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ELECTRON-IMPACT AND FIELD-DESORPTION MASS SPECTRAL STUDIES OF IRON COMPLEXES OF TYPE $Fe_x(CO)_y(C_2R_2)_2$: FRAGMENTATION PATTERNS OF FERROLE DERIVATIVES AND RELATED COMPLEXES

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Summary

Field-desorption and electron-impact mass spectral investigations of mono- and oligo-nuclear ferracyclic ring systems of type $Fe_x(CO)_y(C_2R_2)_2$ ($x = 1, 2, 3$: $y = 6, 8$) are described which for the first time show intense molecular ion peaks, which enable ready recognition of the molecular composition. The fragmentations and their dependence on the ion source and sample temperature, electron energy and sample-inlet mode under electron-impact conditions are discussed.

The application of electron-impact (EI) mass spectrometry (MS) to transition metal carbonyls and their derivatives has mainly been directed towards study of fragmentations of metal–metal and metal–ligand bonds [1]. Several accounts of the fragmentation of mono- and poly-nuclear carbonyls and their derivatives have appeared [2]. Much less is known about the mass spectra of metallacyclic systems which are coordinated via π-bonds to metal carbonyl moieties [3]. There are mainly two reasons for this: (a) most metallacycles are thermally labile and air-sensitive; (b) because of this instability their EI mass spectra rarely exhibit molecular ion peaks, which would provide a rapid indication of the elementary composition of such species, because they readily decompose before ionisation, and this is sometimes leading to misinterpretation of the constitution or the degree of purity of the compound [4]. The mass spectra of some iron, osmium, and ruthenium metallacycles have been described [5]. Interestingly, in case of osmium and ruthenium ($M_2(CO)_6(C_2Ph_2)_2$, M = Os, Ru), molecular ion peaks of moderate to high relative intensity (27–62%) were observed, whereas the analogous iron complex exhibited an extremely weak M^+ peak (0.5%) which was hard to distinguish from minor impurities or peaks resulting from thermal decomposition. Other ferroles showed only

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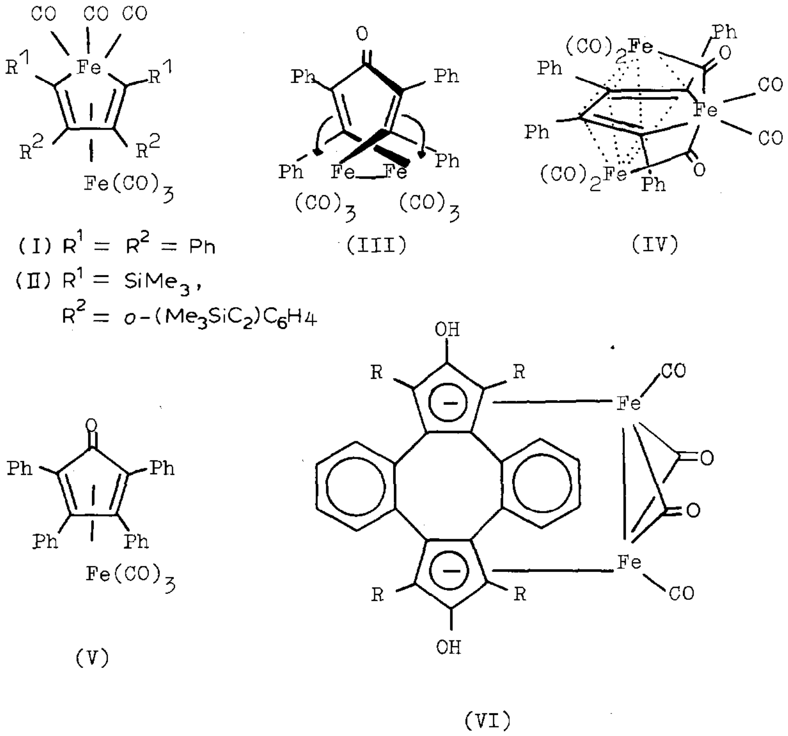
fragment ions and/or ions of stable decomposition products with lower and/or higher mass units than expected [6].

Field-desorption (FD) mass spectrometry, is an analytical tool particularly well suited for the characterisation of compounds which are thermally unstable or have negligible vapor pressures. Surprisingly, this method has been little used in elucidation of the composition of organometallic or inorganic complexes to which such problems apply [7]. Since many organometallic complexes contain elements possessing a number of stable isotopes, observation of the distinctive isotope patterns in the cluster of peaks is a particularly effective way to find out whether the assumed composition is correct.

During our research on the reactions of iron carbonyls with acetylenic compounds [8,9] we isolated some ferrole derivatives, the EI mass spectra of which were rather unsatisfactory. To overcome this problem we synthesised some additional mono-, di-, and trinuclear iron complexes (I, III–V [10]) (Scheme 1) and systematically investigated their EI and FD mass spectra [6].

SCHEME 1



Results and discussion

A. Field-desorption mass spectra (FDMS)

As indicated above, we were interested in both, (a) observation of the molecular ions of high relative abundance which are useful for the establishment of composition in cases in which it is not possible to obtain satisfactory elemental analysis because of rapid decomposition or because of formation of crystals incorporating one or several molecules of solvent, and (b) the fragmentation patterns of the complexes.

In the FDMS of (I–VI) the molecular ion is the peak of highest abundance (Fig. 1). Fragments, if any, had much lower abundances than the molecular ion, and corresponded to loss of $Fe(CO)_2$ ($m/e = 524$, 1%) in the case of I, CO ($m/e = 794$, 0.5%), and 2 CO ($m/e = 766$, 3%) in the case of II, $Fe(CO)_3$ ($m/e = 524$, 6%) in III and tetracyclone $(C_2Ph_2)_2CO$ ($m/e = 384$, 1%) in the case of IV. Complex VI formed crystals incorporating one molecule of benzene (as shown by X-ray crystallography [11]). The FDMS, however, indicated that the molecular weight of this complex was 822 (found: $m/e = 822.1044$. $C_{38}H_{46}O_6Si_4Fe_2$ calcd.: $m/e = 822.1035$.)

Alongside the spectrum in the region of the molecular ion peaks (A) in Fig. 1, in B are shown plots of the total ion current (Σ ion_{tot}) and M^+-ion current (Σ ion_{M^+}) against the temperature. The curve for complex III is of special interest as it shows the disappearance of Σ ion_{M^+} at T_e and the appearance of a new beam at $T > T_e$. This observation may explain the absence of the parent ion under electron-impact conditions (direct inlet: $T_{\text{ion source}}$ (T_{is}) 200°C; in beam inlet: T_{is} 140°C). Under these conditions III is unstable and decomposes readily to yield fragment ions and ions derived from stable decomposition products of higher molecular weight than III (see also paragraph B).

