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Hydrocarbation—Formation of Diiron μ-Alkylidyne Complexes from the Addition of the Carbon–Hydrogen Bond of a μ-Methylidyne Complex across Alkenes

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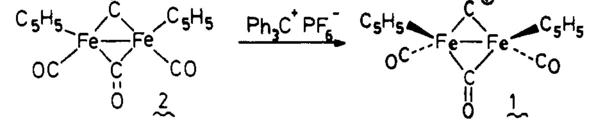
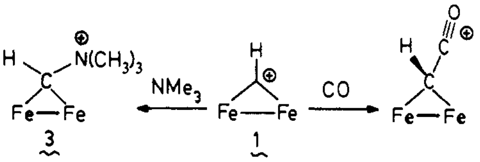
Abstract: The reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$, **1**, with ethylene produced $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)^+PF_6^-$, **4**, in 68% yield. **4** reacted with trimethylamine to give $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$, **5**, in 84% yield. **1** reacted regioselectively with propene, 1-butene, 1-pentene, *tert*-butylethylene, styrene, butadiene, allylbenzene, and isobutylene to give similar μ-alkylidyne products in 76–85% yields. The syn addition of hydrocarbation was established by the reaction of **1** with (*E*)- and (*Z*)-1,2-dideuterio-3,3-dimethyl-1-butene, **23-E** and **23-Z**. The rate of the reaction of **1** with *trans*-2-butene at −50 °C followed second-order kinetics with $k_2 = 9.2 \pm 0.7 \times 10^{-3}\ M^{-1}\ s^{-1}$. Competition techniques were used to measure the relative reactivity of **1** toward alkenes at −50 °C, and electron-donating alkyl substituents substantially increased the reactivity of the alkene. The deuterium kinetic isotope effect for the reaction of **1** with propene and isobutylene at −50 °C was found to be 0.74 ± 0.03 and 0.80 ± 0.03. The regiochemistry, relative rates, and kinetic isotope effects are consistent with a transition state for the rate-determining step of hydrocarbation which involves only initiation of a bond from the methylidyne carbon of **1** to the less substituted carbon of the carbon–carbon double bond.

The Fischer–Tropsch reaction on heterogeneous iron and cobalt catalysts is now thought to proceed via initial dissociative chemisorption of carbon monoxide to give surface carbide species.[1] Hydrogenation of these carbides is thought to proceed by successive formation of surface-bound CH, CH_2, and CH_3 groups. Carbon–carbon bond formation has been proposed to occur via coupling of surface-bound CH_2 and alkyl groups.[2] Recent interest in bridging methylene complexes[3] is directly traceable to their proposed involvement in CO reduction. Several years ago our group[4] and Pettit's group[5] developed a new route to bridging methylene complexes from the reaction of $(C_5H_5)(CO)_2FeCH_2OAc$ and $(C_5H_5)(CO)_2Fe^-$. The same bridging methylene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, **2**, has also been prepared from $[(C_5H_5)(CO)_2Fe]_2$ and $(C_6H_5)_3P{=}CH_2$ by Ziegler[6] and from $(C_5H_5)(CO)_2Fe^-$ and $Me_3CCO_2CH_2Cl$ by Nelson.[7]



Reaction of bridging methylene complex **2** with the hydride abstracting reagent $(C_6H_5)_3C^+PF_6^-$ led to the formation of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$, **1**, the first complex in which a methylidyne group bridges between two metals.[4] The mononuclear methylidyne complex $W(CH)Cl(PMe_3)_4$[8] and compounds such as $Co_3(CO)_9(\mu_3\text{-}CH)$,[9] $H_3Os_3(CO)_9(\mu_3\text{-}CH)$,[10] $H_3Ru_3(CO)_9(\mu_3\text{-}CH)$,[11] $(C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)^+$,[12] and $HOs_3(CO)_{10}(\mu_3\text{-}CH)$[13] in which the methylidyne group bridges three metals, and $HFe_4(CO)_{12}(\mu_4\text{-}CH)$[14] in which the methylidyne group bridges four metals have been synthesized. The methylidyne complex **1** is unstable above 40 °C in CH_2Cl_2 solution. Other examples of isolated doubly bridging methylidyne complexes are still limited to $[(C_5Me_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$,[15] $(C_5H_5)(C_5Me_5)(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)^+$,[16] $[(C_5H_4Me)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$,[17] $[(C_5H_5)(\mu\text{-}NO)Fe]_2(\mu\text{-}CH)^+$,[18] $[(C_5H_5)_2(dppm)Ru_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$,[19] and $[(C_5H_5)(CO)Ru]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$.[20]



The cationic methylidyne complex **1** can be viewed as a relatively stable carbonium ion—certainly more stable than the triphenylmethyl cation from which it was prepared. Extensive electron donation from the two iron centers must be responsible for the stability of the methylidyne complex. In spite of its thermodynamic stability, the bridging methylidyne complex is kinetically very reactive toward nucleophiles. The methylidyne

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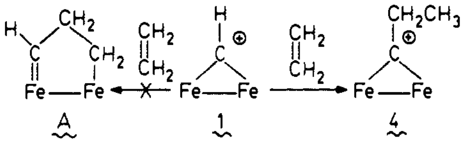
carbon of **1** is electrophilic and is attacked by nucleophiles such as trimethylamine, which produces the adduct $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHN(CH_3)_3]^+PF_6^-$ (**3**, 80%).[21] Carbon monoxide adds to the methylidyne carbon of **1** to produce the acylium complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+PF_6^-$.[21]

In the course of surveying the reactivity of **1**, we studied its reaction with ethylene in the hope that we might observe insertion of ethylene into a carbon–iron bond of the μ-methylidyne unit and produce a diiron cyclopentene structure such as **A**. Instead, we observed the addition of the C–H bond of the methylidyne ligand across the carbon–carbon double bond of ethylene to produce μ-propylidyne complex **4**.[22] Here we present our detailed studies of the scope and mechanism of this "hydrocarbation".



In the following paper, we will describe another new carbon–carbon bond forming reaction of **1** with alkenes that leads to μ-alkenyl complexes, and we will discuss the factors controlling whether a μ-alkylidyne or μ-alkenyl products are obtained from **1** and a given alkene.

Results

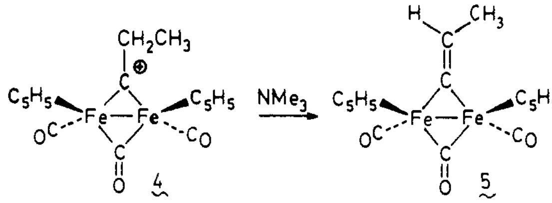
Reaction of μ-Methylidyne Complex 1 with Ethylene. When a suspension of the red methylidyne complex **1** in CH_2Cl_2 was stirred under an ethylene atmosphere and warmed from −78 °C to ambient temperature, a dark red solution was produced. Evaporation of solvent and recrystallization from acetone–ether led to the isolation of the μ-propylidyne complex *cis*-$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)^+PF_6^-$, **4**, in 68% yield. When the reaction of **1** with ethylene in CD_2Cl_2 at −20 °C was followed by ^1H NMR, the time for 50% conversion of **1** to **4** was about 15 min, and no detectable intermediate or side products were observed. The conversion of **1** to **4** involves an unprecedented addition of a C–H bond across an unactivated carbon–carbon double bond, and we have named this reaction "hydrocarbation".

μ-Alkylidyne complexes such as **4** are readily characterized by ^1H and ^{13}C NMR and by IR spectroscopy. In the ^1H NMR, protons on the carbon α to the cationic center are shifted downfield and appear near δ 5.5, and protons on more remote carbons are shifted downfield to a lesser degree. In propylidyne complex **4**, the ethyl group appears as a quartet (J = 7 Hz) at δ 5.49 and a triplet at δ 1.82. The equivalence of the chemical shift for the two methylene hydrogens supports the formulation of **4** as a complex with cis cyclopentadienyl ligands. If the cyclopentadienyl ligands were trans, the two methylene hydrogens would be diastereotopic and two different chemicals shifts for the methylene protons might have been seen.

In the ^{13}C NMR of μ-alkylidyne complexes, the bridging carbyne carbon appears far downfield. For μ-propylidyne complex **4**, the bridging carbyne carbon resonance is seen at δ 504.7. The ethyl group of **4** gives rise to resonances at δ 70.6 (CH_2) and 16.2 (CH_3). The resonance for the bridging carbonyl group appears at δ 252.4 somewhat downfield of the terminal carbonyls at δ 209.8.

The infrared spectrum of **4** provides the strongest evidence for the cis arrangement of the terminal carbonyl ligands. For a cis compound, two infrared active bands are expected, an intense band for the high energy symmetric stretch and a weaker band for the lower energy asymmetric stretch. For a trans compound, only the lower energy asymmetric stretch is infrared active.[16,23] The infrared spectrum of **4** has a very strong symmetric stretch at 2039 cm^{-1} and a weaker asymmetric stretch at 2006 cm^{-1} in addition to the bridging carbonyl stretch at 1855 cm^{-1}; this establishes the cis relationship of the terminal carbonyls in **4**.

The μ-propylidyne complex **4** was also independently synthesized in 33% yield by reaction of ethyllithium with $[(C_5H_5)(CO)_2Fe]_2$ followed by treatment with HPF_6. Other μ-alkylidyne complexes that were previously prepared by the organolithium route include $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_3)^+$,[24] $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$,[24,25] $(C_5H_5)_2(CO)_2FeRu(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$,[26] and $[(C_5H_5)(CO)Ru]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$.[27] Alkylidyne complexes have also been synthesized by a variety of other methods which include protonation of alkenylidene complexes,[27] reaction of $Li(C_5H_5)(CO)_2Fe$ with epoxides,[24] reaction of metal–carbyne complexes, such as $(C_5H_5)(CO)_2W{\equiv}CR$ with low valent metal species,[28,29] and the attack of anionic nucleophiles at bridging alkylidene ligands containing a methoxide substituent.[25,29]



In many cases we have further characterized the cationic μ-alkylidyne complexes by deprotonation to give neutral μ-alkenylidene complexes which are readily purified by chromatography and are easily analyzed by mass spectrometry. Treatment of an acetone solution of the dark red μ-propylidyne complex **4** with trimethylamine led to the isolation of the bright red microcrystalline μ-prop-1-enylidene complex *cis*-$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$, **5**, in 84% yield.

The structure of **5** was readily established spectroscopically. The key feature in the ^1H NMR of **5** is the quartet (J = 7 Hz) at δ 7.12 due to the vinylic proton. In **5**, the resonances for the nonequivalent cyclopentadienyl groups appear at δ 4.97 and 4.89. In the ^{13}C NMR of **5**, two resonances at δ 269.8 and 266.5 are assigned to the bridging carbonyl and bridging vinyl carbon. The nonbridging vinyl carbon appears at δ 133.6. The cis arrangement of the terminal carbonyl groups of **5** is established by the appearance of a strong symmetric stretch at 1994 cm^{-1} and a weaker asymmetric stretch at 1955 cm^{-1}.

While the addition of the C–H bond of **1** across alkenes is rapid at low temperature, we have never observed the addition of a C-alkyl bond of a μ-alkylidyne complex across an alkene. Thus, the reaction of **1** with ethylene rapidly produces **4**, but **4** does not react further with ethylene.

1,2-Addition in Hydrocarbation. Two possible mechanisns were initially considered for the formation of μ-propylidyne complex **4** from **1** and ethylene. One involves a 1,2-addition of the C–H bond of the alkylidyne across ethylene. The other involved electrophilic addition of the methylidyne carbon to one carbon of ethylene to give intermediate **B** followed by two 1,2 hydride shifts. To distinguish between these possibilities, the reaction of **1** with ethylene-d_4 was studied. The ^1H NMR of the labeled μ-propylidyne product had a broad singlet at δ 1.8 and no resonance at δ 5.5 which indicated exclusive formation of a μ-CCD_2CD_2H group.

