Supplementary Material Available: A listing of observed structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) A recent review in this area is given by K. Wade, *Chem. Brit.*, **11**, 177 (1975). See also (b) K. Wade, *J. Chem. Soc. D*, 792 (1971); (c) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559, 563, and 823 (1972); (d) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); (e) D. M. P. Mingos, *Nature (London) Phys. Sci.*, **236**, 99 (1972); (f) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973); (g) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
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(26) Typical values are in the range of 1.7–1.9 Å, but bonded B–B distances of 2.0 Å or larger have been observed in "normal" $2n + 2$ electron closed polyhedral metallocarboranes, e.g., in the tricapped trigonal prismatic species $(\eta^5\text{-}C_5H_5)CoCB_7H_8^-$ [27] and 1,7,5,6-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$.[21]
(27) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1393 (1974).
(28) **Note Added in Proof.** The cobalt–boron cluster $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ recently reported from our laboratory (V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 1600 (1976)) is an electron-hyperdeficient ($2n$-electron) framework for which a capped pentagonal bipyramidal structure is possible in the solid state. However, NMR evidence strongly favors D_{2d} dodecahedral geometry in solution.

Chemistry of Dicarbonyl η^5-Cyclopentadienyl-η^1-allyl- and -η^2-olefiniron Complexes. Preparation and Cycloaddition Reactions

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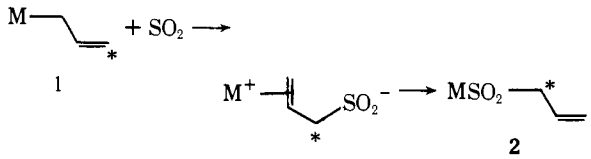
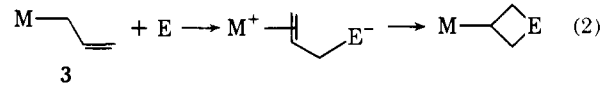
Abstract: A number of η^1-allylmetal complexes of iron, tungsten, molybdenum, cobalt, and chromium enter in (3 + 2) cycloaddition reactions with tetracyanoethylene (TCNE). Of these η^5-$C_5H_5Fe(CO)_2$-η^1-allyl **3a** is the most reactive. This substance and its analogues **7** and **8** may be prepared by metalation of allyl halides or tosylates with η^5-$C_5H_5Fe(CO)_2Na$ or by deprotonation of η^5-$C_5H_5Fe(CO)_2$(olefin) cations 9 and **10.** The scope of the metalation reaction is considered and evidence is provided for rapid equilibration in these complexes. Several general methods are available for the preparation of these iron(olefin) cations. These include olefin exchange with η^5-$C_5H_5Fe(CO)_2$(isobutylene)$^+$ or epoxide deoxygenation with η^5-$C_5H_5Fe(CO)_2Na$. The deprotonation of η^5-$C_5H_5Fe(CO)_2$(olefin) cations is simply achieved by treatment with tertiary amines and is shown to involve preferential loss of a proton trans to the iron–olefin bond. Acyclic and cyclic allyl complexes are readily converted to their TCNE adducts, or in the presence of isocyanates to butyrolactams. These cycloaddition reactions are shown to occur stereospecifically by a suprafacial addition of the electrophile trans to the η^5-$C_5H_5Fe(CO)_2$ group. An analysis of the NMR spectra of several of these iron complexes, both neutral and cationic, indicates a significant diamagnetic anisotropy for the η^5-$C_5H_5Fe(CO)_2$ group in which regions of space close to the fivefold axis of the C_5H_5 ring are relatively shielding. A number of processes are shown to compete with closure of the zwitterion formed as an intermediate in cycloaddition reactions. These include proton transfer, intramolecular decomposition of the zwitterion, and displacement of the anionic terminus at the metal center. Acceptor components such as dicyanodichloroquinone, methylene malonate, and sulfene are also shown to enter into cycloaddition reactions with η^5-$C_5H_5Fe(CO)_2$-η^1-allyl complexes.

Recently we suggested that formation of chain inverted metal allyl sulfones from the reaction of sulfur dioxide with η^1-allyl transition metal complexes was best interpreted in terms of the two-step process depicted in eq 1,[1] rather than by a concerted mechanism.[2]



1 2 (1)

At that time we were led to consider the possibility that dipolar ions analogous to **2** might alternatively collapse through addition of the nucleophile to the activated olefin rather than by ligand displacement (eq 2).

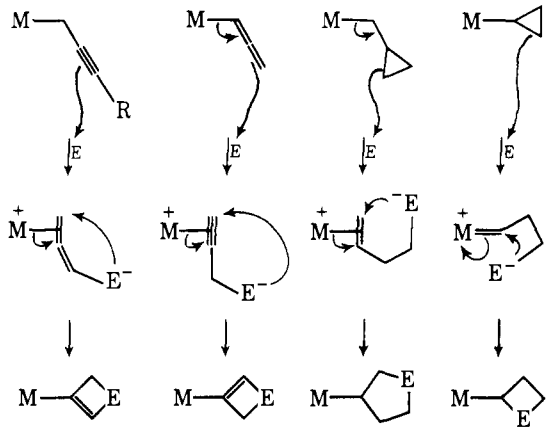


3 (2)

Such metal assisted cycloadditions have since been shown to be very general for a number of electrophiles and η^1-allylmetal complexes.[1,3] A closely related mechanism was also

proposed[1] to account for products reported from the reaction of sulfur dioxide[4] and of *N*-phenylthionylamines[5] with η^1-propargylmetal complexes, and this mechanism was subsequently adopted to account for the reactions of these complexes with sulfur trioxide[6] and with isocyanates.[3a,b] Similar metal assisted cycloadditions have also been observed with η^1-allenyliron,[7] cyclopropylmethyliron,[1] and cyclopropyliron complexes.[8] These transformations constitute a family of metal assisted cycloaddition reactions, closely related in form, and dominated by the ability of the metal to function as an electron donor center (Scheme I).

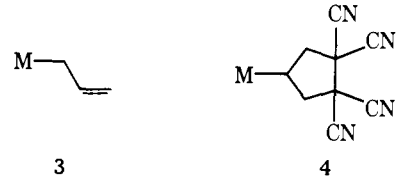
Scheme I



The present paper provides a full account of the chemistry of η^1-allyliron complexes communicated earlier in preliminary form.[1,3a]

Results and Discussion

Relative Reactivity of η^1-Allylmetal Complexes. Following the initial observation that the η^1-allyliron complex **3a**[9] entered into a (3 + 2) cycloaddition reaction with tetracyanoethylene (TCNE) to give the adduct **4a**,[1] we were led to examine the relative reactivity of other η^1-allylmetal complexes, among them the tungsten,[10] cobalt,[11] and chromium complexes **3b,d,e.** The reaction of the related molybdenum complex **3c**[12] with TCNE has been independently reported by Wojcicki and Su.[3d]



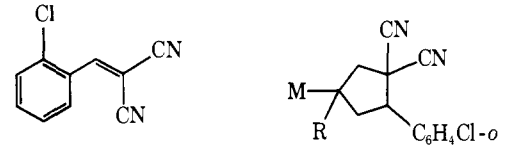
3 4

a, M = η^5-$C_5H_5Fe(CO)_2$
b, M = η^5-$C_5H_5W(CO)_3$
c, M = η^5-$C_5H_5Mo(CO)_3$
d, M = (pyridine)bis(dimethylglyoximato)cobalt
e, M = η^5-$C_5H_5Cr(NO)_2$

Of these allylmetal complexes, only the cobaloxime derivative **3d** was a solid at room temperature. However, its solubility and spectral properties were not convenient and further investigations of its chemistry beyond its reaction with TCNE were not pursued. Complex **3e,** previously unreported, was obtained in poor and variable yield from the reaction of dinitrosylcyclopentadienylchromium chloride[13] and allylmagnesium chloride, while the known iron[9] and tungsten[10] complexes are readily available through reaction of the corresponding carbonyl cyclopentadienylmetal anion with allyl halide.

Differences in reactivity between these latter three complexes are not apparent with the highly reactive TCNE. However, a measure of their relative reactivity can be obtained with the less reactive *o*-chlorodicyanostyrene (**5**). The iron complex reacts with **5** to give a 40% isolated yield of adduct **6a** after 3 h at room temperature, whereas the tungsten complex affords only 6% of the corresponding adduct after 4 h of reaction in refluxing tetrahydrofuran. The chromium complex failed to react with **5** even after 8 h in refluxing tetrahydrofuran.

Owing to the accessibility and high reactivity of the iron complex **3a,** all further experiments were carried out with this substance and its congeners.

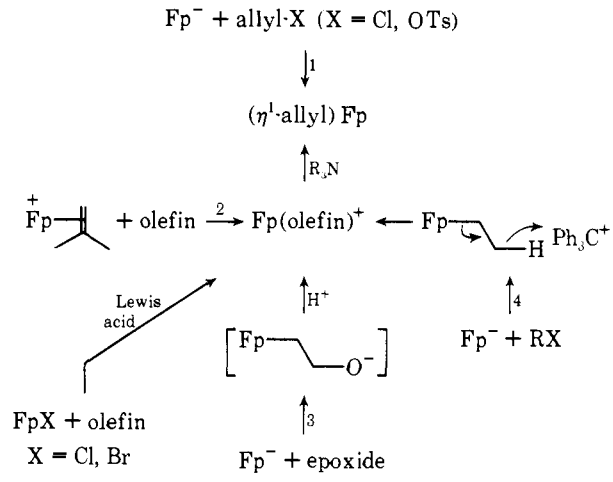


5 6

a, M = η^5-$C_5H_5Fe(CO)_2$; R = H
b, M = η^5-$C_5H_5W(CO)_3$; R = H
c, M = η^5-$C_5H_5Fe(CO)_2$; R = Me

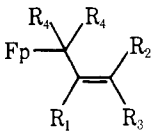
General Methods for the Preparation of (η^1-allyl)Fp Complexes. These substances are available either by metalation of allyl halides[9] or tosylates with η^5-$C_5H_5Fe(CO)_2$ anion[13] (hereafter designated by the symbol Fp), or by deprotonation of Fp(olefin) cations.[3a] The olefin complexes may in turn be prepared either by treatment of FpX (X = Cl, Br) with an olefin in the presence of a Lewis acid,[14] through an exchange reaction with the readily dissociable Fp(isobutylene) cation,[15] from the reaction of Fp anion with an epoxide followed by treatment with acid,[16] or by hydride abstraction from (alkyl)Fp complexes.[17] Scheme II summarizes these transformations, which are treated in detail below.

