Carbon–Carbon Bond Forming Reactions of η^3-Allyl Iron Tricarbonyl Anions with Carbon Electrophiles

Seok Chang, Jaeyon Yoon, and Maurice Brookhart*

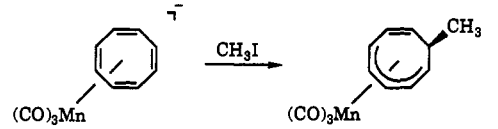
Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

*Received August 30, 1993**

Abstract: Reaction of the η^3-allyl iron tricarbonyl anion, **1**, with alkyl halides (RX, R = $-CH_3$, $-CH_2Ph$, $-(CH_2)_3CH_3$, $-CH(CH_3)_2$, $-CH_2CH{=}CH_2$) followed by treatment with PPh_3 gives η^4-$(CH_3CH{=}CHC(O)R)Fe(CO)_2PPh_3$ complexes, **2a–e**, respectively, in good yields. $P(OPh)_3$ and $P(OCH_3)_3$ also serves as effective trapping ligands. Low-temperature ^1H NMR studies show that CH_3I and $PhCH_2Br$ react with **1** to give η^3-$(CH_2{\cdots}CH{\cdots}CH_2)Fe(CO)_3$-R (**7**, R = $-CH_3$; **8**, R = $-CH_2Ph$). These complexes react with PPh_3 in less than 5 min at −78 °C to give acyl complexes η^3-$(CH_2{\cdots}CH{\cdots}CH_2)Fe(CO)_2PPh_3C(O)R$ (R = $-CH_3$, $-CH_2Ph$) which undergo acyl migration at 21 °C ($\Delta G^{\ddagger}$ ca. 21 kcal/mol) to give the observed η^4-enone-$Fe(CO)_2PPh_3$ products **2a** and **2b**, respectively. Free enones were obtained from **2b** and **2c** by reaction with CH_3CN. Reaction of either *syn*- or *anti*-1-methallyl-$Fe(CO)_3^-$ with CH_3I followed by trapping with PPh_3 yields the same set of products in identical ratios: η^4-(*E*)-$(CH_3CH{=}C(CH_3)C(O)CH_3)Fe(CO)_2PPh_3$, **13a**, η^4-(*Z*)-$(CH_3CH{=}C(CH_3)C(O)CH_3)Fe(CO)_2PPh_3$, **13b**, and η^4-$(CH_2{=}C(CH_2CH_3)C(O)CH_3)Fe(CO)_2PPh_3$, **13c**. Similiar results were obtained using $PhCH_2Br$. Product structures indicate highly regioselective acyl migration to C_1 when PPh_3 is used as the trapping ligand. Moderate regioselective migration to C_3 is observed when CH_3CN or CO is used as the trapping ligand in these systems. When CH_3CN is used as the trapping ligand, the major product isolated are the free β,γ-enones formed from interception of the β,γ-enone complexes prior to 1,3-hydrogen shift and formation of the conjugated α,β-enone iron complexes. A low-temperature *in situ* ^1H NMR study of this reaction using *anti*-methallyl-$Fe(CO)_3^-$ allows the NMR observation and determination of the rates of conversion for the complete set of sequentially formed intermediates: η^3-*anti*-$(CH_3CH{\cdots}CH{\cdots}CH_2)Fe(CO)_3$-$CH_3$, *anti*-**17**, → η^3-*anti*-$(CH_3CH{\cdots}CH{\cdots}CH_2)Fe(CO)_2(PPh_3)(C(O)CH_3)$, *anti*-**18**, → η^3-*syn*-$(CH_3CH{\cdots}CH{\cdots}CH_2)Fe(CO)_2(PPh_3)(C(O)CH_3)$, *syn*-**18**, → η^4-$(CH_2{=}CHCH(CH_3)C(O)CH_3)Fe(CO)_2PPh_3$, **19**, → **13a–c**. The *anti*-to-*syn* conversion of *anti*-**18** to *syn*-**18** is exceedingly rapid relative to model systems. This rate acceleration is ascribed to formation of an η^2-acyl intermediate. Reaction of *syn*-1-phenallyl-$Fe(CO)_3^-$ with CH_3I and $PhCH_2Br$ followed by trapping with PPh_3 yields η^4-(*E*)-$(PhCH_2CH{=}CH(CH_3)C{=}O)Fe(CO)_2PPh_3$ and η^4-(*E*)-$(PhCH_2CH{=}CH$-$(CH_2Ph)C{=}O)Fe(CO)_2PPh_3$, respectively, as the major products. High regioselective acyl migration to C_3 is observed in each case which is ascribed to the conjugative stabilization of the phenyl group. Reactions of 1-propallyl-$Fe(CO)_3^-$, 2-methallyl-$Fe(CO)_3^-$, and *syn*-1-phenyl-*anti*-3-methallyl-$Fe(CO)_3^-$ with CH_3I and $PhCH_2Br$ followed by trapping with PPh_3 and CH_3CN are also reported.

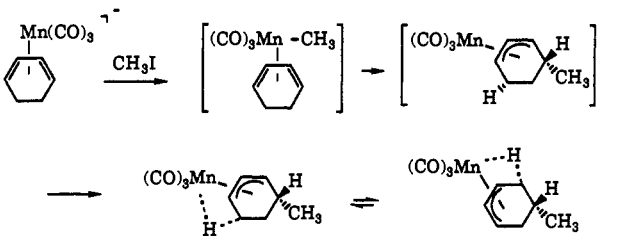
Introduction

Low-valent anionic transition-metal carbonyl complexes often display high nucleophilicity and react readily with simple organic electrophilies. When the anionic metal carbonyl complex also contains an unsaturated hydrocarbon ligand in the coordination sphere, reactions with carbon electrophiles can result in carbon–carbon bond forming reactions involving the unsaturated π-system.[1] In cases where the unsaturated moiety contains one or more uncomplexed π-bonds, *exo* addition is normally observed suggesting that the electrophile attacks the free double bond which results in direct formation of an 18-electron complex. For example, methylation of η^4-$(C_8H_8)Mn(CO)_3^-$ gives the η^5-(*exo*-8-methylcyclooctatrienyl)$Mn(CO)_3$ complex[2] as shown below:



Other well-documented cases include alkylation of η^4-$(C_6H_6)Cr(CO)_3^{2-}$ studied by Cooper[3] and methylation of η^4-(1,3,5-cycloheptatriene)$Mn(CO)_3^-$.[2]

For systems which contain no uncomplexed double bonds such as (diene)$Mn(CO)_3^-$ complexes,[4] (cyclohexadienyl)$Cr(CO)_3^-$,[5,6] (cycloheptadienyl)$Fe(CO)_2^-$,[7] and (arene)$Mn(CO)_2^-$ complexes[8] the electrophile adds *endo* which suggests initial attack at the metal center. An example of a simple *endo* carbon–carbon bond formation is the reaction of (cyclohexadiene)$Mn(CO)_3^-$ with CH_3I to yield the agostic *endo*-methylcyclohexenyl-$Mn(CO)_3$ complex:[4]



The reaction presumably occurs through the manganese–methyl complex. Following methyl migration, the initially formed 16-electron allyl complex is stabilized through an agostic interaction with the *endo* C–H bond.

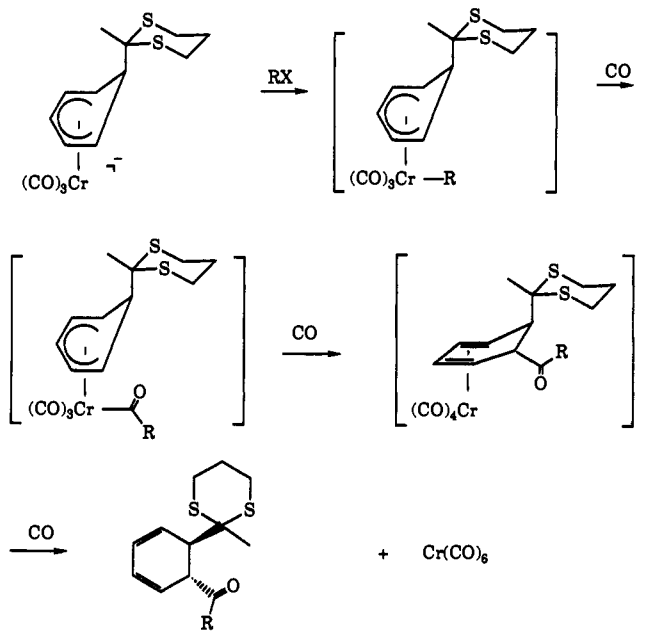
* Abstract published in *Advance ACS Abstracts*, February 1, 1994.

(1) For a review of such reactions, see: Brookhart, M.; Volpe, A. F., Jr.; Yoon, J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ed.; Pergamon Press: 1991; Vol 4, Section 3.5.

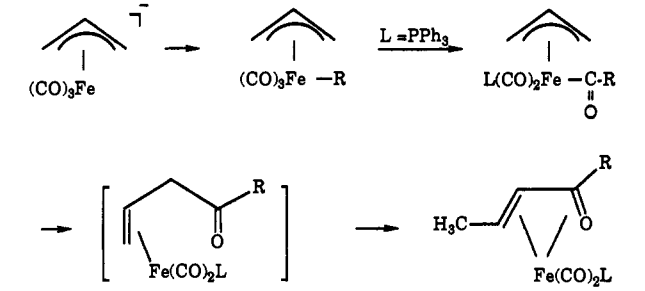
(2) (a) Brookhart, M.; Noh, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829. (b) Brookhart, M.; Noh, S. K.; Timmers, F. J.; Hong, Y. H. *Organometallics* **1988**, *7*, 2458.

0002-7863/94/1516-1869$04.50/0

Acyl products are frequently isolated in these reactions indicating alkylation at metal followed by CO insertion prior to migration.[5,6] An early and synthetically useful example of this reactivity pattern reported by Kundig[5b,6] involves alkylation of 6-*exo*-substituted cyclohexadienyl-$Cr(CO)_3^-$ anions. Reactions of these anionic chromium complexes with alkyl halides, followed by addition of CO yields the *trans*-5,6-disubstituted cyclohexadiene with complete regio- and stereospecificity:



In a preliminary study,[9] we investigated the reaction of η^3-(allyl)$Fe(CO)_3^-$ anion with carbon electrophiles followed by trapping with PPh_3. The following reaction sequence was elucidated:



This manuscript reports an extensive investigation of the reactions of allyl iron tricarbonyl anions with carbon electrophiles. Of particular focus is (1) the regiochemistry of acyl migration and the factors which control the regioselectivity, (2) the effect of *syn* versus *anti* substitution on the product distributions and regioselectivity, and (3) elucidation of the detailed mechanism of the reaction through low-temperature *in situ* ^1H NMR studies.

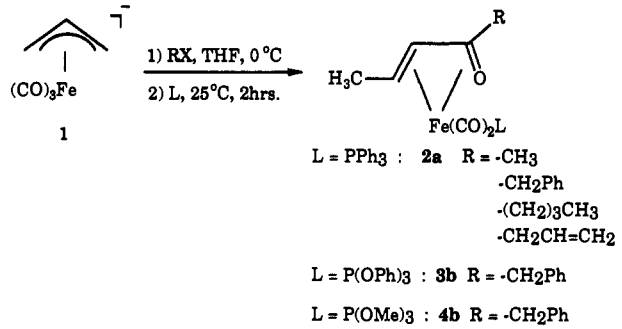
Table 1. Yields of the Reactions of **1** with Carbon Electrophiles

entry	RX	L	product	yield (%)
a	CH_3I	PPh_3	**2a**	74,[a] 79[b]
b	$PhCH_2Br$	PPh_3	**2b**	87,[a] 93[b]
c	$PhCH_2Br$	$P(OPh)_3$	**3b**	84[a]
d	$PhCH_2Br$	P(OMe)3	**4b**	88[a]
e	$CH_3(CH_2)_3I$	PPh_3	**2c**	78[a]
f	$(CH_3)_2CHBr$	PPh_3	**2d**	73[a]
g	$CH_2{=}CH{-}CH_2Br$	PPh_3	**2e**	61[a,c]

[a] Yields are based on the starting $C_3H_5Fe(CO)_3I$ used to generate the sodium salt *in situ*. [b] Yields based on reaction with pure isolated $C_3H_5Fe(CO)_3$–PPN^+. [c] $(\eta^3\text{-}C_3H_5)_2Fe(CO)_2$ is also obtained as reported previously.[11]

Results and Discussion

A. Reactions of the η^3-Allyl Iron Tricarbonyl Anion, 1, with Alkyl Halides. 1. Alkylation of 1 Followed by Trapping with PPh_3: Formation of α,β-Unsaturated Enone-$Fe(CO)_2PPh_3$ Complexes. The η^3-allyl iron tricarbonyl anion is conveniently prepared *in situ* by sodium amalgam reduction of either allyl iron tricarbonyl bromide or iodide.[8,10] The PPN^+ salt of the anion can be isolated *via* counterion exchange as a highly air-sensitive solid. Alkylation reactions were carried out by adding 1 equiv of the alkyl halide to the anion **1** in THF at 0 °C followed by addition of triphenylphosphine (2 equiv) to the solution and warming to 25 °C. The net result of these reactions is summarized below and yields of the product enone complexes are tabulated in Table 1.

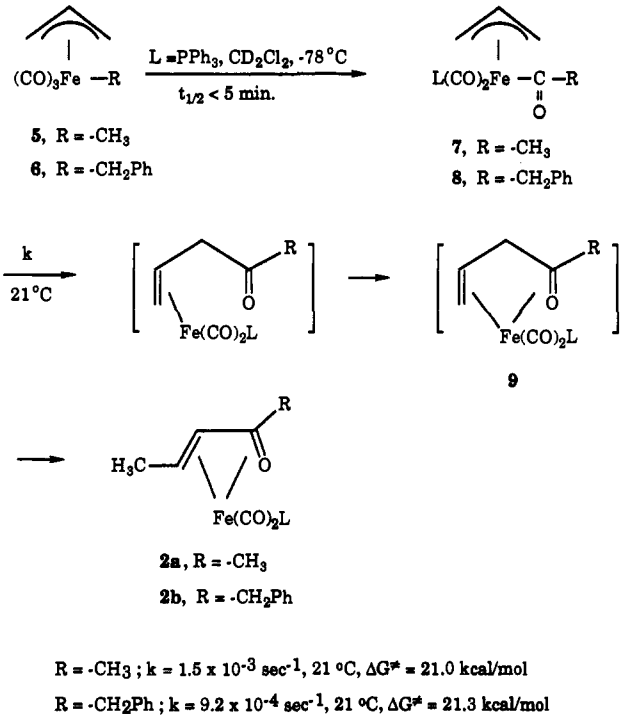


Stereochemistry about the α,β bond in the product enone complexes is exclusively *E*. Good yields (70–90%) were obtained for primary and secondary alkyl halides with the exception of allyl bromide where formation of $(\eta^3\text{-allyl})_2Fe(CO)_2$[11] is competitive with formation of the enone complex. While most trapping reactions were carried out using L = PPh_3, entries c and d in Table 1 show that $P(OPh)_3$ and $P(OMe)_3$ are equally effective trapping ligands. Yields are slightly higher for reactions carried out with the isolated PPN^+ salt of **1**, but the *in situ* generation procedure is far more convenient.

