Cyclopropanes from Reactions of Transition-Metal–Carbene Complexes with Olefins

MAURICE BROOKHART* and WILLIAM B. STUDABAKER

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, 27514

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Contents

I. Introduction

A rich chemistry of transition-metal–carbene complexes has evolved in the quarter century since the original synthesis of $(CO)_5W{=}C(OMe)Ph$ by Fischer and Maasböl.[1] The preparation, characterization, and reactivity of a wide variety of such complexes has been documented including, for example, heteroatom-stabilized electrophilic carbene complexes, electrophilic species which lack heteroatom stabilization, early transition metal alkylidene complexes which display nucleophilic character, several examples of simple methylene complexes, and numerous types of binuclear systems in which a carbene ligand bridges two metal centers.[2] A particular interest in such complexes arises from their postulated or demonstrated intermediacy in a variety of catalytic processes such as olefin metathesis,[2e] Fischer–Tropsch processes,[2f] and metal-catalyzed carbene transfers using diazo compounds.[2j]

Maurice Brookhart is Professor of Chemistry at the University of North Carolina, Chapel Hill. He was born in Cumberland, MD, in 1942 and received a B.A. degree in chemistry from Johns Hopkins in 1964. His Ph.D. studies in organic chemistry were completed in 1968 at UCLA under Professor Saul Winstein. After completing an NSF postdoctoral fellowship at UCLA (1968) and NATO postdoctoral fellowship at University of Southampton (1968–1969), he joined the UNC faculty in 1969. He has held visiting positions at Wisconsin (1974), University of Rennes, France (1981), and the Inorganic Chemistry Laboratories, Oxford (1982–1983). At North Carolina, his research has been in the area of mechanistic and synthetic organometallic chemistry.

William B. Studabaker received his B.A. from Rice University in 1977. After brief employment with Bentley Laboratories in Irvine, CA, he joined the electrochemistry group under Dr. Raymond Jasinski at Occidental Research Corp. in Irvine. In 1981 he began his graduate studies at the University of North Carolina under the direction of Prof. Brookhart and received his Ph.D. in 1986. He is currently a postdoctoral scholar at The Pennsylvania State University, under the direction of Prof. Steven M. Weinreb.

Stoichiometric reactions of carbene complexes directed toward utility in synthetic transformations have recently come under careful scrutiny.[3] This review concerns one aspect of these studies, the reactions of

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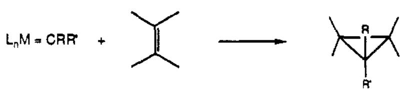
mononuclear electrophilic transition metal carbene complexes with olefins to produce cyclopropanes:



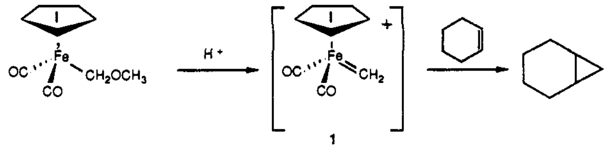
The patterns of reactivity observed in such reactions and the range of carbene moieties which may be transferred via an intermediate organometallic species demonstrate that this new class of reactions is often complementary to the well-established techniques of preparing cyclopropanes from alkenes using classical carbenoid reagents, free carbenes, or diazo reagents. This review includes (1) a description of the synthesis of electrophilic carbene complexes and their precursors, (2) a comprehensive tabulation and comparison of the results of carbene-transfer reactions involving a variety of organometallic species and olefinic substrates, and (3) a discussion of the current understanding of the mechanistic details of carbene-transfer reactions. We will consider only stoichiometric reactions of (a) stable, well-characterized mononuclear carbene complexes and (b) similar complexes generated in situ where there is no ambiguity concerning the nature of the reactive species. Catalytic processes thought to involve the intermediacy of metal–carbene complexes (for example, the reactions of transition-metal reagents with diazo compounds[2j]) will not be discussed.

Nomenclature for simple metal–carbene complexes may be based on naming the compounds as derivatives of carbene complexes or as transition metal ylide derivatives. For example, $L_nM{=}CHPh$ can be termed a phenylcarbene complex or a benzylidene complex. Both nomenclatures are in common use and many authors, ourselves included, have not been consistent even for a set of analogous complexes in using one system or the other. The general historical trend has been to use the "alkylidene" nomenclature when the polarity of the metal–carbon double bond is such that C_α bears a net partial negative charge (C_α nucleophilic) while the carbene nomenclature has been used when the polarity is such that C_α bears a partial positive charge (C_α electrophilic). This trend has already been noted by Grubbs.[4] A problem with this system is that a knowledge of reactivity is required and there are inevitably borderline cases. Nevertheless, since all the complexes discussed in this review are electrophilic in nature, we will conform to this system and consistently use the metal carbene terminology.

II. Early Work

A. Discovery. Heteroatom-Stabilized Carbene Complexes

The first suggestion that transition metal carbene complexes might serve as carbene transfer reagents emerged from the work of Pettit and Jolly[5a] who found that treatment of $CpFe(CO)_2CH_2OCH_3$ with acid in the presence of cyclohexene produced norcarane in 46% yield. The intermediacy of $CpFe(CO)_2{=}CH_2^+$ (1) was suggested and the results of later studies lend strong support to this original proposal.[6-8]



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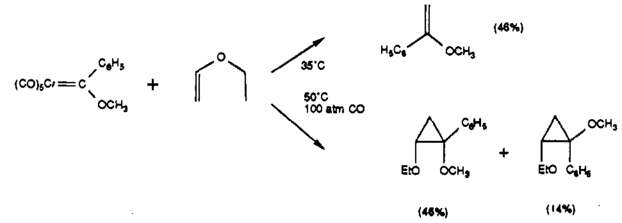
Despite the promise of the above results, the area of metal–carbene-transfer chemistry remained unexplored for some time. Fischer et al. reopened the field with the observation that the complexes $(CO)_5M{=}C(OMe)Ph$ (M = Cr, Mo, W) react with olefins to give cyclopropanes in fair yields although vigorous conditions were often required (90–140 °C).[9-11] Only olefins containing either strongly electron-withdrawing groups (e.g. α,β-unsaturated esters) or electron-donating groups (e.g., vinyl ethers) were successful; simple alkyl-substituted olefins were unreactive. Olefin scission was a commonly observed side reaction. For example, in the reaction with ethyl vinyl ether high CO pressures were required to suppress formation of the scission product $CH_3O(Ph)C{=}CH_2$.[10a]



Early studies of transition-metal–carbene complexes were fueled by speculation that such complexes might be sources of free carbenes. Fischer demonstrated that such was clearly not the case here since (a) the syn:anti cyclopropane isomer ratio found in the reactions of $(CO)_5M{=}C(OCH_3)Ph$ (M = Cr, Mo, W) with *trans*-methyl crotonate is dependent upon the metal[9a] and (b) use of optically active $(CO)_4(P(CH_3)(CH_2CH_2CH_3)Ph)Cr{=}C(OCH_3)Ph$ results in some optical activity in the cyclopropane produced from dimethyl fumarate.[11] Metal–carbon double bond dissociation energies are quite high and in the numerous carbene-transfer reactions carried out since these early studies, no evidence supports involvement of free carbenes.

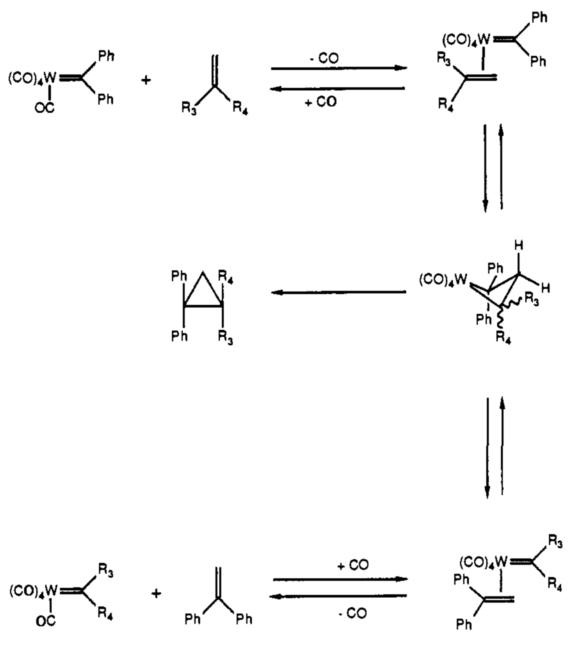
B. Nonheteroatom-Stabilized Carbene Complexes

The requirement for a highly activated or deactivated olefin and forcing conditions places constraints on the use of Fischer carbene complexes for cyclopropane synthesis. Casey found that $(CO)_5W{=}CPh_2$ (2), which lacks a stabilizing heteroatom adjacent to the carbene carbon, is more reactive toward activated olefins than the Fischer carbene complexes and is also reactive (to a much lesser extent) with simple alkenes. Olefin scission was either a side reaction or led to the major product, depending on the substrate.[12] The bis(*p*-tolyl) carbene complex $(CO)_5W{=}C(tol)_2$ gave similar results.[13]

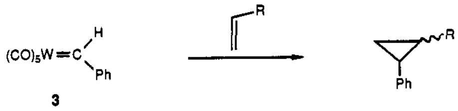
Mechanistic studies by Casey showed that reactions occur only at temperatures at or above those where CO loss from $(CO)_5W{=}CPh_2$ (2) is facile.[14] This led to the mechanistic proposal that reactions with alkenes involve displacement of CO and initial formation of a carbene–alkene complex which is in equilibrium with a metallacyclic intermediate. This reaction scheme accounts for both olefin scission and cyclopropane formation (Scheme I).

In 1977 two key papers appeared which marked the introduction of transition-metal–carbene complexes as practical carbene-transfer reagents. In further studies

SCHEME I



of the tungsten system, Casey et al. prepared and characterized in solution the very reactive *monosubstituted*, electrophilic phenylcarbene complex $(CO)_5W{=}CHPh$ (3).[15] (This species has now been isolated by Fischer.[15c]) This complex was shown to react rapidly with a wide variety of simple alkyl- and aryl-substituted alkenes at low temperatures to yield only cyclopropanes. No olefin scission products were observed. Transfers occurred well below temperatures required for CO dissociation. Such observations indicated direct transfer without formation of intermediate carbene–alkene complexes. Concurrently, Brookhart and Nelson isolated the highly electrophilic cationic phenylcarbene complexes $Cp(CO)(L)Fe{=}CHPh^+$ and found them to be very effective transfer agents at low temperatures.[16]



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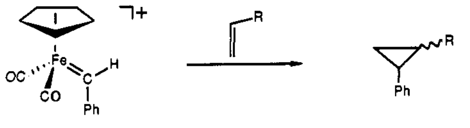

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Based on these papers and Pettit's report, the work of Schrock in particular on early transition metal alkylidene complexes,[2h] and the large extant body of general synthetic and structural work on carbene complexes,[2c] two key concepts concerning the use of metal–carbene complexes as transfer reagents were emerging in the late 1970s: (1) that direct carbene transfers to alkenes were characteristic of highly electrophilic carbene complexes and not a property of nucleophilic alkylidene complexes, and (2) although electrophilic complexes were normally stabilized by heteroatom substitution (Fischer-type carbenes), highly electrophilic systems possessing only simple aryl, alkyl, and hydrogen substituents at C_α could be isolated or at least generated in situ.

Thus, following the 1977 reports, extensive studies appeared regarding the transfer chemistry of stable or in situ generated complexes of the type $(CO)_5W{=}CHPh$, $Cp(CO)(L)Fe{=}CRR'^+$ (L = CO, phosphine, phosphite; R, R′ = H, alkyl, aryl, vinyl, cyclopropyl), $Cp(CO)_2(L)M{=}CH_2^+$ (M = Mo, W; L = phosphine), and $Cp(L)Ni{=}CH_2^+$ (L = phosphine, phosphite). The primary focus of this review will be on the work reported since 1977. The early work of Pettit, Fischer, and Casey ($(CO)_5W{=}CPh_2$) has been reviewed.[2a,b]

III. Synthetic Aspects of Transfer Reactions

A. Synthesis of Carbene Complexes and Their Precursors

1. Via α-Ionization

By far the most widely used technique for generating electrophilic nonheteroatom-substituted metal–carbene complexes is by ionization of a leaving group located at the α position of a metal–alkyl complex:

$$L_nM{-}C(X)RR'^{n} \xrightarrow{-X^-} L_nM{=}CR'R^{n+1} \qquad (1)$$

The leaving group X^- may be RO^-, H^-, halide, or SRR′, and its removal can be accomplished using Brönsted or Lewis acids or simply by thermal ionization in polar solvents. Several representative systems are summarized below.

