Iron-Mediated C–C Bond Formation. Preparation of (Trimethylenemethane)iron Complexes via Reaction of Weak Carbon Nucleophiles with in Situ Generated Cross-Conjugated Pentadienyl Cations. Nucleophilic Attack on (Trimethylenemethane)iron Complexes with Carbanions

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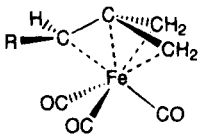
The reaction of (2-(acetoxymethylene)-1,3-butadiene)$Fe(CO)_3$ (**8**) or ((acetoxymethylene)trimethylenemethane)$Fe(CO)_3$ (**9**) with weak carbon nucleophiles in the presence of $BF_3{\cdot}Et_2O$ gives the corresponding substituted (trimethylenemethane)$Fe(CO)_3$ complexes as the major product. Applicable nucleophiles include trialkylaluminums, allyltrimethylsilane, and 2-((trimethylsilyl)oxy)-1-propene. This reaction proceeds in a stereospecific fashion; reaction of **12** gives a single (trimethylenemethane)iron product. The reaction of (1,2-bis(acetoxymethylene)-1,3-butadiene)$Fe(CO)_3$ (**20**) with allyltrimethylsilane gives a (TMM)$Fe(CO)_3$ product in which two new C–C bonds have been formed in one reaction. Reaction of TMM$Fe(CO)_3$ (**1a**) and substituted derivatives with carbanions, followed by workup with trifluoroacetic acid, gives the corresponding methallylated product. Applicable nucleophiles include anions derived from diphenylmethane, ethyl isobutyrate, isobutylnitrile, and 2-phenyl-1,3-dithiane. Use of allyl bromide in place of trifluoroacetic acid gives 6-substituted 5-methylene-1-hexenes as products, the result of a three-component coupling.

Introduction

"Free" trimethylenemethane (TMM) is a highly reactive triplet species which has only been detected by ESR spectroscopy at low temperature (<−150 °C).[1] It had been suggested in 1956 that TMM could be stabilized by complexation to a transition metal.[2] Trimethylenemethane complexes of iron (**1**) were those first reported,[3] and complexes of chromium,[4] molybdenum,[4,5] ruthenium,[6] rhodium,[6] palladium,[7] osmium,[6] iridium,[6] and platinum[8] subsequently became known. In situ generated, zwitterionic η^3-trimethylenemethane Pd complexes undergo cycloaddition reactions with electron deficient olefins to give methylenecyclopentanes in excellent yields.[7] This methodology has found application in the total synthesis of (+)-brefeldin A,[9a] loganin aglycon,[9b] and (±)-albene[9c] and a formal synthesis of chrysomelidial.[9d] *In comparison*, initial interest in the use of neutral TMM$Fe(CO)_3$ complexes as a source of TMM faded when it was reported that oxidative decomplexation of compounds **1** in the presence of olefins afforded only dismal yields of methylenecyclopentane products.[4,10] It has been suggested that this lack of reactivity may be the result of the electron poor nature of **1**.[11] The reaction of *isolable* cyclic and acyclic pentadienyl iron cations with carbon nucleophiles provides a useful method for chemo-, regio-, and stereoselective C–C bond formation. Since the resultant diene ligand can be liberated under a variety of conditions applications of this chemistry to natural product synthesis are of continued interest.[12]



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Uemura has reported that dienyl acetates **2** undergo substitution with weak carbon nucleophiles in a stereospecific fashion to afford diene complexes **4** (Scheme 1) with net retention of configuration.[13] This reaction is believed to occur via the intermediacy of an *in situ* generated transoid pentadienyl iron cation **3**. Isomeric cross-conjugated pentadienyl cations (**5**) have been generated by treatment of (2-(hydroxymethylene)-1,3-butadiene)$Fe(CO)_3$ under super acid conditions; however, attempts to isolate these cations have been unsuccess-

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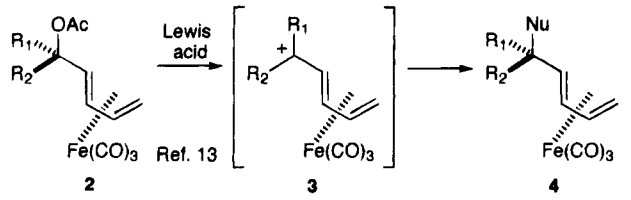
Scheme 1



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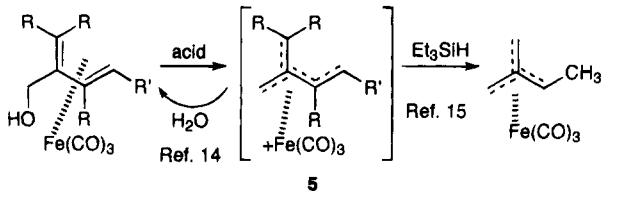
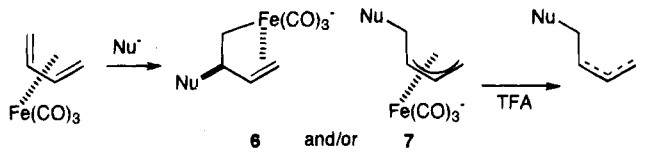


Scheme 3



ful.[14] In general, the cross-conjugated pentadienyl cations reacted with water or methanol to afford the corresponding diene complexes (Scheme 2).[14] During the course of our work, the reactivity of cations **5** with triethylsilane was reported to afford predominantly TMM products.[15]

The diene ligand may be liberated by oxidation,[16] photochemical reduction,[17] or reaction with strong carbon nucleophiles.[18,19] In this latter reaction, nucleophilic attack may occur at either the internal (*kinetic*) or terminal (*thermodynamic*) sites of the diene ligand to afford 1,3,4-η^3-butenyl (**6**) or π-allyl (**7**) iron anionic intermediates (Scheme 3). Protic workup of the intermediate **7** gives the olefinic products in which a new C–C bond has been formed.

As part of our interest in the use of π-organometallic complexes of iron in organic synthesis,[20] we have examined methods for the preparation of substituted TMMFe(CO)$_3$ complexes and for the liberation of the TMM ligand. In particular, we here provide a full account on the reaction of *in situ* generated cross-conjugated pentadienyl

Scheme 4

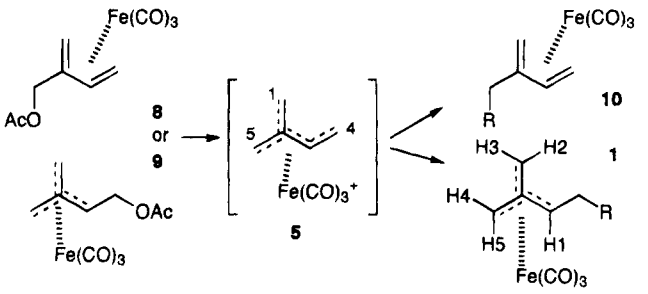


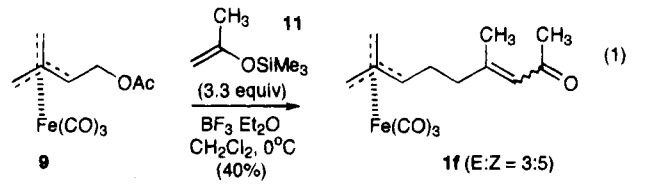
Table 1

conditions	yield (%)	TMM:diene products	
8 $Me_3Al/BF_3{\cdot}Et_2O$	(64–69)	5 (**1b**):1 (**10b**)	(R = Me)
8 $Et_3Al/BF_3{\cdot}Et_2O$	(76)	1 (**1c**):0	(R = Et)
8 allylTMS/$BF_3{\cdot}Et_2O$	(72–91)	7 (**1d**):1 (**10d**)	(R = $CH_2CH{=}CH_2$)
9 allylTMS/$BF_3{\cdot}Et_2O$	(79–99)	8 (**1d**):1 (**10d**)	(R = $CH_2CH{=}CH_2$)
8 $H_2C{=}C(OTMS)CH_3$ (0.4 equiv)/$BF_3{\cdot}Et_2O$	(66)	20 (**1e**):1 (**10e**)	(R = CH_2COCH_3)

cations **5** with weak carbon nucleophiles and the reaction of neutral TMM iron complexes **1** with strong carbon nucleophiles.[21]

