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A STUDY OF FUNDAMENTAL REACTION PATHWAYS FOR TRANSITION METAL
ALKYL COMPLEXES ²

- I. THE REACTION OF A NICKEL METHYL COMPLEX WITH ALKYNES
- II. THE MECHANISM OF ALDEHYDE FORMATION IN THE REACTION OF
A MOLYBDENUM HYDRIDE WITH MOLYBDENUM ALKYL

John Mitchell Huggins
(Ph.D. thesis)

June 1980

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REACTION OF A MOLYBDENUM HYDRIDE WITH
MOLYBDENUM ALKYLs.

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ABSTRACT

I: This study reports the rapid reaction under mild conditions of internal or terminal alkynes with methyl(acetylacetonato)(triphenylphosphine)nickel (1) in either aromatic or ether solvents. In all cases vinylnickel products 2 are formed by insertion of the alkyne into the nickel-methyl bond. These complexes may be converted into a variety of organic products (e.g. alkenes, esters, vinyl halides) by treatment with appropriate reagents. Unsymmetrical alkynes give selectively the one regioisomer with the sterically largest substituent next to the nickel atom. In order to investigate the stereochemistry of the initial insertion, a x-ray diffraction study of the reaction of 1 with diphenylacetylene was carried out. This showed that the vinylnickel complex formed by overall trans insertion was the product of the reaction. Furthermore, subsequent slow isomerization of this complex, to a mixture of it and the corresponding cis isomer, demonstrated that this trans addition product is the kinetic product of the reaction. In studies with other alkynes, the product of trans addition was not always exclusively (or even predominantly) formed, but the ratio of the stereoisomers formed kinetically was substantially different from the thermodynamic ratio. Isotope labeling, added phosphine, and other experiments have allowed us to conclude that the mechanism of this reaction does involve initial cis addition. However, a coordinatively unsaturated vinylnickel complex is initially formed, which can undergo rapid, phosphine-catalyzed cis-trans isomerization in competition with its conversion to the isolable

phosphine-substituted kinetic reaction products.

II. The reaction of $\text{CpMo(CO)}_3\text{H}$ (1a) with $\text{CpMo(CO)}_3\text{R}$ (2, R = CH_3 , C_2H_5) at 50°C in THF gives the aldehyde RCHO and the dimers $[\text{CpMo(CO)}_3]_2$ (3a) and $[\text{CpMo(CO)}_2]_2$ (4a). Labeling one of the reactants with a methylcyclopentadienyl ligand it was possible to show that the mixed dimers $\text{MeCpMo(CO)}_3\text{-(CO)}_3\text{MoCp}$ (3b) and $\text{MeCpMo(CO)}_2\text{=(CO)}_2\text{MoCp}$ (4b) are the predominant kinetic products of the reaction. Additionally labeling the carbonyl ligands of 1a with ^{13}CO led to the conclusion that all three of the carbonyl ligands in 1a end up in the tetracarbonyl dimers 4a if the reaction is carried out under a continuous purge of argon. Trapping studies failed to find any evidence for the intermediacy of either $[\text{CpMo(CO)}_3]^-$ or $[\text{CpMo(CO)}_3]^+$ in this reaction. A mechanism is proposed that involves the initial migration of the alkyl ligand in 2 to CO forming an unsaturated acyl complex which reacts with 1a to give a binuclear complex containing a three center-two electron Mo-H-Mo bond. This complex then selectively loses a carbonyl from the acyl molybdenum, migrates the hydride to that same metal, and forms a metal-metal bond. This binuclear complex with the hydride and acyl ligands on one metal reductively eliminates aldehyde, and migrates a carbonyl ligand, to give 4a directly. The other product 3a is formed by addition of two molecules of free CO to 4a.

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PART I

THE REACTION OF A NICKEL METHYL
COMPLEX WITH ALKYNES

INTRODUCTION

The propagation step in the low pressure polymerization of alkenes and alkynes by Ziegler-Natta catalysts is generally believed to be the concerted cis insertion of the unsaturated monomer into the metal carbon bond of the growing polymer chain.¹ The concerted cis nature of this reaction, which can perhaps better be thought of as an alkyl migration, or 1,2-addition to the alkene or alkyne, has gone unchallenged until quite recently, despite the exceedingly rare occurrence of stoichiometric models involving the 1,2-addition of transition metal alkyls to alkenes or alkynes, which should also proceed by a cis concerted pathway. The corresponding reaction involving metal hydrides is quite common, proceeding selectively cis with only a few exceptions.²

The few stoichiometric insertion reactions of transition metal alkyls that have been reported are usually specific to a few highly "activated" alkenes or alkynes, such as tetrafluoroethylene, hexafluoro-2-butyne, or diphenylacetylene,³⁻⁶ with a few exceptions.^{7,8} More important, a number of the reactions of metal alkyl and hydride complexes with alkynes have recently been observed to give either stereorandom or exclusively trans products, sometimes under kinetic conditions.^{2,5,6} Some complexes have even been observed to give exclusively trans addition for one alkyne, and exclusively cis addition for others. Moreover, two recent studies have reported the observation of reactions involving trans addition mechanisms, by backside attack upon coordinated alkyne by a second molecule of alkylating agent.⁶

Finding an explanation for these highly variable results has presented considerable difficulty, and this has led in turn to suggestions of alternative mechanisms for this process, some of which are shown in Scheme I. One such suggestion would account for trans addition products with a concerted trans addition pathway.⁵ A more radical proposition by M.L.H. Green and coworkers⁹ involves an initial α -hydride migration step, to form a metal alkylidene hydride intermediate. This intermediate can then add alkene(or alkyne) to the alkylidene ligand to form a metallocyclobutane(butene) complex. The reverse of the original α -hydride migration step specifically to the original carbon atom then leads to overall cis addition by a stepwise mechanism. The significance of these proposals is not that present evidence is sufficient to establish their viability, but rather that the existing studies cannot rule out these possibilities.

In the present study we have observed the facile reaction at room temperature of a variety of alkynes with methyl(acetylacetonato)(triphenylphosphine)nickel (1) to give vinylnickel complexes (the product of 1,2-addition) in nearly quantitative yield. The mechanism of this reaction has significant bearing on both the question of cis vs trans addition and Green's α -hydride migration pathway. In particular this reaction was observed to give both cis and trans addition products under kinetically controlled conditions; for some alkynes the trans addition product was found to be predominant. Nevertheless we have obtained evidence that this reaction involves initial cis

addition, giving an intermediate which forms E-and Z-vinylnickel products by kinetically controlled pathways.¹⁰

SCHEME I

cis Concerted: *trans* Concerted: α -Hydride Migration:

RESULTS AND DISCUSSION

A. The Synthesis and Properties of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_3$.

In 1973 Yamamoto and coworkers reported the synthesis and characterization of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_2\text{CH}_3$ and $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$ (acac = 2,4-pentanedionato).¹¹ The square-planar geometry of the ethyl complex was firmly established in a subsequent x-ray crystal structure analysis by Cotton and coworkers.¹² The ^1H , ^{13}C , and ^{31}P NMR spectra of these complexes were used to establish that the phosphine ligand is very labile at room temperature (vide infra), and that both acac exchange and β -hydride elimination processes are quite slow. These complexes have been observed to insert carbon monoxide at low temperature to give acyl derivatives which decompose by disproportionation upon warming.¹³ In addition the synthesis and characterization of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{C}_6\text{H}_5$ and its reaction with olefins and alkyl halides was reported recently.⁸

$\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_3$ (1) was prepared by the method of Cotton¹² for the corresponding ethyl complex from $\text{Ni}(\text{acac})_2$, PPh_3 , and $\text{Al}(\text{CH}_3)_2\text{OCH}_3$. The crude reaction product contains considerable excess PPh_3 which may be removed by repeated recrystallization from toluene-hexane or toluene-acetonitrile mixtures. Analytically pure 1 crystallizes as yellow-brown needles; ^1H NMR (C_6D_6): δ 0.07 (s, 3H, Ni- CH_3), 1.40, 1.90 (s, 3H each, acac- CH_3 's), 5.28 (s, 1H, acac-H), 6.9-7.1, 7.6-8.0 ppm (complex, 15H, -Ph). Complex 1 is stable as a solid, but solutions decompose rapidly upon exposure to air, and it is soluble in aromatic and ether

solvents and insoluble in hydrocarbons.

By elemental and spectral analysis 1 is clearly a monophosphine complex in the solid state and in solution. Observation of two distinct singlets in the ^1H NMR for the methyl absorptions of the acac ligand indicates a rigid square-planar geometry. The absence of splitting of the nickel methyl resonance at room temperature can be explained by the rapid exchange of phosphine on the NMR time scale. Using the temperature dependence of the ^{31}P NMR spectrum, Yamamoto was able to determine that the rate constant for phosphine exchange is $1.6 \times 10^2 \text{ sec}^{-1}$ for $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_2\text{CH}_3$ and $2.8 \times 10^3 \text{ sec}^{-1}$ for $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$ in toluene. In a similar manner acac exchange was determined to be much slower; a rate constant of $1.1 \times 10^1 \text{ sec}^{-1}$ was measured for $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_2\text{CH}_3$ at 40°C in toluene.¹¹

In contrast to the reported isolation by Yamamoto and coworkers of the bisphosphine complex $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$,¹¹ we were unable to detect this species in solutions of 1 and added phosphine. Likewise we were unable to isolate a bisphosphine complex, even when 1 was recrystallized from solutions saturated in PPh_3 . The room temperature ^1H NMR spectra of 1 with and without added PPh_3 are completely superimposable, except for some broadening of the acac-methyl resonances.¹⁴ Cooling a toluene- d_8 solution of 1 results in a downfield shift of the nickel-methyl resonance; below -75°C this resonance splits into a broad doublet, $J = 5 \text{ Hz}$, at $\delta 0.30 \text{ ppm}$. In the presence of added PPh_3 the nickel methyl resonance shifts in a similar manner. However

no coupling to phosphorous is observed at -75°C .

The ^{31}P NMR spectra of **1** are much more informative. The spectrum of **1** in toluene- d_8 contains one singlet at 42.5 ppm downfield from external free PPh_3 . Upon cooling to -90°C this signal remains sharp shifting slightly to 43.8 ppm downfield (Figure 1) and no coalescence or broadening was observed at intermediate temperatures. Addition of PPh_3 to these solutions, however, results in drastic changes in these spectra. The ^{31}P NMR spectrum of solutions of **1** and one equivalent added PPh_3 exists as a very broad singlet centered at 24 ppm downfield at room temperature (Figure 2). Upon cooling the spectrum virtually disappears until temperatures below -60°C are reached. At -90°C two sharp singlets at 43 and -3.8 ppm are observed in roughly equal intensity (Figure 3). In the presence of only half an equivalent of added PPh_3 analogous behavior is observed. At room temperature a broad singlet at 28 ppm downfield is observed; upon cooling to -90°C two absorptions appear at 43 ppm and -3.8 ppm in a ratio of 2:1. These spectra can be explained by the existence of a very rapid exchange between free and bound PPh_3 , which becomes slower than the NMR time scale only below about -75°C . Furthermore the integrated intensities of the absorptions for bound and free PPh_3 at -90°C , and the position of the averaged signal at room temperature, indicate that added PPh_3 is largely dissociated both at room temperature and below.

These observations lead to the conclusion that solutions of **1** and added PPh_3 do not contain any observable concentration of

Figure 1. ^{31}P NMR Spectrum of 1 in toluene- d_8 at -90°C .

Figure 2. ^{31}P NMR Spectrum of 1 and One Equivalent PPh_3 in Toluene- d_8 at 30°C .

Figure 3. ^{31}P NMR Spectrum of 1 and One Equivalent Added PPh_3 in Toluene- d_8 at -90°C .

the bisphosphine complex $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$. This behavior is entirely consistent with the observations by Yamamoto and Cotton for $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CH}_2\text{CH}_3$,^{11,12} which does not form a bisphosphine complex. It is, however, inconsistent with the reported preparation of $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$ and its properties.¹¹ We are at a loss for a good explanation for this discrepancy.¹⁵

The analogues of **1** $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CD}_3$ (**1-d₃**), $\text{Ni}(\text{acac})-(\text{PPh}_3)\text{C}_6\text{H}_5$ (**5**)⁸, and $\text{Ni}(\text{acac})(\text{PCy}_3)\text{CH}_3$ (**6**)¹⁶ were prepared from the appropriate aluminum reagents. Both **5** and **6** have been reported previously. These complexes all have similar properties, except that in the ^1H NMR spectrum of **6** in benzene-d₆ the nickel methyl resonance (δ -0.18 ppm) is a doublet due the coupling to phosphorous ($J_{\text{PH}} = 5$ Hz), indicating that the PCy_3 ligand in **6** is not labile on the NMR time scale.

B. The Reaction of **1** with Alkynes

Stoichiometry and Kinetics. Complex **1** reacts rapidly at room temperature with equimolar amounts of a number of both terminal and internal alkynes to give nearly quantitative yields of vinylnickel complexes formed by the 1,2-addition of the metal carbon bond to the alkyne (Scheme II). These alkynes include; diphenylacetylene, phenyl-1-propyne, phenylacetylene, dimethylacetylenedicarboxylate, tert-butylacetylene, and 4,4-dimethyl-2-pentyne. Internal alkyl alkynes such as 2-butyne and 3-hexyne also react with **1**; in these cases, however, more than one equivalent of alkyne is consumed and mixtures of products

Scheme II

result.¹⁷ Only 1-pentyne and acetylene itself failed to give tractable products.¹⁸ These vinylnickel complexes can be treated with either LiAlH_4 or acid to give mixtures of E- and Z-alkenes in good yield (Scheme II). In this manner it was possible to confirm the structure of the organic ligand in these complexes. Similarly $\text{Ni}(\text{acac})(\text{PCy}_3)\text{CH}_3$ (**6**) reacts with alkynes, but much more sluggishly; for example reaction of **6** with an equimolar amount of $\text{PhC}\equiv\text{CCH}_3$, both 0.1M in benzene, has a half life of about 10 hours at 40°C.

The reaction of **1** with alkynes follows bimolecular kinetics, first order in both **1** and alkyne. Comparable rates are observed in THF and benzene solvent. Qualitatively the relative rates of reaction follow the order:

This order follows a trend of increasing reactivity with increasing ability of the alkyne substituents to support π -back bonding in a metal-alkyne π -bond. In addition terminal alkynes appear to react somewhat faster than their methyl substituted analogues, suggesting some steric control of alkyne reactivity as well.

Complex **1** does not react with alkenes at room temperature. With prolonged heating (56°C) minimal conversions have been observed for a few highly activated alkenes (e.g. dimethylmaleate). Other alkenes either do not react or polymerize without consumption of the nickel complex. This is in contrast to the

facile reaction of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{C}_6\text{H}_5$ (5) with alkenes reported by Yamamoto and coworkers.⁸

A significant secondary deuterium isotope effect is observed in a comparison of the reactivity of **1** and **1-d₃**. Diphenylacetylene was allowed to react with an excess of a mixture of **1** and **1-d₃** at room temperature. Protonation of the resulting product gave a mixture of E-and Z-1,2-diphenylpropenes-d₀ and -d₃. After purification by preparative gas chromatography, analysis of these alkenes by 180 MHz ¹H NMR and mass spectroscopy determined that $k(\text{1})/k(\text{1-d}_3) = 1.24 (\pm .05)$. This corresponds to a deuterium isotope effect of $\sqrt[3]{1.24} = 1.07$ per deuterium.

The reaction of **1** with alkynes is strongly inhibited by added phosphine. A plot of the second order rate constant for the reaction of **1** with diphenylacetylene at 40°C vs $1/[\text{PPh}_3]$ gives a straight line dependence, as shown in Figure 4. Two mechanisms which could give this observed inhibition are illustrated in Scheme III. The crucial distinction is that in mechanism A phosphine inhibition can occur only if significant concentrations of $\text{Ni}(\text{acac})(\text{PPh}_3)_2\text{CH}_3$ build up under the reaction conditions, whereas in mechanism B a preequilibrium involving loss of phosphine accounts for the observed inhibition. Because solutions of **1** and added PPh_3 contain no detectable concentrations of this bisphosphine complex (vide supra), we conclude that the initial step in this reaction is the reversible substitution at nickel of phosphine by alkyne (mechanism B).

Figure 4. Rate of reaction of I with $PhC\equiv CPh$ vs PPh_3 conc.

Scheme III

Mechanism A

Mechanism B

In a competition experiment, a mixture of $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CCH}_3$ was allowed to react with a deficiency of **1** ($\text{L} = \text{PPh}_3$), yielding a mixture of vinylnickel complexes corresponding to a ratio $k(\text{PhC}\equiv\text{CPh})/k(\text{PhC}\equiv\text{CCH}_3) = 1.4$. In a parallel experiment reaction of **6** ($\text{L} = \text{PCy}_3$) with a mixture of $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CCH}_3$ gave a ratio $k(\text{PhC}\equiv\text{CPh})/k(\text{PhC}\equiv\text{CCH}_3) = 1.2$. This result, that the reactivity ratio depends upon the nature of the phosphine, suggests that the substitution of phosphine by alkyne proceeds by an associative mechanism. A dissociative mechanism would have predicted a constant ratio independent of the phosphine present or the concentration of the dissociated nickel species. Consistent with this conclusion is the observed broadening of the acac-CH_3 resonances in the ^1H NMR spectrum of **1** upon addition of excess phosphine, which can be explained by an associative phosphine catalyzed acac exchange process.¹⁴

Taken together, these observations suggest that the square-planar complex $\text{Ni}(\text{acac})(\text{RC}\equiv\text{CR})\text{CH}_3$ is most likely the intermediate which precedes the insertion step. The absence of phosphine in this intermediate will be significant in our later discussion of the mechanism of this reaction. This conclusion, that the alkyne must enter a square-planar coordination site prior to insertion, has precedent in the reaction of the square-planar complexes $\text{Pt}(\text{L})_2(\text{X})(\text{vinyl})$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$; insertion occurs only if X is an easily displaced ligand such as acetone, but not at all for non-labile ligands such as chloride.¹⁹

Regioselectivity. The reaction of 1 with unsymmetrical alkynes was observed to be highly regioselective, always giving only one regioisomeric vinylnickel complex. The direction of this specificity was confirmed by treatment of the vinylnickel complexes with either LiAlH_4 or acid to give mixtures of E- and Z-alkenes in high yield. These results, presented in Table 1, show that even alkynes with only alkyl substituents (for example 3,3-dimethyl-1-butyne) give only one regioisomer. Interestingly alkynes with sterically dissimilar substituents always give the vinylnickel complex with the larger group nearest the nickel atom.

That this selectivity arises from steric and not electronic influences was confirmed by a study of the reaction of a variety of p-substituted diphenylacetylenes $\text{p-X-PhC}\equiv\text{CPh}$ ($\text{X} = \text{CH}_3, \text{OCH}_3, \text{Cl}$) with 1. The ^1H NMR spectra of the resulting vinylnickel products clearly show two sets of trans vinyl- CH_3 and two sets of downfield shifted o-phenyl proton resonances in nearly equal concentrations; in no case was a significant excess of one regioisomer observed.

Somewhat unexpectedly these observations are consistent with a transition state for insertion that is sensitive only to steric crowding, furthermore, the metal end of the Ni-CH_3 bond is sterically less active than the methyl group in the insertion transition state. Although sterically controlled selectivity of this kind exists in the hydrozirconation reaction, the reversed preference is observed. In the hydrozirconation reaction the

Table 1. Products Formed on Reaction of Vinylnickel
Complexes With Acid and LiAlH_4 .

Alkyne	Alkenes	Reagent	Yield
$\text{PhC}\equiv\text{CPh}$	$\text{E, Z-Ph(H)C=C(CH}_3\text{)Ph}$	TsOH^{a}	100%
$\text{PhC}\equiv\text{CPh}$	$\text{E, Z-Ph(H)C=C(CH}_3\text{)Ph}$	LiAlH_4	79%
$\text{PhC}\equiv\text{CCH}_3$	$\text{Ph(H)C=C(CH}_3\text{)}_2$	LiAlH_4	78%
$\text{PhC}\equiv\text{CH}$	$\text{E, Z-Ph(H)C=C(H)CH}_3$	TsOH	68%
$\text{t-BuC}\equiv\text{CH}$	$\text{E, Z-(t-Bu)(H)C=C(H)CH}_3$	LiAlH_4	-
$\text{CH}_3\text{C}\equiv\text{CCH}_3$	$\text{CH}_3\text{(H)C=C(CH}_3\text{)}_2$	TsOH	$60\%^{\text{b}}$
$\text{EtC}\equiv\text{CEt}$	$\text{E, Z-(Et)(H)C=C(CH}_3\text{)Et}$	LiAlH_4	47%
$\text{t-BuC}\equiv\text{CCH}_3$	$\text{t-Bu(H)C=C(CH}_3\text{)}_2$	TsOH	-

^a TsOH = p-Toluenesulfonic acid. ^bA two fold excess of 2-butyne was employed. GC of the organic products revealed 3 longer retention time products in circa 10% yield each; these products were not identified.

zirconium hydride preferentially migrates to the most hindered carbon in unsymmetrical alkynes.²⁰

Reactions of the Vinylnickel Complexes. In addition to acid or LiAlH_4 , a variety of reagents convert the vinylnickel complexes into organic products (Scheme II, Table 2). Nucleophilic reagents such as CH_3Li , LiAlH_4 , and $\text{Al}(\text{CH}_3)_3$, as well as electrophilic reagents such as H^+ and I_2 give reasonable yields of their respective organic products. The organometallic products formed in these reactions have not been well-characterized, but importantly all gave mixtures of E-and Z-alkene products in variable ratios. In no case was a single stereoisomer observed in good yield. The lack of stereoselectivity in the reactions of the vinylnickel complexes required that an alternate method for determining the stereochemistry of these complexes be found.

C. Stereochemistry of Addition.

Reaction of 1 with Diphenylacetylene. We have examined the reaction of 1 with diphenylacetylene especially closely. A solution of 205 mg (1.15 mmol) of $\text{PhC}\equiv\text{CPh}$ in 1 ml toluene was added to 500 mg (1.15 mmol) of 1 in 20 ml toluene at room temperature to give $\text{Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_3]$ (3) in quantitative yield. Precipitation with hexane allowed isolation of 3 as an orange solid in 89% overall yield. The conversion of 1 into 3 can be conveniently monitored by NMR; no intermediates could be observed. In benzene this reaction, 0.1M in both reagents, is complete in less than 30 minutes at room

Table 2. Reactions of the Vinylnickel Complexes,
 $\text{Ni}(\text{acac})(\text{PPh}_3)(\text{C}(\text{R}_1)=\text{C}(\text{R}_2)\text{CH}_3)$.

