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Hydride Reduction of (Diene)iron Tricarbonyl Complexes as a Route to Substituted (Allyl)iron Tricarbonyl Anions. Detection of a Formyl Intermediate in the Hydride Reduction of (1,3-Butadiene)iron Tricarbonyl by Et_3BH^-

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Reactions of (butadiene)iron tricarbonyl or (1-phenylbutadiene)iron tricarbonyl with Et_3BH^- in tetrahydrofuran monitored by IR spectroscopy showed efficient conversion to the corresponding (allyl)iron tricarbonyl anions $(CH_3CH\text{---}CH\text{---}CH_2)Fe(CO)_3^-$ and $(CH_3CH\text{---}CH\text{---}CHC_6H_5)Fe(CO)_3^-$. Treatment of these solutions with $(CH_3)_3SnCl$ resulted in formation of (*anti*-methallyl)$Fe(CO)_3$–$SnMe_3$, *anti*-**12** and (*anti*-1-methyl-*syn*-3-phenylallyl)$Fe(CO)_3$–$SnMe_3$, *anti,syn*-**13**. These *anti* isomers thermally isomerize to their *syn* isomers by clean first-order kinetics (*anti*-**12** to *syn*-**12**, $k = 2.6 \times 10^{-5}$ s^{-1}, 55 °C; *anti,syn*-**13** to *syn,syn*-**13**, $k = 5.8 \times 10^{-6}$ s^{-1}, 25 °C). The sterochemistry of *syn,syn*-**13** was confirmed by X-ray analysis (monoclinic, $P2_1/n$, $a = 14.830(3)$ Å, $b = 7.5651(18)$ Å, $c = 15.7202(18)$ Å, $\beta = 102.001(13)°$, $Z = 4$). Treatment of the (allyl)iron tin complexes *anti*-**12**, *syn*-**12**, *anti,syn*-**13**, and *syn,syn*-**13** with KH results in clean formation of the corresponding (allyl)iron tricarbonyl anions which can be isolated in good yields as their potassium salts. The configuration of the allyl unit is maintained in the reduction reaction. Low temperature ^1H, ^2H, and ^{13}C NMR experiments reveal that the anionic formyl complex $(C_4H_6)(CO)_2FeCHO^-$ is an intermediate in the formation of (*anti*-methallyl)$Fe(CO)_3^-$ from Et_3BH^- and (butadiene)iron tricarbonyl. Hydride migration from formyl to C_1 of the butadiene ligand occurs at −50 °C, $k = 8.3 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger} = 17$ kcal/mol.

Introduction

Unsaturated hydrocarbons can be activated toward attack by nucleophiles by binding them to electrophilic cationic or neutral transition metal carbonyl moieties. There are numerous reports of the use of this strategy in synthesis for stereo- and regioselective carbon–carbon bond formation.[1] The complementary reaction, attack of carbon electrophiles on unsaturated hydrocarbon ligands bound to *anionic* and thus nucleophilic metal carbonyl moieties is less common but is receiving increasing attention.[2-7] Examples of such complexes which result in carbon–carbon bond formation upon reaction with carbon electrophiles include (diene)$Mn(CO)_3^-$ complexes,[2] (cyclohexadienyl)$Cr(CO)_3^-$,[3] (cycloheptadienyl)$Fe(CO)_2^-$,[4] (arene)$Mn(CO)_2^-$ complexes,[5] $(\eta^4\text{-}C_6H_6)Cr(CO)_3^{-2}$,[7] and $(\eta^4\text{-}C_8H_8)Mn(CO)_3^-$.[2e,f] The electrophile adds *endo*[2a-d,3,4,5] to the ring in most of these systems which suggests the intermediacy of a metal alkyl complex. The metal–alkyl intermediate has been observed in some cases.[5] Acyl products are sometimes observed, indicating CO insertion prior to migration.[3-5,6] In a few cases, such as $(\eta^4$-1,3,5-cycloheptatriene)$Mn(CO)_3^-$, $(\eta^4$-cyclooctatetraene)$Mn(CO)_3^-$, and $(\eta^4\text{-}C_6H_6)Cr(CO)_3^{2-}$, the electrophile attacks *exo*,[2e,f,7] suggesting direct reaction with the free double bond.

A system we have investigated in this regard is the reaction of $(\eta^3\text{-allyl})Fe(CO)_3^-$, **1**, with carbon electrophiles.[6] The sequence of reactions observed when this species reacts with $PhCH_2Br$ in the presence of trapping ligands is illustrated in Scheme I. Treatment of **1** with $PhCH_2Br$ yields $(\eta^3\text{-allyl})(CO)_3FeCH_2Ph$, **2**. The benzyl group in **2** does not migrate to the allyl unit, but upon treatment of **2** with PPh_3, CO insertion occurs to give the acyl complex **3**. At room temperature, acyl migration occurs to give **4** which rapidly isomerizes to the α,β-unsaturated ketone complex **5**. The enone can be displaced from **5** with CH_3-

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[1] (a) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. (b) Pearson, A. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, 1991; Vol. 4, Section 3.4. (c) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (d) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, 1991; Vol. 4, Section 2.4. (e) Kundig, E. P.; Desobry, V.; Simmons, D. P.; Wenger, E. *J. Am. Chem. Soc.* **1989**, *111*, 1804. (f) Birch, A. J. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 101. (g) Rosenblum, M.; Lennon, P.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8426. (h) Rosenblum, M. *Pure Appl. Chem.* **1984**, *56*, 129. (i) Hegedus, L. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, 1991; Vol. 4, Section 3.1 and 3.2. (j) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.

[2] (a) Brookhart, M.; Lamanna, W. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *Ibid.* **1982**, *104*, 2117. (c) Brookhart, M.; Lukacs, A. *Ibid.* **1984**, *106*, 4161. (d) Brookhart, M.; Timmers, F. J. *Organometallics* **1985**, *4*, 1365. (e) Brookhart, M.; Noh, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829. (f) Brookhart, M.; Noh, S. K.; Timmers, F. J.; Hong, Y. H. *Organometallics* **1988**, *7*, 2458.

[3] (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. (c) Kundig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P. *Helv. Chim. Acta* **1990**, *73*, 386.

[4] (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.

[5] Brookhart, M.; Rush, P. K.; Noh, S. K. *Organometallics* **1986**, *5*, 1745.

[6] Brookhart, M.; Yoon, J.; Noh, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 4117.

[7] Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.

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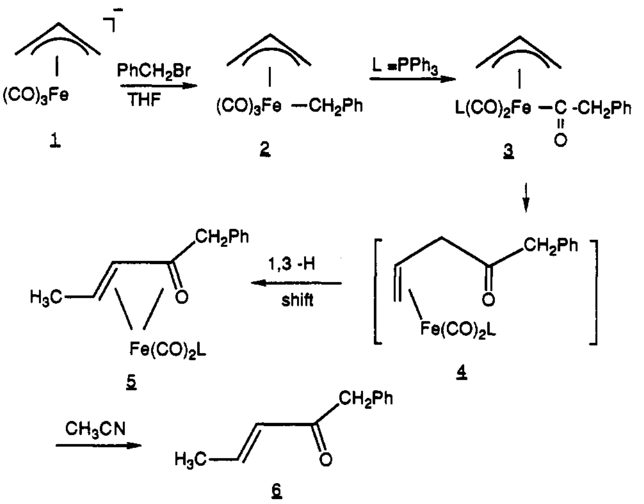
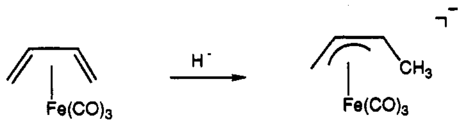
Scheme I

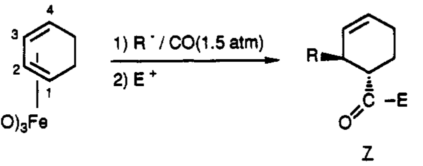


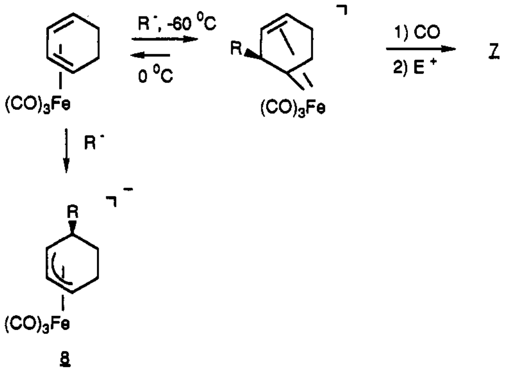
CN. Alkylation of 1 in CH_3CN results in interception and displacement of the β,γ-enone from 4 prior to isomerization.

The parent (allyl)$Fe(CO)_3^-$ anion is readily available from reduction of (allyl)$Fe(CO)_3I$ which is prepared from allyl iodide and $Fe_2(CO)_9$. Yields for formation of substituted (allyl)$Fe(CO)_3X$ derivatives are generally moderate to poor, and thus these complexes are not attractive precursors to substituted (allyl)iron anions. We sought alternative routes to simple substituted (allyl)$Fe(CO)_3^-$ systems. One attractive possibility involved hydride addition to readily available (diene)iron tricarbonyl complexes, as shown for the parent system.