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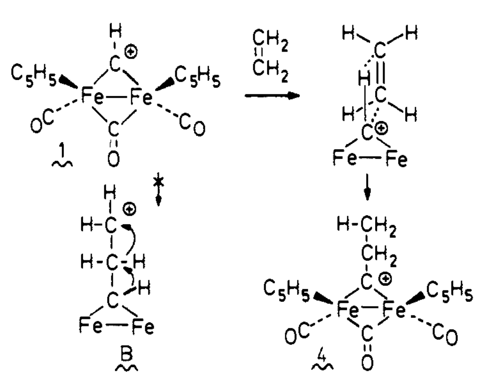
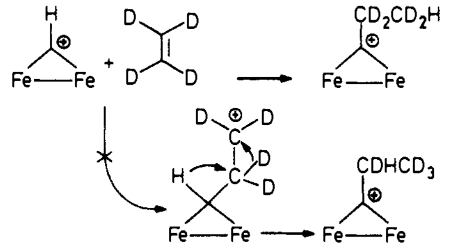
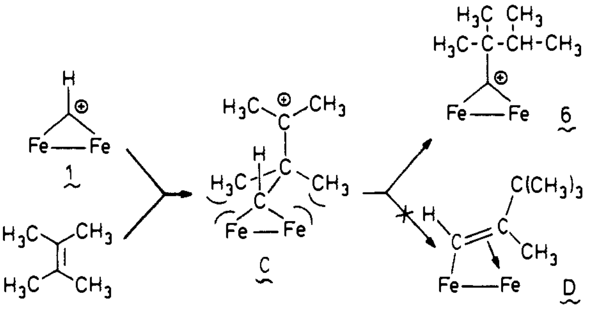




Exclusive 1,2 addition of the methylidyne C–H unit was also seen in the hydrocarbation of tetramethylethylene which produced $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CC(CH_3)_2CH(CH_3)_2]^+PF_6^-$, **6**, in 74% yield. If this reaction proceeds via an intermediate carbocation C, then 1,3 hydrogen migration from the methylidyne carbon to the carbocation must be faster than a 1,2-methyl shift to the carbocation since none of the rearranged μ-alkenyl product D was seen. Tetramethylethylene is the only tetrasubstituted alkene that has been observed to react with **1**; neither 1,2-dimethylcyclohexene nor *trans*-1,2-dimethylstilbene react with **1**.



Further instances of the 1,2 addition of the C–D bond of deuterated methylidyne complex **1-*d*** to ethylene, propene, isobutylene, *cis*-2-butene, *trans*-2-butene, cyclohexene, a β-methylstyrene have also been observed as described later.

Regiochemistry of Hydrocarbation. Diiron methylidyne complex **1** reacts with monosubstituted and 1,1-disubstituted alkenes regioselectively to add the electron deficient carbon of **1** to the least substituted carbon of the alkene and hydrogen to the most substituted carbon atom. Bridging alkylidyne products similar to **4** were obtained from reaction of **1** with propene, 1-butene, 1-pentene, *tert*-butylethylene, styrene, butadiene, allylbenzene, and isobutylene. Isolated yields ranged from 76% for 1-butene to 85% for *tert*-butylethylene as shown in Table I.

In the reaction of **1** with *tert*-butylethylene only μ-alkylidyne complex **10** was observed. No evidence was seen for products resulting from initial addition of the methylidyne carbon to give intermediate E followed by methyl migration. If E is an intermediate then the 1,3 hydride shift to give μ-alkylidyne product **10** must be much faster than 1,2-methyl migration.

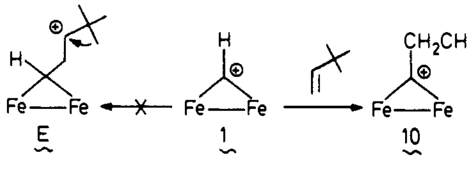
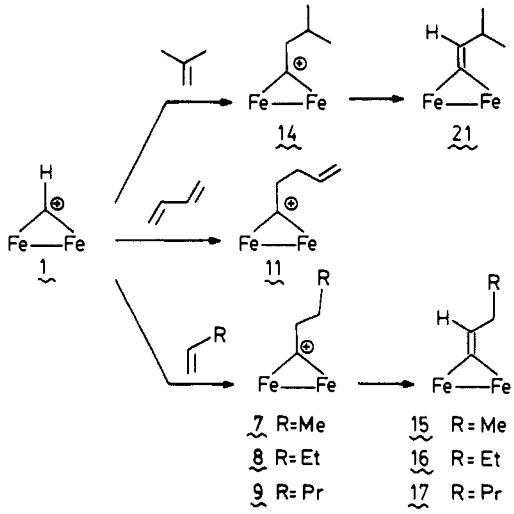


Table I. Product Yields from the Reaction of **1** with Various Alkenes To Give Alkylidynes or Alkenylidenes

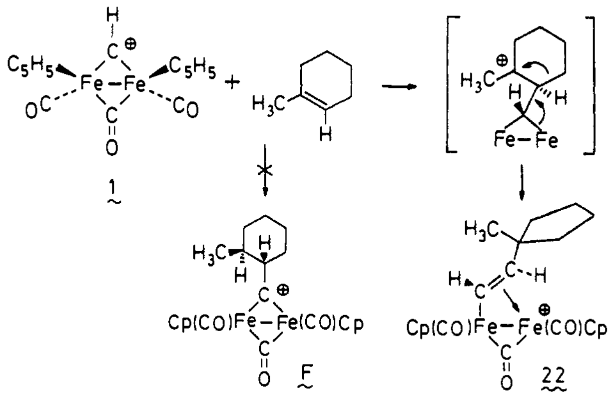
	alkylidyne		alkenylidene	
alkene	prod.	yield (%)	prod.	yield (%)
$CH_2{=}CH_2$	4	68	**5**	77[a]
$CH_2{=}CHMe$	7	78	**15**	61[b]
$CH_2{=}CHEt$	8	76	**16**	87[a]
$CH_2{=}CHPr$	9	78	**17**	75[b]
$CH_2{=}CH\text{-}t\text{-}Bu$	10	85	**18**	33[b]
$CH_2{=}CHCH{=}CH_2$	11	84		
$CH_2{=}CHC_6H_5$	12	81	19	86[a]
$CH_2{=}CHCH_2C_6H_5$	13	83	**20**	80[a]
$CH_2{=}CMe_2$	14	80	**21**	51[b]
$Me_2C{=}CMe_2$	6	74		

[a] Yield from reaction of isolated alkylidyne with base. [b] Yield from reaction of a solution of **1** and alkene with base.

The alkylidyne products **6**–**14** were characterized spectroscopically. All have far downfield ^{13}C NMR resonances for the bridging carbyne carbon ranging from δ 526.4 for **6** to δ 501.7 for **12**. The cationic μ-alkylidyne complexes **7**, **8**, **9**, **10**, **12**, **13**, and **14** were also characterized by deproponation which produced neutral μ-alkenylidene complexes.



Syn Addition in Hydrocarbation. The reaction of **1** with 1-methylcyclohexene was studied in an effort to determine the stereochemistry of hydrocarbation. However, the reaction did not produce μ-alkylidyne complex F but instead led directly to the μ-alkenyl complex **22**. In the following paper, detailed studies of the scope and mechanism of μ-alkenyl complex formation are presented.[30]



The stereochemistry of hydrocarbation was eventually established by studying the reaction of **1** with *Z*- and (*E*)-1,2-dideuterio-3,3-dimethyl-1-butene, **23**.[31] **23-E** was prepared by

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[30] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.*, following paper in this issue.

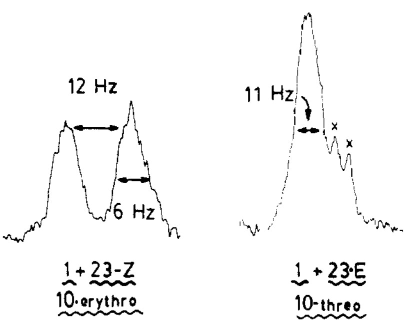
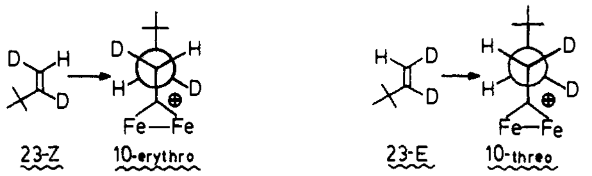


Figure 1. ^{1}H NMR spectra for the *t*-BuC*H*D resonances at δ 1.95 for **10**-erythro and **10**-threo obtained from **1** and **23-Z** and **23-E** (X = impurity).

hydrozirconation of 3,3-dimethyl-1-butyne with $(C_5H_5)_2Zr(D)Cl$ followed by quenching with D_2SO_4–D_2O. **23-Z** was prepared by hydrozirconation of 1-deuterio-3,3-dimethyl-1-butyne with $(C_5H_5)_2Zr(D)Cl$ followed by quenching with H_2SO_4–H_2O.

Whitesides was the first to use the deuterated 3,3-dimethylbutyl system as a probe of reaction stereochemistry.[32] The method relies on the fact that the *tert*-butyl group prefers the anti configuration. In our system, analysis of the NMR spectrum of **10** established that the predominant configuration had anti *tert*-butyl and μ-carbyne centers with $J_{\text{anti}} = 11.0$ Hz, $J_{\text{gauche}} = 6.5$ Hz, $J_{\text{gem}} \approx J'_{\text{gem}} \approx 15$ Hz for the AA'XX' system. Syn addition of the C–H bond of **1** across **23-Z** would produce **10**-erythro while anti addition would produce **10**-threo. **10**-threo ($J_{HH} = 6.5$ Hz) and **10**-erythro ($J = 11$ Hz) are readily distinguished based on the appearance of the resonance at δ 1.95 due to the *tert*-BuC*H*D proton.



When the product of the reaction of **1** with **23-Z** in CD_2Cl_2 was observed directly by ^{1}H NMR, the resonance due to the *t*-BuC*H*D proton at δ 1.95 appeared as a broad doublet with $J = 11.9$ Hz (Figure 1). Each peak of the doublet is broadened ($\omega_{1/2} = 6$ Hz) by coupling to vicinal (1 Hz) and geminal (2 Hz) deuterium. The spectra agreed well with the calculated spectrum of **10**-erythro. When the product of the reaction of **1** with **23-E** in CD_2Cl_2 was studied by ^{1}H NMR, the resonance due to the *t*-BuC*H*D proton at δ 1.95 appeared as a broadened ($\omega_{1/2} = 11$ Hz) singlet. This broadening is due to $J_{HH} = 6.5$ Hz and vicinal (1.6 Hz) and geminal (2 Hz) deuterium coupling. The spectrum agreed well with the calculated spectrum of **10**-threo.

These two results conclusively establish the syn addition of the C–H bond of **1** across the double bond of *tert*-butylethylene.

Second-Order Kinetics. The absolute rate of the reaction of **1** with *trans*-2-butene at −50 °C was determined to establish the rate law for a hydrocarbation reaction. *trans*-2-Butene was chosen for study because of its convenient rate of reaction at −50 °C and the ease of analysis of the neutral product obtained after base workup and not because of the simplicity of its chemistry. In fact, the reaction of **1** with *trans*-2-butene and the subsequent deprotonation are complex and were sorted out only after extensive experimentation. In a separate paper,[33] we provide evidence that the reaction of **1** with *trans*-2-butene at −50 °C initially produces the μ-2-methylbutylidyne complex **24**. Upon warming to −13 °C, **24** undergoes a 1,2-hydride shift to produce an equilibrating 2.3:1.5:1.0 mixture of **24**, and μ-2-methyl-1-butenyl complexes **25-Z** and **25-E**. At room temperature, aqueous bicarbonate deprotonates only μ-2-methylbutylidyne complex **24**, and the entire equilibrium mixture is drained off to the neutral μ-2-methyl-1-butenylidene complex **26**. The kinetically formed **24** reacts with NMe_3 at −78 °C to produce **26**. However, when the equilibrium mixture of **24**, **25-E**, and **25-Z** is treated with NMe_3 at room temperature, deprotonation of **25-E** and **25-Z** occurs to produce vinyl carbene complexes **27** and **28** in addition to **26** obtained from **24**.[34] Therefore, in working up the products from the reaction of **1** with *trans*-2-butene, either aqueous bicarbonate or NMe_3 at −78 °C was employed to cleanly convert the hydrocarbation product to the neutral μ-2-methyl-1-butenylidene complex **26** for analysis.