2. Mechanistic Investigations: ^1H NMR Spectroscopic Detection of Intermediates in the Reaction. The mechanism of the reactions of **1** with RX = CH_3I and $C_6H_5CH_2Br$ (see entries a and b, Table 1) were investigated by low-temperature ^1H NMR spectroscopy. The initial alkylation products $(\eta^3\text{-allyl})(CO)_3FeR$ (R = $-CH_3$, CH_2Ph) (eq 1) could be isolated by low-temperature techniques. The methyl complex **5** exists as a 15:1 mixture of *exo* and *endo* isomers[9] at −58 °C exhibiting methyl singlets at δ −0.51 (major isomer) and δ −0.42 (minor isomer). Typical allyl patterns confirm the structural assignments. Benzyl complex **6** exists as a 5:1 mixture of isomers (−13 °C) and exhibits

(3) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.
(4) (a) Brookhart, M.; Lamanna, W. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 683. (d) Brookhart, M.; Lukacs, A. *Organometallics* **1984**, *106*, 4161. (e) Brookhart, M.; Timmers, F. J. *Organometallics* **1985**, *4*, 1365.
(5) (a) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957. (b) Kundig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855.
(6) Kundig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P. *Helv. Chim. Acta* **1990**, *73*, 386.
(7) (a) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357. (b) Williams, G. M.; Rudisill, D. E.; Barnum, B. A.; Hardcastle, K.; Heyn, R. H.; Kozak, C. Z.; McMillan, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 205.
(8) Brookhart, M.; Rush, P. K.; Noh, S. K. *Organometallics* **1986**, *5*, 1745.
(9) Brookhart, M.; Yoon, J.; Noh, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 4117.
(10) Gubin, S. P.; Denisovich, L. A. *J. Organomet. Chem.* **1968**, *15*, 471.

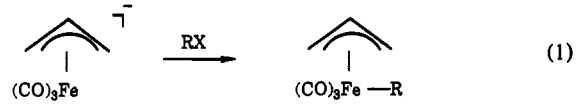
Scheme 1



R = -CH3 ; k = 1.5 x 10^{-3} sec^{-1}, 21 °C, $\Delta G^{\ddagger}$ = 21.0 kcal/mol

R = -CH_2Ph ; k = 9.2 x 10^{-4} sec^{-1}, 21 °C, $\Delta G^{\ddagger}$ = 21.3 kcal/mol

two sets of allyl signals and overlapping resonances for the benzyl hydrogens at δ 1.80.



(1)

5 : R = -CH_3

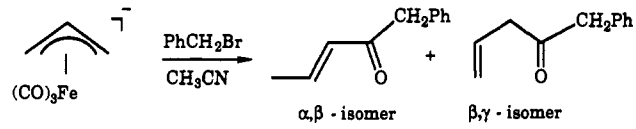
6 : R = -CH_2Ph

Treatment of either **5** or **6** with PPh_3 at −70 °C in CD_2Cl_2 results in immediate disappearance of these species ($t_{1/2}$ < ca. 5 min as monitored by ^{1}H NMR spectroscopy) and formation of acyl complexes **7** and **8**, respectively (see Scheme 1). The most characteristic feature of these complexes are the acyl resonances at δ 2.92 for the Fe–C(O)CH_3 moiety and δ 4.81 for Fe–C(O)CH_2-Ph (full ^{1}H NMR data appear in the Experimental Section). Both **7** and **8** are sufficiently stable that IR spectra could be recorded at 25 °C and showed acyl bands at 1639 cm^{-1} for **7** and 1630 cm^{-1} for **8** in addition to ν_{CO} bands at 1991 and 1932 for **7** and 1990 and 1930 for **8**.

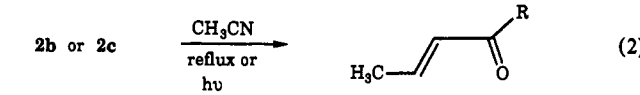
Solutions of **7** and **8** at 21 °C form enone complexes **2a** and **2b**, respectively. These transformations follow first-order kinetics with $k_{7\rightarrow 2a}$ = 1.5 × 10^{-3} s^{-1}, $\Delta G^{\ddagger}$ = 21.0 kcal/mol and $k_{8\rightarrow 2b}$ = 9.2 × 10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 21.3 kcal/mol. No intermediates are observed in the transformation, and thus we assume that the acyl migration step is rate-determining. A β,γ-enone–$Fe(CO)_3$ complex may form following acyl migration (see Scheme 1); it is undetected in these systems, but it has been observed in a similar transfer involving a methallyl complex (see below). Following acyl migration, a 1,3-hydrogen migration is required to form the α,β-enone complexes **2a,b**. Based on numerous analogous 1,3-metal-mediated hydrogen transfers,[12] this migration likely occurs *via* a π-allyl iron hydride intermediate.

3. Isolation of Metal-Free Enones. It has been well-established that enone–$Fe(CO)_3$ complexes are good sources of the $Fe(CO)_3$ moiety and that the enone ligand is readily displaced.[13] Thus, the free α,β-unsaturated ketones can be readily recovered from complexes **2a–g** by simple ligand displacement reactions. Illustrative reactions were carried out with enone complexes **2b,c**. Refluxing either **2b** or **2c** in CH_3CN (2–6 h) gave enones **10** and **11** in good yields (70–77%) (eq 2). Alternatively, irradiation of CH_3CN solutions of **2b** or **2c** at 0 °C led to slightly better yields of the free enones (80–85%).

Scheme 2



Reaction Conditions	Ratio of α,β / β,γ-isomer	Yield
1) $PhCH_2Br$, 0 °C, THF 2) CH_3CN addn., 25°C, 12hrs.	7 : 2	78 %
1) $PhCH_2Br$, 0 °C, THF 2) CH_3CN addn., irradiation, 0 °C	1 : 9	80 %



(2)

10 R = -CH_2Ph

11 R = -$CH_2(CH_2)_2CH_3$

If the β,γ-unsaturated enone complexes **9** (see Scheme 1) could be intercepted prior to 1,3-hydrogen migration, then a reaction sequence would be available for the preparation of the unconjugated β,γ-enones as well as the conjugated isomers. Several reaction sequences were investigated using **1**, benzyl bromide as the alkylating reagent and excess acetonitrile as the trapping ligand. Typical results are summarized below in Scheme 2. Benzylation followed by addition of a very large excess of CH_3-CN and warming to 25 °C for 12 h results in recovery of the conjugated enone (*E*)-CH_3CH=$CHCOCH_2C_6H_5$ and some unconjugated enone CH_2=$CHCH_2COCH_2C_6H_5$ (7:2 ratio, 78% yield). A more effective method for maximizing the yield of the β,γ-isomer involved benzylation in THF, addition of CH_3CN and irradiation, with all procedures carried out at 0 °C. This process results in formation of a 9:1 ratio of β,γ- to α,β-isomers in a total isolated yield of 80%.

B. Reactions of η^3-Methallyl Iron Tricarbonyl Anions with Alkyl Halides. 1. Alkylation Reactions. Reactions of *syn*- and *anti*-methallyl iron tricarbonyl anions, *syn*-**12** and *anti*-**12**, with alkyl halides followed by trapping with PPh_3 to form α,β-unsaturated enone–$Fe(CO)_2PPh_3$ complexes were carried out to determine how an alkyl substituent controls the regiochemistry of acyl migration and to assess how *syn* versus *anti* substitution affects this regiochemistry and the distribution of products. In these studies the *syn*-**12** anion was generated from sodium amalgam reduction of *syn*-methallyl iron tricarbonyl iodide or bromide. An alternate method developed subsequent to this work involves generation by reductive cleavage of (*syn*-methallyl)Fe-$(CO)_3SnMe_3$ using KH.[14] The *anti*-**12** anion can be generated *in situ* from Et_3BH^- reduction of (butadiene)$Fe(CO)_3$. Alternatively, reductive cleavage of (*anti*-methallyl)$Fe(CO)_3SnMe_3$

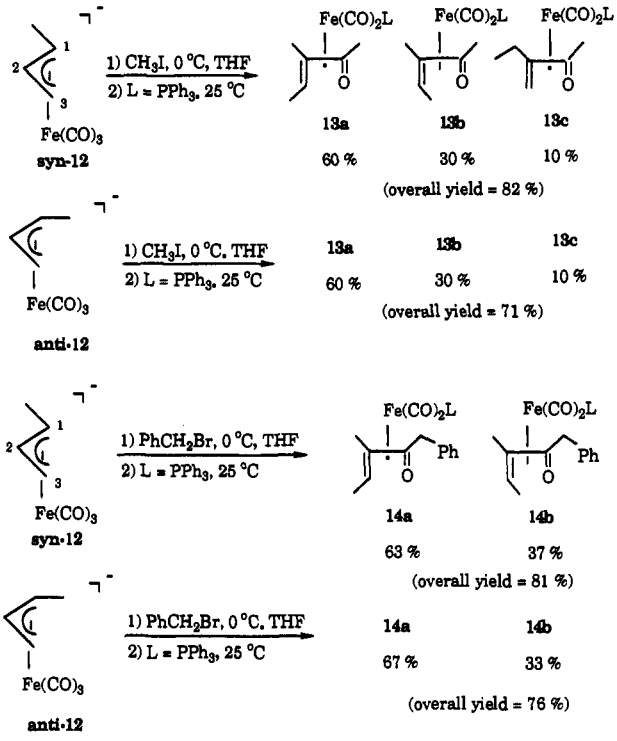
(11) Nesmeyanov, A. N.; Kritskaya, I. I.; Ustynyuk, Y. A.; Fedin, E. I. *Dokl Akad. Nauk. SSSR* **1968**, *176*, 341.

(12) (a) Manuel, T. A. *J. Org. Chem.* **1962**, *27*, 3941. (b) Alper, H.; Leport, P. C.; Wolfe, S. *J. Am. Chem. Soc.* **1969**, *91*, 7553. (c) Cowherd, F. G.; von Rosenberg, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 2157.

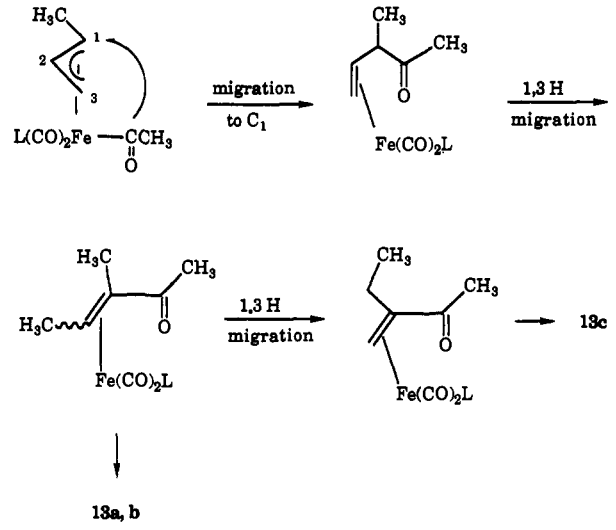
(13) (a) Howell, J. A. S.; Kola, J. C.; Dixon, D. T.; Burkinshaw, P. M.; Thomas, M. J. *J. Organomet. Chem.* **1984**, *266*, 83. (b) Graham, C. R.; Scholes, G.; Brookhart, M. *J. Am. Chem. Soc.* **1977**, *99*, 1180.

(14) Chang, S.; White, P. S.; Brookhart, M. *Organometallics* **1993**, *12*, 3636.

Scheme 3



Scheme 4



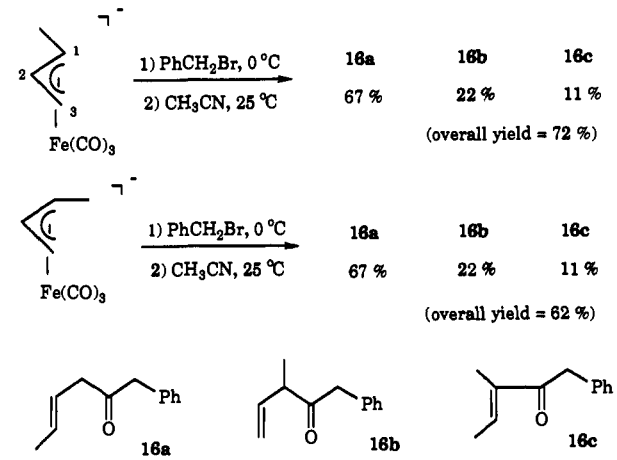
using CH_3Li or KH provides high yields of *anti*-**12**.[14] Using any of these methods gives similar results; however, KH cleavage of the tin complexes results in generation of pure, isolable potassium salts of both *syn*-**12** and *anti*-**12** and thus this is our currently preferred procedure.

Products of the reactions of *syn*-**12** and *anti*-**12** with CH_3I and $C_6H_5CH_2Br$ in THF at 0 °C followed by PPh_3 addition are shown in Scheme 3. The reaction sequence employing CH_3I and either *syn*- or *anti*-**12** gives the identical ratio of enone complexes **13a**:**13b**:**13c** in similar overall yields. The assignment of *E* stereochemistry to **13a** is based on the typical higher field shift of the "inside" hydrogen on the β-carbon of the enone (δ 1.57) relative to the "outside" hydrogen on the β-carbon of **13b** (δ 2.61).[15] The products **13a**,**b** arise from a single 1,3-hydrogen migration while isomer **13c** arises from a second sequential 1,3 H-migration as shown in Scheme 4.

All products (**13a**, **13b**, and **13c**) result from migration of the acyl unit to the methyl-substituted carbon, C_1. Thus, although

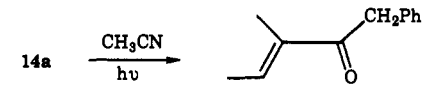
(15) Howell, J. A. S.; Dixon, D. T.; Kola, J. C. *J. Organomet. Chem.* **1984**, *266*, 69.

Scheme 5



three products were formed, the regioselectivity of the migration with PPh_3 as the trapping ligand is quite high.

Results of the benzylation reactions are similar to those of methylation. The major products obtained from either *syn*- or *anti*-**12** are the *E* and *Z* isomers **14a** and **14b** which exhibit ^1H chemical shifts for H_β at δ 1.54 for *E* isomer, **14a**, and δ 2.58 for *Z* isomer, **14b**. (In the case of the benzylation of *syn*-**12**, trace amounts of the isomerized product $[CH_2{=}CH(CH_2CH_3)COCH_2Ph]Fe(CO)_2PPh_3$, **14c**, were also detected). Product ratios from either *syn*- or *anti*-**12** are within experimental error. Again, products arise exclusively from migration of the acyl group, $-COCH_2Ph$, to the methyl-substituted carbon, C_1. To illustrate recovery of free ligands in these systems, isomer **14a** was irradiated in CH_3CN solution which resulted in isolation of enone, **15a**, in 78% yield (eq 3).



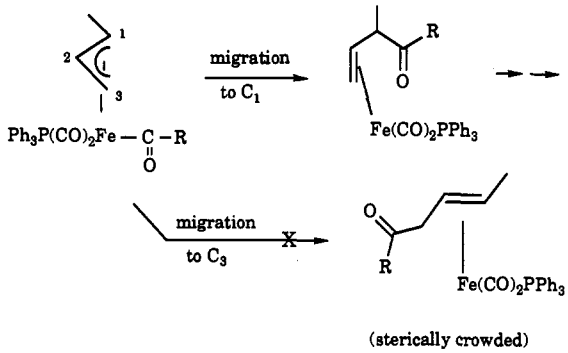
(3)

The regiochemistry of the acyl migration can be substantially altered by variation of the trapping ligand. Illustrated below are the results of benzylation of *syn*- and *anti*-**12** followed by trapping with CH_3CN. In these cases excess CH_3CN results in displacement of the enone ligands which are recovered in good overall yields (Scheme 5). The major products produced are the β,γ-enones, **16a** and **16b**, which are obtained *via* displacement prior to 1,3-hydrogen shift. The product ratios are the same whether *syn*- or *anti*-**12** is employed.

