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THE CHEMISTRY OF DICARBONYLCYCLOPENTADIENYLIRON COMPLEXES: PROGRESS AND PROSPECTS

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Prologue

My introduction to organo-transition metal chemistry came unexpectedly one January morning in 1952. I was then in my second year of graduate research, with R.B. Woodward, caught up in an attempted synthesis of fulvalene, a substance later prepared by Doering and Matzner [1]. Bob Woodward came into my lab and asked casually whether I had seen a recent paper in Nature [2] on a curious compound derived from the reaction of cyclopentadienylmagnesium bromide and ferric chloride. Since I had not, he proceeded to summarize this report, and concluded by drawing on the small blackboard nearby, in his characteristically meticulous architectural style, the sandwich structure now so familiar a representation of ferrocene, the two cyclopentadienyl rings shown in perspective, with delocalized electrons, and ten dashed lines from each of the carbon centers to the iron atom to represent their bonding equivalency. "There", he said "I believe this is the correct structure", then almost as an aside, "Why don't you take off a few days, make some, and let us have a look at it." And so I did. By mid-March 1952, working with Goef Wilkinson and Mark Whiting, strong evidence in support of the sandwich structure had been gathered [3a]. Shortly thereafter, as we were taking our seats before the traditional Thursday evening seminar, Bob Woodward casually suggested that I might want to examine the substance for possible aromatic character. By the next Monday, a Friedel–Crafts acetylation reaction was set up. Later that day a new, bright red crystalline substance was isolated and its infrared spectrum, showing an intense carbonyl band, was in hand. Within a few weeks, evidence for the aromatic character of the molecule was overwhelming [3b]. Suffice it to say that what had begun as a brief chemical excursion has long since become a pleasurably long journey.

Complexes of dicarbonylcyclopentadienyliron

Some twenty years later, in the course of research concerned with the preparation of $CpFe(CO)_2(\eta^2\text{-olefin})$ cations, our attention was drawn to the reactions of η^1-allyl metal complexes with SO_2. This came about through study of the reaction of the cyclopropylmethyl complex **1** with SO_2, carried out by Warren Giering, who was

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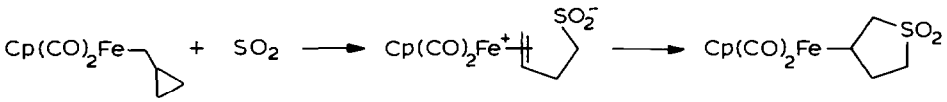
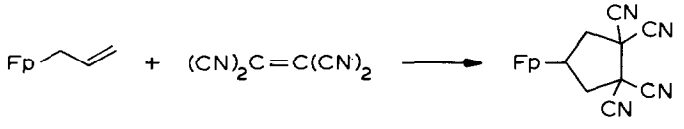
then working with me as a postdoctoral associate. The product was clearly an organic sulfone on the basis of its IR spectrum, not the metal alkyl sulfone to be expected from a simple "insertion" reaction by analogy to similar reactions of alkylmetal complexes which had been investigated extensively by Wojcicki [4a]. We formulated the product as **2**, and wrote the mechanism shown below, in which SO_2



(1) (2)

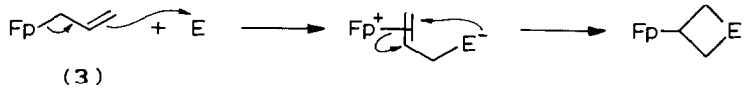
functioned initially as an electrophile in promoting the cleavage of a cyclopropane bond. The formulation of the reaction in terms of an electrophile-initiated two step process was crucial, for it seemed apparent, in terms of such a mechanism, that similar processes should obtain with η^1-allyl-, η^1-propargyl- and η^1-cyclopropyl metal complexes as well. An examination of the literature soon provided reference to the reaction of the first two of these with sulfur dioxide and *N*-thionylamines, but those reactions had generally been written as concerted "insertion" processes [4]. It also seemed plausible to suppose, in terms of the stepwise, ionic mechanism shown above, that other electrophiles, in particular carbon electrophiles, might also be capable of entering these reactions. We were gratified to find that this was indeed so. Tetracyanoethylene, our first candidate, appeared to react instantly with the η^1-allyliron complex **3**, yielding the crystalline cyclopentyl derivative **4**. Since our primary initial focus was on reactions of the ligand σ-bonded to the unchanging organometallic residue, it became convenient to identify this group in a shorthand manner, and we introduced the symbol Fp to signify the $CpFe(CO)_2$ group [5]. We will use this symbol throughout this account.



(3) (4)

Cycloaddition reactions of (η^1-allyl)Fp complexes

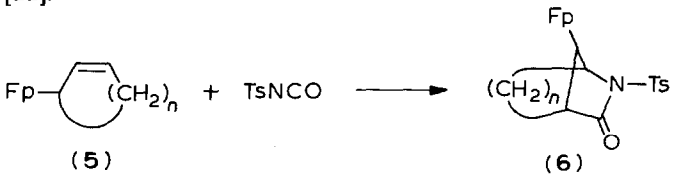
The reactions of Fp complexes may be conveniently considered in terms of the several general types of ligands to which the organometallic radical is bound. These are σ-allyl, π-olefin, π-acetylene and σ-alkyl ligands. A neat division in considering the chemistry of each such complex type is not always possible. For example, the cycloaddition reactions of (η^1-allyl)Fp complexes exemplify the characteristic nucleophilic behavior of the allyl ligand as well as the electrophilic behavior of the intermediate olefin complex.



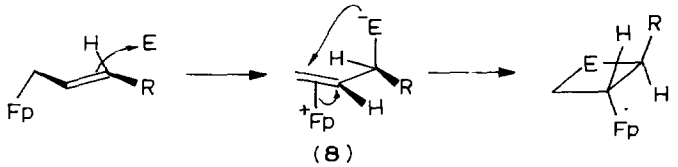
(3)

These reactions, in which the (η^1-allyl)Fp complex behaves as a 1,3-carbon dipole, attracted much of our early attention [6–9]. A brief review of these early results was

given in 1974 [10], and there is consequently no need to duplicate that account here, except to summarize the salient findings so as to set them in the perspective of more recent results. At the outset, it is important to note the very important stereoelectronic role played by the Fp group, in both the reactions of the neutral (η^1-allyl)Fp complexes and those of the cationic Fp(η^2-olefin) complexes. A good example of this is provided by the cycloaddition reactions of cyclic (η^1-allyl)Fp complexes with uncharged carbon electrophiles. Thus, the cyclopentenyl- or (cyclohexenyl)-Fp complexes **5a,b** react with tosylisocyanate to give a single stereoisomeric cycloadduct **6a,b** [11].

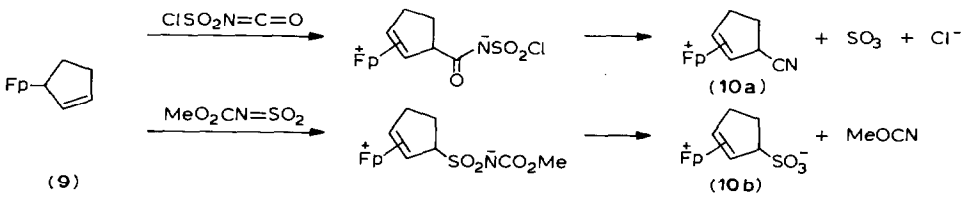


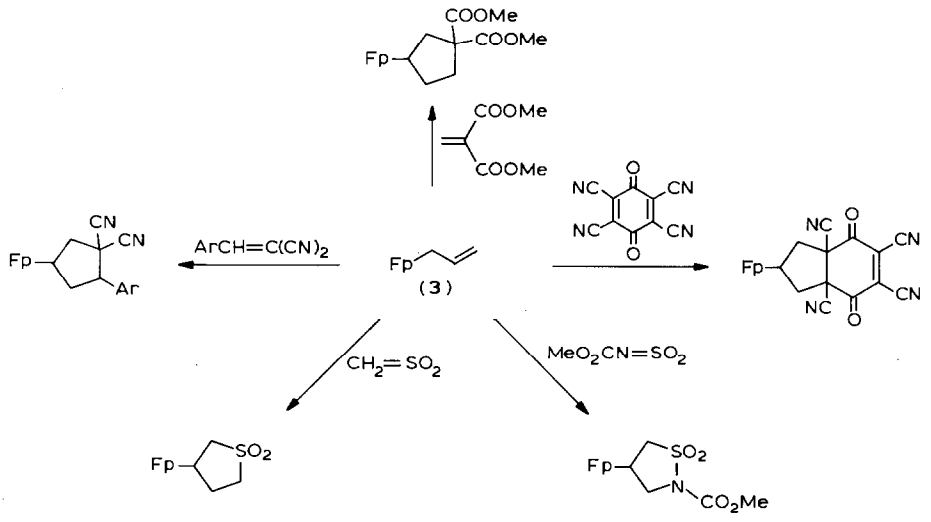
Similar cycloadducts of **5a,b** were isolated from their reactions with tetracyanoethylene [7]. In all of these reactions the stereochemical outcome corresponds to a suprafacial 1,3-addition of the acceptor component to the allyl complex, the result of which is to preserve geometrical isomerism associated with a substituent at C(1) in the reactant by its relationship to the Fp group in the product. In terms of the two step mechanism, both initial electrophilic attack on the allyl complex as well as nucleophile addition to the intermediate olefin complex must therefore occur antiperiplanar to the Fe–ligand bond.



The (η^1-allyl)Fp complexes are comparatively mild nucleophiles and consequently cycloaddition reactions are initiated only by fairly reactive electrophiles. A summary of some of these reactions is given in Scheme 1 for the parent complex **3**.

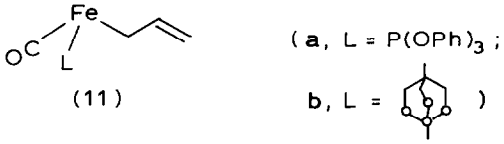
Unanticipated evidence for the intermediacy of dipolar intermediates **8** in these cycloaddition reactions was provided by the isolation of the cations **10a,b** respectively from the reaction of (η^1-cyclopentenyl)Fp (**9**) with chlorosulfonyl isocyanate and with *N*-sulfonylurethane. Here, fragmentation of the dipolar intermediate competes with cyclization to a comparatively strained bicyclic system.





SCHEME 1

Not surprisingly, the replacement of a carbonyl ligand in **3** by a poorer π-acceptor ligand results in a substantial increase in reactivity toward electrophiles. Thus, **11a** is 180 times as reactive as **3** toward β,β-dicyanostyrene, while **11b** is nearly 1000 times as reactive as **3**. The latter phosphite complex reacts readily with 1-ethoxy-2,2-dicyanoethylene at room temperature, while **3** is inert [12].



