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Synthesis, Spectral Characterization, and Alkylidene Transfer Reactions of Electrophilic Iron Carbene Complexes $Cp(CO)(L)Fe{=}CHR^+$, $L = CO, P(C_6H_5)_3$; $R = CH_3, CH_2CH_3, CH(CH_3)_2$

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Abstract: The α-ether complexes $Cp(CO)(L)FeCH(OCH_3)R$ ($L = CO, P(C_6H_5)_3$; $R = CH_3, CH_2CH_3, CH(CH_3)_2$) have been prepared in good yields from readily available acetyl complexes, $Cp(CO)(L)FeCOR$, by O-methylation followed by reduction with borohydride. These ether complexes are rapidly converted to the corresponding cationic carbene complexes, $Cp(CO)(L)Fe{=}CHR^+$, via ionization with trimethylsilyl triflate at −78 °C. The triphenylphosphine-substituted species, $Cp(CO)(P(C_6H_5)_3)Fe{=}CHR^+$, have been characterized in solution with ^1H and ^{13}C NMR spectroscopy. The $Cp(CO)_2Fe{=}CHR^+$ species are too unstable to observe directly; however, decomposition products have been characterized. For $R = CH_3$ an unusual cationic binuclear complex **6** is formed, while for $R = CH_2CH_3$ and $CH(CH_3)_2$ intramolecular hydride migration occurs to give the alkene complexes $Cp(CO)_2Fe(CH_3CH{=}CH_2)^+$ and $Cp(CO)_2Fe((CH_3)_2C{=}CH_2)^+$. When $Cp(CO)_2Fe{=}CHCH_3^+$ is generated in situ at −78 °C in the presence of a variety of alkenes, ethylidene transfer occurs to give methylcyclopropanes in good yields. Very high to moderate cis stereoselectivity is generally observed for polysubstituted alkenes. The ease of preparation and handling of $Cp(CO)_2FeCH(OCH_3)CH_3$ and mild reaction conditions make this ethylidene transfer procedure attractive for synthesis of methyl-substituted cyclopropanes.

Although numerous electrophilic transition-metal carbene complexes stabilized by α-heteroatoms or α-aryl substituents are known,[1] few simple complexes possessing only α-hydrogens or α-alkyl substituents have been characterized. The latter complexes can be rapidly enumerated: $Cp(NO)(P(C_6H_5)_3)Re{=}CH_2^+$;[2] $Cp(diphos)Fe{=}CH_2^+$;[3] $Cp(CO)_2M{=}C(CH_3)_2$, ($M = Mn, Re$);[4] $Cp(NO)(P(C_6H_5)_3)Re{=}CHR^+$, ($R = CH_3, CH_2CH_3$);[5] $Cp(diphos)Fe{=}CHC(CH_3)_3^+$;[6] $Cp(CO)_2Re{=}C(CH_3)(Si(CH_3)_3)$.[7] As part of the work described herein, we report the spectral characterization of $Cp(P(C_6H_5)_3)(CO)Fe{=}CHR^+$, ($R = CH_3, CH_2CH_3, CH(CH_3)_2$). $Cp(L)(CO)Fe{=}CHCH_3^+$, ($L = P(C_6H_5)_3, P(OC_6H_5)_3$) has also been characterized by Cutler.[8]

Evidence has steadily accumulated that, unlike heteroatom-stabilized complexes,[9] highly electrophilic carbene complexes readily transfer the carbene ligand to unactivated olefins to form the corresponding cyclopropane. Thus, rapid methylene transfer to simple alkenes has been observed for the species $Cp(CO)(L)Fe{=}CH_2^+$, ($L = CO, P(C_6H_5)_3$)[10] generated in situ via ionization of various $Cp(CO)(L)FeCH_2X$ derivatives.[11] Within this series, the readily isolable complex $Cp(CO)_2FeCH_2S(CH_3)_2^+\ BF_4^-$ developed by Helquist appears most useful as a synthetic methylene transfer reagent.[11d] Stabilization of the methylene complex is observed in $Cp(diphos)Fe{=}CH_2^+$ where carbene transfer is slow.[3] Reactions of $Cp(NO)(P(C_6H_5)_3)Re{=}CH_2^+$ with alkenes have not been described.[2]

Efficient and stereoselective transfer of benzylidene has been effected with $(CO)_5W{=}CHC_6H_5$[12] and $Cp(CO)_2Fe{=}CHC_6H_5^+$.[13] Employing the latter system, we have obtained good yields of phenylcyclopropanes (ranging from 75–93%) from a wide variety of alkenes. For all alkenes studied, the *cis-* or *syn*-phenylcyclopropanes were formed with high stereoselectivity. For example, monosubstituted ethylenes react to form cis isomers with ratios varying from 4.6 to >100. These early results suggested that transition-metal carbene complexes can be developed as general reagents for cyclopropane formation. Furthermore, a clear need exists for efficient methods to transfer simple, alkyl-substituted carbenes to olefins.

Current routes to alkylcyclopropanes via intermolecular transfer of alkylcarbenes to alkenes are usually inefficient, with yields limited by intramolecular rearrangement of the carbene or carbenoid.[14,15] Observations by Casey[16] and Rosenblum[17] suggest

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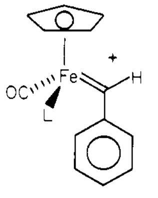
Table I. Characterization of $Cp(L)(CO)FeCH(OCH_3)R$

L	R	% yield			^1H NMR (C_6D_6), δ, and ^{13}C NMR (C_6D_6), ppm				IR (CH_2Cl_2), 25 °C, ν_{CO}, cm^{-1}
					Cp	CH	OCH_3	other absorptions, R, CO, etc.	
CO	CH_3	91		^1H	4.39 (s)	4.94 (q, J_{HH} = 6 Hz)	3.23 (s)	1.81 (d, J_{HH} = 6 Hz, CH_3)	1998, 1938
				^{13}C	87.2	81.1 (J_{PC} = 22 Hz)	58.0	29.1 (CH_3) 217.9, 219 (CO)	
	CH_2CH_3	86		^1H	4.33 (s)	4.69, (dd, J_{HH} = 3, 9 Hz)	3.25 (s)	2.01 (m, CH_2) 1.14 (t, J_{HH} = 6 Hz, CH_3)	1995, 1935
	$CH(CH_3)_2$	82		^1H	4.34 (s)	4.57 (br d, J_{HH} = 6.9 Hz)	3.27 (s)	1.99 (m, CH) 1.10, 1.28 (d, d, J_{HH} = 6.9 Hz, CH_3)	1996, 1940
$P(C_6H_5)_3$[a]	CH_3	95	A 41%	^1H	4.44	3.95 (m)	3.37 (s)	1.92 (d, J_{HH} = 6 Hz, CH_3)	1896
				^{13}C	85.6	81.7 (J_{PC} = 17 Hz)	57.85	31.6 (CH_3) 222.6 (J_{PC} = 33 Hz, CO)	
			B 59%	^1H	4.48	3.95 (m)	3.06 (s)	1.94 (d, d, J_{HH} = 6 Hz, J_{PH} = 1 Hz, CH_3)	
				^{13}C	85.6	81.1 (J_{PC} = 22 Hz)	58.9	29.1 (CH_3) 223.9 (J_{PC} = 28 Hz, CO)	
	CH_2CH_3	72	A 76%	^1H	4.50	3.99 (m)	3.52 (s)	1.98 (m, CH_2) 0.98 (t, J = 6.6 Hz, CH_3)	1910
				^{13}C	84.7	89.1 (J_{PC} = 25 Hz)	58.8	15.5 (CH_2) 50.9 (CH_3) 222.6 (J_{PC} = 25 Hz, CO)	
			B 24%	^1H	4.52	3.99 (m)	2.98 (s)	1.85 (m, CH_2) 1.25 (t, J = 6.6 Hz, CH_3)	
				^{13}C	85.5	90.1 (J_{PC} = 27 Hz)		223.9 (J_{PC} = 33 Hz, CO)	
	$CH(CH_3)_2$	60	A 49%	^1H	4.04	4.35 (m)	3.54 (s)	1.69 (m, CH) 1.44, 0.88 (d, J_{HH} = 6.1 Hz, CH_3)	1898
			B 51%	^1H	4.06	4.35 (m)	3.40 (s)	1.69 (m, CH) 1.44, 0.88 (d, J_{HH} = 6.1 Hz, CH_3)	

