Organoiron Complexes as Potential Reagents in Organic Synthesis

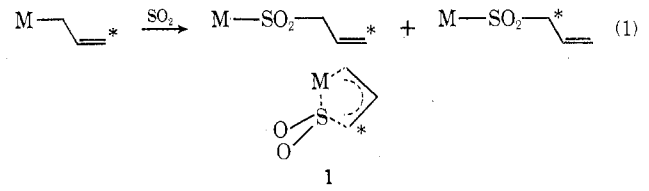
Myron Rosenblum

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

Received September 4, 1973

Metal Assisted Cycloaddition Reactions

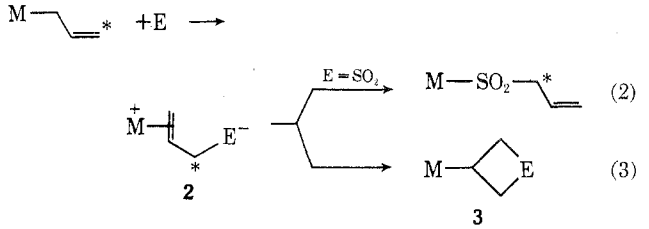
***monohapto*Allylmetal Complexes.** Three years ago our attention was drawn to the reactions of *monohapto*allyl-transition metal complexes[1] with SO_2.[2] These reactions generally led to the formation of metal allyl sulfones and were observed to occur with both retention and inversion of the allylic ligand (eq 1). The latter product was attributed to a concerted insertion process involving simultaneous interaction of SO_2 with the metal and the olefinic terminus (**1**).[2]



(1)

1

However, if SO_2 is viewed as an electrophile, it is apparent that the rearrangement reaction may alternatively be depicted as a two-step process involving initial formation of a dipolar ion (**2**, E = SO_2) and its subsequent collapse through displacement of the coordinated olefin by the anion (eq 2).

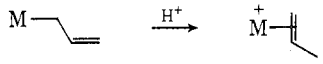


(2)

(3)

2 **3**

The first step of such a mechanism has ample analogy in the conversion of *monohapto*allyl-transition metal complexes to cationic olefin-metal complexes on protonation (eq 4)[3] while the second involving ligand exchange at a metal site (eq 5) is a process ubiquitous in transition metal chemistry.[4] More significantly, a nonconcerted mechanism exposes the possibility, not available to a one-step process, that the dipolar ion **2** may collapse through an internal cyclization reaction to give products of structure **3**[5] (eq 3).

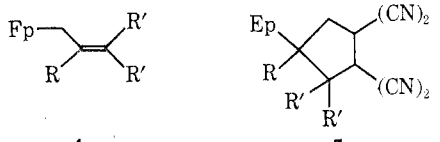


(4)

$$M{-}L + L' \rightleftharpoons M{-}L' + L \qquad (5)$$

While not observed with SO_2, the latter reaction path becomes the exclusive one with electrophilic olefins such as tetracyanoethylene (TCNE). This observation provided at once substantive evidence for a two-step process, a simple means for rationalizing the formation of similar products reported to be formed from *monohapto*propargylmetal complexes (*vide infra*), and a theoretical basis for extending these "metal-assisted cycloaddition reactions" to a larger variety of organometallic complexes and uncharged electrophiles.

Although these reactions appear to be quite general for *monohapto*allylmetal complexes, the most extensive investigations have been carried out with *monohapto*allyl derivatives of dicarbonyl*pentahapto*cyclopentadienyliron (**4**). (In structure 4 and elsewhere, Fp stands for the h^5-$C_5H_5Fe(CO)_2$ moiety.) These were found to react within minutes, at room temperature, with TCNE, to give tetracyanocyclopentyl complexes of structure **5** in good yield.[5-7] The high reactivity of the double bond in these complexes no doubt reflects the capacity of the metal to



4 **5**

a, R, R′ = H
b, R = Me; R′ = H
c, R = H; R′ = Me

Myron Rosenblum was born in New York City in 1925. He obtained his A.B. degree from Columbia University and his Ph.D. degree from Harvard University under R. B. Woodward. After spending 2 years at Columbia University in postdoctoral work with Gilbert Stork, he joined the Illinois Institute of Technology. He remained there until 1958 when he moved to Brandeis University, where he is Professor of Chemistry. His principal scientific interests are in organometallic chemistry.

(1) The nomenclature is that introduced by F. A. Cotton, *J. Amer. Chem. Soc.*, 90, 6230 (1968), in which the h^n prefix (h^1, monohapto; h^2, dihapto, etc.) specifies the number of ligand atoms which are formally bonded to the metal.

(2) (a) F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Amer. Chem. Soc.*, 89, 2493 (1967); (b) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, 2, 289 (1968); (c) A. Wojcicki, *Accounts Chem. Res.*, 4, 344 (1971).

(3) (a) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963); (b) M. L. H. Green and A. N. Stear, *J. Organometal. Chem.*, 1, 230 (1964); (c) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(4) It is not clear whether this step is best depicted as a concerted displacement reaction, or as one involving prior dissociation of the olefinic ligand and subsequent collapse of the resulting ion pair. Among six-coordinate complexes the latter mechanism is the prevalent path of substitution.

(5) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 93, 5299 (1971).

(6) S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, 31, C34 (1971).

