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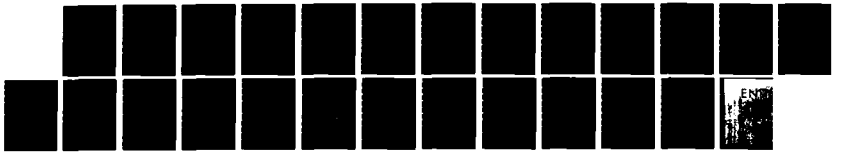

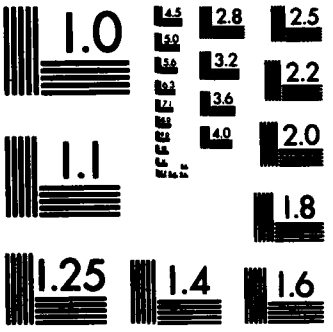

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"The Chemistry of Transition Metal Carbene Complexes"

FINAL TECHNICAL REPORT

G. RONALD HUSK

20 August 1983

U. S. ARMY RESEARCH OFFICE

DAAG-79-D-1002

UNIVERSITY OF NORTH CAROLINA
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Iron-Complexes	Tungsten	

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Significant contributions to the understanding of the synthesis, structure and reactivity of d^4 and d^6 metal carbene complexes of the type $Cp(CO)(L)Fe=CHR^+$ (R=aryl, alkyl; L=$P(C_6H_5)_3$, CO) and $Cp(CO)_2LM=CHR^+$ (M=Mo, W; R=H, aryl) are described. The increasing interest in these complexes can be attributed to their unique reactivity patterns and to their potential importance as intermediates in catalytic processes (olefin metathesis, polymerization and carbene transfer reactions). Recent studies of the cyclopropanation of styrene have provided an excellent model for establishing the role of metal chirality in the conversion of prochiral substrates into optically-active products.

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Abstract

Significant contributions to the understanding of the synthesis, structure and reactivity of d^4 and d^6 metal carbene complexes of the type $Cp(CO)(L)Fe=CHR^+$ (R=aryl, alkyl; L=$P(C_6H_5)_3$, CO) and $Cp(CO)_2LM=CHR^+$ (M=Mo, W; R=H, aryl) are described. The increasing interest in these complexes can be attributed to their unique reactivity patterns and to their potential importance as intermediates in catalytic processes (olefin metathesis, polymerization and carbene transfer reactions). Recent studies of the cyclopropanation of styrene have provided an excellent model for establishing the role of metal chirality in the conversion of prochiral substrates into optically-active products.

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Introduction

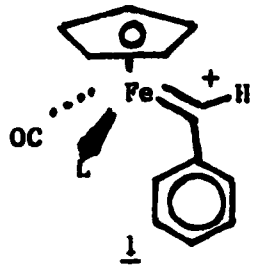
Although numerous electrophilic transition-metal carbene complexes stabilized by α-heteroatoms or α-acyl substituents are known,[1] few simple complexes possessing only α-hydrogens or α-alkyl substituents have been characterized. The latter complexes can be rapidly enumerated: $Cp(NO)(P(C_6H_5)_3)Re=CH_2^+$;[2]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

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

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

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

and Rosenblum[17] suggest that similar limitations might exist with electrophilic alkylcarbene transition-metal complexes due to a propensity to isomerize to olefin complexes. Nevertheless, stable alkylcarbene complexes analogous to the benzylidene complexes 1[13,18] previously studied



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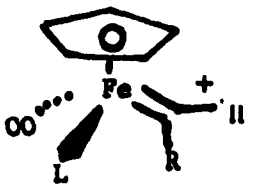
L = CO, $P(C_6H_5)_3$



2

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

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

2b, L = CO

in these laboratories, have been reported. This led us to investigate the synthesis, stability and transfer chemistry of the alkyl-substituted complexes, 2. The results of these studies will be discussed in the Section I.

