Mass Spectrometry of Compounds of the Type $[Fe(CO)_2(\eta\text{-}C_5H_5)R]$ (R = alkyl)

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The electron-impact mass spectra of a series of compounds of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)R]$ (R = alkyl) have been obtained. Three major fragmentation routes commence with loss of alkyl (R), alkene (R–H), or carbonyl groups. Particularly intense peaks are also formed by loss of one, two, or three molecules of H_2 from the $[M - 2CO]^+$ ions, leading to species which presumably contain η^3-allylic and η^5-pentadienyl moieties.

THERE has been considerable interest in recent years in the mass spectra of organotransition-metal compounds.[1,2] The interest has arisen in part because of the usefulness of the technique for the characterization of volatile compounds, and because of the wealth of information in the fragmentation patterns observed for important series of compounds such as the metallocenes.[2]

To date, however, a systematic study of a homologous series of σ-alkyl compounds has not been carried out. We now present, therefore, the mass spectral patterns for a variety of compounds of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)R]$ (R = alkyl). The fragmentation patterns are interpreted in terms of decomposition pathways deduced using information from metastable ions and high-resolution mass determinations. Although some data are available in the literature for R = Ph,[3] CH_2Ph,[4] and COMe,[3] the present investigation is the first to examine thoroughly this important system of alkylmetal compounds.

EXPERIMENTAL

The mass spectra were obtained on a JEOL-OISC mass spectrometer with Mattauch-Herzog geometry under standard conditions: electron energy, 70 eV; and ion-source temperature, *ca.* 170 °C.† Samples were introduced directly into the ion source from a glass capillary set in a metal probe which could be heated or cooled by a stream of nitrogen to precisely controlled temperatures. Metastable ions were absent from the normal mass spectra but could be observed in the first field-free region by decoupling the electrostatic sector and accelerating voltages.

The preparation and purification of the compounds is described elsewhere.[5]

One of the problems faced when working with organometallic compounds is the possibility that the mass spectrum will be complicated by the presence of pyrolysis products formed either in the sample-inlet system or in the ionization chamber. King [3] found that acyl compounds of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)(COR)]$ exhibit ions in their mass spectra arising from ferrocene and substituted ferrocenes. Thermal decomposition of the compounds during sample introduction was suspected.

In the present work, large yields of $[Fe(C_5H_5)_2]^+$ were initially encountered even though spectra could be obtained for most compounds at sample temperatures in the range 10—20 °C. On running a sample to exhaustion, it was found that the contribution of $[Fe(C_5H_5)_2]^+$ (*m/e* 186) to the total ionization diminished with time, and its contribution to the spectrum when most of the sample was vaporized was minimal. This suggests that pyrolysis was not occurring to any significant extent in the mass spectrometer. Samples which showed significant peaks at *m/e* 186 were purified immediately prior to introduction into the ion source. This minimized the yield of this ion. Apart from the molecular ion, the only ions of significance in the spectrum of ferrocene are at *m/e* 121 $\{[Fe(C_5H_5)]^+\}$ and *m/e* 56 (Fe^+) both of which are small compared with *m/e* 186: the presence of a small amount of ferrocene in any compound does not therefore obscure any significant details of the spectrum.

RESULTS AND DISCUSSION

Nineteen compounds of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)R]$ were studied, and are designated (1)—(19). Shown in Figure 1 are the mass spectra of compounds (8), (12), and (14), illustrating the typical patterns for alkyl, alkyl substituted terminally with a saturated ring, and alkyl substituted terminally with an aromatic ring. Also shown for reference is the spectrum of ferrocene obtained under similar conditions.

Figure 2 shows the fragmentation scheme for compound (8) as established by high-resolution mass determinations and observed metastable ions. A solid line indicates that a metastable transition was observed, a broken line that no transition was observed.

The Table gives the major ions for each compound, arranged in a manner devised to correlate the overall general features for this class of compound. Except for the methyl compound (1), molecular ion yields are low. As indicated in Figure 2, no metastables are observed for the decomposition of the molecular ions, although there clearly are three competing decomposition pathways of comparable significance. These commence with loss of alkyl, loss of alkene, or loss of carbonyl groups.

