Early Transition Metal Organometallic Reactivity. Catalytic Acetylene Hydrogenation and Dimerization, Carbene Migratory Insertion Reactions

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1980

(Submitted February 4, 1980)

ACKNOWLEDGMENT

Grateful acknowledgment is made to all the members of the Bercaw group who have constantly reminded me how full of it I am during the last four years. Juan Manriguez, Don McAlister, Bob Bell, Bob Sanner, John Thich, Dave Erwin, Pete Wolczanski, Steve Cohen, Mike Flysuk, Buzz Curtis, Ayusmen Sen, Paul Barger, and Jimmy Mayer have all taught me something about chemistry. Some who tried harder than others might bear special mention except that I'll probably never par the eighth hole at Brookside or attempt a hopelessly disordered crystal structure in the near future. I would like to especially thank John Bercaw. In addition to his good advice in lab, I have appreciated his chemical curiosity to find out what the hell is really going on.

I must also thank the Fannie and John Hertz Foundation for their financial support for the last three years. Finally, the expert typing job by Henriette Wymar is greatly appreciated.

ABSTRACT

The synthesis of several bis-pentamethylcyclopentadienyl titanium and zirconium mono-acetylene complexes from the dinitrogen complexes, $[(C_5Me_5)_2Ti]_2N_2$ and $[(C_5Me_5)_2ZrN_2]_2N_2$, is reported. The steric bulk of the pentamethylcyclopentadiene ligands prevents metallocyclopentadiene formation commonly observed in normal titanocene acetylene reactions. These mono-acetylene complexes are efficient hydrogenation catalysts for acetylenes. A mechanistic inverstigation indicates that $(C_5Me_5)_2TiH_2$ or $(C_5Me_5)_2ZrH_2$ are the active hydrogenating reagents. $(C_5Me_5)_2Ti$ also catalyzes the dimerization of terminal acetylenes such as propyne to form $CH_3{-}C{\equiv}C{-}C(CH_3)=CH_2$.

A series of substituted niobocene zirconoxy carbenes, $(C_5H_5)_2Nb(R)=CHOZr(H)(C_5Me_5)_2$, are prepared by reaction of $(C_5Me_5)_2ZrH_2$ with $(C_5H_5)_2Nb(R)CO$ ($R = H$, CH_3, $CH_2\phi$, and ϕ). These oxycarbenes readily undergo migratory insertion into the niobocene substituent bond. The product of hydride migration can be trapped with CO to form $(C_5H_5)_2Nb(CO)CH_2OZr(H)(C_5Me_5)_2$. The alkyl migration products β-eliminate to yield zirconoxy enolates, $(C_5Me_5)_2Zr(H)OCH=CH_2$ and $(C_5Me_5)_2Zr(H)OCH=CH\phi$. Phenyl does not migrate at a significant rate at 70°C.

Kinetics of the alkyl migrations indicate the rate limiting step is the carbene-alkyl migratory insertion. The carbene-hydride migration which is reversable is studied using saturation transfer nmr techniques. The relative rates for migratory insertion are determined to be $H \gg CH_3 > CH_2\phi \gg \phi$. This series of migratory aptidudes is discussed in terms of the electrophilic nature of migratory insertions.

The syntheses of several substituted $(C_5Me_5)_2Nb$ derivatives is described. $(C_5Me_5)_2NbBH_4$ is a useful precursor for $(C_5Me_5)_2NbH_3$, $(C_5Me_5)_2Nb(H)CO$, $(C_5Me_5)_2Nb(CH_3)CO$, and $(C_5Me_5)_2NbCl_2$. Low valent niobocene derivatives such as $(C_5Me_5)_2NbCO$ and $(C_5Me_5)_2Nb$ seem to be viable synthetic goals.

ABBREVIATIONS

Cp	C_5H_5	cyclopentadiene
Cp^*	$C_5(CH_3)_5$	pentamethylcyclopentadiene
Zr	Cp_2^*Zr	Unless otherwise indicated, zirconium and titanium are always bound to two Cp^* ligands.
Ti	Cp_2^*Ti	
Nb	Cp_2Nb	Unless otherwise indicated, niobium, tantalum, and tungsten are always bound to two Cp ligands.
Ta	Cp_2Ta	
W	Cp_2W	
ϕ	C_6H_5	phenyl
tolane	$\phi\cdot C\equiv C\cdot\phi$	diphenyl acetylene
L	A two electron donating ligand	
R	A one electron donating substituent	
FT-nmr	Fourrier transform nuclear magnetic resonance	

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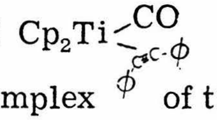
Chapter 1

Acetylene Reactions with Bis-Pentamethylcyclopentadienyl Titanium and Zirconium.

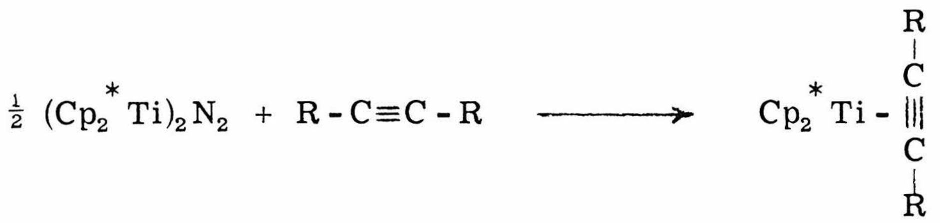
INTRODUCTION

The search for new polymerization and hydrogenation catalysts has stimulated interest in the reactions of bis-cyclopentadienyl titanium complexes with acetylenes. $Cp_2Ti(CO)_2$ catalytically hydrogenates acetylenes to alkenes and alkanes.[1] Because the only isolable titanium products of these reactions are unreactive metallocyclopentadienes, an unsaturated titanium monoacetylene complex was proposed as the active catalyst. This hypothesis was consistent with the higher activity of  $Cp_2Ti(CO)(\phi C{\equiv}C\phi)$ in acetylene hydrogenations.[2] A mono-acetylene complex of titanium was not isolable due to the facile metallocycle formation.

The steric crowding observed for bis-cyclopentadienyl complexes[3] suggested that increased steric bulk around the metal would prevent coordination of a second acetylene. The permethyl titanocene system, in addition to yielding titanium II complexes cleanly, seemed to fulfill this requirement.[4, 5] The synthesis of several group IV metallocene acetylene complexes is reported. Their behavior as hydrogenation catalysts enables further insight into the hydrogenation mechanism. In addition, the lackof metallocycle formation enables the titanium complex to catalytically dimerize terminal acetylenes.

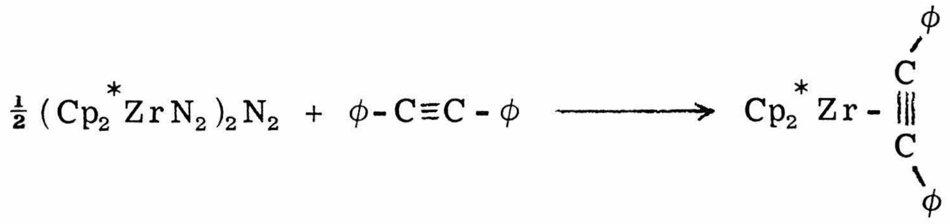
RESULTS

Diphenyl acetylene reacts with $\{[\eta^5\text{-}C_5(CH_3)_5]_2Ti\}_2N_2$ to yield a brown crystalline compound which nmr, ir, elemental analysis, and molecular weight studies indicate is a monomeric monoacetylene complex. The analogous reaction with 2-butyne yields a mono-acetylene product. $\{[\eta^5\text{-}C_5(CH_3)_5]_2ZrN_2\}_2N_2$ also reacts with one equivalent of diphenyl acetylene per zirconium. However, two equivalents of 2-butyne react per zirconium to yield a zirconocyclopentadiene. An increase in steric crowding is apparent between the normal titanocene acetylene derivatives and the permethylated titanocene and zirconocene



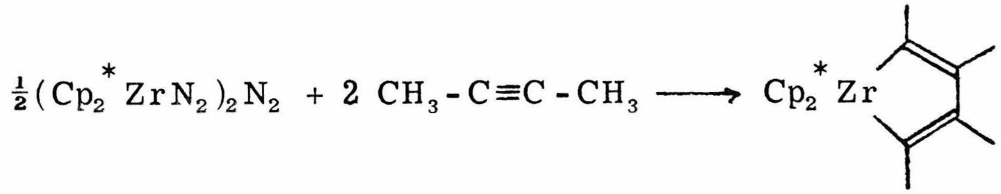
$$\frac{1}{2}\,(Cp_2^*Ti)_2N_2 + R-C\equiv C-R \longrightarrow Cp_2^*Ti-\begin{array}{c}R\\ |\\ C\\ |||\\ C\\ |\\ R\end{array}$$

R equals C_6H_5, 1, and CH_3, 2



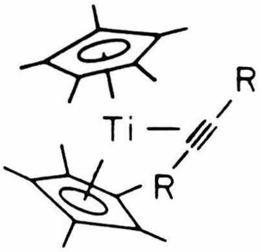
3

$$\frac{1}{2}\,(Cp_2^*ZrN_2)_2N_2 + \phi-C\equiv C-\phi \longrightarrow Cp_2^*Zr-\begin{array}{c}\phi\\ /\\ C\\ |||\\ C\\ \backslash\\ \phi\end{array}$$

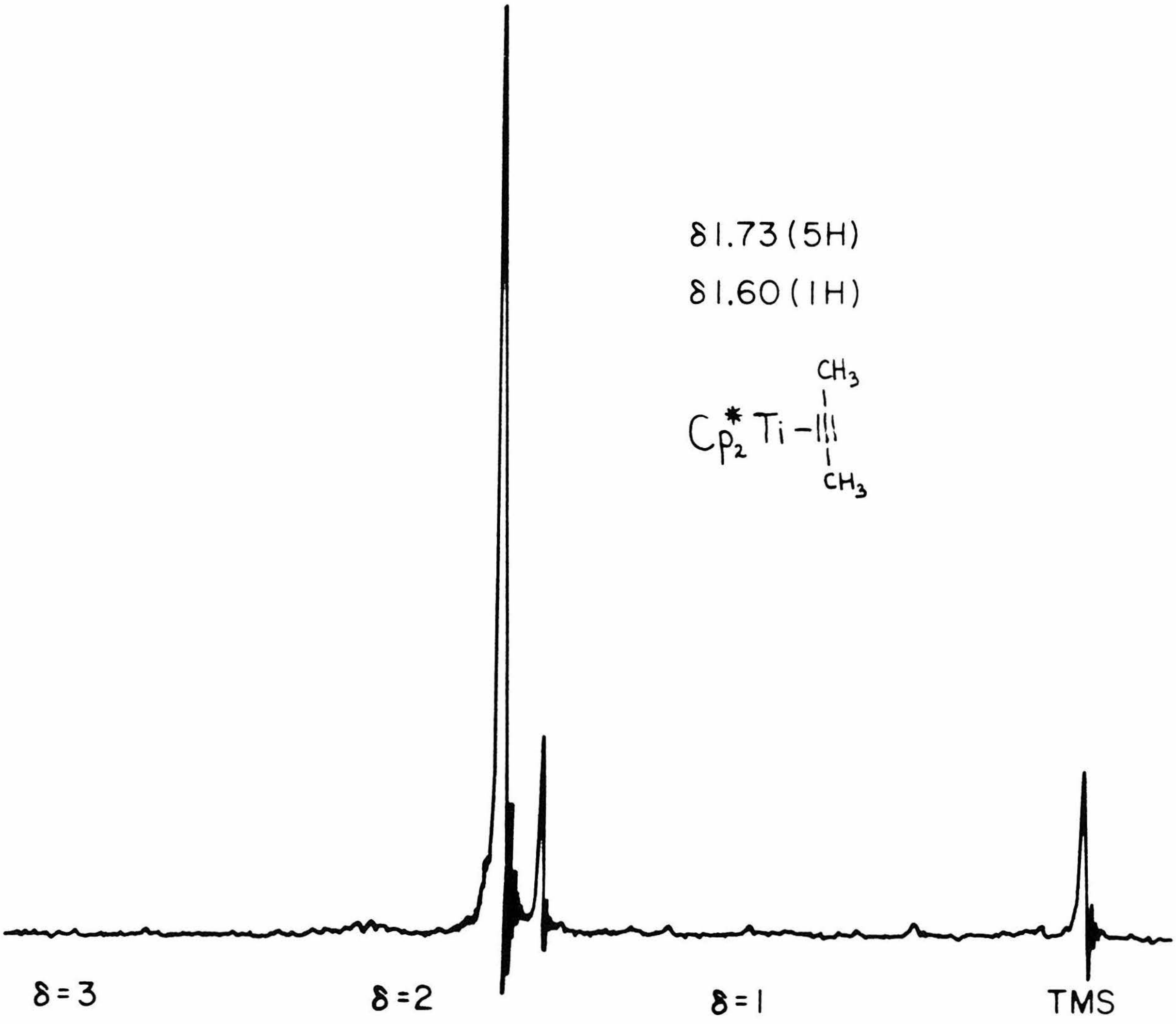


4

$$\frac{1}{2}\,(Cp_2^*ZrN_2)_2N_2 + 2\ CH_3-C\equiv C-CH_3 \longrightarrow Cp_2^*Zr$$



M	R	ν(C≡C)
Ti	CH_3	1683 cm^{-1}
Ti	C_6H_5	1647 cm^{-1}
Zr	C_6H_5	< 1600 cm^{-1}

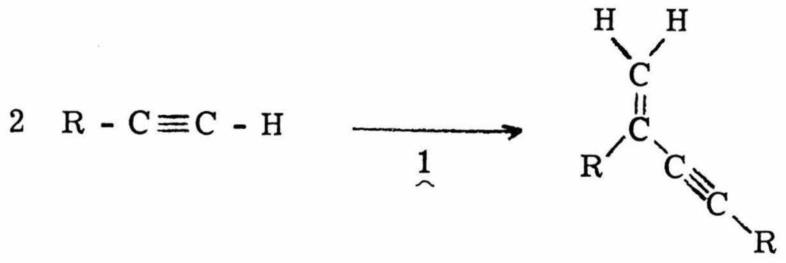


complexes. Whereas metallocyclopentadienes are the most stable acetylene products with normal titanocene,[1] only the larger permethyl zirconocene can accomodate two small acetylenes. Otherwise the permethyl metallocenes are too crowded to allow metallocycle formation.

These mono-acetylene complexes are efficient acetylene hydrogenation catalysts. The general features of the reaction are that unactivated acetylenes such as 2-butyne and propyne are reduced to olefins much faster than activated acetylenes such as phenyl acetylene. The hydrogenation of unactivated acetylenes yields olefins whereas activated acetylenes become fully saturated. This double hydrogenation is stepwise. Stilbene is the initial product which is reduced further once a significant concentration is formed. For similar acetylenes, titanium is a more efficient catalyst than zirconium. All acetylenes cannot be compared due to metallocycle formation with 2-butyne and zirconium. Unlike the normal ring metallocycles, 4 does function as a catalyst at elevated temperatures.

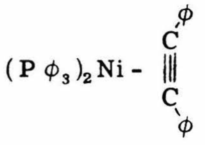
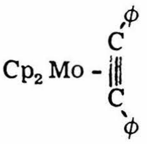
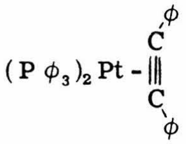
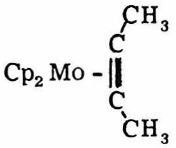
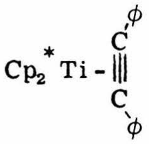
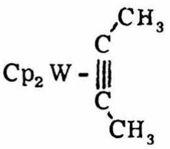
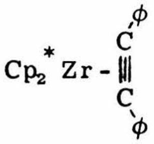
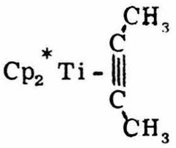
These hydrogenation catalysts behave similarly to the normal ring titanocene system. The main difference is the relative reaction rates. Reasonable rates using $Cp_2Ti(CO)_2$ required fifty atmospheres of hydrogen at 55-60° C. The reduction of 2-butyne to cis-butene by Cp_2^*Ti— has a turnover rate of greater than 0.75 equivalents of butyne per titanium per minute at -21° C. Even at -21° C, the reaction rate is stir-rate dependent at maximum stirring speeds.

By preventing metallocycle formation, permethyl titanocene is able to catalytically dimerize terminal acetylenes. The reaction of propyne and 1 followed by nmr shows two multiplets grow in the vinyl region as the acetylenic hydrogen signal loses intensity. On a preparative scale, $CH_3C{\equiv}C-C(=CH_2)CH_3$ is isolated as the only product in as high as 50 to one turnovers of propyne to titanium.[6] A similar reaction is observed with phenyl acetylene.[7] Unfortunately, it appears that both acetylenes which are coupled must be terminal. Even in neat 2-butyne with a small amount of propyne present, only the propyne dimer is formed.

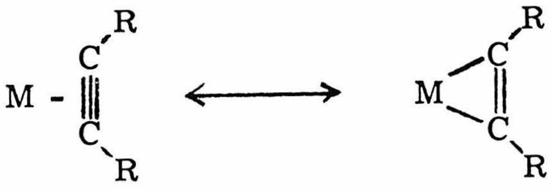


DISCUSSION

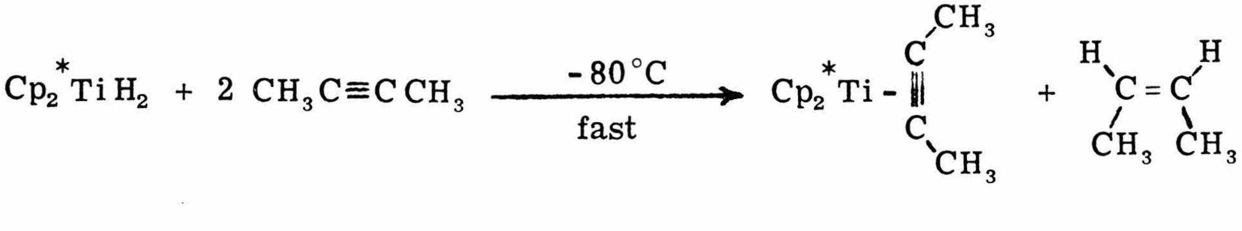
The infrared stretching frequencies of the triple bond of the acetylene complexes and some similar complexes is shown in Figure 1.

	C≡C Stretch (reference)		C≡C Stretch (reference)
 $(P\phi_3)_2Ni-(\phi C{\equiv}C\phi)$	1800 cm^{-1} (9)	 $Cp_2Mo-(\phi C{\equiv}C\phi)$	1771 cm^{-1} (10)
 $(P\phi_3)_2Pt-(\phi C{\equiv}C\phi)$	1740, 1768 cm^{-1} (9)	 $Cp_2Mo-(CH_3C{\equiv}CCH_3)$	1830 cm^{-1} (11)
 $Cp_2^*Ti-(\phi C{\equiv}C\phi)$	1647 cm^{-1}	 $Cp_2W-(CH_3C{\equiv}CCH_3)$	1750 cm^{-1} (11)
 $Cp_2^*Zr-(\phi C{\equiv}C\phi)$	$<$ 1600 cm^{-1}	 $Cp_2^*Ti-(CH_3C{\equiv}CCH_3)$	1683 cm^{-1}

The difference between the free acetylene and the bound acetylene stretching frequencies, is usually rationalized on the basis of orbital overlap of the π and π^* acetylene orbitals with the metal d-orbitals. For a series of structurally similar complexes, the size of this shift $\Delta\nu(C{\equiv}C)$ has been interpreted as a gauge of metal acetylene bond strength.[8] In general, $\Delta\nu(C{\equiv}C)$ increases going down a particular column (Ni → Pt or Mo → W). The ir spectrum of **3**, otherwise indentical to **1**, shows no obvious C≡C stretch between 1600 and 2000 cm^{-1}. A likely explanation is that relative to titanium, the lower energy C≡C stretch of **3** has shifted into the phenyl C=C stretch region at 1585 cm^{-1}. The acetylene stretching vibrations of **1**, **2**, and **3** indicate that of the two resonant structures,[8b] the metallocyclopropene is a better representation of the group IV metal acetylene complexes.



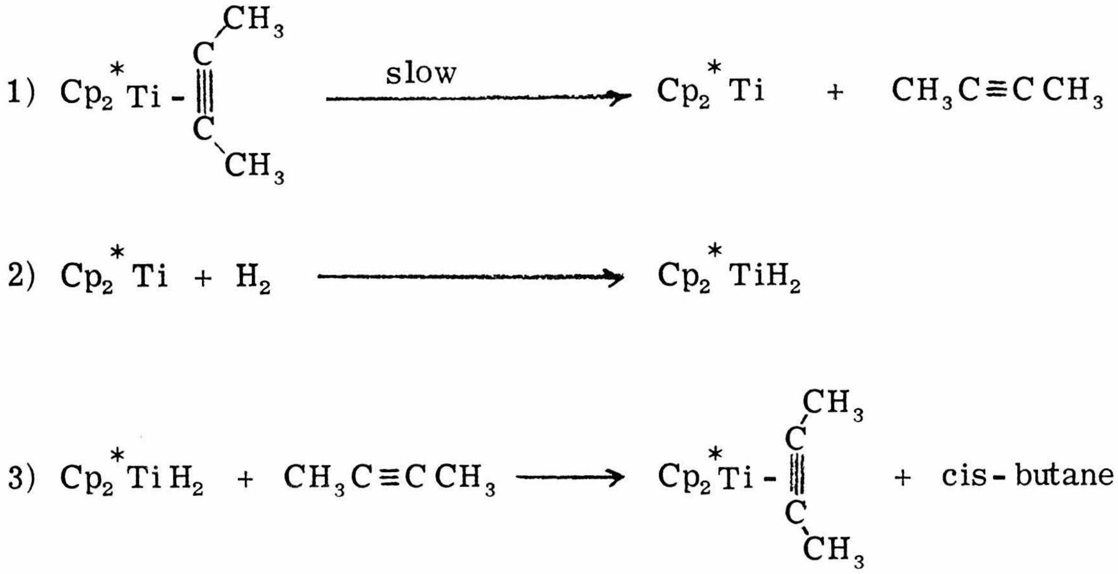
The metal acetylene bond strength is inversely proportional to the rates of acetylene hydrogenation. Activated acetylenes are hydrogenated slower than unactivated ones and the zirconium system is slower than the titanium catalyst. This behavior implies that dissociation of the acetylene from the metal is a necessary step of the catalytic cycle. Because permethyl titanocene oxidatively adds hydrogen very rapidly at -21° C to form $Cp_2^*TiH_2$,[12] dissociative substitution of the acetylene with hydrogen may generate the active hydrogenating agent. In fact, $Cp_2^*TiH_2$ is observed by nmr to react



$$Cp_2^*TiH_2 + 2\ CH_3C{\equiv}CCH_3 \xrightarrow[\text{fast}]{-80\,^\circ C} Cp_2^*Ti\text{-}(CH_3C{\equiv}CCH_3) + (H)(CH_3)C{=}C(H)(CH_3)$$

with 2-butyne at -80° C to produce one equivalent of cis-butene and 2. At -80° C, the 2-butyne complex 2 only slowly hydrogenates 2-butyne. These data are consistent with the mechanism shown in Scheme I. Step one is rate limiting because both steps two and three are

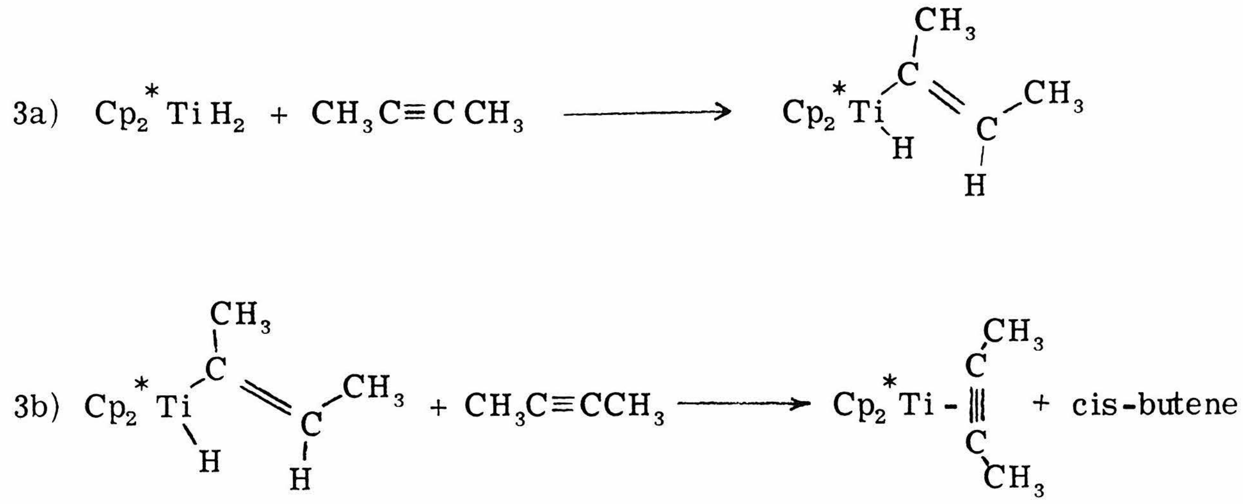
Scheme I



observed to be faster than the overall hydrogenation rate. In addition, Cp_2^*Ti reacts at -80° C with hydrogen and 2-butyne to consume only one equivalent of hydrogen and form 2 and cis-butene. This reaction confirms the slowness of step one relative to steps two and three.[13] For every equivalent of titanocene formed, only one equivalent of butyne is hydrogenated.

Unfortunately, the most interesting transformation, step three, is obscured by the rate-limiting acetylene dissociation. Scheme II depicts a possible scenario for step three. The acetylene inserts into

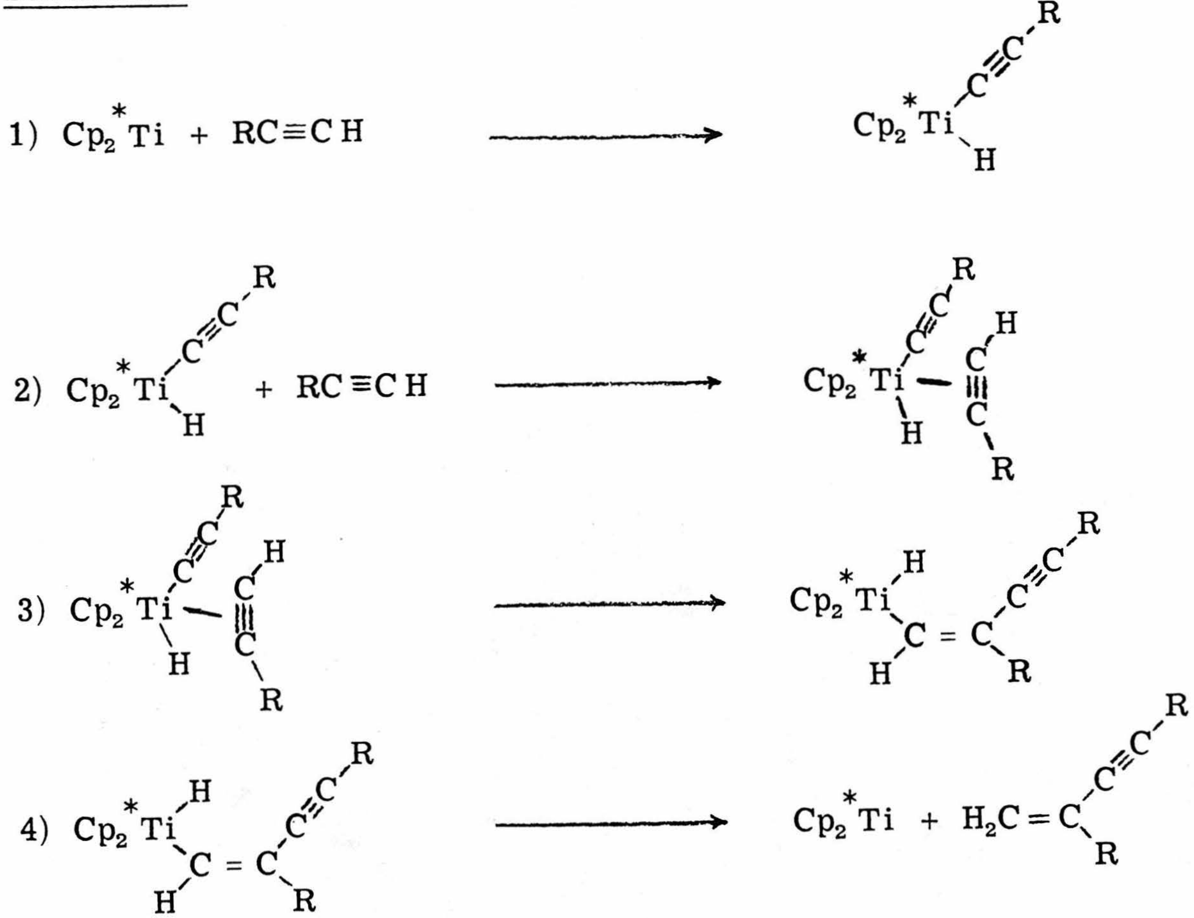
Scheme II



the titanium hydride forming a vinyl hydride. Reductive elimination is promoted by another equivalent of acetylene. Note that either unassisted reductive elimination or hydrogen-assisted reductive elimination of the vinyl hydride violates the requirement of one hydrogenation per titanocene formation.