An early and still widely exploited approach to the generation of electrophilic carbene complexes is the reaction of an α-ether precursor with an electrophile, often acid. Methylene complexes $Cp(CO)_2Fe{=}CH_2^{+}$[5] and phenylcarbene complexes $(CO)_5W{=}CHPh$[15] and $Cp(CO)_2Fe{=}CHPh^{+}$[16] were all obtained from such reactions:

$$\underset{\mathbf{5}}{Cp(CO)_2Fe{-}CH_2(OCH_3)} \xrightarrow{H^+} \underset{\mathbf{1}}{Cp(CO)_2Fe{=}CH_2^+} + CH_3OH_2^+ \qquad (2)$$

$$\underset{\mathbf{6}}{[(CO)_5W{-}CH(OCH_3)Ph]^-} \xrightarrow{H^+} \underset{\mathbf{3}}{(CO)_5W{=}CHPh} + CH_3OH_2^+ \qquad (3)$$

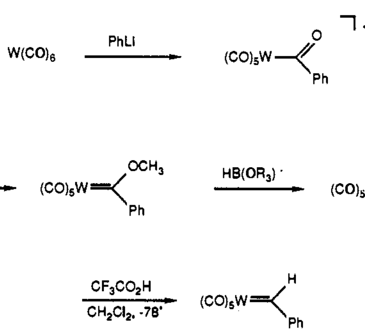
$$\underset{\mathbf{7}}{Cp(CO)_2Fe{-}CH(OCH_3)Ph} \xrightarrow{H^+} \underset{\mathbf{4}}{Cp(CO)_2Fe{=}CHPh^+} + CH_3OH_2^+ \qquad (4)$$

The tungsten α-ether complex 6 was obtained by hydride reduction of the Fischer complex $(CO)_5W{=}C(OCH_3)Ph$.[15] The iron α-ether complexes 5 and 7 were obtained from $Cp(CO)_2Fe^-Na^+$ and an α-haloalkyl methyl ether.[16] α-Halolakyl methyl ethers are generally

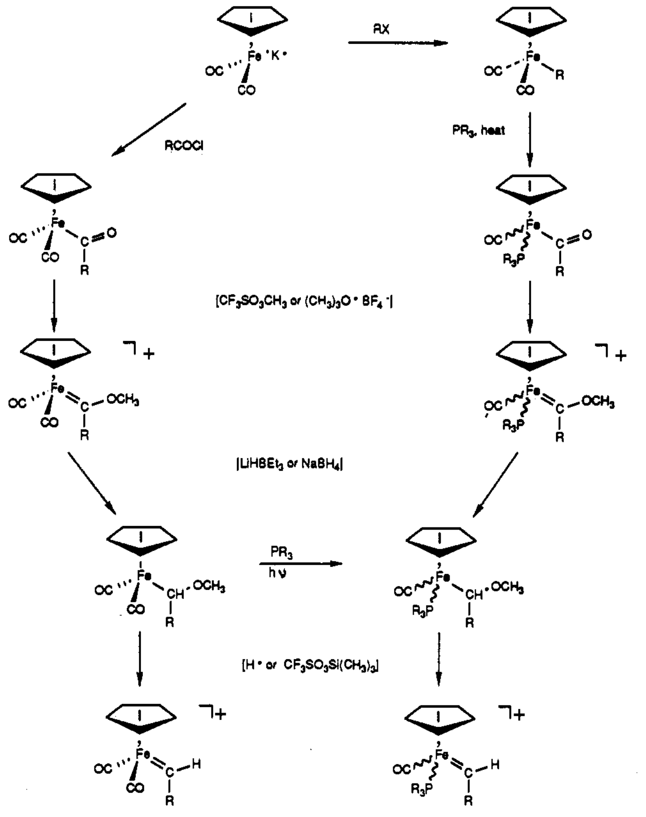
$$CpFe(CO)_2^- + CH_3OCHClR \rightarrow \underset{\substack{\mathbf{5}\ R = H \\ \mathbf{7}\ R = Ph}}{CpFe(CO)_2{-}CH(OCH_3)R} \qquad (5)$$

toxic and often difficult to prepare. In an adaptation of the synthesis of $[(CO)_5W{-}CH(OCH_3)Ph]^-$ (Scheme II), a general synthesis of complexes $CpFe(CO)(L){-}CH(OCH_3)R$ (L = CO, phosphine; R = alkyl, cyclopropyl, aryl) has been devised (Scheme III).[17-22] The key step in Scheme III is the hydride reduction of the Fischer carbene complex $CpFe(CO)_2{=}C(OCH_3)R^+$ to

SCHEME II



SCHEME III



give the α-ether precursors. Cutler has successfully used $LiHBEt_3$ as the reducing agent;[20] Davies has used $NaBH_4$ or $LiAlH_4$ at low temperatures.[18c] Under some conditions overreduction to the alkyl complexes has been observed,[20,21] probably via an alkylidene complex derived from acid-catalyzed elimination of the α-ether. Basic solutions of $NaBH_4$ help avoid overreduction of the α-ether although β-proton abstraction from the alkoxycarbene (to give an η^1-vinyl complex) may compete with hydride addition.[18] A dimethyl α-ether complex was obtained from the reaction of the alkoxycarbene complex $Cp(CO)_2Fe{=}C(OCH_3)CH_3^+$ with CH_3Li or $LiCu(CH_3)_2$.[23a,c] This method appears to be general and complexes of the type $Cp(CO)_2FeCHR(OCH_3)$ have been prepared via RLi addition to $Cp(CO)_2Fe{=}CHOCH_3^+$.[23d]

α-Ether complexes of the type $Cp(CO)(L)Fe{-}CH(OCH_3)R$ exhibit varying degrees of sensitivity to air, temperature, and weakly acidic media. All will decompose in solution on standing at room temperature; in the solid form they are generally more robust and can be stored cold. While the α-ether complexes, L = CO, are frequently purified by column chromatography, the phosphine-substituted analogues lose CH_3OH to give η^1-vinyl species on passage over alumina at room temperature. They are chromatographed successfully at dry ice temperatures.[24]

The use of trimethylsilyl triflate in lieu of a strong acid is effective at generating carbene complexes from their α-ether precursors (eq 6).[16b,21] This approach

$$\mathrm{Cp(CO)_2Fe{-}CHR(OCH_3) + CF_3SO_3Si(CH_3)_3 \rightarrow Cp(CO)_2Fe{=}CHR^+CF_3SO_3^- + CH_3OSi(CH_3)_3} \tag{6}$$

circumvents the possibility of acid-catalyzed rearrangements of cyclopropanes produced in carbene-transfer reactions and also avoids acid-catalyzed polymerization of the olefinic substrates. Trityl cation has also been employed to abstract alkoxide from α-ether precursor, but its application is not general: hydride abstraction can be observed as a competing or exclusive reaction (eq 7, 8).[6,8,25] The carbene transfer reactions

$$\mathrm{Cp(CO)_2(PPh_3)Mo{-}CH_2OCH_3 + Ph_3C^+ \rightarrow Cp(CO)_2(PPh_3)Mo{=}CH_2^+ + Cp(CO)_2(PPh_3)Mo{=}CHOCH_3^+} \tag{7}$$

$$\mathrm{Cp(CO)_2Fe{-}CH_2OCH_3 + Ph_3C^+ \rightarrow Cp(CO)_2Fe{=}CHOCH_3^+} \tag{8}$$

have generally been accomplished by generating the carbene complex in situ in the presence of the olefinic substrate.

Helquist et al. have devised a means of generating carbene complexes $Cp(CO)_2Fe{=}CHR^+$ which is chemically less harsh than the methods described above. The reaction of $CpFe(CO)_2^-K^+$ with α-halo thioethers gives α-thioether complexes $Cp(CO)_2Fe{-}CH(SR')R$.[26,27] Methylation of these complexes with FSO_3CH_3 or $(CH_3)_3O^+BF_4^-$ gives the sulfonium salts $Cp(CO)_2Fe{-}CHR(SCH_3R')^+$ which react directly with olefins (100 °C, R′ = CH_3; 25 °C, R′ = C_6H_5) to produce cyclopropanes, presumably via the intermediacy of carbene complexes $Cp(CO)_2Fe{=}CHR^+$. The dimethylsulfonium salts are particularly attractive reagents, as they are quite stable and may be stored in the air at room temperature for years.[26]

Barefield has recently applied some of the methods described above to the preparation and transfer reactions of the nickel complexes $Cp(L)Ni{-}CH_2S(CH_3)_2^+$ (L = PPh_3, $PPhMe_2$, $P(OMe)_3$).[28] The sulfonium salts could be obtained either by reaction of the α-lithio thioether with CpNi(L)X followed by methylation or by reaction of the metal halide with a sulfur ylide (eq 9–11). Heating these complexes in the presence of

$$\mathrm{Cp(L)NiX + CH_3SCH_2Li \rightarrow Cp(L)Ni{-}CH_2SCH_3} \tag{9}$$

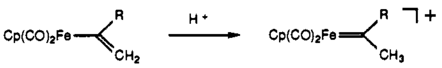
$$\mathrm{Cp(L)Ni{-}CH_2SCH_3 + CF_3SO_3CH_3 \rightarrow Cp(L)Ni{-}CH_2S(CH_3)_2^+CF_3SO_3^-} \tag{10}$$

$$\mathrm{Cp(L)NiX + (CH_3)_2SCH_2 \rightarrow Cp(L)Ni{-}CH_2S(CH_3)_2^+} \tag{11}$$

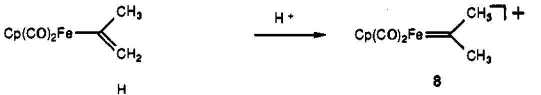
cyclooctene gave varying yields of bicyclo[6.1.0]nonane.

2. *Via Protonation of η^1-Vinyl Systems*

An alternative approach to α-ionization is the generation of carbene complexes via the protonation of η^1-vinyl complexes:



For example, the propenyl species is protonated at the β-carbon to give the dimethyl carbene complex **8** (eq 12).[23a,c,29] If the vinyl group is part of a conjugated diene the δ-carbon is protonated to give a vinyl carbene complex, **9** (eq 13).[29] In a closely related reaction a γ-hydroxyvinyl complex loses water upon protonation to yield **9** (eq 14).[23b,c]



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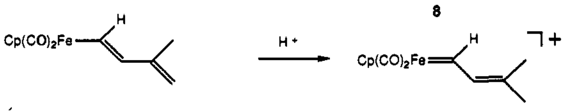

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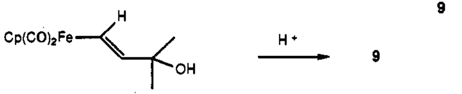


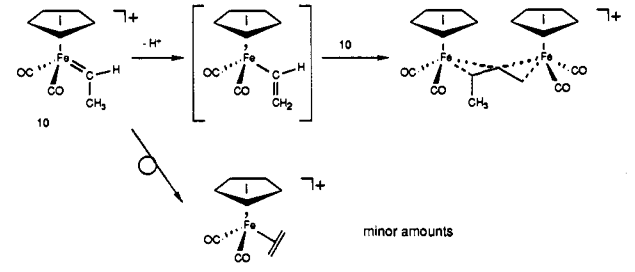
(14)

B. Side Reactions

A variety of side reactions related to the decomposition of the intermediate carbene species may limit the cyclopropane yields in the transfer reactions. As noted above, $Cp(CO)_2Fe{=}CH_2^+$ disproportionates to $Cp(CO)_2Fe^+$ and $Cp(CO)_2Fe(CH_2{=}CH_2)^+$;[5a] similarly, *trans*-stilbene has been isolated as a decomposition product of $Cp(CO)_2Fe{=}CH(C_6H_5)^+$[16] and of $(CO)_5W{=}CH(C_6H_5)$.[15] A second type of disproportionation may be observed if the carbene complex is formed slowly or incompletely: the intermediate carbene may abstract hydride from the starting α-ether complex, giving an alkyl complex and an alkoxycarbene complex (eq 15).[6,8,25]

$$Cp(CO)_3Mo{=}CH_2^+ + Cp(CO)_3Mo{-}CH_2OCH_3 \rightarrow Cp(CO)_3Mo{-}CH_3 + Cp(CO)_3Mo{=}CHOCH_3^+ \quad (15)$$

Bodnar and Cutler have found a unique biomolecular mechanism for the decomposition of methylcarbenes $Cp(CO)(L)Fe{=}CHCH_3^+$.[20] The decomposition product is believed to arise from deprotonation of the methyl group to give the η^1-vinyl complex, which then reacts with a second molecule of the methylcarbene to form a binuclear complex. Hydride migration in methylcarbene complexes to yield ethylene complexes is observed only to a very small extent. In contrast, in higher alkylcarbene complexes, hydride migration to give η^2-olefin complexes is the only mode of decomposition observed and often results in more rapid decay of these species than the methyl-carbene complexes. For example, whereas $Cp(CO)(PPh_3)Fe{=}CHCH_3^+$ is stable up to 25 °C, $Cp(CO)(PPh_3)Fe{=}CHCH_2CH_3^+$ rearranges to $Cp(CO)(PPh_3)Fe(CH_2{=}CHCH_3)^+$ at -40 °C ($t_{1/2}$ = 1 h).[16b] These results suggest that positive charge builds up at C_β in the transition state for hydride migration. The instability of the higher alkylcarbene complexes relative to the methylcarbene complexes also explains the lack of efficient transfer methods for the higher alkylcarbene complexes although low transfer yields have been achieved with $Cp(CO)(PPh_3)Fe{=}CHCH_2CH_3^+$[22] and entropically favored intramolecular transfers are feasible.[29,30]



In the case of the dimethylcarbene complexes $Cp(CO)(L)Fe{=}C(CH_3)_2^+$ (L = CO, PPh_3), hydride migration is relatively slow to yield $Cp(CO)(L)Fe(CH_2{=}CHCH_3)^+$; however, the increased bulk and decreased electrophilicity at C_α also inhibit the transfer reaction to such an extent that hydride migration is still a competitive side reaction.[22a,c]

C. Results of Transfer Experiments

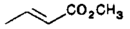
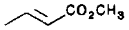
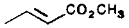
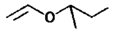
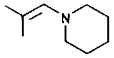
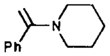
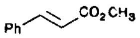
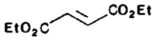
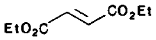
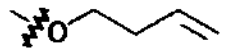
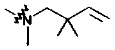
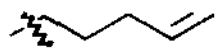
Table I is an extensive summary of the reactions of electrophilic transition metal carbene complexes with olefins which yield cyclopropanes. The table is organized generally according to the structure of the carbene moiety transferred and not according to metal or olefin used.

Several general points should be noted concerning the entries in the table. The transfers are sometimes accomplished by use of stable carbene complexes, but more often via in situ generation of the complex in the presence of the olefin. The method used in a particular case is evident from an examination of the entries under "precursor" and "conditions". As noted above, the yields of cyclopropanes are often diminished by decomposition reactions of the carbene complexes and not by alternative competing reactions with the olefin. Thus in those cases high conversion of olefins to cyclopropanes can be achieved by use of excess metal carbene reagent. Similarly, if the metal carbene reagent is precious, side reactions can be minimized by rapid trapping with large excesses of alkenes. Entries 107–120 illustrate this point. The majority of cases reported in the table involve use of excess olefin.