Loss of Alkyl.—Loss of the alkyl group leads to the $[Fe(CO)_2(\eta\text{-}C_5H_5)]^+$ ion (*m/e* 177). This ion in general is of low intensity for all compounds and the intensities do not correlate with the relative strengths of ground state metal–carbon bonds, *i.e.* primary > secondary > tertiary.[6] For example the two isomeric butyl compounds (3) and (4) give identical yields of $[Fe(CO)_2(\eta\text{-}C_5H_5)]^+$. Such comparisons are not in general fruitful in mass spectrometry, however, since it is the whole decomposition sequence that must be considered.

As observed previously,[3] the $[Fe(CO)_2(\eta\text{-}C_5H_5)]^+$ ion decays by successive loss of carbonyl groups to give $[Fe(C_5H_5)]^+$ $\{[M - (R + 2CO)]^+\}$. This latter ion is also a product of the other fragmentation routes (Figure

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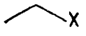
† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

2) and yields an intense peak in all spectra. It is also the major fragment ion in the ferrocene spectrum, but the contribution from ferrocene impurity in any spectrum is not significant. The ion $[Fe(C_5H_5)]^+$ usually fragments directly to Fe^+ but fragmentation of the cyclopentadienyl ring leads to low yields of $[Fe(C_3H_3)]^+$, $[Fe(C_3H_2)]^+$, and $[Fe(C_3H)]^+$ and a little $C_5H_5^+$ is also observed.

CH_3-X

(1)



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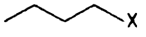

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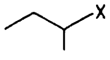

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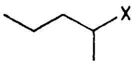

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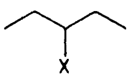

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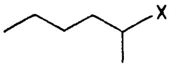

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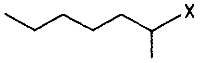
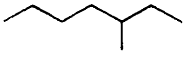


(8)



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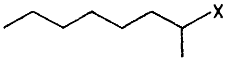

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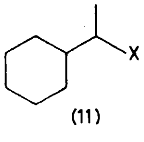

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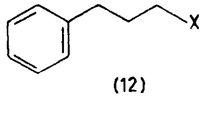

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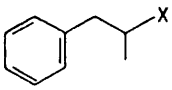

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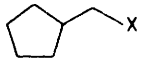

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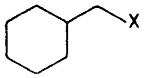

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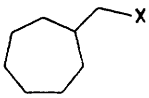

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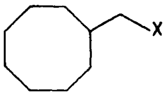

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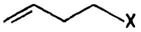

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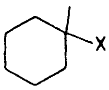


(19)

X = $Fe(CO)_2(\eta\text{-}C_5H_5)$

Loss of Alkene.—In competition with loss of the alkyl group is loss of alkene, accompanied by transfer of H to iron to yield $[Fe(CO)_2(\eta\text{-}C_5H_5)H]^+$ (*m/e* 178). The latter then undergoes successive loss of carbonyl groups, followed ultimately by loss of H. This mode of elimination of olefin is unusual in that it occurs prior to the formation of a vacant site on Fe by elimination of CO. In solution, derivatives of the compounds studied here, of the general formula $[Fe(CO)(\eta\text{-}C_5H_5)R(PPh_3)]$, eliminate olefin in a process which involves prior dissociation of the tertiary phosphine.[7] The hydrogen migrates to the vacant site to give the hydrido-olefin species [Fe(CO)-

Ion	Compound																		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)
M^+	26	8	8	7	8	3	2	8	3	4	3	4	1	3	2	<1	<1	8	2
$[M - CO]^+$	31	27	30	30	34	18	16	30	35	23	25	9	2	13	13	13	13	7	5
$[M - 2CO]^+$	7	31	7	8	5	5	7	3	<1	4	<1	90	16	7	<1	10	4	100	<1
$[M - (2CO + H_2)]^+$	42	3	100	100	100	19	59	100	74	29	79			37	9	100	100	22	35
$[M - (2CO + 2H_2)]^+$			18	13	21	3	10	21	15	20				100	54	62	50	25	7
$[M - (2CO + 3H_2)]^+$			<1	<1	26	16	26	43	28	90							25		
$[M - R]^+$	5	3	20	20	9	41	10	18	34	14	7	15	3	4	4	7	9	18	31
$[M - (R + CO)]^+$		14	19	25	22	28	23	32	33	34	19	33	6	11	24	19	18	28	24
$[M - (R + 2CO)]^+$	100	59	75	63	54	62	86	98	100	100	53	100	22	39	48	52	50	93	56
$[M - \text{olefin}]^+$		27	7	8	10	<1	7	21	<1	21	15	5	3	2	<1	5	21	2	31
$[M - (\text{olefin} + CO)]^+$		31	49	27	29	21	29	45	61	34	26	9	8	7	7	12	13	8	17
$[M - (\text{olefin} + 2CO)]^+$		100	46	47	36	32	54	46	66	45	23	21	9	19	18	22	18	63	24
Fe^+	26	65	46	60	38	53	100	67	77	58	38	59	10	31	45	34	31	76	64
$[M - (RH + CO)]^+$		3	24	19	9	12	5	8	23	10	9	41	10		100	10	13	75	100
$[Fe(C_5H_5)(C_3H_5)]^+$					21	17	17	13	15	14	100		2	5		67	3		
$[Fe(C_5H_5)(C_4H_7)]^+$			100	100		41	10	18	34	16				2		3	17	100	
R^+								3			11	96 *	35 *						60

