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Laser Induced Evaporation of $\{FeCp(CO)_2[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}]\}$ and some Analogous Compounds for Their Mass Spectrometric Characterization

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Electron Impact (EI) mass spectrometry is widely employed for structural characterization and reactivity studies of organometallic compounds [1, 2]. Unfortunately, very often the low volatility and/or thermal instability of the complexes does not allow such an approach, and the only results obtained are mass spectra of pyrolysis products. For these reasons many efforts have been made in recent decades to develop new ionization/evaporation techniques, e.g. field desorption [3], fast atom bombardment [4] and laser desorption [5].

In our previous paper [6] we described a simple instrumental approach which leads to laser induced evaporation of the samples with only minor instrumental modifications. While the EI source and the ion source housing remain unchanged, the sample is introduced in a glass capillary mounted in a hollow probe, containing a glass fiber which carries the laser beam. The results so obtained are generally exciting, and here we discuss the data for some organometallic compounds containing a σ-metal carbon bond. We discuss in detail the results for $\{FeCp(CO)_2[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}]\}$.

Experimental

The compounds $\{FeCp(CO)_2[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}]\}$ (**1**) [7]; $[PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2]$ (**2**) [8]; *trans*-$\{PtCl[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}](PPh_3)_2\}$ (**3**) [8]; $[PtCl(\eta^1\text{-}C_3H_5)(Ph_2PC_2H_2PPh_2)]$ (**4**) [8] and *trans*-$\{PtCl[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}](Ph_2PC_2H_2PPh_2)\}$ (**5**) [8] were prepared according to literature procedures.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument [9] operating in EI conditions (70 eV, 200 μA). The samples were introduced either by the usual insertion probe, or by the fiber optic probe previously described [6]. The laser employed was a ruby laser with an output energy of about 3 J. Metastable transitions were detected by B/E linked scans [10] which are indicated in Scheme 1 by asterisks.

Results and Discussion

In Fig. 1A the usual EI mass spectrum of compound **1**, obtained introducing the sample with the heatable–coolable insertion probe, is reported. The low abundance of high mass ionic species is noteworthy. The molecular ion is absent, as observed for several iron complexes [11] and the higher mass value is at *m/z* 305, probably due to a thermally induced 5-membered ring decomposition with allyl group elimination and maintenance of tetracyanoethylene on the metal centre. The base peak is at *m/z* 39, a fragment arising from the decomposition of cyclopentadienyl moiety (*m/z* 65, 57%).

In Fig. 1B the spectrum of compound **1** obtained in laser induced evaporation conditions is shown. The difference is immediately evident: the results obtained are well related to the original structure. By means of B/E linked scans [10] the fragmentation pattern reported in Scheme 1 has been obtained. Well detectable molecular ion at *m/z* 346 (1.5%) is present; it shows metastable supported $C_3H_5^{\bullet}$ loss leading to ionic species at *m/z* 305 followed by sequential CO losses yielding ions at *m/z* 277 and 249. Molecular ion loses the $^{\bullet}\overline{CHCH_2C(CN)_2C(CN)_2CH_2}$ group leading to ions at *m/z* 177, from which, by sequential CO losses ionic species at *m/z* 149 and 121 (the base peak) originate. From molecular ion, sequential CO losses are observed leading to ionic species at *m/z* 318 and 290. A fragmentation pathway involving the 5-membered ring originates from the ionic species at *m/z* 290. The lack of EI induced primary cyclopentadienyl loss is to be emphasized proving that the abundant ions at *m/z* 65 in the usual EI spectrum of **1** (see Fig. 1A) are thermally generated.

In conclusion the data obtained demonstrate that, in the present case, the use of ionization methods alternative to EI is not necessary. Differences in spectra 1A and 1B arise from thermal decomposition during evaporation of **1**. The use of a 'hard' evaporation method [6] such as the laser induced one, allows a clear structural characterization of **1**.

We also performed the mass spectra, in the same operative conditions described for **1**, for compounds **2**, **3**, **4** and **5**. In these cases we obtained mass spectra indicating fragmentation patterns analogous to those obtained in normal EI conditions [12], but molecular ions are more abundant. So, the $M^{+\bullet}$ abundance for **2** grows up from 0.01 to 1.2%, for **3** from 0.1 to 2.5%. For compound **4** a general increase of high mass ion abundance is found; furthermore in laser