R_1	R_2	Reagent	Products	Yield
Ph	Ph	TsOH^a	$\text{E,Z-Ph(H)C}=\text{C}(\text{CH}_3)\text{Ph}$	100%
Ph	Ph	LiAlH_4	$\text{E,Z-Ph(H)C}=\text{C}(\text{CH}_3)\text{Ph}$	79%
Ph	Ph	AlMe_3	$\text{E,Z-Ph(CH}_3\text{)C}=\text{C}(\text{CH}_3)\text{Ph}$	88%
Ph	Ph	MeLi	$\text{E,Z-Ph(CH}_3\text{)C}=\text{C}(\text{CH}_3)\text{Ph}$	52%
Ph	Ph	I_2	$\text{E,Z-Ph(I)C}=\text{C}(\text{CH}_3)\text{Ph}$	66%
Ph	Ph	CO/MeOH	$\text{E,Z-Ph(MeO}_2\text{C)C}=\text{C}(\text{CH}_3)\text{Ph}$	39%
Ph	H	TsOH	$\text{E,Z-Ph(H)C}=\text{C(H)CH}_3$	68%
Ph	H	I_2	$\text{E,Z-Ph(I)C}=\text{C(H)CH}_3$	30%
Ph	H	CO/MeOH	$\text{E,Z-Ph(MeO}_2\text{C)C}=\text{C(H)CH}_3$	29%

^ap-Toluenesulfonic acid.

temperature.

The vinylnickel complex 3 is an orange-red solid with solubility properties similar to 1. Treatment of a solution of 3 in THF with excess p-toluenesulfonic acid gave E-and Z-1,2-diphenylpropenes in quantitative yield. The ^1H NMR spectrum of 3 has acac absorptions at δ 1.18 and 1.78 (s, 3H each) and 5.09 ppm (s, 1H), and a vinyl methyl resonance at δ 2.03 ppm (d, $J_{\text{PH}} = 1.5$ Hz, 3H). The vinyl methyl signal is split by coupling to phosphorous ($J_{\text{PH}} = 1.5$ Hz), indicating that in this complex phosphine exchange is slow on the NMR time scale. This slower phosphine exchange is general for all the vinylnickel complexes. In addition there is an unusual aromatic proton resonance, a doublet of doublets at δ 8.70 ppm integrating as two protons (A_2MM' quartet, $J_{\text{AM}} = 1$, $J_{\text{AM}'} = 7$ Hz). This low field absorption, assigned to a pair of o-phenyl protons on the β -phenyl group of the vinyl ligand, will be discussed further below.

Complex 3 is the initial product of the reaction. However after standing in solution at room temperature for several days, or heating to 56°C , 3 is converted partially into a new vinyl complex 4. Complex 4 has a new set of acac absorptions at δ 5.20, 1.87, and 1.41 ppm and a new vinyl methyl doublet shifted strongly downfield at δ 3.37 ppm ($J_{\text{PH}} = 1$ Hz). Additionally the absorption at δ 8.70 ppm in 3 is absent in 4. The similarity of 3 and 4 has prevented separation of these two compounds; however, based upon the NMR, and the fact that protonation of mixtures of 3 and 4 also give only 1,2-diphenylpropenes, we conclude that 3

and 4 are cis/trans isomeric about the double bond. This conclusion is supported by the observation that on continued heating the above solution of 3 and 4 reaches an equilibrium ratio for 3/4 of about 3.0 in about one hour at 56°C. Clearly 3 is the kinetic product of the reaction of 1 and $\text{PhC}\equiv\text{CPh}$, and heating converts it to an equilibrium mixture of two isomers.

Crystal and Molecular Structure of 3. Assignment of the stereochemistry of the vinyl ligand in 3 was essential to this investigation. This prompted us to undertake the structure determination of 3 by x-ray diffraction. Complex 3 was conclusively shown to be the *Z*-isomer, the product of trans addition, by x-ray crystallography on a single crystal obtained from a toluene-hexane solution. An ORTEP drawing of 3, excluding the phosphine phenyls, is shown in Figure 5 and relevant interatomic distances and angles are presented in Appendix A. Complex 3 is a square-planar vinylnickel complex with the carbon-carbon double bond almost perpendicular to the plane of the complex. Both the carbon-carbon double bond distance of 1.327 Å and the Ni1-Cl-C7 angle of 123.7° support the characterization of the organic ligand as a vinyl group.

Assuming the structure of 3 in solution is similar to that in the solid state, the x-ray study allows us to rationalize the unusual NMR chemical shift of the aromatic resonance at δ 8.70 ppm. This resonance is assigned to the two o-phenyl protons on the β -phenyl group cis to the nickel for several reasons. With the vinyl ligand at right angles to the plane of the nickel

Figure 5. ORTEP drawing of $Z\text{-Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_3]$ ($\underline{3}$).

complex these ortho protons are placed directly over the nickel atom, although the distance in the crystal is non-bonding (greater than $2.0 \text{ \AA}$). A similar effect is observed in the strong downfield shift of the cis vinyl methyl in 4 relative to the trans vinyl methyl in 3. Relative shifts of this kind are observed in the products of the reaction of 6 with $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CCH}_3$. In $\text{Z-Ni}(\text{acac})(\text{PCy}_3)[\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_3]$ (13) absorptions at 9.28 ($\text{A}_2\text{MM}'$ quartet, $J_{\text{AM}} = 1 \text{ Hz}$, $J_{\text{AM}'} = 7 \text{ Hz}$) and 8.0 ppm ($\text{A}_2\text{MM}'$ quartet, $J_{\text{AM}} = 1 \text{ Hz}$, $J_{\text{AM}'} = 7 \text{ Hz}$) are observed, whereas in $\text{Ni}(\text{acac})(\text{PCy}_3)[\text{C}(\text{Ph})=\text{C}(\text{CH}_3)_2]$ (14) the only low field absorption is at $\delta 7.95 \text{ ppm}$ ($\text{A}_2\text{MM}'$ quartet, $J_{\text{AM}} = 1 \text{ Hz}$, $J_{\text{AM}'} = 7 \text{ Hz}$). Since there is no triphenylphosphine in these complexes to confuse the assignment, it is clear that the ortho-phenyl protons of both the α - and β -vinyl phenyl's are strongly shifted downfield, with the cis β -phenyl protons shifted furthest downfield of the two. Overlap of the triphenylphosphine absorptions probably obscures the protons for the α -phenyl group in complexes 3 and 4. The observed coupling pattern in these absorptions is also consistent with their assignment as o-phenyl protons.

Reaction of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{Ph}$ (5) with $\text{PhC}\equiv\text{CCH}_3$. The unusual result that 3, the kinetic product of the reaction of 1 and $\text{PhC}\equiv\text{CPh}$, was the product of overall trans addition led us to investigate the reaction of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{Ph}$ (5) with $\text{PhC}\equiv\text{CCH}_3$. If this reaction also proceeded with trans stereoselectivity then 4, the isomer opposite to 3, should be the kinetic product. Contrary to this prediction, 3 was the only kinetic product of

the reaction of 5 with $\text{PhC}\equiv\text{CCH}_3$. This reaction proceeded at a rate comparable to that for $\text{PhC}\equiv\text{CPh}$ with 1, and again heating the product solution led to an equilibrium mixture of 3 and 4. Clearly 3 is the sole kinetic product of both reactions, and heating leads to an equilibrium mixture of the cis and trans vinyl products (Scheme IV).

Reaction of 1 With $\text{PhC}\equiv\text{CCH}_3$. Complex 1 reacts with $\text{PhC}\equiv\text{CCH}_3$ to give $\text{Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{Ph})=\text{C}(\text{CH}_3)_2]$ (7) as the only product. The ^1H NMR spectrum of 7 shows two vinyl methyl signals. One at 2.95 ppm (d, $J_{\text{PH}} = 1$ Hz) can be assigned as cis, and the other at 1.75 ppm (d, $J_{\text{PH}} = 1$ Hz) as trans to the nickel atom by analogy to 3 and 4. Treatment of 7 with LiAlH_4 gave 1-phenyl-2-methylpropene in 78% yield. In this reaction, using a deuterium labeled methyl group, it is possible to distinguish cis and trans reaction pathways directly.

Reaction of 1- d_3 with $\text{PhC}\equiv\text{CCH}_3$ gave a ratio of cis- CD_3 /trans- CD_3 -7 = 1.6 ($\pm .1$) as kinetic products. Likewise the reaction of 1 with $\text{PhC}\equiv\text{CCD}_3$ gave a ratio of cis- CH_3 /trans- CH_3 = 1.8 ($\pm .1$) (Scheme V). Both product mixtures approach an equilibrium ratio of about 1.0 after several hours. The inversion of the product ratio in these two reactions excludes a deuterium isotope effect as the cause of the observed predominance of cis addition.²¹

Reaction of 1 With Other Alkynes. Using the strong downfield shift of the cis-vinyl methyl in the ^1H NMR spectrum to assign stereochemistry, it was possible to determine both the kinetic

Scheme IV

Scheme V

1.8 : 1.0

1.0

1

29

1.0 : 1.6

1.6

1-d₃

and thermodynamic ratios of cis and trans addition products for a number of alkynes. These results, summarized in Table 3, contribute to several important conclusions: a) in all cases, different kinetic and thermodynamic ratios of E-and Z-vinylnickel products are observed; b) the subsequent and slower isomerization of the initially obtained products to an equilibrium mixture of isomers establishes that they are the result of kinetically controlled pathways; c) depending upon the alkyne involved, either the E-or Z-isomer can be the favored kinetic product; and d) the predominant thermodynamic product has the larger substituent on the β -carbon cis to nickel.

D. The Mechanism of Addition.

One way to account for the stereochemical and kinetic observations presented here would be to postulate a mechanism involving parallel concerted cis and trans addition pathways, where slight changes in the structure of the alkyne involved can strongly affect the relative rates of cis and trans addition. This mechanism would require that $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CCH}_3$, as well as $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ and $\text{PhC}\equiv\text{CH}$, have opposite stereochemical preferences. Moreover this mechanism would require some pathway for cis-trans isomerization of the products that is independent of the mechanism of addition. We find these requirements rather arbitrary and prefer the alternative hypothesis that only one addition pathway exists. This requires that there exist an intermediate capable of isomerization about the carbon-carbon double bond.

Table 3. Stereochemistry of Addition of Nickel Complexes to

Rxn	R ₁	R ₂	R ₃	Kinetic Prod. ^a		Thermo. Prod. ^a	
				<u>cis</u>	<u>trans</u>	<u>cis</u>	<u>trans</u>
1	CH ₃	Ph	Ph	0	100	25	75
2	Ph	Ph	CH ₃	100	0	75	25
3	CH ₃	Ph	CD ₃	65	35	50	50
4	CD ₃	Ph	CH ₃	61	39	50	50
5 ^b	CH ₃	t-Bu	H	30	70	100	0
6 ^b	CH ₃	Ph	H	65	35	100	0

^a relative percent. ^b for these alkynes determining the kinetic ratio of products is approximate, because isomerization of the products is competitive with the initial insertion reaction.

A mechanism of this type that reasonably accounts for our results is presented in Scheme VI. The initial step is the reversible substitution at nickel of phosphine by alkyne to form the intermediate $\text{Ni}(\text{acac})(\text{RC}\equiv\text{CR})\text{CH}_3$. Then, in what is probably the slow step in the reaction, the alkyne inserts into the nickel methyl bond in a cis manner to give a coordinatively unsaturated intermediate cis-B. Cis-B is the crucial intermediate that can either add phosphine to give the coordinatively saturated cis addition product, or isomerize to give trans-B. (See section E for a discussion of the effect of $[\text{PPh}_3]$ on the rate of this isomerization.) Trans-B can then add phosphine to give the trans addition product.

The results summarized in Table 3 require that k_1 be competitive with (if not faster than) k_2 . The predominant kinetic product under these circumstances will depend upon the relative rates of k_1 , k_{-1} , k_2 , and k_3 and not on either the cis/trans product equilibrium or the stereochemistry of the insertion step. Only in the case where both R_1 and R_3 are CH_3 or CD_3 (Reactions 3 and 4, Table 3) can the stereochemistry of the insertion step be observed in the products. In this case k_1 and k_{-1} , and k_2 and k_3 are expected to be nearly equal; and the predominance of one isomer among the products can only arise from a competition between k_1 and k_2 . Therefore the observation of more cis than trans product in reactions 3 and 4 requires that cis-B is formed first, that is the insertion step proceeds cis.

Scheme VI

These stereochemical observations do not provide detailed information about the mechanism of the insertion process itself. The observed predominance of the cis addition product in reactions 3 and 4 argues against a direct trans addition pathway. An alternative hypothesis involving α -hydride migration (Scheme I) might also give a cis specific result, but this mechanism would predict a primary kinetic deuterium isotope effect. The observed kinetic ratio $k(\underline{1})/k(\underline{1}-d_3) = 1.24$ is too small to be primary, and clearly represents a secondary effect. On the basis of these arguments we conclude that the most likely mechanism involves a concerted cis insertion process.

E. The Mechanism of Isomerization.

The most direct mechanism for the cis-B $\rightleftharpoons$ trans-B isomerization involves a simple unimolecular rotation about the π -bond (perhaps assisted by contributions from resonance forms of type 15). This mechanism, or any other involving a unimolecular

pathway for isomerization of B, would predict a strong phosphine concentration dependence on the ratio of cis and trans products in reactions 3 and 4, where the rate of isomerization is

competitive with the rate of addition of phosphine to give product. This dependence was not observed: over concentrations ranging from zero to 1.0 M added PPh_3 (.1M in 1) the cis/trans product ratio from the reaction of 1-d₃ with $\text{PhC}\equiv\text{CCH}_3$ changed very little. Likewise, highly charge-separated transition states can be discounted because virtually no effect upon the cis/trans product ratio was observed in changing solvent from benzene to THF, or adding 0.2M NaBPh_4 in THF.

In order to account for these observation, we suggest that both the isomerization and the product-forming steps involve phosphine. Phosphine can catalyze isomerization of the carbon-carbon double bond if free PPh_3 has two modes of addition to the intermediate B. Addition at the nickel center gives product, whereas reversible addition to the β -vinyl carbon leads to complex 16, resulting in isomerization of the double bond. Addition of phosphine to the vinyl ligand might be enhanced in B by delocalization of electron density toward nickel, through resonance forms of the type 15, making the β -carbon somewhat electrophilic. Equilibration of the kinetic products would then

involve loss of phosphine to regenerate intermediate B (dotted arrows in Scheme VI), followed by competitive readdition of phosphine either at nickel or at carbon. This mechanism is supported by the observation that phosphine is much less labile in the vinylnickel complexes than in 1, accounting for the slow approach to equilibrium. As expected in this mechanism the rate of approach to equilibrium is retarded by addition of excess phosphine.

SUMMARY AND CONCLUSION

The reaction of the methylnickel complex 1 with alkynes occurs rapidly under mild conditions to give vinylnickel complexes, the product of 1,2-addition to the alkyne, in high yield. A wide variety of both internal and terminal alkynes can be employed. This reaction is bimolecular, first order in both 1 and alkyne, and gives highly regioselective products. Only the regioisomer resulting from migration of the methyl ligand to the least hindered alkyne carbon is observed. Thus this system constitutes a general example of the 1,2-addition of a transition metal alkyl to alkynes.

The formation of both cis and trans addition products in kinetically controlled pathways demonstrates that 1,2-addition reactions can give products which have stereochemistry that differs significantly from the stereochemistry of the addition process itself. To account for this we have suggested the initially concerted cis insertion of the alkyne into the nickel methyl bond gives a coordinatively unsaturated vinylnickel intermediate capable of isomerization of the carbon-carbon double bond at a rate competitive with product formation. Kinetic competition between the rates of isomerization and of formation of cis and trans products then leads to product stereochemistry that may be independent of the stereochemistry of addition. The observed stereochemistry is also independent of the relative thermodynamic stabilities of the cis and trans addition products, and is not affected by changes in phosphine concentration.

Mechanisms of this type help explain how different alkynes can give opposite stereochemistry in reactions with the same metal alkyl, even under kinetic conditions, without postulating different addition pathways in each case.^{5,6}

In this study the observation of products stereochemically distinct from the pathway for addition was dependent upon phosphine catalysis for the isomerization of an intermediate. Nevertheless, independent of the mechanism of isomerization, the following conclusion concerning stereochemical studies in organometallic addition reactions still pertains: the observation of a given stereochemical mode of addition, even when the observed complex is found to be the kinetic product of the reaction, does not necessarily mean that the crucial insertion step proceeds with that same stereochemistry.

EXPERIMENTAL

General. All manipulations involving organonickel or aluminum compounds were done under either nitrogen or argon using standard Schlenk techniques or in a Vacuum/Atmospheres Corporation model HE-553 inert atmosphere glove box with a model MO-40 recirculating purification system, and continuously circulating nitrogen. All organonickel compounds were stored in the glove box. All solvents were thoroughly dried and degassed prior to use. Tetrahydrofuran (THF) and diethyl ether were vacuum distilled directly from sodium benzophenone ketyl solution. Benzene, toluene, and hexanes were added to a solution of sodium benzophenone ketyl preformed in tetraglyme, then vacuum distilled. Additionally hexane was also extensively washed with sulfuric acid, potassium permanganate (10% H_2SO_4 solution), and water to remove olefins, prior to ketyl formation.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian EM-390, or a 180 MHz FT-NMR instrument equipped with a Bruecker superconducting magnet and a Nicolet Instrument Corp. model 1180 data system, and electrons assembled by Mr. Rudi Nunlist (U.C. Berkeley). ^{31}P spectra were obtained at 72.9016 MHz on the later instrument. All ^1H NMR spectra are reported in ppm downfield from tetramethylsilane, and ^{31}P spectra are reported in δ ppm downfield from external PPh_3 (-5.9 ppm vs trimethylphosphite in benzene). The following abbreviations are used for the observed peak multiplicities: s = singlet, d = doublet, dd = doublet or doublets, t = triplet, q =

quartet, m = complex multiplet. Most chemical shifts were determined using the residual proton absorption of benzene- d_6 absorption at δ 7.15 ppm, THF- d_8 at δ 3.58 ppm, or added Cp_2Fe 3.96 ppm. Infrared spectra were recorded on a Perkin-Elmer 237 Grating Spectrophotometer. Gas chromatography (GC) was performed on Hewlett-Packard 5750 and Varian 90-P chromatograph, with helium as the carrier gas. Two columns were employed: A) 10' x 1/8" 20% SE-30 on 100/120 chromasorb P, B) 2' x 1/4" 5% SE-30 on 60-80 chromasorb W. All peak areas were determined by electronic integration using a Spectra-Physics Autolab System I integrator.

$Ni(acac)_2$ was prepared by drying commercially available $Ni(acac)_2(H_2O)$ ($100^\circ C$, 24 hrs. at full vacuum). Triphenylphosphine (Alfa) and diphenylacetylene (Aldrich) were recrystallized from hexanes. Liquid alkynes were purified by distillation or preparative gas chromatography where necessary.

Preparation of $Ni(acac)(PPh_3)CH_3$ (1). Compound 1 was prepared by analogy to the method of Cotton, et.al.¹² for the synthesis of $Ni(acac)(PPh_3)CH_2CH_3$. A solution of 0.68 g (7.8 mmol) $Al(CH_3)_2OCH_3$ ²² in 7 mL hexanes was added dropwise over 20 minutes to a ice/salt bath cooled ($-15^\circ C$), stirred suspension of 4.0 g (15.6 mmol) $Ni(acac)_2$ and 4.5 g (17 mmol) PPh_3 in 50 mL diethyl ether under nitrogen. The solution was allowed to warm to about $0^\circ C$ for about 2 hours. Then the solution was cooled to $-15^\circ C$ again and the yellow precipitate was collected by filtration. The crude product was washed three times with cold ether, residual solvent was removed at reduced pressure, and taken into

the drybox. This gave 5.75 gms crude product containing considerable excess PPh_3 as evidenced by NMR integration. This crude product was purified by repeated recrystallization from toluene-hexane (1/10) or toluene-acetonitrile (1/4) to give 3.5 g (51% yield) of pure 1. Compound 1 does not sublime; it has m.p. (sealed tube) $150-2^\circ\text{C}$ dec.; ^1H NMR (benzene- d_6): δ 0.07 (s, 3H), 1.40, 1.90 (s, 3H each), 5.28 (s, 1H), 6.9-7.1, 7.6-8.0 (complex, 15H); IR(CH_2Cl_2): 3300 (br.), 1580 (s), 1520 (s), 1440 (w), 1400 (s), 1190 (w), 1100 (m), 1020 (m), 860 (w), 830 (s) cm^{-1} ; Anal. Calcd. for $\text{C}_{24}\text{H}_{25}\text{O}_2\text{NiP}$: C, 66.24; H, 5.79; Ni, 13.49%. Found: C, 65.92; H, 5.85; Ni, 13.65%.

Preparation of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{CD}_3$ (1- d_3). Compound 1- d_3 was prepared as described above from 2.0 g (7.8 mmol) $\text{Ni}(\text{acac})_2$, 2.05 g (7.8 mmol) PPh_3 , and $\text{Al}(\text{CD}_3)_2\text{OCH}_3$ prepared in situ from $\text{Al}(\text{CD}_3)_3(\text{Et}_2\text{O})$ (0.65 g, 3.9 mmol) and CH_3OH (157 μL , 3.9 mmol) in 20 mL hexane-ether (1/3). Three recrystallizations from toluene-hexane yielded 0.75 g (22% Theory) of pure 1- d_3 . Anal. Calcd. for $\text{C}_{24}\text{D}_3\text{H}_{22}\text{O}_2\text{NiP}$: C, 65.79; H + D, 6.44%. Found: C, 66.20, H + D, 6.66%.

Preparation of $\text{Ni}(\text{acac})(\text{PCy}_3)\text{CH}_3$ (6).¹⁶ Compound 6 was prepared in an analogous manner from $\text{Ni}(\text{acac})_2$ (7.8 mmol), PCy_3 (7.8 mmol), and $\text{Al}(\text{CH}_3)_2\text{OCH}_3$ (3.9 mmol), to yield 1.32 g crude product. The crude product was purified by repeated recrystallization from ether, yield 0.73 gms (21% theory) dark brown cubic crystals. ^1H NMR (benzene- d_6): δ -0.18 (d, $J = 5$ Hz, 3H), 1.68, 1.85 (s), 1.0-1.4, 1.4-2.2 (m), 5.28 ppm (s, 1H).

(lit.¹⁶ ^1H NMR: δ -0.32 (d, $J = 5$ Hz), 0.75-1.75 (m), 1.69, 1.84 (s), 5.28 ppm (s)).

Preparation of $\text{Ni}(\text{acac})(\text{PPh}_3)\text{Ph}$ (5). Attempts to prepare 5 by the method of Maruyama, *et.al.*⁸ gave very poor yields of product and large amounts of $\text{Ni}(\text{PPh}_3)_n$ ($n = 3, 4$) as impurity. Results were highly variable, sometimes giving no product at all. The following modified procedure enabled the isolation of 5 sufficient for these experiments.