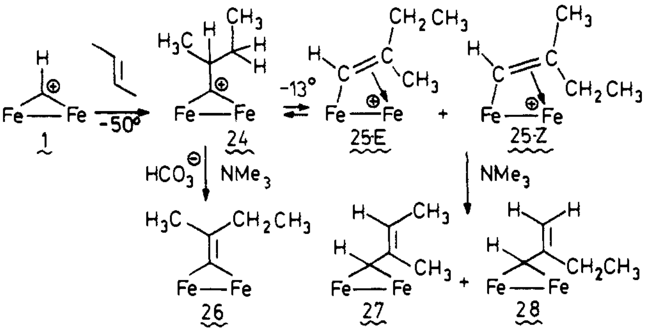


Table II. Rate of Reaction of *trans*-2-Butene with **1** at −50 °C

10^3[**1**], M	$10^3[C_4H_8]$, M	time, s	10^3[**26**], M	10^3k_2, M^{-1} s^{-1}
2.6	40	1260	0.73	10.2
2.6	79	1260	1.16	10.2
2.6	60	∞	1.82	
2.2	40	1500	0.77	9.6
2.2	80	1500	1.15	8.8
2.2	48	∞	1.76	
1.5	24	1800	0.38	8.6
1.5	47	1800	0.62	8.4
1.5	39	∞	1.22	
1.4	80	1500	0.65	9.1
2.8	80	1500	1.30	9.1
2.8	80	∞	1.96	

The reaction of **1** with *trans*-2-butene at −50 °C was carried out under pseudo-first-order conditions by using a 16–36-fold excess of alkene. For a given kinetic run, a solution of **1** in CH_2Cl_2 containing triphenylmethane as an internal standard for subsequent NMR analysis was divided into 3 portions. Different concentrations of *trans*-2-butene was added to the first 2 portions. After an identical reaction time of about 30 min, the reactions were quenched by cooling to −78 °C. Most of the *trans*-2-butene was removed under high vacuum at −78 °C, and then aqueous sodium bicarbonate was added at −78 °C to convert alkylidyne product **24** to alkenylidene complex **26**. The extent of reaction was measured by comparison of the ^{1}H NMR integrals the alkenylidene complex **26** and of the triphenylmethane internal standard. The third portion of **1** was reacted with alkene for a much longer time (4 h) and then warmed to room temperature before quenching with base.

The kinetic results shown in Table II establish a second-order rate law, rate = k_2[**1**][alkene]. Qualitatively, it is apparent that the rate of formation of product is increased by increasing the concentration of either **1** or *trans*-2-butene. A pseudo-first-order rate constant for each point was calculated by using the equation, $k_{\text{obsd}} = -(1/t)\ln(1 - [\mathbf{26}]_t/[\mathbf{26}]_\infty)$, which takes into account the fact that the reaction does not proceed quantitatively. The second-order rate constants, $k_2 = k_{\text{obsd}}$[2-butene], calculated for each point were independent of the concentration of **1** and of *trans*-2-butene. The magnitude of k_2 was $9.2 \pm 0.7 \times 10^{-3}$ M^{-1} s^{-1} at

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Table III. Relative Reactivity of Alkenes Toward **1** and Other Electrophiles

	1	$(CO)_5W{=}CHPh$[45]	H^+, H_2O[46]	CH_3CO_3H[47]	CH_3SCl[48]	$Br_2/MeOH$[49]	$(CO)_5W{=}CAr_2$[50]
$CH_2{=}CH_2$	1			1		1	fast
trans-$CH_3CH{=}CHCH_3$	25	25	18		22	1700	
$CH_2{=}CHEt$	32	40	54[a]	23[b]	30		49[b]
$CH_2{=}CHMe$	56	82.5	25	22		61	
$CH_2{=}CPh_2$	90			253			
$CH_2{=}CHPh$	160	292.5	188	58.4			
cis-$CH_3CH{=}CHCH_3$	470	55	42	489	390	2600	1
$CH_2{=}CMe_2$	6900	25000	187000	484	23	5400	10

[a] Value reported is for 1-hexene. [b] Value reported is for 1-pentene.

Table IV. Deuterium Kinetic Isotope Effects on the Reaction of **1** and **1-d** with Alkenes at −50 °C

alkene	k_H/k_D[a]
$CH_2{=}CH_2$[b]	0.81 ± 0.02
$CH_2{=}CHMe$	0.74 ± 0.03
$CH_2{=}CMe_2$	0.80 ± 0.03
trans-$CH_3CH{=}CHCH_3$	0.77 ± 0.03
cis-$CH_3CH{=}CHCH_3$	1.45 ± 0.06
$CH_2{=}CMe(t\text{-}Bu)$[c]	0.72 ± 0.02

[a] Average of three (M^+, $M - CO^+$, $M - 2CO^+$) MS determinations for 3–4 separate experiments. [b] Because of the low reactivity of $CH_2{=}CH_2$, runs were at −25 °C. [c] Only M^+ and $M - CO^+$ peaks were analyzed.

−50 °C which corresponds with $\Delta G^{\ddagger} = 14.9$ kcal mol^{-1}.

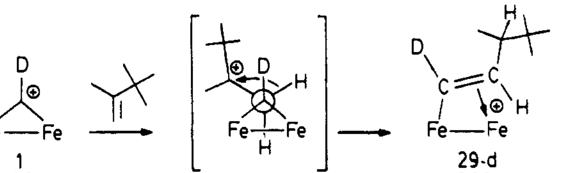
Relative Reactivity of Alkenes toward 1. Competition techniques were used to measure the relative reactivity of alkenes toward **1** in CH_2Cl_2 at −50 °C. Typically a 0.002 M solution of **1** in CH_2Cl_2 was added to a 100–1000-fold excess of a mixture of alkenes with a total concentration of 0.1–1.0 M alkene. After 1 h, the reaction was quenched by addition of either NMe_3 or aqueous bicarbonate which deprotonated the cationic μ-alkylidyne products and produced neutral μ-alkenylidene products which were isolated and analyzed by integration of ^1H NMR spectra. The ratio of alkenes was adjusted so that substantial amounts of each alkenylidene complex were obtained. When cross comparisons of the reactivity of alkenes allowed more than one estimate of relative reactivity, the results agreed to within 20%.

The results summarized in Table III indicate that electron-donating alkyl substituents substantially increase the reactivity of the alkene; the relative reactivity of ethylene:propene:isobutylene is 1:56:6900. Two alkyl groups substituted on the same carbon of the alkene increase the reactivity more than when one alkyl group was substituted on each carbon of the double bond; thus, isobutylene (6900) is more reactive than either *trans*-2-butene (25) or *cis*-2-butene (470).

The regiochemistry of hydrocarbation and the acceleration of hydrocarbation by electron-donating substituents on one carbon of the alkene double bond provide substantial evidence for extensive bonding from the methylidyne carbon of **1** to one carbon of the alkene at the transition state. However, these experiments provide no evidence for or against concerted transfer of hydrogen from the methylidyne carbon to the alkene.

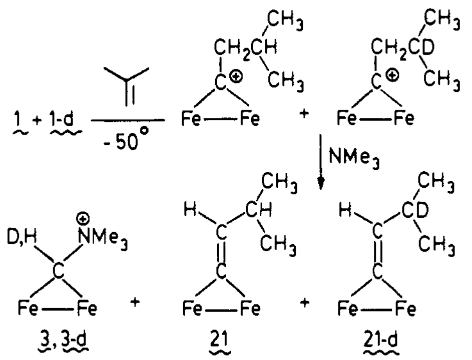
Deuterium Isotope Effect. In an attempt to distinguish between a concerted addition of the C–H bond of the methylidyne group of **1** across the alkene and a stepwise mechanism involving addition of the methylidyne carbon to the alkene followed by a 1,3-hydride shift within a carbocation intermediate, we measured the deuterium isotope effect for the addition of the C–D bond of deuterated methylidyne complex **1-*d*** to alkenes. For the nonlinear transition state of a concerted C–H addition mechanism, we anticipated a primary isotope effect of $k_H/k_D = 2$–7. The cis elimination of LiH from *n*-octyllithium has an isotope effect of 3.6.[35] The cis elimination of an iridium hydride from an iridium alkyl has an isotope effect of 2.28.[36] For the cis addition of R_2BH to 1-hexene, tritium isotope effects of 1.5–4.7 were seen.[37]

Since it was difficult to predict the isotope effect for the stepwise mechanism involving a carbocation intermediate, we determined the isotope effect for the reaction of **1** and **1-*d*** with 2,3,3-trimethyl-1-butene which involved no cleavage of the methylidyne C–H bond. As detailed in the accompanying paper, **1-*d*** reacts with 2,3,3-trimethyl-1-butene to produce the μ-alkenyl product **29-*d*** in which the C–D bond is intact.[30] The reaction proceeds



by rate-determining addition of the methylidyne carbon to the alkene followed by a 1,2-hydride shift to produce **29-*d***. An inverse secondary isotope effect of $k_H/k_D = 0.72$ was seen for this reaction. This provides an excellent model for the isotope effect to be expected if **1-*d*** adds its C–H bond to alkenes by a two-step mechanism.

The reaction of the deuterated methylidyne complex **1-*d*** with ethylene, propene, and isobutylene gave clean 1,2-addition of the C–D bond across the carbon–carbon double bond and after deprotonation gave **5-*d*** (94%), **15-*d*** (95%), and **21-*d*** (75%). The



isotope effect for the reaction of **1** with isobutylene was determined by using a competition technique in which **1** (0.1 mmol) and **1-*d*** (0.1 mmol) competed for a deficiency of isobutylene (0.1 mmol) in CH_2Cl_2 at −50 °C. At this temperature the reaction of **1** with isobutylene is very rapid. Addition of NMe_3 to the reaction mixture after 0.5 h at −50 °C resulted in deprotonation of the cationic μ-alkylidyne complexes and generation of the neutral μ-alkenylidene complexes **21** and **21-*d***. Any unreacted methylidyne complex was converted to the cationic NMe_3 addition products **3** and **3-*d*** which were insoluble in diethyl ether and easily separated from **21** and **21-*d***. The mixture of **21** and **21-*d*** was isolated and purified by column chromatography and HPLC prior to analysis.

The relative amounts of **21** and **21-*d*** were determined by slowly scanning the M^+, $M - CO^+$ and $M - 2CO^+$ envelopes in the mass spectrum and averaging 20 scans. The ratio of **21**:**21-*d*** was found to be 45.9:54.1 by using the M^+ envelope, 45.5:54.5 by using the

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M − CO$^+$ envelope, and 45.3:54.7 by using the M − 2CO$^+$ envelope. The isotope effect was calculated to be k_H/k_D = 0.79, 0.78, and 0.77 by using the three different regions. In four independent experiments, the value of k_H/k_D for the three envelopes varied over the range 0.77–0.83.

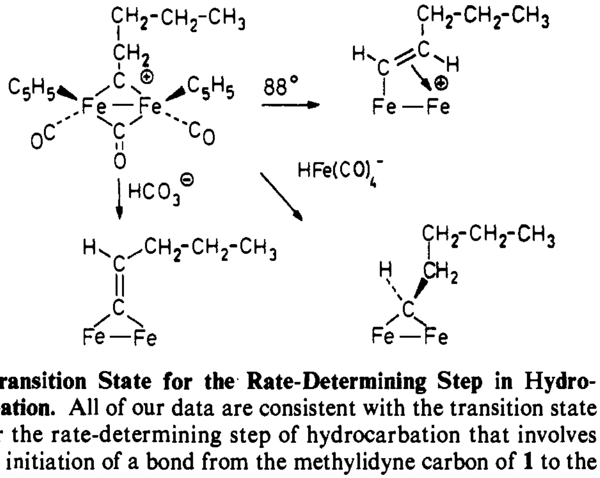
The ratio of **21**:**21-*d*** was independently confirmed by ^{1}H NMR. Comparison of the integral for the methine hydrogen at δ 2.80 to the integral for the vinyl hydrogen at δ 6.95 indicated a ratio of 46.0:54.0. In four experiments, the value of the isotope effect determined by ^{1}H NMR varied from 0.80 to 0.90.

