Metal Assisted Carbon–Carbon Bond Formation. Addition of Carbon Nucleophiles to Dicarbonyl η^5-Cyclopentadienyl(olefin)iron Cations[1]

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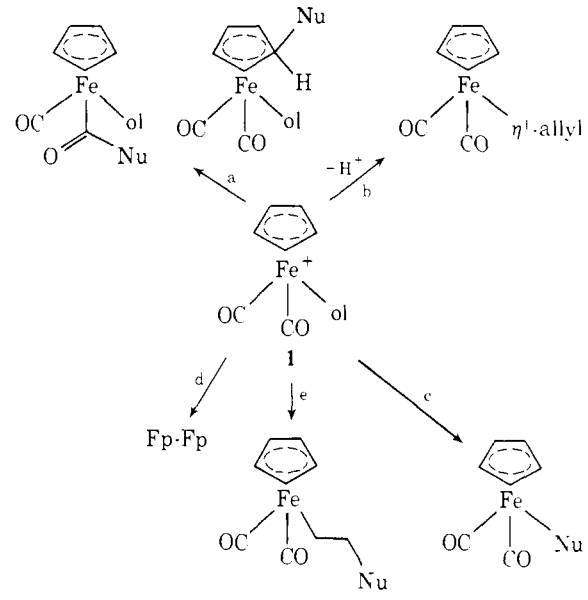
Abstract: A new carbon-carbon bond synthesis is described, which involves the addition of carbon nucleophiles to olefins, activated as dicarbonyl η^5-cyclopentadienyl(olefin)iron cations (**10**, **13**, **14**). Enolates derived from malonates, acetoacetates, cyanoacetates, and nitromethane as well as enamines of isobutyraldehyde, cyclopentanone, and cyclohexanone have been condensed with a number of such olefin complexes including those of ethylene, propylene, styrene, butadiene, cyclopentene, cyclohexene, and allene. The addition of nucleophile occurs trans to the iron olefin bond in the complex. The regiospecificity of these additions is low for the propylene complex, but generally high for the styrene complex, the products being derived from addition of nucleophile to the benzylic carbon atom. Direct addition to the coordinated bond in the butadiene complex (**10d**) is observed with malonate, but mixtures of products derived from direct and conjugate addition are obtained with cyclohexanone pyrrolidine enamine. The 1,2 adduct (**37**) undergoes ligand transfer (RFeCO → FeCOR) and chelation with high diastereoselectivity. The factors promoting such selectivity are examined. Treatment of enolate adducts (**11**) with trityl cation generally led to reversion, by abstraction of the nucleophile fragment. However, with the cyclopentene complex (**13**) the sequence of nucleophile addition, hydride abstraction, and nucleophile addition was successfully employed in the synthesis of a trans,trans 1,2,3-trisubstituted cyclopentane derivative (**21**). In general, the reaction of either Grignard (excluding phenyl Grignard) or lithio reagents with the olefin-iron complexes leads to olefin displacement and reduction of the organometallic radical. Lithium dimethylcuprate is a more generally satisfactory reagent for addition reactions. The stabilized ylide (**51**) adds to the ethylene complex (**10a**) and the adduct (**52**) was successfully transformed to an ylide and thence to an olefin (**54**) by Wittig condensation with benzaldehyde.

Reactions which lead to the formation of carbon-carbon bonds are of central importance in organic synthesis. Of this class, those which proceed through an inversion of the normal charge affinity[2] of one of the reactants provide rich synthetic opportunities. An example of one such reaction is the addition of nucleophiles to olefinic centers coordinated to a transition metal. The literature is by now replete with examples of such additions to metal coordinated polyene and polyenyl systems,[3] but, with the exception of the very extensive chemistry of palladium and platinum,[4] the reactions of nucleophiles with simple olefinic complexes have not been widely examined.

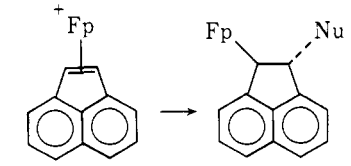
The present report provides an account of the reactions of dicarbonyl η^5-cyclopentadienyl(olefin)iron cations (**1**) with a number of simple carbon nucleophiles (in Scheme I and elsewhere, Fp stands for the η^5-$C_5H_5Fe(CO)_2$ radical). A separate account of the addition of heteroatomic nucleophiles[5] to these complex cations and a summary of the methods available for their synthesis[6] has recently been given.

Generalized Pathways for the Reaction of Nucleophiles with Fp(olefin) Cations. A number of pathways are in principle available for the reaction of nucleophiles with the complex cation (**1**). These are summarized in Scheme I. Of these, nucleophilic addition to either the cyclopentadienyl ring or to a carbonyl ligand (path a), which has been observed with Fp(allene)[7] or FpL cations[8] (L = CO, CS, PPh_3), is not observed with simple olefin complexes. Allylic deprotonation (path b) does not generally compete effectively with the remaining reaction modes, except with the very acidic Fp(cyclopentadiene) and Fp(indene) cations. However, for some nucleophiles, processes leading to displacement of the ligating olefin (path c) and to formation of complex dimer $(C_5H_5Fe(CO)_2)_2$ (path d) can compete effectively with the desired addition reaction (path e). Displacement becomes the dominant reaction mode with Fp(cyclooctene) and *exo*-Fp(norbornene) cations where steric effects block trans addition to the coordinated olefin, or, as with heteroatomic nucleophiles, the addition process may be reversible. Although this latter complication has not generally been observed with carbon nucleophiles, reductive reactions (path d) are, however, especially common with simple unstabilized carbanions such as alkyllithium and alkyl Grignard reagents.

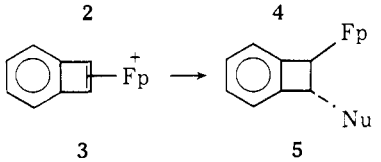
Scheme I



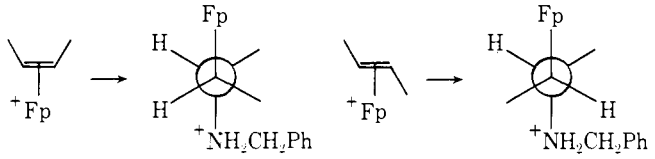
Stereochemistry of Nucleophilic Addition. While the stereochemistry of nucleophilic addition to Fp(olefin) cations has not been examined for each of the reactions carried out, the addition of both carbon and heteroatomic nucleophiles has been shown to proceed stereospecifically with the acenaphthalene[9] and benzocyclobutadiene[10] complexes (**2** and **3**) producing the trans adducts only. Trans addition has also been shown to be the course of addition of benzylamine to *cis*- and *trans*-Fp(2-butene) cations (**6** and **7**),[29] affording the diastereomeric adducts **8a** and **8b**. Furthermore, nucleophilic addition to polyene and polyenyl metal complexes has generally been observed to take place trans to the metal-ligand bond.[3,11] Accordingly a similar course of reaction has been assumed to apply to all addition reactions reported here.



2 4



3 5

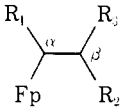


6 8a 7 8b

Addition of Enolate Anions. The addition of enolate anions to Fp(olefin) cations is particularly facile and uncomplicated by side reactions. The enolates (**9a–f**), generated by treatment of the activated methylene compounds with lithium bis(trimethylsilyl)amide,[12] react readily with a suspension of the olefin salt in THF at temperatures below 0 °C. The products, either amber, air-stable oils or yellow solids, were purified by column chromatography on alumina. Analytical and spectral data for these are given in Table I.

	R_1	R_2	R_3
9a	H	COOMe	COOMe
b	H	COMe	COOEt
c	Me	COOEt	COOEt
d	H	CN	COOEt
e	H	H	NO_2
f	Ph	COOEt	COOEt

	R
10a	H
b	Me
c	Ph
d	$CH=CH_2$
e	CH_2CH_2Ph
f	$CMe=CH_2$



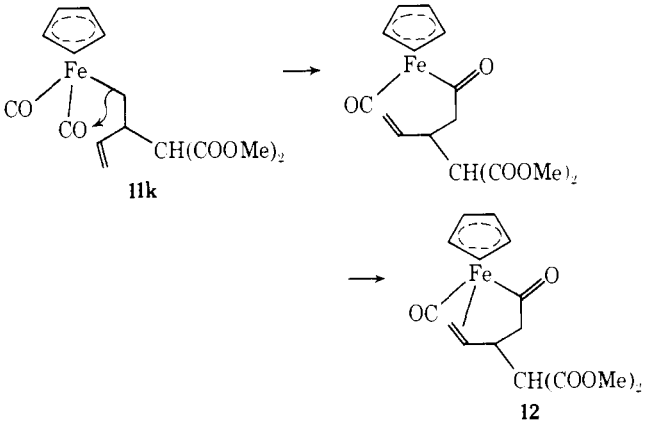
	R_1	R_2	R_3
11a	H	H	$CH(COOMe)_2$
b	H	H	CH(COMe)(COOEt)
c	H	H	$C(Me)(COOEt)_2$
d	H	H	CH_2NO_2
e	H	Me	$CH(COOMe)_2$
f	Me	H	$CH(COOMe)_2$
g	H	Me	CH(CN)(COOEt)
h	Me	H	CH(CN)(COOEt)
i	H	Ph	$CH(COOMe)_2$
j	H	Ph	CH(CN)(COOEt)
k	H	$CH=CH_2$	$CH(COOMe)_2$
l	H	$CH=CH_2$	H

A measure of the regiospecificity of these reactions is provided by an examination of the products derived from the propene and styrene complexes (**10b,c**). The addition of lithium dimethylmalonate or ethyl cyanoacetate to the propene complex proceeds in high yield and affords a mixture of regioisomers, as is clearly evidenced by the appearance of two η^5-cyclopentadienyl proton signals in the spectrum of each of the reaction mixtures. With the propene complex and malonate ion, the isomers are formed in a ratio of 2:1. These are assigned structures **11e** and **11f,** respectively, based on the integrated intensity of methyl doublet signals at τ 9.05 and 8.75 in the product. An examination of a number of (alkyl) Fp complexes has shown that in general a methyl substituent at C_β is more highly shielded than one bound to C_α (see structure **11**).[13]

The reaction of cyanoacetate anion with the propene complex is somewhat more regiospecific. The products, formed in a ratio of 3:1, are assigned structures **11g** and **11h.** Furthermore, the presence in the product spectrum of two doublet resonances (τ 6.67, 6.53, J = 5 Hz) of almost equal intensity, which are assigned to the γ-methine proton (-C*H*CN(COOEt)) in **11g,** suggests that the two diastereomeric adducts related to the principal regioisomer are formed in about equal amounts. An examination of the ^{13}C NMR spectrum of the product mixture confirms these assignments. In particular, off-resonance decoupling experiments provide identification of signals for α, β, γ, and methyl carbon atoms in each of the four diastereomeric products. The multiplicity of products is further evidenced by the presence of signals for four metal carbonyl, three ester carbonyl, and two cyano carbon nuclei in the product. These data are collected in Table IV.