A possible mechanism for the dimerization of terminal acetylenes is shown in Scheme III. The reaction is formally the addition of an acetylene hydrogen bond across another acetylene triple bond. Somewhat analogous to the acetylene hydrogenations, Cp_2^*Ti oxidatively adds across the acetylene hydrogen bond. Although any acetylene might react with the acetylene hydride in step two, only a terminal acetylene can coordinate and insert to form the en-yne hydride. The resulting reductive elimination yields the cis-acetylene hydrogen addition product.

Scheme III



EXPERIMENTAL

All manipulations were performed under rigorously oxygen- and moisture-free conditions using either vacuum line techniques or a Vacuum Atmospheres glove box. All solvents were purified by distillation from titanocene immediately prior to use. 2-Butyne and phenyl acetylene were purified by distillation from molecular sieves. Propyne was freeze-pump-thawed and distilled at -78° C. Diphenyl acetylene (Aldrich) was used without purification. The nitrogen complexes of titanium and zirconium as well as the dihydrides were prepared by literature methods.[5, 14, 15] Proton nmr were obtained from either a Varian A-60 or 220 MHz spectrometer. Infrared spectra were recorded on a Beckman IR-12. Molecular weights were determined cryoscopically in freezing benzene using a standardized molality-freezing point curve with a ferrocene standard. Hydrogenation product ratios were measured by peak weights of gas chromatograph output from a Varian 920 gas aerograph equipped with a 5% SE-30 on chromosorb column.

Preparation of $Cp_2^*TiC_2(C_6H_5)_2$, 2

400 Mgs of $(Cp_2^*Ti)_2N_2$ and 200 mgs of tolane was dissolved in fifteen mls of toluene in a 50-ml flask attached to a swivel frit. The reaction proceeded at 0° C and the solution changed color from blue to brown. The toluene was pumped away and pentane distilled onto the reaction mixture. Pentane removal left microcrystalline product which was recrystallized from octane. Anal. Calcd for $C_{34}H_{40}Ti$: C, 82.23; H, 8.12; Ti, 9.65. Found, C, 81.93; H, 8.02; Ti, 9.90.

^{1}H nmr (d_6 benzene) δ 1.92 (singlet, 3H), δ 6.9 (complex, 1H). Ir (nujol) 1647 cm^{-1} ($\nu C\equiv C$). Molecular weight 463 ± 40.

Preparation of $Cp_2^*TiC_2(CH_3)_2$, **2**

500 Mgs of $(Cp_2^*Ti)_2N_2$ was dissolved in fifteen mls of toluene in a 50 mls flask attached to a swivel frit. An excess of 2-butyne was distilled onto the solution at -78° C and warmed to 25° C. ^{1}H nmr of the green solid shows pure **2**, (d^8 toluene) δ 1.89 (singlet, 5H), δ 1.74 (singlet, 1H). Ir (nujol) 1683 ($\nu C\equiv C$).

Preparation of $Cp_2^*ZrC_2(C_6H_5)$, **3**

The same procedure used for **1** substituting $(Cp_2^*ZrN_2)_2N_2$[6] yielded a dark-green crystalline compound, Anal. Calcd. for $C_{34}H_{10}Zr$: C, 75.60; H, 7.41; Zr, 16.90. Found C, 75.39; H, 7.60; Zr, 16.81. ^{1}H nmrs (d_6 benzene) δ 1.80 (singlet, 3H), δ 7.5 (complex, 1H).

Preparation of $Cp_2^*ZrC_4(CH_3)_4$, **4**

400 Mgs of $(Cp_2^*ZrN_2)_2N_2$ was dissolved in fifteen mls of toluene in a 50-ml flask attached to a swivel frit. An excess of 2-butyne was distilled onto the solution. This mixture reacted at -20° C yielding an orange solution. After removing the toluene, seven mls of pentane was added. Slow cooling to -78° C yielded microcrystalline **4**. Anal. Calcd. for $C_{28}H_{45}Zr$: C, 71.53; H, 8.94; Zr, 19.45. Found C, 71.25; H, 8.98; Zr, 19.62. ^{1}H nmr δ 1.80 (singlet, 5H), δ 1.79 (singlet, 1H); δ 1.58 (singlet, 1H). Yields in the syntheses of compounds **1** through **4** were all in excess of 90 percent.

Hydrogenations

The hydrogenations were performed in a 50-ml flask with a septum adapter. A typical run used between 0.1 to 0.25 mmoles of

$Cp_2^*TiH_2$ in eleven mls of toluene. 33 Mmoles of 2-butyne was frozen into solution at -78° C. One atmosphere of hydrogen was put over the solution and the reaction immersed in a -21° C temperature bath. Immediately on warming, the orange solution of $Cp_2^*TiH_2$ turned green. The solution remained green until all 2-butyne was gone then returned to orange. The reaction was monitored by removing 30 μl aliquots periodically throughout the reaction. The relative ratios of alkyne versus alkene were determined by G.C. peak weights. A kinetic study was impossible because the reaction was stir-rate dependent. An average turnover of 2-butyne was 0.75 equivalents per minute per titanium. Hydrogenations of tolane though much slower were complicated by further reduction to dibenzyl.

The reaction of $Cp_2^*TiH_2$ with 2-butyne under hydrogen at -50° C by nmr was very rapid; the reaction was 75% reacted to form $\underset{\frown}{2}$ and cis-butene in five minutes. Once the dihydride had completely reacted, further hydrogenation continued slowly until the hydrogen in the nmr tube was consumed.

The reaction of 0.5 mmoles of Cp_2^*Ti with hydrogen and 2-butyne was performed by adding 5 mmoles of 2-butyne at -196° C and 1.70 mmoles of hydrogen. Stirring the reaction for three minutes at -78° C and then collecting all volatiles through -196° C traps by toepler pump yielded 1.22 mmoles of hydrogen. Gas chromatography of the remaining hydrocarbons showed a ratio of nine to one 2-butyne to 2-butene.

Dimerization of Terminal Acetylenes

The catalytic dimerization of propyne was performed by dissolving 0.12 mmoles of 1 in toluene and adding five mmoles of propyne at -78° C. Warming to 25° C resulted in a red solution which was stirred for 24 hours. The solution slowly turned brown. All volatile products were pumped through a -78° C trap. The involatile product at -78° C proved to be 2-methyl-pentene-3-yne. The ir and nmr matched those of an authentic sample.[16]

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13. If step one is reversible then less than one equivalent of hydrogen would have been consumed.

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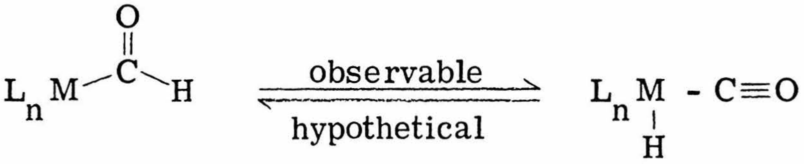
16. Prepared by reacting $CH_2=C(CH_3)-C\equiv C\ominus$, 2-propenyl acetylide anion with CH_3I.

Chapter 2

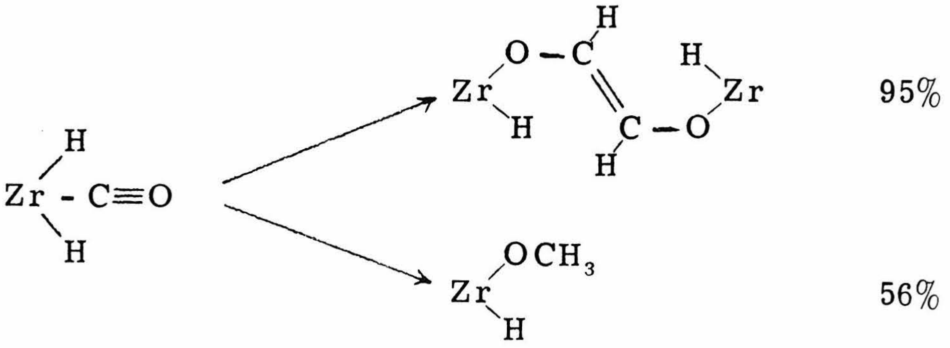
The Kinetics and Mechanism of the Zirconoxy Carbene Migratory Insertion Reaction

INTRODUCTION

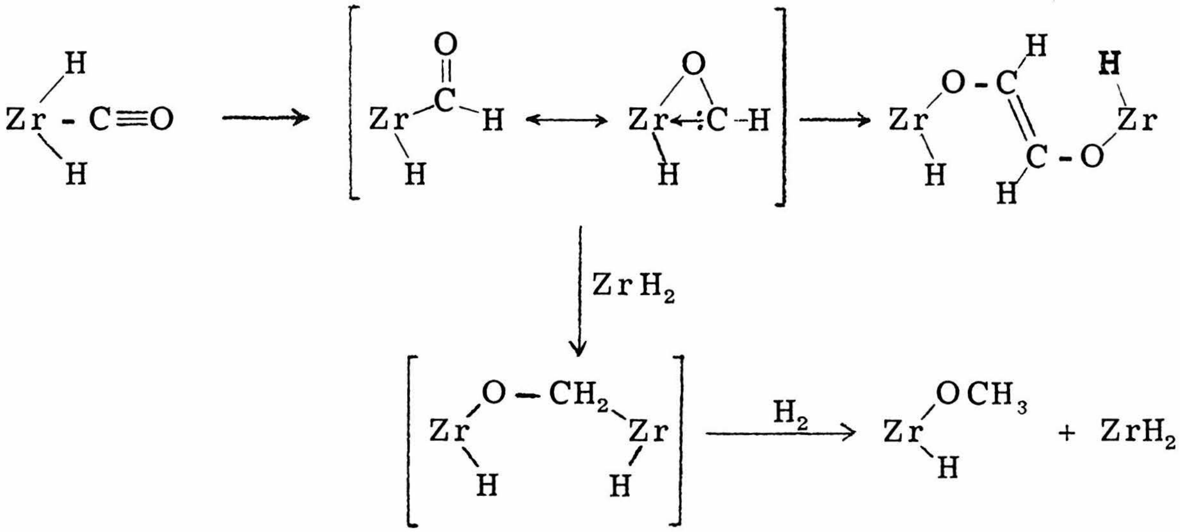
Growing interest in the selective conversion of carbon monoxide and hydrogen to hydrocarbons has focused attention on the requisite reduction of CO. The fundamental process of forming a hydrogen bond to CO mediated by transition metal catalysts has been the center of considerable research.[1-3] Migratory insertion of a metal carbonyl hydride to produce a metal formyl has been postulated as the initial step in Fischer-Tropsch hydrocarbon syntheses. To date however, only the reverse reaction has been directly observed.[2]



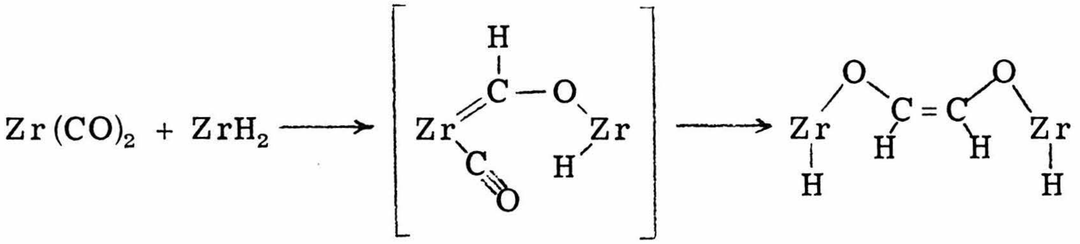
The stoichiometric reduction of CO by ZrH_2 may be an exception.[1] ZrH_2 coordinates one equivalent of CO at low temperature producing $Zr(H)_2CO$. Above -30° C, $Zr(H)_2CO$ decomposes to form trans-$HZrOCH{=}CHOZrH$ and $HZrOCH_3$. The relative amount of each product depends on the amount of excess ZrH_2 in solution during the decomposition of $Zr(H)_2CO$. Only the trans-enolate is formed when no excess ZrH_2 is present. $HZrOCH_3$ is the major product when four equivalents of ZrH_2 are in solution with $Zr(H)_2CO$. Both the trans-enolate and the methoxy-hydride result from CO hydrogenation

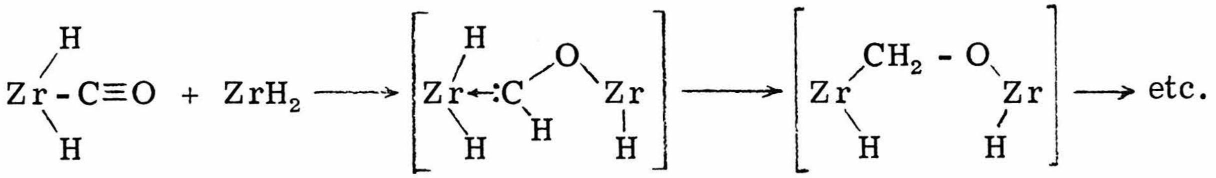


mediated by ZrH_2. The most straightforward mechanism of this reaction involves migratory insertion of CO into a zirconium hydride bond of $Zr(H)_2CO$ to yield a formyl intermediate. Subsequent dimerization of the formyl intermediate with accompanied rearrangement formally yields the trans-enolate. ZrH_2 can trap the formyl yielding $HZrOCH_2ZrH$ which reductively eliminates $HZrOCH_3$ under hydrogen.



Although intramolecular insertion into a zirconium hydride bond is consistent with ZrH_2 reactions with free CO, the nearly quantitative yield of cis-enolate, HZrOCH=HCOZrH, from the reaction of ZrH_2 with $Zr(CO)_2$ implies a direct reaction of ZrH_2 with $Zr(CO)_2$.[3] This observation also raises questions concerning the molecularity of the $Zr(H)_2CO$ decomposition. The mechanistic implications of inter-



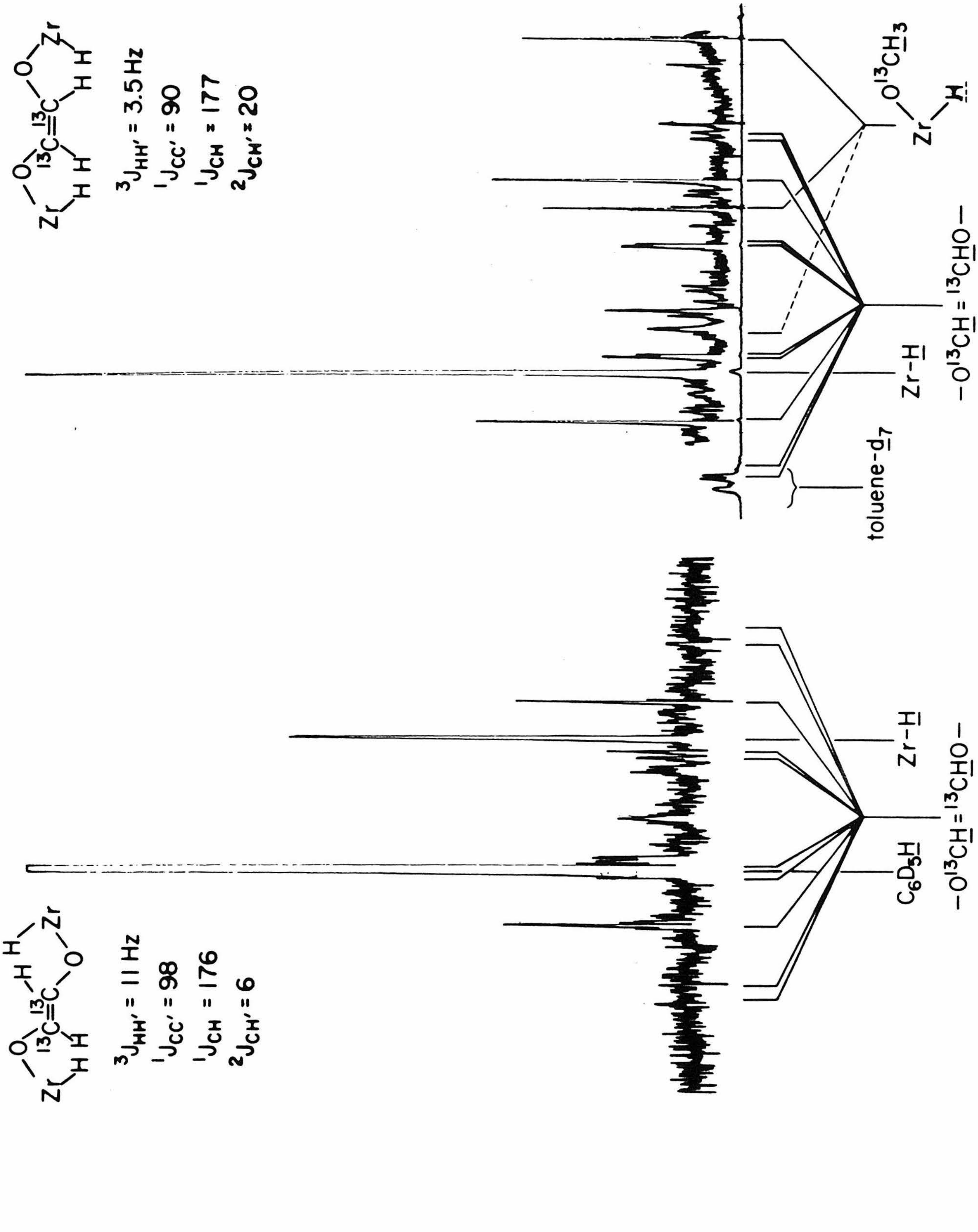


molecular CO reduction in the $Zr(H)_2CO$ system are too broad to discuss in detail here. In general, intermolecular CO reduction by ZrH_2 is viewed as hydride transfer from zirconium to carbon analogous to borohydride reductions of metal carbonyls.[2] Unlike borohydride

$$M-C\equiv O \; + \; ZrH_2 \longrightarrow M=\underset{\displaystyle H}{\underset{|}{C}}-O-\underset{\displaystyle H}{\underset{|}{Zr}}$$

reductions, the zirconium oxygen bond remains intact. A zirconoxy carbene results instead of a formyl anion. The zirconium zirconoxy carbene, (CO)Zr=CH-O-ZrH, has never been observed, probably due to its inherent instability. In addition to the steric crowding resulting from the proximity of two Cp_2^*Zr moieties, zirconium II has only two d electrons to stabilize the two π acidic ligands, CO and oxycarbene.

Models for this hydride transfer product were sought which would yield stable carbene complexes. Electron-rich mono-carbonyls were the first choice to avoid the stability problems previously discussed. The reactions of ZrH_2 with group VI metallocene carbonyls yield the zirconoxy carbenes, Cp_2M=CH-O-ZrH, (M = W, Mo, and Cr).[3] Hydride transfer is rapid at -80° C and the molybdenum and tungsten products are stable above 100° C. The closely related niobocene carbenes, RNb=CH-O-ZrH, are perhaps more interesting chemically. Several niobocene substituents readily migrate to the carbene. The mechanism of this rarely observed migratory insertion[4] is investigated herein. The syntheses of several substituted niobocene carbenes are described.


Zr
O
13C
13C
H H H H
Zr
3JHH' = 3.5 Hz
1JCC' = 90
1JCH = 177
2JCH' = 20
O13CH3
Zr–H
–O13CH = 13CHO–
Zr–H
toluene-d7
Zr
O
13C
13C
H H H
Zr
3JHH' = 11 Hz
1JCC' = 98
1JCH = 176
2JCH' = 6
Zr–H
C6D5H
–O13CH = 13CHO–

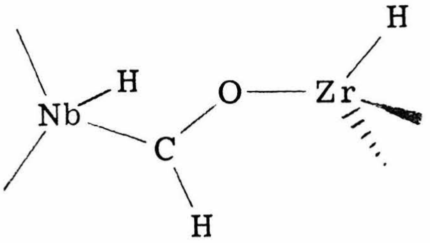
RESULTS

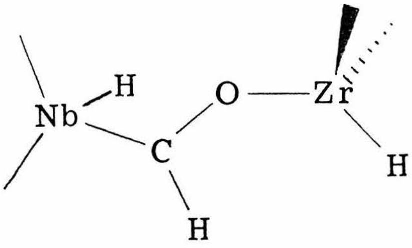
1) Reactions of ZrH_2 with metal carbonyls: Preparation of substituted niobocene zirconoxy carbenes.

ZrH_2 reacts with $Zr(CO)_2$ underhydrogen at 25° C to form the cis-enolate, HZrOCH=CHOZrH in two hours. The ^1H nmr of the cis-enolate, has an olefinic proton upfield from the zirconium hydride peak in contrast to the trans-enolate.[1] The ^{13}C substituted cis-enolate displays the classic ten-line AA'XX' ^1H nmr pattern[5] for the olefinic proton $J_{HH'}$ is three hertz for the cis compared to eleven for the trans-enolate.

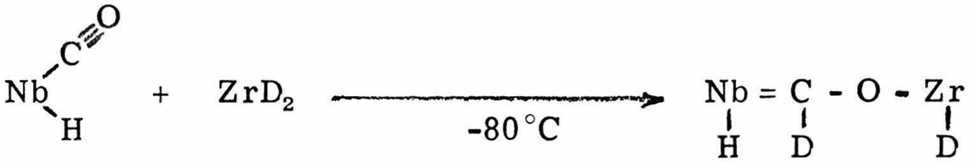
ZrH_2 reacts rapidly with other metallocene carbonyls. At -78° C, ZrH_2 reacts as soon as it dissolves with Nb(H)CO to form HNb=CH–O–ZrH. The ^1H nmr of HNb=CH–O–ZrH is similar to the nearly isostructural W=CH–O–ZrH.[3] The carbene hydrogen resonance is found at low field at δ 11.63. The Cp protons are a singlet at 25° C but separate into the two expected equal intensity peaks about 0.01 ppm apart below -35° C. Bonding in the metallocene equatorial plane to the carbene p-orbital directs oxygen toward one Cp and hydrogen toward the other Cp.[6] The zirconium hydride and niobium hydride signals are at δ 5.70 and δ -3.14, respectively.

HNb=CH–O–ZrH also exhibits a temperature-dependent ^{13}C nmr spectrum. At 30° C the carbene carbon peak is a broad doublet at δ 265.5. The resonance coalesces to a broad lump at -30° C. At -90° C, the signal resolves into two doublets at δ 272.8 and δ 215.1 of seven to one relative intensity. Apparently a process not involving any C–H bond making or breaking occurs rapidly which equilibrates two isomers of HNb=CH–O–ZrH. Rotation about the niobium carbon double bond cannot be the dynamic process because the two ppm separated Cp resonances remain constant over the entire temperature range. Of the remaining bonds in the molecule, rotation around the carbon oxygen bond is impossible. Models suggest that two rotomers of the zirconium oxygen bond ought to be stable conformations. In one conformation, the zirconium hydride points away from the carbene-hydrogen bond as in W=CH–O–ZrH. The zirconium hydride is directed away from the carbene hydrogen in the other conformer.

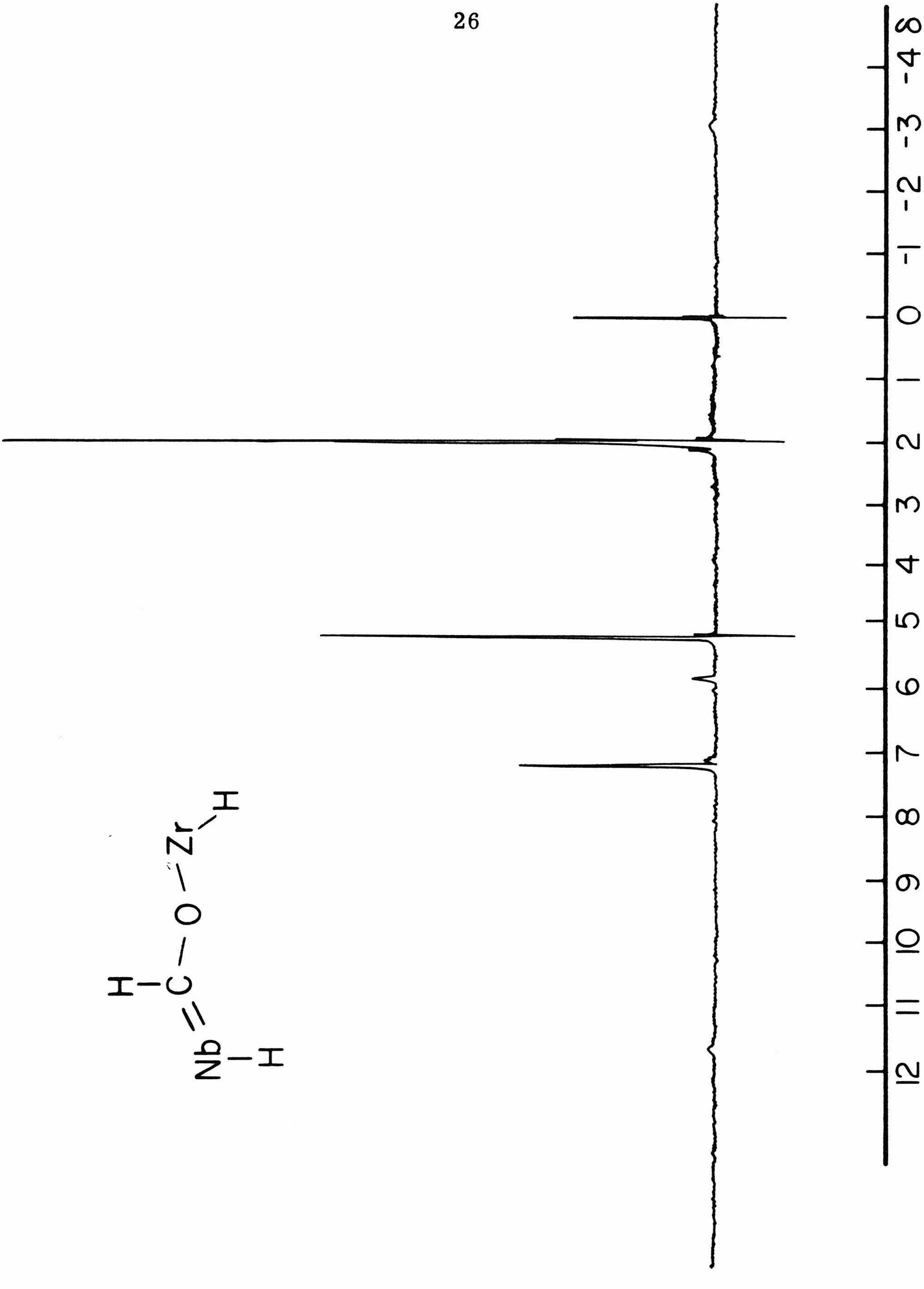




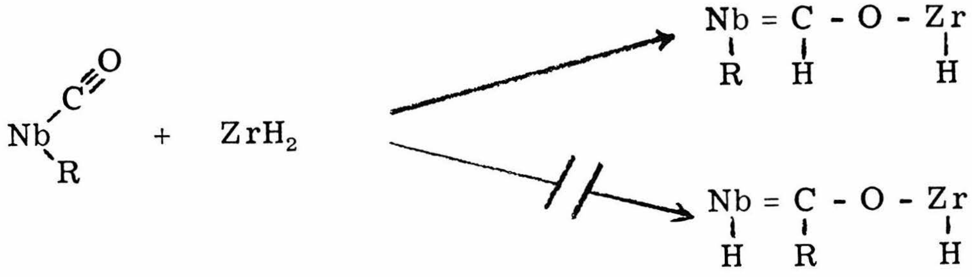
Reactions of ZrD_2 with Nb(H)CO show zirconium dihydride reacts as a hydride transfer reagent to CO. Additionally ZrH_2 does not