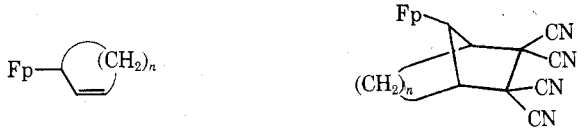
(7) The closely related h^5-$C_5H_5M(CO)_3(h^1$-allyl) (M = Mo,[6] W[8]) as well as h^5-$C_5H_5Cr(NO)_2(h^1$-allyl)[9] and (h^1-allylcobaloxime)-pyridine[8] also react with TCNE to give cycloaddition products. Qualitative observations suggest that the iron complex is the most reactive of these.[9]

(8) D. Wells, unpublished results.

(9) S. Raghu, unpublished results.

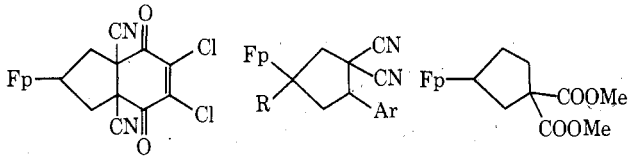
stabilize the positive charge in both the dipolar intermediate **2** and in the transition state leading to it.

Such (3 + 2) metal-assisted cycloaddition reactions may also be effected with cycloalkenyl derivatives. This is exemplified by the conversion of **6a–d** to the bicyclic derivatives **7a–d**.[10,11]



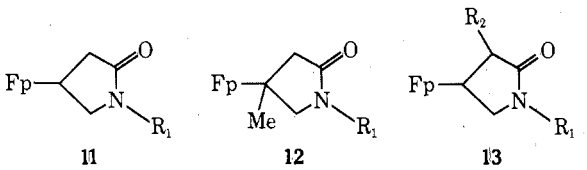
6 **a–d**, $n = 1–4$ **7**

Furthermore, other electrophilic olefins such as dichlorodicyanoquinone,[5] β,β-dicyano-*o*-chlorostyrene,[9,12] and dimethyl methylenemalonate[9] undergo (3 + 2) cycloaddition reactions with **4**, affording the adducts **8**,[13] **9**,[13] and **10**.



8 **9** **10**

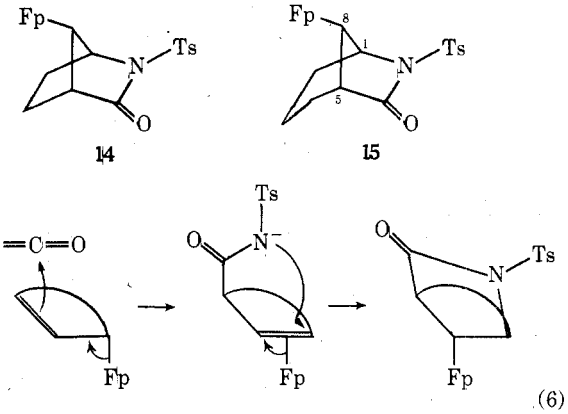
Although neither alkyl nor phenyl isocyanate reacts with **4**, more reactive electrophiles such as toluenesulfonyl,[14] methoxysulfonyl,[14] and especially chlorosulfonyl isocyanate[14,15] enter smoothly into cycloaddition reactions with a number of (*monohapto*)allyliron complexes affording butyrolactam derivatives (**11**, **12**, and **13**).



11 **12** **13**

R_1 = SO_2Cl, Ts, R_2 = Me, Ph, CH_2Fp

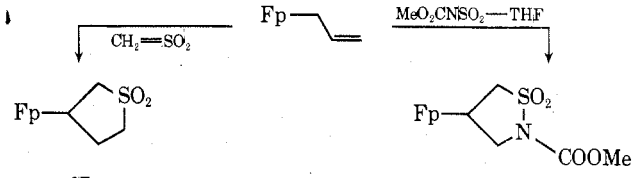
Reaction of the cycloalkenyl complexes **6b** and **6c** with toluenesulfonyl isocyanate yields the bicyclic lactams **14** and **15** as single stereoisomers.[14] The stereospecificity of the reactions is perhaps not surprising since on steric as well as on stereoelectronic grounds attack of the isocyanate might be expected to occur preferentially trans to the activating Fp group (eq 6). Support for this conclusion is provided by the nmr spectrum of **15** which shows triplet absorption for H-8 ($J_{1,8} = J_{5,8} = 5$ Hz), consistent with an anti orientation for the Fp group.[16]



14 **15**

(6)

Preliminary experiments with *N*-sulfonylurethane[17] and sulfene have shown that these react readily with **4a** affording the isothiazoline dioxide **16**[14] and the sulfone **17**.[9]

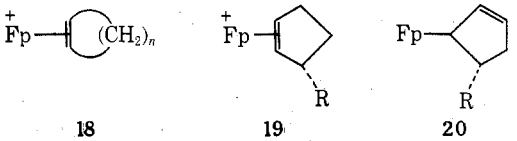


17 **16**

Synthesis of (*monohapto*Allyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron Complexes. The parent complex was first prepared in 1963 by metalation of allyl chloride with the complex Fp anion.[3a] This method, which has been widely used for the preparation of many alkyl- and acyl-transition metal complexes, has been extended to the synthesis of a number of allyl-Fp and *monohapto*allyl-$M(CO)_5$ (M = Mn, Re)[2b] complexes substituted at C-1 and C-2 of the allyl chain. The parent cycloalkenyl complexes **6b–d** have also been prepared by this method in good yield from the corresponding cycloalkenyl chlorides.[10,14]