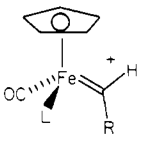
[a] Diastereomeric products resulted. Isomers, labeled A and B, could be observed spectroscopically. Relative amounts are shown here as a percentage of overall yield. In NMR studies, phenyl protons absorb broadly, δ 7.0–8.0, with aryl carbons at 125–140 ppm. All ^1H Cp resonances in this series appear as doublets with J_{PH} ca. 0.9 Hz.

that similar limitations might exist with electrophilic alkylcarbene transition-metal complexes due to a propensity to isomerize to olefin complexes. Nevertheless, stable alkylcarbene complexes analogous to the benzylidene complexes **1**[13,18] previously studied in these laboratories, have been reported. This led us to investigate the synthesis, stability, and transfer chemistry of the alkyl-substituted complexes, **2**.



1

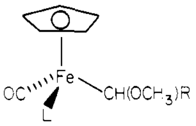
L = CO, $P(C_6H_5)_3$



2

R = CH_3, CH_2CH_3, $CH(CH_3)_2$

2a, L = $P(C_6H_5)_3$
2b, L = CO



3

R = CH_3, CH_2CH_3, $CH(CH_3)_2$

3a, L = $P(C_6H_5)_3$
3b, L = CO

We report here: (1) a simple, general synthesis of precursors to **2**, the series of α ethers $Cp(CO)(L)FeCH(OCH_3)R$ **3**, (2) the generation and spectral characterization of carbene complexes **2a**, (3) the mode of decomposition for complexes **2b**, and (4) the susccessful transfer of ethylidene from **3b** (R = CH_3) to simple alkenes to form methyl cyclopropanes. A preliminary account of part of this work has previously appeared.[19] Concurrently, Helquist described the use of $Cp(CO)_2FeCH(CH_3)S(CH_3)_2^+$ for transfer of ethylidene to alkenes.[20]

Results and Discussion

Summarized in Scheme I are the general syntheses of the carbene precursors, **3a**,**b**, their conversion to the corresponding alkylidene complexes, **2a**,**b**, and the transfer of the ethylidene moiety to olefins to form methylcyclopropanes. A detailed account of these results follows.

Synthesis and Characterization of Carbene Precursors. Alkylation of readily accessible acyl complexes **4** (Scheme I) with excess methyl triflate in methylene chloride at 25 °C proceeds rapidly and quantitatively to generate the methoxy carbene complexes **5**. Methylation of the more basic phosphine-substituted acyls normally requires only ca. 6 h, while the less basic dicarbonyl complexes require ca. 24 h for complete methylation. Metal carbonyl stretching frequencies provide a good method for monitoring the progress of these reactions (see Experimental Section). Hydride reduction of the heteroatom-stabilized carbenes is accomplished by quenching the methylene chloride solutions of **5a** and **5b** into $CH_3OH/CH_3O^-/BH_4^-$ at −78 °C. Dilution with water, followed by extraction with methylene chloride, gave the spectroscopically pure ethers **3a** and **3b** in good yields. For ethers **3a**, formation of two diastereomers is possible, and in all cases examined, substantial amounts of both diastereomers are observed. No attempt was made to separate the diastereomers. Yields, diastereomer ratios, and spectroscopic data for these α ethers are summarized in Table I.

Efficient conversions of acyl complexes, $Cp(CO)(L)FeC(O)CH_3$, to the corresponding α ethers have been reported by Green utilizing $NaBH_4/C_2H_5OH$.[21] Davison and Reger, however, report

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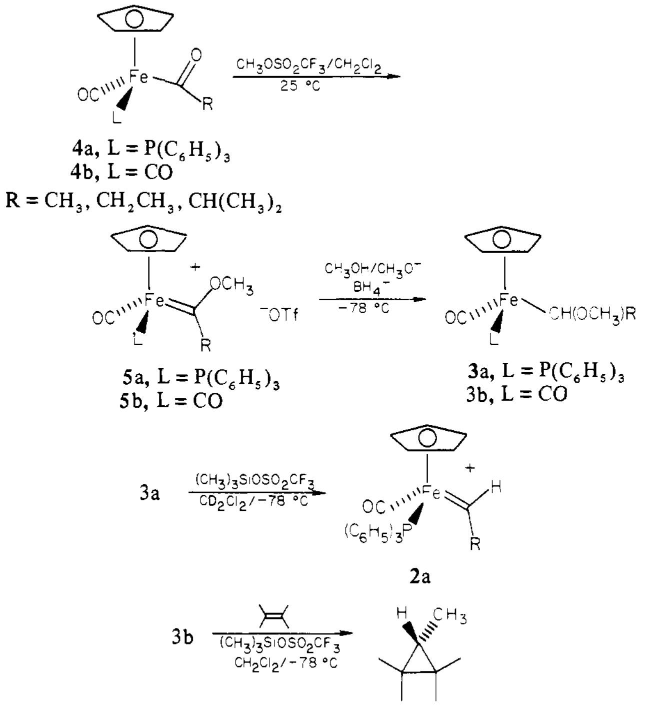
Table II. Spectral Characterization of Alkylidene Complexes, $Cp(CO)(L)Fe{=}CHR^+$

L	R	$t_{1/2}$, h (T, °C)		^1H NMR (CD_2Cl_2), δ, ^{13}C NMR (CD_2Cl_2), ppm				
				Cp	$P(C_6H_5)_3$	CO	CH_α	other absorptions, R
$P(C_6H_5)_3$	CH_3[a]	3 (25)	^1H	5.25 (d, J_{Ph} = 2 Hz)	7.1-7.8 (m)		17.94 (q, J_{HH} = 7.8 Hz)	2.8 (d, J_{HH} = 7.8 Hz, CH_3)
			^{13}C	93.4 (s)	125-135	213.4 (d, J_{PC} = 28.7 Hz)	380.0 (J_{PC} = 25.1 Hz)	51.0 (s, CH_3)
	CH_2CH_3[b]	1 (−40)	^1H	5.25 (br s)	7.1-7.8 (m)		17.52 (br s)	2.96 (br s, CH_2) 0.90 (br s, CH_3)
			^{13}C	93.0 (s)	125-135	213 (d, J_{PC} = 28.6 Hz)	383.2 (d, J_{PC} = 25.1 Hz)	48.3 (s, CH_2), CH_3 (obscured by Me_3Si)
	$CH(CH_3)_2$[c]	<0.5 (−65)	^1H				(17.8)	
CO	R[d]							

[a] Spectra at 0 °C. [b] Spectra at −78 °C. [c] Spectra at −78 °C. Spectra broad and complex. Rapid decomposition even at −78 °C. [d] Decomposition of all compounds is rapid at low temperatures. No carbene spectra were observed. See text.

Scheme I

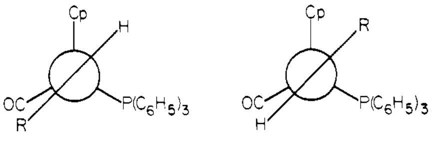


overreduction with these reagents, yielding mixtures of α-ethers and alkyl complexes.[22] An alkyl complex most likely arises from reduction of an alkylidene complex derived from acid-catalyzed elimination of the α ether. Under basic conditions, we have been able to avoid overreduction to the metal alkyls.