Enone **16a** results from migration of the acyl moiety to C_3, the unsubstituted terminal carbon, while enones **16b** and **16c** result from migration to C_1, the methyl-substituted carbon. Thus, in this case, although regioselectivity is low, migration to C_3 is favored by ca. 2:1 in contrast to the PPh_3 case where migration occurs exclusively to C_1.

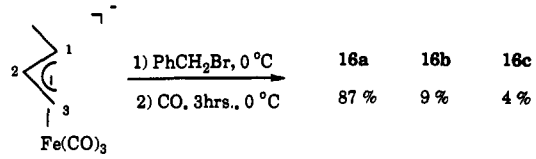
What differences between CH_3CN and PPh_3 result in the opposite regioselectivity of acyl migration? Even though CH_3CN and PPh_3 are electronically quite different (PPh_3 is a much better π-acid than CH_3CN), we believe that the most likely explanation lies in the extreme contrast in the relative sizes of these ligands. We propose that the very bulky PPh_3 ligand directs migration of the acyl group to C_1 to produce initially a monosubstituted alkene complex as noted below. Migration to C_3 to form a much more sterically crowded disubstituted alkene complex is disfavored.

In contrast, for the much smaller CH_3CN ligand there is no discrimination based on the formation of mono- versus disubstituted alkene complexes. In this case it would appear that the slight selectivity for migration to C_3 may be controlled by the



steric preference for σ-bond formation between the acyl unit and an unsubstituted allyl carbon atom.

To further probe the role of ligands in determining the regioselectivity of migration, CO was employed as a trapping ligand. In this case CO possesses π-acid character similar to PPh_3 but steric bulk equivalent to CH_3CN. Benzylation of *syn*-**12** followed by exposure to CO for 3 h at 0 °C resulted in isolation of the free enones, **16a–c**, shown below.



16a	16b	16c
87 %	9 %	4 %

In this case the major product observed, **16a**, is a result of migration to C_3 which supports the idea that steric effects play the major role in determining regioselectivity.

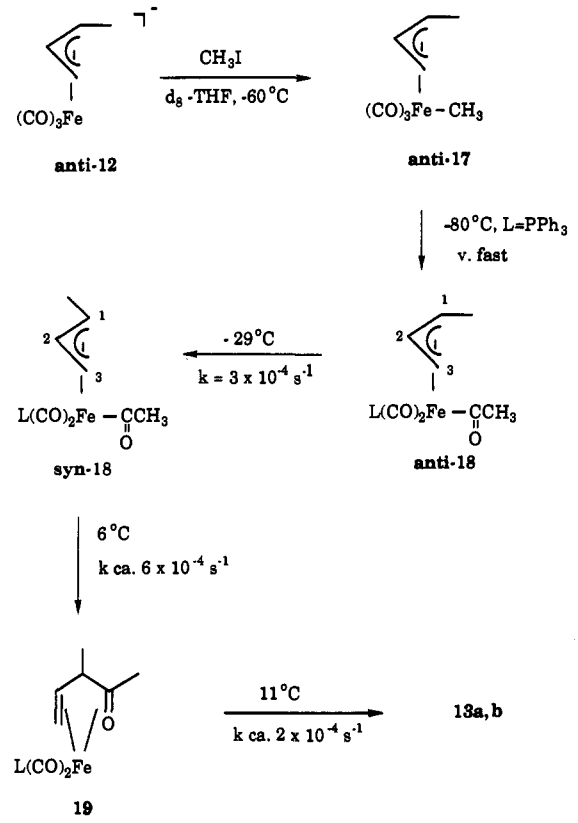
2. *In Situ* ^{1}H NMR Spectroscopic Investigation of the Reaction of *anti*-Methallyl Iron Tricarbonyl Anion, *anti*-12, with CH_3I Followed by Trapping with PPh_3. The fact that *syn*- and *anti*-methallyl iron tricarbonyl anions both yield the same ratio of products **13a–c** upon methylation and subsequent treatment with PPh_3 led us to suspect that at some stage in the reaction prior to acyl migration the *anti* isomer isomerizes to the more stable *syn* isomer to reach a common intermediate. To probe this possibility, an *in situ* ^{1}H NMR study was carried out using *anti*-**12** in an effort to detect any *anti*-to-*syn* transformations which might occur during the course of the reaction.

Remarkably, four sequentially formed intermediates could be identified in the conversion *anti*-**12** to products **13a–c**. The spectroscopic observations are summarized in Scheme 6. Methylation of *anti*-**12** using CH_3I at –60 °C in THF-d_8 gave cleanly (*anti*-methallyl)$Fe(CO)_3CH_3$, *anti*-**17**. The $FeCH_3$ signal appears at δ –0.47. A typical methallyl pattern is observed with the central proton, H_2, appearing as a doublet of triplets ($J_{H1-H2} = J_{Hsyn-H2}$ = 7.4 Hz, $J_{Hanti-H2}$ = 12.9 Hz). The J_{H1-H2} value of 7.4 Hz, typical of a *syn* coupling, establishes that the methyl group has remained *anti*. Treatment of *anti*-**17** with PPh_3 at –80 °C results in immediate conversion to acyl complex, *anti*-**18**. The acetyl methyl of *anti*-**18** appears at δ 2.76. Again a pattern characteristic of an *anti*-methallyl group is evident: δ 4.08 (H_2), 3.64 (H_1), 3.09 (*syn*-H_3), 3.00 (*anti*-H_3), 1.00 (CH_3). The H_2 resonance exhibits a J_{H1-H2} = 8.1 Hz indicative of a *syn* coupling and proof that the methyl group has remained *anti*.

Warming the solution of *anti*-**18** to –29 °C results in *anti*-to-*syn* isomerization and formation of (*syn*-methallyl)$Fe(CO)_2PPh_3$-$C(O)CH_3$, *syn*-**18**. The transformation follows first-order kinetics with $k = 3.0 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ = 18.1 kcal/mol. The acetyl methyl resonance appears at δ 2.87 together with a set of resonances characteristic of a *syn*-methallyl moiety: δ 4.31 (H_2), 2.85 (H_1), 2.24 (*syn*-H_3), 1.65 (*anti*-H_3), and 1.11 (CH_3). Again, the H_2 signal shows a J_{H1-H2} = 13 Hz typical of an *anti* coupling and proof that the methyl group is now *syn*.

When solutions of *syn*-**18** are warmed at 25 °C, rapid conversion to products **13a–c** occurs. However, holding the solution of *syn*-**18** at 6 °C results in observation of an intermediate formed prior to final product formation. While several of the resonances of this species are obscured by *syn*-**18** and products **13a,b** being formed, clearly visible is a new acyl signal at δ 1.82 and a new methyl doublet at δ 1.43 (J = 8.0 Hz). A reasonable assignment for this fleeting intermediate is the β,γ-enone complex **19**, as shown in Scheme 6. Warming this solution to 11 °C results in conversion to products **13a,b**. (On the scale of this experiment, the minor product **13c** could not be observed.) The first-order rate constants obtained for these conversions were $k_{syn\text{-}18 \rightarrow 19} = 6 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ ca. 20 kcal/mol; $k_{19 \rightarrow 13a,b} = 2 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ ca. 21 kcal/mol.

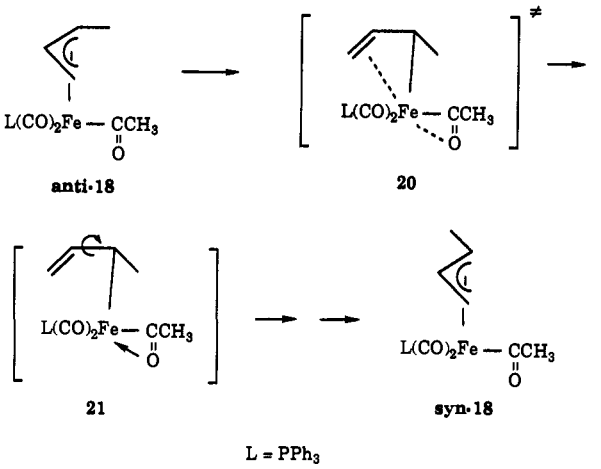
Scheme 6



The observation that *anti*-**18** isomerizes to *syn*-**18** at a rate much faster than acyl migration demonstrates why the same product distributions are obtained from either *syn*- or *anti*-**12** when PPh_3 is used as a trapping ligand. The observation that the same ratio of free enone products are produced upon benzylation of *anti*- or *syn*-**12** and trapping with CH_3CN also suggests isomerization of the intermediate *anti*-acyl complex, *anti*-methallyl $Fe(CO)_2(CH_3CN)C(O)CH_3$, to its *syn* isomer prior to acyl migration. In addition the fact that the major product, **16a**, possesses *E* stereochemistry about the β,γ-double bond further supports *anti*-to-*syn* isomerization in the CH_3CN systems.

The rate of *anti*- to *syn*-**18** isomerization is enormously accelerated relative to *anti* → *syn* isomerization in rather similiar systems. For example, isomerization of *syn*-(CH_3CH–CH–CH_2)$Fe(CO)_3SnMe_3$ to its *anti* isomer occurs at 55 °C with $k = 2.6 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger}$ = 26.2 kcal/mol. This corresponds to a $\Delta\Delta G^{\ddagger}$ of 8 kcal/mol or a rate difference of nearly 10^6 at 25 °C. Although there are several other features which may result in this rate effect (e.g., PPh_3 versus CO substitution), we suggest that the acyl ligand is responsible for this large rate acceleration. The acyl ligand can function in an η^2 fashion and thus is capable of stabilizing the 16-electron σ-allyl intermediate responsible for *anti*-to-*syn* isomerization (Scheme 7). More specifically, as the η^3-*anti*-methallyl ligand transforms to the σ-allyl complex, the acyl oxygen, in a concerted fashion, can stabilize the developing vacant coordination site as shown below in structure **20**. The

Scheme 7

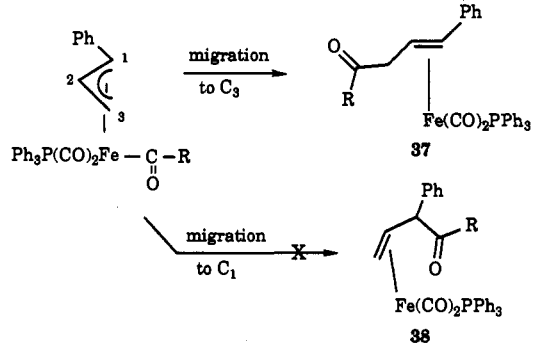


resulting intermediate σ-complex can be formulated as the 18-electron η^2-acyl species, **21**.

C. Reactions of Other Substituted Allyl Iron Tricarbonyl Anions with Alkyl Halide Followed by Trapping with PPh_3 and CH_3CN. Reactions of *syn*-1-propallyl-$Fe(CO)_3^-$, **22**, *syn*-1-phenallyl-$Fe(CO)_3^-$, **23**, 2-methallyl-$Fe(CO)_3^-$, **24**, and *syn*-1-phenyl-*anti*-3-methallyl-$Fe(CO)_3^-$, **25**, with methyl iodide and benzyl bromide have been examined. Anions **22**, **23**, and **24** were generated by sodium amalgam reduction of the corresponding allyl iron tricarbonyl halides; anion **25** was generated by hydride reduction ($KBHEt_3$) of (*trans*-1-phenylbutadiene)$Fe(CO)_3$.[14]

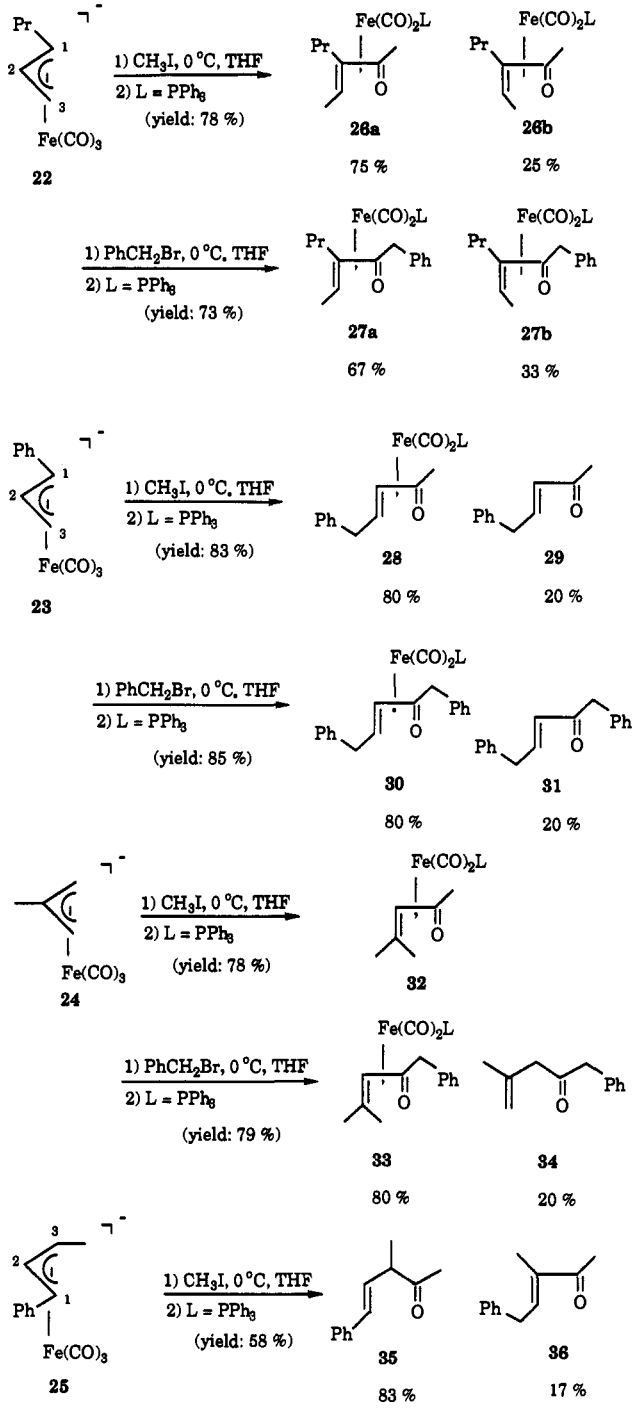
Scheme 8 summarizes results of the alkylation reactions carried out in THF at 0 °C followed by treatment of these solutions with PPh_3. In all cases except **25**, α,β-unsaturated enone–$Fe(CO)_2PPh_3$ complexes were isolated in good yields. While not spectroscopically monitored, we assume the mechanism of formation of these products is similar to the mechanisms deduced for the analogous (allyl)$Fe(CO)_3^-$ and (methallyl)$Fe(CO)_3^-$ reactions.

In the case of the *anti*-1-propyl substituted anion, **22**, enone–$Fe(CO)_2L$ products are analogous to those obtained for the *syn*- and *anti*-methallyl-$Fe(CO)_3^-$ anions. As with the methallyl systems, the acyl group migrates regioselectively to C_1, the propyl-substituted allyl carbon atom. The phenallyl system, **23**, shows the opposite regiochemistry with products **28**, **29** and **30**, **31** arising from acyl migration to C_3 in the case of both $-C(O)CH_3$ and $-C(O)CH_2Ph$ groups. The likely reason for the change in regioselectivity is that, as shown below, migration to C_3 results in initial formation of an alkene complex **37** in which the phenyl group remains conjugated with the C_1–C_2 double bond as shown below. Had migration to C_1 occurred, conjugation of the phenyl group would have been sacrificed in **38**. Apparently in this case, the conjugative interaction outweighs the differences in steric crowding.