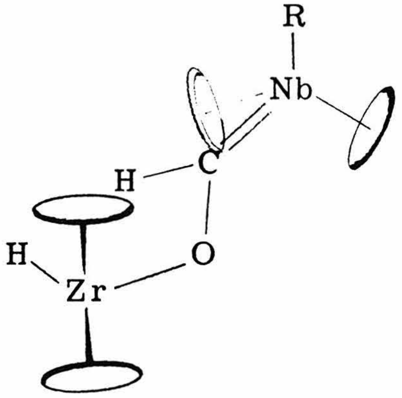
promote the migratory insertion of CO into the niobium substitutent bond in the hydride transfers to niobocene alkyl carbonyls. In all cases the niobocene substituent remains on niobium during hydride transfer. A proton substituted carbene is formed characterized by a

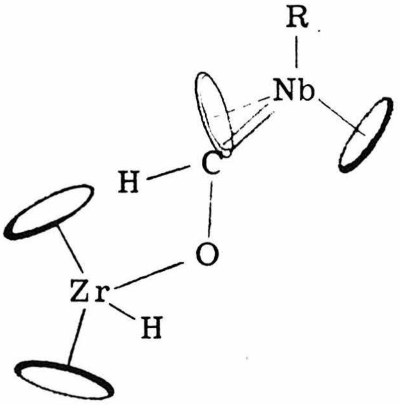

Nb
H
C
H
O
Zr
H
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ

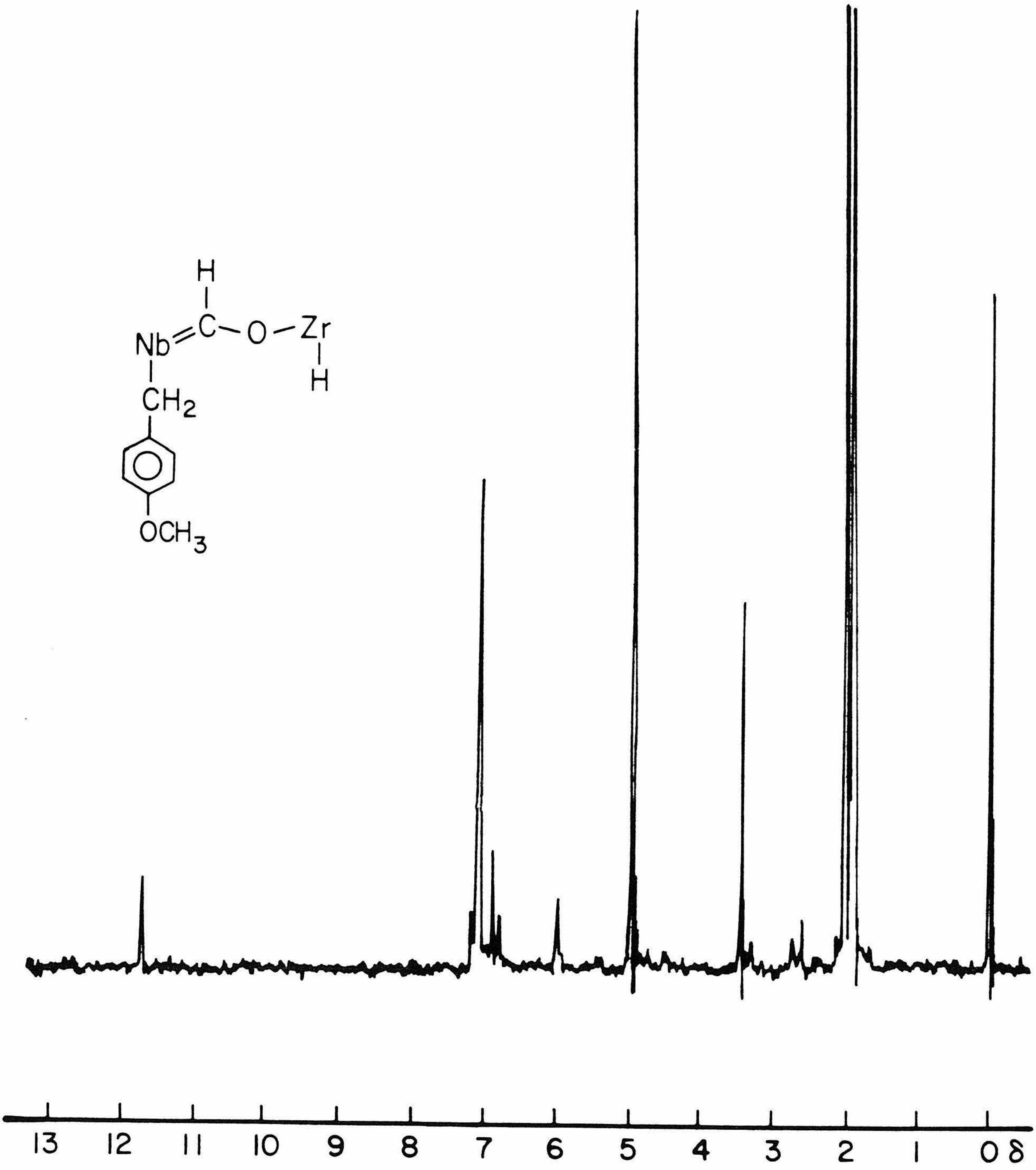
low field resonance in the ^{1}H nmr at δ 11-12.



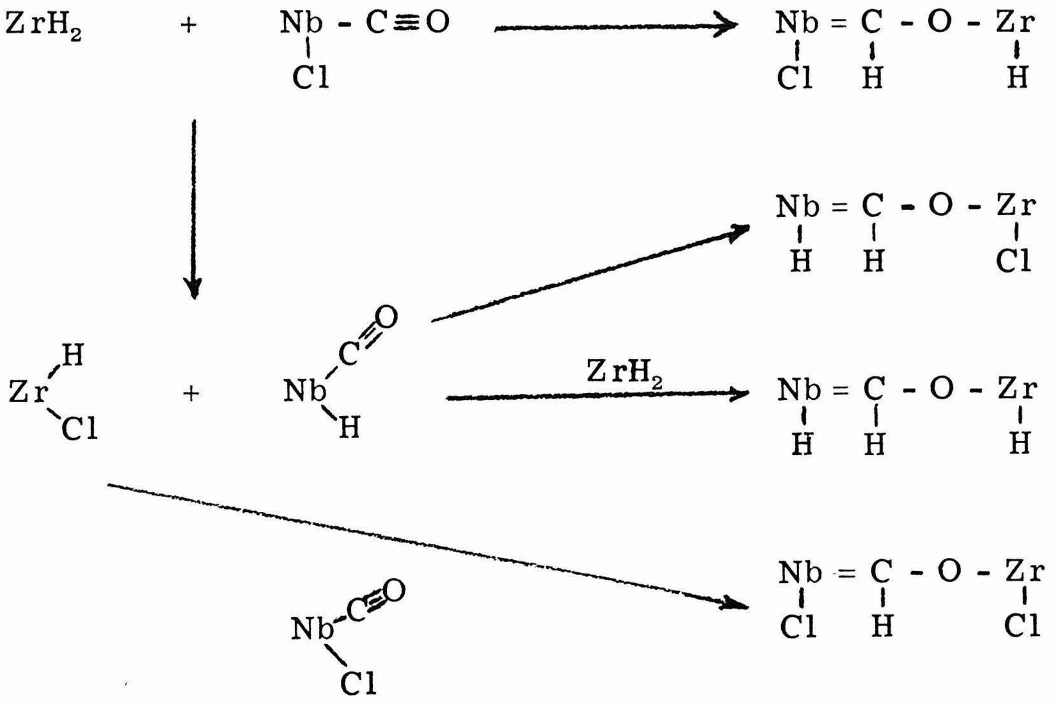
The reaction of ZrH_2 with Nb(CH_2ϕ)CO produces ϕCH_2Nb=CH–O–ZrH isolated in greater than 90% yield. Similar to HNb=CH–O–ZrH, the Cp ligands appear equivalent at higher temperatures by ^{1}H nmr. Below 40° C the Cp signals separate by 0.02 ppm. The Cp* methyl resonances are also inequivalent. Similar to $(ZrN_2)_2N_2$,[7] the Cp and Cp* ligands must stagger. Because niobium has two ligands in the equatorial plane, each Cp* is in a different environment. This effect is observed for all niobocene carbenes except the hydride.






H
Nb=C—O—Zr
H
CH2
OCH3
13
12
11
10
9
8
7
6
5
4
3
2
1
0 δ

A variety of substituted niobocene carbenes have been prepared in this manner, including methyl, ethyl, vinyl, phenyl, benzyl, and zirconoxymethylene. A limitation to this procedure is Nb(Cl)CO. In addition to hydride transfer to the carbonyl, ZrH_2 also exchanges with chloride to form Nb(H)CO and ZrHCl. A mixture is obtained from the

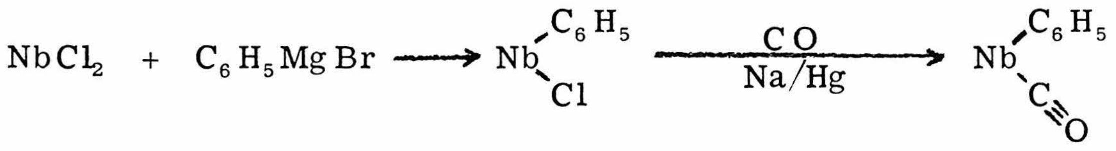


ZrH_2 reaction with Nb(Cl)CO whose ^1H nmr is consistent with the above scheme. That ZrHCl will transfer hydride is verified independently by the formation of HNb=CH–O–ZrCl from ZrHCl and Nb(H)CO. ZrHF reacts similarly. However, ZrHCl or ZrHF will not transfer hydride to $Nb(CH_2\phi)CO$. Apparently the halide reduces the hydricity of the zirconium hydride enough that hydride transfer is unfavorable to the more sterically crowded $Nb(CH_2\phi)CO$.

2) Synthesis of substituted niobocene carbonyls

Most of the substituted niobocene carbonyls used in the carbene syntheses have not been reported. In the case of $Nb(CH_3)CO$, the literature preparation is unreproduceable.[8] Methyl lithium and $Nb(Cl)CO$ produce $Nb(CH_3)CO$ in less than one percent yield under a variety of conditions. $Nb(CH_3)CO$ is prepared in 40 percent yield by slow addition of methyl grignard to $Nb(Cl)CO$.

Similar reactions of both phenyl grignard and benzyl grignard with $Nb(Cl)CO$ failed to yield a significant amount of the desired carbonyl. $Nb(\phi)CO$ is prepared by the reduction of $Nb\phi Cl$ with Na/Hg under CO in 40% yield. One equivalent of phenyl grignard reacts with

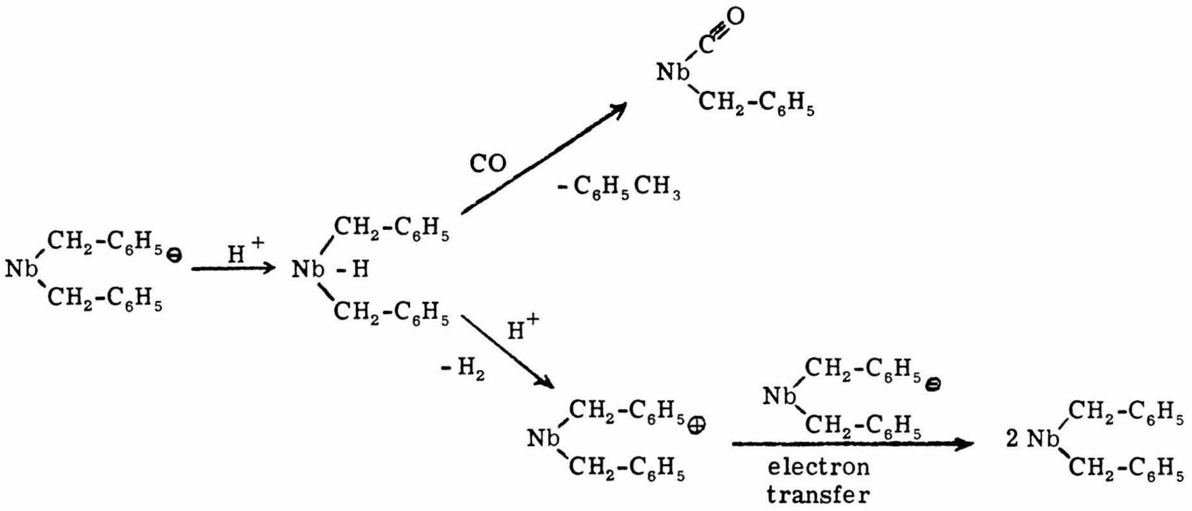


$$NbCl_2 + C_6H_5MgBr \longrightarrow Nb(C_6H_5)(Cl) \xrightarrow[Na/Hg]{CO} Nb(C_6H_5)(C{\equiv}O)$$

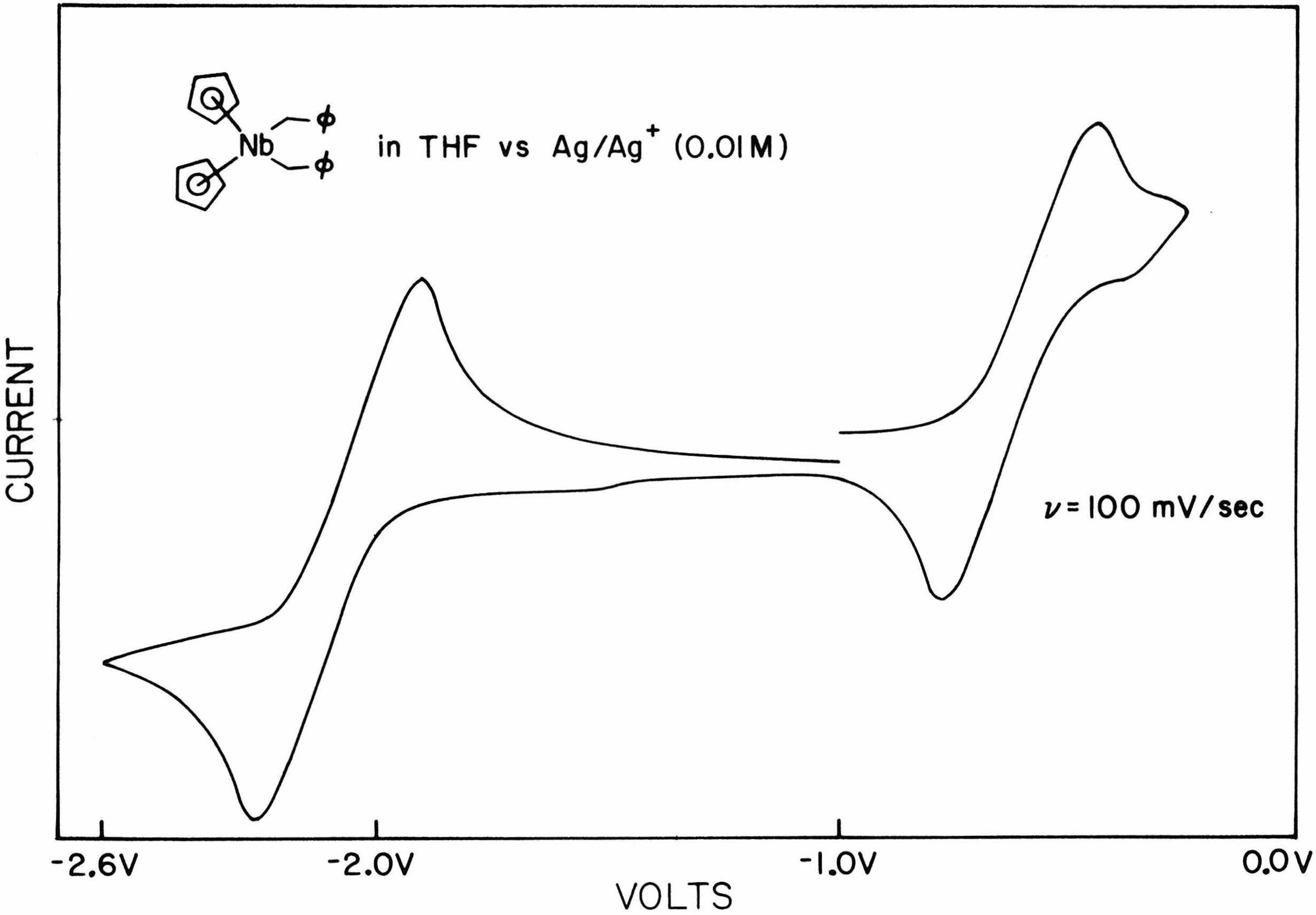
$NbCl_2$ to produce $Nb\phi Cl$. The same synthetic method fails to yield $Nb(CH_2\phi)CO$. $Nb(CH_2\phi)Cl$ appears to be unstable with respect to $Nb(CH_2\phi)_2$ and $NbCl_2$. One equivalent of benzyl grignard with $NbCl_2$ forms only half an equivalent of $Nb(CH_2\phi)_2$. One equivalent of HCl reacts with $Nb(CH_2\phi)_2$ yielding half $NbCl_2$ and half unreacted $Nb(CH_2\phi)_2$. A scheme similar to the preparation of $W(CH_2\phi)_2$[9] from WH_2 also fails. The deprotonation of $Nb(H)CO$ by LDA followed by reaction with benzyl bromide yields no $Nb(CH_2\phi)CO$.

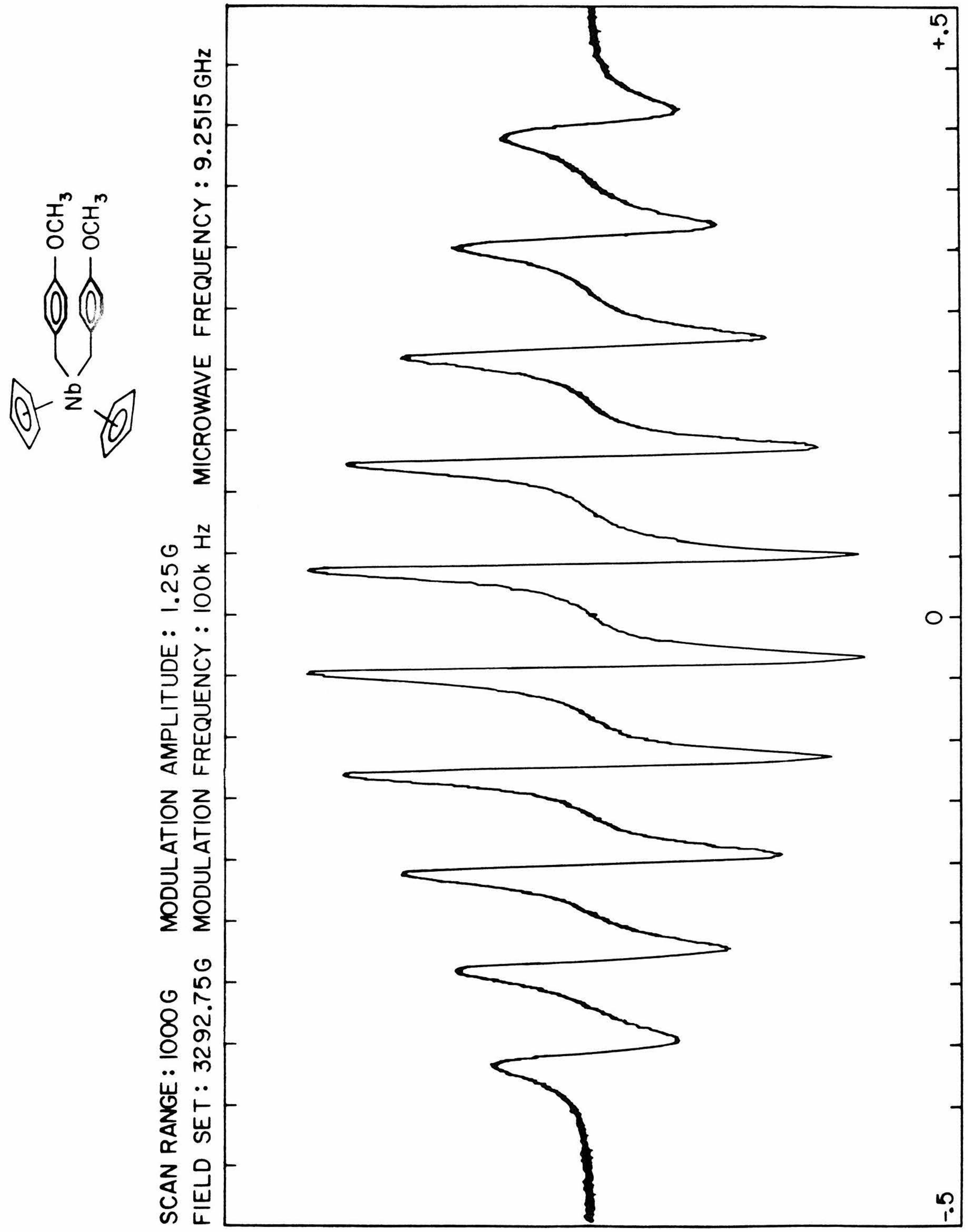
$Nb(CH_2\phi)CO$ is formed in 60% yield by the reduction of $Nb(CH_2\phi)_2$ followed by protonation under CO. The cyclic voltamogram of

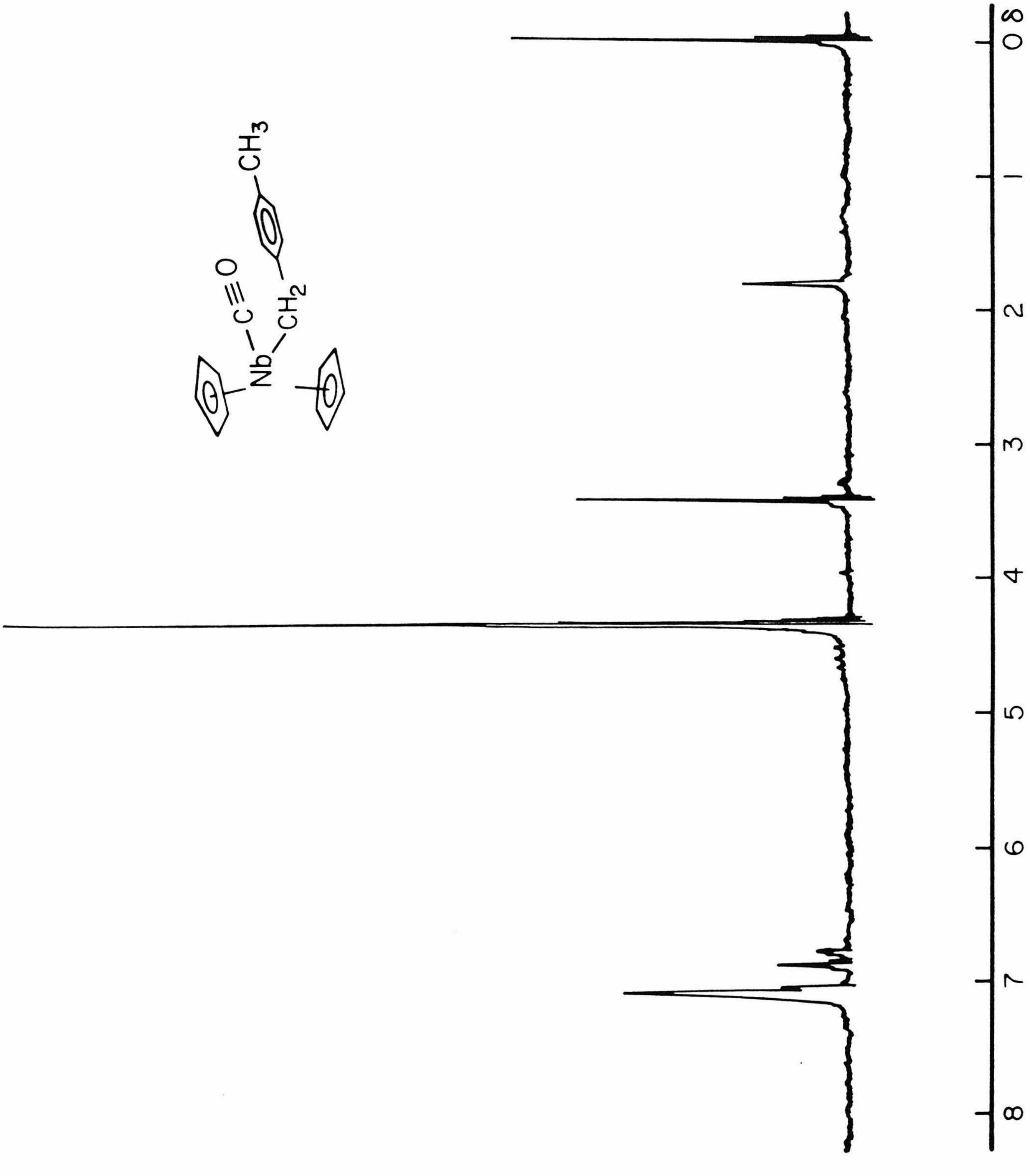
$Nb(CH_2\phi)_2$ shows the seventeen-electron complex has reversible redox potentials of equal intensity at -2.08 V and -0.62 V relative to a Ag/Ag^+ reference. Coulometry of the most cathodic process proves the reduction is a one-electron transfer to form the expected anion $Nb(CH_2\phi)_2^{\ominus}$. The slow protonation with CF_3CH_2OH of dilute solutions of $Nb(CH_2\phi)_2^{\ominus}$ under CO yields $Nb(CH_2\phi)CO$. The dilute conditions required and



$Nb(CH_2\phi)_2$ the major by-product indicate a likely side reaction is the protonation of the intermediate hydride to form $Nb(CH_2\phi)_2^{\oplus}$ and hydrogen. $NbH(CH_2\phi)_2$, similar to NbH_3, ought to be hydridic enough to reduce protons. Subsequent electron transfer from $Nb(CH_2\phi)_2^{\ominus}$ to the cation $Nb(CH_2\phi)_2^{\oplus}$ is favorable by 1.46 V based on the cyclic voltamogram.

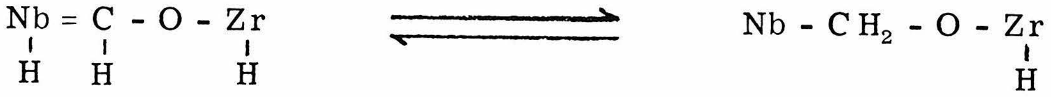

Nb
ϕ
ϕ
in THF vs Ag/Ag+ (0.01M)
ν = 100 mV/sec
CURRENT
VOLTS
-2.6V
-2.0V
-1.0V
0.0V


SCAN RANGE : 1000 G
MODULATION AMPLITUDE : 1.25 G
FIELD SET : 3292.75 G
MODULATION FREQUENCY : 100k Hz
MICROWAVE FREQUENCY : 9.2515 GHz
Nb
OCH3
OCH3
-.5
0
+.5


Nb
C≡O
CH$_2$
CH$_3$
8
7
6
5
4
3
2
1
0 δ

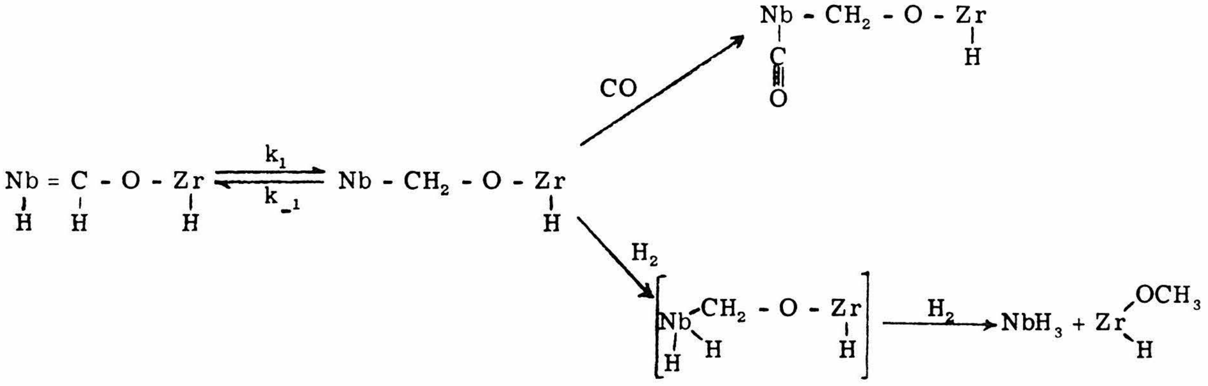
3) Migratory insertions of the zirconoxy-carbene into the niobocene hydride bond

The tautomerization of the eighteen-electron HNb=CH–O–ZrH, formally the product of α-elimination by Nb–CH_2–O–ZrH, occurs readily at 25° C. The sixteen-electron tautomer ought to be unstable



$$\underset{H}{Nb} = \underset{H}{C} - O - \underset{H}{Zr} \rightleftharpoons Nb - CH_2 - O - \underset{H}{Zr}$$

analogous to NbH,[10] $NbCH_2CH_3$,[11] and NbCl.[12] Solutions of the carbene-hydride darken slowly at 25° C and decomposition is much faster at higher temperatures. Added ligand can trap the unsaturated niobium III species. Carbon monoxide reacts with the carbene-hydride to form (CO)Nb–CH_2–O–ZrH. Hydrogen oxidatively adds to form the transient niobium V alkyl dihydride. The resultant alkyl-hydride reduction elimination and further reaction with H_2 yields NbH_3 and Zr(H)OCH_3.