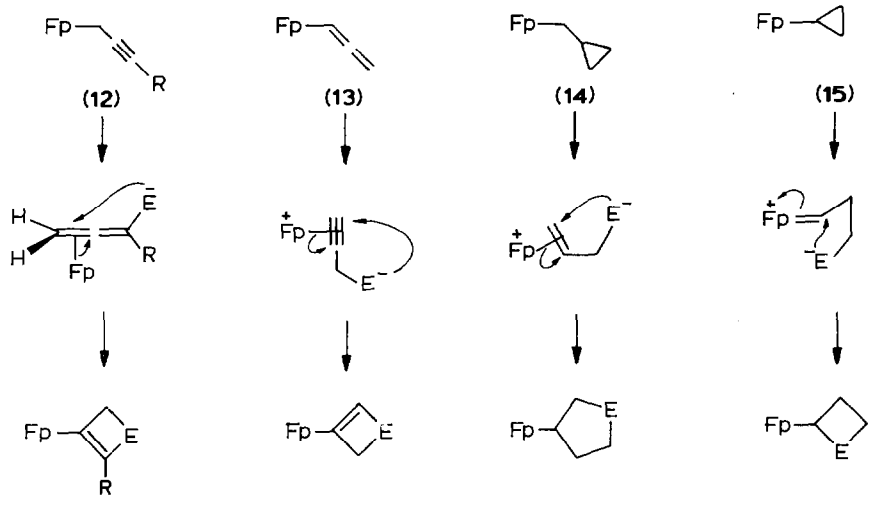
(11)

(**a**, L = $P(OPh)_3$;

b, L =)

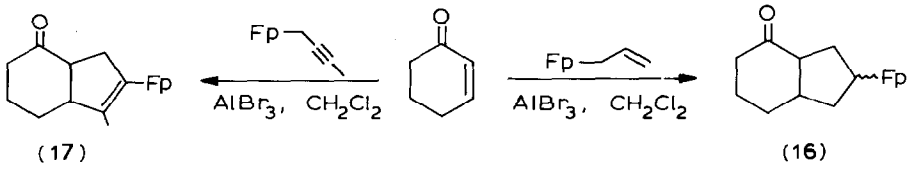
Much of the same form of cycloaddition reaction is manifested by analogs of **3** such as the propargyl **12**, allenyl **13**, cyclopropylmethyl **14** and cyclopropyl **15** complexes. Scheme 2 summarizes these conversions and the postulated dipolar intermediates associated with them. Together these constitute a family of 1,3-carbon dipoles whose cycloadducts complement those formed with (η^1-allyl)Fp complexes. The intermediate cation generated in the reactions of (cyclopropyl)Fp with electrophiles is unique in the group as a "carbene" type cation; the first of its class. Such cations have more recently been prepared by other means by Brookhart and by Helquist, and have been shown to function as electrophilic carbenes [13].

Among the cycloaddition reactions depicted in Scheme 2, those in which E is a 2-carbon electrophile are of particular interest, since they provide a [3 + 2]-cycloaddition route to cyclopentanes, complementing familiar [4 + 2]-cycloadditions of the Diels–Alder type. Only the most electron deficient of olefins, CH_2=$C(COOR)_2$, $ArCH{=}C(CN)_2$, $(CN)_2C{=}C(CN)_2$, appear to be capable of initiating cycloadditions with (η^1-allyl)Fp and its congeners. The more reactive phosphine and phosphite derivatives of these, such as **11** have not been examined as yet. Nevertheless, even cyclohexenone has been found to initiate cyclopentaannulation with **3** and with (η^1-butynyl)Fp in the presence of $AlBr_3$ as catalyst to give the *cis*-hy-

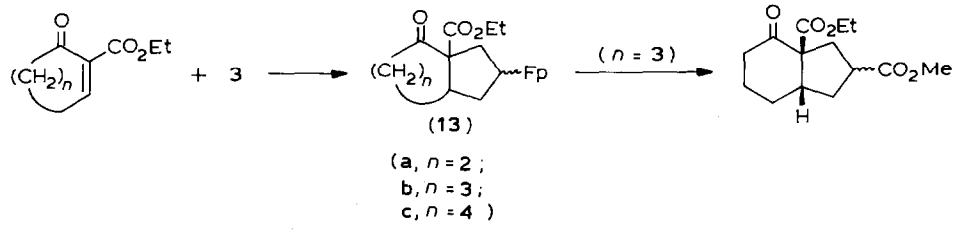


SCHEME 2

drindanones **12** and **13**. However, 3-methylcyclohexenone does not react with **3** under these conditions.

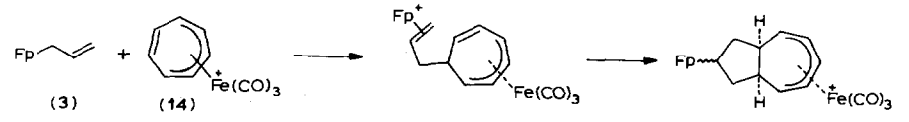


The readily accessible 2-carbethoxycycloalkenones undergo uncatalyzed cycloaddition with **3** in moderate yield, and the hydroindanone product **13b**, has been



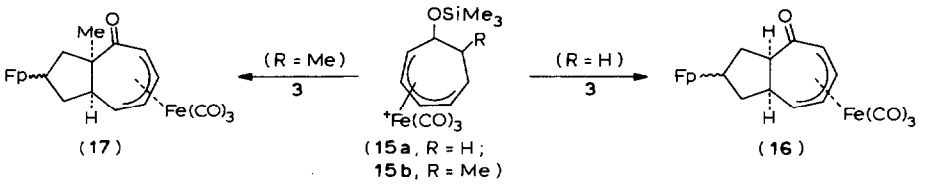
converted into a mixture of stereoisomeric methyl esters on oxidation with Ce^{IV} in methanol solution [14].

A variant of these cycloaddition reactions, in which the dipolarophile is itself an organometallic complex, **14**, provides a facile entry into the hydroazulene ring system [15].



These reactions have more recently been extended to oxygenated tropylium salts **15a,b**, which notwithstanding the fluxional character of these complex cations, react with **3** and its congeners to give a single product **16,17**. These may serve as useful

starting materials for the synthesis of guaianolides and pseudoguaianolides [16,17], a point which remains to be examined.

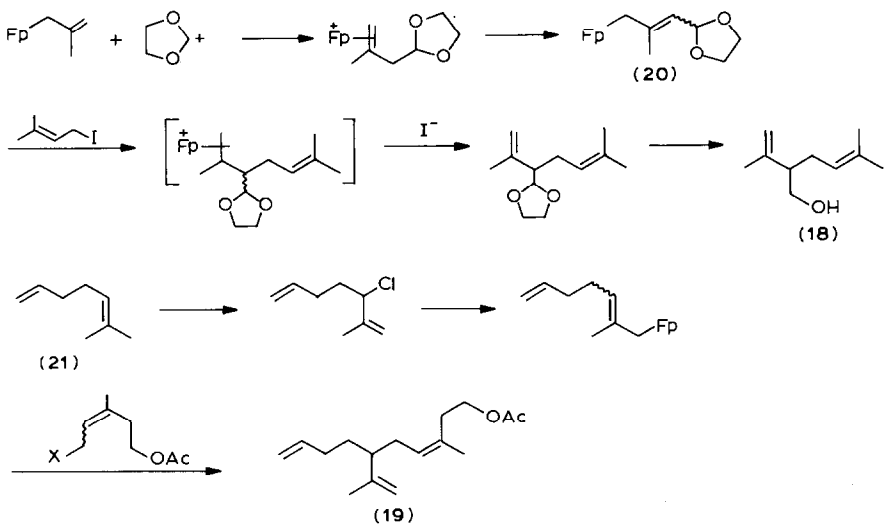


Reactions of (η^1-allyl)Fp and related complexes with electrophiles

Like allyl-silanes [18] and -stannanes [19], (η^1-allyl)Fp complexes react with a range of charged electrophiles. The stability of Fp(η^2-olefin) cations allows the cationic products of these reactions to be isolated, an outcome not possible with allylsilanes or allylstannanes. Moreover, protons allylic to the coordinated olefin are highly acidified, making it possible to remove them with a base as weak as a tertiary amine. The overall sequence provides a general method for elaboration and functionalization of simple (η^1-allyl)Fp complexes, and hence a route to the preparation of more highly functionalized cycloaddition products [20].

Some straightforward synthetic applications of the electrophilic substitution reactions are exemplified by the synthesis of lavandulol **18** and the red scale pheromone **19** [21].

The first synthesis proceeds through an initial alkylation, deprotonation sequence of (η^1-isobutenyl)Fp. It is of interest to note that the alkylation of the substituted

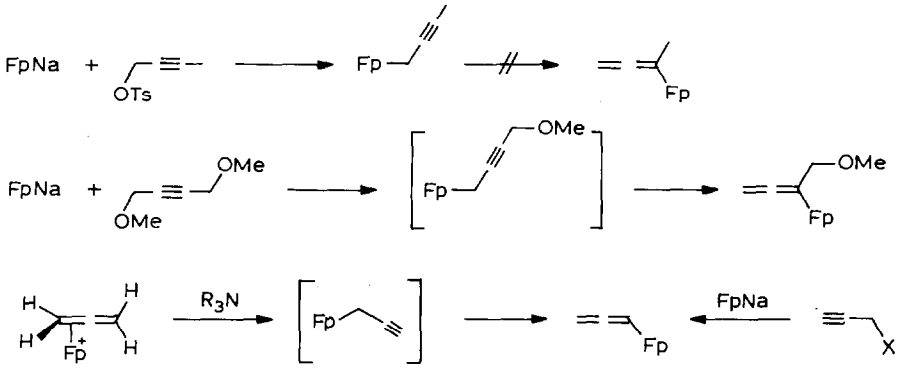


(η^1-allyl)Fp complex **20** may be achieved with as mild an electrophilic reactant as an allylic iodide. The intermediate olefin complex is demetallated in the course of the condensation by the iodide released.

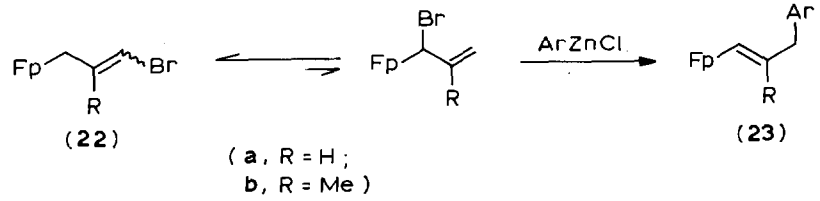
The starting material employed in the red scale pheromone synthesis was prepared from the commercially available diene **21** by selective halogenation following the method of Wolinsky [22]. This reaction illustrates an important distinction

between the behavior of allyl-silanes or -stannanes and (η^1-allyl)Fp complexes. Because of the weaker metal–carbon bond in Fp complexes, sigmatropic rearrangement to the more stable allyl complex takes place rapidly [23]. These reactions have been shown to proceed not intramolecularly but by a radical chain mechanism in which the chain carrying species is the relatively stable Fp radical [24].