A solution of $[\text{Al}(\text{Ph})_3(\text{Et}_2\text{O})]$ (0.35 g, 1.3 mmol) in 25 mL toluene-ether (1/4) was added very slowly to a slurry of 2.0 g (7.8 mmol) $\text{Ni}(\text{acac})_2$ and 2.15 g (8.2 mmol) PPh_3 in 35 mL diethyl ether with cooling to -78°C . Upon warming to -20°C a yellow color developed and 50 mL cold hexane was added. The solution was cooled to -78°C and filtered. Only a small amount of a yellow-green solid was collected. The filtrate was allowed to warm to room temperature, turning yellow-brown (no precipitate). The solvent was removed to yield a red residue. Extensive washing of this crude product with ether at room temperature gave 0.55 g (14% Theory) of essentially pure 5 as a yellow powder. Compound 5 could be recrystallization from toluene-ether. ^1H NMR (benzene- d_6); δ 1.40, 1.72 (s, 3H each), 5.30 (s, 1H), 6.8-7.1, 7.4-7.6 ppm (m). (lit.⁸ ^1H NMR: 1.50 (s, 3H), 1.72 (s, 3H), 5.30 (s, 1H), 6.8-7.1, 7.4-7.8 ppm (m))

The reaction of 1 with alkynes. General: The reaction of 1 with alkynes was carried out in either THF or benzene under air free conditions by one of two methods. Method A: In the glove box

a solution of **1** was prepared (typically around 0.1 M in **1**) and an equimolar amount of the alkyne was added. The resulting solution was transferred to an NMR tube, capped, and the cap wrapped with parafilm. The reaction was then monitored by NMR over a period of hours or days depending upon the alkyne. Method B: A solution of **1** prepared in the glove box was transferred to an NMR tube and capped with a rubber septum. Outside the drybox the alkyne was then added through the septum via syringe, and the reaction was monitored by NMR. All reactions involving heating of the reaction solution were carried out in sealed NMR tubes. Typically the solutions changed from a light yellow-brown color to red as the reaction progressed. The ^1H NMR spectra of the resulting vinylnickel complexes are summarized in Table 4. With the exception of **3** these complexes were not isolated. The structures of these complexes was deduced from their NMR spectra and through identification of the organic product resulting from cleavage of the nickel-carbon bond with acid or LiAlH_4 (Table 1).

Reaction of **1 with $\text{PhC}\equiv\text{CPh}$. Protonation.** A solution of 205 mg (1.15 mmol) $\text{PhC}\equiv\text{CPh}$ in 1 mL toluene was added to 500 mg (1.15 mmol) **1** in 20 mL toluene in the glove box. After stirring at room temperature overnight the solvent was reduced by evaporation to 8-10 mL and diluted with 200 mL hexanes. An orange precipitate (280 mg) was collected. A second crop was realized by reducing the filtrate to yield a total of 450 mg (89% theory) of a mixture of **3** and **4**. In a similar experiment addition of excess $\text{PhC}\equiv\text{CPh}$ had no effect upon the reaction, other than to accelerate it; no

evidence of multiple insertion could be detected by NMR.

In a separate experiment a solution of **3** prepared in THF from 75 mg (0.17 mmol) **1** and 31 mg (0.17 mmol) $\text{PhC}\equiv\text{CPh}$ was treated with 0.4 mL (0.4 mmol) 1M p-toluenesulfonic acid in THF. Analysis of the resulting solution by gas chromatography identified E- and Z-1,2-diphenylpropenes in 104% calculated yield and a ratio of Z/E = 5/4, using naphthalene as an internal standard and molar response factors determined using an authentic sample. However this Z/E ratio was variable experiment to experiment. The 1,2-diphenylpropenes were identified by coinjection of an authentic mixture,²³ and by mass spectral analysis on a sample purified by preparative gas chromatography (column B; 110-130°C, flow rate 60 ml/min).

Reaction of **1 with $\text{PhC}\equiv\text{CPh}$ and added PPh_3 .** A solution of 235 mg (0.54 mmol) **1**, 78 mg (0.298 mmol) PPh_3 , and 50 mg (0.269 mmol) Cp_2Fe (internal standard) in exactly 6 mL benzene- d_6 was prepared in the glove box. Then 96 mg (0.54 mmol) $\text{PhC}\equiv\text{CPh}$ was dissolved in the solution and 1 ml aliquots were added to weighed amounts of PPh_3 . The resulting solutions were then transferred to NMR tubes, frozen and sealed off under a vacuum. Six NMR tubes were prepared in this manner containing the concentrations listed in Table 5. These NMR tubes were heated in a temperature controlled water bath at 40 (± 1)°C, and the concentration of **1** was determined by cooling the NMR tube in ice/water and integrating the nickel-methyl resonance vs Cp_2Fe . The second order rate constants determined in this way are presented in

Table 4. ^1H NMR Data for vinylnickel complexes of general structure $\text{Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{R}_1)=\text{C}(\text{R}_2)\text{CH}_3]$.

Complex: vinyl ligand	Chemical Shifts ^a			
	$=\text{C}(\text{CH}_3)$	R_1	R_2	acac
3: ~ Ph Me	2.03 (d, J= 1)	6.9-7.6 (m)	6.9-7.6 (m)	1.78, 1.18 (s, 3H) 5.09 (s, 1H)
4: ~ Ph Ph	3.37 (d, J= 1)	6.9-7.6 (m)	6.9-7.6 (m)	1.87, 1.41 (s, 3H) 5.20 (s, 1H)
7: ~ Ph Me	2.95 (d, J= 1)	6.9-7.1 7.6-7.9 (m)	1.75 (d, J= 1)	1.88, 1.30 (s, 3H) 5.22 (s, 1H)
9: ~ Ph H	2.80 (dd, J= 1, 7)	6.9-7.2 7.6-7.9 (m)	5.05 (q, J= 1)	1.83, 1.38 (s, 3H) 5.22 (s, 1H)
10: ~ t-Bu H	2.75 (dd, J= 1, 6)	1.50 (s)	4.65 (q, J=6)	1.80, 1.30 (s, 3H) 5.25 (s, 1H)
11: ~ t-Bu Me	3.12 (d, J= 1.5)	1.58 (s)	1.85 (d, J= 1)	1.87, 1.38 (s, 3H) 5.28 (s, 1H)
12: ~ E E	2.72 (s)	3.32 (s)	3.56 (s)	1.78, 1.22 (s, 3H) 5.15 (s, 1H)

^a δ ppm in benzene- d_6 , J is in Hz. ^bE = $-\text{CO}_2\text{CH}_3$.

Figure 6. Plot of $1/[\eta]_t - 1/[\eta]_0$ vs time at 40°C , $[\text{PPh}_3] = 0.05\text{ M}$.

Table 5. Rate constants for the reaction of $\underset{\sim}{1}$ with $\text{PhC}\equiv\text{CPh}$ and added PPh_3 at $40 \pm 1^\circ\text{C}$.

$[\underset{\sim}{1}]^b$	$[\text{PPh}_3]$	$k(\text{obs})^a \text{ L}\cdot\text{M}^{-1}\text{sec}^{-1}$
0.0945 M	0.05 M	6.2×10^{-3}
0.945 M	0.71 M	3.63×10^{-3}
0.855 M	0.107 M	2.98×10^{-3}
0.085 M	0.197 M	1.70×10^{-3}
0.080 M	0.43 M	7.33×10^{-4}
0.070 M	1.05 M	3.0×10^{-4}

^arate constant from plot of $1/[\underset{\sim}{1}] - 1/[\underset{\sim}{1}]_0$ vs time. ^b $[\underset{\sim}{1}] = [\text{PhC}\equiv\text{CPh}]$.

Table 5. A sample second order plot is presented in Figure 6. The plot of $k(\text{obs})$ vs $1/[\text{PPh}_3]_{\text{added}}$ is shown in Figure 4.

Reaction of 1 with $\text{ArC}\equiv\text{CPh}$. Solutions of 1 (0.05 mmol) and equimolar amounts of $\text{ArC}\equiv\text{CPh}$ ($\text{Ar} = \text{p-CH}_3\text{O-C}_6\text{H}_4^-$, $\text{p-Cl-C}_6\text{H}_4^-$, $\text{p-Me-C}_6\text{H}_4^-$) in 0.5-.7 mL benzene- d_6 were prepared in the glove box, transferred to NMR tubes and capped. The reactions all proceed at room temperature to give the ^1H NMR spectra summarized here. These spectra are consistent with the presence of both possible regioisomers of the p-substituted analogs of compound 3.

A. The product of 1 and $\text{p-MeOC}_6\text{H}_4\text{C}\equiv\text{CPh}$.

^1H NMR: δ 1.23 (s, 3H), 1.85 (s, 3H), 2.10 (two d, $J = 1.5$ Hz, 3H), 3.42, 3.50 (s, 3H, ratio 1.45), 5.17 (s, 1H), 7.0-7.8 (m), 8.65 (d, $J = 9$ Hz), 8.75 ppm (dd, $J = 1, 7$ Hz).

B. The product of 1 and $\text{p-ClC}_6\text{H}_4\text{C}\equiv\text{CPh}$.

^1H NMR; δ 1.27 (d, $J < 1$ Hz, 3H), 1.85 (d, $J = 1.5$ Hz, 3H), 2.03 (two d, $J = 1.5$ Hz, 3H), 5.12 (s, 1H), 6.9-7.6 (m), 8.48 (d, $J = 9$ Hz), 8.67 ppm (d, $J = 6$ Hz).

C. The product of 1 and $\text{p-MeC}_6\text{H}_4\text{C}\equiv\text{CPh}$.

^1H NMR: δ 1.20 (s, 3H), 1.78 (s, 3H), 2.05 (d, $J = 1$ Hz, 3H), 2.12 (s), 2.25 (s), 5.05 (s, 1H), 6.7-7.8 (m), 8.60 (d, $J = 6$ Hz), 8.78 ppm (dd, $J = 1, 6$ Hz).

Reaction of 1 with $\text{PhC}\equiv\text{CCD}_3$ and 1- d_3 with $\text{PhC}\equiv\text{CCH}_3$. A solution of 40 mg (0.09 mmol) 1 and 11 mg (0.09 mmol) $\text{PhC}\equiv\text{CCH}_3$ in exactly 1 mL benzene- d_6 was prepared in the glove box, transferred to an NMR tube, and capped. Monitoring by NMR showed the reaction was 70% complete in less than 30 minutes, and

complete in 1.25 hours at room temperature. A ratio of the cis/trans isomers could be calculated by comparing the integrations for the acac-H at δ 5.22 ppm and the cis-vinyl-CH₃ at δ 2.95 ppm and correcting for the theoretical number of protons. Integration of the trans-vinyl-CH₃ at δ 1.75 ppm was very unreliable due to the proximity of the acac-CH₃ absorption at 1.88 ppm. In this way the initial ratio was calculated to be cis-CH₃/trans-CH₃ = 1.70 ($\pm$.1). Alternatively, in a separate experiment in protiobenzene integration of the deuterium NMR (180 MHz FT NMR) resonances for the vinyl-CD₃ at δ 2.95 and 1.75 ppm directly gave a ratio of trans-CD₃/cis-CD₃ = 1.87; the later experiment was considered more accurate.

A similar reaction involving 68 mg (0.15 mmol) 1-d₃ and 18 mg (0.15 mmol) PhC $\equiv$ CCH₃ in 1 ml benzene gave a ratio of cis-CD₃/trans-CD₃ = 1.56 by deuterium NMR.

These product ratios were found to be almost totally insensitive to added PPh₃ or solvent. In the reaction of 1-d₃ with PhC $\equiv$ CCH₃ in benzene-d₆ the cis/trans product ratio was 1.55 ($\pm$.1) with no added PPh₃, 1.67 ($\pm$.1) with 0.1 M added PPh₃, and 1.85 ($\pm$.1) with 1.0 M added PPh₃ (both at 60°C). In the reaction of 1 with PhC $\equiv$ CCD₃ the cis/trans product ratio was 1.6 ($\pm$.1) in THF-d₈, and 1.7 ($\pm$ 0.1) in 0.2 M NaBPh₄ in THF-d₈.

The Kinetic Deuterium Isotope Effect. A solution of 9 mg (0.05 mmol) PhC $\equiv$ CPh was added to a solution of 102 mg (0.23 mmol) 1 and 114 mg (0.26 mmol) 1-d₃ in 4.5 ml THF. After 2 hours a solution of 430 mg (2.2 mmol) p-toluenesulfonic acid in 2 ml THF

was added. The solvent was removed and the residue was extracted with H₂O/ether in air. The combined ether fractions were dried, then evaporated to dryness, to yield a white solid. About 1-2 mg of E-and Z-1,2-diphenylpropenes were isolated from this mixture by preparative gas chromatography (column B; 130°C, 80 ml/min). Mass spectral analysis gave a d₀/d₃ ratio of 1.05 and 1.085 for the Z-and E-1,2-diphenylpropenes, respectively. Similarly the 180 MHz NMR spectrum of Z-1,2-diphenylpropene gave a d₀/d₃ ratio of 1.16. Averaging and correcting for the starting concentrations gives a value for $k(l)/k(l-d_3) = 1.24 (\pm .05)$

X-Ray Crystal Structure of 3. A crystal of 3 measuring 0.36 x 0.24 x 0.28 mm obtained from a toluene-hexane solution was shown to be exclusively 3, not 4, by examination of the NMR spectrum of the remaining crystals in the same batch. Compound 3 crystallizes in space group $P\bar{1}$ with cell parameters: $a = 17.892$, $b = 12.339$, $c = 16.732 \text{ \AA}$, $\alpha = 106.27^\circ$, $\beta = 73.17^\circ$, $\gamma = 110.77^\circ$, $z = 4$. The calculated density is 1.26 gm/cc, and a density of 1.19 gm/cc was measured by flotation of a crystal from the same batch. Intensity data on 5258 reflections $2\theta \leq 38$ were collected on a Syntex P2₁ diffractometer with monochromatic Mo K α radiation using $0-2\theta$ scanning. By monitoring ten standard reflections it was determined that no significant crystal decomposition occurred. The locations of the two nickel and two phosphorus atoms were obtained by examination of a Patterson map. Fourier-transform electron density maps then identified the positions of the other 80 non-hydrogen atoms. The nickel and phosphorus atom thermal

parameters were refined anisotropically, and the other 80 non-hydrogen atoms only isotropically. A difference Fourier map identified no sites of electron density greater than $1.0 \text{ e}^-/\text{\AA}^2$ except within $2.0 \text{ \AA}$ of the nickel atoms. Finally H atom positions were calculated assuming a carbon hydrogen bond length of $0.95 \text{ \AA}$ and a B value one greater than for the attached carbon atom. Final refinement after a total of four least-squares routines gave $R = 0.082$ and a 'goodness of fit' = 1.54 for all 5258 reflections ($2\theta \leq 38^\circ$), and $R = 0.053$ for the 3198 reflections [$F_o > 3\sigma(F_o)$]. An ORTEP drawing of 3 is shown in Figures 5. More crystallographic data are given in Appendix A.

Competition Experiment Between $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CCH}_3$. A solution of 20 mg (0.181 mmol) $\text{PhC}\equiv\text{CCH}_3$, 30 mg (0.168 mmol) $\text{PhC}\equiv\text{CPh}$ and 21 mg (0.046 mmol) 6 in 1 mL benzene- d_6 was prepared in the glove box, transferred to an NMR tube, and sealed off under vacuum. After heating to 44°C for 2.5 h a ratio of $\text{Ni}(\text{acac})(\text{PCy}_3)[\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_3]$ to $\text{Ni}(\text{acac})(\text{PCy}_3)[\text{C}(\text{Ph})=\text{C}(\text{CH}_3)_2]$ of $1.1 (\pm .1)$ was determined by integration of the NMR spectrum of the resulting solution, at this point 40% of 6 had been consumed. Correcting for the initial concentrations gives a ratio for $k(\text{PhC}\equiv\text{CPh})/k(\text{PhC}\equiv\text{CCH}_3) = 1.2 (\pm .1)$.

In a similar manner a mixture of 30 mg (0.168 mmol) $\text{PhC}\equiv\text{CPh}$, 21 mg (0.181 mmol) $\text{PhC}\equiv\text{CCH}_3$, 21 mg (0.048 mmol) 1, and 13 mg (0.049 mmol) PPh_3 (to slow the reaction at room temperature) in 1.0 mL benzene- d_6 gave a value for the ratio of $k(\text{PhC}\equiv\text{CPh})/k(\text{PhC}\equiv\text{CCH}_3) = 1.40 (\pm .05)$ after heating to 45°C for

100 minutes. Another experiment involving no added PPh_3 and conducted at room temperature resulted in an identical ratio within experimental error.

Reactions of the Vinylnickel Complexes. General. The vinylnickel complexes $\text{Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_3]$ (3) and $\text{Ni}(\text{acac})(\text{PPh}_3)[\text{C}(\text{Ph})=\text{C}(\text{H})\text{CH}_3]$ (8) were prepared in situ, usually in THF solvent, from equimolar amounts of 1 and either $\text{PhC}\equiv\text{CPh}$ or $\text{PhC}\equiv\text{CH}$. After about 1 hour at room temperature these solutions were treated with the appropriate reagent under air free conditions. The resulting organic products were analyzed by gas chromatography and/or NMR, and identified by comparison with authentic samples in most cases. These results are summarized in Table 2. Below are descriptions of the reactions of 3 with some of these reagents; the reactions of 8 were carried out in a similar manner.

LiAlH_4 . A solution of 12 mg (0.32 mmol) LiAlH_4 in 10 mL THF was added to a solution of 0.2 mmol 3, prepared as above, in 3 mL THF with 15 mg biphenyl as internal standard. At various time intervals 1 mL aliquots were removed, quenched with 1 mL saturated Na_2SO_4 and analyzed by gas chromatography (column A, 195°C , 60 ml/min). After 15 minutes a maximum yield of 85% of E- and Z-1,2-diphenylpropenes²³ was realized. However the E/Z ratio changed over the course of the reaction from an initial value of 1.1 to 1.8.

$\text{Al}(\text{CH}_3)_3$. A 1 mL solution of $\text{Al}(\text{CH}_3)_3$ (25% in hexane) was added dropwise to a solution of 0.1 mmol 3 in 2 mL benzene.

After 5 min, 4 h and 24 h, 1 mL aliquots were quenched with 2 mL saturated Na_2SO_4 . After 4 h a maximum yield of 88% E- and Z-2,3-diphenyl-2-butenes²⁴ were identified by gas chromatography.

CH_3Li . To a solution of 0.047 mmol 3 in 1 mL of ether was added dropwise 0.5 mL of 1.45 M CH_3Li at room temperature. Extraction with H_2O /ether allowed isolation of a 52% yield of E-2,3-diphenyl-2-butene²⁴, identified by its mass spectrum and NMR.

I_2 . A solution of 150 mg (0.59 mmol) I_2 and 50 μL pyridine in 12 mL CH_2Cl_2 was added to a solution of 0.57 mmol 3 in 5 mL THF. After stirring overnight addition of 230 μL CH_3I (to precipitate PPh_3) and filtration through a plug of silica gel yielded 168 mg of a mixture of E-1,2-diphenylpropene, and E- and Z-1-iodo-1,2-diphenyl propenes, in yields of 24 and 66% respectively.

CO/MeOH. A solution of 520 mg (0.5 ml) 25% methanolic $\text{Bu}_4\text{N}^+\text{OH}^-$ in 33 mL benzene was added to a solution of 0.051 mmol 3 in 2 mL benzene under carbon monoxide purge. After 30 min CO flow was discontinued, and then after 1 h the solution was extracted with 10% HCl/ether. The combined ether layers were dried with MgSO_4 then evaporated to yield a mixture of E- and Z-methyl-2,3-diphenyl-2-butenate, in 39% yield, identified by NMR and mass spec. of a sample purified by preparative GC.

Preparation of $\text{Al}(\text{CD}_3)_3\cdot\text{Et}_2\text{O}$. $\text{Al}(\text{CD}_3)_3(\text{Et}_2\text{O})$ was prepared by the method of Krause and Wendt²⁵ for the corresponding protio compound. A solution of CD_3MgI , prepared from 6.9 mL (0.108 mol) CD_3I (99+% D, Aldrich) and 3.15 g (0.13 mol) Mg turnings in 40 mL

ether, was added to a solution of 4.0 g (0.03 mol) freshly sublimed AlCl_3 in 25 mL ether (the ether should be added to the AlCl_3 with cooling to control the strongly exothermic formation of the etherate) over 10 minutes with cooling from an ice bath, all under nitrogen. The resulting solution was brought to a reflux for 5.5 h. The reflux condenser was replaced with a distillation head, condenser and receiver flask under nitrogen flow and the ether was distilled out of the flask at atmospheric pressure. The oily residue was heated with an oil bath to around 200 C at reduced pressure, and $\text{Al}(\text{CD}_3)_3(\text{Et}_2\text{O})$ distills over as a clear liquid: b.p. 50-65°C at aspirator pressure (~15 mm Hg). (lit.²⁵ b.p. 68°C at 15 mm Hg) Yield 3.02 gms (60% theory). Virtually no Al-CH_3 can be observed by NMR just the coordinated ether. This preparation was repeated with protio methyl iodide to give $\text{Al}(\text{CH}_3)_3(\text{Et}_2\text{O})$. ^1H NMR: δ -0.42 (s), 0.76 (t, $J = 6.5$ Hz), 3.35 ppm (q, $J = 6.5$ Hz).

Preparation of AlPh_3 . AlPh_3 was prepared by the method of Eisch and Kaska.²⁶ Under nitrogen a solution of 30.9 g (0.087 moles) HgPh_2 in 150 mL xylenes was brought to reflux in a three necked flask containing 11.1 gms (0.41 mmol) Al turnings, and equipped with a second three necked flask attached through a side arm. After heating at reflux for 4 days the solution was poured hot through the side arm into a the second flask containing 5 gms Al turnings, leaving behind the Al/Hg solids in the original flask. The solution was heated at reflux for an additional 2 days, then decanted hot into a third flask. Roughly two thirds of

the solvent was distilled out of the flask, and the solution was cooled to -30°C to give the white crystalline product. Yield 8.86 gms AlPh_3 (59% theory); m.p. $235-42^{\circ}\text{C}$ (lit.²⁶ $229-242^{\circ}\text{C}$). The product could be recrystallized as the etherate from toluene-ether. $\text{AlPh}_3(\text{Et}_2\text{O})$: m.p. $127-9^{\circ}\text{C}$ (lit.²⁶ $129-129.5^{\circ}\text{C}$).

Preparation of $\text{PhC}\equiv\text{CCD}_3$.²⁷ A 22 mL solution of BuLi (0.053 mol, 2.4 M) in hexane was added dropwise over 20 minutes to a solution of 5.5 mL (0.05 mol) freshly distilled $\text{PhC}\equiv\text{CH}$ in 40 mL anhydrous ether with cooling to -20°C under nitrogen. The solution was allowed to warm to room temperature and 25 mL dry THF was added, followed by 3.2 mL (0.05 moles) CD_3I (Aldrich 99+% D) over 10 minutes. The reaction was exothermic, warming the solution considerably. The addition funnel was washed down with an additional 10 mL THF. After 17 hours the solution was poured over 100 ml ice/water, then extracted with ether. The combined ether extracts were dried with MgSO_4 and distilled at reduced pressure to yield 2.40 g (40% theory) $\text{PhC}\equiv\text{CCD}_3$; b.p. $73-75^{\circ}\text{C}$ (17 mm Hg). By ms the product was determined to be > 98 atom % D. Anal. Calcd. for $\text{C}_9\text{H}_5\text{D}_3$: C, 90.70; H + D, 9.30. Found: C, 90.23; H + D, 9.52.