The addition of malonate or cyanoacetate to the styrene complex (**10c**) is by contrast highly stereospecific, affording a single regioisomer (**11i,j**) in each reaction. In each, the presence of a (β-phenethyl)Fp fragment is signaled by two proton multiplet absorptions in the product NMR spectrum between τ 8.0 and 8.8, which are assigned to α-methylene protons in these complexes. Similarly situated protons in (β-phenethyl)Fp[14] are observed at τ 8.3, while those in (benzyl)Fp are at τ 7.23.[15] The proximity of methoxyl protons in the malonate adduct (**11i**) to the chiral center is further evidenced by two widely separated resonance signals for these protons at τ 6.37 and 6.87. For the cyanoacetic ester adduct, structure **11j** is supported by the presence in its NMR spectrum of two equally intense doublet signals at τ 6.33 and 6.55. These are assigned to the γ-methine proton in each of the two diastereomers of **11j,** which are evidently formed in equal amounts. The presence of two such closely related structural isomers is further confirmed by an examination of the ^1H NMR spectrum of this product taken in benzene solution at 270 MHz, which exhibits two equally intense cyclopentadienyl resonances separated by 5 Hz.

Nucleophilic addition to the butadiene complex (**10d**) can take place either by conjugate or direct addition to the coordinated double bond. With lithium dimethylmalonate a single product is formed in 86% yield. This substance exhibits resonance absorption for three vinylic protons between τ 4.5 and 5.3 (ABX set) and two single proton multiplets at τ 8.3 and 9.12. These data require that it be assigned structure **11k,**



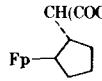
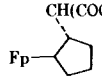
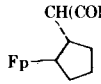
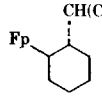
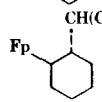
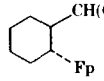
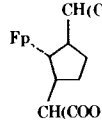
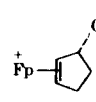
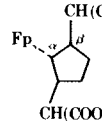
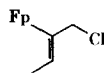
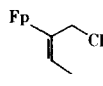
11k 12

derived from direct addition to C_2. Prolonged heating of the adduct in THF solution led to its recovery in high yield. Only a small amount of the chelate (**12**) derived from ligand transfer and olefin capture by the coordinatively unsaturated intermediate could be isolated. The closely related unsubstituted (3-butenyl)Fp complex has also been observed to resist thermal conversion to the acyl chelate on heating in THF.[16,17]

The cyclopentene and cyclohexene complexes (**13** and **14**) were examined as models for enolate addition to cyclic Fp-

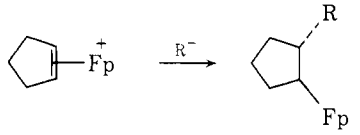
Table I. Enolate Addition to Fp(olefin) Cations

Olefin complex	Enolate	Product	Yield, %	Mp, °C	ν_{CO}, cm^{-1}	^1H NMR absorptions, τ	Anal. data Calcd	C, H, N Found
^+Fp—‖	$^-CH(COOMe)_2$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}CH(COOMe)_2$	98	Oil	2002, 1946[a]	8.84 (m, 2, α-CH_2), 8.08 (m, 2, β-CH_2) 6.80 (t, 1, J = 7 Hz, γ-CH), 6.43 (s, 6, OCH_3), 5.27 (s, 5, Cp)[d]	50.03 4.83	49.90 4.84
	$^-CH(COCH_3)COOEt$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}CH(COCH_3)(COOEt)$	80	47–48	2004, 1953[a]	8.75, (t, 5, CH_3, α-CH_2), 8.17 (m, 2, β-CH_2), 6.76 (t, 1, J = 7 Hz, γ-CH), 5.94 (q, 2, CH_2O), 5.27 (s, Cp), 7.92 (s, 3, CH_3CO)[d]	54.00 5.86	54.01 5.94
	$^-C(CH_3)(COOEt)_2$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}C(CH_3)(COOEt)_2$	84	Oil	2008, 1953[b]	8.84 (t, 8, CH_3 α-CH_2), 8.82 (s, 3, CH_3), 8.15 (m, 2, β-CH_2) 5.96 (q, 4, CH_2O), 5.30 (s, 5, Cp)	[e]	
	$^-CH_2NO_2$	$FpCH_2CH_2CH_2NO_2$	35	34–34.5	2016, 1953[c]	8.80 (m, 2, α-CH_2), 8.00 (m, 2, β-CH_2), 5.76 (t, 2, J = 6.5 Hz, γ-CH_2), 5.28 (s, 5, Cp)[d]	40.32 4.18 5.28	44.78 3.94 5.23
^+Fp—‖	$^-CH(COOMe)_2$	$Fp\overset{CH_3}{\overset{\vert}{\underset{\alpha}{CH}}}\overset{\beta}{CH_2}\overset{\gamma}{CH}(COOMe)_2$ $\overset{\alpha}{Fp}CH_2\underset{CH_3}{\underset{\vert}{\overset{\beta}{CH}}}\overset{\gamma}{CH}(COOMe)_2$	80	Oil	2005, 1955[a]	9.05 (d, J = 7 Hz, β-CH_3), 8.75 (d, J = 6.5 Hz, α-CH_3) 6.5–6.9 (d and t, γ-CH, both isomers), 7.4–8.5 (m, α and β CH, CH_2, both isomers) 6.38, 6.35 (2 s, OCH_3), 5.23, 5.18 (2 s, Cp)[d]	51.46 5.14	51.49 5.04
	$^-CH(CN)(CO_2Et)$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}\underset{CH_3}{\underset{\vert}{\overset{\gamma}{CH}}}CH(CN)(COOEt)$ $FpCH\underset{CH_3}{\underset{\vert}{CH_2}}CH(CN)(COOEt)$	90	Oil	2000, 1955[a]	8.93 (d, J = 6 Hz, β-CH_3), 8.71 (t, ester CH_3, α-CH_3) 7.5–8.5 (m, CH, CH_2), 6.67 6.53 (2 d, J = 5 Hz, γ-CH), 5.23, 5.25 (2 s, Cp)[d]	54.41 5.18 4.23	54.27 5.13 4.31
^+Fp—‖ Ph	$^-CH(COOMe)_2$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}CHPhCH(COOMe)_2$	85	Oil	2004, 1950[a]	8.75 (t, 1, $J_{\alpha\alpha'} = J_{\alpha'\beta}$ = 10 Hz, α-CH_2), 8.15 (dd, 1, $J_{\alpha\alpha'}$ = 10, $J_{\alpha\beta}$ = 2 Hz, α-CH_2), 6.87, 6.37 (2 s, 6, OCH_3), 6.4–6.6 (m, 2, CHPh, $CH(COOMe)_2$), 5.32 (s, 5, Cp) 2.87 (s, 5, Ph)[d]	58.28 4.88	57.99 4.88
	$^-CH(CN)(COOEt)$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}CHPhCH(CN)(COOEt)$	99	Oil	2020, 1957[a]	8.97 (2 t, 3, CH_3), 8.0–8.5 (m, 2, α-CH_2), 6.7–7.0 (m, 1, CHPh), 6.55, 6.33 (2 d, 1, J = 7.0, 6.5 Hz, CH(CN) (COOEt), 6.08 (2 q, 2, CH_2O), 5.45 (s, 5, Cp), 2.83 (s, 5, Ph)[d]	61.10 4.87 3.56	61.02 4.87 3.54
^+Fp—‖	$^-CH(COOMe)_2$	$\overset{\alpha}{Fp}\overset{\beta}{CH_2}\overset{\gamma}{CH}(\overset{\delta}{CH}{=}CH_2)(CH(COOMe)_2)$	86	40–42	2005, 1940[a]	9.12 (t, 1, $J_{\alpha\alpha'} = J_{\alpha\beta}$ = 10 Hz, α-CH_2), 8.3 (dd, 1, $J_{\alpha\alpha'}$ = 10, $J_{\alpha'\beta}$ = 2.5 Hz, α-CH_2), 7.5 (m, 1, β-CH), 6.76 (d, 1, J = 9 Hz, $CH(COOMe)_2$), 6.46, 6.38 (2 s, 6, OCH_3), 5.24 (s, 5, Cp), 4.5–5.3 (m, 3, $CH{=}CH_2$)[d]	53.08 5.01	53.03 5.14

	$^{-}CH(COOMe)_2$		93	Oil	2008, 1942[a]	7.5–8.7 (m, 8, CH, CH_2), 6.53 (d, 1, J = 5.5 Hz, $CH(COOMe)_2$), 6.44, 6.42 (2 s, 6, OCH_3), 5.28 (s, 5, Cp)[d]	54.00 5.86	54.04 5.83
	$^{-}CH(COOEt)_2$		89	Oil	2000, 1940[a]	8.81, 8.77 (2 t, 6, J = 7.0 Hz, CH_3), 7.8–8.8 (m, 8, CH, CH_2), 6.2 (d, 1, J = 4 Hz, $CH(COOEt)_2$), 6.0, 5.92 (2 q, 4, J = 7.0 Hz, CH_2O), 5.29 (s, 5, Cp)[d]	58.15 6.15	58.23 6.23
	$^{-}CH(COMe)(COOMe)$		61	Oil	2008, 1938[a]	8.45 (br s, 8, CH, CH_2), 7.9, 7.92 (2 s, 3, CH_3CO), 6.33, 6.36 (2 s, 3, OCH_3), 6.66, 6.43 (2 d, 1, CH(COMe) (CO_2Me)), 5.25 (s, 5, Cp)[d]	56.71 5.60	56.33 5.70
	$^{-}CH(COOEt)_2$		65	69.5–71	2000, 1942[c]	8.83, 8.77 (2 t, 6, CH_3), 7.7–8.8 (m, 10, CH, CH_2), 6.2 (d, 1, J = 4 Hz, $CH(COOEt)_2$), 6.0, 5.92 (2 q, 4, OCH_2), 5.28 (s, 5, Cp)[d]	57.43 6.26	57.52 6.38
	$^{-}CH(COMe)(CO_2Et)$		76	Oil	1996, 1938[a]	8.80, 8.75 (2 t, 3, CH_3), 7.95 (2 s, 3, $COCH_3$), 7.0–8.8 (m, 10, CH,CH_2), 5.7–6.3 (m, 3, OCH_2, CH(COOEt), 5.31, 5.28 (2 s, 5, Cp)[d]	58.79 6.23	58.78 6.22
	$^{-}CH(CN)(CO_2Et)$		94	132–133	1992, 1930[c]	8.70 (t, 3, CH_3), 7.5–8.8 (m, 10, CH, CH_2), 5.74 (q, d, 3, J = 7 Hz, OCH_2, J = 2 Hz, CHCN), 5.23 (s, 5, Cp)[d]	58.24 5.71 3.77	58.04 5.70 3.66
	$^{-}CH(COOMe)_2$		41	Oil	2004, 1949[a]	8.80 (t, 6, J = 7 Hz, CH_3), 6.4 (s, 6, OCH_3), 5.92 (q, 4, J = 7 Hz, OCH_2), 5.18 (s, 5, Cp)[d]	53.94 5.66	54.57 5.63
	$^{-}CH(COOMe)_2$		23	Oil	2004, 1921[c]	8.1–8.8 (m, 4, CH_2CH_2), 7.61 (br s, 3, α- and β-CH), 6.60 (d, 2, J = 6 Hz, $CH(COOMe)_2$), 6.38 (s, 12, OMe), 5.20 (s, 5, Cp)[d]	52.19 5.18	51.92 5.05
	$^{-}CH(COOMe)_2$		88	54.5–55.5	2010, 1955[a]	8.35 (dt, 3, J = 7, 1 Hz, CH_3), 7.23 (br d, 2, J = 7 Hz, CH_2), 6.40 (s, 6, OCH_3), 6.19 (t, 1, J = 7 Hz, $CH(COOMe)_2$), 5.14 (s, 5, Cp), 4.14 (q, 1, J = 7 Hz, CH═)[d]	53.08 5.01	53.06 4.98
	$^{-}CH(COOMe)_2$		*e*		2010, 1955[a]	8.38 (d, 3, J = 7 Hz, CH_3), 7.25 (br d, 2, J = 7 Hz, CH_2), 6.40 (s, 6, OCH_3), 6.2 (t, 1, J = 7 Hz, $CH(COOMe)_2$), 5.22 (s, 5, Cp), 4.66 (q, 1, J = 7 Hz, CH═)[d]		