These few examples illustrate the value of FDMS for characterisation at least of heterocyclic systems containing iron atoms, and π-bonded iron carbonyl species. The technique provides simple, highly specific data and is applicable even when quantities are small. It provides a valuable supplement to other physical methods routinely used for such compounds.

B. Electron-impact mass spectra (EIMS)

Compared with the FDMS results the EIMS (direct inlet, T_{is} 200°C, T_{sample} (T_s) 100–200°C, 70 eV) of I–VI were very unsatisfactorily in revealing the molecular ion peaks (Table 1). Only VI exhibited a parent ion of moderate intensity (15%), whereas tricarbonyl(tetracyclone)iron(0) (V) and ferrole complex II showed relatively weak M^+-peaks (2%) [12] and no detectable decomposition product. In the spectrum of IV the parent ion was observed only at T_s 150°C, and with an extremely small intensity of ca. 0.1%, which did not permit a confident assignment of the composition. I and III showed no parent peak; fragment ions (from I, $M^+ - CO$ and from III: $M^+ - Fe(CO)_3$) and peaks resulting from stable decomposition products with molecular weights higher than I and III were observed; such results could easily lead to faulty identification. A possible route for the decomposition is outlined in Scheme 2(a). In this, thermal decomposition of IV yields complex I, which is converted thermally into V and tetracyclone VII, as described earlier [10]. Reaction of V and VII might give $(C_4Ph_4CO)_2Fe(CO)$ (VIII) (M^+: $m/e = 852$) with elimination of two CO molecules. We recently described a structurally related intramolecular complex [8].

Use of an in-beam sample inlet system, which seems to be more precise, and lowering T_{is} and T_s to 40–50°C below the melting/decomposition points results in observation of moderately intense parent ions for all the compounds except III, without any ions from decomposition products (Table 1); in the case of III in addition to fragment ions there was a peak at $m/e = 794$ arising from decomposi-

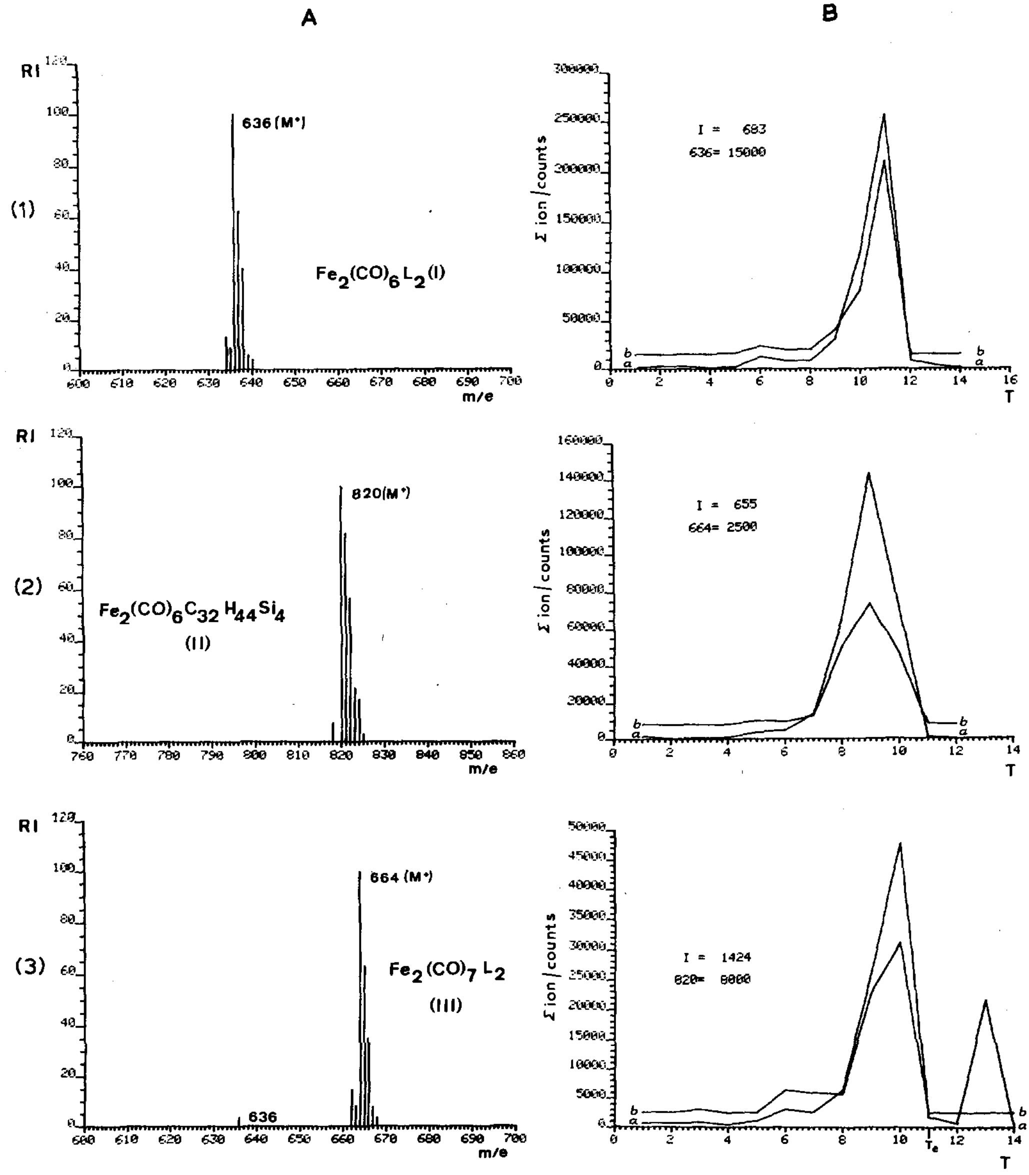
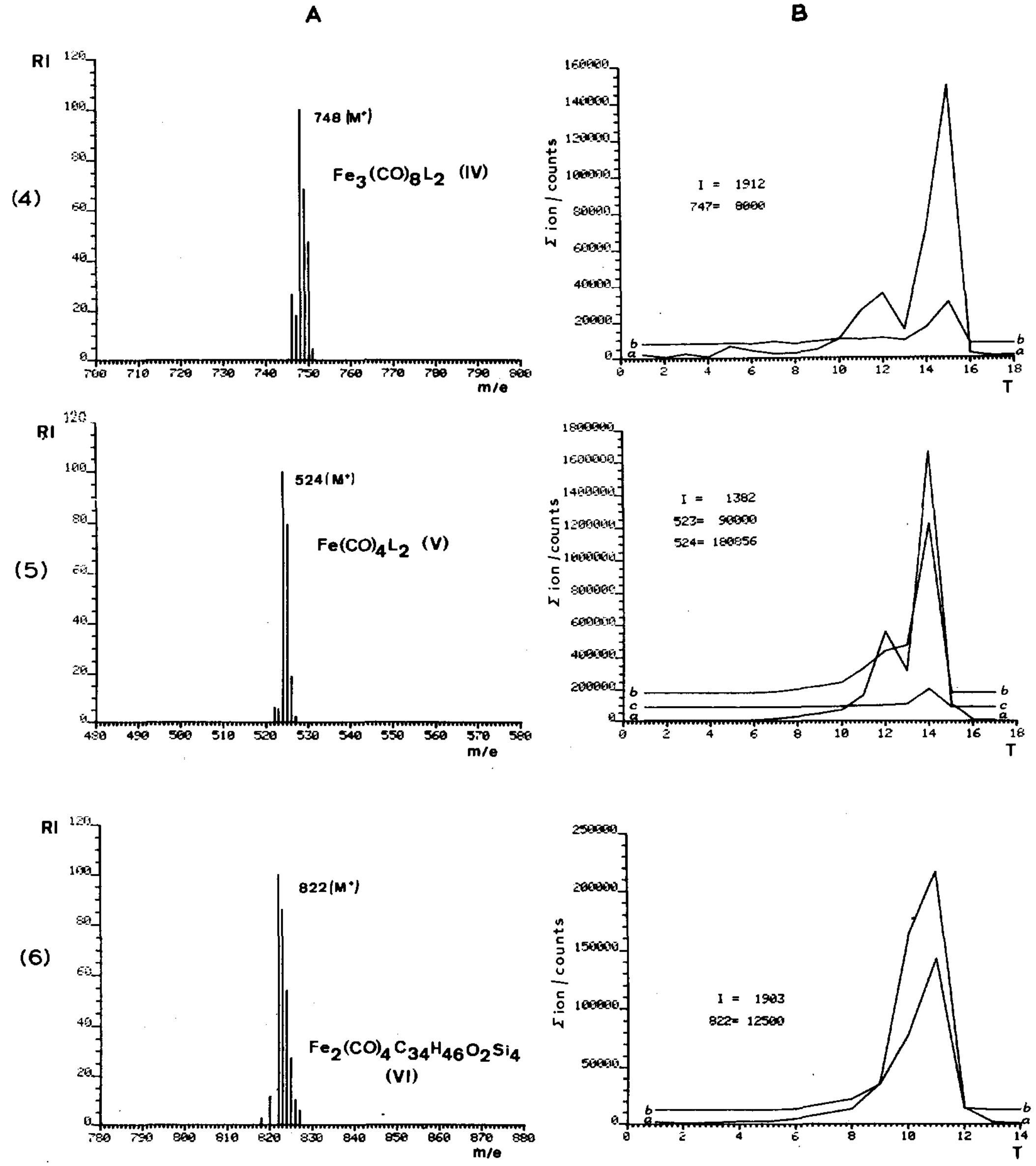


