

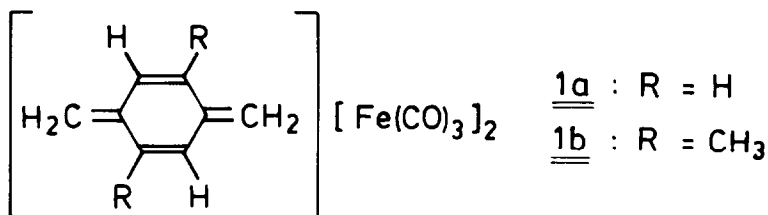
BIS(TRICARBONYLIRON) COMPLEXES OF p-QUINODIMETHANES:
 FRAGMENTATION AND ISOMERISATION UNDER ELECTRON IMPACT

Marina Rentzea*, Ali R. Koray and Heinz A. Staab

Abteilung Organische Chemie
 Max-Planck-Institut für medizinische Forschung
 Jahnstrasse 29, D-6900 Heidelberg

Summary: EI mass spectra of trans- η^4, η^4 -[3,6-bis(methylene)-1,4-cyclohexadiene]-bis-(tricarbonyliron) complexes 1a, b are reported. The fragmentation pathway is rationalized by assuming a rearrangement of the trans-bis(tricarbonyliron) complexes into the cis-isomers under electron impact.

Recently the [3,6-bis(methylene)-1,4-cyclohexadiene]-bis(tricarbonyliron) complexes 1a and b have been prepared and characterized ¹⁾. For 1b a centrosymmetrical structure with a trans-arrangement of the iron nuclei on opposite sides of the p-quinodimethane ligand was determined by X-ray structure analysis (Fig. 1).



Mass spectra of 1a and b (Fig. 2) provided some interesting results concerning the fragmentation of these p-quinodimethane-iron complexes. The fragmentation pathway presented in Scheme 1 for 1b was derived from B/E and B/E² linked scans and exact mass measurements; for 1a very similar results were obtained.

Elimination of five CO units from the molecular ion [QFe₂(CO)₆]⁺ resulted in the formation of an ion [QFe₂CO]⁺ to which the base peak in the spectra of 1a and b is assigned (Q = p-quinodimethane). As has been observed for a large variety of other iron carbonyl complexes ²⁾ the ions formed by successive elimination of CO from the parent ion did not exhibit significant loss of any fragments other than carbon monoxide. An exception was observed, however, for the ions [QFe₂CO]⁺ which also lose the FeCO species. Another feature of interest in these spectra is the simultaneous loss of two CO units ³⁾ from the parent ions and from

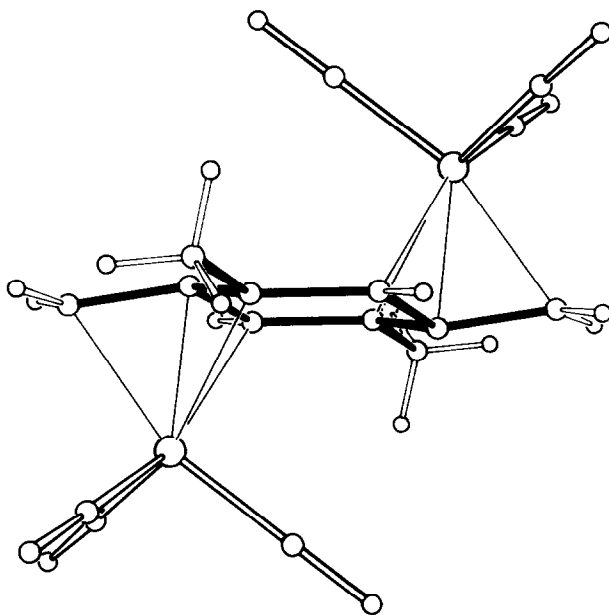


Fig. 1. Molecular structure of 1b ¹).