In the case of the methallyl anion **24**, the terminal allyl carbons are equivalent and only one α,β-enone–$Fe(CO)_2L$ isomer can

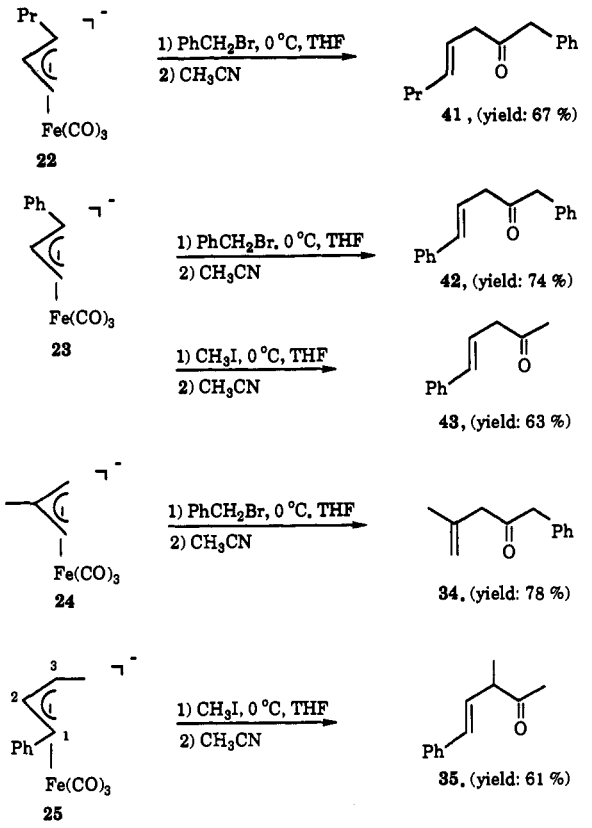
Scheme 8



result, **32** in the case of CH_3I and **33** in the case of $C_6H_5CH_2Br$. The benzylation reaction results in formation of a small amount of the free β,γ-enone, **34**. The 1-phenyl-3-methallyl-$Fe(CO)_3^-$ anion, **25**, as expected based on the behavior of **12** and **23**, exhibits acyl migration exclusively to C_3 upon benzylation and trapping with PPh_3. However, in this case, displacement of the β,γ-enone occurs prior to isomerization to give **35** as the major product. A minor amount of the isomerized α,β-enone, **36**, is also observed. Again, to demonstrate that the free enones can be displaced in good yields for enone–$Fe(CO)_2PPh_3$ systems, complexes **27a**, **28**, **30**, and **33** were irradiated with refluxing or stirred at 25 °C without irradiation in CH_3CN solutions. The α,β-unsaturated enones (**39**, **29**, **31**, and **40**, respectively) were isolated in yields of 65–75%. Details appear in the Experimental Section.

Experiments were also carried out in which anions **22**, **23**, **24**, and **25** were alkylated and then treated with acetonitrile as the trapping ligand. In each of these four cases the β,γ-enones were isolated in good yields as the only products. Results are

Scheme 9



summarized in Scheme 9. Based on the mechanisms delineated earlier for PPh_3 reactions we assume that the acyl species (allyl)$Fe(CO)_2(CH_3CN)C(O)R$ is formed which then undergoes acyl migration to form the β,γ-enone complex. The β,γ-enone is then displaced from these complexes by excess CH_3CN before 1,3-hydrogen migration and formation of the α,β-enone complexes can occur.

The regiochemistry of acyl migration is clear from the structures of the β,γ-enones isolated. Acyl migration in the 1-propyl substituted system occurs exclusively (>15:1) to C_3 to yield **41** as the sole product. This selectivity is substantially higher than in the 1-methallyl system which shows at ca. 2:1 preference for migration to C_3 versus C_1. Steric factors must be responsible for this increased selectivity. Of course the regioselectivity is the opposite of that observed when PPh_3 is used as a trapping ligand where products **26a,b** and **27a,b** result from exclusive migration to C_1.

In the phenyl-substituted system, products **42** and **43** demonstrate that migration of CH_3CO and $C_6H_5CH_2CO$ occurs exclusively to C_3. This is the expected result based on the fact that high regioselectivity for migration to C_3 is observed in the PPh_3 case and the smaller CH_3CN ligand would only serve to enhance that regioselectivity. In the case of the *syn*-1-phenyl-*anti*-3-methallyl-$Fe(CO)_3^-$ system, migration of $-C(O)CH_3$ occurs exclusively to C_3, the methyl-substituted carbon. The free β,γ-enone, **35**, is the sole product. This result further illustrates that the phenyl group strongly prefers to remain conjugated with the double bond of the β,γ-enone initially formed upon acyl migration.

Summary

The following major points have been established.

1. Alkylation (RX = CH_3I, $PhCH_2Br$, $CH_3(CH_2)_3I$, $(CH_3)_2CHBr$, $CH_2{=}CHCH_2Br$) of (allyl)$Fe(CO)_3^-$ followed by trapping with PPh_3 gives good yields of η^4-((*E*)-$CH_3CH{=}CHC(O)R)Fe(CO)_2PPh_3$. The free enones can be readily isolated by displacement with acetonitrile. Using CH_3CN in place of PPh_3 as the trapping ligand at 0 °C under photolysis results in good yields of the free β,γ-enones, the product of acyl migration prior to 1,3-hydrogen shift.

2. Methylation or benzylation of *syn*- or *anti*-methallyl-$Fe(CO)_3^-$ was carried out using either PPh_3 or CH_3CN as the trapping ligand. Results demonstrated that the product ratios are independent of *syn* versus *anti* substitution but the regiochemistry of migration can be controlled by choice of trapping ligand. When PPh_3 is used, acyl migration occurs exclusively to C_1, the methyl-substituted allyl carbon, and α,β-enone–$Fe(CO)_2PPh_3$ complexes are ultimately formed. When CH_3CN is used as the trapping ligand, free β,γ-enones are formed. Regioselectivity is reversed and acyl migration occurs predominantly to C_3. When CO is used as the trapping ligand, selective migration to C_3 is also observed which suggests steric control of the regioselectivity of migration.

3. Methylation or benzylation of 1-phenallyl-$Fe(CO)_3$ followed by trapping with PPh_3 yields α,β-enone complexes, $(PhCH_2CH{=}CHC(O)R)Fe(CO)_2PPh_3$. Regiochemistry of acyl migration is reversed relatively to the methallyl system and occurs exclusively to C_3, presumably due to the conjugative effect of the phenyl group. Use of CH_3CN as the trapping ligand gives good yields of the free β,γ-enones with regioselective acyl migration to C_3. Methylation of the disubstituted system 1-phenyl-3-methallyl-$Fe(CO)_3^-$ and trapping with PPh_3 or CH_3CN gives products indicative of acyl migration exclusively to C_3. In both cases the major product is the free β,γ-enone.

4. *In situ* ^1H NMR studies have allowed detection of several intermediates in the reaction and thus elucidated several mechanistic details. Methylation or benzylation of allyl–$Fe(CO)_3^-$ yields allyl–$Fe(CO)_3$–R complexes (R = $-CH_3$, $-CH_2C_6H_5$). Exposure to PPh_3 at −78 °C gives the acyl complexes allyl–$Fe(CO)_2PPh_3$–C(O)R in less than 5 min. The acyl group migrates to C_1 of the allyl moiety at 20 °C. Free energies of activation for this migration are ca. 21 kcal/mol. In both cases the α,β-enone complexes are formed; no β,γ-enone complexes, presumed intermediates, are detected during migration.

5. ^1H NMR investigation of methylation of the *anti*-1-methylallyl-$Fe(CO)_3^-$ anion revealed a similar behavior but two additional significant observations were made. First, the *anti*-methyl–acyl complex, *anti*-1-methylallyl-$Fe(CO)_2PPh_3C(O)CH_3$ undergoes isomerization to the *syn*-methyl isomer prior to migration. The rate of this isomerization is ca. 10^6 faster than model systems which we attribute to stabilization of the σ-allyl intermediate through η^2-acyl formation. This observation explains why product ratios are independent of *syn*- vs *anti*-methyl substitution. Secondly, acyl migration in this system yields a transient intermediate assigned to the β,γ-enone complex. This observation completes the identification of every plausible intermediate in the conversion allyl-$Fe(CO)_3^-$ anions to α,β-enone–$Fe(CO)_2PPh_3$ complexes through alkylation and trapping with PPh_3.

Experimental Section

General procedures were the same as those previously published.[14] High-resolution mass spectroscopy was performed by Midwest Center for Mass Spectroscopy at University of Nebraska, Lincoln. Elemental analyses for (*Z*)-$CH_3CH{=}CHCOCH_2Ph$, **2a–e**, **3b**, **4b**, **11**, **13a–c**, **14a–c**, **16b–c**, **26a,b**, **27a,b**, **28**, **29**, **30**, **31**, **32**, **33**, **34**, **39**, **40**, and **43** and high-resolution mass spectral data for **10**, **16a**, **41**, **42**, and $CH_2{=}CHCH_2COCH_2Ph$ are contained in the supplementary material. The following compounds were prepared as previously described:[14] *trans*-η^4-$[PhCH{=}CHCH{=}CH_2]Fe(CO)_3$, *anti*-$[CH_3CH{-}CH{-}CH_2]Fe(CO)_3(SnMe_3)$, *syn*-$[CH_3CH{-}CH{-}CH_2]Fe(CO)_3(SnMe_3)$, *anti,syn*-$[CH_3CH{-}CH{-}CHPh]Fe(CO)_3(SnMe_3)$, *syn,syn*-$[CH_3CH{-}CH{-}CHPh]Fe(CO)_3(SnMe_3)$.

η^3-$[CH_2{-}CH{-}CH_2]Fe(CO)_3I$. A modification of the procedure of Murdoch and Weiss was used.[16] To a solution of allyl iodide (20 g, 0.12

(16) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1962**, *225*, 1927.
(17) Nesmeyanov, A. N.; Nekrasov, Y. S.; Avakyan, N. P.; Kritskaya, I. I. *J. Organomet. Chem.* **1971**, *33*, 375.
(18) Plowman, R. A.; Stone, F. G. A. *Z. Naturforsch.* **1962**, *176*, 575.

mol) in hexane (300 mL) was added $Fe(CO)_5$ (47 g, 0.24 mol). The mixture was warmed to 40 °C, and then stirring was continued for 5 h. Ethyl ether was added, and the solution was filtered through silica gel. The solvent was removed to give the crude product as a mixture of two isomers (1.4:1 at 25 °C, 67%, 24.8 g): IR ν_{CO} (THF, cm^{-1}) 2073, 2018, 2011; ^1H NMR ($CDCl_3$, δ), major isomer 4.62 (tt, J = 13.3, 7.9 Hz, 1H, CH_2-CH-), 4.21 (d, J = 7.9 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 3.82 (d, J = 13.3 Hz, 2H, *anti*-H of (CH_2-CH-CH_2), minor isomer 5.71 (tt, J = 13.0, 7.9 Hz, 1H, CH_2-CH-), 3.71 (td, J = 7.9, 1.1 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 2.38 (d, J = 13.0 Hz, 2H, *anti*-H or CH_2-CH-CH_2).

Generation of [(η^3-allyl)tricarbonyliron]$^-Na^+$.[10] To stirring mercury (20 g, 0.1 mol) was added sodium (1.2 g, 0.05 mol) under a nitrogen atmosphere. After formation of the sodium amalgam, the mixture was cooled to 0 °C. A solution of η^3-[CH_2-CH-CH_2]$Fe(CO)_3I$ (1.0 g, 3.2 mol) in THF (30 mL) was added dropwise to the rapidly stirring sodium amalgam. During the addition, a temporary deep red color appeared and then turned to yellow (10–20 min). The yellow solution was filtered through Celite under nitrogen to give η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ in THF solution.

η^3-[CH_2-CH-CH_2]$Fe(CO)_3^-PPN^+$. To freshly prepared η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ (from η^3-[CH_2-CH-CH_2]$FeCO_3I$ (0.5 1.6 mmol)) in THF solution was added bis(triphenylphosphoranylidene)-ammonium chloride (PPNCl, 0.92 g, 1.6 mmol) at 0 °C. After stirring for 10 min, the solution was filtered through Celite under nitrogen; solvent was evaporated to give crude η^3-[CH_2-CH-CH_2]$Fe(CO)_3PPN$. Several recrystallizations using THF/hexane gave the pure product as a bright ivory solid which was unstable in the air but could be stored under nitrogen at −10 °C for several days: IR ν_{CO} (THF, cm^{-1}) 1933, 1830; ^1H NMR (THF-d_8, δ) 4.21 (tt, J = 8.9, 5.3 Hz, 1H, CH_2-CH-CH_2), 1.58 (d, J = 5.3 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 0.92 (d, J = 8.9 Hz, 2H, *anti*-H of CH_2-CH-CH_2).

η^3-[CH_2-CH-CH_2]$Fe(CO)_3(CH_3)$, 5. To η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ (from η^3-[CH_2-CH-CH_2]$Fe(CO)_3I$ (0.5 g, 1.6 mmol)) in THF (30 mL) at 0 °C was added CH_3I (0.28 g, 1.92 mmol). After stirring for 20 min at 0 °C, sodium iodide was removed by filtering through Celite. Evaporation of solvent under reduced pressure gave the crude product which was purified by low-temperature column chromatography using silica gel and hexane/CH_2Cl_2. The product, which was thermally unstable and decomposed in the air, was obtained as a mixture of two isomers (yellow oil, 15:1 at −58 °C): IR ν_{CO} (THF, cm^{-1}) 2050, 1985; major isomer, ^1H NMR ($CDCl_3$, −58 °C, δ) 3.92 (tt, J = 12.2, 7.5 Hz, 1H, CH_2-CH-CH_2), 3.04 (d, J = 7.5 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 2.18 (d, J = 12.2 Hz, 2H, *anti*-H of CH_2-CH-CH_2), −0.51 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, δ {^1H}) 105.6 (CH_2-CH-CH_2), 49.0 (CH_2-CH-CH_2), −2.7 (CH_3); minor isomer, ^1H NMR ($CDCl_3$, −58 °C, δ) 4.20 (m, 1H, CH_2-CH-CH_2), 3.52 (d, J = 7.6 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 1.74 (d, J = 12.5 Hz, 2H, *anti*-H of CH_2-CH-CH_2), −0.42 (s, 3H, CH_3).

η^3-[CH_2-CH-CH_2]$Fe(CO)_3(CH_2Ph)$, 6. Following the same procedure as above using $PhCH_2Br$ (0.33 g, 1.92 mmol) yielded a mixture of two isomers (yellow oil, 5:1 at −13 °C): IR ν_{CO} (THF, cm^{-1}) 2057, 1994, 1711; ^1H NMR (CD_2Cl_2, −13 °C, δ) major isomer, 7.18–6.92 (m, 5H, Ph), 3.92 (tt, J = 12.4, 7.5 Hz, 1H, CH_2-CH-CH_2), 3.16 (d, J = 7.5 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 2.36 (d, J = 12.4 Hz, 2H, *anti*-H of CH_2-CH-CH_2), 1.80 (s, 2H, CH_2Ph), minor isomer, 7.18–6.92 (m, 5H, Ph), 4.21 (tt, J = 11.7, 6.8 Hz, 1H, CH_2-CH-CH_2), 3.58 (d, J = 6.8 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 1.90 (d, J = 11.7 Hz, 2H, *anti*-H of CH_2-CH-CH_2), 1.80 (s, 2H, CH_2Ph).