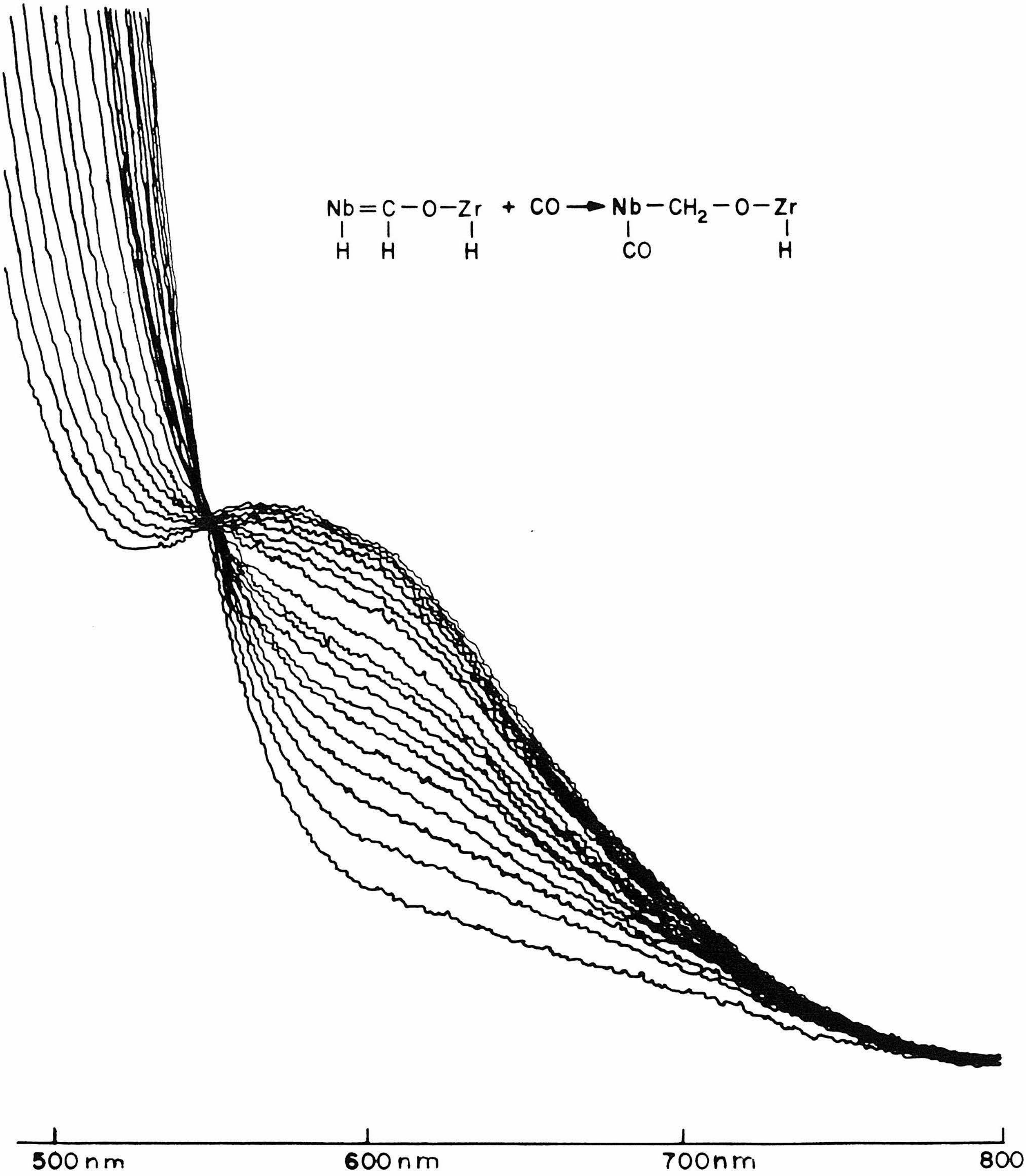
The CO reaction with HNb=CH–O–ZrH is conveniently followed by visible spectroscopy as the orange carbene hydride converts to the green (CO)Nb–CH_2–O–ZrH. Under pseudo-first-order conditions in CO, the rate is first-order in carbene hydride concentration. First-order dependence on CO pressure is demonstrated up to five atmospheres. The CO concentration at these pressures is two to forty mmolar[13] compared to the 16 mmolar initial carbene hydride concentration. The rate of dissolving CO must be faster than the CO trapping of Nb–CH_2–O–ZrH or else the observed rate is only a measure of the CO solvation rate. A limiting CO diffusion rate is unlikely because the reaction rate was insensitive to the stirring speed. The rate expression for the CO mediated hydride migration is:

$$\text{Rate} = k_{obs}\left[\underset{\text{H}}{\overset{|}{\text{Nb}}} = \underset{\text{H}}{\overset{|}{\text{C}}} - \text{O} - \underset{\text{H}}{\overset{|}{\text{Zr}}}\right] P_{co} = \frac{k_1 k_2 \left[\text{HNb} = \text{CH} - \text{O} - \text{ZrH}\right] P_{co}}{k_1 + k_2 P_{co}}$$

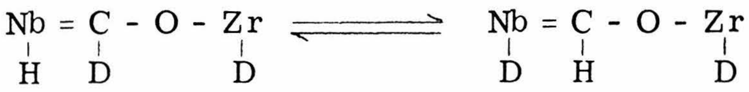
$$k_{obs} = \frac{k_1 k_2}{k_1} = 7.6 \times 10^{-3}\ \text{sec}^{-1}\ \text{atm}^{-1}$$

Apparently α-elimination is much faster than trapping by CO.

The unlikelihood of an associative process by CO with HNb=CH–O–ZrH implies a rapid pre-equilibrium of carbene insertion-α-elimination. The niobium hydride and the carbene hydrogen ought to exchange during this pre-equilibrium. This process is observed directly by nmr at low temperature in the spectrum of HNb=CD–O–ZrD. At -80° C, HNb=CD–O–ZrD displays the characteristic carbene


Nb=C−O−Zr + CO → Nb−CH₂−O−Zr
H H H CO H
500 nm
600 nm
700 nm
800

spectrum lacking the zirconium hydride and carbene-hydrogen peaks.



$$\underset{H}{Nb} = \underset{D}{C} - O - \underset{D}{Zr} \rightleftharpoons \underset{D}{Nb} = \underset{H}{C} - O - \underset{D}{Zr}$$

Even at -80° C the niobium hydride signal slowly loses intensity concommitant with the appearance of the carbene-hydrogen resonance. At room temperature this exchange occurs very rapidly. The resonance for the carbene-hydrogen and the niobium hydride do not average on the nmr time scale. This places an upper limit on the exchange rate of 2.7×10^3 sec^{-1}.[14]

Another direct measurement of this equilibrium is the saturation transfer technique using nmr.[15] If the exchange process between the carbene hydrogen and the niobium hydride occurs on the order of their proton relaxation times, then saturating one resonance will reduce the intensity of the other. This saturation transfer experiment succeeds for HNb=CH—O–ZrH. A more quantiative understanding of the exchange rate is gained by relating the intensities of the saturated peak to the exchanging peak as a function of delay time from the moment of complete saturation. A typical experiment involves saturating one signal, then waiting a specified time before recording the spectrum. The correlation of the difference in intensity of the two peaks as a function of delay time with the magnetization equation

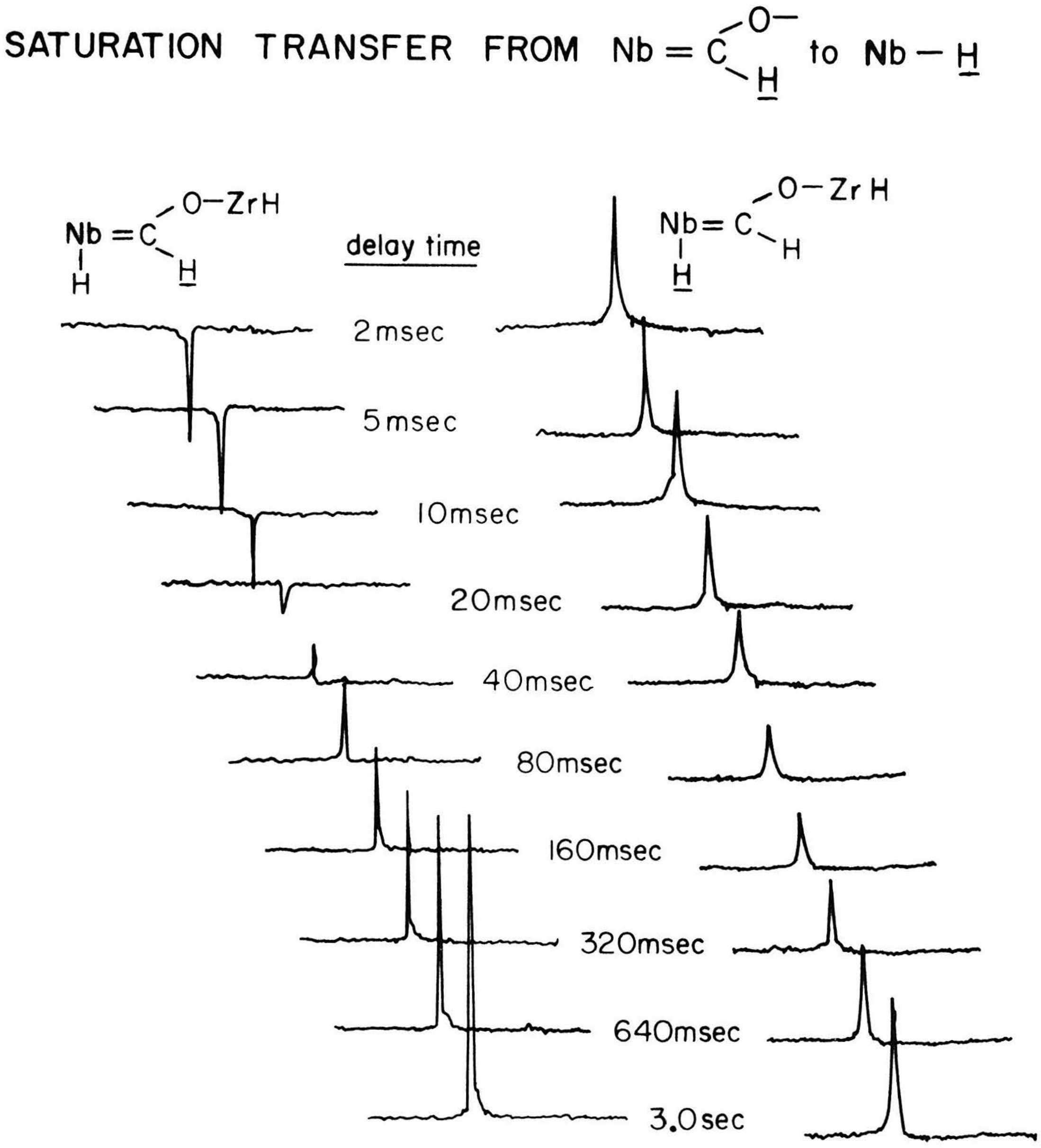
$$\frac{\partial(M_A - M_B)}{\partial t} = -\frac{(M_A - M_B)}{T_1} - 2k_{ex}(M_A - M_B)$$

[16] yields the exchange rate. M_A and M_B are the saturated resonance and the exchanging peak magni-

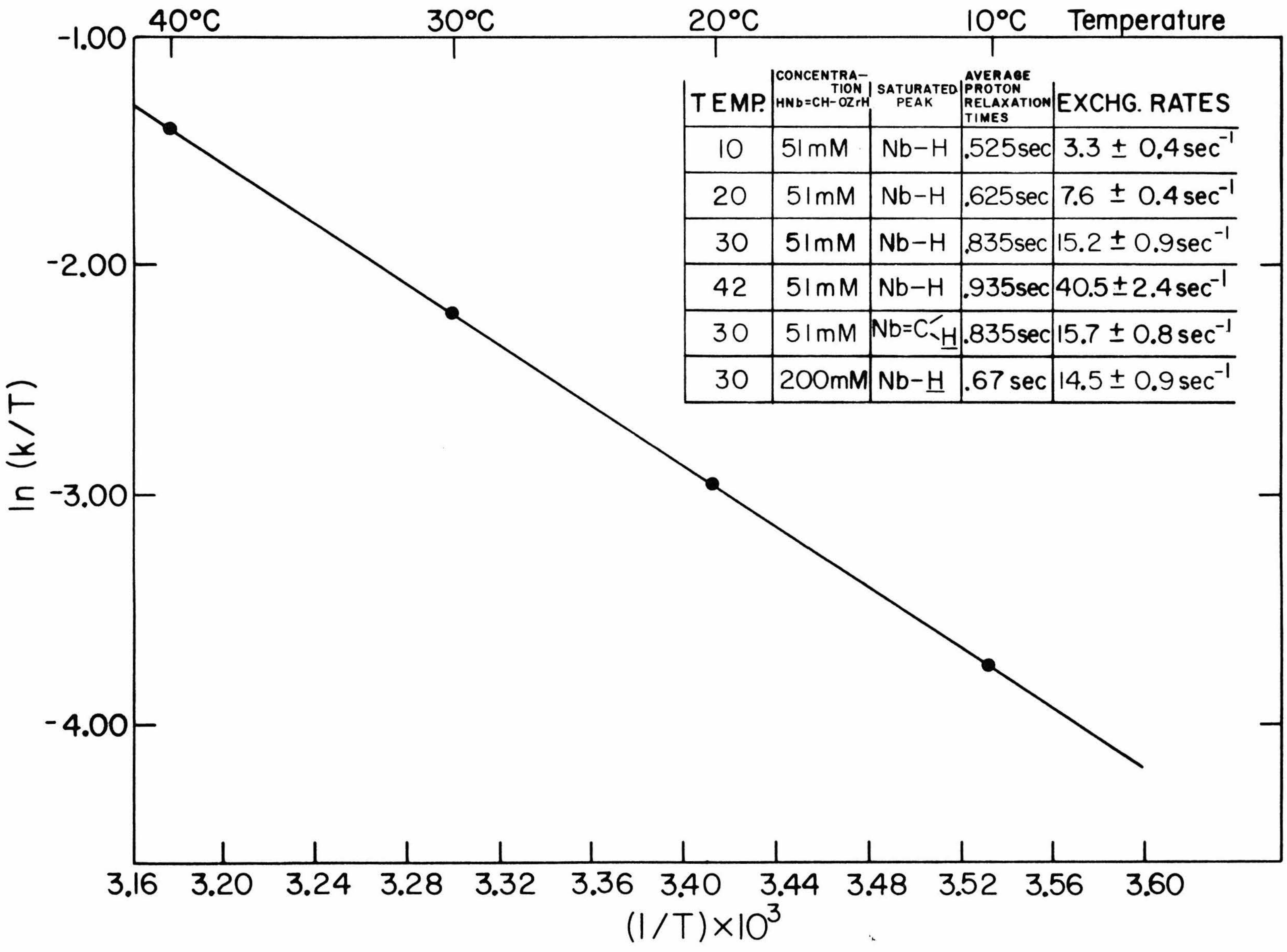
tudes, respectively. T_1 is the average relaxation of these two protons. K_{ex} equals the exchange rate.

Figure I shows the series of spectra for the saturation transfer of magnetization from the carbene hydrogen to the niobium hydride. Intuitively, saturation appears to have transferred at the time when the niobium-hydride signal has no intensity and the carbene hydrogen has minimum intensity. The reciprocal of the delay time of this spectrum ought to be an estimate of the rate of exchange. At 32.5° C, the minimum spectrum is near 0.036 sec. A guess for the rate is therefore $\ln 2(1 \div 0.036) = 19\ \mathrm{sec}^{-1}$.[17] The non-linear least-squares fit of the series of spectra to the magnetization equation yields a rate of 15.7 sec^{-1}. The rate is identical when either the niobium hydride or the carbene hydride resonance is saturated. Since either methylene proton can α-eliminate from $Nb-CH_2-O-ZrH$, the insertion rate equals twice this exchange rate: 31.4 sec^{-1}. The rate invariance over a four-fold concentration range of carbene indicates the hydride migration is unimolecular. These results, in conjunction with the CO kinetics, indicate α-elimination is roughly 200 times faster than CO trapping at one atmosphere.

Above 10° C the exchange rate satisfies the condition of being faster than the average proton relaxation time. Exchange rates were measured from 10° C to near the decomposition temperature of $HNb{=}CH-O-ZrH$ at 40° C. An Arrhenius rate plot at four temperatures yields the activation parameters of $\Delta H^{\ddagger} = 13.06$ kcal/mole and $\Delta S^{\ddagger} = -9.6$ e.u. (Figure 2). $\Delta S^{\ddagger}$ is not significantly negative to raise questions of the molecularity.



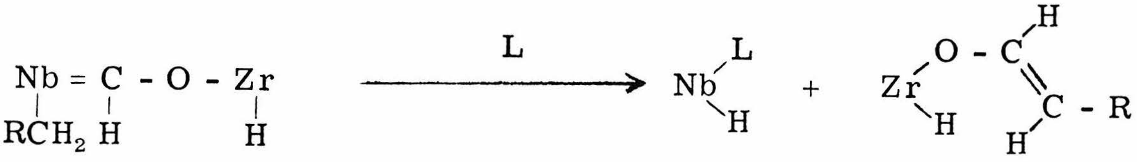
SATURATION TRANSFER FROM $Nb=C(O-)\underline{H}$ to $Nb-\underline{H}$



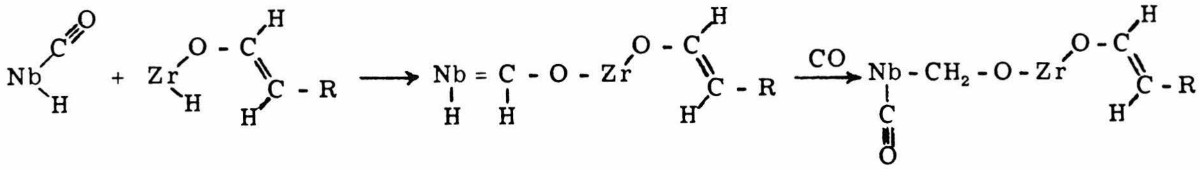
TEMP.	CONCENTRATION HNb=CH-OZrH	SATURATED PEAK	AVERAGE PROTON RELAXATION TIMES	EXCHG. RATES
10	51mM	Nb-H	.525sec	3.3 ± 0.4sec^{-1}
20	51mM	Nb-H	.625sec	7.6 ± 0.4sec^{-1}
30	51mM	Nb-H	.835sec	15.2 ± 0.9sec^{-1}
42	51mM	Nb-H	.935sec	40.5 ± 2.4sec^{-1}
30	51mM	Nb=C$\langle\underline{H}$	.835sec	15.7 ± 0.8sec^{-1}
30	200mM	Nb-$\underline{H}$	.67 sec	14.5 ± 0.9sec^{-1}

4) Migratory insertions of the zirconoxy carbene into niobocene alkyl bonds

The alkyl substituted niobocene carbenes react w th added ligands to form Nb(H)L and Zr(H)OCH=CHR. R equals hydrogen, phenyl,

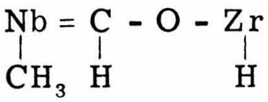
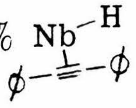
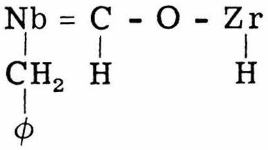
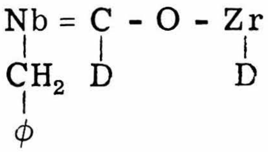
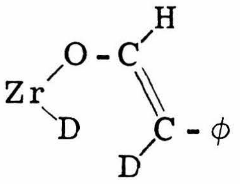
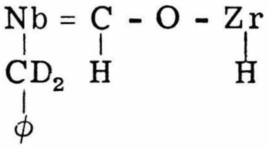
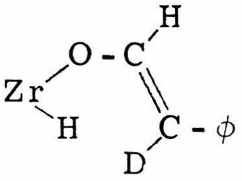
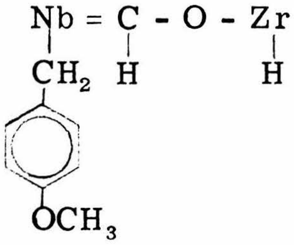
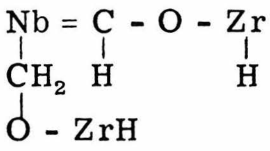
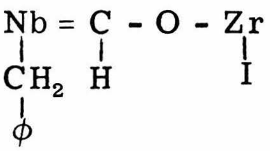
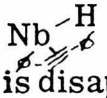


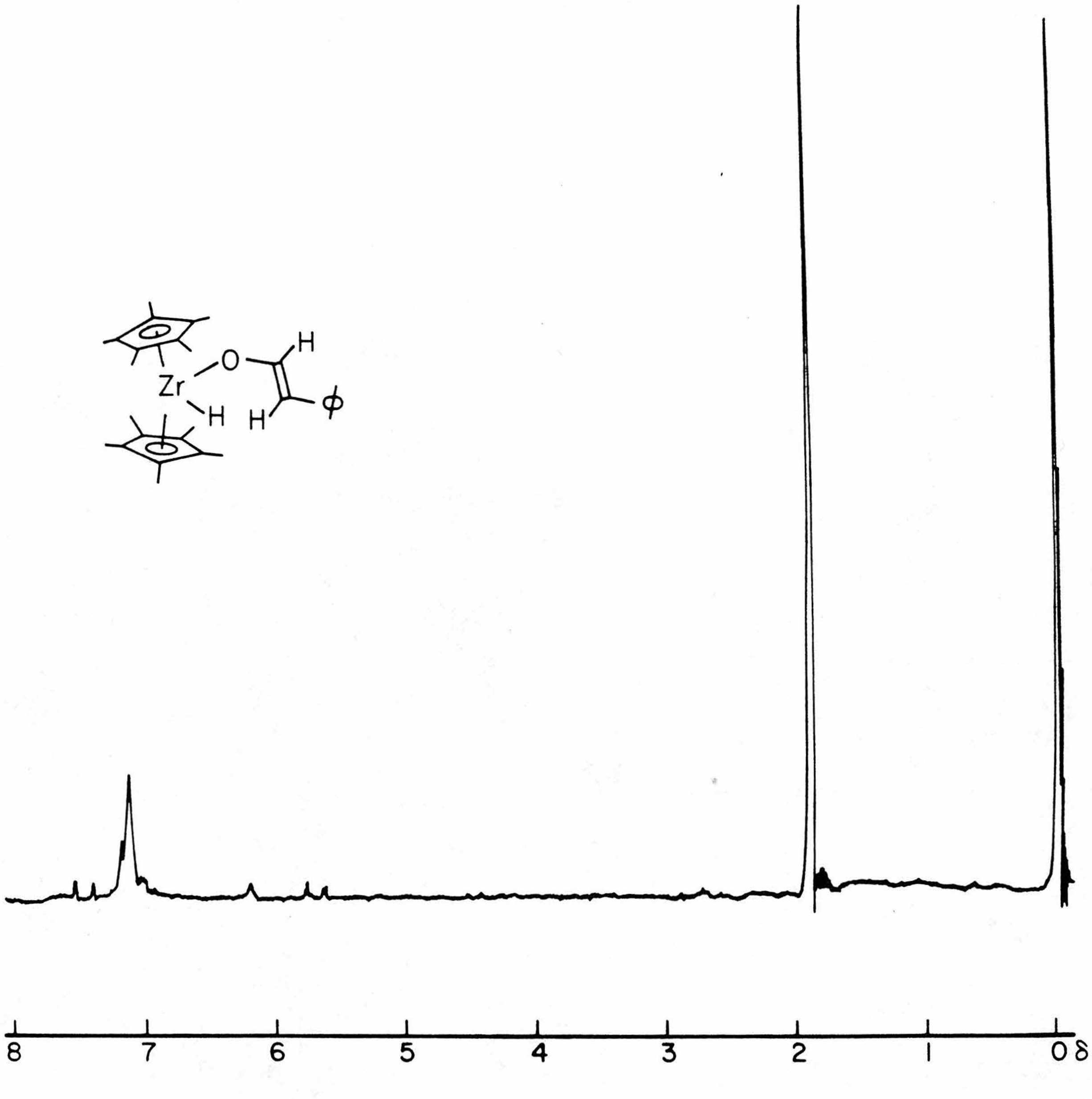
p-methoxy phenyl and -OZrH. In all cases, the enolate has trans geometry. The ligands include carbon monoxide, hydrogen, and tolane. The yield is greater than 95% by nmr when the promoting ligands are hydrogen or tolane. A secondary reaction occurs when CO is the promoting ligand. The initial products, Nb(H)CO and Zr(H)OCH=CHϕ react forming a new compound with an AB pattern for the olefin (still trans) and a new Cp resonance. Zr(H)OCH=CHϕ probably transfers hydride to Nb(H)CO, a reaction similar to ZrHCl hydride transfer to Nb(H)CO. The subsequent carbene insertion yields (CO)Nb$-$CH$_2$$-O-Zr-$OCH=CH$\phi$.



The best kinetic data are obtained from the tolane reactions. The products, $\underset{\phi - \equiv - \phi}{\text{Nb}}$$-$H and Zr(H)OCH=CHR are stable to reaction conditions.