Results and Discussion

Nucleophilic Additions to Cross-Conjugated Pentadienyl Cations. Dienyl acetate **8**[23] and TMM acetate **9**[14b,15a] were prepared by literature methods. Reaction of **8** with excess trimethylaluminum, triethylaluminum, or allyltrimethylsilane in the presence of $BF_3{\cdot}Et_2O$ gave substituted TMMFe(CO)$_3$ complexes **1b–d** as the major products along with minor amounts of diene products **10** (Table 1). Similarly, reaction of **9** with excess allyltrimethylsilane/$BF_3{\cdot}Et_2O$ gave **1d** as the predominant product. Reaction of **9** with 2-((trimethylsilyl)oxy)propene **11** (0.4 equiv) in the presence of $BF_3{\cdot}Et_2O$ gave the methyl ketone TMMFe(CO)$_3$ complex (**1e**) along with trace amounts of the diene isomer (**10e**) (Scheme 4 and Table 1). Reaction of excess 2-((trimethylsilyl)oxy)propene with **9** gave predominantly the enone complex (**1f**, eq 1) as a



separable mixture of *E*- and *Z*-isomers. The enones **1f** presumably arise via Lewis acid mediated aldol condensation of the excess **11** with **1e**.

Separation of the mixture of **1b** and **10b** was not attempted; instead, these compounds were identified by comparison to literature spectral data.[24,25] The TMMFe(CO)$_3$ complexes **1d**, **1e**, and **1f** could be separated by

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(22) All compounds are racemic mixtures of enantiomers. Only one enantiomer has been diagrammed for clarity.

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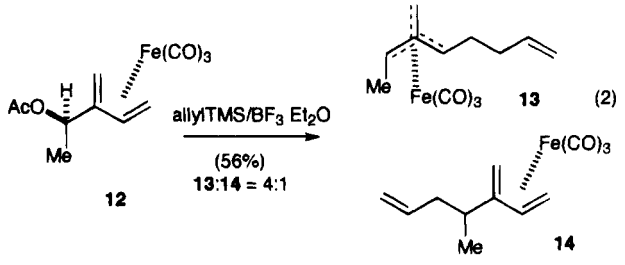
repeated column chromatography; however, the diene products (**10**) were characterized only as mixtures with their isomeric TMM counterparts. All of the products **1b–f** exhibited five signals in their ^{1}H NMR spectra at ca. δ 2.9 (m), 2.5 (d, J = ca. 4.5 Hz), 2.15 (d, J = ca. 2.2 Hz), 1.77 (s), and 1.65 (d, J = 4.5 Hz) ppm corresponding to the TMM protons H_1, H_2, H_3, H_4, and H_5 (see structure **1**, Scheme 4, for numbering). Additionally, the ^{13}C NMR spectra of **1b–f** exhibit three distinct signals at ca. δ 211 ppm corresponding to the three carbonyl ligands and signals at ca. δ 103, 80, 52, and 50 ppm, corresponding to the central and terminal carbons of the TMM ligand. These chemical shifts and coupling constants are characteristic of TMMFe(CO)$_3$ complexes bearing a single alkyl substituent.[3b,24]

Isolation of the same product mixture from the reaction of either **8** or **9** with allyltrimethylsilane/BF_3·Et_2O suggests a common intermediate. We propose that the products arise via acetate ionization to generate the cross-conjugated pentadienyl cation **5**. Nucleophilic attack predominantly at C4 gives the TMM products **1** while attack at C5 gives the minor diene products **10**. Notably, the NMR spectral data and extended Hückel calculations for **5** (R = R′ = H) strongly suggest that C4 bears greater partial positive charge than does C1 or C5.[14b] Conversely, dieneFe(CO)$_3$ complexes are more thermodynamically stable than the corresponding TMMFe(CO)$_3$ complexes, as exemplified by isomerization of **1b** to **10b** under acidic conditions.[3b,15] Thus, the formation of TMM products **1** from the reaction of **5** with weak carbon nucleophiles may be rationalized as the result of kinetically controlled, irreversible attack at the carbon bearing the greatest partial charge (C4 of cation **5**), while thermodynamically controlled, reversible attack by water/alcohol gives the more stable diene products.

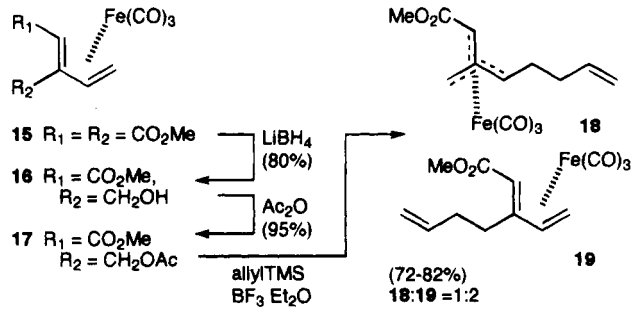
The dienyl acetate **12** was prepared according to the literature procedure.[15a] The reaction of **12** with allyltrimethylsilane/BF_3·Et_2O gave a 4:1 mixture of TMM complex **13** and diene complex **14** (eq 2). Separation of



(2)

the mixture was not attempted. The structure of **13** was assigned on the basis of its ^{1}H NMR spectral data. In particular, the signal for the proton adjacent to the butenyl substituent appears at δ 3.55 (dt, J = 2.5, 7.6 Hz), while the signal for the proton adjacent to the methyl substituent appears at δ 2.75 (q, J = 7.1 Hz). The absence of the "W" coupling[3b] for the proton adjacent to the methyl group and the presence of the "W" coupling (2.5 Hz) for the proton adjacent to the butenyl group indicates that the methyl substituent is anti, and the butenyl substituent is syn, with respect to the unsubstituted terminal TMM carbon. While the diene product **14** appears to be a single diastereomer on the basis of its NMR spectral data, it has not been possible to assign the relative configuration of **14**. The isolation of **13** and **14** as single diastereomers indicates that the

Scheme 5



substitution reaction is stereospecific.[26] This may be rationalized by ionization of the acetate in an orientation opposite to the Fe(CO)$_3$ adjunct followed by nucleophilic attack of allyltrimethylsilane before rotation about any of the C–C bonds of the cross-conjugated pentadienyl ligand.

Reduction of the known[28] diester **15** with lithium borohydride gave a single monoester–alcohol complex (Scheme 5). The product, which arises from selective reduction of the cross-conjugated ester in preference to the conjugated ester, was assigned structure **16** on the basis of its ^{1}H NMR spectral data. In particular, the appearance of the H2 signal as a singlet at δ 1.91 indicates that the C1 ester functionality was *not* reduced. The acetate **17** could be prepared from **16** by standard procedures. The reaction of **17** with allyltrimethylsilane/BF_3·Et_2O gave a 1:2 mixture of TMM complex **18** and diene complex **19**. Separation of the mixture was not attempted. Clearly, the presence of the electron-withdrawing methoxycarbonyl substituent in **17** effects the regioselectivity of attack on the cross-conjugated pentadienyl cation. The structures of **18** and **19** were assigned on the basis of their ^{1}H NMR spectral data. For **18**, the signal for the proton adjacent to the butenyl substituent appears at δ 2.87 (t, J = 7.7 Hz). The absence of the "W" coupling[3b] for this proton indicates that the butenyl substituent is anti, and the methoxycarbonyl substituent is syn, with respect to the unsubstituted terminal TMM carbon. Signals at δ 5.20 (dd), 1.86 (dd), 0.62 (s), and 0.52 (dd) in the ^{1}H NMR spectrum of **19** are assigned to the H4, H5exo, H2endo, and H5 endo protons of the 3-substituted 2,4-pentadienoate fragment.