Cutler[8] has recently succeeded in preparing organoiron η^1-α-alkoxyethyl compounds, $Cp(CO)(L)FeCH(OCH_3)CH_3$(L = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$), from the requisite alkoxycarbene complexes by reduction with lithium triethylborohydride in THF at −80 °C. Yields of 70–95% were obtained. No overreduction to the alkyl metal complex was noted. Either $NaBH_4$ or $Li(C_2H_5)_3BH$ appears to be a more versatile reducing agent for this purpose than the organoiron hydride, Cp(dppe)FeH, previously reported by Cutler.[23] This organotransition-metal hydride has been shown to dealkylate certain heteroatom carbenes to the corresponding acyl complexes. In none of these cases have attempts been reported to prepare other than the α-alkoxyethyl complexes.

Spectroscopic Observations of Alkylidene Complexes and Their Rearrangement Products. A. $Cp(CO)(P(C_6H_5)_3)Fe{=}CHR^+$ Complexes, 2a. Diastereomeric mixtures of the α-methyl ethers, **3a**, react quantitatively in CD_2Cl_2 at −78 °C with trimethylsilyl triflate (Me_3SiOTf) to yield the corresponding alkylidene complexes **2a**. Both the ethylidene (R = CH_3) and propylidene (R = CH_2CH_3) complexes are readily characterized by ^1H and ^{13}C NMR spectroscopy. Table II summarizes spectral details. At −78 °C in CD_2Cl_2 characteristic ^1H absorptions for H_α appear at δ 17.94 (J_{H-CH_3} = 7.8 Hz) for the former and δ 17.52 (br) for the latter. Furthermore, the low-field ^{13}C resonances of the carbene carbon at 380 ppm (CD_2Cl_2, O °C) and 383 ppm (CD_2Cl_2, −78 °C), respectively, clearly establish these solution species as cationic alkylidene complexes analogous to other highly electrophilic carbene complexes.[2,3,5,6,13,18] Only tentative evidence has been obtained for the existence of the isobutylidene complex **2a** (R = $CH(CH_3)_2$) at −78 °C.[24]

The ^1H shifts reported for **2a** (R = CH_3) agree with those reported by Cutler[8] for **2a** (R = CH_3) (δ 17.85) generated in TFA. The close correspondence of these chemical shifts to those of the analogous benzylidene complexes, as well as the lack of coupling to ^{31}P, suggests a similarity in structure between alkylidene and benzylidene complexes. Although the precise geometry remains uncertain, calculations suggest that in unsymmetrically substituted complexes of the type, $CpLL'M{=}CR_2$, the carbene plane will be aligned with the Fe–L bond of the better π acceptor.[25] This prediction is supported by the X-ray structure of $CpRe(NO)(PPh_3)CHO$.[26a] Such geometries have also been verified by Gladysz for $Cp(NO)(PPh_3)Re{=}CHC_6H_5$.[5,26b] Thus, the two most likely structures for the alkylidene complexes are anticlinal **2a** and synclinal **2a**. On the basis of steric considerations, anticlinal **2a** is likely the more stable.



anticlinal 2a synclinal 2a

The effect of the added β-CH_3 substituent in the propylidene complex **2a** (R = CH_2CH_3) on the rate and mechanism of thermal decomposition relative to **2a** (R = CH_3) is of considerable interest. Whereas the triflate salt of the ethylidene complex is stable for short periods of time at 25 °C ($t_{1/2}$ ca. 3 h, CH_2Cl_2), the propylidene complex undergoes isomerization exclusively by the in-

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[24] A broad ^1H NMR spectrum is obtained at −78 °C. A rapidly fading, broad low-field absorption observed at δ 17.8 may indicate the presence of the carbene complex; however, its integrated intensity relative to the 15 H $P(C_6H_5)_3$ absorption is considerably less than that of 1 H.

[25] (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592–598. (b) Extended Hückel calculations by R. Hoffmann and O. Eisenstein (unpublished results) indicate that the lowest energy conformations for $CpFe(PH_3)(NO)(CH_2)^{2+}$ are those in which the methylene plane is aligned with the iron–nitrosyl bond.

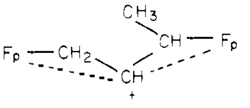
[26] (a) Wong, W.-K.; Tam. W.; Strouse, E. C.; Gladysz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 530–532. (b) Gladysz has recently determined the structure of the thermodynamically most stable isomer of $Cp(PPh_3)(NO)Re{=}CHC_6H_5^+$ by X-ray diffraction. It is the anticlinal isomer with the carbene plane aligned with the nitrosyl ligand: Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

tramolecular hydrogen migration even at −40 °C ($t_{1/2}$ ca. 1 h CD_2Cl_2) to the two diastereomeric propene complexes, $Cp(CO)(PPh_3)Fe(CH_3CH{=}CH_2)^+$. This isomerization results initially in preferential formation of the thermodynamically less stable diastereomer (>90%). At higher temperature equilibration with the thermodynamically favored diastereomer (>80%) occurs, likely via dissociation of the propene.[27]

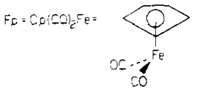
In contrast to the propylidene system, only a minor amount (<10%) of the olefin complex $Cp(CO)(PPh_3)Fe(C_2H_4)^+$ is formed during thermal decomposition of the ethylidene complex **2a** (R = CH_3).[29] The decomposition material, due to excessively broad and complex spectra, has not been characterized. It may be a binuclear, cationic complex analogous to that observed by Cutler for $Cp(CO)_2Fe{=}CHCH_3^+$[8] (see below).

It is clear from these results that the activation energy for the intramolecular hydrogen migration in the propylidene complex is much less than that for the ethylidene complex. Such a difference in activation energies seems best explained by viewing the isomerization as a hydride migration to a neighboring carbonium ion center with substantial accumulation of positive charge on the β-carbon in the transition state. Thus, carbonium ion stabilizing substituents at the β-carbon, such as alkyl groups, would be expected to accelerate the hydride migration. The expected additional increase in rate of hydride migration in the isobutylidene complex may account for our inability to cleanly generate and observe this species at −78 °C.[24]

B. Attempted Spectral Observation of $Cp(CO)_2Fe{=}CHR^+$ Complexes 2b. The series of α ethers $Cp(CO)_2FeCH(OCH_3)R$, **3b**, were ionized (Me_3SiOTf/CD_2Cl_2/−78 °C) by using procedures similar to those used for **3a**. In no case could any carbene complex be detected spectroscopically when solutions were monitored immediately after generation at −78 °C. Although apparently formed (see below), all these alkylidene complexes react/rearrange rapidly at −78 °C. The unobserved ethylidene complex **2b** (R = CH_3) yields a mixture of two fluxional cationic diastereomeric binuclear complexes **6** which have been identified and characterized by Cutler.[8] These complexes apparently arise via elimination of a proton from **2b** (R = CH_3) to form σ-vinyl complex, $Cp(CO)_2FeCH{=}CH_2$, followed by reaction of this vinyl complex with remaining **2b** (R = CH_3).[8] Under the conditions we employ, less than 10% of the ethylene complex, $Cp(CO)_2Fe(C_2H_4)^+$, is observed.[29]

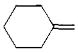
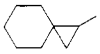
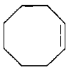
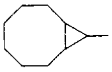
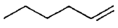
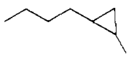
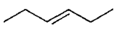
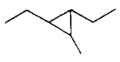
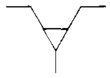
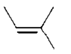
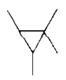
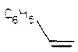
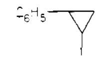


6

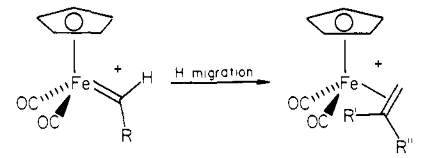


Similar to their triphenylphosphine analogues, propylidene **2b** (R = CH_2CH_3) and isobutylidene **2c** (R = $CH(CH_3)_2$) complexes rearrange quantitatively to $Cp(CO)_2Fe(CH_3CH{=}CH_2)^+$ (**7**) and $Cp(CO)_2Fe((CH_3)_2C{=}CH_2)^+$ (**8**) via intramolecular hydride migrations.