Scheme II

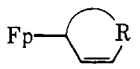


Metalation. This method has been most commonly used for the preparation of primary and secondary (η^1-allyl)Fp complexes. Table II provides a summary of spectral properties and yields of (η^1-allyl)Fp complexes prepared in the course of this work by the metalation reactions. In general, allyl chlorides constitute the best reactants; lower yields are obtained with either the bromides or tosylates. Those substrates which in principle could give either primary or secondary (η^1-allyl)Fp complexes are found to yield only the former. Thus, metalation of crotyl chloride or 3-chloro-1-butene is reported to give *cis*- and *trans*-(crotyl)Fp (**7b,c**), while metalation of either cinnamyl chloride or α-phenylallyl chloride yields only the cinnamyl complex **7e.**[18]

These results may be due to either preferential metalation at a primary carbon atom or to metalation followed by allylic

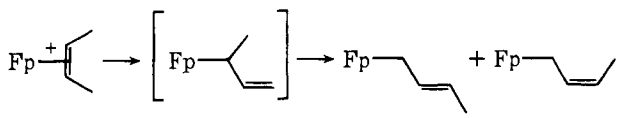


	R_1	R_2	R_3	R_4
7a	Me	H	H	H
b	H	Me	H	H
c	H	H	Me	H
d	H	Me	Me	H
e	H	H	Ph	H
f	H	H	H	Me, H
g	H	D	D	H
h	H	H	H	D
i	Me	H	H	D
j	Me	D	D	H
k	H	H	OMe	H
l	H	OMe	H	H



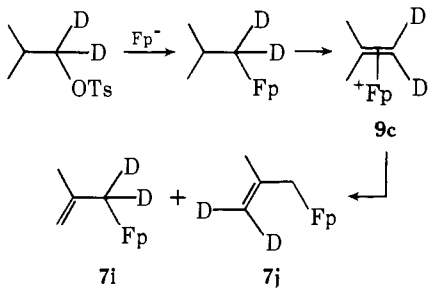
	R
8a	(CH_2)
b	$(CH_2)_2$
c	$(CH_2)_3$
d	$(CH_2)_4$
e	(CH=CH)

rearrangement to the more stable complex. That the latter pathway is available is to be seen in the formation of *cis*- and *trans*-(crotyl)Fp (**7b,c**) from the deprotonation of the Fp(*cis*-2-butene) cation (**9d**) with triethylamine. The isomeric (α-methallyl)Fp complex **7f** must be the initial product of deprotonation, but evidently undergoes rapid and complete isomerization to the crotyl complex. Furthermore, the energy barrier separating **7b,c** from **7f** may be in excess of 20 kcal/mol, since mixtures of **7b,c** of differing composition are not observed to equilibrate on standing at room temperature for several hours. Such isomerization would be expected to proceed through the intermediacy of the α-methallyl complex **7f.**



9d **7f** **7c** **7b**

Rapid equilibration is observed in the formally symmetric (3,3-dideuterioisobutenyl complex) **7i,** prepared from the corresponding dideuterioisobutyl complex, as shown below. Deprotonation of the labeled isobutylene complex **9c** with *N*-methylmorpholine either at room temperature or at 0° gave a mixture of deuterated (isobutenyl)Fp complexes (**7i,j**). A similar, but slower equilibration of (1,1-dideuterioallyl)Fp (**7g**) has also been observed.[18]



9c

7i **7j**

These phenomena find a close parallel in the behavior of related Grignard reagents,[19] but the rates of site exchange in (η^1-allyl)Fp complexes must be significantly slower than those in allyl Grignard reagents, since proton averaging is not observed for the iron complex but is for Grignard reagents.[20] Even at temperatures up to 100° no change indicative of exchange averaging is observed in the NMR spectra of **3a.**

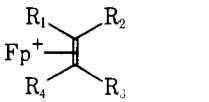
Synthesis of Fp(olefin) Cations. In those circumstances in which the requisite allyl halide or tosylate may not be available, deprotonation of Fp(olefin) cations (**9, 10**) constitutes an attractive method for the synthesis of (η^1-allyl)Fp complexes.

The exchange reaction[15] (reaction 2, Scheme II) has proven to be a direct and effective method for the preparation of a number of simple Fp(olefin) complexes. The reaction is effected by brief warming of the isobutylene complex **9b** in 1,2-dichloroethane in the presence of excess olefin. The isobutylene complex is a crystalline, air-stable substance, which can be stored indefinitely at 0° and is readily available by protonation of **7a.** Since the exchange reaction is confined to the preparation of Fp(olefin) cations more stable than **9b,** and stability generally decreases with olefin substitution, monosubstituted olefins are particularly well suited as exchange partners. A number of cycloalkene complexes have also been prepared by this technique. Of these, cyclohexene is the least successful, affording the olefin complex in very low yield, owing apparently to steric interactions between the organometallic radical and an axial homoallylic proton on the ring.

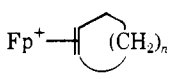
In such circumstances, the epoxide reaction sequence[16] (reaction 3, Scheme II) provides an effective alternative method for the preparation of the requisite complex cation. The Fp anion, which is among the most powerful organometallic nucleophiles known,[22] readily converts epoxides, at room temperature, to the corresponding alkoxide. These, on protonation in situ with 2 equiv of fluoroboric or hexafluorophosphoric acid, are instantaneously converted to the corresponding Fp(olefin) cations, which may be isolated by precipitation with ether. Table III provides a summary of the physical properties and analytical data for those cations prepared either by the exchange reaction or from the epoxide.

The conversion of epoxide to olefin complex is a highly stereospecific process, as evidenced by the transformation of *cis*- and *trans*-2-butene, *cis*- and *trans*-stilbene, and *trans*-ethyl crotonate epoxides to the corresponding olefin complexes **9d–h** with greater than 98% retention of configuration. Since the free olefin may be liberated from the complex by brief exposure to sodium iodide in acetone solution, the sequence also constitutes a useful complement to other methods by which epoxides are transformed to olefins of either inverted[23] or retained[24] stereochemistry.

The reaction of Fp anion with epoxides forms a close parallel with the reactions of cobalt tetracarbonyl,[25a] hydridoiron tetracarbonyl,[25b] and pyridinebis(dimethylglyoximato)cobalt(I) anions with epoxides.[26]



	R_1	R_2	R_3	R_4
9a	H	H	H	H
b	Me	Me	H	H
c	Me	Me	D	D
d	H	Me	Me	H
e	Me	H	Me	H
f	H	Ph	Ph	H
g	Ph	H	Ph	H
h	CO_2Et	H	Me	H
i	CHO	H	H	H
j	H	H	H	CH_2CPh_3



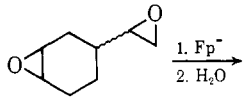
10a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$
e, $n = 5$

11 **12**

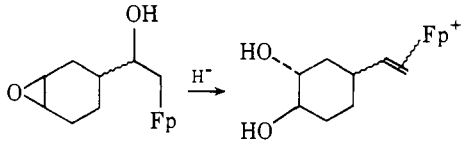
Since the intermediate alkoxides may be converted to cationic olefin complexes by protonation at very low temperatures (−78°), the epoxide sequence is particularly well suited to the synthesis of relatively unstable olefin complexes. Among these are the cations of *cis*- and *trans*-stilbene (**9f,g**), cyclohexene (**10c**), *trans*-ethyl crotonate (**9h**), and acrolein (**9i**). The stilbene and crotonate complexes are particularly unstable and decompose rapidly at −15° in solution. When decomposition of the stilbene salt is allowed to proceed in nitromethane solution, the nitromethane complex **11** may be isolated as an air-stable, orange crystalline solid. The cyclooctatetraene

complex **12,** prepared from the monoepoxide[27] is likewise unstable and decomposes above 0° in nitromethane. Below this temperature an examination of its NMR spectrum gave no evidence for fluxional behavior.

The large steric demand of the Fp anion is reflected in the great difference in rates of reaction of this reagent with terminal and internal epoxides (Table III), and in the failure of either *exo*-norbornene or cyclooctene epoxides to undergo ring opening. It is possible to make use of this attribute in selective reductions of bisepoxides, as is illustrated by the conversion of **13** to the glycols (**14**).



13



14

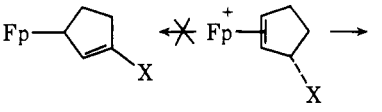
Epoxides possessing other functional groups susceptible to nucleophilic attack may be entered successfully into this reaction, as is seen in the conversion of crotonate and acrolein epoxides in high yield to the corresponding olefin complexes **9h,i.** The NMR spectrum of the intermediate alcohol derived from *trans*-crotonate shows that ring opening by the organometallic anion has taken place at the α-carbon atom. This is evidenced by the presence of a doublet signal for H_α at τ 7.67 and multiplet absorption for H_β at τ 6.07. The unusual stability of this alcohol may be due in part to electronic interaction of the metal with the ester carbonyl, as is indicated by the abnormally low frequency carbonyl absorption in this complex at 1675 cm^{-1}.

The overall stereochemistry of the reductive sequence is best accounted for in terms of two successive trans processes: epoxide opening and elimination of water.

Deprotonation of Fp(olefin) Cations. Conversion of the complexed cations **9** and **10** to (η^1-allyl)iron complexes is readily achieved by treatment with triethylamine.[28] The reaction is rapid at room temperature in methylene chloride solution and is generally complete within 30 min. Its progress is readily monitored by following the replacement of carbonyl bands near 2030 and 2070 cm^{-1} in the cation by those of the product near 1950 and 2005 cm^{-1}.

The deprotonation reaction is highly stereospecific, proceeding by loss of an allylic proton trans to the metal olefin bond. This is well illustrated by the cyclopentene complexes **15a–c,** which yield the cyclopentenyl derivatives **16a–c** exclusively. The result is especially striking for **15a,b,** in which the cyano or sulfonic acid groups would otherwise be expected to control the course of deprotonation. Deprotonation of **15d** gave the η^1-cyclopentadienyl complex **8e** as the only isolable product. Its formation is likewise best depicted as proceeding through **16d,** followed by elimination of bromide and subsequent deprotonation. The importance of steric factors is illustrated by the triphenylmethyl derivative **15e** which resists deprotonation by triethylamine. The acyclic olefin complex **9j** similarly is not deprotonated by triethylamine but instead slowly decomposes to the dimer (Fp_2).

The cycloheptene complex **10d** provides a further interesting example of stereoelectronic control in the deprotonation reaction. It alone among the cycloalkene complexes (**10a–e**) resists deprotonation with triethylamine. Models indicate that for the sterically preferred conformation, in which the Fp group is pendent exo to the ring (**17**), no allylic protons trans to the Fp-olefin bond are available in either the chair or boat conformations of the ring.[29] This is in sharp contrast to the other cycloalkene complexes, all of which possess allylic C–H bonds with the requisite trans stereochemistry.



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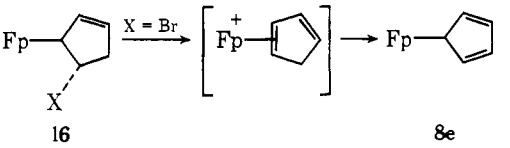
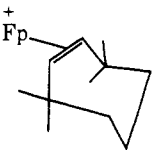


16 8e

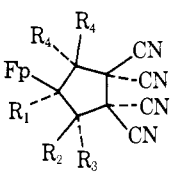
a, CN
b, SO_3H
c, Me
d, Br
e, CPh_3



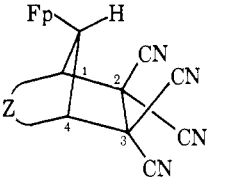
17

In those circumstances in which neither a suitable allyl halide nor olefin are readily available a three-step dehydrogenation sequence starting with an alkyl halide (reaction 4, Scheme II) may be expedient. This sequence is illustrated by the conversion of cyclobutyl bromide to (cyclobutyl)Fp and thence with trityl tetrafluoroborate to Fp(cyclobutene) (**10a**). Deprotonation with ethyldiisopropylamine gave the cyclobutenyl complex **8a** in moderate yield.[30]

Cycloaddition Reactions. Tetracyanoethylene. The reaction of tetracyanoethylene with (η^1-allyl)Fp complexes is very rapid at room temperature. The adducts are generally air-stable, yellow crystalline materials, easily purified by crystallization or chromatography, and constitute convenient derivatives for the characterization of (η^1-allyl)Fp complexes. Adducts prepared from simple acyclic and cyclic (η^1-allyl)Fp complexes are enumerated by structures **18** and **19.**[31] Their physical



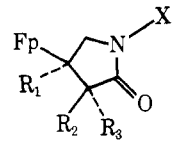
	R_1	R_2	R_3	R_4
18a	H	H	H	H
b	Me	H	H	H
c	H	H	Me	H
d	H	Me	H	H
e	H	Me	Me	H
f	H	H	Ph	H
g	H	H	$COCHMe_2$	H



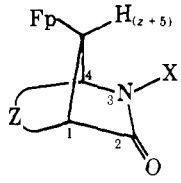
19a, Z = CH_2
b, Z = $(CH_2)_2$
c, Z = $(CH_2)_3$
d, Z = $(CH_2)_4$
e, Z = (CH=CH)
f, Z = *endo*-$(CHCNCH_2)$
g, Z = *endo*-$(CHCH_3CH_2)$

properties are given in Table IV.