Deprotonation of the readily available cationic h^5-$C_5H_5Fe(CO)_2$(olefin) [(Fp(olefin))$^+$] complexes with tertiary amines occurs readily below room temperature and constitutes a second general route to *monohapto*allyl-Fp complexes. The deprotonation reaction appears to be highly stereospecific and to require the presence of a C–H bond trans to the metal–olefin bond. Thus, while **18a–c** are smoothly deprotonated, the cycloheptene complex **18d** is inert. Models show that, in contrast to the situation in the four-, five-, and six-membered-ring complexes, no allylic protons trans to the iron–olefin bond are available in the cycloheptene complex.[14]

A dramatic example of the stereospecificity of the deprotonation process is to be seen in the conversion of the cyclopentene complexes **19a,b** to **20a,b**, re-



18 **19** **20**

a–d, $n = 2–5$ **a**, R = CN; **b**, R = SO_3H

(10) A. Cutler, unpublished results.

(11) The reactions of substituted cyclopentenyldicarbonyl(*pentahapto*-cyclopentadienyl)iron complexes[10] and of **6** with isocyanates (*vide infra*) provide evidence for the stereochemical course of these reactions in which cycloaddition trans to the activating organometallic group is assumed.

(12) W. P. Giering, unpublished results.

(13) With the exception of **9** (R = Me) each adduct is obtained as a single stereoisomer, but their stereochemistry has not been established.

(14) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *J. Amer. Chem. Soc.*, **94**, 8251 (1972).

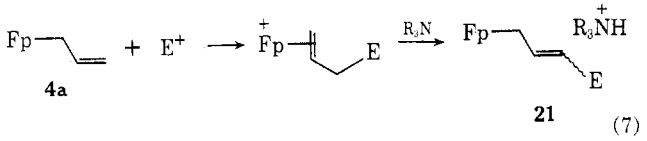
(15) Y. Yamamoto and A. Wojcicki, *Inorg. Nucl. Chem. Lett.*, 883 (1972); Y. Yamamoto and A. Wojcicki, *Inorg. Chem.*, **12**, 1779 (1973).

(16) E. Munck, C. S. Sodano, R. L. McLean, and T. H. Haskell, *J. Amer. Chem. Soc.*, **89**, 4158 (1967); C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965); A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965); T. N. Margulis, L. Schiff, and M. Rosenblum, *J. Amer. Chem. Soc.*, **87**, 3269 (1965).

(17) E. M. Burgess and W. M. Williams, *J. Amer. Chem. Soc.*, **94**, 4386 (1972).

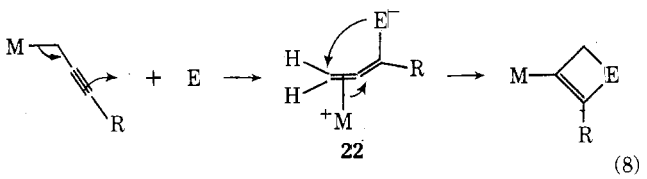
spectively, notwithstanding the presence of the activating cyano and sulfonic acid groups.[14]

A number of 1-substituted allyl-Fp complexes have been prepared from the parent compound by the two-step process outlined below (eq 7), which can be carried out conveniently at low temperatures, without isolation of the intermediate cationic complex.

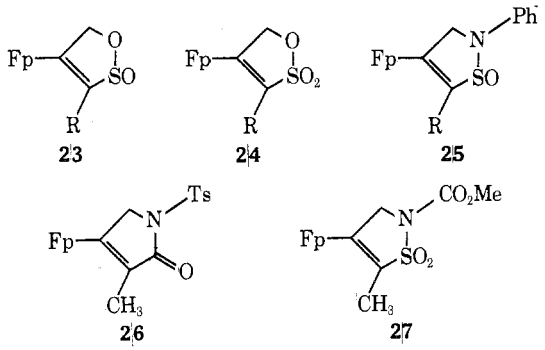


The stereochemistry of the product **21** is highly dependent on the nature of E^+. Thus, acetylation with methyloxocarbonium tetrafluoroborate or alkylation with di- or trialkoxycarbonium ions followed by deprotonation with triethylamine gives exclusively the trans isomers **21** (E = Ac, $(RO)_2CR'$, $(RO)_3C$).[9,18] However, bromination with *N*-bromopyridinium bromide yielded only the cis bromo derivative (**21**, E = Br)[19] and alkylation with trimethyloxonium tetrafluoroborate gave an equal mixture of both cis and trans isomers (**21**, E = Me).[9] When **4a** is treated with SO_2 in the presence of $Me_3O^+BF_4^-$ the intermediate dipolar ion (**2**, E = SO_2, M = Fp) may be trapped by alkylation. Deprotonation yields the sulfone **21** (E = SO_2Me) as the trans isomer. With the exception of the bromo derivative, all of these 1-substituted allyl complexes yield normal cycloaddition products with TCNE.[9,20]

Reactions of (*monohapto*Propargyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron Complexes. The general form of metal-assisted cycloaddition reactions of *monohapto*allylmetal complexes is readily extended to other systems, among them *monohapto*propargylmetal complexes.[21] These substances are available by metalation of propargyl halides or benzenesulfonates and their reaction with electrophiles may be depicted as proceeding through the formation and cyclization of a dipolar metal-allene complex (**22**;[5,22] eq 8).