Related to this transformation is work reported by Semmelhack in a series of papers[8a–f] on addition of carbon nucleophiles to (diene)$Fe(CO)_3$ complexes. Semmelhack and co-workers initially reported that treatment of (cyclohexadiene)$Fe(CO)_3$ with stabilized carbanions followed by acid quenching resulted in mixtures of isomeric substituted cyclohexenes.[8a] The regioisomers produced upon reaction of (1,3-butadiene)$Fe(CO)_3$ indicated that addition of the nucleophile occurred at C_2. Later, Semmelhack and co-workers showed that reaction between (cyclohexadiene)$Fe(CO)_3$ and stabilized carbon nucleophiles under 1.5 atm of CO resulted in acyl complexes, 7, after quenching with electrophiles.[8b] This result also pointed to R^- addition at C_2, which was later confirmed by ^1H and ^{13}C NMR studies of intermediates generated at low temperatures.[8c] This NMR study in conjunction with product studies under a variety of conditions showed that C_2 addition resulted in the kinetically controlled product at low temperatures.[8e] Above ca. 0 °C, addition of the stabilized carbanion is reversible and, ultimately, attack occurs at C_1 to give the thermodynamically controlled product, the substituted (allyl)iron tricarbonyl anion, 8.



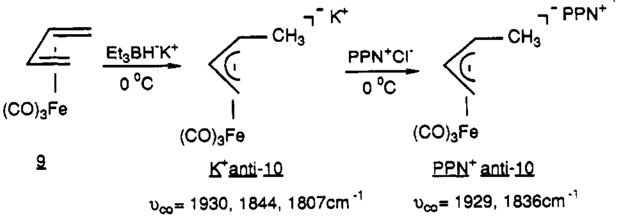


We report here the development of a convenient procedure for hydride addition to (diene)$Fe(CO)_3$ complexes to generate substituted (allyl)iron anions. Quenching these anions, generated *via* hydride addition procedures, with Me_3SnCl gives (allyl)$Fe(CO)_3$–$SnMe_3$ derivatives in good yields. These tin derivatives represent excellent precursors to (allyl)$Fe(CO)_3^-K^+$ salts through cleavage of the Fe–Sn bond with KH in tetrahydrofuran. Low temperature NMR studies of the hydride addition step using Et_3BH^- and Et_3BD^- reveal the intermediacy of a formyl complex which transfers hydride from the CO ligand to the bound diene.

Results and Discussion

1. Hydride Reduction Reactions of (Butadiene)-$Fe(CO)_3$, 9. Several hydride reducing reagents were screened using IR studies to determine which reagent was most efficient for conversion of (butadiene)$Fe(CO)_3$, 9, to (η^3-$CH_3CH\text{---}CH\text{---}CH_2$)$Fe(CO)_3^-$. Reaction of 9 with 2.5 equiv of $LiAlH_4$ in THF at 0 °C resulted in very rapid reduction, complete in less than 10 min. The IR spectrum revealed two bands typical of the (allyl)iron anion (ν_{CO} = 1930, 1834 cm^{-1}), but substantial amounts of an unknown CO-containing material with a broad ν_{CO} at 1699 cm^{-1} were also present. Similarly, (*sec*-butyl)$_3BH^-$ gave rapid reduction of 9 but considerable contamination of the (methallyl)iron anion with unknown carbonyl complexes was evident.

Clean transformations of 9 to the (methallyl)iron tricarbonyl anion K^+*anti*-10 were achieved using either $Na^+(CH_3OCH_2CH_2O)_2AlH_2^-$(Red-Al) or $K^+Et_3BH^-$ as judged by the sole appearance of bands at 1930, 1836, 1805 cm^{-1} (Red-Al) and at 1930, 1844, 1807 cm^{-1} (Et_3BH^-) in the IR spectrum. To avoid contamination of the anion



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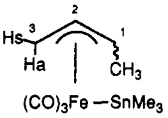
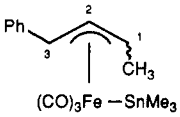
[8] (a) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (b) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (c) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15. (d) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885. (e) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715. (f) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1985**, *107*, 1456.

Table I. ^1H NMR Chemical Shifts and Coupling Constants for (Allyl)iron Trimethyltin Complexes in C_6D_6



Anti-methallyl isomer, anti-12
Syn-methallyl isomer, syn-12



Anti-methallyl isomer, anti,syn-13
Syn-methallyl isomer, syn,syn-13

	δ (ppm)							*J* (Hz)					
	H_1			H_3									
complex	syn	anti	H_2	syn	anti	CH_3	$SnMe_3$	H_{1-2}	H_{2-3s}	H_{2-3a}	H_{1-Me}	H_{s-a}	H_{1-3s}
***anti*-12**	3.36 (quin)		4.09 (dt)	2.36 (dt)	1.97 (d)	0.92 (d)	0.29 (s)	7.4	6.7	11.5	7.4	1.7	1.5
***syn*-12**		2.52 (dq)	4.09 (td)	1.94 (dd)	1.05 (d)	1.28 (d)	0.39 (s)	10.7	6.5	10.6	6.2	1.7	
***anti,syn*-13**	3.54 (quin)		5.26 (dd)		3.72 (dd)	1.05 (d)	0.34 (s)	7.1		11.7	7.1		
***syn,syn*-13**		2.46 (dq)	5.19 (t)		2.82 (d)	1.44 (d)	0.37 (s)	10.7		10.8	6.2		

with excess hydride reagents (usually more than 2 equiv of hydride is required for the complete generation of anion in this reaction) or by the BEt_3 or $AlH(CH_3OCH_2CH_2O)_2$ byproducts, we attempted to isolate pure potassium or PPN^+ salts (PPN^+ = $(Ph_3P)_2N^+$) from these solutions.

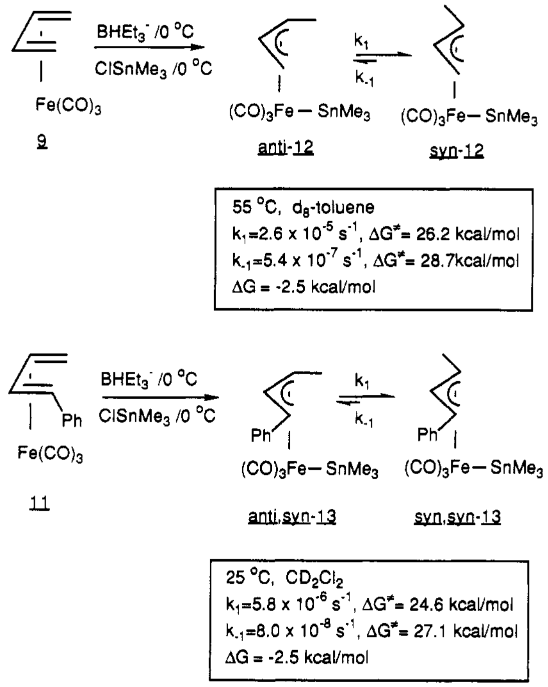
Limited success was obtained. The best preparation of PPN^+*anti*-**10** was achieved by adding 2.4 equiv of PPN^+Cl^- to the *in situ* generated K^+*anti*-**10** (2.4 equiv of Et_3BH^- plus **9**, 0 °C, THF). Filtration followed by solvent removal and trituration of the solid with ether and hexane give PPN^+*anti*-**10** as a yellow powder but in less than 10% yield. This salt was identified as the *anti*-methallyl derivative based on the typical cis $J_{H_{1S}-H_2}$ coupling constant of 6.6 Hz[9] (complete ^1H and ^{13}C data for this anion will be presented below).

To ultimately carry out clean organic reactions of these (allyl)iron anions, we felt it was necessary to begin with uncontaminated salts. Since direct isolation of salts from Et_3BH^- reduction reactions appeared difficult, an alternative procedure was devised whereby the anionic (allyl)iron complexes are first converted to their trimethyltin derivatives (which are readily purified) and then converted back to the (allyl)iron anions cleanly and in good yields by reduction of the Fe–Sn bond. This chemistry is described in the next two sections.

2. Generation of (η^3-Allyl)(CO)$_3$Fe–SnMe$_3$ Complexes *via* Trapping of (η^3-Allyl)Fe(CO)$_3$ Anions with Me$_3$SnCl. As noted above, reaction of Et_3BH^- with (diene)$Fe(CO)_3$ complexes in THF gives clean *in situ* generation of (allyl)$Fe(CO)_3$ anions. Reaction of these anions with Me_3SnCl results in good yields of the corresponding (η^3-allyl)(CO)$_3$Fe–SnMe$_3$ complexes which are easily handled and purified.