Similar rearrangements of propargylic and allenic complexes which may also involve radical intermediates have also been observed, but no evidence on this point is available. The thermodynamic balance between these isomeric complexes is apparently a sensitive function of ligand substituents, as evidenced by the following reactions.



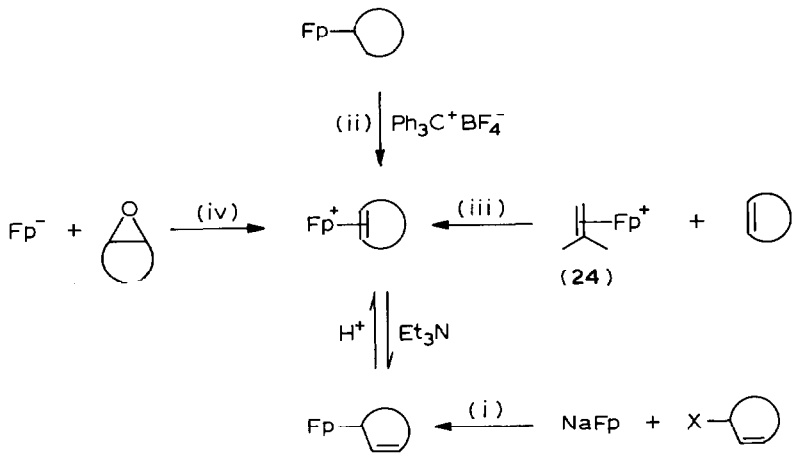
Although not observed in the NMR spectrum, the thermodynamically less stable isomeric Fp complex may nevertheless be present in equilibrium with the major tautomer. Evidence on this point has recently been obtained in examining the reactions of **22a,b** with arylzinc chloride. The products **23a,b**, which form slowly, have been shown through deuterium labelling studies to be formed through S_N2' attack on the isomeric (η^1-allyl)Fp complex [25].



Olefin complexes – formation and primary transformations

Fp(η^2-olefin)BF_4 salts are readily accessible by a number of routes. These are summarized below in generalized terms for a cyclic olefin (Scheme 3).

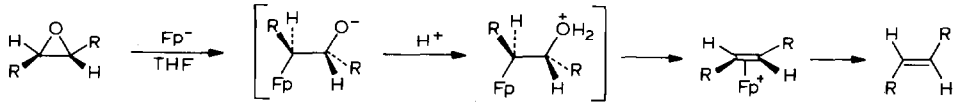
The first of these, shown in sequence (i), is based on the early work of Green [26], and provides a general route to acyclic and cyclic (η^1-allyl)Fp complexes from allyl bromides, chlorides or tosylates. These, on protonation, yield cationic olefin complexes. This latter reaction is reversible, and deprotonation may generally be achieved by a tertiary amine base [8,11]. The deprotonation step is also highly stereoselective and proceeds by preferential removal of an allylic proton *trans* to the



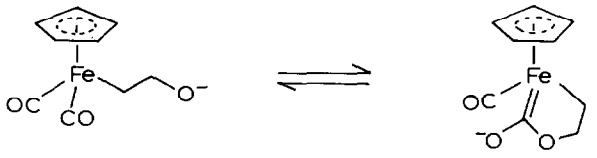
SCHEME 3

Fp-olefin bond. β-Hydride abstraction, from alkyl Fp complexes [27], shown in sequence (ii), also appears to be highly stereoselective, proceeding through preferential removal of the *trans*-hydride. This reaction has been less extensively examined as a synthetic route to Fp(η^2-olefin) complexes. Fp(η^2-isobutylene)BF_4 (**24**), prepared by metallation of isobutenyl chloride followed by protonation, is a thermodynamically unstable complex. Good advantage may be taken of this property by carrying out the thermal decompostion of **24** in the presence of an acceptor olefin. This exchange complexation, sequence (iii), which can be carried out in refluxing methylene chloride (2–3 h) or 1,2-dichloroethane (65°C, 20–30 min), has proven to be a highly convenient method for the synthesis of Fp(olefin) complexes. It is, however, clearly confined to those complexes which are stable under conditions of the exchange. These include mono- and *cis*-disubstituted acyclic olefins as well as cyclic olefins. Olefins substituted by electron-withdrawing groups are not good partners in the exchange reactions, since the donor property of the olefin π-orbital, which is the principal contributor to bonding in Fp(η^2-olefin) complexes, is diminished by conjugation with the electron-withdrawing group. These olefin complexes consequently exhibit low thermal stability. They can, however, be prepared from the epoxide of the α,β-unsaturated carbonyl compound, by treatment with the strongly nucleophilic reagent NaFp. The resulting (β-oxidoalkyl) Fp complex is then protonated at low temperature to give these olefin complexes (sequence (iv)) [28,11].

Since Fp(olefin) cations are generally decomposed by brief treatment with sodium iodide in acetone solution at room temperature, the overall sequence is an effective one for the reduction of epoxides. Moreover, both epoxide opening and Fp assisted loss of water from the intermediate hydronium salt occur with high *trans*-stereospecificity, so that the overall stereochemical result is retention of configuration. Other reducible functional groups such as aldehydes and esters are unaffected.

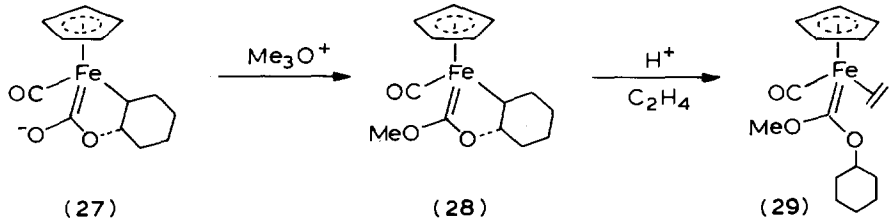


If instead of being protonated, the oxido complex **25** is thermally decomposed in refluxing THF solution or by heating neat in vacuo, the olefin with inverted stereochemistry is produced. The reaction is highly stereospecific for dialkyl and diaryl epoxides, but is less effective for the preparation of *cis*-α,β-unsaturated esters which are readily isomerized [29]. The mechanism of this reaction has not been examined, but it is known that (β-oxidoalkyl)Fp complexes exist in equilibrium with the ring tautomers such as **26** [30], and the latter may be intermediates in the thermal reaction. Indeed, such carbenoid complexes were subsequently trapped by alkylation with trimethyloxonium salts [30,31]. Complex **27**, which is formed from cyclohexene



(25) (26)

epoxide as a single diastereomer [31], is converted into **28** on treatment with trimethyloxonium tetrafluoroborate. Protonation of this latter substance in the presence of ethylene yielded **29**, the first stable mononuclear metal complex with

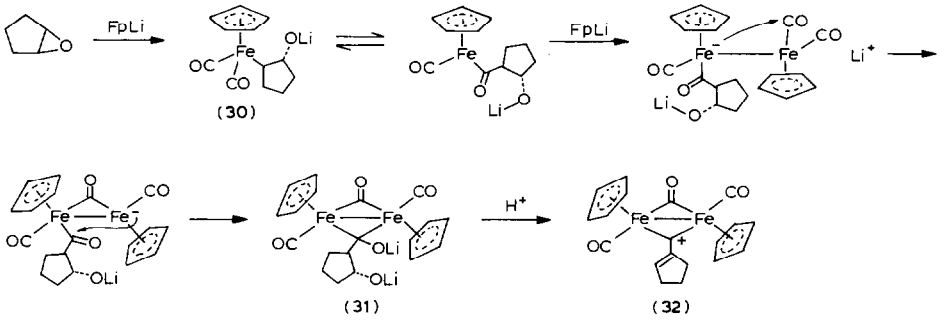


(27) (28) (29)

both carbene and olefin ligands [32]. Such complexes are presumed to be intermediates in olefin metathesis reactions.

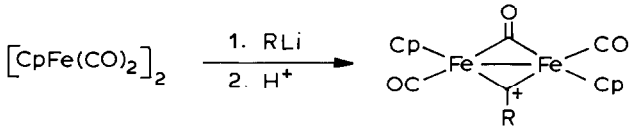
Although the sodium salt of Fp^-, conveniently prepared in THF solution by reduction of Fp with sodium amalgam, has been the most commonly used form of this powerful organometallic nucleophile, the importance of the alkali metal cation, especially in reactions of epoxides is evident. LiFp opens epoxides with considerably greater ease than NaFp, as a consequence, no doubt, of lithium coordination with the epoxide oxygen [33]. For example, a 20-fold excess of cyclohexene epoxide reacts with NaFp within 4 h at room temperature, but the same reaction is complete with LiFp within 2 min.

The oxophilic character of lithium cations is undoubtedly also important in promoting a rearrangement which occurs in the opening of certain cyclic epoxides with FpLi but not FpNa [34]. We observed that when cyclopentene epoxide was treated with FpLi and the product immediately acidified, the expected olefin salt was formed. But, if these solutions were allowed to stand for several hours at room temperature before acidification, the binuclear salt **32** was formed instead. The course of this change is depicted below. The formation of a bicyclic complex does not occur with acyclic epoxides or with cyclohexene or cycloheptene epoxide. It



(30) (31) (32)

appears that rearrangement is confined to cyclic epoxides, such as cyclopentene epoxide, in which the intermediate (β-oxidoalkyl)Fp complex exists preferentially in the acyclic form **30**. Lithium ion may then promote migratory insertions in the compound, and the resulting coordinatively unsaturated complex is then activated for nucleophilic addition by FpLi and closure to the penultimate bridged species **31**. A more general method for the preparation of such cationic bridging carbyne complexes was found in the reaction of alkyl or aryllithium reagents with Fp_2, followed by acidification. Cations **32** and **33** represent the first examples of cationic binuclear carbyne complexes.