Table III. Ethylidene Transfers to Alkenes from $Cp(CO)_2FeCH(OCH_3)CH_3$

alkene	cyclopropane	% yield of alkene:precursor ratio 4:1	2:1	1:1	1:2	isomer ratio, cis/trans, syn/anti
			86	67	99	*a*
			60	25	87	>25:1
		48	28			1:1
			3.4			*a*
			58			>50:1[a]
			52			>50:1[a]
			75	47	91	4.7:1

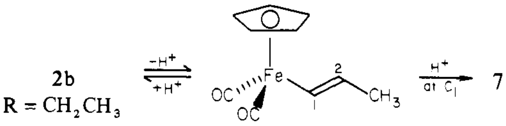
[a] Only one product could be detected.



2b
R = CH_2CH_3, $CH(CH_3)_2$

7, R′ = CH_3; R″ = H
8, R′, R″ = CH_3

An alternative route via a σ-vinyl complex, **9**, was ruled out by ionization of the methyl ether **3b** (R = CH_2CH_3) in TFA-*d*. No deuterium is incorporated into the olefin complex. Our results may be compared to those of Rosenblum[17] who observed that protonation of $Fp\text{-}c\text{-}C_3H_5$ at 25 °C led only to the propene complex, **7**, presumably via the intermediacy of **2b** (R = CH_2CH_3).



Ethylidene Transfer Reactions. Despite its thermal instability, the short-lived ethylidene complex **2b** (R = CH_3) reacts with olefins at −78 °C to form methylcyclopropanes (see Scheme I). Rapid and efficient transfer of ethylidene is observed when a 2-fold excess of complex **3b** (R = CH_3) is treated in situ with Me_3SiOTf (CH_2Cl_2, −78 °C) in the presence of alkene. A summary of product yields and stereochemistries are shown in Table III while the respective spectral data are given in the Experimental Section. Yields of cyclopropane decrease when the molar ratio of **3b** (R = CH_3) to alkene is lowered to 1:1. This suggests that decomposition of the carbene is competitive with transfer of the ethylidene. In accord with this interpretation, yields again increase when olefin is employed in 2-fold excess. The short reaction time (5 min) and a rapid, basic workup are necessary to prevent acid-catalyzed isomerization of the cyclopropanes to olefins.

The stereochemistries of the methylcyclopropanes can be established unambiguously by ^1H and ^{13}C NMR spectroscopy. The *cis*- and *trans*-1-methyl-2-phenylcyclopropanes exhibit spectra identical with those previously reported.[12b,30] Characteristic cis

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(27) (a) These two diastereomeric propene complexes have been previously spectroscopically observed upon protonation of $Cp(CO)(P(C_6H_5)_3)FeCH_2CH{=}CH_2$. The ^1H NMR data reported by Brown in SO_2 at −10 °C agree closely with those reported here. The major isomer observed by Brown at −10 °C corresponds to our "thermodynamic" isomer which grows in rapidly at −10 °C.: Aris, K. R.; Brown, J. M.; Taylor, K. A. *J. Chem. Soc. Dalton Trans.* **1974**, 2222. (b) Observation of two species could be accounted for by assuming formation of only *one* diastereomer which exists as two rotameric forms with a high barrier to rotation about the iron–propene bond. The observed barrier for ethylene rotation in $Cp(CO)(P(C_5H_5)_3)Fe(C_2H_4)^+$ is 10 kcal/mol.[28a] If a similar barrier applies to the propene complex, it is far too low to account for our observations. Reger has isolated diastereomeric mixtures of propene complex for $Cp(CO)(P(OC_6H_5)_3)Fe(CH_3CH{=}CH_2)^+$.[28a]

(28) (a) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3270–3273. (b) Reger, D. L.; Coleman, C. J. *Ibid.* **1979**, *18*, 3155–3160.

(29) In the decomposition of both $Cp(CO)_2Fe{=}CHCH_3^+$ and $Cp(CO)(P(C_6H_5)_3)Fe{=}CHCH_3^+$ in TFA, Cutler[8] observes substantially more of the isomeric ethylene complexes than reported here. This suggests that the competition between the intramolecular hydrogen migration reactions and the other modes of decomposition is likely solvent dependent.

(30) (a) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042–4053. (b) Mathias, R.; Weyerstahl, P. *Chem. Ber.* **1979**, *112*, 3041–3053.

vicinal coupling, $J_{H_1H_9} = J_{H_8H_9} = 8.5$ Hz, established the *endo*-9-methylbicyclo[6.1.0]nonane as the major product isolated from cyclooctene. A minor product (<4%) contaminated with isomeric olefins gives an ^{1}H NMR consistent with the exo-methyl isomer.

Chemical shift analysis established the stereochemistry of the 1-butyl-2-methylcyclopropanes. Cyclopropyl protons are shielded by *cis* alkyl groups. Thus, *cis*-1-butyl-2-methylcyclopropane, with one methylene proton cis to both substituents, is characterized by one unique high-field resonance, δ -0.38. The three remaining ring hydrogens fall in a broad complex envelope, δ 0.5–0.8. In the trans isomer where all cyclopropyl protons are cis to one alkyl group, both methylene protons absorb together, δ 0.11, as do the two tertiary cyclopropyl protons, δ 0.34. Similar arguments establish the stereochemistry of the single product detected from ethylidene addition to *cis*-3-hexene. All cyclopropyl resonances absorb below δ 0.5 with no high-field resonance noted. Thus, the *all-cis*-1,1-diethyl-3-methylcyclopropane was obtained with isomer ratio >50:1. In contrast, the *trans*-1,2-diethyl-3-methylcyclopropane, the only possible cyclopropane from *trans*-3-hexene, gives an expected high-field resonance, δ -0.03, for the unique proton cis to two alkyl groups, with the remaining cyclopropyl absorptions at δ 0.30 and δ 0.45.

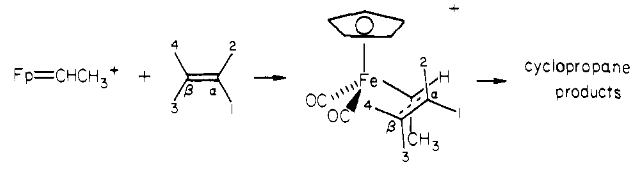
The diasterotopic *gem*-dimethyl groups of 1,1-cis-2,3-tetramethylcyclopropane observed in both the ^{1}H and ^{13}C NMR spectra provide positive identification for the single isolated product of ethylidene addition to 2-methyl-2-butene. As above, the limit of the cis/trans isomer ratio was estimated at >50:1.

As demonstrated by the product ratios (Table III), stereoselectivity of ethylidene transfer varies widely with structure of the olefin substrate. Very little to moderate stereoselectivity is observed with monosubstituted terminal olefins. In contrast, alkylidene addition to internal olefins proceeds with high selectivity in a cis fashion. Stereochemical integrity of the alkene substituent is preserved in the final product in both *cis*- and *trans*-3-hexene.