Basic structures of the product cyclopropanes are obvious and are not explicitly illustrated in the table. In column D comments are made regarding the stereochemistry of the product cyclopropanes and any other structural features worth noting. In general the stereochemistry about the original carbon–carbon double bond is maintained, but there is an important exception which cautions us that this may not always be the case.[37] Additionally, the general trend for transfers involving monosubstituted carbene complexes is that the sterically least favored stereoisomer is the major product, e.g., for monosubstituted olefins the cis isomers and for cycloalkenes, the endo isomers. This trend is not always observed and ratios of stereoisomers can vary widely with changes in the ancillary ligands on the metal center. For example, styrene reacts with $Cp(CO)_2Fe{=}CHCH_3^+$ to give predominantly *cis*-1-methyl-2-phenylcyclopropane[16b] while $Cp(CO)(PPh_2R)Fe{=}CHCH_3^+$ yields predominantly the trans isomer.[31]

Both general trends and quite specific data regarding the transfer reactions can be gleaned by scanning the

TABLE I. Results of Carbene-Transfer Reactions

entry	L_nM	=CRR'		precursor	substrate	conditions	carbene: olefin	cyclopropane yield, %		cyclopropane stereochem	ref
		R	R'					isolated	GC		
1	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		90–140 °C	1:10	60		7:3 (anti:syn)	9a
2	$(CO)_5Mo$	OCH_3	C_6H_5	stable complex		90–140 °C	1:10	60		6:1	9a
3	$(CO)_5W$	OCH_3	C_6H_5	stable complex		90–140 °C	1:10	60		7:3	9a
4	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		120 °C	1:10	5–11		76:13:11 (anti:syn: trans diester)	9b
5	$(CO)_5Mo$	OCH_3	C_6H_5	stable complex		120 °C	1:10	5–11		13:6:81	9b
6	$(CO)_5W$	OCH_3	C_6H_5	stable complex		120 °C	1:10	5–11		5:5:90	9b
7	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex	$CH_2=CHOEt$	100 atm CO, 50 °C, 65 h	1:10	61		1:3 (anti:syn)	10a
8	$(CO)_5Mo$	OCH_3	C_6H_5	stable complex	$CH_2=CHOEt$	100 atm CO, 50 °C, 65 h	1:10	61		1:4	10a
9	$(CO)_5W$	OCH_3	C_6H_5	stable complex	$CH_2=CHOEt$	100 atm CO, 50 °C, 65 h	1:10	61		1:2	10a
10	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		100 atm CO, 50 °C, 65 h	1:10	60		4.4:1	10a
11	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		150 atm CO, 80 °C, 60 h	1:1	1.6		n/a	10b
12	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		120 °C	1:1	16		n/a	53
13	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		110 °C, 3 h	1:10	34		4:1	9b
14	$(CO)_5Cr$	OCH_3	C_6H_5	stable complex		100 °C, 3 h	1:10	49			9b
15	$((R_p)$-PMePrPh)-$(CO)_4Cr$	OCH_3	C_6H_5	stable complex			1:9	n/a		optically active	11
16	$(CO)_5W$	p-$C_6H_4CH_3$		stable complex	R' (intramolecular)	40 °C, C_6D_6		>80 (NMR)			40
17	$(CO)_5W$	p-$C_6H_4CH_3$		stable complex	R' (intramolecular)	99 °C, C_6D_6, 75 h		18			41
18	$(CO)_5W$	OCH_3		stable complex	R' (intramolecular)	60 °C, 2 h		100			42
19	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	(E)-2-butene	50 °C, 4 h	neat olefin	trace			12
20	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	$(CH_3)_2C=CH_2$	100 °C, 2.5 h	neat olefin	10			12
21	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	$EtOCH=CH_2$	37 °C, 3 h	neat olefin	65			12
22	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	$EtOCH=CH_2$	37 °C	1:200	61			55
23	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	$EtOCH=CH_2$	37 °C, C_6H_6	1:20	20			55

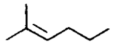
24	$(CO)_5W$	C_6H_5	C_6H_5	stable complex	$EtOCH{=}CH_2$	37 °C, C_5H_{12}	1:20	5			55
25	$(CO)_5W$	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	stable complex	1-pentene	70 °C, 3 h	neat olefin		27		13
26	$(CO)_5W$	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	stable complex	$(CH_3)_2C{=}CH_2$	70 °C, 3 h	neat olefin		5		13
27	$(CO)_5W$	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	stable complex	styrene	70 °C, 3 h	neat olefin		8		13
28	$(CO)_5W$	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	stable complex		70 °C, 3 h	neat olefin		0		13
29	$(CO)_5W$	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	stable complex	(Z)-2-butene	70 °C, 3 h	neat olefin		2		13
30	$(CO)_5W$	C_6H_5	H	α-ether	ethene	H^+, CH_2Cl_2, −78 °C, 4 h	1:100		<0.1		15
31	$(CO)_5W$	C_6H_5	H	α-ether	propene	H^+, CH_2Cl_2, −78 °C, 4 h	1:100		79	2:1 (cis:trans)	15
32	$(CO)_5W$	C_6H_5	H	α-ether	1-butene	H^+, CH_2Cl_2, −78 °C, 4 h	1:200		73	0.9:1	15
33	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CHCH(CH_3)_2$	H^+, CH_2Cl_2, −78 °C, 4 h	1:200		72	1:2.8	15
34	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CHC(CH_3)_3$	H^+, CH_2Cl_2, −78 °C, 4 h	1:150		67	1:100	15
35	$(CO)_5W$	C_6H_5	H	α-ether	$(CH_3)_2C{=}CH_2$	H^+, CH_2Cl_2, −78 °C, 4 h	1:650		98		15
36	$(CO)_5W$	C_6H_5	H	α-ether	(E)-2-butene	H^+, CH_2Cl_2, −78 °C, 4 h	1:700		82		15
37	$(CO)_5W$	C_6H_5	H	α-ether	(Z)-2-butene	H^+, CH_2Cl_2, −78 °C, 4 h	1:400		59	40:1	15
38	$(CO)_5W$	C_6H_5	H	α-ether	$CH_3CH{=}C(CH_3)_2$	H^+, CH_2Cl_2, −78 °C, 4 h	1:200		82	>100:1 (cis:trans)	15
39	$(CO)_5W$	C_6H_5	H	α-ether	$(CH_3)_2C{=}C(CH_3)_2$	H^+, CH_2Cl_2, −78 °C, 4 h	1:200		37		15
40	$(CO)_5W$	C_6H_5	H	α-ether	styrene	H^+, CH_2Cl_2, −78 °C, 4 h	1:200		39	11:1	15
41	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}C(C_6H_4CH_3\text{-}p)_2$	H^+, CH_2Cl_2, −78 °C, 4 h	1:1.1		37		15
42	$(CO)_5W$	C_6H_5	H	α-ether	cyclopentene	H^+, CH_2Cl_2, −78 °C, 4 h	1:250		40	2.6:1 (endo:exo)	15
43	$(CO)_5W$	C_6H_5	H	α-ether	1-methylcyclopentene	H^+, CH_2Cl_2, −78 °C, 4 h	n/a		50	7:1	15
44	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CPhOCH_3$	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		89	1:1.8 (syn:anti)	35
45	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}C(OCH_3)_2$	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		98	1.4:1	35
46	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}C(OCH_3)$-t-Bu	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		96	1:91	35
47	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CHOBu$	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		96	5.8:1 (cis:trans)	35
48	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CHOEt$	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		89	7.6:1	35
49	$(CO)_5W$	C_6H_5	H	α-ether	$CH_2{=}CHOAc$	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		85	10.5:1	35
50	$(CO)_5W$	C_6H_5	H	α-ether	1-hexene	H^+, CH_2Cl_2, −78 °C, 1–4 h	1:50		37	1:1.2	35

TABLE I (Continued)

		=CRR′						cyclopropane yield, %			
entry	L_nM	R	R′	precursor	substrate	conditions	carbene:olefin	isolated	GC	cyclopropane stereochem	ref
51	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	ethene	H^+, CH_2Cl_2, −78 °C	1:2	47	75		16
52	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	propene	H^+, CH_2Cl_2, −78 °C	1:2	54	90	7.8:1 (cis:trans)	16
53	$(Cp(CO)_2Fe$	C_6H_5	H	α-ether	1-butene	H^+, CH_2Cl_2, −78 °C	1:2	75		6.5:1	16
54	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	$CH_2{=}CHCH(CH_3)_2$	H^+, CH_2Cl_2, −78 °C	1:2	76		4.6:1	16
55	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	styrene	H^+, CH_2Cl_2, −78 °C	1:2	88		>100:1	16
56	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	(*E*)-2-butene	H^+, CH_2Cl_2, −78 °C	1:2	52	89		16
57	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	(*Z*)-2-butene	H^+, CH_2Cl_2, −78 °C	1:2	57	93	>100:1	16
58	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	cyclopentene	H^+, CH_2Cl_2, −78 °C	1:2	78		>200:1 (endo:exo)	16
59	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	$(CH_3)_2C{=}CH_2$	H^+, CH_2Cl_2, −78 °C	1:2	45	82		16
60	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	$Ph_2C{=}CH_2$	H^+, CH_2Cl_2, −78 °C	1:2	75			16
61	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	(*E*)-PhCH=CHPh	H^+, CH_2Cl_2, −78 °C	1:2	96			16
62	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	$CH_3CH{=}C(CH_3)_2$	H^+, CH_2Cl_2, −78 °C	1:2	91		>50:1 (cis:trans)	16
63	$Cp(CO)_2Fe$	C_6H_5	H	α-ether	$(CH_3)_2C{=}C(CH_3)_2$	H^+, CH_2Cl_2, −78 °C	1:2	59			16
64	$Cp(CO)_2Fe$	*p*-$C_6H_4OCH_3$	H	α-ether	propene	H^+, CH_2Cl_2, 0 °C	excess olefin	85		2.0:1 (cis:trans)	36
65	$Cp(CO)_2Fe$	*p*-C_6H_4F	H	α-ether	propene	H^+, CH_2Cl_2, 0 °C	excess olefin	80		9.4:1	36
66	$Cp(CO)_2Fe$	*p*-$C_6H_4CF_3$	H	α-ether	propene	H^+, CH_2Cl_2, 0 °C	excess olefin	67		7.3:1	36
67	$Cp(CO)_2Fe$	*p*-$C_6H_4CH_3$	H	α-ether	propene	H^+, CH_2Cl_2, 0 °C	excess olefin	60		9.0:1	36
68	$Cp(CO)_2Fe$	*m*-$C_6H_4OCH_3$	H	α-ether	propene	H^+, CH_2Cl_2, 0 °C	excess olefin	81		9.6:1	36
69	$Cp(CO)_2Fe$	H	H	α-ether	cyclohexene	H^+, acetone, 0 °C	n/a	46			5
70	$Cp(CO)_2Fe$	H	H	α-ether	(*Z*)-2-butene	H^+, acetone, 0 °C	n/a	n/a		all cis	5
71	$Cp(CO)_2Fe$	H	H	α-ether	(*E*)-2-butene	H^+, acetone, 0 °C	n/a	n/a		all trans	5
72	$Cp(CO)_2Fe$	H	H	α-bromide	cyclohexene	50 °C	n/a	80			5a
73	$Cp(CO)_2Fe$	H	H	α-ether	cyclohexene	gas-phase ionization	n/a	n/a			54
74a	$Cp(CO)_2Fe$	H	H	dimethylsulfonium salt	cyclooctene	dioxane, 100 °C, 4–12 h	2:1	76	92		26
74b	$Cp(CO)_2Fe$	H	H	diphenylsulfonium salt	cyclooctene	22 °C, 3 h	1:1	85			28b
75	$Cp(CO)_2Fe$	H	H	dimethylsulfonium salt	1:1 cis:trans cyclododecane	dioxane, 100 °C, 4–12 h	2:1		90	1:1 (cis:trans isomers)	26

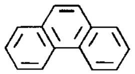
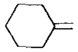
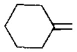
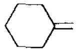
76	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt	(*E*)-PhCH=CHPh	dioxane, 100 °C, 4–12 h	2:1		40	all trans	26
77	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt	Ph$_2$C=CH$_2$	dioxane, 100 °C, 4–12 h	2:1	88	99		26
78	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt		dioxane, 100 °C, 4–12 h	2:1		31		26
79	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt	1-decene	dioxane, 100 °C, 4–12 h	2:1		56		26
80	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt	(*E*)-5-decene	dioxane, 100 °C, 4–12 h	2:1		33	all trans	26
81	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt	(*Z*)-5-decene	dioxane, 100 °C, 4–12 h	2:1		51	all cis	26
82	(R_{Fe})-Cp(CO)(PPh$_3$)Fe	H	H	α-menthyl ether	PhCH=CHMe	HBF$_4$	neat olefin	n/a		26% ee (1*R*,2*R*)	32
83	(S_{Fe})-Cp(CO)(PPh$_3$)Fe	H	H	α-menthyl ether	PhCH=CHMe	HBF$_4$	neat olefin	n/a		38% ee	32
84	(R_{Fe})-Cp(CO)(PPh$_3$)Fe	H	H	α-bromide	PhCH=CHMe	4 h, dark (neat olefin)	1:7		47	10% ee (1*S*,2*S*)	34
85	Cp(CO)(PPh$_3$)Fe	H	H	α-ether	cyclohexene	H$^+$, acetone, 25 °C	n/a		11		5b
86	Cp(CO)(PPh$_3$)Fe	H	H	α-ether	cyclohexene	H$^+$, acetone, −78 → 25 °C	n/a		63		5b
87	Cp(diphos)Fe	H	H	α-ether	cyclohexene	H$^+$, acetone, 25 °C	n/a		0		5b
88	Cp(diphos)Fe	H	H	α-ether	cyclohexene	H$^+$, acetone, −78 °C	n/a		1.6		5b
89	Cp(diphos)Fe	H	H	α-ether	cyclohexene	H$^+$, Ac$_2$O, −20 °C	n/a		23		5b
90	Cp(diphos)Fe	H	H	α-ether	CH$_2$=CHOEt	H$^+$, CH$_2$Cl$_2$	n/a	98			33
91	Cp(diphos)Fe	H	H	α-ether	1-pentene	H$^+$, CH$_2$Cl$_2$	n/a	10			33
92	Cp(diphos)Fe	H	H	α-ether	cyclohexene	H$^+$, CH$_2$Cl$_2$	n/a	30			33
93	(C$_5$Me$_5$)(CO)$_2$Fe	H	H	α-ether	styrene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −90 °C	n/a	70	100		7
94	Cp(CO)$_3$Mo	H	H	α-ether	cyclohexene	H$^+$	n/a	n/a			5a
95	Cp(CO)$_2$(PPh$_3$)Mo	H	H	α-pivalate	styrene	CF$_3$SO$_3$ SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		50		25
96	Cp(CO)$_2$(PPh$_3$)W	H	H	methyl complex	styrene	Ph$_3$C$^+$, CH$_2$Cl$_2$, −78 °C	1:2		52		25
97	Cp(CO)$_2$(PEt$_3$)W	H	H	methyl complex	styrene	Ph$_3$C$^+$, CH$_2$Cl$_2$, −78 °C	1:2		50		25
98	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	THF, 67 °C, 26 h	1:2		27		28
99	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	dioxane, 100 °C, 16 h	1:2		9		28
100	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	CH$_3$CN, 82 °C, 17 h	1:2		49		28
101	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	CH$_3$CN, 82 °C, 15 h	2:1		28		28
102	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	CH$_3$CN, 82 °C, 42 h	1:5		47		28
103	Cp(PPh$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	145 °C, 24 h	neat olefin		30		28