* *m/e* 91.

(η-C_5H_5)(olefin)H], followed by displacement of olefin by phosphine to give products. Attempts to pyrolyze some of the present compounds by rapid heating in the ion source of the mass spectrometer failed to show any production of olefin. The $[Fe(CO)_2(\eta\text{-}C_5H_5)H]^+$ ion is therefore a product of ion dissociation. Clearly olefin elimination by the dissociative mechanism favoured for molecules in solution does not occur in the mass spectrometer.

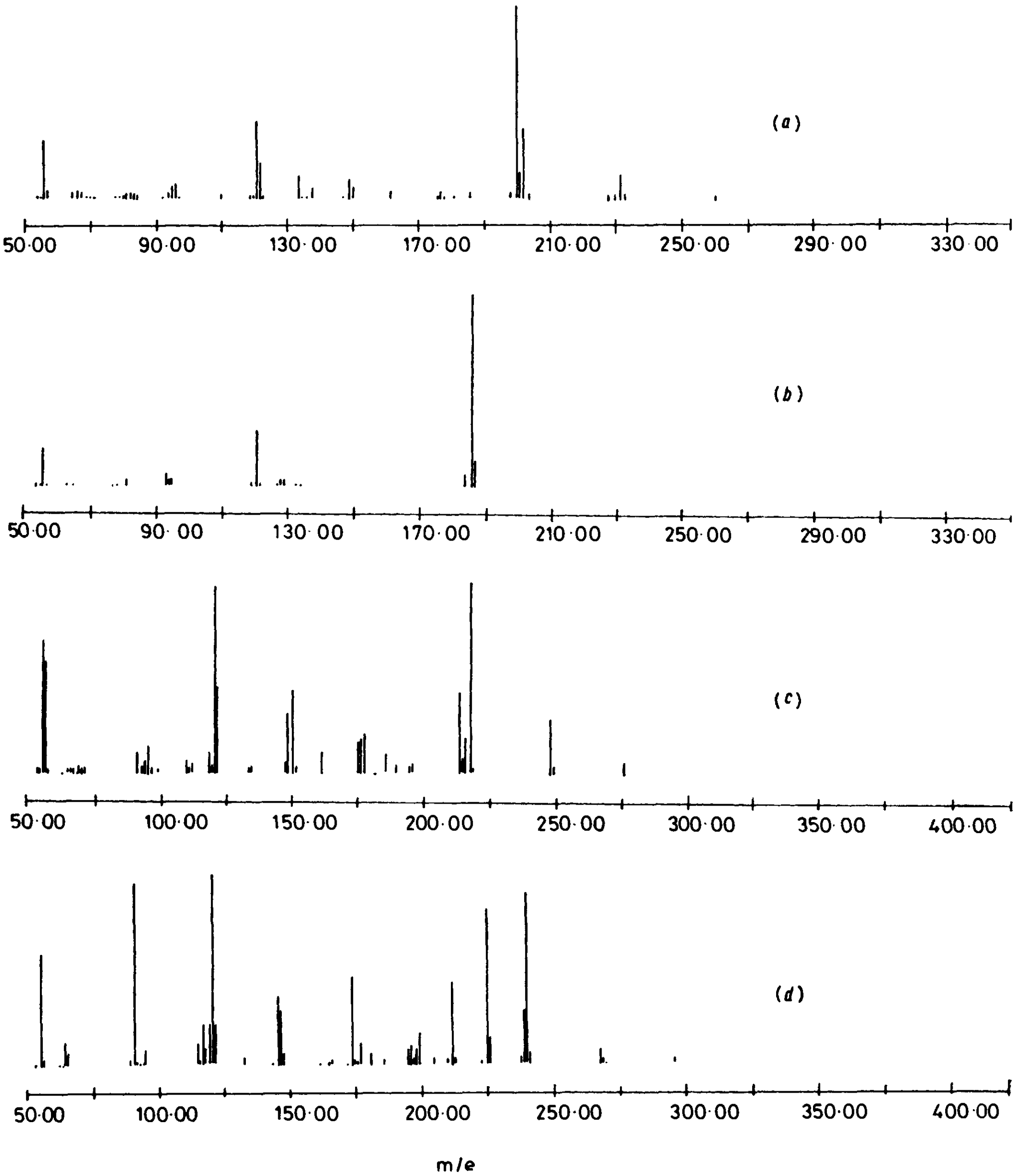
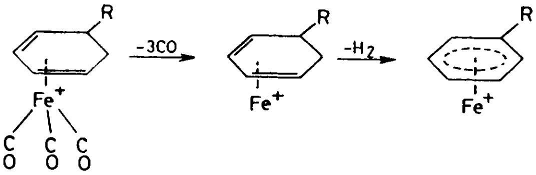


