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Nucleophilic Attacks on Tricarbonyl(cyclooctadienyl)Fe(0) Cations

G. SCHIAVON, C. PARADISI and C. BOANINI

Istituto di Chimica Generale "Giacomo Ciamician", Università di Bologna, Italy

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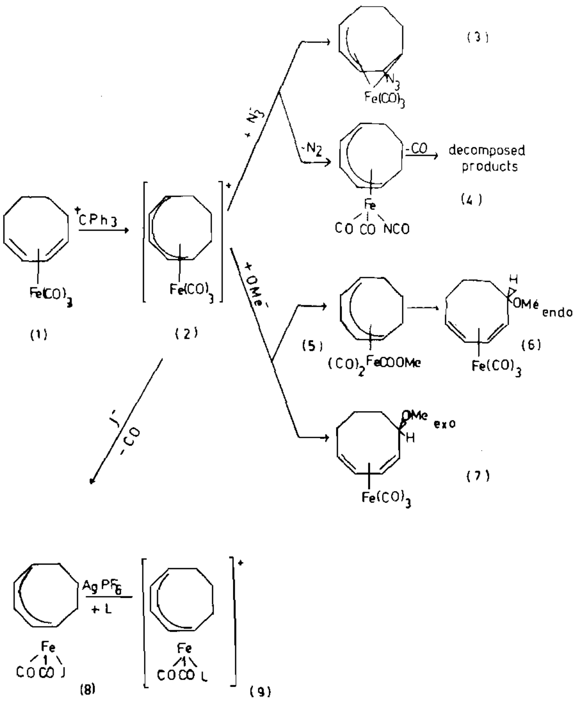
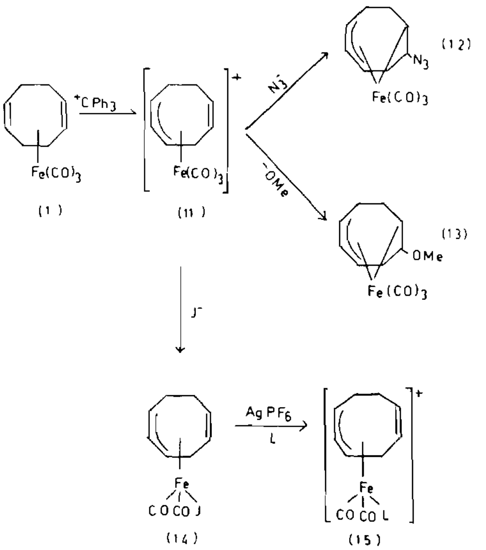
It is known that treatment of the complexes (1,3cyclooctadiene)$Fe(CO)_3$ (1) and (1,5cyclooctadiene)$Fe(CO)_3$ (10) with triphenylmethyl tetrafluoroborate results in hydride abstraction and formation of cationic species[1]. With complex (1) the product was the dienyl salt (2) and with complex (10) the product was the allyl–olefin salt (11). We have studied the reaction between the salts (2) and (11) and the nucleophiles N_3^-, CH_3O^- and I^-. These reactions are summarized in the Schemes. When using the salt (2) and the azide ion, we isolated product (3), a compound in which the diene fragment is coordinated to the iron by σ,η^3allylic bonds. However, during the reaction, nitrogen was evolved and a band appeared in the IR spectrum of the reaction mixture at $\nu = 2173$ cm^{-1}. This band increased in intensity with time and it did not appear in the spectrum of the final product. We think that the azide ion attacks the cation (2) either at the organic moiety to give product (3), or at the carbonyl group to give, via loss of one molecule of nitrogen and rearrangement, the intermediate compound (4), which undergoes decomposition with development of carbon monoxide at the end of the reaction. We have assigned the band at $\nu = 2173$ cm^{-1} to an NCO group coordinated to the iron in the compound (4). Both nitrogen and carbon monoxide were analysed by the gas chromatographic method.





With salt (2) and the methoxide ion we had also two modes of attack. Attack at the carbonyl group gave an ester (5). This product smoothly reacted to the methoxy-substituted diene derivative (6). The existence of (5) was inferred by the appearance of a band at $\nu = 1720$ cm^{-1} in the infrared spectrum of the reaction mixture. As the reaction progressed, this ketonic band decreased in intensity and disappeared altogether by the end of the reaction. Attack at the diene fragment gave the methoxy-substituted diene derivative (7). Compounds (6) and (7) exhibited the same IR spectrum, perhaps from the two isomers *endo* (6) and *exo* (7). Similar behaviour was observed with the analogous tricarbonyl(cyclohexadienyl) derivatives of ruthenium and osmium; the *endo*-isomer is the thermodynamically more stable product, the *exo*-isomer is the kinetically controlled product of a reversible reaction[2].

With salt (2) and the iodide ion we have obtained compound (8). The product results from a soft–soft acid–base interaction between the soft acid Fe(0) and the soft base I^-. With salt (11) and the nucleophiles N_3^- and CH_3O^- we have obtained the σ,η-^{3}allyl complexes (12) and (13) as the sole products. With salt (11) and the iodide ion we have obtained the neutral complex (14) in which the diene was coordinated to the iron atom by allyl–olefinic bonds. Compounds (8) and (14) are related to the previously reported derivatives of tricarbonylcyclohexa- and cycloheptadienyliron cations[3].

In addition to complexes (8) and (14), we have prepared substituted compounds (9) and (15), where L = phosphines, arsines and cyanide.

The compounds obtained were characterized by IR and NMR analyses.

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