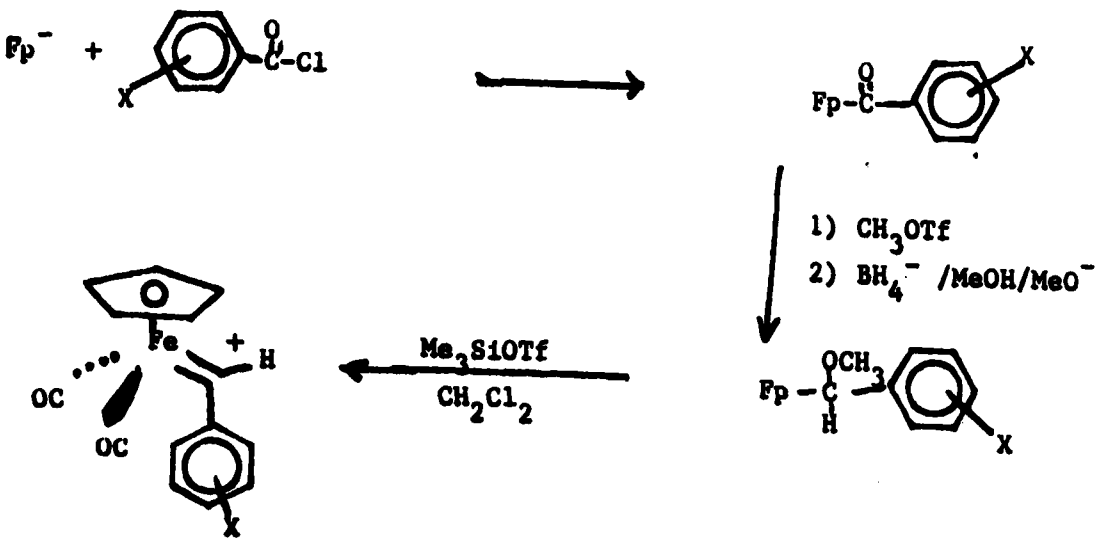
Although our current research efforts have centered primarily on iron complexes, the chemistry of d^6 electrophilic carbene complexes of the general type $CpL_1L_2M{=}CRR'$ is also of considerable interest. A variety of both heteroatom and nonheteroatom-stabilized species is now known. Several structures have been examined crystallographically,[19] while both structure and dynamics have been scrutinized spectroscopically and theoretically.[3,13a,18,20] The more electrophilic species exhibit high reactivity toward nucleophilic reagents.[2,5,20,23] In contrast, relatively few electrophilic carbene complexes in the parallel d^4 series with general structure $CpL_3M{=}CRR'$ have been studied. Isolable or spectroscopically chacterized examples include only

heteroatom-stabilized complexes; for example, $Cp(CO)_2(PH_3M)M'=Cr(OR')$ (M= Sn,Ge; M'=Mo,W; R=CH_3,C_6H_5).[24] $Cp(CO)_2(PPh_3)Mo=C(CH_3)(OCH_3)^+$,[25] $Cp(CO)_2LMo=CFR^+$ (L = CO,PPh_3; ,R=F,C_2F_5),[26] ,$Cp(CO)_2(PPh_3)Mo=CCH_2CH_2CH_2O^+$[27] and $Cp(CO)_2W=C(NEt_2)CH(CH_3)CO$.[28] No nonheteratom-stabilized species have been well characterized.[29] These efforts are discussed in Section II.

I. Chemistry of the d^6 electrophilic complexes $Cp(CO)(L)Fe=CHR^+$ and related species.

A. $Cp(CO)_2Fe=CHAr-X^+$ Systems.

A series of ring-substituted benzylidene carbene complexes, 1, have been generated via the following sequence:



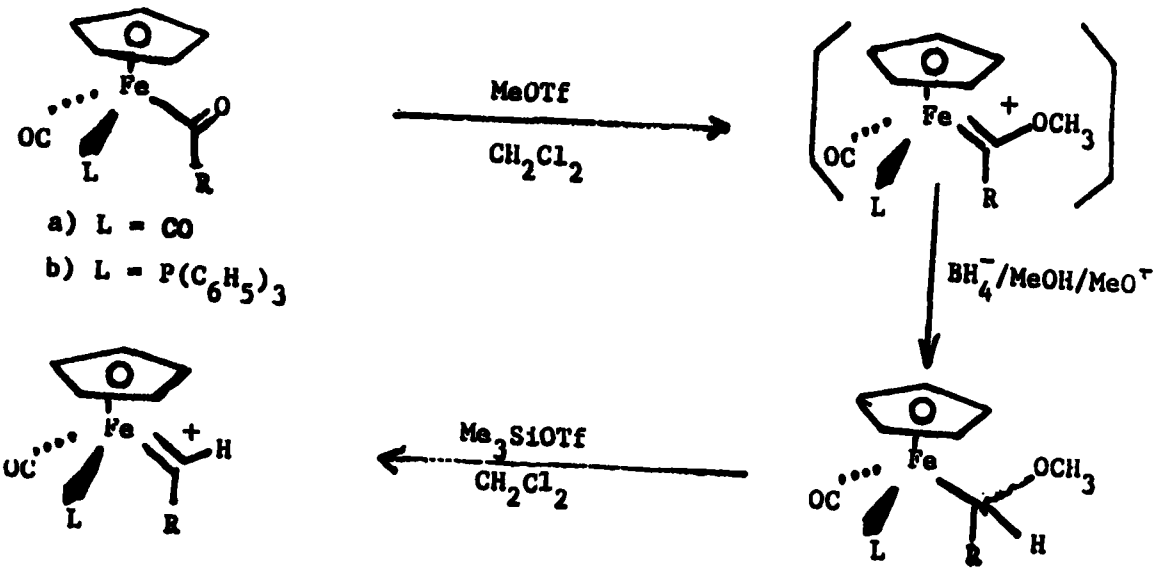
Fp = $Cp(CO)_2Fe$

X = a) H, b) p-CH_3, c) p-F, d) p-OCH_3, e) m-OCH_3, f) p-CF_3

Complexes 1a-1d have been directly observed by NMR spectroscopy and the activation barriers to rotation about the C_{carb}-C_{aryl} bond measured using dynamic ^1H NMR, correlate well with σ^+ substituent values. This offers good evidence that the carbene carbon is "carbonium ion like" in character. Part of this work has been published.[18] Transfers of the benzylidene moiety of 1(a) - 1(f) to propene to give cis and trans 1-aryl-2-methylcyclopropanes have been carried out.[30]