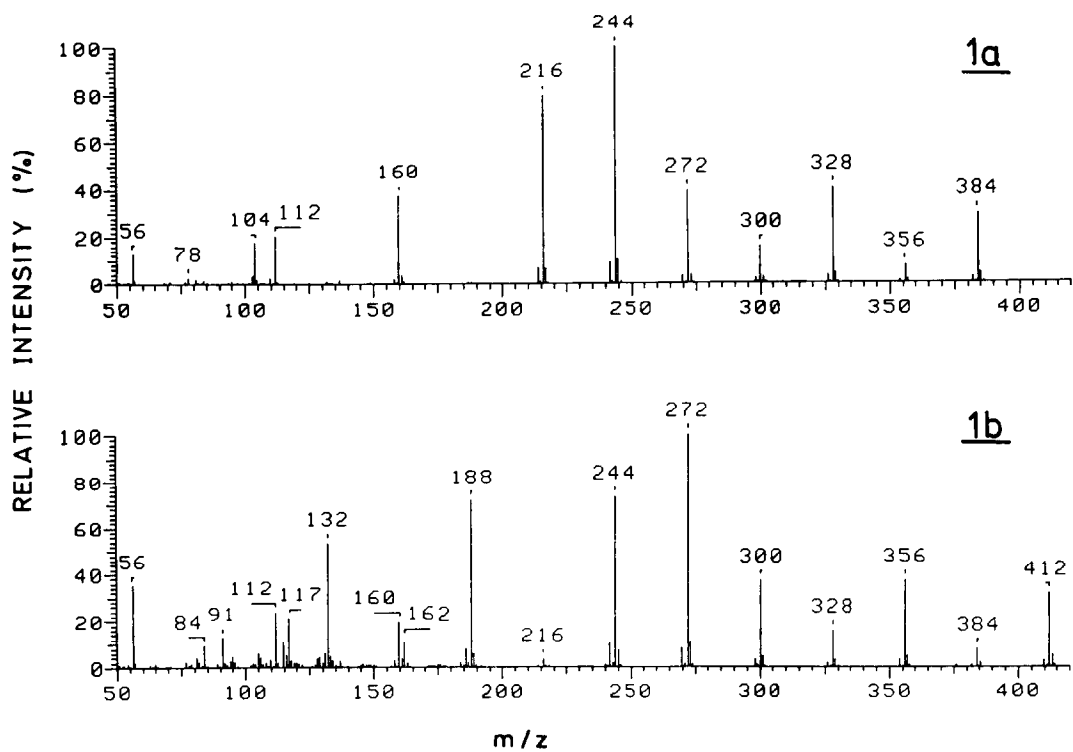
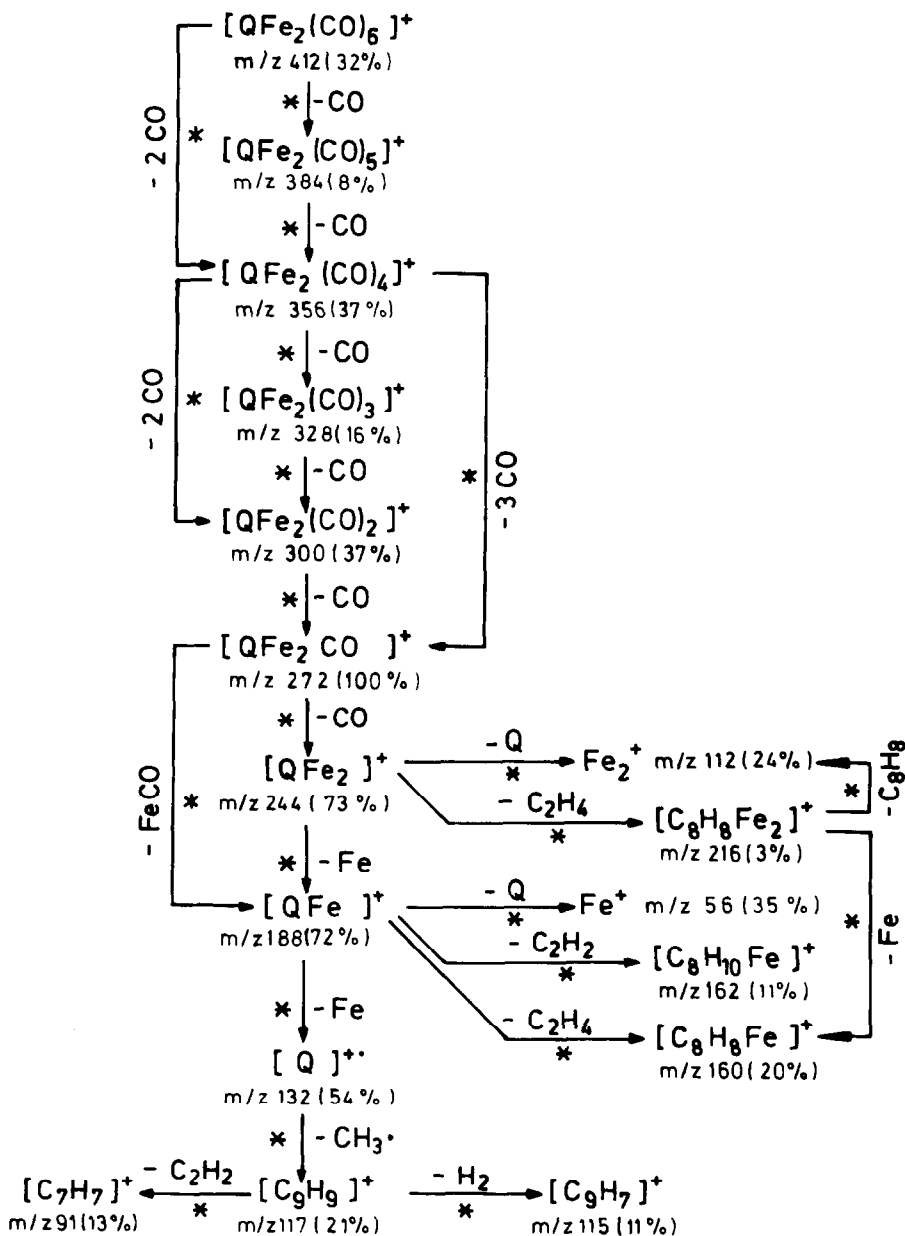


Fig. 2. EI mass spectra of 1a and 1b (70eV).