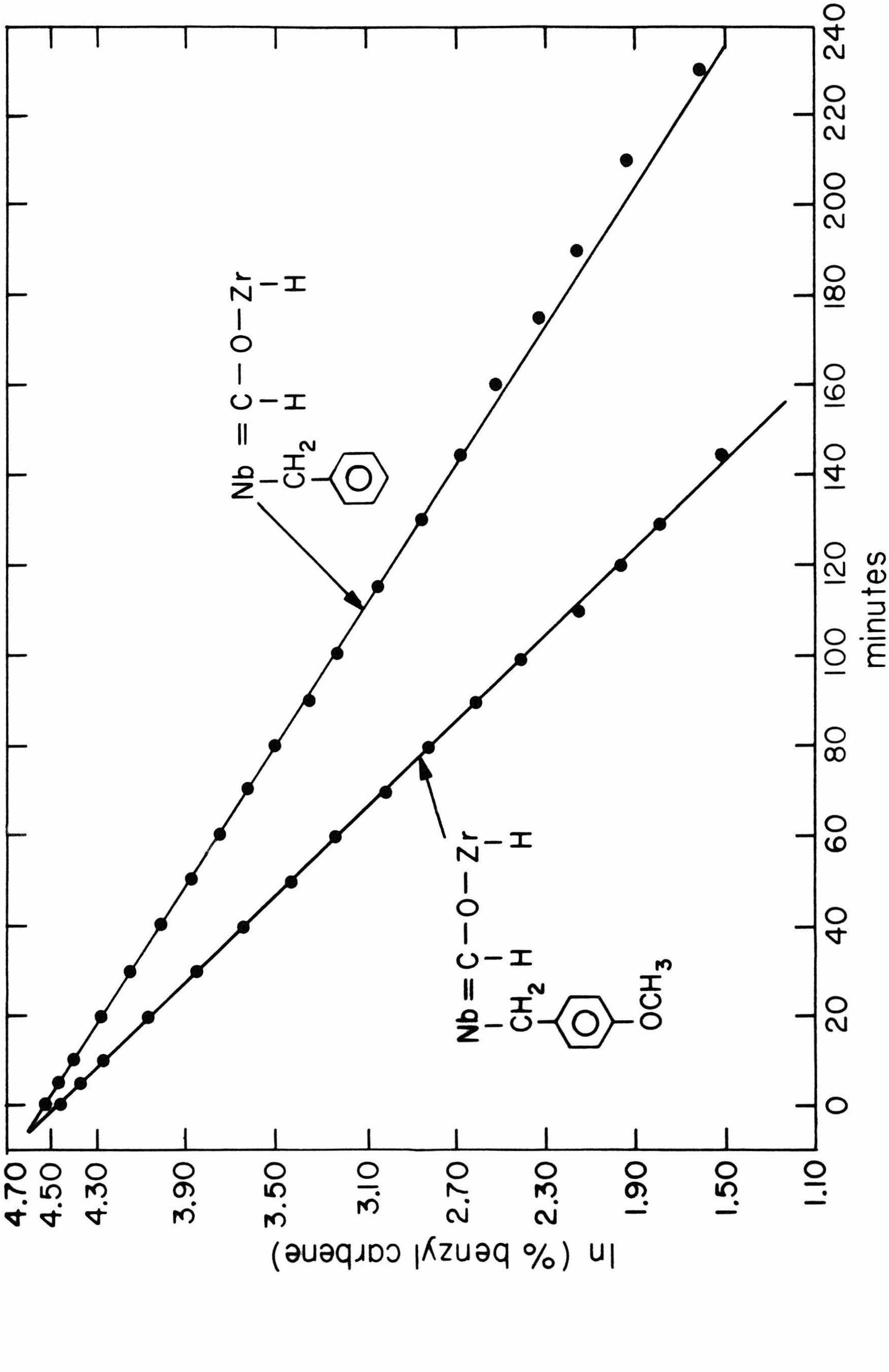
Table I

Compound	Rate (50°C)	Notes
 $\underset{CH_3}{\mathrm{Nb}} = \underset{H}{\mathrm{C}} - \mathrm{O} - \underset{H}{\mathrm{Zr}}$	$7.71 \times 10^{-4}\ \mathrm{sec}^{-1}$	Only 87%  was formed. The remaining 13% was not identified.
 $\underset{\underset{\phi}{CH_2}}{\mathrm{Nb}} = \underset{H}{\mathrm{C}} - \mathrm{O} - \underset{H}{\mathrm{Zr}}$	$2.09 \times 10^{-4}\ \mathrm{sec}^{-1}$	
 $\underset{\underset{\phi}{CH_2}}{\mathrm{Nb}} = \underset{D}{\mathrm{C}} - \mathrm{O} - \underset{D}{\mathrm{Zr}}$	$2.65 \times 10^{-4}\ \mathrm{sec}^{-1}$	No  is formed.
 $\underset{\underset{\phi}{CD_2}}{\mathrm{Nb}} = \underset{H}{\mathrm{C}} - \mathrm{O} - \underset{H}{\mathrm{Zr}}$	$1.79 \times 10^{-4}\ \mathrm{sec}^{-1}$	Only  is formed.
	$3.37 \times 10^{-4}\ \mathrm{sec}^{-1}$	
 $\underset{\underset{\mathrm{O-ZrH}}{CH_2}}{\mathrm{Nb}} = \underset{H}{\mathrm{C}} - \mathrm{O} - \underset{H}{\mathrm{Zr}}$	$3.33 \times 10^{-4}\ \mathrm{sec}^{-1}$	
 $\underset{\underset{\phi}{CH_2}}{\mathrm{Nb}} = \underset{H}{\mathrm{C}} - \mathrm{O} - \underset{I}{\mathrm{Zr}}$	$5.07 \times 10^{-5}\ \mathrm{sec}^{-1}$	Only 50%  was formed. The rate is disappearance of carbene Cp resonance.


Zr
O
H
H
H
φ
8
7
6
5
4
3
2
1
0 δ

A convenient rate is obtained at 50° C. By either visible spectroscopy or FT-nmr, the reaction rate is first order in alkyl-carbene for three to five half-lives. The rate is independent of tolane concentration. The rate constants for several alkyl migratory insertions are listed in Table I. The isotope effect for the deuterium-substituted benzylic carbene is 1.17. An inverse isotope effect is observed in the deuterium labeled carbene: $k_H/k_D = 0.79$. A ρ value for the benzylic migrations is -1.77.

The insertion rates for $\phi CH_2Nb{=}CH{-}O{-}ZrH$ and $CH_3Nb{=}CH{-}O{-}ZrH$ were monitored at several temperatures between 32.5° C and 80° C. The Arrhenius rate plots are shown in Figure 3. The activation parameters for the benzyl migration are $\Delta H^\ddagger = 25.3$ kcal/mole and $\Delta S^\ddagger = 2.7$ e.u. For the methyl migration, $\Delta H^\ddagger = 23.5$ kcal/mole and $\Delta S^\ddagger = 0.2$ e.u.


ln (% benzyl carbene)
4.70
4.50
4.30
3.90
3.50
3.10
2.70
2.30
1.90
1.50
1.10
minutes
0
20
40
60
80
100
120
140
160
180
200
220
240
Nb = C — O — Zr
CH2 H H
Nb = C — O — Zr
CH2 H H
OCH3

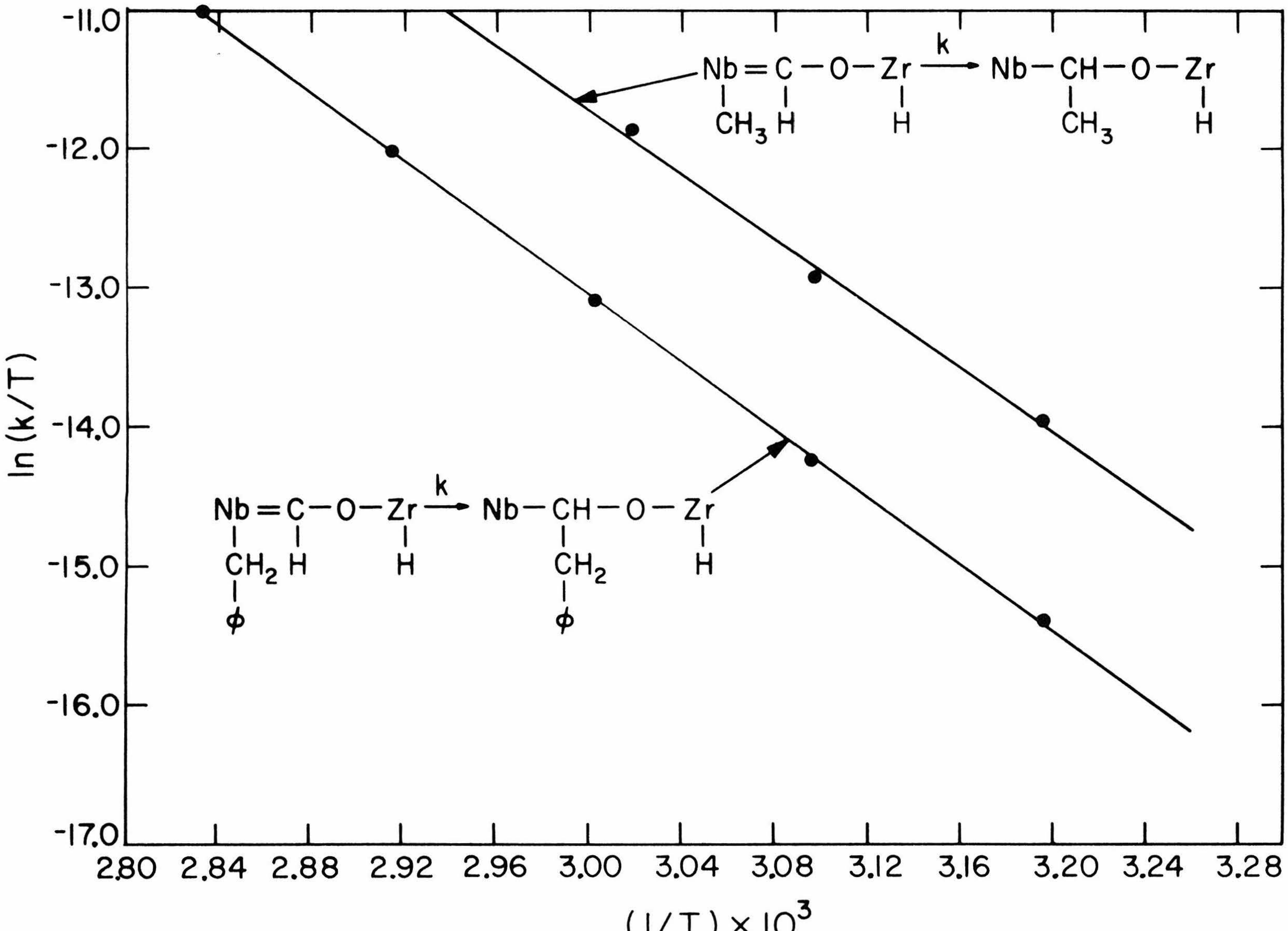
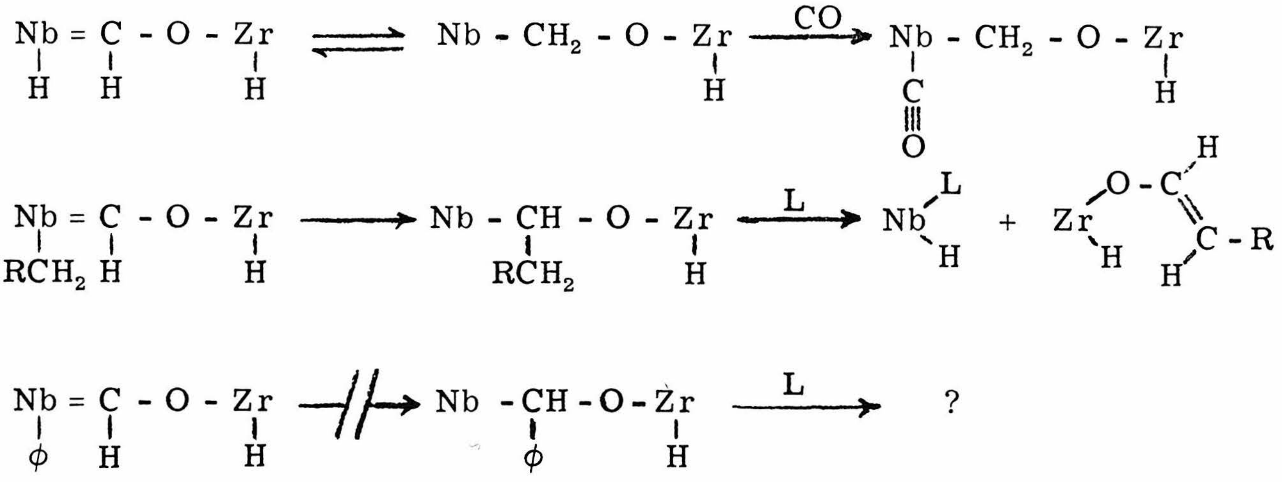

-11.0
-12.0
-13.0
-14.0
-15.0
-16.0
-17.0
ln (k/T)
2.80
2.84
2.88
2.92
2.96
3.00
3.04
3.08
3.12
3.16
3.20
3.24
3.28
(1/T) × 10^3
Nb=C(CH3)H−O−Zr(H) →k Nb−CH(CH3)−O−Zr(H)
Nb=C(CH2ϕ)H−O−Zr(H) →k Nb−CH(CH2ϕ)−O−Zr(H)

Figure 3

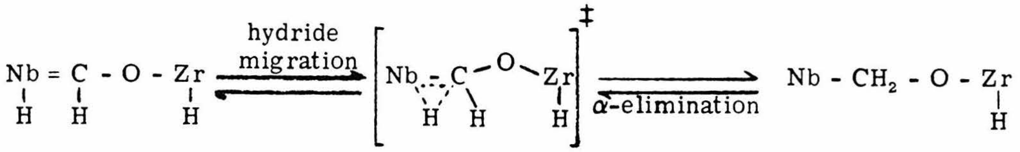
DISCUSSION

The facile formation of several substituted niobocene carbenes has enabled a systematic study of the carbene insertion reaction. In the most direct observation of the carbene insertion, HNb=CD–O–ZrD isomerizes to DNb=CH–O–ZrD at low temperature. Carbon monoxide traps the intermediate tautomer to form (CO)Nb–CH_2–O–ZrH. At higher temperatures, carbene insertion into the niobocene alkyl bond yields an intermediate which β-eliminates faster than ligand trapping. Only zirconoxy enolates are produced along with substituted niobocene hydrides. Saturation transfer experiments verify the rapid rate of hydride migration relative to alkyl migration. In the only case where β-hydrogens would not be present on the intermediate insertion product, no migration of phenyl to carbene is observed. The order of migratory aptitudes of niobocene substituents is hydride ≫ methyl > benzyl ≫ phenyl.



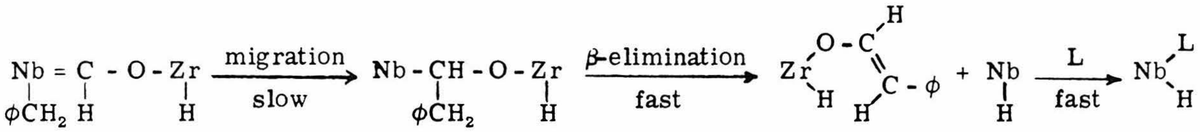
Considering the relative stabilities of the species involved in hydride migration there must be at least a two kcal energy difference between the tautomers. Nb–CH_2–O–ZrH is never observed by nmr although the tautomerization occurs radily at 25 ° C. There could be as much as a sixteen kcal difference between tautomers if the α-elimination has no activation energy. The hydride migration appears to be a one-step process, formally breaking the niobium-carbene π bond and the niobium hydride bond to form a carbon-hydrogen bond. The estimated bond strengths for the niobium carbene π bond and the niobium hydride bond are considerably more than the measured activation energy of thirteen kcals. A reasonable carbene π bond strength is eighteen kcals based on activation energies for carbene rotation in Ta(CHϕ)(CH$_2\phi$) and Nb(CHCMe$_3$)Cl.[18] A lower limit for theniobium hydride bond is sixty kcals based on some first-row metal hydride bond strengths.[19] The new carbon hydrogen bond of the methylene tautomer must be formed to a significant extent in the transition state to lower the energy requirement from 78 to sixteen kcals.

Scheme I



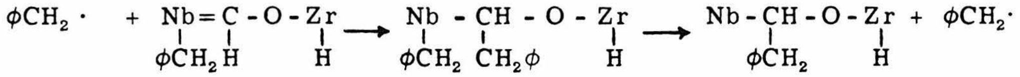
The mechanism of alkyl migration is masked because the migration product cannot be trapped with added ligands. Additional steps produce zirconoxy enolates. Scheme II shows the simplest

Scheme II



mechanism for the reaction. Ligand trapping of NbH must be faster than the rate limiting step because the rate law is independent of ligand concentration. β-Elimination cannot be rate determining since no intermediates are observed by nmr. A fast pre-equilibrium prior to rate limiting β-elimination is unlikely because this requires repeated carbon-carbon bond breakage and formation. By process of elimination alkyl migration is the slow step for the mechanism of scheme II. The observed inverse isotope effect for the deuterium substituted carbene insertion is consistent with rate limiting migratory-insertion. An inverse isotope effect indicates the carbene p-hybridization increases in the transition state.[20] Neither β-elimination nor ligand trapping satisfy this criterion.

Another mechanism which satisfies some of the above conditions is the addition of benzyl radical to the carbene followed by niobium benzyl bond cleavage. This alternative seems possible considering the



$$\phi CH_2\cdot + \underset{\phi CH_2}{Nb}=\underset{H}{C}-O-\underset{H}{Zr} \longrightarrow \underset{\phi CH_2}{Nb}-\underset{CH_2\phi}{CH}-O-\underset{H}{Zr} \longrightarrow Nb-\underset{\phi CH_2}{CH}-O-\underset{H}{Zr} + \phi CH_2\cdot$$

25 kcal activation energy relative to a cobalt benzyl bond strength of 19 kcals.[21] However, a crossover experiment indicates no niobium benzyl bond homolysis occurs during the reaction. A mixture of $\phi CD_2Nb=CH-O-ZrH$ and $\phi CH_2Nb=CD-O-ZrD$ produce no $Zr(H)OCH=CH\phi$.

The primary thermodynamic difference between the alkyl migration and the hydride migration is the relative strengths of the reacting bonds. The bond energy difference for hydride migration

$$\underset{H}{Nb}=\underset{H}{C}-O-\underset{H}{Zr} \longrightarrow Nb-\underset{H}{CH}-O-\underset{H}{Zr}$$

Niobium hydride bond broken
Carbon hydrogen bond formed

$$\underset{CH_3}{Nb}=\underset{H}{C}-O-\underset{H}{Zr} \longrightarrow Nb-\underset{CH_3}{CH}-O-\underset{H}{Zr}$$

Niobium alkyl bond broken
Carbon carbon bond formed

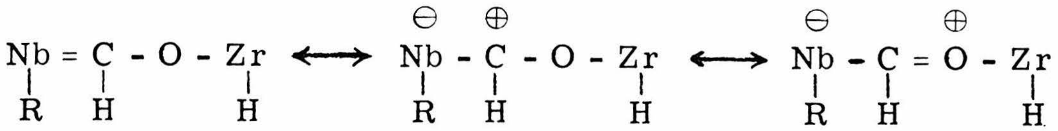
equals -35 kcal: sixty kcals for the niobium hydride bond broken minus 95 kcals for the carbon hydrogen bond formed. The bond energy difference for alkyl migration is -45 kcal: 35 kcal for the niobium alkyl bond broken minus 80 kcals for the carbon-carbon bond formed. First-row transition metal alkyls are roughly 25 kcals weaker than the corresponding hydrides. Though these bonds may be stronger for second-row transition metals, the differences are probably the same. These bond energy differences must be revised to obtain heats of reaction. Other contributions to the overall energy include carbene π bonds broken during migration as well as energy changes of carbon oxygen and carbon hydrogen bonds as a result of rehybridization.[22] However, these factors are probably equal for each migration so that the net difference is ten kcals. This reacting bond energy difference implies alkyl migration is less endothermic than hydride migration.

These ground state thermodynamic effects fail to explain the series of migratory aptitudes: hydrogen $\gg$ methyl $>$ benzyl $\gg$ phenyl. The most endothermic migration is the fastest. If the mechanisms are similar, the relative migratory aptitudes must be a reflection of some ligand property which affects the three-center transition state. Indeed, alkyl migrations appear to be concerted three-center reactions analogous to the hydride migration. The 53 kcal sum of the niobium π bond plus the niobium alkyl bond is much more than the measured 25 kcal activation energy.

The trend of migratory aptitudes is significantly different for carbene insertions compared to carbonyl insertions. Hydride migration to CO has never been directly observed,[23] although the relative rates of methyl versus benzyl migration are nearly the same for CO and oxycarbenes.[24] From what little is known about isonitrile migratory insertions, hydrides and alkyls migrate at more comparable rates.[25]

The presence of substituents on the carbene (zirconoxy) and isonitrile (methyl of phenyl) increase the electrophilic character of the inserting groups and enhance their rate of migratory insertion. $Nb(CH_3)CO$ does not undergo migratory insertion,[26] whereas the carbene-methyl, $(CH_3)Nb{=}CH{-}O{-}ZrH$, readily inserts. A similar effect rationalizes the lewis acid promotion of CO insertions.[27] The failure of a variety of nucleophilic carbenes, $Ta(CHR)CH_2R$, to insert[28] supports the notion of the electrophilic nature of carbene migratory insertions.

The electrophilic reactivity of an oxycarbene could explain the trend of migratory aptitudes. The resonance structures of oxycarbenes display interactions stabilizing the positively charged carbene carbon.



$$\underset{R}{Nb} = \underset{H}{C} - O - \underset{H}{Zr} \longleftrightarrow \underset{R}{\overset{\ominus}{Nb}} - \underset{H}{\overset{\oplus}{C}} - O - \underset{H}{Zr} \longleftrightarrow \underset{R}{\overset{\ominus}{Nb}} - \underset{H}{C} = \overset{\oplus}{O} - \underset{H}{Zr}$$

If the migrating group moves with its pair of electrons to the electrophilic carbene analogous to CO insertions,[29] electron donating groups should migrate easier. The negative ρ value measured for benzyl migrations is consistent with this supposition. Electronegativity is perhaps a more general measure of the electron donating ability of a migrating group. Less electronegative groups are more electron donating. The order of electronegativity increases in the order: hydrogen, methyl, benzyl, phenyl.[30] The trend of migratory aptitudes to the zirconoxy carbene correlates with this series of group electronegativities.

The carbene migratory insertion is structurally similar to several organic rearrangements. In the Wagner-Meerwien and Pinacol rearrangements, a migrating group moves to an adjacent positively charged carbon.[31] Migratory aptitudes in these reactions are usually hydrogen > aryl > alkyl,[32] The degree of s-character in the bond of the migrating atom correlates with the general order of migrating groups. This correlation is usually rationalized on the basis of the orbital overlap of the migrating group to the molecular framework of the transition state. In general, hydrogen bonds are stronger than aryl bonds which are stronger than alkyl bonds. Presumably, the transition state is stabilized the most by the stronger hydrogen bond.

Electronegativity and hybridization seem to be interrelated factors determining the stability of the transition state. Electron donating groups cannot stabilize the transition state if there is no overlap with the migrating group. Good overlap of a strongly electron-withdrawing group to the electrophilic carbene destabilizes the transition state. These considerations probably apply to most electrophilic insertion reactions. In this vein, one expects similar trends for carbonyl insertions across the transition metals compared to carbene insertions. Carbonyl insertion into transition metal hydrides are unprecedented, although ZrH_2CO appears to react by carbonyl insertion into the hydride.[33] The most hydridic of the transition metal hydrides, zirconium hydride is most likely to migrate to CO. Presumably, the hydridic niobium hydride[34] also shows a greater tendency to migrate to carbenes than later transition metal hydrides. For the acidic hydrides of group VIII, one would expect slower carbene-hydride migratory insertions, at least relative to alkyl migrations. Hopefully, the rate correlation of migratory insertion to the electronegativity of the migrating group will be clarified by studies of some iron oxycarbene insertions.

EXPERIMENTAL

All manipulations were performed in an inert atmosphere using a glove box or vacuum techniques. Ether solvents such as glyme and THF were distilled from sodium benzophenone ketyl. All other solvents including nmr solvents were purified by distillation from titanocene.[35] Hydrogen, argon and nitrogen were passed through MnO on vermiculite[36] and 4 Å molecular sieves. Carbon monoxide (MCB) was used without purification. Tolane was recrystallized from octane. ZrH_2 and $NbCl_2$[37] were prepared by literature methods. ZrHF was prepared from ZrH_2 and ZrF_2 analogous to ZrHCl.[38]

^1H nmr spectra were obtained using a Varian EM 390 and a JEOL FX90Q spectrometers. ^{13}C nmr were also measured on the JEOL. Infrared spectra were recorded on a Beckman 4240 spectrophotometer. Esr spectra were obtained on an X-band Varian E-line Century Series spectrometer. Visible spectra were observed using a Cary 14 spectrophotometer. Cyclic voltamograms were conducted on a PAR 174A Polarographic analyzer. Coulometry was analyzed on a PAR Potentiostat 173.

1) Preparation of $Nb(CH_3)CO$

2.0 Grams of NbClCO (7.0 mmoles) was suspended in 140 mls of warm toluene. 2.0 Mls of 3.2 M methyl magnesium bromide (6.4 mm was added in the following manner. Ten percent was added at once followed by the slow addition over a period of fifteen minutes. The toluene was then immediately removed by vacuum transfer. Several pentane extractions followed by treatment with methyl iodide yielded a green solid after solvent removal. The green residue was extracted with pentane to separate $Nb(CH_3)CO$ from NbICO. Sublimation yielded 0.8 gram of $Nb(CH_3)CO$, 43% yield.

2) Preparation of $Nb(\phi)CO$.

2.0 Grams of $NbCl_2$ (6.8 mmoles) was reacted with 2.1 mls of 3.2 M phenyl magnesium bromide (6.7 mmoles) in THF at 25° C. After eight hours, all the $NbCl_2$ had dissolved and the brown solution had considerable white precipitate. All solvent was removed by vacuum transfer and 70 mls of toluene added. A warm filtration followed by solvent removal left green-brown crystals of presumably $Nb(\phi)Cl$. After redissolving in toluene and cooling to -80° C, four mls of one percent Na/Hg was added via syringe. All gas was removed and the reaction mixture was stirred at 25° C under one atmosphere of CO for eight hours. The resulting green solution was decanted from the amalgam and filtered prior to solvent removal. The green solid was sublimed at 120° C to yield 0.9 gram of $Nb(\phi)CO$, 40 percent based on $NbCl_2$.

3) Preparation and Characterization of $Nb(CH_2C_6H_4X)_2$, X = H and OCH_3

2.0 Grams of $NbCl_2$ (6.8 mmoles) was suspended in 100 mls of THF. 17 Mls of 0.92 M benzyl magnesium chloride (15.6 mmoles) was added and the reaction stirred for six hours. The resultant purple solution was quenched of excess grignard with one ml of deoxygenated methanol. All solvent was immediately removed by vacuum transfer. 100 Mls of benzene was added to the mixture and warmed to 40° to dissolve the product. The solution was filtered and the benzene volume reduced to 25 mls. The resultant purple crystals were redissolved by warming before cooling to yield 2.4 grams of Nb($CH_2\phi$)$_2$. A further recrystallization from toluene separated more impurity from the compound. Final yield was 2.0 grams of dibenzyl niobocene. The same methodology yielded Nb($CH_2C_6H_4OCH_3$)$_2$ in a similar yield. The esr of these compounds displayed a ten-line spectra with g values of 2.01 for both Nb($CH_2C_6H_5$) and Nb($CH_2C_6H_4OCH_3$)$_2$. Cyclic voltamograms of the dibenzyl compounds were conducted in THF with 0.1 M tetrabutyl ammonium tetrafluoroborate. The reference potential was Ag/Ag^+ (0.01 M in CH_3CN). Peak to peak separations were 90 mV at 200 mV/sec scan rate. These were considered reversible based on the identical peak to peak separation of added ferrocene at +0.2 V.[39] The redox potentials for Nb($CH_2C_6H_5$)$_2$ were -2.02 volts for reduction and -0.62 volt for oxidation relative to Ag/Ag^+. For Nb($CH_2C_6H_4OCH_3$)$_2$ the potentials were -2.12 V reducing and -0.79 V oxidizing. Coulometry consumed 1.01 electrons per equivalent for the reaction of Nb($CH_2C_6H_5$)$_2$.

4) Preparation of Nb($CH_2\phi$)CO

810 Mgs of Nb($CH_2\phi$)$_2$ (2 mmoles) are dissolved in 200 mls of THF. Four mls of one percent Na/Hg was added and stirred for two hours when the solution was dark brown. The solution of dibenzyl anion was separated from the amalgam by decantation and filtration. A solution of 0.14 mls of CF_3CH_2OH in twenty mls of THF was added slowly over a period of twelve hours to the anion solution under one atmosphere of CO. The solvent was removed. The benzyl carbonyl was extracted fromthe brown residue with 70 mls of warm octane. A green powder was isolated which was washed with cold pentane.

375 Mgs of Nb(CH$_2\phi$)CO were obtained from the sublimation of green powder at 90° C: 5 percent yield.

5) Preparation of RNb=CH–O–ZrH; General Syntheses

1.0 Grams of NbHCO (4 mmoles) and 1.6 grams of ZrH$_2$ were reacted in thirty mls of toluene. This orange solution was filtered and toluene removed by vacuum transfer. The orange residue was suspended in pentane and filtered to yield 2.2 grams of HNb=CH–O–ZrH: 90 percent yield.

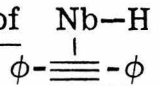
5) Preparation of RNb=CH–O–ZrH; General Syntheses

1.0 Grams of NbHCO (4 mmoles) and 1.6 grams of ZrH$_2$ were reacted in thirty mls of toluene. This orange solution was filtered and toluene removed by vacuum transfer. The orange residue was suspended in pentane and filtered to yield 2.2 grams of HNb=CH–O–ZrH: 90 percent yield. All carbenes were prepared in this manner and stored at -20° C.