B. $Cp(CO)(L)Fe=CHR^+$ (L=CO, PPh_3, R=-CH_3, -CH_2CH_3, -$CH(CH_3)_2$).

A general highly efficient synthesis for α-ether complexes 3 has been devised:[20,31,32]



a) L = CO

b) L = $P(C_6H_5)_3$

3 a)L= CO

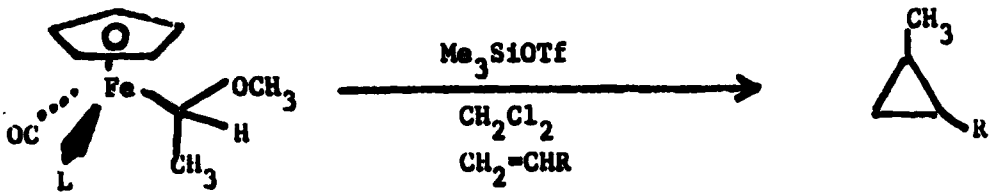
b)L= $P(C_6H_5)_3$

2 a)L = CO

b)L = $P(C_6H_5)_3$

The α-ethers, 3, serve as direct precursors to the alkylidene species, 2, which have been generated by ionization with $(CH_3)_3SiOTf$ in CH_2Cl_2. For 3(b) (L = PPh_3) the alkylidene complexes were directly observed by NMR spectroscopy and their rates and products of thermal decomposition were studied. For 3(a) (L = CO) the alkylidene species were too unstable to observe, but their thermal decomposition products were characterized.

Despite the short lifetimes of 3a, (R=CH_3) its high reactivity permits its use as an efficient ethylidene transfer reagent. Transfer of alkylidenes using classical means is normally quite difficult and characterized by low yields; thus, the α-ether 2a was developed as a synthetically useful ethylidene transfer reagent using the following procedure:



A variety of substituted olefins has been examined. Most transfers occur with high yields and high cis or syn stereoselectivity. Part of this work has been published.[20,31] and a further detailed manuscript is being prepared.

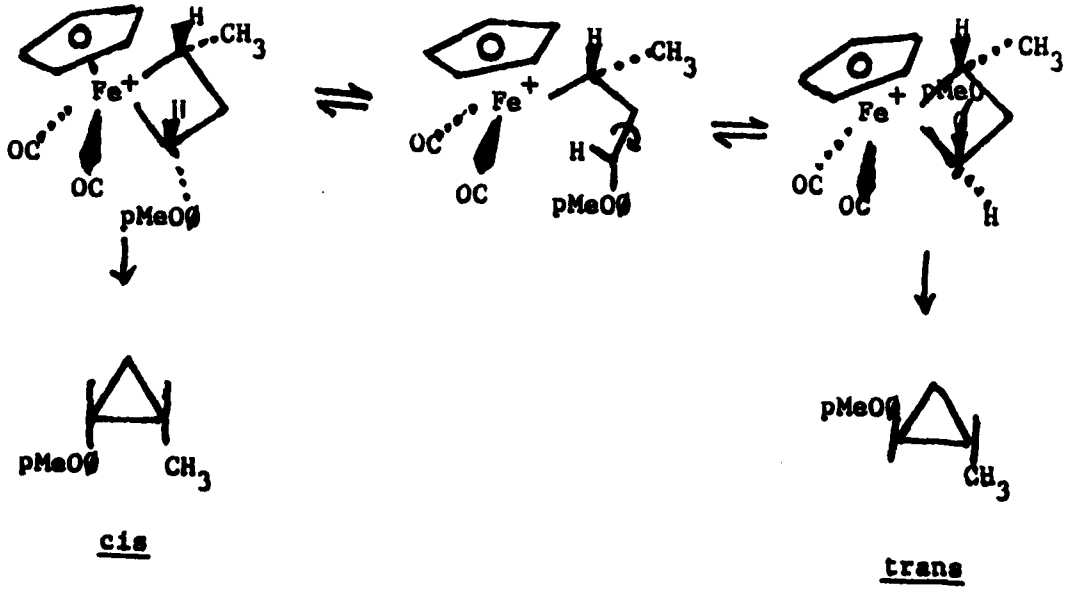
C. The mechanism of the ethylidene transfer reaction.
Studies using ring-substituted and deuterium-labeled styrenes.