Deuterium kinetic isotope effects were also measured for alkylidyne complex formation from several other alkenes (Table IV). Because of the slower rates involved in these cases, an excess of alkene was employed, and the reactions were quenched with NMe_3 after partial consumption of **1** and **1-*d***. The isotope effects seen for alkylidyne formation from **1** and isobutylene are very similar to the inverse secondary isotope effect seen in the reaction of **1** with 2,3,3-trimethyl-1-butene which produces a μ-alkenyl complex without any breaking of the methylidyne C–D bond.

Discussion

The hydrocarbation reactions of **1** constitute the first examples of the addition of a carbon–hydrogen bond across the carbon–carbon double bond of a simple alkene. Previously, Arigoni suggested the addition of the C–H bond of a carbocation across a carbon–carbon double bond to explain the stereochemistry seen in the biosynthesis of avocetin.[38] The addition of B–H,[39,40] Al–H,[41] and Zr–H[42] bonds across alkenes are, of course, well-known.

The hydrocarbation reactions of **1** make available a wide range of new μ-alkylidyne complexes. These μ-alkylidyne complexes can be deprotonated to give μ-alkenylidene complexes, thermally rearranged to μ-alkenyl complexes[43] or reduced with $HFe(CO)_4^-$ to μ-alkylidene complexes.[5] We are now attempting to develop the chemistry of these new organoiron functional groups to make them useful in organic synthesis.



Transition State for the Rate-Determining Step in Hydrocarbation. All of our data are consistent with the transition state I for the rate-determining step of hydrocarbation that involves only initiation of a bond from the methylidyne carbon of **1** to the less substituted carbon of the carbon–carbon double bond. There is no indication that transfer of hydrogen from the methylidyne group to the alkene is occurring in the transition state.

The high regioselectivity seen in hydrocarbation provides evidence that positive charge is building up at the more substituted carbon of the carbon–carbon double bond at the transition state. The relative rates of reaction of alkenes with **1** (Table III) are consistent with buildup of positive charge predominantly at the more substituted carbon of the double bond. An additional electron-donating alkyl group causes the rate to increase by a factor of 56 in going from ethylene to propene. A second additional alkyl group to the same carbon causes a further rate increase of 123 in going from propene to isobutylene which has a relative rate of 6900 compared with ethylene. Much smaller rate effects are seen if the two carbon substituents are attached to opposite ends of the double bond. For example, *trans*-2-butene is only 0.45 times as reactive as propene and 0.8 as reactive as 1-butene. *cis*-2-Butene is 19 times more reactive than the trans isomer but only eight times more reactive than propene and 15 times less reactive than isobutylene.

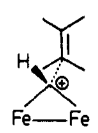


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Table III also provides a comparison of the relative rates of hydrocarbation with those of other electrophilic additions to alkenes.[44] Three patterns of reactivity can be seen. First, the accelerating effect of electron-donating alkyl substituents is cumulative only if the substituents are on the same end of the double bond as seen for hydrocarbation by **1**, cyclopropanation by $(CO)_5W{=}CHC_6H_5$,[45] and acid-catalyzed hydration.[46] This is consistent with positive charge localization at the more substituted alkene carbon. Second, alkyl groups at either end of the double bond accelerate epoxidation by CH_3CO_3H,[47] addition of CH_3SCl,[48] and bromination in methanol.[49] This is consistent with a cyclic transition state in which the positive charge is distributed over both carbons of the double bond. The third case is the reaction of $(CO)_5W{=}C(C_6H_4\text{-}p\text{-}CH_3)_2$ with alkenes where the least-substituted alkene is the most reactive.[50] This is consistent with competition of alkenes for a vacant site on the metal.

While rate differences for the hydrocarbation of alkenes with different number of alkyl substituents are substantial, they are not consistent with a transition state which bears a full positive charge at the more substituted alkene carbon. The rate difference of 123 between propene and isobutylene at −50 °C corresponds to a free energy difference of 2.1 kcal mol^{-1}. This energy difference is small compared with the 14.9 kcal mol^{-1} energy difference between the gas phase stabilities of $(CH_3)_2CH^+$ and $(CH_3)_3C^+$[51] or with the 11–15 kcal mol^{-1} energy difference between $[(CH_3)_2CH](CH_3)CH^+$ and $CH_3CH_2(CH_3)_2C^+$ in $SO_2ClF\text{-}SbF_5$.[52] It is also small compared with the 11 kcal mol^{-1} energy difference between the S_N1 transition states leading to secondary and tertiary 2-adamantyl cations[53] or with the 6.4 kcal mol^{-1} energy difference between the S_N1 transition states for solvolysis of $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ in ethanol.[54] Most of the positive charge in the transition state for hydrocarbation must therefore still be associated with the diiron methylidyne unit.

The inverse deuterium kinetic isotope effects seen for hydrocarbation are consistent with transition state I in which the C–H bond of the methylidyne group is not being broken but is un-

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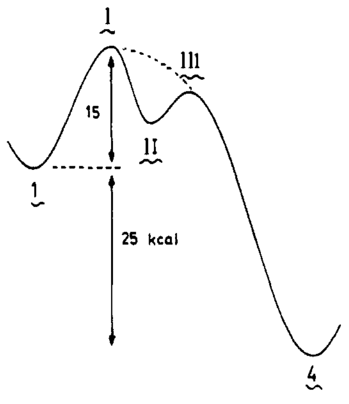
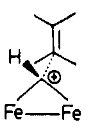
dergoing a hybridization change from sp^2 to sp^3. This provides evidence for a transition state whose structure is between that of **1** and carbocation II. Inverse secondary deuterium isotope effects are commonly seen in reactions involving change in the hybridization of the C–H bond from sp^2–sp^3.[55–57] Examples of inverse deuterium kinetic isotope effects for reactions involving an sp^2–sp^3 change in hybridization include 0.76 for the first step in the oxidation of *trans*-cinnamic acid by acidic permanganate[58] and 0.84 for the cycloaddition of a ketene to a deuterated cyclopentadiene.[59] The similarity of the isotope effects seen for reactions of **1** and alkenes that produce μ-alkylidyne complexes and those that produce μ-alkenyl complexes suggest that the transition states for both reactions are very similar. The carbon and hydrogen migrations seen for μ-alkenyl complex formation imply the existence of an intermediate carbocation capable of rearrangement.

Carbocation Intermediates? The existence of a carbocation intermediate in hydrocarbation is open to question. We know that a 1,3-hydrogen migration must take place after the transition state and that this should require the geometry shown for III. However, we have no way of discerning whether carbocation intermediate II is an energy minimum between transition state I and the geometry III leading to the μ-alkylidyne product. Thus, III is either the transition state for the product-determining step in hydrocarbation or simply another point on the reaction coordinate.





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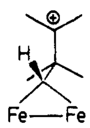

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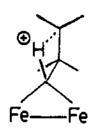


III

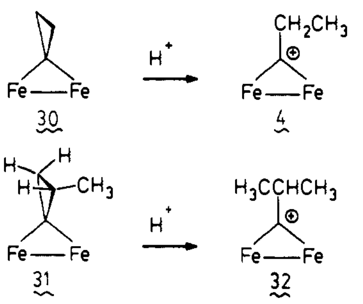
If there is an intermediate carbocation such as II in the hydrocarbation reaction, the 1,3-hydride shift to give a μ-alkylidyne product must be extremely rapid. In particular, the 1,3-hydride shift would have to be more rapid than 1,2-carbon or hydrogen shifts to give μ-alkenyl products, more rapid than the 1,2-carbon migration possible in the reaction with *tert*-butylethylene, and more rapid than carbon–carbon bond rotation of the possible intermediate in the addition of **1** to **23-E** and **23-Z**. In addition, the fact that we observed no isomerization of excess *cis*-2-butene recovered from reaction with **1** requires that the 1,3-hydride shift to produce a μ-alkylidyne product be much faster than carbon–carbon bond rotation followed by reversal of C–C bond formation to regenerate **1**.[17]

The requirement for a very rapid 1,3-hydride shift of the carbocation intermediate to give μ-alkylidyne products is not unreasonable since energetically degenerate 1,3-hydride shifts in the 2,4-dimethyl-2-pentyl cation have a barrier of 8.5 kcal mol^{-1} and since the 1,3-hydride shift leading to a μ-alkylidyne complex should be very exothermic.[60]

Are carbocations such as II energetically possible intermediates in hydrocarbation? To be intermediates they would have to be more stable than transition state I ($\Delta G^{\ddagger} = 14.9$ kcal mol^{-1} for *trans*-2-butene) and less stable than the μ-alkylidyne product. The relative energies of **1** and the μ-alkylidyne product can be crudely estimated as similar to the energy difference between an sp^2 hybridized C–H unit plus ethylene and an sp^2 hybridized C–Et unit which has $\Delta H = -25.4$ kcal mol^{-1}.[61] This is a minimum estimate since no extra stabilization of the positive carbyne center in the alkylidyne complex relative to the methylidyne complex is assumed. Thus, carbocation II is an energetically possible intermediate in hydrocarbation since it's energy must surely be less than 40 kcal mol^{-1} higher than that of the μ-alkylidyne product.

The basic difference between carbocation intermediate II and the μ-alkylidyne product is that the positive carbon center of II is stabilized only by alkyl groups whereas the positive center in the alkylidyne complex is greatly stabilized by two strongly electron-donating iron centers as well as an alkyl group. The methylidyne complex **1** is prepared by hydride abstraction from μ-methylene complex **2** with the triphenylmethyl cation; therefore, the methylidyne complex must be at least as stable as triphenylmethyl cation. A good model for carbocation intermediate II would be a secondary carbonium ion. The transition states leading to $(CH_3)_2CH^+$ and $(C_6H_5)_3C^+$ via S_N1 solvolysis of the corresponding chlorides differ in energy by about 16 kcal mol^{-1}.[54] This is within the 40 kcal mol^{-1} window for a possible intermediate. Therefore, it is likely that the very exothermic σ bond formation in going from I to II would make it energetically feasible to generate even a primary carbocation intermediate in hydrocarbation.

A geometry similar to III is required for the 1,3-hydride shift leading to μ-alkylidyne product. We do not know whether III is a transition state connecting a carbocation intermediate II with the μ-alkylidyne product or whether it is just a geometry along a downhill pathway from the rate-determing transition state I to μ-alkylidyne product. It should be noted that III has the geometry of an edge-protonated cyclopropane. Recently Hoel prepared the diiron cyclopropylidene complex **30**[62] and showed that it is ring opened by acid to μ-propylidyne complex **4**.[63] The methylcyclopropylidene complex **31** is also ring opened by acid, but the branched alkylidyne complex **32** formed has a different regiochemistry than that obtained from hydrocarbation. The failure of the ring opening of **31** to give the same regiochemistry as hydrocarbation is probably the result of the tendency of cyclopropanes to ring open by attack of acid at the less-substituted carbon.[64]



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Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Brucker WP270, AM500, or WP200 spectrometer. ^{13}C NMR spectra at 50.1 MHz of samples containing 0.07 M Cr(acac)$_3$ as a shiftless relaxation reagent and ^{2}H NMR at 30.6 MHz containing $CDCl_3$ as an internal standard were obtained on a JEOL FX200 spectrometer. CD_2Cl_2 and CD_3NO_2 were dried over P_2O_5, acetone-d_6 was dried over molecular sieves or B_2O_3, and benzene-d_6 was distilled from solutions of sodium and benzophenone. CD_3CN was distilled from P_2O_5 and then from CaH_2. NMR samples were prepared and sealed on a vacuum line and centrifuged prior to analysis. IR spectra were recorded on a Beckman 4230 infrared spectrometer calibrated with polystyrene film.

Mass spectrum were obtained on an AEI-MS-902 or Kratos MS-80RF mass spectrometer. The data for the quantitative MS runs were acquired by using the standard scanning mode of the Kratos MS-80RF. The instrument resolution was set at 1000 $M/\Delta M$, and the magnet was scanned at 100 s per decade. The signal detection threshold was set intentionally low to minimize errors in intensity measurements. Twenty consecutive scans were averaged together to give normalized values for each envelope region.