Fig. 1. A. Positive ion field desorption mass spectra of complexes I–VI. I, II, III, V: dissolved in $CHCl_3$; IV: dissolved in THF; VI: dissolved in $CHCl_3$/THF. The emitter current was 14 mA. B. Total ion

tion. Scheme 2(b) represents a possible thermal degradation sequence. Hübel observed [13] that III decomposes thermally to give predominantly tetraphenylquinone (IX) along with tetracyclone (VII). These compounds could have undergone a Diels–Alder type reaction in the mass spectrometer to form X (M^+: $m/e = 796$). The EI in-beam technique seems to be a much better method for parent ion detection, but in contrast to FDMS, the range of application is limited to complexes with melting/decomposition points above 160°C.



current (Σ ion$_{tot}$) (a) and M^+ –ion current (Σ ion$_{M^+}$) (b) as functions of the sample temperature T. B_5 also shows the $M^+ - 1$-ion current (Σ ion$_{M^+-1}$) (c). (L = C_2Ph_2; RI = relative intensity in %).

The heterocyclic complexes I–IV and tricarbonyl(cyclopentadienone)iron(0) (V) showed similar fragmentation patterns, the first process being the expected stepwise loss of CO groups to give $[Fe_2(CO)_n(C_2Ph_2)_2]^+$ (n = 0–6) before any more fundamental breakdown of the molecule, such as loss of C_2Ph_2 or Fe, occurs. The mass spectra of I, IV, and V are of particular interest, since enough metastable ions (Table 2) were observed to confirm the fragmentation scheme depicted in Scheme 3.

In I ions $[Fe_2(CO)_n(C_2Ph_2)_2]^+$ (n = 0, 1, 3) were present in high abundance

TABLE 1

RELATIVE INTENSITIES OF THE MOLECULAR ION PEAKS (%) UNDER ELECTRON-IMPACT OF COMPLEXES (I–VI): direct inlet: T_{is} 200°C, T_s 140°C; in beam inlet: T_{is} 140°C, T_s 140°C

Compound	M^+ (m/e)	Direct	In beam
I	636	– [a,b]	6
II	820	2	4
III	664	– [a,c]	– [a,d]
IV	748	0.1 [b]	8
V	524	2	14
VI	822	15	58

[a] No molecular ion peak detected. [b] Highest observed peak: $m/e = 852$ (1%). [c] Highest observed peak: $m/e = 524$ (3%, $M^+ - Fe(CO)_3$). [d] Highest observed peak: $m/e = 794$.

