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Preliminary communication

CATIONIC METAL π-ENYL COMPLEXES AS ELECTROPHILIC REAGENTS ON AROMATIC MOLECULES

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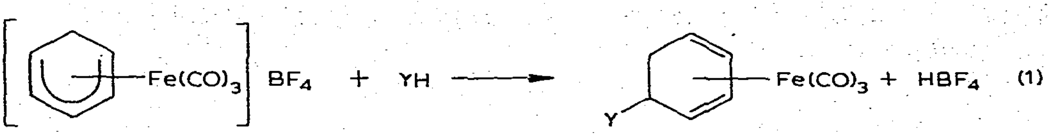
Summary

The electrophile $[C_6H_7Fe(CO)_3]^+$ has been shown to attack the activated arenes 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene to yield diene-substituted benzenoid derivatives.

We recently demonstrated [1] that the cationic dienyl complex $[C_6H_7Fe(CO)_3]BF_4$ (I) can function as an electrophile towards aromatic heterocycles to yield substituted dienes (II), according to eq. 1 (YH = indole methylindoles, pyrrole, furan, thiophene). However, even under exhaustive conditions, no reaction was observed with benzene, alkylbenzenes, anisole or phenol. This seemed unfortunate in view of the synthetic interest in benzenoid derivatives.



(I)

(II)

We now wish to report that the activated arenes 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene react smoothly with (I) in polar organic solvents to give the appropriate diene-substituted benzenoids. The reactions proceed to completion, as evidenced by the disappearance of the dienyl carbonyl IR bands at 2120 and 2055 cm^{-1} and the growth of product peaks at 2040 and 1980 cm^{-1}, characteristic of substituted tricarbonyl (diene)iron species. In the case of 1,2,3-trimethoxybenzene, the product was isolated as pale yellow crystals (m.p. 109°C) by evaporating the reaction mixture (acetonitrile solvent) to dryness, and recrystallising from methanol/water. [Found: C, 56.0; H, 4.7. $C_{18}H_{18}FeO_6$ calcd.: C, 56.0; H, 4.7.] Its ^1H NMR spectrum is consistent with structure (II), while the strong IR band (nujol mull) around 1600 cm^{-1} confirms the presence of the arene.

Table 1 summarises some kinetic data for the reaction of (I) with these methoxybenzenes, and compares their reactivity with heterocyclic aromatics. The 1,3,5-trimethoxybenzene substrate is seen to be almost as susceptible towards electrophilic attack as furan, while both are more reactive than thiophene. Differences between the present data and the earlier report [1] arise from a redetermination of the rate for thiophene, for which only an approximate value was then available. Also the previous [1] rate constant for pyrrole was somewhat low, since at the pyrrole concentrations employed ($\geqslant 0.1M$) some association was expected [2]. The present pyrrole data were obtained employing equimolar concentrations ($0.005M$) of reagents.

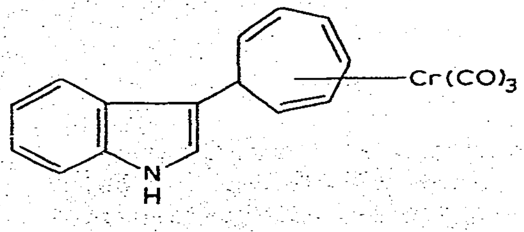
TABLE 1

REACTION OF [$C_6H_7Fe(CO)_3$]BF_4 ($0.005M$) WITH AROMATIC SUBSTRATES IN NITROMETHANE (temperature 20.8°C)

Substrate	Relative k_2 [a]
Pyrrole	10^7
Indole	1.8×10^6
Furan	1.1×10^4
1,3,5-Trimethoxybenzene	3.7×10^3
1,3-Dimethoxybenzene	75
Thiophene	1

[a] Obtained by following the disappearance of the dienyl band at 2120 cm^{-1}.

Preliminary observations indicate that aromatic substrates may in fact be successfully attacked with a range of cationic organometallic complexes, providing extensive synthetic possibilities. For example the tropylium complex [$C_7H_7Cr(CO)_3$]BF_4 (III) performs a similar, but less extended series of electrophilic substitutions. In particular, reaction with indole in acetone solution, followed by addition of water, gave fine orange crystals of the substituted triene (IV). [Found: C, 63.1; H, 3.7; N, 3.9. $C_{18}H_{14}CrNO_3$ calcd.: C, 63.0; H, 3.8; N, 4.1%.] Structure (IV) is supported by ^{1}H NMR, IR and mass spectral [3] data.



(IV)

In order to drive the last mentioned reaction to completion a large excess of indole is required, at which concentrations the process is too rapid to follow by IR spectroscopy. However, the rate of the corresponding reaction of (III) with acetylacetone could be readily followed in dichloroethane, giving a second-order rate constant of 7.26×10^{-6} l mol^{-1} s^{-1}. This compares with

$k_2 = 1.21 \times 10^{-4}$ l mol^{-1} s^{-1} for the analogous reaction of acetylacetone with [$C_6H_6OMeFe(CO)_3$]BF_4 (V).

Since the 2-methoxycyclohexadienyl salt is known [4] to be 9 times less reactive than the parent (I) towards nucleophiles, (III) is seen to be a much weaker electrophile than [$C_6H_7Fe(CO)_3$]BF_4 (I) (factor of 150). This provides the first quantitative comparison of the electrophilic reactivities of dienyliron tricarbonyl and tropyliumchromium tricarbonyl species.

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