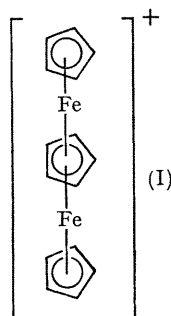


## Electron Impact Studies on Cyclopentadienyliron Carbonyl Tetramer: a Novel Route to a "Triple-decker" Sandwich Ion

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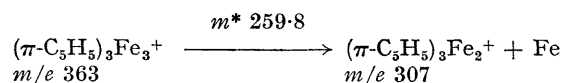
THE tetranuclear cyclopentadienylmetal carbonyl derivative<sup>1</sup>  $[(\pi\text{-C}_5\text{H}_5)\text{FeCO}]_4$  has a symmetrical structure<sup>2</sup> with a tetrahedral cluster of iron atoms, a  $\pi$ -cyclopentadienyl ring bonded to each iron atom, and a three-way bridging carbonyl group in each of the four faces of the iron tetrahedron.



Its mass spectrum (inlet temp. *ca.* 200°; source pressure  $3 \times 10^{-6}$  mm.) exhibits a parent ion ( $m/e$  596) and a tetrametallic ion  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4^+$  formed by loss of all four carbonyl groups. The ions  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_n^+$  ( $n = 3, 2,$  and  $1$ ) formed by partial loss of carbonyl groups from the parent ion are also observed, but are unusually weak, having relative abundances  $< 10\%$  of  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4^+$  and  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4^+$ . The ions  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_n^+$  ( $n = 2$  and  $0$ ) formed by carbon-oxygen fission are also found, and, surprisingly, have relative abundances similar to those of  $(\pi\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_n^+$  ( $n = 3, 2,$  and  $1$ ). The mass spectrum

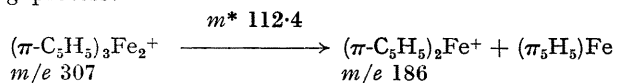
of  $[(\pi\text{-C}_5\text{H}_5)\text{FeCO}]_4$  thus differs from the mass spectra of other metal carbonyl derivatives<sup>3</sup> [*e.g.*  $\text{W}(\text{CO})_6^+$ ], where ions formed by carbon-oxygen fission [*e.g.*  $\text{W}(\text{CO})_n\text{C}^+$ ], if observed at all, are very weak compared with the ions formed by metal-carbon fission [*e.g.*  $\text{W}(\text{CO})_n^+$ ]. This suggests that, in  $[(\pi\text{-C}_5\text{H}_5)\text{FeCO}]_4$  the metal-carbon bonds to the carbonyl groups are relatively strong and the carbon-oxygen bonds of the carbonyl groups are relatively weak. The strength of the iron-carbonyl bonds is consistent with the three-way bridging of the carbonyl groups demonstrated by *X*-ray crystallography.<sup>2</sup> The weakness of the carbon-oxygen bonds is consistent with the unusually low  $\nu_{\text{CO}}$  frequency (1620  $\text{cm}^{-1}$ ).

The mass spectrum of  $[(\pi\text{-C}_5\text{H}_5)\text{FeCO}]_4$  also exhibits the series of trimetallic ions  $(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_3(\text{CO})_n^+$  ( $n = 2, 1,$  and  $0$ ) in addition to the trimetallic ion  $(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_3\text{C}^+$  formed by carbon-oxygen bond cleavage. The carbonyl-free trimetallic ion  $(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_3^+$  undergoes further decay by loss of a neutral iron atom according to the following process:



The  $(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_2^+$  ion has been previously observed in very low abundance by Schumacher and Taubenest<sup>5</sup> in the mass spectrum of ferrocene at pressures sufficiently high for a bimolecular process to take place (*ca.*  $1 \times 10^{-5}$  mm.). This ion may have the "triple-decker" sandwich structure (I). This suggested structure is supported by the tendency for the  $(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_2^+$  ion to form the  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}^+$  ion by

elimination of a neutral  $(\pi\text{-C}_5\text{H}_5)\text{Fe}$  fragment in the following process:



This is the only example in our work with a great variety of  $\pi$ -cyclopentadienylmetal derivatives where the elimination of a neutral  $\text{C}_5\text{H}_5\text{M}$  fragment has been supported by the presence of a metastable ion. Furthermore, in the previously reported<sup>5</sup> work with  $(\text{C}_5\text{H}_5)_3\text{Fe}_2^+$  generated from the mass spectrum of ferrocene, the abundance of the "triple-decker" sandwich ion was too low to permit the observation of its formation and decay by metastable ion analysis.

These preliminary results indicate that the electron impact of polynuclear cyclopentadienylmetal derivatives may provide sources of "triple-decker" sandwich ions in higher abundances than previous<sup>5</sup> methods. Unfortunately not all polynuclear cyclopentadienylmetal derivatives generate "triple-decker" sandwich ions upon electron impact, as indicated by the failure to observe significant abundances of the  $(\text{C}_5\text{H}_5)_3\text{M}_2^+$  ions or the metastable ions corresponding to their generation or decay in the mass spectra of  $[(\pi\text{-C}_5\text{H}_5)\text{CoCO}]_3^+$ <sup>1</sup> or  $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2^+$ .<sup>6</sup>

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<sup>6</sup> E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 1966, **49**, 1447.