Application of Electron-impact and Field-desorption Mass Spectra in the Characterisation of Thermally Labile Ferracyclic Complexes

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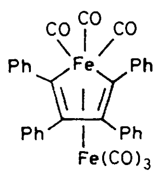
Mass spectral studies of the thermally labile ferracyclic complexes (**1**)—(**4**) and the related systems (**5**) and (**6**) result for the first time in the observation of intense molecular ion peaks by the use of special electron-impact and field-desorption techniques which enable a rapid determination of the basic composition of this type of compound.

Recently, metallacyclic compounds have received increasing attention as they represent valuable and important intermediates in many transition metal catalysed and mediated syntheses[1] of natural products[2] and strained organic molecules of theoretical interest.[3] Owing to their thermally labile and air-sensitive nature an easy and fast characterisation of their basic composition by mass-spectroscopic determination has hitherto been unsuccessful.[4] As described earlier,[5] most organic tricarbonyl-iron(0)-π-complexes exhibit molecular ions of very small relative intensity which are hard to differentiate from peaks of minor impurities. In many cases only fragment ions from the loss of ligand molecules prior to ionisation and/or molecular ions of stable decomposition products have been observed. On the other hand, loss of carbon monoxide molecules in σ-bonded iron carbonyl species is a more facile process than that for its π-analogues.[6]

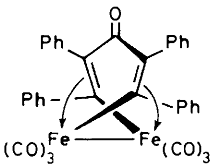
To overcome this obstacle we synthesised mono-, di-, and tri-nuclear ferracyclic complexes (**1**)—(**4**)[7] which represent a combination of σ- and π-bonded iron atoms and the related species (**5**) and (**6**).[7] We then measured their electron-impact (EI) and field-desorption (FD) mass spectra by systematically changing electron energy (15—70 eV), sample-inlet mode (direct, in beam), and ion source (is) and sample (s) temperature (70—200 °C), in order to find the optimum conditions for observation of intense molecular ion peaks.

Indeed, initial routine EI-measurements (T_{IS} = 200 °C, direct, T_S = 70—200 °C, 70 eV) led only to fragment ions [**1**, **3**: M^+ − CO; **2**: M^+ − Fe(CO)$_3$] and ion peaks resulting from stable decomposition products (**1**, **3**) with higher mass units. Variation in electron energy did not result in the detection of the desired M^+-peaks.

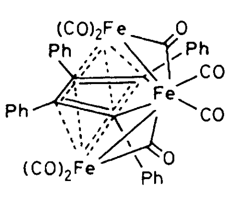
However, lowering T_{IS} and T_S to 40—50 °C below melting/



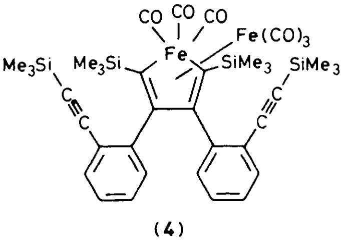
(1)



(2)



(3)



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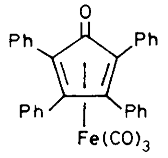

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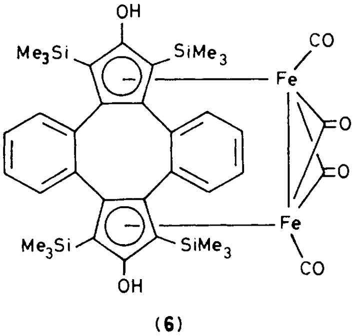

(6)

Table 1. Relative intensities of the molecular ion peaks (%) of complexes (**1**)—(**6**).

Complex	M^+	EI direct[a]	EI in beam[b,g]	FD direct[b]
(**1**)	636	—[c,d]	6	100
(**2**)	664	—[c,e]	—[f]	100
(**3**)	748	0.1[d]	8	100
(**4**)	820	2	4	100
(**5**)	524	2	14	100
(**6**)	822	15	58	100

[a] Varian-MAT 711 mass spectrometer. [b] Varian-MAT 212 mass spectrometer. [c] No molecular ion peak detected. [d] Highest observed peak *m/e* 852 (1%). [e] Highest observed peak *m/e* 524 [3%, $M^+ - \mathrm{Fe(CO)_3}$]. [f] Highest observed peak *m/e* 794. [g] Accelerating potential +3 kV, ion source temperature 140 °C, electron energy 70 eV, emitter heating current 16 mA, pressure in the ionisation chamber 1×10^{-6} Torr.