SCHEME 2

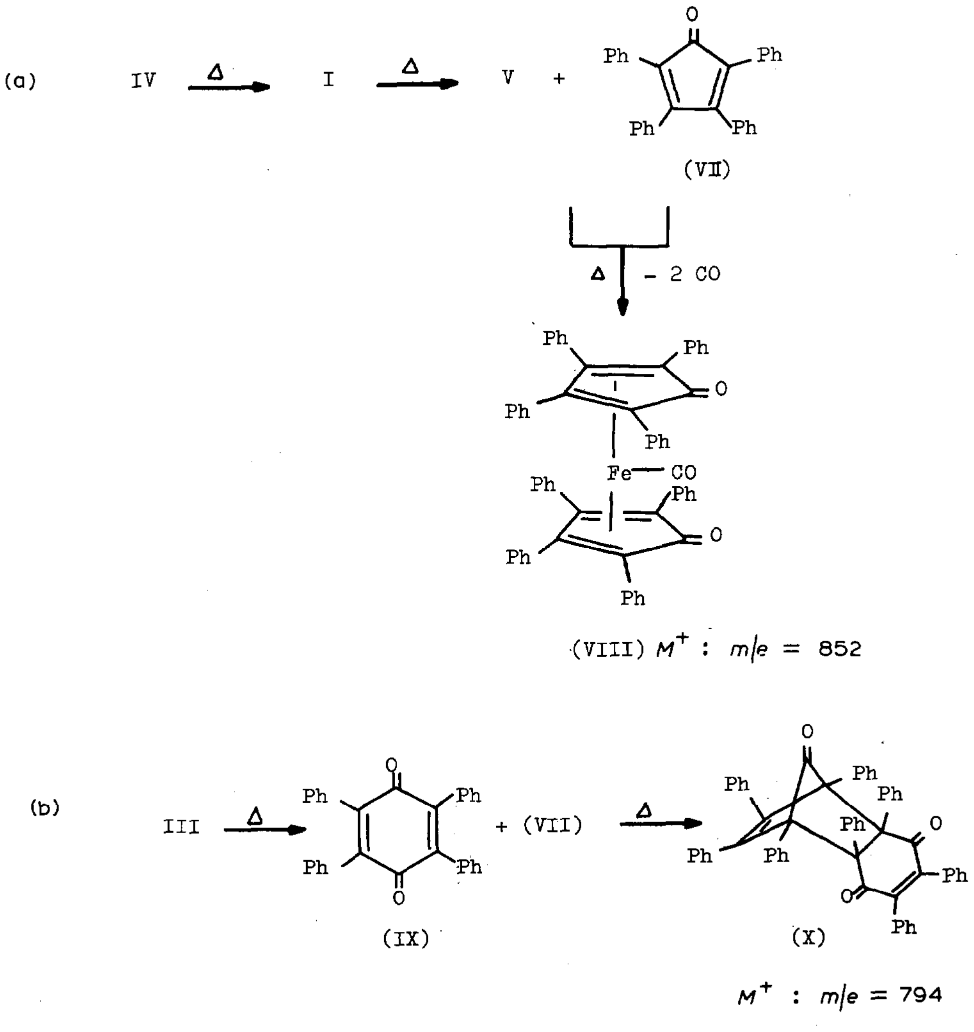


TABLE 2

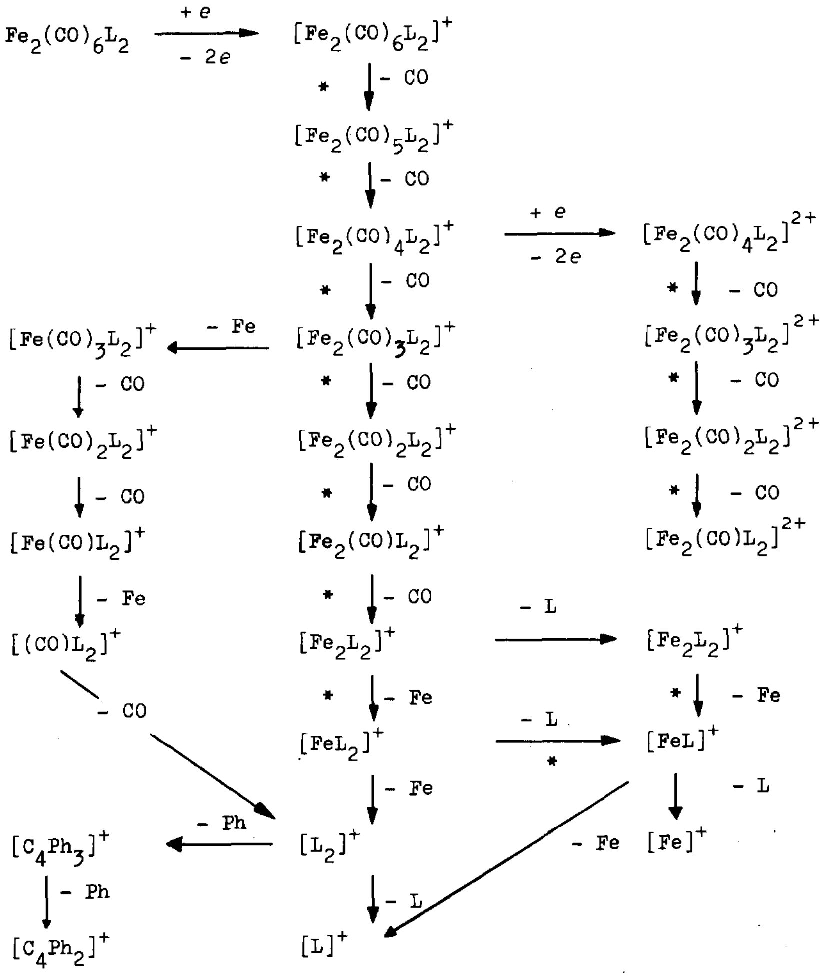
METASTABLE IONS OF COMPLEXES I, IV and V

