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Preliminary communication

METALLOCYCLE CARBENES

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Summary

Intramolecular reactions of dicarbonyl-η^5-cyclopentadienyl (β-hydroxyalkyl)iron anions provide a route to chelated metal carbenes Some preliminary reactions of these are given

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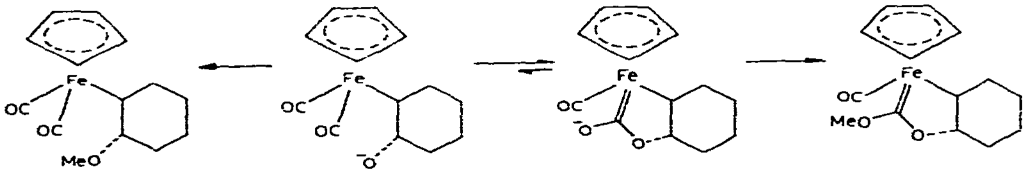
Of the numerous and growing number of transition metal carbene complexes which have been characterized [1], relatively few are known in which the metal—carbene bond is part of a ring [2]. The present report describes the preparation and some preliminary transformations of several new members of this class of complex, which incorporate an unusual ferrofuran ring.

Treatment of the (η^5-C_5H_5)Fe(CO)$_2$ anion with cyclohexene oxide affords an anion, which is best formulated as II rather than its acyclic tautomer I* [4] Structure II is clearly evidenced by the presence of a single metal carbonyl absorption in the IR spectrum at 1880 cm^{-1} and by additional absortion at 1530 cm^{-1}, assigned to the lactone function. When the anion is quenched with $Me_3O^+ BF_4^-$ at 0°C, a mixture of the carbene complex III** and its isomer IV are formed, each in 40% yield; III, IR (CH_2Cl_2) 1920 cm^{-1}, PMR (acetone-d_6) δ (ppm) 4.48 (s, Cp), 3.9 (s+m, OCH_3, OCH), 2.8—1 (m, CH, CH_2); ^{13}C NMR (CD_3NO_2) δ 265.70 ppm (carbene C).



(IV) (I) (II) (III)

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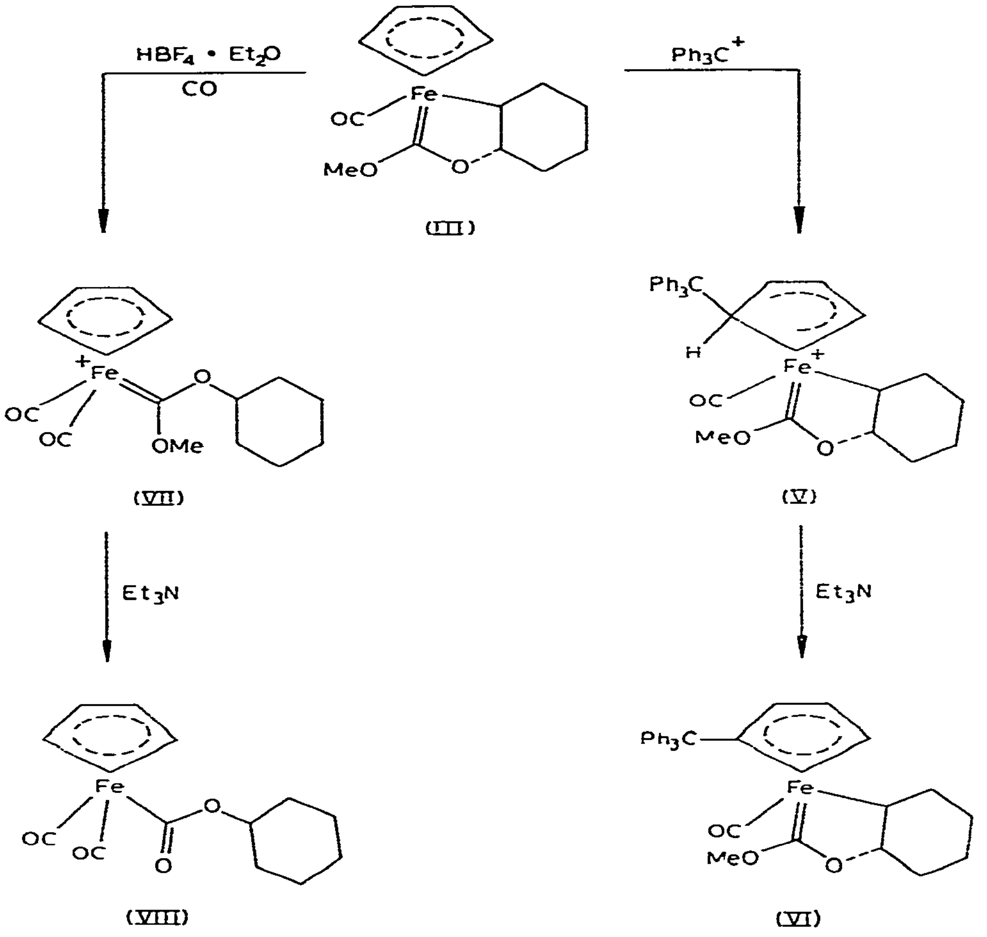
*Knoth [3] has observed similar equilibria in Group VI metal complexes

