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STEREOSELECTIVE LOSS OF HYDROGEN DURING FRAGMENTATION OF CYCLOHEXADIENE IRON TRICARBONYL IN THE MASS SPECTROMETER

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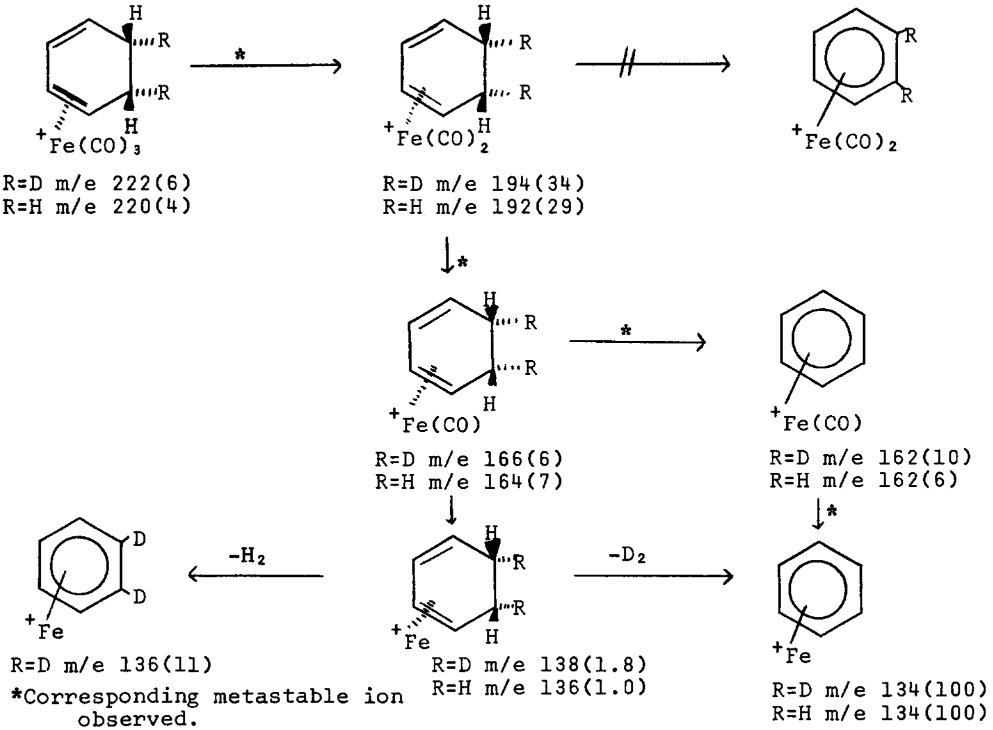
The mass spectra of transition metal organometallic compounds have recently attracted much attention.[1,2] Among carbonyl compounds, cyclohexadiene iron tricarbonyls are particularly interesting in that major fragments correspond to $C_6H_6Fe(CO)_n^+$ (n=0,1).[3,4] In order to compete favorably with CO loss, this pathway must be of very low energy.

We have recently[5] developed a synthesis of stereospecifically labeled cyclohexadiene iron tricarbonyl, and now report that the loss of hydrogen from the decarbonylated fragments of this molecule is highly, but not completely, stereoselective. The major fragmentation pathways[6] are indicated in the Scheme. As pointed out by Haas and Wilson[4], fragments involving aromatization become more important as the degree of coordinative unsaturation of the iron increases. Thus in the unlabeled compound the ratio $r = C_6H_6Fe(CO)_n^+/C_6H_6R_2Fe(CO)_n^+$ varies with n as follows: n=3,2, r=0; n=1, r=0.9; n=0, r=100. The corresponding numbers for the labeled species are: n=3,2, r=0; n=1, r=1.6; n=0, r=63±10. Significantly, the amount of deuterium loss is much greater than either H_2 or HD loss, indicating a high degree of stereospecificity. Thus, for the n=1 ion, H_2 loss is just detectable, D_2 loss being favored by a factor of at least 100. Specificity in the n=0 ion is much reduced, D_2 loss being favored only by a factor of 9, and this factor is too large, since a substantial quantity of the m/e 134 ion is formed by CO loss from m/e 162, and not by direct aromatization. Thus as reactivity increases, the selectivity decreases, as expected.

The results obtained here demonstrate that the iron atom directs the stereochemistry of this fragmentation. A reasonable explanation for this effect might involve prior transfer of H_2 from the ligand to the metal, followed by H_2 loss by cleavage of metal hydride bonds.

SCHEME (Value in parenthesis is the relative intensity of the ion of appropriate mass)



*Corresponding metastable ion observed.

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6. Mass spectra were obtained on an AEI MS 9 instrument at an ionizing voltage of 70 ev. The sample of deuterated material used had the isotopic composition 0% d_3, 83 ± 1% d_2, 16 ± 1.5% d_1, and 1.0 ± 0.5% d_0, and the relative intensities are corrected to 100% d_2.