+ 120 $(LFe_2—C_3H_4)^+$
	(XXIV), (XXV)	100	100	61(—CH_3) 39(—CH_3, CH_2O)		
	(XXIX)	100	100	79(—H) 8(—2H) 14(—3H) 94(—CH_3) 57(—CH_4) 50(—C_2H_4)	116(—2H) 54(—4H) 30(—C_2H_4)	103 LFe_2^+ 120 $(LFe_2—2H)^+$ 53 $(LFe_2—4H)^+$
	(XXX)	100	100	12(—H) 34(—4H) 18(—6H) 69(—CH_3) 8(—CH_4) 11(—CH_5) 77(—C_2H_4) 104(—C_2H_5) 52(—C_2H_6) 72(—C_3H_7)	241(—4H)	211 LFe_2^+ 136 $(LFe_2—4H)^+$

TABLE 2

RELATIVE ABUNDANCES OF MAJOR IRON-CONTAINING FRAGMENTS IN THE MASS SPECTRA OF UNSUBSTITUTED AND SOME METHYL-SUBSTITUTED BIS(TRICARBONYLIRON)—STYRENE COMPLEXES

No.	Complex[a]			$[M{-}CO]^+$	$[M{-}2CO]^+$	$[M{-}3CO]^+$	$[M{-}4CO]^+$	$[M{-}5CO]^+$	LFe_2^+	$[M{-}Fe(CO)_5]^+$	LFe^+	$[LFe{-}CH_4]^+$	$[LFe{-}(\ \ )]^+$
	R^α	R^β	X										
(I)	H	H	H	15	9	27	34	93	51	15	100		
(II)	CH_3	H	H	11	7	12	16	60	52	15	100	48	
(III)	CH_3	H	3-CH_3	18	11	19	23	76	67	13	100	55	
(IV)	CH_3	H	4-CH_3	18	16	37	46	104	87	12	100	53	
(V)	CH_3	H	5-CH_3	15	13	28	28	85	79	11	100	59	
(VI)	CH_3	H	6-CH_3	24	13	37	33	87	97	15	100	46	
(VII)	CH_3	H	3-C_6H_5	7	2	22	16	37	55	20	100	33	
(VIII)	CH_3	H	4-C_6H_5	8	2	22	17	55	45	16	100	30	
(IX)	CH_3	H	5-C_6H_5	25	9	49	42	83	98	12	100	41	
(X)	CH_3	H	4-CH_3O	17	9	23	25	73	62	16	100	31	8$(-CH_2O)$
(XI)	CH_3	H	5-CH_3O	4	4	13	13	44	48	18	100	22	
(XII)	H	CH_3	H	30	35	50	45	70	100	35	100		80$(-C_2H_2)$
(XIII)	H	CH_3	4-CH_3O	19	18	40	36	76	107	21	100		61$(-C_2H_2)$
(XIV)	H	H	4-CH_3	9	3	11	13	47	41	13	100		

[a] See structure (A) as model of substitution.

TABLE 3

RELATIVE ABUNDANCES (%) OF MAJOR IRON-CONTAINING FRAGMENTS IN THE MASS SPECTRA OF HALOGENOBIS(TRICARBONYLIRON)—α-METHYLSTYRENE COMPLEXES ($R^\alpha = CH_3$, $R^\beta = H$, X = hal)

No.	X	$(M{-}CO)^+$	$(M{-}2CO)^+$	$(M{-}3CO)^+$	$(M{-}4CO)^+$	$(M{-}5CO)^+$	$(M{-}6CO)^+$ LFe_2^+	$(LFe_2{-}C_3H_4)^+$	LFe^+	$(LFe{-}CH_4)^+$	$(LFe{-}HX)^+$
(XV)	4-F	29	22	41	37	112	117	5	100	30	12
(XVI)	4-Cl	45	40	47	49	61	318	75	100		48
(XVII)	4-Br	25	36	18	64	48	396	120	100		84
(XVIII)	3-Br	74	56	37	132	68	594	224	100		69
(XIX)	5-Br	88	99	51	173	106	485	260	100		92