Isocyanates. As in classical cycloaddition reactions,[32] (η^1-allyl)Fp complexes enter into reaction with a number of heterocumulenes, among these the isocyanates. The reaction fails with ethyl or phenyl isocyanate, is slow with 2,5-dichlorophenyl isocyanate, but is rapid with the more reactive trichloroacetyl, toluenesulfonyl, methoxysulfonyl, and chlorosulfonyl isocyanates. These adducts, like the TCNE adducts, are generally crystalline, air-stable products. A summary of condensation products obtained from acyclic and cyclic (η^1-allyl)Fp complexes is provided by structures **20** and **21.** Table



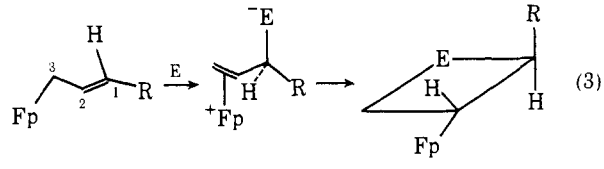
	R_1	R_2	R_3	X
20a	H	H	H	Ts
b	H	H	H	$ClSO_2$
c	H	H	H	H
d	H	H	H	2,5-$C_6H_3Cl_2$–
e	Me	H	H	Ts
f	H	Me	Me	Ts
g	H	Me	Me	CCl_3CO
h	H	Me	Me	H
i	H	H	Ph	Ts
j	H	OMe	H	Ts
k	H	H	OMe	Ts



	Z	X
21a	$(CH_2)_2$	Ts
b	$(CH_2)_3$	Ts
c	$(CH_2)_3$	$MeOSO_2$

V summarizes the physical properties for these substances.

Stereochemistry of Cycloaddition. The stereochemistry of cycloaddition may be shown to correspond to a suprafacial addition of the acceptor component to the allyl complex. Under these circumstances, any geometric isomerism associated with a substituent at C_1 in the reactant complex is preserved in the product by the relationship between this substituent and the adjacent Fp group. This is shown schematically by eq 3.



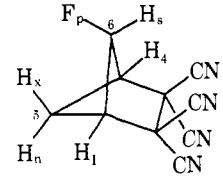
(3)

However, the stereochemical results with acyclic (η^1-allyl)Fp complexes do not distinguish between the process depicted in eq 3 and an equivalent suprafacial addition which takes place cis to the Fp-C bond. The results obtained with cyclic (η^1-allyl)Fp complexes clearly exclude the latter path.

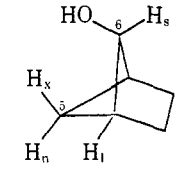
It was not possible to analyze the ^1H NMR spectrum of the TCNE adduct of the *trans*-cinnamyl complex (**7e**), but the *trans*-butenyl adduct (**7c**) proved more amenable. The reaction of **7c**, containing 15% of the cis isomer **7b**, with TCNE, gave a mixture of adducts in the same proportion. The major component exhibited methyl doublet absorption at τ 8.51 while the minor product showed this doublet at τ 8.67. These absorptions correspond closely to methyl proton resonances at τ 8.46 and 8.68 exhibited by the dimethyl adduct **18e**, derived from the isopentenyl complex **7d**. The high and low field resonances in the spectra of these adducts are assigned to methyl protons cis and trans, respectively, to the Fp group. Therefore TCNE adducts derived from **7b** and **7c** are assigned structures **18d** and **18c**, respectively. These assignments conform to the stereochemical outcome anticipated for a suprafacial addition of electrophilic olefin to the allyl complex (eq 3), and rest in turn upon spectral observations for a number of Fp complexes, which suggest that regions of space close to the fivefold cyclopentadienyl-iron axis are relatively shielding. Similar anisotropy effects are observed for allyl protons in cyclopentadienyl(η^3-allyl)molybdenum,[33a] -tungsten,[33a] and -iron[33b] carbonyls, and appear to correlate well with fields induced by cyclopentadienyl ring currents.[33a]

The NMR spectrum of (cyclopropyl)Fp[8] (**22**) in CS_2 shows a 2-proton multiplet at unusually high field (τ 10.12), in addition to a 3-proton multiplet at τ 9.48, for cyclopropyl ring protons. Similarly, homoallylic methylene protons in the Fp(cyclopentene) cation (**10b**) give rise to a high field signal at τ 9.41 as well as one at τ 8.26. Although these unusual resonances cannot be unambiguously assigned, models show that protons H_b which are cis to the Fp group in **22** and **10b** all lie close to the cyclopentadienyl-iron axis in sterically preferred conformations of the Fp-ligand bond.[3b,46]

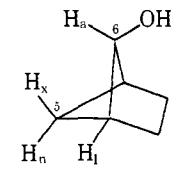
Table I. Coupling Constants (Hz) in Bicyclo[2.1.1]hexanes



19a



25a

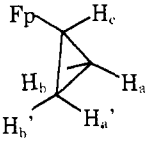


25b

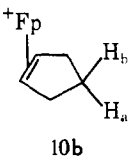
	J_{1-5x}	J_{5x-5n}	J_{6s-5n}	J_{1-6a}
19a	2.5	10.0	10.0	—
25a	2.8	6.8	6.8	—
25b	2.9	7.6	—	2.9

In (3-cyclobutenyl)Fp (**8a**) and in (vinyl)Fp (**23**), stereoisomeric methylene protons may be unambiguously assigned from their vicinal coupling constants (**8a**, J_{ab} = 3 Hz, J_{ac} < 1 Hz; **23**, J_{ab} = 9 Hz, J_{ac} = 17 Hz). In both complexes proton H_c, cis to the proximate Fp group and therefore closer to the cyclopentadienyl-iron axis in all conformations of the Fp-ligand bond, is found to be more highly shielded than the trans proton H_b (**8a**, τ_{H_c} 7.66, τ_{H_b} 7.00; **23**, τ_{H_c} 4.67, τ_{H_b} 4.16).

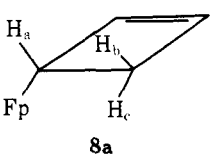
The complex cation **24** provides perhaps the most dramatic illustration of magnetic anisotropy effects associated with the Fp group. Methylene protons H_{7s} and H_{7a} give rise to two multiplet resonances at τ 9.23 and 10.20. The latter signal may be assigned to H_{7s} through double resonance decoupling of long range coupling with $H_{5n,6n}$ (J = 2 Hz). Models show that the sterically preferred conformation of **24** is one in which the carbonyl ligands straddle C_7.[3b] In such a conformation, H_{7s} lies much further within the shielding region defined by the cyclopentadienyl ring current than does H_{7a}, although both are evidently shielded. The related norbornadiene complex shows similar differential shielding of C_7 protons (τ 8.11 and 9.38).



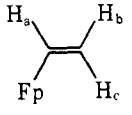
22



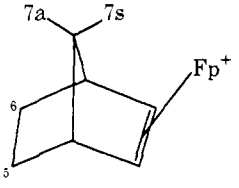
10b



8a



23



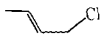
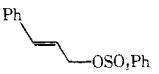
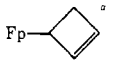
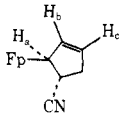
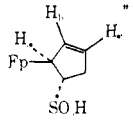
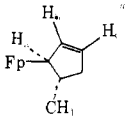
24

The reactions of (η^1-cycloalkenyl)Fp complexes with TCNE and with toluenesulfonyl isocyanate give the bicyclic adducts as a single stereoisomer in each case. The stereochemistry of these products (**19, 21**) corresponds to suprafacial 1,3-addition of the acceptor trans to the Fp-C bond in the donor complex (eq 3).

For **19a** the stereochemical assignment follows from the presence of long range coupling between H_6 and H_{5n} indicative of the "W" configuration of these protons, as has been observed for a number of bicyclo[2.1.1]hexanes.[34] A comparison of the coupling constants for **19a** and the epimeric bicyclohexanols **25a** and **25b**,[35] summarized in Table I, reveals the close correspondence between the iron complex and the isostructural alcohol **25a**.

Similar arguments can be made for the adducts **19b** and **19e**, although the long range coupling constants cannot be explicitly

Table II. (η^1-Allyl) Fp Complexes, Preparation and Spectral Data

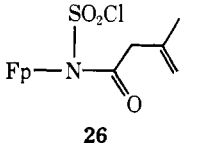
Allyl halide	Product	Yield (%)	ν_{CO} (cm^{-1})[c]	^1H NMR absorption[d] (τ)
	**3a**	91	2000, 1952	4.06 (ddt, 1, J = 16.0, 10.0, 8.0 Hz, CH═), 5.04–5.63 (m, 2, CH_2═), 5.46 (s, 5, Cp), 7.95 (d, 2, J = 8.0 Hz, CH_2)
	**3a**	25		
	**7a**	88	1998, 1950	5.39 (s, 5, Cp), 5.41 (m, 2, CH_2═), 7.87 (s, 2, CH_2), 8.22 (s, 3, CH_3)[e]
	7b + c	94	2005, 1945	
	7b + c 7c	84		4.32 (5q, 1, J = 15.0, 7.5, 1.0 Hz, CH═), 4.94 (dq, 1, J = 15.0, 6.0 Hz, CH═), 5.43 (s, 5, Cp), 7.93 (dm, 2, J = 7.5 Hz, CH_2), 8.47 (dm, 3, J = 6.0 Hz, CH_3)
	7d	52	2005, 1950[f]	4.66 (t, 1, J = 9.0 Hz, CH═), 5.42 (s, 5, Cp), 7.86 (br, d, 2, J = 9.0 Hz, CH_2), 8.43 (brs, 6, CH_3)
	7e	22	2010, 1960	2.85 (brs, 5, Ph), 3.57 (dt, 1, J = 15.0, 7.5 Hz, CH═), 3.85 (d, 1, J = 15.0 Hz, CH═), 5.44 (s, 5, Cp)
			1999, 1947	3.69 (d, 1, J = 2.5 Hz, FpCCH═), 4.21 (m, 1, FpCC═CH), 5.26 (s, 5, Cp), 6.14 (br d, 1, J = 3.0 Hz, FpCH), 7.00 (dd, 1, J = 14.0, 3.0 Hz, *trans*-FpCCH), 7.66 (d, 1, J = 14 Hz, *cis*-FpCCH)[e]
	8b	60	1997, 1945	3.80–4.06 (m, 1, FpCCH═), 4.40–4.63 (m, 1, FpCC═CH), 5.30 (s, 5, Cp), 6.08–6.40 (m, 1, FpCH), 7.48–8.42 (m, 4, CH_2)[e]
	8c	91	1998, 1947	3.96–4.32 (m, 1, FpCCH═), 4.46–4.80 (m, 1, FpCC═CH), 5.32 (s, 5, Cp), 6.50–6.86 (m, 1, FpCH), 7.66–8.66 (m, 6, CH_2)[e]
	**8c**	6[b]		
		70	2005, 1957	3.90–4.14 (m, 1, H_b), 4.48–4.72 (m, 1, H_c), 5.14 (s, 5, Cp), 6.04–6.24 (m, 1, H_a), 6.88–7.44 (m, 3, CH, CH_2)[e]
		50	1988, 1930	3.8–4.1 (m, 1, H_b), 4.4–4.6 (m, 1, H_c), 5.2 (s, 5, Cp), 6.16 (m, 1, H_a), 7.5–8.0 (m, 3, CH, CH_2)[e]
			2002, 1950	*b*, *g*

[a] Prepared by deprotonation of Fp (olefin) cation. [b] Characterized as TCNE adduct. [c] In CH_2Cl_2 unless otherwise specified. [d] In CS_2 unless otherwise specified. [e] In $CDCl_3$ solution. [f] Neat. [g] Not recorded, unstable.

derived from the spectral data. In both these adducts, the methylene bridge proton appears as a broad unresolved multiplet (half height line width 4 Hz) indicative of long range coupling of this proton with endo ethano[36] or ethylene protons, rather than as a triplet to be expected for the C_7-stereoisomer.