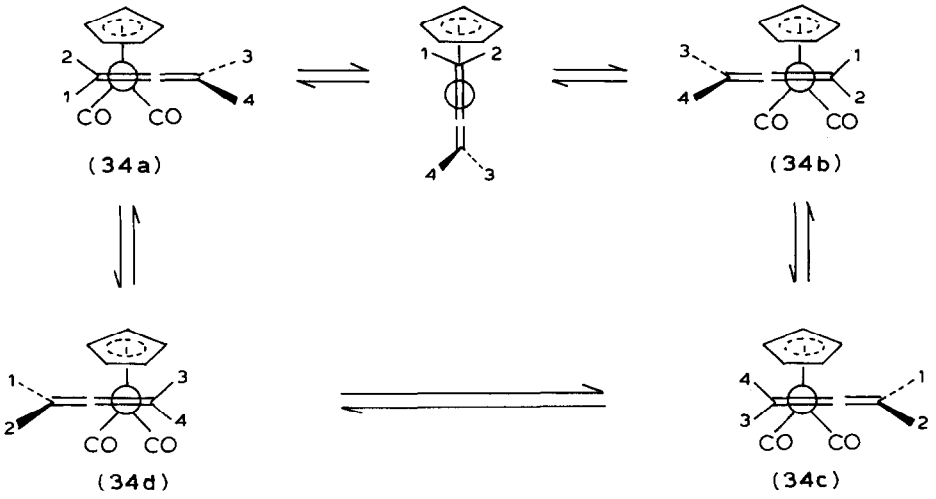


(33)

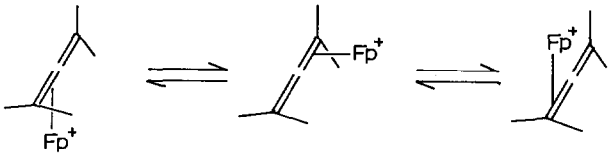
(R = Me, n-Bu, Ph)

Cationic Fp(allene) complexes **34** provided us with interestingly mobile systems, whose fluxional behavior resembled that of tetramethylalleneiron tetracarbonyl, examined earlier by Ben Shoshan and Pettit [35]. Metal coordination to the ligand in these complexes appears to be significantly stronger than in simple olefin complexes, as indicated by the shorter metal bond to the internal carbon center in the Fp(η^2-tetramethylallene) cation [36,37]. As a consequence, the exchange reaction of allenes with Fp(η^2-isobutylene)BF_4 serves as a convenient, high yield method for preparing these complexes [37]. In this way, the parent complex as well as several methylated Fp(η^2-alkene)complexes were prepared. Two dynamic processes are evident in these complexes, which are best exemplified in the behavior of the tetramethylallene complex, summarized in Scheme 4.

At $-60°C$ the proton NMR spectrum of this complex exhibits four singlet resonances. Two of these, assigned to methyl groups 1 and 2 in **34a,b** collapse above $-25°C$, due to averaging through rotation of the ligand about the metal–olefin bond. At higher temperatures, averaging of the remaining pair of methyl groups among themselves and with the other pair, takes place through a 1,2-shift. The activaton energies for these two processes (12.7 and 16.3 kcal mol^{-1}) are sufficiently different so that one is rapid on the NMR time scale before appreciable onset of the second. Further experiments showed that the 1,2-shift takes place by a non-dissociative mechanism.



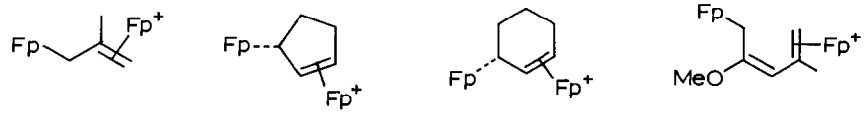
Scheme 4



Fluxional behavior has been observed in dinuclear systems, which we like to refer to as "teetertautomers", the first one of which, **35**, was reported some years ago by King and Bisnette [38]. The infrared spectrum of this complex shows the presence of both neutral and cationic Fp groups, but the NMR spectrum shows a single proton

(35)

resonance down to $-90°C$ [39]. Some charge dispersal in these cations, and hence increased thermodynamic stability, is evident from the fact that **36** can be prepared by exchange complexation with Fp(η^2-isobutylene). The complex also shows thermal stability in nitromethane solution significantly greater than Fp(η^2-isobutylene). The NMR spectrum of this compound, and those of the cyclic analogs **37** and **38**, also

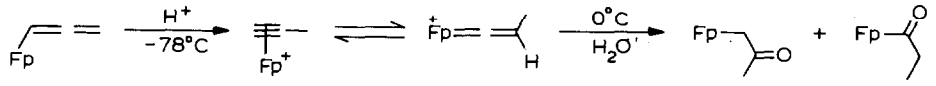


(36) (37) (38) (39)

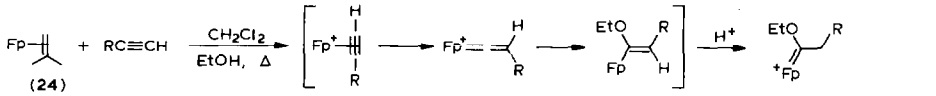
show Fp averaging, the latter even down to $-110°C$. The dinuclear complex **39** shows very complex temperature-dependent NMR spectra behavior associated with both fluxional exchange of the two nonequivalent Fp centers as well as rotational isomerism about the framework C–C single and double bonds [40]. Doubtless many more such conjugated, fluxional σ,π-systems, both homo, and heteronuclear are constructable.

Acetylene complexes

Compared with the Fp(η^2-olefin) complexes, the corresponding acetylene complexes have been less extensively studied. The first such cation, **41**, was prepared by protonation of **40** at low temperature. Rearrangement of **41** to the vinylidene complex **42** is suggested by the fact that hydrolysis, which takes place rapidly at 0°C, gives a mixture of ketones, expected from **41** and **42**.

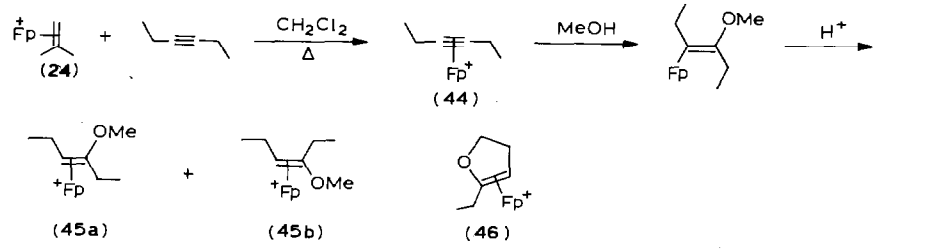


A more general method for the synthesis of stabilized carboxonium ions derived from cations such as **42**, consists simply in carrying out the Fp^+ cation exchange reaction with Fp(η^2-isobutylene)BF_4 and a terminal acetylene in the presence of an alcohol [41]. In this way complexes such as **43a,b,c** are readily obtained. The

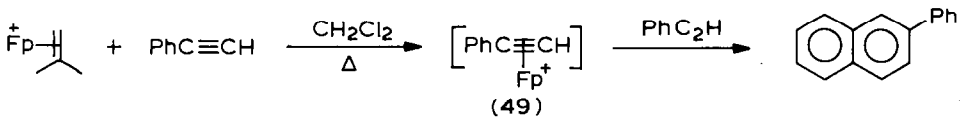


(**43a**, R = n-C_3H_7; **43b**, R = n-C_4H_9; **43c**, R = Ph)

rearrangement of the acetylene complex to the vinylidene complex in this sequence is intramolecular, since when it is carried out in EtOD only one deuterium is incorporated α- to the carboxonium ion in the product [42]. Concurrent complexation and alcoholysis cannot be applied to internal acetylenes, but the 3-hexyne complex **44**, prepared by the exchange reaction with **24**, can be converted into a 3/1 mixture of **45a** and **46b** by subsequent treatment with methanol. With 3-hexyne-1-ol, exchange complexation and intramolecular alcohol addition take place, to give the dihydrofuran complex **46**.



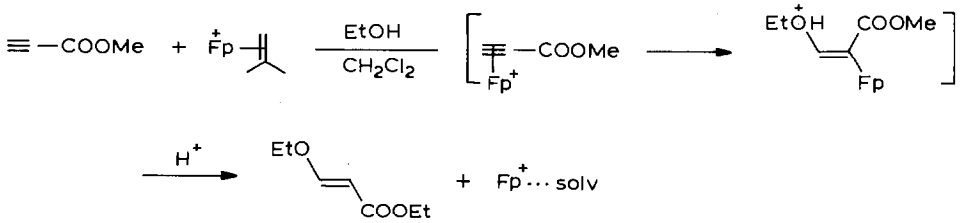
It is apparent from the above results that Fp(η^2-acetylene) complexes are highly reactive electrophiles, in many respects more reactive than the corresponding olefin complexes. One measure of this is to be seen in the formation of 2-phenylnaphthalene when the exchange reaction of Fp(η^2-isobutylene) is carried out with phenylacetylene. The reaction is mildly catalytic in Fp(η^2-isobutylene), and the reactive species is apparently the unrearranged terminal acetylene complex **49**, not the isomeric vinylidene cation, since with 1-deuteriophenylacetylene the product is found to be labelled only at C(1) and C(3) [43].



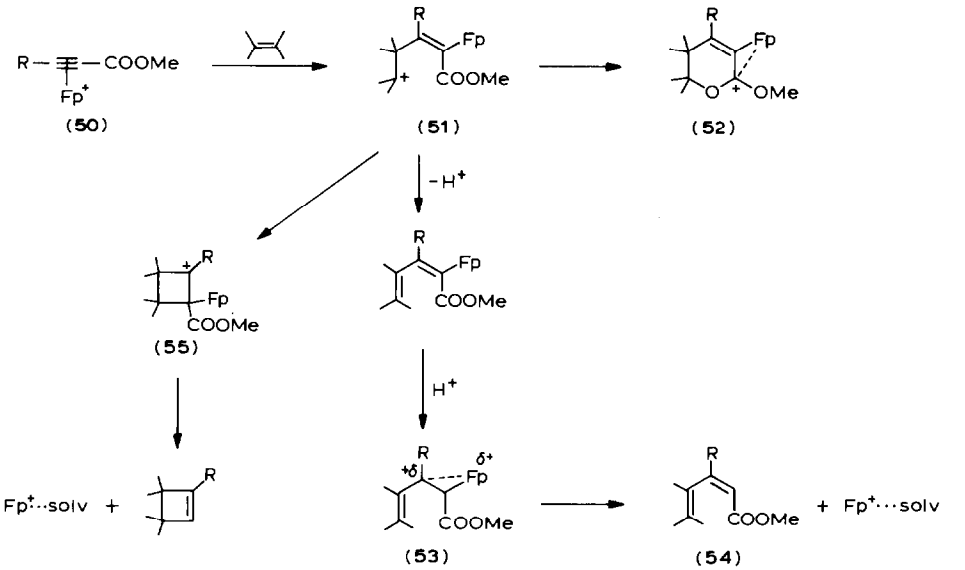
(49)

The precise mode by which the product is formed has not been defined, but it may involve electrophilic attack of **49** on uncomplexed phenylacetylene.

In contrast to olefins substituted by electron-withdrawing groups, which do not yield Fp complexes by the exchange reaction, propiolic esters are apparently complexed in this reaction. These complexes have not been isolated, but their formation may be reasonably inferred from the products of the reaction. Thus, in the presence of ethanol, exchange complexation of methyl propiolate gives methyl *trans*-3-ethoxyacrylate, in a reaction which is catalytic in Fp(η^2-isobutylene)BF_4 [41].