FIGURE 1 Mass spectra of the compounds (14) (*a*), ferrocene (*b*), (8) (*c*), and (12) (*d*)

Ions containing H bonded to metal are, as expected, of low intensity for the methyl compound (1) for which loss of methylene is not energetically favourable. They are also of low intensity for compounds (12) and (13), whose spectra also show hydrocarbon ions such as those at *m*/*e* 91 and 105 characteristic of alkyl-substituted aromatics. All other compounds, with the exception of (19), show only minor contributions to total ionization from ions arising from the alkyl group.

Loss of Carbon Monoxide.—Carbon monoxide, being a weak donor ligand, is readily lost from the molecular ions.[3] Metastable transitions (Figure 2) indicate that loss of the second CO occurs in two ways, either alone, followed by loss of H_2, or by loss of COH_2 in what appears to be a single step. The latter step could involve direct loss of formaldehyde, as has been proposed for carbonyl-substituted phenylferrocenes,[8] but it seems more probable that losses of CO and H_2 are occurring consecutively in the time of flight through the first field-free region of the mass spectrometer (a distance of *ca*. 1 m).

Loss of H_2 has been reported for a number of tricarbonylcyclohexa-1,3-dieneiron derivatives.[9] It was suggested that after the elimination of one or more carbonyl groups the iron becomes electron deficient. Loss of H_2 converts the hydrocarbon ligand from a 4π η^4-diene to a 6π η^6-arene system.



The present alkyl complexes lose up to three H_2 molecules subsequent to the loss of carbonyl. In the case of the methyl compound (1) it has been shown that H_2 loss after loss of carbonyl occurs with scrambling of the hydrogens of the methyl and of the cyclopentadienyl ring.[10] The resulting ion may be the arene species $[Fe(C_6H_6)]^+$. The formation of this ion is not observed for the other alkyl compounds and it is probable that the scrambling of H atoms between alkyl and ring is unique to compound (1).

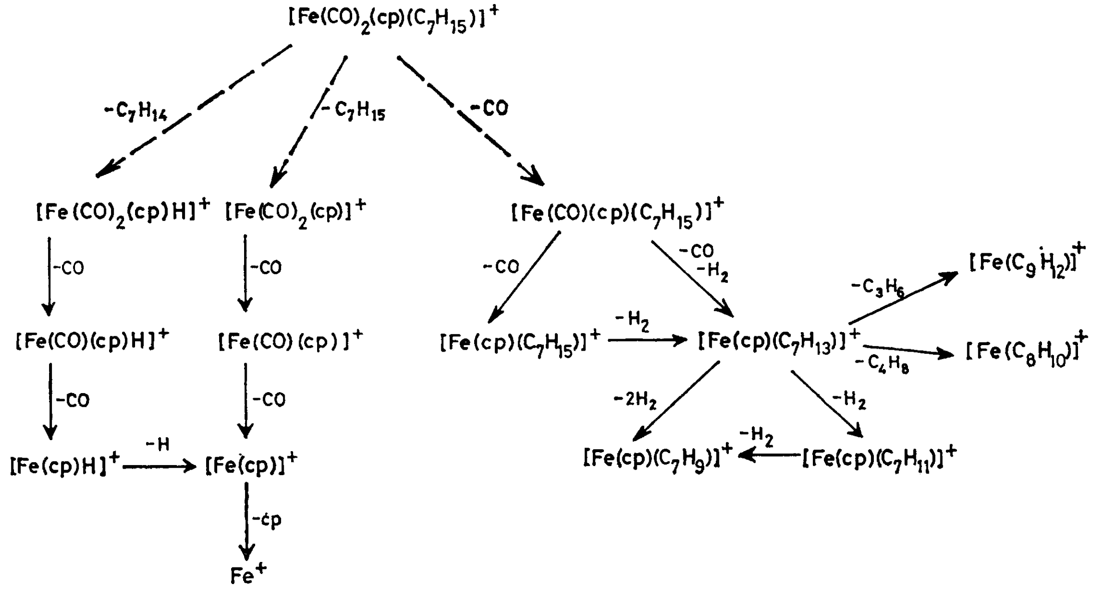
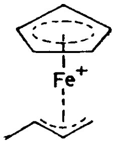