TABLE 4. RELATIVE ABUNDANCES (%) OF MAJOR IRON-CONTAINING FRAGMENTS IN THE MASS SPECTRA OF BIS(TRICARBONYLIRON)—CHLOROSTYRENE COMPLEXES ($R^{\alpha} = R^{\beta} = H$)

No.	X	$(M-CO)^+$	$(M-2CO)^+$	$(M-3CO)^+$	$(M-4CO)^+$	$(M-5CO)^+$	LFe_2^+	$(LFe_2-C_2H_2)^+$	LFe^+	$(LFe-HCl)^+$
(XX)	6-Cl	146	80	40	64	66	730	312	100	350
(XXI)	5-Cl	46	19	17	33	45	267	91	100	143
(XXII)	4-Cl	52	20	33	36	49	281	75	100	95

TABLE 5. RELATIVE ABUNDANCES (%) OF MAJOR IRON-CONTAINING FRAGMENTS IN THE MASS SPECTRA OF BIS(TRICARBONYLIRON)—PHENYLSTYRENE COMPLEXES

No.	R^{α}	R^{β}	X	$(M-CO)^+$	$(M-2CO)^+$	$(M-3CO)^+$	$(M-4CO)^+$	$(M-5CO)^+$	LFe_2^+	$[LFe_2-(\ )]$	$[M-Fe(CO)_5]^+$	LFe^+	$[LFe-(\ )]^+$
(XXIII)	C_6H_5	H	H	15	9	27	34	93	51		15	100	
(XXIV)	C_6H_5	H	$4-CH_3O$	16	6	32	39	100	51		12	100	4 ($-CH_3$) 3 ($-CH_2O$) 8 ($-CH_3OH$)
(XXV)	$p-CH_3OC_6H_4$	H	H	6	2	10	14	42	23		18	100	3 ($-CH_3$) 2 ($-CH_2O$) 4 ($-CH_3OH$)
(XXVI)	C_6H_5	H	$4-CH_3$	19	8	31	40	123	51	12 ($-H_2$)	4	100	21 ($-H_2$)
(XXVII)	$p-CH_3C_6H_4$	H	H	25	10	38	46	120	59	17 ($-H_2$)	6	100	27 ($-H_2$)
(XXVIII)	$o-CH_3C_6H_4$	H	H	40	5	62	74	140	63	118 ($-H_2$)	15	100	74 ($-H_2$) 16 ($-CH_3$) 27 ($-CH_4$)

TABLE 6. RELATIVE ABUNDANCES (%) OF MAJOR IRON-CONTAINING FRAGMENTS IN THE MASS SPECTRA OF BIS(TRICARBONYLIRON)—1-PHENYLCYCLOALKENE COMPLEXES[a]

No.	n	$(M-CO)^+$	$(M-2CO)^+$	$(M-3CO)^+$	$(M-4CO)^+$	$(M-5CO)^+$	LFe_2^+	$(LFe_2-2H)^+$	$(LFe_2-4H)^+$	$[M-Fe(CO)_5]^+$	LFe^+	$(LFe-2H)^+$	$(LFe-4H)^+$	$(LFe-C_2H_4)^+$
(XXIX)	3	43	36	73	89	179	103	120	53	32	100	116	54	30
(XXX)	4	71	38	137	115	179	211		136	31	100		241	

[a] For model, see structure (B).