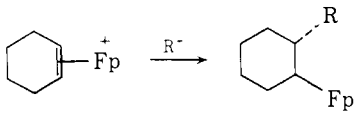
[a] Thin film, determined directly after chromatography before crystallization. [b] In hexane. [c] In KBr. [d] In CS_2. [e] Not determined. [f] In deuteriobenzene. [g] TCNE adduct. [h] In CD_3NO_2. [i] Data obtained at 270 MHz. [k] From a separate experiment.

(olefin) cations. Both of these complexes proved to be excellent substrates, affording high yields of adducts (**15** and **16**) as amber, air-stable oils with a number of stabilized enolates. As with acyclic olefin complexes, deprotonation of these cations (path b, Scheme I) does not compete with nucleophile addition to the activated olefin. However, reductive displacement of the ligand (path d) appears to be the predominant mode of reaction for the cyclohexene complex with the more hindered diethyl methylmalonate or diethyl phenylmalonate anions.



13 15

a, R = $CH(COOMe)_2$
b, R = $CH(COOEt)_2$
c, R = CH(COMe)(COOMe)
d, R =



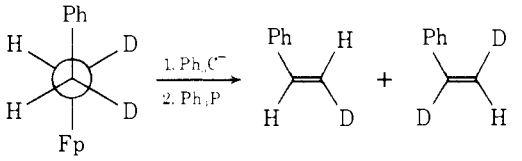
14 16

a, R = $CH(COOMe)_2$
b, R = CH(COMe)(COOEt)
c, R = CH(CN)(COOEt)

The relatively large magnetic anisotropy associated with the Fp group is reflected in the ^1H NMR spectra of the malonate adducts (**15a,b, 16a**), which clearly show the presence of diastereotopic ester groups by the doubling of signals for methyl and methylene ester protons. For adducts derived from the reaction of acetoacetic ester enolates (**15c, 16b**), the presence of equal proportions of diastereomers is likewise evidenced by the multiplicity and relative intensity of these signals in the ^1H NMR spectra of the products. Finally, the small coupling of the substituent methine proton in the cyanoacetic ester adduct (**16c**) with the adjacent ring proton (J = 2 Hz) is consistent with an equatorial conformation for this group,[18] as would be anticipated for trans addition of the nucleophile to the coordinated double bond.

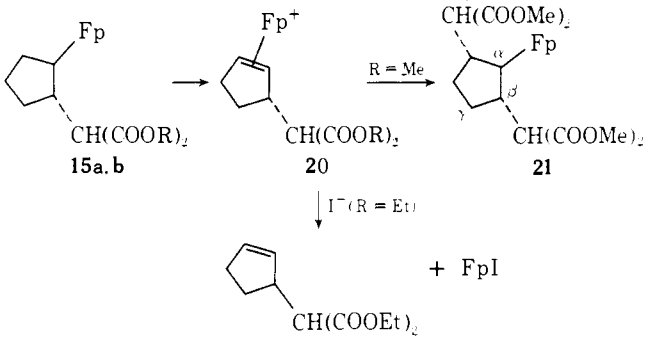
The prospect of effecting a double addition of nucleophile to an Fp(olefin) cation through the sequence of nucleophile addition, β-hydride abstraction,[19] and repeated addition appeared attractive and was therefore examined. In practice this sequence was found to be circumscribed by preferential loss of the substituent rather than hydride when the adducts are treated with trityl cation. Thus, although the malonate adduct (**11a**) is unchanged on treatment with trityl tetrafluoroborate in methylene chloride at 0 °C, reaction is rapid at 45 °C and leads to reversion of the adduct to the ethylene cation (**10a**). Reaction of the acetoacetate adduct (**11b**) with trityl cation is more rapid, but the results are the same, and **10a** is isolated in 67% yield after 1 h of reaction at 0 °C. In neither of these reactions was there evidence for the formation of a substituted ethylene complex. By contrast, the nitromethylate adduct (**11d**) resisted attack by trityl cation and could be recovered in high yield after extended reaction at 45 °C.

Preferential abstraction of malonate or acetoacetate by trityl cation may be due in part to stereoelectronic effects, which favor Fp-assisted elimination of the group antiperiplanar to the organometallic radical in the acyclic adducts. Thus, hydride abstraction from (*threo*-1,2-dideuterio-2-phenethyl)Fp (**17**), followed by displacement of the coordinated olefin by triphenylphosphine, has been reported to give **18** and **19** (in 1:2.5 ratio) in accord with expectations based on these stereochemical constraints.[20]



17 18 19

The cyclohexene-malonate adduct (**16a**) as well as the cyclopentene-acetoacetate adduct (**15c**), like their acyclic analogues, suffered reversion to unsubstituted olefin complex when treated with trityl cation at 0 °C. However, the cyclopentene-malonate adducts (**15a,b**) behaved differently and afforded the product of hydride abstraction (**20**) in high yield.



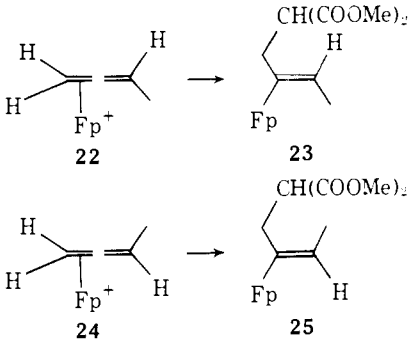
15a,b 20 21

The structure of the cation is evidenced by its ^1H NMR spectrum, which shows the presence of two vinyl protons. Treatment of **20** (R = Et) with sodium iodide in acetone solution liberated the free olefin, and this was further identified by comparison with an authentic sample prepared from 3-chlorocyclopentene and sodium diethylmalonate.[21]

The factors controlling the course of these abstraction reactions are not well defined, although hydride abstraction from (cyclohexyl)Fp complexes apparently occurs preferentially through a conformation in which the Fp group is axial.[22]

The addition of lithium dimethylmalonate to the substituted cyclopentene complex (**20**) proceeds in good yield and affords a single product, which is assigned structure **21** on the basis of its ^{13}C nmr spectrum. This shows a single metal carbonyl resonance at δ 218.98 and two closely spaced ester carbonyl signals at δ 170.67 and 171.32, in accord with a structure having a plane of symmetry passing through the Fp group. The presence of only seven other resonances assignable to cyclopentadienyl ring carbons, a pair of diastereotopic methoxyl carbons, cyclopentane carbon atoms, and the remaining malonate methine center confirms this assignment.

The reaction of heteroatomic nucleophiles with Fp(allene) cations has been shown to proceed generally by addition at C_1 of the allene ligand.[5,7] Similarly, the addition of lithium dimethylmalonate of Fp(*syn*-3-methylallene) (**22**) gave a (vinyl)Fp complex as a single stereoisomer (**23**) in high yield. Its assigned stereochemistry follows from trans addition to the



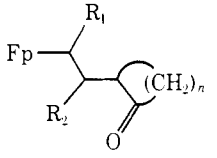
22 23 24 25

coordinated double bond. The isomeric product (**25**) is obtained with **23** when a mixture of *syn*- and (*anti*-3-methylallene)Fp cations (**22, 24**), obtained by thermal equilibration of **22**,[23] is treated with malonate.

Addition of Enamines. Enamines proved to be as useful in addition reactions with Fp(olefin) cations as are enolate anions. These reactions provide a general and simple route to ketone or aldehyde functionalized (alkyl)Fp complexes. Deprotonation of the Fp(olefin) cation, a reaction readily effected by tertiary amines, is not in general a complicating side reaction with enamines, possibly owing to the reduced basicity of these substances. Preferential N-alkylation of isobutyraldehyde enamine, which is the commonly observed reaction path with alkyl halides,[24] has not been encountered with either Fp(ethylene) or Fp(propene) cations. These results parallel those reported recently for the alkylation of isobutyraldehyde enamine by a cyclohexadienyliron tricarbonyl cation.[25]

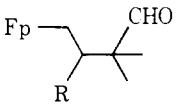
The reactions reported here were found to proceed readily at 0 °C in acetonitrile solution, and may be conveniently followed by observing the changes in metal–carbonyl absorptions typical of reactants (2060, 2020 cm^{-1}) and products (2005, 1950 cm^{-1}). Although it proved possible in a number of reactions to isolate the intermediate iminium salt by precipitation with ether, in situ hydrolysis of these with aqueous oxalic acid, or better with dilute aqueous sodium hydroxide, proved to be more practical. Analytical and spectral data for all compounds prepared are collected in Table II.

The pyrrolidine enamines of cyclopentanone and cyclohexanone afforded alkyl complexes **26a** and **26b,** in good yield, on reaction with ethylene complex (**10a**), while isobutyraldehyde enamine gave **27a** in quantitative yield with this cation.