**Correct chemical analysis were obtained for complexes III, VI, VII, and XII

Both *cis*- and *trans*-2-butene epoxide also react with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ to give a chelated anion analogous to II*. However, treatment of these solutions with $Me_3O^+ BF_4^-$, under a variety of conditions gave only mixtures of *cis*- and *trans*-2-butene and the dimer $[(\eta^2\text{-}C_5H_5)Fe(CO)_2]_2$, but no carbene complex**.

Electrophilic attack on III leads either to addition to the cyclopentadienyl ring or cleavage of the Fe—C single bond Treatment of III with trityl tetrafluoroborate in methylene chloride, followed by addition of ether led to the



SCHEME 1

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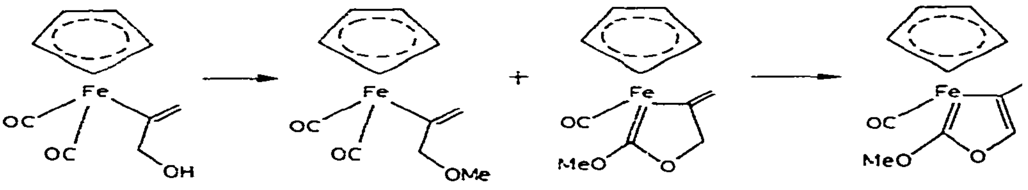
*The IR spectra of these solutions like that derived from the reaction of cyclohexene epoxide and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ show carbonyl absorption only at 1880 and 1530 cm^{-1} on completion of the reaction.

**It is possible that the open chain alkoxides derived from *cis*- or *trans*-2-butene epoxides are methylated much more rapidly than the ring tautomer. Alternatively rapid intramolecular rearrangement of the carbene to a CpFe(CO)(COOMe)(2-butene) complex, followed by loss of olefin cannot be ruled out.

precipitation of a reactive purple solid in high yield, which is formulated as the 16-electron cation V*; IR (CH_2Cl_2) 2020 cm^{-1}. Its high reactivity in solution has thus far prevented full characterization However, deprotonation of V with triethylamine affords the neutral carbene complex VI (80%), IR (CS_2) 1930 cm^{-1}; PMR (CS_2) δ (ppm) 7 11 (s, Ph), 4.2 (m, Cp), 3.76 (s, OCH_3), 3.65 (m, OCH), 2 3—1.2 (m, CH, CH_2). In the presence of $HBF_4 \cdot Et_2O$ and excess CO, the carbene complex III is transformed to VII (80%); IR (CH_2Cl_2) 2030, 2075 cm^{-1}; PMR (CD_3NO_2) δ (ppm) 5.44 (s, Cp), 5.40 (m, CHO), 4.35 (s, OCH_3) 2.2—1.3 (m, CH, CH_2). Demethylation of this cation with triethylamine gave the neutral acyl complex VIII** (83%) which was further characterized by decomposition with $HBF_4 \cdot Et_2O$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_3^+$ BF_4^- and cyclohexanol. These transformations are depicted in Scheme 1.

A second series of metallocycle carbene complexes is obtained from the allyl alcohol IX***, prepared in turn by hydration of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(allene) cation [8]. Treatment of IX with t-BuLi at −20°C, followed by methylation of the anion with Me_3OBF_4 gave a mixture of X and XI (80%, X/XI 3/1). On brief exposure of the carbene complex XI to neutral alumina, it is smoothly transformed to XII; IR (CH_2Cl_2) 1938 cm^{-1}, PMR (CS_2) δ (ppm) 6.6 (q, J 2 0 Hz, CH=), 4 46 (s, Cp), 3 96 (s, OCH_3), 2 03 (d, J 2 0 Hz, CH_3). Preliminary attempts to effect a Diels—Alder reaction of XII with maleic anhydride either thermally or photochemically have been unsuccessful



(IX) (X) (XI) (XII)

In principle, the sequences described here should be applicable to a wide range of organometallic complexes. An investigation of the scope of these reactions is in progress.

Acknowledgement

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*An analogous 16-electron cation $CpFe(R_2PCH_2CH_2PR_2)^+$ has recently been reported [5]

**King et al. [6] have reported the preparation of the methyl and ethyl esters corresponding to VIII

***Lichtenberg and Wojcicki [7] have reported the preparation of the 3-phenyl- and 3-methyl-substituted allyl alcohol complexes related to IX.

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