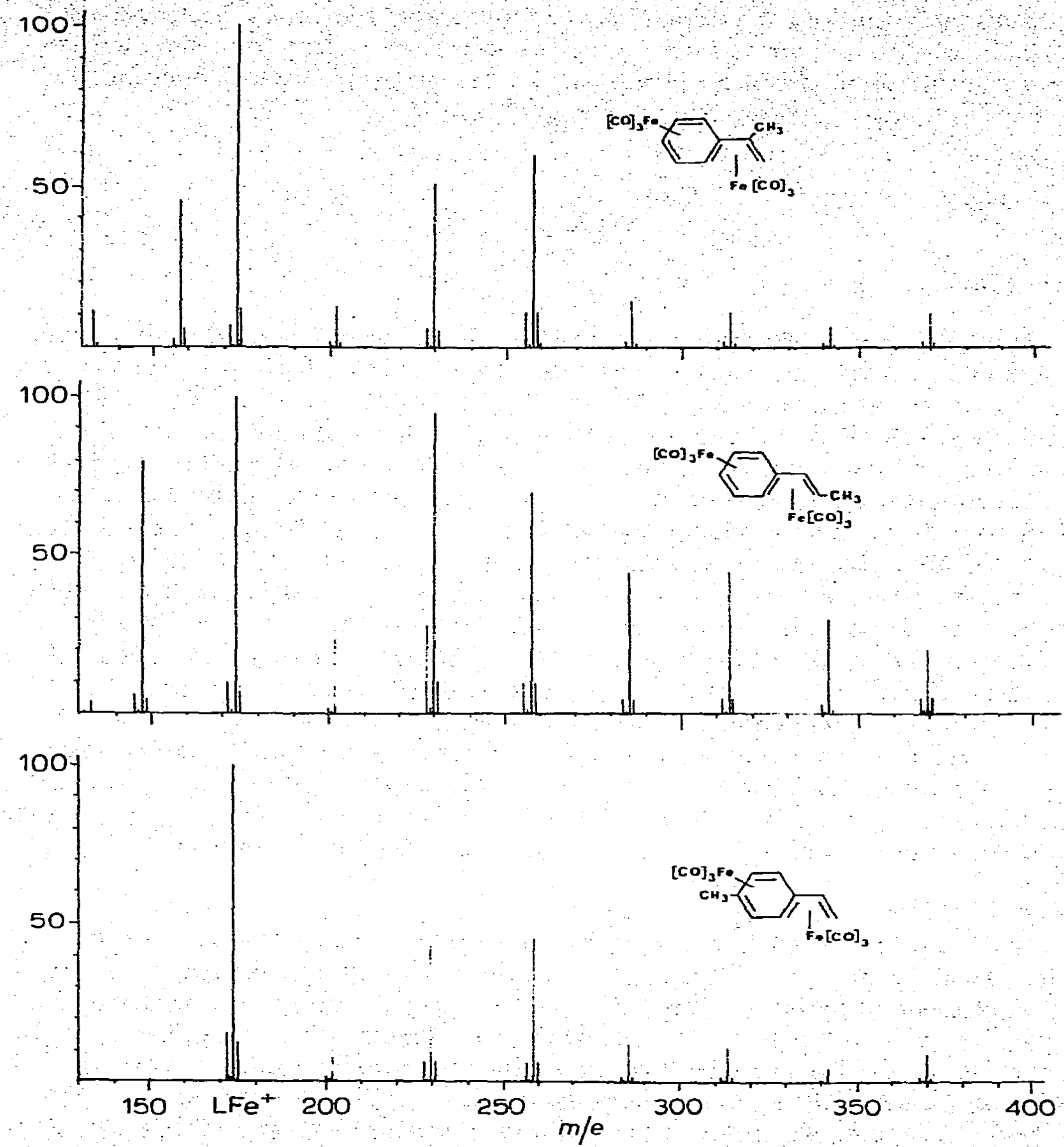


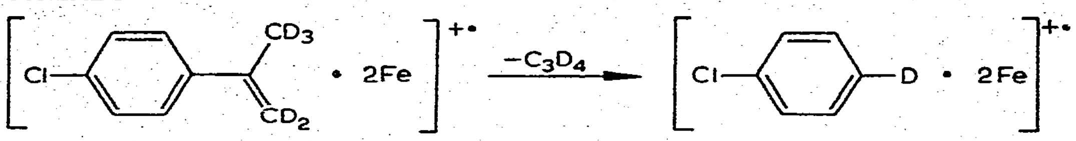
Fig. 1. Mass spectra of methylstyrene—bis(tricarbonyliron) isomers.