η^3-[CH_2-CH-CH_2]$Fe(CO)_2PPh_3(COCH_3)$, 7. To a solution of η^3-[CH_2-CH-CH_2]$Fe(CO)_3CH_3$ (0.01 g, 0.05 mmol) in CD_2Cl_2 (0.3 mL) in an NMR tube was added PPh_3 (0.027 g, 0.10 mmol) in CD_2Cl_2 (0.3 mL) at −78 °C. The NMR spectrum indicated the immediate disappearance of the Fe–CH_3 peak (−0.5 ppm) and formation of a new metal acyl peak (2.92 ppm). The product (single isomer) is stable under −10 °C but above that temperature acyl migration begins: IR ν_{CO} (CH_2Cl_2, cm^{-1}) 1991, 1932, 1639; ^1H NMR (CD_2Cl_2, −40 °C, δ) 7.56–7.24 (m, 15H, 3Ph), 4.20 (m, 1H, CH_2-CH-CH_2), 2.92 (s, 3H, $COCH_3$), 2.86 (d, J = 6.9 Hz, 2H, *syn*-H 1.92 (dd, J = 12.2, J_{H-P} = 3.7 Hz, 2H, *anti*-H of CH_2-CH-CH_2).

η^3-[CH_2-CH-CH_2]$Fe(CO)_2PPh_3(COCH_2Ph)$, 8. Following the same procedure as above using η^3-[CH_2-CH-CH_2]$Fe(CO)_3(CH_2Ph)$ gave a single isomer, **8**: IR ν_{CO} (CH_2Cl_2, cm^{-1}) 1990, 1930, 1630; ^1H NMR (CD_2Cl_2, −45 °C, δ) 7.80–7.12 (m, 20H, 4Ph), 4.81 (s, 2H, CH_2Ph), 4.21 (m, 1H, CH_2-CH-CH_2), 2.98 (d, J = 7.5 Hz, 2H, *syn*-H of CH_2-CH-CH_2), 2.04 (dd, J = 12.3, J_{H-P} = 3.5 Hz, 2H, *anti*-H of CH_2-CH-CH_2).

Synthetic Method for Preparation of 2a–e, 3b, and 4b. To a stirred solution of freshly prepared η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ (from η^3-[CH_2-CH-CH_2]$Fe(CO)_3I$ (0.5 g, 1.6 mmol)) in THF (30 mL) at 0 °C under nitrogen was added 1.9 mmol of RX. After stirring for 30 min at 0 °C, 3.2 mmol of the appropriate phosphine or phosphite was added. Stirring was continued at 25 °C for 2 h followed by the normal workup procedure to give the crude product. Products were purified by flash column chromatography using silica gel and CH_2Cl_2/hexane.

η^4-(*E*)-[CH_3CH=$CHCOCH_3$]$Fe(CO)_2PPh_3$, 2a (RX = CH_3I): yellow solid; IR ν_{CO} (THF, cm^{-1}) 1990, 1930, 1835, 1475, 1435; ^1H NMR (C_6D_6, δ) 7.78–7.65 (m, 5H, Ph), 7.10–6.95 (m, 10H, 2Ph), 4.82 (dd, J = 8.2, J_{H-P} = 2.3 Hz, 1H, =CHCO), 2.10 (d, J_{H-P} = 2.5 Hz, 3H, $COCH_3$), 1.56 (m, 1H, CH_3CH=), 1.10 (dd, J = 6.4, 1.8 Hz, 3H, CH_3-CH=); ^{13}C NMR (C_6D_6, δ {H}) 17.1 (CH_3CH=), 21.1 ($COCH_3$), 55.2 (CH_3CH=), 84.2 (=CHCO); yield = 74%.

η^4-(*E*)-[CH_3CH=$CHCOCH_2Ph$]$Fe(CO)_2PPh_3$, 2b (RX = $PhCH_2$-Br): yellow solid; IR ν_{CO} (THF, cm^{-1}) 1990, 1925, 1470, 1430; ^1H NMR (C_6D_6, δ) 7.78–7.68, 7.11–6.98 (m, 15H, 3Ph), 4.95 (dd, J = 8.4, J_{H-P} = 2.0 Hz, 1H, =CHCO), 4.04, 3.69 (2dd, J = 14.8, J_{H-P} = 1.7 Hz, 2H, CH_2Ph), 1.52 (qd, J = 7.3, 2.0 Hz, 1H, CH_3CH=), 0.99 (dd, J = 7.3, 0.6 Hz, 3H, CH_3CH=); ^{13}C NMR ($CDCl_3$, δ {H}) 17.6 (CH_3CH=), 42.4 ($COCH_2Ph$), 56.5 (CH_3CH=), 85.0 (=CHCO); yield = 87%.

η^4-(*E*)-[CH_3CH=$CHCOCH_2CH_2CH_2CH_3$]$Fe(CO)_2PPh_3$, 2c (RX = $CH_3(CH_2)_3I$): yellow solid; IR ν_{CO} (THF, cm^{-1}) 1988, 1926, 1331; ^1H NMR (C_6D_6, δ) 7.80–7.62 (m, 5H, Ph), 7.11–6.92 (m, 15H, 3Ph), 4.98 (dd, J = 8.3, J_{H-P} = 2.0 Hz, 1H, =CHCO), 2.76–2.40 (m, 2H, $COCH_2$), 1.78–1.20 (m, 5H, CH_3CH=, $COCH_2CH_2CH_2$-), 1.14 (dd, J = 6.4, J_{H-P} = 0.8 Hz, 3H, CH_3CH=), 0.84 (t, J = 7.3 Hz, 3H, -CH_2CH_3); ^{13}C NMR (C_6D_6, δ {^1H}) 14.0, 23.0, 30.9, 35.3 ($CH_2CH_2CH_2CH_3$), 17.2 (CH_3CH=), 55.9 (CH_3CH=), 83.5 (=CHCO); yield = 78%.

η^4-(*E*)-[CH_3CH=$CHCOCH(CH_3)_2$]$Fe(CO)_2PPh_3$, 2d (RX = $(CH_3)_2CHBr$): yellow solid; IR ν_{CO} (THF, cm^{-1}) 1950, 1935, 1630; ^1H NMR (C_6D_6, δ) 7.82–7.70, 7.12–6.95 (m, 15H, 3Ph), 5.08 (dd, J = 8.4, J_{H-P} = 2.4 Hz, 1H, =CHCO), 2.86 (septets of d, J = 6.9, J_{H-P} = 1.7 Hz, 1H, -$CH(CH_3)_2$), 1.50 (m, 1H, CH_3CH=), 1.36, 1.30 (2d, J = 6.9, 6.9 Hz, 6H, $CH(CH_3)_2$), 1.10 (d, J = 6.2 Hz, 3H, CH_3CH=); ^{13}C NMR (C_6D_6, δ, {^1H}) 17.1 (CH_3CH=), 20.8, 21.7 ($CH(CH_3)_2$), 33.7 (CH-$(CH_3)_2$), 57.0 (CH_3CH=), 80.9 (=CHCO); yield = 73%.

η^4-(*E*)-[CH_3CH=$CHCOCH_2CH$=CH_2]$Fe(CO)_2PPh_3$, 2e (RX = CH_2=$CHCH_2I$): yellow solid; IR ν_{CO} (THF, cm^{-1}) 1994, 1931, 1721, 1482, 1434; ^1H NMR (C_6D_6, δ) 7.78–7.65, 7.12–6.92 (m, 15H, 3Ph), 6.22–6.12 (m, 1H, -CH=CH_2), 5.15 (dq, J = 17.0, 1.5 Hz, 1H, one of CH=CH_2), 5.10–4.98 (m, 2H, =CHCO, one of CH=CH_2), 3.45–3.12 (m, 2H, $COCH_2$), 1.56 (m, 1H, CH_3CH=), 1.08 (d, J = 6.3 Hz, 3H, CH_3CH=); ^{13}C NMR (C_6D_6, δ, {^1H}) 17.5 (CH_3CH=), 40.6 ($COCH_2$), 56.8 (CH_3CH=), 84.3 (=CHCO), 118.4, 134 (CH=CH_2); yield = 61%. A minor product η^3-$(C_3H_5)_2Fe(CO)_2$, was also obtained in this case and identified by comparison to known material.[11]

η^4-(*E*)-[CH_3CH=$CHCOCH_2Ph$]$Fe(CO)_2P(OMe)_3$, 4b (RX = $PhCH_2Br$): yellow oil; IR ν_{CO} (THF, cm^{-1}) 1999, 1937, 1645; ^1H NMR (C_6D_6, δ) 7.46–7.36, 7.22–7.01 (m, 5H, Ph), 4.95 (dd, J = 8.4, J_{H-P} = 2.7 Hz, 1H, =CHCO), 4.02 (dd, J = 14.8, J_{H-P} = 3.1 Hz, 1H, one of CH_2Ph), 3.76 (dd, J = 14.8, J_{H-P} = 3.9 Hz, 1H, one of CH_2Ph), 3.48 (s, 9H, 3(OMe)), 2.05–1.82 (m, 1H, CH_3CH=), 1.35 (dd, J = 6.4, J_{H-P} = 2.7 Hz, 3H, CH_3CH=); yield = 85%.

η^4-(*E*)-[CH_3CH=$CHCOCH_2Ph$]$Fe(CO)_2P(OPh)_3$, 3b (RX = $PhCH_2Br$): yellow oil; IR ν_{CO} (THF, cm^{-1}) 1998, 1965, 1585, 1475; ^1H NMR (C_6D_6, δ) 7.37–7.28, 7.10–6.98, 6.92–6.80 (m, 20H, 4Ph), 4.95 (dd, J = 8.3, J_{H-P} = 2.7 Hz, 1H, =CHCO), 3.90 (dd, J = 15.2, J_{H-P} = 3.9 Hz, 1H, one of CH_2Ph), 3.68 (dd, J = 15.2, J_{H-P} = 4.9 Hz, 1H, one of CH_2Ph), 2.18 (m, 1H, CH_3CH=), 1.40 (dd, J = 6.4, J_{H-P} = 3.0 Hz, 3H, CH_3CH=); yield = 84%.

Reaction of η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ with $PhCH_2Br$ under Various Conditions. To η^3-[CH_2-CH-CH_2]$Fe(CO)_3Na$ (from η^3-[CH_2-CH-CH_2]$Fe(CO)_3I$, 0.5 g, 1.6 mmol) in THF (30 mL) solution was added $PhCH_2Br$ (1.2 equiv) at 0 °C. The mixture was stirred for 30 min at 0 °C, and then the procedure was varied as follows: (1) CO was purged through the solution for 20 h at 0 °C. The normal workup procedure gave a mixture of three compounds which were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2. (2) Acetonitrile (20 mL) was added. The reaction mixture was stirred at room temperature for 12 h, followed by the normal workup procedure to give the products which were purified as above. (3) Acetonitrile (20 mL) was added. The reaction mixture was irradiated using a sun lamp for 3 h at 0 °C, then filtered through silica gel, and solvent evaporated to give the products which were purified as above.

The ratio of (*E*):(*Z*)-$CH_3CH{=}CHCOCH_2Ph$/$CH_2{=}CHCH_2COCH_2Ph$ and the overall yield is as follows: (1) 2:1:2, 145 mg, 81%; (2) 3.5:trace:1, 140 mg, 78%; and (3) 1:trace:9, 143 mg, 80%.

Product Characterizations. **(*E*)-$CH_3CH{=}CHCOCH_2Ph$, 10**: colorless oil; IR ν_{CO} (THF, cm^{-1}) 1641; ^1H NMR (C_6D_6, δ) 7.20–6.98 (m, 5H, Ph), 6.58 (dq, J = 15.6, 6.9 Hz, 1H, $=CHCO$), 5.90 (dq, J = 15.6, 1.7 Hz, 1H, $CH_3CH{=}$), 3.46 (s, 2H, CH_2Ph), 1.25 (dd, J = 6.9, 1.7 Hz, 3H, CH_3).

$CH_2{=}CHCH_2COCH_2Ph$: colorless oil; IR ν_{CO} (THF, cm^{-1}) 1721; ^1H NMR (C_6D_6, δ) 7.18–7.00 (m, 5H, Ph), 5.89 (m, 1H, $CH_2{=}CH$-), 5.00 (dq, J = 10.3, 1.6 Hz, 1H, *trans*-H of $CH_2{=}CH$-), 4.88 (dq, J = 17.0, 1.6 Hz, 1H, *cis*-H of $CH_2{=}CH$-), 3.27 (s, 2H, CH_2Ph), 2.81 (dt, J = 6.9, 1.6 Hz, 2H, $=CHCH_2$).

(*Z*)-$CH_3CH{=}CHCOCH_2Ph$: colorless oil; IR ν_{CO} (THF, cm^{-1}) 1621; ^1H NMR ($CDCl_3$, δ) 7.10–6.94 (m, 5H, Ph), 5.84 (dq, J = 15.4, 1.7 Hz, 1H, $CH_3CH{=}$), 5.65 (dq, J = 15.4, 6.8 Hz, 1H, $=CHCO$), 3.38 (s, 2H, CH_2Ph), 1.98 (dd, J = 6.8, 1.7 Hz, 3H, CH_3).

η^3-*syn*-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3I$. A modified literature procedure was used.[16] To a solution of *cis*- and *trans*-crotyl iodide (10 g, 55 mmol) in hexane (300 mL) was added $Fe_2(CO)_9$ (40 g, 2 equiv). The mixture was warmed to 40 °C, and stirring was continued for 5 h. Ethyl ether was added and the solution was filtered through silica gel. The solvent was removed to give a mixture of two isomers (only *syn* isomers were obtained, 1:1 mixture of *endo* and *exo* isomers at 25 °C, 4.4 g, yield = 25%):[16] IR ν_{CO} (THF, cm^{-1}) 2075, 2020, 2010; ^1H NMR (C_6D_6, δ) 4.45 (ddd, J = 12.6, 6.3, 6.3 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 3.38 (td, J = 12.5, 7.6 Hz, 1H, $CH_3CH\cdot\cdot$), 3.21 (d, J = 7.6 Hz, 1H, *syn*-H of $\cdot\cdot CH_2$), 3.05 (d, J = 13.5 Hz, 1H, *anti*-H of $\cdot\cdot CH_2$), 1.18 (d, J = 6.3 Hz, 3H, CH_3); second isomer: 5.31 (td, J = 12.4, 7.8 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 2.84 (dd, J = 7.7, 1.5 Hz, 1H, *syn*-H of $\cdot\cdot CH_2$), 2.24–2.04 (m, 1H, $CH_3CH\cdot\cdot$), 1.42 (d, J = 6.1 Hz, 3H, CH_3), 1.26 (d, J = 12.3 Hz, 1H, *anti*-H of $\cdot\cdot CH_2$).

η^3-*syn*-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3Br$. Following the same procedure as previously reported[16] using crotyl bromide gave the product in 40% yield: IR ν_{CO} ($CHCl_3$, cm^{-1}) 2083, 2030, 2009; ^1H NMR ($CDCl_3$, δ) major isomer, 4.82 (td, J = 12.9, 7.9 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 4.94 (m, 1H, $CH_3CH\cdot\cdot$), 4.38 (d, J = 7.9 Hz, 1H, *syn*-H of $\cdot\cdot CH_2$), 3.18 (d, J = 12.9 Hz, 1H, *anti*-H of $\cdot\cdot CH_2$), 2.01 (d, J = 6.3 Hz, 3H, CH_3); minor isomer, signals obscured by major isomer.