TABLE I (Continued)

		=CRR′					carbene:	cyclopropane yield, %		cyclopropane	
entry	L_nM	R	R′	precursor	substrate	conditions	olefin	isolated	GC	stereochem	ref
104	Cp(PhPMe$_2$)Ni	H	H	dimethylsulfonium salt	cyclooctene	CH$_3$CN, 82 °C, 24 h	1:2		19		28
105	Cp(P(OMe)$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	CH$_3$CN, 82 °C, 20 h	1:3		47		28
106	Cp(P(OMe)$_3$)Ni	H	H	dimethylsulfonium salt	cyclooctene	dioxane, 100 °C, 20 h	1:2		25		28
107	Cp(CO)$_2$Fe	CH$_3$	H	α-ether		CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		86		21
108	Cp(CO)$_2$Fe	CH$_3$	H	α-ether		CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:1		67		21
109	Cp(CO)$_2$Fe	CH$_3$	H	α-ether		CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	2:1		99		21
110	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	cyclooctene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		60	>25:1 (endo:exo)	21
111	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	cyclooctene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:1		25	>25:1	21
112	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	cyclooctene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	2:1		87	>25:1	21
113	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	1-hexene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:4		48	1:1 (cis:trans)	21
114	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	1-hexene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		28	1:1	21
115	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	(*E*)-3-hexene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		3.4		21
116	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	(*Z*)-3-hexene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		58	>50:1	21
117	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_3CH{=}C(CH_3)_2$	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		52	>50:1	21
118	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	styrene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:2		75	4.7:1 (cis:trans)	21
119	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	styrene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:1		47	4.7:1	21
120	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	styrene	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	2:1		91	4.7:1	21
121	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	(*Z*)-DCH=CHPh	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		70	6.5:1 (no D trans to Ph)	37
122	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_3OC_6H_4CH{=}C''H_2$-*p*	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		50	0.9:1	37
					(*Z*)-DCH=CHC$_6$H$_4$OCH$_3$-*p*					D trans to Ar (loss of stereochem)	
123	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4CH_3$-*p*	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		75	6.0:1	37
					(*Z*)-DCH=CHC$_6$H$_4$CH$_3$-*p*					no D trans to Ar	
124	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4F$-*p*	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		83	7.0:1 (cis:trans)	37
125	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4Cl$-*p*	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		35	6.0:1	37
126	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4CF_3$-*p*	CF$_3$SO$_3$SiMe$_3$, CH$_2$Cl$_2$, −78 °C	1:5		10	5.0:1	37

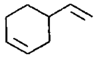
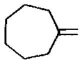
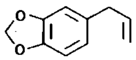
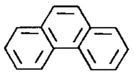
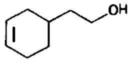
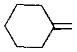
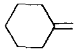
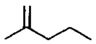
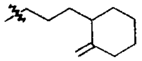
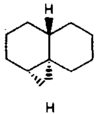
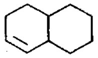
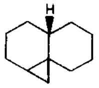
127	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4NO_2$-*p*	$CF_3SOSiMe_3$, CH_2Cl_2, −78 °C	1:5	0		51
128	Cp(CO)$_2$Fe	CH$_3$	H	α-ether	$CH_2{=}CHC_6H_4NMe_2$-*p*	$CF_3SO_3SiMe_3$, CH_2Cl_2, −78 °C	1:5	0		51
129	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	cyclooctene	$(CH_3)_3O^+BF_4^-$, CH_2Cl_2, 25 °C	1:1	73	all endo	27
130	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	cyclooctene	FSO_3CH_3, CH_2Cl_2, 25 °C	1:1	60	all endo	27
131	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	cyclododecene	CH_2Cl_2, 25 °C FSO_3CH_3	1:1	34	1:1 (endo:exo)	27
132	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	1-decene	$(CH_3)_3O^+BF_4^-$	1:1	47	1:1 (cis:trans)	27
133	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	1-decene	FSO_3CH_3	1:1	39	1:1	27
134	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*E*)-5-decene	$(CH_3)_3O^+BF_4^-$	1:1	14		27
135	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*E*)-5-decene	FSO_3CH_3	1:1	0		27
136	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	$(CH_3)_3O^+BF_4^-$	1:1	43	all cis	27
137	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	$(CH_3)_3O^+BF_4^-$	2:1	50	all cis	27
138	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	FSO_3CH_3	1:1	27	all cis	27
139	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	$(CH_3CH_2)_3O^+BF_4^-$	1:1	25	all cis	27
140	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	CH_3I	1:1	<2	all cis	27
141	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*Z*)-5-decene	$(CH_3)_3O^+SbCl_6^-$	1:1	0		27
142	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	styrene	$(CH_3)_3O^+BF_4^-$	1:1	67	all cis	27
143	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	styrene	FSO_3CH_3	1:1	54	all cis	27
144	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$PhC(CH_3){=}CH_2$	$(CH_3)_3O^+BF_4^-$	1:1	65	2.5:1 (syn:anti)	27
145	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$PhC(CH_3){=}CH_2$	FSO_3CH_3	1:1	58	2.5:1	27
146	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$Ph_2C{=}CH_2$	FSO_3CH_3, CH_2Cl_2, 25 °C	1:1	48		27
147	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	1-methylcyclohexene	$(CH_3)_3O^+BF_4^-$	1:1	22	5.6:1 (endo:exo)	27
148	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	40	1:1 (cis:trans addition to exocyclic bond only)	27
149	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	100		27
150	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$CH_2{=}CH(CH_2)_4Br$	$(CH_3)_3O^+BF_4^-$	1:1	50	0.9:1	27
151	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	37	1:1.3	27
152	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$CH_3CO(CH_2)_2CH{=}CH_2$	$(CH_3)_3O^+BF_4^-$	1:1	21	1:1.7	27
153	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	(*E*)-$CH_3CH{=}CH_2CO_2CH_3$	$(CH_3)_3O^+BF_4^-$	1:1	0		27
154	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	3-methylcyclohexene	$(CH_3)_3O^+BF_4^-$	1:1	0		27
155	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	0		27
156	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	0		27
157	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	3-bromocyclohexene	$(CH_3)_3O^+BF_4^-$	1:1	0		27
158	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	0		27
159	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$CH_2{=}CH(CH_2)_3OH$	$(CH_3)_3O^+BF_4^-$	1:1	0		27
160	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide	$CH_2{=}CHCH_2SPh$	$(CH_3)_3O^+BF_4^-$	1:1	0		27
161	Cp(CO)$_2$Fe	CH$_3$	H	α-phenyl sulfide		$(CH_3)_3O^+BF_4^-$	1:1	0		27

TABLE I (Continued)

		=CRR'					carbene:	cyclopropane yield, %		cyclopropane	
entry	L_nM	R	R'	precursor	substrate	conditions	olefin	isolated	GC	stereochem	ref
162	$(C_5Me_5)(CO)_2Fe$	CH_3	H	α-ether	(*Z*)-DCH=CHPh	H^+, CH_2Cl_2, −78 °C	1:3		80	>100:1 (cis:trans; Ar, D all cis)	51
163	$(C_5Me_5)(CO)_2Fe$	CH_3	H	α-ether	(*Z*)-DCH=CHC$_6$H$_4$OCH$_3$-*p*	H^+, CH_2Cl_2, −78 °C	1:3		n/a	>100:1 (Ar, D all cis)	51
164	Cp(CO)(PPh$_3$)Fe	CH_3	H	α-ether	(*Z*)-DCH=CHPh	H^+, CH_2Cl_2, −78 °C	1:3		47	1:3 (Ph, D all cis)	51
165	Cp(CO)(PPh$_3$)Fe	CH_3	H	α-ether	(*Z*)-DCH=CHC$_6$H$_4$OCH$_3$-*p*	H^+, CH_2Cl_2, −78 °C	1:3		n/a	1:1.5 (Ar, D all cis)	51
166	(S_{Fe})-Cp(CO)-(PPh$_2$R)Fe (R = 2-methylbutyl)	CH_3	H	α-ether	styrene	$CF_3SO_3SiMe_3$, CH_2Cl_2, −78 °C	1:7		75	1:3.5 (cis:trans; (*RS*):(*RR*))	31
167	(R_{Fe})-Cp(CO)-(PPh$_2$R)Fe (R = 2-methylbutyl)	CH_3	H	α-ether	styrene	$CF_3SO_3SiMe_3$, CH_2Cl_2, −78 °C	1:7		75	1:4.0 ((*SR*):(*SS*))	31
168	Cp(CO)$_2$Fe	CH_3	H	vinyl complex	PhC(CH$_3$)=CH$_2$	H^+, CH_2Cl_2	1:10–20		10–40	(mostly syn)	29
169	Cp(CO)$_2$Fe	CH_3	H	vinyl complex	PhC(CH$_3$)=CH$_2$	H^+, CH_2Cl_2	1:10–20		10–40	(all endo)	29
170	Cp(CO)$_2$Fe	CH_2CH_3	H	α-ether		$CF_3SO_3SiMe_3$, CH_2Cl_2, −78 °C	1:2		8		22
171	Cp(CO)$_2$Fe	$CH(CH_3)_2$	H	α-ether		$CF_3SO_3SiMe_3$, CH_2Cl_2, −78 °C	1:2		<1		22
172	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	PhC(CH$_3$)=CH$_2$	H^+, CH_2Cl_2, −78 °C	1:10–20		10–40		29
173	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	1-decene	H^+, CH_2Cl_2, −78 °C	1:10–20		10–40		29
174	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex		H^+, CH_2Cl_2, −78 °C	1:10–20		0		29
175	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	(*Z*)-5-decene	H^+, CH_2Cl_2, −78 °C	1:10–20		0		29
176	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	3-methylcyclohexene	H^+, CH_2Cl_2, −78 °C	1:10–20		0		29
177	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	cyclooctene	H^+, CH_2Cl_2, −78 °C	1:10–20		0		29
178	Cp(CO)$_2$Fe	CH_3	CH_3	2-propenyl complex	cyclododecene	H^+, CH_2Cl_2, −78 °C	1:10–20		0		29
179	Cp(CO)$_2$Fe	CH_3	CH_3	α-ether	(CH$_3$)$_2$C=CH$_2$	CH_2Cl_2, −40 °C	1:6		20		23
180	Cp(CO)$_2$Fe	CH_3	CH_3	α-ether	styrene	CH_2Cl_2, −65 °C	1:12		45		23
181	Cp(CO)$_2$Fe		H	α,ω-diene	R (intramolecular)	H^+, CH_2Cl_2, −50 °C			<10		29
182	Cp(CO)$_2$Fe		H	α-phenyl	R (intramolecular)	(CH$_3$)$_3$O$^+$BF$_4^-$, −50 °C		80			30
183	Cp(CO)$_2$Fe	H	H	dimethyl-sulfonium salt		dioxane, 100 °C	1:1	n/a			30
184	Cp(CO)$_2$Fe	HC=C(CH$_3$)$_2$	H	γ-allyl alcohol	(CH$_3$)$_2$C=CH$_2$	CH_2Cl_2, −23 °C	1:300		56		23
185	Cp(CO)$_2$Fe	HC=C(CH$_3$)$_2$	H	γ-allyl alcohol	cyclooctene	CH_2Cl_2, −15 °C	1:3		37	all endo	23

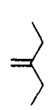
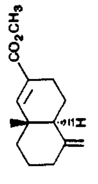
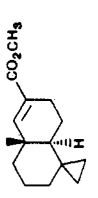
186	Cp(CO)$_2$Fe	HC═C(CH$_3$)$_2$	H	γ-allyl alcohol	styrene	CH$_2$Cl$_2$, −15 °C	1:3		45	1:2 (cis:trans)	23
187	Cp(CO)-(P(OMe)$_3$)Fe	HC═C(CH$_3$)$_2$	H	α,γ-diene complex	styrene	H$^+$, CH$_2$Cl$_2$, −20 °C	large excess olefin	15		5:1 (cis:trans)	38
188	Cp(CO)$_2$Fe	c-C$_3$H$_5$	H	α-ether	styrene	H$^+$, CH$_2$Cl$_2$, −50 °C	1:2		66	1:3.4	39
189	Cp(CO)$_2$Fe	c-C$_3$H$_5$	H	α-ether		H$^+$, CH$_2$Cl$_2$, −50 °C	1:2		64		39
190	Cp(CO)$_2$Fe	H	H	dimethylsulfonium salt		25 °C, 4 h	n/a	86			26c

table. Clearly a variety of combinations of metals, ligands, and carbene substituents may be used in the transfer reactions. Although we will not discuss each entry in detail, a few general comments will be offered as regards the transfer of each type of carbene moiety.