6) Preparation of (CO)Nb–CH$_2$–O–ZrH

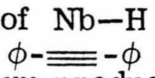
1.0 Gr (1.62 mmole) of NHb=CH–O–ZrH was reacted in 35 mls of toluene with one atmosphere of CO for eight hours at 45° C. After cooling and filtration, the volume was reduced to about eight mls. The green precipitate was recrystallized and washed with pentane. 825 Mgs of (CO)Nb–CH$_2$–O–ZrH was isolated for a 80 percent yield.

7) Preparation of



$$\begin{array}{c}\mathrm{Nb{-}H}\\ |\\ \phi{-}\equiv{-}\phi\end{array}$$

300 Mgs of NbH$_3$[34] (1.33 mmoles) and 230 mgs of tolane (1.3 mmole) were heated to 65° C in toluene for two hours. The reaction was cooled to 35° C, then filtered. Solvent removal resulted in a

brown oil. A yellow powder results from the repeated addition and removal of pentane by vacuum transfer. This powder was recrystallized from 40 mls of octane, yielding 400 mgs of  $\underset{\phi-\equiv-\phi}{\text{Nb—H}}$ in 75% yield. The ^{1}H nmr spectrum is identidcal to the niobium product of the alkyl carbene migratory insertions.

8) Preparation of Zr(H)OCH=CHϕ(trans)

700 Mgs of ϕCH$_2$Nb=CH–O–ZrH (1 mmole) and 175 mgs of tolane (1 mmole) were reacted in toluene at 25° C for two days. Toluene was removed by vacuum transfer. Several pentane addition-removal cycles yielded a tractable powder. Most of the zirconium enolate was extracted by filtration of a 15 ml pentane solution at 0° C. The resultant yellow solution was reduced to three mls and cooled to -80° C to form colorless crystalline product. Cold filtration yielded 300 mgs of Zr(H)OCH=CHϕ in 62 percent yield.

A mixture of the cis and trans-zirconium phenyl enolates was prepared by reacting NaOCH=CHϕ with ZrHCl. 80 Mgs of NaH was suspended in 80 mls of THF. 0.35 Mls of phenyl acetaldehyde was added at -30° C and reacted for eight hours at 25° C. This solution was filtered onto 800 mgs of ZrHCl and stirred four hours. The THF was removed and replaced with pentane. A yellow powder was isolated after filtration whose nmr showed both the cis and trans-enolate hydrides.

9) Kinetics of the hydride migration mediated by CO

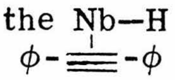
A typical experiment involved 40 mgs of HNb=CH–O–ZrH dissolved in 40 mls of benzene (16.2 mmolar) in a ten mm quartz cell with a 50 ml total volume. The reaction was run at 22° C under a measured CO pressure. The visible spectrum was recorded periodically as the reaction proceeded. The reaction was stirred between recordings but little rate deviation occurred without stirring. Plots of $\ln(A_\infty\text{-}A)$ at 600 nm versus time were linear for three half lives. Rate plots of CO pressure indicated first order CO dependence.

10) Kinetics of hydrogen exchange using saturation transfer

The pulsing technique employed is described by Freeman.[40] The relaxation times for the protons of HNb=CH–O–ZrH were measured using the inversion recovery program of the JEOL FX90Q.[41] Saturation transfer spectra were obtained using a pulse sequence program written by Perkins.[42] It involves the timing for saturating a specific resonance and delaying the observation pulse a specified interval. A three parameter non-linear least squares fit[43] of the data to the magnetization equation was performed on a Commodore Pet computer.

11) Kinetic measurements of alkyl migrations

The rates of alkyl migrations were followed by FT-nmr. Less than 45 degree observation pulses were used. Repetition rates were greater than twice the relaxation times of the niobium resonances. Reaction temperatures were maintained by the probe temperature controller and observed to be constant to within one degree by the peak separations of ethylene glycol.[44] A typical reaction involved 30 mgs of $\phi CH_2Nb{=}CH{-}O{-}ZrH$ (42.4 μmoles) and 30 mgs of tolane (168 μmoles) dissolved in 0.45 mls of d_6 benzene. As the reaction proceeded, the niobium carbene Cp resonance lost intensity as the $\underset{\phi-\equiv-\phi}{\underset{|}{\mathrm{Nb}}}\text{—H}$ Cp signal appeared. The plot of the carbene Cp decay

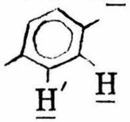


showed first-order behavior for better than three half lives. The rate for benzyl migration was independent of tolane concentration over a fifty-fold range. Most migration rates were studied with only a three-fold excess of tolane yet showed first-order carbene decay kinetics for at least three half lives.

12) Benzyl migration crossover experiment

25 Mgs each of $\phi CD_2Nb{=}CH{-}O{-}ZrH$ and $\phi CH_2Nb{=}CD{-}O{-}ZrD$ were reacted with 30 mgs of tolane in d_6 benzene. The reaction was monitored by nmr. The olefinic proton at 5.73 δ appears as a singlet for $Zr(H)OCH{=}CD\phi$. No doublet is observed for $Zr(H)OCH{=}CH\phi$.

Compound	Solvent	Group		Chemical Shift	
$(C_5H_5)_2Nb(H){=}CH{-}O{-}Zr(H)(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	5.01	
		$C_5\underline{H}_5$	s	5.02	
Anal. Calcd. %C, 60.46; %H, 7.04		Nb-$\underline{H}$	s	-3.14	
Found, %C, 58.76; %H, 6.80		$=C\underline{H}$-O-	s	11.63	
		Zr$\underline{H}$	s	5.70	
		$C_5(C\underline{H}_3)_5$	s	1.99	
$(C_5H_5)_2Nb(CH_3){=}CH{-}O{-}Zr(H)(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	4.97	
		$C_5\underline{H}'_5$	s	5.01	
Anal. Calcd. %C, 61.02; %H, 7.20; %Zr, 14.48;		Nb-$C\underline{H}_3$	s	?	
Found: %C, 60.85; %H, 7.10; %Zr, 14.21.		$=C\underline{H}$-O-	s	11.72	
		Zr-$\underline{H}$	s	5.90	
		$C_5(C\underline{H}_3)_5$	s	1.95	
		$C_5(C\underline{H}_3)_5$	s	1.97	
$(C_5H_5)_2Nb(CH_2\phi){=}CH{-}O{-}Zr(H)(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	4.98	
		$C_5\underline{H}'_5$	s	4.96	
Anal. Calcd. %C, 64.65; %H, 7.00; %Zr, 12.92; %Nb, 13.16;		Nb-$C\underline{H}_2$-ϕ	d	2.73	$J_{HH'} = 11$ Hz

Compound	Solvent	Group		Chemical Shift	
Found: %C, 61.64; %H, 6.56; %Zr, 12.48; %Nb, 12.85.	d_6 benzene	$=C\underline{H}-O-$	s	11.87	
		$Zr-\underline{H}$	s	6.05	
		$C_5(C\underline{H}_3)_5$	s	1.96	
		$C_5(C\underline{H}_3)_5$	s	2.03	
		$C_6\underline{H}_5$	m	7.28	
$(C_5H_5)_2Nb(CH_2\phi)=CD-O-Zr(D)(C_5(CD_3)_5)_2$		$C_5\underline{H}_5$	s	4.98	
		$C_5\underline{H}'_5$	s	4.96	
		$Nb-C\underline{H}H-\phi$	d	2.73	J_{HH} = 11 Hz
		$Nb-CH\underline{H}-\phi$	d	1.99	
		$C_6\underline{H}_5$	m	7.28	
$(C_5H_5)_2Nb(CH_2C_6H_4OCH_3)=CH-O-Zr(H)(C_5Me_5)_2$		$C_5\underline{H}_5$	s	4.99	
Anal. Calcd: %C, 63.65; %H, 6.98:		$Nb-C\underline{H}_2-$	d	2.68	J_{HH} = 11 Hz
Found: %C, 61.53; %H, 6.81;		$Nb=C\underline{H}-O-$	s	11.76	
			d	6.87	J_{HH} = 8 Hz
			d	7.70	
		$OC\underline{H}_3$	s	3.45	
		$Zr-\underline{H}$	s	6.02	
		$C_5(C\underline{H}_3)_5$	s	1.93, 2.02	

Compound	Solvent	Group		Chemical Shift
$(C_5H_5)_2Nb(C_6H_5)$=CH-O-Zr(H)$(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	5.14
		$C_5\underline{H}'_5$	s	5.23
		Nb-$C_6\underline{H}_5$	m	7.2
		Nb=C$\underline{H}$-O-	s	12.23
		Zr-$\underline{H}$	s	6.90
		$C_5(C\underline{H}_3)_5$	s	2.01
$(C_5H_5)_2Nb(CH_2OZr(H)(C_5Me_5)_2)$=CH-OZr(H)$(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_6$	s	5.12
Anal. Calcd: %C, 61.99; %H, 7.50; %Zr, 18.11;		$C_5\underline{H}'_5$	s	5.33
Found: %C, 61.85; %H, 7.39; %Zr, 18.33.		Nb-$C\underline{H}_2$-O	s	5.93
		Zr$\underline{H}$	s	6.10
		Zr$\underline{H}'$	s	6.65
		$C_5(C\underline{H}_3)_5$	s	1.94
			s	1.99
			s	2.04
			s	2.10

Compound	Solvent	Group		Chemical Shift	
$(C_5H_5)_2Nb(CH_2C_6H_5)=CH-O-Zr(I)(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	4.97	
		$C_5\underline{H}_5$	s	5.06	
		$Nb-C\underline{H}_2-$	d	2.65	J_{HH} = 10 Hz
		$-CH_2-C_6\underline{H}_5$	m	7.23	
		$Nb=C\underline{H}-O-$	s	11.30	
		$C_5(C\underline{H}_3)_5$	s	1.90	
		$C_5(C\underline{H}_3)_5$	s	1.97	
$(C_5H_5)_2Nb(CH_2C_6H_5)CO$	d_6 benzene	$C_5\underline{H}_5$	s	4.39	
Anal. Calcd: %C, 63.17; %H, 5.01; %Nb, 27.15;		$Nb-C\underline{H}_2-$	s	1.82	
Found: %C, 63.04; %H, 5.15; %Nb, 27.00.		$CH_2-C_6\underline{H}_5$	m	7.23	
$(C_5H_5)_2Nb(CH_2C_6H_4OCH_3)CO$	d_6 benzene	$C_5\underline{H}_5$	s	4.40	
		$Nb-C\underline{H}_2-$	s	1.84	
		$CH_2-C_6\underline{H}_4-O$	d	6.88	J_{HH} = 8 Hz
			d	7.17	
		$OC\underline{H}_3$	s	3.45	

Compound	Solvent	Group		Chemical Shift
$(C_5H_5)_2Nb(C_6H_5)CO$	d_6 benzene	$C_5\underline{H}_5$	s	4.53
		$C_6\underline{H}_5$	m	7.05, 7.70
$(C_5H_5)_2Nb(CO)CH_2OZr(H)(C_5Me_5)_2$	d_6 benzene	$C_5\underline{H}_5$	s	4.68
Anal. Cald: %C, 59.70; %H, 6.58; %Zr, 14.17		Nb-C$\underline{H}_2$-O-	s	5.20
Found: %C, 59.36; %H, 6.94; %Zr, 14.33		Zr$\underline{H}$	s	5.20
		$C_5(C\underline{H}_3)_5$	s	2.00
$(C_5H_5)_2Nb(H)(C_6H_5)_2C_2$	d_6 benzene	$C_5\underline{H}_5$	s	4.85
Anal. Calcd: %C, 71.64; %H, 5.26; %Nb, 23.09;		Nb-$\underline{H}$	s	-0.28
Found: %C, 71.67; %H, 5.37, %Nb, 23.05.		$-C_6\underline{H}_5$	m	7.5
$(C_5Me_5)_2Zr(H)OCH{=}CH\phi$ trans	d_6 benzene	$C_5(C\underline{H}_3)_5$	s	1.93
Anal. Calcd: %C, 69.80; %H, 7.95;		Zr$\underline{H}$	s	6.23
Found: %C, 70.80; %H, 7.55.		-O-C$\underline{H}$=	d	5.73
		=C$\underline{H}\phi$	d	7.52
		$-C_6\underline{H}_5$	m	7.08

Compound		Solvent	Group		Chemical Shift	
$(C_5Me_5)_2Zr(H)OCH{=}CH\phi$	cis	d_6 benzene	$C_5(C\underline{H}_3)_5$	s	1.88	
			$Zr\underline{H}$	s	6.43	
			$-OC\underline{H}=$	d	6.69	$J_{HH'} = 7$ Hz
			$=C\underline{H}\phi$	d	5.10	
			$-C_6\underline{H}_5$	m	7.08	
$(C_5Me_5)_2Zr(H)OCH{=}CH_2$		d_6 benzene	$C_5(C\underline{H}_3)_5$	s	1.92	
			$Zr\underline{H}$	s	6.10	
			$O-C\underline{H}=$	dd	6.77	
			$=CH_2$ t	d	4.10	$J_{HH'} = 17$ Hz
			$=CH_2$ c	d	3.89	$J_{HH'} = 5$ Hz

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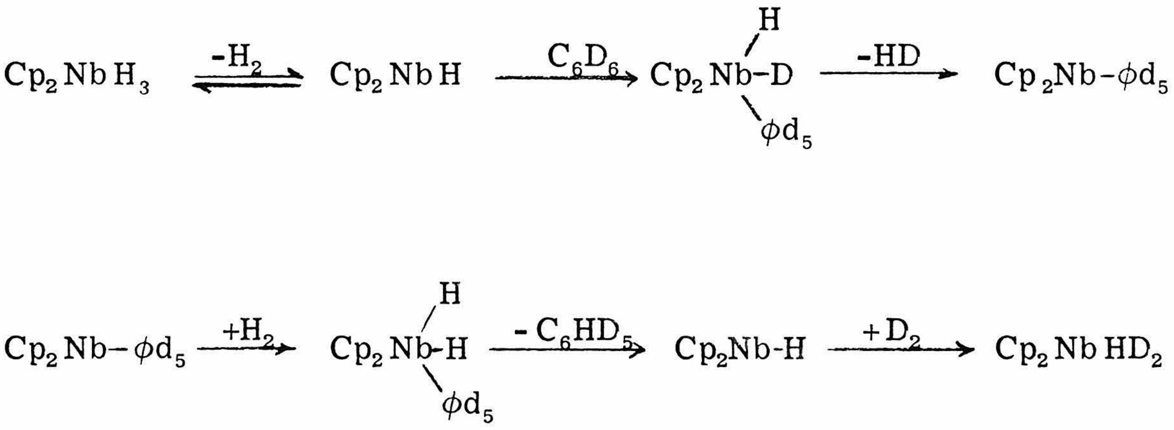
Chapter 3

Synthesis of Bis-Pentamethylcyclopentadienyl Niobocene Compounds

INTRODUCTION

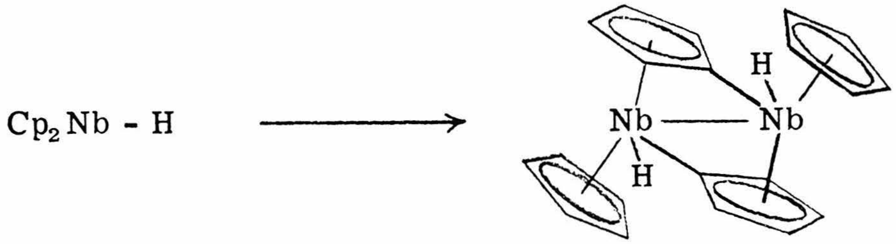
The organometallic chemistry of niobium has only recently been investigated. For reasons of stability and availability, most research has been directed toward an understanding of the niobocene moiety. These niobium complexes have displayed rich and diverse chemistry.[1-3, 5-9] Niobocene trihydride, Cp_2NbH_3, catalyzes exchange of molecular hydrogen with d_6-benzene.[1] The absence of pairwise exchange led Parshall to propose a mechanism involving reversible



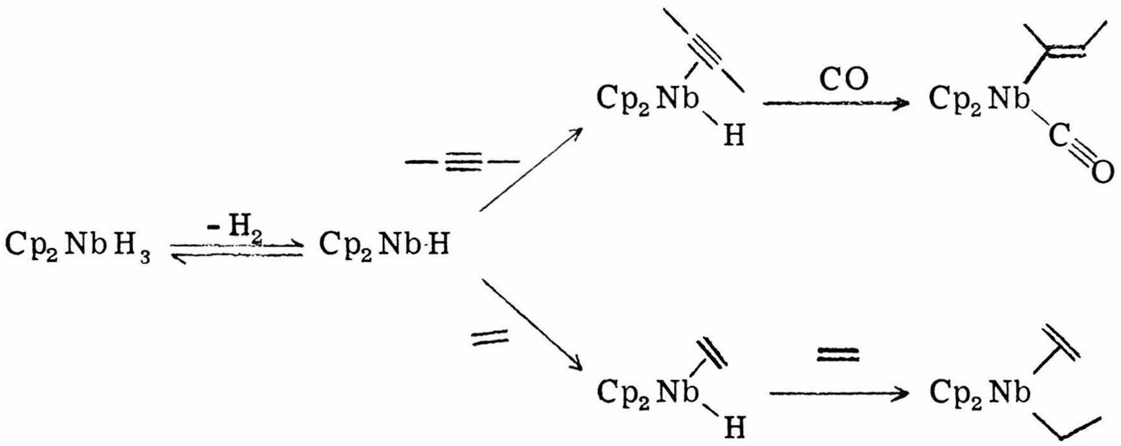
$$Cp_2NbH_3 \overset{-H_2}{\rightleftharpoons} Cp_2NbH \xrightarrow{C_6D_6} Cp_2\underset{\phi d_5}{\overset{H}{Nb}}\text{-}D \xrightarrow{-HD} Cp_2Nb\text{-}\phi d_5$$

$$Cp_2Nb\text{-}\phi d_5 \xrightarrow{+H_2} Cp_2\underset{\phi d_5}{\overset{H}{Nb}}\text{-}H \xrightarrow{-C_6HD_5} Cp_2Nb\text{-}H \xrightarrow{+D_2} Cp_2NbHD_2$$

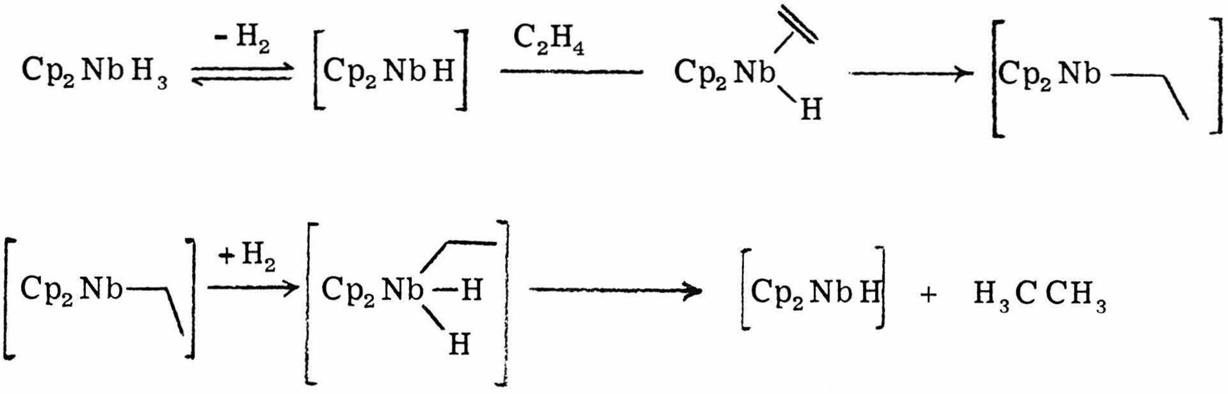
oxidative addition of an aryl hydrogen bond to coordinatively unsaturated niobocene hydride.[2] The very reactive niobocene hydride is generated by reductive elimination of H_2 from the trihydride. In the absence of added ligands, this compound appears to react with its own carbon hydrogen bonds to form niobocene dimer,[3] somewhat analogous to titanocene chemistry.[4] With added ligands, niobocene hydride is trapped and several interesting products have been isolated by this



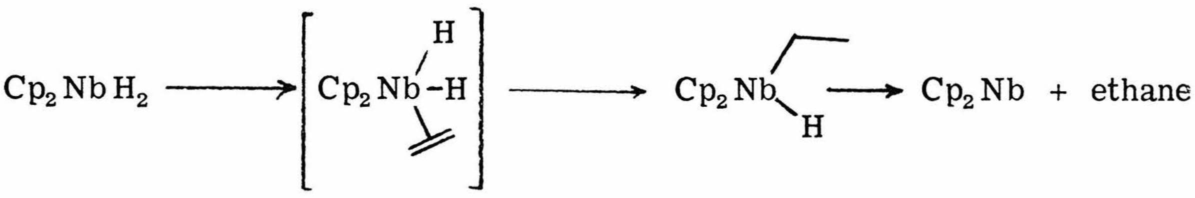
procedure. Carbon monoxide traps niobocene hydride to form $Cp_2Nb(H)CO$.[2] Both acetylenes and olefins react with Cp_2NbH_3 to yield acetylene[5] and olefin[6] hydride complexes. These rarely observed complexes readily undergo migratory insertion to form vinyl and alkyl



complexes. Similar chemistry has been observed for the tantalum analogs of these compounds. The trihydrides are also hydrogenation catalysts for olefins. In view of the observed sequence of events leading from Cp_2NbH_3 to $Cp_2Nb(L)C_2H_5$ in the reaction with ethylene, the mechanism shown below was proposed for hydrogenation.



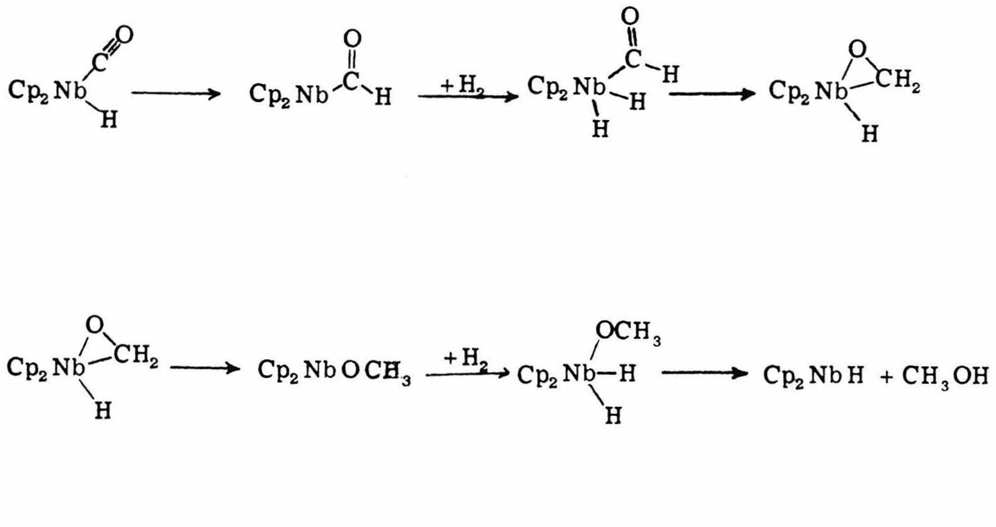
Another possibility was proposed by Kochi who observed the rapid low temperature reaction of Cp_2NbH_2 with olefins.[7] Cp_2NbH_2 was prepared by hydrogen atom abstraction from Cp_2NbH_3 with t-butyl peroxide.[8] Esr signals consistent with Cp_2NbH_2, $Cp_2Nb(H)C_2H_5$ and Cp_2Nb were observed consecutively suggesting a hydrogenation mechanism involving



paramagnetic species. In fact, there appears to be an equilibrium involving Cp_2NbH_3 and Cp_2NbH_2.[9] (Vide infra.)

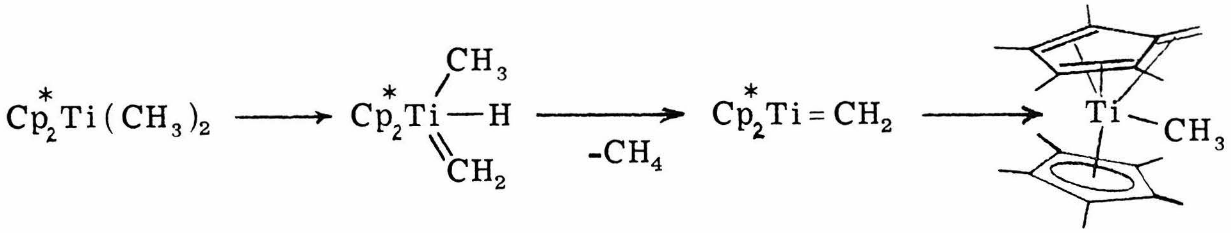
$$Cp_2NbH_3 \underset{+H_2}{\overset{-H_2}{\rightleftarrows}} Cp_2NbH \xrightarrow{Cp_2NbH_3} 2\ Cp_2NbH_2$$

It is clear that oxidation states of two through five are common in niobocene chemistry. Several of the intermediates of the above reactions are interesting molecules which could not be isolated due to irreversible reactions involving the carbon hydrogen bonds of the cyclopentadienyl ligands. It was hoped that substitution of pentamethyl cyclopentadiene would alleviate this problem and facilitate isolation of coordinatively unsaturated complexes.[10] Additionally, we hoped niobium would mimic some of the carbon monoxide chemistry observed with zirconium.[11] Perhaps the expected weaker niobium oxygen bonds would permit reductive elimination of methanol and enable catalytic carbon monoxide reduction with hydrogen.



By and large, these goals have not been achieved. For the CO reaction, the failure of CO to insert, even into a niobium methyl bond, precludes any possibility of CO reduction. The synthesis of several bis-pentamethyl cyclopentadienyl niobium complexes which bear on this question are reported.

More promising results are the syntheses of several paramagnetic niobocene derivatives. The impetus for studying paramagnetic niobocene chemistry originated from the similar behavior of titanocene[10] and niobocene dialkyls.[12] Both are thermally sensitive and explosively release methane under certain conditions. The use of pentamethyl cyclopentadiene ligands in the titanium system stabilized the chemistry enough to understand the reaction.[13] $Cp_2^*Ti(CD_3)_2$ loses d_4 methane at 90 °C to yield the fulvene complex. This reaction is the first step of



the permethyl titanocene synthesis.[10] We hope to observe similar reactivity with niobium to obtain low valent niobium compounds. The starting point for the investigation of niobocene and singly substituted niobocene derivatives is presented.

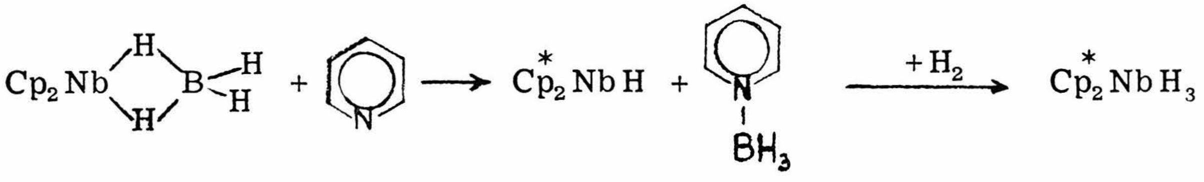
RESULTS AND DISCUSSION

The entry into all permethyl niobocene chemistry is $Cp_2^*NbBH_4$. It is prepared by reaction of niobium pentachloride with lithium permethyl cyclopentadiene and $NaBH_4$ in dimethoxyethane. Yields as

$$2\ Li^+\ C_5(CH_3)_5^- + NbCl_5 + NaBH_4 \longrightarrow Cp_2^*NbBH_4$$

high as 45% are obtained which depend critically on the solvent purity as well as the purity of all starting materials. The nmr of the green borohydride shows a singlet for the Cp^* methyl hydrogens. In addition to broadening due to boron quadrupole coupling, the possibility for fluxionality renders a complex analysis for the borohydride proton resonances.[10]

The borohydride complex reacts with pyridine under hydrogen to produce $Cp_2^*NbH_3$ in 80% yield. Presumably, pyridine reacts with



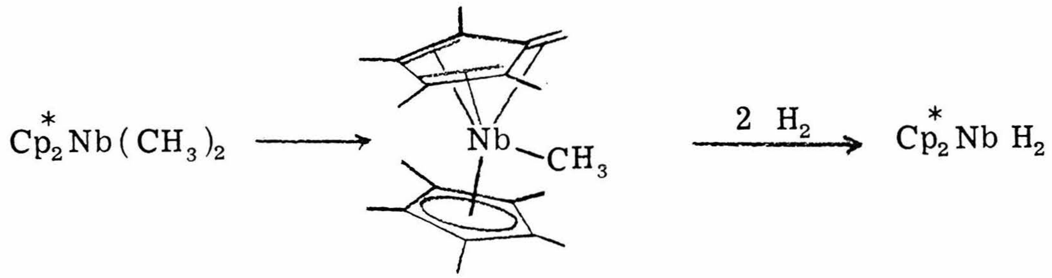
borohydride complexes similar to the phosphine BH_3 abstractions.[15] The trihydride is unstable in solution in the absence of hydrogen analogous to the normal ring niobocene trihydride. Heating speeds the hydrogen reductive elimination. Attempts to isolate Cp_2^*NbH resulted in intractable oils.