α-, the β- and the *p*-positions of the ligand are represented in Fig. 1 to show the dramatic difference in their modes of fragmentation.

Halogen substitution

When halogen (Br, Cl, F) is present on a ring position the predominant fragment containing iron is that comprised of the original styrene ligand and two iron atoms ($LFe_2^{+\cdot}$, Tables 3 and 4). From this ion there is an observed loss of acetylene or propyne when the sidechain is comprised of a vinyl group or an isopropenyl group, respectively [mode (*b*), Scheme 1]. It could be shown from deuterium labelling that the neutral alkyne lost is derived solely from the sidechain (Scheme 3). In contrast, while the loss of propyne from α-methyl-substituted free styrene ligands is an important process in most cases, it becomes minor when halogen is present on the ring (Table 1).

SCHEME 3



The LFe$^{+\cdot}$ ions containing halogen at a ring position are in relatively lower abundance in the spectra, probably because they undergo facile elimination of a hydrohalide molecule [mode (*f*), Scheme 1]. The order is HBr > HCl > HF, and for α-methyl-substituted members of this series such fragmentation is at the expense of methane elimination from the sidechain (Table 3). Halide elimination from the corresponding free ligand was a comparable process to the loss of hydrohalide from the complexed species (Table 1). At first glance it seems that the ion formed might have a ferrobenzyne structure as a result of 1,2-dehydrohalogenation from the ring. We found, however, that from the *p*-chloro-α-methylstyrene-d_5 complex where all deuterium is in the sidechain, HCl and DCl were eliminated to about the same extent. Furthermore, it appears that hydrogen loss from the sidechain is preferred on comparison of HCl elimination from the chlorostyrene isomers (Table 4), the 6-chloro-isomer showing far more than that of the 4- and 5-chloro isomers. It is suggested that the elimination takes place by way of a cyclic transition state in which iron plays a central role. Further evidence for the interaction between iron and halogen is given by the appearance of the FeX$^+$ ion in most of the mass spectra of the halogen complexes*.

Aryl substitution

In a series of complexes in which an aryl group is present at the α-position of the ligand, there is no observed elimination of a neutral arene species from LFe$^+$ analogous to methane elimination in the α-methyl series, nor is there rupture of the aromatic carbon skeleton while iron remains on the fragment in which the aryl substituent is at an α- or ring-position. Fragmentation of the organic portion is derived only from substituents on the complexed portion or on the free aryl group; e.g., elimination of methane from the isopropenylbiphenyl complexes [(VII)—(IX), Table 2] and minor loss of methyl radical, formaldehyde and methanol from the two isomers of *p*-methoxy-α-phenylstyrene [(XXIV) and (XXV), Table 5]. When methyl is present at the *p*-position of either the α-aryl substituent or the complexed ring, there is minor cleavage of a molecule of hydrogen [(XXVI) and (XXVII), Table 5], but when the methyl group is at the *o*-position of the aryl substituent**, the elimination of neutral hydrogen from

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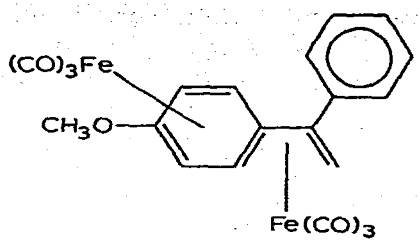
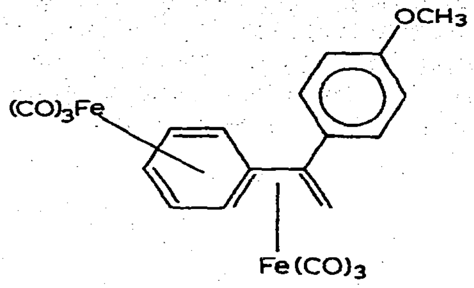
* Similar loss of Hhal from the mono(tricarbonyliron)—halostyrene complexes [5] indicates that the elimination of Hhal is indeed from the LFe$^+$ ion and not elimination of HFehal from the LFe$_2^+$ ion.