In accord with the electrophilic nature of the ethylidene complex **2b** (R = CH_3), cyclopropane yields are greatest with those olefins most activated toward electrophilic attack (see Table III). Thus the high yields observed in reactions with methylenecyclohexane and styrene are somewhat diminished with cyclooctene and *cis*-3-hexene, and even further so in 1-hexene. A stereochemical influence is suggested in the low yields of addition to *trans*-3-hexene which may have been partially overcome in 2-methyl-2-butene (52%) by the electron-donating effect of the additional alkyl substituent.

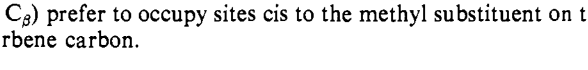
These overall yields compare favorably with the procedures established by Kawabata[15f] using $CH_3CHI_2/(CH_3CH_2)_2Zn$ as the ethylidene-transfer reagent. Ethylidene transfer to cyclohexene was reported in 66% yield with a syn:anti ratio of 1.5:1. A somewhat more direct comparison can be made with the recent report by Helquist[20] of ethylidene transfer from $Cp(CO)_2FeCH(SC_6H_5)(CH_3)$ over a period of 12–20 h at 20 °C in methyl fluorosulfonate/CH_2Cl_2. Although yields of methylcyclopropanes are somewhat less overall than those obtained in the present study, similar trends in product stereochemistry and olefin reactivity are noted.[31]

Mechanistic Considerations of Ethylidene Transfer. The highly electrophilic nature of the metal carbene complexes, $Cp(CO)_2Fe{=}CHR^+$, is reflected in their attack on alkenes. The carbene moiety is most readily transferred to the most electronically activated alkenes. This is clearly observed in the yields of methylcyclopropanes derived from reaction with the series of alkenes listed in Table III as well as in rate ratios for ethylidene transfer to ring-substituted styrenes determined in competition studies.[32] Model **10** for the transition state for ethylidene can be proposed. The electrophilic carbene attacks at C_α (the least substituted carbon) with positive charge development at C_β. Ultimately, following the transition state, the developing electrophilic center at C_β may displace Fp^+ with synchronous $C_{carbene}–C_\beta$ bond formation. Alternatively, a discrete Fe(IV) metallacycle may be formed, followed by reductive elimination.[33] Several points should be noted in connection with this model: (1) Substituents at C_β have little effect on selectivity. Thus, for styrene and 1-hexene, with single substituents at C_β, moderate to no selectivity is observed, respectively. This suggests in **10** the steric environments of sites 3 and 4 at C_β are similar. (2) Substitutents at C_α strongly control stereoselectivity. This is illustrated most clearly with 2-methyl-2-butene where the high cis selectivity (>50:1) must be dictated by the single C_α methyl substituent. The high selectivities noted for *cis*-cyclooctene and *cis*-3-hexene are then consistent with stereochemical control by the C_α substituent. The model **10** accounts for this selectivity if a staggered conformation about a well-developed $C_{carbene}–C_\alpha$ bond is assumed in which substituents will prefer to occupy site 1 between H and CH_3 as opposed to the sterically more crowded site 2 between Fp and H.[34] (3) Stereochemistry of the original double bond is maintained for both *cis*- and *trans*-3-hexene, indicating, at least for these systems, that carbonium ion development at C_β with sufficient lifetime for $C_\alpha–C_\beta$ bond rotation does not occur. (4) The extent of stereochemical control by substituents (especially at C_β) may be a sensitive function of the position of the transition state along the reaction coordinate ("early" vs. "late") as controlled by the nature of the substituents and the resulting nucleophilicity of the alkene.



10

Although this model of the transition state is a reasonable one, other models are possible and cannot yet be conclusively eliminated. Solvolysis of certain γ-SnR_3 derivatives of general structure **11** leads to cyclopropanes apparently via *backside* displacement of R_3Sn^+ by the developing carbonium ion.[34] Applying this mechanism to the present system suggests that the developing electrophilic center at C_β may displace Fp^+ in a backside manner. However, a transition state similar to **12** which resembles product cyclopropanes, predicts trans stereoselectivity which we do not observe. On the other hand, an early transition state, such as **13**, could be invoked in which substituents at C_α (and to a lesser extent at C_β) prefer to occupy sites cis to the methyl substituent on the carbene carbon.



11

Summary

Highly electrophilic monoalkyl-substituted alkylidene complexes of the type $Cp(CO)(L)Fe{=}CHR^+$ (L = CO, $P(C_6H_5)_3$, R = CH_3,

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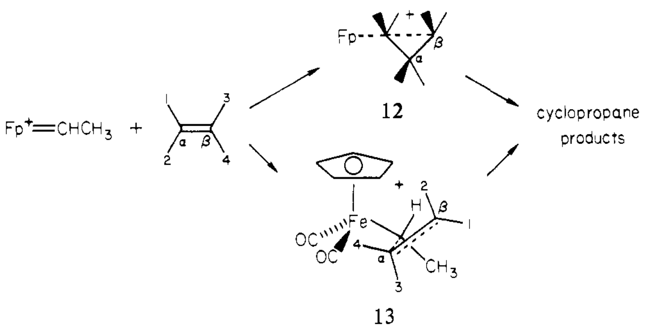
(31) A notable exception is the observation that *cis*-cyclododecene yields a 1:1 ratio of endo:exo addition products.[20] For both cis disubstituted olefins that we have examined, only the all-cis cyclopropane isomers could be observed.

(32) Kegley, S.; Brookhart, M.; Husk, G. R., unpublished results.

(33) A referee has raised the possibility that some olefin scission via a metallacyclobutane may be occurring in these systems. Such a reaction could serve to reduce the yields of cyclopropanes. We see no evidence for substantial amounts of scission products: no cyclopropanes as noted which would come from the secondary, "metathesized" alkylidene nor are Fp–alkene complexes observed from isomerization of the secondary alkylidene. However, small amounts of these materials probably would have gone undetected.

(34) Previously, high cis stereoselectivities in transfers of benzylidene moieties from $(CO)_5W{=}CH(C_6H_5)$ and $Cp(CO)_2Fe{=}CH(C_6H_5)^+$ have been attributed to a stabilizing interaction between C_β and the aryl group.[12,13b] No such interaction is possible here. It is interesting to note that in these cases high stereoselectivities are also observed when stereochemistry is controlled by α substituents.

(35) (a) Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576. (b) McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *Ibid.* **1978**, *100*, 6407.



CH_2CH_3, $CH(CH_3)_2$) can be generated in situ by ionization of α ethers, $Cp(CO)(L)FeCH(OCH_3)R$. The triphenylphosphine-substituted complexes have been spectrally characterized in solution; however, lifetimes of $Cp(CO)(P(C_6H_5)_3)Fe{=}CHR^+$ (R = CH_2CH_3, $CH(CH_3)_2$) are short even at low temperatures due to β-hydride migration. The more electrophilic species, $Cp(CO)_2Fe{=}CHR^+$, could not be directly observed even at low temperatures due to rapid decomposition initiated either by β-hydride migration to give alkene complexes (R = CH_2CH_3, $CH(CH_3)_2$) or by β-hydride elimination (R = CH_3).

Rapid ethylidene transfer to alkenes to form methylcyclopropanes has been efficiently carried out under mild conditions utilizing $Cp(CO)_2Fe{=}CHCH_3^+$ generated in situ. In most cases, cyclopropane formation is competitive with carbene decomposition. Transfer reactions occur most readily to electron-rich mono-, 1,1-di-, and cis 1,2-disubstituted alkenes. Trisubstituted olefins also react readily; however, transfer to trans 1,2-disubstituted alkenes occurs in low yield. A marked cis stereoselectivity is normally observed in the transfer reactions. The ease of preparation of large quantities of the solid, easily handled α ether precursor, $Cp(CO)_2FeCH(OCH_3)CH_3$, and the generally high stereoselectivity and mild conditions (−78 °C) of the subsequent ethylidene transfer to alkenes makes this a potentially attractive synthetic reaction.

