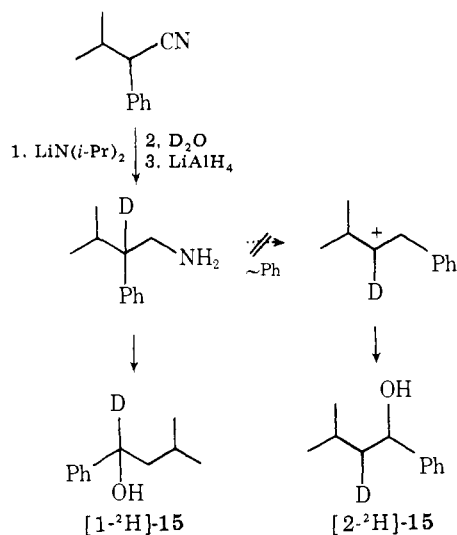Scheme III

[1-²H]-15   [2-²H]-15

Both deamination and solvolysis induce sequential rearrangements which are regio- and stereospecific.[18] The widely different reaction conditions exclude ion pairing as a possible cause of the observed stereochemistry. Phenyl, isopropyl, and hydrogen shifts compete efficiently in the deamination of **3**, whereas the tosylate **2** reacts predominantly by phenyl migration. These variations conform with previous experience[19] and are readily understood in terms of an increased demand for anchimeric assistance in tosylate solvolysis.

Our results demonstrate that phenonium ions can undergo sequential rearrangements in competition with attack by external nucleophiles, although the driving force for such processes is not obvious. The regioselectivity of sequential rearrangements provides an additional criterion for distinguishing open and bridged ions.

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Lithium Ion Promotion in the Synthesis of Novel Dinuclear Iron–Carbyne Complexes

Sir:

The importance of ion pairing in intra- and intermolecular reactions of organometallic salts has recently been emphasized.[1] These interactions are now shown to play an important role in the synthesis of a new class of stereochemically dynamic binuclear iron–carbyne complexes.

Earlier, we reported the conversion of epoxides to Fp(olefin) cations (Fp ≡ η⁵-C₅H₅Fe(CO)₂) by the sequence outlined in Scheme I.[2] In these reactions, the anionic intermediate (**1**) has been shown to exist preferentially in the lactone form (**2**).[3]

The use of FpLi in place of FpNa in these reactions results in a marked increase in the rate of epoxide ring opening, but for acyclic epoxides the overall course of reaction is unchanged.[4] However, the behavior of cyclopentene oxide is

