Cationic Metal-dienyl Complexes as Electrophilic Reagents on Aromatic Molecules

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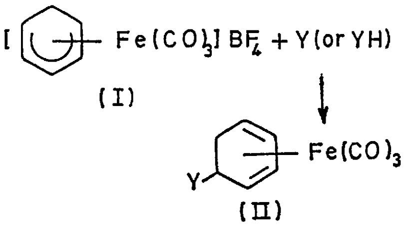
Summary The cation $[C_6H_7Fe(CO)_3]^+$ has been shown to act as an electrophile towards a wide variety of aromatic molecules, yielding new diene-substituted derivatives.

It is known[1] that cationic dienyl complexes of the type (I) are readily attacked by nucleophiles to yield substituted dienes (II) [equation (1); Y = CN⁻, OR⁻, H⁻, Acac⁻, morpholine, *etc.*]. These reactions may be alternatively considered to involve attack on Y by the species (I) acting as electrophiles. Such considerations led us to examine the feasibility of employing organometallic cations as electrophilic reagents on aromatic molecules.



We now report that $[C_6H_7Fe(CO)_3]BF_4$ reacts with a wide variety of aromatic compounds, yielding complexes of the general type (II; Y = indolyl, methylindolyl, pyrrolyl, furyl, thienyl, imidazolyl, and ferrocenyl). The reaction proceeds in water or polar organic solvents. No reaction was observed with benzene, alkylbenzene, anisole, or phenol. The indole, methylindole, and pyrrole products separated from aqueous solution as white crystalline solids which gave excellent analyses, mass spectra,[2] and sharp m.p.'s. Formation of the other products was indicated by i.r. spectral studies showing the formation of two intense carbonyl bands at *ca.* 2040 and *ca.* 1970 cm⁻¹, characteristic of substituted tricarbonyl(diene)iron species.

Reaction of $[C_6H_7Fe(CO)_3]BF$ (0·005M) *with aromatic substrates in acetonitrile; temp* 20 °C.

Substrate	Relative k_2[a]
2-Methylindole	35×10^5
N-Methylindole	30×10^5
Indole	5×10^5
Pyrrole	5×10^5
Furan	3×10^3
Thiophen	1

[a] Obtained by following the disappearance of the dienyl carbonyl band at 2120 cm⁻¹.

I.r., ^1H n.m.r., and kinetic studies are consistent with structure (II) for the indole products (Y = indol-3-yl and 2-methylindol-3-yl). The presence of an N–H stretching band at 3410 cm⁻¹ eliminates the possibility of nucleophilic attack by indole on salt (I) *via* the nitrogen centre. Electrophilic attack on indoles is known[3] to occur almost exclusively at C-3, and is confirmed for species (II) from their ^1H n.m.r. spectra. Also supporting attack at C-3 are kinetic results (Table) showing that while methyl substitution at N and C_2 enhances the rate of electrophilic attack by $[C_6H_7Fe(CO)_3]BF_4$, no observable reaction occurs on 3-methylindoles. The absence of a kinetic isotope effect using 1,3-deuteriated indole indicates a mechanism essentially identical to that previously found[4] for electrophilic attack by *p*-nitrodiazonium salt on indole, *i.e.* rate-determining addition on indole, followed by rapid proton loss from C-3. A similar mechanism seems likely for the other five-membered ring aromatics.

This novel concept of employing cationic organometallic complexes as electrophiles on aromatic molecules promises to provide simple synthetic routes to a wide variety of substituted organic compounds. Preliminary tests have shown that $[C_6H_7Ru(CO)_3]BF_4$ and the tropylium complexes $[C_7H_7M(CO)_3]BF_4$ (M = Cr, Mo, W)[5] yield a similar series of products. The preparation of complex (II; Y = ferrocenyl) indicates the potential of the method for producing unusual bi-metallic complexes.

Reaction (1) also provides an ideal series for comparative studies of the reactivity of aromatic systems towards electrophiles. Such studies have often been tedious or impossible in the past because of the complex nature of the reactions employed or the changes in solvent involved. The Table shows some preliminary kinetic results with $[C_6H_7Fe(CO)_3]BF_4$, which indicate a similar reactivity order to that previously established[3] for other electrophiles. These data provide a rare quantitative comparison of the electrophilic susceptibility of indole and pyrrole molecules.

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