The transfer of ethylidene from 3a, $Cp(CO)_2Fe{=}CHCH_3^+$, 3b, $Cp(CO)(PPh_3)$-$Fe{=}CHCH_3^+$ and 4, $(C_5Me_5)(CO)_2Fe{=}CHCH_3^+$ to a series of ring-substituted and specifically deuterated styrenes has been examined.[33]

For 3a the cis to trans ratio of 1-aryl-2-methylcyclopropane is ca. 5.0:1 for all substituents (X=H, p-F, p-Cl, p-CH_3, p-CF_3) except p-OCH_3, where the

ratio falls to 1:1. The results of carbene transfers to specifically deuterium labeled styrenes, cis-β-deuteriostyrene, 5, and cis-β-deuterio-p-methoxystyrene 6, were examined to probe whether the stereochemistry about the carbon-carbon double bond was retained. The cyclopropane products from labeled styrene exhibit no deuterium scrambling and the recovered, unreacted styrene is also unscrambled. In contrast, the p-methoxy system shows extensive deuterium scrambling in the products but no scrambling of unreacted p-methoxystyrene. Furthermore, cycloporpane products are not scrambled under the reaction conditions. A detailed consideration of the scrambling results and control experiments allow the folling conclusions: (1) loss of stereochemistry about the carbene-carbon double bond occurs during the reaction, but after the rate-determining step and (2) the "approach ratio" (cis vs. trans) is ca. 4:1, close to that for all the other styrenes.

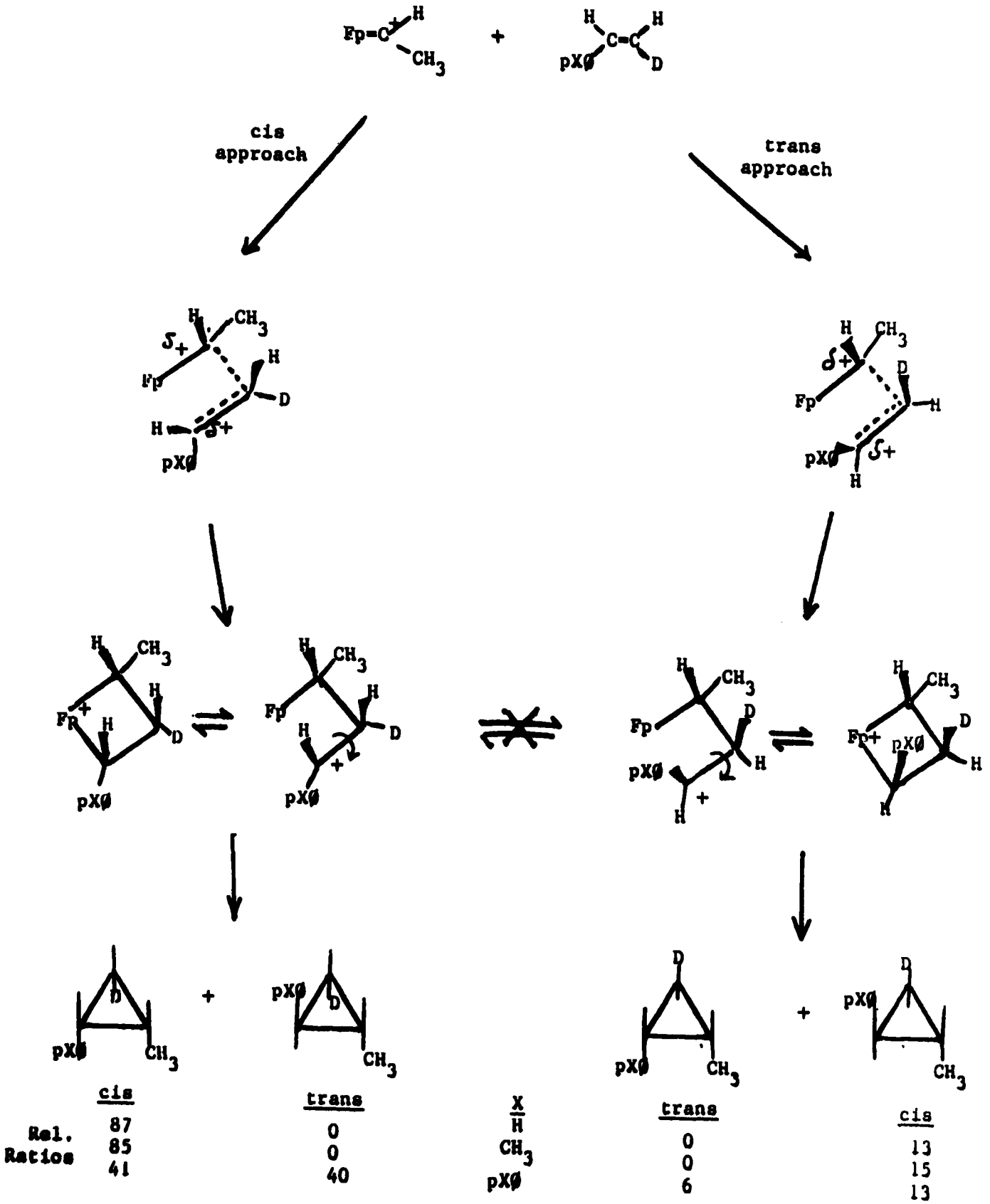
What is the structure of the intermediate occurring after the rate-determining step which allows scrambling for p-methoxystyrene? The results are consistent with the formation of a metallacyclic intermediate which can scramble as follows:



cis trans

For X=H, reductive elimination to give cyclopropane products is required to be faster than scrambling; however, for X=p-methoxy, scrambling can occur competitively with cyclopropane formation due to the stabilization of the carbonium ion intermediate. It should be noted that metallacycles are not required intermediates. For example, direct formation of a carbonium ion intermediate which rapidly collapses to products for X=H but which has sufficient lifetime for C-C bond rotation for X=pOMe also explains the results.