1. Methylene Complexes (Table Entries 69–106)

Electrophilic methylene complexes are the structurally simplest systems, were the earliest transfer reagents examined, and have received wide attention. The broad range of metal/ligand combinations which have been used in such transfers suggests that there is considerable latitude available for the development of general carbene transfer reagents.

The method of Jolly and Pettit (acid-induced ionization of an α-ether or ester complex) has been used for in situ generation and transfer of methylene from Cp(CO)$_2$Fe═CH$_2^+$ (1),[5] Cp(diphos)Fe═CH$_2^+$ (11),[5b,33] Cp(CO)$_3$Mo═CH$_2^+$ (12),[5a] (C$_5$Me$_5$)(CO)$_2$Fe═CH$_2^+$ (13),[7] Cp(CO)(PPh$_3$)Fe═CH$_2^+$ (14),[32] and Cp(CO)$_2$(PPh$_3$)Mo═CH$_2^+$ (15).[25] Only a limited range of olefins have been examined (styrene, β-methylstyrene, cyclooctene, and *trans*-2-butene). Yields, where reported, are moderate (50%). Hydride abstraction (by Ph$_3$C$^+$) from the appropriate methyl complex was used to generate and spectroscopically characterize complexes Cp(CO)$_2$(PPh$_3$)W═CH$_2^+$ (16) and Cp(CO)$_2$(PEt$_3$)W═CH$_2^+$ (17).[25] These species react with styrene to give ca. 50% yields of cyclopropane. The presence of a good electron-donating ligand at the metal center is responsible for the relative stability of complexes **15**, **16**, and **17**. Additional donor ligands further increase the stability of methylene complexes while suppressing their reactivity. A combination of reduction of electrophilic character and increase in steric bulk is probably responsible. Thus, the complex Cp(diphos)Fe═CH$_2^+$ **11** is relatively stable at temperatures below 0 °C and gives low-transfer yields with cyclohexene but high yields with the electron-rich ethyl vinyl ether.[5b,33]

Thermolysis of the complex Cp(CO)$_2$Fe–CH$_2$S(CH$_3$)$_2^+$ (18) (with presumed in situ generation of 1) in the presence of olefins is an efficient means for the synthesis of cyclopropanes.[26] This has been the most extensively studied methylene transfer system to date. The reactions of **18** with a variety of olefins demonstrated that moderate to very good yields of cyclopropanes could be obtained; it was also found that the stereochemistry about the carbon–carbon double bond was completely retained in the product. The ease of preparation, handling, and storage of **18** add to its attractiveness as a synthetic reagent. When yields are low, starting olefins are often recovered, so high conversions to cyclopropanes can be achieved by use of excesses of **16**. Complex **18** has recently been used by Wender in the synthesis of warburganal.[26c]

The thermally-induced reactions of the complexes Cp(PCH$_3$Ph$_2$)Ni–CH$_2$S(CH$_3$)$_2^+$ and Cp(P(OCH$_3$)$_3$)Ni–CH$_2$S(CH$_3$)$_2^+$ with cyclooctene under a variety of conditions have also been studied.[28] Generally lower yields are obtained with these latter complexes relative to the analogous iron reagent **18**.

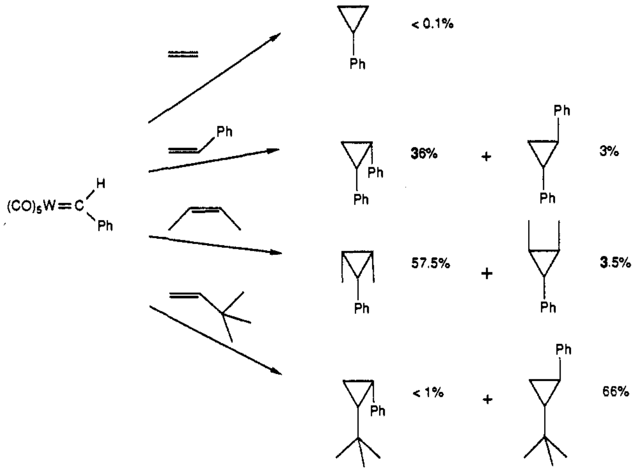
The chiral-at-iron complex Cp(CO)(PPh$_3$)Fe═CH$_2^+$ (14) was used by two groups to demonstrate the potential applications of carbene complexes to enantioselective syntheses. The reaction of (+)-Cp(CO)-

(PPh$_3$)Fe–CH$_2$–((L)-OMenthyl) (**19**), HBF$_4$, and neat *trans*-β-methylstyrene gave a 26% ee of (1*R*,2*R*)-*trans*-1-methyl-2-phenylcyclopropane.[32] (+)-Cp(CO)(PPh$_3$)Fe–CH$_2$Br, prepared by treatment of (+)-**17** with HBr, reacted with the same substrate directly to give a 10% ee of (1*S*,2*S*)-*trans*-1-methyl-2-phenylcyclopropane in 55% yield.[34] The precise reasons for these conflicting results are not clear. As later results indicate (see below) much higher ee's can be achieved when the carbene carbon is prochiral. Enantioselectivity does not then depend as here on *si* versus *re* facial selection of attack on the alkene.

2. Phenylcarbene Complexes (Table Entries 30–68)

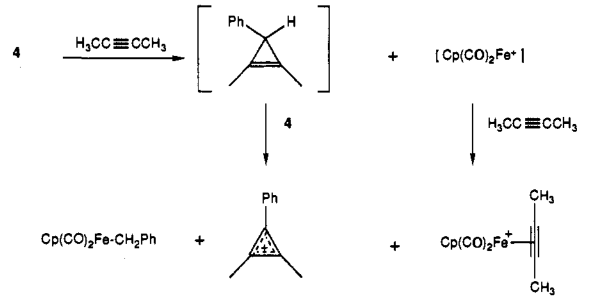
The first study of phenylcarbene transfer reactions was reported by Casey et al. using (CO)$_5$W=CHPh **3** generated in situ.[15] An extensive range of olefinic substrates was examined. Transfers were carried out at −78 °C for 4 h by using large excesses of olefins, usually 100-fold or greater. Moderate to excellent yields were obtained for all alkyl and aryl substituted olefins studied except ethylene (yield <0.1%). Relative rate studies were reported and are considered in the next section.

Stereochemistry about the double bond was maintained and, in general, cis or syn selectivity in the product cyclopropane was observed. For example, *cis*-2-butene gave a 40:1 ratio of 1-phenyl-*cis*,*cis*-2,3-dimethylcyclopropane:1-phenyl-*trans*,*trans*-2,3-dimethylcyclopropane and styrene gave 11:1 *cis*:*trans* 1,2-diphenylcyclopropane. Propene gave a 2:1 *cis*:*trans* selectivity, but as the single alkyl substituent increased in size a remarkable shift toward trans selectivity was noted (R = *i*-Pr, c:t = 1:2; R = *t*-Bu, c:t = 1:100). Mechanistic implications of this trend are discussed below.



Several additional transfers using (CO)$_5$W=CHPh (**3**) are reported in a later study by Doyle who draws parallels between Rh$_2$(OAc)$_4$-catalyzed additions of :CHPh using PhCHN$_2$ and stoichiometric additions using (**3**).[35] Of particular note is the observation that alkoxy- and acetoxy-substituted alkenes give cyclopropanes in high yields. For example, ethyl vinyl ether and vinyl acetate give phenylcyclopropanes in 89% and 85% yields with cis:trans ratios of 7.6 and 10.5, respectively.

Phenylcarbene transfers can also be accomplished using Cp(CO)$_2$Fe=CHPh$^+$ (**4**) as a stable salt or generated in situ.[16] Yields of transfer products are good to excellent for all alkyl and aryl substituted olefins studied including ethylene (see Table I). This contrast in reactivity toward ethylene together with spectroscopic studies suggest the cationic complex **4** is more electrophilic than the neutral **3**. As a part of this study Brookhart et al. also reported phenylcarbene transfer to an alkyne, 2-butyne, which yields a cyclopropenium salt probably via the following pathway:



This appears to be the only report of such a transfer to an alkyne.

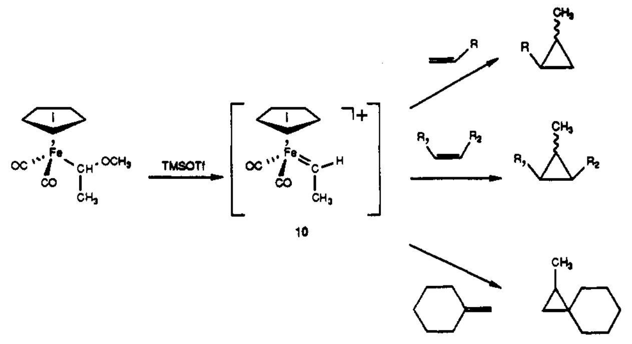
Stereochemical results reported for **4** parallel those for **3**. Stereochemistry about the original double bond is maintained. Cis or syn selectivity is observed; however, the iron phenylcarbene complex is more selective than the tungsten complex. For example, compare the results of phenylcarbene transfer to styrene: the product cis:trans ratio = 11:1 for **3** versus >100:1 for **4**. Brookhart and Broom found that substitutions of electron-donating and withdrawing groups on the aryl ring in **4** had little effect on the stereoselectivity of the carbene complexes in reaction with propene, although the p-methoxy derivative of **4** yielded 1-methyl-2-(*p*-methoxyphenyl)cyclopropane with an anomalously low cis:trans ratio.[36]

3. Methylcarbene and Other Alkylcarbene Complexes (Table Entries 107–183)

The synthesis of methylcyclopropanes using iron methylcarbene complexes has been the origin of much of the interest in the chemistry of carbene complex transfer reactions. In contrast to methylene transfer where Simmons–Smith type reagents and metal-catalyzed diazomethane reactions are extensively used for :CH$_2$ transfer, techniques for transferring methylcarbene using conventional carbenoid reagents are much less successful. Rearrangements of the free carbene or the carbenoid via hydrogen migration to give ethylene are normally dominant relative to addition to alkenes.

Brookhart et al. observed that treatment of Cp(CO)$_2$Fe–CH(OCH$_3$)CH$_3$ with strong acid or trimethylsilyl triflate at low temperatures in the presence of olefins gave methylcyclopropanes.[21] The reaction presumably proceeds via the intermediate methylcarbene complex Cp(CO)$_2$Fe=CHCH$_3$$^+$ **10**, although that species has escaped direct observation.

The electrophilic nature of the addition is evident by noting the qualitative trend in the yields (see the table). Lower yields are observed with simple terminal alkyl substituted olefins in contrast to higher yields obtained for styrene and 1,1′-disubstituted alkenes. A steric effect on rate of addition is evident in the very low yields obtained from *trans*-3-hexene relative to moderate yields from *cis*-3-hexene. Low yields normally result from competitive decay of the carbene complex,



thus much higher conversions of olefin to cyclopropane can be achieved by using excess carbene complex.

With one notable exception, the stereochemistry about the double bond was preserved in the product cyclopropane. (The exception involved methylcarbene addition to cis-β-deuterio-*p*-methoxystyrene where a stable *p*-methoxyphenyl-substituted carbocation can be formed.[37] See mechanistic section for further discussion.) Where two product isomers were possible there was a general preference for formation of the cis (or syn or endo) isomer; in some cases only the cis isomer was observed within the detection limits (<2% trans). More stereocontrol is exerted by substituents at C_1 (the initial site of attack of the electrophilic carbene complex) than at C_2 as evidenced by the nearly 1:1 cis:trans cyclopropane isomer ratio from 1-hexene and the >50:1 isomer ratio for 2-methyl-2-butene and cis-3-hexene.

Product isomer ratios are quite sensitive to the ancillary ligands at the iron center. For example in transfer of methylcarbene to styrene the product cis:trans isomer ratios vary from 5:1 for $Cp(CO)_2Fe{=}CHCH_3^+$ (**10**)[16] to >99:1 for $C_5Me_5(CO)_2Fe{=}CHCH_3^+$ (**20**)[25] to 1:3.5 (i.e. trans selectivity) for $Cp(CO)(CH_3CH_2CH(CH_3)CH_2PPh_2)Fe{=}CHCH_3^+$ (**21**).[31]

The reactions of **10** with a series of para-substituted styrenes helped evaluate which factors are important in determining the course of the transfer reaction. The cis:trans ratio of the product cyclopropanes was fairly insensitive to the electron-donating or withdrawing capacity of the para substituent.[37] Stereoselection in these reactions is therefore primarily a steric effect. On the other hand, strongly electron-withdrawing substituents (Cl, CF_3) gave significantly reduced yields of cyclopropanes. This is not surprising; the electron-deficient olefins should be less rapidly attacked by electrophiles. These last results are examined more closely in the discussion of reaction mechanisms below.

Kremer and Helquist have studied the methylcarbene transfer reactions of $Cp(CO)_2Fe{-}CH(SPhCH_3)CH_3^+$ (**22**), generated in situ by the reaction of $Cp(CO)_2Fe{-}CH(SPh)CH_3$ with methylating agents, typically $(CH_3)_3O^+BF_4^-$. Efficient methylcarbene transfer to a variety of olefins was observed, most likely via the intermediate methylcarbene complex **10** (see below).[27] The results were qualitatively similar to those obtained using $Cp(CO)_2FeCH(OCH_3)CH_3$ + Me_3SiOTf, in particular the cis, syn, or endo selectivity of the transfer reaction. (The only substantially different results as regards stereoselection concern methylcarbene transfer to styrene. Brookhart reports a 5:1 cis:trans isomer ratio in the product cyclopropanes whereas Helquist reports formation of only the cis isomer.) The reaction of **22** with 4-vinylcyclohexene was regiospecific, the only observed products being a 1:1 mixture of cis and trans-1-(3-cyclohexenyl)-2-methylcyclopropane. Transfers to remotely functionalized olefins were successful (table entries 150–152), although allylic substituents (e.g. acyl, Br) apparently deactivated olefins to methylcarbene transfer. Alcohols were also found to be unreactive in a transfer sense. Other olefins containing nucleophilic substituents should be expected to exhibit similar problems as a result of direct nucleophilic attack on the electrophilic carbene complex.