When the reaction partner is an olefin, for which complexation by Fp^+ is unfavorable, *trans* addition of the olefin to the cationic complexed acetylenic ester **50** yields **51**. Three courses of reaction are apparently open to this intermediate, depending on the structure of the olefin. These are summarized in Scheme 5. With 1,1-disubstituted olefins, closure of cation **51** through the ester carbonyl, yields the

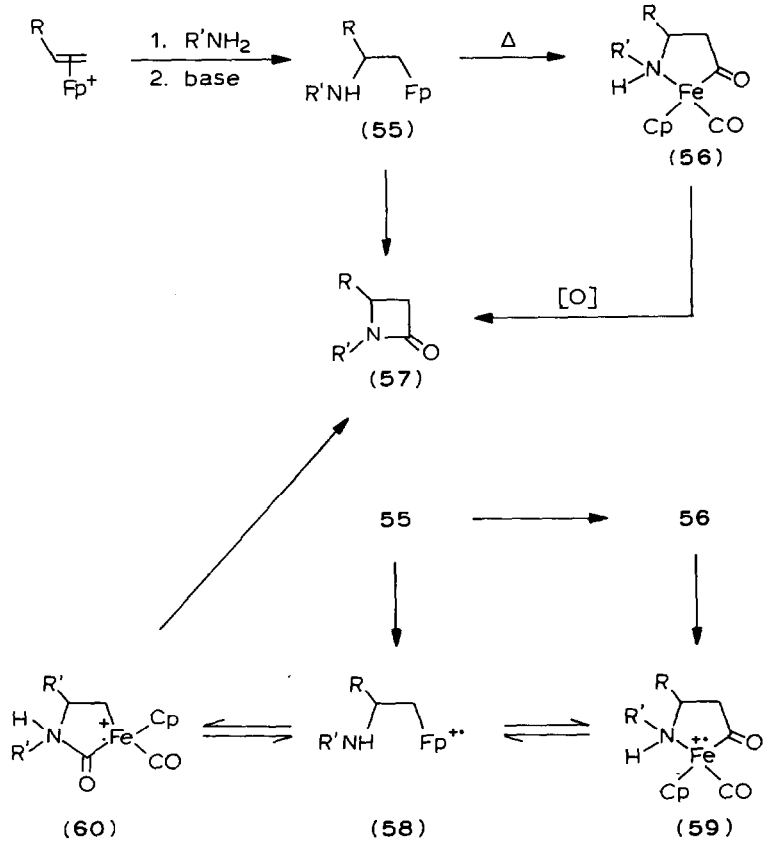


SCHEME 5

metal stabilized methylated lactone cation **52**. Alternatively, proton transfer from **51**, gives the metal stabilized cation **53**, and thence the diene **54**, in a reaction catalytic in Fp(η^2-isobutylene)BF_4. Finally, **51** may cyclize to the metal stabilized cyclobutyl cation **55** and then lose Fp^+ to give a cyclobutene. As would be expected, the formation of this product is also catalytic in Fp(η^2-isobutylene)BF_4. These latter two products are observed to form with cyclic and 1,2-disubstituted products. With acyclic olefins, closure of **51** to the cyclobutenes or transformation to **54** takes place with retention of stereochemistry [44].

Reactions of Fp(η^2-olefin) cations

The reactions of Fp(η^2-olefin) cations with nucleophiles and the subsequent chemical transformation of these adducts constitutes an area rich in synthetic potential, which is currently an important focus of our work. We recognized very early in our research that Fp(η^2-olefin) cations should be suceptible to nucleophilic attack. Indeed the two-step mechanism proposed initially for the cycloaddition reactions of (η^1-allyl)Fp complexes presupposed such a reaction, and ample precedent existed at the time for nucleophile addition to polyene- and polyenyl-metal systems [45].



SCHEME 6

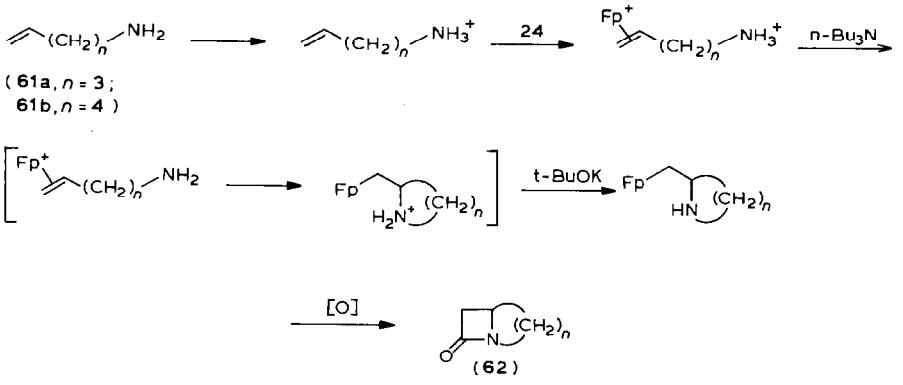
Since the Fp(η^2-olefin) cation represents a coordinatively saturated 18-electron complex, nucleophile addition to the olefin ligand cannot occur intramolecularly by a path involving prior coordination of the reagent to the metal, but must occur intermolecularly through addition *trans* to the metal–olefin bond. Thus far no exceptions to this generalization have been observed [46].

In the absence of strongly polarizing substituents on the coordinated olefin ligand, the regioselectivity of nucleophile addition to unsymmetrically substituted olefins is generally low. This is illustrated by the reactions of Fp(η^2-propene)BF_4 with malonate, acetoacetate, cyanoacetate or cyclohexanone pyrrolidine enamine, which yield mixtures of regioisomeric adducts. By contrast, the addition of such heteroatomic nucleophiles as amines and methanol, but not thiols, to this cation takes place with high regioselectivity at the more highly substituted carbon center, in analogy to the reactions of bromonium ions with such nucleophiles. These two reactions of Fp(η^2-olefin) cations may not, however, be mechanistically comparable, since the first is likely to be kinetically controlled, while there is some evidence that with amines, methanol and phosphines the additions are reversible, and consequently under thermodynamic control [47].

The addition of 1°-amines or ammonia to Fp(olefin) cations provides the first step in a useful synthesis of mono- and bicyclic β-lactams. This is outlined below [48].

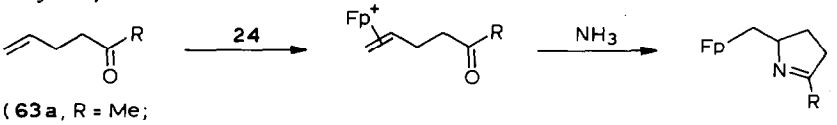
The transformation of the (β-aminoalkyl)Fp adduct may be accomplished in two steps, by thermal rearrangement to chelate **56**, followed by oxidation with PbO_2, AgO or air. Alternatively direct oxidation of **55** has been observed to give the β-lactam as well. These reactions were believed to proceed through the 17-electron chelate **59**, formed either from **56** directly, or through acceleration of the migratory insertion reaction in the intermediate **58**. More recent work by Giering [49] now suggests that the isomeric amido-chelate **60**, formed either from **59** or directly from **58**, is the true precursor of the β-lactam (see Scheme 6).

A simple permutation of the basic sequence, using ω-amino 1-alkenes **61a,b**, permits construction of bicyclic β-lactams **62a,b**. The amino group is first protected against attack by the Fp cation, in the exchange reaction, by protonation. Exposure of the free amino group, results in spontaneous nucleophilic addition and the resulting products are then oxidatively transformed to β-lactams.

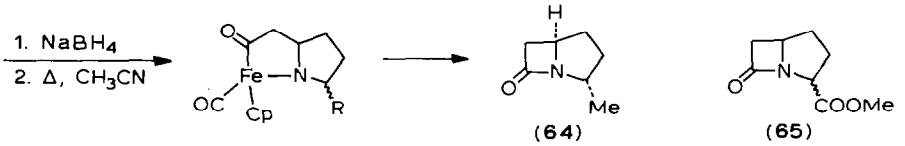


Construction of the pyrrolidine ring in the bicyclic β-lactam may alternatively be achieved using a keto-olefin as starting material, as shown for the synthesis of **64**

from **63a** [50]. An analogous sequence carried out on the pyruvic ester **63b** gave the bicyclic β-lactam **65** as a mixture of stereoisomers.



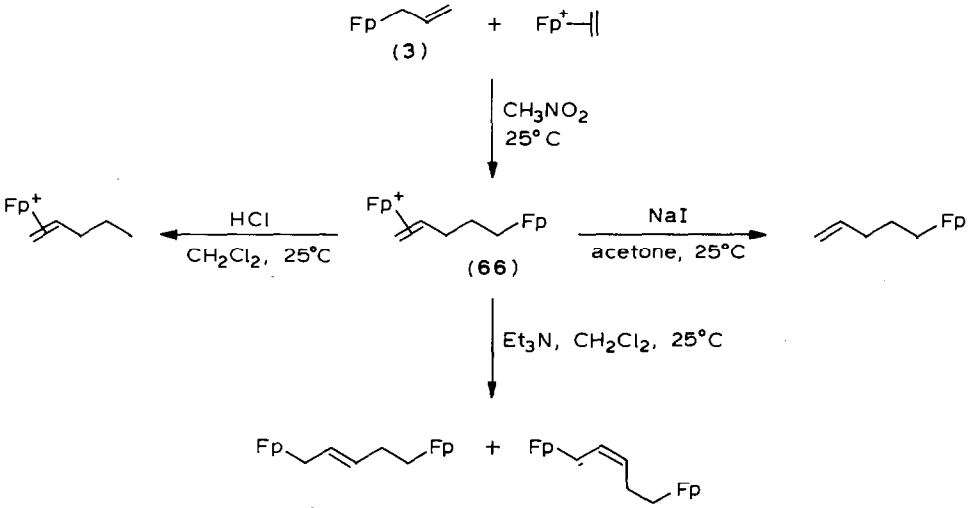
(**63a**, R = Me;
63b, R = COOMe)



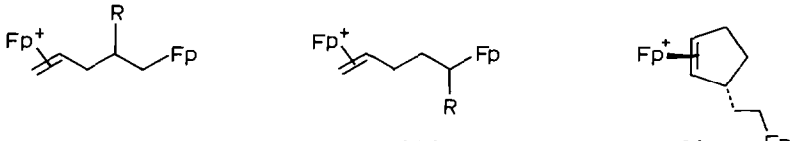
(**64**) (**65**)

The use of this chemistry in the elaboration of β-lactams of pharmacological importance remains a subject of continued interest in our laboratories.

(η^1-Allyl)Fp complexes were among those nucleophiles which we considered, early in our research, as possible reaction partners for Fp(η^2-olefin) cations. The parent complexes condense readily at room temperature, affording the dinuclear product **66**, which may be selectively degraded or transformed as shown below. Since (η^1-allyl)Fp complexes are only mild nucleophiles, this form of condensation appears to be confined to the more reactive of Fp(η^2-olefin) cations. Thus, **3**



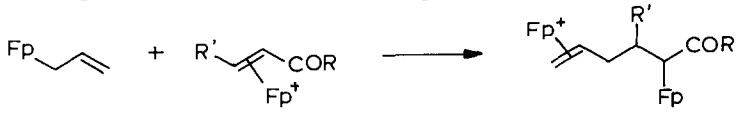
condenses with both Fp(η^2-propene) and Fp(η^2-styrene) cations at room temperature to give mixtures of regioisomeric products **67** and **68**, and (η^1-cyclopentenyl)Fp condenses with Fp(η^2-ethylene)BF_4 to give **69**, but no reaction occurs between **3** and Fp(η^2-cyclopentene)BF_4.