Synthesis of $p\text{-X-C}_6\text{H}_4\text{C}\equiv\text{CPh}$. The substituted diphenylacetylenes $p\text{-X-PhC}\equiv\text{CPh}$ were prepared from $\text{PhC}\equiv\text{CCu}$ and the appropriate p -iodobenzene by the method of Castro and Stephens.²⁸ The iodobenzenes were all obtained from Pfaltz and Bauer and used without further purification. In all cases the resulting acetylene was recrystallized from methanol or hexanes until no

change in melting point was observed (at least twice).

p-ClC₆H₄C≡CPh : m.p. 80.5-81.5°C (lit.²⁹ 81.5-82°C).

IR(CCl₄): 2225 (w), 1605 (sh), 1595 (s), 1495 (s), 1445 (s), 1400 (s), 1090 (s), 1015 (s), 825 (s), 685 (s) cm⁻¹.

p-CH₃C₆H₄C≡CPh: m.p. 70 - 71°C. (lit.³⁰ m.p. 72-74°C)

IR(CCl₄): 2215 (w), 1600 (s), 1515 (s), 1487 (s), 1445 (s), 685 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 1.99 (s, 3H), 6.97 (m, 5H), 7.50 ppm (m, 4H).

p-MeOC₆H₄C≡CPh: m.p. 57-61°C (lit.^{30,31} m.p. 58-60°C).

IR(CCl₄): 2210 (w), 1500 (s), 1435 (m), 1242 (s), 1168 (m), 1030 (s), 825 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 3.17 (s, 3H), 6.5-7.4 ppm (m, 9H).

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PART II

THE MECHANISM OF ALDEHYDE FORMATION IN THE
REACTION OF A MOLYBDENUM HYDRIDE WITH
MOLYBDENUM ALKYLs.

INTRODUCTION

In a recent communication Bergman and Jones¹ reported the clean bimolecular reaction of $\text{CpMo(CO)}_3\text{H}$ with $\text{CpMo(CO)}_3\text{R}$ in THF to give the aldehyde RCHO and molybdenum dimers under mild conditions (Scheme I). This reaction is significant both as an example of reductive elimination involving two metal centers, and as a model for the aldehyde forming step in the oxo process. Mechanistic studies on the cobalt catalyzed hydroformylation of alkenes by carbon monoxide and hydrogen, the oxo process, have firmly established that hydrido cobalt tetracarbonyl is the active chain carrying intermediate in this system.^{2,3} However despite evidence^{2B} that the bimolecular reaction of HCo(CO)_4 with a cobalt acyl complex is the mechanism for aldehyde formation under stoichiometric conditions (25°C , 1 atm), researchers in this field have argued that direct reduction of a cobalt acyl by H_2 is responsible for aldehyde production under reaction conditions.² This conclusion and most of the arguments in support of it have been brought into considerable question by a recent re-examination of the equilibrium $\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightleftharpoons 2 \text{HCo(CO)}_4$ under high pressure and high temperature conditions.³ The reaction of molybdenum hydride 1 with molybdenum alkyls 2 to give aldehydes, therefore, represents an important stoichiometric model system supporting the proposition that aldehyde formation occurs by the reaction of HCo(CO)_4 with cobalt acyls in the hydroformylation of alkenes.

Scheme I

+

64

+

The reaction of $\text{CpMo(CO)}_3\text{H}$ (1) with $\text{CpMo(CO)}_3\text{R}$ (2, $\text{R} = \text{CH}_3$, C_2H_5 , CH_2Ph) in THF at between 25 and 50°C was observed to be bimolecular (first order in each reactant) leading to a quantitative yield of aldehyde and the molybdenum dimers $[\text{CpMo(CO)}_3]_2$ (3a) and $[\text{CpMo(CO)}_2]_2$ (4a) (Scheme I). Some of the observed second order rate constants are listed in Table 1. The rate of this reaction was found to be highly dependent upon the molybdenum alkyl involved, following the reactivity order $\text{C}_2\text{H}_5 > \text{CH}_3 > \text{CH}_2\text{Ph}$. In addition the reaction rate was found to exhibit a moderate solvent dependence, proceeding at least an order of magnitude faster in THF than in benzene, and no reaction was observed in hexane solution after 7 days at 70°C. The reaction become first order (independent of the concentration of 1) in benzene.⁴ The rate of reaction of 1 with 2b in THF was unaffected by 10 atmospheres of carbon monoxide pressure.

These observations are analogous to some earlier work on the reaction of molybdenum alkyls with phosphines, only with the inverse solvent dependence. In 1967 Butler, Basolo, and Pearson⁵ reported a kinetic study of the reaction of $\text{CpMo(CO)}_3\text{CH}_3$ (2a) with phosphines and phosphites to give the acyl complexes $\text{CpMo(CO)}_2(\text{PR}_3)[\text{C(O)R}]$ (6). They found that the reaction was first order (in 2a) and reasonably independent of the added ligand and its concentration in THF. However in toluene the reaction was found to be much slower, following second order kinetics. Similarly Craig and Green found that this same reaction was first order in acetonitrile and chloroform.⁶ These results were

Table 1. Second Order Rate Constants for the Reaction of 1a
with $\text{CpMo}(\text{CO})_3\text{R}$ in THF.

Complex	R	T ($^{\circ}\text{C}$)	k ($\text{M}^{-1}\text{sec}^{-1}$)
2a	$-\text{CH}_3$	50	4.0×10^{-3}
2b	$-\text{CH}_2\text{CH}_3$	25	8.5×10^{-4}
2c	$-\text{CH}_2\text{Ph}$	50	2.5×10^{-5}

interpreted as being consistent with a mechanism involving a preequilibrium to give the unsaturated intermediate acyl complex $\text{CpMo(CO)}_2[\text{C(O)R}]$ (5) followed by addition of phosphine (Scheme II).^{5,6} The second order rate law observed in toluene was attributed to a slow direct bimolecular reaction pathway. The rate expression for the mechanism outlined in Scheme II has the form shown in eq (1).

$$\frac{-d[2]}{dt} = \frac{k_1 k_2 [2] [\text{PR}_3]}{k_{-1} + k_2 [\text{PR}_3]} \quad (1)$$

Bergman and Jones¹ were able to show that reaction of 1 with phosphine complex $\text{CpMo(CO)}_2(\text{PPh}_3)[\text{C(O)R}]$ (6b, R = C_2H_5) in THF does not proceed at temperatures near 50°C, but only at more elevated temperatures where loss of phosphine can occur. Under these conditions formation of aldehyde was accompanied by the observation of small amounts of 2b. Independent kinetic measurements have determined an approximate value for the ratio k_2/k_3 of about 2.

Bergman and Jones used crossover labeling studies to rule out an alternative mechanism involving homolysis of the metal-acyl bond, to give acyl free radicals, followed by reaction with molybdenum hydride to give aldehyde. However, in the case of R = CH_2Ph a minor competitive mechanism, involving homolysis of the metal-alkyl bond leading to toluene, was observed.

The reaction of 1 with 2 to give aldehydes is one of the few examples known for in which bond formation between alkyl and hydride ligands involving two metal centers occurs. The mechanism

Scheme II

of reductive elimination of alkanes and carbonyl compounds from mononuclear hydrido alkyls and acyls is generally considered to be a facile intramolecular process. Yet isolable hydrido alkyl, and dialkyl complexes have been observed to reductively eliminate alkane by both intra- and inter-molecular mechanisms.^{7,8} At least four general mechanisms for the reductive elimination of R-H from hydride and alkyl ligands bound to two different metal centers have been identified:¹ a) alkyl migration to form an intermediate acyl complex, followed by reaction with metal hydride to give aldehyde (e.g., the reaction of 1 with 2); b) alkyl migration to form an intermediate metal acyl, followed by reaction with metal hydride to give alkane;⁸ c) loss of carbonyl, followed by reaction with metal hydride to give alkane;⁹ and d) metal-carbon bond homolysis to give an organic radical,⁹ followed by abstraction of a hydrogen atom from the metal hydride. A fifth alternative, involving a concerted carbon hydrogen bond forming process from organic ligands bound to adjacent metal centers in binuclear and larger metal complexes, has been widely discussed.¹⁰ However no well documented examples of this "binuclear" reductive elimination mechanism exist.¹¹

Considering the paucity of well behaved stoichiometric examples of "bimolecular" reductive elimination reactions, and the continuing inter- vs intra-molecular controversy in mononuclear systems, the details of the mechanism of reductive elimination of aldehydes from the reaction of molybdenum hydride with molybdenum alkyls is of particular interest. Bergman and

Jones proposed that the bimolecular reaction of the unsaturated intermediate 5 with molybdenum hydride gives the hydride bridged intermediate 7 containing a Mo-H-Mo three center, two electron bond. A number of stable complexes containing linear hydride bridges of this kind have been characterized.¹² However the mechanism through which this complex proceeds to give aldehyde was not established. It is this process, in which the intermediate 7 gives aldehyde, that the experiments presented here were designed to probe.

RESULTS

The Reaction of $\text{CpMo(CO)}_3\text{H}$ and MeCpMo(CO)CH_3 . As described in the previous section the reaction of molybdenum hydride 1 and molybdenum alkyls 2 gives two metal containing products, the dimers $[\text{CpMo(CO)}_3]_2$ (3), and $[\text{CpMo(CO)}_2]_2$ (4), in roughly equal amounts. The fate of the Mo atoms can be followed by labeling one of the reactants with a methylcyclopentadienyl ligand ($\text{MeCp} = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$). This can give six possible dimers 3a,b,c and 4a,b,c.

3a

4a

3b

4b

3c

4c

All six of these dimers are known and authentic mixtures can readily be prepared. The dimers 4a,b,c have a metal-metal triple bond, confirmed by an x-ray crystal structure on 4a; they exhibit a rich chemistry including the rapid addition of two molecules of carbon monoxide at room temperature to give the dimers 3a,b,c.¹³ The dimers 3a,b,c can be photochemically¹⁴ and thermally¹³ converted to 4a,b,c provided free CO is removed from the system.

Following the reaction of $\text{CpMo(CO)}_3\text{H}$ (1a) with $\text{MeCpMo(CO)}_3\text{CH}_3$ (2b), $\text{MeCpMo(CO)}_3\text{H}$ (1b) with $\text{CpMo(CO)}_3\text{CH}_3$ (2a), or 1b with $\text{CpMo(CO)}_3\text{Et}$ (2b) in THF-d_8 at 50°C by ^1H NMR shows these reactions cleanly give a mixture of dimers containing the

resonances for the fragments $\text{CpMo}(\text{CO})_3$, $\text{CpMo}(\text{CO})_2$, $\text{MeCpMo}(\text{CO})_3$, and $\text{MeCpMo}(\text{CO})_2$. However, distinguishing the two unsymmetrical dimers **3b** and **4b** from mixtures of the symmetrical dimers **3a** + **3c** and **4a** + **4c** is impossible by either NMR, IR or normal column chromatography. Whereas mass spectral analysis of mixtures of **3a,b,c** and **4a,b,c** has been achieved by others,¹³ the inherent complexity of such analysis with the present mixture led us to seek another method of analysis.

It was found that high pressure liquid chromatography (HPLC) using a reversed phase column (1 x 25 cm, Altex Corp. Ultrasphere-ODS, claiming virtually complete coverage) with water/acetonitrile (1:5) as eluant gives almost baseline separation of an authentic mixture of all dimers (see Figure 1).¹⁵ Under these conditions the most polar dimer, **4a**, elutes first and the least polar dimer, **3c**, elutes last.

Analysis of the products of the reaction of **1a** with **2d**, **1b** with **2a**, or **1b** with **2b** by HPLC revealed that the major metal containing products are the two unsymmetrical dimers **3b** and **4b** and only minor amounts of the other four dimers are formed (Figure 2). Thus two of the possible six dimers predominate in the reaction of molybdenum hydride and molybdenum alkyls when one of them contains a labeled cyclopentadienyl ligand, independent of the original location of the label. The analysis is complicated by the conversion of unreacted molybdenum hydride to the hexacarbonyl dimers in acetonitrile. Molybdenum hydride was shown to decompose in acetonitrile solution (the HPLC solvent) to

Figure 1. HPLC chromatogram of a Mixture of 3a,b,c and 4a,b,c.

Figure 2. HPLC Chromatogram of the Products of the Reaction
of 1b and 2b.

give the corresponding hexacarbonyl dimer (either 3a or 3c), in addition to some unidentified products. However, if all the molybdenum hydride has been consumed prior to the HPLC analysis, no spurious source of dimers hinders the analysis. The molybdenum alkyls and the dimers are stable to the analysis conditions.

The two dimers 3b and 4b are formed in roughly equal concentration, independent of the original position of the methylcyclopentadienyl "label" (i.e. 1b or 2d), or the molybdenum alkyl involved. If, however, a solution of 1a and 2d in THF is heated to 100°C for 15 hours, a nearly thermodynamic mixture of all six dimers is formed. At this temperature conversion of the initially obtained dimers 3b and 4b to the thermodynamic mixture of all six dimers can occur by a mechanism involving the thermal cleavage of the Mo-Mo bond (Scheme 3). This series of reactions is well established to occur at temperatures above 80°C.^{13,14,16}

The Reaction of $\text{CpMo}(^{13}\text{CO})_3\text{H}$ with $\text{CpMo}(\text{CO})_3\text{CH}_3$. Molybdenum hydride containing 93.8 atom % ^{13}CO was prepared from $[\text{CpMo}(^{13}\text{CO})_3]_2$ via the standard method involving reduction, followed by protonation.¹⁷ The labeled dimer was prepared by the repeated photochemical exchange¹⁴ of carbonyl ligands under an atmosphere of ^{13}CO . The carbonyl absorptions in the IR spectrum of the ^{13}CO labeled molybdenum hydride shift from 2020 and 1948 to 1977 and 1890 cm^{-1} , consistent with the expected isotope effect. Furthermore the ^1H NMR resonance for the hydride exists as a 1:3:1:3:1 quintet corresponding to coupling constants to the

trans and cis ^{13}CO 's of about 13 Hz. $\text{CpMo}(\text{CO})_3\text{H}$ is believed to have a square-pyramidal structure.¹⁷

Monitoring the reaction of 1 and 2 in THF by NMR shows that the primary product of the reaction is the triply bonded dimer 4, and only slowly does free CO add to give 0.5 equivalents of 3. Therefore, our analysis of the reaction of $\text{CpMo}(^{13}\text{CO})_3\text{H}$ with 2 concentrated upon the ^{13}CO content of 4. To analyze for this dimer the reaction solvent was removed and then 4 was isolated by either column chromatography (Florisil, eluting with hexanes/benzene) or by HPLC (reverse phase, 20% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ as eluant); for this separation column chromatography proved more convenient. The resulting purified dimer was then subjected to mass spectral analysis (50 eV, 150°C inlet temp.). Since molybdenum contains seven isotopes distributed over a mass range of 9 units, in significant amounts, the mass spectrum of $[\text{CpMo}(\text{CO})_2]_2$ containing a natural abundance of the elements has parent ions at 18 different m/e values (Figure 3). Analysis of these spectra when the dimers contain ^{13}C carbonyls was achieved by a least squares fit of the relative intensities of the parent ions assuming each of the isotopomers gave the same relative ratios at $(m/e + n)$ for n ^{13}CO 's. This method of analysis is explained in greater detail in appendix B. The net result is the percentage of 4 that contains $n = 0, 1, 2, 3$, or 4 ^{13}CO 's, and thus the average percentage of ^{13}CO in the product.

The reaction of $\text{CpMo}(^{13}\text{CO})_3\text{H}$ (1a) with 2a was carried out under two distinctly different conditions, and then analyzed for

Scheme III

the ^{13}CO content in 4 as described above. These results are presented in Table 2. In reaction 1 $1(^{13}\text{CO})_3$ and 2a were heated in sealed NMR tube to 50°C for 26 hours. Under these conditions any CO liberated during the reaction cannot escape and has time to add to 4 and result in scrambling of the carbonyl labels. In reactions 2 and 3 the reaction solution was heated to 50°C under a moderately vigorous purge of nitrogen or argon; in this case liberated CO is swept out of the system.

The observation of large amounts of 4a containing 0, 1 and 4 ^{13}CO 's immediately indicates the existence of a scrambling mechanism. It was conclusively shown that some scrambling of the CO's (presumably between product molecules) occurs under the mass spectral conditions. In a control experiment a sample of 4 from reaction 2 was mixed with some unlabeled 4 and then analyzed by mass spectrometry. The relative ratios of the ^{13}CO containing products changed in the resulting mass spectrum, implicating exchange of CO's between the natural abundance dimer and the ^{13}CO containing products. No conditions could be found that would completely eliminate this apparent scrambling; however, the total ^{13}CO content of the products always remained about the same. The similarity of the total ^{13}CO content in 4 from both experiments 2 and 3, where different reaction times are involved, suggests that any such scrambling must occur after the total CO content of the product has been determined. Curtis and Klingler have established that scrambling of the $\text{CpMo}(\text{CO})_2$ fragments in 4 does occur, but this mechanism is much too slow to account for our

Figure 3. Parent Ion Mass Spectrum of Natural Abundance 4a.

observations.¹³

In an attempt to eliminate this scrambling the product, 4, was converted to $\text{CpMo(CO)}_2(\text{PMe}_3)\text{CH}_3$ (2e) which is much more volatile. Analysis of 2e derived from reaction 3 in this way gives the results shown in Table 3. These results corroborate those in Table 2, and will be discussed in more detail in the next section.

Trapping Experiments. The following trapping experiments were designed that might trap possible intermediates of the type $[\text{CpMo(CO)}_3]^+$ or $[\text{CpMo(CO)}_3]^-$. In all cases no significant amounts of trapping products could be observed.

a) CH_3I . Bergman and Jones¹ reported that addition of a 10-fold excess of MeI to the reaction of 1a and 2b did not yield any observable $\text{CpMo(CO)}_3\text{CH}_3$, the expected product of reaction of $[\text{CpMo(CO)}_3]^-$ and CH_3I .¹⁸

b) LiCl . Addition of excess LiCl ($> 1\text{M}$) to the reaction of 1a with 2a at 50°C in THF did not result in any detectable formation of CpMo(CO)Cl by NMR or IR either during or after the reaction. The presence of the intermediate $[\text{CpMo(CO)}_3]^+$, a known compound,¹⁹ would have been expected to lead to reaction with chloride ion to give $\text{CpMo(CO)}_3\text{Cl}$.

c) $\text{CpMo(CO)}_3\text{Cl}$ and $\text{CpMo(CO)}_3\text{D}$. Attempts to trap the intermediate $[\text{CpMo(CO)}_3]^+$ in the reaction of 1a with 2 by the processes in equations (1) and (2) were thwarted by the facile exchange of chloride and hydride ligands in the starting complexes, equations (3) and (4).

Table 2. ^{13}CO Distribution in $(\text{CpMo}(\text{CO})_2)_2$ From the Reaction of $\text{CpMo}(^{13}\text{CO})_3\text{H}$ with $\text{CpMo}(\text{CO})_3\text{CH}_3$.

Rxn	Rxn ^a time	Percent of Molecules With n ^{13}CO 's					Corrected Average % ^{13}CO
		n= 0	1	2	3	4	
1 ^b	26	7	21	32	29	12	59
2 ^c	5	2	11	29	38	20	69
3 ^d	21	1	10	28	39	22	72.5
2 + 4a ^e	-	40	12	20	20	8	-
$\text{CpMo}(^{13}\text{CO})\text{H}$		0	1	16	83	-	93.8

^a50°C. ^bsealed tube. ^cunder a purge of Ar. ^dunder a purge of N_2 .

^ethe product of Rxn 2 was diluted with unlabeled 4a, then analyzed by mass spec.

Table 3. ^{13}CO Distribution in $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{CH}_3$ Derived from The Product of Reaction 3.

n = 0	Percent of Molecules With n ^{13}CO 's		Corrected Average % ^{13}CO
	1	2	
12	45	44	70.5

DISCUSSION

The reaction of molybdenum hydride (1) with molybdenum alkyls (2) in THF proceeds to give aldehyde and the two molybdenum dimers $[\text{CpMo}(\text{CO})_3]_2$ (3) and $[\text{CpMo}(\text{CO})_2]_2$ (4) as the sole metal containing products. Using a methylcyclopentadienyl ligand to label either the molybdenum hydride or molybdenum alkyl it was possible to determine the origin of the molybdenum centers in these dimers. At temperatures of 50°C and below it was found that the mixed dimers 3b and 4b, containing one labeled and one unlabeled cyclopentadienyl ligand, predominate. This result was found to be independent of which starting material was labeled. At temperatures greater than 80°C, however, a thermodynamic mixture of all six dimers was observed. At these temperatures secondary reactions involving metal-metal bond cleavage lead to equilibration of the product mixture (Scheme III). Thus the dimers 3b and 4b are the kinetic products of the reaction.

These observations qualitatively suggest, but do not require, that the metal-metal bond is formed prior to or concomitant with reductive elimination of aldehyde from intermediate 7. This kind of "concerted" mechanism would give dimers that contain one metal center derived from each reactant, in a process involving the intramolecular reductive elimination of aldehyde from intermediate 7 (vide infra). Alternatives to a "concerted" mechanism of this kind involve either proton or hydride transfer. Both of these possibilities lead to charged

intermediates that can still give unsymmetrical or mixed products under these conditions.

Bergman and Jones¹ were able to exclude proton transfer on the basis of three observations: a) the much less acidic $\text{CpMo(CO)}_2(\text{PMe}_3)\text{H}$ (**1c**) reacted with **2b** at a rate ($k_{25} = 2 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$) comparable to that for **1a**; b) addition of a 10 fold excess of CH_3I to the reaction of **1a** and **2b** did not trap any of the molybdenum anion $[\text{CpMo(CO)}_3]^-$; c) no reaction was observed between **2a** and acetic acid in THF-d_8 after 24 hours at 50°C ,²⁰ whereas trifluoroacetic acid reacts with **2a** (presumably via direct protonation of the unrearranged alkyl) to give methane.

A second alternative involving hydride transfer cannot be so easily ruled out. In this mechanism (Scheme IV) hydride transfer from **1** to the intermediate **5** gives $[\text{CpMo(CO)}_3]^+$ and the anionic hydrido acyl intermediate **9**. Reductive elimination of aldehyde from **9** to form an anionic $[\text{CpMo(CO)}_2]^-$ species, followed by recombination of this species with $[\text{CpMo(CO)}_3]^+$ could give the pentacarbonyl dimer **10**. Dimer **10** can either lose or add carbon monoxide to give the observed products **4** and **3** respectively. The inability of chloride ion to trap the proposed intermediate $[\text{CpMo(CO)}_3]^+$ is not sufficient to exclude this mechanism, because it cannot be shown that $\text{CpMo(CO)}_3\text{Cl}$ is stable to the reaction conditions (e.g. displacement of chloride by CpMo(CO)_n^- the other charged fragment in solution).