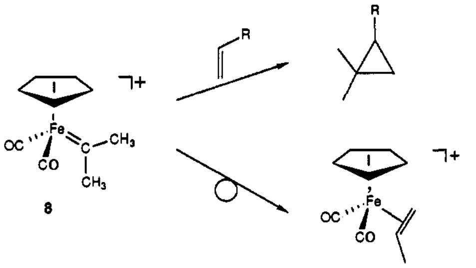
As regards comparison of the synthetic utilities of $Cp(CO)_2Fe{-}CH(CH_3)S(CH_3)Ph^+$ and $Cp(CO)_2Fe{-}CH(OCH_3)CH_3$, the sulfonium route gives somewhat higher yields, but isomerization (acid-catalyzed?) of cyclopropane products can occur (e.g. 3-ethylcyclooctene from cyclooctene) at the required reaction temperatures (25 °C). Transfer reactions using $Cp(CO)_2Fe{-}CH(OCH_3)CH_3$ can be carried out at −80 °C (better yields are obtained at even −100 °C)[24] and cold, basic workup can be used to avoid any cyclopropane ring-opening isomerizations. Both precursors are readily prepared and stored as solids.

Results reported by Brookhart et al. indicate that the chiral-at-iron complexes Cp(CO)((*S*)-$CH_3CH_2CH(Me)CH_2PPh_2)Fe{=}CHCH_3^+$ **21**, analogous to the chiral methylene complex **14** studied by Davison[32] and Flood,[34] are quite good reagents for the enantioselective synthesis of methyl-substituted cyclopropanes.[31] The spectroscopically characterized complex (S_{Fe},S_C)-**21** reacted with styrene to give a 3.5:1 mixture of (1*R*,2*R*)-*trans*-1-methyl-2-phenylcyclopropane (**23**) (88% ee) and (1*R*,2*S*)-*cis*-**23** (84% ee). The (R_{Fe},S_C) isomer of **21** reacted with styrene to give quantitatively similar yields producing the opposite pair of enantiomers, (1*S*,2*S*)-*trans*-**22** and (1*S*,2*R*)-*cis*-**23**. A major difference between these chiral carbene complexes and the chiral methylene complexes described by Davison and by Flood is that the C_α carbon is prochiral in the former systems but not the latter systems.

The methylcarbene complex $Cp(CO)_2Fe{=}CHCH_3^+$ **10** has been generated in situ by protonation of the η^1-vinyl species $Cp(CO)_2Fe{-}CH{=}CH_2$.[29] Carried out in the presence of 10–20 equiv of olefin, transfers occur with 10–40% yields; for *cis*-cyclooctene and α-methylstyrene syn selectivity is observed consistent with earlier results.

More highly alkylated species relative to the simple methylcarbene complex (**10**) as noted earlier, suffer more rapid decay via 1,2 hydride migrations to yield alkenes or alkene complexes. This fact, coupled with increased steric hindrance and in disubstituted systems decreased electrophilicity, greatly reduces transfer yields of these species relative to methylcarbene. For example in situ generation of $Cp(CO)_2Fe{=}CHCH_2CH_3^+$ in the presence of methylenecyclohexane gives the cyclopropane in only ca. 8% yield.[22] Protonation of $Cp(CO)_2Fe{-}C(Ph){=}CH_2$ in the presence of olefins yields only $Cp(CO)_2Fe(CH_2{=}CHPh)^+$ and no cyclopropanes.[29]

More success has been achieved with the dimethylcarbene species $Cp(CO)_2Fe{=}C(CH_3)_2^+$ **8**. Casey et al. have reported preparation of stable salts of this species via either protonation of $Cp(CO)_2Fe{-}C(CH_3){=}CH_2$ or $Cp(CO)_2Fe{-}C(CH_3)_2OCH_3$.[23] The complex undergoes 1,2 hydride migration quantitatively at −11 °C ($t_{1/2}$ = 70 min) to give $Cp(CO)_2Fe(CH_2{=}CHCH_3)^+$. However, for reactive alkenes carbene transfer is competitive with



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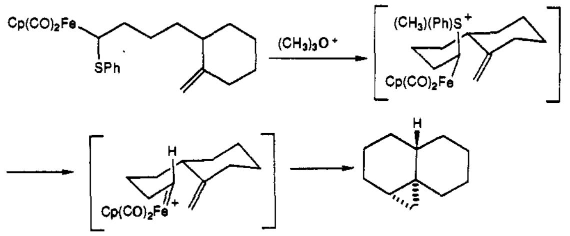
decay and *gem*-dimethylcyclopropanes are produced in 20–33% yield from isobutene and 45% yield from styrene. No transfer to the less reactive 1-octene could be observed. Helquist has also carried out in situ generation of 8 via protonation of $Cp(CO)_2Fe{-}C(CH_3){=}CH_2$ and observed *gem*-dimethylcyclopropanes from isobutene, styrene, α-methylstyrene, 1,1-diphenylethylene, and 1-decene (yields not reported).[29] No transfer products could be detected using 2-methyl-1-pentene, *cis*-5-decene, 4-methylcyclohexene, *cis*-cyclooctene, and *cis*-cyclodecene.

Helquist et al. have demonstrated that intramolecular trapping can compete effectively with hydride migrations in alkylidene complexes of the type $Cp(CO)_2Fe{=}CHCHRR'^+$ where R or R′ contain a double bond remote to C_α. The stereochemical control exhibited by such reactions suggests synthetic utility for such reactions in constructing polycyclic ring systems.[29,30]



4. *Other Carbene Complexes (Table Entries 184–189)*

Generation and transfer reactions of stable monosubstituted carbene complexes of the type $Cp(CO)(L)Fe{=}CHR^+$ have been reported for R = vinyl and cyclopropyl, both carbocation-stabilizing substituents. As regards synthetic utility, these are interesting species in that free carbenes and classical carbenoid reagents containing these substituents undergo rapid intramolecular rearrangements; thus, transfer reactions are normally unsuccessful.

Casey[23a,c] and Helquist[38] independently prepared the vinylcarbene complex $Cp(CO)_2Fe{=}CH(CH{=}C(CH_3)_2)^+$ 9. Casey found 9 to be modestly useful as a carbene-transfer reagent; Helquist obtained a similar result for the derivative $Cp(CO)(P(OCH_3)_3)Fe{=}CH(CH{=}C(CH_3)_2)^+$. Vinylcyclopropanes were obtained from styrene, isobutene, and cyclooctene. Casey noted that contrary to normal cis selectivity, transfer of dimethylvinylcarbene to styrene gives predominantly the trans vinylcyclopropane isomer.

Brookhart, Studabaker, and Husk prepared and spectroscopically characterized the cyclopropyl-substituted carbene complex $Cp(CO)_2Fe{=}CH\text{-}c\text{-}C_3H_5^+$ (24), which was shown to be an effective reagent for the synthesis of dicyclopropanes. Good yields were obtained in transfers to 2-ethyl-1-butene and styrene, with a trans selectivity noted in transfer to styrene (cis:trans = 1:3.5).[39]

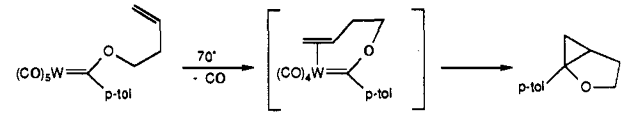
IV. Mechanistic Aspects of the Carbene-Transfer Reaction

A. Transfers Involving Transition-Metal–Carbene–Alkene Complexes as Intermediates

As outlined above, early studies by Casey suggested that reactions of $(CO)_5W{=}CPh_2$ with alkenes occurred via loss of CO and formation of carbene alkene complexes, $(CO)_4(alkene)W{=}CPh_2$.[12] Through equilibration with a metallacyclobutane, both cyclopropane and olefin scission products could be generated (Scheme I). Based on these results (and consistent with those for the more reactive $(CO)_5W{=}CHPh$ for which transfers are observed without CO loss), Casey proposed an explanation for the unusual observations by Fischer wherein only highly activated or highly deactivated alkenes are reactive toward $(CO)_5M{=}C(OR)Ph$.[2b] Two different reaction pathways are suggested to be involved. Vinyl ethers are sufficiently electron rich that they can undergo direct reaction (without CO loss) with the weakly electrophilic alkoxy-stabilized carbene complexes. This pathway is favored by high CO pressures which suppress formation of alkene–carbene complexes. On the other hand, α,β-unsaturated esters are very weakly nucleophilic but good π-acid ligands for low valent metal complexes and thus react only via CO loss and formation of intermediate metal–alkene–carbene complexes.

Strong support for the involvement of carbene alkene complexes in these reactions has come from the work of Casey[40,41] and of Rudler[42] who have prepared stable chelated metal–carbene–alkene complexes and found in certain cases that these thermolyze to form cyclopropanes.

Mechanistically the most revealing study involves the thermolysis of 25 to form cyclopropane 27:[40b]



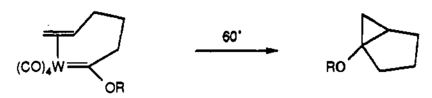
25 26 27

Spectroscopic studies establish the carbene–alkene complex 26 as an intermediate. Kinetically complex, the reaction exhibits an induction period and autocatalysis. Casey has proposed the following mechanism in which autocatalysis is due to CO abstraction from 25 by product $W(CO)_4$. The key feature is that $W(CO)_4$ is capable of abstracting CO from 2 equiv of 25 to form 2 equivalents of 26. Stated another way, decomposition

$$\begin{array}{ll} \text{induction} & 25 \rightarrow 26 + CO \\ \text{autocatalysis} & 26 \rightarrow 27 + W(CO)_4 \\ & W(CO)_4 + 25 \rightarrow 26 + W(CO)_5 \\ & W(CO)_5 + 25 \rightarrow 26 + W(CO)_6 \end{array} \tag{16}$$

of 1 equivalent of 26 leads to formation of 1 equiv of 27 and $W(CO)_6$ and regenerates not 1 but 2 equiv of 26.

Two other similar carbene–alkene complexes have been prepared which yield cyclopropane products. Both are six-membered ring chelates which form cyclopropanes with bicyclic [3.1.0] structures. Rudler has demonstrated by X-ray analysis of 28 that the carbene



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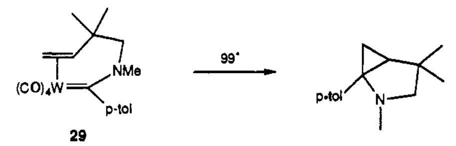

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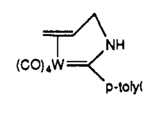
and alkene functions lie in a parallel face-to-face arrangement which is the requisite geometry for metallacyclobutane formation and subsequent extrusion of cyclopropane.[42] Complex **29** can adopt two conformations, one in which the carbene and alkene functions are nearly perpendicular and the parallel arrangement required for C–C coupling. These conformers equilibrate rapidly at 25 °C; cyclopropane formation probably occurs via the conformer with the parallel carbene–alkene conformation.[41]

Other similar stable chelated carbene–alkene complexes have been characterized but do not form cyclopropanes, for example **30**,[41a] **31**,[42] and **32**.[43] There are two key differences between these systems and those above which yield cyclopropanes: (1) the chelate ring is five-membered and X-ray analysis reveals unfavorable perpendicular carbene–alkene geometries, and (2) cyclopropane formation would result in highly strained [2.1.0] bicyclic products.



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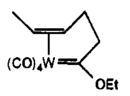

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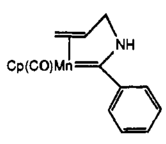

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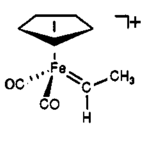
B. Transfers Occurring without Involvement of Transition-Metal-Carbene-Alkene Intermediates

The majority of the transfer reactions observed make use of highly electrophilic carbene complexes such as $(CO)_5W{=}CHPh$ and $Cp(CO)(L)Fe{=}CRR'^+$. These species react with alkenes at very low temperatures, far below those required for ligand dissociation. In addition, no alkene scission products are observed. All available evidence points to direct reaction of these metal carbene complexes with alkenes without prior formation of carbene–alkene complexes via ligand substitution.

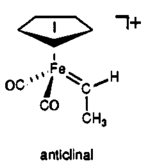
Substantial data relevant to the transfer mechanism are available: relative reactivities of a wide variety of alkenes with several carbene complexes; studies of the variation of cis:trans stereoselectivities as a function of alkene structure, substituents at the carbene carbon, and the L_nM fragment employed; and enantioselectivities observed using optically pure chiral-at-metal carbene complexes with known absolute configurations. We note from the outset of this discussion that to date there is no single general mechanistic model which accounts for all of the data and, ignoring subtleties, there is still a fundamental question concerning the basic mode of ring closure which remains to be answered (see below). Thus, although for specific systems there have been reasonable models proposed in each case, these still must be regarded as hypothetical.

Indeed, a truly complete mechanistic understanding of the transfers will be difficult to achieve since there are several variables which have a substantial impact on the rates and stereoselectivity of the reactions, including alkene substituents, carbene substituents, and variations of the ancillary metal ligands. Relative electrophilicities of the carbene complex and nucleophilicities of the alkene fragment can dictate early vs. late transition states. Steric interactions between the incoming alkene and the ligands on the metal as well as the carbene ligand orientation within the metal complex can play a major role in determining stereoselectivity. For example, consider the cis:trans cyclopropane product ratios observed for carbene transfer to styrene using these closely related species: $Cp(CO)_2Fe{=}CHCH_3^+$ (6.5:1, table entry 121), $(C_5Me_5)(CO)_2Fe{=}CHCH_3^+$ (>100:1, 162), $Cp(CO)(PPh_3)Fe{=}CHCH_3^+$ (1:3, 164), and $Cp(CO)_2Fe{=}CHcC_3H_5^+$ (1:3.4, 188).