(**67**) **a**, **R=Me**; **b**, **R=Ph** (**68**) (**69**)

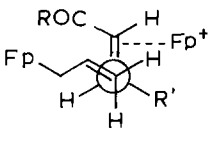
As might be anticipated, Fp(η^2-olefin) cations bearing an electron-withdrawing function, such as **70a,b** or **c** are better acceptor components in these reactions, which

generally proceed rapidly at 0°C. In addition, the products **71b** and **71c**, which possess two chiral centers, are apparently formed with high diastereoselection, a result perhaps better accounted for by a *gauche*-configuration **72a** for the transition state complex rather than the *anti*-configuration **72b**.

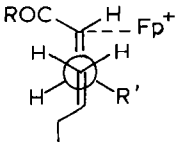


(70) (71)

(**a**, R = OMe, R' = Me;
b, R = H, R' = H;
c, R = Me, R' = H)



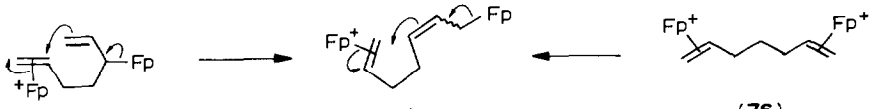
(72a)



(72b)

With $Fp(\eta^2$-butadiene)BF_4 (**73**) as acceptor component, reaction of **3** allows sequential condensations leading to cyclized products **77** and **78**. The formation of intermediate **75** may be accounted for either as a result of nucleophile addition to C(1) of the diene complex, followed by sigmatropic rearrangement, or by conjugate addition at C(4). This intermediate may also be prepared by monodeprotonation of the 1,6-heptadiene complex **76**, and it is noteworthy that the *trans*-stereochemistry of the cyclized product **78** can be accounted for only in terms of a *gauche* transition state conformation **79a**. However, models suggest that the corresponding *anti* transition state configuration **79b** may be relatively strained.

(3) (73)

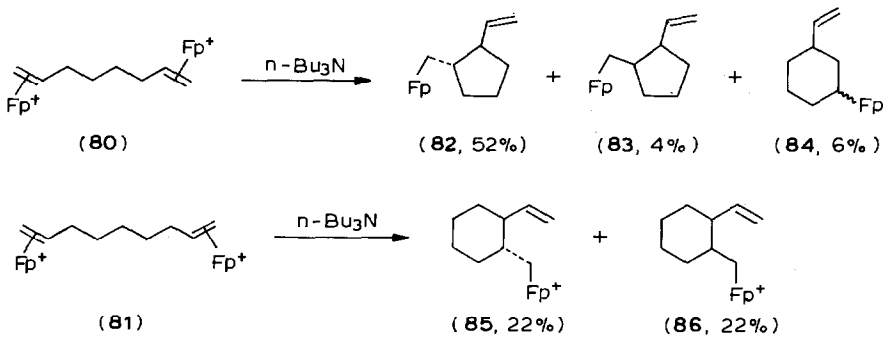


(74) (75) (76)

(77) (78)

(79a) (79b)

These results, in particular the generation of **75** from **76**, prompted us to examine the reactions of homologous diene complexes. Monodeprotonation of the diene complexes **80** and **81**, followed by selective demetallation of the dinuclear products with iodide, was shown to give a mixture of cyclization products **82–86**.



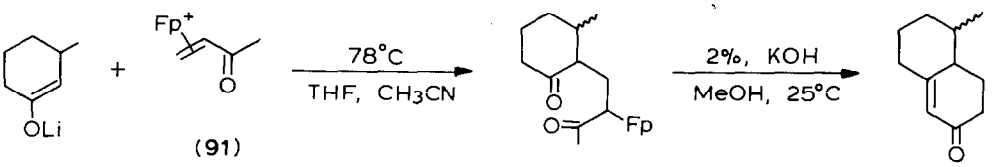
Since the deprotonation step in these reactions is expected to give mixtures of *cis* and *trans* (η^1-allyl)Fp type intermediates (cf. **75**), we were led to examine the possible relationship between geometrical isomerism in these intermediates and the product stereochemistry [53]. The requisite *cis* and *trans* monocationic dinuclear complexes **89** and **90** were prepared by monoprotonation of the corresponding *cis,cis*- or *trans,trans*-bis(η^1-allyl)Fp complexes **87** and **88**. Each of these complexes showed a significant, although incomplete correlation of product stereochemistry with geometrical isomerism in the dienes. Complex **88a** gave principally **82**, while the *cis*-isomer **87** gave significant amounts of **83** with **82**. Similarly **88b** gave **85** and **86** in a 2/1 ratio but **87b** gave these isomers in a 1/3 ratio. The latter ratios represent minimum stereoselectivities, since recovered diene complexes **87b** and **88b** were observed to be substantially isomerized.

(**a**, n = 2;
b, n = 3)

(**a**, n = 2;
b, n = 3)

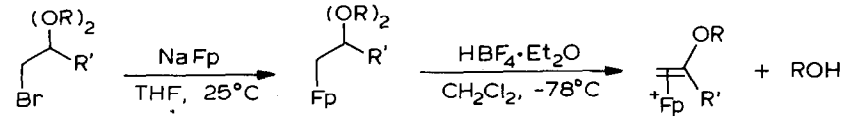
The factors affecting the stereoselectivity of cyclization are not defined, but it may be noted, that if proton transfer to **87** and **88** is assumed to occur preferentially to an extended form of these complexes, so as to allow for electrophile interaction with both double bonds, then isomeric *gauche*-configurations of a transition complex would be generated and would lead respectively to *cis* and *trans* cyclization products. These questions, and the possible elaboration of such metal assisted cyclizations in a synthetic context, remain to be examined.

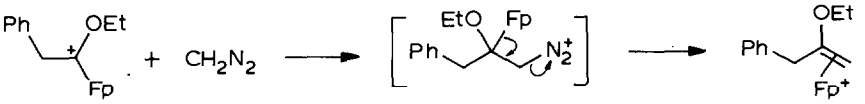
We return now to the general theme with which this last section was begun, namely the addition of nucleophiles, especially carbon nucleophiles, to Fp(η^2-olefin) cations. The low regioselectivity of these reactions with alkyl-substituted olefin complexes prompted us to examine the reactions of more highly polarized Fp(η^2-olefin) cations. An example of such a complex is provided by **91**. This substance, prepared from methyl vinyl ketone epoxide (Scheme 3) has been used as a Michael component in reactions with kinetically generated enolates. Its use, illustrated below, for 3-methylcyclohexanone enolate constitutes a solution to the problem of polymerization of the acceptor component when Michael reactions are carried out in aprotic media. The sequence also illustrates the ease with which an Fp group adjacent to a carbonyl group may be removed by base, much as similarly positioned R_3Si groups undergo displacement by base.



(91)

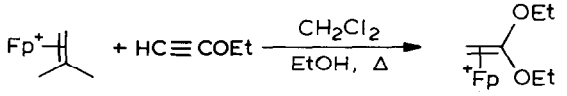
Fp complexes of vinyl ethers constitute a second class of Fp(η^2-olefin) cations rich in synthetic potential. These complexes may be prepared from α-bromoacetals or ketals through the sequence outlined below [55]. An alternative synthesis, which makes use of Fp stabilized alkoxyl carbonium ions **43** and diazomethane or diazoalkanes, has not been widely examined [42]. The exchange reaction of Fp(iso-





(43)

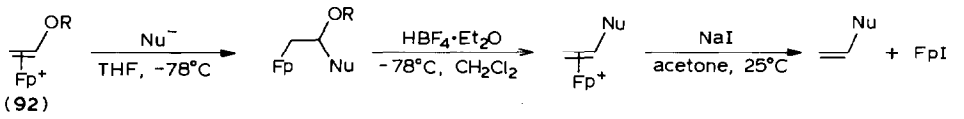
butylene)BF_4 (**24**) cannot be used to prepare Fp(η^2-vinyl ether)BF_4 complexes since the strongly electrophilic Fp cation induces polymerization of simple vinyl ethers. However **24** reacts with ethoxyacetylene in the presence of ethanol to give a ketene acetal complex [42].



(24)

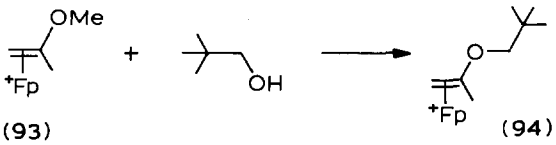
The synthetic value of Fp(η^2-vinyl ether) cations **92** derives from the high regioselectivity of their reactions with a broad range of both heteroatomic and carbon nucleophiles together with their capacity to function as vinyl cation equiv-

alents, as illustrated in the generalized reaction sequence shown below.



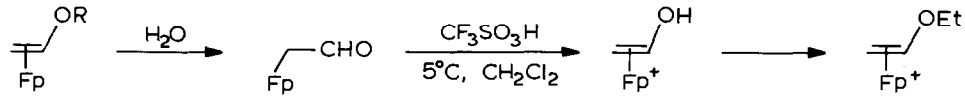
(92)

Both primary and secondary alcohols may also serve as nucleophiles in this sequence, so that dissolution of a methyl alkenyl ether complex in the presence of an excess of such an alcohol effects rapid exchange of the alkyl group, as illustrated by the conversion of the methyl i-propenyl ether complex **93** into the neopentyl complex **94**.



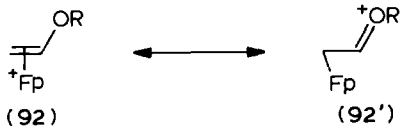
(93) (94)

Free enol complexes are also preparable by hydrolysis of the vinyl ether complexes (an instantaneous reaction at room temperature) followed by treatment of the free aldehyde or ketone complex with $HBF_4 \cdot Et_2O$. Not surprisingly, these cationic enol complexes are strong acids. That derived from acetaldehyde **95** has a pK_a in aqueous sulfuric acid of -0.75, and undergoes rapid etherification to give **96** on dissolution in ethanol.



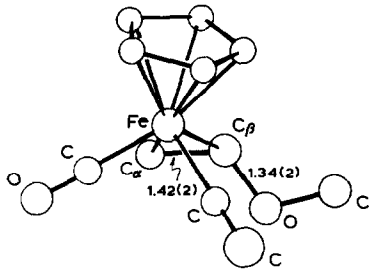
(92) (95) (96)

The distortion in the metal–olefin bonding in these complexes, which is implicit in canonical form **92'**, was confirmed by an X-ray crystallographic structure determination of Fp(η^2-methyl vinyl ether) BF_4 (Fig. 1a) [56].