In preliminary transfer reactions of more complex, monosubstituted alkylidene complexes, yields of cyclopropanes are significantly diminished due to the shorter lifetimes of the cationic carbene complexes. For example, transfer of propylidene from $Cp(CO)_2Fe{=}CH(CH_2CH_3)^+$ generated in situ to methylenecyclohexane occurs in only ca. 8% yield.[36] Even though less reactive, the longer lifetimes of $Cp(CO)(P(C_6H_5)_3)Fe{=}CHR^+$ may offer a method for increasing yields of transfer products from more complex alkylidene species. Preliminary results indicate that $Cp(CO)(P(C_6H_5)_3)Fe{=}CHCH_3^+$ transfers ethylidene to styrene in good yields (25 °C); however, *trans*-1-methyl-2-phenylcyclopropane is formed preferentially (cis:trans ca. 1:3).

The precise mechanistic details of these transfer reactions are unknown at the present time. Although the general character of the reaction is clearly an electrophilic attack by the carbene carbon on the alkene, the precise structure of the transition state is unclear and may be a sensitive function of substituents on the alkene. Further mechanistic information is expected from observing the variation in stereoselectivities from a series of substituted styrenes where electronic character can be varied independent of steric character. In addition, studies of alkylidene transfers from chiral alkylidene complexes will provide insight into the structure of the transition state. These studies are in progress.

Experimental Section

General Information. All metal carbonyl compounds were manipulated under an atmosphere of dry, oxygen-free nitrogen. Hydrolysis and alcoholysis reactions were effected with degassed reagents. Photolyses were performed in a quartz immersion well with a Hanovia 450-W, medium-pressure, mercury vapor lamp. Infrared spectra were recorded on a Beckman 4250 spectrometer. ^1H- and ^{13}C NMR spectra were recorded on either a Varian XL-100 or a Bruker WM-250 spectrometer. Chemical shifts for ^1H NMR spectra were determined by utilizing residual C_6HD_5 (δ 7.15), $CHCl_3$ (δ 7.24), or $CHDCl_2$ (δ 5.28) as an internal reference. ^{13}C NMR resonances were measured from CD_2Cl_2 (53.8 ppm) or C_6D_6(δ 128.0). Analytical GLC data were obtained on a Hewlett-Packard 5750 chromatograph with a flame ionization detector. Preparative GLC was performed on a Varian Aerograph 90-P.

$C_5H_5(CO)_2FeCOR$, 4b, R = CH_3, CH_2CH_3, $CH(CH_3)_2$. General Procedure. The reactions of $Cp(CO)_2FeNa$ with appropriate acyl chlorides were carried out by using procedures similar to those described by King.[37] The crude, red, oily products were chromatographed on neutral alumina (activity 3) with petroleum ether: yields R = CH_3 78%, CH_2CH_3 86%, $CH(CH_3)_2$ 91%; ^1H NMR (C_6D_6) R = CH_3 δ 2.42 (s, 3 H), 4.88 (s, 5 H); CH_2CH_3 1.05 (t, 3 H, J = 8 Hz), 2.78 (q, 2 H, J = 8 Hz), 4.25 (s, 5 H); $CH(CH_3)_2$ 1.03 (d, 6 H, J = 7 Hz), 3.01 (sept, 1 H, J = 7 Hz), 4.37 (s, 5 H); IR ν_{CO}, ν_{RCO} (CH_2Cl_2) R = CH_3 2010, 1960, 1638, 1680 cm^{-1}; CH_2CH_3 1955, 2005, 1637 cm^{-1}; $CH(CH_3)_2$ 2010, 1950, 1665, 1618 cm^{-1}.

$C_5H_5(CO)(P(C_6H_5)_3)FeCOR$, 4b, R = CH_3, CH_2CH_3,$CH(CH_3)_2$. General Procedure. Alkyl complexes, $Cp(CO)_2FeR$, readily prepared from reactions of $Cp(CO)_3FeNa$ and corresponding alkyl halides,[37] were heated at reflux with 1.1 equiv of $(C_6H_5)_3P$ in acetonitrile. The reaction was terminated when the ν_{CO} band (ca. 1915 cm^{-1}) for **4b** reached a maximum (12–24 h). The acyl complexes were precipitated with pentane and chromatographed on neutral alumina with 1:5 benzene:petroleum ether: yields R = CH_3 82%, CH_2CH_3 66%, $CH(CH_3)_2$ 70%, ^1H NMR (C_6D_6) R = CH_3 δ 2.62 (d, 3 H, J_{PH} = 1.8 Hz), 4.31 (d, 5 H, J_{PH} = 1.9 Hz), 6.7–8.0 (m, 15 H); CH_2CH_3 0.94 (t, 3 H, J = 6.5 Hz), 2.98 (q, 2 H, J = 6.5 Hz), 4.36 (d, 5 H, J_{PH} = 1.8 Hz), 6.8–8.0 (m, 15 H); R = $CH(CH_3)_2$ 1.69 (d, 3 H, J = 6.9 Hz), 2.23 (d, 3 H, J 6.9 Hz), 3.11 (sept, 1 H, J = 6.9 Hz), 4.41 (d, 5 H, J_{PH} = 1.8 Hz), 6.8–8.0 (m, 15 H); IR ν_{CO}) νRCO (CH_2Cl_2) R = CH_3 1915, 1600 cm^{-1}; CH_2CH_3 1916, 1605 cm^{-1}; $CH(CH_3)_2$ 1909, 1590 cm^{-1}.

$C_5H_5(CO)_2FeCH(OCH_3)R$, 3b, R = CH_3, CH_2CH_3, $CH(CH_3)_2$. General Procedure. The iron acyl **3b** (0.0066 mol) in 25 mL of dry CH_2Cl_2 was stirred at 25 °C with methyl triflate (0.025–0.040 mol) for ca. 24 h. The progress of the alkylation was monitored by the decrease of the ν_{CO} bands at ca. 2010 and 1960 cm^{-1} for **4b** and the increase of bands at ca. 2060 and 2015 cm^{-1} for the heterocarbenes **5b**. The CH_2Cl_2 solution of the heterocarbene was then reduced by dropwise addition into a rapidly stirring slurry of $NaBH_4$ (2-fold molar excess with respect to $CH_3OSO_2CF_3$) in 250 mL of CH_3OH/CH_3ONa (4-fold molar excess with respect to methyl triflate). (The $NaBH_4/CH_3OH$ must be stirred 1 h prior to the quench to ensure a saturated borohydride solution.) The resulting CH_3OH/CH_2Cl_2 solution was diluted with 1.5 L of water and extracted with 3 × 25 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts wre dried and solvent removed to yield spectroscopically pure (>90%) α-ether complexes **3b**. Further purification can be achieved by elution from neutral alumina with pentane. Table I summarizes yields and spectroscopic data for **3b**, R = CH_3, CH_2CH_3, and $CH(CH_3)_2$. Anal. Calcd for **3b** (R = CH_3), $C_{10}H_{12}O_3Fe$: C, 50.88; H, 5.12; Fe, 23.66. Found: C, 50.9]; H, 5.14; Fe, 23.48.

$C_5H_5(CO)(P(C_6H_5)_3)FeCH(OCH_3)R$, 3a, R = CH_3, CH_2CH_3, $CH(CH_3)_2$. General Procedure. A slight modification of the procedure used for **3b** was employed. Alkylation of **3a** (0.0044 mol) with methyl triflate (0.0088–0.013 mol) was complete in less than 12 h as the ν_{CO} band at ca. 1915 cm^{-1} of **4a** is replaced by the 1980-cm^{-1} band of the heterocarbene **5a**. The α ethers **3a** are precipitated from CH_2Cl_2 by addition of 2-methylbutane and further purified by reprecipitation. (The complexes are unstable on alumina.) Significant amounts of both diastereomers are formed in each reaction, and no attempt was made to separate them. Table I summarizes the yields and ^1H NMR data for each diastereomer. Anal. Calcd for **3a** (R = CH_3), $C_{27}H_{27}O_2FeP$: C, 68.95; H, 5.79; Fe, 11.87. Found: C, 68.74; H, 5.73; Fe, 11.66.