Air sensitive compounds were handled by using standard Schlenk procedures and glovebox manipulations. Diethyl ether, THF, hexane, and toluene were distilled from purple solutions of sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2, and acetone was dried over molecular sieves or B_2O_3. HPLC was performed on a Beckman 334 gradient liquid chromatography with a Beckman 421 controller. A nonaqueous reverse phase column, Ultrasphere-ODS, was chosen, and HPLC grade methanol was the mobile phase.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CH)^+PF_6^-$ (1). The μ-methylene complex **2** was prepared by the procedure of Ziegler.[6] A solution of $(C_6H_5)_3P{=}CH_2$ (Ph_3PCH_3Br 13.56 g, 37.9 mmol; *n*-BuLi; 23 mL 1.61 M in hexane, 37 mmol; THF 600 mL) and $[(C_5H_5)(CO)_2Fe]_2$ (**33**) (6.00 g, 17.0 mmol) was refluxed gently for 30 h to give a 3:1 mixture of **2**:**33** (4.16 g, 9.2 mmol) after column chromatography (alumina, hexane). This mixture of **2**:**33** and $(C_6H_5)_3C^+PF_6^-$ (3.35 g, 8.62 mmol) was stirred in CH_2Cl_2 (40 mL) for 1 h at 0 °C. The resulting red microcrystalline solid was isolated by filtration, washed with CH_2Cl_2 (3 × 5 mL), and dried under high vacuum to give **1** (3.71 g, 45.2% based on **33**): ^{1}H NMR (CD_2Cl_2) cis:trans 19:1; cis δ 22.85 (s, 1 H), 5.37 (s, 10 H); trans δ 22.94 (s, 1 H), 5.29 (s, 10 H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 490.2 (μ-CH), 252.7 (μ-CO), 204.8 (CO), 92.0 (C_5H_5); IR (CH_2Cl_2) 2052 (s) and 1856 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{11}F_6Fe_2O_3P$: C, 34.75; H, 2.29; P, 6.40. Found: C, 34.51; H, 2.36; P, 6.18.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CD)^+PF_6^-$ (1-*d*). A 4:1 mixture of **2**:**33** (2.6 g, 6.1 mmol of **2**) and CF_3CO_2D (25 g, 217 mmol) was stirred at −10 °C under N_2 to give a deep blue solution of $[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CH_2D)^+CF_3CO_2^-$ (**34**).[4] Addition of D_2O (1.5 mL, 83 mmol) at −5 °C set up an equilibrium between **34** and **2**. Aliquots of D_2O (1.5 mL, 83 mmol) were added every 10 min until the suspension was a bright red (typically 8 mL). D_2O (20 mL) was added, and the suspension was filtered, washed with D_2O (4 × 10 mL), and dried under high vacuum overnight. The resulting solid was purified by column chromatography (alumina, toluene) and recrystallized from toluene–hexane to give a 10:1 mixture of **2-*d*$_2$**:**33** (1.80 g, 78%). Analysis by ^{1}H NMR revealed no μ-CH_2 resonances and >99% d_2. ^{2}H {^{1}H} NMR (acetone) cis δ 10.4, 8.34; trans 9.65.

The reaction of $(C_6H_5)_3C^+PF_6^-$ (1.51, 3.89 mmol) with this mixture of **2-*d*$_2$**:**33** in CH_2Cl_2 (80 mL) gave **1-*d*** (1.72 g, 91% based on Ph_3C^+).

To analyze the deuterium content of **1-*d***, $[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CDCH_3)$ (**35**) was made from reaction[25] of MeLi and **1-*d***. No signal for the μ-C*H*Me resonance was observed in the ^{1}H NMR which indicates >99% deuterium incorporation. ^{1}H NMR (acetone-d_6) δ 4.84 (10 H, C_5H_5), 3.10 (s, 3 H, CH_3); ^{2}H{^{1}H} NMR (acetone) δ 12.1.

Reaction of 1 with Alkenes. The procedure detailed for the preparation of **4** from **1** was also used to prepare **6**–**11** and **14**.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH_3)^+PF_6^-$ (4). Ethylene (0.79 atm, 350 mL, 11.3 mmol) was condensed into a stirred suspension of **1** (0.21 g, 0.43 mmol) in CH_2Cl_2 (15 mL) at −78 °C. The reaction mixture was warmed to ambient temperature. Solvent was evaporated, and the residue was dried under high vacuum. Acetone (10 mL) was condensed onto the solids. The resulting solution was filtered and concentrated to 3 mL. Diethyl ether (10 mL) was added, and the resulting red precipitate was filtered, washed with diethyl ether (3 × 5 mL), and dried under vacuum to give **4** (0.15 g, 68%): ^{1}H NMR (acetone-d_6) δ 5.69 (s, 10 H, C_5H_5), 5.49 (q, J = 7 Hz, CH_2), 1.82 (t, J = 7 Hz, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6) δ 504.7 (μ-CR), 252.4 (μ-CO), 208.9 (CO), 93.1 (C_5H_5), 70.6 (CH_2), 16.2 (CH_3); IR (Nujol) 2039 (s), 2006 (m), 1855 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{15}F_6Fe_2O_3P$: C, 37.54; H, 2.95; P, 6.05. Found: C, 37.88; H, 3.22; P, 5.99.

4 from EtLi and $[(C_5H_5)(CO)_2Fe]_2$. CH_3CH_2Li (30 mL, 1.5 M, 45 mmol) was added to a stirred solution of **33** (7.06 g, 22.49 mmol) in THF (300 mL) at −40 °C. The reaction mixture was stirred at ambient temperature for 40 min. Aqueous HPF_6 (17 mL, 65% by weight in solution, 115 mmol) was added slowly at −20 °C. The resulting bright red solution was stirred at ambient temperature for 30 min. The solution was concentrated to 200 mL under vacuum, and diethyl ether (250 mL) was added. The resulting red precipitate was filtered, washed successively with ether, toluene, hexane, and ether, and dried under vacuum to give 4 (3.75 g, 33%).

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH_2CH_3)^+PF_6^-$ (7). Reaction of propene (0.33 atm, 300 mL, 4.0 mmol) with **1** (0.127 g, 0.262 mmol) in CH_2Cl_2 (8 mL) gave 7 (0.105 g, 78%): ^{1}H NMR (acetone-d_6) δ 5.68 (s, 10 H, C_5H_5), 5.50 (t, J = 7 Hz, CH_2Et), 2.32 (sextet, J = 7 Hz, CH_2Me), 1.23 (t, J = 7 Hz, CH_3); ^{13}C NMR (acetone-d_6) δ 503.5 (μ-CR), 252.4 (μ-CO), 207.8 (CO), 93.4 (d, J = 184 Hz, C_5H_5), 79.6 (t, J = 131 Hz, CH_2Et), 26.3 (t, J = 125 Hz, CH_2Me), 14.3 (q, J = 121 Hz, CH_3); IR (Nujol) 2038 (s), 2003 (m), 1858 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{17}F_6Fe_2O_3P$: C, 38.82; H, 3.26; P, 5.89. Found: C, 38.78; H, 3.47; P, 5:51.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH_2CH_2CH_3)^+PF_6^-$ (8). Reaction of 1-butene (0.10 atm, 100 mL, 0.42 mmol) with **1** (0.200 g, 0.415 mmol) in CH_2Cl_2 (15 mL) gave **8** (0.169 g, 76%): ^{1}H NMR (acetone-d_6) δ 5.66 (s, 10 H, C_5H_5), 5.52 (m, μ-CCH_2), 2.27 (m, CH_2Et), 1.64 (sextet, J = 7.4 Hz, CH_2Me), 1.04 (t, J = 7.4 Hz, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6) δ 502.5 (μ-CR), 250.7 (μ-CO), 209.9 (CO), 92.3 (C_5H_5), 76.7 (μ-C*C*H_2), 33.7 (CH_2Et), 22.1 (CH_2Me), 12.4 (CH_3); IR (Nujol) 2040 (s), 2004 (m), 1870 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{19}F_6Fe_2O_3P$: C, 40.04; H, 3.55. Found: C, 39.88; H, 3.69.

8 was also prepared by addition of *n*-butyllithium (36 mL, 1.60 M in hexane, 58 mmol) to a suspension of **33** (20.0 g, 56.4 mmol) in 200 mL THF at −78 °C. The reaction mixture was warmed to room temperature. HPF_6 (20 mL, 60% aqueous solution, 136 mmol) was added at −78 °C, and the reaction mixture was warmed to room temperature. The resulting red precipitate was isolated by filtration and washed with toluene and then ether. The solid was dissolved in acetone, the solution was filtered, and ether was added to precipitate red microcrystalline **8** (7.37 g, 26%).

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$C(CH_2)_4CH_3)^+PF_6^-$ (9). Reaction of 1-pentene (0.11 mL, 70 mg, 1.0 mmol) with **1** (400 mg, 0.83 mmol) in CH_2Cl_2 (16 mL) gave 9 (358 mg, 78%): ^{1}H NMR (acetone-d_6) δ 5.66 (s, 10 H, C_5H_5), 5.52 (m, CCH_2), 2.30 (m, CCH_2CH_2), 1.67–1.37 (m, $CH_2CH_2CH_3$), 0.93 (t, J = 7 Hz, CH_3); ^{13}C{^{1}H} NMR (CD_3NO_2) δ 504.1 (μ-CR), 252.6 (μ-CO), 207.7 (CO), 93.7 (C_5H_5), 78.8 (μ-C*C*H_2), 33.0, 32.8 (μ-$CCH_2CH_2CH_2$), 23.2 (CH_2CH_3), 14.3 (CH_3); IR (CH_2Cl_2) 2037 (s), 2002 (m), 1861 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{21}F_6Fe_2O_3P$: C, 41.19; H, 3.82. Found: C, 40.95; H, 4.05.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH_2C(CH_3)_3)^+PF_6^-$ (10). Reaction of 3,3-dimethyl-1-butene (0.090 mL, 0.70 mmol) with **1** (154 mg, 0.318 mmol) in CH_2Cl_2 (8 mL) gave **10** (153 mg, 85%): ^{1}H NMR (acetone-d_6) δ 5.65 (s, 10 H, C_5H_5), 5.52 (m, 2 H, μ-CCH_2), 2.14 (m, 2 H, CH_2-*t*-Bu), 1.12 (s, 9 H, CH_3); ^{13}C NMR (CD_3NO_2) δ 503.5 (μ-CR), 253.6 (μ-CO), 207.7 (CO), 93.6 (d, J = 181 Hz, C_5H_5), 74.6 (t, J = 133 Hz, μ-C*C*H_2), 45.7 (t, J = 138 Hz, CH_2-*t*-Bu), 32.0 (CMe_3), 29.4 (q, J = 123 Hz; CH_3); IR (Nujol) 2040 (s), 2002 (m), 1842 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{23}F_6Fe_2O_3P$: C, 42.29; H, 4.08; P, 5.45. Found: C, 42.57; H, 3.84; P, 5.39.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH_2CH{=}CH_2)^+PF_6$ (11). Reaction of 1,3-butadiene (0.53 atm, 250 mL, 5.4 mmol) with **1** (124 mg, 0.256 mmol) in CH_2Cl_2 (10 mL) gave **11** (116 mg, 84%): ^{1}H NMR (acetone-d_6) δ 6.06 (ddt, J = 17, 10.2, 6.3 Hz, $CH_2CH{=}CH_2$), 5.68 (s, 10 H, C_5H_5), 5.59 (t, J = 7.5 Hz, μ-CCH_2), 5.27 (dq, J = 17, 1.5 Hz, $CH_2CH{=}CHH$), 5.10 (dq, J = 10.2, 1.5 Hz, $CH_2CH{=}CHH$), 3.09 (m, 2 H, μ-CCH_2CH_2); ^{13}C NMR (acetone-d_6) δ 502.7 (μ-CR), 252.2 (μ-CO), 207.6 (CO), 136.6 (d, J = 154 Hz, CH=), 116.9 (t, J = 155 Hz, $=CH_2$), 93.3 (d, J = 184 Hz, CH_2), 76.4 (t, J = 133 Hz, μ-C*C*H_2), 36.4 (t, J = 133 Hz, CH_2); IR (Nujol) 2050 (s), 2013 (m), 1851 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_3P$: C, 40.19; H, 3.19. Found: C, 40.04; H, 3.04.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$CCH_2CH(CH_3)_2)^+PF_6^-$ (14). Reaction of 2-methylpropene (0.33 atm, 250 mL, 3.4 mmol) with **1** (168 mg, 0.347 mmol) in CH_2Cl_2 (6 mL) gave **14** (150 mg, 80%); ^{1}H NMR (acetone-d_6) δ 5.66 (s, 10 H, C_5H_5), 5.46 (d, J = 7 Hz, CH_2), 3.01 (nonet, J = 7 Hz, CH), 1.13 (d, J = 7 Hz, 6 H, CH_3); ^{13}C NMR (acetone-d_6) δ 504.6 (μ-CR), 252.7 (μ-CO), 208.4 (CO) 93.6 (d, J = 179 Hz, C_5H_5), 86.9 (t, J = 128 Hz, CH_2), 35.9 (d, J = 136 Hz, CH), 23.5 (q, J = 121 Hz, CH_3); IR (Nujol) 2040 (s), 2008 (m), 1850 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{19}F_6Fe_2O_3P$: C, 40.04; H, 3.55; P, 5.74. Found: C, 39.97; H, 3.65; P, 5.78.