$Cp_2^*Nb(H)CO$ is produced quantitatively from the CO reaction with the trihydride. Nmr and ir spectra are similar to the normal ring niobocene hydride carbonyl. $Cp_2^*Nb(H)CO$ is unreactive toward several atmospheres of hydrogen at elevated temperatures. The reaction of $Cp_2^*Nb(H)CO$ with HCl yields $Cp_2^*Nb(Cl)CO$. At low temperature, the initial product appears to $Cp_2^*NbH_2CO.^{\oplus}$ This yellow cation is isoelectronic with $Cp_2^*ZrH_2CO$. It is amusing that this d^0 dihydride carbonyl only undergoes reductive elimination on warming to yield hydrogen and $Cp_2^*Nb(Cl)CO$. Unfortunately, $Cp_2^*NbH_2CO^{\oplus}$ is not sufficiently long-lived to allow measurement of the ir stretch of the d^0 carbonyl. The use of non-coordinating acids such as CF_3CO_2H and $HClO_4$ to produce $Cp_2^*NbH_2CO^{\oplus}$ did not prevent facile reductive elimination above 0°C.

$Cp_2^*Nb(Cl)CO$ reacts with methyl lithium to form $Cp_2Nb(CH_3)CO$ in high yield. Under high pressures of CO or several equivalents of trimethyl phosphine, methyl migration to form an acyl is not observed. An experiment yet to be done is the protonation reaction to form $Cp_2^*Nb(H)(CH_3)CO.^{\oplus}$ In light of the facile CO insertion into the alkyl bond of isoelectronic $Cp_2^*Zr(CH_2CH(CH_3)_2)(H)CO$, one expects acyl formation from the niobium methyl hydride carbonyl cation.

$Cp_2^*NbBH_4$ reacts with aqueous HCl to yield $Cp_2^*NbCl_2$ in 70 percent yield. The esr of $Cp_2^*NbCl_2$ displays a ten-line spectra with a g value of 2.01 characteristic of niobium IV. Magnetic susceptability indicates the compound has a magnetic moment of 1.91 BM. Reduction of the dichloride with Na/Hg under CO yields a brown complex which esr and ir evidence indicates is a niobium II carbonyl. A similar reduction under hydrogen produced a red crystalline compound whose esr displayed a ten-line pattern with proton hyperfine indicative of two protons per metal. However, the purity is ambiguous because the same compound shows an nmr spectrum chracteristic of $Cp_2^*NbH_3$. Apparently an equilibrium exists under hydrogen between the dihydride and the trihydride.

Low-temperature preparation of $Cp_2^*NbH_2$ may circumvent this problem. Oxidative addition of H_2 to niobocene is an attractive synthesis, presuming that niobocene is synthetically attainable. In this vein, attempts to duplicate the permethyl titanocene preparation are underway. Additionally, reductive elimination of an alkyl hydride may



$$Cp_2^*Nb\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown H} \longrightarrow Cp_2^*Nb + CH_4$$

be an attractive route to niobocene at low temperature. The reaction of methyl lithium produces $Cp_2^*Nb(CH_3)Cl$. Reactions with suitable hydride reagents should yield the methyl hydride.

CONCLUSION

The main barrier to studying the permethylcyclopentadienyl chemistry of niobocene has been surmounted. Low valent permethyl niobocene complexes can be easily studied now that $Cp_2^*NbCl_2$ is readily available. In addition to providing theoretically interesting molecules such as niobocene, these compounds have potential for interesting ligand transformations such as carbon hydrogen bond activation, olefin oligomerization and migratory insertion reactions.

EXPERIMENTAL

All manipulations were performed in an inert atmosphere using a glove box or vacuum line techniques. Ether solvents such as glyme and THF were distilled from sodium benzophenone ketyl. Halogenated solvents were distilled in vacuo from 4 Å molecular sieves. Toluene, benzene, and pentane were purified by distillation from titanocene.[17] Hydrogen, argon, and nitrogen were passed through MnO on vermiculite[18] and 4 Å molecular sieves. Carbon monoxide (MCB) was used without purification. Pyridine was refluxed over CaH_2 for a day and stored in vacuo over 4 Å molecular sieves. Lithium pentamethylcyclopentadienide was prepared by literature methods.[19] $NbCl_5$ was carefully purified by two sublimations. The initial sublimation at 110° C separated $NbCl_5$ from most of the oxychloride impurities. A second sublimation at 100° C yielded pure $NbCl_5$ which showed no niobium oxide stretches in the ir.

^1H nmr spectra were obtained using a Varian EM 390 spectrometer. Infrared spectra were recorded on aBeckman 4240 spectrophotometer. Esr spectra were measured on an X-band Varian E-line Century Series spectrometer. Magnetic susceptibilities were determined using a Cahn/Ventron susceptibility balance.

Preparation of $Cp_2^*NbBH_4$

18.15 Grams of pentamethylcyclopentadiene and 55.5 mls of 2.4 M BuLi(Alfa/Ventron) were added at -78° C to 300 mls of glyme. This reaction was stirred at 25° C for six hours before nine grams of $NaBH_4$ was added. The solution was cooled to -78° C and 16 grams of freshly sublimed $NbCl_5$ was slowly added with vigorous stirring. After the addition is complete, the solution is warmed to 25 ° C, then heated at reflux for three days. The glyme is then removed by vacuum transfer. The resulting purple residue is extracted four times with pentane. The pentane volume is reduced to yield green crystals from the maroon solution. Recrystallization from octane as well as subliming the purple residue yield 8.5 grams of $Cp_2^*NbBH_4$: 45% based on $NbCl_5$. Nmr (d_6 benzene) δ 1.67 (s, 30H); δ 5.17 (d, 2H); δ -18.2 (s, 2H). Anal. Calcd. %C; H, 9.06; Nb, 24.56; B, 2.86; Found: %C, 63.36; H, 8.96; Nb, 25.04; B, 2.92.

Preparation of $Cp_2^*NbH_3$

4.1 Grams of $Cp_2^*NbBH_4$ and ten mls of pyridine were added to 40 mls of toluene at -78 ° C. The mixture was warmed to 25 ° C under one atmosphere of hydrogen and stirred eight hours. All volatile materials are removed by vacuum transfer and the orange residue was extracted with 40 mls of diethyl ether. The solvent volume was reduced to ten mls and the resulting yellow crystals were collected by filtration. The extraction process was repeated twice and the crude trihydride recrystallized from octane under hydrogen. 3.3 Grams of pale-yellow $Cp_2^*NbH_3$ were obtained in 82% yield. Nmr (d_6 benzene) δ 1.90 (s, 30H); δ -1.20 (brd, 1H); δ -2.30 (d, 2H).

Preparation of $Cp_2^*Nb(H)CO$

1.2 Grams of $Cp_2^*NbH_3$, dissolved in 25 mls of toluene, was stirred under one atmosphere of CO at 95 ° C for sixteen hours. The toluene was removed from the red solution by vacuum transfer and the residue was extracted with 25 mls of octane at -30 ° C. The octane volume was reduced to seven mls and the red precipitate was recrystallized to yield 1.1 grams of $Cp_2^*Nb(H)CO$: 90%. Nmr (d_6 benzene) δ 1.80 (s, 30H); δ -5.6 (brd, 1H). Ir (nujol) $\nu_{C\equiv O}$ 1880 cm^{-1}, $\nu_{Nb\text{-}H}$ 1700 cm^{-1}.

Preparation of $Cp_2^*Nb(Cl)CO$

300 Mgs of $Cp_2^*Nb(H)CO$ were dissolved in 30 mls of toluene. Two equivalents of HCl gas were frozen into the reaction pot at -196° C. The reaction was warmed to -60° C to melt all the toluene, then re-cooled to -78° C. The red solution is then stirred for several minutes until the solution is yellow. All excess HCl is then pumped off. Toepler experiments indicate that no hydrogen was evolved. Warming above -10° C resulted in a significant rate of gas evolution which was complete after 30 minutes. One equivalent of hydrogen was formed to produce green $Cp_2^*Nb(Cl)CO$. The compound was washed with pentane. Nmr (d_6 benzene) δ 1.60 singlet. Ir (nujol) $\nu_{C\equiv O}$ 1890 cm^{-1}.

Preparation of $Cp_2^*Nb(CH_3)CO$

210 Mgs of $Cp_2^*Nb(Cl)CO$ was dissolved in diethyl ether along with 0.4 mls of 1.6 M methyl lithium (three-fold excess). The reaction was stirred for a day with no color change. The diethyl ether was removed and the green residue extracted with toluene. The toluene was removed by vacuum transfer and the resulting green crystals suspended in cold pentane and filtered. 190 Mgs were collected in 90 percent yield. Nmr (d_6 benzene) δ 1.53 (s, 30H); δ -0.93 (s, 3H).

Preparation of $Cp_2^*NbCl_2$

5.3 Grams of $Cp_2^*NbBH_4$ dissolved in 100 mls of benzene was reacted with 15 mls of deoxygenated 3M HCl at 0° C. The solution evolves gas vigorously and turns brown with yellow precipitate.

After stirring for 20 minutes, all volatiles were pumped away. The brown residue was soxelut extracted with benzene. The brown microcrystalline product was dissolved in 120 mls of CH_2Cl_2. This solution was added to 500 mgs of degassed grade III alumina. Filtration separated $Cp_2^*NbCl_2$ from all hydroxy niobium compounds. Recrystallization from toluene yielded 4.1 grams of $Cp_2^*NbCl_2$: 67%. Esr (benzene) ten line spectrum, g = 2.01. Magnetic susceptibility = 1.91 BM. Anal. Calcd. %C, 55.31; H, 6.96; Nb, 21.39; Cl, 16.33; Found, %C, 55.41; H, 7.03; Nb, 21.52; Cl, 16.29.

Reduction of $Cp_2^*NbCl_2$ under hydrogen

970 Mgs of $Cp_2^*NbCl_2$ was reduced in benzene with Na/Hg under one atmosphere of hydrogen for one day. The resulting red solution was decanted from the amalgam and filtered. Benzene was replaced with twenty mls of octane by vacuum transfer. The mixture was heated under hydrogen (mistake) to dissolve the red crystals, then filtered. Slow cooling to -40° C yielded 600 mgs of red crystalline compound. Esr (benzene) ten-line spectrum, g = 2.01. Nmr (d_6 benzene) identical to $Cp_2^*NbH_3$.

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PROPOSITIONS

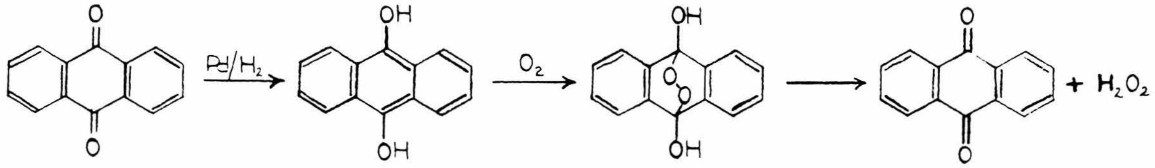
PROPOSITION I

Abstract: A series of electrochemical measurements is proposed for several quinone derivatives complexed to transition metals. It is hoped that a four-electron redox process will occur when the two-electron quinone potential couples with the two-electron metal redox potential. By varying substituents on both the metal and the quinone, the net four-electron potential might be adjusted to significantly positive values to efficiently reduce oxygen to water.

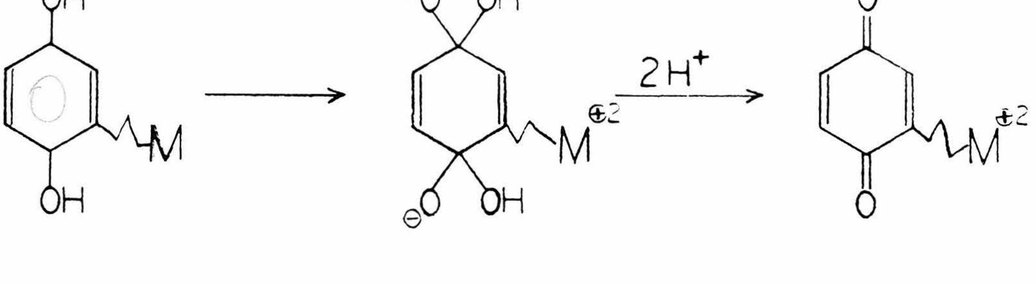
Attempts to efficiently electrochemically reduce oxygen have generated considerable interest in the requisite four-electron transfer process. Several complications have clouded the understanding of this deceptively simple process: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. The four-electron reduction primarily occurs in some poorly understood enzyme reactions.[1] Simple molecules have thus far shown no propensity toward four-electron redox processes so their relevant molecular properties are undefined. Oxygen reduction has been studied with metal complexes known to be unstable to oxygen. Unfortunately the reducing agents form hydrogen peroxide instead of water.[2] With respect to fuel cell efficiency, this two-electron reduction at 0.68 V represents a major loss in energy relative to the O_2/H_2O couple at 1.23 V.[3]

A modification currently under investigation involves bimolecular catalysis by face to face porphyrins.[4] Geometrical modifications will hopefully enhance the known bimetallic oxygen reduction by iron porphyrins[5] such that peroxide formation is suppressed. Some success has been achieved in this vein.[4] No peroxide was formed when oxygen is reduced by a Cobalt-Cobalt porphyrin complex. However, the 650 mV reduction potential of the cobalt complex still represents a substantial overpotential. In addition, the electrochemistry appears to be a series of one-electron steps which somehow net an overall four-electron process. Modifications which could improve the catalyst seem obscure and synthetically formidable. A system which has two coupled two-electron processes might allow more insight into the four-electron process. Also a simpler system would offer more flexibility in adjusting the overall potential to approach 1.23 V.

The quinone functionality is one of the most extensively studied two-electron redox processes.[6] A wide variety of quinones are commercially available with substituents that predictably alter the quinone/hydroquinone potential. Of special relevance to the oxygen electrode problem is the commercial importance of anthroquinone catalysts for the production of H_2O_2.[7] The reduced form reduces



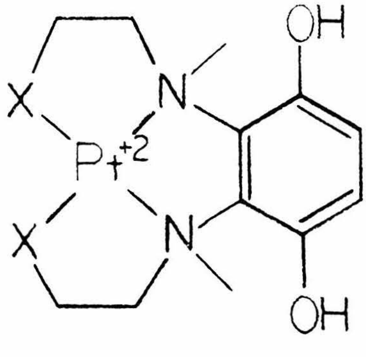
oxygen, albeit to H_2O_2. To efficiently use the oxygen reduction energy of 1.23 V, peroxide formation must be avoided. Although the two-electron oxygen reduction to H_2O_2 is 0.68 V exothermic, this process does not use the additional 0.5 volts of energy electrochemically available from complete oxygen reduction. In the quinone system,



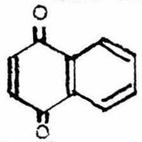
complete reduction will result by cleaving the oxygen-oxygen bond of the peroxide intermediate before H_2O_2 extrusion. In fact, this bond is the weakest in the molecule. The proximity of a sufficiently strong reducing agent such as a metal complex could reductively cleave the oxygen-oxygen bond.

Stability of the reduced and oxidized catalyst and a large metal-quinone interaction is necesssary to electrocatalytically reduce oxygen. Chemical reversibility may not be fortuitous due to the expected ligand reorganizations involved with the two-electron metal couple. Strong interaction of the metal and the quinone is needed for fast electron transfer to break the oxygen-oxygen bond. When the metal^{+2}/metal and quinone/hydroquinone potentials are nearly the same, the metal quinone interaction will facilitate a simultaneous four-electron reduction. Once this potential is adjusted more positive than 0.68 V, peroxide formation becomes endothermic.

A model which may satisfy these requirements is:



Other metals can be Pd^{+2} and Ir^{+1}

Other quinones can be 

X can be an amine or a hydroxy group

Chemical reversibility between the plus two and plus four oxidation states should be enhanced by the macrocyclic ligand.[8] The proximity of the metal to the quinone ought to facilitate rapid electron transfer from the metal to the intermediate peroxide. Considerable modifications are possible to match the metal and quinone reduction potentials. Substituted quinones have reduction potentials ranging from 0.0 V to 1.1 V.[6] Platinum amine reduction potentials range from 0.5 V to 0.9 V.[9] By varying the nature of the macrocycle as well as substituents on the quinone, a voltage significantly more positive than 0.7 volts seems attainable.

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PROPOSITION II

Abstract: An electrochemical study of a series of bimetallic complexes is proposed. The two-electron nature of metal-metal bonds will hopefully cause two-electron redox electrochemistry instead of one-electron transfer observed for most transition metal complexes. The metal-metal bond formed by electron transfer ought to substantially affect the potential.

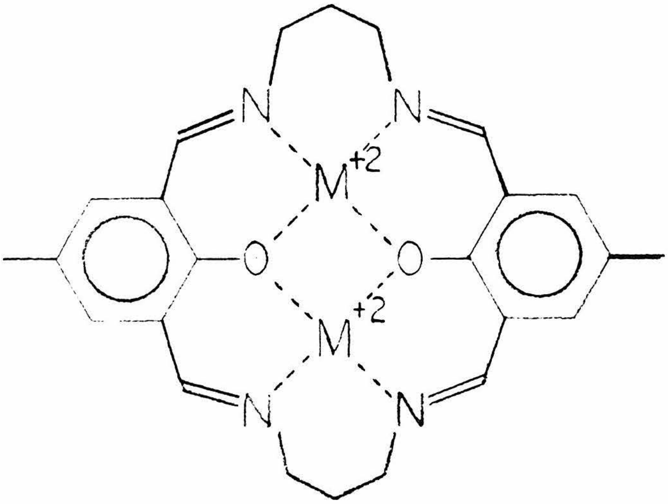
The paucity of two-electron redox processes of transition metal complexes[1] is probably related to the small energy difference between M^{+n} and M^{+n+1} oxidation states. Compared to p-orbital energies, most d^n states are closer in energy to d^{n-1} than p^n states are to p^{n-1}.[2] Thus one-electron metal oxidation is stabilized by relatively minor ligand reorganizations. In p-orbital redox processes, ligand reorganization may not be sufficient to stabilize a different oxidation state. More drastic changes can result such as bond formation. Because most bonds involve two electrons, many p-orbital redox processes are two electron transfers.[3]

Analogous to bonding responsible for two-electron transfers in p-bonded compounds, metal-metal bonding could favor a single two-electron process. A two-electron process is favored over two one-electron steps by the metal-metal bond energy. Many examples of metal-metal bonded complexes are known.[4] Singly as well as multiply bonded bimetallic complexes are substantially stabilized by metal-metal interactions.

$$M^+ + M^+ \xrightarrow{1\,e^-} M\cdots\cdots M^+ \xrightarrow{1\,e^-} M - M$$

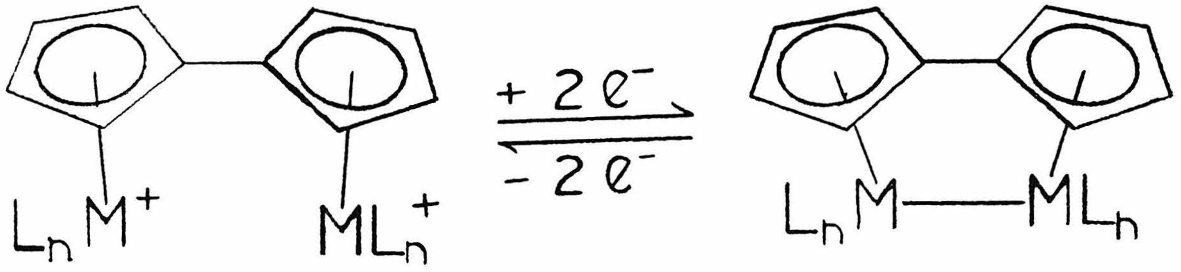
$$M^+ + M^+ \xrightarrow{2\,e^-} M - M$$

Some bimetallic compounds have shown a tendency toward two-electron electrochemistry. $[(CO)_5Mn]_2$ and $[CpCr(CO)_3]_2$ are reduced by two electrons to form $(CO)_5Mn^-$ and $CpCr(CO)_3^-$.[5] The reductions are electrochemically irreversible due to dissociation. In several bimetallic macrocycles where dissociation does not occur, two-electron processes are not observed.[6] Well separated one-electron transfers are obtained. However, the distance between metals is too long to permit metal-metal bonding.

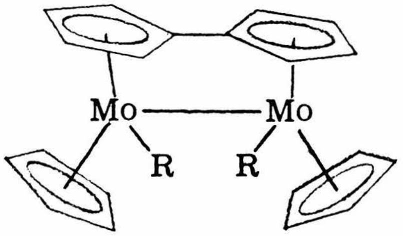


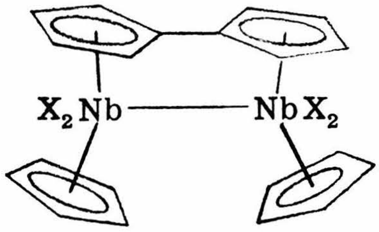
M = Cu, Ni, Co, Fe

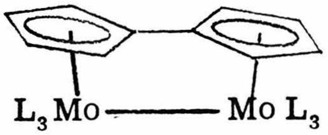
The fulvalene bimetallic complexes offer promise of two-electron processes. The bidentate fulvalene is capable of holding the metals close together whether or not there is a metal-metal bond. Two-electron oxidative or reductive cleavage of a metal-metal bonded fulvalene complex would not totally separate the metals. Since only one electron is transferred per metal, ligand reorganization should not be too severe to prevent electrochemical reversibility. The redox potential of the the two-electron couple, $L_xM_2^{+2}/L_xM_2$, should be one half the metal-metal bond energy more positive than the single electron couple, L_xM^+/L_xM. Only a single two-electron redox potential should result.



Several metal-metal bonded fulvalene complexes which may serve as two-electron transfer agents are:[7, 8]







The metal-metal bonds of the first two compounds will cleave upon two-electron oxidation. Two-electron reduction should cleave the metal-metal bond of all three complexes. Several related complexes have been studied. The bis-fulvalene complexes of vanadium, chromium, iron, cobalt, and nickel all have two well separated one-electron potentials.[9] The separation of one-electron redox potentials of greater than 230 mV indicates the metals of these bis-fulvalenes are close enough to interact. A significant two-electron bond does not form because the bis-fulvalene ligand environment keeps the metals out of bonding distance. The molybdenum and niobium fulvalenes are better suited to two-electron transfer because their larger size permits metal-metal bonding at the 2.9-3.4 Å distance permitted by the fulvalene.[10] Unless solvent interacts strongly with the non-bonded complexes, two-electron reversible electrochemistry of these second-row fulvalenes appears imminent.

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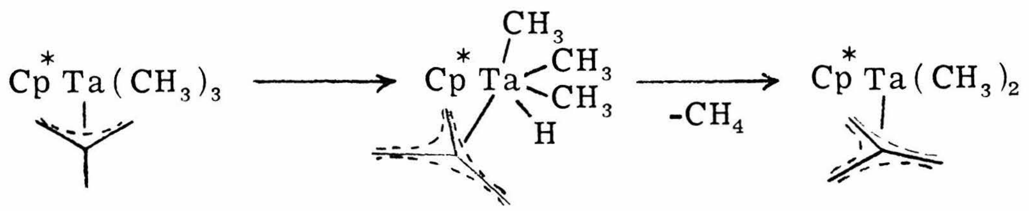
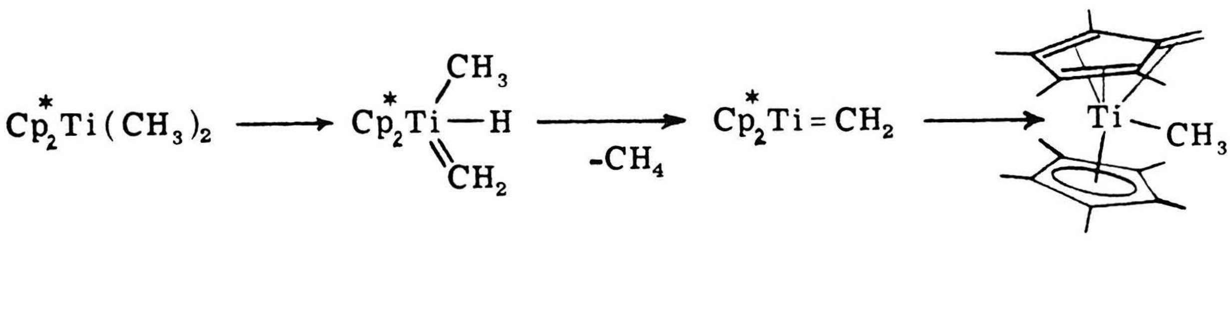
PROPOSITION III

The synthesis of several novel substituted cyclopentadienyl tantalum and niobium compounds is proposed. Hydrogen abstraction from alkyl or allyl ligands can yield coordinated ligands which are normally difficult to prepare. The resulting compounds are potentially interesting with respect to reductive elimination, carbon-hydrogen bond activation and small molecule reactions.

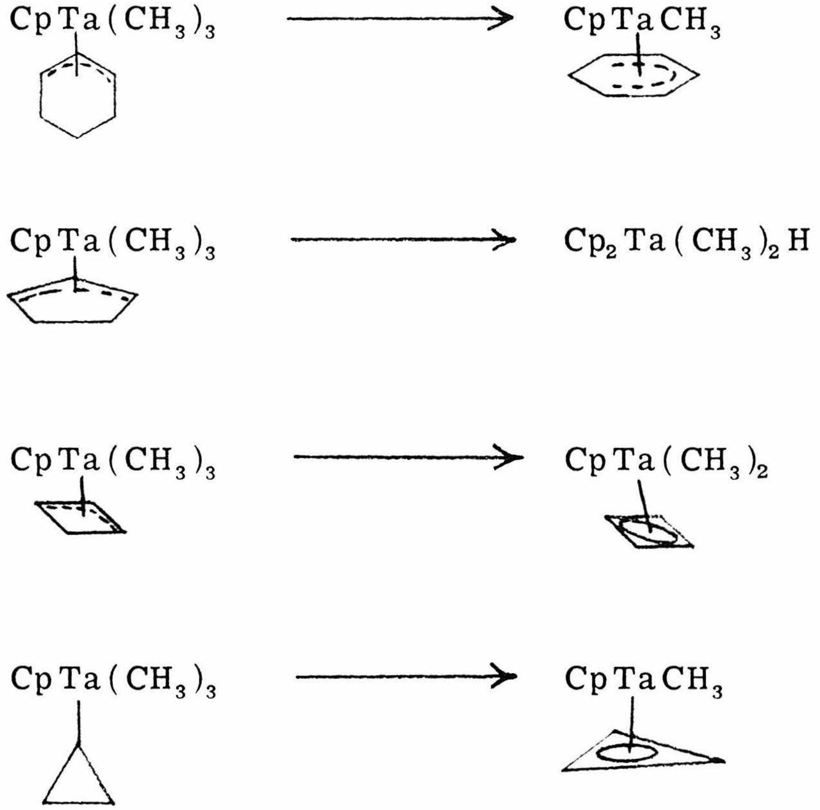
Intramolecular hydrogen abstraction occurs in several reactions of early transition metal complexes. Abstraction of a phenyl hydrogen to form a benzyne complex has been implicated in the decomposition of diphenyl zirconocene.[1] The benzyne complex, $C_5Me_5Ta(CH_3)_2C_6H_4$, was isolated from the decomposition of $C_5Me_5Ta(CH_3)_3\phi$.[2] Presumably, hydrogen abstraction of a phenyl hydrogen by either the metal or a methyl preceeds reductive elimination of methane to form the benzyne complex. A similar reaction involving $C_5Me_5Ta(CH_3)_3CH_2C(CH_3)_2CH_2$ produced the trimethylene methane complex, $C_5Me_5Ta(CH_3)_2C(CH_2)_3$ and methane.[3] A closer look at the mechanism indicates methane reductive elimination follows hydrogen transfer from the methyl allyl



to yield the trimethylene methane product. A similar mechanism is postulated for the decomposition of bis-permethyl cyclopentedienyl titanium dimethyl.[4] Thermolysis of $Cp^*_2Ti(CD_3)_2$ yielded only CD_4. The resulting titanium product is the fulvene complex.