Two diene complexes were studied, the parent (butadiene)$Fe(CO)_3$, **9**, and (*trans*-1-phenylbutadiene)$Fe(CO)_3$, **11**. Results are summarized in Scheme II. From **9**, only the (*anti*-methallyl)$Fe(CO)_3$–$SnMe_3$, *anti*-**12**, complex was isolated. Key ^1H NMR data for *anti*-**12** are summarized in Table I. The stereochemistry is assigned on the basis of the $J_{H_1-H_2}$ value of 7.4 Hz, typical of a *cis* coupling constant. Formation of the *anti* isomer indicates that the stereochemistry of the C_2–C_3 bond is maintained during the sequence of reactions leading to *anti*-**12**. Clean, first-order thermal isomerization of *anti*-**12** to the more stable *syn* isomer, *syn*-**12**, occurs at 55 °C in toluene (k_1 = 2.6 × 10^{-5} s^{-1}, $t_{1/2}$ = 7.4 h, ΔG^* = 26.2 kcal/mol). At equilibrium the *syn*-**12**:*anti*-**12** ratio is 47 (ΔG = −2.5 kcal/mol) from which k_{-1} can be estimated as 5.4 × 10^{-7} s^{-1}. A typical rate plot is presented in the supplementary material. The *syn* isomer can be isolated in near quantitative yield after isomerization. ^1H NMR data appear in Table I; the $J_{H_1-H_2}$ value of 10.7 Hz establishes the stereochemistry of *syn*-**12** and confirms the assignment of the *anti*-**12** isomer.[9]

Scheme II



55 °C, d_8-toluene
k_1=2.6 x 10^{-5} s^{-1}, $\Delta G^{\neq}$= 26.2 kcal/mol
k_{-1}=5.4 x 10^{-7} s^{-1}, $\Delta G^{\neq}$= 28.7kcal/mol
ΔG = -2.5 kcal/mol

25 °C, CD_2Cl_2
k_1=5.8 x 10^{-6} s^{-1}, $\Delta G^{\neq}$= 24.6 kcal/mol
k_{-1}=8.0 x 10^{-8} s^{-1}, $\Delta G^{\neq}$= 27.1 kcal/mol
ΔG = -2.5 kcal/mol

Using a similiar procedure, only the (*anti*-1-methyl-*syn*-3-phenylallyl)$Fe(CO)_3$–$SnMe_3$, *anti,syn*-**13**, complex was isolated from the reaction of (*trans*-1-phenylbutadiene)$Fe(CO)_3$, **11**. Again, stereochemistry is established on the basis of $J_{H_1-H_2}$ (7.1 Hz, *cis*) and $J_{H_2-H_3}$ (11.7 Hz, *trans*) tabulated in Table I. Clean first-order thermal isomerization of *anti,syn*-**13** to *syn,syn*-**13** occurs at 25 °C in CH_2Cl_2 (k_1 = 5.8 × 10^{-6} s^{-1}, $t_{1/2}$ = 33 h, ΔG^* = 24.6 kcal/mol). The measured K_{eq} at 25 °C is 72, corresponding to ΔG = −2.5 kcal/mol, k_{-1} = 8.0 × 10^{-8} s^{-1}. The *syn,syn* isomer can be isolated in near quantitative yield, and as seen in Table I, the $J_{H_1-H_2}$ and $J_{H_2-H_3}$ values of 10.7 and 10.8 Hz, respectively, establish the stereochemistry. This configuration was confirmed by a single crystal X-ray structural determination which is reported below.

The *anti* to *syn* isomerization likely proceeds *via* the general and well-established mechanism for such metal allyl isomerizations. This involves η^3 to η^1 conversion followed by rotation of the uncomplexed double bond and recoordination. Thus for *anti*-**12** to *syn*-**12** the process below is proposed to occur.

The more rapid isomerization of *anti,syn*-**13** relative to *anti*-**12** probably reflects easier formation of the η^1-allyl intermediate as a result of conjugation of the free

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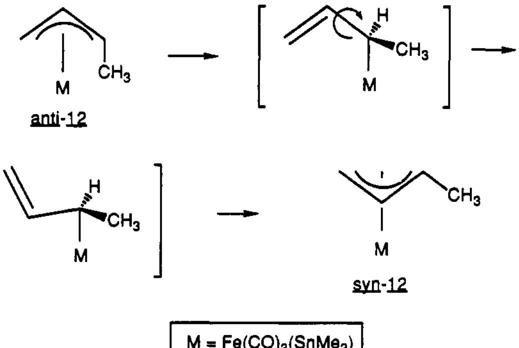
(9) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 177. (b) Nesmeyanov, A. N.; Ustynyuk, Yu. A.; Kritskaya, I. I.; Shchembelov, G. A. *J. Organomet. Chem.* **1968**, *14*, 395.

Table II. Crystallographic Data and Collection Parameters and Refinement Parameters for *syn,syn*-$[CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CHPh]Fe(CO)_3(SnMe_3)$, *syn,syn*-13

molecular formula	$C_{16}H_{20}FeO_3Sn$
fw	434.86
cryst dimens, mm	0.15 × 0.15 × 0.30
space group	$P2_1/n$
cell params	
a, Å	14.830(3)
b, Å	7.5651(18)
c, Å	15.7202(18)
β, deg	102.001(13)
V, Å^3	1725.1(6)
Z	4
d(calcd), Mg/m^3	1.674
F(000)	862.07
radiation wavelength, Å	0.710 73
monochromator	graphite
linear abs coeff, mm^{-1}	2.30
scan mode	ω–2θ
background	10% of full scan width on both side
2θ limit, deg	45
octants collcd	$\pm k,\pm h,\pm l$
total no. of unique reflns	2238
data with $I \geq 2.5\sigma(I)$	1525
R (including unobserveds)	0.051 (0.184)
R_w (including unobserveds)	0.069 (0.083)
GoF	1.93
no. of params	191
largest param shift/error	0.171
max density in final difference synthesis, e/Å^3	1.060

double bond with the aryl group in the 16-electron intermediate and greater relief of steric crowding.



X-ray Structure Determination of *syn,syn*-13. Single crystals of *syn,syn*-13 for X-ray analysis were grown from a hexane solution at −78 °C. Complex *syn,syn*-13 crystallizes in the monoclinic system with space group $P2_1/n$. The unit cell contains four molecules separated by the normal van der Waals distances. Crystallographic data are collected in Table II, and atomic coordinates are listed in Table III. An ORTEP diagram of *syn,syn*-13 is shown in Figure 1, and selected bond distances and angles are summarized in Table IV.

The X-ray structure confirms the *syn,syn* stereochemical assignment made on the basis of ^1H NMR spectral data. The phenyl group is twisted slightly out of the plane of the C_5–C_6–C_7 allyl moiety (21.5°), but this twist angle still allows for substantial π-interaction between these two groups. The bond distances in the allyl unit are normal, as is the Fe–Sn distance of 2.62 Å.[10,11] (Allyl)iron tricarbonyl halide complexes exhibit significant populations of both *exo* and *endo* isomers at room temperature.[9b,12] We observe only one isomer in solution for *syn,syn*-13 at temperatures from −80 to +25 °C and assume

Table III. Fractional Atomic Coordinates and Isotrophic Thermal Parameters for *syn,syn*-$[CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CHPh]Fe(CO)_3(SnMe_3)$, *syn,syn*-13

atom	x	y	z	B_{iso}, Å^2 [a]
Fe	0.51653(13)	0.1613(3)	0.33518(11)	1.28(8)
C(1)	0.4354(9)	0.1519(24)	0.4034(8)	2.3(8)
O(1)	0.3836(7)	0.1435(16)	0.4486(6)	2.7(5)
C(2)	0.5428(9)	−0.0712(20)	0.3438(8)	1.4(6)
O(2)	0.5585(7)	−0.2189(14)	0.3499(5)	2.2(5)
C(3)	0.4613(8)	0.3530(19)	0.2851(8)	1.2(6)
O(3)	0.4236(6)	0.4843(14)	0.2564(6)	2.1(5)
Sn	0.42300(7)	0.03355(14)	0.18782(6)	1.38(4)
C(4)	0.6137(10)	0.3527(24)	0.5166(9)	2.7(8)
C(5)	0.6287(10)	0.2427(20)	0.4439(8)	1.7(6)
C(6)	0.6385(9)	0.3062(20)	0.3645(8)	1.5(6)
C(7)	0.6494(9)	0.1956(20)	0.2959(8)	1.4(6)
C(8)	0.3055(10)	−0.1066(21)	0.2134(9)	2.1(7)
C(9)	0.5029(11)	−0.1483(22)	0.1286(9)	2.5(8)
C(10)	0.3764(11)	0.2285(24)	0.0907(9)	2.8(7)
C(11)	0.6570(9)	0.2536(19)	0.2078(8)	1.1(6)
C(12)	0.6276(9)	0.4180(19)	0.1728(8)	1.4(7)
C(13)	0.6389(9)	0.4762(19)	0.0913(8)	1.3(6)
C(14)	0.6799(9)	0.3571(21)	0.0416(8)	1.6(7)
C(15)	0.7101(9)	0.1958(22)	0.0745(8)	2.1(7)
C(16)	0.6978(9)	0.1397(22)	0.1554(8)	1.9(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

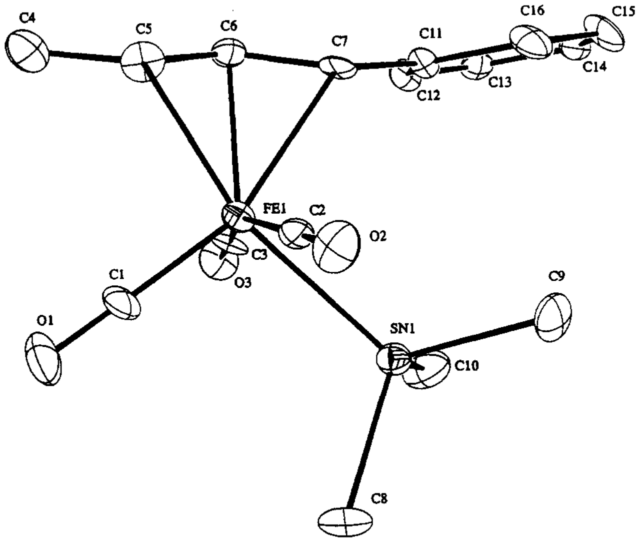


Figure 1. ORTEP diagram of *syn,syn*-13.