The substitution of pentadienyl acetates **2** has been previously noted (Scheme 1). In order to examine if substitution via the pentadienyl cation and via the cross-conjugated pentadienyl cation were compatable, a dienyl complex which incorporated two acetoxymethylene substituents was designed. Further reduction of **16** could be accomplished using DIBAL, and acetylation of the resultant diol gave the diacetate **20**. Reaction of **20** with excess allyltrimethylsilane/BF_3·Et_2O gave the TMM complex **21** (Scheme 6). The unsymmetrical (syn,anti) structure of **21** was assigned on the basis of its NMR spectral data. In particular, the ^{13}C NMR spectrum contains four signals (δ 101.7, 76.5, 74.1, 49.5) for the TMM portion of the ligand and the ^{1}H NMR spectrum contains four signals (δ 3.50, 2.62, 2.30, and 1.77) for each of the four

(26) Stereoselective substitution has been reported for the reaction of **12** with triethylsilane[15a] and for the reaction of allyltrimethylsilane with the alcohol corresponding to **12**.[27] These observations have been rationalized by a similar mechanism.

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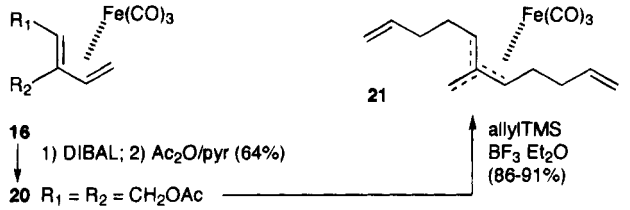
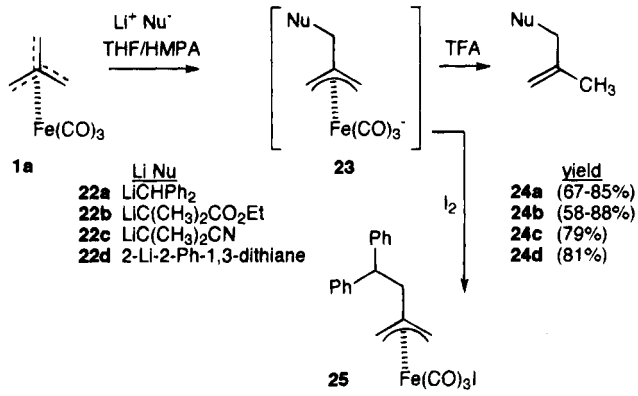
Scheme 6



Scheme 7

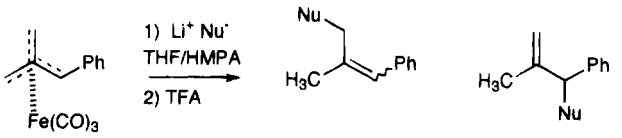


different protons attached to the TMM ligand. The two new C–C bond formations of **21** are most likely formed in a sequential fashion. The reaction of **20** with 0.8 equiv of allyltrimethylsilane/BF_3·Et_2O gave unreacted starting material and the TMM complex **21**. This result indicates that substitution of the second acetate occurs at a rate faster than substitution of the first acetate, and thus, it is not possible to determine which acetate (pentadienyl vs cross-conjugated pentadienyl) is the first to undergo substitution.

Liberation of the TMM Ligand via Nucleophilic Addition. The parent TMM complex **1a**[3b] and the carbanions **22a–d**[18a] were prepared by literature methods. Reaction of **1a** with the carbanions **22a–d** (THF/HMPA), followed by protic workup, gave the corresponding methallylated species **24** in good yields (Scheme 7). The products **24a–c** are known compounds and were identified by comparison to literature data.[29] The dithiane **24d** was obtained as a mixture with unreacted 2-phenyl-1,3-dithiane. Hydrolysis of the mixture gave 3-methyl-1-phenyl-3-buten-1-one and the conjugated isomer, 3-methyl-1-phenyl-2-buten-1-one, which were identified by comparison to literature spectral data.[30] Notably, reaction of **1a** with sodium dimethylmalonate gave only recovered **1a**.

We propose that the products arise via nucleophilic attack on the TMM ligand[31] to form an intermediate allyl(tricarbonyl)iron anion **23**, followed by protonolysis (Scheme 7). There is ample precedent for the formation of anions of this type by the reaction of carbanions with dieneFe(CO)$_3$ complexes.[18,32] Additionally, protonation of anions similar to **23** has resulted in the formation of olefins.[18] The reaction of **1a** with **22a** followed by workup with I_2 gave a labile complex tentatively identified as **25**. In particular, carbonyl stretching peaks in the IR spectrum of **25** (2073, 2023, 2004 cm^{-1}) and signals in the ^{1}H NMR spectrum of **25** corresponding to the syn and anti allyl protons (δ 3.80 and 3.61, respectively) are consistent with other known allylFe(CO)$_3$I complexes.[33] The formation of **25** provides further evidence to support the intermediacy of an allyliron anion species.

Scheme 8



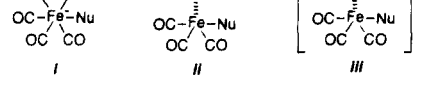
	Nu	yield		
1g	$CHPh_2$	**26a** (34%)	**27a** (40%)	
	$C(CH_3)_2CO_2Et$	**26b** (93%)		
	$C(CH_3)_2CN$	**26c** (95%)	**27c** (trace)	

The results in Scheme 7 are of limited synthetic applicability, since the products **24** alternatively could have been prepared from the reaction of the nucleophiles **22** with methallyl chloride.[29] Of potentially greater synthetic interest would be the addition of nucleophiles to *substituted* TMMFe(CO)$_3$ complexes. The phenyl-substituted TMM complex **1g** was prepared by the literature method.[3b] Reaction of **1g** with **22a** gave a separable mixture of **26a** and **27a** (ca. 1:1 ratio, Scheme 8). In contrast, the reaction of **1g** with **22b** or **22c** gave predominantly the substituted styrenes **26b** and **26c**. Only in the case of **22c** was a trace of the isomeric **27c** detected. The structures of compounds **26** and **27a** were assigned on the basis of their spectral data. In the ^{1}H NMR spectra of **27a** the signals at δ 4.50 (d, 1H) and 4.18 (d, 1H) indicate that the diphenylmethyl functionality is attached to a methine carbon. Signals in the ^{1}H NMR spectrum of **26a** at δ 6.11 (s, 1H), 2.90 (d, 2H), and 1.78 (narrow d, 3H), in the ^{1}H NMR spectrum of **26b** at δ 6.18 (s, 1H), 2.39 (s, 2H) and 1.73 (narrow d, 3H), and in the ^{1}H NMR spectrum of **26c** at δ 6.39 (s, 1H), 2.43 (s, 2H) and 2.07 (s, 3H) correspond to the vinyl, the allylic methylene, and the allylic methyl groups, respectively, of the styrene functional group. The styrene products **26a–c** were isolated as mixtures of geometrical isomers; the major isomer in each case is assigned the *E*-stereochemistry. In the NOESY spectrum of **26a**, the olefinic signal for the major isomer at δ 6.11 ppm exhibited a cross-peak with the methylene signal at δ 2.39 ppm, indicating a cis relationship of these two groups. In the

(29) (a) Babler, J. H.; Tortorello, A. J. *J. Org. Chem.* **1976**, *41*, 885–7. (b) Gaudemar, M. *Tetrahedron Lett.* **1983**, *24*, 2749–52. (c) Terent'v, A. B. *Bull. Acad. Sci. USSR* **1979**, *28*, 1425–8. (d) Hawthorne, D. G.; Solomon, D. H. *J. Macromol. Sci.-Chem.* **1975**, *A9*, 149–67.

(30) Snowden, R. L.; Linder, S. M.; Muller, B. L.; Schulte-Elte, K. E. *Helv. Chim. Acta* **1987**, *70*, 1858–78.