A full reaction scheme using the metallacyclic intermediate model is shown on the following page.



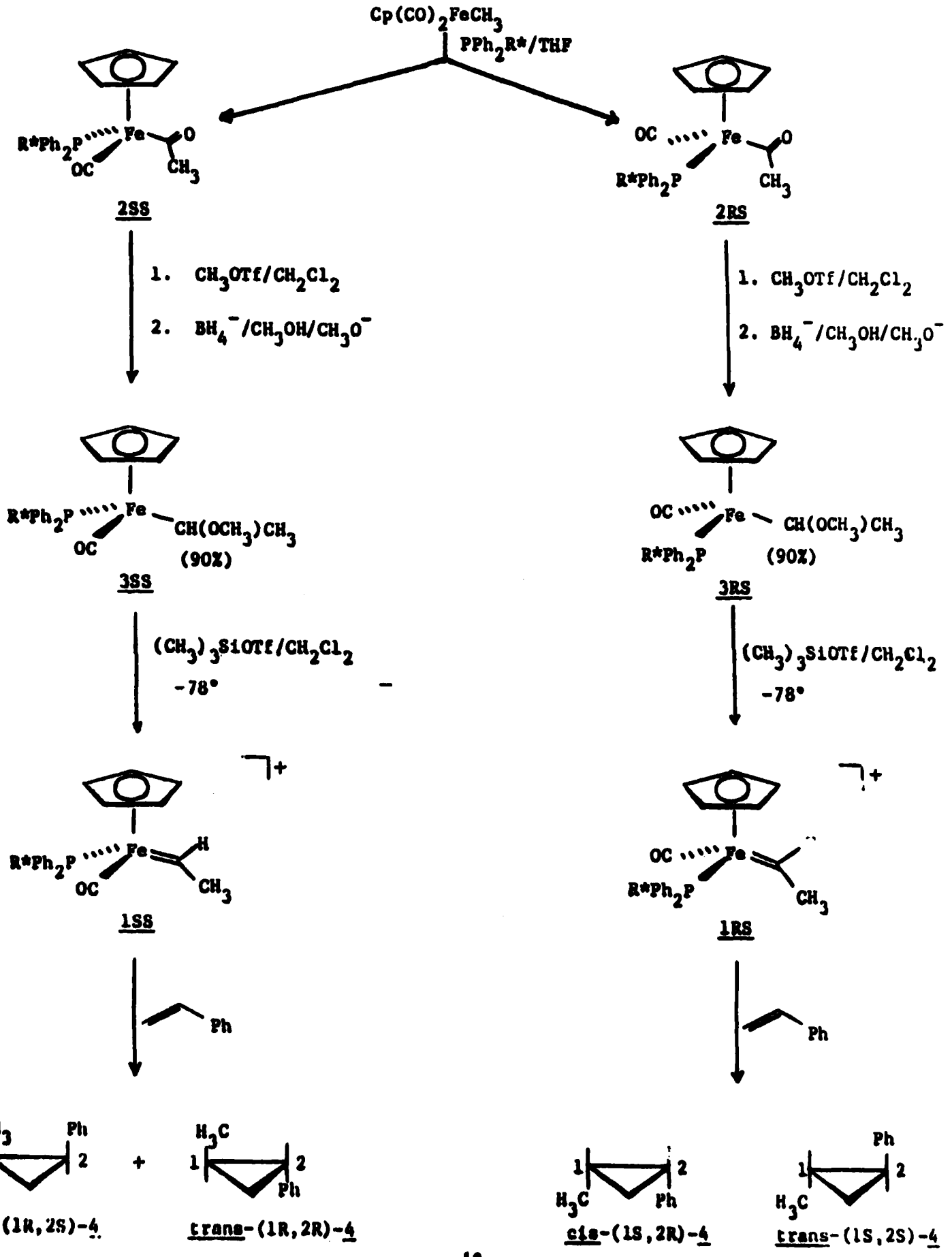
	cis	trans	X	trans	cis
Rel. Ratios	87	0	H	0	13
	85	0	CH_3	0	15
	41	40	pXØ	6	13

The reactions of the phosphine substituted carbene 3b and the pentamethyl derivative 4 with labeled styrenes (p-X=-H,-OCH_3) were also carried out.[34] No scrambling of the deuterium label was observed in the cyclopropane products or in the unreacted styrenes. The predominant cyclopropane products in the reactions using 3b were the trans isomers, opposite to the selectivity observed for products arising from 3a. The pentamethyl ethylidene complex 4 showed a very high cis selectivity (>30:1). These results are preliminary. Further studies are in progress.