The stereospecificity of the cycloaddition reaction involving isocyanates as acceptor components is most evident for the reaction of **8c** with toluenesulfonyl isocyanate. The bicyclic lactam, obtained as a single stereoisomer, exhibits triplet absorption for H_8 (J = 5 Hz) in accord with the stereochemistry depicted for **21b**.[37]

Reactions Competitive With Cycloaddition. A number of processes may compete with closure of the zwitterion formed in the reaction of (η^1-allyl)Fp complexes with heterocumulenes (eq 3). These include proton transfer, intramolecular zwitterion decomposition, and displacement at the metal atom. The latter path leads to so-called "insertion" products, and is exemplified by the reaction of **7a** with chlorosulfonyl isocyanate, which is reported to give **26** as the exclusive product.[3c] By contrast, the same donor complex gives a normal cycloaddition product (**20e**) with toluenesulfonyl isocyanate.[3a] These results may reflect increased anion stabilization and hence higher dipolar ion equilibrium concentration for the former reaction, which would provide a competitive path for irreversible transformation of the dipolar ion. The results do not of course distinguish between such direct competition and a mechanism involving prior dissociation of the dipolar ion **27a** to an ion pair **27b**, followed by its collapse to "insertion" product. Substitution at C_2 in **27a** would be expected to promote such dissociation.



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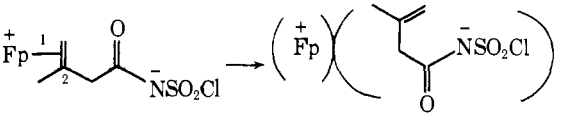
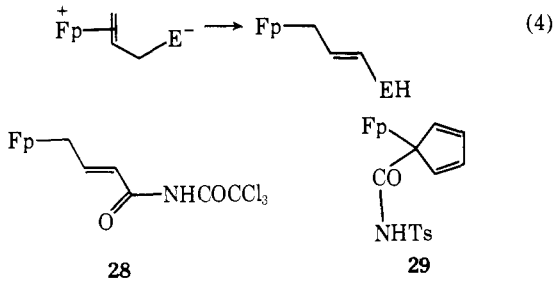


27a **27b**

Proton transfer in the dipolar complex (eq 4) is the dominant mode of reaction with trichloroacetyl isocyanate since the exclusive product of this reaction is the trans substituted (η^1-allyl)Fp complex (**28**). When this process is foreclosed by



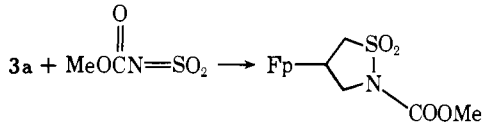
(4)

28 29

employing the 3,3-dimethylallyl complex (**7d**), reaction proceeds normally to give the lactam **20g,** isolated after brief treatment with aqueous base as the unsubstituted lactam **20h.**

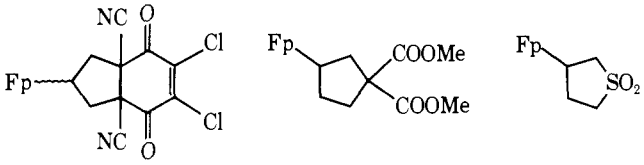
Proton transfer intervenes also in the reaction of (η^1-cyclopentadienyl)Fp (**8e**) with toluenesulfonyl isocyanate. The product **29** is evidently formed through proton transfer in the dipolar ion, followed by sigmatropic shift of the C–metal bond. By contrast this complex reacts normally with TCNE affording the adduct **19e** in good yield.

When the zwitterion is highly stabilized and displacement by the anionic terminus at the metal is not stereochemically possible, cyclization may not be able to compete with irreversible decomposition of the anion, especially if cyclization leads to a strained ring system. This is illustrated by the reactions of chlorosulfonyl isocyanate or methyl *N*-sulfonylurethane[38] with **8b,** which afford cations **15a** and **-b** as the sole products, through loss of chlorosulfonate anion[39] or methyl cyanate from the intermediate dipolar ion. The latter reagent reacts normally with **3a** to give the cycloaddition product **30,** while toluenesulfonyl isocyanate also affords a normal cycloaddition product with **8b.**



30

Other Acceptor Components in Cycloadditions. A number of other electrophiles have been more cursorily examined as partners in cycloaddition reactions with (η^1-allyl)Fp complexes. These include dichlorodicyanoquinone, dimethyl methylenemalonate,[40] and sulfene, which afford adducts **31, 32,** and **33** with the parent complex **3a.**



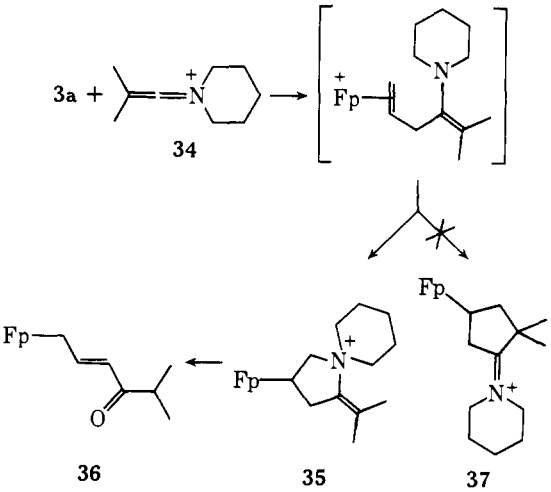
31 32 33

An attempt to prepare a cyclopentanone complex through cycloaddition with the keteneimmonium salt **34**[41] led instead to the ammonium complex **35,** which in the presence of oxalic acid solution gave the ketone **36,** through cycloreversion, enamine hydrolysis, and deprotonation. Attempts to isomerize **35** to **37** by heating in acetonitrile at 82° for 5 h were unsuccessful and led to the recovery of **35.**

Experimental Section

All operations were carried out in a nitrogen atmosphere. Solvents were dried, degassed, and stored under nitrogen and over molecular sieves. Ir spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. ^{1}H NMR spectra were determined on a Varian A-60 spectrometer (NIH GM-13183). Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of (η^1-Allyl)metal Complexes. Metalation of Allyl Halides or Tosylates—General Procedure. A stock solution containing



34 36 35 37

50 mmol of $C_5H_5Fe(CO)_2Na$ in 150 ml of THF was prepared by sodium amalgam reduction of 8.84 g (25 mmol) of the dimer $[C_5H_5Fe(CO)_2]_2$.[14,42] The solution was cooled in a dry ice–acetone bath and the allylic halide or tosylate was added dropwise. After warming to room temperature over a 1-h period, solvent was removed in vacuo and the residue was extracted repeatedly with ether. Combined extracts were filtered through sand in a Schlenk tube, solvent was removed, and the residue was chromatographed on an alumina column (100 g, Camag, neutral activity 3) made up in ether. Elution was with petroleum ether. In general the η^1-allyliron complexes are amber, air and heat sensitive liquids, which are best characterized as their TCNE or SO_2 adducts. In those cases in which the allyl complex is relatively unstable (**8c,d**) the complex was not isolated but derivatized in situ, directly following the metalation reaction.

Preparation of Complex 7c, (*trans*-2-Butenyl)Fp. Treatment of 4.55 g (50 mmol) of 3-chloro-1-butene with an equivalent of NaFp in THF, as described above, gave the product in 94% yield as a mixture of cis and trans isomers (**7b,c**) in the ratio of 1:2, after workup.

When the same reaction was carried out on a commercial mixture of crotyl chloride containing approximately 20% of 3-chloro-1-butene and a 1:1 ratio of *cis*- and *trans*-4-chloro-2-butene, an 84% yield of product **7b,c** in the ratio of 3:4 (cis:trans) was obtained.

Chromatography of 1 g of either of the above mixtures on 160 g of ether washed alumina (Camag, neutral, activity 3) employing petroleum ether as eluent gave a partial separation of isomers. The forerun (100–180 mg) consists of **7c** (90% purity). The NMR spectrum of this substance was identical with an authentic sample of the trans complex prepared by metalation of *trans*-crotyl tosylate.

Deprotonation of Fp(*cis*-2-butene) (9d). Preparation of 7b,c. Treatment of 0.640 g of **9d** (2.0 mmol) in 40 ml of methylene chloride with 0.28 ml (2.0 mmol) of triethylamine at room temperature gave a clear solution within 10 min. Solvent was removed after 30 min. The residue was extracted with ether and filtered, and solvent was removed, leaving 0.450 g (97%) of a caramel colored oil identified by NMR determination as a 1:1 mixture of cis and trans complexes **7b** and **c.**

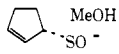
Preparation and Deprotonation of 9c. Methyl isobutyrate was reduced with $LiAlD_4$ in THF and converted to the benzene sulfonate by standard procedures. Metalation of 5.8 g of sulfonate with NaFp, prepared from 7.0 g of dimer, in 60 ml of THF gave 2.9 g of (1,1-dideuterioisobutyryl)Fp, after normal workup. An NMR spectrum showed less than 2% of undeuterated material. Treatment of this material with 2.8 g of trityl tetrafluoroborate in methylene chloride gave 1.9 g of Fp(1,1-dideuterioisobutylene) tetrafluoroborate (**9c**). This was reprecipitated three times from methylene chloride by addition of ether. An NMR spectrum of this material indicates less than 2% of undeuterated material. Treatment of this material with *N*-methylmorpholine at room temperature, followed by washing with water, extraction into Skelly-B, and vacuum distillation of the residue, gave a product whose NMR spectrum indicated a ratio of $FpCH_2/CH_3$ of 1:3. In a second experiment, deprotonation and workup were carried out at 0°, with the same result.