m/e	Process		
(a) $Fe_2(CO)_6(C_2Ph_2)_2$ (I)			
581.2	$[Fe_2(CO)_6(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(CO)_5(C_2Ph_2)_2]^+$	$+CO$
553.3	$[Fe_2(CO)_5(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(CO)_4(C_2Ph_2)_2]^+$	$+CO$
525.4	$[Fe_2(CO)_4(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(CO)_3(C_2Ph_2)_2]^+$	$+CO$
497.2	$[Fe_2(CO)_3(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(CO)_2(C_2Ph_2)_2]^+$	$+CO$
469.5	$[Fe_2(CO)_2(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(CO)(C_2Ph_2)_2]^+$	$+CO$
441.6	$[Fe_2(CO)(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(C_2Ph_2)_2]^+$	$+CO$
362.7	$[Fe_2(C_2Ph_2)_2]^+$	$\rightarrow [Fe(C_2Ph_2)_2]^+$	$+Fe$
262.7	$[Fe_2(CO)_4(C_2Ph_2)_2]^{2+}$	$\rightarrow [Fe_2(CO)_3(C_2Ph_2)_2]^{2+}$	$+CO$
248.7	$[Fe_2(CO)_3(C_2Ph_2)_2]^{2+}$	$\rightarrow [Fe_2(CO)_2(C_2Ph_2)_2]^{2+}$	$+CO$
234.7	$[Fe_2(CO)_2(C_2Ph_2)_2]^{2+}$	$\rightarrow [Fe_2(CO)(C_2Ph_2)_2]^{2+}$	$+CO$
188.8	$[Fe_2(C_2Ph_2)]^+$	$\rightarrow [Fe(C_2Ph_2)]^+$	$+Fe$
132.9	$[Fe(C_2Ph_2)_2]^+$	$\rightarrow [Fe(C_2Ph_2)]^+$	$+C_2Ph_2$
(b) $Fe_3(CO)_8(C_2Ph_2)_2$ (IV)			
693.0	$[Fe_3(CO)_8(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_7(C_2Ph_2)_2]^+$	$+CO$
665.1	$[Fe_3(CO)_7(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_6(C_2Ph_2)_2]^+$	$+CO$
637.1	$[Fe_3(CO)_6(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_5(C_2Ph_2)_2]^+$	$+CO$
609.2	$[Fe_3(CO)_5(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_4(C_2Ph_2)_2]^+$	$+CO$
583.1	$[Fe_3(CO)_4(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_3(C_2Ph_2)_2]^+$	$+CO$
553.3	$[Fe_3(CO)_3(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)_2(C_2Ph_2)_2]^+$	$+CO$
525.4	$[Fe_3(CO)_2(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(CO)(C_2Ph_2)_2]^+$	$+CO$
497.4	$[Fe_3(CO)(C_2Ph_2)_2]^+$	$\rightarrow [Fe_3(C_2Ph_2)_2]^+$	$+CO$
441.4	$[Fe_3(C_2Ph_2)_2]^+$	$\rightarrow [Fe_2(C_2Ph_2)_2]^+$	$+Fe$
362.7	$[Fe_2(C_2Ph_2)_2]^+$	$\rightarrow [Fe(C_2Ph_2)_2]^+$	$+Fe$
(c) $Fe(CO)_4(C_2Ph_2)_2$ (V)			
469.5	$[Fe(CO)_4(C_2Ph_2)_2]^+$	$\rightarrow [Fe(CO)_3(C_2Ph_2)_2]^+$	$+CO$
441.6	$[Fe(CO)_3(C_2Ph_2)_2]^+$	$\rightarrow [Fe(CO)_2(C_2Ph_2)_2]^+$	$+CO$
413.7	$[Fe(CO)_2(C_2Ph_2)_2]^+$	$\rightarrow [Fe(CO)(C_2Ph_2)_2]^+$	$+CO$
385.8	$[Fe(CO)(C_2Ph_2)_2]^+$	$\rightarrow [Fe(C_2Ph_2)_2]^+$	$+CO$
307.6	$[Fe(C_2Ph_2)_2]^+$	$\rightarrow [(C_2Ph_2)_2]^+$	$+Fe$

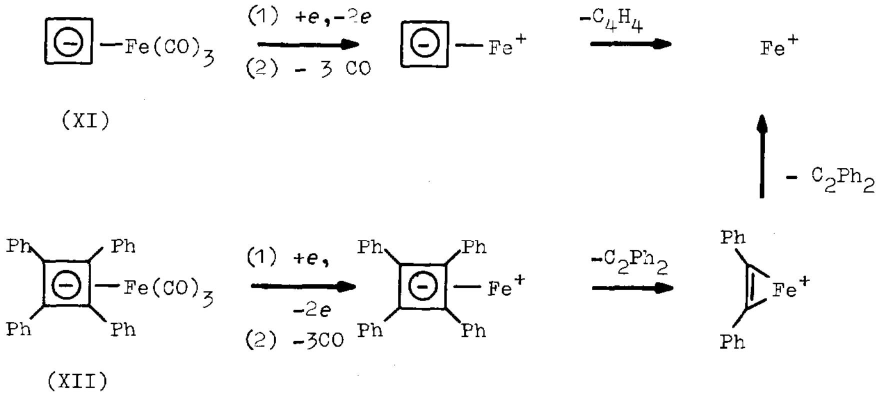
whereas ions with $n = 2$, 4, 5 were only moderately intense. Formation of $[Fe_2(C_2Ph_2)_2]^+$ gives rise to another binuclear ion $[Fe_2(C_2Ph_2)]^+$. The same ion loses iron atoms in two subsequent stages and forms the hydrocarbon ion $[(C_2Ph_2)_2]^+$ in moderate abundance. However, stepwise loss of diphenylacetylene (C_2Ph_2) from $[Fe_2(C_2Ph_2)_2]^+$ and $[Fe(C_2Ph_2)]^+$ is preferred over formation of the tetraphenylcyclobutadiene ion by loss of the iron atoms, as indicated by: (1) The metastable ion at 132.9, and (2) the relatively high abundances of the ions $[Fe_2(C_2Ph_2)]^+$ ($m/e =$ 290), $[Fe(C_2Ph_2)]^+$ ($m/e = 234$), and $[C_2Ph_2]^+$ ($m/e = 178$). These observations are in agreement with those by King and Efraty [14] who demonstrated the relationship between stability and fragmentation by comparing the fragmentation patterns of the tricarbonyl iron(0) complexes derived from parent cyclobutadiene and tetraphenylcyclobutadiene (Scheme 4). The ring–metal bond in XII is more stable than that in XI.

The doubly charged binuclear ions undergo stepwise loss of the CO groups and form ions which still retain the double charge, as shown by the corresponding

SCHEME 3. Fragmentation scheme of $Fe_2(CO)_6(C_2Ph_2)_2$ (I) ($L = C_2Ph_2$).



SCHEME 4



metastable ions (Table 2), but they are not as intense as those of the monocharged ions. The formation of doubly charged ions from other doubly charged ions was first reported by Kiser and Winters [15] for the fragmentation of $W(CO)_6$ and $Fe(CO)_5$; no $[Fe(CO)_3]^+$ ions, and only weak $[Fe(CO)_n]^+$ ($n = 1, 2$) ions were found. Tables 3–6 list the relative intensities of ions from complex I when only one of the possible variables is changed while the others are kept constant.