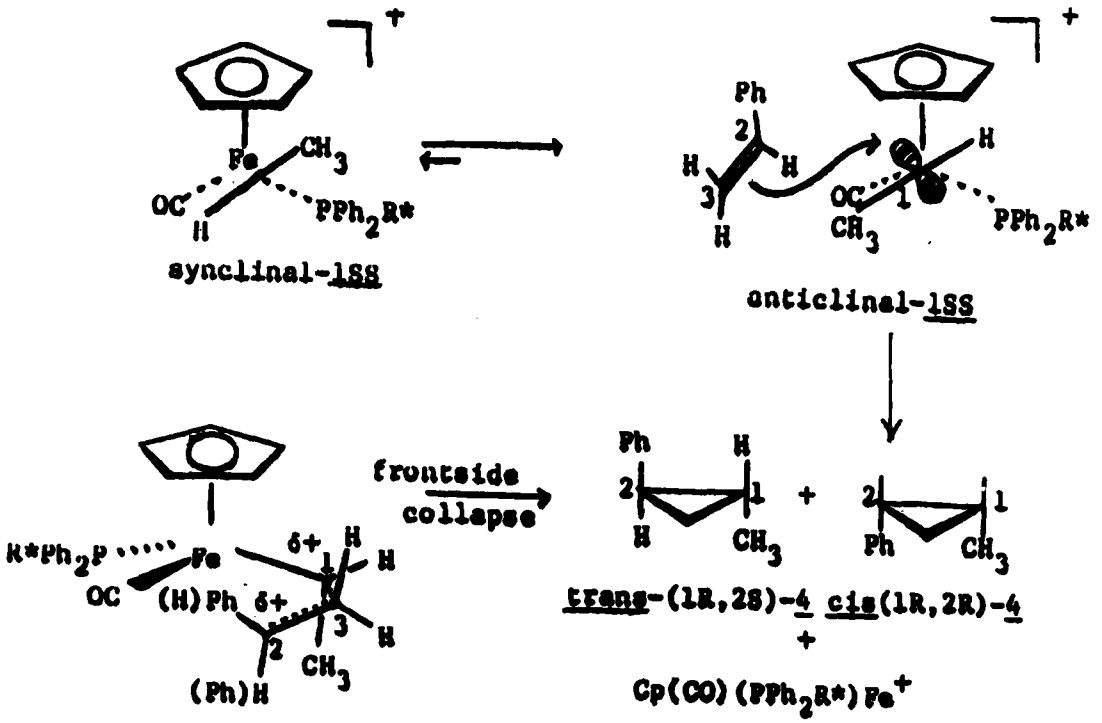
D. Enantiomeric Synthesis Using Chiral Carbene Complexes:

An important breakthrough has been made in the synthesis of chiral-at-metal carbene complexes[35] and subsequent enantiomeric synthesis of cyclopropanes.

The diasteroemeric complexes ($S_{Fe}S_C$)- and ($R_{Fe}S_C$)-$Cp(CO)(Ph_2R^*P)FeCOCH_3$, 2SS and 2RS, (R* = (S)-2-methylbutyl) have been prepared and separated as shown on the Scheme. Conversion of 2SS and 2RS to the corresponding α-ethers, $Cp(CO)(Ph_2R^*P)FeCH(OCH_3)CH_3$ followed by treatment with trimethylsilyl triflate generates in situ ($S_{Fe}S_C$)- and ($R_{Fe}S_C$)-$Cp(CO)(Ph_2R^*P)Fe{=}CHCH_3^+$, 1SS and 1RS. Transfer of ethylidene from 1SS or 1RS to styrene yields cis and trans-1-methyl-2-phenyclcyclopropanes, 4, in good chemical (70-75%) and high optical yield (84-90%). Complex 1SS yields predominantly cis-(1R,2S)-4 and trans-(1R,2R)-4, while 1RS yields cis-(1S, 2R)-4 and trans-(1S,2S)-4. This is represented in the following Scheme.


Cp(CO)2FeCH3
PPh2R*/THF
2SS
2RS
1. CH3OTf/CH2Cl2
2. BH4-/CH3OH/CH3O-
(90%)
3SS
3RS
(CH3)3SiOTf/CH2Cl2
-78°
1SS
1RS
Ph
cis-(1R,2S)-4
trans-(1R,2R)-4
cis-(1S,2R)-4
trans-(1S,2S)-4

These results add to the complex picture of the mechanism of the carbene transfer reactions and when combined with the results in Section C is consistent with the following description.



The nucleophile, styrene, attacks anticlinical-1SS over CO at the si face of the ethylidene with initial interaction between C_1 and C_3. The developing electrophilic center at C_2 then ultimately collapses in a frontside manner (either in a synchronous process or via a metallacyclic intermediate[31]) to give the cis and trans cyclopropane enantiomers observed, depending on whether styrene adds with its si or re face.