$[\text{QFe}_2(\text{CO})_4]^+$ ions, and of three CO from the latter ions. These processes are supported by the observation of appropriate metastable ions.

Scheme 1. General fragmentation pattern of compound 1b.

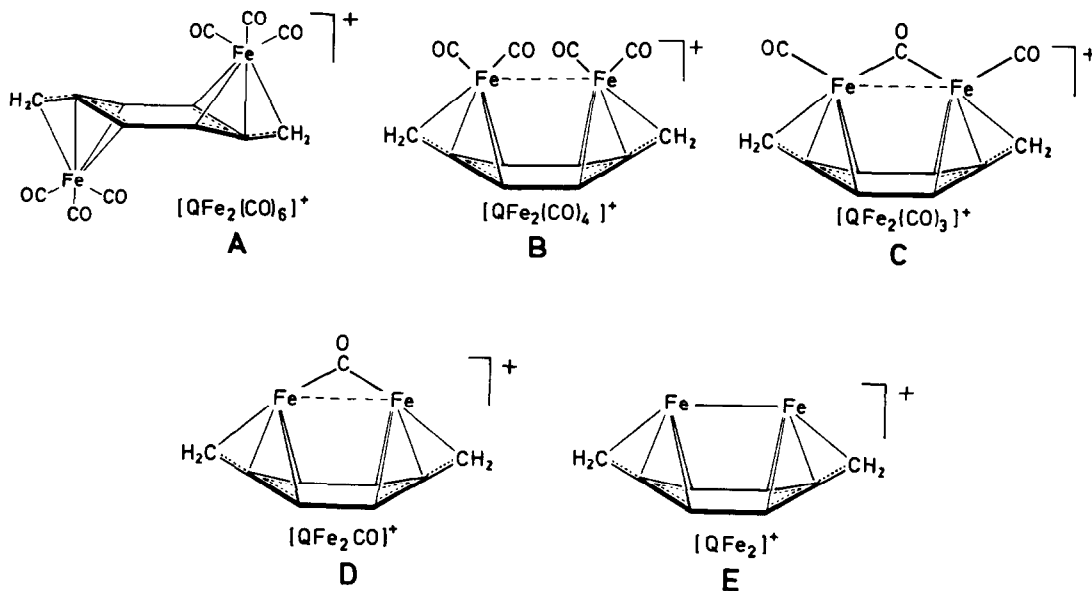
(Q = $\text{C}_{10}\text{H}_{12}$; * fragmentation supported by metastable peaks)



The remarkably stable ions $[\text{QFe}_2\text{CO}]^+$ (base peak of the spectra) lose further CO to an abundant $[\text{QFe}_2]^+$. From there two principal fragmentation paths were detected: 1) loss of Fe

resulting in ions $[QFe]^+$ with subsequent formation of the bare iron ion $[Fe]^+$, and 2) loss of $[Q]$ from $[QFe_2]^+$ resulting in an ion $[Fe_2]^+$ with $m/z = 112$. Whereas for the majority of these fragmentation pathways analogies are known from the mass spectra of other olefine-metalcarbonyl complexes ^{2,4,5}, the most interesting feature and the least predictable one is the formation of $[Fe_2]^+$. This ion was shown to arise from clusters of two or more iron atoms. In the case of the complexes 1a and b the observation of $[Fe_2]^+$ cannot be explained on the basis of the transoid structure which has to be assumed for the molecular ion A, but requires a cisoid arrangement with the two iron atoms on the same side of the quinodimethane ligand. At what step along the fragmentation pathway this rearrangement occurs cannot be decided experimentally. Most probably the isomerisation takes place at the stages of either B, C or D where the rearrangement should be supported by metal-metal interaction. From the ions D, then, the fragment ions E with iron-iron bonding are obtained as the immediate precursors of $[Fe_2]^+$.

Scheme 2.



The $i-C_4H_{10}$ CI mass spectra of 1a and b showed $[M]^+$ as base peak and $[M-2CO]^+$ as major ion species. The negative ion $i-C_4H_{10}$ CI mass spectra of these compounds gave only low intensities of $[M]^-$ and contained predominantly $[M-CO]^-$ ions.

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