Preparation of Complex 10a. Cyclobutyl bromide (5.132 g, 38.0 mmol) was added to a solution of NaFp (57.0 mmol) in THF, cooled to −80°. The reaction was allowed to come to room temperature and proceed for 5 h. Solvent was removed and the residue was extracted with petroleum ether, filtered, and chromatographed on 120 g of

Table III. Fp(olefin)BF_4 Salts

Olefin	Method of preparation	Reaction time	Yield (%)	ν_{CO}[c] (cm^{-1})	^1H NMR absorptions (τ)	Anal. data C/H Calcd	Found
$CH_2{=}CH_2$	*a*	10 min	44	2075, 2040	4.30 (s, 5, Cp), 6.15 (s, 4, $=CH_2$)		*i, j*
	b	30 min	90				
$CH_2{=}CHCH_3$	*b*	30 min	81	2070, 2035	4.38 (s, 5, Cp), 4.80 (m, 1, =CH), 6.02 (d, 1, J = 8 Hz, *cis*-$CH_2{=}$), 6.46 (d, 1, J = 14 Hz, *trans*-$CH_2{=}$), 8.12 (d, 3, J = 6 Hz, CH_3).		*i, j*
$CH_2{=}CHCH_2CH_3$	*b*	30 min	91	2070, 2030	4.33 (s, 5, Cp), 4.87 (m, 1, =CH), 6.03 (d, 1, J = 8 Hz, *cis*-$CH_2{=}$), 6.52 (d, 1, J = 14 Hz, *trans*-$CH_2{=}$), 7.3–8.7 (br m, 5, CH_2CH_3)		*j*
cis-$CH_3CH{=}CHCH_3$	*b*	12 h	64	2065, 2025	4.37 (s, 5, Cp), 4.82 (m, 2, CH=), 8.18 (dd, 6, J = 5.5, 1.5 Hz, CH_3)	41.29 4.07	40.90 3.95
trans-$CH_3CH{=}CHCH_3$	*b*	12 h	50	2065, 2025	4.33 (s, 5, Cp), 5.18 (m, 2, CH=), 8.12 (dd, 6, J = 5.5, 2.0 Hz, CH_3)	41.29 4.07	41.14 4.00
$PhCH{=}CH_2$	*b*	30 min	65	2070, 2035	2.54 (br s, 5, Ph), 3.78 (dd, 1, J = 8, 15 Hz, PhCH=), 4.35 (s, 5, Cp), 5.70 (dd, 1, J = 15, 1 Hz, *trans*-$CH_2{=}$), 5.76 (dd, 1, J = 8, 1 Hz, *cis*-$CH_2{=}$)		*k*
trans-PhCH=CHPh	*b*	4 h	83	2090, 2060[m]	*e*		
cis-PhCH=CHPh	*b*	6 h	82	2075, 2033[d]	*e*		
$CH_2{=}\overset{|}{C}HCH{=}CH_2$	*b*	30 min	91	2070, 2035	4.33 (s + m, 9, Cp, H_2, H_3, H_4), 6.08 (d, 1, J = 8 Hz, *cis*-H_1), 6.27 (d, 1, J = 15 Hz, *trans*-H_1)		*i*
$CH_2{=}CHCHO$	*b*	30 min	94	2100, 2050 1685	0.45 (d, 1, J = 6 Hz, CHO), 4.09 (s, 5, Cp), 4.45 (m, 1, CH=), 5.30 (m, 2, $CH_2{=}$)	31.83 2.38	32.31 2.58
trans-$CH_3CH{=}CHCOOC_2H_5$	*b*	3 h	75	2092, 2049 1724	*e*		
Cyclobutene	*l*		81	2070, 2030[h]	4.23 (t, 2, J = 2.5 Hz, CH=), 4.39 (s, 5, Cp), 7.01 (dt, 2, J = 13.0, 2.5 Hz, CH_2), 8.14 (dm, 2, J = 13.0 Hz, CH_2)	41.56 3.46 Fe 17.57	41.37 3.39 17.39
Cyclopentene	*a*	10 min	100	2066, 2026	4.35 (s + m, 7, Cp, CH=), 7.64 (m, 4, allylic CH_2), 8.26 (m, 1, CH_2), 9.41 (m, 1, CH_2)	36.80 3.21 Fe 13.90	37.07 3.13 13.91
	b	4 h	47				
Cyclohexene	*a*	10 min	2	2065, 2025	4.22 (s + m, 7, Cp, CH=), 7.3–8.88 (br m, 8, CH_2)		*i*
	b	4 h	60				
Cycloheptene	*a*	10 min	100	2075, 2020	4.40 (s, 5, Cp), 4.68 (m, 2, CH=), 7.40 (m, 2, CH_2), 8.33 (br m, 8, CH_2)	Fe 15.5	16.1
	b	9 h	31				
Cyclooctene	*a*	10 min	51	2062, 2023[d]	4.39 (s, 5, Cp), 4.92 (m, 2, CH=), 7.46–8.40 (m, 12, CH_2)	48.2 4.51	47.9 5.19
Norbornene	*a*	10 min	31	2075, 2032[d]	4.39 (s, 5, Cp), 4.83 (s, 2, CH=), 7.10 (brs, 2, CH) 8.20 (m, 2, CH_2CH_2), 8.78 (m, 2, CH_2CH_2), 9.23 (d, 1, J = 11 Hz, anti CH_2), 10.20 (d, 1, J = 11 Hz, syn CH_2)	46.98 4.22	47.06 4.15
	b	8 h	0				

Table III. *(Continued)*

Olefin	Method of preparation	Reaction time	Yield (%)	ν_{CO}[c] (cm^{-1})	^1H NMR absorptions (τ)	Anal. data C/H Calcd	Found
Norbornadiene	*a*	10 min	54	2065, 2030[d]	3.10 (m, 2, CH═), 3.89 (s, 2, CH═ complexed) 4.35 (s, 5, Cp), 6.34 (m, 2, CH), 8.11 (d, J = 11 Hz, 1, anti CH_2), 9.38 (d, J = 11 Hz, 1, syn CH_2)	47.2 3.65	46.9 3.87
Cyclooctatetraene	*b*	4 h	54	2053, 2012[d]	3.83 (m, 4, CH═), 4.16 (brs, 2, CH═), 4.28 (s, 5, Cp), 4.72 (m, 2, complexed CH═)		
	*g*		58	2070, 2032[d] 2230 (CN)	4.20 (m + s, 6, CH═, Cp), 4.48 (d, 1, CH═), 6.40 (d, 1, J = 8 Hz, CHCN), 7.1–8.3 (m, 4, CH_2)	37.62 2.91	37.42 2.88
	*g*		35	2058, 2016[d]	4.12 (m + s, 7, CH═, Cp), 6.35 (s, 3, CH_3OH) 6.95 (m, 1, $CHSO_3$), 7.1 (m, 4, CH_2)	42.63 4.25 S 9.08	43.82 4.49 8.99
	*g*		77	2060, 2022[h]	4.40 (s, 5, Cp), 4.52 (m, 2, CH═), 7.0–8.1 (m, 3, CH, CH_2), 8.4–9.5 (m, 2, CH_2), 8.9 (d, 3, J = 7 Hz, CH_3)	38.64 3.74	38.96 3.74
	*g*		86	2020, 2045[d]	4.25 (s, 5, Cp), 4.32 (m, 2, CH═), 4.88 (d, 1, J = 5 Hz, CHBr), 7.1–8.2 (m, 3, CH_2), 8.5–9.2 (m, 1, CH_2)	30.74 2.59	30.97 2.18
	*g*		90	2060, 2022[h]	2.66 (br s, 15, Ph), 4.45 (s, 5, Cp), 4.58 (m, 2CH═), 5.34 (m, 1, $CHCPh_3$), 7.5–9.0 (m, 4, CH_2)	58.81 4.46	58.64 4.20
	*a*		10	2070, 2020[m]	4.38 (s + m, 9, Cp, CH═, complexed and noncomplexed), 7.02 (m, 4, CH_2)	Fe16.2	15.9
	*a*	40 min	80	2050, 2000[d]	4.47 (s + m, 7, Cp, uncomplexed CH═), 4.9 (m, 2, complexed CH═), 7.2–8.2 (m, 8, CH_2)	48.43 4.60 Fe17.6	48.16 4.34 17.3

[a] By exchange with Fp(isobutylene)tetrafluoroborate. [b] From the epoxide. [c] In nitromethane solution unless otherwise noted. [d] In KBr. [e] Unstable in solution. [f] PF_6^- salt. [g] From reaction of (cyclopentenyl)Fp. [h] In CH_2Cl_2. [i] Reference 14. [j] Reference 9. [k] Reference 43. [l] By hydride abstraction from alkyl complex. [m] In Nujol suspension.

alumina (Camag, neutral, activity 3), with petroleum ether, to give 5.21 g (58%) of the cyclobutyl complex: ir (neat) 2007, 1910 cm^{-1}; NMR (CS_2) τ 5.40 (s, 5, Cp), 6.65 (m, 1, FpCH), 7.60–8.26 (m, 6, CH_2).

The cyclobutyl complex (5.63 g, 24 mmol) was added dropwise into a solution trityl tetrafluoroborate (8.25 g, 25 mmol) in 90 ml of methylene chloride cooled to 0°. After 1 h of reaction at room temperature, the product was precipitated by addition of 400 ml of ether, washed with ether, and dried to give 6.28 g (81%) of Fp(cyclobutene) tetrafluoroborate (**10a**). Spectral data and analysis are given in Table III.

Deprotonation of 10a. Fp(cyclobutene) tetrafluoroborate (0.318 g, 1.00 mmol) in 15 ml of methylene chloride was treated with 0.129 g (1.00 mmol) of ethyldiisopropylamine. After 2 h of reaction, solvent was removed and the gum was extracted with ether, filtered, and concentrated. Chromatography on 12 g of activity 3 alumina with 1:5 ether petroleum ether gave 0.135 g (59%) of (cyclobutenyl)Fp (**8a**).

Preparation of Complex 15a. (Cyclopentenyl)Fp (**8b**) was prepared by deprotonation of 3.12 g (8 mmol) of Fp(cyclopentene) hexafluorophosphate (**10b**) in methylene chloride with triethylamine (1.12 ml, 8 mmol) at room temperature. After filtration, the solution was treated with a methylene chloride stock solution of chlorosulfonyl isocyanate (8 mmol) at room temperature. The granular yellow precipitate was collected, washed with methylene chloride, and recrystallized from acetone–ether to give 1.9 g (58%) of **15a** as the hexafluorophosphate.

Preparation of Complex 15b. A solution of methyl *N*-(chlorosulfonyl)urethane (1.73 g, 10 mmol) in 20 ml of THF was cooled to −78° and sodium hydride (457 mg of 56% oil dispersion) was added. The solution was allowed to warm to 0° and (η^1-cyclopentenyl)Fp (2.4 g, 10 mmol) in 10 ml of THF was added. The solution was allowed to come to room temperature and reaction was continued for another hour. Solvent was removed and the residue was extracted with methylene chloride and filtered. The filtrate was concentrated and the residue was recrystallized from methanol–ether to give 1.3 g (37%) of the product **15b.** Spectral data and analysis are given in Table III.

Preparation of Complex 15c. Trimethyloxonium hexafluorophosphate (1.092 g, 5.30 mmol) was washed with methylene chloride, dried under nitrogen and taken up in a small volume of nitromethane. A nitromethane solution of cyclopentenyl complex (**8b**) (1.293 g, 5.30 mmol) was added to this at room temperature and reaction was al-

lowed to continue for 1 h. The yellow precipitate was collected, washed with ether, and recrystallized twice from acetone–ether to give 1.64 g (85%) of product **15c**. Spectral data and analysis are given in Table III.

Preparation of Complex 15d. A solution of bromine (0.688 g, 4.30 mmol) in 10 ml of ether was added to a solution of **8b** (1.05 g, 4.30 mmol) in 40 ml of ether, cooled to 0°. The yellow precipitate, which formed immediately, was collected, washed with ether, and dried to give 1.68 g (95%) of the salt as the bromide. This was taken up in nitromethane and treated with an equivalent of trimethyloxonium hexafluorophosphate to give the salt as the hexafluorophosphate after precipitation with ether and recrystallization from acetone–ether (86%). Spectral data and analysis are given in Table III.