Table IV. Selected Bond Distances (Å) and Angles (deg) for *syn,syn*-$[CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CHPh]Fe(CO)_3(SnMe_3)$, *syn,syn*-13

Fe–C(1)	1.772(13)	Fe–C(5)	2.210(14)
Fe–C(2)	1.800(15)	Fe–C(6)	2.083(13)
Fe–C(3)	1.768(14)	Fe–C(7)	2.199(13)
C(4)–C(5)	1.467(21)	C(5)–C(6)	1.374(18)
C(6)–C(7)	1.400(19)	C(7)–C(11)	1.479(17)
C(1)–O(1)	1.151(16)	C(2)–O(2)	1.141(18)
C(3)–O(3)	1.182(17)	Fe–Sn	2.6243(21)
C(1)–Fe–C(2)	94.5(7)	C(1)–Fe–C(3)	89.5(7)
C(1)–Fe–Sn	102.6(5)	C(1)–Fe–C(5)	92.2(6)
C(1)–Fe–C(6)	123.7(6)	C(1)–Fe–C(7)	159.3(5)
C(2)–Fe–C(3)	155.2(6)	C(2)–Fe–Sn	76.9(4)
C(2)–Fe–C(5)	95.6(6)	C(2)–Fe–C(6)	109.5(6)
C(2)–Fe–C(7)	86.8(6)	C(3)–Fe–Sn	78.4(4)
C(3)–Fe–C(5)	108.7(6)	C(3)–Fe–C(6)	88.1(6)
C(3)–Fe–C(7)	97.9(6)	Sn–Fe–C(5)	163.7(4)
Sn–Fe–C(6)	131.6(3)	Sn–Fe–C(7)	97.8(3)
C(4)–C(5)–C(6)	124.9(14)	C(5)–C(6)–C(7)	122.8(14)
C(6)–C(7)–C(11)	126.0(13)		

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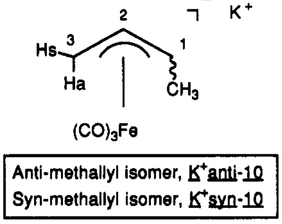
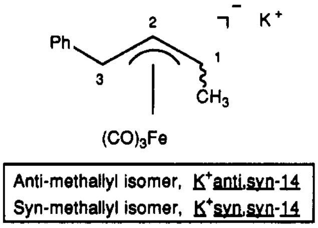
(10) (a) Minasyants, M. Kh.; Struchkov, Yu. T. *J. Struct. Chem.* **1968**, *9*, 577. (b) Minasyants, M. Kh.; Struchkov, Yu. T.; Kritskaya, I. I.; Avoyan, R. L. *J. Struct. Chem.* **1966**, *7*, 840.

(11) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 336.

Table V. ^{1}H NMR Chemical Shifts and Coupling Constants for (Allyl)iron Tricarbonyl Anionic Salts in THF-d_8



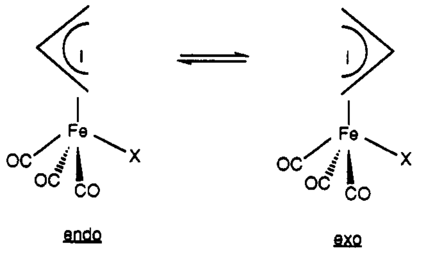
Anti-methallyl isomer, K$^+$anti-10
Syn-methallyl isomer, K$^+$syn-10



Anti-methallyl isomer, K$^+$anti,syn-14
Syn-methallyl isomer, K$^+$syn,syn-14

	δ (ppm)						J (Hz)				
	H_1			H_3							
complex	syn	anti	H_2	syn	anti	CH_3	H_{1-2}	H_{2-3s}	H_{2-3a}	H_{1-Me}	H_{1-3s}
K$^+$*anti*-**10**	3.03 (quin)		4.41 (dt)	2.09 (dd)	1.79 (d)	1.09 (d)	6.6	5.9	9.9	6.6	1.4
K$^+$*syn*-**10**		1.92 (dq)	3.99 (td)	1.63 (d)	0.90 (d)	1.52 (d)	8.7	5.7	9.1	6.1	
K$^+$*anti,syn*-**14**	3.00 (quin)		4.88 (dd)		3.40 (d)	1.25 (d)	6.7		9.4	6.7	
K$^+$*syn,syn*-**14**		2.02 (dq)	4.46 (t)		2.49 (d)	1.61 (d)	8.7		8.3	5.6	

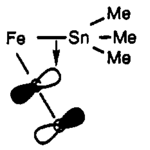
the solid state structure corresponds to the solution structure. The allyl unit can be regarded as *endo* with



respect to the $-SnMe_3$ group but is twisted substantially from an ideal geometry.

The coordination geometry in *syn,syn*-**13** deviates significantly from an ideal octahedral arrangement. The most unusual feature is the strong distortion of two CO groups (C_2O_2 and C_3O_3) toward the trimethyl tin group. The C_2–Fe–Sn angle is 76.9(4)°, while the C_3–Fe–Sn angle is 78.4(4)°. Such distortions have been previously observed in tin transition metal carbonyl derivatives but the present example is a particularly dramatic case. For example the average Sn–Mn–CO(equatorial) angle in $(CH_3)_3SnMn(CO)_5$ is 84.4° while the average Sn–Fe–CO angle in $CpFe(CO)_2$–$Sn(C_6H_5)_3$ is 86.5°.[11,13]

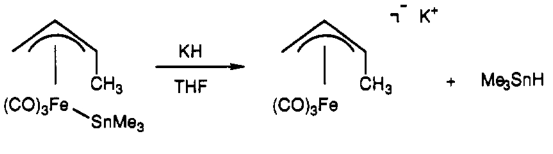
There is no obvious steric reason for this distortion in *syn,syn*-**13**. The stabilization of carbocations by β-substituted R_3M groups (M = Si, Ge, Sn, Pb) *via* σ–π conjugation is well established.[14] Chipperfield[15] has proposed that the increasing rates of electrophilic cleavage of a series of Me_3M–$Mn(CO)_5$ derivatives (M = Si, Ge, Sn, Pb; relative rates = 1:21:10^3:3 × 10^4) is due to σ–π conjugative stabilization between the Mn–MMe_3 σ bond and the π* orbital of the carbonyl groups in a $(CO)_5MnMMe_3$–I_2 intermediate. This kind of σ–π* interaction



I

could also lead to the observed distortions in *syn,syn*-**13**, as illustrated for one CO group in I.

3. Reductive Cleavage of (η^3-Allyl)Fe(CO)$_3$–SnMe$_3$ Complexes. *In Situ* Generation of (η^3-Allyl)Fe(CO)$_3$ Anions. The iron–tin bond in the (η^3-allyl)Fe(CO)$_3$–SnMe$_3$ complexes can be reductively cleaved with a variety of reagents including methyllithium, *n*-butyllithium, and various hydride reagents. IR monitoring of these reactions shows in all cases quantitative generation of (allyl)Fe(CO)$_3$ anions. The most convenient reagent for the preparation of salts is KH. In a typical reaction, (*anti*-methallyl)Fe(CO)$_3$–SnMe$_3$ was treated with excess KH in THF at 0 °C. Stirring for 20 min followed by filtration of unreacted KH and solvent removal gave the yellow potassium salt of (η^3-*anti*-methallyl)Fe(CO)$_3^-$, *K$^+$anti*-**10** in near quantitative yield. ^{1}H NMR data for *K$^+$anti*-**10** are summarized in Table V; the $J_{H_1-H_2}$ of 6.6 Hz establishes the *anti* stereochemistry. Using a similar procedure, the salts (η^3-*syn*-methallyl)Fe(CO)$_3^-$K$^+$, *K$^+$syn*-**10**, (η^3-*anti*-1-methyl-*syn*-3-phenylallyl)Fe (CO)$_3^-$K$^+$, *K$^+$anti,syn*-**14**, and (η^3-*syn*-1-methyl-*syn*-3-phenylallyl)Fe(CO)$_3^-$K$^+$, *K$^+$syn,syn*-**14** were generated from the corresponding tin complexes. ^{1}H NMR data for these anions are summarized in Table V; $J_{1,2}$ and $J_{2,3}$ values establish the stereochemistries of the anions which are unchanged from the precursor tin complexes.



anti-12
K$^+$anti-10

4. Mechanism of Reduction of (Butadiene)Fe(CO)$_3$ by Et$_3$BH$^-$. Detection of a Formyl Intermediate. The reaction sequence described above represents an efficient method for generating (allyl)Fe(CO)$_3$ anions. The key step is the efficient production of allyl anions in solution from reaction of Et_3BH^- with the diene complexes. We have conducted a brief mechanistic study of this hydride addition reaction. Three plausible mechanisms were initially envisioned, as outlined in Scheme III. In analogy with the addition of RLi reagents to iron diene complexes studied by Semmelhack,[8b] mechanism (a) involves hydride addition to C_2 to yield the σ,π complex **15** followed by isomerization to *K$^+$anti*-**10**. Mechanism (b) illustrates attack at C_1 to yield directly *K$^+$anti*-**10** with no intervening intermediate. Mechanism (c) involves formation of a

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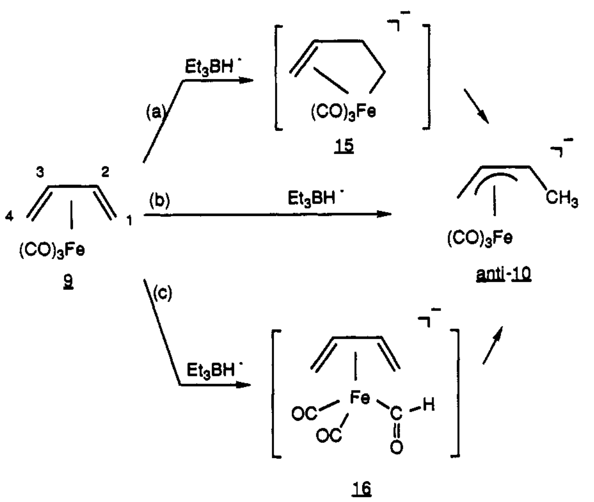
(12) (a) Cotton, J. D.; Doddrell, D.; Heazlewood, R. L.; Kitching, W. *Aust. J. Chem.* **1969**, *22*, 1785. (b) Nesmeyanov, A. N.; Kritskaya, I. I. *J. Organomet. Chem.* **1968**, *14*, 387. (c) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71.