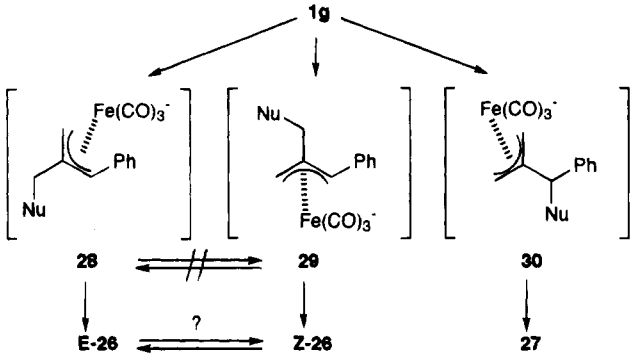
(31) One reviewer has suggested initial nucleophilic attack at iron as an alternative possibility. Direct attack at iron would generate either a 3-methyleneferracyclobutane complex i, an anionic σ-alkyl-π-allylFe(CO)$_3$ complex ii, or the 20e$^-$ σ-alkyl-TMMFe(CO)$_3$ species iii. Since there is no precedent for species of this type within the first row transition metals, we favor direct attack at a ligand [(either TMM or carbon monoxide *vide supra*)]. Additionally, nucleophilic attack on *diene*Fe(CO)$_3$ complexes has been shown to occur only at coordinated ligands.[18,19,32b]



(32) (a) Chang, S.; Yoon, J.; Brookhart, M. *J. Am. Chem. Soc.* **1994**, *116*, 1869–79. (b) Chang, S.; White, P.; Brookhart, M. *Organometallics* **1993**, *12*, 3636–44. (c) Brookhart, M.; Yoon, J.; Noh, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 4117–8.

(33) Andrews, D. C.; Davidson, G. *J. Organomet. Chem.* **1977**, *124*, 181–8. Nesmeyanov, A. N.; Abakyan, N. P.; Kritskaya, I. I. *Bull. Acad. Sci. USSR* **1976**, *25*, 1666–70.

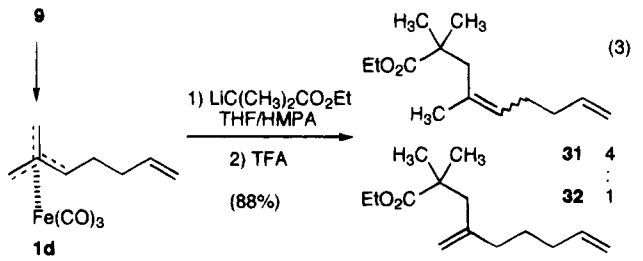
Scheme 9



^{1}H NMR spectra of **26a**, **26b**, and **26c** the signals for the major olefinic isomers (*E*) appear upfield of those of the minor (*Z*) isomers.

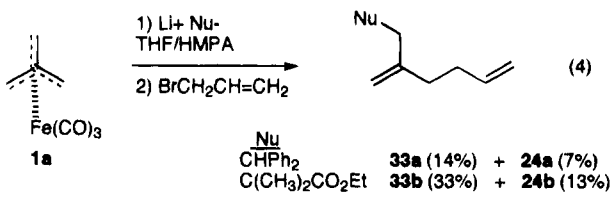
The product **27** arises from protonation of the 2-substituted allylFe(CO)$_3^-$ anion **30** (Scheme 9). Conversely, the styrene products **26** arise from the 1,2-disubstituted allylFe(CO)$_3^-$ anions **28** or **29**. Presumably protonation of **28** and **29** occurs selectively at the unsubstituted terminus due to conjugation of the emerging double bond with the phenyl substituent. Anti−syn isomerization of 1-substituted allylFe(CO)$_3$X[34] and 1-substituted allylFe(CO)$_3^-$ anions[32b] has been shown to occur only at elevated temperature (ca. 55 °C). For this reason interconversion of **28** and **29**, via an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process, is unlikely under the reaction conditions [**22a**, 21 °C; **22b/c**, −78 °C]. While the diphenylmethane anion **22a** generates mixtures of olefinic products, *synthetically useful* regioselectivity is observed for attack by nucleophiles **22b/c**. It is interesting to note that in the X-ray crystal structure[35] of **1g**, the phenyl-substituted TMM carbon-to-iron distance (2.162 Å) is significantly longer than the iron-to-unsubstituted TMM terminal carbons (2.108 Å).

The reaction of **1d** with ethyl isobutyrate anion **22b** (2.2 equiv) gave a mixture of isomeric esters **31** (*E* and *Z*) and **32** along with recovered **1d** (32%) (eq 3). The ester



mixture could be separated from TMM complex by column chromatography, and the yield of **31/32**, based on consumed TMM complex, is excellent (88%). Incomplete consumption of the starting complex may be due to deprotonation of **1d**, by the **22b**, α to the TMM ligand to generate a TMMFe(CO)$_3$ anion. Anions of this type have been reported.[25] The carbon backbone of **31** was identified by comparison of its ^{1}H NMR spectral data with that of ethyl 4-methyl-4,8-nonadienoate.[36] The general structure of **32** was identified by comparison of its ^{1}H NMR spectral data with that of ethyl 2,2-dimethyl-4-methylene-7-octenoate (**33b**, *vide infra*). As in the case of the reaction of **1g** with **22b** (Scheme 8), C−C bond formation between **1d** and **22b** occurs regioselectively at an unsubstituted TMM terminus. However, unlike the reaction of **1g** with **22b**, control of the position and stereochemistry of the internal double bond is not observed.

The intermediacy of anion **23** provides the opportunity for formation of a second C−C bond. The reaction of allylFe(CO)$_3^-$ anions with carbon electrophiles, such as allyl or alkyl halides, is known to lead to the formation of condensed products.[32,34] In our hands, the reaction of **1a** with **22a** or with **22b**, followed by addition of excess allyl bromide, gave the 2-substituted 1,5-hexadienes **33a** and **33b**, respectively, accompanied by the products from protonation **24a** or **24b** (eq 4). Separation of **33** and **24**



could be accomplished by chromatography over AgNO$_3$-impregnated silica gel. The structural assignments for compounds **33** are based on their NMR spectral data. In particular, signals at ca. δ 5.8 (tdd, 1H) and 5.0 (m, 2H) in the ^{1}H NMR and signals at ca. δ 138 and 114 ppm in the ^{13}C NMR spectra of **33a/b** provided evidence for the vinyl functional group. These results indicate that complexes **1** hold promise as a trimethylenemethane synthon in three-component coupling reactions.

Ionization of diene complexes **8**, **12**, or **17** or trimethylenemethane complex **9** under Lewis acid conditions leads to the in situ formation of iron-complexed cross-conjugated pentadienyl cations **5**. Reaction of these cations with weak carbon nucleophiles (trialkylaluminums, allylsilanes, silyl enol ethers) gives TMM products. The regioselectivity observed for cations derived from **8**, **9**, or **12** is proposed to be the result of irreversible kinetically controlled nucleophilic attack. Reaction of neutral TMMFe(CO)$_3$ complexes with strong carbon nucleophiles, followed by electrophilic workup, gives olefinic products in good yields. Reaction of substituted TMM complexes **1d** or **1g** with ethyl isobutryate anion proceeds at the unsubstituted TMM terminus with excellent regioselectivity. Formation of C−C bonds via these two processes may be of use to organic synthesis.

Experimental Section[37]

(Diene)Fe(CO)$_3$ complexes **8**,[23] **12**,[15] and **15**[28] and (trimethylenemethane)Fe(CO)$_3$ complexes **1a**,[3] **1g**,[3] and **9**[14] were prepared by literature methods. Solutions of lithium diphenylmethane (**22a**), lithium ethylisobutyrate (**22b**), 2-lithio-2-methylpropanenitrile (**22c**), or 2-lithio-2-phenyl-1,3-dithiane (**22d**) in THF/HMPA (4:1) were prepared according to the literature procedures[18a] except that nitrogen was used as the inert atmosphere instead of argon.

Reaction of 8 with Trimethylaluminum. To a solution of **8** (0.40 g, 1.50 mmol) and trimethylaluminum (1.13 mL, 2.0 M in hexanes, 2.26 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added BF_3·Et_2O (0.21 mL, 1.7 mmol). The reaction mixture was stirred at −78 °C for 2 h and at 0 °C for 8 h. Saturated aqueous $NaHCO_3$ (50 mL) was added, the mixture was

(34) Nesmeyanov, A. N.; Gubin, S. P.; Rubezhov, A. Z. *J. Organomet. Chem.* **1969**, *16*, 163.
(35) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1969**, *8*, 401−7.
(36) Trust, R. I.; Ireland, R. E. *Org. Synth.* **1973**, *53*, 116−22.