The ferrole complex II gives the parent ion with a relative intensity of 2–4% but does not show $[M - 2\ CO]^+$ and $[M - 3\ CO]^+$ ions, and simultaneous elimination of three carbonyl groups from $[Fe_2(CO)_5C_{32}H_{44}Si_4]^+$ to give $[Fe_2(CO)_2C_{37}H_{44}Si_4]^+$ is observed for both in-beam and direct sample inlet modes. The base peak is the dinuclear carbonyl-free ion $[Fe_2C_{32}H_{44}Si_4]^+$ (Table 7), which itself gives rise to the doubly charged ion $[Fe_2C_{32}H_{44}Si_4]^{2+}$ in moderate abundance ($m/e = 326$, 12%). Neither the direct nor the in-beam inlet technique revealed the parent ion for III. Along with the previously mentioned peaks derived from a decomposition product which structure was tentatively suggested in Scheme 2, only the fragment ions $[M - Fe(CO)_3]^+$ (direct, $m/e = 524$) and $[(CO)(C_2Ph_2)_2]^+$ (in beam, $m/e = 384$) were detected. The reason for this could be that the T_{is} and T_s, both 140°C, may be too high for complex III, the melting/decomposition point of which is 158°C, and we found that use of temperatures of 40–50°C below the melting/decomposition temperature usually yields the best results.

Complex IV exhibited an extremely small molecular ion peak (direct, 150°C) of 0.5% relative intensity. The abundances of the fragment ions resulting from CO and

TABLE 3

EIMS OF $Fe_2(CO)_6(C_2Ph_2)_2$ (I): DIRECT INLET, 70 eV, T_{is} 200°C, ΔT_s ($L = C_2Ph_2$)

Fragment	Relative intensities (%), at T (°C)					
	110	120	140	150	170	200 [a]
$[Fe_2(CO)_6L_2]^+$	–	–	0.1	–	–	–
$[Fe_2(CO)_5L_2]^+$	8	17	15	10	12	1
$[Fe_2(CO)_4L_2]^+$	6	13	18	22	18	2
$[Fe_2(CO)_3L_2]^+$	8	42	70	62	47	3
$[Fe_2(CO)_2L_2]^+$	13	25	35	32	30	5
$[Fe_2(CO)L_2]^+$	39	66	99	100	86	15
$[Fe_2L_2]^+$	38	61	100	93	88	12
$[(CO)L_2]^+$	1	1	1	1	2	0.5
$[L_2]^+$	18	23	24	24	31	10
$[Fe_2L_2]^+$	6	8	3	9	9	2
$[C_4Ph_3]^+$	14	14	6	12	18	11
$[Fe_2(CO)_3L_2]^{2+}$	11	10	5	9	12	6
$[Fe_2(CO)_2L_2]^{2+}$	3	3	3	3	5	–
$[Fe_2(CO)L_2]^{2+}$	7	7	9	8	8	2
$[FeL]^+$	60	77	97	95	98	14
$[C_4Ph_2]^+$	5	3	2	3	3	3
$[L]^+$	100	100	58	92	100	37
$[Fe(CO)_2]^+$	12	11	13	18	13	2
$[Fe]^+$	53	48	69	98	60	18

[a] Base-peak: $m/e = 46$.

(Continued on p. 96)

TABLE 4

EIMS OF I: DIRECT INLET, T_{is} 200°C, T_s 140°C, ΔEe ($L = C_2Ph_2$)

Fragment	Relative intensities (%), at E_e (eV)				
	70	40	30	20	15
$[Fe_2(CO)_6L_2]^+$	–	1	1	1	1
$[Fe_2(CO)_5L_2]^+$	15	41	18	24	38
$[Fe_2(CO)_4L_2]^+$	18	29	19	27	43
$[Fe_2(CO)_3L_2]^+$	70	74	59	81	100
$[Fe_2(CO)_2L_2]^+$	35	36	31	47	38
$[Fe_2(CO)L_2]^+$	99	100	88	100	42
$[Fe_2L_2]^+$	100	96	98	98	19
$[Fe(CO)L_2]^+$	1	2	2	3	3
$[FeL_2]^+$	24	25	33	33	16
$[(CO)L_2]^+$	3	3	4	6	10
$[L_2]^+$	12	10	15	34	34
$[FeL_2]^+$	69	76	100	31	18
$[C_4Ph_3]^+$	6	5	7	12	7
$[Fe_2(CO)_3L_2]^{2+}$	5	6	6	3	3
$[Fe_2(CO)_2L_2]^{2+}$	3	4	4	1	–
$[Fe_2(CO)L_2]^{2+}$	9	7	8	2	1
$[FeL]^+$	97	86	95	16	10
$[C_4Ph_2]^+$	2	2	2	2	0.5
$[L]^+$	58	45	54	59	41
$[Fe(CO)_2]^+$	13	10	12	3	3
$[Fe]^+$	69	22	18	5	4

TABLE 5

EIMS OF I: DIRECT INLET, 40 eV, T_{is} 200°C, T_s ($L = C_2Ph_2$)

Fragment	Relative intensities (%) at T (°C)		
	100	120	140
$[Fe_2(CO)_6L_2]^+$	–	1	1
$[Fe_2(CO)_5L_2]^+$	11	31	41
$[Fe_2(CO)_4L_2]^+$	10	19	29
$[Fe_2(CO)_3L_2]^+$	38	61	74
$[Fe_2(CO)_2L_2]^+$	22	31	36
$[Fe_2(CO)L_2]^+$	62	86	100
$[Fe_2L_2]^+$	72	92	96
$[Fe(CO)_2L_2]^+$	2	2	2
$[FeL_2]^+$	32	27	25
$[(CO)L_2]^+$	6	5	3
$[L_2]^+$	19	12	10
$[Fe_2L]^+$	80	86	76
$[C_4Ph_3]^+$	11	6	5
$[Fe_2(CO)_3L_2]^{2+}$	11	7	6
$[Fe_2(CO)_2L_2]^{2+}$	2	4	4
$[Fe_2(CO)L_2]^{2+}$	3	8	7
$[FeL]^+$	100	100	86
$[C_4Ph_2]^+$	2	2	2
$[L]^+$	92	67	45
$[Fe(CO)_2]^+$	18	17	10
$[Fe]^+$	46	41	22

TABLE 6

EIMS OF I: (a) DIRECT INLET, 70 eV, T_{is} 200°C, T_s 140°C, (b) in beam, 70 eV, T_{is} 140°C, T_s 140°C ($L = C_2Ph_2$)

Fragment	Relative intensities (%)	
	Direct	In beam
$[Fe_2(CO)_6L_2]^+$	–	6
$[Fe_2(CO)_5L_2]^+$	15	62
$[Fe_2(CO)_4L_2]^+$	18	12
$[Fe_2(CO)_3L_2]^+$	70	80
$[Fe_2(CO)_2L_2]^+$	35	22
$[Fe_2(CO)L_2]^+$	99	83
$[Fe_2L_2]^+$	100	88
$[Fe(CO)L_2]^+$	1	2
$[FeL_2]^+$	24	10
$[(CO)L_2]^+$	3	–
$[L_2]^+$	12	–
$[Fe_2L]^+$	69	84
$[C_4Ph_3]^+$	6	8
$[Fe_2(CO)_3L_2]^{2+}$	5	2
$[Fe_2(CO)_2L_2]^{2+}$	3	6
$[Fe_2(CO)L_2]^{2+}$	9	16
$[FeL_2]^+$	97	100
$[C_4Ph_2]^+$	2	2
$[L]^+$	58	30
$[Fe(CO)_2]^+$	13	16
$[Fe]^+$	69	52