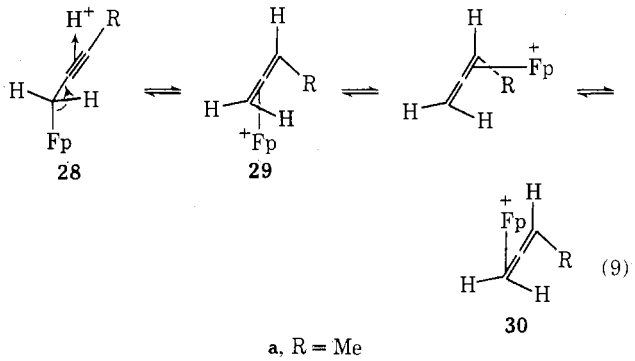


Among the heterocycles which have been prepared from propargyl-Fp complexes employing SO_2,[23] SO_3,[22] *N*-thionylaniline,[24] toluenesulfonyl isocyanate[14,15] and methyl *N*-sulfonylurethane[25a] are **23**–**27**.



R = Me, Ph, CH_2Fp

Simple protonation of *monohapto*propargyl-Fp complexes allows the cationic Fp(allene) complex, postulated as an intermediate in the cycloaddition reactions, to be isolated.[25] The process is apparently highly stereospecific. Thus, protonation of **28a** affords the cis allene complex **29a** exclusively.[25a] This complex isomerizes by a first-order rate process to the more stable trans isomer **30**. The isomerization may be depicted as involving successive orthogonal migrations of the Fp group similar to those postulated to account for the averaging of methyl proton resonances in tetramethylalleneiron tetracarbonyl[26] (eq 9). The stereospecificity of the protonation reaction is best interpreted in terms of a concerted metal-assisted trans periplanar process (eq 9).



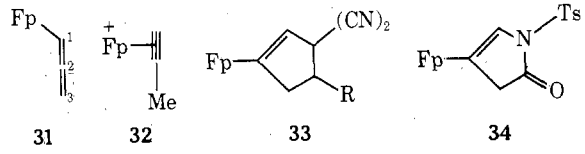
a, R = Me
b, R = Ph

In the reactions of the propargyl complexes with uncharged electrophiles it is undoubtedly this stereospecificity of electrophilic attack combined with distortion of the complexed allene ligand from linearity[27] (see **22**) which makes possible smooth conversion of the dipolar ion to cyclized product through trans addition of the anion to the coordinated double bond (eq 8).

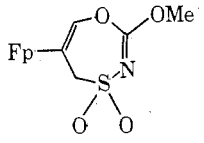
Reactions of (*monohapto*Allenyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron Complexes. Only the parent complex **31** is known, and this is readily prepared by the metalation of propargyl bromide or

(18) D. Ehntholt, unpublished results.
(19) K. Nicholas, unpublished results.
(20) The adduct derived from the (*monohapto*-1-bromoallyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron complex (**21**, E = Br) is a β-bromoalkyldicarbonyl(*pentahapto*cyclopentadienyl)iron complex which apparently decomposes spontaneously by elimination of FpBr.
(21) In point of chronology the cycloaddition reactions of (*monohapto*propargyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron complexes were reported before those of (*monohapto*allyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron complexes, but the mechanism of these processes was apparently not recognized at the time. See, for example, ref 23.
(22) D. W. Lichtenberg and A. Wojcicki, *J. Organometal. Chem.*, **33**, C77 (1971).
(23) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971); M. Churchill, T. Wormald, D. A. Ross, J. E. Thomasson, and A. Wojcicki, *J. Amer. Chem. Soc.*, **92**, 1795 (1970).
(24) P. W. Robinson and A. Wojcicki, *Chem. Commun.*, 951 (1970).
(25) (a) S. Raghu and M. Rosenblum, *J. Amer. Chem. Soc.*, **95**, 3060 (1973); (b) D. W. Lichtenberg and A. Wojcicki, *ibid.*, **94**, 8271 (1972); (c) J. Benaim, J. Merour, and J. Roustan, *C. R. Acad. Sci., Ser. C*, **272**, 789 (1971).
(26) R. Ben-Shoshan and R. Pettit, *C. R. Acad. Sci., Ser. C*, **89**, 2231 (1967).
(27) T. G. Hewitt, K. Anzenhofer, and J. J. Deboer, *J. Organometal. Chem.*, **18**, P19 (1969); P. Racanelli, G. Paritini, A. Immirz, G. Allegra, and L. Povic, *Chem. Commun.*, 361 (1969); T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kukudo, *ibid.*, 317 (1969).

benzenesulfonate with the Fp anion.[28] While, in principle, electrophilic attack may occur at C-1 or C-3 of the allenic ligand, the latter site appears to be preferred. Protonation with $HPF_6 \cdot Et_2O$ at −20° gives the cationic acetylene complex **32** as a very air- and water-sensitive substance. With uncharged electrophiles such as TCNE, β,β-dicyano-*o*-chlorostyrene, and toluenesulfonyl isocyanate, the cycloaddition products (**33, 34**) are formed, the latter two defining the site of initial electrophilic attack at C-3 of the allenic chain. With *N*-carbomethoxysulfonylamine, the bidentate anion in the dipolar intermediate cyclizes preferentially through oxygen to give the oxathiazepine derivative **35**, the first member of this class of heterocycle.