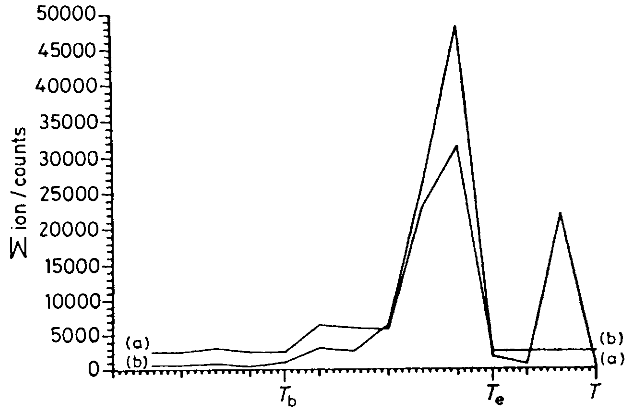

Figure 1. Total ion current (Σ ion$_{tot}$) (a) and M^+-ion current (Σ ion $_{M^+}$) (b) of complex (**2**) as a function of temperature.

decomposition point of the samples and switching to an in beam-sample-inlet mode[8] gave moderately intense molecular ion peaks in all cases except complex (**2**) (see Table 1). The spectra of (**1**) and (**3**)—(**6**) show the expected fragmentation pattern from stepwise loss of the CO ligands.[4] FD-Spectra (direct, $T_{1s} = 80$ °C, cathode potential −5.2 kV, acceleration potential +3 kV) succeeded in detecting M^+ values as the base-peak for (**1**)—(**6**). Total ion current (Σ ion$_{tot}$) and M^+-ion current (Σ ion $_{M^+}$) were plotted as a function of the sample temperature (Figure 1). Figure 1 shows that the molecular ions are detected exclusively in the section T_b—T_e. Temperatures greater than T_e result only in the detection of fragment peaks due to thermal decomposition. The latter observation might explain the registration of peaks with higher mass units than expected for (**1**) and (**3**) in the EI-measurements (direct, $T_{1s} = 200$ °C).

These results indicate that a rapid determination of the basic composition of important metallacyclic intermediates can be carried out by mass spectroscopic studies without running the risk of misinterpretation from thermal decomposition of the samples before ionisation.

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References

1 J. P. Collman and L. S. Hegedus in 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California 1980, and references therein; D. J. Brian, A. Naiman, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 1982, 133.

2 R. L. Funk and K. P. C. Vollhardt, *Chem. Soc. Rev.*, 1980, **9**, 41.

3 G. Ville, K. P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, 1981, **103**, 493; R. L. Hillard and K. P. C. Vollhardt, *Tetrahedron*, 1980, **36**, 2435.

4 In contrast to ruthenium and osmium containing metallacycles their iron analogues exhibit only extremely weak (1%) molecular ion peaks: *e.g.* G. A. Vaglio, O. Gambino, R. P. Ferrari, and G. Cetini, *Org. Mass Spectrom.*, 1971, **5**, 493.

5 W. Flitsch and E. R. F. Gesing, *J. Organomet. Chem.*, 1981, **218**, 377; J. Müller, *Angew. Chem.*, 1972, **84**, 725; *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 653.

6 E. Sappa, M. L. Nanni-Marchino, and V. Raverdino, *Ann. Chim. (Rome)*, 1978, **68**, 349.

7 Synthesis of the investigated complexes (**1**—**3**, **5**): G. N. Schrauzer, *J. Am. Chem. Soc.*, 1959, **81**, 5307; see also W. Hübel in I. Wender and P. Pino, 'Organic Synthesis via Metal Carbonyls,' vol. 1, Interscience, New York, 1968, p. 273; E. R. F. Gesing, *J. Chem. Soc., Chem. Commun.*, 1982, 426; E. R. F. Gesing, unpublished results.

8 For a recent description and application of the EI-in beam-mass spectroscopic technique see: A. Dell, D. H. Williams, H. R. Morris, G. A. Smith, J. Feeney, and G. C. K. Roberts, *J. Am. Chem. Soc.*, 1975, **97**, 2497; M. Ohashi, S. Yamada, H. Kudo, and N. Nakayama, *Biomed. Mass Spectrom.*, 1978, **5**, 578; M. Ohashi and N. Nakayama, *Org. Mass Spectrom.*, 1978, **13**, 642.