Scheme I

1

2

Scheme II

trans-3   4

cis-3
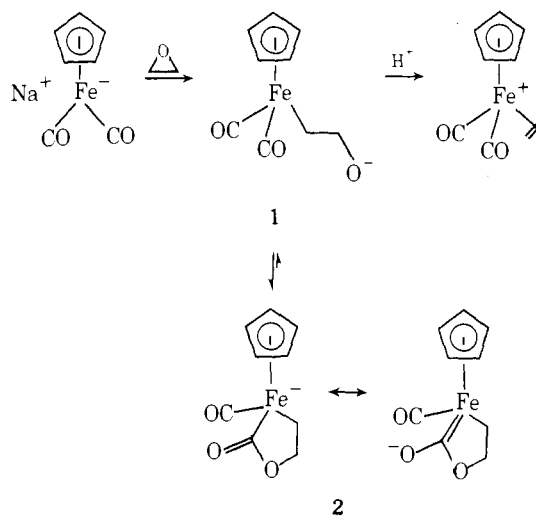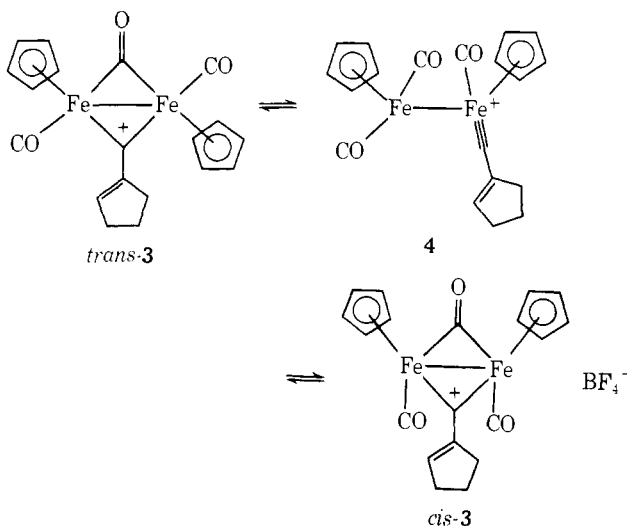
strikingly different. While brief exposure of this epoxide to 0.25 molar equiv of FpLi at 0 °C, followed by acidification with 48% HBF$_4$, leads to the expected olefin complex, prolonged reaction of these components (25 °C, 5 h), especially in the presence of excess FpLi, yields a deep red dinuclear salt (44%), C$_{19}$H$_{17}$Fe$_2$O$_3$BF$_4$, as a mixture of stereoisomers. The principal isomer, separated by fractional crystallization, is formulated as the bridged carbyne complex, *trans*-3:[5a] IR (CH$_2$Cl$_2$) 2040 (w), 2020 (s), 1855 (m) cm^{-1};[6] ^{1}H NMR (CD$_3$NO$_2$) δ 7.4 (br s, 1, CH=), 5.38 (s, 10, Cp), 3.65 (m, 2, CH$_2$), 2.89 (m, 2, CH$_2$), 2.39 (m, 2, CH$_2$); ^{13}C NMR (CD$_3$NO$_2$) δ 448.27 (s, carbyne C), 253.52 (s, CO), 207.45 (s, CO), 174.24 (s, C=), 155.33 (d, CH=), 94.50 (d, Cp), 39.97 (t, CH$_2$), 37.62 (t, CH$_2$), 25.67 (t, CH$_2$). The carbyne carbon in this and related complexes described below are among the most highly deshielded carbon atoms known.[7]

On heating in nitromethane solution, *trans*-3 is converted to the more stable cis isomer (Scheme II) ($K_{eq}^{32°}$ = 7.32):[5a] IR (CH$_2$Cl$_2$) 2040 (s), 2020 (w), 1855 (m) cm^{-1}; ^{13}C NMR (CD$_3$NO$_2$) δ 443.65 (carbyne C), 255.15 (s, CO), 208.68 (s, CO), 171.64 (s, CH=), 163.97 (d, CH=), 93.00 (s, Cp), 40.03 (t, CH$_2$), 37.89 (t, CH$_2$), 25.54 (t, CH$_2$). The activation energy for this process ($\Delta G^{\ddagger}$ = 22.5 kcal/mol) is considerably higher than for cis–trans isomerization of the parent dimer [CpFe(CO)$_2$]$_2$, for which $\Delta G^{\ddagger}$ = 10.4 kcal/mol has been calculated from NMR line shape studies.[6b] We attribute this in large measure to increased charge localization in the nonbridged carbyne intermediate (4), but steric factors may also contribute significantly.[8]

exo-Norbornene epoxide undergoes a similar transformation. This substance fails to react with FpNa on prolonged exposure, but treatment with FpLi (THF, 25 °C, 96 h), followed by acidification with HBF$_4$, yields the bridged carbyne complex (46%) as the cis isomer 5:[5a] IR (CH$_2$Cl$_2$) 2040 (s),

5

2020 (w) 1855 (m) cm^{-1}; ^{13}C NMR (CD$_3$NO$_2$) δ 432.7 (carbene C).

We formulate the changes associated with these reactions as shown in Scheme III for cyclopentene epoxide.

The IR spectrum of 6 shows that it exists in the open form.[9] Lactone formation in 6, as in the analogous anion derived from norbornene epoxide, is probably foreclosed by the s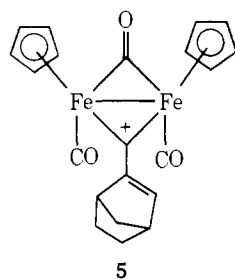tereochemical constraints of the trans substituted cyclopentane ring. These factors are no doubt important in facilitating the ligand transfer step (6 → 7), since dinuclear complexes are not formed in the reactions of FpLi with acyclic olefin epoxides or with either cyclohexene or cycloheptene epoxides, all of which may be shown to yield lactone anions (2) on treatment with Fp anions. Lithium ions are, however, essential in promoting the formation of a dinuclear complex since extended reaction of cyclopentene epoxide with FpNa (25 °C, 19 h) affords only a very low yield of 3. These observations are consistent with a mechanism in which the ligand transfer step is promoted by lithium ion coordination with a carbonyl oxygen.