Finally there exists a "concerted" mechanism in which the bridging hydride in intermediate **7** is transferred to the metal in

Scheme IV

the acyl complex, facilitating formation of a metal-metal bond (Scheme V). In this mechanism loss of CO, hydride migration to the acyl-bound metal, and formation of the metal-metal bond (i.e. oxidative addition of the M-H bond to the second metal center) will give the intermediate 8. This hydrido-acyl complex undergoes reductive elimination of aldehyde and migration of CO from the other metal center to form $[\text{CpMo}(\text{CO})_2]_2$ (4a) directly. The direct formation of 4 in this manner is consistent with the observation that 4 is the principal metal-containing product observed by NMR at early reaction times.

These mechanisms make specific predictions concerning the origin of the carbonyl's that end up in the tetracarbonyl dimer 4. In the hydride transfer mechanism outlined in Scheme IV random loss of a carbonyl ligand from intermediate 10 will lead to 4 that has 3/5, or 60%, carbonyl's that came from the molybdenum hydride. Alternatively if intermediate 7 is not CO labile, then transfer of hydride and formation of a metal-metal bond can give an intermediate of the type 11. Reductive elimination of aldehyde from 11 will give the pentacarbonyl intermediate 10. This mechanism and any other that involves 10 as the intermediate preceding dimer formation will give the same prediction. However the mechanism presented in Scheme V predicts that three of the carbonyl's in 4, or 75%, come from the molybdenum hydride.

Scheme V

Labeling the carbonyl's in the molybdenum hydride starting material with ^{13}CO it now becomes possible to distinguish these mechanisms. The results presented in the Table 2, when corrected for the isotopic purity of the starting material, are in reasonable accord with the mechanism in Scheme V.

Under conditions where CO liberated during the course of the reaction has the chance to escape the system, i.e. under a nitrogen purge, 69 to 72.5 % of the carbonyls in 4 were found to come from 1. This observation approaches the value of 75% predicted by the mechanism in Scheme V, if all carbon monoxide liberated during the reaction is swept out of the system. Considering the inefficiency of the method employed to remove CO during the reaction this agreement seems good. Nevertheless the high degree of CO scrambling evident from the distribution of ^{13}CO 's in 4, Table 2, is worrisome. At least some of this scrambling appears to occur in the mass spectrometer.

In a closed system, where liberated CO cannot escape the system and has time to react with the initially formed products, 59% of the carbonyls in 4 originate from the molybdenum hydride. This is consistent with the fast reversible addition of CO to 4

to give intermediate 10, and the slow addition of a second molecule of free CO to form 3 (Scheme VI).

The dimer 4 was chemically converted to the much more volatile $\text{CpMo(CO)}_2(\text{PMe}_3)\text{CH}_3$ (2e), in an effort to eliminate mass spectral scrambling. Compound 2e was found to have a ^{13}CO content comparable to the original dimer. The distribution of ^{13}CO label in 2e is a less sensitive measure than in 4; however, even here at least some scrambling appears to have taken place. The observed ratios of 12, 45, and 44% should be compared to the values of 4, 50, and 46% for $n = 0, 1$, and 2 ^{13}CO 's predicted by Scheme V (Table 3). The mechanism in Scheme IV on the other hand would predict values of 18, 50, and 32% for this product.

The results presented here cannot be considered conclusive. In particular a good explanation for the origin of the ^{13}CO scrambling in 4 is lacking. However, if indeed the scrambling is occurring after the CO content in the products has been determined (i.e. between product molecules), then the observed average ^{13}CO content in 4 is most consistent with the mechanism in Scheme V.

If this conclusion is correct, then the observed loss of CO from the molybdenum alkyl, prior to product formation strongly suggests that intermediate 7 loses CO, enabling the hydride to migrate to the acyl-bound metal and the formation of a metal-metal bond. Thus it would appear that aldehyde is formed from the intramolecular reductive elimination of a hydrido-acyl metal complex.

Scheme VI

90

4

10

3

EXPERIMENTAL

General. All manipulations involving organomolybdenum complexes were carried out either by standard Schlenk techniques or in a Vacuum/Atmospheres Corp. Model HE-553 inert atmosphere glove box with continuously circulating nitrogen atmosphere and a model MO-40 recirculating purification system. All molybdenum alkyls and hydrides were stored cold (-40°C) and in the dark, except 2a which is more thermally stable. All reactions and subsequent manipulations of products were conducted so as to avoid photochemical side reactions; this involved foil wrapping of NMR tubes and reaction flasks, and the performance of column chromatography under dim, indirect light.

Proton Nuclear magnetic resonance (^1H NMR) spectra were obtained using a Varian EM-390 90 MHz spectrometer, or a 180 MHz FT-NMR instrument equipped with a Bruker superconducting magnet and a Nicolet Instrument Corp. 1180 data system and electronics assembled by Mr. Rudi Nunlist (U. C. Berkeley). Infrared (IR) spectra were obtained on a Perkin-Elmer 237 Grating Spectrophotometer. Microanalyses and mass spectra (MS) were obtained from the analytical facilities of the University of California at Berkeley. Mass spectral samples were prepared in capillaries by introducing the compound as a solution, evaporating the solvent, and then sealing the capillaries under an inert atmosphere. For analysis the capillaries were cracked open, inserted in the mass spectrometer probe, and evacuated with a minimum exposure to air. Photolyses were carried out through

pyrex using an Oriel Corp. focused beam apparatus and power supply equipped with an OSRAM 500 watt HBO Super Pressure Mercury Lamp.

High pressure liquid chromatography (HPLC) employed an Altex Scientific Inc. model 110A high pressure pump, a Rheodyne model 905-42 variable volume injector valve, and an Altex model 153 UV-VIS detector equipped with a 2mm pathlength 254 nm wavelength kit. Separations were achieved using a 1 x 25 cm Ultrasphere-ODS (Altex) reversed phase column claiming complete coverage of the active sites. The solvent was degassed by continuously purging the solvent reservoir with argon.¹⁵

Commercial samples of $[\text{CpMo}(\text{CO})_3]_2$ and $[\text{MeCpMo}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{MeCp} = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$) (Alfa) contained considerable amounts of non-volatile impurities. These impurities could be removed by column chromatography on Florisil, eluting with benzene or THF, and collecting the dimer which elutes as a red band. In less sensitive experiments (for example in the preparation of 2a) this procedure was not always followed, especially where the products could be sublimed away from these impurities. $\text{Mo}(\text{CO})_6$ was used without purification. NaCp and NaMeCp were prepared by the standard method from Na metal and the freshly cracked diene in THF. The compounds $\text{CpMo}(\text{CO})_3\text{H}$ (1a),¹⁷ $\text{CpMo}(\text{CO})_3\text{CH}_3$ (2a),¹⁸ $\text{CpMo}(\text{CO})_3\text{C}_2\text{H}_5$ (2b),¹⁸ $\text{MeCpMo}(\text{CO})_3\text{CH}_3$ (2d),¹⁸ and $\text{Mo}(\text{CO})_3\text{Cl}$ ^{13,15} were prepared by literature procedures, and purified by sublimation. Their IR and NMR spectra are summarized in Tables 4 and 5.

Table 4. ^1H NMR Data for $\text{CpMo}(\text{CO})_3\text{R}$ Complexes.

Complex:	Chemical Shifts ^a	
	Cp	R
1a: $\text{CpMo}(\text{CO})_3\text{H}$	5.56	-5.55
1b: $\text{MeCpMo}(\text{CO})_3\text{H}$	5.45	-5.45 (AA'BB', $J_{\text{AB}} = 17$, $J_{\text{AA'}} = 2.1$)
2a: $\text{CpMo}(\text{CO})_3\text{CH}_3$	5.45	0.40
2b: $\text{CpMo}(\text{CO})_3\text{Et}$	5.30	1.70 (q, $J = 6$) 1.44 (t, $J = 6$)
2c: $\text{CpMo}(\text{CO})_3\text{CH}_2\text{Ph}$	5.29	2.89 (s), 7.16 (m)
2d: $\text{MeCpMo}(\text{CO})_3\text{CH}_3$	5.26	0.32
$\text{CpMo}(\text{CO})_3\text{Cl}$	5.75	

^a in δ ppm in THF-d_8 , J is in Hz, singlets unless otherwise noted.

Table 5. Infrared Data for $\text{CpMo}(\text{CO})_3\text{R}$ Complexes.

Complex:	Solvent	$\nu(\text{CO}) \text{ cm}^{-1}$
1a: $\text{CpMo}(\text{CO})_3\text{H}$	THF	2020, 1948
1b: $\text{MeCpMo}(\text{CO})_3\text{H}$	THF	2020, 1930
1c: $\text{CpMo}({}^{13}\text{CO})_3\text{H}$	THF	1197 (w), 1978 (s), 1915 (sh), 1890 (s)
2a: $\text{CpMo}(\text{CO})_3\text{CH}_3$	THF	2015, 1930
2d: $\text{MeCpMo}(\text{CO})_3\text{CH}_3$	THF	2015, 1930
$\text{CpMo}(\text{CO})_3\text{Cl}$	CH_2Cl_2	2055, 1980

All solvents employed were thoroughly dried and degassed by the methods outlined in the previous chapter. Similarly THF- d_8 was distilled (reduced pressure) from sodium benzophenone ketyl prior to use. High pressure liquid chromatography (HPLC) solvents were not dried, but were millipore filtered to remove particulates prior to use.

The Synthesis of $MeCpMo(CO)_3H$, 1b. The previously unknown $MeCpMo(CO)_3H$ (1b, $MeCp = \eta^5-CH_3C_5H_4$) was prepared by the following adaptation of the standard method of synthesis for 1a. A solution of 1.05 g (3.72 mmol) $[MeCpMo(CO)_3]^-Na^+$ (prepared from $NaMeCp$ and $Mo(CO)_6$ by the literature method¹⁷) in 30 ml THF was treated with 0.7 g (4 mmol) p-toluenesulfonic acid as a THF solution in the glove box. A copious precipitate formed immediately. After 15 minutes an IR spectrum of this solution indicated only molybdenum hydride and no anion. The yellow solution was filtered and the solvent removed in vacuo to yield a red oil. This oil was distilled at reduced pressure to yield 1b as a pale yellow, light and thermally sensitive oil; b.p. 55-60°C (0.01 mmHg). IR(THF) $\nu(CO)$: 2015(s), 1930(s) cm^{-1} . 1H NMR(THF- d_8): δ -5.42 (s, 1H), 2.12 (s, 3H), 5.46 ppm (AA'BB' quartets, $J_{AB} = 17$ Hz, $J_{AA'} = 2.1$ Hz, 4H).

The Synthesis of 3a, 3b, and 3c. Standard Mixture. A solution of 200 mgs (0.4 mmol) $[CpMo(CO)_3]_2$ (3a) and 220 mg (0.42 mmol) $[MeCpMo(CO)_3]_2$ (3c) in 50 ml benzene was irradiated through pyrex for 12 hours with a 500 watt UV lamp, with cooling from a water bath. The solvent was removed in vacuo and the resulting

red residue was chromatographed on basic alumina I (2 x 25 cm column) eluting with THF. One red band was collected, and a blue-grey residue remained at the origin. The solvent was removed to yield a mixture of $[\text{CpMo}(\text{CO})_3]_2$ **3a**, $\text{MeCpMo}(\text{CO})_3-(\text{CO})_3\text{MoCp}$ **3b**, and $[\text{MeCpMo}(\text{CO})_3]_2$ **3c**. The HPLC chromatogram of this mixture is presented in Figure 4. Coinjection of samples of **3a** and **3c** determined the order of elution to be **3a**, **3b**, **3c**. Note that the relative ratios of these compounds is roughly 1:2:1. This is consistent with the expected equilibrium ratio of these isomers. IR(THF) $\nu(\text{CO})$: 2010 (w), 1960 (s), 1915 (s) cm^{-1} . ^1H NMR(THF- d_8): 2.15 (s), 5.30 (AA'BB' multiplet, $J_{AB} = 12$ Hz), 5.40 ppm (s).

The Synthesis of 4a, 4b, 4c. Standard Mixture. Following the procedure of Curtis and Klingler¹² a solution of 250 mg (0.51 mmol) **3a** and 250 mg (0.48 mmol) **3c** in 150 ml toluene was brought to reflux under a gentle N_2 purge. After 18 h the IR spectrum of this solution indicated complete conversion to product. The solvent was removed in vacuo. The resulting residue was extracted thoroughly with hexanes and the resulting solution filtered through a 2 gm plug of florisil. The florisil plug was washed with benzene-hexanes (1:1) to yield a red solution of the products. The solvent was removed to yield a mixture of $[\text{CpMo}(\text{CO})_2]_2$ (**4a**), $\text{MeCpMo}(\text{CO})_2\equiv(\text{CO})_2\text{MoCp}$ (**4b**), and $[\text{MeCpMo}(\text{CO})_2]_2$ (**4c**) as a red solid. The HPLC chromatogram of this mixture is shown in Figure 5. Again a 1:2:1 ratio of isomers is observed in accordance with the expected equilibrium mixture. IR(hexanes) $\nu(\text{CO})$: 1965(w), 1898(s), 1870(s) cm^{-1} . ^1H NMR(THF- d_8): δ 2.05 (s),

Figure 4. HPLC Chromatogram of an Authentic Mixture of
3a, b, c.
~ ~ ~

Figure 5. HPLC Chromatogram of an Authentic Mixture of

4a, b, c.
~ ~ ~

5.15 (AA'BB' d of quart., $J_{AB} = 5.6$, $J_{AA'} = 2.1$ Hz), 5.28 ppm (s).

The Synthesis of $[\text{CpMo}(\text{}^{13}\text{CO})_3]_2$. In a 250 ml round bottomed flask equipped with a vacuum stopcock a solution of 250 mg (0.51 mmol) $[\text{CpMo}(\text{CO})_3]_2$ in 100 ml benzene was degassed then charged with 5.4 mmol ^{13}CO (~94% ^{13}CO) (less than 1 atm pressure). The solution was irradiated with a 500 watt UV lamp for 5 hours with cooling from a water bath. The solution was taken through two freeze-pump-thaw cycles to remove free CO. This procedure was repeated a total of four times, the solvent was removed and the resulting residue was chromatographed on basic alumina I eluting with THF. One red band was collected. The solvent was removed to yield a red solid. Comparing the intensities of the parent ion at 490 and 489 m/e in the mass spectrum a rough isotopic purity of 93.7 atom % ^{13}CO could be calculated. IR(THF) $\nu(\text{CO})$: 1967(w), 1915(s), 1870(s) cm^{-1} .

The Synthesis of $\text{CpMo}(\text{}^{13}\text{CO})_3\text{H}$. A 25 ml Schlenk flask was charged with the entire 250 mg (~.51 mmol) $[\text{CpMo}(\text{}^{13}\text{CO})_3]_2$ in 20 ml THF, then capped with a rubber septum. Under nitrogen 0.5 ml (1.8 mmol) 0.65% Na/Hg amalgam was added via syringe. In less than 30 min the red solution had turned pale yellow indicating conversion to the anion. The solution was then transferred by cannula away from the amalgam to a Schlenk flask that also serves as a sublimator bottom. A solution of 250 mg (1.5 mmol) p-toluenesulfonic acid in 10 ml THF was added via cannula. The yellow solution turned almost clear with the formation of a fine white precipitate. After 15 minutes an IR spectrum of this

solution indicated quantitative formation of the hydride. The solvent was removed in vacuo, and the residue was sublimed (50-60° C, 0.01 mmHg) to yield a somewhat impure hydride. A second sublimation yielded 140 mg (55% overall yield based upon 3a) CpMo(¹³CO)H. Mass spectral analysis (see Appendix B) gave the following percentages of compounds: 1(¹³CO)₃ = 82.8 ±3%, 1(¹³CO)₂ = 15.9 ±3.1%, 1(¹³CO)₁ = 1.2 ±3.1%; or 93.8 atom % ¹³CO. IR(THF) ν(CO): 1997 (w), 1977 (s), 1915 (shoulder, w), 1890 (vs) cm⁻¹. ¹H NMR(THF-d₈): δ 5.55 (s, 5H), -5.52 ppm (1:3:1:3:1 quintet, J=13 Hz, 1H).

The Reactions of 1b with 2a, 1b with 2b, and 1a with 2d. In all cases the two starting materials were weighed into an NMR tube in the glove box. Then on a vacuum line THF-d₈ was condensed into the tube and it was sealed off under vacuum. The resulting solutions were heated in a temperature controlled water bath. The reaction progress was monitored by cooling the NMR tubes and recording the NMR spectrum at room temperature. Light was excluded from these solutions by wrapping the NMR tubes in foil. Analysis of the products was achieved by cracking the NMR tubes open in the dry box, removing the solvent, redissolving the resulting residue in CH₃CN, and analyzing by HPLC. High pressure liquid chromatographic (HPLC) analysis was achieved using a 1 x 25 cm Altex Ultrasphere-ODS reversed phase column, eluting with 20% H₂O/CH₃CN saturated with argon. 20-50 μl injections completely eluted over a 35 minute time period at a flow rate of 0.5 ml/min. Typical pressures at this flow rate were 400-600 psi.

The separation achieved under these conditions is demonstrated in the chromatogram of an authentic mixture of 3a,b,c and 4a,b,c shown in Figure 1.

A) A solution of 19 mg (0.077 mmol) 1a and 20 mg (0.073 mmol) 2d in 0.4 ml THF-d₈ was heated to 50(±.5)°C for 22 hours (approximately 57% reaction) and then analyzed by HPLC. The resulting chromatogram is presented in figure 6. In addition to 2d and products arising from decomposition of 1a in acetonitrile solution²¹, the dimers 3a, 3b, and 4b were observed.

B) A solution of 18 mg (0.07 mmol) 1b and 20 mg (0.077 mmol) 2a in 0.4 mmol THF-d₈ was heated to 50(±.5)°C for 22 hours (approximately 64% reaction) and then analyzed by HPLC. The resulting chromatogram is shown in Figure 7. In addition to unreacted 2a and products from decomposition of 1b in acetonitrile,²¹ significant amounts of the dimers 3b, 3c, and 4b are observed.

C) A solution of 22 mg (0.085 mmol) 1b and 27 mg (0.098 mmol) 2b in 0.58 ml THF-d₈ was allowed to react at room temperature for 48 hours, at which point no unreacted 1b could be observed by NMR. HPLC analysis gave the chromatogram in Figure 2. In addition to unreacted 2b the only other compounds present in significant amounts are the dimers 3b and 4b.

D) A solution of 17 mg (0.065 mmol) 1b and 18 mg (0.069 mmol) 2a in 0.78 ml THF-d₈ was heated to 100°C for 15 hours. HPLC analysis gave the chromatogram in Figure 8. All six dimers 3a,b,c and 4a,b,c are observed in significant concentrations. The

Figure 6. HPLC Chromatogram of the Reaction Products of
The Reaction of 1a and 2d .

^xdecomposition products of molybdenum hydride

Figure 7. HPLC Chromatogram of the Products of the Reaction of 1b and 2a.

^xdecomposition products of molybdenum hydride.

Figure 8. HPLC Chromatogram of the Products of the
Reaction of $\tilde{1b}$ and $\tilde{2a}$ at 100°C for 15 hours.

relative ratio of these dimers closely resembles the equilibrium mixture in Figure 1.

The products are labeled in these chromatograms. All known compounds were identified by coinjection of authentic samples. Reaction of $\text{CpMo}(^{13}\text{CO})_3\text{H}$ with $\text{CpMo}(\text{CO})_3\text{CH}_3$. Reaction 1: In the dry box 7 mg (0.028 mmol) $\text{CpMo}(^{13}\text{CO})_3\text{H}$ and 21 mg (0.08 mmol) 2a were weighed into an NMR tube. Then on a vacuum line 0.5 ml THF-d_8 was condensed into the tube and it was sealed off under a vacuum. The solution was heated to $50(\pm 0.5)^\circ\text{C}$ for 20 hours (88% consumption of hydride). The tube was cracked open in the dry box and the solvent removed. The resulting residue was chromatographed by HPLC on a reversed phase column under conditions identical to those in the previous experiment. Only 3a, 4a, and 2a and a small amount of molybdenum hydride decomposition products could be detected. 4a was collected under argon, the solvent was removed and the resulting red solid was analyzed by mass spectrometry. The relative percentages for molecules containing n ^{13}CO 's ($n = 0, 1, 2, 3, 4$) was evaluated by a least-squares treatment of the relative intensities of the 20 line parent ion "envelope"; details of this analysis are given in Appendix B. The results of the least squares treatment are presented in Table 2.

Reaction 2: A solution of 10 mg (0.04 mmol) $\text{CpMo}(^{13}\text{CO})_3\text{H}$ and 20 mg (0.077 mmol) 2a in 2 ml THF prepared in a 50 ml Schlenk flask equipped with a reflux condenser capped with a rubber septum. The solution was heated to $50(\pm 2)^\circ\text{C}$ in the dark with an oil bath

while a vigorous purge of argon was maintained through needles in the rubber septum. After 5 hours heating was discontinued. The reflux condenser was replaced with a glass stopper and the solvent was removed. 4a was isolated by column chromatography in the dark on a 1 x 15 cm florisil column eluting first with 10% benzene/hexane (50 ml), next with 50% benzene/hexane (50 ml), then 75% benzene/hexane. A pale yellow fraction containing 1a and 2a eluted first, followed by a very small red band containing 3a, 4a eluted last as a yellow-orange band. No compounds appeared to remain on the column and no observable decomposition occurred. Molybdenum hydride is stable to florisil but not alumina or silica. The solvent was removed from the fraction containing 4a and mass spectral samples were prepared in capillaries. Analysis of the mass spectrum in the manner described in Appendix B gave the data presented in Table 2.

Reaction 3: A solution of 20 mg (0.08 mmol) $\text{CpMo}(\text{}^{13}\text{CO})_3\text{H}$ and 22 mg (0.085 mmol) 2a in 2 ml THF was heated to $50(\pm 2)^\circ\text{C}$ for 21 hours under a nitrogen purge. Isolation of 4a by column chromatography and mass spectral analysis gave the results presented in Table 2.

A sample of 4a isolated from this experiment (< 1 mg) was dissolved in 1 ml THF and placed in a 5 ml flask with a teflon stopcock. On a vacuum line an excess of PMe_3 (~10 mmol) was condensed into the flask.¹³ The solution was allowed to stir for 40 minutes at room temperature, and then the volatiles were removed. The resulting red solid was dissolved in 1 ml THF and

treated with an excess of 0.6% Na/Hg amalgam (~2 mmol) it turned a pale yellow color. After 5 minutes the solution was pipetted away from the amalgam and placed in a clean 25 ml Schlenk flask. Then an excess of CH_3I (3 mmol) was added via syringe through a septum. After 10 minutes the solvent was removed to yield $\text{CpMo}(\text{CO})_2(\text{PMe}_3)\text{CH}_3$ (2e), as an off-white solid. An authentic sample of 2e was prepared in the identical manner from natural abundance 4a. Mass spectral analysis in a manner identical to that for 4a gave the data shown in Table 3.