$[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-$C(CH_3)_2CH(CH_3)_2)^+PF_6^-$ (6). Reaction of 2,3-dimethyl-2-butene (0.10 mL, 0.84 mmol) with **1** (130 mg, 0.27

mmol) in CH_2Cl_2 (6 mL) gave **6** (113 mg, 74%): ^1H NMR (acetone-d_6) δ 5.79 (s, 10 H, C_5H_5), 3.19 (septet, J = 7 Hz, CH), 1.81 (s, 6 H, CH_3), 1.00 (d, J = 7 Hz, 6 H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 526.4 (μ-CR), 252.4 (μ-CO), 209.3 (CO), 93.8 (C_5H_5), 80.7 (μ-CC), 42.9 ($CHMe_2$), 27.1, 20.2 (CH_3); IR (Nujol) 2032 (s), 2002 (m), 1857 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{23}F_6Fe_2O_3P$: C, 42.29; H, 4.08; P, 5.45. Found: C, 42.49; H, 4.30; P, 5.23.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2C_6H_5)^+PF_6^-$ (13-P). Addition of allylbenzene (0.1 mL, 0.76 mmol) to a solution of **1** (260 mg, 0.54 mmol) in CH_2Cl_2 (35 mL) at ambient temperature gave **13-P** (270 mg, 83%): ^1H NMR (acetone-d_6) δ 7.34–7.23 (m, 5 H, C_6H_5), 5.65 (s, 10 H, C_5H_5), 5.57 (m, 2 H), 2.96 (t, J = 7.7 Hz, 2 H), 2.61 (m, 2 H); IR (CH_2Cl_2) 2043 (s), 2010 (m), 1865 (s) cm^{-1}.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2C_6H_5)^+BF_4^-$ (13-B). Addition of $HBF_4{\cdot}O(C_2H_5)_2$ (84 μL, 0.68 mmol) to a diethyl ether (25 mL) solution of **20** at −78 °C led to precipitation of **13-B** (105 mg, 42%): ^{13}C NMR (acetone-d_6) δ 502.9 (μ-CR), 252.7 (μ-CO), 207.7 (CO), 142.5 (ipso), 129.9, 127.6 (C_6H_5), 93.7 (C_5H_5), 77.9 (μ-CCH_2), 36.4 (CH_2Ph), 34.8 (CH_2); IR (CH_2Cl_2) 2043 (s), 2008 (m), 1852 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{21}BF_4Fe_2O_3$: C, 50.79; H, 3.89. Found: C, 50.60; H, 3.69.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2C_6H_5)^+PF_6^-$ (12). Styrene (0.09 mL, 0.78 mmol) was added by syringe to a solution of **1** (310 mg, 0.64 mmol) in CH_2Cl_2 (35 mL) at ambient temperature. Workup as described for **4** gave **12** (306 mg, 81%): ^1H NMR (CD_2Cl_2) δ 7.38–7.15 (m, 5 H, C_6H_5), 5.41 (t, J = 7.7 Hz, μ-CH_2), 5.37 (s, 10 H, C_5H_5), 3.38 (t, J = 7.7 Hz, CH_2Ph); ^{13}C NMR (acetone-d_6, 125 MHz) δ 501.3 (μ-CR), 251.5 (μ-CO), 207.2 (CO), 139.5 (C_6H_5), 128.9 (d, J = 156 Hz, C_6H_5), 128.7 (d, J = 156 Hz, C_6H_5), 126.9 (d, J = 156 Hz, C_6H_5), 93.1 (d, J = 181 Hz, C_5H_5), 77.9 (t, J = 130 Hz, μ-CCH_2), 37.6 (t, J = 130 Hz, CH_2Ph); IR (CH_2Cl_2) 2038 (s), 2005 (m), 1860 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{19}F_6Fe_2O_3P$: C, 44.94; H, 3.26. Found: C, 45.22; H, 3.37.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$ (5). Addition of $N(CH_3)_3$ (0.52 atm, 1 L, 21 mmol) to a solution of **4** (0.50 g, 0.98 mmol) in acetone (20 mL) at −78 °C led to an immediate color change from maroon to bright red. Solvent was evaporated under high vacuum. The residue was extracted with diethyl ether and filtered. Evaporation of ether gave red crystalline **5** (0.30 g, 84%).

5 was also prepared by reaction of ethylene (0.79 atm, 400 mL, 12.9 mmol) with **1** (150 mg, 0.31 mmol) in CH_2Cl_2 (8 mL) at ambient temperature followed by addition of $N(CH_3)_3$ (0.39 atm, 400 mL, 6.4 mmol) at −78 °C. Purification as described above gave **5** (87 mg, 77%): ^1H NMR (acetone-d_6) δ 7.12 (q, J = 7 Hz, $=CH$), 4.97, 4.89 (C_5H_5), 2.33 (d, J = 7 Hz, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 269.8, 266.5 (μ-C, μ-CO), 211.8, 211.6 (CO), 133.6 ($=CHMe$), 87.5, 86.7 (C_5H_5), 21.5 (CH_3); IR (CH_2Cl_2) 1994 (s), 1955 (w), 1788 (m) cm^{-1}; HRMS calcd for $C_{16}H_{14}Fe_2O_3$ 365.9637, found 365.9640.

Similarly, a solution of ethylene (0.33 atm, 450 mL, 6.1 mmol) and ***1-d*** (38 mg, 0.078 mmol) in CH_2Cl_2 (20 mL) was reacted with NMe_3 (0.66 atm, 235 mL, 6.4 mmol) to give ***5-d*** (27 mg, 94%) $^2H\{^1H\}$ NMR (acetone) δ 2.40.

$[(CH_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2C_6H_5)$ (20). $N(CH_3)_3$ (0.92 atm, 530 mL, 20 mmol) was added to a solution of **13** (200 mg, 0.33 mmol) in CH_2Cl_2 (30 mL) at −78 °C. Workup as described for **5** gave crude **20** (120 mg, 80%) which was purified by column chromatography (activity III alumina, CH_2Cl_2–hexane): ^1H NMR (acetone-d_6) δ 7.39–7.11 (m, 6 H, C_6H_5 and $=CH$), 4.89, 4.86 (s, 10 H, C_5H_5), 3.03 (m, 2 H, CH_2), 2.92 (m, 2 H, CH_2), $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 271.1, 266.8 (μ-C, μ-CO), 212.8 (CO), 143.6 ($=CH$), 140.0, 129.5, 128.9 (C_6H_5), 88.7, 87.9 (C_5H_5), 39.7, 38.4 (CH_2CH_2); IR (CH_2Cl_2) 1986 (s), 1947 (m), 1780 (m) cm^{-1}; HRMS calcd for $C_{23}H_{20}Fe_2O_3$ 456.0105, found 456.0110.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_3)$ (15). A solution of propene (0.26 atm, 1.06 mL, 11.5 mmol) and **1** (273 mg, 0.564 mmol) in CH_2Cl_2 (20 mL) was warmed from −78 °C to ambient temperature. The solution was cooled to −78 °C, and a large excess of $N(CH_3)_3$ was added. Workup as described for **5** followed by recrystallization from Et_2O–hexane gave **15** (131 mg, 61%) (mp 118–124 °C dec): ^1H NMR (acetone-d_6, 200 MHz) δ 7.08 (dd, J = 6.7, 6.2 Hz, $=CH$); 4.96, 4.89 (s, 10 H, C_5H_5), 2.7 (m, CH_2), 1.17 (dd, J = 7.6, 7.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 273.0, 265.8 (μ-C, μ-CO), 213.6, 213.5 (CO), 142.9 ($=CH$), 88.86, 88.11 (C_5H_5), 31.0 (CH_2), 16.5 (CH_3); IR (CH_2Cl_2) 1992 (s), 1953 (w), 1782 (m) cm^{-1}; HRMS calcd for $C_{17}H_{16}O_3Fe_2$ 379.9793, found 379.9803.

Similarly, a solution of propene (0.092 atm, 235 mL, 0.90 mmol) and ***1-d*** (40 mg, 0.083 mmol) was reacted with NMe_3 (0.66 atm, 235 mL, 6.4 mmol) to give ***15-d*** (30 mg, 95%) $^2H\{^1H\}$ NMR (acetone) δ 2.85, 2.75.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_2CH_3)$ (17). A solution of 1-pentene (0.38 atm, 29.0 mL, 0.45 mmol) and **1** (150 mg, 0.31 mmol) in CH_2Cl_2 (12 mL) was reacted with excess $N(CH_3)_3$ (0.33 atm, 600 mL, 8.2 mmol). Workup as described for **5** gave **17** (95 mg, 75%): ^1H NMR (acetone-d_6) δ 7.09 (dd, J = 7.7, 6.3 Hz, $=CH$), 4.96, 4.89 (s, C_5H_5), 2.91–2.43 (m, $C{=}CHCH_2$), 1.70–1.36 (m, $CH_2CH_2CH_3$), 0.95 (t, J = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 269.8, 265.4 (μ-C, μ-CO), 211.8 (CO), 140.7 (μ-$C{=}CH$), 87.6, 86.8 (C_5H_5), 37.4 (μ-$C{=}CHCH_2$), 34.1 ($CHCH_2CH_2$), 22.9 (CH_2CH_3), 14.5 (CH_3); IR (CH_2Cl_2) 1992 (s), 1952 (m), 1785 (m) cm^{-1}; HRMS calcd for $H_{19}H_{20}Fe_2O_3$ 408.0110, found 408.0099.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2C(CH_3)_3)$ (18). A solution of 3,3-dimethyl-1-butene (0.060 atm, 235 mL, 0.59 mmol) and **1** (170 mg, 0.35 mmol) in CH_2Cl_2 (30 mL) was warmed from −78 °C to ambient temperature. The solution was cooled to −78 °C, and $N(CH_3)_3$ (0.65 atm, 235 mL, 6.3 mmol) was added. Workup as described for **5** followed by column chromatography (alumina, CH_2Cl_2) and crystallization from hexane gave **18** (50 mg, 33%). A small amount of the trans isomer was seen by NMR: ^1H NMR (acetone-d_6) δ 7.20 (dd, J = 8.5, 5.5 Hz, $=CH$), 4.94, 4.91 (s, 10 H, C_5H_5), 2.84 (dd, J = 13.8, 5.5 Hz, $=CHCHH$), 2.63 (dd, J = 13.8, 8.5 Hz, $=CHCHH$), 1.04 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 269.5, 266.6 (μ-C, μ-CO), 211.6 (CO), 137.6 ($=CHR$), 87.5, 86.8 (C_5H_5), 51.6 (CH_2), 31.7 (CMe_3), 29.8 (CH_3); IR (CH_2Cl_2) 1994 (s), 1956 (m), 1783 (m) cm^{-1}; HRMS calcd for $C_{20}H_{22}Fe_2O_3$ 422.0261, found 422.0264.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH(CH_3)_2)$ (21). Reaction of 2-methylpropene (0.20 atm, 270 mL, 2.2 mmol) with **1** (168 mg, 0.347 mmol) in CH_2Cl_2 (12 mL) at −78 °C followed by addition of $N(CH_3)_3$ (0.72 atm, 270 mL, 8.0 mmol) and workup as described for **5** gave **21** (70 mg, 51%): ^1H NMR (acetone-d_6) δ 6.93 (d, J = 9.0 Hz, $=CH$), 4.96, 4.88 (s, 10 H, C_5H_5), 3.01 (m, 1 H, $CHMe_2$), 1.32 (d, J = 6.6 Hz, CH_3), 1.12 (d, J = 6.6 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 271.4, 263.6 (μ-C, μ-CO), 213.1 (CO), 149.0 ($=CH$), 88.2, 88.0 (C_5H_5), 38.0 (CH), 25.3, 24.9 (CH_3); IR (KBr) 1965 (s), 1936 (m), 1778 (m) cm^{-1}; HRMS calcd for $C_{18}H_{18}Fe_2O_3$ 393.9949, found 393.9955.