26

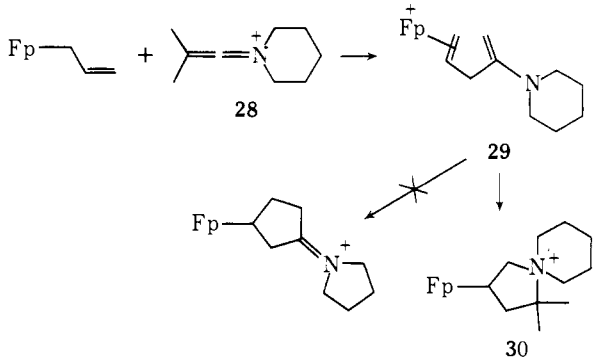
	R_1	R_2	n
a	H	H	3
b	H	H	4
c	Me	H	4
d	H	Me	4
e	Ph	H	4
f	H	Ph	4



27

a, R = H
b, R = Me

The C-alkylation of the latter enamine is particularly striking in view of exclusive N-alkylation which is observed in the closely related intramolecular reaction of the enamine (**29**) formed by condensation of (η^1-allyl)Fp and the keteneiminium cation (**28**).[6] However, the failure of **29** to ring close through



carbon is very likely the consequence of greater stereoelectronic constraints associated with this mode of reaction compared with ring closure through nitrogen.[26,27]

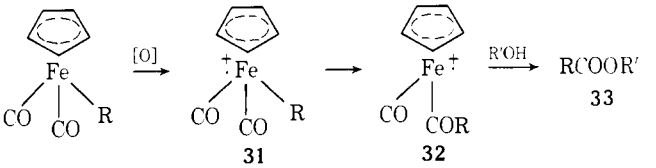
The propylene complex (**10b**) reacts with cyclohexanone pyrrolidine enamine in a manner closely paralleling its reaction with enolates. Two regioisomers (**26c,d**) are formed in not greatly disparate proportions and each is present as a mixture of diastereomers. This is readily evidenced by the presence of four cyclopentadienyl proton signals of nearly equivalent intensity in the NMR spectrum of the product. Further confirmation of this is to be seen in the ^{13}C NMR spectrum of the product, which clearly shows 29 of the expected 32 high-field resonances in addition to two cyclopentadienyl, three ketone, and four metal carbonyl carbon resonances.

The results with isobutyraldehyde piperidine enamine and the propene complex (**10b**) are strikingly different. A single product is obtained in 86% yield, the NMR spectrum of which shows only one cyclopentadienyl resonance, and a high-field methyl signal compatible with methyl substitution at the carbon atom β to iron. Structural assignment (**27b**) for this product is confirmed by an examination of its ^{13}C spectrum, which exhibits a high-field resonance (δ 4.42) typical of the $FpCH_2$ grouping. Off-resonance decoupling shows this peak to be a triplet, and the number of signals shown by the fully decoupled product spectrum is compatible with the presence of a single substance.

As with enolates, the styrene complex (**10c**) reacts with cyclohexanone pyrrolidine enamine to give a single regioisomer. However, the proton resonance spectrum, which shows a single cyclopentadienyl proton resonance, provides no firm basis for the assignment of structure. The ^{13}C spectrum is more informative. Two high-field resonances at δ 9.88 and 5.22 in a ratio of 3:1, which appear as triplets under conditions of partial decoupling, provide unequivocal evidence for the presence of the two diastereomers of structure **26f.** The minor diastereomer constitutes 20–40% of the mixture of products.

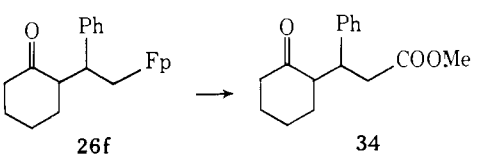
Two transformations of the adduct **26f** deserve comment. Treatment of this substance in ether solution at 0 °C with $HBF_4 \cdot Et_2O$ in an attempt to cleave the Fe–C bond led instead to the immediate and quantitative precipitation of the Fp(styrene) BF_4 salt. Cyclohexanone was identified in the ether solution. The same reversion reaction may be effected with HCl in methylene chloride, although somewhat less rapidly, and is clearly related in form to the cleavage of malonate and acetoacetate adducts by trityl cation.

Although carboalkoxylation of (alkyl)Fp complexes by oxidative demetalation, a process which may be depicted by the changes **31** → **32** → **33**,[28,29] has been effected with a



31 **32**

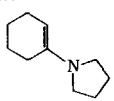
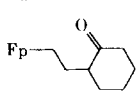
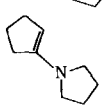
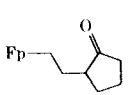
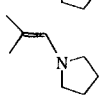
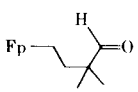
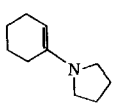
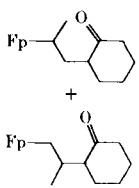
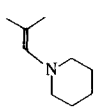
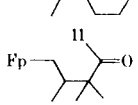
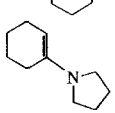
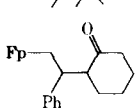
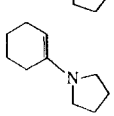
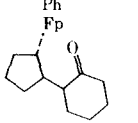
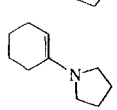
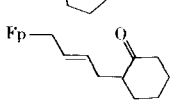
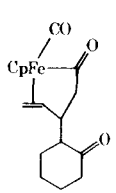
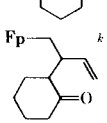
number of simple (alkyl)Fp complexes, the reaction has been little examined with functionalized complexes. When $CuSO_4$ in methanol is used to effect the conversion of **26f** only a low yield of ester (**34**) is obtained, but with excess Ce-



26f **34**

$(NH_4)_2(NO_3)_6$ this ester may be isolated in 90% yield. The sequence of enamine addition followed by oxidative demeta-

Table II. Enamine Addition to Fp(olefin) Cations

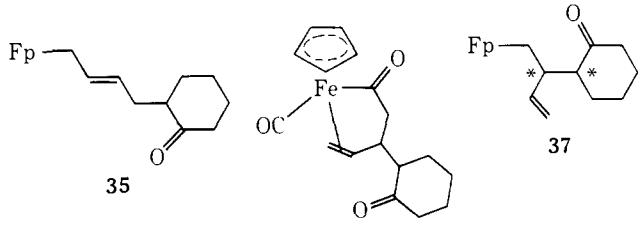
Olefin complex	Enamine	Product	Yield, %	Mp, °C	ν_{CO}, cm^{-1}	^1H NMR absorption, τ	Anal. data C, H	
							Calcd	Found
			60	32.4–33.5	2008, 1942[a]	7.7–8.8 (m, 13, CH, CH_2), 5.23 (s, 5, Cp)[d]	59.63 5.60	59.59 5.55
			71	Oil	2008, 1942[a]	7.7–8.8 (m, 11, CH, CH_2), 5.34 (s, 5, Cp)[d]	58.30 5.60	58.38 5.55
			98	31.5–32.5	2000 1940[a]	8.87 (s, 6, CH_3), 8.2–9.0 (m, 4, CH_2), 5.33 (s, 5, Cp), 0.75 (s, 1, CHO)[d]	56.55 5.84	56.52 5.80
			93	Oil	2012, 1946[a]	7.2–9.1 (br, CH, CH_2, CH_3), 5.33 5.25, 5.20, 5.17 (4 s, Cp)[d]	60.74 6.35	61.14 6.36
			86	Oil	2008, 1934[a]	8.2–9.2 (m, 12, *gem*-CH_3 β-CH_3, CH, CH_2), 5.32 (s, 5, Cp), 0.73 (s, 1, CHO)[d]	57.96 6.25	58.09 6.29
			90	79–80	2004, 1942[a]	6.5–9.0 (m, 12 CH, CH_2), 5.28 (s, 5, Cp), 2.88 (m, 5, Ph)[d]	66.61 5.86	66.80 5.94
			79	Oil	2000, 1934[a]	7.5–8.8 (m, 17, CH, CH_2), 5.30 (s, 5, Cp)[d]	63.23 6.47	63.33 6.36
			26	Oil	1995, 1950[a]	7.6–8.9 (m, 13, CH, CH_2), 5.60 (s, 5, Cp) 4.50 (dt, 1, J = 17, 10 Hz, CH=) 4.06 (dt, 1, J = 17, 10 Hz, CH–)[f,j]	62.22 6.19	63.30 6.13
			31	92.3–93.5	1942, 1638	6.6–8.6 (m 15, CH, CH_2) 5.29 (s, 5, Cp)[h]	62.22 6.19	60.21, 63.36 6.17, 6.47
			56	Oil	2004, 1946[c]	7.6–8.9 (m, 13, CH, CH_2), 5.62 (s, 5, Cp), 5.2–5.3 (m, 3, CH=CH_2)	*e*	

[a–k] See corresponding Footnotes to Table I.

lation may prove useful in those circumstances in which either Michael or enamine alkylation reactions fail. In the present context, the alkylation of cyclohexanone pyrrolidine enamine with methyl cinnamate failed to give appreciable yields of **34** even after prolonged refluxing in dimethylformamide solution.[30]

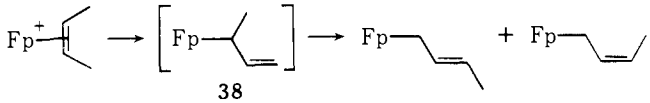
The addition of cyclohexanone pyrrolidine enamine to the Fp(cyclopentene) cation is complete within 3 h at 0 °C, and affords the ketone (**15d**) in 79% yield. As before, a trans stereochemistry is assigned to the cyclopentane ring substituents, and although only one cyclopentadienyl proton resonance is observed in the product spectrum, a mixture of diastereomeric adducts is presumed to be formed in the reaction.[31] A small amount of (3-cyclopentenyl)Fp, formed by deprotonation of the cation by the enamine, is observed in this reaction.

Reaction of cyclohexanone enamine with the Fp(butadiene) cation provides an interesting counterpoint to the reaction of malonate with this cation. When condensation is carried out in acetonitrile solution at 0 °C for 30 min, followed by hydrolysis of the iminium salt by brief heating with aqueous sodium hydroxide, two products are obtained. The first, isolated in 26% yield, is the product of conjugate addition as indicated by the presence of two rather than three vinyl proton signals in its NMR spectrum. Infrared absorption at 960 cm^{-1} suggests that it is the trans isomer (**35**), and this is amply



confirmed by its ^1H NMR spectrum, taken at 270 MHz, which provides a first-order spectrum of the vinyl proton region of this substance.

The exclusive formation of this adduct as the trans isomer suggests that it is formed directly from the butadiene complex (**10d**) by conjugate addition to the more stable s-trans form of this complex, rather than by a two-step process involving enamine addition to C_1, followed by a [1,3] sigmatropic change of the metal radical. Such a reaction would be expected to lead to both cis and trans isomers, since we have shown[6] that deprotonation of Fp(*cis*-2-butene)$^+$, a reaction which must proceed through (α-methallyl)Fp (**38**), affords a mixture of *cis*- and *trans*-(crotyl)Fp complexes.