TABLE 7

EIMS OF FERROLE II: (a) DIRECT INLET: T_{is} 200°C, T_s 110°C, 70 eV, (b) IN BEAM INLET: T_{is} 140°C; t_s 140°C, 70 eV (M^+ parent ion)

Fragment	Relative intensities (%)	
	Direct	In beam
$[M]^+$	2	4
$[M-CO]^+$	8	7
$[M-2\ CO]^+$	–	–
$[M-3\ CO]^+$	–	–
$[M-4\ CO]^+$	50	36
$[M-5\ CO]^+$	48	22
$[M-6\ CO]^+$	100	58
$[M-Fe(CO)_5]^+$	25	–
$[M-Fe(CO)_6]^+$	–	–
$[M-Fe_2(CO)_6]^+$	–	–
$[M-6\ CO]^{++}$	12	36
$[Me_3Si]^+$	62	18

Fe elimination as function of T_s varied more than for I (Table 8). No significant enhancement of the parent peak was brought about by lowering the electron energy to 15 eV. The in-beam technique gives more intense $[Fe_x(CO)_y(C_2Ph_2)_2]^+$ fragments ($x = 1$–3, $y = 1$–7) and less intense hydrocarbon fragments.

Both the iron π-complexes V and VI exhibit parent ions with small to moderate relative intensities, but these are large enough to allow a fast determination of the molecular composition. In contrast to the ferrole type systems, even better results were obtained in respect of the parent ion detection when the electron energy was lowered to 15 eV, since the molecular ion of V was doubled in intensity and that of VI actually became the base peak (Table 9). No decomposition products were observed. The tetracyclone complex V shows the loss of three carbonyl groups, giving $[Fe(CO)(C_2Ph_2)_2]^+$ as intense peak at 70 eV. One possible structure of the $[M - 3\ CO]^+$ ion is shown in XIII, but a carbonyl extrusion mechanism in which XIII is intermediate on the way to XIV could also explain this result. Such behaviour has been proposed previously [16].

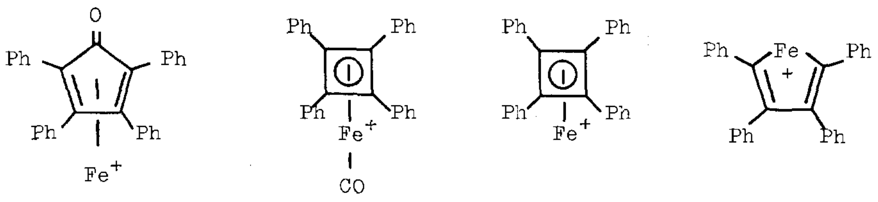
Besides the extrusion of a fourth CO molecule from the ring to give $[Fe(C_2Ph_2)_2]^+$, which might be either the cyclobutadiene complex XV or the ferrole ion XVI

TABLE 8

EIMS OF COMPLEX IV: DIRECT INLET, T_{is} 200°C, 70 eV, T_s; IN BEAM INLET, T_{is} 140°C, T_s 140°C, 70 eV ($L = C_2Ph_2$)

Fragment	Relative intensities (%)				
	Direct, T (°C)				In beam T (°C)
	120	150	170	190	140
$[Fe_3(CO)_8L_2]^+$	–	0.1	–	–	8
$[Fe_3(CO)_7L_2]^+$	2	5	3	–	21
$[Fe_3(CO)_6L_2]^+$	14	40	27	0.5	100
$[Fe_3(CO)_5L_2]^+$	12	33	25	0.5	63
$[Fe_3(CO)_4L_2]^+$	13	32	26	0.5	48
$[Fe_3(CO)_3L_2]^+$	21	49	43	8	64
$[Fe_3(CO)_2L_2]^+$	17	31	32	11	21
$[Fe_2(CO)_3L_2]^+$	30	59	80	47	55
$[Fe_2(CO)_2L_2]^+$	28	51	61	27	62
$[Fe_2(CO)L_2]^+$	11	21	55	81	2
$[Fe_2L_2]^+$	19	36	82	100	10
$[Fe(CO)L_2]^+$	2	2	3	2	–
$[FeL_2]^+$	13	18	27	27	3
$[(CO)L_2]^+$	6	8	9	5	–
$[L_2]^+$	28	37	67	77	25
$[Fe_2L]^+$	23	37	67	77	25
$[C_4Ph_3]^+$	19	24	24	12	6
$[Fe_2(CO)_3L_2]^{2+}$	23	18	18	8	–
$[Fe_2(CO)_2L_2]^{2+}$	26	44	21	4	52
$[FeL]^+$	37	55	80	94	16
$[C_4Ph_2]^+$	11	11	8	4	–
$[L]^+$	100	100	100	80	8
$[Fe(CO)_2]^+$	13	18	16	13	6
$[Fe]^+$	57	92	64	62	20

SCHEME 5



(XIII) (XIV) (XV) (XVI)

resulting from insertion of the iron atom into the C_4-ring [17], another major process is observed. This is the cleavage of the metal–ring bond in either $[Fe(CO)(C_2Ph_2)_2]^+$ or $[Fe(C_2Ph_2)_2]^+$ to give the charged ligand ions, the further fragmentation of which provides the majority of other ions observed. A third important process is elimination of diphenylacetylene from $[Fe(C_2Ph_2)_2]^+$ to give $[Fe(C_2Ph_2)]^+$ in 39% relative abundance.