(13) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, 1599.

(14) (a) Berwin, H. J. *J. Chem. Soc., Chem. Commun.* **1972**, 237. (b) Hanstein, W. G.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829.

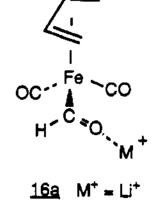
(15) Chipperfield, J. R.; Hayter, A. C.; Webster, D. E. *J. Chem. Soc., Chem. Commun.* **1975**, 625.

Scheme III

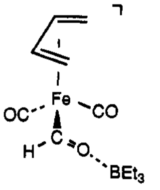


formyl intermediate, **16**, followed by migration of hydride from carbonyl to C$_1$ of the diene unit. Since Fe(CO)$_5$ accepts hydride from B(OCH$_3$)$_3$H$^-$ to yield the anionic formyl complex (CO)$_4$FeCHO$^-$,[16] the formyl intermediate is clearly plausible.

To search for intermediates, low temperature ^{1}H, ^{2}H, and ^{13}C NMR experiments were conducted using Et$_3$BH$^-$ and Et$_3$BD$^-$. Reaction of **9** (ca. 0.03 mM in 0.8 mL of THF/THF-d_8) with 17 equiv of LiBHEt$_3$ at −80 °C resulted, after vigorous stirring, in the formation of a homogeneous yellow solution which at −80 °C exhibited an ^{1}H resonance at 13.4 ppm. This signal falls in the typical range for the formyl hydrogens in metal formyl complexes[16,17] and clearly indicates the intermediacy of the formyl complex which we assign to the lithium coordinated species **16a**. All starting material has been reduced, and small amounts of the *anti*-methallyl complex, *K$^+$anti*-**10**, are evident. Warming to −50 °C results in isomerization of **16a** to *K$^+$anti*-**10**.



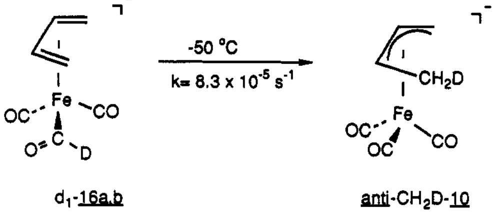
16a M$^+$ = Li$^+$
16c M$^+$ = K$^+$



16b

Using fewer equivalents of **9** (3–6 equiv) results in formation of *two* formyl species exhibiting resonances at 13.4 and 12.0 ppm. All starting material is not consumed under these conditions.[18] We assign the new species with the signal at 12.0 ppm as **16b**, a formyl complex in which BEt$_3$ is coordinated to the formyl oxygen. Two experiments were carried out to support these assignments. First, BEt$_3$ was added to a THF solution containing a 2:1 mixture of **16a**:**16b**. The resulting solution showed a 1:3 ratio of **16a**:**16b**. We presume the decrease in the amount of **16a** and increase of **16b** arises from increased competition of BEt$_3$ with Li$^+$ for the formyl oxygen. Secondly, the reduction reaction was carried out with K$^+$Et$_3$BH$^-$ (3.0 equiv) at −80 °C. ^{1}H NMR spectroscopy again revealed two formyl complexes present, the BEt$_3$-complexed species at 12.0 ppm and a new species at 13.5 ppm which we assign to **16c**, the K$^+$ coordinated formyl complex. Using similar ratios of K$^+$Et$_3$BH$^-$ and Li$^+$Et$_3$BH$^-$, the resulting **16c**:**16b** ratio is less than the **16a**:**16b** ratio presumably due to the weaker Lewis acidity of K$^+$ relative to Li$^+$.

These results were confirmed by ^{2}H NMR experiments. Reaction of **9** with 3–5 equiv of Li$^+$Et$_3$BD$^-$ (−80 °C, THF) results in formation of both **16a**-d_1 and **16b**-d_1, as evidenced by ^{2}H signals at 13.3 and 11.9 ppm. Substantial starting material remains unreduced.[19] The upfield region is now readily examined since no solvent signals interfere. The rate of isomerization of **16a**-d_1, **16b**-d_1 to *anti*-CH$_2$D-**10** can be conveniently monitored by the growth of the ^{2}H band at 0.92 ppm corresponding to the *anti*-CH$_2$D signal and the simultaneous disappearance of the formyl ^{2}H resonances. The migration follows first-order kinetics with $k_{\mathrm{mig}} = 8.3 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger} = 17$ kcal/mol at −50 °C. The starting material which is unreduced at −80 °C is not converted to *anti*-CH$_2$D-**10**. Under these conditions, the ^{2}H resonance of the excess BDEt$_3^-$ appears at δ 0.12, while a second resonance appears at δ −3.18, which we assign to the bridged species Et$_3$BDBEt$_3^-$. Indeed, at higher temperatures (25 °C) these bands broaden and coalesce.



To further verify the identity of the formyl complexes **16a,b**, the reduction was carried out at −80 °C using Li$^+$Et$_3$BH$^-$ and the solution monitored by ^{13}C NMR spectroscopy. A ^{13}C resonance assigned to the formyl carbon of **16a** appears at 297.1 ppm with $J_{\mathrm{CH}} = 123$ Hz, while **16b** exhibits a signal at 299.1 ppm with $J_{\mathrm{CH}} = 128$ Hz. These values are typical of the ^{13}C shifts and J_{CH} values for other metal formyl complexes.[16] The ^{13}CO resonances appear as two distinct bands at δ 218.4 and 226.9 for the Li$^+$ coordinated formyl complex, **16a**, and 217.7 and 225.4 for the BEt$_3$ coordinated formyl complex, **16b**. This observation supports structures for **16a,b** which lack a plane of symmetry, as shown above. The potential fluxional behavior of **16** could not be tested due to its isomerization to *K$^+$anti*-**10** above −50 °C.

The migration of a formyl hydrogen to other bound

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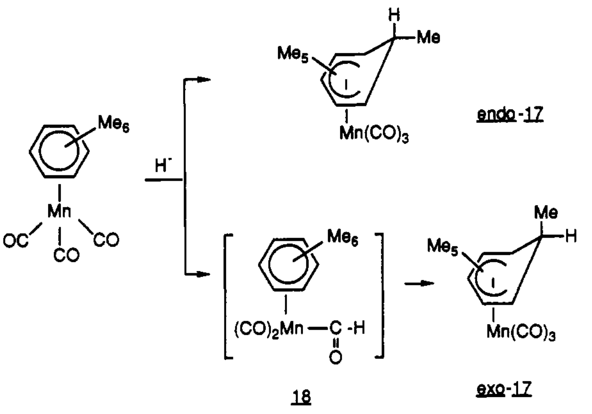
(16) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

(17) (a) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545. (b) Tam, W.; Wang, W. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1 and references therein.

(18) It is not clear why all the diene complex **9** is not reduced under these conditions. Initially, upon addition of the THF solution of Et$_3$BH$^-$ to the THF solution of **9** at −78 °C two layers (yellow and clear) are evident. Mixing for several minutes is required to produce a homogeneous solution. More rapid reduction in local "hot" zones immediately upon mixing is one possibility, but experiments where reductions were carried out at −50 °C followed by rapid cooling resulted in complete conversion of **9** to π-allyl complex *K$^+$anti*-**10** with no formyl complexes detected. More rapid reduction at the interface of two layers (than in homogeneous solution) is a second possibility. In any case, to achieve high yields of formyl complex at −78 °C using these mixing techniques, 15–20 equiv of Et$_3$BH$^-$ was required.

(19) The fact that the remaining starting material is not reduced at −50 °C provides evidence that the hydride addition is not reversible.

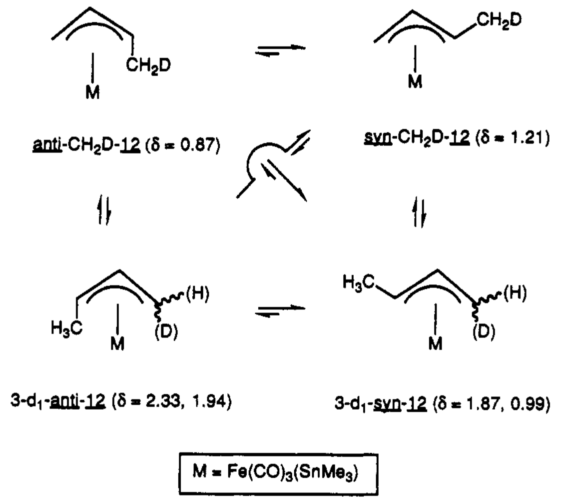
ligands has little precedent. We[20] recently reported low temperature generation of the formyl complex Tp'W(CO)(CHO)(NPh) which isomerizes at −40 °C to the amide complex $Tp'W(CO)_2NHPh$ *via* hydride migration from formyl to the nitrogen atom of the nitrene ligand. More closely related to the present study is the recent observation of Eyman[21] who showed the reduction of $(C_6Me_6)Mn(CO)_3^+$ with various hydride reagents results in substantial amounts (depending on reaction conditions) of ((1,2,3,4,5-η)-*exo*-methylcyclohexadienyl)$Mn(CO)_3$, *exo*-**17**, formed *via* the formyl complex **18**. Sweigart[22] also reported that $(6\text{-}exo\text{-}PhC_6Me_5H)Re(CO)_2NO^+$ reacts with Bu_4NBH_4 at −35 °C to form a neutral formyl intermediate which slowly converts to the cyclohexadiene complex, however in the manganese analog the formyl intermediate was not detected.