Preparation of Complex 15e. Treatment of **8b** (0.657 g, 2.7 mmol) in methylene chloride solution at room temperature with trityl hexafluorophosphate (1.048 g, 2.7 mmol), followed by precipitation of the product with ether, gave 1.236 g (100%) of **15e** after recrystallization from acetone–ether. Spectral data and analysis are given in Table III.

Preparation of Fp(olefin)BF_4 Salts by the Exchange Reaction. General Procedure. A 1,2-dichloroethane solution of Fp(isobutylene)BF_4 containing 2 to 3 molar equiv of the exchanging olefin was maintained briefly at 60°. After cooling the solution to room temperature, ether was added and the precipitated salt was collected and washed with ether.

Preparation of Fp(olefin)BF_4 Salts from Epoxides. General Procedure. The epoxide was added slowly to an equimolar solution of NaFp,[14,42] in THF at 0°. After addition was complete, the solution was allowed to come to room temperature and reaction was allowed to continue for the specified time (Table III). The solution turned dark green when reaction was complete. The solution was then cooled to 0° (to −78° for unstable cations) and either 48% fluoroboric acid or 70% hexafluorophosphoric acid was added slowly. Diethyl ether was then added until precipitation of the salt was complete. The product could be recrystallized from a methylene chloride–acetone or nitromethane–ether solvent mixture. The salts are generally yellow, air-stable solids which decompose rather than melt on heating.

Table III lists the salts prepared either by the exchange reaction above or from the epoxide, as well as their spectral properties and analytical data.

Preparation of the Complex Cations 14 from 4-Vinylcyclohexene Diepoxide (13). A solution of NaFp (20 ml, 0.5 M) in THF was added dropwise and with stirring to 1.40 g (10.0 mmol) of 4-vinylcyclohexene diepoxide (**13**), dissolved in 5 ml of THF cooled to 0°. The solution turned dark green. After 1 h additional reaction at room temperature, the solution was poured into degassed water and extracted with ether. Workup gave a red oil which was placed on a Fluorisil column (60–100 mesh). Elution with Skelly B–ether (1:1) gave two bands, the first identified as Fp_2. The second, yellow band yielded 2.09 g (50%) of the intermediate epoxy alcohol: ir (neat) 1946, 2000 (C≡O), 3484 cm^{-1} (OH); NMR (CS_2) τ 5.10 (s, 5, Cp), 7.05, (m, 3, epoxide H and C*H*OH), 7.4–9.0 (br m, 10, CH, CH_2, OH).

A solution of the epoxy alcohol (1.0 g, 3.1 mmol) dissolved in 20 ml of anhydrous ether was added dropwise to excess fluoroboric acid (5.0 mmol). The precipitate was filtered, washed with ether, and dried in a stream of nitrogen to give 0.87 g (67%) of **14** as a yellow solid; ir (KBr) 3401 (OH), 2066, 2024 cm^{-1} (C≡O); NMR (CD_3NO_2) τ 4.28 (s, 5, Cp), 5.00 (m, 1, -CH=), 6.33 (m, 6, C*H*OH), CH_2=), 7.7 −8.8 (br m, 7, CH, CH_2). The PF_6 salt was prepared for analysis.

Anal. Calcd for $C_{15}H_{19}FeO_4PF_6 \cdot 2H_2O$: C, 36.00; H, 4.60; Fe, 11.20. Found: C, 35.40; H, 4.59; Fe, 11.23.

Preparation of Intermediate Complex Alcohol from *trans*-Crotonate Epoxide. Ethyl *trans*-2,3-epoxybutyrate (1.0 g, 10 mmol) was added at room temperature to a THF solution containing an equivalent of NaFp. After stirring for 7 h, the solution was poured in 100 ml of degassed water and then extracted with ether. The product was chromatographed on 50 g of neutral, activity 3 alumina. Elution with Skelly B, then 1% methanol–methylene chloride, gave Fp_2 followed by the alcohol (1 g, 32%) as yellow orange crystals: mp 64–65.5°; ir (KBr) 1675, 1969, 2024 cm^{-1}; NMR (CD_3NO_2) τ 5.07 (s, 5, Cp), 6.07 (q + m, 3, OCH_2 and C*H*OH), 6.75 (d, 1, J = 6 Hz, OH), 7.67 (d, 1, J = 6 Hz, FpCH), 8.73 (t, 3, J = 7 Hz, OCH_2CH_3), 8.79 (d, 3, J = 6 Hz, CH_3CHOH).

Anal. Calcd for $C_{13}H_{16}FeO_5$: C, 50.67; H, 5.20. Found: C, 50.84; H, 5.22.

Preparation of Intermediate Complex Alcohol from Cyclohexene Epoxide. Cyclohexene epoxide (1.47 g, 10 mmol) was added to an equivalent of NaFp in 20 ml of THF at room temperature. After 4 h of reaction, the dark green solution was poured into degassed water and worked up. The crude product as an amber oil was crystallized from Skelly-B to give 1.4 g (51%) of the alcohol as yellow crystals: mp 74.5–75°; ir (KBr) 1927, 2000, 3436 cm^{-1}; NMR (CS_2) τ 5.34 (s, 5, Cp), 6.88 (br m, 1, C*H*(OH)), 8.49 (br m, 10, CH_2, CH, OH). The complex is relatively stable in air, but decomposes in solution.

General Procedure for the Decomposition of Fp(olefin) Cations with Sodium Iodide. The olefin complex (0.2 mmol) was taken up in 0.5 ml of acetone-d_6 containing 0.2 mmol of benzene in a centrifuge tube. Sodium iodide (0.22 mmol) was added and the mixture was shaken until all of the salt was consumed. This varied with the olefin, being instantaneously with complexes of *cis*- and *trans*-stilbene and with ethyl crotonate, 2–5 min with complexes of styrene, acrolein, and cyclohexene, 15 min for propene, and 30 min with cyclopentene and cycloheptene. The ethylene complex failed to react under these conditions.

The reaction mixture was centrifuged and an NMR spectrum was taken of the supernatant. In all cases, quantitative conversion of the complex to FpI was observed. The NMR spectra of solutions derived from decomposition of *cis*- or *trans*-stilbene or ethyl *trans*-crotonate complexes failed to reveal the presence of isomeric olefin. Analysis of the olefins derived from decomposition of *cis*- or *trans*-2-butene complexes was carried out by GLC on a 40% silver nitrate–ethylene glycol on Chromosorb P column, employing authentic samples of olefins for calibration of retention times. These analyses failed to show the presence of isomeric olefins derived from each of the complexes.

Decomposition of *cis*- or *trans*-Stilbene Complex in Nitromethane. Isolation of Nitromethane Complex. The intermediate alkoxide (1.7 g, 3.4 mmol) formed in the reaction of *cis*- or *trans*-stilbene epoxide with NaFp, was suspended in 40 ml of ether cooled to −20°. A solution of 65% hexafluorophosphoric acid (1.5 ml, 6.9 mmol) dissolved in 20 ml of ether was added. The alkoxide went into solution and the olefin salt precipitated. This was collected and dissolved in nitromethane at room temperature. After filtering off sodium hexafluorophosphate, the nitromethane complex (**11**) was isolated (0.93 g, 73%) as an orange air-stable crystalline solid: ir (KBr) 2033, 2075 (C≡O), 1342, 1538 cm^{-1} (NO_2); NMR (CD_3NO_2) τ 4.50 (s, 5, Cp), 5.63 (s, 3, CH_3NO_2).

Anal. Calcd for $C_8H_8FeO_4NPF_6$: C, 25.08; H, 2.09. Found: C, 25.40; H, 2.12.

Preparation of TCNE Adducts (18 and 19). General Procedure. A 10% excess of TCNE in THF solution was added to a solution of the allyl complex in either THF or CH_2Cl_2 at 0° or room temperature. The yellow crystalline product was either recrystallized directly from CH_2Cl_2–hexane or purified by chromatography on neutral Camag activity 3 alumina. The physical properties and analytical data for the TCNE adducts are given in Table IV.

Preparation of TCNE Adduct 4b. A solution of **3b**[10] (0.400 g, 1.07 mmol) and TCNE (0.160 g, 1.25 mmol) in 20 ml of benzene was allowed to react for 30 min at room temperature. The pale yellow solid which formed was collected and recrystallized from acetone–benzene to give 0.480 g (88%) of **4b**. Spectral data and analysis are given in Table IV.

Preparation of Cobaloxime Complex 3d and Its TCNE Adduct 4d. Complex **3d** was prepared following the literature procedure[11] and employing allyl chloride as alkylating reagent. The orange compound was recrystallized from methylene chloride–ether, 150° dec.

Anal. Calcd for $C_{16}H_{24}CoN_5O_4$: C, 46.94; H, 5.88; N, 17.10 Found: C, 46.74; H, 5.64; N, 17.04.

The allyl complex **3d** (0.780 g, 1.91 mmol) and TCNE (0.246 g, 1.95 mmol) were taken up in 40 ml of benzene and stirred at room temperature for 2 h. The yellow precipitate was filtered to give 0.50 g of product. An additional 0.43 g was obtained from the solution, to give a total of 0.93 g (93%) of **4d**, 200° dec. An analytical sample was prepared by recrystallization from acetone–benzene.

Anal. Calcd for $C_{22}H_{24}CoN_9O_4$: C, 49.16; H, 4.50; N, 23.44. Found: C, 49.52; H, 4.52; N, 22.87.

Preparation of Chromium Complex 3e and Its TCNE Adduct 4e. Allylmagnesium chloride (12.5 ml, 2 M solution) was added dropwise to a solution of cyclopentadienylchromium dinitrosyl chloride[13] (5.35 g, 0.025 mol) in THF. Reaction was continued for 1 h, then solvent was removed and the residue was extracted with pentane. The extracts were chromatographed on 100 g of neutral, activity III alumina. Elution with hexane afforded a green band which yielded 200 mg of

