Preliminary communication

IMPORTANCE OF CATIONIC ASSISTANCE IN THE REACTIONS OF M[(η5-C5H5)Fe(CO)2] SALTS WITH EPOXIDES

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Summary

The high bonding power of lithium toward oxygen is indicated by the absorption frequency for the carbonyl bridged ion pair Li[η^5-C$_5$H$_5$)Fe(CO)$_2$] and by the relative concentration of this species in THF solutions of this salt. Li[(η^5-C$_5$H$_5$)Fe(CO)$_2$] is much more reactive towards epoxides than is the corresponding sodium salt, and this difference may be attributed to more effective coordination of epoxide oxygen by lithium cation.

Although the complex anion [(η^5-C$_5$H$_5$)Fe(CO)$_2$]⁻ (hereafter designated as Fp⁻) is recognized as one of the most powerful of organometallic nucleophiles in S_N2 processes with alkyl halides [1]*, the role of its gegenion in these and related reactions has not been examined. Our interest in the anion as a metallating reagent [2] prompted us to examine the reactivity of its lithium salt, since we anticipated that for some reactions of the salt, Lewis acid coordination might play an important role.

A number of MFp salts are known, among them the sodium, potassium, tri-n-butylammonium and magnesium salts, but the lithium salt does not appear to have been reported. However, it like the sodium salt may readily be prepared by reduction of Fp$_2$ with excess lithium amalgam in THF solution**. A comparison of the carbonyl bands for LiFp with those of other known salts is instructive. These data are collected in Table 1.
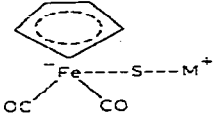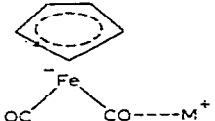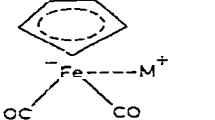
The infrared spectrum of LiFp in THF solution, like that of the magnesium salt [3], exhibits four bands of approximately equal intensity. These, following the interpretation of Pannell and Jackson [4], are assigned to the tight ion pair III and to the carbonyl bridged ion pair II. In addition, two relatively weak absorptions, comparable to those observed in the spectrum of

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*It has recently been shown that for reactive halides and especially for alkyl iodides, electron transfer processes may intervene substantially [1c].

**0.3% lithium amalgam.

TABLE 1

METAL CARBONYL INFRARED ABSORPTIONS OF $M[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ IN THF

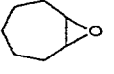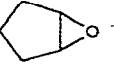| Ion pair type		C—O stretching frequency (cm^{-1})				
		NBu$_4$	K	Na	Li	Mg
—Fe----S---M$^+$ (I)		1865,1788	1868,1792	1862,1786	1865,1785	
—Fe, CO----M$^+$ (II)			1868,1772	1862,1770	1865,1745	1884,1713
—Fe----M$^+$ (III)				1877,1806	1880,1805	1918,1854

n-Bu$_4$NFp [5] are also present and these are assigned to the solvent separated ion pair I. When an equivalent of hexamethylphosphoramide is added to these solutions, the bands corresponding to II and III disappear and only the bands corresponding to I are observed.

A significant feature of the spectral data is the relatively low carbonyl absorption frequency exhibited by the bridged ion pair (II) in the lithium salt compared with the other alkali metal salts. The displacement of carbonyl stretching to lower frequency is almost as great as is observed when the cation is the dipositive magnesium ion, and no doubt reflects the considerable binding strength of lithium for oxygen [6]. This is further supported by the observation that both species II and III are present in roughly equal proportions in THF solutions of LiFp, while III is the predominant species for the sodium salt.
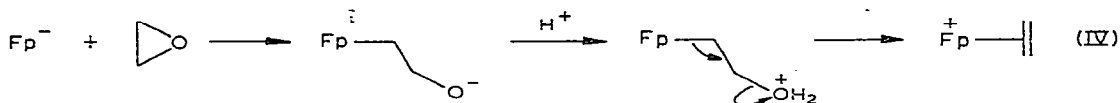
The importance of the gegenion in the reactions of Fp anion is dramatically illustrated by the data of Table 2, which compares the reactivities of NaFp and LiFp towards a number of epoxides. While in general the sodium salt reacts rapidly with the terminal olefin epoxides at 0°C in THF solution, higher temperatures and much longer reaction times are required to effect the opening of internal or cyclic olefin epoxides. By contrast LiFp reacts with these latter substrates rapidly even at 0°C to give comparable yields of the corresponding olefin salts IV, after acidification of the reaction mixture. As with NaFp, overall transformation of the epoxide occurs with retention of stereochemistry [7] (Table entries 3 and 4).

Infrared monitoring of the reactions of these salts in THF solution (0.05 M) with a 20-fold excess of cyclohexene epoxide at 25°C provides a measure of

TABLE 2

REACTIVITY OF M[(η⁵-C₅H₅)Fe(CO)₂] WITH EPOXIDES[a]

Epoxides	M	T (°C)	t (h)	% Yield[b] of Fp—‖
(cyclohexene oxide)	Li	0	0.5	75
	Na	25	4.0	60
(cycloheptene oxide)	Li	25	1.0	47
	Na	25	9.0	31
(isobutylene oxide)	Li	0	0.5	60
	Na	25	20.0	64
(2-methyl-1,2-epoxypentane)	Li	0	0.5	47
	Na	25	20.0	50
(cyclopentene oxide)	Li[c]	0	0.5	50
	Na	25	20	47

[a] Mole ratio of Fp⁻/epoxide 1:1. [b] Isolated product. [c] Mole ratio of Fp⁻/epoxide 1:4.

$$Fp^- \ + \ \text{(cyclohexene oxide)} \longrightarrow Fp\text{—}\overset{\bar{\cdot}}{\diagdown}\text{—O}^- \ \xrightarrow{H^+} \ Fp\diagdown\overset{+}{OH_2} \longrightarrow \overset{+}{Fp}\text{—‖} \quad (IV)$$

their relative reaction rates. Under these conditions, anion consumption for LiFp is complete within 2 min, while 4 h are required for complete reaction of NaFp.

The importance of the cation in these reactions is further revealed by the observation that THF solutions of LiFp, containing an equivalent of hexamethylphosphoramide, as well as those of n-Bu₄NFp failed to react with cyclohexene epoxide on prolonged standing at room temperature*.

Ion pairing by Li and Na cations with carbonyl oxygen has been implicated in promoting ligand transfer (RMCO → MCOR) in the RFe(CO)₄⁻ anion [9], and more specific acid catalysis has been inferred from a comparison of the rates of reaction of epoxides with HCo(CO)₄ and with NaCo(CO)₄ [10]. The present results provide strong evidence for the importance of Lewis acid

*The rates of reaction of MMn(CO)₄L with alkyl halides has been shown to be markedly lowered by the presence of hexamethylphosphoramide, which has been shown to promote formation of solvent separated ion pairs [8].

promotion in epoxide reactions even for anions of high nucleophilicity. A further evaluation of these effects in other reactions of the Fp⁻ anion is in progress.

Acknowledgement

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