η^3-*syn*-$[CH_3CH_2CH_2CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3I$. Following the same procedure as above using a mixture of *cis* and *trans*-1-iodo-2-hexene (10 g, 48 mmol) and $Fe_2(CO)_9$ (34.6 g, 96 mmol) gave the product as a dark brown solid (33% yield, 5.54 g, 1.4:1 isomer mixture): IR ν_{CO} ($CHCl_3$, cm^{-1}) 2075, 2025, 2010; ^1H NMR ($CDCl_3$, δ) major isomer, 4.72 (m, 1H, $-CH_2CH\cdot\cdot CH\cdot\cdot$), 4.41 (td, J = 12.9, 7.9 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 3.98 (dd, J = 7.9, 1.5 Hz, 1H, *syn*-H of $\cdot\cdot CH\cdot\cdot CH_2$, 3.48 (d, J = 12.9 Hz, 1H, *anti*-H of $\cdot\cdot CH\cdot\cdot CH_2$), 2.40–1.20 (m, 4H, $-CH_2CH_2-$), 1.04 (t, J = 7.3 Hz, 3H, CH_3); minor isomer, 5.68 (td, J = 12.3, 7.8 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 4.80–4.65 (m, 1H, $-CH_2CH\cdot\cdot CH_2\cdot\cdot$), 3.50 (d, J = 7.8 Hz, 1H, *syn*-H of $\cdot\cdot CH\cdot\cdot CH_2$), other peaks are obscured.

η^3-*syn*-$[CH_3CH_2CH_2CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3Br$. Following the same procedure as above using *cis,trans*-1-bromo-2-hexane (10 g, 61 mmol) and $Fe_2(CO)_9$ (44.2 g, 122 mmol) gave the product as a dark brown solid (34% yield, 6.3 g, single isomer): IR ν_{CO} (Et_2O, cm^{-1}) 2083, 2035, 2007; ^1H NMR ($CDCl_3$, δ) 4.80 (td, J = 12.8, 7.9 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 4.44 (m, 1H, $-CH_2CH\cdot\cdot$), 4.21 (d, J = 7.7 Hz, 1H, *syn*-H of $\cdot\cdot CH\cdot\cdot CH_2$), 3.21 (dt, J = 13.0, 1.1 Hz, 1H, *anti*-H of $\cdot\cdot CH\cdot\cdot CH_2$), 2.58–2.41 (m, 1H, one of $-CH_2CH\cdot\cdot$), 2.08–1.50 (m, 3H, one of $-CH_2CH\cdot\cdot$, CH_3CH_2), 1.04 (t, J = 7.2 Hz, 3H, CH_3).

syn-η^3-$[PhCH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3Br$. Following the same procedure as reported previously[17] gave the the title compound as a dark yellow solid (60% yield, 11.1 g, two isomers, 5.8:1): ^1H NMR ($CDCl_3$, δ) major isomer, 7.50–7.30 (m, 5H, Ph), 5.62 (td, J = 13.0, 7.9 Hz, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 5.38 (d, J = 13.0 Hz, 1H, $PhCH\cdot\cdot$), 4.31 (dd, J = 7.9, 1.1 Hz, 1H, *syn*-H of $\cdot\cdot CH_2$), 3.45 (dt, J = 13.0, 1.1 Hz, 1H, *anti*-H of $\cdot\cdot CH_2$); minor isomer, 6.05 (m, 1H, $\cdot\cdot CH\cdot\cdot CH_2$), 4.42 (d, J = 13.5 Hz, 1H, $PhCH\cdot\cdot$), 3.86 (dd, J = 8.0, 1.1 Hz, 1H, *syn*-H of $\cdot\cdot CH_2$), 2.52 (dt, J = 13.5, 1.1 Hz, 1H, *anti*-H of $\cdot\cdot CH_2$).

η^3-$[CH_2{\cdot\cdot}C(CH_3){\cdot\cdot}CH_2]Fe(CO)_3I$. Following the same procedure as reported previously[18] gave the the title compound as a dark brown solid (75% yield, 13.3 g, single isomer): ^1H NMR ($CDCl_3$, δ) 4.08 (s, 2H, *syn*-H of $CH_2{\cdot\cdot}C(CH_3){\cdot\cdot}CH_2$), 3.79 (t, J = 1.1 Hz, 2H, *anti*-H of $CH_2{\cdot\cdot}C(CH_3){\cdot\cdot}CH_2$), 2.02 (s, 3H, $CH_2{\cdot\cdot}C(CH_3){\cdot\cdot}CH_2$).

Reaction of syn-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3Na$ with RX (R = $-CH_3$, $-CH_2Ph$). Trapping with PPh_3. To *syn*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3Na$ (from *syn*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3I$, 0.5 g, 1.6 mmol) in THF (30 mL) at 0 °C was added RX (1.92 mmol). After stirring for 20 min at 0 °C, PPh_3 (0.84 g, 3.2 mmol) was added as a solid. Stirring was continued at 25 °C for 2 h. The normal workup procedure gave the crude product as a mixture of three complexes which were purified by flash column chromatography using hexane/CH_2Cl_2 (For RX = MeI, **13a/13b/13c** = 6:3:1, 0.62 g, 82%, for RX = $PhCH_2Br$, **14a/14b/14c** = 2:1:trace, 81%, 0.71 g). Characterization of these complexes is described below.

The Reaction of *anti*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3^-$ with CH_3I. Trapping with PPh_3. *anti*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3^-$ was prepared *in situ* from the reaction of butadiene iron tricarbonyl (0.3 g, 1.5 mmol) with $KB(CH_2CH_3)_3H$ (3.7 mL 1 M THF solution, 2.4 equiv) at 0 °C in THF (30 mL). MeI (0.26 mL, 4 mmol) was added, and the solution was stirred for 5 min. PPh_3 (0.52 g, 2.0 mmol) was added, and stirring was continued for another 2 h at 25 °C. The reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and filtered through silica gel, and the solvent was evaporated to give three products (**13a/13b/13c** = 6:3:1) in 71% yield (0.5 g). Further separation was performed by flash column chromatography on silica gel eluting with petroleum ether/ether, 20:1–5:1. Elution order: **13b, 13a, 13c**.

Reaction of *anti*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3^-$ with $PhCH_2Br$. Trapping with PPh_3. *anti*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3^-$ was generated *in situ* from the reaction of *anti*-η^3-$[CH_3CH{\cdot\cdot}CH{\cdot\cdot}CH_2]Fe(CO)_3(SnMe_3)$ (0.5 g, 1.4 mmol) with MeLi (1.6 M in diethyl ether, 1.2 equiv, 1.1 mL) in THF (30 mL) at 0 °C. To this solution was added $PhCH_2Br$ (0.2 mL, 1.7 mmol). After stirring for 5 min, PPh_3 (0.43 g, 1.7 mmol) was added, and the mixture was stirred for 2 h at 25 °C. The reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and filtered through silica gel, and solvent was evaporated to give two products (**14a/14b** = 2:1) in 75% yield (0.58 g). Further separation was performed by flash column chromatography on silica gel eluting with petroleum ether/ether, 20:1–5:1. Elution order: **14b, 14a**.

Product Characterizations. **η^4-(*E*)-$[CH_3CH{=}C(CH_3)COCH_3]Fe(CO)_2PPh_3$, 13a**: yellow solid; IR ν_{CO} (C_6D_6, cm^{-1}) 1988, 1923; ^1H NMR (C_6D_6, *THF-d_8*, δ) 7.80–7.65, 7.11–6.94 (m, 15H, 3Ph), 2.18, *2.19* (d, J_{H-P} = 2.5 Hz, 3H, $COCH_3$), 1.85, *2.09* (d, J_{H-P} = 2.2 Hz, 3H, $=C(CH_3)CO$), 1.57, *1.26* (quin, J = 6.8 Hz, 1H, $CH_3CH{=}$), 1.12, *1.08* (dd, J = 6.5, J_{H-P} = 1.4 Hz, 3H, $CH_3CH{=}$); ^{13}C NMR (C_6D_6, δ) 13.9, 14.7, 18.7 (q, J = 127, 126, 127 Hz, $CH_3CH{=}$, $=C(CH_3)CO$, $=CCOCH_3$), 58.3 (d, J = 160 Hz, $CH_3CH{=}$), 95.1 (s, $=C(CH_3)COCH_3$), 211.1 (s, CH_3CO), 216.5 (d, J_{H-P} = 7.3 Hz, $Fe(CO)_2$); ^{31}P NMR (C_6D_6, δ), 56.7; ^{13}C NMR (C_6D_6, δ, $\{^{31}P\}$, $\{^1H\}$) 216.5 (s, $Fe(CO)_2$).

η^4-(*Z*)-$[CH_3CH{=}C(CH_3)COCH_3]Fe(CO)_2PPh_3$, 13b: yellow solid; IR ν_{CO} (C_6D_6, cm^{-1}) 1990, 1927; ^1H NMR (C_6D_6, *THF-d_8*, δ) 7.80–7.65, 7.11–6.94 (m, 15H, 3Ph), 2.61, *2.47* (qd, J = 6.7, J_{H-P} = 1.5 Hz, 1H, $CH_3CH{=}$), 1.97, 1.94, *2.13*, *1.96* (2d, J_{H-P} = 1.6, 1.9 Hz, 6H, $COCH_3$, $=C(CH_3)CO$), 1.19, *0.85* (dd, J_{H-P} = 3.3, J = 6.7 Hz, 3H, $CH_3CH{=}$); ^{13}C NMR (C_6D_6, δ) 13.2, 19.3, 20.4 (q, J = 127, 119, 119 Hz, $CH_3CH{=}$, $=C(CH_3)CO$, $=CCOCH_3$), 55.3 (d, J = 145 Hz, $CH_3CH{=}$), 91.7 (s, $=C(CH_3)COCH_3$), 211.1 (s, CH_3CO), 216.5 (d, J_{H-P} = 7.3 Hz, $Fe(CO)_2$).

η^4-$[CH_2{=}C(CH_2CH_3)COCH_3]Fe(CO)_2PPh_3$, 13c: yellow solid; IR ν_{CO} (C_6D_6, cm^{-1}) 1988, 1923; ^1H NMR (C_6D_6, δ) 7.80–7.65, 7.11–6.94 (m, 15H, 3Ph), 2.68–2.45 (m, 1H, *trans*-H of $CH_2{=}$), 2.31 (d, J_{H-P} = 2.7 Hz, 3H, $COCH_3$), 1.45–1.18 (m, 3H, *cis*-H of $CH_2{=}$, $=C(CH_2CH_3)$), 1.08 (t, J = 7.5 Hz, 3H, $=C(CH_2CH_3)$).

η^4-(*E*)-$[CH_2CH{=}C(CH_3)COCH_2Ph]Fe(CO)_2PPh_3$, 14a: yellow solid; IR ν_{CO} (C_6D_6, cm^{-1}) 1988, 1925; ^1H NMR (C_6D_6, δ) 7.79–7.62, 7.40–6.95 (m, 20H, 4Ph), 4.40 (dd, J = 14.4, J_{H-P} = 2.0 Hz, 1H, one of CH_2Ph), 3.65 (d, J = 14.4 Hz, 1H, one of CH_2Ph), 1.94 (d, J_{H-P} = 2.1 Hz, 3H, $=C(CH_3)CO$), 1.54 (quin, J = 6.9 Hz, 1H, $CH_3CH{=}$), 1.06 (dd, J = 6.6, J_{H-P} = 1.5 Hz, 3H, $CH_3CH{=}$); ^{13}C NMR (C_6D_6, δ) 13.8, 14.4 (q, J = 127, 126 Hz, $CH_3CH{=}$, $=C(CH_3)(CO)$, 39.8 (t, J = 129 Hz, CH_2Ph), 59.6 (d, J = 129 Hz, $CH_3CH{=}$), 96.4 (s, $=C(CH_3)CO$), 126.6 (d, J = 160 Hz, C_p of CH_2Ph), 128.7, 129.4 (d, J = overlap, 156 Hz, C_m, C_o of CH_2Ph), 138.7 (s, C_i of CH_2Ph), 210.8 (s, CH_2PhCO), 216.3 (d, J_{H-P} = 7.4 Hz, $Fe(CO)_2$).

η^4-(*Z*)-$[CH_3CH{=}C(CH_3)COCH_2Ph]Fe(CO)_2PPh_3$, 14b: yellow solid; IR ν_{CO} (C_6D_6, cm^{-1}) 1993, 1929; ^1H NMR (C_6D_6, δ) 7.79–7.62, 7.40–6.95 (m, 20H, 4Ph), 4.16 (d, J = 14.4 Hz, 1H, one of CH_2Ph), 3.24 (d, J = 14.4 Hz, 1H, one of CH_2Ph), 2.58 (qd, J = 6.8, J_{H-P} = 1.4 Hz, 1H, $CH_3CH{=}$), 2.02 (d, J_{H-P} = 1.5 Hz, 3H, $=C(CH_3)CO$), 1.14 (dd, J = 6.6, J_{H-P} = 3.3 Hz, 3H, $CH_3CH{=}$); ^{13}C NMR (C_6D_6, δ) 13.0, 20.3 (q, J = 127, 127 Hz, $CH_3CH{=}$, $=C(CH_3)CO$), 40.22 (t, J = 127 Hz, CH_2Ph) 55.9 (d, J = 138 Hz, $CH_3CH{=}$), 92.9 (s, $=C(CH_3)CO$), 126.6 (d, J = 161 Hz, C_p of CH_2Ph), 128.8, 129.1 (d, J = overlap, 156 Hz, C_m, C_o of CH_2Ph), 138.6 (s, C_i of CH_2Ph), 210.8 (s, CH_2PhCO), 216.3 (d, J_{H-P} = 7.4 Hz $Fe(CO)_2$).

η^4-[CH_2=C(CH_2CH_3)$COCH_2Ph$]$Fe(CO)_2PPh_3$, 14c: yellow oil; IR ν_{CO} (THF, cm^{-1}) 1990, 1923; ^1H NMR (C_6D_6, δ) 7.79–7.62, 7.40–6.95 (m, 20H, 4Ph), 4.45 (dd, J = 14.4, J_{H-P} = 2.0 Hz, 1H, one of CH_2Ph), 3.94 (d, J = 14.4 Hz, 1H, one of CH_2Ph), 2.71 (m, 1H, *trans*-H of CH_2=), 1.70–1.40 (m, 3H, =C(CH_2CH_3), *cis*-H of CH_2=), 0.98 (t, J = 7.5 Hz, 3H, =C(CH_2CH_3)).

Reactions of *syn*-η^3-[CH_3CH-CH-CH_2]$Fe(CO)_3Na$ with $PhCH_2Br$ under Various Conditions. To *syn*-η^3-[CH_3CH-CH-CH_2]$Fe(CO)_3$Na (from *syn*-η^3-[CH_3CH-CH-H_2]$Fe(CO)_3I$, 0.5 g, 1.6 mmol) in THF (20 mL) solution was added $PhCH_2Br$ (1.2 equiv) at 0 °C. The mixture was stirred for 30 min at 0 °C, and then the procedure was varied as follows: (1) Acetonitrile (20 mL) was added. The reaction mixture was stirred at 25 °C for 18 h, then filtered through Celite, and solvent evaporated to give the crude products which were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2. (2) Acetonitrile (20 mL) was added. The reaction mixture was irradiated using a sun lamp for 1 h at 0 °C and worked up as above. (3) CO was purged through the solution for 3 h at 0 °C and worked up as above.

The ratio of the products and overall yield is as follows: (1) **16a/16b/16c** = 6:2:1, 72%, 200 mg, (2) 7:2.8:1, 73%, 200 mg; and (3) 20:2:1, 77%, 210 mg.

Reaction of *anti*-η^3-[CH_3CH-CH-CH_2]$Fe(CO)_3^-$ with $PhCH_2Br$. Trapping with CH_3CN. *anti*-η^3-[CH_3CH-CH-CH_2]$Fe(CO)_3^-$ was generated *in situ* from the reaction of *anti*-η^3-[CH_3CH-CH-CH_2]-$Fe(CO)_3(SnMe_3)$ (0.3 g, 0.8 mmol) with MeLi (1.2 equiv, 0.63 mL) in THF (30 mL) at 0 °C. To this solution was added $PhCH_2Br$ (0.12 mL, 1.0 mmol). After stirring for 5 min at 0 °C, acetonitrile (30 mL) was added and stirred for 3 days at 25 °C. Standard workup gave three products (**16a/16b/16c** = 6:2:1) in 62% yield (86 mg). Further separation was performed by preparative thin-layer chromatography using hexane/EtOAc. Elution order: **16b, 16a, 16c**.