TABLE 9

EIMS OF COMPLEXES V AND VI IN BEAM AND DIRECT AT 15 AND 70 eV ($L = C_2Ph_2$)

Fragment	Relative intensities (%)		
	Direct		In beam
	70	15	70
(a) $Fe(CO)_4(C_2Ph_2)_2$ *(V)*			
$[Fe(CO)_4L_2]^+$	2	4	14
$[Fe(CO)_3L_2]^+$	8	10	16
$[Fe(CO)_2L_2]^+$	22	32	16
$[Fe(CO)L_2]^+$	93	24	100
$[FeL_2]^+$	3	1	–
$[(CO)L_2]^+$	44	100	4
$[L_2]^+$	30	24	–
$[FeL]^+$	31	3	22
$[L]^+$	100	10	12
$[Fe(CO)]^+$	–	–	44
$[Fe]^+$	12	–	10
(b) $Fe_2(CO)_4C_{34}H_{46}O_2Si_4$ *(VI)*			
$[Fe_2(CO)_4C_{34}H_{46}O_2Si_4]^+$	18	100	56
$[Fe_2(CO)_3C_{34}H_{46}O_2Si_4]^+$	1	4	2
$[Fe_2(CO)_2C_{34}H_{46}O_2Si_4]^+$	19	20	28
$[Fe_2(CO)C_{34}H_{46}O_2Si_4]^+$	55	60	74
$[Fe_2C_{34}H_{46}O_2Si_4]^+$	100	22	100
$[Fe_2C_{34}H_{45}O_2Si_4]^+$	61	13	62
$[Fe_2C_{34}H_{44}O_2Si_4]^+$	91	23	81
$[Fe_2C_{34}H_{46}OSi_4]^+$	24	3	20
$[Fe_2C_{34}H_{45}OSi_4]^+$	15	1	12
$[Fe_2C_{34}H_{44}OSi_4]^+$	22	3	20
$[Si(CH_3)_3]^+$	80	5	84
$[Fe]^+$	–	–	20

The dinuclear complex VI shows the expected fragmentation involving stepwise loss of four carbonyl groups and then elimination of molecular hydrogen from $[Fe_2C_{34}H_{44}O_2Si_4]^+$, followed by loss of an oxygen atom before an iron atom is eliminated.

Conclusion

For studies on organometallic compounds the choice of MS technique is of considerable importance, and the temperatures of the ion source and sample inlet system are crucial. With both types of complex studied, those containing π- and σ-bonded iron atoms and the pure iron π-complexes the FDMS technique generally gives excellent results, and the parent ion appears as the base peak without interfering peaks from decomposition products. In contrast, the EIMS technique is useful mainly in studying the fragmentation pathways of metallacyclic systems, because the more drastic conditions needed for these complexes and the low vapor pressure result in ready decomposition in the ion source to give only fragment ions and/or ions derived from stable decomposition products, which occasionally give ions with higher mass units than that of the complex under study. The fact that the parent ion, if detected, is usually present in very small abundances ($< 1\%$) and so is not easily distinguished from minor impurities, could lead to misinterpretations. Two different sample inlet modes were tested: direct and in-beam inlets. The latter is more precise and gives the parent ions even for ferracyclic systems provided the ion source temperature is kept 40–50° below the melting/decomposition point of the complex under study. Pure iron π-complexes, however, give moderately intense molecular ions at 70 eV. With these complexes lowering the electron energy to 15 eV yields more intense parent ions, and in one case the parent ion even is the base peak, whereas only little or no improvement was observed with the ferracycles.

Experimental

Electron-impact mass spectra were run (a) at 15–70 eV on a Varian-MAT 711 mass spectrometer with an SS-100 computer system (ion source temperature: 200°C; water cooled direct inlet system on an aluminium crucible; accelerating potential: +8 kV) at the University of Zürich-Irchel, (b) at 70 eV on a Varian-MAT 212 mass spectrometer (accelerating potential: +3 kV; ion source temperature: 140°C) at SANDOZ A.G. in Basel, and (c) at 70 eV on a Varian-MAT CH7 mass spectrometer at the Westfälische Wilhelms University in Münster. Field-desorption mass spectra were recorded on a Varian-MAT 212 mass spectrometer (accelerating potential: +3 kV, cathode potential: −5.2 kV, ion source temperature: 90°C, direct sample inlet mode) at SANDOZ A.G. in Basel.

Complexes I, III–V were prepared from commercially available pentacarbonyl iron, diphenylacetylene and 2,3,4,5-tetraphenylcyclopentadienone by photolysis in refluxing benzene [10], but for III ether was used as solvent instead of benzene in order to keep the reflux temperature lower and so avoid decomposition. This solvent change increased the yield from 3 to 46%. The synthesis of II from *o*-bis(trimethylsilylethynyl)benzene and $Fe_2(CO)_9$ in refluxing benzene was described recently [8]; VI can be obtained from the same reaction in 7% yield [9].

TABLE 10

FORMULAS, MOLECULAR WEIGHTS, MELTING/DECOMPOSITION POINTS, AND ELEMENTARY ANALYSES OF COMPLEXES I–VI

Complex	Formula	Molecular weight	M.p. (dec.) (°C)	Elementary analysis (Found (calcd.) (%))	
				C	H
I	$C_{34}H_{20}O_6Fe_2$	636.22	181 [a]	64.21	3.19
				(64.19)	(3.17)
II	$C_{38}H_{44}O_6Si_4Fe_2$	820.80	184	55.64	5.25
				(55.61)	(5.40)
III	$C_{35}H_{20}O_7Fe_2$	664.23	158	62.79	3.24
				(63.29)	(3.04)
IV	$C_{36}H_{20}O_8Fe_3$	748.09	214 [b]	57.62	2.67
				(57.80)	(2.69)
V	$C_{32}H_{20}O_4Fe$	524.36	174	73.22	3.80
				(73.30)	(3.84)
VI	$C_{38}H_{46}O_6Si_4Fe_2$	822.81 [c]	184		
	$C_{38}H_{46}O_6Si_4Fe_2 \cdot C_6H_6$	900.02		58.66	5.78
				(58.66)	(5.82)

[a] Lit. [10], 174°C. [b] Lit. [10], 208°C. [c] Exact mass: calcd. 822.1044, found 822.1035.

TABLE 11

IR DATA OF COMPLEXES I–VI RECORDED ON A PERKIN-ELMER SPECTROMETER (MODEL 298) AS KBr PELLETS

Complex	$\tilde{\nu}$ (cm^{-1})
I	2065, 2020, 1999, 1987, 1970, 1925 (Fe–CO)
II	2140 (C≡C), 2060, 2015, 1995, 1975, 1912 (Fe–CO)
III	2070, 2040, 2010, 1990 (Fe–CO), 1667 (ketonic CO)
IV	2055, 2010, 1999, 1987, 1965 (Fe–CO), 1855, 1848 (Fe–CO–Fe)
V	2060, 2010, 1990 (Fe–CO), 1645 (ketonic CO)
VI	2060, 2030, 1985, 1950 (Fe–CO), 1780 (Fe–CO–Fe)

Each complex was recrystallized five times and dried at 22°C/5 × 10^{-3} Torr for three days. IR data and elemental analysis for I–VI are listed in Tables 10 and 11.

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