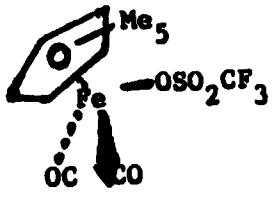
In the rapidly growing field of enantioselective catalysis by transition metal complexes, optically-active ligands, usually phosphines, carrying the chiral information are used.[36] During catalysis the transition metal atom

itself frequently becomes a chiral center, and there have been speculations on the role of the metal chirality in the conversion of prochiral substrates into optically-active products remains undetermined.[36-39] The present cyclopropanation of styrene is an excellent model for this problem. 1SS and 1RS contain the same optically-active phosphine ligand and have opposite metal configurations. The fact that 1SS and 1RS give cyclopropanes of opposite configurations and almost identical optical purities indicate that the chirality at the iron center is primarily responsible for asymmetric induction and that the optically-active phosphine plays little or no role, demonstrating the potential of control by the metal configuration in enantioselective catalysis.

The present results, coupled with the developing synthetic utility of iron carbene complexes,[13a,b,11d,20,23,31,40] show that chiral carbene complexes of the type $Cp(CO)(PR_3)Fe{=}CHR^+$ will be generally useful for asymmetric syntheses of cyclopropanes. In this regard, we are presently examining additional ethylidene transfer from 1SS and 1RS and synthetic routes to other chiral carbene complexes.

E. Related X-ray structural work:

X-ray crystal structures of two complexes related to the present studies have been determined:[33,41]



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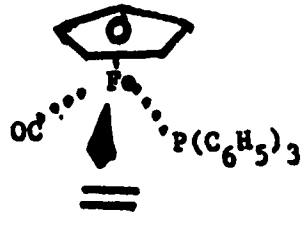


6

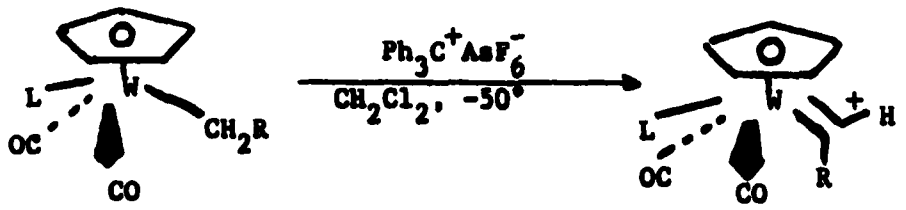
The structure of 5 shows that the very labile triflate ligand is strongly coordinated via oxygen, and the bond is largely ionic in nature.

Structure 6 shows that the ethylene unit nearly aligns with CO, in contrast to what might be expected based on simple MO calculations. Detailed MO calculations are being carried out on this system by R. Hoffman (Cornell) and O. Eisenstein (Michigan) in a joint effort.

II. Chemistry of the d^4 electrophilic complexes $Cp(CO)_2(L)M{=}CHR^+$:

In contrast to the d^6 systems, the chemistry of the d^4 series is relatively unexplored. We have spectrally characterized the first examples of d^4 nonheteroatom-stabilized carbene complexes of the type $Cp(CO)_2LM{=}CHR^+$.[13C]

The tungsten carbene complexes $Cp(CO)_2(L)W{=}CHR^+$ 7a ($L{=}PPh_3$, R=H), 7b($L{=}PEt_3$, R=H) and 7c ($L{=}PPh_3$, R=Ph) can be prepared from the corresponding alkyl precursors by hydride abstraction using $Ph_3C^+AsF_6^-$.



7 a L = $P(C_6H_5)_3$, R = H
b L = PEt_3, R = H
c L = $P(C_6H_5)_3$, R = C_6H_5

The low temperature (-110^0) ^1H NMR spectrum of 7a and 7b shows that the two methylene hydrogens are nonequivalent. By using rate measurements from dynamic NMR spectra, the barriers to rotation around the W-C bond have been calculated. The lower barrier observed for 7a (8.3 Kcal/mole) compared to 7b (9.0 Kcal/mole) is consistent with the better donor properties of PEt_3 relative to PPh_3. The methylene carbenes 10a and 10b decompose above -20^0 by

disproportionation to $Cp(CO)_2(L)W\text{-}(C_2H_4)^+$ and the solvated $Cp(CO)_2(L)W^+$. In contrast to 7a and 7b, the benzylidene carbene 7b is very stable and can be isolated as a crystalline salt.

The molybdenum methylene complex $Cp(CO)_2(PPh_3)Mo{=}CH_2^+$, 8 was synthesized by the route outlined below:

$$[Cp(CO)_3Mo]_2 \xrightarrow{I_2} Cp(CO)_3Mo\text{-}I \xrightarrow{PPh_3} Cp(CO)_2(PPh_3)Mo\text{-}I \xrightarrow{Na(Hg)}$$

$$Cp(CO)_2(PPh_3)Mo \xrightarrow{Cl\text{-}CH_2OR} Cp(CO)_2(PPh_3)Mo\text{-}CH_2OR \xrightarrow[-90^\circ]{Me_3SiOTf} \underline{8}$$

A single resonance for the methylene hydrogens of 8 is observed to as low as -90° which indicates that rapid rotation around the Mo=C bond is occurring even at -90° ($\Delta G^{\ddagger}_{rot}$ 6.7 Kcal/mole). Decomposition of 8 to the ethylene complex $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+$ and the solvent coordinated $Cp(CO)_2(PPh_3)Mo^+$ is rapid above $-50^\circ C$.