Product Characterizations. (*E*)-CH_2CH=$CHCH_2COCH_2Ph$, 16a: IR ν_{CO} (THF, cm^{-1}) 1718; ^1H NMR (C_6D_6, δ) 7.12–6.90 (m, 5H, Ph), 5.48 (m, 1H, CH_3CH=C*H*-), 5.21 (m, 1H, CH_3CH=CH-), 3.27 (s, 2H, CH_2Ph), 2.78 (m, 2H, =$CHCH_2CO$), 1.47 (dq, J = 6.3, 1.4 Hz, 3H, CH_3CH=); decoupling exp., irradiation at CH_3 gives 5.48 (dt, J = 15.1, 6.9 Hz, 1H, CH_3CH=C*H*CH_2), 5.21 (d, J_{tr} = 15.1 Hz, 1H, CH_3CH=CH-); ^{13}C NMR ($CDCl_3$, δ {H}) 18.0 (CH_3), 45.9, 49.4 (-CH_2-$COCH_2Ph$), 122.9, 134.2 (-CH=CH-).

CH_2=$CHCH(CH_3)COCH_2Ph$, 16b: IR ν_{CO} (hexane/CH_2Cl_2, cm^{-1}) 1721; ^1H NMR (C_6D_6, δ) 7.15–6.90 (m, 5H, Ph), 5.60 (m, 1H, CH_2=C*H*), 4.88 (m, 2H, CH_2=CH-), 3.28 (s, 2H, $COCH_2Ph$), 2.95 (quin, J = 6.9 Hz, 1H, =$CHCH(CH_3)$-), 1.00 (d, J = 6.8 Hz, 3H, CH_3).

(*E*)-CH_3CH=$C(CH_3)COCH_2Ph$, 16c: IR ν_{CO} (THF, cm^{-1}) 1628; ^1H NMR (C_6D_6, δ) 7.17–6.98 (m, 5H, Ph), 6.35 (qq, J = 6.9, 1.4 Hz, 1H, CH_3CH=), 3.66 (s, 2H, CH_2Ph), 1.68 (m, 3H, =$C(CH_3)$), 1.30 (dq, J = 6.9, 1.0 Hz, 3H, CH_3CH=).

Low-Temperature ^1H NMR Monitoring of the Reaction of *anti*-Methallyl Iron Tricarbonyl Anion, *anti*-12, with CH_3I Followed by Trapping with PPh_3. To an *anti*-[CH_3CH-CH-CH_2]$Fe(CO)_3^-K^+$ (8 mg, 0.03 mmol)[14] in THF-d_8 (0.55 mL) was added MeI (4.3 μL, 2 equiv) at –78 °C. All starting material was converted to (*anti*-methallyl)$Fe(CO)_3$-(CH_3), *anti*-**17**, at –60 °C. To this solution was added PPh_3 (24 mg, 0.10 mmol) in THF-d_8 (0.06 mL) at –78 °C. The NMR spectrum indicated the immediate disappearance of the Fe–CH_3 peak (–0.47 ppm) and formation of new metal–acyl peak (2.76 ppm) at this temperature. Upon warming to –29 °C, *anti* complex, *anti*-**18**, generated *in situ*, isomerized to the thermodynamically more stable *syn* isomer, *syn*-**18**. The rate of isomerization of *anti*-**18** to *syn*-**18** was measured at –29 °C. The decrease in the intensity of the signal at δ 1.00 assigned to *anti*-**18** was monitored relative to the increase in the intensity of the signal at δ 1.11 assigned to *syn*-**18**. After *syn*-**18** was formed the solution was warmed to 6 °C, and the acyl group ($CH_3C(O)$-) in *syn*-**18** migrated exclusively to the substituted carbon (C_1) of the allyl moiety to generate the η^4-β,γ complex, **19**. The rate of migration was measured at 6 °C. The decrease in the intensity at δ 2.83 assigned to *syn*-**18** was monitored relative to the THF-d_8 signal at δ 3.58. Upon warming to 11 °C, hydride migration occurred from the η^4-β,γ complex, **19**, to yield the more stable η^4-α,β complexes, **13a,b**. The decrease in the intensity at δ 1.82 assigned to the acyl group of β,γ complex, **19**, was monitored relative to the constant THF-d_8 signal at δ 3.58. The ^1H NMR data for all intermediates observed are summarized below.

***anti*-[CH_3CH-CH-CH_2]$Fe(CO)_3(CH_3)$, *anti*-17**: ^1H NMR (THF-d_8, δ) 4.18 (quin, J = 7.0 Hz, 1H, -$CHCH_3$), 3.81 (dt, J_{tr} = 12.9, J_{cis} = 7.4 Hz, 1H, CH_2-C*H*), 3.34 (d, J = 7.4 Hz, 1H, *syn*-H of CH_2-), 2.88 (d, J = 12.9 Hz, 1H, *anti*-H of CH_2-), 1.32 (d, J = 7.1 Hz, 3H, -$CHCH_3$), –0.47 (s, 3H, $Fe(CH_3)$).

***anti*-[CH_3CH-CH-CH_2]$Fe(CO)_2(PPh_3)(COCH_3)$, *anti*-18**: ^1H NMR (THF-d_8, δ, –30 °C) 4.08 (ddt, J_{H-P} = 18.1, J_{tr} = 13.7, J_{cis} = 8.1 Hz, 1H, CH_2-C*H*), 3.64 (quin, J = 7.6 Hz, 1H, -$CHCH_3$), 3.09 (d, J = 8.1 Hz, 1H, *syn*-H of CH_2-), 3.00 (dd, J = 13.4, J_{H-P} = 3.2 Hz, 1H, *anti*-H of CH_2-), 2.76 (s, 3H, $Fe(COCH_3)$), 1.00 (d, J = 6.4 Hz, 3H, -$CHCH_3$).

***syn*-[CH_3CH-CH-CH_2]$Fe(CO)_2(PPh_3)(COCH_3)$, *syn*-18**: ^1H NMR (THF-d_8, δ, –30 °C) 4.31 (qd, J_{H-P} = 13, J_{tr} = 13, J_{cis} = 8 Hz, 1H, CH_2-C*H*), 2.87 (s, 3H, $Fe(COCH_3)$), 2.85 (m, 1H, -$CHCH_3$), 2.24 (d, J = 7.6 Hz, 1H, *syn*-H of CH_2-), 1.65 (dd, J = 13.1, J_{H-P} = 6.8 Hz, 1H, *anti*-H of CH_2-), 1.11 (d, J = 6.4 Hz, 3H, -$CHCH_3$).

η^4-[CH_2=$CHCH(CH_3)COCH_3$]$Fe(CO)_2PPh_3$, 19: ^1H NMR (THF-d_8, δ, 6 °C) 1.82 (s, $COCH_3$), 1.43 (d, J = 8.0 Hz, =$CHCH(CH_3)$). The remaining signals were obscured.

Reaction of *syn*-η^3-[CH_2-CH-$CHCH_2CH_2CH_2$]$Fe(CO)_3Na$ with CH_3I. Trapping with PPh_3. Following the same procedure as that for *syn*-η^3-[CH_3CH-CH-CH_2]$Fe(CO)_3Na$, reaction of η^3-[CH_2-CH-$CHCH_2CH_2CH_3$]$Fe(CO)_3Na$ (1.43 mmol) with CH_3I (0.24 g, 1.72 mmol) and PPh_3 (0.73 g, 2.9 mmol) gave complexes **26a** and **26b** as the major products. These were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (1.1 g, 78%).

η^4-(*E*)-[CH_2CH=$C(CH_2CH_2CH_3)COCH_3$]$Fe(CO)_2PPh_3$, 26a: yellow oil; IR ν_{CO} ($CHCl_3$, cm^{-1}) 1988, 1927; ^1H NMR (C_6D_6, δ) 7.80–7.68, 7.12–6.94 (m, 15H, 3Ph), 2.46 (m, 1H, one of =$C(CH_2CH_2CH_3)$), 2.21 (m, 1H, one of =$C(CH_2CH_2CH_3)$), 2.22 (d, J_{H-P} = 2.5 Hz, 3H, $COCH_3$), 1.64–1.40 (m, 3H, CH_3CH=, =$C(CH_2CH_2CH_3)$), 1.20 (dd, J = 6.6, J_{H-P} = 1.4 Hz, 3H, CH_3CH=), 0.88 (t, J = 7.3 Hz, 3H, =$C(CH_2CH_2CH_3)$); ^{13}C NMR (C_6D_6, δ {H}) 14.0, 14.1, 18.4, 23.3, 31.1, 57.8, 93.7 (CH_3CH=$C(CH_2CH_2CH_3)COCH_3$).

η^4-(*Z*)-[CH_2CH=$C(CH_2CH_2CH_3)COCH_3$]$Fe(CO)_2PPh_3$, 26b: yellow oil; IR ν_{CO} (hexane, cm^{-1}) 1982, 1924; ^1H NMR (C_6D_6, δ) 7.81–7.62, 7.12–6.91 (m, 15H, 3Ph), 2.68 (m, 1H, CH_3CH=), 2.50–2.10 (m, 2H, =$C(CH_2CH_2CH_3)$), 2.20 (d, J_{H-P} = 2.2 Hz, 3H, $COCH_3$), 1.18 (dd, J = 7.1, J_{H-P} = 1.3 Hz, 3H, CH_3CH=), 0.86 (t, J = 7.0 Hz, 3H, =$C(CH_2CH_2CH_3)$).

Reaction of *syn*-η^3-[CH_2-CH-$CHCH_2CH_2CH_2$]$Fe(CO)_3Na$ with $PhCH_2Br$. Following the same procedure as described above, η^3-[CH_2-CH-$CHCH_2CH_2CH_3$]$Fe(CO)_3Na$ (1.43 mmol), $PhCH_2Br$ (0.29 g, 1.72 mmol) and PPh_3 (0.73 g, 2.9 mmol) gave complexes **27a** and **27b** as the major products. These were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (0.6 g, 73%).

η^4-(*E*)-[CH_3CH=$C(CH_2CH_2CH_3)COCH_2Ph$]$Fe(CO)_2PPh_3$, 27a: yellow oil; IR ν_{CO} ($CHCl_3$, cm^{-1}) 1993, 1927; ^1H NMR (C_6D_6, δ) 7.80–7.68, 7.42–7.36, 7.15–6.95 (m, 20H, 4Ph), 4.38 (dd, J = 13.7, J_{H-P} = 2.0 Hz, 1H, one of CH_2Ph), 3.82 (d, J = 13.7 Hz, 1H, one of CH_2Ph), 2.70–2.52, 2.36–2.16 (m, 2H, =$C(CH_2CH_2CH_3)$), 1.59 (m, 1H, CH_3CH=), 1.48–1.18 (m, 2H, =$C(CH_2CH_2CH_3)$), 1.18 (dd, J = 7.0, J_{H-P} = 1.4 Hz, 3H, CH_3CH=), 0.82 (t, J = 7.2 Hz, 3H, =$C(CH_2CH_2CH_3)$); ^{13}C NMR (C_6D_6, δ {^{1}H}) 13.8, 14.4, 23.5, 31.5, 39.2, 58.9, 100.0 (CH_3CH=$C(CH_2CH_2CH_3)COCH_2Ph$).

η^4-(*Z*)-[CH_3CH=$C(CH_2CH_2CH_3)COCH_2Ph$]$Fe(CO)_2PPh_3$, 27b: yellow oil; IR ν_{CO} (THF, cm^{-1}) 1992, 1927; ^1H NMR (C_6D_6, δ) 7.80–7.68, 7.20–6.95 (m, 20H, 4Ph), 4.25 (d, J = 13.7 Hz, 1H, one of CH_2Ph), 3.38 (d, J = 13.7 Hz, 1H, one of CH_2Ph), 2.70 (m, 1H, CH_3CH=), 2.00–1.20 (m, 4H, =$C(CH_2CH_2CH_3)$), 1.24 (dd, J = 7.0, J_{H-P} = 3.0 Hz, 3H, CH_3CH=), 0.89 (t, J = 7.1 Hz, 3H, =$C(CH_2CH_2CH_3)$).

Reaction of *syn*-η^3-[$PhCH$-CH-CH_2]$Fe(CO)_3Na$ with CH_3I. Following the same procedure as described above using *syn*-η^3-[$PhCH$-CH-CH_2]$Fe(CO)_3Na$ (1.5 mmol), CH_3I (0.26 g, 1.8 mmol), and PPh_3 (0.79 g, 3.0 mmol) gave the product as a mixture of **28a** and **29**. These were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (83%, 4:1).

η^4-*E*-[$PhCH_2CH$=$CHCOCH_3$]$Fe(CO)_2PPh_3$, 28: yellow solid; IR ν_{CO} (THF, cm^{-1}) 1990, 1928; ^1H NMR (C_6D_6, δ) 7.79–7.65, 7.15–6.91 (m, 20H, 4Ph), 4.99 (dd, J = 8.3, J_{H-P} = 2.2 Hz, 1H, =CHCO), 2.69 (dd, J = 14.0, 5.6 Hz, 1H, one of $PhCH_2$), 2.55 (dd, J = 14.0, 9.8 Hz, 1H, one of $PhCH_2$), 2.06 (d, J_{H-P} = 2.6 Hz, 3H, $COCH_3$), 1.80 (m, 1H, $PhCH_2CH$=).

(*E*)-$PhCH_2CH$=$CHCOCH_3$, 29: IR ν_{CO} (THF, cm^{-1}) 1672; ^1H NMR ($CDCl_3$, δ) 7.30–7.18 (m, 5H, Ph), 6.85 (dt, J = 15.9, 6.8 Hz, 1H, $PhCH_2CH$=), 6.01 (dt, J = 15.9, 1.6 Hz, 1H, =CHCO), 3.48 (dd, J = 6.8, 1.4 Hz, 2H, $PhCH_2$-), 2.18 (s, 3H, CH_3).

The Reaction of *syn*-η^3-[$PhCH$-CH-CH_2]$Fe(CO)_3Na$ with $PhCH_2Br$. Trapping with PPh_3. Following the same procedure as described above, using *syn*-η^3-[$PhCH$-CH-CH_2]$Fe(CO)_3Na$ (1.5 mmol), $PhCH_2Br$ (0.31 g, 1.8 mmol), and PPh_3 (0.79 g, 3.0 mmol) gave a mixture

of two compounds, **30** and **31**, which were purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (0.51 g, 85%, 4:1).

η^4-(*E*)-[PhCH$_2$CH=CHCOCH$_2$Ph]Fe(CO)$_2$PPh$_3$, 30: IR ν_{CO} (THF, cm^{-1}) 1990, 1929; ^1H NMR (C_6D_6, δ) 7.78–7.65, 7.38–7.30, 7.15–6.72 (m, 25H, 5Ph), 5.10 (dd, J = 8.1, J_{H-P} = 2.2 Hz, 1H, =C*H*CO), 3.98 (dd, J = 15.0, J_{H-P} = 1.6 Hz, 1H, one of COC*H*$_2$Ph), 3.67 (d, J = 15.0 Hz, 1H, one of COC*H*$_2$Ph), 2.64 (dd, J = 14.6, 5.3 Hz, one of PhC*H*$_2$-CH=), 2.50 (dd, J = 14.6, 9.8 Hz, one of PhC*H*$_2$CH=), 1.79 (m, 1H, PhCH$_2$C*H*=); ^{13}C NMR (C_6D_6, δ {^1H} 38.7, 41.9 (Ph*C*H$_2$CH=, CO*C*H$_2$-Ph), 61.8 (PhCH$_2$*C*H=), 82.7 (=*C*HCO).