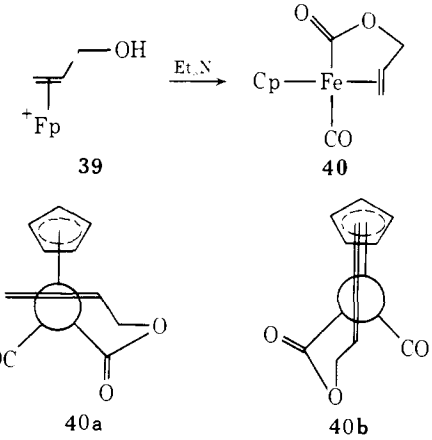
38

A second, crystalline and more polar product is isolated from the reaction of Fp(butadiene) cation and cyclohexanone enamine, in 31% yield. Its infrared spectrum shows only a single metal carbonyl absorption at 1942 cm^{-1} in addition to cyclohexanone absorption at 1702 cm^{-1} and an intense peak at 1638 cm^{-1}. Structure **36** is consistent with these data,[32] and is further supported by a ^1H NMR spectrum of the substance which shows no low-field vinyl proton resonances, but instead absorptions at τ 6.5–7.5, which are within the range expected for vinyl protons in an uncharged complex.[33] Finally, a mass spectrum of the complex shows a parent peak at *m/e* 328, in accord with structure **36.**

Complex **37**, the likely precursor of **36,** can be isolated from the condensation reaction of **10d** and cyclohexanone enamine in 56% yield by low-temperature hydrolysis of the reaction mixture, followed by rapid chromatography on alumina. The substance is identified by the presence of two metal-carbonyl absorptions in its infrared spectrum at 2004 and 1946 cm^{-1} and by three vinyl proton resonances in its ^1H NMR spectrum. The presence of two cyclopentadienyl proton signals of almost equal intensity suggests that the two possible diastereomeric products are present in roughly equal amounts. The resolution of diastereomeric cyclopentadienyl proton signals in this product is reminiscent of the adduct derived from cyclohexanone enamine and the Fp(propylene) cation, which also exhibited separate signals for **26c,d**. On heating **37** briefly in acetonitrile, it is converted to **36.**

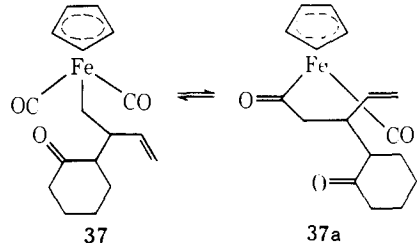
A striking aspect of this reaction is the high degree of its diastereoselectivity. Examination of the ^{13}C NMR spectrum of **36** shows only three signals in the region of cyclopentadienyl carbon resonances, at δ 88.26, 88.10, and 87.89, in a ratio of 52:35:13. Thus, of a total of eight possible diastereomers, only three are formed and of these one is a relatively minor component.

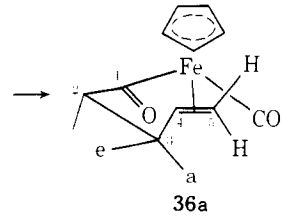
In a closely related example of diastereoselectivity, we showed that deprotonation of **39** led to the formation of the lactone **40** as a single diastereomer.[34] This may be assigned structure **40a,** since the second isomer (**40b**) is excessively



crowded owing to significant nonbonded interactions between the cyclopentadienyl ring hydrogens and those of the methylene group in the rigidly held complexed olefin ligand.

In the present context, the formation of two principal diastereomeric forms of **36** from **37** requires that one or both of



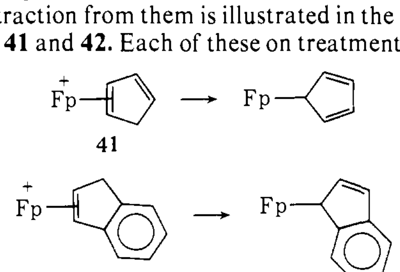


the chiral centers in the latter complex effectively control the stereochemistry of the process which leads through the coordinatively unsaturated intermediate (**37a**)[35a] to the final chelation step.

The precise mode by which chirality is induced at the iron center cannot be defined, but could in principle derive either from kinetically controlled relaxation of an achiral "planar"

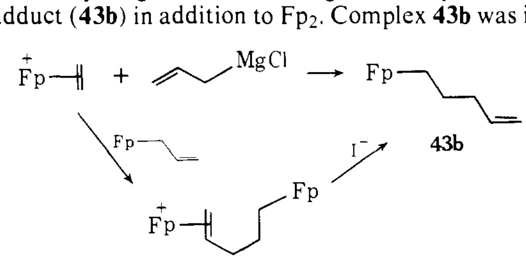
iron center in **37a** or through rapid equilibration of a chiral form of **37a**.[35b d] However, regardless of the precise details of this process, it is essential to recognize that the conversion of **37** to **36** simultaneously establishes both the configuration at the iron atom and the stereochemistry of substituents at C_3 on the chelate ring. Furthermore, models[34] show that, in the preferred diastereomeric form of the chelate ring, in which the olefin axis is roughly parallel to the Cp ring, the chelate ring may adopt a chairlike conformation in which the cyclohexanone substituent at C_3 is either equatorial or axial. In the latter configuration significant ,teric interactions exist between the substituent and cis hydrogens at C_2 and C_5. If then, as seems likely, the chelation step (**37a** → **36a**) is essentially irreversible under the reaction conditions, asymmetric induction at iron may be attributed to kinetically controlled formation of the preferred, equatorially substituted chelate ring. Furthermore, the activation energy for the chelation step must be greater than that associated with interconversion of nonplanar, enantiomeric iron configurations in **37a**.

Side Reactions. Deprotonation. The delicate balance between nucleophilic addition to these cationic complexes and proton abstraction from them is illustrated in the reactions of the cations **41** and **42**. Each of these on treatment with either



isobutyraldehyde or cyclohexanone pyrrolidine enamine gave the corresponding (η^1-allyl)Fp complexes derived from simple deprotonation. Similar proton transfer occurred when **41** was treated with lithium methyl acetoacetate at −70 °C. The results are not perhaps surprising since both of the complex cations would be expected to exhibit enhanced acidities.

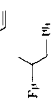
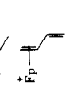
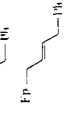
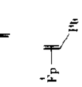
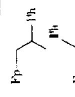
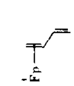
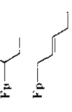
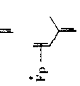
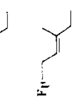
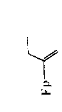
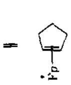
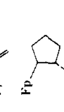
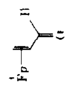
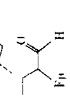
Unstabilized Carbanions. In general the reaction of either Grignard or lithio reagents with Fp(olefin) cations leads principally to olefin displacement by the anion and to reduction of the organometallic radical to the dimer Fp_2. Thus, methyllithium gave mainly Fp_2 and a small amount of (methyl)Fp when the reaction with Fp(ethylene)$^+$ was carried out either at room temperature or at −78 °C. A similar result was obtained with phenyllithium, but the adduct **43a** was also isolated from this reaction in 7% yield, in addition to biphenyl. Lithio-1,3-dithiane gave only Fp_2 with Fp(ethylene)$^+$, while lithium phenylacetylide gave principally the dimer Fp_2 and a small amount (10%) of displacement product, FpC≡CPh.[36] Methyl and vinyl Grignard reagents behaved similarly with Fp(ethylene)$^+$, the latter affording $FpCH{=}CH_2$,[37] in 25% yield, but allylmagnesium chloride gave a low yield (14%) of the adduct (**43b**) in addition to Fp_2. Complex **43b** was identi-



fied by comparison with the substance obtained by condensation of (η^1-allyl)Fp and Fp(ethylene)$^+$, followed by demetalation with iodide.[3]

Phenylmagnesium chloride proved to be more effective in additions to Fp(olefin) cations. With ethylene complex, a 66% yield of the adduct **43a** was obtained, while the propylene

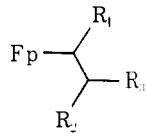
Table III. Carbanion Addition to Fp(olefin) Cations

Olefin complex	Carbanionic reagent	Product	Yield, %	Mp, °C	ν_{CO}, cm^{-1}	^{1}H NMR absorption, τ	Anal. data C,H,N Calcd	Anal. data C,H,N Found
	allyl-MgCl		14	Oil	2004, 1946[a]	8.53 (m, 4, CH_2), 7.98 (m, 2, CH_2), 5.35 (s, 5, Cp), 5.13 (m, 2, CH_2=), 4.30 (m, 1, CH=)[d]	58.57 5.69	58.40 5.86
	PhMgCl		43	Oil	2004, 1942[a]	8.82 (d, 3, J = 6 Hz, CH_3), 6.8–7.5 (m, 3, CH, CH_2), 5.07 (s, 5, Cp), 2.78 (s, 5, Ph)[h]	64.84 5.46	64.84 5.14
	PhMgCl		55	Oil	2000, 1942[a]	7.92 (d, 2, J = 7.0 Hz, $FpCH_2$), 6.82 (d, 2, J = 5.5 Hz, $PhCH_2$), 5.50 (s, 5, Cp), 4–5 (m, 2, CH=CH)[d]	66.12 5.24	66.00 5.42
	$LiCuMe_2$	 (major) (minor)	58	Oil	1996, 1931[a]	9.25 (t, 3, J = 7 Hz, CH_3 (minor isomer)), 8.74 (d, 3, J = 7 Hz, CH_3 (major isomer)), 5.66 (s, 5, Cp (minor isomer)), 5.55 (s, 5, Cp (major isomer))[d]	64.84 5.46	64.72 5.40
	$LiCuMe_2$		62	117–118[g]	2000, 1950[a]	9.08 (t, 3, J = 7 Hz, CH_3), 8.17 (m, 2, J = 7 Hz, CH_2), 7.94 (d, 2, J = 7 Hz, $FpCH_2$), 4–5 (m, 2, CH=CH), 5.44 (s, 5, Cp)[d]	57.78[g] 3.77 14.98	57.67 3.65 14.90
	$LiCuMe_2$		72	123–124[g]	1995, 1942[a]	9.08 (t, 3, J = 7.5 Hz, CH_3), 8.47 (s, 3, CH_3), 8.13 (q, 2, J = 7 Hz, CH_2), 7.88 (d, 2, J = 9 Hz, $FpCH_2$), 5.42 (s, 5, Cp), 4.67 (mt, 1, CH=)[d]	58.78[g] 4.15 14.44	58.53 4.13 14.25
	$LiCuMe_2$		65	Oil	2028, 1957[a]	8.98 (t, 3, J = 7 Hz, CH_3), 7.7 (m, 2, CH_2), 5.27 (s, 5, Cp), 5.10 (t, 1, J = 1.0 Hz, CH=), 4.45 (t, 1, J = 1.5 Hz, CH=)[d]	56.94 5.21	57.09 5.16
	$LiCuMe_2$		~10	Oil	e	5.3 (s, Cp), 9.03 (Me)[d]		e
	$LiCuMe_2$		22	Oil	2010, 1959[a]	9.16 (t, 3, J = 7 Hz, CH_3), 7.6–8.2 (m, 3, CH_2, CH), 5.34 (s, 5, Cp), 1.09 (d, 1, J = 2.5 Hz, CHO)[d]		e

a–k See corresponding footnotes in Table I.

complex afforded a single adduct (43%) shown by off-resonance decoupling of its ^{13}C NMR spectrum to have structure **43c.** Data for carbanion adducts are collected in Table III.