Table IV. TCNE Adducts. Analytical Data and Properties

Adduct	Dec pt (°C)	Anal. data (C/H/N) Calcd	Found	ν_{CO} (cm^{-1})[a]	^1H NMR absorptions[b] (τ)
4b	205	40.64 2.08 11.15	40.50 2.17 11.05	2050, 1940	4.41 (s, 5, Cp), 6.8–7.7 (m, 5, CH_2, CH)[d]
4e	155	48.56 2.89 24.28	48.40 2.86 24.13	1792, 1666 (NO)	4.30 (s, 5, Cp), 6.4–7.3 (m, 5, CH, CH_2)
18a	200–204	55.49 2.89	55.54 2.81	2000, 1940	4.93 (s, 5, Cp), 6.58–7.74 (m, 5, CH_2, CH)
18b	147–148	56.67 3.33	56.42 3.37	2010, 1950	4.94 (s, 5, Cp), 6.64 (d, 2, J = 14.5 Hz, *trans*-FpCCH) 7.02 (d, 2, J = 14.5 Hz, *cis*-FpCCH), 8.36 (s, 3, CH_3)
18c	162	56.67 3.33	56.63 3.27	2005, 1945	4.88 (s, 5, Cp), 6.74–7.86 (m, 4, CH, CH_2), 8.51 (d, J = 6.0 Hz, CH_3)
18e	155	57.78 3.77	57.78 3.78	2010, 1950	4.87 (s, 5, Cp), 6.65–7.25 (m, 3, CH, CH_2), 8.46 (s, 3, CH_3), 8.68 (s, 3, CH_3)
18f	134	62.58 3.34	62.41 3.36	2010, 1960	2.46 (s, 5, Ph), 5.05 (s, 5, Cp), 6.00–7.30 (m, 4, CH, CH_2)
18g	*e*	57.72 3.88	57.74 3.94	2030, 1975 1720	4.94 (s, 5, Cp), 6.08 (dd, 1, J = 8.5, 1.5 Hz, FpCHC*H*) 6.60–7.54 (m, 4, CH, CH_2), 8.68 (d, 3, J = 5.0 Hz, CH_3), 8.78 (d, 3, J = 5.0 Hz, CH_3)
19a	178	57.01 2.81	57.15 3.10	2001, 1941	4.93 (s, 5, Cp), 6.78 (d, 2, J = 2.5 Hz, $H_{1,4}$) 7.08 (dt, 1, J = 2.5, 10 Hz, H_{5x}), 7.54 (d, 1, J = 10.0 Hz, H_6), 8.34 (t, 1, J = 10.0 Hz, H_{5n})
19b	137	58.09 3.25	57.86 3.36	2010, 1945	4.91 (s, 5, Cp), 6.87 (brs, 2, $H_{1,4}$), 7.09 (brs, 1, H_7) 7.65–8.49 (m, 4, CH_2)
19c	125	59.09 3.65	58.80 3.67	2010, 1950	4.90 (s, 5, Cp), 6.88 (brs, 3, $H_{1,4,8}$), 7.70–8.65 (m, 6, CH_2)
19d	91	60.02 4.03	59.84 4.15	2000, 1950	4.91 (s, 5, Cp), 6.65 (brs, 3, $H_{1,4,9}$), 7.55–8.65 (m, 8, CH_2)
19e	108	58.41 2.72	58.13 2.58	2015, 1960	3.40 (m, 2, $H_{5,6}$), 5.10 (s, 5, Cp), 6.12 (m, 2, $H_{1,4}$), 7.13 (m, 1, H_7)[c]
19f[f]	122	49.82 2.72	50.13 2.85	2010, 1950	4.57 (s, 2, CH_2Cl_2), 4.86 (s, 5, Cp), 6.29 (ddd, 1, J = 12.0, 7.0, 3.5 Hz, CHCN), 6.57–6.93 (m, 2, CH) 6.93–7.05 (m, 1, FpCH), 7.1–8.2 (m, 2, CH_2)
19g	55	59.09 3.65	59.21 3.83	2005, 1945	4.93 (s, 5, Cp), 6.82–7.50 (m, 4, CH), 7.5–8.3 (m, 2, CH_2), 8.62 (d, 3, J = 6.5 Hz, CH_3)

[a] In KBr. [b] Determined in CD_3NO_2 solution unless otherwise noted. [c] Determined in CD_2Cl_2 solution. [d] Determined in $(CD_3)_2CO$ solution. [e] Not determined. [f] Obtained as a methylene chloride monosolvate.

3e as a yellow-green oil (3.6%); NMR (CS_2) τ 3.9 (m, 1, CH=), 4.75 (s, 5, Cp), 5.15–5.8 (m, 2, CH_2=), 7.55 (d, 2, J = 8 Hz, CH_2).

The allyl complex (200 mg, 0.9 mmol) and TCNE (100 mg, 0.8 mmol) were stirred together in 10 ml of THF for 15 min. Solvent was then removed and the residue was recrystallized from methylene chloride–hexane to give 200 mg of **4e** (71%), mp 155–156°. Spectral data and analysis are given in Table IV.

Preparation of Adduct 6a. Complex **3a** (0.63 g, 2.9 mmol) in 10 ml of methylene chloride was added to **5** (0.55 g, 2.9 mmol) dissolved in 5 ml of the same solvent. After 3 h of reaction at room temperature, the solution was concentrated and hexane was added. The yellow solid was collected and recrystallized from ether–hexane to give 0.50 g (40%) of **6a**: mp 125–128°; ir (KBr) 1930, 2000 cm^{-1}; NMR ($CDCl_3$) τ 2.3–2.9 (m, 4, Ar), 5.15 (s, 5, Cp), 5.35–5.7 (m, 1, ArCH), 6.9–7.8 (m, 5, CH, CH_2).

Anal. Calcd for $C_{20}H_{15}ClFeN_2O_2$: C, 59.11; H, 3.69; N, 6.89; Cl, 8.74. Found: C, 59.01; H, 3.73; N, 6.82; Cl, 8.83.

Preparation of Adduct 6b. Complex **3b** (0.75 g, 2 mmol) and **5** (0.38 g, 2 mmol) were taken up in THF, and the solution was refluxed for 4 h. The solution was cooled, solvent was removed, and the residue was chromatographed on 100 g of neutral, activity III alumina. Starting complex was eluted with hexane and then the adduct was eluted with ether. Recrystallization of this product from ether–hexane gave 70 mg (6%) of **6b**: mp 159–161°; ir (KBr) 2030, 1900 cm^{-1}; NMR ($CDCl_3$) 2.66 (m, 4, Ar), 4.50 (s, 5, Cp), 5.70 (dd, 1, J = 7, 10 Hz, ArCH), 6.95–7.85 (m, 5, CH, CH_2).

Anal. Calcd for $C_{21}H_{15}ClN_2O_3W$: C, 44.80; H, 2.67; N, 4.98; Cl, 6.31. Found: C, 44.63; H, 2.75; N, 4.87; Cl, 6.35.

Preparation of Adduct 6c. Complex **7a** (2.32 g, 10 mmol) and **5** (1.7 g, 9.0 mmol), dissolved in 30 ml of methylene chloride, were refluxed for 2 h. Workup as with **6a** gave 3.2 g (85%) of **6c**: mp 123–124°; ir (KBr) 2020, 1960 cm^{-1}; NMR ($CDCl_3$) τ 2.66 (m, 4, Ar), 5.18 (s, 5, Cp), 5.33 (m, 1, ArCH), 7.06 (m, 2, CH_2), 7.6 (m, 2, CH_2) 8.20, 8.41 (2s, 3, two isomeric CH_3).

Anal. Calcd for $C_{21}H_{17}ClN_2O_2Fe$: C, 59.94; H, 4.04; N, 6.66; Cl, 8.44. Found: C, 59.83; H, 3.99; N, 6.66; Cl, 8.63.

Preparation of Toluenesulfonyl Isocyanate Adducts 20 and 21. General Procedure. A solution of the allyl complex in methylene chloride was added to an equivalent of toluenesulfonyl isocyanate in the same solvent. The crude product, obtained by removal of solvent after 30 min at room temperature, was purified either by crystallization from ether or by chromatography on alumina. Physical properties and analytical data for the lactams are summarized in Table V. The *trans*-methoxyallyl complex (**7k**)[3b] was prepared by metalation of *trans*-3-chloro-1-methoxy-1-propene.[44] Its tosyl isocyanate is recorded in the table along with that derived from the isomeric *cis*-methoxyallyl complex (**7l**), previously reported,[3b] for comparison purposes.

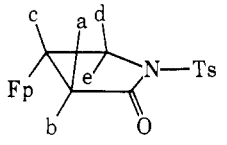
Preparation of Other Lactams. Lactams 20b and -c. The allyl complex **3a** (1.34 g, 6.12 mmol) in 60 ml of methylene chloride was cooled to −80°. A stock solution containing 6.12 mmol of $ClSO_2NCO$ was added by syringe. A yellow precipitate formed immediately. The cooling bath was removed and the solution was allowed to come to room temperature. The solution showed the presence of lactam by ir absorption at 2015, 1966, and 1766 cm^{-1}.

The solution was cooled to −40° and treated with 6.2 mmol of sodium methoxide and 12.4 mmol of thiophenol in 31 ml of methanol. The solution was allowed to warm to room temperature. Solvent was removed, leaving a yellow-brown gum. This was taken up in methylene chloride and precipitated with hexane and the precipitate was washed with hexane. Chromatography on alumina (Camag, neutral, activity 3) with methylene chloride gave 1.15 g (72%) of lactam **20c**: mp 180–181° dec; ir (KBr) 1996, 1942, 1675 cm^{-1}; NMR ($CDCl_3$) τ 3.55 (br s, 1, NH), 5.17 (s, 5, Cp), 6.25–8.10 (m, 5, CH, CH_2).

Anal. Calcd for $C_{11}H_{11}FeNO_3$: C, 50.57; H, 4.21; N, 5.36. Found: C, 49.79; H, 4.04; N, 5.22.

Lactam 20d. A methylene chloride solution containing 1.04 g (5.5 mmol) of 2,5-dichlorophenyl isocyanate (50 ml) and 1.20 g (5.5 mmol)

Table V. Tosyl Isocyanate Adducts. Analytical Data and Properties



20

Adduct	Mp (°C)	Anal. data (C/H) Calcd	Found	ν_{CO} (cm^{-1})	^1H NMR absorption (τ)[a]
20a	120–122	52.06 4.13	52.36 4.08	2005, 1950[b] 1725	2.10 (d, 2, J = 8.5 Hz, Ar), 2.58 (d, 2, J = 8.5 Hz, Ar) 5.02 (s, 5, Cp), 5.83 (dd, 1, J = 7.5, 9.5 Hz, H_d), 6.27 (t, 1, J,J' = 9.5 Hz, H_e), 7.10–7.95 (m, 3, H_a, H_b, H_c) 7.57 (s, 3, CH_3)
20e	99–100	53.15 4.47	52.97 4.51	2010, 1950[c] 1740	2.11 (d, 2, J = 8.5 Hz, Ar), 2.58 (d, 2, J = 8.5 Hz, Ar) 5.01 (s, 5, Cp), 5.84 (d, 1, J = 10.5 Hz, H_d), 6.14 (d, 1, J = 10.5 Hz, H_e), 7.36 (d, 1, J = 17.0 Hz, H_a) 7.78 (d, 1, J = 17.0 Hz, H_b), 7.57 (s, 3, CH_3Ar), 8.75 (s, 3, CH_3)
20f	71–73	54.19 4.78	54.03 4.81	1995, 1940[b] 1730	2.12 (d, 2, J = 8.5 Hz, Ar), 2.61 (d, 2, J = 8.5 Hz, Ar), 4.95 (s, 5, Cp), 6.04 (dd, 1, J = 8.5, 10.0 Hz, H_d) 6.29 (t, 1, J = 10.0 Hz, H_e), 7.27 (dd, 1, J = 8.5, 10.0 Hz, H_c), 7.57 (s, 3, CH_3Ar), 8.96 (s, 3, $CH_3)_a$, 9.24 (s, 3, $CH_3)_b$
20i		58.67 4.31	59.11 4.36	2010, 1950[c] 1740	2.06 (d, 2, J = 8.5, Ar), 2.45–3.0 (m, 7, Ph + Ar), 5.19 (s, 5, Cp), 5.74 (dd, 1, J = 7.5, 10.0 Hz, H_d), 6.18 (t, 1, J = 10.0 Hz, H_e), 6.63 (d, 1, J = 12.0 Hz, H_b), 7.25 (ddd, 1, J = 7.5, 10.0, 12.0 Hz, H_c), 7.29 (s, 3, CH_3)
20j	135–136		*e*	2012, 1953[b] 1715	2.06 (d, 2, J = 8.0 Hz, Ar), 2.66 (d, 2, J = 8.0 Hz, Ar) 5.16 (s, 5, Cp), 6.13 (dd, 2, H_d, H_e), 6.70 (s, 3, OCH_3), 6.72 (d, 1, J = 5 Hz, H_a), 7.40 (ddd, 1, J = 9, 9, 5 Hz, H_c), 7.58 (s, 3, $ArCH_3$)
20k	120–121	51.25 4.32 N 3.15	51.09 4.28 3.17	2010, 1958[b] 1720	2.02 (d, 2, J = 8.0 Hz, Ar), 2.64 (d, 2, J = 8.0 Hz, Ar), 5.08 (s, 5, Cp), 6.00 (dd, 1, J = 10.5, 8.5 Hz, H_d), 6.37 (t, 1, J = 10.5, 10.5 Hz, H_e), 6.37 (s, 3, OCH_3), 6.40 (d, 1, J = 12.0 Hz, H_b), 7.55 (ddd, J = 8.5, 10.5, 12 Hz, H_c), 7.55 (s, 3, $ArCH_3$)
21a	97–99	54.43 4.35	54.36 4.38	2000, 1925[b] 1725	2.12 (d, 2, J = 8.5 Hz, Ar), 2.56 (d, 2, J = 8.5 Hz, Ar), 5.02 (s, 5, Cp), 5.51 (brs, 1, CHN), 7.17 (brs, 1, CHFp), 7.56 (s, 3, CH_3), 7.5–9.0 (m, 5, CH_2, CHCO)
21b	102–103	55.39 4.66	55.70 4.63	2010, 1940[c] 1720	2.02 (d, 2, J = 8.5 Hz, Ar), 2.55 (d, 2, J = 8.5 Hz, Ar), 4.98 (s, 5, Cp), 5.58 (brs, 1, CHN), 6.76 (t, 1, J = 4.5 Hz, CHFp), 7.55 (s, 3, CH_3), 7.7–9.0 (m, 7, CH_2, CHCO)
29	153	54.68 3.90	54.55 4.07	2025, 1960[d] 1670	2.02 (d, 2, J = 8.5 Hz, Ar), 2.63 (d, 2, J = 8.5 Hz, Ar) 3.42 (m, 2, CH=), 4.26 (m, 2, CH=), 5.10 (s, 5, Cp) 7.55 (s, 3, CH_3), 7.5–8.0 (m, 1, NH)