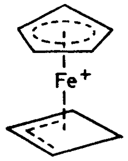
FIGURE 2 Fragmentation scheme for compound (8). A solid arrow signifies that the metastable ion was observed

The higher alkyl compounds lose more than one molecule of hydrogen, the number lost correlating approximately with the length of the alkyl chain. Thus loss of only one H_2 leads to the base peak of each butyl complex [(3) and (4)] [interestingly, the same ion forms the base peak of the butenyl complex (18)]. While this ion, $[Fe(C_9H_{12})]^+$, cannot be identified with certainty, and indeed may not even be the same species for all three systems, it seems most likely that it is the methylallyl complex $[Fe(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3H_4Me)]^+$.

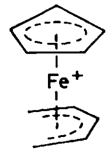


The same species could be derived from all three precursors *via* double-bond migration, and would be stabilized by the great stability of the η^3-alkyliron moiety.[11] The reported gas-phase reaction of $[Rh(\eta\text{-}C_5H_5)H]^+$ with propane, yielding the allyl complex $[Rh(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)]^+$ and 2 mol of H_2[12] may involve a similar interaction.

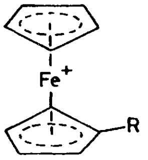
Loss of a second H_2 occurs to some extent for compounds (3) and (4), giving a species of formula $[Fe(C_9H_{10})]^+$ which could be $[Fe(C_5H_5)(C_4H_5)]^+$ as shown below.



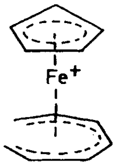
Compounds (4)—(11) and (14)—(17) also lose 1 mol of H_2 after loss of 2CO, presumably forming allylic species of the type discussed above. Abundant ions due to the loss of $2H_2$ are presumably pentadienyl complexes, *e.g.* as below from (5). Such species are also expected to be very



stable. Loss of 3 mol of H_2 occurs from the longer-chain compounds (5)—(10), presumably leading to substituted ferricinium ions.



An alternative type of structure, possible for the C_7 and C_8 straight-chain species, is a heptatrienyl complex.



Such a structure is without precedent in ground-state organometallic chemistry. That the ferricinium structure is more likely is shown by the fact that while the cycloalkyl species (14)—(17) readily form the allylic and pentadienyl ions, as expected, they do not produce ions by loss of $3H_2$. The seven- and eight-membered rings should be capable of existence as heptatrienyl species, but might not be expected to readily undergo contraction to five-membered rings by loss of H_2 only. The heptatrienyl species illustrated would, furthermore, be a 19-electron system and would not be expected to be stable.[13] The driving force in the formation of the ferricinium species would be the carbon–carbon bond formation as well as the great stability of the Fe(η-C_5H_5) moiety.[9]

As shown in the Table, the allylic species $[Fe(C_5H_5)(C_3H_5)]^+$ and $[Fe(C_5H_5)(C_4H_7)]^+$ occur in the mass spectra of a large number of compounds. In the case of compound (8), as shown in Figure 1, these species are formed by loss of olefins (butene and propene, respectively) from the $[M - (2CO + H_2)]^+$ ion. Thus the loss of olefin *via* carbon–carbon bond cleavage competes with loss of hydrogen from the heavier alkyl species (C_5—C_8).

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