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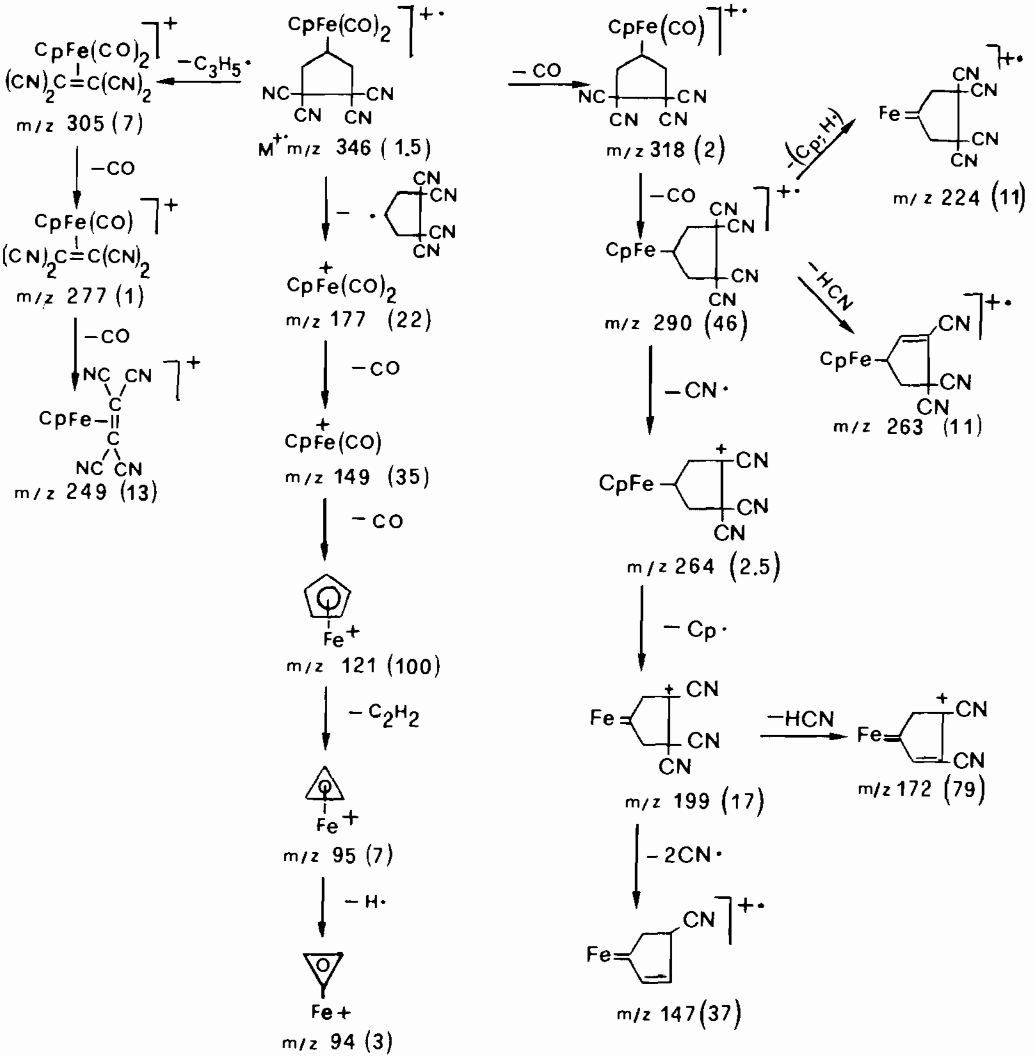

Scheme 1.

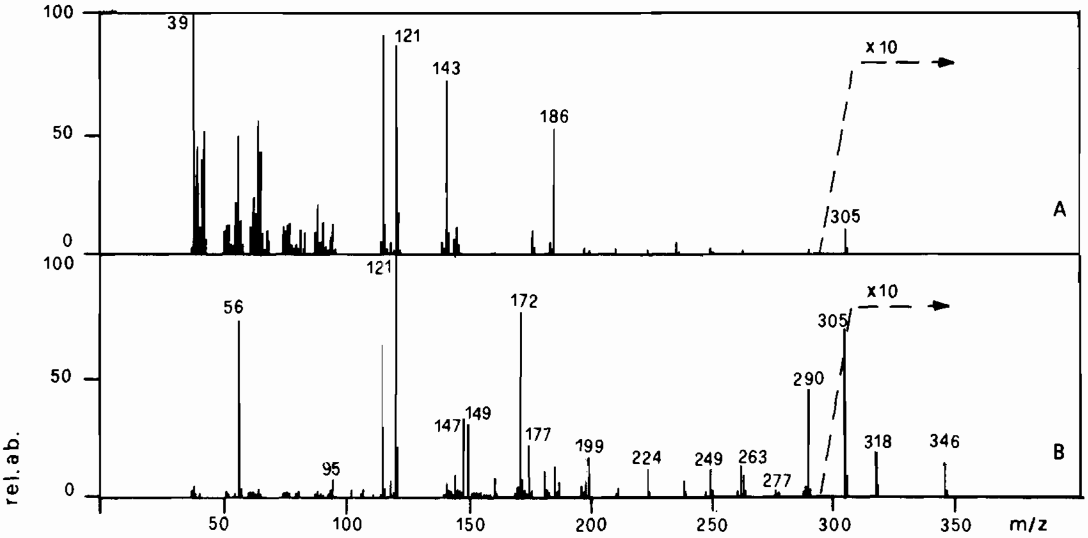

Fig. 1. (A) EI mass spectrum of **1**. (B) EI mass spectrum of **1** obtained in laser induced evaporation conditions.

sample vaporization conditions the only primary fragmentation process is due to Cl$^•$ loss, leading to ions at *m/z* 632 (64%) followed by $C_3H_5^•$ release yielding ions at *m/z* 591 (23.4%). Finally for compound **5** the $M^{+•}$ abundance grows up from 0.01 to 5.0%.

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