(37) For general experimental conditions see ref 20c.

extracted with CH_2Cl_2 (2 × 50 mL), the combined organic extracts were washed with brine (50 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes) to give a yellow oil (0.23 g, 69%). This was determined to be a mixture of **1b** and **10b** (5:1) by NMR spectroscopy. Further separation of the mixture was not attempted. The products, **1b** and **10b**, were identified by comparison to literature spectral data.[24,25]

1b: ^{1}H NMR ($CDCl_3$) δ 2.95 (dt, J = 1.2, 7.6 Hz, 1H), 2.50 (d, J = 4.2 Hz, 1H), 2.15 (d, J = 1.2 Hz, 1H), 1.76 (s, 1H), 1.62 (d, J = 4.2 Hz, 1H), 1.53–1.43 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.9, 211.6, 211.1, 102.9, 82.3, 52.5, 50.6, 22.9, 16.7.

10b: ^{1}H NMR ($CDCl_3$) δ 5.26 (br t, J = 8.8 Hz, 1H), 2.37 (m, 2H), 1.82 (br t, J = 2.0, 1H), 1.68 (dd, J = 2.5, 6.7, 1H), 1.29 (t, J = 7.3 Hz, 3H), 0.28 (dd, J = 0.8, 2.1, 1H), 0.10 (dd, J = 2.0, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 104.9, 83.0, 42.7, 38.1, 29.9, 14.1.

Reaction of 8 with Triethylaluminum. To a solution of **8** (0.25 g, 0.98 mmol) and triethylaluminum (2.0 mL, 1.0 M in hexanes, 2.0 mmol) in CH_2Cl_2 (15 mL) at −78 °C was added BF_3·Et_2O (0.2 mL, 1.6 mmol). The reaction mixture was stirred at −78 °C for 4 h. Saturated aqueous $NaHCO_3$ (25 mL) was added, the mixture was extracted with CH_2Cl_2 (2 × 25 mL), the combined organic extracts were washed with brine (25 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes) to give **1c** as a yellow oil (0.18 g, 76%).

1c: ^{1}H NMR ($CDCl_3$) δ 2.98 (br t, J = 6.0 Hz, 1H), 2.50 (d, J = 4.2 Hz, 1H), 2.17 (d, J = 2.0 Hz, 1H), 1.77 (s, 1H), 1.61 (d, J = 4.2 Hz, 1H), 1.57–1.42 (m, 4H), 0.92 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 212.0, 211.6, 211.1, 103.2, 79.8, 52.5, 50.5, 31.7, 25.5, 15.6; EI-HRMS m/z 180.0261 (calcd for $C_8H_{12}OFe$ m/z 180.0260).

Reaction of 8 with Allyltrimethylsilane. To a solution of **8** (1.10 g, 4.14 mmol) and allyltrimethylsilane (1.3 mL, 8.3 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added BF_3·Et_2O (0.75 mL, 6.2 mmol). The reaction mixture was stirred at 0 °C for 10 min and then allowed to warm to 23 °C over a 3 h period. Saturated aqueous $NaHCO_3$ (50 mL) was added, the mixture was extracted with CH_2Cl_2 (2 × 50 mL), the combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes) to give a yellow oil (0.93 g, 91%). This was determined to be a mixture of **1d** and **10d** (7:1) by NMR spectroscopy. A pure sample of **1d** could be obtained by further chromatography of this mixture (SiO_2, hexanes).

1d: R_f 0.45 (hexanes); IR (CCl_4, cm^{-1}) 2068, 2002, 1970, 970; ^{1}H NMR ($CDCl_3$) δ 5.81 (ddt, J = 17.1, 10.1, 6.8 Hz, 1H), 5.05 (d, J = 17.1 Hz, 1H), 5.01 (d, J = 10.1 Hz, 1H), 2.96 (dt, J = 2.1, 7.6 Hz, 1H), 2.51 (d, J = 4.4, Hz 1H), 2.17, (d, J = 2.1 Hz, 1H), 2.28–2.06 (m, 2H), 1.78 (s, 1H), 1.65 (d, J = 4.4 Hz, 1H), 1.68–1.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 212.0, 211.9, 211.7, 137.4, 115.4, 103.3, 78.9, 52.6, 50.6, 36.4, 29.1; GC/MS (m/z) 248 (M^+, 3), 220 (4), 192 (17), 164 (39), 110 (28), 84 (29), 56 (100); EI-HRMS m/z 248.0137 (calcd for $C_{11}H_{12}O_3Fe$ m/z 248.0136).

10d: ^{1}H NMR ($CDCl_3$, partial) δ 5.95 (m), 5.27 (br t, J = 8.5 Hz), 5.08–5.00 (m), 2.45 (m, 2H), 2.7–2.1 (m, 2H), 1.81 (dd, J = 1.6, 2.2 Hz, 1H), 1.62 (dd, J = 1.6, 7.8, Hz 1H), 0.29 (dd, J = 1.2, 2.0 Hz, 1H), 0.08 (dd, J = 2.2, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 137.2, 115.5, 84.3, 43.0, 38.2, 37.0, 35.9.

Reaction of 9 with Allyltrimethylsilane. To a solution of **9** (0.500 g, 1.88 mmol) and allyltrimethylsilane (0.6 mL) in CH_2Cl_2 (28 mL) at 0 °C was added BF_3·Et_2O (0.35 mL, 6.2 mmol). The reaction mixture was stirred at 0 °C for 10 min and then allowed to warm to 23 °C over a 3 h period. Workup as above gave a yellow oil (0.460 g, 99%) which was determined to be a mixture of **1d** and **10d** (8:1) by NMR spectroscopy.

Reaction of 9 with 2-(Trimethylsiloxy)propene (0.4 Equiv). To a solution of **9** (0.40 g, 1.5 mmol) and (trimethylsiloxy)propene (0.1 mL, 0.6 mmol) in CH_2Cl_2 (22 mL) at 0 °C was added BF_3·Et_2O (0.28 mL, 2.3 mmol). The reaction mixture was warmed to 23 °C over a 2.5 h period. Saturated aqueous $NaHCO_3$ (25 mL) was added, the mixture was extracted with CH_2Cl_2 (2 × 25 mL), the combined organic extracts were washed with water (25 mL) followed by brine (25 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes–ethyl acetate (10:1)) to give unreacted **9** followed by **1e** as a yellow oil (105 mg, 66%) followed by a mixture of **1e** and **10e** (ca. 1:1, 10 mg).

1e: R_f 0.31 (hexanes–ethyl acetate (10:1)); IR ($CDCl_3$, cm^{-1}) 2052, 1973, 1719; ^{1}H NMR ($CDCl_3$) δ 2.88 (dt, J = 2.4, 7.6 Hz, 1H), 2.55 (t, J = 7.1 Hz, 2H), 2.54 (d, J = 4.2 Hz, 1H), 2.18 (d, J = 2.3 Hz, 1H), 2.15 (s, 3H), 1.86 (m, 1H), 1.78 (s, 1H), 1.72 (m, 1H), 1.64 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 211.6, 211.1, 210.8, 207.4, 103.3, 77.7, 52.8, 50.9, 45.7, 30.0, 23.7; GC/MS (m/z) 264 (M^+, <1), 236 (8), 208 (19), 180 (29), 152 (23), 124 (20), 110 (41), 56 (100); EI-HRMS m/z 236.0125 (calcd for $C_{10}H_{12}O_3Fe$ (M − CO) m/z 236.0136).

10e: ^{1}H NMR ($CDCl_3$, partial) δ 5.27 (br t, J = 8.5 Hz), 2.45 (m, 2H), 2.80 (m), 2.55 (m), 2.21 (s), 1.79 (br d, J = 2.2 Hz), 1.64 (dd, J = 1.5, 7.7 Hz), 0.24 (br d, J = 2.2 Hz), 0.06 (dd, J = 1.5, 8.7 Hz).

Reaction of 9 with 2-(Trimethylsiloxy)propene (2.3 Equiv). To a solution of **9** (0.35 g, 1.3 mmol) and (trimethylsiloxy)propene (0.5 mL, 3.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added BF_3·Et_2O (0.24 mL, 2.0 mmol). Workup as above and purification by chromatography (SiO_2, hexanes–ethyl acetate (10:1)) gave (*Z*)-**1f** as a yellow oil (100 mg, 25%) followed by (*E*)-**1f** as a yellow oil (60 mg, 15%).