** The corresponding isomer in which the *o*-methyl group is present on the complexed ring was not detected in the reaction in which (XXVIII) was synthesized. The steric requirements in such a complex would presume a strong interaction between the methyl group and the α-phenyl substituent.

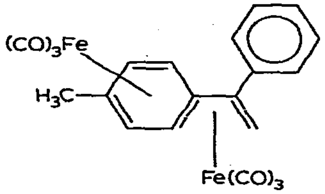
LFe$_2^{+\cdot}$ and LFe$^{+\cdot}$ becomes a major process [(XXVIII), Table 5]. It is assumed for the latter case that a cyclic transition is involved in which the original methyl carbon serves as the bridge between the two ring systems.



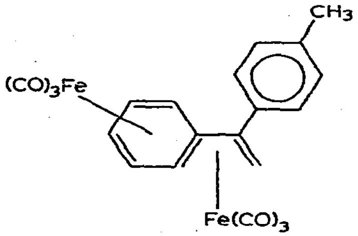
(XXIV)



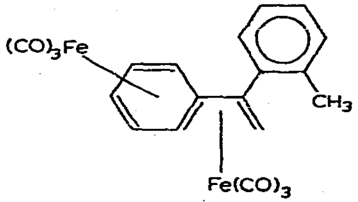
(XXV)



(XXVI)



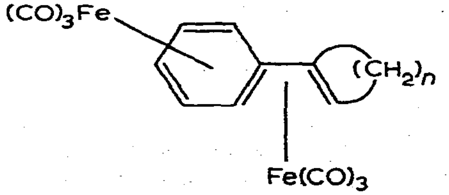
(XXVII)



(XXVIII)

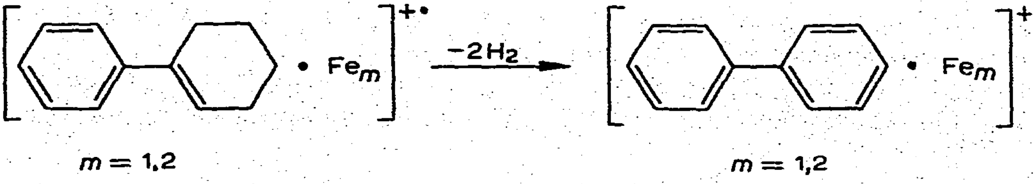
α,β-Polymethylene substitution (1-phenylcycloalkene complexes)

Two complexes derived from 1-phenylcycloalkenes (B) showed dominant fragments resulting from the loss of neutral hydrogen molecules (Table 6). In the case of the 1-phenylcyclohexene complex (XXX) the direct loss of 4 hydrogens points to a straightforward aromatization of the cyclohexene (Scheme 4), for which precedence has been shown in the study of cyclohexadienetricarbonyliron [7]. Though such elimination is also observed in the free 1-phenylcyclohexene ligand, it is not the exclusive pathway of fragmentation; instead it is subdued by modes in which carbon-containing species are cleaved (Table 1).