The addition of phenylmagnesium chloride to the Fp(butadiene) cation afforded the conjugate adduct in 55% yield. The product is a single isomer, as shown by a comparison of its ^1H NMR spectrum with that of a mixture of *cis*- and *trans*-1-phenyl-4-Fp-2-butene (**43d,e**), prepared by deprotonation of Fp(4-phenyl-1-butene) (**10e**) with triethylamine. The presence of infrared adsorption at 960 cm^{-1} suggests that it is the trans isomer (**43e**), formed as are the enolate and enamine adducts of this diene complex by conjugate addition to the more stable s-trans conformer of the complex. A small amount of the 1,2 adduct (**43f**) may also be present in the reaction mixture.



43

	R_1	R_2	R_3
a	H	H	Ph
b	H	H	$CH_2CH{=}CH_2$
c	Me	H	Ph
d	H	H	*cis*-$=CHCH_2Ph$
e	H	H	*trans*-$=CHCH_2Ph$
f	H	Ph	$CH{=}CH_2$

Lithium dimethylcuprate proved to be a more generally effective reagent for additions to a number of Fp(olefin) cations. But even here, cyclopentene and cyclohexene complexes, and those derived from acrolein or methyl crotonate, gave low yields of adducts. The principal product was the dimer Fp_2. These results are summarized in Scheme II.

The reaction of $LiCuMe_2$ with the propene complex shows no regiospecificity; both (isobutyl)- and (*sec*-butyl)Fp (**44, 45**) are formed in equal amounts in 70% overall yield. However, the styrene complex reacts with somewhat greater specificity, the isomers **46** and **47** being formed in 41 and 18% yield, respectively. As with phenylmagnesium chloride, the reaction of $LiCuMe_2$ with the butadiene complex yields predominantly the conjugate adduct **48.** A substantial amount of the displacement product, FpMe, is also formed when this reaction is carried out at −20 °C, but this side reaction can be completely suppressed by carrying out the reaction at −50 °C. The trans stereochemistry of the adduct is evidenced by infrared absorption at 960 cm^{-1}, and this is confirmed by ^1H NMR decoupling experiments. Less than 2% of the cis isomer is present in the product as is shown by a comparison of the ^1H NMR spectrum of this product with the 1:1 mixture of *cis*- and *trans*-(2-pentenyl)Fp, prepared by deprotonation of Fp(1-pentene)$^+$.

An extension of these reactions to the isoprene complex (**10f**) provides an opportunity to prepare a trisubstituted (η^1-allyl)Fp complex with defined stereochemistry. When the reaction of **10f** with lithium dimethylcuprate was carried out at −78 °C, the adduct **49** was obtained in 72% yield. Its ^1H NMR spectrum suggested that it was a simple stereoisomer, derived from conjugate addition to the diene complex. This was confirmed by conversion of the product in 75% yield to a crystalline TCNE adduct. A comparison of the methyl proton chemical shifts for this substance with those observed for the TCNE adducts of methyl-substituted (η^1-allyl)Fp complexes of defined stereochemistry provides strong evidence for the cis relationship of the methyl and Fp substituents on the cyclopentane ring. These data are summarized in Table V.

Since we have previously shown[6] that cycloadditions of (η^1-allyl)Fp complexes proceed so that geometrical isomerism about the olefinic bond in the reactant complex is preserved in the product, it follows that the stereochemistry of the isoprene adduct must be as depicted by **49.** The result is as anticipated for conjugate addition to the s-trans form of the isoprene complex (**10f**).

As with malonate ion, lithium dimethylcuprate added smoothly to the allene complex at C_1, affording the vinyl complex (**50**) in 65% yield.

Ylides. Although ylides have been shown to function as ligands in transition metal complexes,[38] their use as nucleophiles toward metal olefin and polyene complexes does not appear to have been examined. Adducts derived from such reactions should be useful synthetic intermediates since they might be transformable to Wittig reagents with potential functionalities derived from the organometallic radical.

The relatively stable ylide **51** was briefly examined since it, like the stabilized enolates or the enamines, gave promise of simple addition to Fp(olefin) cations uncomplicated by reduction processes. The addition of **51** to the Fp(ethylene) cation was found to proceed readily in acetonitrile solution at 0 °C. The adduct **52,** isolated in 50% yield, was readily deprotonated with aqueous sodium hydroxide, to give the ylide

Scheme II

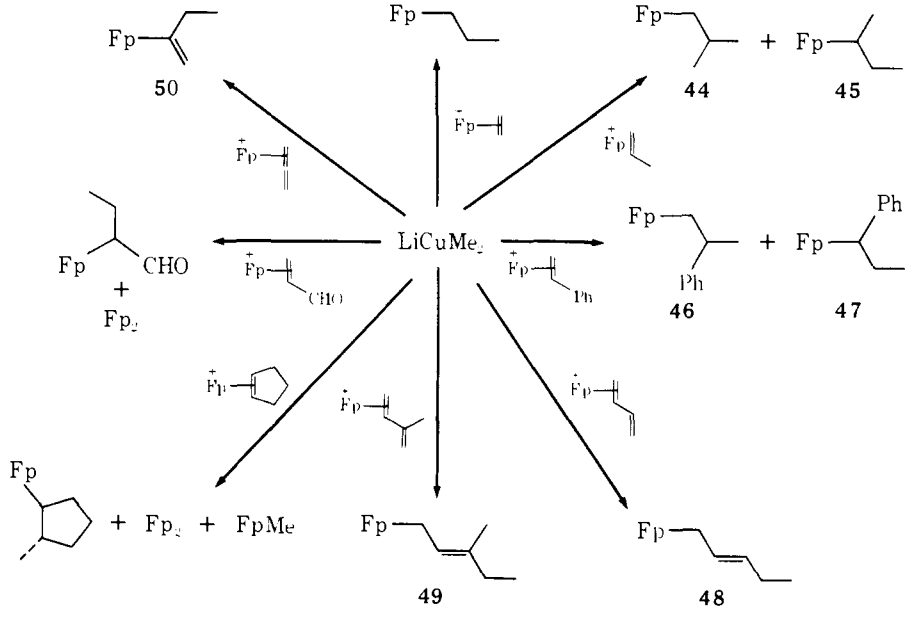
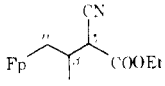
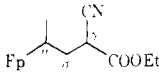
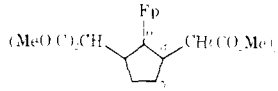
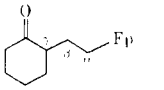
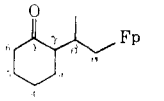
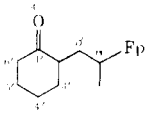
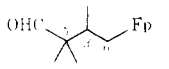
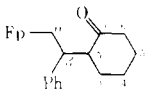
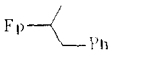
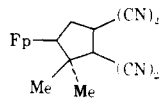
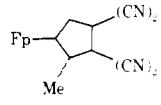
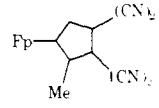
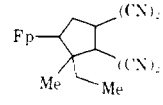


Table IV. ^{13}C NMR Spectral Data

	Chemical shift, δ [a,c]					
	α	β	γ	Me	Cp	Other resonances
	7.09[b] 4.03	41.22[b] 41.81	47.59[b] 48.50	19.77[b] 20.94	86.74 86.74	14.24 (OCH_2CH_3), 62.87 (OCH_2CH_3), 116.90, 117.10 (CN), 167.36, 167.68, 167.55 (COOEt), 217.88, 218.20, 218.40,
	13.85[b] 14.95	38.30[b] 37.30	45.90[b] 46.42	27.63[b] 28.28	86.74 86.74	218.85 (M−CO)
	26.53		29.58		87.89	52.80, 53.06, 53.58, 56.18 (β-CH, $CHCO_2Me$, OCH_3), 170.67, 171.32 (CO_2R), 218.98 (MCO)
	1.43	42.46	55.92		86.61	25.42, 28.87, 34.39, 38.49 (CH_2), 213.98 (C=O), 219.18 (MCO)
	9.92[b] 7.51	50.94 47.40	58.71 59.82	17.85 19.28	*e*	36.12, 37.19 (C_3), 33.06, 37.74 (C_3), 25.13 25.29, 25.45 (C_4, C_4'), 27.63, 27.73, 28.25, 28.64, 28.93, 29.06 (C_5, C_5', Me), 42.08, 42.26, 42.42, 42.65 (C_6, C_6'), 86.48, 86.70
	20.74[b] 16.68	*d*	45.45[e] 50.00	*d*	*e*	(Cp), 212.87, 213.26, 213.65 (C=O), 218.22, 218.59, 218.92, 219.24 (MCO)
	4.42	43.82	54.81	19.18 17.49 16.84	86.35	207.41 (CHO), (MCO), 281.00, 218.92
	[b] 9.88	52.80	62.35		87.13	25.36, 30.30, 35.18 (C_3, C_4, C_5), 43.50 (C_6), 127.43 (*p*-Ph), 129.45, 130.10 (*o*-, *m*-Ph), 147.33 (ipso-Ph), 216.12 (CO), 218.59, 219.11 (MCO)
	5.27	*d*	*d*		87.13	24.71, 29.45, 42.72, 51.76 (C_3, C_4, C_5, C_6), 129.26, 130.43, 147.72 (*o*-, *m*-, *p*-Ph), 214.30 (CO)
	22.04	52.86		28.41	86.61	125.94 (*p*-Ph), 128.61, 129.26 (*o*, *m*-Ph), 144.60 (ipso-Ph)

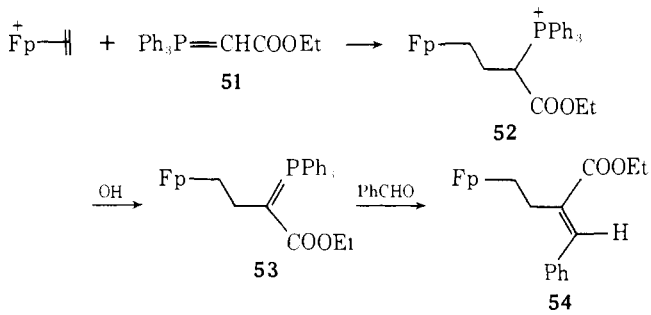
[a] In parts per million from internal Me_4Si; assignments based on off-resonance decoupling. [b] Major diastereomer. [c] In CD_3NO_2. [d] Resonance not assigned. [e] Diastereomer assignment not certain.

Table V. Methyl Proton Chemical Shifts in TCNE Adducts

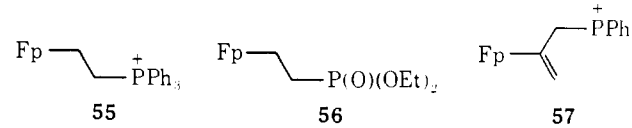
				
	Chemical shifts, τ			
cis-Me	8.68[a]		8.61[b]	8.70[a]
trans-Me	8.46	8.51[b]		

[a] In $(CD_3)_2CO$ solution. [b] In CD_3NO_2 solution.