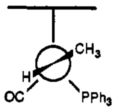
The structure of the dicarbonyl complexes, based on theory[44,45], X-ray analyses of related species,[46-48] and NMR analysis of $Cp(diphos)Fe{=}CH_2^+$,[33] almost certainly contains the carbene ligand in a plane bisecting the CO–Fe–CO angle. However, for monosubstituted systems, two isomers, anticlinal and synclinal, are possible. Although the anticlinal is *assumed* to be more stable (no direct proof is available), the barrier to equilibration must be quite low and no experiments have resolved through which isomer transfer reactions proceed or if both are possibly involved. Similarly, in the case of phosphine substituted systems the work of Gladysz clearly suggests anticlinal and synclinal isomers with the carbene plane aligned with CO.[48] Again, however, the barrier to interconversion in the iron systems is low, the equilibrium ratios have not been established,[49] and no experiments demonstrate conclusively which isomer (if not both) is the reactive one in the transfer reactions.



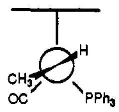
synclinal



anticlinal



synclinal

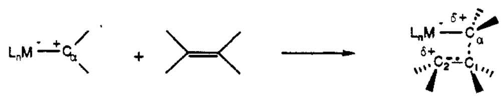


anticlinal

With these conditions and limitations in mind, we will review some of the relevant mechanistic data concerning the transfer reactions. Rather than chronological, we focus on the transfer mechanism in such a way that we consider first broad, generally-agreed-upon features and then more hypothetical proposals of specific transition-state models for transfers in several systems.

1. Electrophilic Nature of the Transfer Reaction

It is clearly established that for the transfer reactions considered in this review the electrophilic carbene complex attacks the nucleophilic alkene with substantial charge development in the transition state: (For purposes of further mechanistic discussions the carbene



33

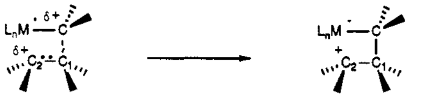
carbon and the two alkene carbons will be designated C_α, C_1, and C_2 as shown.)

Several studies support this view. In early work Casey et al. examined the relative reactivities of $(CO)_5W{=}CHPh$ with a series of alkenes.[15] Relative rates found for representative olefins were C_2H_4 (ca. 0), $CH_3CH{=}CH_2$ (11), cis-$CH_3CH{=}CHCH_3$ (8), $CH_2{=}C(CH_3)_2$ (3500), $CH_3CH{=}C(CH_3)_2$ (920), and $PhCH{=}CH_2$ (410). These results, especially the similarity of 2-butene to propene rather than isobutene, are consistent with a transition state involving unsymmetrical attack with partial charge build up on only C_2 and not a more symmetrical model where equal charge builds up at C_1 and C_2. Steric effects on rates are evident in the drop in reactivity of $(CH_3)_2C{=}CHCH_3$ and $(CH_3)_2C{=}C(CH_3)_2$ relative to $(CH_3)_2{=}CH_2$.

Kegley and Brookhart studied relative rates of reaction of $Cp(CO)_2Fe{=}CHCH_3^+$ with a series of para-substituted styrenes which effectively eliminates the influence of steric effects on relative reactivity. A good Hammett $\sigma^+\rho$ correlation was found with $\rho = -2.2$, which implies substantial positive charge buildup at C_2 in the transition state and supports a transition state similar to **33**.[51]

Although no other quantitative rate studies are reported, general trends in yields (See Table I) for most transfer reactions also support this transition-state model. Steric effects also play a significant role, e.g., compare generally lower yields of trans 1,2 disubstituted olefins with their corresponding cis isomers. (Table entries **80** and **81**, **115** and **116**, and **134–137**.)

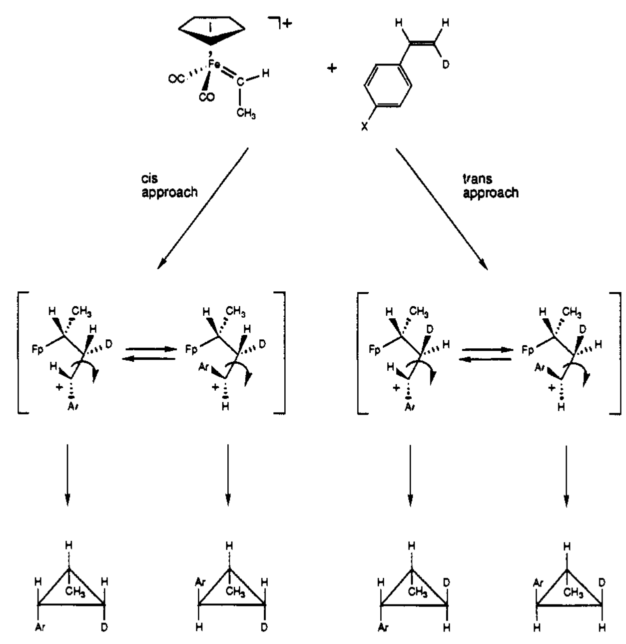
A question raised initially by Casey was whether subsequent to the transition state and prior to ring closure free carbocationic intermediates **34** may intervene.[15] Two observations were made which argue against this in phenylcarbene transfers from $(CO)_5W{=}CHPh$.[15] First, using *tert*-butylethylene no products from 1,2 methyl migration were observed. Second, the original alkene stereochemistry was always maintained in the product cyclopropane. Thus, no rotation around C_1–C_2 occurred as might be expected from **34**. In fact, for all transfer products reported in the table where stereochemistry was determined, the original olefin stereochemistry is maintained in nearly every case. Thus, if intermediates such as **34** are formed, collapse must be faster than rotation about C_1–C_2.



33 **34**

There is one important exception reported which introduces a note of caution in concluding alkene stereochemistry is always maintained. Kegley, Brookhart, and Husk studied the reaction of $Cp(CO)_2Fe{=}CHCH_3^+$ with a series of para-substituted styrenes.[37] With the exception of *p*-methoxystyrene (which yielded a cis:trans ratio of approximately 2:1) all substituted styrenes gave similar cis:trans ratios (ca. 6). Using *β-cis*-deuterio-*p*-methoxystyrene, the unusually low cis:trans ratio was shown to be due to loss of stereochemistry about the double bond which occurs *after* the rate determining step, no doubt via a carbocation intermediate analogous to **33**. The simplest mechanistic explanation is shown in Scheme IV. These results indicated that the cis:trans approach ratio was similar to that observed for other substituted styrenes (ca. 5) and that this is a "borderline" case for loss of stereochemistry, that is, C_1–C_2 rotation occurs on a similar time scale as collapse. This point is emphasized by the fact that no loss of stereochemistry is noted in the reaction of $Cp(CO)_2Fe{=}CHCH_3^+$ with *cis-β*-deuterio-*p*-methylstyrene nor does loss occur in reaction of the *less* electrophilic $Cp(CO)(PPh_3)Fe{=}CHCH_3^+$ with cis-*β*-deuterio-*p*-methoxystyrene. The results support the logical contention that olefin stereochemistry is most likely to be lost when the carbene complex is highly electrophilic and the alkene substituents allow formation of a stabilized carbocation.

SCHEME IV

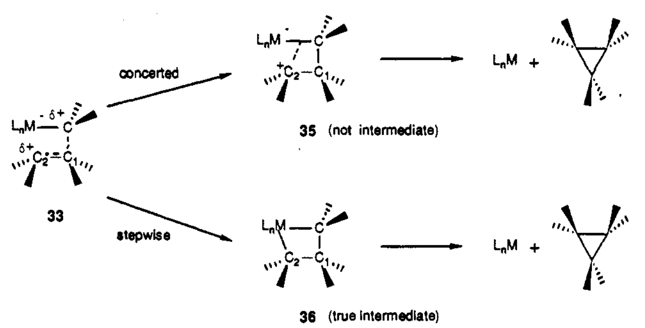


X				
H	87%	None observed (<2%)	None observed (<2%)	13%
CH_3	85%	None observed (<2%)	None observed (<2%)	15%
OCH_3	41%	41%	6%	13%

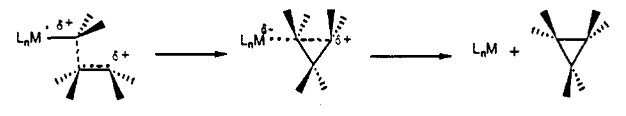
2. *Mode of Ring Closure*

Production of cyclopropanes fro our model transition state **33** must involve formation of a carbon–carbon bond between the electrophilic center C_2 and C_α with release of the ML_n fragment. There are two stereochemically distinct modes of ring closure. First a *frontside* attack of the developing electrophilic center C_2 on the M-C_α bond may occur in a concerted manner to yield a cyclopropane with retention of stereochemistry at C_α (from **33**). This pathway is stereochemically indistinguishable from collapse of **33** to yield a metallacyclic intermediate followed by reductive elimination. Since most electrophilic displacements are frontside in nature, the earlier mechanistic proposals assumed a pathway similar to those represented in Scheme V. However, there is a reasonable alternative pathway, *backside* closure of **33** with inversion of stereochemistry at C_α (We note here that transition state **33** is meant

SCHEME V

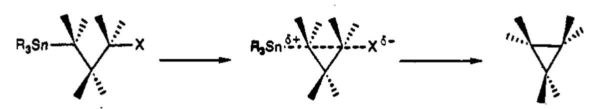


as a very general representation. We do not mean to imply a specific structure, nor can substantial interaction of C_2 with C_α or M be precluded. Transition states could be late and structures would then resemble, for example, **35** and **37**. Relative rate studies indicate only partial positive charge buildup on C_2.)



33 37

This mode of closure was first considered by Brookhart, Tucker, and Husk.[21b] It was noted that electrophilic cleavage of M–C bonds can occur with inversion and there is a close mechanistic analogy with cyclopropane formation from solvolysis of γ-Sn derivatives where stereochemical studies suggest a backside closure mechanism.[52] In the carbene-transfer reactions, closure via a backside mechanism looks sterically attractive.



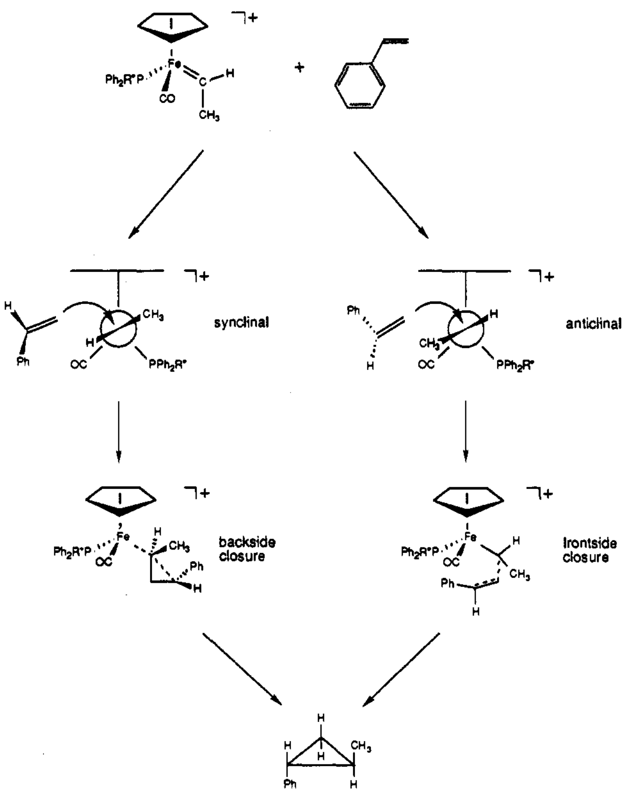
Remarkably, although absolutely fundamental to the mechanism, in no system yet examined has the nature of the ring closure, backside or frontside, been determined. Thus all models so far proposed for the transfers are limited by the lack of knowledge of this critical feature.

The system studied which comes closest to resolving this question is the enantioselective ethylidene transfer to styrene from the optically pure chiral-at-iron complexes (R_{Fe},S_C)- and (S_{Fe},S_C)-**20**.[31] The absolute configurations of the iron centers and of the product *cis*- and *trans*-1-phenyl-2-methylcyclopropanes were determined. The stereochemical outcome of the transfer is determined by several factors: the absolute configuration of the metal center, the reactive isomer (synclinal or anticlinal), the mode of approach of the olefin (over CO or over PPh_3), and the nature of ring closure (frontside or backside). The iron configuration is known and, based on the work of Gladysz,[48] approach of styrene over CO can be confidently assumed. The results are consistent only with reaction via the anticlinal isomer with frontside closure or via the synclinal isomer with backside closure. These pathways are illustrated in Scheme VI.

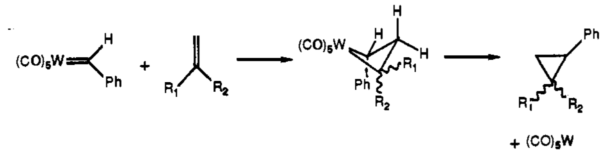
3. Specific Transition-State Models for Carbene Transfers

Although the mode of ring closure has yet to be determined, through the course of the many transfer studies which have been carried out, several specific transition state models have been proposed to account for the observed results. These are briefly summarized below.

SCHEME VI

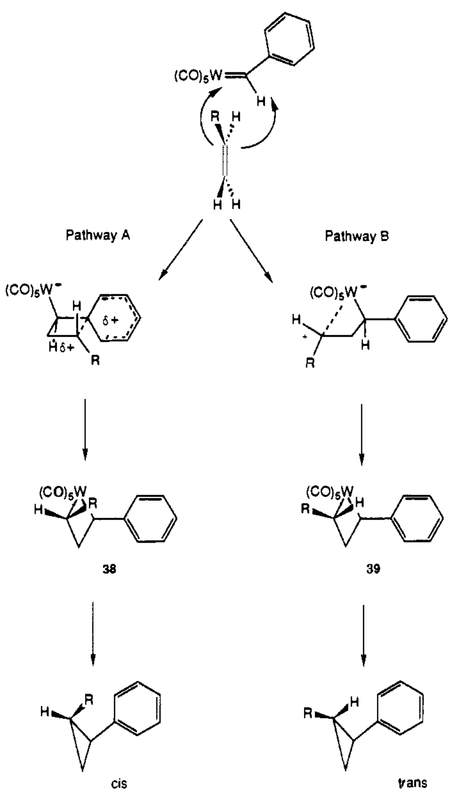


The first detailed proposals of transfer mechanisms were advanced by Casey et al. for carbene transfers involving $(CO)_5W{=}CHPh$ (**3**). Initially, metallacyclobutanes were presumed intermediates and models for the transition states of transfer reactions.[15a] However, later stereochemical results using an extensive series of substituted alkenes were incompatible with "bent" (puckered) metallacycles as transition-state models.[15b] The mechanistic model favored by Casey involves two competitive pathways whose relative rates for a given system are largely determined by steric effects. The transition states **38** and **39** for these pathways are illustrated for the reaction of a monosubstituted alkene with **3** (Scheme VII). Both involve frontside closure. (Metallacycles may or may not be involved *after* the transition state. There is no evidence for or against their existence.)