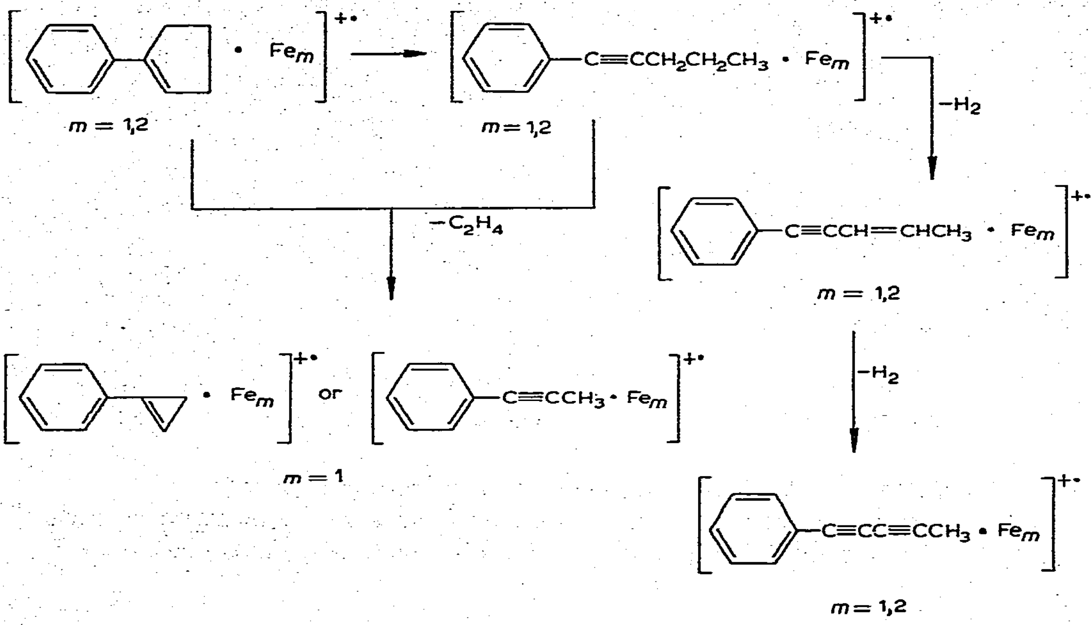
(B) $n = 1,2$

SCHEME 4



The cleavage of one and two molecules of hydrogen and a molecule of ethylene from the cyclopentyl complex (XXIX) cannot be interpreted in terms of aromatization. It is suggested rather that a part if not all of these processes occur concerted with or after ring opening of the cyclopentene. Such ring-opening might proceed in analogy to methane elimination from α-methylstyrene complexes; i.e., with the formation of phenylalkyne (Scheme 5). Cleavage within the free ligand also indicates rupture of the cyclopentene ring but with elimination of radical fragments.

SCHEME 5



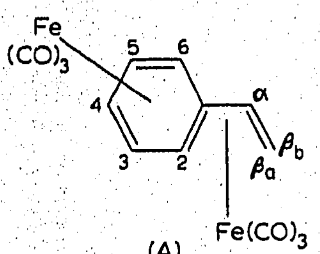
Experimental

Mass spectra were carried out on a MAT CH-5 Spectrometer, using the direct inlet system. The electron energy was maintained at 70 eV and the ionization current was maintained at 300 μA. The abundances of ions are given in percentages relative to the $LFe^{+\cdot}$ peak ion.

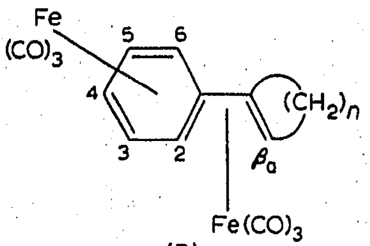
All styrene—bis(tricarbonyliron) complexes were synthesized by photochemical reaction of the styrene substrate with $Fe(CO)_5$ according to the procedure given in ref. 5. The free styrene ligands of previously unreported complexes were prepared from Grignard reaction of appropriate substrates and dehydration of the resulting alcohols by refluxing with 20-40% H_2SO_4 or distilling from solid $KHSO_4$. These substrates and their precursors include: *m*-phenyl-α-methylstyrene [8], (acetone, *m*-$C_6H_5C_6H_4MgBr$), *m*-methoxy-α-methylstyrene [9] (*m*-methoxyacetophenone, CH_3MgI), *p*-methylstyrene [10] (*p*-tolualdehyde, CH_3MgI), 1-phenyl-1-(*p*-tolyl)ethylene [11] (acetophenone, *p*-$CH_3C_6H_4MgBr$), 1-phenyl-1-(*o*-tolyl)ethylene [12] (*o*-methylacetophenone, C_6H_5MgBr), 1-phenylcyclopentene [13] (cyclopentanone, C_6H_5MgBr) and 1-phenylcyclohexene [14] (cyclohexanone, C_6H_5MgBr). The bis(tricarbonyliron) complexes