53 as an orange, hygroscopic oil. This substance behaves normally as a Wittig reagent, affording a single olefinic product in moderate yield on condensation with benzaldehyde in refluxing benzene solution. Structure **54** is tentatively assigned to this product since stablized ylides such as **51** are normally observed to give a preponderance of product in which the ester group is trans to the larger substituent of the carbonyl reactant.[39]



Similar attempts to generate ylides from the salt **55,** derived by addition of triphenylphosphine to the Fp(ethylene) cation,[5] were unsuccessful. The phosphonium salt failed to show deuterium exchange with sodium methoxide in methanol or when treated with *n*-butyllithium followed by D_2O. The phosphonate **56,** derived by addition of triethyl phosphite to **10a** followed by reaction with iodide, also failed to deprotonate with *n*-butyllithium. Lastly, an attempt to effect a Wittig condensation with benzaldehyde, employing the phosphonium salt **57** and sodium hydride in DMF, also failed. It seems likely that steric factors largely associated with the Fp group are re-



sponsible for retarding proton removal in these complexes. Models show that the activated protons are shielded on one side by the PR_3 and on the other by the carbonyl ligands of the Fp group in the most stable conformation of these substances.

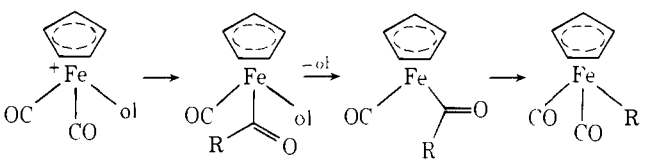
Some General Observations. regiospecificity and Reductive Processes. The regiospecificity exhibited by nucleophiles in their addition to monosubstituted Fp(olefin) cations necessarily depends upon the balance between bond making and breaking in the transition state, in much the same manner as for reactions of bromonium ions[40] or for the acid-catalyzed opening of epoxides.[41] This balance is in turn a function of the electron-releasing capacity of the olefin substituent and of the reactivity and polarizability of the nucleophile. Bond making appears to be more important for *tert*-butyl thiol than for enolates or enamines since the former affords an adduct derived from attack at the methylene carbon atom in the Fp(styrene) cation, while the latter afford products derived from addition to the benzylic center. As might be anticipated, the reactions of these latter nucleophiles with the propylene complex or of the more reactive methyl cuprates with the styrene complex exhibit low regiospecificity.

For the allene complexes, substitution at the terminal carbon atom appears to be an invariant pattern both for heteroatomic as well as for carbon nucleophiles.[5,7,42] For these cations, charge on the ligand would be expected to reside principally at this site.

Steric factors may play a large role in the reactions of the butadiene and isoprene complexes with Grignard and organocopper reagents, since these give products derived principally from addition to the more accessible terminal carbon center. Such factors are evidently less important for enamines and malonates which give increasing proportions of products derived from direct addition to the coordinated olefinic center.

It is unlikely that FpR complexes, formed in the reactions of Fp(olefin) cations with organomagnesium and lithium reagents, owe their origin to processes involving direct displacement of the olefin by nucleophile. The Fp(olefin) cations represent 6-coordinate d^6 species and hence are coordinatively saturated. An S_N2 type of displacement mechanism for such complexes has little if any precedent.[43] An S_N1 mechanism involving dissociation of the olefinic ligand may also be discarded, since first-order solvolysis of the relatively unstable Fp(isobutylene) cation in nitromethane proceeds slowly at 50 °C ($t_{1/2}^{50}$ = 40 min), while the formation of FpR complexes in the above reactions takes place rapidly well below 0 °C.[44]

These products may be formed instead through competitive addition of the carbanion to a carbonyl group of the Fp(olefin) cation. Loss of olefin cation from the resulting neutral complex, followed by rearrangement of the coordinatively unsaturated complex,[35a] would then yield the products of olefin displacement.



Alternatively a mechanism involving one-electron transfer from the Grignard or organolithium reagent to the complex cation may be responsible for both the displacement product as well as for the formation of dinuclear complex, Fp_2.

$$R^- + Fp(ol)^+ \longrightarrow \{R\cdot + Fp(ol)\cdot\} \quad (58)$$

$$\{R\cdot + Fp(ol)\cdot\} \longrightarrow FpR + Fp\text{-}Fp$$

Such electron transfer, well recognized in the reactions of organocuprates,[45] would be expected to weaken the metal-ligand bonds in the resulting complex radical and to promote olefin dissociation, since the orbital populated by such a transfer is antibonding with respect to the metal and ligands. Radical recombination within the solvent cage or escape of Fp, followed by dimerization, accounts for the observed products. The isolation of biphenyl from the reaction of phenyllithium with the Fp(ethylene) cation is in accord with this mechanism.

Rapid transfer of a methyl group from the cuprate to the organoiron radical (**58**), in a process competitive with dissociation of **58**, may account for the successful addition of this reagent to Fp(olefin) cations. It is also possible that the electrochemical reduction potential of this reagent is not sufficiently great to effect electron transfer.

Experimental Section

All reaction 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. ^1H NMR spectra were determined on either a Varian A-60 spectrometer (NIH GM-13183), a Perkin-Elmer R-32 spectrometer (NSF GU 3852), a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156) or a 270 MHz spectrometer.[46] ^{13}C NMR spectra were determined at 22.62 MHz on the latter instrument. Mass spectra were obtained on an AEI MS-12 direct inlet spectrometer (NSF GP 3644). Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Procedure for Enolate Additions. To a solution of $Li[N(SiMe_3)_2]$ in THF at −78 °C was added 1 equiv of the active methylene compound. After 15 min, the resultant clear solution was added to a THF suspension of the Fp(olefin) salt at −78 °C. The reaction mixture was allowed to warm over a period of 2–3 h to room temperature, and solvent was evaporated under reduced pressure. The residue was purified by chromatography on neutral alumina (Camag, activity III). Elution with ether or methylene chloride gave the products as amber oils or yellow crystals.

Preparation of $FpCH_2NO_2$. A suspension of lithium nitromethide was prepared from 0.68 mL (15 mmol) of CH_3NO_2 and 2.10 g of $Li[N(SiMe_3)_2]$ (15 mmol) in 200 mL of THF at 0 °C. A solution of FpCl (2.12 g, 10 mmol) in 35 mL of THF was added to this and the resulting mixture was stirred at 34 °C for 2 h. The mixture was filtered, solvent was evaporated, and the residue was recrystallized from CH_2Cl_2/hexane to give 1.26 g (55%) of product: mp 102–104 °C; IR (KBr) 2041, 1996, 1496, 1348 cm^{-1}; NMR ($CDCl_3$) τ 5.03 (s, 5, Cp), 5.55 (s, 2, CH_2).

Anal. Calcd for $C_8H_7FeNO_4$: C, 40.54; H, 2.97; N, 5.91. Found: C, 40.48; H, 2.81; N, 5.76.

Reaction of Fp(ethylene)BF_4 with Sodium Nitromethide. Adduct 11d. To a suspension of $NaCH_2NO_2$ (3.5 mmol) prepared from NaH (0.85 g, 3.5 mmol) in 5 mL of nitromethane was added a solution of Fp(ethylene)BF_4 (1.0 g, 3.4 mmol) in 45 mL of nitromethane. An immediate color change from orange to brown occurred. The reaction was continued for 90 min, solvent was then removed in vacuo, and the residue was chromatographed on 50 g of activity III neutral alumina. Elution with ether gave 352 mg of crude product shown by its ^1H NMR spectrum to be a 9:1 mixture of **11d** and $FpCH_2NO_2$. Careful chromatography of this product on alumina gave pure adduct (**11d**) (spectral and analytical data, Table I).

Hydride Abstraction from Adduct 15a. Preparation of 20. A solution of the adduct **15a** (0.67 g, 1.8 mmol) in 5 mL of methylene chloride was treated with a solution of trityl tetrafluoroborate (0.58 g, 1.7 mmol) in 5 mL of methylene chloride at 0 °C. After continued reaction at 0 °C for 3 h, anhydrous ether was added, and the product was collected and recrystallized from CH_3CN–Et_2O at 0 °C to give 0.58 g (72%) of **20** (R = Me): mp 104.5–105.5 °C; IR (KBr) 2053, 2004, 1745, 1736 cm^{-1}; NMR (CD_3NO_2) τ 8.4–9.2 (m, 2, CH_2), 7.3–7.8 (m, 2, CH_2), 6.6–6.8 (m, 2, CH, $CH(CO_2R)_2$), 6.22, 6.25 (2 s, 6, OCH_3), 4.32 (s, 5, Cp), 4.68 (m, 2, CH=CH).

Anal. Calcd for $C_{17}H_{19}BF_4FeO_6$: C, 44.16; H, 4.14. Found: C, 44.18; H, 4.10.

Similar treatment of **15b** with trityl tetrafluoroborate gave **20** (R = Et) in 76% yield: IR (KBr) 2062, 2004, 1745, 1739 cm^{-1}.

Anal. Calcd for $C_{19}H_{23}BF_4FeO_4$: C, 46.79; H, 4.74. Found: C, 46.40; H, 4.61.

Reaction of 20 with Sodium Iodide. Diethyl 2-Cyclopentenylmalonate. The cation **20** (R = Et) (0.065 g, 0.132 mmol) in 0.4 mL of acetone-d_6 in an NMR tube was treated with 0.022 g (0.145 mmol) of NaI. After centrifugation, an NMR spectrum indicated complete conversion of the salt to FpI and free olefin. Chromatography on 10 g of activity III neutral alumina and elution with ether–petroleum ether (1:4) gave 0.025 g (84%) of olefin: NMR (acetone-d_6) τ 8.78 (t, 6, CH_3), 7.7 (m, 2, CH_2), 6.7 (m, 2, CH_2), 6.4 (m, 2, CH), 5.83 (q, 4, OCH_2), 4.23 (m, 2, CH=).

Treatment of Adduct 26f with HBF_4·Et_2O. Reversion Reaction. The adduct **26f** (0.108 mg, 0.285 mmol) was dissolved in 2 mL of ether and 0.04 mL of HBF_4·Et_2O was added to this at 0 °C. A yellow solid precipitated, and this was collected and identified as Fp(styrene)BF_4 (100 mg, 100%). The ether-soluble portion was identified as cyclohexanone by its IR spectrum.

Oxidation of Adduct 26f with Ce(IV). Conversion to Ester 34. To a solution of adduct **26f** (0.400 g, 1.05 mmol) in 15 mL of methanol, previously saturated with carbon monoxide, was added $Ce(NH_4)_2(NO_3)_6$ (2.70 g, 6.0 mmol) in one portion at room temperature. Carbon monoxide was bubbled through the solution while reaction was continued for 5 h. The dark brown solution was then poured into 25 mL of water, extracted with ether, and worked up. Chromatography of the crude product on 25 g of activity III alumina and elution with ether gave 0.245 g of ester: mp 90–91 °C (90%); IR (KBr) 1728, 1704 cm^{-1}.

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.75. Found: C, 73.64; H, 7.73.

General Procedure for Enamine Additions. One equivalent of the enamine, either neat or in acetonitrile solution, was added to a solution of the Fp(olefin) salt in acetonitrile at 0 °C. The reaction could be conveniently followed by observing the changing pattern of metal-carbonyl bands in the IR spectrum of the solution. The solution was then briefly heated on the steam bath (5–20 min) with one equivalent of NaOH in aqueous ethanol and the product was extracted into ether, worked up, and purified by chromatography on neutral, activity III alumina.