Generation and Spectral Characterization of $Cp(CO)(P(C_6H_5)_3)Fe{=}CHR^+$ 2a (R = CH_3, CH_2CH_3, $CH(CH_3)_2$). A standard 5-mm NMR tube adapted for alternate high vacuum–inert atmosphere operation was used for generation and observation of the alkylidene complexes. Typically, the α-ether precursor, **3a**, (0.03 mmol) was placed in the NMR tube and dissolved in 0.3 mL of CD_2Cl_2 at −78 °C. The solution was degassed by a freeze–pump–thaw cycle. Transfer of trimethylsilyl triflate (0.06 mmol) by calibrated pipette to the cooled reaction mixture (−78 °C) followed by mixing resulted in a rapid and usually quantitative formation of the red solution of the alkylidene complex. The NMR tube was then frozen, evacuated, and sealed at liquid N_2 temperatures. The tubes were thawed at −78 °C just prior to introduction into the precooled NMR sample probe. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy; data are summarized in Table II.

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[36] The resulting product, 1-ethylspiro[2,5]octane exhibits the following ^1H NMR ($CDCl_3$): δ −0.18 (br t, 1 H, apparent J ca. 4.7 Hz), 0.29 (dd, 1 H, J = 3.8, 9.6 Hz), 0.38 (m, 1 H, C*H*CH$_2$CH$_3$), 0.96 (t, 3 H, J. = 7 Hz, CH_3), 1.1–1.5 (m, 12 H, CH_2's).

[37] King, R. B.; Bisnette, M. *J. Organomet. Chem.* **1964**, *2*, 15.

Thermal Decomposition of Carbene Complexes, 2a. Solutions of the carbene complexes **2a** generated as described above, were warmed in the NMR probe. The decomposition was monitored by ^{1}H NMR spectroscopy.

2a, R = CH$_3$ ($t_{1/2}$ ca. 3 h, 25 °C, CD$_2$Cl$_2$). The extremely complex, broad spectrum (25 °C) precludes structural assignment for the major decomposition products. Only minor amounts (<10%) of the ethylene complex can be detected as evidenced by a broad signal at δ 3.4.

2a, R = CH$_2$CH$_3$ ($t_{1/2}$ ca. 1 h, −40 °C, CD$_2$Cl$_2$). The first-formed product at −78 °C is apparently one (>90%) of the two possible diastereomers of the isomeric propene complex, Cp(CO)(P(C$_6$H$_5$)$_3$)Fe(CH$_3$CH = CH$_2$)$^+$ and exhibits ^{1}H NMR signals (−40 °C) at δ 4.75 (5 H, C$_5$H$_5$), 3.96 (d, 1 H, J = 9.6 Hz, olefinic CH), 2.35 (apparent t, 1 H, olefinic CH) and 1.25 (d, 3 H, CH$_3$). (One olefinic CH is obscured.) As the probe temperature is raised in 10-deg increments from −40 t 0 °C, the kinetic diastereomer isomerizes to the thermodynamically more stable diastereomer (ca. 80%) which shows resonances at δ 4.80 (5 H, C$_5$H$_5$), 4.00 (d, 1 H, J = 13.5 Hz), 3.13 (M, 1 H, olefinic CH), 2.83 (apparent t, 1 H, olefinic CH) and 1.77 (d, 3 H, CH$_3$, J = 6.9 Hz). These data agree with those previously reported.[27]

Ionization of Cp(CO)$_2$FeCH(OCH$_3$)R, 3b, R = CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$. Ionization of α ethers **3b** was carried out with Me$_3$SiOTf by using the same procedures described for generation of 2a. In no case could the carbene complexes be observed even when solutions were monitored immediately at −78 °C. For R = CH$_3$ the first-observed products of ionization corresponded to the mixture of diastereomeric binuclear species, **6**, previously reported by Cutler.[8] (Our ^{1}H NMR spectrum of isolated product matched spectra provided by Cutler.) For R = CH$_2$CH$_3$ and CH(CH$_3$)$_2$, the products of ionization were the olefinic complexes Fp(CH$_3$CH=CH$_2$)$^+$ and Fp((CH$_3$)$_2$C=CH$_2$)$^+$, respectively, whose ^{1}H NMR spectra matched those previously reported. Dissolution and ionization of **3b** (R = CH$_2$CH$_3$) in TFA-*d* resulted in quantitative formation of Fp(CH$_3$CH=CH$_2$)$^+$ with no observable incorporation of deuterium.

Ethylidene Transfers to Alkenes with Cp(CO)$_2$FeCH(OCH$_3$)CH$_3$, 3b, R = CH$_3$. As a general procedure, trimethylsilyl triflate (0.77g, 3.47 mmol) was syringed into rapidly stirring CH$_2$Cl$_2$ (12 mL, −78 °C) containing **3b** (1.0g, 3.17 mmol) and alkene (1.5–12.6 mmol). After 5 min, iron salts were precipitated by the addition of a large volume (ca. 60 mL) of 2-methylbutane. The cold solution was filtered and washed quickly with saturated sodium bicarbonate solution, then filter-dried through neutral alumina. Both low-temperature workup and subsequent neutralization are needed to prevent acid-catalyzed ring opening of the cyclopropanes. Simple distillation effected solvent removal.

The resulting mixture of cyclopropanes and unreacted alkene was purified by preparative GLC using either column A ($^1/_4$ in. × 17 ft, 20% SE-30 on Chrom W) or column B ($^1/_4$ in. × 12 ft 25% QF 1 on Chrom W). Analytical GLC was done with $^1/_8$ in. × 12 ft stainless steel columns packed as above. Yields were determined by standard GLC methods (flame ionization detection) in which straight chain alkanes were used as internal standards. Relative response factors were determined by using known ratios of the cyclopropane:alkane. Internal standards were added to the reaction mixtures prior to ethylidene transfer. No products other than cyclopropanes and sometimes traces of isomeric alkenes could be detected. Although not quantitated for all cases, material balance, when determined, was accounted for by the presence of unreacted alkene.

A summary of the ethylidene transfer reactions is given in Table III. Isomer ratios of cyclopropanes derived from *cis*-3-hexene and 2-methyl-2-butene were estimated as >50:1 on the basis of observation of a single peak by GLC and lack of other resonances in 250-MHz ^{1}H NMR spectra with S/N ≥ 400. Spectral data for the isolated cyclopropanes are given below. Noted after each compound is the column and temperature used for GLC analysis and, where isomeric cyclopropanes are formed, relative retention times for each.

From Methylenecyclohexane: 1-Methylspiro[2.5]octane (column A, 120 °C).[38] ^{1}H NMR (CDCl$_3$) δ −0.21 (br t, 1 H, apparent J ca. 4.8 Hz, methylene H cis to methyl), 0.31 (dd, 1 H, J = 3.8, 8.0 Hz, methylene H trans to methyl), 0.48 (m, 1 H, C*H*CH$_3$), 1.02 (d, 3 H, J = 6.3 Hz, CH$_3$), 1.18–1.45 (m, 10 H, C$_6$ ring CH$_2$'s).