Trapping Experiments using LiCl. A solution of 20 mg (0.08 mmol) 1a, 20 mg (0.077 mmol) 2a and 120 mg (3 mmol) LiCl in 1 ml THF was heated to 50°C in a Schlenk flask equipped with a reflux condenser for 40 hours while monitoring by IR at regular intervals. A very weak absorption at 2050 cm^{-1} was observed, in addition to the expected absorptions at 2015, 1960, 1930, 1855 cm^{-1} , but no strong absorption at 1980 cm^{-1} (characteristic of $\text{CpMo}(\text{CO})_3\text{Cl}$) was observed.

In a similar experiment 17 mg (0.07 mmol) 1a, 18 mg (0.07 mmol) 2a and 20 mg (0.5 mmol) LiCl were weighed into an NMR tube. On a vacuum line 0.65 ml THF-d_8 was condensed into the NMR tube and it was sealed off under a vacuum. The solution was heated to 50°C in a water bath and NMR spectra were recorded at regular intervals at room temperature. No Cp resonance at $\delta 5.65$ ppm for $\text{CpMo}(\text{CO})_3\text{Cl}$ could be observed. After 16 hours of heating the NMR tube was cracked open and an IR spectrum recorded in $\text{d}_6\text{-THF}$. Again a very weak absorption at 2050 cm^{-1} was observed, however

the absence of a band at 1980 cm^{-1} leads to the conclusion that LiCl does not trap $[\text{CpMo}(\text{CO})_3]^+$ to give $\text{CpMo}(\text{CO})_3\text{Cl}$ in these reactions.

The Reaction of lb with $\text{CpMo}(\text{CO})_3\text{Cl}$. In the dry box 10 mg (0.038 mmol) lb , 20 mg (0.077 mmol) 2a , and 20 mg (0.093 mmol) $\text{CpMo}(\text{CO})_3\text{Cl}$ were weighed into an NMR tube. Then on a vacuum line 0.5 ml THF-d_8 was condensed in the tube and it was sealed off under a vacuum. The initial NMR spectrum after warming to room temperature already contained 1a , and a new MeCp resonance at 1.98 ppm, most likely $\text{MeCpMo}(\text{CO})_3\text{Cl}$. No lb could be observed. Clearly all of lb was converted to 1a , presumably with concomitant formation of $\text{MeCpMo}(\text{CO})_3\text{Cl}$, at a point where no reaction between 1 and 2a had taken place yet.

The Reaction of $\text{CpMo}(\text{CO})_3\text{D}$ with lb . In the dry box 20 mg (0.081 mmol) $\text{CpMo}(\text{CO})_3\text{D}$, $\text{1a(d}_1\text{)}$, 21 mg (0.08 mmol) lb , and 11 mg (0.042 mmol) 2a were weighed into an NMR tube. On a vacuum line 0.5 ml THF-d_8 was condensed into the NMR tube and it as sealed off under a vacuum. After 30 minutes at room temperature the NMR spectrum revealed that virtually equal amounts of 1a and lb were present in solution. A similar reaction in benzene- d_6 of 10 mg (0.04 mmol) $\text{1a(d}_1\text{)}$ and 15 mg (0.06 mmol) lb also gave considerable 1a at room temperature in less than 10 minutes. These reactions appear to have reached equilibrium faster than their NMR spectra could be recorded.

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APPENDIX A

X-ray Crystal Structure Data For
Z-Ni(acac)(PPh₃) [C(Ph)=C(CH₃)Ph].

Contents

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Figure 1. ORTEP drawing of full asymmetric unit.

Figure 2: Schematic of atom numbering scheme.

Molecule A Molecule B

Table 1. Interatomic Distances (Å) and Angles (°).

Molecule A Distances:

Nil-P1	2.1783
Nil-C1	1.8970
Nil-O1	1.9101
Nil-O2	1.9228
P1-C21	1.8205
P1-C20	1.8287
P1-C33	1.8197
O1-C3	1.2748
O2-C5	1.2822
C1-C7	1.3271
C1-C9	1.4685
C2-C3	1.5015
C3-C4	1.3589
C4-C5	1.3554
C5-C6	1.5054
C7-C8	1.5268
C7-15	1.4825
C9-C10	1.3772
C9-C14	1.4002
C10-C11	1.4037
C11-C12	1.3639
C12-C13	1.3576
C13-C14	1.3964
C15-C16	1.3823
C15-C20	1.4087
C16-C17	1.3883
C17-C18	1.3845
C18-C19	1.3386

Molecule A Distances (cont):

C19-C20	1.3812
C21-C22	1.3843
C21-C26	1.3662
C22-C23	1.3962
C23-C24	1.3668
C24-C25	1.3734
C25-C26	1.3898
C27-C28	1.3826
C27-C32	1.3864
C28-C29	1.4116
C29-C30	1.3554
C30-C31	1.3677
C31-C32	1.4037
C33-C34	1.3698
C33-C38	1.4025
C34-C35	1.3876
C35-C36	1.3575
C36-C37	1.3623
C37-C38	1.4146

Molecule B Distances:

Ni2-P2	2.1634
Ni2-O3	1.8970
Ni2-O4	1.8948
Ni2-C44	1.8935
P2-C58	1.8057
P2-C65	1.8102
P2-C71	1.8196

Table 1. Continued

<u>Molecule B Distances (cont):</u>		<u>Molecule B Distances (cont):</u>			
O3-C42	1.2985	C59-C64	1.3737		
O4-C40	1.2770	C60-C61	1.3898		
C39-C40	1.5310	C61-C62	1.3841		
C40-C41	1.3432	C62-C63	1.3534		
C41-C42	1.3560	C63-C64	1.3975		
C42-C43	1.5317	C65-C66	1.4042		
C44-C45	1.3093	C65-C70	1.3764		
C44-C47	1.4695	C66-C67	1.3877		
C45-C46	1.5546	C67-C68	1.3661		
C45-C53	1.4812	C68-C69	1.3649		
C47-C48	1.4110	C69-C70	1.3940		
C47-C52	1.3556	C71-C72	1.3762		
C48-C49	1.4128	C71-C76	1.3923		
C49-C50	1.3579	C72-C73	1.4127		
C50-C51	1.3536	C73-C74	1.3559		
C51-C52	1.3815	C74-C75	1.3594		
C53-C54	1.3960	C75-C76	1.4042		
C53-C58	1.3980	<u>Molecule A Angles:</u>			
C54-C55	1.3905	O1	Nil	P1	175.79
C55-C56	1.3441	O2	Nil	P1	87.01
C56-C57	1.3591	O2	Nil	O1	92.90
C57-C58	1.4053	O2	Nil	Cl	176.22
C59-C60	1.3843	Cl	Nil	P1	93.16

Table 1. Continued

Molecule A Angles (cont):

C1	Nil	O1	87.20
C21	P1	Nil	109.48
C27	P1	Nil	122.64
C27	P1	C21	103.32
C27	P1	C33	102.05
C33	P1	Nil	113.11
C33	P1	C21	104.43
C3	O1	Nil	124.73
C5	O2	Nil	123.94
C7	C1	Nil	123.95
C7	C1	C9	127.93
C7	C1	Nil	109.71
C2	C3	O1	114.38
C2	C3	C4	120.40
C4	C3	O1	125.19
C5	C4	C3	125.29
C4	C5	O2	125.86
C6	C5	O2	112.95
C6	C5	C4	121.17
C8	C7	C1	123.57
C15	C7	C1	122.57
C15	C7	C8	113.85
C10	C9	C1	122.35
C14	C9	C1	120.49
C14	C9	C10	116.97
C11	C10	C9	121.96
C12	C11	C10	119.58

Molecule A Angles (cont):

C13	C12	C11	120.00
C14	C13	C12	120.86
C13	C14	C9	120.62
C16	C15	C7	123.52
C20	C15	C7	119.65
C20	C15	C16	116.83
C17	C16	C15	121.56
C18	C17	C16	118.97
C19	C18	C17	121.31
C20	C19	C18	119.87
C19	C20	C15	121.44
C22	C21	P1	117.83
C26	C21	P1	124.34
C26	C21	C22	117.83
C23	C22	C21	121.69
C24	C23	C22	119.08
C25	C24	C23	120.02
C26	C25	C24	120.17
C25	C26	C21	121.20
C28	C27	P1	121.89
C32	C27	P1	119.11
C32	C27	C28	118.99
C29	C28	C27	119.80
C30	C29	C28	119.47
C31	C30	C29	122.46
C30	C31	C32	118.02

Table 1. Continued

Molecule A Angles (cont):

C31	C32	C27	121.26
C34	C33	P1	120.29
C38	C33	P1	121.20
C38	C33	C34	118.51
C35	C34	C33	120.80
C36	C35	C34	121.19
C37	C36	C35	119.73
C36	C37	C38	120.33
C37	C38	C33	119.44

Molecule B Angles:

O3	Ni2	P2	85.81
O4	Ni2	P2	176.43
O4	Ni2	O3	92.88
C44	Ni2	P2	93.21
C44	Ni2	O3	172.97
C44	Ni2	O4	88.50
C59	P2	Ni2	112.83
C65	P2	Ni2	107.48
C65	P2	C59	103.42
C71	P2	Ni2	124.43
C71	P2	C59	103.13
C71	P2	C65	103.38
C42	O3	Ni2	126.15
C40	O4	Ni2	124.75
C39	C40	O4	112.84
C41	C40	O4	127.35
C41	C40	C39	119.81
C42	C41	C40	124.43
C41	C42	O3	124.25

Molecule B Angles (cont):

C43	C42	O3	111.55
C43	C42	C41	124.21
C45	C44	C47	124.15
C45	C44	Ni2	126.18
C47	C44	Ni2	109.36
C46	C45	C44	123.77
C52	C45	C44	122.09
C53	C45	C46	114.13
C48	C47	C44	119.38
C52	C47	C44	124.91
C52	C47	C48	115.60
C49	C48	C47	121.03
C50	C49	C48	120.08
C51	C50	C49	119.07
C52	C51	C50	120.98
C51	C52	C47	123.18
C54	C53	C45	120.23
C58	C53	C45	122.98
C58	C53	C54	116.76
C55	C54	C53	120.59
C56	C55	C54	121.34
C57	C56	C55	120.50
C58	C57	C56	119.48
C57	C58	C53	121.30
C60	C59	P2	119.09
C64	C59	P2	123.03

Table 1. Continued
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Molecule B Angles (cont):

C64	C59	C60	117.88
C61	C60	C59	120.68
C62	C61	C60	119.57
C61	C62	C63	120.91
C62	C63	C64	118.65
C63	C64	C59	122.20
C66	C56	C70	118.44
C66	C65	P2	117.74
C70	C65	P2	123.76
C67	C66	C65	119.72
C66	C67	C68	120.60
C67	C68	C69	120.48
C68	C69	C70	119.67
C65	C70	C69	121.07
C72	C71	P2	122.15
C76	C71	P2	119.74
C76	C71	C72	118.04
C73	C72	C71	121.03
C74	C73	C72	119.04
C75	C74	C73	121.84
C76	C75	C74	119.11
C75	C76	C71	120.89

Table 2. Fractional Coordinates.

	X	Y	Z	U11	U22	U33	U12	U13	U23
Nil	73930 (6)	29967 (9)	51551 (6)	410 (7)	389 (7)	449 (7)	118 (5)	-117 (5)	5 (5)
P1	65425 (12)	39544 (18)	52611 (13)	380 (14)	389 (14)	406 (14)	118 (11)	- 57 (11)	65 (11)

	X	Y	Z	B
O1	8166 (3)	2106 (5)	4976 (3)	3.93 (0.11)
O2	6552 (3)	1572 (5)	4840 (3)	4.12 (0.12)
C1	8196 (5)	4389 (7)	5542 (5)	3.53 (0.17)
C2	8838 (5)	716 (8)	4399 (6)	5.58 (0.21)
C3	8091 (5)	1104 (7)	4568 (5)	3.82 (0.18)
C4	7401 (5)	336 (7)	4318 (5)	4.36 (0.19)
C5	6679 (5)	569 (7)	4484 (5)	4.15 (0.19)
C6	5931 (6)	-372 (8)	4234 (6)	6.80 (0.24)
C7	1297 (5)	4854 (7)	4946 (5)	3.91 (0.18)
C8	675 (5)	3711 (8)	4621 (5)	5.46 (0.21)
C9	8233 (5)	4411 (7)	6412 (5)	3.48 (0.17)
C10	7553 (5)	4309 (7)	7068 (5)	4.11 (0.18)
C11	7578 (6)	4238 (8)	7881 (6)	5.41 (0.21)
C12	8294 (6)	4254 (8)	8032 (6)	5.89 (0.22)
C13	8976 (6)	4352 (9)	7398 (6)	6.56 (0.24)
C14	8958 (5)	4441 (7)	6591 (5)	4.99 (0.20)
C15	8703 (5)	4964 (7)	4139 (5)	3.61 (0.18)
C16	8693 (5)	5828 (8)	3770 (6)	5.35 (0.20)
C17	8677 (6)	5611 (8)	2914 (6)	6.11 (0.22)
C18	8694 (5)	4511 (8)	2416 (6)	5.62 (0.22)
C19	8715 (5)	3655 (8)	2747 (6)	5.08 (0.21)
C20	8717 (5)	3862 (7)	3601 (5)	3.95 (0.13)
C21	6041 (5)	3338 (7)	4360 (5)	3.38 (0.17)
C22	6531 (5)	3232 (8)	3550 (6)	5.38 (0.21)
C23	6199 (6)	2795 (9)	2822 (6)	6.33 (0.24)
C24	5369 (6)	2445 (8)	2913 (6)	5.97 (0.22)
C25	4873 (6)	2534 (8)	3712 (6)	5.53 (0.21)
C26	5213 (5)	2976 (7)	4430 (5)	4.51 (0.19)
C27	3134 (5)	4452 (7)	4695 (5)	3.54 (0.17)
C28	3235 (5)	3986 (8)	5304 (5)	4.84 (0.19)
C29	2982 (6)	2748 (9)	5239 (6)	5.93 (0.22)
C30	2643 (6)	2030 (8)	4577 (6)	5.81 (0.23)
C31	2534 (6)	2457 (8)	3961 (6)	5.66 (0.22)
C32	2788 (5)	3687 (7)	4026 (5)	4.28 (0.18)

Table 2. (continued)

	X	Y	Z	B
C33	5708 (4)	3789 (7)	6191 (5)	3.15 (0.16)
C34	5528 (5)	2887 (7)	6607 (5)	3.91 (0.18)
C35	4903 (5)	2766 (8)	7326 (6)	5.05 (0.20)
C36	4445 (5)	3525 (8)	7633 (5)	5.03
C37	4604 (6)	4432 (8)	7237 (6)	6.11 (0.23)
C38	5241 (5)	4583 (8)	6505 (6)	5.14 (0.20)

	X	Y	Z	U11	U22	U33	U12	U13	U23
Ni2	76322 (6)	7100 (10)	88218 (6)	466 (7)	695 (8)	379 (7)	256 (6)	-74 (5)	101 (6)
P2	84188 (13)	4491 (19)	94735 (13)	425 (14)	529 (15)	313 (13)	167 (12)	-60 (11)	74 (11)

	X	Y	Z	B
03	8530 (3)	810 (5)	7876 (4)	5.07 (0.13)
04	6942 (3)	845 (5)	8207 (4)	4.73 (0.12)
C39	6458 (6)	1009 (8)	7099 (6)	6.63 (0.24)
C40	7158 (5)	973 (7)	7434 (6)	4.81 (0.19)
C41	7900 (6)	1062 (8)	6919 (6)	4.90 (0.21)
C42	8551 (5)	998 (8)	7143 (6)	5.20 (0.20)
C43	9404 (7)	1141 (10)	6564 (7)	9.00 (0.30)
C44	6799 (5)	808 (7)	9817 (5)	4.13 (0.19)
C45	3753 (5)	85 (7)	-127 (5)	4.26 (0.18)
C46	4406 (6)	-52 (8)	-965 (6)	6.11 (0.22)
C47	6806 (5)	2047 (7)	144 (5)	4.46 (0.19)
C48	6143 (7)	2391 (10)	114 (7)	8.14 (0.28)
C49	6152 (8)	3587 (12)	369 (8)	9.16 (0.33)
C50	6798 (6)	4425 (9)	664 (6)	6.66 (0.24)
C51	7426 (6)	4095 (8)	712 (6)	5.41 (0.21)
C52	7432 (5)	2932 (8)	437 (5)	4.92 (0.20)
C53	3794 (5)	1328 (7)	289 (5)	4.31 (0.19)
C54	3783 (5)	1708 (7)	1160 (5)	4.69 (0.19)
C55	3834 (6)	2878 (8)	1954 (6)	5.72 (0.22)
C56	3893 (6)	3674 (9)	1113 (7)	7.10 (0.25)
C57	3911 (6)	3353 (10)	263 (7)	7.72 (0.27)
C58	3870 (6)	2180 (9)	-154 (6)	6.33 (0.24)
C59	9232 (5)	1776 (7)	9733 (5)	3.61 (0.17)
C60	9500 (6)	2633 (8)	9244 (6)	5.98 (0.22)

Table 2. (continued)

	X	Y	Z	B
	-----	-----	-----	-----
C61	10149 (7)	3641 (10)	9401 (7)	7.77 (0.27)
C62	10523 (6)	3794 (9)	10059 (7)	7.39 (0.26)
C63	10248 (6)	2995 (9)	10571 (6)	5.82 (0.22)
C64	9610 (5)	1972 (7)	10389 (5)	4.48 (0.19)
C65	11043 (5)	547 (7)	1271 (5)	3.54 (0.17)
C66	11513 (5)	1661 (7)	1635 (5)	4.31 (0.19)
C67	11126 (5)	2446 (8)	2219 (5)	5.18 (0.20)
C68	10293 (5)	2135 (8)	2460 (5)	4.99 (0.20)
C69	9826 (5)	1050 (7)	2123 (5)	4.50 (0.19)
C70	10205 (5)	256 (7)	1527 (5)	4.04 (0.18)
C71	1940 (5)	154 (7)	9561 (5)	3.58 (0.17)
C72	1793 (5)	1158 (7)	9522 (5)	4.80 (0.20)
C73	2064 (6)	1595 (9)	8759 (6)	6.00 (0.23)
C74	2466 (5)	1002 (8)	8056 (6)	5.65 (0.22)
C75	2602 (5)	-12 (8)	8060 (6)	5.52 (0.21)
C76	2343 (5)	-437 (7)	8821 (5)	4.34 (0.19)

UIJ HAS BEEN MULTIPLIED BY 10^{**4} . THE CONVERSION OF BIJ TO UIJ FOR I.NE.J INCLUDES MULTIPLICATION BY $1/2$.

	X	Y	Z	B
	-----	-----	-----	-----
HS1	0.742979	-0.044699	0.397262	5.45
HS2	0.798219	0.116739	0.633481	6.37
HS3	0.655458	0.272330	0.225769	7.52
HS4	0.513092	0.214594	0.240832	6.94
HS5	0.428094	0.226918	0.376183	6.67
HS6	0.485158	0.303181	0.499767	5.69
HS7	0.712489	0.348345	0.349502	4.62
HS8	0.583876	0.230460	0.638456	4.94
HS9	0.478924	0.212312	0.762955	6.28
HS10	0.400598	0.342580	0.813126	6.09
HS11	0.428158	0.499232	0.746227	7.12
HS12	0.536168	0.523070	0.621885	6.14
HS13	0.349010	0.451275	0.577305	5.85
HS14	0.303754	0.240500	0.566263	7.16

Table 2. (continued)

	X	Y	Z	B
HS15	0.246607	0.117478	0.452751	6.98
HS16	0.229334	0.192398	0.347583	6.86
HS17	0.271174	0.401579	0.359953	5.31
HS18	0.922081	0.252366	0.878536	6.82
HS19	1.032929	0.423325	0.904219	8.76
HS20	1.099657	0.449220	1.014875	8.41
HS21	1.048945	0.313754	1.105506	6.10
HS22	0.942588	0.136666	1.073197	5.75
HS23	0.149159	0.156134	1.003105	5.87
HS24	0.197050	0.231999	0.875150	7.14
HS25	0.265037	0.130110	0.753146	6.77
HS26	0.288772	-0.041984	0.754037	6.56
HS27	0.245073	-0.116125	0.883574	5.54
HS28	0.987171	-0.050632	0.126341	5.21
HS29	0.923060	0.082959	0.229917	5.57
HS30	1.002822	0.268011	0.288081	6.24
HS31	1.145084	0.323445	0.245763	6.09
HS32	1.210933	0.186921	0.147128	5.47
HS33	0.703386	0.426837	0.695544	5.21
HS34	0.708861	0.417746	0.833424	6.63
HS35	0.831789	0.421576	0.860299	7.15
HS36	0.948070	0.436978	0.751501	7.56
HS37	0.944885	0.449402	0.614344	5.85
HS38	0.870718	0.661569	0.413781	6.29
HS39	0.866718	0.622729	0.266222	7.12
HS40	0.866723	0.435280	0.181625	6.78
HS41	0.873404	0.288284	0.237853	6.28
HS42	0.873112	0.322117	0.383187	5.18
HS43	0.375758	0.114592	0.149141	5.80
HS44	0.382897	0.312739	0.216080	6.70
HS45	0.392984	0.449908	0.140641	7.95
HS46	0.393654	0.394423	-0.004594	8.85
HS47	0.391351	0.193885	-0.077962	7.57
HS48	0.565158	0.177600	-0.004613	9.22
HS49	0.571797	0.381625	0.029512	10.62
HS50	0.680502	0.526800	0.084546	7.66
HS51	0.788274	0.469304	0.093996	6.56

Table 2. (continued)

	X	Y	Z	B
HS52	0.791604	0.275121	0.045076	6.14
HS53	0.9300	0.1274	0.4126	6.59
HS54	0.8919	0.07091	0.4939	6.59
HS55	0.87673	-0.00447	0.40034	6.59
HS56	0.4918	0.0092	-0.0795	7.64
HS57	0.43124	-0.08886	-0.12202	7.64
HS58	0.4360	0.034	-0.135	7.64
HS59	0.66362	0.11954	0.65578	7.68
HS60	0.605	0.0148	0.705	7.68
HS61	0.62027	0.15787	0.74934	7.68
HS62	0.9805	0.1838	0.6795	9.93
HS63	0.94076	0.04486	0.61245	9.93
HS64	0.947	0.181	0.628	9.93
HS65	0.082	0.302	0.4620	6.36
HS66	0.01221	0.37574	0.48757	6.36
HS67	0.0727	0.3643	0.401	6.36
HS68	0.6070	-0.1062	0.3875	7.05
HS69	0.55241	-0.06010	0.47286	7.05
HS70	0.57038	-0.01153	0.38913	7.05

APPENDIX B

Analysis of the Mass Spectral Data

For $[\text{CpMo}(*\text{CO})_2]_2$ (4a).