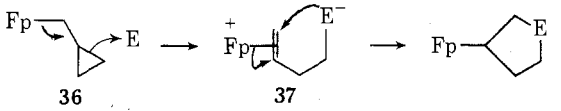
31 **32** **33** **34**



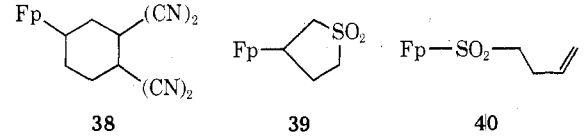
35

R = $(CN)_2$, *o*-C_6H_4Cl

Reactions of (*monohapto*Cyclopropylmethyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron Complexes. Activation of metal-bonded ligands toward electrophilic attack is not confined to those having centers of unsaturation, but may also be observed with ligands possessing a strained single bond. The parent cyclopropylmethyl–Fp complex (**36**), prepared from cyclopropylmethyl tosylate and the complex anion, reacts with TCNE and with SO_2 to give **38** and **39**, respectively.[5] Each of these products is apparently derived from metal-assisted electrophilic attack on the cyclopropyl ring, followed by closure of the dipolar ion **37**, homologous to that generated with the allyl complex (eq 10).



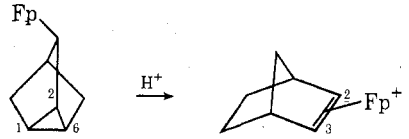
36 **37** (10)



38 **39** **40**

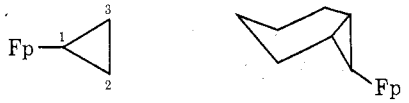
The sulfone **39** is evidently the kinetic product in the reaction of SO_2 with **36** since on brief heating it isomerizes, possibly through reversion to **37** (E = SO_2), to the sulfone **40**.

Cyclopropyl ring opening is apparently a metal-assisted stereoselective trans process since protonation of the tricyclane complex **41**, in which the stereochemical relationships of the cyclopropyl C–C bonds with respect to Fp–C are clearly defined, yields only the exo norbornene complex **42** (60%), derived by cleavage of C-2–C-6 (eq 11). However, the endo isomer is unknown, and consequently its formation and decomposition in the course of the reaction cannot be excluded.



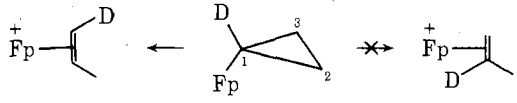
41 **42** (11)

Reactions of (*monohapto*Cyclopropyl)dicarbonyl(*pentahapto*cyclopentadienyl)iron. Two such substances, the parent compound **43** and the norcarane complex **44**, have been prepared either by metalation of cyclopropyl bromide with Fp^- or by alkylation of FpBr with cyclopropyllithium.[29] The reactions of these substances with electrophiles differ significantly from those of the isomeric *monohapto*allyl –Fp complexes.



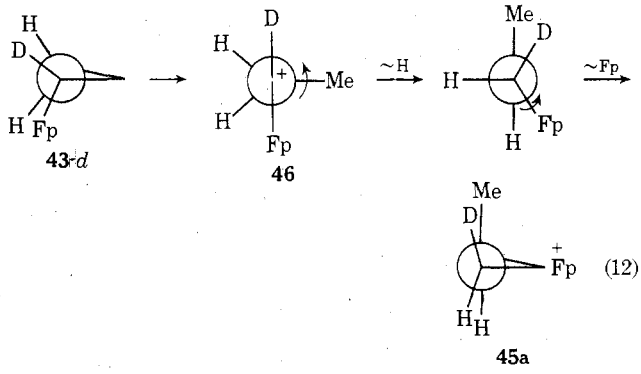
43 **44**

Although protonation of **43** gives Fp(propene)$^+$, as does the isomeric *monohapto*allyl–Fp complex **4a**, the reaction evidently does not proceed through cleavage of C-2–C-3 and migration of the Fp group since the orthogonality of the Fp–C-1 and C-2–C-3 bonds precludes a concerted metal-assisted process. Thus, treatment of the 1-deuterio derivative (**43-*d***) with HBF_4 does not yield the 2-deuterio cation (**45b**) to be expected from a one-step synchronous reaction. The product is instead the 1-deuterio derivative, and more strikingly it is exclusively the cis isomer **45a**.



45a **43-*d*** **45b**

Both the stereospecificity of the reaction and the position of deuterium in the product may be accounted for by protonolysis of C-1,2 and initial formation of a metal-stabilized α-carbonium ion (**46**), followed by its prototopic rearrangement and collapse to the olefin complex through minimum energy conformational changes (eq 12).[29]



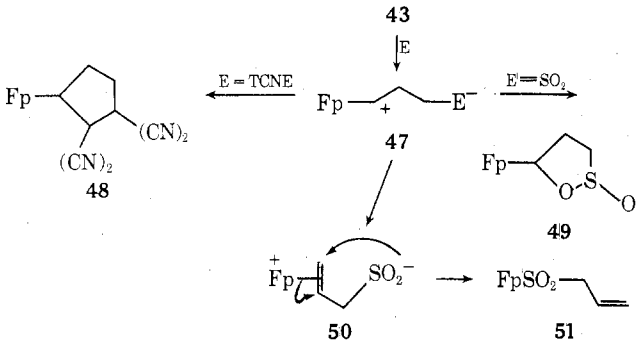
43-*d* **46** **45a** (12)

Metal-stabilized α-carbonium ions (**47**) are apparently also formed as intermediates in the reactions of the neutral electrophiles TCNE and SO_2 with **43**,

(28) J. Roustan and P. Cadiot, *C. R. Acad. Sci., Ser. C*, **268**, 734 (1969); P. W. Jolly and R. Pettit, *J. Organometal. Chem.*, **12**, 491 (1968); M. D. Johnson and C. Mayle, *Chem. Commun.*, 192 (1969).