General Procedure for Cuprate Additions. Lithium dimethylcuprate was prepared by addition of 1 equiv of ethereal methyllithium to a suspension of cuprous iodide in dry ether. This solution was added to the Fp(olefin) salt suspended in THF at temperatures between −78 and −20 °C. After 1 h, solvent was removed, and the product was taken up in petroleum ether and chromatographed on activity III, neutral alumina.

Preparation of Fp(4-phenyl-1-butene)BF_4 (10e). To a solution of Fp(isobutylene)BF_4 (0.96 g, 3 mmol) in 25 mL of 1,2-dichloroethane was added 4 mL (30 mmol) of 4-phenyl-1-butene. The solution was heated to 75 °C for 5 min and cooled to 0 °C, and ether was added. The product was collected and recrystallized from methylene chloride–ether to give 1.01 g of **10e** (85%): mp 77–78 °C; IR (KBr) 2080, 2040 cm^{-1}; NMR (CD_3NO_2) τ 2.71 (s, 5, Ph), 4.38 (s, 5, Cp), 5.00 (m, 1, CH=), 6.10 (d, 1, J = 8.0 Hz, *cis*-CH_2=), 6.70 (d, 1, J = 14.5 Hz, *trans*-CH_2=), 7.0–7.5 (m, 3, CH_2), 8.33 (m, 1, CH_2).

Anal. Calcd for $C_{17}H_{17}FeBF_4O_2$: C, 51.57; H, 4.32. Found: C, 51.41; H, 4.24.

Deprotonation of 10e. Preparation of *cis*- and *trans*-1-Phenyl-4-Fp-2-butene. A solution of **10e** (0.396 g, 1.0 mmol) in 5 mL of methylene chloride was treated with triethylamine (0.106 g, 1.05 mmol) at 0 °C. Reaction was continued for 60 min at this temperature, then solvent was removed and the residue was chromatographed on 25 g of activity III alumina, previously deactivated with ether. Elution with ether–hexane (1:1) gave 0.33 g of product (99%): IR (film) 2010, 1955 cm^{-1}; NMR (CS_2) τ 7.93 (d, 2, J = 7.0 Hz, $FpCH_2$, trans isomer), 7.83 (d, 2, J = 9.0 Hz, $FpCH_2$, cis isomer), 6.80 (d, 2, J = 6.0 Hz, $PhCH_2$, trans isomer), 6.67 (d, 2, J = 8.0 Hz, $PhCH_2$, cis isomer), 5.45, 5.50 (2 s, 10, Cp), 3.9–5.1 (m, 4, *cis*- and *trans*-CH=CH).

The TCNE adduct of the mixture was obtained in 79% yield on treatment of the product with tetracyanoethylene in methylene chloride–tetrahydrofuran solution, mp 200 °C dec.

Anal. Calcd for $C_{23}H_{16}FeN_4O_2$: C, 63.32; H, 3.70; N, 12.84. Found: C, 63.44; H, 3.58; N, 12.44.

Preparation of Fp(1-pentene)BF_4. To a solution of Fp(isobutylene)BF_4 (0.96 g, 3 mmol) in 10 mL of 1,2-dichloroethane was added 3.5 mL (30 mmol) of 1-pentene. The solution was heated at 75 °C for 5 min, then cooled and the product precipitated by addition of ether. Recrystallization from CH_2Cl_2–ether gave the 1-pentene salt (0.71 g, 71%): IR (KBr) 2070, 2033 cm^{-1}; NMR (CD_3NO_2) τ 4.33 (s, 5, Cp), 4.93 (m, 1, CH=), 6.05 (d, 1, J = 8.0 Hz, *cis*-CH_2=), 6.50 (d, 1, J = 15.0 Hz, *trans*-CH_2=), 7.3–9.2 (m, 7, CH_2, CH_3).

Preparation of *cis*- and *trans*-1-Fp-2-pentene. A solution of the above salt (0.50 g, 1.5 mmol) in 10 mL of methylene chloride was treated with 0.21 mL (1.7 mmol) of triethylamine at 0 °C. After 45 min, solvent was removed and the residue was chromatographed on alumina to give 0.29 g (79%) of product: IR (neat) 2008, 1946 cm^{-1}; NMR (CS_2) τ 4.0–5.2 (m, 2, CH=CH), 5.35, 5.40 (2 s, 5, Cp), 7.9 (2 d, 2, J = 7.0, 9.0 Hz, $FpCH_2$), 8.1 (m, 2, CH_2), 9.07 (t, 3, J = 7.0 Hz, CH_3).

TCNE Adduct of *trans*-1-Fp-2-pentene. A solution of the allyl complex (**48**) (0.054 g, 0.22 mmol) in methylene chloride was treated with 1 equiv of TCNE in THF at 0 °C. After 15 min, the product was crystallized by addition of hexane. Further purification by chromatography on alumina gave pure adduct (0.064 g, 86%): mp 117.5–118.5 °C; IR 2257, 2024, 1980 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}N_4O_2Fe$: C, 57.78; H, 3.77; N, 14.98. Found: C, 57.67; H, 3.65; N, 14.90.

TCNE Adduct of 49. The allyl complex **49** (0.05 g, 0.2 mmol) was taken up in 2 mL of methylene chloride and treated with 0.025 g (0.2 mmol) of TCNE in 2 mL of THF at 0 °C. After 10 min at room temperature, the product was precipitated by addition of hexane and this was collected and further purified by chromatography on alumina. Recrystallization from methylene chloride–hexane gave 0.06 g (78%) of adduct: mp 122–123 °C; IR (KBr) 2278, 2028, 1961 cm^{-1}; NMR (acetone-d_6) τ 4.77 (s, 5, Cp), 6.65 (dd, 1, J = 13, 8 Hz, $FpCCH_2$), 6.96 (dd, 1, J = 13, 13 Hz, $FpCCH_2$), 7.27 (dd, 1, J = 13, 8 Hz, FpCH), 7.74 (m, 1, $FpCCCH_2$), 8.25 (m, 1, $FpCCCH_2$), 8.70 (s, 3, $FpCCCH_3$), 8.82 (t, 3 J = 7 Hz, CH_3CH_2).

Anal. Calcd for $C_{19}H_{16}N_4O_2Fe$: C, 58.78; H, 4.25; N, 14.44. Found: C, 58.53; H, 4.13; N, 14.25.

Addition of Carboethoxymethylenetriphenylphosphorane to Fp(ethylene)BF_4. To a solution of Fp(ethylene)BF_4 (0.58 g, 2.0 mmol) in 5 mL of acetonitrile at 0 °C was added 0.70 g (2.0 mmol) of carboethoxymethylenetriphenylphosphorane. After 1 h of reaction, the mixture was added to ether and the precipitate which separated was removed and chromatographed on 25 g of Florisil. Elution with methylene chloride gave an orange band which yielded 0.65 g (50%) of product: mp 143 °C dec; IR (KBr) 2001, 1942, 1731 cm^{-1}; NMR (CD_3NO_2) τ 2.1–2.3 (m, 15, Ph), 5.26 (s, 5, Cp), 5.95 (q, 2, J = 7 Hz, CH_2CH_3), 7.5–8.3 (m, 5, CH_2, CH), 8.95 (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{31}H_{30}BF_4FeO_4P$: C, 58.16; H, 4.72; P, 4.84. Found: C, 58.30; H, 5.30; P, 4.71.

Preparation of Ylide 53. A solution of the phosphonium salt **52** (0.18 g, 0.28 mmol) in 5 mL of methylene chloride was treated with 5 mL of 0.056 M NaOH in water. The mixture was shaken and the organic layer was separated and dried over magnesium sulfate. Removal of solvent left a yellow oil, which was chromatographed on neutral activity III alumina to give 0.11 g (70%) of the ylide as an orange, hygroscopic oil: IR (film) 2004, 1949, 1603 cm^{-1}; NMR ($CDCl_3$) τ 2.1–2.6 (m, 15, Ph), 5.34 (s, 5, Cp), 6.13 (q, 2, J = 7 Hz, CH_2CH_3), 7.5–8.3 (m, 2, $FpCH_2$), 8.3–8.9 (m, 2, CH_2), 9.15 (m, 3, CH_3).

Wittig Condensation. Preparation of 54. A solution of the ylide (0.42 g, 0.76 mmol) and benzaldehyde (0.80 g, 7.5 mmol) in 5 mL of benzene was refluxed for 5.5 h. The reaction mixture was cooled, solvent was evaporated, and the residue was extracted with ether. Chromatography on alumina, eluting with ether, gave 0.15 g (46%) of product: mp 67–69 °C; IR (CH_2Cl_2) 2004, 1946, 1701, 1635 cm^{-1}; NMR ($CDCl_3$) τ 2.59 (s, 1, PhCH=), 2.61 (br s, 5, Ph), 5.25 (s, 5, Cp), 5.75 (q, 2, J = 7 Hz, CH_2CH_3), 7.37 (m, 2, CH_2), 8.50 (m, 2, $FpCH_2$), 8.67 (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{20}H_{20}FeO_4$: C, 63.20; H, 5.30. Found: C, 63.50; H, 5.28.

Conversion of Compound 37 to the Chelate 36. Compound **37** was dissolved in 20 mL of acetonitrile and heated at 60–80 °C in a flask equipped with a reflux condenser for 15 min. The solution gradually reddened and darkened. After removal of solvent, the residue was chromatographed on activity III basic alumina. The chelate **36** was eluted slowly with methylene chloride: ^{13}C NMR (CD_3NO_2) δ 24.84, 25.23, 28.00, 29.36, 32.96, 34.00, 42.62, 42.75, 43.82, 44.80, 45.12, 58.56, 73.83, 75.81, 77.37, 87.39, 88.10, 88.26, 213.81, 214.07, 220.64, 221.10, 266.48, 266.61.

The peaks at δ 87.39, 88.10, and 88.26 are assigned to η^5-C_5H_5

carbon atoms on the basis of a single frequency proton decoupling experiment. Low-power irradiation at the frequency corresponding to cyclopentadienyl proton resonance decoupled the three signals above while the rest of the high-field portion of the ^{13}C spectrum appeared as an off-resonance decoupled spectrum.

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References and Notes

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(32) Compare **12**, 1969 (MCO), 1639 cm^{-1} (MCOR); CpFe(CO)(CO-$CH_2CH_2CH{=}CH_2$),[17] 1944, 1625 cm^{-1}; and CpFe(CO(COCMe$_2$-$CH_2CH{=}CH_2$),[16,17] 1945, 1635 cm^{-1}.
(33) Compare CpFe(CO)($COCH_2CH_2CH{=}CH_2$),[16,17] τ 6.77, 7.47; CpFe(CO)-($COCMe_2CH_2CH{=}CH_2$), τ 7.4, 8.1; CpFe(CO)($COOCH_2CH{=}CH_2$),[34] τ 6.70, 7.18.
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