(*Z*)-1f: ^{1}H NMR ($CDCl_3$) δ 6.09 (s, 1H), 3.00 (ddd, J = 2.4, 6.3, 8.8 Hz, 1H), 2.88 (ddd, J = 6.6, 9.5, 11.7 Hz, 1H), 2.57 (d, J = 4.4 Hz, 1H), 2.47 (ddd, J = 5.6, 9.5, 11.7 Hz, 1H), 2.17 (d, J = 2.2 Hz, 1H), 2.16 (s, 3H), 1.87 (d, J = 1.2 Hz, 3H), 1.77 (s, 1H), 1.65 (d, J = 4.4 Hz, and m, 3H); ^{13}C NMR ($CDCl_3$) δ 211.7, 211.3, 210.9, 197.9, 157.1, 124.6, 103.3, 78.5, 52.6, 50.8, 36.5, 31.6, 28.5, 25.5; GC/MS (m/z) 304 (M^+, <1), 276 (3), 248 (21), 220 (51), 176 (22), 162 (19), 134 (22), 56 (100); EI-HRMS m/z 248.0500 (calcd for $C_{12}H_{16}O_2Fe$ (M − 2CO) m/z 248.0500).

(*E*)-1f: IR ($CDCl_3$, cm^{-1}) 2054, 1981, 1690; ^{1}H NMR ($CDCl_3$) δ 6.08 (d, J = 0.5 Hz, 1H), 2.84 (t, J = 7.5 Hz, 1H), 2.49 (d, J = 4.4 Hz, 1H), 2.17 (d, J = 2.2 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.28–2.00 (m, 2H), 1.80 (s, 1H), 1.80–1.60 (m, 2H), 1.66 (d, J = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 211.6, 211.1, 210.9, 198.6, 156.3, 124.4, 103.4, 77.8, 52.6, 50.8, 43.6, 31.7, 27.7, 19.0; GC/MS (m/z) 304 (M^+, <1), 276 (4), 248 (26), 220 (66), 176 (30), 162 (22), 134 (21), 56 (100).

Reaction of 12 with Allyltrimethylsilane. The reaction of **12** (0.14 g, 0.50 mmol) with allyltrimethylsilane (0.16 mL, 1.0 mmol) was carried out in a fashion similar to the reaction of **8** with allyltrimethylsilane. The crude product was purified by chromatography (SiO_2, hexanes) to give a yellow oil (0.93 g, 91%). This was determined to be a mixture of **13** and **14** (4:1) by NMR spectroscopy. Further separation of the mixture was not attempted.

13: ^{1}H NMR ($CDCl_3$) δ 5.83 (ddt, J = 17.1, 10.0, 6.6 Hz, 1H), 5.1–4.9 (m, 2H), 3.55 (dt, J = 2.5, 7.6 Hz, 1H), 2.75 (q, J = 7.1, Hz 1H), 2.27 (s, 1H), 2.18 (m, 2H), 1.75 (d, J = 2.3 Hz, 1H), 1.68–1.60 (m, 2H), 1.31 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.3, 137.5, 115.3, 102.5, 76.0, 68.1, 49.0, 36.6, 28.9, 13.9.

14: ^{1}H NMR ($CDCl_3$, partial) δ 5.20 (t, J = 7.7 Hz), 1.27 (d, J = 6.6 Hz), 0.25 (br s), 0.13 (dd, J = 2.2, 8.7 Hz); ^{13}C NMR ($CDCl_3$, partial) δ 135.9, 116.9, 81.0, 44.7, 42.9, 39.1, 38.2, 17.0.

[Methyl 2-(acetoxymethylene)-2,4-pentadienoate]tricarbonyliron (17). To a solution of **15** (0.73 g, 2.3 mmol) in ether (80 mL) at −78 °C was added a solution of $LiBH_4$ in THF (1.2 mL, 2.0 M, 2.4 mmol). The reaction was allowed to warm to 23 °C over a 2 h period and stirred at this temperature for 16 h. The mixture was diluted with water (45 mL) and extracted with ether (2 × 80 mL). The combined organic layers were washed with brine (80 mL) and dried, and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes–benzene (1:1)) to afford **16** as a yellow oil (0.52 g, 80%). **16**: ^{1}H NMR ($CDCl_3$) δ 5.87 (br t, J = 7.6 Hz, 1H), 5.23 (d, J = 13.4 Hz, 1H), 4.98 (d, J = 13.4 Hz, 1H), 3.67 (s, 3H), 1.97 (dd J = 2.5, 6.6 Hz, 1H), 1.91 (s, 1H), 1.23 (s, 1H), 0.24 (dd, J = 2.2, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 173.6, 106.4, 86.2, 62.3, 51.7, 45.4, 38.4. This product was used without

further characterization. To a solution of **16** (1.41 g, 5.00 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added pyridine (5 mL) and excess acetic anhydride (5 mL). After being stirred for 18 h, the mixture was diluted with water (50 mL) and extracted with ether (2 × 25 mL), the combined organic extracts were washed with 1 N HCl (2 × 25 mL) followed by saturated aqueous $NaHCO_3$ (25 mL) and dried, and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes–ethyl acetate (9:1)) to afford **17** as a light orange solid (1.54 g, 95%).

17: mp 62–63 °C; IR (CCl_4, cm^{-1}) 2050, 1975, 1747, 1735; ^1H NMR ($CDCl_3$) δ 5.47 (d, J = 12.5 Hz, 1H), 5.46 (br t, J = 8.4 Hz, 1H), 5.20 (d, J = 12.5 Hz, 1H), 3.64 (s, 3H), 2.11 (s, 3H), 1.93 (dd, J = 2.9, 7.3 Hz, 1H), 0.67 (s, 1H), 0.58 (dd, J = 2.9, 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 171.6, 169.5, 99.7, 86.7, 70.6, 47.1, 39.4, 27.8, 19.0; EI-HRMS m/z 268.0036 (calcd for $C_{10}H_{12}O_5Fe$ (M − 2CO) m/z 268.0033).

Reaction of 17 with Allyltrimethylsilane. The reaction of **17** (0.32 mg, 0.21 mmol) with allyltrimethylsilane (0.30 mL, 2.0 mmol) was carried out in a fashion similar to the reaction of **8** with allyltrimethylsilane. The crude product was purified by chromatography (SiO_2, hexanes–ethyl acetate (49:1)) to give a light orange oil (0.25 g, 82%). This was determined to be a mixture of **18** and **19** (1:2) by NMR spectroscopy. Further separation of the mixture was not attempted: IR (CCl_4, cm^{-1}) 2044, 1979, 1724; EI-HRMS m/z 222.0347 (calcd for $C_{10}H_{14}O_2Fe$ (M − 3CO) m/z 222.0342).

18: ^1H NMR ($CDCl_3$) δ 5.80 (ddt, J = 16.9, 10.3, 6.8 Hz), 5.1–5.0 (m), 3.68 (s, 0.5H), 3.62 (s, 1.5H), 3.38 (d, J = 2.4 Hz, 0.5H), 2.87 (t, J = 7.7 Hz, 0.5H), 2.20 (m), 2.04 (d, J = 2.4 Hz, 0.5H), 1.70 (m).

19: ^1H NMR ($CDCl_3$) δ 5.89 (ddt, J = 17.1, 10.3, 6.8 Hz), 5.20 (ddd, J = 1.1, 7.1, 9.2 Hz, 1H), 5.1–5.0 (m), 3.66 (s, 3H), 3.46 (ddd, J = 5.9, 7.8, 13.7 Hz, 1H), 2.52 (m, 1H), 2.36 (m, 2H), 1.86 (dd, J = 3.0, 7.1 Hz, 1H), 0.62 (s, 1H), 0.52 (dd, J = 3.0, 9.2 Hz, 1H).