(29) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 4354 (1972).

which lead to the products **48** and **49**.[29] A small amount of the allyl sulfone **51** is also formed in the latter reaction through prototopic rearrangement of **47** (E = SO_2^-) to **50**, a process evidently competitive with the closure of **47** to the sultine **49**.

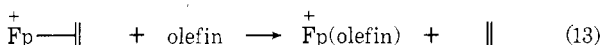


Reactions of Cationic Fp(olefin) Complexes

The addition of nucleophiles to metal-coordinated olefins and acetylenes is a reaction widely encountered in organometallic chemistry.[30] Since the second step of the cycloaddition reactions described above involves such a process, we were prompted to examine the chemistry of Fp(olefin) cations and in particular their reactions with nucleophiles.

Preparation of Fp(olefin) Cations. Several methods are available for the synthesis of these complexes. A number of these cations were first prepared by the reaction of dicarbonylcyclopentadienyliron bromide (FpBr) with simple olefins in the presence of Lewis acids,[31] by protonation of *monohapto*allyl-Fp complexes[3a] or by hydride abstraction from alkyl-Fp complexes.[32]

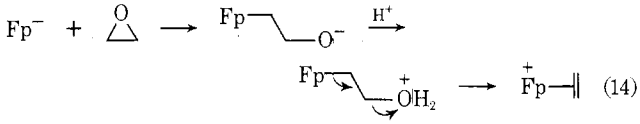
Two other methods have more recently augmented these. The first makes use of the Fp(isobutylene) cation **52**, which is readily prepared by protonation of methallyl-Fp **4b**. The reagent can be stored for prolonged periods at 0° without decomposition. When chlorocarbon solutions of this complex are heated briefly at 60° in the presence of an excess of olefin, exchange occurs leading to the formation of an Fp(olefin) cation (eq 13).[33]



52 (13)

The reaction is necessarily limited to the preparation of those olefin complexes which are thermally stable in solution under conditions used to effect exchange with the isobutylene complex.[34]

An alternative method which does not suffer from this limitation, and which may also be used for the preparation of olefin complexes having functional groups, makes use of epoxides as starting materials.[35] Treatment of these with the Fp anion affords alkoxy-Fp complexes, and these on protonation *in situ* and at low temperatures are converted to the corresponding Fp(olefin) cations. Equation 14 illustrates this transformation for ethylene oxide.



(14)

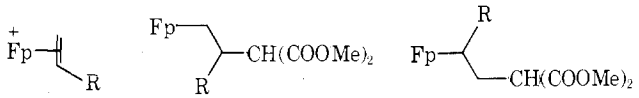
The reaction sequence has been applied successfully to a variety of cyclic and acyclic epoxides as well as to acrolein and crotonic ester epoxide and may also be used to prepare relatively unstable cations such as Fp(*trans*-stilbene)$^+$. The transformation of epoxide to olefin complex proceeds with retention of configuration and constitutes an effective method for the stereospecific reduction of epoxides to olefins, since the cationic olefin complexes are readily decomposed on brief treatment with iodide, liberating the olefin.[35]

Nucleophilic Additions to Fp(olefin) Cations. Nucleophiles react with Fp(olefin) cations by one or more of three pathways. Direct addition of nucleophile to the complexed double bond is a very general process, but one which may be reversible with uncharged nucleophiles. Displacement of the olefin by the nucleophile as well as reductive processes resulting in the formation of dicarbonylcyclopentadienyliron dimer (Fp_2) often compete with the addition reaction. These latter two reactions generally become important and often predominant with reactive anionic nucleophiles, such as alkyl-Grignard or lithio reagents. However, lithium enolates, generated in THF solution with lithium bis(trimethylsilyl)amide,[36] add smoothly at −78° to a variety of acyclic and cyclic Fp(olefin) cations, affording neutral adducts such as **53** and **54**.[30,37]

53 **54**, $n = 2, 3$

R = $CH_2(COOMe)_2$; CH(COMe)COOEt; $CMe(COOEt)_2$

Dimethyl malonate adds to the Fp(propene) cation **55b**to give a 1:1 mixture of the adducts **56a** and **57a**, but the styrene complex **55c** reacts with greater regiospecificity, affording only **56b** in high yield.[38]



55a, R = H
b, R = Me
c, R = Ph

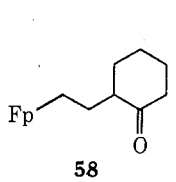
56a, R = Me
b, R = Ph

57a, R = Me

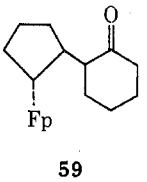
Cyclohexanone pyrrolidine enamine reacts rapidly at 0° with cationic Fp(olefin) complexes, affording adducts such as **58** and **59** in high yield. With pro-