[a] Taken in CD_3NO_2; assignments of H_d + H_e in 29a,e,f,i are tentative. [b] In KBr. [c] In CH_2Cl_2. [d] In acetone-d_6. [e] Reference 3b.

of **3a** was refluxed for 75 h. The solution was passed through an alumina column and the eluate, containing lactam was rechromatographed eluting with ether. The crude product was recrystallized from methylene chloride–hexane to give 352 mg (15%) of **20d**: mp 153–155°; ir (KBr) 1930, 1995, 1687 cm^{-1}; NMR ($CDCl_3$) τ 2.7 (m, 3, Ar), 5.14 (s, 5, Cp), 6.21 (d, 2, J = 8.5 Hz, CH_2N), 7.1 (m, 1, CH), 7.40 (d, 2, J = 6 Hz, CH_2CO).

Anal. Calcd for $C_{17}H_{13}FeCl_2NO_3$: C, 48.38; H, 3.08; N, 3.32. Found: C, 48.10; H, 3.15; N, 3.29.

Reaction of 7d with Trichloroacetyl Isocyanate. Preparation of Complex 20h. Complex **7d** (2.46 g, 10 mmol) and trichloroacetyl isocyanate (2.08 g, 11 mmol) were mixed together in 40 ml of methylene chloride at −78°. The solution was allowed to come to room temperature and allowed to react for 2 h. Sodium hydroxide (100 ml, 0.1 N) was then added, followed by 50 ml of methylene chloride. The mixture was shaken for 15 min, the organic layer was separated, solvent was removed, and the residue was recrystallized from methylene chloride–hexane to give 2.1 g (73%) of **20h**: mp 191–192° (lit.[3c] 191–193°); ir (KBr) 2010, 1940, 1670 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}NFeO_3$: C, 53.97; H, 5.19; N, 4.84. Found: C, 53.91; H, 5.22; N, 4.80.

Lactam 21c. (Cyclohexene)Fp tetrafluoroborate (**10c**) (1.04 g, 3 mmol) in 40 ml of methylene chloride was cooled to 0° and treated with 0.42 ml (3 mmol) of triethylamine by dropwise addition. Deprotonation was immediate. A stock solution of methoxysulfonyl isocyanate[45] in methylene chloride (3 mmol) was added at 0°. After 30 min, the reaction mixture was poured into water and extracted with methylene chloride. Removal of solvent from the dried extracts left a red gum which was extracted with ether. On concentration, 265 mg (22%) of yellow-orange crystals, mp 78–80°, were obtained; ir (CH_2Cl_2) 1958, 2005, 1740, 987, 1180 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}FeNO_6S$: C, 44.66; H, 4.24; N, 3.47. Found: C, 45.47; H, 4.40; N, 3.38.

Reaction of 3a with Trichloroacetyl Isocyanate. Preparation of Complex 28. The allyl complex **3a** (1.20 g, 5.5 mmol) in 7 ml of methylene chloride was treated with trichloroacetyl isocyanate (1.04 g, 5.5 mmol) at room temperature. After 1 h, solvent was removed and the residue was crystallized from methylene chloride–hexane to afford 0.9 g (40%) of **28** as an orange solid: ir (KBr) 2020, 1960 (C≡O) 1710, 1650 (C=O), 1560 cm^{-1} (C=C); NMR ($CDCl_3$) τ 0.97 (br s, 1, NH), 2.3 (m, 1, CH=) 3.42 (d, 1, J = 15 Hz, CH=), 5.21 (s, 5, Cp), 7.87 (d, 2, J = 10 Hz, CH_2).

Anal. Calcd for $C_{13}H_{10}FeCl_3NO_4$: C, 38.40; H, 2.46; N, 3.44; Cl, 26.19. Found: C, 38.42; H, 2.46; N, 3.45; Cl, 26.23.

Reaction of 3a with Methyl *N*-Sulfonylurethane. Preparation of Complex 30. A solution of methyl *N*-(chlorosulfonyl)urethane (1.39 g, 8.0 mmol) in 20 ml of THF was cooled to −78°. Sodium hydride (0.2 g, 8.3 mmol) was added and the mixture was stirred for 5 min and then allowed to warm to −10°. The allyl complex **3a** (1.71 g, 8 mmol), dissolved in 10 ml of THF, was then added and the solution was allowed to come to room temperature. After 2 h, solvent was removed, methylene chloride was added, and NaCl was filtered off. The filtrate was concentrated and the residue was recrystallized from methylene chloride–ether to give 1.2 g (46%) of **30**: mp 128–129°; ir (KBr) 2000,

1940 cm^{-1} (C≡O), 1700 (C=O), 1340, 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 4.95 (s, 5, Cp), 6.05 (s, 3, CH_3), 5.9–7.2 (m, 5, CH, CH_2).

Anal. Calcd for $C_{12}H_{13}NSO_6Fe$: C, 40.56; H, 3.66; N, 3.94; S, 9.01. Found: C, 40.33; H, 3.49; N, 3.78; S, 8.78.

Reaction of 3a with Dimethyl Methylenemalonate. Preparation of Complex 32. A solution of **3a** (0.87 g, 4.0 mmol) and freshly prepared dimethyl methylenemalonate[40] (0.72 g, 5.0 mmol) in 20 ml of ether was stirred overnight at room temperature. Solvent was removed and the residue was chromatographed on activity III alumina. Starting material was eluted with pentane, followed by Fp_2 with hexane–ether (4:1). Continued elution with hexane–ether (3:2) gave the product **32** as yellow crystals after slow recrystallization from ether–hexane, 0.95 g (66%): mp 82–82.5°; ir (KBr) 2020, 1940 (C≡O), 1730 cm^{-1} (C=O); NMR ($CDCl_3$) τ 5.21 (s, 5, Cp), 6.30 (s, 6, CH_3), 7.15–8.5 (m, 7, CH, CH_2).

Anal. Calcd for $C_{16}H_{18}FeO_6$: C, 53.04; H, 4.97. Found: C, 53.21; H, 5.04.

Reaction of 3a with Sulfene. Preparation of Complex 33. A solution of **3a** (1.09 g, 5.0 mmol) and methane sulfonyl chloride (2.29 g, 20 mmol) in 20 ml of methylene chloride was cooled to 0°. Triethylamine (2.02 g, 20 mmol) was added and the solution was stirred for 1 h. Solvent was removed in vacuo and the residue was chromatographed on activity III alumina. After eluting starting material with hexane and Fp_2 with ether–hexane (1:4), the product was eluted with methylene chloride and recrystallized from methylene chloride–hexane to give 180 mg (12%) of **33**: mp 125–127°; ir (KBr) 2015, 1950 (C≡O), 1280, 1110 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 5.11 (s, 5, Cp), 6.6–8.1 (m, 7, CH, CH_2).

Reaction of (Dimethyl ketene)piperidineimmonium Hexafluorophosphate (34) with 3a. *N*-(1-Chloro-2-methylpropenyl)piperidine was prepared from *N*-piperidinoisobutyramide and phosgene.[41] Silver hexafluorophosphate (1.04 g, 4.10 mmol) was dissolved in 40 ml of methylene chloride and the α-chloroenamine (0.712 g, 4.10 mmol) was added dropwise with stirring at −80°. The reaction was allowed to proceed at −60° for 30 min, then **3a** (0.894 g, 4.10 mmol) was added. The mixture was allowed to come to room temperature, and was then filtered and the filtrate was concentrated. Trituration with ether gave the product **35** as a pale-yellow solid (2.04 g, 100%): ir (KBr) 2005, 1955 (C≡O), no absorption between 1620 and 1690 (C=N^+<), 835 cm^{-1} (PF_6); NMR (CD_3NO_2) τ 4.98 (s, 5, Cp) 5.7–8.3 (several m, 15, CH, CH_2), 8.20, 8.31 (2s, 6, CH_3).

Anal. Calcd for $C_{19}H_{26}FeO_2NPF_6$: C, 45.53; H, 5.23. Found: C, 45.34; H, 5.24.

Hydrolysis of Complex 35. A solution of **35** (1.168 g, 2.33 mmol) in 40 ml of acetone was stirred for 12 h with 100 ml of 1% aqueous oxalic acid. After ether extraction and chromatography on 15 g of alumina (Camag, neutral, activity 3) product **36** was obtained as an orange oil (0.121 g, 19%): ir (neat) 2010, 1950 (C≡O), 1640 (C=O), 1570 cm^{-1} (C=C); NMR (CD_3NO_2) τ 2.97 (dt, 1, J = 15.0, 9.0 Hz, =CH), 4.18 (d, 1, J = 15.0 Hz, =CHCO), 5.31 (s, 5, Cp), 7.31 (septet, 1, J = 7.0 Hz, CHCO), 7.95 (d, 2, J = 9.0 Hz, CH_2Fp), 9.01 (d, 6, J = 7.0 Hz, CH_3).

Treatment of this product with TCNE gave the adduct as greenish yellow crystals in 60% yield: ir (KBr) 2030, 1975 (C≡O), 1720 cm^{-1} (C=O); NMR (CD_3NO_2) 4.94 (s, 5, Cp), 6.08 (dd, 1, J = 8.5, 1.5 Hz, $CHC(CN)_2$), 6.6–7.5 (m, 4, CH, CH_2), 8.68 (d, 3, J = 5.0 Hz, CH_3), 8.78 (d, 3, J = 5.0 Hz, CH_3).

Anal. Calcd for $C_{20}H_{16}FeN_4O_3$: C, 57.72; H, 3.88; N, 13.46. Found: C, 57.74; H, 3.94; N, 13.29.

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