Similarly, a solution of 2-methylpropene (0.20 atm, 270 mL, 2.22 mmol) and ***1-d*** (170 mg, 0.35 mmol) was reacted with NMe_3 (0.72 atm, 270 mL, 8.0 mmol) to give ***21-d*** (104 mg, 75%): $^2H\{^1H\}$ NMR (acetone) δ 3.0.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_3)$ (16). A mixture of **8** (0.50 g, 0.93 mmol), 25 mL of acetone, 25 mL of diethyl ether, and 25 mL of saturated aqueous sodium bicarbonate was stirred rapidly for 1 h. The aqueous layer was separated and extracted with additional ether. The combined ether extracts were dried ($MgSO_4$), filtered, and evaporated to give **16** (0.32 g, 87%): ^1H NMR (acetone-d_6) δ 7.09 (dd, J = 7.8, 5.9 Hz, $=CH$), 4.96, 4.89 (s, 10 H, C_5H_5), 2.86 (m, $C{=}CHCHH$), 2.66 (m, $C{=}CHCHH$), 1.62 (m, CH_2CH_3), 1.03 (t, J = 7.4 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 271.4, 262.3 (μ-C, μ-CO), 212.9 (CO), 140.6 ($C{=}CHCH_2$), 88.7, 80.0 (C_5H_5), 39.7 ($C{=}CHCH_2$), 25.0 (CH_2Me), 14.1 (CH_3); IR (THF) 1998 (s), 1960 (w), 1801 (m) cm^{-1}; HRMS calcd for $C_{18}H_{18}Fe_2O_3$ 393.9949, found 393.9954.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2C_6H_5)$ (19). A solution of **12** (260 mg, 0.44 mmol) in acetone (5 mL) and saturated sodium bicarbonate solution (5 mL) in ether (10 mL) was stirred for 15 min, and workup as described for **16** gave **19** (178 mg, 91%). A small amount (<5%) of the rearranged vinyl carbene isomer was seen by NMR: ^1H NMR (acetone-d_6, 500 MHz) δ 7.45 (d, J = 7 Hz, o-C_6H_5), 7.30 (t, J = 7 Hz, m-C_6H_5), 7.23 (t, J = 7 Hz, $=CH$), 7.17 (t, J = 7 Hz, p-C_6H_5), 5.00 (s, C_5H_5), 4.95 (s, C_5H_5), 4.18 (dq, J = 15.3, 6.4 Hz, 1 H, CHH), 4.08 (dq, J = 15.3, 7.7 Hz, 1 H, CHH); $^{13}C\{^1H\}$ NMR (acetone-d_6, 125 MHz) δ 270.6, 267.8 (μ-C and μ-CO), 212.7 (CO), 144.2 (ipso, C_6H_5), 139.1 ($=CH$), 129.0 (C_6H_5), 126.3 (C_6H_5), 88.8 (C_5H_5), 88.0 (C_5H_5), 43.8 (CH_2); IR (CH_2Cl_2) 1997 (s), 1959 (m), 1788 (m) cm^{-1}; HRMS calcd for $C_{22}H_{18}Fe_2O_3$ 441.9954, found 441.9954.

Kinetics of Reaction of 1 with *trans*-2-Butene. A solution of **1** (38 mg, 0.079 mmol) and triphenylmethane (19 mg, 0.078 mmol) in CH_2Cl_2 (34 mL) was prepared in a dry box. Three 10-mL aliquots were each added to a 50-mL flask containing a magnetic stirring bar, fitted with a Teflon vacuum stopcock adapter, and cooled immediately in liquid nitrogen to prevent slow decomposition of **1**. Each of the flasks was attached to a vacuum line, and a known volume (112 mL) and pressure of *trans*-2-butene (0.37 mmol, 0.73 mmol, and 0.56 mmol) were condensed into the flask. The stopcock was closed, and the flask was removed from the vacuum line. The mixtures were stirred briefly at −78 °C to ensure dissolution of **1** and then placed in a thermostated bath at −50 ± 1 °C. The concentrations of reactants reported in Table II are corrected for the contraction of solvent upon cooling to −50 °C (the density of CH_2Cl_2 is 1.33 at 20 °C and 1.44 at −50 °C). After 21 min, the flasks initially containing 0.37 and 0.73 mmol of *trans*-2-butene were thermally quenched in a −78 °C bath. The third sample ("infinity") was main-

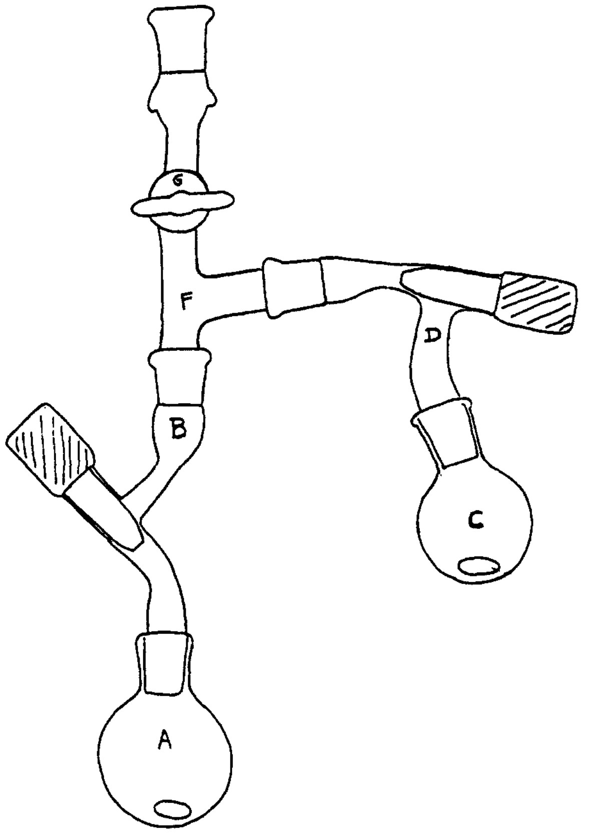

Figure 2. Apparatus used in the determination of relative rates of reaction.

tained at −50 °C for 4 h and then warmed to ambient temperature prior to workup.

The flask was reconnected to the vacuum line, and excess butene and some CH_2Cl_2 were evaporated at −78 °C under high vacuum over 1 h. The flask was again disconnected from the vacuum line, and acetone (0.5 mL) and saturated aqueous sodium bicarbonate (0.2 mL) were added at −78 °C to convert the alkylidyne complex **24** to the neutral alkenylidene complex **26**. After being warmed to ambient temperature, solvents were removed under high vacuum. The residual solids were dissolved in 10 mL of ether. The ether solution was filtered and evaporated to dryness under high vacuum. The resulting mixture of **26** and triphenylmethane was dissolved in benzene-d_6 for ^1H NMR analysis. The three samples in each of the five parallel sets of measurements summarized in Table II were treated identically. Control experiments using an alternate NMe_3 base workup at −78 °C gave similar results.

Relative Rates of Reaction of Alkenes with 1. A representative reaction using the apparatus shown in Figure 2 will be described. **1** (15 mg, 0.031 mmol) was added to flask C in a dry box. The apparatus was connected to a vacuum line, CH_2Cl_2 (5 mL) was condensed into flask C, and the mixture was stirred at −78 °C until **1** dissolved. The contents of flask C were placed under about 1 atm nitrogen pressure and stopcock D was closed. A known volume and pressure of propene (22.8 mmol), 2-methylpropene (0.45 mmol), and CH_2Cl_2 (10 mL) were condensed into flask A at liquid nitrogen temperature. With the system under high vacuum except for flask C, stopcock G was closed, and both flasks A and C were immersed in a thermostated bath at −50 °C. The cold solution of **1** was rapidly forced from C to A by inverting flask C and then sequentially opening stopcocks D and B.

After 1 h at −50 °C, the reaction was quenched by cooling to −78 °C. The apparatus was reconnected to a vacuum line, excess alkenes were removed under high vacuum at −78 °C, and a large excess of NMe_3 (~4 mmol) was condensed into the system. After 1 h at −78 °C, the mixture was warmed to ambient temperature and evaporated to dryness under high vacuum. The residue and ether (5 mL) were stirred and filtered to remove solid $NMe_3H^+PF_6^-$ and **3**. The ether solution was evaporated, and the resulting mixture of **15** and **21** was dissolved in acetone-d_6 and analyzed by quantitative integration of ^1H NMR spectra by using pulse delays of 30–60 s to avoid discrepancies in the integration due to different relaxation times.

In several cases, the base quench was performed by using 0.5 mL of saturated aqueous sodium bicarbonate. When ethylene was one of the reactants, reactions were carried out in a Fisher–Porter bottle, and the amount of ethylene in solution was estimated by condensing a known volume of ethylene into the system at −196 °C and measuring the free volume of the system and the pressure of the ethylene in the gas phase over the CH_2Cl_2 solution at −50 °C. When 1,1-diphenylethylene or styrene was used, they were measured into flask A by syringe. Poor quantitative results were obtained when styrene was one of the alkenes since extensive polymer formation made product isolation more difficult and led to uncertainties in the concentration of styrene.

Table V. Relative Rates of Reaction of Alkenes with **1**

alkenes		alkene ratio	prod. ratio	rel. rate
$CH_2{=}CHEt$	$CH_2{=}CH_2$	0.045	1.48	33
		0.024	0.72	30
$CH_2{=}CMe_2$	$CH_2{=}CHMe$	0.020	2.49	126
		0.015	1.80	120
$CH_2{=}CMe_2$	$CH_2{=}CHEt$	0.030	7.43	247
		0.026	4.95	191
trans-MeCH=CHMe	$CH_2{=}CHEt$	0.901	0.86	0.95
		0.854	0.74	0.87
cis-MeCH=CHMe	$CH_2{=}CHEt$	0.408	5.82	14.3
		0.469	6.21	13.2
$CH_2{=}CMe_2$	*trans*-MeCH=CHMe	0.019	5.99	315
$CH_2{=}CMe_2$	*cis*-MeCH=CHMe	0.156	2.29	14.7
		0.060	0.76	12.7
$CH_2{=}CHPh$	*trans*-MeCH=CHMe	1.20	6	5
		0.74	6	8
$CH_2{=}CPh_2$	$CH_2{=}CHEt$	0.294	0.82	2.8
		0.625	1.79	2.9

Table VI. Kinetic Isotope Effects[a] Determined at −50 °C

	k_H/k_D (M^+)	k_H/k_D ($M - CO^+$)	k_H/k_D ($M - 2CO^+$)	k_H/k_D NMR
$CH_2{=}CMe_2$	0.79	0.78	0.77	0.80
	0.81	0.80	0.77	0.81
	0.83	0.81	0.81	0.84
	0.83	0.82	0.80	0.86
$CH_2{=}CHMe$	0.75	0.73	0.75	0.79
	0.76	0.77	0.76	0.84
	0.71	0.70	0.70	0.72
$CH_2{=}CH_2$[b]	0.78	0.80	0.81	0.80
	0.81	0.80	0.80	0.94
	0.84	0.83	0.84	1.00
$CH_2{=}CMe(CMe_3)$	0.74	0.76		0.73
	0.69	0.70		0.67
	0.72	0.72		0.70
	0.73	0.73		0.66
trans-MeCH=CHMe	0.75	0.73	0.75	0.78
	0.77	0.74	0.75	0.73
	0.82	0.75	0.81	0.76
cis-MeCH=CHMe	1.46	1.39	1.42	1.42
	1.42	1.36	1.38	1.46
	1.51	1.42	1.49	1.72
	1.55	1.47	1.51	1.53

[a] Each line represents an independent isotope effect determination.
[b] Determined at −25 °C.