(30) For leading references see A. M. Rosan, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, **95**, 3062 (1973).
(31) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961); **95**, 2063 (1962).
(32) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).
(33) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).
(34) The mechanism of this exchange reaction is not known, but may involve dissociation of the isobutylene complex rather than displacement of one ligand by another.
(35) W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, **94**, 7170 (1972).
(36) M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970).
(37) The trans stereochemical assignments made for the cyclic adducts are well supported by the general course of additions of nucleophiles to metal coordinated olefins: A. Panunzi, A. De Renzi, and G. Parao, *J. Amer. Chem. Soc.*, **92**, 3489 (1970); J. K. Stille and R. H. Morgan, *ibid.*, **88**, 5135 (1966); M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967); C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.*, **7**, 181 (1967); J. K. Stille and D. B. Fox, *Inorg. Chem. Lett.*, **5**, 157 (1969).
(38) A. M. Rosan, unpublished results.

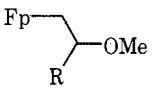
pene and styrene complexes, the regiospecificity of these reactions parallels that observed with enolate anions. By contrast, the reactions of heteroatomic nucleophiles are highly regiospecific. The adducts **60** and **61** are the exclusive products obtained with these nucleophiles and the propene or styrene complexes.



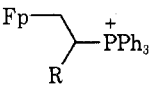
58



59

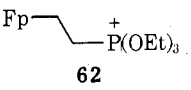


60, R = Me, Ph

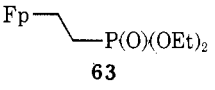


61, R = Me, Ph

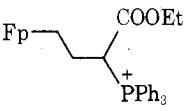
Attempts to employ complexes **61** or the phosphonate **63**, derived from **62**, as Wittig reagents have thus far been unsuccessful, but the stabilized phosphorane, prepared from the adduct **64**, reacts with benzaldehyde to give **65**.[38]



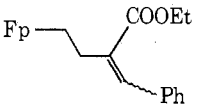
62



63

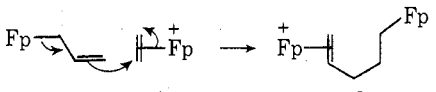


64



65

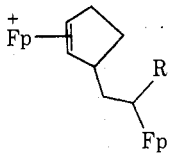
Organometallic Condensation Reactions. The combination of organometallic electrophile and nucleophile leads to a new condensation reaction. Thus, an equimolar mixture of **4a** and **55a** condenses at room temperature to give the dinuclear complex **66** in 60% yield.[30]



(15)

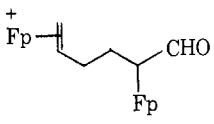
4a **55** **66**

Similar condensations may be effected with **4a** or the cyclopentenyl complex **6a** as donor and the cationic ethylene, acrolein, or crotonic ester complexes as acceptors, yielding products such as **67–69.**

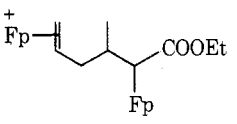


R = H, CHO

67



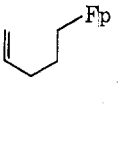
68



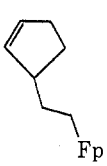
69

Each of the Fp groups in the dinuclear condensation products may be selectively removed. Thus, brief treatment of **66**, **67** (R = H), **68**, or **69** with sodium iodide in acetone solution at room temperature yields the mononuclear complexes **70–73**, while short contact of **66** with HCl at room temperature in methylene chloride solution affords **74**.

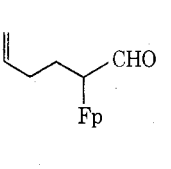
When the acceptor component is the Fp(1,3-butadiene) cation **75**, the condensation with allyl-Fp (**4a**) apparently proceeds through initial formation of **76**



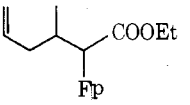
70



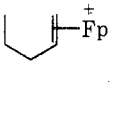
71



72

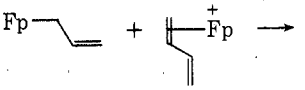


73

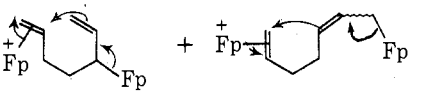


74

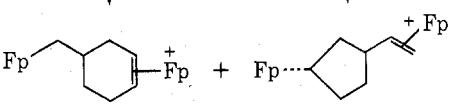
affording **78** and **79**.[39] These products were isolated as the neutral mononuclear complexes **81** and **82** in 40% yield after treatment of the reaction mixture with sodium iodide. The facile cyclization of **76** and **77** is not surprising since these intermediates contain both donor and acceptor components suitably disposed for intramolecular reaction.



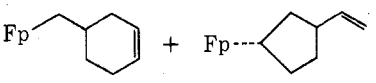
75



76 **77**

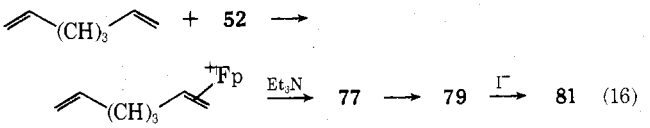


78 **79**



80 **81**

An alternative synthesis of **77** and thence **79**, whose more general synthetic application remains to be examined, makes use of 1,6-heptadiene as starting material and the sequence outlined below (eq 16).



(16)

Demetalation Reactions

Since many of the reactions of *monohapto*allyl-Fp and Fp(olefin) complexes lead to the formation of alkyl-Fp complexes, it is natural to consider methods by which the organometallic group in these latter complexes might be replaced by an organic function.