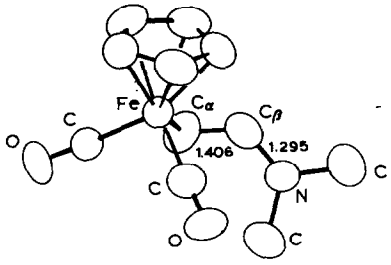
(92) (92')

As might be anticipated, bonding dissymmetry in the related vinyl dimethylamino complex is further magnified (Fig. 1b). This complex lies closer to the σ-bonded structural form in the continuum of σ-alkyl to π-alkene bonding modes. Nevertheless, some olefinic character, and hence residual bonding with C_β, is evidenced in this complex by the short C_α–C_β bond length and an Fe–C–C–N torsional angle of 102.3°. The barrier to rotation about the C_α–C_β bond, 10.5 kcal mol^{-1}, is also well above the value expected for a C–C single bond in the vinyl amine complex. The vinyl ether complexes show, as anticipated, higher C–C rotational barriers. These, determined either kinetically or by coalescence measurements, are summarized below.



(a)

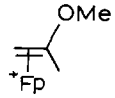
Fe-Cα 2.09(2) Å
Fe-Cβ 2.32(2) Å



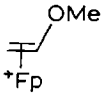
(b)

Fe-Cα 2.121(5) Å
Fe-Cβ 2.819(5) Å

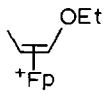
Fig. 1. Molecular structures: (a) $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CHOCH_3)$ cation; (b) $(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2CHN(CH_3)_2]$ cation.



14.8 [56]

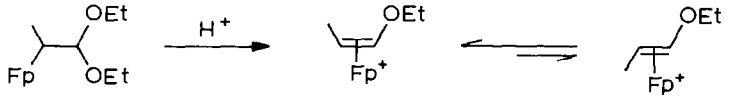


>18 [56]



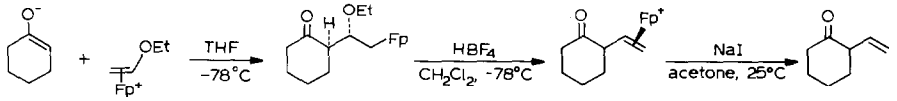
21.9 [57]

An important chemical consequence of the relatively low rotation barrier in vinyl ether complexes is evident in the conversion of the metallated acetal **97** exclusively to the *cis*-propenyl ether ether complex **98**. This result is the consequence of the greater thermodynamic stability of the *cis*-complex [58] together with a low energy path for its interconversion with the *trans*-isomer.



(97) (*cis*-98) (*trans*-98)

The use of Fp(η^2-vinyl ether) cations in the vinylation of enolates has been examined for a number of cyclohexanone lithium enolates. Condensation of **96** with cyclohexanone lithium enolate yields a single diastereomer **99** [59], which is converted by protonation and demetallation into 2-vinylcyclohexanone. The initial formulation of the adduct as **99** was predicated on a postulated antiperiplanar configuration of reacting components in the transition state, in which the larger OR substituent is placed *exo* to the cyclohexanone ring, where additional stabilization

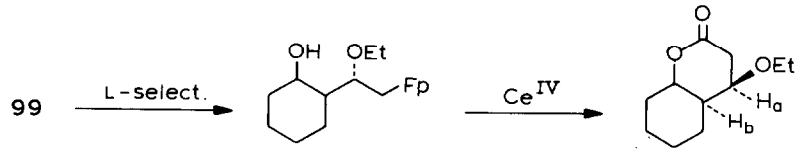


(96) (99)

(*t*-99) (*g*-99)

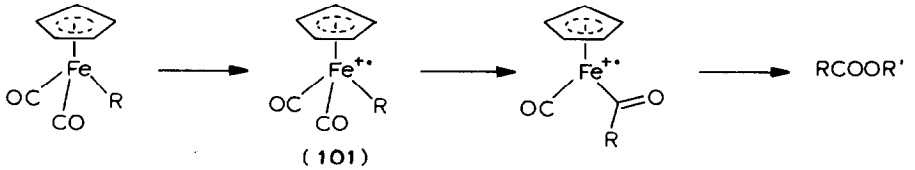
might be available through lithium ion chelation [59]. The *gauche* conformation *g*-**99**, which follows more closely the prescriptions adduced recently by Seebach and

Golinski [60] for classical condensation reactions, would yield the same diastereomer. Structure **99** has now been confirmed through reduction of the ketone to the *cis*-alcohol and conversion into the lactone **100**, in which H_a, H_b are shown to be *cis* [61]. The lactonization step, which is based on the conversion of (alkyl)Fp



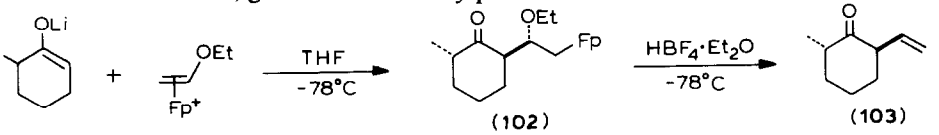
(100)

complexes into esters, a reaction first reported by Anderson, Fong and Johnson [62], probably proceeds through the cation radical **101**, which undergoes rapid migratory insertion and subsequent nucleophilic attack by solvent alcohol. The migratory insertion step has been shown to be highly stereospecific, proceeding with retention of configuration at the migrating alkyl group [63].



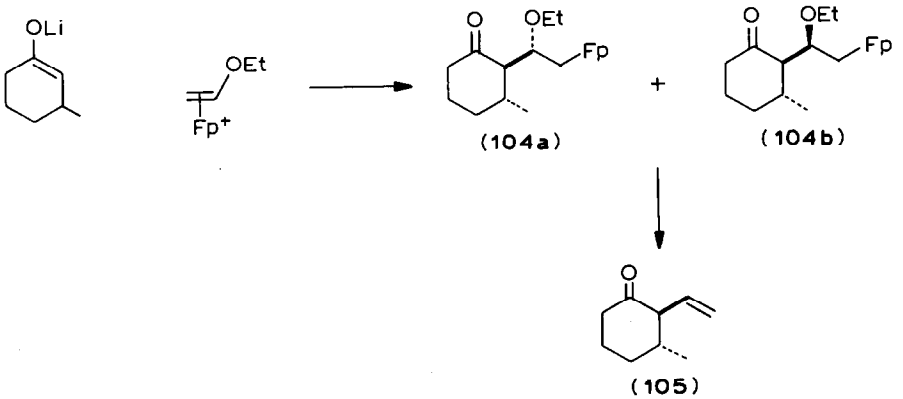
(101)

Electrophilic addition to cyclohexanone enolates by Fp(vinyl ether) cations takes place axially, as indicated by the exclusive formation of the *trans*-2,6-disubstituted cyclohexanone adduct **102** from 6-methylcyclohexanone lithium enolate. Furthermore, this substance, like **99**, is formed as a single diastereomer with the structure shown [61]. Its conversion through acid treatment and demetallation by warming in acetonitrile solution, give **103** as the only product.



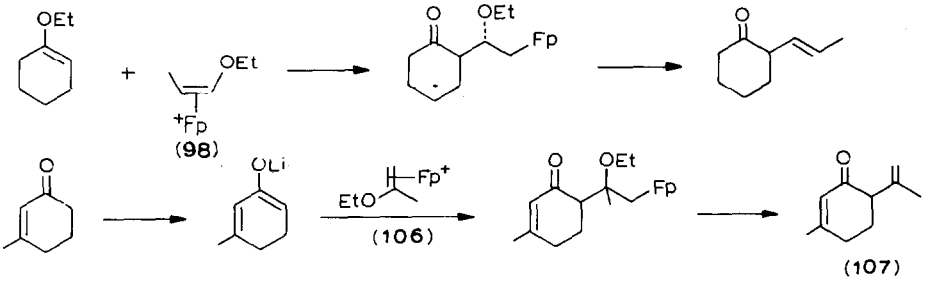
(102) (103)

Vinylation of 3-methylcyclohexanone lithium enolate occurs preferentially *trans*, to give the adduct as a mixture of diastereomers **104a** and **104b** [61] in a ratio of 3/1. The major diastereomer has recently been shown to have structure **104a** [61], and each adduct has been converted into *trans*-2-vinyl-3-methylcyclohexanone **105**.

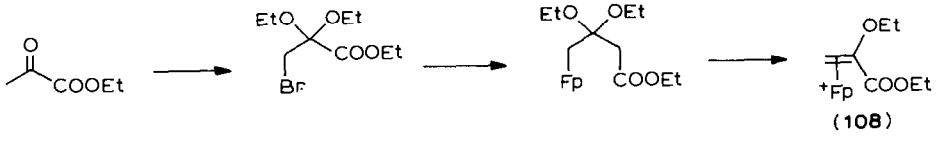


(104a) (104b) (105)

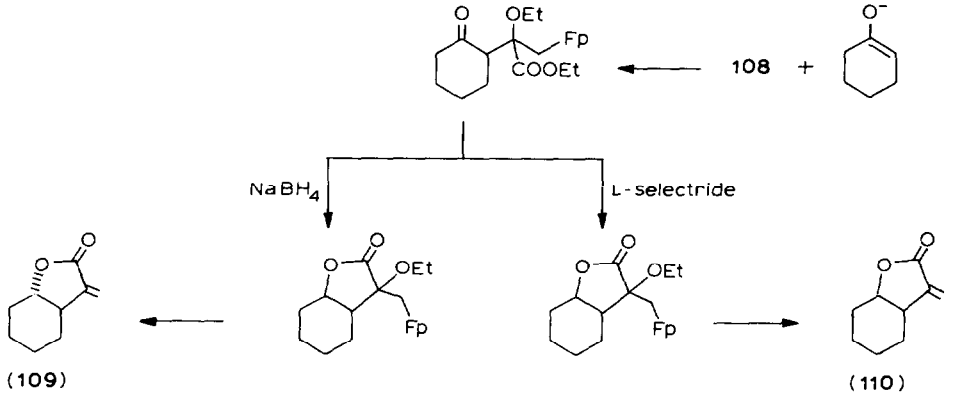
Vinylation of enolates has also been effected with the propenyl ethyl ether complex **98** and the isomeric isopropenyl ethyl ether complex **106** [64]. The first introduces the vinyl group as a *trans*-propenyl substituent, owing to its *cis*-geometry and the successive *trans*-addition, *trans* elimination processes involved in its transformation to free olefins. The second serves as an isopropenyl synthon, and has been used in a short synthesis of isopiperitenone **107** from 3-methylcyclohexenone [64].