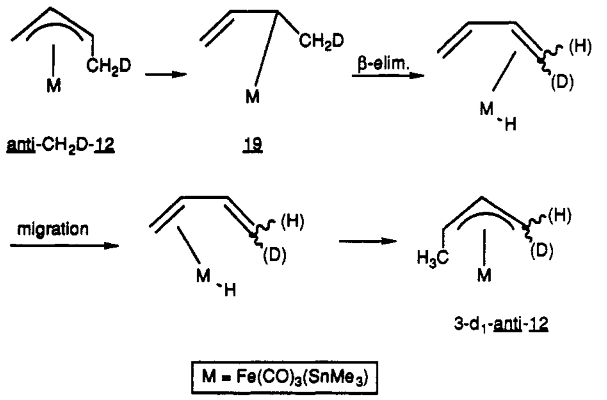
The contrasting regiochemistries of the addition of RLi reagents versus hydride addition to (1-phenylbutadiene)$Fe(CO)_3$, **11**, may be explained by the contrasting mechanisms of addition. Whereas thermodynamic addition of the RLi reagents (e.g. $LiCHPh_2$) reported by Semmelhack[8e] occurs at C_2 (inner carbon) of **11**, hydride addition using Et_3BH^- occurs exclusively at C_1 (outer carbon), as described above.

To confirm that reduction of **9** with Et_3BD^- results in exclusive placement of deuterium in the *anti*-methyl group of *anti*-CH_2D-**10**, the reduction was carried out on a preparative scale and the anion trapped with Me_3SnCl. ^2H NMR analysis indeed confirmed that the initially formed product was *anti*-CH_2D-**12**. However, warming *anti*-CH_2D-**12** to 45 °C revealed a rearrangement process which scrambles deuterium between the methyl group and the *syn* and *anti* positions at C_3. The rate of deuterium scrambling is similar to the *anti* to *syn* isomerization rate, so not only do ^2H signals for *anti*-**12**-*3*-d_1 appear but also signals for *syn*-CH_2D-**12** and *syn*-**12**-*3*-d_1 are observed. Ultimately, the exothermic *anti* to *syn* rearrangement results in conversion to an equilibrium mixture of *syn*-CH_2D-**12** and *syn*-**12**-*3*-d_1 (see Scheme IV).

Scheme IV



The most reasonable mechanism for deuterium scrambling involves the same η^1-intermediate which is invoked in the *anti* to *syn* isomerization. A β-elimination from **19**, followed by 1,3-migration of the η^2-bound $(SnMe_3)Fe(CO)_3H$ moiety across the diene and collapse to the η^4-structure yields the isomerized product *anti*-**12**-*3*-d_1 as shown. The migration of the η^2-bound iron moiety across the face of the diene has precedent in the work of Whitlock[23] on the mechanism of isomerization of (1-phenyl-6-*p*-tolyl-1,3,5-hexatriene)iron tricarbonyl complexes.



If the above mechanism is correct, there is a pathway available involving the transoid form of **19** which would permit direct isomerization of *anti*-CH_2D-**12** to *syn*-**12**-*3*-d_1 and interconversion of the two *syn* isomers. The similar rates of deuterium scrambling and *anti* to *syn* isomerization and the substantial overlap of the ^2H signals of *syn*-**12**-*3*-d_1 (δ 0.99, 1.87) with *anti*-CH_2D-**12** (δ 0.87) and *anti*-**12**-*3*-d_1 (δ 1.94, 2.33) preclude gathering sufficiently accurate experimental data to address this point.

Summary

Reaction of Et_3BH^- with (butadiene)- or (1-phenylbutadiene)iron tricarbonyl in THF efficiently generates (allyl)iron tricarbonyl anions, but pure salts could not be isolated in good yields from these solutions. Low temperature ^1H, ^2H, and ^{13}C NMR experiments demonstrate that formyl complexes are intermediates in the formation of the allyl complexes. Trapping of these (allyl)iron anions with Me_3SnCl results in good yields of (*anti*-methallyl)$Fe(CO)_3$–$SnMe_3$, and (*anti*-1-methyl-*syn*-3-phenylallyl)$Fe(CO)_3$–$SnMe_3$, respectively. The *syn* isomers can be prepared by clean thermal isomerization of these *anti* isomers. Reductive cleavage of any of these isomers with KH results in formation of the corresponding allyl anions

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[20] Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433.

[21] Morken, A. M.; Eyman, D. P.; Wolff, M. A.; Schauer, S. J. *Organometallics* **1993**, *12*, 725.

[22] Pike, R. D.; Ryan, W. J.; Lennhoff, N. S.; Epp, J. V.; Sweigart, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4798.

[23] Whitlock, H. W., Jr.; Chuah, Y. N. *J. Am. Chem. Soc.* **1965**, *87*, 3605.

which can be isolated in good yields as their potassium salts. The stereochemistry of the allyl moieties is maintained in these reduction reactions.

This two step procedure is an efficient method for preparation of substituted (allyl)iron tricarbonyl anions with control of the configuration of the allyl unit. These anions have nucleophilic properties similar to those of $Cp(CO)_2Fe^-$ and, as previously demonstrated,[6] can be used for various carbon–carbon bond forming reactions through the series of transformations illustrated in Scheme I. While this two step procedure for generation of (allyl)iron tricarbonyl anions has been demonstrated for (butadiene)- and (1-phenylbutadiene)iron tricarbonyl complexes, it should clearly be generally applicable to a wide range of (diene)iron tricarbonyl complexes.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry, deoxygenated nitrogen using Schlenk techniques with a double manifold vacuum line, unless otherwise noted. Nitrogen gas was purified by passage through a column of BASF catalyst (R3-11) heated to 130 °C followed by activated molecular sieves. NMR spectra were recorded at either 200, 250, 300, or 400 MHz; ^{1}H chemical shifts were referenced to residual protio solvent peaks ($CHDCl_2$ δ 5.32; C_6D_5H δ 7.15; THF-d_7 δ 1.73, 3.58; toluene-d_7 δ 2.09, 6.98, 7.00, 7.09), and ^{2}H chemical shifts were referenced to C_6D_6 (δ 7.15). ^{13}C chemical shifts were referenced to ^{13}C solvent signals (CD_2Cl_2 53.8; C_6D_6 128.0; THF-d_8 25.3, 67.4; toluene-d_8 δ 20.4, 125.2, 128.0, 128.9, 137.5). Infrared spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. Solvents (THF, hexane, diethyl ether) were distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use. NMR solvents were degassed by successive freeze/pump/thaw cycles and stored over 4-Å molecular sieves under nitrogen. Elemental analyses were performed by Oneida Research Services, Inc. $KBHEt_3$, $LiBHEt_3$, $LiBDEt_3$, and BEt_3 (Aldrich, 1 M in THF) and Me_3SnCl (Alfa) and $C_4H_6Fe(CO)_3$ (Pfaltz & Bauer or Janssen Chimica) were stored cold under nitrogen.

Synthesis of *trans*-η^4-[PhCH=CHCH=CH$_2$]Fe(CO)$_3$, 11. This procedure is an optimized modification of the previously reported synthesis by Mahler.[24] To a hexane solution of *trans*-1-phenylbutadiene (11 g, 85 mmol, obtained from the reaction of PhMgBr with *trans*-crotonaldehyde in diethyl ether followed by dehydration[25]) was added $Fe_2(CO)_9$ (46 g, 0.13 mol). The solution was refluxed for 2.5 h with stirring under nitrogen. The mixture was filtered through Celite, and the volatile materials were removed under vacuum. The crude product was purified by column chromatography on neutral alumina, eluting with hexane. Removal of solvent from the yellow band provided 11 as yellow crystals (18.4 g, 68 mmol, 81% yield based on the diene used).

IR, ν_{CO} (C_6D_6, cm^{-1}): 2043, 1979. ^{1}H NMR (C_6D_6, δ): 6.99 (m, 5H, Ph), 5.22 (dd, J = 9.4, 5.1 Hz, 1H, $\mathrm{CH_2{=}C}\mathit{H}$), 4.66 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CHPh}$), 1.73 (d, J = 9.4 Hz, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{Ph}$), 1.38 (dd, J = 7.0, 2.6 Hz, 1H, H_{tr} of $\mathrm{C}\mathit{H_2}\mathrm{{=}CH}$), 0.18 (dd, J = 9.3, 2.4 Hz, 1H, H_{cis} of $\mathrm{C}\mathit{H_2}\mathrm{{=}CH}$). ^{13}C NMR ($CD_2Cl_2$, δ): 212.0 (s, Fe(CO)$_3$), 140.3 (s, C_{ipso} of Ph), 129.0, 126.5 (d, J = 160, 157 Hz, C_{ortho} and C_{meta} of Ph), 126.9 (d, J = 160 Hz, C_{para} of Ph), 84.0 (d, J = 167 Hz, $\mathit{C}\mathrm{H{=}CHPh}$), 81.9 (d, J = 170 Hz, $\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 61.9 (d, J = 156 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HPh}$), 40.1 (t, J = 160 Hz, $\mathit{C}\mathrm{H_2{=}CH}$). Anal. Calcd for $C_{13}H_{10}O_3Fe$: C, 57.82; H, 3.73. Found: C, 58.14; H, 3.78.