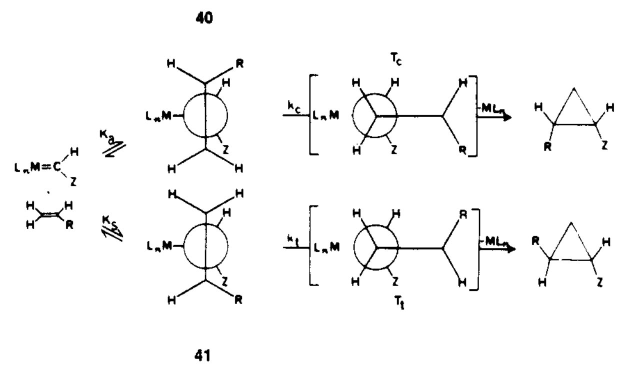


Pathway A involves stabilization of the developing positive charge at C_2 by interaction with the ipso carbon of the arene ring. Substituents have a slight steric preference to be trans to $(CO)_5W$ and, upon frontside collapse, the cis cyclopropane will predominate. The overall rate via this pathway will decrease with increasing bulk of R. Pathway B involves interaction at C_2 with the metal, the trans isomer is strongly favored, and rates are presumed insensitive to steric effects.

SCHEME VII



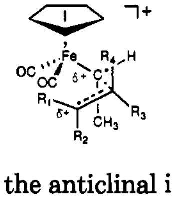
SCHEME VIII



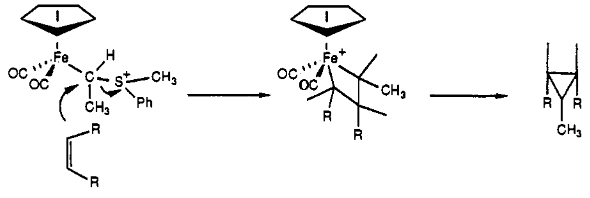
Thus, as the bulk of the substituent increases more product arises via pathway B and an increasing proportion of trans product is observed. This model also rationalizes why high cis selectivity is observed for trimethylethylene: the single methyl group at C_1 strongly prefers to be trans to $(CO)_5W$ in **38** (pathway A). Similar considerations apply to *cis*-2-butene.

The Casey model was also consistent with initial results obtained by Brookhart et al. for transfer of phenylcarbenes from $Cp(CO)_2Fe{=}CHPh^+$ (**4**) to a series of substituted alkenes.[16b] However, in later studies the cis:trans cyclopropane isomer ratio obtained from reaction of propene with a series of substituted phenylcarbene complexes $Cp(CO)_2Fe{=}CHC_6H_4X^+$ (Table entries 64–68) showed virtually no sensitivity to X (c/t ca. 7).[36] These results suggest the Casey model does not apply to phenylcarbene transfers in the iron systems. (The exception is for X = *p*-OCH_3 which shows a *low* c/t of 2. An ipso interaction mechanism as in Scheme VII would predict a *higher* cis:trans ratio. Spectroscopic results suggest this complex may react from a different conformation.[24])

A similar but less pronounced cis or syn selectivity was also noted for methylcarbene transfers from $Cp(CO)_2Fe{=}CHCH_3^+$ (**18**).[21,27] Unlike the aryl substituent in **3** or **4**, no special stabilizing interactions can be attributed to the carbene substituent, the methyl group. A transition-state model involving frontside closure was proposed by Brookhart et al.[21b] It was suggested that reaction occurs from the anticlinal isomer (in which the methyl group points away from the cyclopentadienyl ring) and that substituents at C_2 have a slight preference for the position cis to $-CH_3$, while substituents at C_1 have a stronger preference for the cis position based on more unfavorable interaction with the Cp group. This model is consistent with the increased cis selectivity observed for the reactions of $(C_5(CH_3)_5)(CO)_2Fe{=}CHCH_3^+$ **19** with alkenes (entries 162, 163).[51] It is less obvious how the model can account for trans selectivity of $Cp(CO)(PR_3)Fe{=}CHCH_3^+$ (**20**)[22,31,51] although the stable conformation of **20** is no doubt different from **18**.



Helquist has suggested that in the case of methylcarbene transfer from the sulfonium salt $Cp(CO)_2Fe{-}CH(CH_3)S(CH_3)Ph^+$ (**21**) consideration be given to a bimolecular displacement mechanism in which the olefin acts as the nucleophile.[27b] Recent observations by Barefield[28b] show that substitution reactions of $Cp(CO)_2FeCH_2SPh_2^+$ proceed by dissociative mechanisms and thus argue against this pathway in favor of the cationic iron methylcarbene as the reactive intermediate.



In conjunction with work analyzing the parallel between phenylcarbene transfers using stable transition-metal–phenylcarbene complexes and metal-catalyzed transfers, Doyle has proposed a general model for carbene transfers (Scheme VIII).[35] This mechanism invokes formation of π-complexes **40** and **41** prior to backside closures through transition states T_c and T_t. Doyle in part uses estimated relative values of K_a and K_s to rationalize observed cis:trans ratios. However, since **40** and **41** intermediates have never been observed in transfer reactions and must be higher in energy than the ground state $L_nM{=}CHZ + H_2C{=}CHR$, the cis:trans partitioning must be controlled *solely* by the differences in energy between T_c and T_t. Examining transition state models T_c and T_t, there appears to be no interaction between L_nM and the alkene substituent, R. Thus, one can account neither for the stereochemical results observed in phenylcarbene transfers, nor for transfer results obtained for other monosubstituted carbene complexes. In addition, it is not clear how such a model could account for variations and even reversals of cis:trans ratios with variation of the "ML_n" fragment (see table entries 162 and 164, for example).

V. Summary

Numerous electrophilic transition metal carbene complexes transfer the carbene ligand to alkenes to form cyclopropanes. Convenient synthetic procedures have been developed which allow ready access to stable carbene complexes as well as carbene complex precursors for in situ generation of less stable species. The most versatile and easily prepared reagents are complexes of the type $Cp(CO)(L)Fe{=}CRR'^{+}$.

Although synthetic chemists still employ diazo compounds or classical carbenoid reagents to convert alkenes to cyclopropanes, recent results as summarized here make these attractive reagents for certain applications. High selectivity can often be achieved. Transfers frequently occur with nearly exclusive formation of the sterically more crowded, thermodynamically less stable cyclopropane isomer; some control by variation of metal and ligand is possible. Initial experiments indicate optically pure chiral-at-metal complexes can be used to achieve high enantioselectivities. Further synthetic advantages arise in cases where classical carbenoid reagents are generally too unstable to permit efficient transfers. Stereochemical control in intramolecular additions is a promising development in the synthesis of polycyclic compounds.

The current systems have obvious limitations which represent areas for future research. (1) Most transfers are successful only for nucleophilic alkenes possessing electron-donating substituents; reagents are needed which have both the stability and reactivity to transfer carbenes to electron deficient alkenes. (2) Transfer yields are often limited by rapid intramolecular rearrangements or other modes of decomposition, especially 1,2 hydride migration, and would benefit from complexes in which such decomposition was slow relative to carbene transfer. (3) All currently useful reagents involve simple methylene complexes or derivatives in which the carbene substituents are electron-donating. Stable systems involving electron-withdrawing substituents at C_α are lacking but may be accessible through use of more electron-rich L_nM fragments. (4) Although chiral-at-metal complexes hold promise for enantioselective syntheses, general routes to a family of such species are not yet available.

The mechanism of the transfer reaction and the way in which the metal, ligands, and carbene substituents influence reactivity and selectivity has been studied by several research groups. Certain systems, especially those in which cyclopropane formation and olefin scission occur competitively, undoubtedly involve intermediate metal–carbene–alkene complexes. Stable carbene–alkene complexes have been isolated and substantial mechanistic detail has been elucidated with regard to the mode of and necessary features required for decomposition of these species to cyclopropanes. However, the large majority of transfer reactions occur without ligand dissociation from the metal carbene complexes and without intervention of carbene–alkene complexes. In addition, there is no evidence for metallacycle formation in the course of transfer reactions. Relative reactivity studies have established the electrophilic nature of the transfer and a *general* picture of the transition state. However, detailed pictures of the transition states have not been developed and there are still fundamental mechanistic questions to be answered regarding transition state structures, the reasons for the observed selectivities and the modes of ring closure and metal-carbon bond cleavage. These will not be easy questions to answer and will require a careful and mechanistically sophisticated analysis of structurally well-defined systems.

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VI. References

(1) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645.

(2) Reviews: (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1 (General). (b) Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, p 135 (General). (c) Dötz, K. H.; Fischer, H.; Hoffmann, P.; Kreissl, F.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (d) Dötz, K. H. *Angew. Chem., Int. Ed. Eng.* **1984**, *23*, 587 (Synthetic applications). (e) Ivin, J. J. *Olefin Metathesis*; Academic Press: New York, 1983. (f) Anderson, R. B. *The Fischer–Tropsch Synthesis*; Academic Press: New York, 1984; pp 174–228. (g) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25 (Tungsten alkylidenes). (h) Schrock, R. R. *Science* **1983**, *219*, 13. Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98 (Early transition metal complexes). (i) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319 (Bridging methylene complexes). (j) Doyle, M. I. *Chem. Rev.*, in press (Catalytic applications).

(3) Some recent citations, outside the scope of this review: (a) Polymerization catalysis: Ho, T. H.; Katz, T. J. *J. Mol. Cat.* **1985**, *28*, 359. Clark, T. C.; Yannoni, C. S.; Katz, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 7787. (b) Coupling and cycloaddition reactions: Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. Semmelhack, M. F.; Tamura, R.; Schantter, W.; Springer, J. *Ibid.* **1984**, *106*, 5363. Semmelhack, M. F.; Tamura, R. *Ibid.* **1983**, *105*, 4099. Semmelhack, M. F.; Tamura, R. *Ibid.* **1983**, *105*, 6750. Yamashita, A. *Ibid* **1985**, *107*, 5823. Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *Ibid.* **1985**, *107*, 1060. Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461. Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (c) Enolate-related reactions: Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (d) Reaction with ethers: Fischer, H.; Schmid, J.; Markel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 572. (e) β-Lactam synthesis: Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijum, C. *Tetrahedron* **1985**, *41*, 5833.

(4) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

(5) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1955**, *88*, 5044. (b) Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408.

(6) Markham, J.; Tolman, W.; Menard, K.; Cutler, A. *J. Organomet. Chem.* **1985**, *294*, 45.

(7) Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 835.

(8) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 894.

(9) (a) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Ibid.* **1972**, *105*, 1356.

(10) (a) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 3966. (b) Dorrer, B.; Fischer, E. O.; Kalbfus, W. *J. Organomet. Chem.* **1974**, *81*, C20.

(11) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.

(12) Burkhardt, T. J.; Casey, C. P. *J. Am. Chem. Soc.* **1973**, *95*, 5833.

(13) Casey, C. P.; Tuinstra, H. E.; Saeman, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 608.

(14) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.

(15) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282. (c) Fischer, H.; Zeuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684.

(16) (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *Ibid.* **1980**, *102*, 7802.

(17) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794.

(18) (a) Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745. (c) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764.

(19) Felkin, H.; Meunier, B.; Pascard, C.; Prange, T. *J. Organomet. Chem.* **1977**, *135*, 361.

(20) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

(21) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258.

(22) Tucker, J. R. Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1981.

(23) (a) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (b) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808. (c) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (d) Casey, C. P.; Miles, W. H. *J. Organomet. Chem.* **1984**, *254*, 333.

(24) Studabaker, W. B. Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1981.

(25) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(26) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (b) Certain unpublished yields and product ratios have been included in the table: P. Helquist, personal communication. (c) Wender, P. A.; Eck, S. L. *Tetrahedron Lett.* **1982**, *23*, 1871.

(27) (a) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862. (b) Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231.

(28) (a) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1178. (b) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Ibid.* **1985**, *4*, 1682.

(29) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119.

(30) Iyer, R. S.; Kuo, G.-H.; Helquist, P. *J. Org. Chem.* **1985**, *50*, 5898.

(31) Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6721.

(32) Davison, A.; Krussell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7.

(33) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

(34) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

(35) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 56.

(36) Broom, M. B. H. Ph.D. Dissertation, University of North Carolina, 1982.

(37) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

(38) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.

(39) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943.

(40) (a) Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1980**, *8*, 1. (b) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736.

(41) (a) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *Ibid.* **1984**, *106*, 375.

(42) Toledano, C. A.; Rudler, H.; Karan, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574.

(43) McGeary, M. J.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 2102.

(44) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(45) (a) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(46) Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830.

(47) Knors, C. J.; Kuo, G.-H.; Helquist, P. *Abstracts of Papers* 191st National Meeting of the American Chemical Society New York, NY; American Chemical Society: Washington, DC; ORGN 126.

(48) (a) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *Ibid.* **1982**, *104*, 4865.

(49) Both synclinal and anticlinal isomers have been observed for the complexes $Cp(CO)(L)Fe{=}CHCH_3^+$ **20** (L = PPh_3,[24] PEt_3,[50] PPh_2((S)-2-methylbutyl)[50]).

(50) Dominey, E. W. G.; Brookhart, M. Presented at the Eleventh International Conference on Organometallic Chemistry, Callaway Gardens, GA, October 10–14, 1983.

(51) Kegley, S. E. Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1982.

(52) (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.

(53) Dōtz, K. H.; Pruskil, I. *Chem. Ber.* **1981**, *114*, 1980.

(54) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2584.

(55) Weiss, K.; Hoffmann, K. *J. Organomet. Chem.* **1983**, *255*, C24.