Molybdenum has seven isotopes in significant natural abundance, distributed over a mass range of 9 units, resulting in a mass spectrum for natural abundance $[\text{CpMo}(\text{CO})_2]_2$ (4a) containing parent ions at 18 different m/e values ranging from 426 to 443 (Figure 3, Chapter II). The relative intensities of these ions under the conditions employed in this study (50 eV, 150°C inlet temperature) are summarized in Table 1. The observed parent ion intensities for the ^{13}CO labeled 4a for reactions 1, 2, and 3 (Table 2, Chapter II) is also presented in Table 1. In all cases these relative intensities are the averaged result of at least 4 measurements.

This data were analyzed by a least squares fit to the equation;

$$I_m = a_m \times C_0 + a_{(m-1)} \times C_1 + a_{(m-2)} \times C_2 + a_{(m-3)} \times C_3 \\ + a_{(m-4)} \times C_4$$

Where;

I_m = observed relative intensity at mass m .

a_m = observed normalized intensity of natural abundance 4a at mass m .

C_n = calculated coefficient, the relative contribution of $[\text{CpMo}(\text{}^{13}\text{CO})_n(\text{}^{12}\text{CO})_{4-n}]_2$ to the observed mass spectrum.

The values of C_0 , C_1 , C_2 , C_3 , and C_4 calculated in this manner were then converted into percentages to give the data in Table 2, Chapter II. This analysis ignores changes in the $(m + 1)$ contribution to these relative intensities as a result of the

replacement of natural abundance CO by labeled ^{13}CO . This calculation was accomplished using the least squares regression routine available at the U. C. Berkeley Computer Center as part of the Statistical Package for the Social Sciences program (SPSS).¹ The statistical error in these calculations was quite good ($\leq 1.5\%$). The sensitivity to throwing out weak data was within these error limits. With 20 data points ($m/e = 427 - 446$) and only five variables the system is highly overdetermined. A similar analysis was used in evaluation of the mass spectral data for 2e. It is expected that errors in the mass spectral data collection, and through differences in reaction conditions highly outweigh the error inherent in this analysis of the mass spectra.

Reference

1. Nie, N. H., Hull, C. H., Jenkins, J. G., Steinbrenner, K., Bent D. H., "SPSS-Statistical Package for the Social Sciences", Second edition, McGraw-Hill, New York, N.Y., 1975, pg 320-367.

Table 1. The Observed Relative intensities of the Parent Ions in The Mass Spectra for 4a.

m/e	nat. ab. ^b	Reaction # ^a		
		1	2	3
426	0.1460	—	—	—
427	0.0198	392	379	918
428	0.1870	929	1086	2644
429	0.3518	1628	1850	4600
430	0.4471	2712	3056	7232
431	0.4699	4664	5144	12544
432	0.9506	6624	7840	19232
433	0.6304	8400	10576	25888
434	1.0	10352	13248	33152
435	0.9101	12032	16000	40128
436	0.8834	13248	17280	44480
437	0.6581	13376	18528	46912
438	0.7184	12704	18432	47296
439	0.2399	11248	16544	42880
440	0.3533	9024	14096	36480
441	0.0527	6720	10832	28192
442	0.0736	4368	7224	19392
443	0.0100	2664	4480	11904
444	—	1110	2392	6472
445	—	418	1032	2700
446	—	—	471	1156
447	—	—	206	—

^aSee Table 2, Chapter II. ^bnatural abundance, normalized to I₄₃₄ = 1.0

PART III
THE PROPOSITIONS

Abstracts

A. A Stereoselective Synthesis Mediated by a Chiral Transition Metal Complex.

A series of selective reactions of organic ligands bound to a chiral transition metal complex, where the metal center is chiral, will be employed to effect the overall selective synthesis of chiral organic products. This stereoselective synthesis involves the use of an optically active phosphine ligand to allow the separation of diastereomeric mixtures of organometallic compounds, and the ability of an optically active transition metal complex to induce stereoselective reactions of organic ligands.

B. Nucleophilicity and Transition Metal Carbonyl Anions: A Study Of the Relationship between Ion-Pairing and the Competition between Sn2 Displacement and Electron Transfer Mechanisms.

The ion-pairing equilibria of $\text{CpFe(CO)}_2^-\text{Na}^+$ (1) will be studied by infrared and conductivity methods. Knowledge of the ion-pairing equilibrium position under a number of conditions will be employed to analyze the relative rates of Sn2 and electron transfer processes in the reaction of 1 with alkyl halides. In particular cyclopropylcarbonyl halides will be used to evaluate the contribution of electron transfer processes to

the observed rate. In the second part of this proposal the relative rates of the reaction of a number of metal anions with alkyl halides under "pure" $\text{S}_\text{N}2$ conditions, involving only free ions, will be re-evaluated.

C. The Synthesis and Reactivity of a Novel σ -Alkyl- μ -Alkylidene Iron Complex. A Model for the Carbon-Carbon Bond Forming Process in Fischer-Tropsch Catalysis?

Two novel synthetic approaches to the preparation of μ -alkylidene complexes are proposed. These methods will be investigated as routes to the σ -alkyl- μ -alkylidene complexes $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CH}_2)(\mu\text{-CO})\text{Fe}(\text{R})(\text{CO})_3$, and their vinylidene analogues. Once prepared, the reactions of these complexes will be studied. In particular reactions that lead to carbon-carbon bond formation are sought.

D. The Absolute Rate Constant for Cis-Trans Isomerization of Vinyl Radicals.

It is proposed to measure the absolute rate constant for the cis-trans isomerization of vinyl radicals by using a steady state analysis on the reduction of vinyl fluorides by sodium naphthalenide. The rate of reduction of the vinyl radicals to stable vinyl carbanions is assumed to be $1.6 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$, the value obtained for the reduction of alkyl radicals to carbanions by sodium naphthalenide.

E. The Study of Cationic Bisphosphine Methylnickel(II) and Methylplatinum(II) Complexes: The Search for Evidence of an α -Hydride Migration Process.

It is proposed to study the reactions of cationic methylnickel and methylplatinum complexes of the type $[(L)_2M(CH_3)(\text{acetone})]^+PF_6^-$ with phosphines and alkenes. These reactions will be analyzed in an effort to gain evidence for the intermediacy of an α -hydride migration process.

A STEREOSELECTIVE SYNTHESIS MEDIATED BY A CHIRAL TRANSITIONMETAL COMPLEX

INTRODUCTION

In organic synthesis the selective construction of asymmetric centers remains one of the most difficult challenges for the synthetic chemist. The use of organotransition metal reagents in stereoselective syntheses has been growing rapidly in recent years.¹ To date, however, most of these efforts have centered around the asymmetric induction provided by chiral ligands, in particular chiral bisphosphine ligands. Recently Brunner and his coworkers² have studied both the synthesis and properties of a wide variety of asymmetric transition metal complexes, where the chiral center is at the metal atom. Brunner has proposed that the use of such chiral transition metal complexes in asymmetric synthesis can result in high optical yields due to the ability of the chiral metal atom to closely approach the reactive center when the substrate is bound to the metal complex.^{2a} An asymmetric synthesis of this kind involving a chiral transition metal complex is proposed here.

The synthesis and reactivity of the cationic alkene complexes $[\text{CpFe}(\text{CO})_2(\text{alkene})]^+$ has been extensively studied and the use of these organoiron complexes in organic synthesis has been reviewed recently.^{3,4} These complexes have been shown to undergo a number of highly selective reactions of the organic

ligand. For example it was found that protonation of the σ -allyl complex $\text{CpFe}(\text{CO})_2[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]$ (1a) with dry DCl occurs at the 3 position to give exclusively $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{C}(\text{H})(\text{CH}_2\text{D}))]^+$ (2a). Furthermore reduction of the 2a with a number of hydride reagents can give either $\text{CpFe}(\text{CO})_2[\text{CH}(\text{CH}_3)_2]$ (3a) or $\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{CH}_3)$ (4a). Some reagents have been found that reduce 2a selectively to 3a.³⁻⁵ In this later reaction a new asymmetric center is generated at the carbon atom bound to iron. The stereochemistry of this carbon center is determined by which face of the alkene is bound to iron in 2a, and is independent of whether hydride attack occurs exo or endo to the metal center. Thus the stereochemistry of the carbon center in 3a is predetermined in the enantiomeric cationic complex 2a. These reactions and the stereochemistry of 2a are shown in Scheme I.

If one of the carbonyl ligands in the complexes 1, 2, 3, or 4 is substituted by a phosphine ligand then the metal center becomes chiral. Brunner has prepared an analogue of 1a $\text{CpFe}(\text{CO})(\text{PR}_3^*)\text{CH}_3$ using the optically active phosphine ligand (S)- $\text{PPh}_2[\text{N}(\text{CH}_3)-\text{CH}(\text{CH}_3)(\text{Ph})]$, PPh_2R^* .^{2,6} This complex has two diastereomeric isomers, related by inversion of stereochemistry at the metal center, which can be separated by high pressure liquid chromatography. A similar approach, substituting the complexes 1, and 2 with an optically active phosphine, will be employed in this proposal.

SCHEME I

THE PROPOSAL

It is proposed to synthesize the chiral complexes $[\text{CpFe}(\text{CO})(\text{PPh}_2\text{R}^*)(\text{CH}_2=\text{CHR})]^+$ (2) in high optical purity. Then the reduction of these complexes to the secondary alkyliron complexes $\text{CpFe}(\text{CO})(\text{PPh}_2\text{R}^*)[\text{CH}(\text{CH}_3)(\text{R})]$ (3), will be investigated. The subsequent conversion of 3b into organic products without loss of optical activity will result in the overall stereoselective synthesis of a chiral secondary center from achiral alkenes using stoichiometric reactions of a transition metal complex. Two somewhat distinct approaches to the preparation of the required optically active alkene complexes 2b will be investigated.

A. The first approach involves the substitution of the complexes 1a, which are readily prepared from $\text{CpFe}(\text{CO})_2\text{Na}$ and allylic halides, with the optically active phosphine PPh_2R^* to give a mixture of two diastereomers. These diastereomers will then be separated by high pressure liquid chromatography in a manner analogous to that employed by Brunner and coworkers.⁵ Protonation of the resolved diastereomers should give optically active 2b (Scheme II). The optical purity of 2b will depend upon both the optical purity of 1b and the amount of asymmetric induction in the protonation step. Two suggested conformations of the σ -allyl ligand in the transition state for protonation, leading to different stereochemistry, are shown in Scheme III. These conformers are related as object and mirror image, and since the geometry about the metal center is chiral it can

SCHEME II

SCHEME III

or

reasonably be expected that one of these transition states will be of lower energy than the other. Previous studies found that deprotonation of cyclic alkene complexes to give analogues of 1a occurs only if the proton can obtain a configuration trans to iron, supporting the hypothesis that the transition states for both protonation and deprotonation are highly organized.⁴

Separation of the optically active complexes 1b should be aided by asymmetric induction in the phosphine substitution step, where the influence of the optically active center in the phosphine ligand results in the predominance of one isomer. An effect of this kind was observed by Brunner and coworkers.⁴ Loss of the organic substrate can be minimized by epimerization of the unwanted diastereomer followed by repetition of the separation procedure. For example it has been shown that the optically active complex $\text{CpFe(CO)(PPh}_2\text{R}^*)\text{CH}_3$ loses most of its optical activity upon heating to 96°C for 10 hours.⁶

B. An alternative approach involves the separation of the diastereomeric alkene complexes 2b. Using an optically active phosphine four possible diastereomers can result (Scheme IV). These alkene complexes can be prepared by a number of methods; a) protonation of the σ -allyl complexes 1b (approach A), b) displacement of isobutene from the complex $[\text{CpFe(CO)(L)(isobutene)}]^+$, and c) by nucleophilic attack of $[\text{CpFe(CO)(L)}]^-$ on epoxides followed by protonation (Scheme IV). In this last case retention of the stereochemistry in the epoxide is observed.^{3,4}

SCHEME IV

Separation of this diastereomeric mixture of complexes by high pressure liquid chromatography could prove difficult considering the number of isomers. However it should be noted that the isomers a & c and b & d have the olefin coordinated on the same side, and will therefore give the same stereochemistry at carbon upon reduction. Thus only separation of a & c from b & d becomes necessary. Treatment of the undesired isomers with NaI or I₂ in acetone allows the recovery of the alkene substrate in good yield.^{4b}

Green and Nagy³ reported that the reduction of $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{CH}(\text{CH}_3))]^+$ (2a) with NaBH₄ gave exclusively $\text{CpFe}(\text{CO})_2(\text{CH}(\text{CH}_3)_2)$ (3a) and no $\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{CH}_3)$ (4a). However Rosenblum and coworkers⁴ reported that this same reduction gives a 3a/4a ratio of 1:3. Reduction with NaBH₃CN,⁷ $\text{CpFe}(\text{CO})(\text{PPh}_3)_2$,⁵ and $\text{HFe}(\text{CO})_4^- \text{NEt}_4^+$ have been reported to give exclusively 3a. This reduction is strongly effected by the presence of electron withdrawing groups on the alkene, causing attack of hydride to occur at the substituted carbon. Likewise both carbon and heteroatom nucleophiles have been observed to add preferentially at the substituted alkene carbon. For the purposes of this proposal the selective reduction of the cationic alkene complexes to secondary alkyliron complexes is desired. An investigation of the selectivity of this reaction as a function of reducing agent and functionality on the alkene will be required.

The optically active alkyliron complexes 3b can then be converted to a variety of useful organic functionalities

without loss of optical activity (Scheme V).⁸ For example carbonylation in methanol gives the corresponding methyl ester with retention of configuration,⁸ and bromination in CS₂ gives the corresponding bromide with inversion of stereochemistry at carbon.^{8,9}

DISCUSSION

This proposal involves the stereoselective conversion of either a terminal alkene or allylic halide into optically active secondary esters or halides using stoichiometric organometallic reactions (Scheme VI). This goal is achieved by taking advantage of the ability of an asymmetric transition metal center to induce stereoselectivity in reactions that occur at either σ - or π -bound ligands, and through the use of an optically active phosphine ligand to produce diastereomeric organometallic complexes which can be separated.

Two distinct approaches are proposed. The first approach described here involves the synthesis of the diastereomeric σ -allyl complexes **1b** from allylic halides, CpFe(CO)₂Na, and an optically active phosphine, PPh₂R*. Separation of these diastereomers by high pressure liquid chromatography, followed by protonation, gives the optically active alkene complex **2b**. Selective reduction of this complex to a secondary alkyliron complex then generates a new chiral center at carbon. The second approach involves the synthesis of mixtures of diastereomeric alkene complexes **2b**, followed by separation of the resulting four

SCHEME V

SCHEME VI

diastereomers. Again reduction will give optically active alkyliron complexes. This second approach should give optically pure products, provided the diastereomers of **2b** can be cleanly separated, and selective reduction of **2b** can be achieved. The protonation of **1b**, however, is expected to yield variable amounts of asymmetric induction, depending upon the nature of the substituent R, and the phosphine ligand, resulting in products of variable optical purity. In all cases the organic substrate that ends up in metal complexes with undesirable stereochemistry can be recovered and used again to produce more product. The beauty of this synthesis is that the separation of diastereomers occurs after the stereochemistry in the product has been determined, i.e. in the alkene complex, but prior to product formation. And all of the steps including the reduction are reversible,^{3,4} allowing recovery of the organic substrate.

In conclusion it is proposed to use a series of stoichiometric reactions of asymmetric transition metal complexes to effect the overall conversion of achiral organic substrates into chiral organic products in high optical yield. This stereoselective transformation employs the use of an optically active phosphine ligand to allow separation of diastereomeric mixtures of organometallic compounds, and the ability of an optically active transition metal center to induce stereoselective reactions of organic ligands. This proposal is unique in that it is one of the first examples of the use of an asymmetric transition metal complex, where the metal center is

chiral, to effect a stereoselective transformation of an organic substrate.

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NUCLEOPHILICITY AND TRANSITION METAL CARBONYL ANIONS: A STUDY OF THE RELATIONSHIP BETWEEN ION-PAIRING AND THE COMPETITION BETWEEN S_N2 DISPLACEMENT AND ELECTRON TRANSFER MECHANISMS.

Introduction

The reaction of transition metal anions with alkyl halides or tosylates is one of the major synthetic routes for the preparation of transition metal alkyl complexes.¹ The similarity between this reaction and ordinary organic displacement reactions has led to a number of attempts at a comparison of transition metal anions with traditional organic and main group nucleophiles.^{2,3} The conclusion that these reactions proceed by an S_N2 displacement mechanism is supported by a number of observations; a) the reaction invariably follows bimolecular kinetics, b) the relative rates of reaction normally follow the order $1^\circ > 2^\circ > 3^\circ$ for the carbon center, and $I > Br \approx OTs > Cl$ for the leaving group, and finally c) the reaction of $[CpFe(CO)_2]^-M^+$ ($M = Na^+, Li^+$) with a diastereomeric primary tosylate or bromide,⁴ and the reaction of $Na_2Fe(CO)_4$ with an optically active 2-octyl tosylate,⁵ were observed to result in inversion at carbon. The observation of inversion of stereochemistry at carbon is usually considered conclusive proof for an S_N2 displacement mechanism.

The generality of this conclusion for all substrates and metal anions has become suspect recently, as the facility of electron transfer processes in organometallic reactions has

become increasingly clear.⁶ For example the related reaction, the oxidative addition of alkyl halides to transition metals has been shown to occur by electron transfer pathways in some cases.⁷ However more convincingly the reaction of $[\text{CpFe}(\text{CO})_2]^- \text{Na}^+$ with cyclopropylcarbinyl iodide in THF was observed to give about 30% of the ring opened product.⁸ In this case ring opening would be expected to arise from a unimolecular rearrangement of a free cyclopropylcarbinyl radical, indicating an electron transfer mechanism. These two mechanisms, $\text{S}_\text{N}2$ displacement and dissociative electron transfer, are presented in Scheme I.

Two studies have attempted to evaluate the relative nucleophilicity of transition metal anions by examining their relative rates of reaction with MeI or MeOTs.^{2,3} An early study by Dessy, Pohl, and King² found the relative reactivity of metal anions with MeI in DME to follow the order: $\text{CpFe}(\text{CO})_2^- > \text{Re}(\text{CO})_5^- > \text{CpW}(\text{CO})_3^- > \text{Mn}(\text{CO})_5^- > \text{CpMo}(\text{CO})_3^- > \text{CpCr}(\text{CO})_3^- > \text{Co}(\text{CO})_4^-$. More recently Pearson and Figdore³ have studied the rates of the reaction of a number of metal nucleophiles with MeI and MeOTs in THF. Whereas $\text{CpCr}(\text{CO})_3^-$ was found to react with MeI faster than $\text{CpMo}(\text{CO})_3^-$ and $\text{CpW}(\text{CO})_3^-$, and likewise $\text{CpFe}(\text{CO})_2^-$ faster than $\text{CpRu}(\text{CO})_2^-$, $\text{Mn}(\text{CO})_5^-$ was found to react an order of magnitude slower than $\text{Re}(\text{CO})_5^-$. To further confuse things the entropy of activation for the reaction of MeOTs with $\text{CpCr}(\text{CO})_3^-$ was large and negative (-20.2 e.u.), small but still negative for .PA $\text{CpMo}(\text{CO})_3^-$ (-2.5 e.u.), but positive for $\text{CpW}(\text{CO})_3^-$ (11.3 e.u.). The explanation for these results presented by the authors

SCHEME I

Sn2 Electron Transfer

evaluated the MeI/MeOTs ratio in terms of hard and soft nucleophiles and leaving groups. However the observation of highly variable entropies and enthalpies of activation is a serious warning sign that strong solvent influences effecting the ground and transition states differently are perturbing these systems.⁹ These results are both confusing and contradictory, making conclusions about relative nucleophilicity of the metal anions by the authors dubious at best.

To a large extent these studies of the reaction of transition metal anions with alkyl halides have ignored, or else dealt inadequately with, solvent effects and the influence of ion-pairing on both the rate of reaction and the competition between electron transfer and Sn2 displacement mechanisms, with two exceptions.^{10,11} The ion-pairing of transition metal anions with alkali metal cations has been extensively studied for $[\text{Co}(\text{CO})_4]^-$,¹² $[\text{Fe}(\text{CO})_4]^{-2}$,¹⁰ $[\text{RFe}(\text{CO})_4]^-$,^{10,13} $[\text{CpFe}(\text{CO})_2]^-$,¹⁴ and $[\text{Mn}(\text{CO})_4\text{L}]^-$ ($\text{L} = \text{PMe}_2\text{Ph}$, PPh_3 , $\text{P}(\text{OPh})_3$, CO).¹¹ And in all cases both tight and loose, or solvent separated ion pairs have been identified. Most significantly, however, all these ions are substantially if not entirely tight ion paired in THF solution, the solvent in which almost all of the kinetic and mechanistic data available was obtained.

An exhaustive study of the reaction of $\text{Na}_2\text{Fe}(\text{CO})_4$ with alkyl halides and tosylates has shown that the rate of Sn2 displacement is highly dependent upon the nature of the ion-pairing; tight ion pairs are almost completely unreactive, and the mono anion appears

to react somewhat faster than the free dianion in NMP solution.^{5,10} In this system no evidence for the participation of electron transfer pathways was observed. In a second study the rate of the reaction of NaMn(CO)_5 with PhCH_2Cl in THF was found to be inhibited upon addition of HMPA, contrary to expectations.¹¹ These results lead to serious questions concerning the reliability of existing relative rate comparisons. Without knowledge of the position of the tight vs solvent separated ion pair equilibrium, and the relative rates of displacement for each of these ions in a given solvent, comparisons are meaningless.

Furthermore, other than in the specific cases where the stereochemistry has been determined, the existence of at least a partial contribution to the rates from electron transfer processes cannot be ruled out. In fact in the one system that has been studied for a number of leaving groups, the CpFe(CO)_2^- anion, the reaction was found to proceed by $\text{S}_\text{N}2$ displacement for primary tosylates or bromides,⁴ but for primary iodides electron transfer processes were identified.⁸

The Proposal

It is the intention of this proposal to carefully examine the relative rates of $\text{S}_\text{N}2$ displacement and electron transfer reactions for $[\text{CpFe(CO)}_2]^- \text{M}^+$ as a function of solvent, ion-pairing equilibria, and added sequestering agent. Then with this knowledge in hand the relative rates of a series of metal anions with alkyl halides and tosylates under identical conditions,

where an S_N2 pathway is assured, will be re-examined. Two important issues need to be addressed in this study. First it is necessary to determine the position of the tight vs loose or solvent separated ion-pair equilibrium as a function of solvent, counter-ion, and added sequestering agent. Secondly it will be necessary to determine the relative rates of S_N2 displacement vs electron transfer pathways as a function of the structure of the ion pair, the counter ion, the solvent, and the leaving group. Only then will it be possible to examine the relative rates of the reaction of a number of transition metal anions with alkyl halides and tosylates, where only free ions and non-coordinating counter ions are involved, such that the relative nucleophilicities of these anions in solution can be evaluated.