However, the presence of an oxido function, derived from the epoxide ring, is not essential for promotion of ligand transfer, since (benzyl)Fp (8) may be transformed to a mixture of cis and trans dinuclear complexes (10)[5] on treatment with

Scheme III
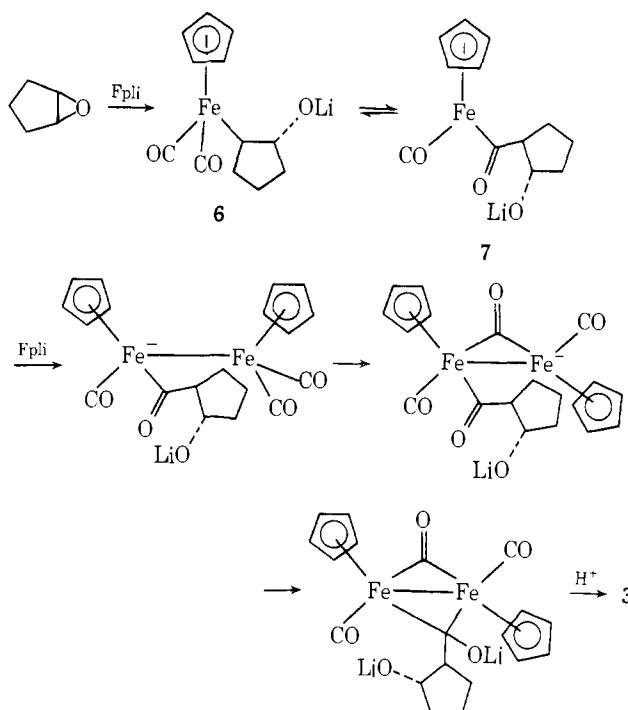
Scheme IV
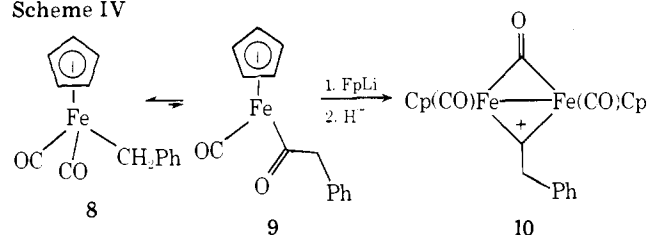
FpLi, followed by acidification (Scheme IV).

This reaction, like that of NaMn(CO)$_5$ with RMn(CO)$_5$ to give (CO)$_5$MnMn(COR)(CO)$_4$Na,[10] may proceed through capture of the coordinatively unsaturated complex (9) by Fp anion. The importance of lithium cation in this process is demonstrated by the fact that the reaction fails when FpLi is replaced by FpNa.[11] A similar reaction of FpLi, carried out on the relatively stable coordinatively unsaturated carbene complex (11),[12] affords the dinuclear complex (12):[5] IR (CS$_2$) 1945 (s), 1780 (w) 1740 (s) cm^{-1}.

11

12

13a, R = Me
b, R = *n*-Bu
c, R = Ph

Finally, the synthesis of these dinuclear carbyne complexes may be achieved alternatively and more directly in moderate yield, by treatment of the parent dimer [CpFe(CO)$_2$]$_2$ with alkyl- or aryllithium reagents, followed by acidification with HBF$_4$. In this manner complexes **13b** and **13c** are obtained as cis isomers and **13a** as a mixture of cis and trans isomers.

Further examination of these reactions and of the chemistry of the carbyne complexes is in progress.

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(9) In contrast to salts derived from FpNa or FpLi and either acyclic epoxides or cyclohexene epoxide, which exhibit IR absorption at 1850 and 1530 cm^{-1} (**2**), the product from cyclopentene epoxide shows two terminal carbonyl absorptions at 1995 and 1945 cm^{-1}.