[1,2-Bis(acetoxymethylene)-1,3-butadiene]tricarbonyliron (20). To a solution of **16** (0.70 g, 2.5 mmol) in THF (100 mL) at 0 °C was added a solution of DIBAL in toluene (7.5 mL, 1.0 M, 7.5 mmol). The reaction was allowed to warm to 23 °C over a 2 h period and stirred at this temperature for 16 h. The mixture was poured into saturated aqueous Na_2SO_4 (150 mL) and extracted with ethyl acetate (2 × 100 mL). The combined organic layers were washed with brine (100 mL) and dried and the solvent evaporated. The residue was purified by chromatography (SiO_2, hexanes–ethyl acetate (3:1)) to afford a yellow oil (0.42 g, 72%): ^1H NMR ($CDCl_3$) δ 5.68 (br t, J = 8.6 Hz, 1H), 5.11 (d, J = 13.4 Hz, 1H), 4.68 (d, J = 13.4 Hz, 1H), 4.81 (m, 2H), 2.19 (br s, 2H), 1.80 (dd, J = 2.2, 7.0 Hz, 1H), 1.39 (m, 1H), 0.25 (dd, J = 2.1, 9.0 Hz, 1H). This product was used without further characterization. To a solution of the diol (100 mg, 0.380 mmol in CH_2Cl_2 (25 mL) at 0 °C was added pyridine (5 mL) and excess acetic anhydride (4 mL). After being stirred for 16 h, the mixture was diluted with water (25 mL) and extracted with ether (2 × 25 mL), the combined organic extracts were washed with 1 N HCl (25 mL) followed by saturated aqueous $NaHCO_3$ (25 mL) and dried, and the solvent was evaporated. The residue was purified by chromatography (SiO_2, hexanes–ethyl acetate (9:1)) to afford **20** as a pale yellow oil (110 mg, 89%).

20: ^1H NMR ($CDCl_3$) δ 5.52 (br t, J = 8.3 Hz, 1H), 4.93 (d, J = 12.7 Hz, 1H), 4.84 (d, J = 13.4 Hz, 1H), 4.25 (m, 2H), 2.11 (s, 3H), 2.04 (s, 3H), 1.78 (dd, J = 2.7, 7.1 Hz, 1H), 0.86 (t, J = 7.5 Hz, 1H), 0.39 (dd, J = 2.7, 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 209.9, 170.4, 170.2, 98.3, 85.1, 63.1, 62.6, 55.5, 38.5, 20.7; EI-HRMS m/z 282.0191 (calcd for $C_{11}H_{14}O_5Fe$ (M − 2CO) m/z 282.0189).

Reaction of 20 with Allyltrimethylsilane. The reaction of **20** (70 mg, 0.21 mmol) with allyltrimethylsilane (0.10 mL, 0.62 mmol) was carried out in a fashion similar to the reaction of **8** with allyltrimethylsilane. The crude product was purified by chromatography (SiO_2, hexanes) to afford **21** as a yellow oil (55 mg, 86%).

21: IR (CCl_4, cm^{-1}) 2051, 1977, 917; ^1H NMR ($CDCl_3$) δ 5.80 (m, 2H), 5.1–5.0 (m, 4H), 3.50 (dt, J = 2.2, 7.6 Hz, 1H), 2.62 (t, J = 7.6 Hz, 1H), 2.30 (s, 1H), 2.25–2.05 (m, 4H), 1.77 (d, J = 2.4 Hz, 1H), 1.73–1.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 212.0, 211.7, 211.2, 137.5, 115.5, 115.4, 101.7, 76.5, 74.1, 49.5, 36.6, 36.3, 28.9, 28.1; EI-HRMS m/z 248.0711 (calcd for $C_{13}H_{18}OFe$ (M − 2CO) m/z 248.0708).

General Procedure for Reaction of Carbanions with Tricarbonyl(trimethylenemethane)iron Complexes Followed by Protonation. A solution of the (TMM)$Fe(CO)_3$ complex (0.5–1.0 mmol) in THF (2 mL) was rapidly added to a solution of the anion in THF/HMPA (2 equiv) at −78 °C. The reaction mixture was stirred at the temperature and for the amount of time indicated in each entry. To the reaction mixture, at −78 °C, was added trifluoroacetic acid (1 mL). After being stirred at −78 °C for 30 min, the mixture was poured into saturated aqueous $NaHCO_3$ and extracted with petroleum ether (2 × 25 mL). The combined organic extracts were washed with brine (25 mL) and dried ($MgSO_4$) and the solvent evaporated. The residue was purified as indicated in the following procedures.

2-Methyl-4,4-diphenyl-1-butene (24a). Purification of the residue from the reaction (23 °C, 1.5 h) of **1a** (194 mg, 1.00 mmol) with **22a** by flash chromatography (SiO_2 impregnated with 15% $AgNO_3$, hexanes) gave **24a** as a colorless oil (188 mg, 85%). The ^1H and MS spectral data for this compound were identical with the literature values.[29a]

24a: ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, 10H), 4.68 (br s, 1H), 4.59 (br s, 1H), 4.17 (t, J = 8.1 Hz, 1H), 2.77, (d, J = 8.1 Hz, 2H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 144.7, 143.4, 128.9, 128.4, 126.1, 112.6, 49.4, 43.9, 22.6; GC/MS m/z 222 (M^+, 3), 167 (100), 165 (34), 152 (20), 115 (7).

Ethyl 2,2,4-Trimethyl-4-pentenoate (24b). Purification of the residue from the reaction (−78 °C, 1 h) of **1a** (200 mg, 1.03 mmol) with **22b** by flash chromatography (hexanes–ethyl acetate (20:1)) gave **24b** as a colorless liquid (102 mg, 58%). The ^1H NMR spectral data for this compound were similar to that of the known methyl ester.[29c]

24b: IR (neat, cm^{-1}) 1735, 918; ^1H NMR ($CDCl_3$) δ 4.79 (br s, 1H), 4.64 (br s, 1H), 4.11 (q, J = 7.3 Hz, 2H), 2.30 (br s, 2H), 1.65 (br s, 3H), 1.25 (t, J = 7.3 Hz, 1H), 1.16 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 178.0, 142.6, 114.1, 60.3, 48.4, 41.4, 25.6, 23.5, 14.1; GC/MS m/z 170 (M^+, 2), 155 (6), 97 (100), 81 (16), 55 (98), 41 (73).

2,2,4-Trimethyl-4-pentenenitrile (24c). Purification of the residue from the reaction (−78 °C, 1 h) of **1a** (100 mg, 0.515 mmol) with **22c** by flash chromatography (hexanes–ethyl acetate (4:1)) gave **24c** as a colorless liquid (50 mg, 79%). The spectral data for this compound were identical with the literature values.[29d]

24c: ^1H NMR ($CDCl_3$) δ 4.97 (narrow m, 1H), 4.83 (narrow m, 1H), 2.25 (br s, 2H), 1.89 (br s, 3H), 1.35 (s, 6H); GC/MS m/z 123 (M^+, 45), 122 (13), 105 (43), 81 (23), 55 (100).

2-(2-Methyl-2-propenyl)-2-phenyl-1,3-dithiane (24d). Purification of the residue from the reaction (−78 °C, 1 h) of **1a** (194 mg, 1.00 mmol) with **22d** by flash chromatography (hexanes–ethyl acetate (9:1)) gave **24d** as a pale yellow oil (202 mg). This sample contained ca. 16% of 2-phenyl-1,3-dithiane which could not be separated. Hydrolysis ($HgCl_2$, $CdCO_3$, H_2O) of this mixture gave the known[30] 3-methyl-1-phenyl-3-buten-1-one and 3-methyl-1-phenyl-2-buten-1-one.

24d: ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m), 4.81 (br s, 1H), 4.62 (br s, 1H), 2.80 (s, 2H), 2.74 (m, 4H), 1.92 (m, 2H), 1.45 (s, 3H); GC/MS m/z 250 (M^+, 2), 195 (100), 161 (30), 121 (73), 77 (42).

2-Methyl-1,4,4-triphenyl-1-butene (26a) and 2-Methyl-3,4,4-triphenyl-1-butene (27a). The ^1H NMR spectrum of the crude residue from the reaction (23 °C, 1.5 h) of **1g** (270 mg, 1.00 mmol) with **22a** indicated this to be a mixture of **26a** and **27a** (9:11) along with diphenylmethane. The residue was purified by flash chromatography (SiO_2 impregnated with 15% $AgNO_3$). Elution with hexanes–ethyl acetate (20:1) gave diphenylmethane (120 mg). Further elution with hexanes–ethyl acetate (9:1) gave **26a** (100 mg, 34%) as a pale yellow oil followed by **27a** (120 mg, 40%) as a tan solid.