The results are summarized in Table V. The relative rate ratio was calculated by dividing the ratio of products by the ratio of starting alkenes. Since a large excess of each alkene was used, no correction was made for depletion of alkenes during the reaction.

Kinetic Isotope Effect Measurements. Details are presented for one run with isobutylene and one run with propene. The propene procedure was followed for all other alkenes except ethylene which was studied at −25 °C. The isotope effects were calculated by using the equation, $k_H/k_D = [\ln([\mathbf{1}]_t/[\mathbf{1}]_0)]/[\ln([\mathbf{1}\text{-}\boldsymbol{d}]_t/[\mathbf{1}\text{-}\boldsymbol{d}]_0)]$, where $[\mathbf{1}]_t = [\mathbf{1}]_0 - (\%d_0)$[product] and $[\mathbf{1}\text{-}\boldsymbol{d}]_t = [\mathbf{1}\text{-}\boldsymbol{d}]_0 - (\%d_1)$[product]. Table VI summarizes the results.

Isobutylene (0.04 atm, 60 mL, 0.10 mmol) was condensed into a red solution of **1** (49 mg, 0.101 mmol) and **1-*d*** (48 mg, 0.099 mmol, 100% d_1) in CH_2Cl_2 (140 mL) at −50 °C. After stirring for 25 min at −50 °C, an excess of $N(CH_3)_3$ (1.0 atm, 235 mL, 10 mmol) was added, and an immediate color change to bright red was observed. The solution was warmed to ambient temperature, and the solvent was reduced to 5 mL. Upon addition of diethyl ether (20 mL), bright red solids precipitated, and the dark red filtrate was collected. Column chromatography of the filtrate (alumina, 3:1 hexane:CH_2Cl_2) gave a mixture of **21** and **21-*d*** (23 mg, 0.058 mmol, 29%) which was further purified by HPLC.

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MS analysis: separate analysis of $\mathrm{M^+}$, $\mathrm{M - CO^+}$, and $\mathrm{M - 2CO^+}$ gave independent measures of deuterium content: **21** *m/e* (int) $\mathrm{M^+}$ 397 (0), 396 (4.1), 395 (25.1), 394 (100), 393 (3.5), 392 (13.4); $\mathrm{M - CO^+}$ 369 (0), 368 (3.7), 367 (23.5), 366 (100), 365 (3.7), 364 (13.5); $\mathrm{M - 2CO^+}$ 341 (0), 340 4.4), 339 (22.3), 338 (100), 337 (4.0), 336 (13.7). **21** + **21-*d*** *m/e* (int) $\mathrm{M^+}$ 397 (0.0), 396 (31.7), 395 (137.4), 394 (100), 393 (17.3), 392 (12.3) [45.9% **21**, 54.1% **21-*d***]; $\mathrm{M - CO^+}$ 369 (4.5), 368 (29.9), 367 (137.0), 366 (100), 365 (17.6), 364 (12.5) [45.5% **21**, 54.5% **21-*d***]; $\mathrm{M - 2CO^+}$ 341 (6.3), 340 (30.2), 339 (136.3), 338 (100), 337 (17.5), 336 (12.4) [45.3% **21**, 54.7% **21-*d***]. ^{1}H NMR analysis ($\mathrm{CD_2Cl_2}$) δ 6.95 (1.00 H, =CH), 4.96 (9.96 H, $\mathrm{C_5H_5}$), 2.80 (0.460 H, CH), 1.25 (6.08 H, $\mathrm{CH_3}$) [46.0% **21**, 54.0% **21-*d***].

Reaction of propene (0.13 atm, 60 mL, 0.33 mmol) with **1** (66 mg, 0.136 mmol) and **1-*d*** (64 mg, 0.132 mmol, 100% d_1) in $\mathrm{CH_2Cl_2}$ (130 mL) at −50 °C for 2 h followed by a $\mathrm{N(CH_3)_3}$ (1.0 atm, 235 mL, 10 mmol) qunch gave **15** and **15-*d*** (23 mg, 0.061 mmol, 23%) which were purified by column chromatography and HPLC before analysis.

MS analysis: separate analysis of $\mathrm{M^+}$, $\mathrm{M - CO^+}$, and $\mathrm{M - 2CO^+}$ gave independent measures of deuterium content: **15** *m/e* (int) $\mathrm{M^+}$ 383 (0), 382 (3.8), 381 (23.5), 380 (100), 379 (3.0), 378 (13.0); $\mathrm{M - CO^+}$ 355 (0), 354 (3.8), 353 (22.3), 352 (100), 351 (3.2), 350 (13.3); $\mathrm{M - 2CO^+}$ 327 (0), 326 (6.0), 325 (21.5), 324 (100), 323 (3.4), 322 (13.1). **15** + **15-*d*** *m/e* (int) $\mathrm{M^+}$ 383 (4.9), 382 (31.9), 381 (141.5), 380 (100), 379 (18.0), 378 (12.8) [44.8% **15**, 55.2% **15-*d***]; $\mathrm{M - CO^+}$ 355 (4.6), 354 (30.3), 353 (142.2), 352 (100), 351 (19.3), 350 (14.0) [44.3% **15**, 55.7% **15-*d***]; $\mathrm{M - 2CO^+}$ 327 (0.0), 326 (37.2), 325 (139.0), 324 (100), 323 (18.8), 322 (13.0), [44.8% **15**, 55.2% **15-*d***]. ^{1}H NMR analysis ($\mathrm{CD_2Cl_2}$) δ 7.08 (1.00 H, =CH), 4.9 (10.00 H, $\mathrm{C_5H_5}$), 2.7 (1.456 H, $\mathrm{CH_2}$ and CHD), 1.17 (3.05 H, $\mathrm{CH_3}$) [45.6% **15**, 54.4% **15-*d***].

(*E*)-1,2-Dideuterio-3,3-dimethyl-1-butene (23-*E*).[31] 3,3-Dimethyl-1-butyne (1.32 atm, 235 mL, 12.8 mmol) was condensed into a solution of $\mathrm{(C_5H_5)_2ZrDCl}$ (3.11 g, 12.02 mmol) in toluene (120 mL) at −78 °C. The reaction mixture was stirred at ambient temperature for 2 h. Solvent was evaporated, and the residue was dried under high vacuum for 3 h. Dilute $\mathrm{D_2SO_4}$ (20 mL, 1 M) was added to the residue at −78 °C via syringe. The aqueous solution was stirred for 2 h at ambient temperature. Volatiles were vacuum transferred onto $\mathrm{P_2O_5}$ and then into a storage vessel. **23-E** was isolated as a clear liquid (0.75 atm, 235 mL, 7.3 mmol, 61%) without further purification: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 4.902 (t, J_{DH} = 2.64 Hz, =CHD), 1.015 (s, $\mathrm{C(CH_3)_3}$).

(*Z*)-1,2-Dideutertio-3,3-dimethyl-1-butene (23-Z).[31] 1-Deuterio-3,3-dimethyl-1-butene (1.71 atm, 235 mL, 16.6 mmol) was added to a solution of $\mathrm{(C_5H_5)_2ZrDCl}$ (3.9 g, 15.1 mmol) in toluene (250 mL) at −78 °C. Workup with $\mathrm{H_2SO_4}$ as described above gave **23-Z** (0.95 atm, 235 mL, 9.2 mmol, 61%) as a clear liquid: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 4.817 (t, J_{DH} = 1.7 Hz, =CHD), 1.015 (s, $\mathrm{C(CH_3)_3}$).

Reaction of 1 with 23-E. **23-E** (0.20 atm, 8 mL, 65 µmol) was condensed into an NMR tube containing a suspension of **1** (13 mg, 27 µmol) in $\mathrm{CD_2Cl_2}$ (0.51 mL) at −78 °C. The NMR tube was sealed under vacuum, warmed to ambient temperature, and centrifuged. Prompt ^{1}H NMR analysis revealed **10**-threo and **23-E** as the major components: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 5.36 (s, $\mathrm{C_5H_5}$), 1.95 (br d, J = 11.91 Hz, $\omega_{1/2}$ = 6 Hz, µ-CCHDC*H*D), 1.14 (s, $\mathrm{C(CH_3)_3}$).

Reaction of 1 with 23-Z. **23-Z** (0.20 atm, 8 mL, 65 µmol) was condensed into a suspension of **1** (12 mg, 25 µmol) in $\mathrm{CD_2Cl_2}$ (0.42 mL) at −78 °C. Prompt ^{1}H NMR analysis revealed **10**-erythro and **23-Z** as the major components: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 5.36 (s, $\mathrm{C_5H_5}$), 1.96 (br s, $\omega_{1/2}$ = 11 Hz, µ-CHDC*H*D), 1.14 (s, $\mathrm{C(CH_3)_3}$).

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Formation of Diiron µ-Alkenyl Complexes from the Reaction of a µ-Methylidyne Complex with Selected Alkenes

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Abstract: Reaction of $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-}$, **1**, with 1-methylcyclohexene produced $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(\mathit{E})\text{-}CH{=}CH\overline{C(CH_3)CH_2CH_2CH_2C}H_2]^+PF_6^-}$, **2**, in 72% yield. (2-Methyl-1-propenyl)benzene and *trans*-stilbene reacted with **1** to give $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(\mathit{E})\text{-}CH{=}CHC(CH_3)_2(C_6H_5)]^+PF_6^-}$, **3**, and $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(\mathit{E})\text{-}CH{=}CHCH(C_6H_5)_2]^+PF_6^-}$, **4**, in 71% and 57% yields. **4** was also obtained from reaction of **1** with 1,1-diphenylethylene in 83% yield. **1** reacted with α-methylstyrene and 2,3,3-trimethyl-1-butene to give $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(\mathit{E})\text{-}CH{=}CHCH(CH_3)(C_6H_5)]^+PF_6^-}$, **6**, and $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(\mathit{E})\text{-}CH{=}CHCH(CH_3)C(CH_3)_3]^+PF_6^-}$, **7**; in 59% and 78% yields. The reaction of **1-d** with 1-methylcyclohexene, 1,1-diphenylethylene, α-methylstyrene, and 2,3,3-trimethyl-1-butene gave the µ-alkenyl complexes with the deuterium label exclusively on the bridging alkenyl carbon. The secondary deuterium kinetic isotope effect for the reaction of 2,3,3-trimethyl-1-butene with **1** was found to be 0.72. The regiochemistry and kinetic isotope effect are consistent with electrophilic addition of **1** to the alkene which produces a carbocation intermediate. Subsequently, this intermediate rearranges by a 1,2-hydrogen or carbon shift to produce the µ-alkenyl product.

The cationic µ-methylidyne complex $\mathrm{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-}$, **1**, forms 1:1 adducts with nucleophiles such as $\mathrm{NMe_3}$ and CO.[1,2] **1** also reacts with alkenes such as ethylene, propene, and isobutylene to add the C–H bond of the methylidyne ligand across the carbon–carbon double bond and to produce new µ-alkylidyne complexes.[3,4] The regiochemistry of this hydrocarbation reaction indicates that the methylidyne carbon acts as an electrophile which adds to the least-substituted carbon of the carbon–carbon double bond.

In the course of examining the scope of the reaction of methylidyne complex **1** with alkenes, we discovered that several

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