TABLE 7

NMR SPECTRAL PARAMETERS[a,b] OF PREVIOUSLY UNREPORTED BIS(TRICARBONYLIRON) COMPLEXES



(A)



(B)

No.	Model	Substituents	Chemical shift (τ)							
			βa	βb	α	2	3	4	5	6
(VII)	(A)	α-CH_3, 3-C_6H_5	9.55d	8.30d	7.88s	≈ 7.88[c]	≈ 2.64m	3.40d	3.31dd	6.20dd
(IX)		α-CH_3, 5-C_6H_5	9.77d	8.40d	7.83s	8.04d[c]	6.55dd	3.55dd	≈ 2.26m(2H) ≈ 2.59m(3H)	5.81d[d]
(XI)		α-CH_3, 5-CH_3O	9.84d	8.44d	7.89s	8.13d[d]	7.02dd	4.16dd	6.10s	≈ 6.10[e]
(XIV)		4-CH_3	9.94dd	8.52dd	5.01dd	7.90d[d]	6.64dd	7.66s	3.62dd	6.57dd
(XXVI)		α-C_6H_5, 4-CH_3	9.62d	8.15d	2.40 — 2.78m	7.97dd	6.59dd	7.62s	3.55dd	6.52dd
(XXVII)		α-(p-$CH_3C_6H_4$)	9.60d	8.12d	2.58d(2H) 2.86d(2H) 7.65s(3H)	7.96d[d]	6.58m	3.85m	3.45m	6.33d[d]
(XXVIII)		α-(o-$CH_3C_6H_4$)	9.35d	8.31d	≈ 2.82m(4H) 7.53s(3H)	7.89d[d]	6.56m	3.91m	3.58m	6.77m
(XXIX)	(B)	$n = 3$	7.3 — 8.5 (unresolved)				6.57m	3.93m	3.47m	6.32d[d]
(XXX)		$n = 4$	7.2 — 8.8 (unresolved)				6.52m	3.91m	3.52m	6.29d[d]

[a] Solutions in $CDCl_3$, TMS internal standard. [b] J taken for all compounds (Hz): $H_{\beta a}H_{\beta b}$ = 2.0 — 2.6; $H_{\beta a}H_{\alpha}$ = 8.4; $H_{\beta b}H_{\alpha}$ = 6.5; H_2H_3 = 4.4 — 5.0; H_2H_6 = 1.4; H_3H_4 = 6.0 — 6.5; H_3H_5 = 1.6 — 2.2; H_4H_5 = 4.4; H_5H_6 = 6.4 — 6.6. [c] Hidden under methyl proton resonance. [d] Broad due to further coupling. [e] Hidden under methoxy proton resonance.