Synthesis of *anti*-[$\mathrm{CH_3CH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}$]Fe(CO)$_3$(SnMe$_3$), *anti*-12. (Butadiene)iron tricarbonyl (900 mg, 4.64 mmol) in tetrahydrofuran solution at 0 °C was treated with potassium triethylborohydride (1 M in THF, 2.4 equiv/11.1 mL) and then stirred for about 20 min. Me_3SnCl (2.4 equiv, 2.2 g) was added to this solution, and the resulting mixture was stirred for about 5 min. Removal of the volatiles under vacuum and then extraction with hexane (100 mL) gave the product as a yellow oil in 79% yield (1.32 g, 3.66 mmol). Recrystallization from hexane at −78 °C gave *anti*-12 as yellow crystals.

IR ν_{CO}(THF): 2025, 1967, 1946, cm^{-1}. All ^{1}H NMR data except J^2_{Sn-Me} = 45.9, 47.6 Hz are reported in Table I. ^{13}C NMR (C_6D_6, δ): 212.2 (s, CO), 84.8 (d, J = 161 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CH\,CH_3}$), 64.1 (d, J = 155 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathit{C}\mathrm{HCH_3}$), 42.5 (t, J = 160 Hz, $\mathit{C}\mathrm{H_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHCH_3}$), 18.6 (q, J = 128 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH}\mathit{C}\mathrm{H_3}$), −6.7 (q, J = 129 Hz, J_{Sn-C} = 243, 253 Hz, Sn(CH$_3$)$_3$). Anal. Calcd for $C_{10}H_{16}FeO_3Sn$: C, 33.48; H, 4.49. Found: C, 33.41; H, 4.48.

Synthesis of *syn*-[$\mathrm{CH_3CH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}$]Fe(CO)$_3$(SnMe$_3$), *syn*-12. Thermal Isomerization of *anti*-12. (*anti*-Methallyl)iron tricarbonyl trimethyltin, *anti*-12 (700 mg, 2.0 mmol), was added to 20 mL of toluene in a Schlenk flask and heated at 55 °C for 4 days. No decomposition was evident during a thermolysis, and after solvent removal *syn*-12 was isolated in quantitative yield. Recrystallization from hexane at −78 °C gave *anti*-12 as yellow crystals. The rate of isomerization of *anti*-12 to *syn*-12 was measured in a sealed NMR tube at 55 °C in toluene-d_8. The decrease in intensity of signals at δ 3.38 and 4.11 assigned to *anti*-12 was monitored relative to the increase in intensity of the signal at δ 4.07 assigned to *syn*-12. A typical rate plot is given in the supplementary material. Kinetic data obtained are summarized in the Results and Discussion.

IR, ν_{CO} (THF): 2025, 1967, 1946 cm^{-1}. All ^{1}H NMR data except J^2_{Sn-Me} = 45.9, 47.6 Hz are reported in Table I. ^{13}C NMR (C_6D_6, δ) 212.4 (s, J_{Sn-C} = 80 Hz, CO), 86.7 (d, J = 160 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CHCH_3}$), 66.4 (d, J = 158 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathit{C}\mathrm{HCH_3}$), 37.0 (t, J = 160 Hz, $\mathit{C}\mathrm{H_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHCH_3}$), 19.2 (q, J = 127 Hz, $\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH}\mathit{C}\mathrm{H_3}$), −5.2 (q, J = 129 Hz, J_{Sn-C} = 243, 254 Hz, Sn(CH$_3$)$_3$). Anal. Calcd for $C_{10}H_{16}FeO_3Sn$: C, 33.48; H, 4.49. Found: C, 33.92; H, 4.58.

Synthesis of *anti,syn*-[$\mathrm{CH_3CH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHPh}$]Fe(CO)$_3$Sn(CH$_3$), *anti,syn*-13. Starting with (*trans*-1-phenylbutadiene)iron tricarbonyl, 11 (900 mg, 3.33 mmol), the same method was used as described above for the preparation of *anti*-12. Yellow crystals of *anti,syn*-13 were obtained (1.45 g, 2.40 mmol) after recrystallization of the crude product from hexane at −78 °C. IR, ν_{CO} (THF): 2017, 1960, 1943 cm^{-1}. All ^{1}H NMR data except phenyl resonance (δ 7.05–6.93, m) and J^2_{Sn-Me} = 46.5, 48.5 Hz are reported in Table I. ^{13}C NMR (C_6D_6, δ): 212.5 (s, J_{Sn-C} = 90 Hz, CO), 139.9 (s, C_{ipso} of Ph), 129.1, 126.4 (d, J = 161, 157 Hz, C_{ortho}, C_{meta} of Ph), 127.2 (d, J = 161 Hz, C_{para} of Ph), 83.9 (d, J = 160 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CHCH_3}$), 66.3 (d, J = 155 Hz, $\mathrm{Ph}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHCH_3}$), 58.7 (d, J = 156 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathit{C}\mathrm{HCH_3}$), 18.5 (q, J = 129 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHCH_3}$), −5.0 (q, J = 129 Hz, J_{Sn-C} = 252, 264 Hz, Sn(CH$_3$)$_3$). Anal. Calcd for $C_{16}H_{20}FeO_3Sn$: C, 44.19; H, 4.64. Found: C, 44.51; H, 4.64.

Synthesis of *syn,syn*-[$\mathrm{CH_3CH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHPh}$]Fe(CO)$_3$(SnMe$_3$), *syn,syn*-13. Thermal Isomerization of *anti,syn*-13. The same method was used as described above for the preparation of *syn*-12. The isomerization was carried out in CD_2Cl_2, and the rate was measured in a sealing NMR tube at 25 °C. No decomposition was evident, and the yield was quantitative. The rate measurements were carried out by monitoring the increase in intensity of the resonance at δ 1.85 (for the *syn* isomer) and the decrease in integration of the signal at δ 1.39 (for the *anti* isomer).

IR, ν_{CO} (THF): 2017, 1960, 1943 cm^{-1}. All ^{1}H NMR data except the phenyl resonances (δ 7.02–6.93, m) and J^2_{Sn-Me} = 46.5, 48.5 Hz are reported in Table I. ^{13}C NMR (C_6D_6, δ): 212.7 (s, J_{Sn-C} = 96 Hz, CO), 140.3 (s, C_{ipso} of Ph), 129.1, 126.3 (d, J = 158, 160 Hz, C_{ortho}, C_{meta} of Ph), 126.9 (d, J = 160 Hz, C_{para} of Ph), 87.2 (d, J = 158 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CHCH_3}$), 61.5 (d, J = 156 Hz, $\mathrm{Ph}\mathit{C}\mathrm{H}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CHCH_3}$), 60.5 (d, J = 157 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathit{C}\mathrm{HCH_3}$), 20.1 (q, J = 127 Hz, $\mathrm{PhCH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH}\mathit{C}\mathrm{H_3}$),

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(24) Mahler, J. E. Thesis for Ph.D., The University of Texas, 1967; pp 106–107.

(25) Koelsch, C. F.; Steinhauer, A. F. *J. Org. Chem.* **1953**, *18*, 1516.

−5.0 (s, $J_{\mathrm{Sn-C}}$ = 252, 264 Hz, $\mathrm{Sn(CH_3)_3}$). Anal. Calcd for $\mathrm{C_{16}H_{20}FeO_3Sn}$: C, 44.19; H, 4.64. Found: C, 43.81; H, 4.59.

General Procedure for the Synthesis of Potassium Salts of (Allyl)iron Tricarbonyl Anions. Addition of the (allyl)iron tin complexes (*anti*-**12**, *syn*-**12**, *anti,syn*-**13**, *syn,syn*-**13**) to an excess of KH in THF at 0 °C followed by stirring for about 20 min produces the (allyl)iron tricarbonyl potassium salts. Reactions are conveniently monitored by IR spectroscopy. This solution was filtered *via* cannula, and then the solvent was removed *in vacuuo*. The remaining solid was washed with hexane and dried to give solid yellow potassium salts in near quantiative yields. These salts are highly air sensitive and somewhat thermally sensitive, precluding microanalysis. As proof of purity, representative spectra are displayed in the supplementary material.

***anti*-[$\mathbf{CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$]Fe(CO)$_3^-K^+$, K$^+$*anti*-10.** IR, ν_{CO} (THF): 1929, 1844, 1807 cm^{-1}. All ^{1}H NMR data are reported in Table V. ^{13}C NMR (THF-d_8, δ): 228.5 (s, *C*O), 72.2 (d, J = 161 Hz, $\mathrm{CH_2\overset{\cdots}{-}\mathit{C}H\overset{\cdots}{-}CHCH_3}$), 54.6 (d, J = 131 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}\mathit{C}HCH_3}$), 35.8 (t, J = 154 Hz, $\mathrm{\mathit{C}H_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}$), 19.5 (q, J = 125 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH\mathit{C}H_3}$).

***syn*-[$\mathbf{CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$]Fe(CO)$_3^-K^+$, K$^+$*syn*-10.** IR, ν_{CO} (THF): 1929, 1844, 1807 cm^{-1}. All ^{1}H NMR data are reported in Table V. ^{13}C NMR (THF-d_8, δ): 228.9 (s, *C*O), 72.7 (d, J = 161 Hz, $\mathrm{CH_2\overset{\cdots}{-}\mathit{C}H\overset{\cdots}{-}CHCH_3}$), 51.2 (d, J = 156 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}\mathit{C}HCH_3}$), 31.8 (t, J = 155 Hz, $\mathrm{\mathit{C}H_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}$), 21.2 (q, J = 124 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH\mathit{C}H_3}$).