(*E*)-PhCH$_2$CH=CHCOCH$_2$Ph, 31: IR ν_{CO} (THF, cm^{-1}) 1612; ^1H NMR ($CDCl_3$, δ) 7.39–7.10 (m, 10H, 2Ph), 7.00 (dt, J = 15.7, 6.9 Hz, 1H, PhCH$_2$C*H*=), 6.14 (dt, J = 15.7, 1.5 Hz, 1H, =C*H*CO), 3.82 (s, 2H, COC*H*$_2$Ph), 3.51 (dd, J = 6.9, 1.2 Hz, 2H, PhC*H*$_2$CH=).

Synthesis of η^4-(*E*)-[(CH$_3$)$_2$C=CHCOCH$_3$]Fe(CO)$_2$PPh$_3$, 32. Following the normal procedure, *syn*-η^3-[CH$_2$⁻⁻CH(CH$_3$)⁻⁻CH$_2$]Fe(CO)$_3$Na (1.6 mmol), CH_3I (0.27 g, 1.92 mmol), and PPh_3 (0.84 g, 3.2 mmol) gave the product, **32**, as a yellow solid, which was purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (0.59 g, 78%): IR ν_{CO} ($CHCl_3$, cm^{-1}) 1988, 1924, 1481, 1436; ^1H NMR (C_6D_6, δ) 7.68–7.56, 7.09–6.92 (m, 15H, 3Ph), 4.71 (s, 1H, =C*H*CO), 1.65 (d, J = 4.5 Hz, 3H, COC*H*$_3$), 1.52–1.45 (m, 6H, 2C*H*$_3$).

Synthesis of η^4-(*E*)-[(CH$_3$)$_2$C=CHCOCH$_2$Ph]Fe(CO)$_2$PPh$_3$, 33: Following the normal procedure, η^3-[CH$_2$⁻⁻CH(CH$_3$)⁻⁻CH$_2$]Fe(CO)$_3$Na (1.6 mmol), PhCH$_2$Br (0.31 g, 1.92 mmol), and PPh_3 (0.84 g, 3.2 mmol) gave **33** (yellow solid) as a major product, together with CH_2=C(CH$_3$)CH$_2$COCH$_2$Ph (4:1, 79%), which were purified by flash chromatography using silica gel and hexane/CH_2Cl_2: IR ν_{CO} ($CHCl_3$, cm^{-1}) 1992, 1929; ^1H NMR ($CDCl_3$, δ) 7.58–6.92 (m, 15H, 3Ph), 5.02 (s, 1H, =C*H*CO), 3.53, 2.58 (2d, J = 14.2 Hz, 2H, C*H*$_2$Ph), 1.42 (d, J = 2.9 Hz, 3H, *trans*-C*H*$_3$), 1.31 (d, J = 4.5 Hz, 3H, *cis*-C*H*$_3$).

Synthesis of CH$_2$=C(CH$_3$)CH$_2$COCH$_2$Ph, 34: To η^3-[CH$_2$⁻⁻CH(CH$_3$)⁻⁻CH$_2$]Fe(CO)$_3$Na (1.6 mmol) in THF (30 mL) at 0 °C was added PhCH$_2$Br (0.33 g, 1.92 mmol). After stirring for 20 min at 0 °C, acetonitrile (30 mL) was added, and then the reaction mixture was irradiated using a sun lamp at 0 °C for 2 h. Stirring for 12 h at 25 °C without light gave the same product. The mixture was filtered through silica gel to give a colorless oil which was purified by flash column chromatography using silica gel and hexane/CH_2Cl_2 (0.22 g, 78%): IR ν_{CO} ($CHCl_3$, cm^{-1}) 1716; ^1H NMR ($CDCl_3$, δ) 7.38–7.15 (m, 5H, Ph), 4.98 (t, J = 1.5 Hz, 1H, *cis*-H of C*H*$_2$=), 4.81 (s, 1H, *trans*-H of C*H*$_2$=), 3.75 (s, 2H, C*H*$_2$Ph), 3.16 (s, 2H, C*H*$_2$CO), 1.72 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, δ {^1H} 22.6 (*C*H$_3$), 49.1, 51.3 (*C*H$_2$Ph, *C*H$_2$CO), 115.3 (*C*H$_2$=), 134.1 (=*C*(CH$_3$)).

The Reaction of *anti,syn*-η^3-[PhCH⁻⁻CH⁻⁻CHCH$_3$]Fe(CO)$_3^-$ with CH$_3$I. Trapping with PPh$_3$. *anti,syn*-η^3-[PhCH⁻⁻CH⁻⁻CHCH$_3$]Fe(CO)$_3^-$ was generated *in situ* from the reaction of *trans*-1-phenylbutadiene iron tricarbonyl (300 mg, 1.11 mmol) with KBHEt$_3$ (2.4 equiv, 2.7 mL) in THF (30 mL) at 0 °C. To this solution was added CH_3I (0.26 mL, 4.0 mmol). After stirring for 5 min, PPh_3 (580 mg, 2.22 mmol) was added. Stirring was continued for 5 h at 25 °C. The mixture was filtered through silica gel and solvent evaporated to give crude product (**35**/**36** = 5:1) which was purified by flash column chromatography on silica gel eluting with hexane/methylene chloride (85 mg, 58%). Elution order: **35**, **36**.

(*E*)-PhCH=CHCH(CH$_3$)COCH$_3$, 35: IR ν_{CO} ($CDCl_3$, cm^{-1}) 1709; ^1H NMR ($CDCl_3$, δ) 7.36–7.22 (m, 5H, Ph), 6.51 (d, J = 15.9 Hz, 1H, PhC*H*=CH), 6.16 (dd, J_{tr} = 15.9, J = 8.5 Hz, 1H, =C*H*CH(CH$_3$)), 3.34 (quin, J = 7.4 Hz, 1H, =CHC*H*(CH$_3$)), 2.19 (s, 3H, CH(CH$_3$)-COC*H*$_3$), 1.26 (d, J = 6.9 Hz, 3H, CH(C*H*$_3$)COCH$_3$); ^{13}C NMR ($CDCl_3$, δ) 209.4 (s, *C*OCH$_3$), 136.7 (s, C_i of Ph), 132.1 (d, J = 151 Hz, PhC*H*=CH), 128.7 (d, J = 153 Hz, PhCH=C*H*), 128.6 (d, J = 160 Hz, C_o of Ph), 127.6 (d, J = 161 Hz, C_p of Ph), 126.2 (d, J = 157 Hz, C_m of Ph), 51.3 (d, J = 129 Hz, =CH*C*H(CH$_3$)), 28.2 (q, J = 127 Hz, CO*C*H$_3$), 16.1 (q, J = 129 Hz, CH(*C*H$_3$)CO).

(*E*)-PhCH$_2$CH=C(CH$_3$)C(O)CH$_3$, 36: IR ν_{CO} (C_6D_6, cm^{-1}) 1672; ^1H NMR (C_6D_6, δ) 7.36–7.22 (m, 5H, Ph), 6.32 (dt, J = 7.3, 1.5 Hz, 1H, PhCH$_2$C*H*=), 3.13 (d, J = 7.3 Hz, 2H, PhC*H*$_2$CH=), 1.87 (s, 3H, =C(CH$_3$)COC*H*$_3$), 1.81 (s, 3H, =C(C*H*$_3$)COCH$_3$).

The Reaction of *anti,syn*-η^3-[PhCH⁻⁻CH⁻⁻CHCH$_2$]Fe(CO)$_3^-$ with CH$_3$I. Trapping with CH$_3$CN. *anti,syn*-η^3-[PhCH⁻⁻CH⁻⁻CHCH$_3$]Fe(CO)$_3^-$ was generated in THF as described above. To this solution CH_3I (0.26 mL, 4.0 mmol) was added. After stirring for 5 min, acetonitrile (30 mL) was added. Stirring was continued for 2 h at 0 °C under irradiation. The mixture was filtered through silica gel and solvent evaporated to give the crude product which was purified by flash column chromatography (silica gel, hexane/methylene chloride) to yield only (*E*)-PhCH=CHCH(CH$_3$)COCH$_3$, **35** (174 mg, 61%).

Synthesis of (*E*)-CH$_3$CH$_2$CH$_2$CH=CHCH$_2$COCH$_2$Ph, 41. To *syn*-η^3-[CH$_3$CH$_2$CH$_2$CH⁻⁻CH⁻⁻CH$_2$]Fe(CO)$_3$Na (1.43 mmol) in THF (30 mL) at 0 °C was added PhCH$_2$Br (0.29 g, 1.72 mmol). After stirring for 20 min at 0 °C, acetonitrile (30 mL) was added, the reaction mixture was irradiated for 2 h and filtered through silica gel to give a colorless oil, which was purified by preparative thin-layer chromatography using hexane/CH_2Cl_2 (0.19 g, 67%): IR ν_{CO} (Et_2O, cm^{-1}) 1710; ^1H NMR (C_6D_6, δ) 7.18–7.00 (m, 5H, Ph), 5.58–5.22 (m, 2H, -C*H*=C*H*-), 3.34 (s, 2H, COC*H*$_2$Ph), 2.86 (dd, J = 6.6, 0.7 Hz, 2H, COC*H*$_2$CH=), 1.89 (dq, J = 6.8, 1.0 Hz, 2H, -C*H*$_2$CH=CH-), 1.30 (sextet, J = 7.2 Hz, 2H, CH$_3$C*H*$_2$-), 0.86 (t, J = 7.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (C_6D_6, δ {^1H}) 13.6 (-*C*H$_3$), 22.4 (-*C*H$_2$CH$_3$), 34.7 (=CH*C*H$_2$-), 46.0 (-*C*H$_2$CH=), 49.3 (-*C*H$_2$Ph), 121.8, 135.3 (-*C*H$_2$=*C*H$_2$-), 127.0, 128.7, 129.5 (Ph).

Synthesis of (*E*)-PhCH=CHCH$_2$COCH$_2$Ph, 42. To *syn*-η^3-[PhCH⁻⁻CH⁻⁻CH$_2$]Fe(CO)$_3$Na (1.5 mmol) in THF (30 mL) at 0 °C was added PhCH$_2$Br (0.31 g, 1.8 mmol). After stirring for 20 min at 0 °C, acetonitrile (30 mL) was added, and the mixture irradiated at 0 °C for 2 h and then filtered through a short column of silica gel to give the crude title compound as a colorless oil which was purified by preparative thin-layer chromatography (0.24 g, 74%): IR ν_{CO} (hexane, cm^{-1}) 1710; ^1H NMR ($CDCl_3$, δ) 7.39–7.11 (m, 10H, 2Ph), 6.42 (d, J = 15.7 Hz, 1H, PhC*H*=), 6.24 (dt, J = 15.7, 6.6 Hz, 1H, =C*H*CH$_2$), 3.76 (s, 2H, COC*H*$_2$Ph), 3.56 (d, J = 6.6 Hz, 2H, =CHC*H*$_2$CO).

Synthesis of (*E*)-PhCH=CHCH$_2$COCH$_3$, 43. Following the same procedure as above and using CH_3I (0.28 g, 1.92 mmol) gave the title product as a colorless oil which was purified as above (0.15 g, 63%). IR ν_{CO} ($CHCl_3$, cm^{-1}) 1713; ^1H NMR ($CDCl_3$, δ) 7.40–7.31 (m, 5H, Ph), 6.47 (d, J = 15.1 Hz, 1H, PhC*H*=), 6.29 (dt, J = 15.1, 6.2 Hz, 1H, =C*H*CH$_2$-), 3.32 (d, J = 6.2 Hz, 2H, =CHC*H*$_2$-), 2.20 (s, 3H, COC*H*$_3$).

Synthesis of α-β-Enones 10, 11, 29, 31, 39, 40 by Decomplexation of η^4-Enone-Fe(CO)$_2$PPh$_3$ Complexes with CH$_3$CN. A solution of the η^4-enone-Fe(CO)$_2$PPh$_3$ complex [(η^4-(*E*)-[CH$_3$CH=CHCOCH$_2$Ph]Fe(CO)$_2$PPh$_3$ (0.5 g, 0.94 mmol), η^4-(*E*)-[CH$_3$CH=CHCO(CH$_2$)$_3$-CH$_3$]Fe(CO)$_2$PPh$_3$ (0.5 g, 1.0 mmol), **27a** (0.5 g, 0.9 mmol), **28** (0.3 g, 0.58 mmol), **30** (0.3 g, 0.67 mmol), or **33** (0.4 g, 0.78 mmol)] in acetonitrile (30 mL) was refluxed or irradiated with a sunlamp until no metal carbonyl peak was detected by IR. The solution was then filtered through silica gel, and solvent was removed to give the crude product as a colorless oil which was purified as above.

(*E*)-CH$_3$CH=CHCOCH$_2$Ph, 10: characterization reported above; yield = 85%.

(*E*)-CH$_2$CH=CHCOCH$_2$CH$_2$CH$_2$CH$_3$, 11: IR ν_{CO} (hexane, cm^{-1}) 1604; ^1H NMR ($CDCl_3$, δ) 6.76 (dq, J = 15.8, 6.8 Hz, 1H, =C*H*CO), 6.05 (dq, J = 15.8, 1.8 Hz, 1H, CH$_3$C*H*=), 2.44 (t, J = 6.5 Hz, 2H, COC*H*$_2$), 1.82 (dd, J = 15.8, 1.8 Hz, 3H, C*H*$_3$CH=), 1.50–1.15 (m, 4H, COCH$_2$C*H*$_2$), 0.82 (t, J = 6.3 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); yield = 80%.

(*E*)-PhCH$_2$CH=CHCOCH$_3$, 29: characterization reported above; yield = 71%.

(*E*)-PhCH$_2$CH=CHCOCH$_2$Ph, 31: characterization reported above; yield = 74%.

(*E*)-CH$_3$CH=C(CH$_2$CH$_2$CH$_3$)COCH$_2$Ph, 39: IR ν_{CO} (Et_2O, cm^{-1}) 1615; ^1H NMR (C_6D_6, δ), 7.20–7.05 (m, 5H, Ph), 6.42 (q, J = 7.0 Hz, 1H, CH$_3$C*H*=), 3.76 (s, 2H, C*H*$_2$Ph), 2.38 (t, J = 7.5 Hz, 2H, C*H*$_2$-CH$_2$CH$_3$), 1.50–1.24 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 1.42 (d, J = 7.0 Hz, 3H, C*H*$_3$CH=), 0.88 (t, J = 7.0 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); yield = 64%.

(CH$_3$)$_2$C=CHCOCH$_2$Ph, 40: IR ν_{CO} ($CHCl_3$, cm^{-1}) 1617; ^1H NMR ($CDCl_3$, δ) 7.38–7.20 (m, 5H, Ph), 6.12 (t, J = 1.5 Hz, 1H, =C*H*CO), 3.71 (s, 2H, C*H*$_2$Ph), 2.18, 1.88 (2d, J = 1.0, 0.8 Hz, 6H, 2C*H*$_3$); yield = 74%.

Acknowledgment is made to the National Institute of Health (GM 28938) for financial support of this research.

Supplementary Material Available: Elemental analyses and high-resolution mass spectral data for compounds as listed in the general procedure of the experimental section. Rate plots for (1) the isomerization of *anti*-**18** to *syn*-**18**, (2) the acyl migration from *syn*-**18** to **19**, and (3) the hydride migration of **19** to **13a,b** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.