From Cyclooctene: *endo*-9-Methylbicyclo[6.1.0]nonane (column A, 70 °C, 10.4 min). ^{1}H NMR (CDCl$_3$) δ 0.53 (m, 2 H, H$_1$,H$_8$), 0.74 (m, 1 H, C*H*CH$_3$), 0.92 (d, 3 H, J = 6.25 Hz), 1.0–1.8 (m, 12 H, CH$_2$'s). Computer simulation of variously decoupled 250-MHz spectra unambiguously establishes $J_{1,8}$ = 8.65 Hz, $J_{1,9}$ = $J_{8,9}$ = 8.50 Hz. ^{13}C NMR (CDCl$_3$, off-resonance) δ 7.7 (q, CH$_3$), 11.2 (d, *C*HCH$_3$), 17.8 (d, *C*HCH$_2$), 21.5 (t, CH$_2$), 26.7 (t, CH$_2$), 29.7 (t, CH$_2$).

***exo*-9-Methylbicyclo[6.1.0]nonane (column A, 70 °C, 9.4 min).** Identification of this material is tentative. Collection of a trace peak (ca. 5%) at 9.4 min and analysis by 250-MHz NMR reveals the presence of olefinic product (>50%) and a minor material (<50%) which is tentatively identified as the exo-methyl isomer on the basis of ^{1}H NMR resonances (CDCl$_3$) δ −0.03 (m, 1 H *C*HCH$_3$), 0.20 (m, 2 H, H$_1$, H$_8$), 1.0 (d, 3 H, CH$_3$, J = 6.3 Hz), 1.2–2.1 (m, CH$_2$'s, overlapping resonances of olefinic isomer(s)). The endo:exo isomer ratio can be conservatively estimated as >25:1.

From Styrene: *cis*- and *trans*-1-Methyl-2-phenylcyclopropane (column B, 100 °C, relative retention times 8.9:10.2, cis:trans). ^{1}H NMR (CDCl$_3$): identical with published spectra.[12b,30]

From 1-Hexene: *cis*-1-Butyl-2-methylcyclopropane (column A, 80 °C, 7.8 min). ^{1}H NMR (CDCl$_3$) δ −0.38 (m, 1 H, methylene H cis to CH$_3$), 0.5–0.8 (m, 3 H, remaining cyclopropyl H's), 0.88 (t, 3H J = 6.7 Hz, CH$_2$*CH*$_3$), 1.0 (d, 3 H, J = 6.3 Hz, CH*CH*$_3$), 1.2–1.4 (m, 6 H, CH$_2$'s).

***trans*-1-Butyl-2-methylcyclopropane (column A, 80 °C, 6.0 min).** ^{1}H NMR (CDCl$_3$) δ 0.11 (m, 2 H, ring-*CH*$_2$), δ 0.34 (m, 2 H overlapping *CH*CH$_3$ and *CH*CH$_2$CH$_3$), 0.82–1.42 (complex m, 12 H, the CH*CH*$_3$ doublet is visible at δ 1.0, J = 6.1 Hz).

From *cis*-3-Hexene: *cis*-1,2-Diethyl-3-methylcyclopropane (column A, 80 °C). ^{1}H NMR (CDCl$_3$) δ 0.58 (m, 2H, *CH*CH$_2$), 0.76 (m, 1 H, *CH*CH$_3$), 0.9 (d, 3 H, CH*CH*$_3$, J = 6 Hz), 0.94 (t, 6 H, *CH*$_3$CH$_2$, J = 6.8 Hz), 1.23 (m, 4 H, CH$_2$'s) (only detectable product).

From *trans*-3-Hexene: *trans*-1,2-Diethyl-3-methylcyclopropane (column A, 80 °C). ^{1}H NMR (CDCl$_3$) δ −0.03 (m, 1 H, *CH*CH$_2$CH$_3$ cis to CH$_3$), 0.30 and 0.45 (m, 1 H and 1 H, C*H*CH$_2$CH$_3$ cis to CH$_3$ and C*H*CH$_3$, unassigned), 0.9–1.0 (m, 9 H, CH$_3$'s), 1.0–1.4 (m, 4 H, CH$_2$'s). ^{2}H FT NMR analysis indicates the 0.9–1.0 multiplet is composed of two triplets (CH$_2$*CH*$_3$'s, J = 7.2 Hz) and one doublet (CH*CH*$_3$, J = 6.0 Hz).

From 2-Methyl-2-butene: *cis*-1,2,3,3-Tetramethylcyclopropane (column A, 25 °C). ^{1}H NMR (CDCl$_3$) δ 0.40 (m, 2 H, *CH*CH$_3$), 0.80 (s, 3 H, *CH*$_3$), 0.82 (m, 6 H, CH*CH*$_3$), 0.97 (s, 3 H, *CH*$_3$). Additional confirmation of structure is provided by diastereotopic resonances of the *gem*-dimethyl groups in the off-resonance ^{13}C NMR spectra (CDCl$_3$): 7.86 (q, one gem C(CH$_3$)$_2$), 9.96 (s, *C*(CH$_3$)$_2$), 14.13 (q, one gem C(*C*H$_3$)$_2$), 19.71 (d, *C*HCH$_3$), 28.98 (q, C*C*H$_3$).

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Registry No. 2a (R = CH$_3$), 76624-87-8; **2a** (R = CH$_2$CH$_3$), 83802-12-4; **2a** (R = CH(CH$_3$)$_2$), 83802-13-5; **3a** (R = CH$_3$, isomer A), 76624-85-6; **3a** (R = CH$_3$, isomer B), 76648-52-7; **3a** (R = CH$_2$CH$_3$, isomer A), 83802-10-2; **3a** (R = CH$_2$CH$_3$, isomer B), 83860-17-7; **3a** (R = CH(CH$_3$)$_2$, isomer A), 83802-11-3; **3a** (R = CH(CH$_3$)$_2$, isomer B), 83860-18-8; **3b** (R = CH$_3$), 74171-11-2; **3b** (R = CH$_2$CH$_3$), 83802-08-8; **3b** (R = CH(CH$_3$)$_2$), 83802-09-9; **4a** (R = CH$_3$), 12101-02-9; **4a** (R = CH$_2$CH$_3$), 32611-01-1; **4a** (R = CH(CH$_3$)$_2$), 32661-71-5; **4b** (R = CH$_3$), 12108-22-4; **4b** (R = CH$_2$CH$_3$), 32983-18-9; **4b** (R = CH(CH$_3$)$_2$), 65295-16-1; methylenecyclohexane, 1192-37-6; cyclooctene, 931-88-4; *exo*-9-methylbicyclo[6.1.0]nonane, 62862-04-8; *cis*-1-butyl-2-methylcyclopropane, 38851-69-3; *trans*-1-butyl-2-methylcyclopropane, 38851-70-6; *trans*-1,2-diethyl-3-methylcyclopropane, 83802-14-6; *cis*-1,2-diethyl-3-methylcyclopropane, 83860-19-9; *cis*-1,2,3,3-tetramethylcyclopropane, 83860-20-2; *cis*-1-methyl-2-phenylcyclopropane, 4866-54-0; *trans*-1-methyl-2-phenylcyclopropane, 5070-01-9; 1-methylspiro[5.2]octane, 41417-81-6; *endo*-9-methylbicyclo[6.1.0]nonane, 62929-24-2; 1-hexene, 592-41-6; (*E*)-3-hexene, 13269-52-8; (*Z*)-3-hexene, 7642-09-3; 2-methyl-2-butene, 513-35-9; ethenylbenzene, 100-42-5; 1-isopropylcyclohexene, 4292-04-0.

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(38) In early experiments in which workups were done less carefully, an acid-catalyzed rearrangement product could also be isolated and was identified as 1-isopropylcyclohexene on the basis of ^{1}H NMR (CDCl$_3$): δ 0.93 (d, 6 H, J = 6.4 Hz, CH(CH$_3$)$_2$), 1.5–2.0 (m, 8 h, CH$_2$'s), 2.06 (sept, 1 H, J = 6.4 Hz, C*H*(CH$_3$)$_2$), 5.28 (br s, 1 H, C*H*=).