***anti,syn*-[$\mathbf{CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CHPh}$]Fe(CO)$_3^-K^+$, K$^+$*anti,syn*-14.** IR, ν_{CO} (THF): 1933, 1854, 1817 cm^{-1}. All ^{1}H NMR data except phenyl resonance (δ 7.18–6.73, m) are reported in Table V. ^{13}C NMR (THF-d_8, δ): 227.7 (s, *C*O), 149.3 (s, C_{ipso} of Ph), 128.0, 126.5 (d, J = 152, 150 Hz, C_{ortho}, C_{meta} of Ph), 122.8 (d, J = 154 Hz, C_{para} of Ph), 74.1 (d, J = 163 Hz, $\mathrm{PhCH\overset{\cdots}{-}\mathit{C}H\overset{\cdots}{-}CHCH_3}$), 54.6 (d, J = 155 Hz, $\mathrm{Ph\mathit{C}H\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}$), 50.1 (d, J = 152 Hz, $\mathrm{PhCH\overset{\cdots}{-}CH\overset{\cdots}{-}\mathit{C}HCH_3}$), 20.7 (q, J = 125 Hz, $\mathrm{PhCH\overset{\cdots}{-}CH\overset{\cdots}{-}CH\mathit{C}H_3}$).

***syn,syn*-[$\mathbf{CH_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CHPhFe}$](CO)$_3^-K^+$, K$^+$*syn,syn*-14.** IR, ν_{CO} (THF): 1933, 1854, 1815 cm^{-1}. All ^{1}H NMR data except phenyl resonance (δ 7.18–6.69, m) are reported in Table V. ^{13}C NMR (THF-d_8, δ): 228.1 (s, *C*O), 149.9 (s, C_{ipso} of Ph), 129.7, 126.4 (d, J = 156, 155 Hz, C_{ortho}, C_{meta} of Ph), 122.4 (d, J = 156 Hz, C_{para} of Ph), 74.6 (d, J = 160 Hz, $\mathrm{PhCH\overset{\cdots}{-}\mathit{C}H\overset{\cdots}{-}CHCH_3}$), 51.7 (d, J = 156 Hz, $\mathrm{Ph\mathit{C}H\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}$), 47.0 (d, J = 155 Hz, $\mathrm{PhCH\overset{\cdots}{-}CH\overset{\cdots}{-}\mathit{C}HCH_3}$), 21.2 (q, J = 124 Hz, $\mathrm{PhCH\overset{\cdots}{-}CH\overset{\cdots}{-}CH\mathit{C}H_3}$).

Synthesis of *anti*-[$\mathbf{CH_2DCH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$]Fe(CO)$_3$(SnMe$_3$), *anti*-CH$_2$D-12. The same method was used as described above for *anti*-**12** except LiBDEt$_3$ was used as a reducing agent. The yield was 70%.

IR, ν_{CO} (THF): 2025, 1967, 1946 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 4.09 (dt, J = 11.6, J = 6.7 Hz, 1H, $\mathrm{CH_2\overset{\cdots}{-}C\mathit{H}\overset{\cdots}{-}CHCH_2D}$), 3.36 (q, J = 6.8 Hz, 1H, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}C\mathit{H}CH_2D}$), 2.36 (dt, J = 6.7 Hz, ^3J = 1.5 Hz, J_{gem} = 1.7 Hz, 1H, *syn*-H of $\mathrm{C\mathit{H}_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_2D}$), 1.97 (d, J = 11.6 Hz, 1H, *anti*-H of $\mathrm{C\mathit{H}_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_2D}$), 0.92 (m, 2H, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHC\mathit{H}_2D}$), 0.29 (s, $^2J_{\mathrm{Sn-Me}}$ = 46.1, 47.6 Hz, $\mathrm{Sn(C\mathit{H}_3)_3}$). ^{13}C NMR (C$_6D_6$, δ): 212.1 (s, *C*O), 84.9 (d, J = 161 Hz, $\mathrm{CH_2\overset{\cdots}{-}\mathit{C}H\overset{\cdots}{-}CHCH_2D}$), 64.0 (d, J = 155 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}\mathit{C}HCH_2D}$), 42.5 (t, J = 156 Hz, $\mathrm{\mathit{C}H_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_2D}$), 18.6 (tt, $J_{\mathrm{C-H}}$ = 128 Hz, $J_{\mathrm{C-D}}$ = 19 Hz, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH\mathit{C}H_2D}$), −6.7 (q, J = 129 Hz, $J_{\mathrm{Sn-C}}$ = 243, 253 Hz, $\mathrm{Sn(\mathit{C}H_3)_3}$). ^{2}H NMR (C$_6H_6$, δ): 0.87 (br s, $\mathrm{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_2\mathit{D}}$).

Low Temperature ^{1}H NMR Experiments. Detection of Formyl Complexes from Hydride Reduction of (Butadiene)iron Tricarbonyl. (Butadiene)iron tricarbonyl (5–10 mg, 0.03–0.05 mmol) was transferred to an NMR tube and then dissolved in THF-d_8 under nitrogen, and solution was cooled to −78 °C. LiBEt$_3$H (0.15–0.45 mL) or KBEt$_3$H (0.15–0.2 mL) was slowly added to the NMR tube. The solution was then stirred until it became homogeneous, and the NMR tube was sealed. At −80 °C, two formyl hydrogen signals were detected in the reactions with LiBEt$_3$H, one at 13.4 ppm, which was assigned to the Li$^+$ coordinated formyl complex, and one at 12.0 ppm, which was assigned to the BEt$_3$ coordinated formyl complex. In the reactions with KBEt$_3$H two formyl resonances are again observed. The signal at 13.5 ppm was assigned to K$^+$ coordinated formyl complex, and again the one at 12.0 ppm was assigned to the BEt$_3$ coordinated formyl complex.

(2) Addition of Triethylborane to the Formyl Intermediates. Triethylborane (0.15 mL of 1.0 M THF solution, 3 equiv *versus* **9**) was added to a solution of the formyl complex generated *in situ* from **9** (10 mg, 0.05 mmol) and LiBEt$_3$H (0.15 mL of 1.0 M THF solution, 3 equiv) at −78 °C. The initial ratio of the formyl complex **16a**:**16b** was 2:1, as judged by the integral ratio of the signals at δ 13.4 and 12.0. After BEt$_3$ was added, the ratio changed to 1:3.

Low Temperature ^{2}H NMR Experiments. Detection of Formyl Complexes. THF-h_8 was degassed and stored over Na and 4-Å molecular sieves for several days prior to use. (Butadiene)iron tricarbonyl (8 mg, 0.04 mmol) was transferred to an NMR tube and then dissolved in THF-h_8 under nitrogen. Trace amounts of C$_6$D$_6$ were added for an internal ^{2}H reference. This solution was cooled to −78 °C. Degassed LiBEt$_3$D (0.17 mL, 4 equiv) was added slowly and then the NMR tube was sealed. Confirming the ^{1}H NMR results, two formyl resonances were observed by ^{2}H NMR at δ 13.3 and 11.9. At −50 °C, the resonances of these formyl complexes decreased while the resonance attributed to the −CH$_2$D group of *anti*-CH$_2$D-**10** of the methyl position (δ 0.89) increased. Kinetic analysis gave good first-order plots for this conversion with $k = 8.3 \times 10^{-5}$ s^{-1}.

Low Temperature ^{13}C NMR Experiments. (Butadiene)iron tricarbonyl (20 mg, 0.10 mmol) was transferred to an NMR tube and dissolved in THF-d_8 under nitrogen, and the solution was cooled to −78 °C. LiBEt$_3$H (1 mL, 1 mmol in THF) was transferred to a Schlenk tube and concentrated to 0.1 mL, and 0.3 mL of THF-d_8 was added. Part of this solution (0.3 mL, 5 equiv) was added slowly to the NMR tube, and then the tube was sealed. At −80 °C a ^{13}C resonance for the Li coordinated formyl complex appeared at δ 297.1 (J = 123 Hz), while that for the BEt$_3$ coordinated complex appeared at δ 299.1 (J = 128 Hz). ^{13}CO resonances for the Li coordinated formyl complex appeared at δ 218.4 and 226.9 and for the BEt$_3$ coordinated species at δ 217.7 and 225.4.

X-ray Structure Determination. Data were collected on a Rigaku AFC6/S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using a ω–2θ scans; reflections with $I > 2.5\sigma(I)$ were considered observed and included in subsequent calculations. The structures were solved by direct methods. Refinement was by full-matrix least squares with weights based on counter statistics. Hydrogen atoms were included in the final cycles of refinement in calculated positions with thermal parameters derived from the atom to which they were bonded. Crystal data and experimental conditions are given in Table II. All computations were performed using the NRCVAX suite of programs[26] and scattering factors were taken from ref 27.

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Supplementary Material Available: Tables of crystal data and data collection parameters, fractional coordinates of hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles for *syn,syn*-**13**, kinetic plots for rates of isomerization of *anti*-**12** to *syn*-**12** and *anti,syn*-**13** to *syn,syn*-**13** and rate of hydride migration from d$_1$-**16** to *anti*-CH$_2$D-**10**, and ^{1}H and ^{13}C NMR spectra for *K$^+$syn*-**10** and *K$^+$syn,syn*-**14** (13 pages). Ordering information is given on any current masthead page.

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[26] Gabe, E. J.; Le, Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[27] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.