The high electrophilicity of these complexes is substantiated by their observed reactivity with olefins. Transfer of the methylene moiety of 7a, 7b and 8 to styrene in CH_2Cl_2 occurs at -78° within 10-15 min. to produce phenylcyclopropane in >50% yields.

Because of their observed electrophilicity, these easily-modified d^4 carbene systems appear to have potential as carbene transfer reagents.

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List of Publications

1. "Measurement of Barriers to Aryl Rotation in $CP(CO)_2Fe=CHC_6H_5^+$ and $CP(CO)_2Fe=CH(pCH_3C_6H_4)^+$," Brookhart; M.; Tucker, J. R.; Husk, G. R.; J. Organometal. Chem., 1980, 193, C23.

2. "Facile Synthesis, Spectral Characterization and Ethylidene Transfer Reactions of Complexes of the Type $Cp(CO)(L)Fe=CHCH_3^+$," Brookhart, M.; Tucker, J. R.,; Husk, G. R., J. Am. Chem. Soc., 1981, 103, 979.

3. "Spectroscopic Characterization of Electrophilic d^4 Methylene and Benzylidene Complexes of the Type $Cp(CO)_2(L)M=CHR^+$ ($L=PPh_3$, PEt_3; M=Mo, W; R=H,Ph)." "Experimental Determination of Barriers to Rotation About the Tungsten-Methylene Multiple Bond," Kegley, S. E.; Brookhart, M.; Husk, G. R., Organometallics, 1982, 1, 760-762.

4. "Synthesis, Spectral Characterization and Alkylidene Transfer Reactions of Electrophilic Iron Carbene Complexes, $Cp(CO)(L)Fe=CHR^+$, L=CO, $P(C_6H_5)_3$; R=CH3, CH_2CH_3, $CH(CH_3)_2$," Brookhart, M.; Tucker, J. R.; Husk, G. R.; J. Am. Chem. Soc., 1983, 105, 258.

5. "The Crystal and Molecular Structure of η^5-Pentamethylcyclopentadienyl (trifluoromethanesulfonato) Iron (II) Dicarbonyl: A Strong Eletrostatic Iron-Triflate Interaction," Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R., in press Inorg. Chem., October 1983.

6. "Enantioselective Cyclopropane Synthesis Using the Chiral Carbene Complexes $(S_{Fe}S_C)$- and $(R_{Fe}S_C)$-$(C_5H_5)(CO)(C_6H_5)_2R^*P)Fe=CHCH_3^+$($R^*$=(S)-2-Methylbutyl). Role of Metal vs. Ligand Chirality in the Optical Induction," Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B., accepted for publication, J. Am. Chem. Soc., September 1983.

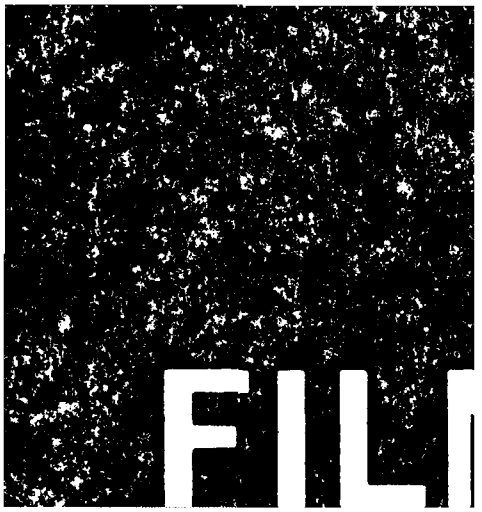
7. "Mechanistic Studies of Cycloproponation Reactions. Loss of Stereospecificity in Electrophilic Carbene Transfers from $(C_5H_5)(CO)_2Fe=CHCH_3^+$ to cis-β-Deuteriostyrenes," Brookhart, M.; Kegley, S. E.; Husk, G. R., submitted to Organometallics, September 1983.

8. "Synthesis and Transfer Reactions of Electrophilic Iron Carbene Complexes $(C_5H_5)(CO)(L)Fe=CHR^+$ L=CO, $P(C_6H_5)_3$, R=CH_3Aryl and $(C_5(CH_3)_5)$ $(CO)_2Fe=CHCH_3^+$," Brookhart, M.; Kegley, S. E.; Humphrey, M. B.; Rossen, K.; Husk, G. R., in preparation.

At least two further papers are anticipated from this work.

List of Scientific Personnel, Supported or Partially Supported

James R. Tucker, Ph.D., 1982
Susan E. Kegley, Ph.D., 1983
William Lamanna
M. Beth Humphrey
Deborah Smith-Timmers
Gregory D. Williams
M. S. Brookhart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