Brominolysis of transition metal–carbon bonds appears to be a reaction of some generality, and while there remains some controversy regarding the stereochemistry of some of these reactions,[40,41] inversion of

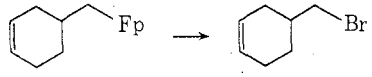
(39) It is possible that the exclusive initial product is **76** and that **77** is formed from it by an allylic rearrangement.

(40) R. G. Pearson and W. R. Muir, *Inorg. Chem. Lett.*, 92, 5519 (1970); R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970); J. A. Labinger, R. J. Baus, D. Dolphin, and J. H. Osborn, *ibid.*, 612 (1970); F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 93, 5283 (1971).

configuration in the reaction of bromine with a primary Fp–C bond appears well established.[42] It has recently been suggested that these and other electrophilic substitution reactions of metal–alkyl complexes proceed by nucleophilic attack on the oxidized complex (eq 17).[41]

$$M{-}R \xrightarrow{X_2} \overset{+\cdot}{M}{-}R + X^- \longrightarrow RX + M^{\cdot} \qquad (17)$$

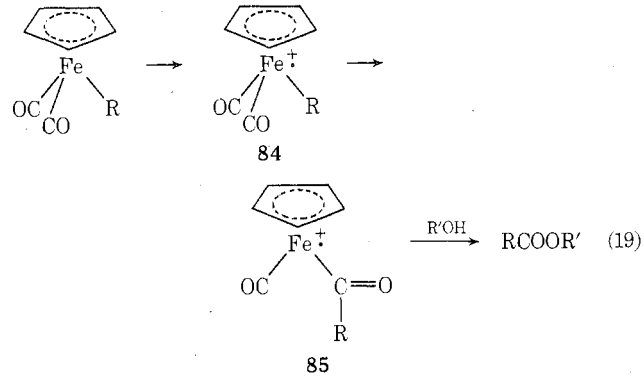
The brominolysis of Fp–C bonds is a very rapid reaction which may be carried out employing either bromine, pyridinium perbromide, or bromopyridinium bromide. So rapid is the reaction that it may be effected selectively at −78° in the presence of an olefin bond, as is illustrated by the conversion of **82** to **83**[19] (eq 18).



82 **83** (18)

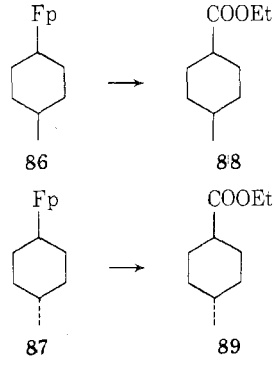
The conversion of transition metal–alkyl complexes to metal alkyl sulfone complexes by treatment with SO_2 has been examined for a number of complexes[43] and shown to proceed with inversion of configuration with FpCHDCHD(*t*-Bu).[42] By contrast, cleavage of the Fe–C bond in this latter complex with $HgCl_2$ proceeds with retention of configuration in the product, RHgCl.[42]

One-step replacement of the Fp group by either a carboxylic ester or acid function has more recently been achieved, through oxidation of alkyl–Fp complexes with either cupric chloride,[44] ferric chloride,[19] dichlorodicyanoquinone,[19] or ceric salts.[45] When the reaction is carried out in alcohol solution, the ester is obtained in good yield,[44,45] while in aqueous acetone the acid is formed.[19] It seems likely that the reaction proceeds through the oxidized form of the iron complex (**84**),[44,45] and that ligand transfer (R to carbonyl) in this intermediate is facilitated by the cationic charge which diminishes metal–carbonyl back-bonding and increases the positive charge at the carbonyl carbon atom. Nucleophilic displacement at the carbonyl group of the rearranged cation **85** is also likely to be facilitated by the positive charge on the metal (eq 19).



(19)

The reaction has been applied successfully to both primary and secondary alkyl–Fp complexes and appears to be highly stereospecific. Thus, oxidative carboxylation of *cis*- and *trans*-4-methylcyclohexyl–Fp (**86** and **87**) with cupric chloride in ethanol solution gave the corresponding cis and trans ethyl esters, respectively (**88** and **89**).[44]



Much of the chemistry described in this Account represents the work of my research associates and students during the past 3 years. It is a pleasure to acknowledge my indebtedness to Dr. Warren P. Giering who began this research, and to Drs. Daniel Ehntholt, R. W. Fish, S. Raghu, Kenneth Nicholas, Darrell Wells, Messrs. Alan Cutler, Alan Rosan, and Jean Tancrede who have carried it forward so ably and with such spirit. The research has been supported by grants from the National Institutes of Health, by the National Science Foundation, and by the Army Research Office, Durham, which I gratefully acknowledge. This paper was written while I was on leave at the Hebrew University, Jerusalem, Israel. I wish to express my appreciation to the members of the Institute of Chemistry for their hospitality.

(41) S. N. Anderson, D. M. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).

(42) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971).

(43) J. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966); A. Wojcicki and F. A. Hartman, *ibid.*, **88**, 844 (1966); F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968); M. Giaziani, J. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).

(44) K. M. Nicholas and M. Rosenblum, *J. Amer. Chem. Soc.*, **95**, (1973).

(45) S. N. Anderson, C. W. Fong, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 163 (1973).