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(13) The NMR spectrum of this substance in acetone-d_6 exhibits two cyclopentadienyl proton resonances below 18 °C at δ 4.72 and 4.57 of unequal intensity, which collapse to a single peak at room temperature. These changes may be associated with rapid transfer of the carbene ligand between the two metal centers and a slower rate of cis–trans interconversion.

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Methanesulfenic Acid[1]

Sir:

Sulfenic acids play a pivotal role in mechanistic organosulfur chemistry;[2] yet with rare exceptions these lowest members of the sulfur oxy acid family have defied isolation and structural characterization. The sulfenic acids that have been isolated in pure form[3] are sufficiently encumbered with polar linkages to obscure key structural aspects such as the preferred position of hydrogen

$$R\text{–}S\text{–}O\text{–}H \underset{\rightleftharpoons}{\overset{?}{}} RS(O)H$$

$$\text{A} \qquad\qquad \text{B}$$

as well as conformational features of the singly bonded isomer (form A, eq 1). Simpler sulfenic acids have eluded isolation because of their high reactivity as either electrophiles or nucleophiles[4] and because of their very facile conversion to thiosulfinate esters (eq 2; the mechanism shown[2b] incorporates

$$\longrightarrow \quad RS(O)SR + H_2O \qquad (2)$$

the dual electrophilic/nucleophilic character of sulfenic acids). Thus information on these intriguing molecules is based for the most part on kinetic and trapping studies.[2,5] Structural characterization of sulfenic acids takes on added importance with the recent demonstration that specific sulfhydryl groups in some enzymes can be oxidized to stable sulfenic acids and that these modified enzymes show altered catalytic activity.[7] We now wish to report that we have succeeded in generating by flash vacuum pyrolysis (FVP) the simplest organic sulfenic acid, methanesulfenic acid (**1**), and have fully characterized it by microwave spectroscopy. We report herein aspects of the structure and chemistry of this elusive molecule.

FVP–mass spectrometric examination[1b,8] of *tert*-butyl methyl sulfoxide (**2**), a likely precursor to methanesulfenic acid,[9,10] indicated the conversion of **2** above 250 °C to species with molecular ions of m/e 56 and 64. Definitive evidence for the formation of methanesulfenic acid and 2-methylpropene (m/e 64 and 56, respectively) from **2** under FVP conditions was obtained by following the decomposition of **2** by microwave spectroscopy. When **2** at its vapor pressure of 0.1–0.2 Torr was evaporated through a pyrolysis tube into a microwave absorption cell, generation of methanesulfenic acid and 2-methylpropene (whose microwave spectrum is known[11]) was detected first at a pyrolysis temperature of 240 °C and was complete above 400 °C; above 750 °C the microwave spectrum of methanesulfenic acid had been replaced by that of thioformaldehyde. A tandem pyrolysis experiment confirmed the gas phase dehydration of methanesulfenic acid to thioformaldehyde.[12] When condensed at −196 °C methanesulfenic acid could not be recovered on warming in vacuum. Analysis of the condensate warmed to room temperature revealed the presence of methyl methanethiosulfinate (**3**), water, 2-methylpropene, and traces of dimethyl disulfide (a known disproportionation product of **3**[2b,13]). It was also shown that methanesulfenic acid readily exchanges with D$_2$O in the wave guide affording methanesulfenic acid-*hydroxy-d$_1$*. The several reactions of methanesulfenic acid are summarized in eq 3.

$$CH_3S(O)C_4H_9\text{-}t \xrightarrow{\text{FVP}} (CH_3)_2C{=}CH_2 + CH_3SOH \xrightarrow[\text{750 °C}]{-H_2O} CH_2{=}S$$

$$\text{2} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{1}$$

$$\xrightarrow[\text{25 °C}]{-H_2O} CH_3S(O)SCH_3$$

$$\text{3}$$

$$\xrightarrow[\text{25 °C}]{D_2O} CH_3SOD \qquad (3)$$

A number of other thermal sources of methanesulfenic acid were found using FVP–microwave techniques, although none of these sources were as efficient as **2**. Methyl methanethiosulfinate (**3**) at 250 °C afforded methanesulfenic acid and thioformaldehyde presumably by a mechanism previously described by one of us (eq 4).[2b] Dimethyl sulfoxide also proved

$$\longrightarrow \quad CH_3SOH + CH_2{=}S \qquad (4)$$

$$\text{3}$$