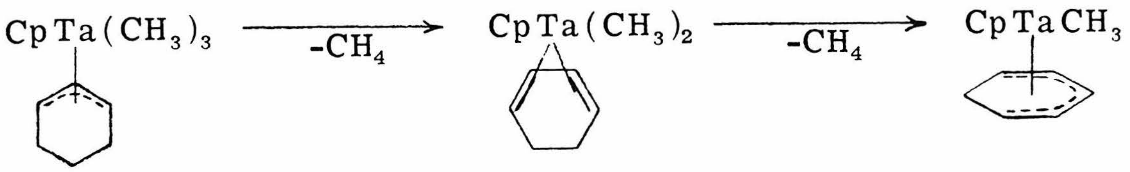


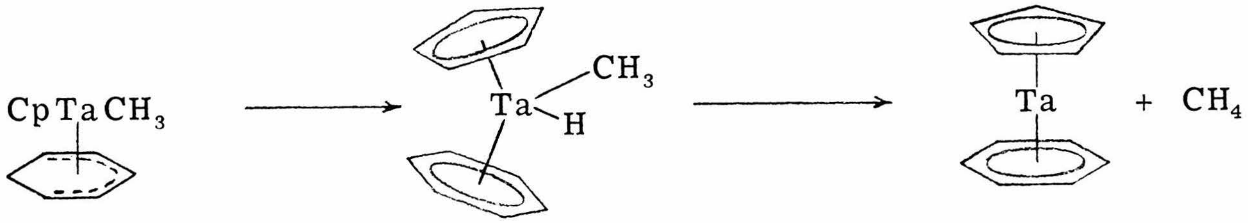
These interesting ligand transformations are mediated by an unsaturated metal center. Hydrogen abstraction in the tantalum complexes, $CpTa(CH_3)_3X$, followed by reductive elimination regenerates unsaturation of the metal. Consecutive hydrogen abstraction and reductive elimination cycles of appropriately substituted tantalum complex should produce interesting products. Several possibilities include:



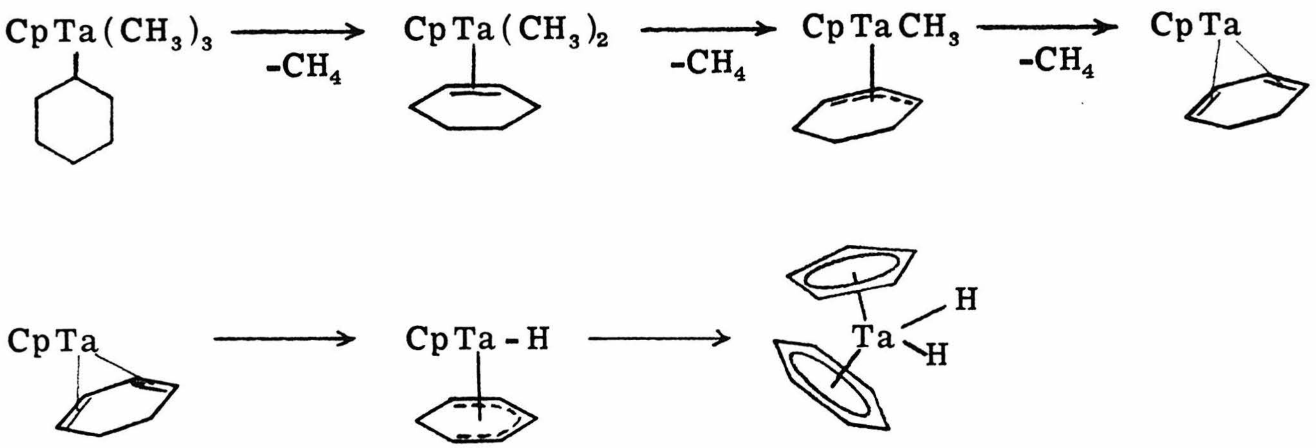
In general, three experiments are envisioned for each cyclic ligand: decomposition of the cycloallyl, decomposition of the cycloalkyl, and substitution of the cyclic ligands to block hydrogen abstraction. Several interesting compounds are expected which may lend themselves to studies of reductive elimination and carbon-hydrogen bond activation.

The proposed decomposition of the cyclohexallyl-substituted complex is shown below. Two consecutive hydrogen abstractions

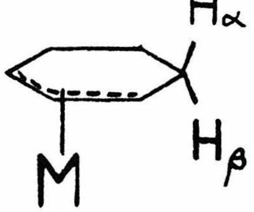


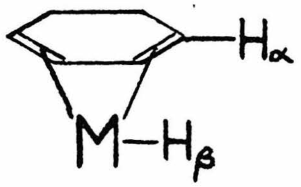


yield the sixteen-electron η^5-cyclohexadienyl complex. The final hydrogen abstraction yields the eighteen-electron cyclopentadienyl benzene tantalum methyl hydride. In light of the unusually high stability of a zirconium alkyl hydride,[5] the possibility of reductive elimination to form CpTaBz should be interesting. Decomposition of the cyclohexyl rather than cyclohexallyl could yield the dihydride tantalum sandwich complex. The driving force for the reaction is the eventual eighteen-electron complex. Whether or not any of the intermediates will be isolable seems unfathomable at this point. However, some steps may be prevented by methyl substitution.

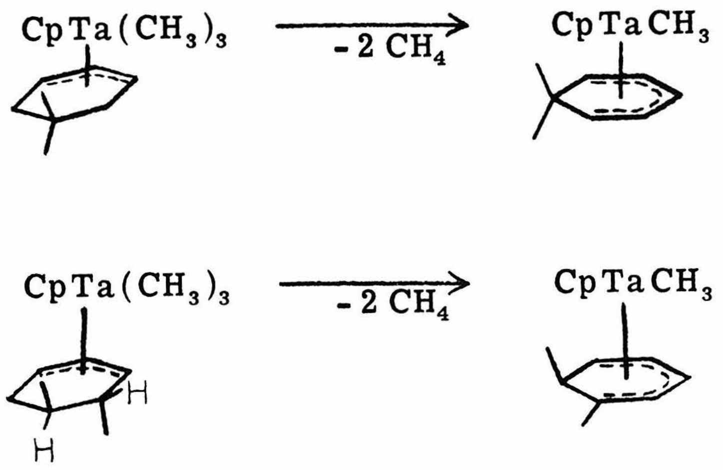


Presumably, a hydrogen must point toward the metal for hydrogen abstraction to occur.[6] Another group besides hydrogen should

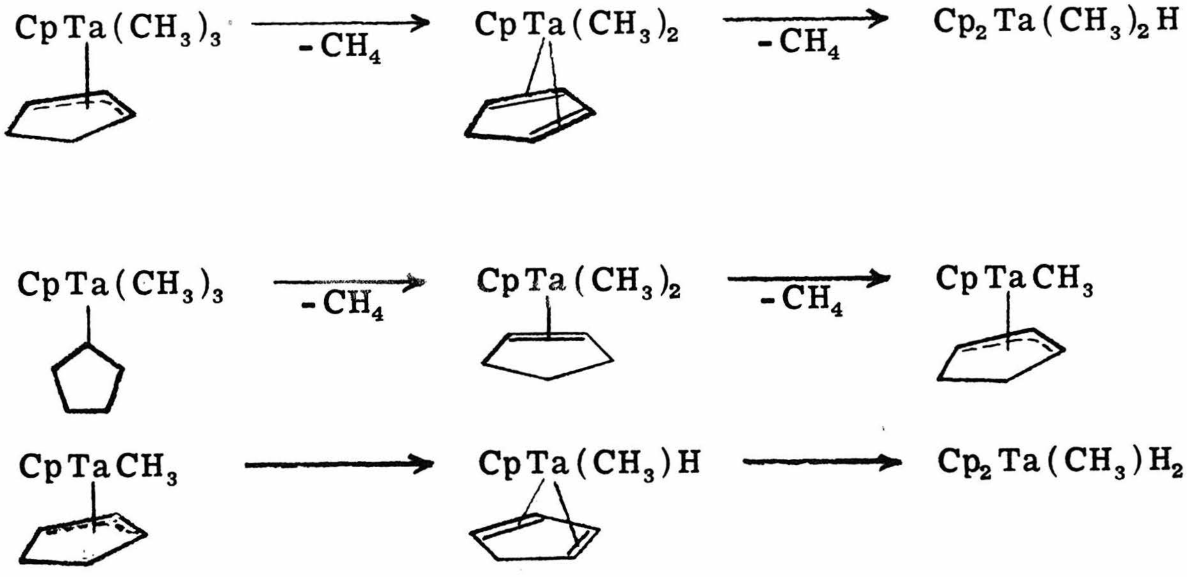




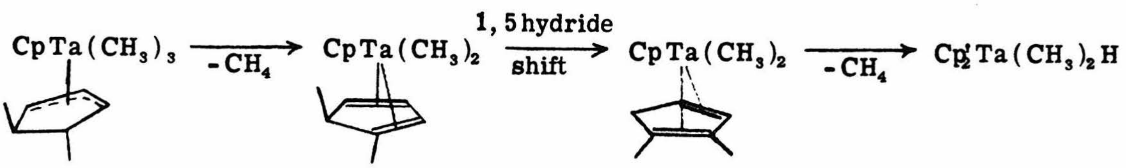
prevent hydrogen abstraction. 5,5 Dimethyl cyclohexallyl cannot easily form a benzene complex. Trans-4,5-dimethyl cyclohexallyl cannot transfer the last hydrogen to tantalum unless there is a hydride shift.



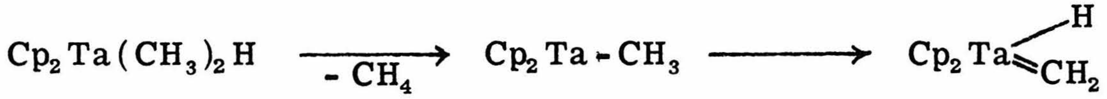
Similar considerations for the cyclopentallyl and cyclopentyl are shown below. Once again, consecutive hydrogen abstractions are facilitated by the unsaturated metal. The use of trans-4,5-dimethyl cyclopentallyl could permit a closer look at the 1-5 hydride shift.



These syntheses of bis-cyclopentadienyl tantalum complexes are



particularly attractive for bis-permethylcyclopentadienyl tantalum compounds. $Cp_2^*TaX_n$ cannot be prepared by conventional techniques.[7] These alkyl hydrides lend themselves to reductive elimination studies. Hopefully the alkyl hydrides will be produced under mild enough conditions to permit their isolation. Reductive elimination of methane from $Cp_2Ta(CH_3)_2H$ yields Cp_2TaCH_3 which is known to be very



$$\mathrm{Cp_2Ta(CH_3)_2H \xrightarrow[-\,CH_4]{} Cp_2Ta \leftarrow CH_3 \longrightarrow Cp_2Ta\genfrac{}{}{0pt}{}{\diagup H}{\leqslant CH_2}}$$

reactive.[8] Providing the reductive elimination is facile at low temperature, $Cp_2Ta(H)CH_2$ could be isolable via the α-elimination reaction.

Decompositions of both the four- and three-membered rings should lead to similar products. All the cycloalkyl decompositions are interesting reactions yielding products conducive to considerable investigation. The coordinatively unsaturated products lend themselves to further study with small molecules such as ethylene, carbon monoxide and hydrogen. The alkyl hydrides are also potentially reactive due to their expected facile reductive elimination. Finally, the low temperatures involved in the hydrogen abstraction may allow isolation of reactive intermediates.

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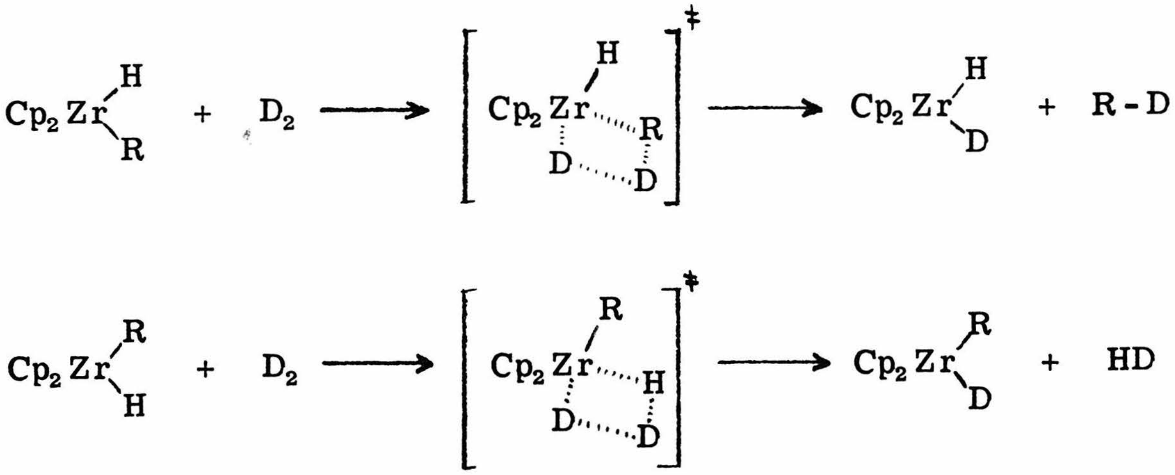
PROPOSITION IV

Abstract: The mechanism of propene insertion into a hydride followed by reductive elimination of propane is probed. The products of the deuterium promoted reaction should indicate the reaction pathway.

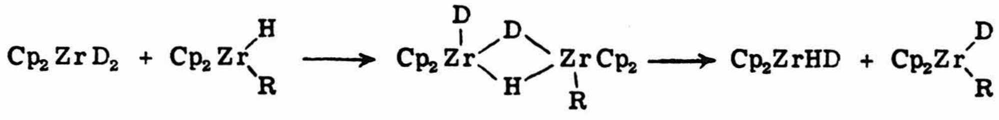
The high reactivity of several d^0 zirconium complexes toward hydrogen has provoked controversy regarding the reaction mechanism. Deuterium is observed to exchange with $Cp_2^*ZrH_2$ at -80° C forming primarily HD.[1] Hydrogen also significantly promotes the reductive elimination of alkanes from several zirconocene alkyl hydrides.[2,3] Oxidative addition of hydrogen to the d^0 complexes seems unlikely. Two mechanisms have been proposed to explain the promoting effect of hydrogen.

The first explanation involves a four-center exchange reaction whereby the two atoms of H_2 and the two atoms of the cleaving metal substituted bond interact.[3] The mechanism explains why the alkane



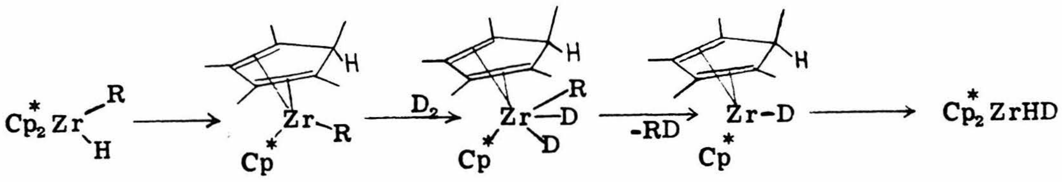
product of reductive elimination is exclusively deuterium substituted. It also rationalizes the incorporation of deuterium into the hydride position of the alkyl hydride, Cp_2ZrHR, prior to alkane formation. However, an efficient pathway involving H-D exchange catalyzed by

Cp_2ZrD_2 followed by intermolecular deuteride transfer also explains



the alkyl hydride deuterium incorporation. This seems feasible considering the dimeric nature of Cp_2ZrRH. Additionally, Cp_2ZrH_2 is expected to a very efficient catalyst for H-D exchange from D_2.

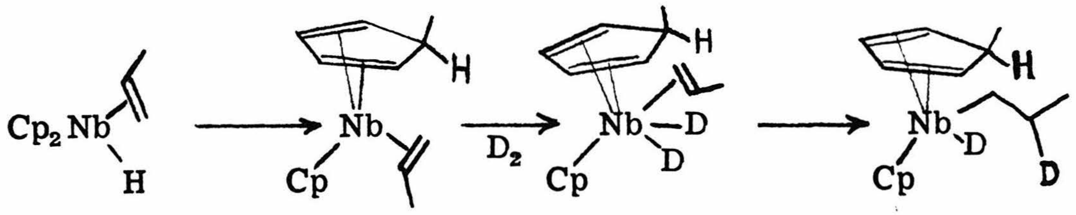
A second mechanism involves intitial reductive elimination of the hydrogen and the Cp^*.[2] Oxidative addition of D_2 is then possible.



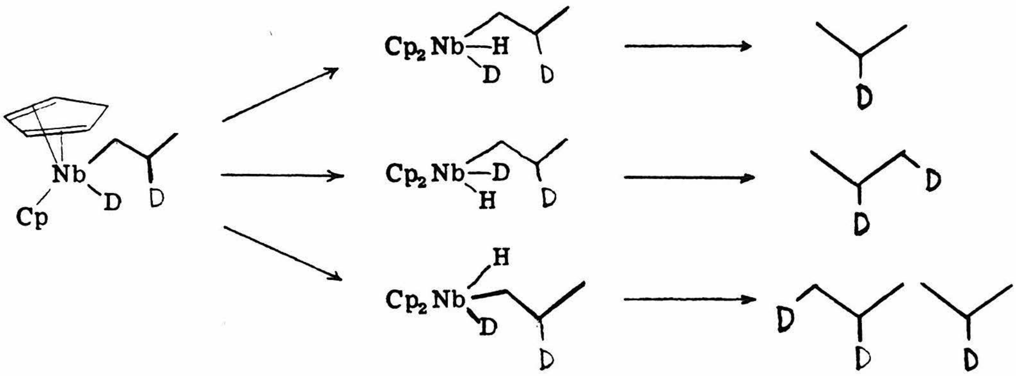
Only alkyl deuterium results from reductive elimination. In contrast to the normal ring system, deuterium does not exchange with alkyl hydride prior to reductive elimination. If a four-center mechanism is responsible for the H-D exchange, it is hard to believe the alkyl hydride would not exchange with D_2. $Cp_2^*ZrH_2$ rapidly exchanges with D_2 at -80° C. The second mechanism does not allow H-D exchange for the alkyl hydride. H-D exchange can occur from the dihydride because hydride Cp^* reductive elimination still leaves one hydride on zirconium.

Both mechanisms bespeak the high energy of the simple reductive elimination product, Cp_2Zr. Whereas most transition metal alkyl hydrides undergo facile reductive elimination,[4] Cp_2ZrHR goes to extremes to avoid forming Cp_2Zr. Several early transition metal biscyclopentadienyl complexes share zirconiums aversion for the unsaturated structure.[5] Cp_2Nb-X and Cp_2Ta-X are extremely unstable sixteen electron complexes.[6] Several olefin hydrides of bis-cyclopentadienyl niobium and tantalum readily undergo olefin migratory insertion at low temperatures.[7] Although the simple migration to form the alkyl seems obvious, the olefin hydride $Cp_2M(CH_2{=}CHR)H$ may shun the unsaturated complex Cp_2Nb-R′ in favor of the intramolecular gymnastics proposed for Cp_2ZrRH.

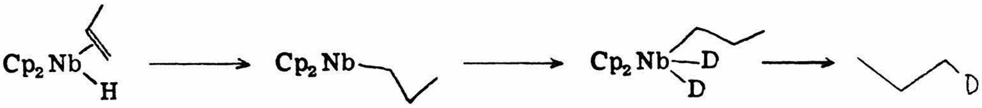
The deuterium promoted migratory insertion and reductive elimination of the niobocene propene hydride[9] is capable of uncovering this devious reactivity. If the hydride migrates to the ring prior to oxidative addition of deuterium, olefin insertion will yield a secondary



deuterio-propyl group. At this point, several possibilities exist. Reductive elimination of the propyl deuteride followed by deuterium trapping would yield 1,2-dideuteriopropane. If the hydrogen moves back from the ring first, either 1,2-dideuteriopropane or



2-deuteriopropane will result, depending on how the hydrogen comes back. If the olefin inserts prior to deuterium oxidative addition, only 1-deuteriopropane will result.



Both schemes assume olefin insertion will yield only the primary alkyl complex. This seems reasonable considering other metallocene hydride additions to olefins.[8] The yield of 2-deuteriopropane differentiates the two schemes as to whether or not the olefin insertion is reversible. In scheme II, deuterium incorporation into the secondary carbene is not allowed. The presence of two deuteriums on the secondary carbon of propane would indicate reversible olefin insertion in scheme I. The two possible reaction modes are thus clearly differentiable by analysis of the deuterium-substituted propane products.

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PROPOSITION V

The generation of acetylene and substituted acetylene carbonium ions is proposed by oxidation of acetylene radicals by copper II. Formation of a stable copper acetylide and the high endothermicity for the process $HC{\equiv}C\bullet \longrightarrow HC{\equiv}C^{\oplus} + e^{\ominus}$ are problems which can hopefully be overcome by the proper choice of solvent and supporting media.

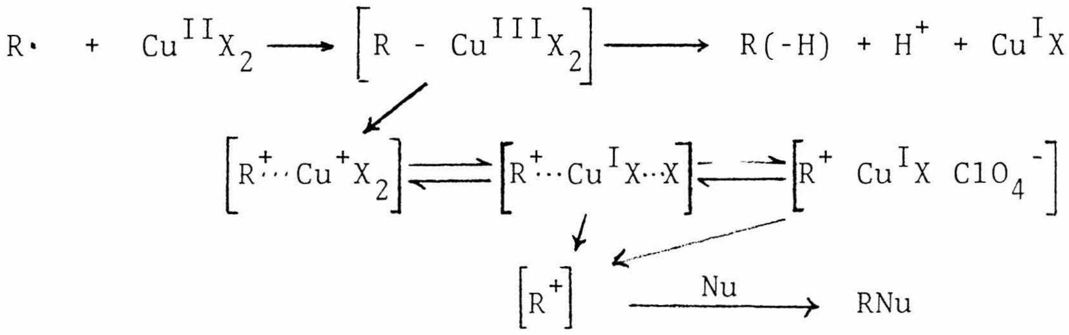
Although nucleophilic substitutions at acetylene carbons are not common, such substitutions have been observed to be facile.[1] Unlike substitutions at saturated carbons, there has been no evidence to implicate an acetylene carbonium ion as an intermediate in an S N1 type reaction. The reason for this is probably the high heat of formation of $HC{\equiv}C^{\oplus}$ which is 397 kcal/mole. Indeed, reported attempts have failed to produce such a cation when a haloacetylene was reacted with silver oxide. Diazotation of acetylene amine followed by loss of nitrogen to form the desired cation is complicated by the instability of acetylene amines.

Another approach is to take two steps to reach the high energy cation, each step being relatively endothermic in terms of the acetylene. Step one would be to generate an acetylene radical and step two would be to oxidize that radical to the acetylene carbonium ion. An important requirement for step two is that it must be as fast as radical coupling in order to avoid simple dimerization of acetylene radicals.

Two ways to generate acetylene radicals which allow a variety of acetylene substituents are the loss of CO or CO_2 from an acyl ar acyloxy radical respectively.[2] Although these reactions have not been utilized to generate acetylene radicals in the past, these fractionations hve been used to generate a variety of alkyl radicals including methyl radical. The acyl radical can be generated by radical abstraction of a hydrogen atom from an aldehyde,[3] and the acyloxy radical can be generated by the thermolysis of a peroxy-diacid.[4] The latter is preferred as one might get complications from radical addition to the acetylene rather than hydrogen abstraction from an aldehyde. Also, loss of CO_2 is more exothermic than loss of CO.[5]

In order to oxidize the acetylene radical, the oxidation rate must be faster than the radical formation and comparable to radical dimerization. For this reason, conventional strong oxidants may not be fast enough to catch the acetylene radical. In an extensive series of organic radical oxidations, Kochi found that copper II was an efficient radical scavenger[6] and that the rate of oxidation approached diffusion controlled.[7] Although copperIIseems to be an unlikely choice due to its relatively low oxidation potential,[8] Kochi observed extensively rearranged products attributable to carbonium ion rearrangement from the oxidation of neopentyl and cyclobutyl radicals. No coupled product from the corresponding radicals was detected.[9] Mechanistic studies of the oxidation of carbon radicals implicated unstable organocopper III whose decomposition could be controlled by choice of solvent and the variation of counterions of copper II.[10]

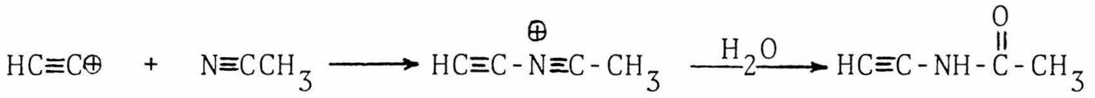
In particular, it is known that use of acetonitrile as solvent significantly increases the oxidation potential of copper II.[11] Non-coordinating counterions increased the amount of oxidation products attributable to carbonium ion intermediates. Also, $LiClO_4$, associated with the "special salt effect" observed in nucleophilic substitutions,[14] increased the apparent carbonium-ion derived products.[10] Sufficient control of copper II



as an oxidant appears to be present to make oxidation of acetylene radicals possible.

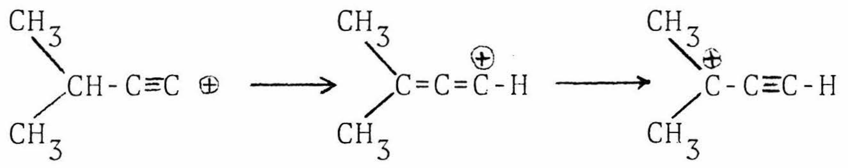
Because copper III is not very stable in general,[12] the acetylene copper complex will probably decompose somehow. Once the copper III acetylide has formed, will it decompose to form the carbonium ion and copper I or will it merely cleave homolytically as it formed? The formation of only diacetylene would indicate homolysis predominates over oxidation. If the acetylene carbonium ion does form, trapping ought to be relatively easy.

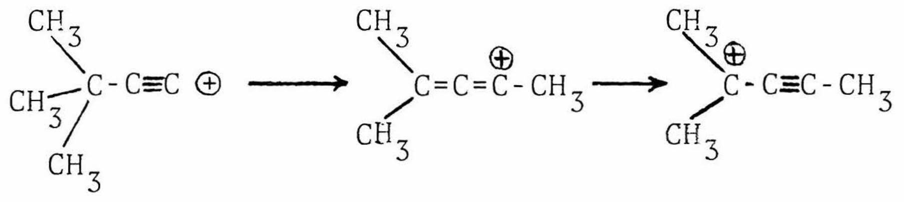
Solvent trapping is most likely. Trapping by acetonitrile would yield acetylene amides on aqueous workup.[13]



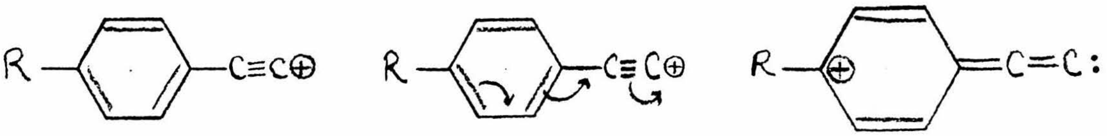
$$HC\equiv C^{\oplus} + N\equiv CCH_3 \longrightarrow HC\equiv C-\overset{\oplus}{N}\equiv C-CH_3 \xrightarrow{H_2O} HC\equiv C-NH-\overset{\overset{O}{\|}}{C}-CH_3$$

Although it may be difficult to prove that acetonitrile traps free acetylene carbonium ions rather than the copper III acetylide complex, other acetylenes with different substituents may show carbonium ion reactivity. For example, i-propyl acetylene or t-butyl acetylene cations may rearrange to the more stable allene cations. Methyl acetylene cation may react by





in a similar fashion. Phenyl substituted acetylenes should stabilize the cations. Additionally, varying the phenyl substituents could significantly alter the acetylide reactivity. By sufficiently stabilizing the positive charge in the phenyl ring, vinylidene reactivity might be observed.



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