26a: ^1H NMR ($CDCl_3$) δ 7.3–7.0 (m, 15H), 6.11 (br s, 1H), 4.24 (t, J = 7.8 Hz, 1H), 2.90 (d, J = 7.8 Hz, 2H), 1.78 (d, J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 144.6, 138.8, 136.3, 128.7, 128.3, 128.2, 128.0, 127.6, 126.1, 125.8, 49.7, 46.6, 17.9; GC/

MS *m/z* 298 (M^+, 2), 219 (19), 167 (100), 165 (14), 91 (53); EI-HRMS *m/z* 298.1720 (calcd for $C_{23}H_{22}$ *m/z* 298.1716).

27a: mp 88–91 °C, ^1H NMR ($CDCl_3$) δ 7.3–7.0 (m, 15H), 4.86 (d, J = 0.5 Hz, 1H), 4.71 (br t, J = 1.5 Hz, 1H), 4.50 (d, J = 12.2 Hz, 1H), 4.18 (d, J = 12.5 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146.0, 144.0, 143.5, 141.7, 130.0, 128.3, 128.2, 128.1, 128.0, 127.8, 125.9, 125.6, 112.8, 57.3, 54.3, 21.2; GC/MS *m/z* 298 (M^+, 1), 167 (100), 165 (13), 91 (6); EI-HRMS *m/z* 298.1731 (calcd for $C_{23}H_{22}$ *m/z* 298.1716).

Ethyl 2,2,4-Trimethyl-5-phenyl-4-pentenoate (26b). Purification of the residue from the reaction (−78 °C, 1 h) of **1g** (135 mg, 0.50 mmol) with **22b** by flash chromatography (hexanes–ethyl acetate (20:1)) gave **26b** as a colorless liquid: 115 mg, 93%.

26b: IR (neat, cm^{-1}) 1735, 1471; ^1H NMR ($CDCl_3$) δ 7.26–7.07 (m, 5H), 6.18 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 2.39 (s, 2H), 1.73 (d, J = 1.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 1H), 1.16 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 177.9, 138.2, 135.7, 128.9, 128.0, 127.9, 126.1, 60.3, 51.5, 42.6, 25.6, 19.1, 14.1; GC/MS *m/z* 246 (M^+, 6), 131 (100), 115 (19), 91 (38), 41 (13); EI-HRMS *m/z* 246.1611 (calcd for $C_{16}H_{22}O_2$ *m/z* 246.1621).

2,2,4-Trimethyl-5-phenyl-4-pentenenitrile (26c). Purification of the residue from the reaction (−78 °C, 1 h) of **1g** (135 mg, 0.50 mmol) with **22c** by flash chromatography (hexanes–ethyl acetate (20:1)) gave a mixture of (*E*)-**26c** and (*Z*)-**26c** (4.7:1) as a colorless liquid: 95 mg, 95%.

26c: IR (neat, cm^{-1}) 2245, 1460; ^1H NMR ($CDCl_3$) δ 7.41–7.17 (m, 5H), 6.56 (*Z*) and 6.39 (*E*, two s, 1H), 2.53 (*Z*) and 2.43 (*E*, two s, 2H), 2.12 (*Z*) and 2.07 (*E*, two d, J = 1.4 Hz, 3H), 1.42 (*E*) and 1.25 (*Z*, two s, 6H); EI-HRMS *m/z* 199.1356 (calcd for $C_{14}H_{17}N$ *m/z* 199.1362).

3-Ethyl 2,2,4-Trimethyl-4,8-nonadienoate (31) and Ethyl 2,2-Dimethyl-4-methylene-8-nonenoate (32). The residue from the reaction (−78 °C, 2.5 h) of **1d** (220 mg, 0.89 mmol) with **22b** was purified by flash chromatography (SiO_2). Elution with hexanes gave recovered **1d** (70 mg). Further elution with hexanes–ethyl acetate (10:1) gave a mixture of (*E*)-**31**, (*Z*)-**31**, and **32** (2:2:1) as indicated by ^1H NMR spectroscopy (120 mg, 88% based on consumed **1d**): ^1H NMR ($CDCl_3$) δ 5.8 (m, 1H), 5.23 (m, 0.4H), 5.10 (m, 0.4H), 5.03–4.90 (complex m, 2H), 4.79 (br s, 0.2H), 4.68 (br s, 0.2H), 4.09 (overlapping q, 2H), 2.35 (s, 0.8H), 2.30 (s, 0.4H), 2.25 (s, 0.8H), 2.05 (m, 4H), 1.59 (s, 1.2H), 1.52 (s, 1.2H), 1.25 (overlapping t, 3H), 1.16 (s, 1.2H), 1.15 (s, 2.4H), 1.12 (s, 2.4H), 0.85 (m, 0.4H); EI-HRMS *m/z* 224.1777 (calcd for $C_{14}H_{24}O_2$ *m/z* 224.1776).

General Procedure for Reaction of Carbanions with Tricarbonyl(trimethylenemethane)iron: Allyl Bromide Workup. A solution of the (TMM)$Fe(CO)_3$ complex (0.5–1.0 mmol) in THF (2 mL) was rapidly added to a solution of the anion in THF/HMPA (2 equiv) at −78 °C. The reaction mixture was stirred for the amount of time and at the temperature indicated in each entry. To the reaction mixture, at −78 °C, was added allyl bromide (0.5 mL) over a 1 min period. After being stirred at −78 °C for 1 h, the mixture was stirred for the amount of time and at the temperature indicated in each entry. The reaction mixture was then diluted with water (25 mL) and extracted with petroleum ether (3 × 15 mL). The combined organic extracts were washed with brine (25 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified as indicated in the following procedures.

5-Methylene-7,7-diphenyl-1-heptene (33a). The reaction (23 °C, 2 h) of **1a** (200 mg, 1.03 mmol) with **22a** followed by allyl bromide (60 °C, 3 h) gave a residue which was purified by flash chromatography (SiO_2, hexanes–ethyl acetate (100:1)) followed by column chromatography (SiO_2 impregnated with 15% $AgNO_3$, hexanes–ethyl acetate (100:1)) to give **33a** as a colorless oil (39 mg, 14%) along with **24a** (16 mg, 7%).

33a: ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, 10H), 5.80 (tdd, J = 6.2, 10.3, 17.0 Hz, 1H), 5.01 (br d, J = 17.0 Hz, 1H), 4.96 (br d, J = 10.3 Hz, 1H), 4.74 (br s, 1H), 4.67 (br s, 1H), 4.20 (t, J = 7.8 Hz, 1H), 2.80 (d, J = 7.8 Hz, 2H), 2.20 (m, 2H), 2.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 146.4, 144.7, 138.3, 128.3, 127.9, 126.1, 114.6, 111.8, 49.2, 42.1, 35.4, 31.9; EI-HRMS *m/z* 262.1718 (calcd for $C_{20}H_{22}$ *m/z* 262.1723).

Ethyl 2,2-Dimethyl-4-methylene-7-octenoate (33b). The reaction (−78 °C, 3 h) of **1a** (200 mg, 1.03 mmol) with **22b**, followed by allyl bromide (23 °C, 5 h), gave a residue which was purified by flash chromatography (SiO_2, hexanes–ethyl acetate (20:1)) followed by column chromatography (SiO_2 impregnated with 15% $AgNO_3$, hexanes–ethyl acetate (10:1)) gave **33b** as a colorless oil (71 mg, 33%) along with **24b** (23 mg, 13%).

33b: IR (neat, cm^{-1}) 3078, 2950, 1728, 1641, 1186, 1128, 908; ^1H NMR ($CDCl_3$) δ 5.78 (tdd, J = 6.2, 10.3, 17.0 Hz, 1H), 5.07–4.92 (complex m, 2H), 4.82 (br s, 1H), 4.71 (br s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.31 (s, 2H), 2.20 (m, 2H), 2.07 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.17 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 177.9, 145.7, 138.3, 114.5, 113.1, 60.3, 46.5, 42.0, 36.0, 32.1, 25.7, 14.1; EI-HRMS *m/z* 165.1277 (calcd for $C_{11}H_{17}O[M-OC_2H_5]$ *m/z* 165.1280).

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Supplementary Material Available: Copies of ^1H and/or ^{13}C NMR spectra of all new compounds (24 pages). This material is contained in 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.

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