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HYDROGEN TRANSFER IN THE MASS SPECTRAL FRAGMENTATION OF CYCLOHEXADIENYLCYCLOPENTADIENYLIRON

C. C. Lee, R. G. Sutherland and B. J. Thomson
Department of Chemistry and Chemical Engineering
University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

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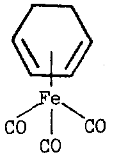
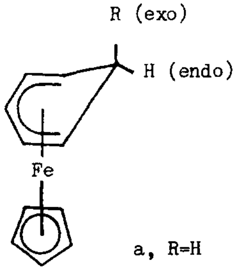
Interest in the mass spectra of transition metal organometallic complexes is growing rapidly[1] and in a number of instances it has been shown that the metal atom may exert considerable influence on the fragmentation mode of the organic ligand[2]. The recent report[3] of stereoselective loss of hydrogen from cyclohexadiene iron tricarbonyl (1), possibly via transfer to the iron atom, prompts us to report our observations on the mass spectral fragmentation of cyclohexadienylcyclopentadienyliron (2a)[4].



(1)



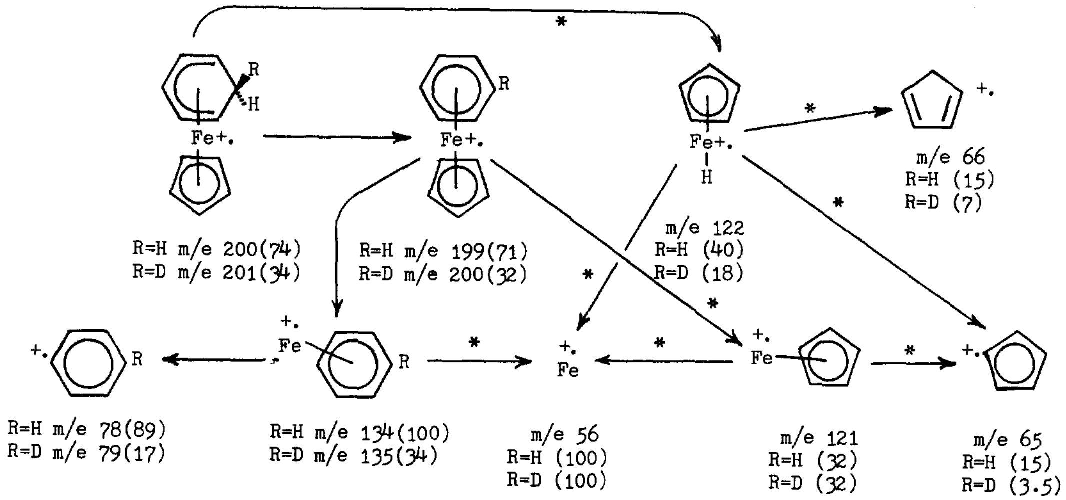
a, R=H
b, R=D

(2)

The mass spectrum[5] of (2a) showed the presence of radical-ions which could be readily ascribed as resulting from hydrogen transfer to iron. The Scheme shows the major fragmentation pathways. Examination of the mass spectrum of the deuterated analogue (2b)[4] established that transfer of the endo-H of (2) to the iron atom was highly specific. The presence of m/e 186 in the mass spectrum of (2) was attributed to ferrocene formation, thought to occur mainly by thermal rearrangement in the source rather than by loss of CHR from $M^{+\cdot}$[6].

The observations here lend support to Whitesides and Arhart's postulated[3] loss of the endo-H_2 of (1) through initial transfer to the iron atom, thence by cleavage of metal hydride bonds. We thank the National Research Council of Canada for financial assistance.

SCHEME



* Corresponding metastable ion observed.
Value in parenthesis is the relative abundance of the ion of appropriate mass.

FOOTNOTES AND REFERENCES

1. R.B. King, Fortschritte der Chemischen Forschung, 1970, 14, 92-126, Springer-Verlag, N.Y.; M. Cais, M.S. Lupin, Adv. Organometal. Chem., 1970, 8, 211; M.I. Bruce, ibid, 1968, 6, 273; T. Lewis, B.F.G. Johnson, Accnts. Chem. Research, 1968, 1, 245.

2. "Recent Developments in Mass Spectroscopy", University of Tokyo Press, Tokyo, Japan, 1970, pp 1210, 1175.

3. T.H. Whitesides and R.W. Arhart, Tet. Lets., 1972, 297.

4. D. Jones, L. Pratt and G. Wilkinson, J. Chem. Soc., 1962, 4458.

5. Mass spectra were determined on an AEI MS 12 instrument at an ionizing voltage of 70 ev. and a source temperature of 100°. The sample of deuterated material used had $>98\%$ d_1 incorporation and the relative abundances are uncorrected.

6. TLC examination showed (2) to be free of ferrocene. However traces of ferrocene were noted after passage of (2) through a VPC column at 95°. Similarly, TLC examination showed cyclohexadienyl(ethylcyclopentadienyl)iron to be free of ethyl- and diethylferrocene, but traces of these compounds were noted in its mass spectrum[5] and after similar VPC treatment. This thermal lability will be commented on more fully at a later date.