derived from these styrene materials are characterized by five to six metal carbonyl bands in the infrared region 1950 to 2060 cm^{-1} (hexane solution): *m*-phenyl-α-methylstyrene—$[Fe(CO)_3]_2$ [(VII), purple needles, m.p. 131° (dec.), five CO bands; (IX), red prisms, m.p. 129° (dec.), five CO bands]; *m*-methoxy-α-methylstyrene—$[Fe(CO)_3]_2$ [(XI), orange needles, m.p. 124° (dec.), five CO bands]*, *p*-methylstyrene—$[Fe(CO)_3]_2$ [(XIV), orange-red needles, m.p. 126° (dec.), five CO bands]; 1-phenyl-1-(*p*-tolyl)ethylene—$[Fe(CO)_3]_2$ [(XXVI), red prisms, m.p. 110° (dec.), six CO bands; (XXVII), orange-red plates, m.p. 120° (dec.), five CO bands]; 1-phenyl-1-(*o*-tolyl)ethylene—$[Fe(CO)_3]_2$ [(XXVIII), purple prisms, m.p. 110° (dec.), five CO bands]**; 1-phenylcyclopentene—$[Fe(CO)_3]_2$ [(XXIX), red crystal, m.p. 146° (dec.), six CO bands]; and 1-phenylcyclohexene—$[Fe(CO)_3]_2$ [(XXX), orange-red crystal, m.p. 152° (dec.), six CO bands].

All new complexes reported here gave satisfactory elementary analyses (C, H; A. Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany).

The NMR spectral data of the new complexes obtained from $CDCl_3$ solutions with TMS internal standard on a Jeol C-60H spectrometer are tabulated in Table 7.

The deuterated bis(tricarbonyliron) complexes of α-methylstyrene-d_5 and *p*-chloro-α-methylstyrene-d_5 were prepared by usual photochemical reaction of the deuterated substrate with $Fe(CO)_5$ [5]. Deuterium labelling of the substrate was achieved by small scale Grignard reaction of phenylmagnesium bromide or *p*-chlorophenylmagnesium bromide (in excess) with acetone-d_6 (1 ml in each case), and dehydration of the aryldimethyl-d_6 carbinol by distillation from a catalytic amount of $KHSO_4$. Mass spectral analyses of the products obtained showed over 90% pentadeutero-substitution in each case.

References

1 (a) M.I. Bruce, Advan. Organometal. Chem., 6 (1968) 273;
(b) M. Cais and M.S. Lupin, ibid., 8 (1970) 211;
(c) J. Muller, Angew. Chem., Int. Ed. Engl., 11 (1972) 653, and references therein.
2 Cf., H. Budzikiewicz, C. Djerassi and D.H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, 1967.
3 R.B. King, Org. Mass Spectrom., 2 (1969) 657.
4 (a) A. Mandelbaum and M. Cais, Tetrahedron Lett., (1964) 3847;
(b) H. Egger, Monatsh. Chem., 97 (1966) 602;
(c) J.D. Hawthorne, M.J. Mays and R.N.F. Simpson, J. Organometal. Chem., 12 (1968) 407.
5 R. Victor, R. Ben-Shoshan and S. Sarel, J. Org. Chem., 37 (1972) 1930.
6 W.G. Dauben and M.E. Lorber, Org. Mass Spectrom., 3 (1970) 211.
7 T.H. Whitesides and R.W. Arhart, Tetrahedron Lett., (1972) 297.
8 D.T. Mowry, J. Dazzi, M. Renoll and R.W. Shortridge, J. Amer. Chem. Soc., 70 (1948) 1916.
9 L.H. Easson and E. Stedman, J. Chem. Soc., (1933) 1094.
10 A.F. Titley, J. Chem. Soc., (1926) 508.
11 M. Tiffeneau, Ann. Chim. Phys., 8 (1907) 322; Chem. Abstr., 2 (1908) 266.
12 M.S. Kharasch, A. Fono, W. Nudenberg and A.C. Poshkus, J. Org. Chem., 15 (1950) 775.
13 Y. Amiel, A. Loffler and D. Ginsburg, J. Amer. Chem. Soc., 76 (1954) 3625.
14 C.C. Price and J.V. Karabinos, J. Amer. Chem. Soc., 62 (1940) 1159.

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* The isomeric bis(tricarbonyliron) complex of (XI) in which the methoxy group is at the 3-position [structure (A)] was not detected in the reaction mixture from which (XI) was isolated.

** See footnote on page 72.