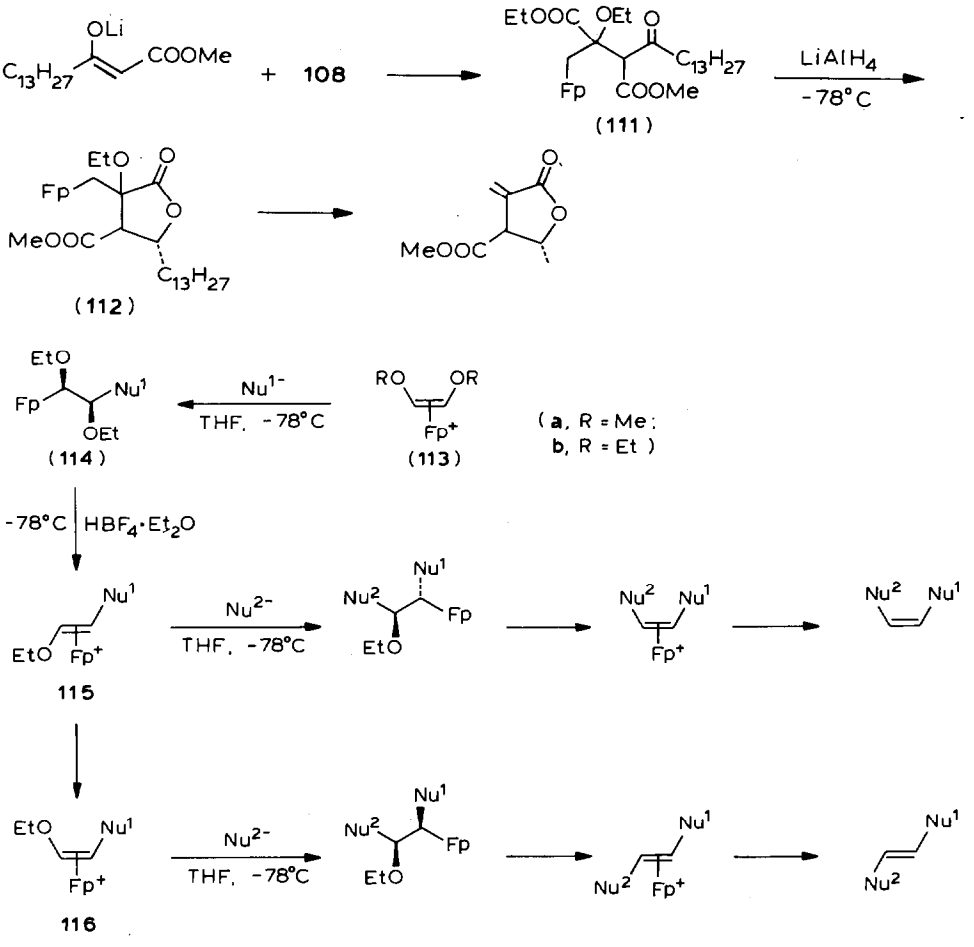
In a further elaboration of this chemistry, the vinyl ether complex **108** was prepared from pyruvic ester. This highly reactive cation, which functions as an



α-acrylic ester cation equivalent, finds synthetic use in the synthesis of α-methylene-γ-lactones from carbonyl compounds [65]. With cyclohexanone, both *cis*- and *trans*-fused lactones **109** and **110** are preparable, as shown below.



An analogous sequence starting from methyl 3-oxohexadecanoate provides a synthesis of protolichesterinic acid ester **112**, but here, because of the high reactivity of **108**, a significant amount of *o*-alkylation product is formed in the first step along with **111** [66].



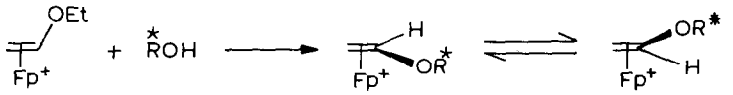
SCHEME 7

The most recent additions to the series of vinyl ether complexes are represented by the *cis*-1,2-dialkoxy olefin cation **113**, its cyclic analog **117**, and the optically active complex **118**. These give promise of being especially useful new synthons.

A brief account of the use of **113** as a vinylene dication was presented recently [57], and is summarized in Scheme 7. Complex **113a**, which is prepared by exchange complexation with Fp(η^2-isobutylene)BF_4, may be converted into **113b** by brief stirring in ethanol and reprecipitation with ether. Such substitution may be advantageous in blocking nucleophilic attack at the alkyl center.

Cation **113** combines with a variety of nucleophiles including phenyl Grignard, lithium dimethylcuprate, and enolates. These additions and, subsequent acid promoted elimination from the neutral adduct **114** are *trans*-stereoselective. Consequently these steps provide a route to the thermodynamically unstable *trans*-alkenyl ether complexes **115**. A second sequence of nucelophile addition, ethanol elimination, and demetalation yields the *cis*-1,2-disubstituted ethylene. If **115** is instead first allowed to isomerize, thermally or in the presence of ethanol at low temperature, to the *cis*-cation **116**, this same sequence provides a route to *trans*-1,2-disubstituted ethylenes.

Our attention was now drawn to the possibility of converting the diastereoselective reactions of vinyl ether complexes, exemplified by the transformation of cyclohexanone enolates to adducts **99** and **102**, into enantioselective processes. Since simple vinyl ether complexes, such as **96**, are chiral, a method for preparing such complexes in optically active form was needed. The solution was simply to take advantage of the facile exchange of alkoxy groups and of the low rotational barrier about the putative double bond in these cations. If the exchanging alcohol is optically active then the product is a rapidly equilibrating mixture of diastereomers.



(96)

A number of primary and secondary optically active alcohols have been examined in this reaction, among them (+)- and (−)-menthol, (−)-borneol, (−)-isoborneol, (−)-myrtanol, (+)-2°-butanol, and (+)-methyl-β-hydroxyl isobutyrate. Of these, the menthols give the highest ratio of diastereomers (4/1) [67]. Condensation of cyclohexanone lithium enolate with the diastereomeric mixture obtained from (−)-menthol, gave a 4/1 mixture of diastereomeric products, which were readily separated on alumina.

In order to determine the absolute configuration of this product we have turned to an examination of the circular dichroism spectra of the mixtures of diastereomeric vinyl ethers derived from the several optically active alcohols. These spectra exhibit three differential absorption peaks near 280, 380 and 480 nm, corresponding closely to absorption peaks or shoulders at 305, 380 and 440 nm in UV-VIS spectra of the salts. The CD spectra for (+)- and (−)-menthol vinyl ether complexes are shown in Fig. 2. As a useful index of absolute configuration at the complexed olefin face we have chosen the CD peak at 480 nm, furthest away in energy from any electronic transition associated with the alkyl group. The intensity of this peak for a number of diastereomeric mixtures has been shown to give a linear correlation with the ratio of diastereomers, as determined from ^{13}C NMR measurements [68].

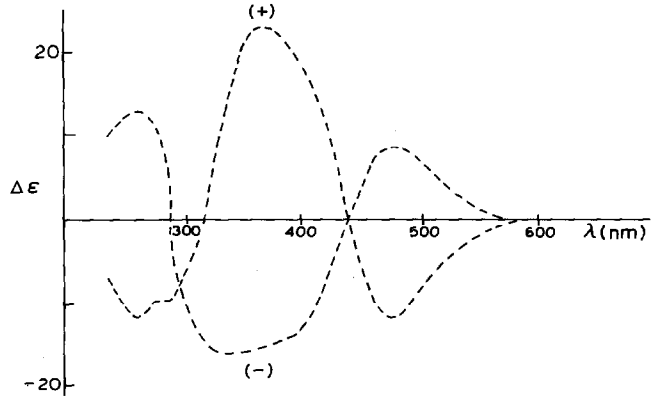
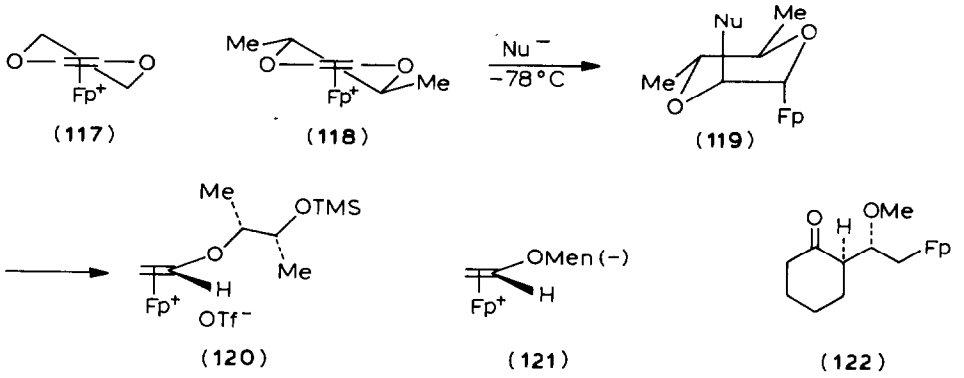


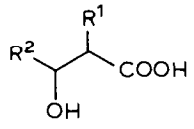
Fig. 2. CD spectra of $Fp(\eta^2\text{-}CH_2CHOR)^+ BF_4^-$ where R is (+)- or (−)-menthyl. Concentration is 1 mg/ml in CH_2Cl_2 with a path length of 1 cm. $\Delta\epsilon$ is in units of l/mol·cm.

The preparation of the cyclic, optically active complex **118** has now provided us with the means of assigning absolute configurations to the simple vinyl ether diastereomers [69]. This complex, like its parent **117** and the simple vinyl ether complexes, enter successfully into addition reactions involving a range of nucleophilic reagents, which include $NaBH_3CN$, LiMeCuCN, PhMgBr, cyclohexanone lithium enolate, Et_4NCN and $PhCH_2SH$. In all these reactions a single regioisomeric and hence stereoisomeric product **119** results, possible due to stereoelectronic control of the addition. When **119** (Nu = H) is opened with TMSOTf at −50°C, the vinyl ether complex **120**, with the absolute configuration shown, is formed. The substance shows



a differential absorption $\Delta\epsilon$ at 480 nm of +1.34. The diastereomeric mixture of vinyl ethers derived from **96** by exchange with (−)-menthol shows $\Delta\epsilon_{480}$ +0.83, which is in accord with a 4/1 ratio of diastereomers determined by ^{13}C NMR measurements. Hence the major diastereomer present in this mixture must have the absolute configuration shown in structure **121**, and the absolute configuration of its adduct with cyclohexanone enolate can therefore be represented by structure **122**.

In principle, complex **118** and its (*S*,*S*)-enantiomer should serve as useful starting materials for the enantio-controlled synthesis of all four optical isomers of α,β-disubstituted β-hydroxy propionic acids **123** through successive additions of two nucleophiles to these cations, as depicted in part in Fig. 1, followed by oxidative carbonylation. These synthetic prospects among others await examination.



(123)

Summation and Acknowledgement

This research had its beginnings some fifteen years ago in a chance, but important observation made by Warren Giering, then working with me as a postdoctoral associate. If it has grown and prospered since, this is largely due to the hardy band of graduate students and postdoctoral associates who during these years carried out the experiments and contributed the ideas which gave it sustenance. In a very real sense this review is dedicated to all of them, whose names appear in the list of references.

I am indebted to the National Science Foundation and the National Institutes of Health, which have abundantly supported this research over the years.

This account was written during the summer of 1985, when I held a Meyerhoff Visiting Professorship at the Weizmann Institute, Rehovot, Israel. It is a pleasure to acknowledge my gratitude to the Institute and to the staff of the department of Organic Chemistry, especially to Dr. Ehud Keinan, for making that brief stay so pleasurable.

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