The cyclopentadienyl(dicarbonyl)iron anion (1) in THF exhibits a complex set of infrared absorptions at 1877, 1862, 1806, 1786, 1770 cm^{-1} . Parnell and Jackson were able to show that three distinct species exist in THF.¹⁴ The proposed structures for these species are presented in Figure 1. The solvent separated ion C where the counter ion is R_4N^+ has absorptions at 1865, 1788 cm^{-1} . The weakly associated ion pair B is believed to have a strong interaction between the counter ion and one carbonyl, thus the strongly shifted absorption at 1770 cm^{-1} . Finally the contact ion pair A has absorptions at 1877, 1806 cm^{-1} . As expected the salts of the non-coordinating counter ion NR_4^+ exists exclusively as the solvent separated ion pair C, and similarly addition of HMPA to a THF solution of the sodium salt

SCHEME II

of 1 results in formation of the ion pair C.

The first part of this proposal will involve the quantitative evaluation of the equilibrium between structures A, B, and C for a variety of solvents and counter ions. Solvents such as tetrahydrofuran (THF), N-methylpyrrolidinone (NMP), hexamethylphosphoric triamide (HMPA) will be used, along with the counter ions Li^+ , Na^+ , K^+ , and the non-coordinating bistrisphenylphosphine imminium cation (PPN^+).

An accurate evaluation of K_2 , the equilibrium between C and A + B can be obtained from a conductimetric titration of 1 in THF or NMP using a cryptand such as Kryptofix 222 as titrant. Kryptofix 222 has a Na^+ complexation constant of 10^8 M^{-1} in MeOH. Provided a sharp breaking point at one molar equivalent added cryptand is observed, and the presence of triple ions can be avoided, then after correcting for mobility differences;

$$K_2 = \alpha / (1 - \alpha)$$

α = degree of dissociation = Λ / Λ_0
 Λ = conductance at zero added cryptand
 Λ_0 = conductance at one equivalent added cryptand

An approximate value of the equilibrium constant K_1 , the equilibrium between A and B, can be obtained in the following manner. In THF with one equivalent added crown ether only the species B and C exists in solution.¹⁴ Evaluation of this equilibrium constant by conductimetry in a manner identical to that just described gives K_1 under these conditions. Then knowing the ratio of B/C the extinction coefficients for the absorptions for the infrared absorptions at 1745, and 1785 cm^{-1} attributable

to these ions can be determined. Furthermore in ether or ether/THF it may be possible to evaluate the extinction coefficients for the IR absorptions for structure A independently. These extinction coefficients will then allow the equilibrium constant K_1 to be measured by IR, assuming Beer's law behavior. The equilibrium constant K_1 evaluated in this manner is bound to be less accurate than K_2 determined by conductimetry due to assumptions concerning extinction coefficients and Beer's law behavior. However since the solvent separated, or free ions are the species that will be of the most interest here this situation will not represent a large problem, vide infra.

In the second part of this proposal an attempt will be made to evaluate the ratio of S_N2 vs electron transfer processes using the a cyclopropylcarbiny1 halides or tosylates under conditions where 1 exists either as solvent separated, or free ions, structure C, or as entirely "tight" ion pairs, structure A or B. First using the cyclopropylcarbiny1 tosylate the rate of S_N2 displacement can be evaluated without interference from electron transfer processes. Alkyl tosylates have not been observed to undergo dissociative electron transfer reactions involving the carbon-oxygen bond. If as expected the rate of displacement for the solvent separated ion pair is faster than for tight ion pairs, then evaluation of the rate of displacement for the tight ion pair may be complicated by minor amounts of free ions present even when K_1 is very small.

The work of San Filippe⁸ suggests that in the reaction of

$[\text{CpFe}(\text{CO})_2]^- \text{Na}^+$ with cyclopropylcarbonyl iodides in THF at least 30% of the reaction pathway involves electron transfer. Whereas the reaction of the corresponding bromide was observed to involve less than 5% of an electron transfer pathway. This kind of leaving group dependence upon the competition between nucleophilic and electron transfer processes has been observed for the reactions of main group anions.^{8,15} Re-evaluation of the ratio of ring opened to ring closed product under solvent and counter ion conditions such that only tight or free ion pairs (A, and B, or C) exist in solution will allow the relative rates of electron transfer and $\text{S}_\text{N}2$ displacement for each of the ions to be determined separately. The best way to evaluate these ratios for each of the limiting cases is to determine the ratio of cyclized/uncyclized product for various concentrations of added cryptand in a solvent such as THF, where in the absence of a sequestering agent the ions exist mostly as tight ion pairs. Then plotting the observed ratio vs K_2 at that concentration of cryptand and extrapolating to $K_2 = 0$ will give the ratio in the total absence of free ions. This same ratio will be determined under different solvent and counter ion conditions, with and without added cryptand to dissociate the ion pairs.

The rate of $\text{S}_\text{N}2$ displacement is expected to be highly dependent upon the leaving group, the solvent, and nature of the ion pair involved. In particular the results with $\text{Na}_2\text{Fe}(\text{CO})_4$ suggests that solvent separated ion pairs should be more reactive than more tightly bound ion pairs in $\text{S}_\text{N}2$ reactions. On the other

hand, no clear prediction can be made for the rate of electron transfer processes from different ion pair structures. Furthermore determining the rate of electron transfer from each of the ion pairs A, B, and C will be considerably more difficult than for the S_N2 pathway. However if the absolute rate of "pure" S_N2 displacement for each ion structure is known, from the alkyl tosylate studies, and a correction for the change in leaving group can be made, then, using the ratio of cyclized to uncyclized product from the reactions of cyclopropylcarbinyl iodide, the approximate rate constants for electron transfer for each limiting structure can be calculated. Repeating this calculation for a series of counter ions should show a stronger dependence for the rate of electron transfer from A or B than for C as a function of counter ion.

The actual situation is in fact even more complicated. the analysis just described assumes that reaction of a metal anion with a cyclopropylcarbinyl halide by an electron transfer process will always lead to ring opening. However this conclusion requires that the organic radical formed upon dissociation of the halide ion a) escapes the solvent cage where electron transfer has taken place, and b) rearranges faster than it proceeds to give product. In an analogous reaction of $CpV(CO)_3H^-$ with alkyl halides a dissociative electron transfer mechanism was identified, and trapping of alkyl radicals was found to be very fast ($k_{25} = 2 \times 10^7 \text{ sec}^{-1}$), competitive with the rate of ring opening for the cyclopropylcarbinyl radical.¹⁶ Some of these

problems can be avoided by using the diastereomeric halides employed by Whitesides,⁴ and studying the stereochemistry of displacement.

The third part of this proposal involves the evaluation of relative rates of displacement for a given substrate and a variety of transition metal anions, under conditions of solvent and counter ion where an S_N2 mechanism and free ions is virtually assured. Using a non-coordinating counter ion, such as PPN^+ , and a polar solvent such as NMP or HMPA only totally dissociated free ions will be involved. Thus the influence of tight vs loose ion-pair equilibria upon the rates of reaction can be eliminated. Using cyclopropylcarbinyl halides the participation of electron transfer processes can be evaluated. Then comparisons of the relative rates of displacement, under pseudo first-order conditions, by a S_N2 pathway will allow the evaluation of the relative nucleophilicities of a number of transition metal anions. The anions to be studied will be $[Co(CO)_4]^-$, $[Rh(CO)_4]^-$, $[Fe(CO)_4]^{-2}$, $[RFe(CO)_4]^-$, $[CpFe(L)_2]^-$, $[CpRu(CO)_2]^-$, $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$, $[CpCr(CO)_3]^-$, $[CpMo(CO)_3]^-$, $[CpW(CO)_3]^-$, ($L = PPh_3$, $dipos$, CO).¹⁷ The interesting comparisons within this series will be between; isostructural anions of the first, second, and third rows, and between isoelectronic anions of the first row. Furthermore a comparison of the effect of substituting carbonyls with phosphines for a given metal will be examined for the anion $[CpFe(L)_2]^-$.

Only two studies of the reactivity of transition metal

anions with alkyl halides have carefully considered the effects of ion-pairing upon the rates of reaction. In both cases solvent, and substrate were chosen so that only an S_N2 process needed consideration. In the present study the effect of ion-pairing upon the competition between dissociative electron transfer and S_N2 displacement mechanisms is evaluated. These studies are complementary, and together define the "boundary" conditions within which S_N2 processes are assured. Under these purely S_N2 conditions with the influence of ion-pairing and the nature of the counter ion virtually eliminated the relative rates of a variety of transition metal anions with alkyl halides will be re-examined. Only a comparison of the reactivity of free metal anions by a common mechanism in the same solvent will be meaningful in evaluating the relative nucleophilicity of the metal centers involved.

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THE SYNTHESIS AND REACTIVITY OF NOVEL σ -ALKYL- μ -ALKYLIDENE IRON COMPLEXES. A MODEL FOR THE CARBON-CARBON BOND FORMING PROCESS IN FISCHER-TROPSCH CATALYSIS?

INTRODUCTION

The catalytic hydrogenation of carbon monoxide by Fischer-Tropsch catalysts, and related systems, will undoubtedly become increasingly important as coal replaces petroleum as the major feedstock for organic chemicals over the next several decades. Even though Fischer-Tropsch Catalysis has been known since the 1920's, the mechanism of this heterogeneous process remains poorly understood. This situation does not arise for a lack of mechanistic proposals.¹

Two major mechanistic schools of thought prevail. The first argues that insertion of carbon monoxide into a metal carbon bond, a process that is facile in homogeneous systems, followed by reduction of the resulting acyl species, results in extension of the carbon chain (Scheme I).¹ A second group argues that carbon monoxide dissociatively absorbs on the catalyst surface under reaction conditions to give surface carbon and oxygen atoms.² This surface carbon species is then sequentially reduced to alkylidyne, alkylidene, and then alkyl species (Scheme II).¹⁻³ The major uncertainty in this later mechanism remains the mechanism of carbon-carbon bond formation. As early as 1926 Fischer and Tropsch proposed that surface methylene intermediates simply polymerize.³ In support of this hypothesis is the observation

SCHEME I

SCHEME II

that diazomethane, a methylene precursor, polymerizes over metal catalysts to give linear hydrocarbons.⁴ Alternatively extension of the growing alkyl chain could involve the insertion of a surface methylene species into a surface bound alkyl, Scheme II.^{2,3}

Homogeneous models for the reduction of carbon monoxide by the mechanisms in Scheme II have been quite few,⁵ and no such examples for any of the carbon-carbon forming steps proposed for this mechanism exist. It is the intension of this proposal to synthesize transition metal complexes that might be expected to exhibit reactivity that model the proposed reaction of a surface alkylidene species with the growing alkyl chain. Surface alkylidenes are most likely bound to two adjacent metal centers, thus bridging μ -alkylidenes represent the most reasonable models for these surface species. In this proposal binuclear complexes that contain both μ -alkylidene and σ -alkyl ligands will be prepared and their reactivity studied. In addition the synthesis and reactivity of the related μ -vinylidene complexes will also be explored.

THE PROPOSAL

It is proposed to synthesize the complexes $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CR}_2)(\mu\text{-CO})\text{Fe}(\text{R}')(\text{CO})_3]$ (1, $\text{R} = \text{H}, \text{CH}_3$, $\text{R}' = \text{CH}_3, \text{C}(\text{O})\text{CH}_3$), and the vinylidene analogues $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}=\text{C}(\text{R})_2)(\mu\text{-CO})\text{Fe}(\text{R}')(\text{CO})_3]$ (2). Two novel synthetic approaches for the preparation of these transition metal complexes will be investigated. Both approaches

involve the reaction of a nucleophilic iron complex either $\text{RFe}(\text{CO})_4^- \text{Na}^+$, or $\text{Na}_2\text{Fe}(\text{CO})_4$, with an electrophilic carbon ligand of a second complex. $\text{Na}_2\text{Fe}(\text{CO})_4$ has been characterized as a "supernucleophile", readily reacting with one molecule of an alkyl bromide to give the complexes $\text{RFe}(\text{CO})_4^- \text{Na}^+$. These complexes in turn react with alkyl halides to give ketones.⁶ This later reaction is believed to proceed through an intermediate of the type $[\text{R}(\text{O})\text{C}](\text{R})\text{Fe}(\text{CO})_3$, which could not be observed. The corresponding Osmium complexes are quite stable and the mechanism of reductive elimination in these complexes has been the subject of considerable study.⁷

The first approach involves the reaction of $(\text{R}')\text{Fe}(\text{CO})_4^- \text{Na}^+$ with the cationic complexes $[\text{Cp}(\text{L})(\text{CO})\text{Fe}_2=\text{CR}_2]^+$ (3), and $[\text{Cp}(\text{L})(\text{CO})\text{Fe}_2=\text{C}=\text{CR}_2]^+$ (4)¹⁰ ($\text{L} = \text{CO}, \text{PPh}_3$, Scheme III). In this reaction attack of the nucleophilic metal on the alkylidene carbon, and the formation of a metal-metal bond, will give a bridging μ -alkylidene complex. The resulting complex, however, may be an acyl- μ -alkylidene complex resulting from migration of the alkyl ligand to carbonyl in $\text{RFe}(\text{CO})_4^-$ prior to attack upon the alkylidene complex. It has been shown that this migration process is involved in the reaction of $\text{RFe}(\text{CO})_4^-$ with alkyl halides.⁶ Furthermore it is well established that nucleophiles react with group VI-VIII alkylidene complexes by attack at carbon,⁸ and recent work has established similar behavior for mononuclear vinylidene complexes as well.¹⁰ In fact some known μ -vinylidene complexes were prepared in this way.⁹

SCHEME III

$\text{L} = \text{CO}, \text{PPh}_3 \quad \text{R} = \text{H}, \text{CH}_3, \text{Ph}$

The second synthetic approach to be employed here involves the reaction of $\text{RFe(CO)}_4^- \text{Na}^+$ with $\text{CpFe(L)}_2\text{-CH}_2\text{-X}$ ($\text{L} = \text{CO}, \text{PPh}_3, \text{X} = \text{Cl}, \text{OMe}, \text{SMe}_2^+$)¹⁰ (Scheme IV). In this reaction displacement of the leaving group by the metal nucleophile is expected to be followed by formation of a metal-metal bond, and the bridging of a carbonyl, resulting in the μ -alkylidene structure shown. It is hoped that this process will be competitive with reductive elimination from the iron atom. The complexes $\text{Cp(CO)}_2\text{FeCH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{OMe}$) have been used as precursors for the unstable cationic alkylidene complex $[\text{Cp(CO)}_2\text{Fe=CH}_2]^+$.¹¹ Alternatively use of the $\text{Fe(CO)}_4^{2-} \text{Na}_2^+$ dianion as the nucleophile followed by alkylation of the resulting binuclear anion may yield the desired σ -alkyl- μ -alkylidene complexes (Scheme IV).

An interesting extension of this method involves the use of iron alkyl complexes with the leaving group at more distant positions on the alkyl ligand. Reactions of these complexes with metal nucleophiles could then result in binuclear complexes linked by carbon chains of two, three, or more carbon atoms. A complex of this type has recently been prepared by Theopold and Bergman, $\text{Cp(CO)Co} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \end{array} \text{Co(CO)Cp}$.¹²

The second part of this proposal involves a study of the reactions of the complexes 1, 2, and 3. Of greatest interest will be reactions involving bond formation between the two organic ligands. This reaction if it gives $\text{CpFe(L)}_2(\text{CR}_2\text{R}')$ can be thought of as similar to the reductive elimination of two σ -bound organic ligands from $\text{R}_2\text{Fe(CO)}_4$. This should be a facile thermal process.⁶

SCHEME IV

However in the absence of thermal or ligand induced reactivity, photolysis, or oxidation of the complex may be employed. Considerable evidence has been acquired in recent years that oxidation often induces carbon-carbon bond coupling reactions.¹³ Alternatively the alkylidene ligand could "insert" into the iron alkyl bond to give $R^1C(O)CR_2Fe(CO)_3-(L)_2FeCp$ (Scheme V).

DISCUSSION

As with all synthetic studies of this kind the stability of the products cannot be predicted directly. However it has been noted that bridging alkylidene and vinylidene complexes are generally more thermally stable than their mononuclear analogues, thus the proliferation of these complexes that have been prepared in recent years.^{10,14}

Stoichiometric models for the proposed chain propagating steps in the Fischer-Tropsch reaction have been lacking, largely because of the absence of known complexes that model the structure of the surface bound intermediates in this reaction. The increase of characterizable μ -alkylidene and μ -vinylidene complexes recently suggests that reasonable models for the reactivity these surface intermediates may be found. This proposal is one such attempt at the synthesis of model complexes that exhibit Fischer-Tropsch reactivity.

In conclusion some novel synthetic procedures for the preparation of μ -alkylidene complexes are proposed. These methods will be employed to prepare binuclear iron complexes containing

both a μ -alkylidene and a σ -alkyl ligand. The reactivity of these σ -alkyl- μ -alkylidene complexes will be studied. In particular reactions that induce carbon-carbon bond formation are of interest. It is believed that the observation of carbon-carbon bond forming processes in these complexes should help substantiate mechanistic proposals for the catalytic hydrogenation of carbon monoxide that involve the active participation of surface alkylidenes in the growth of the carbon chain.

SCHEME V

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THE ABSOLUTE RATE CONSTANT FOR CIS-TRANS ISOMERIZATION OF VINYL RADICALS

INTRODUCTION

Vinyl radicals¹ can be produced through the addition of free radicals to alkynes,^{2,3} through irradiation in an ESR cavity,^{4,5} through the decomposition of α,β -unsaturated peresters,⁶⁻⁸ through the irradiation of vinyl iodides,⁹ and through the reduction of vinyl chlorides by sodium naphthalenide.¹⁰ In all cases mixtures of both *E*- and *Z*-alkenes are obtained upon abstraction of hydrogen from hydrogen donors.

ESR studies of the ethenyl radical, $\text{CH}_2\text{CH}^\bullet$, observed a spectrum characteristic of two species that are rapidly interconverting, consistent with a non-linear ethenyl radical interconverting between *cis* and *trans* geometrical isomers. The half life for this process was determined to be between 3×10^{-8} and 3×10^{-10} sec at -160° to -104°C , which assuming a frequency factor of 10^{13} corresponds to a barrier to isomerization of about 2 kcal/mole.⁴ The authors implicated electron tunneling in this process. By contrast the 1-methyl vinyl radical was found to be configurationally stable at -172°C , indicating a barrier to interconversion of greater than 2.7 kcal/mole.^{4,5}

Early studies found that in the thermal decomposition of *t*-butyl *E*- and *Z*- α,β -dimethylpercinamates, and the corresponding *t*-butyl *E*- and *Z*- α -methyl and α -phenylpercinamates yielded *Z*- and *E*-alkenes in ratios of 1.16 and 1.5 respectively, independent

of the starting isomer.^{6,7} These results can be rationalized either by a symmetrical intermediate, or a pair of rapidly interconverting isomers, where in both cases steric influences control the observed product ratio. Support for this steric control of the product ratios was found in the effect of changes in the hydrogen donor upon the observed Z/E product ratio; for example cumene gave higher Z/E ratios than cyclohexane.^{6,7}

Sargent and Browne reduced isomerically pure E- and Z-3-chloro-3-hexene with sodium naphthalenide and observed a different ratio of Z- and E-alkenes depending upon the starting isomer, with retention of stereochemistry in the predominant isomer. This observation allows for the conclusion that there exist distinct cis and trans vinyl radicals, not a single linear intermediate. More importantly this experiment was able to demonstrate that the rate of trapping of the vinyl radical by sodium naphthalenide, to give the configurationally stable vinyl carbanion, is faster than the rate of cis-trans equilibration for disubstituted vinyl radicals.

THE PROPOSAL

It is proposed to study the reduction of a series of three pairs of E- and Z-vinyl fluorides by sodium naphthalenide in 1,2-dimethoxyethane (DME) solvent. By examining the E/Z ratio of the alkene products it will be possible to determine the absolute rate of isomerization of vinyl radicals. The series of vinyl fluorides to be studied are: E- and Z-3-fluoro-3-hexene (1a, 1b), E- and Z-2-fluoro-2-butene (2a, 2b), and E- and Z-1-fluoro-1-

deutero-1-propene (3a, 3b).

It has been adequately established that the reduction of alkyl halides by sodium naphthalenide, as well as other aromatic radical anions, proceeds by an initial one-electron transfer, followed by dissociation of halide. The resulting alkyl radical is reduced to a carbanion by another molecule of naphthalene radical anion. The resulting carbanion then abstracts a proton from solvent.^{10,11} This mechanism is outlined in Scheme I.

In this mechanism k_3 is rate limiting and halogen dependent. The order of relative rates goes $X = F \ll Cl = Br = I$. When $X = Cl, Br, \text{ or } I$ the reaction proceeds at a rate approaching the rate of mixing of the reactants, while fluorides typically have rate constants of $1 \times 10^{-4} \text{ M}^{-1}\text{sec}^{-1}$.¹¹ The second order rate constant k_2 has been measured by examining the extent of cyclization in the reduction of 5-hexenyl fluoride.¹¹ In that study it was established that $k_2 = 1.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ or almost the diffusion controlled limit. It is an assumption of this proposal that the rate constant k_2 for the reduction of the vinyl radical to the vinyl carbanion is the same as for the reduction of alkyl

radicals to carbanions.

Based on analogy to the reduction of alkyl halides the proposed mechanism for the reduction of isomeric vinyl fluorides is presented in Scheme II. In this scheme k_2 is assumed to be the same for both cis and trans vinyl radicals.

Based upon this mechanism the kinetic analysis goes as follows. Starting from the Z-isomer (I), for example, a steady state approximation is made on the concentration of the opposite vinyl radical isomer, the cis-vinyl radical ($C^\bullet$). Starting from E-vinyl fluorides (II) this assumption is made on the trans-vinyl radical ($T^\bullet$) concentration. Therefore, starting from I:

$$\frac{d[C^\bullet]}{dt} = 0 = k_1[T^\bullet] - k_{-1}[C^\bullet] - k_2[C^\bullet][N^{\bullet-}]$$

$$\text{solving; } \frac{[C^\bullet]}{[T^\bullet]} = \frac{k_1}{k_{-1} + k_2[N^{\bullet-}]} \quad (1)$$

where $[T^\bullet]$ = concentration of trans-vinyl radical
 $[C^\bullet]$ = concentration of cis-vinyl radical
 $[N^{\bullet-}]$ = concentration of sodium naphthalenide
 $[T]$ = concentration of trans-alkene product
 $[C]$ = concentration of cis-alkene product

the observed product ratio is directly proportional to the concentration of these radicals;

$$\left(\frac{[C]}{[T]} \right)_{\text{obs}} = \frac{k_2[C^\bullet][N^{\bullet-}]}{k_2[T^\bullet][N^{\bullet-}]} = \frac{[C^\bullet]}{[T^\bullet]} \quad (2)$$

under equilibrium conditions; $k_{-1} \gg k_2[N^{\bullet-}]$

$$\frac{[C^\bullet]}{[T^\bullet]} = \frac{k_1}{k_{-1}} \quad (3)$$

therefore at equilibrium;

$$\left(\frac{[C]}{[T]} \right)_{eq} = \frac{k_1}{k_{-1}} \quad (4)$$

under non-equilibrium conditions k_{-1} is comparable to $k_2[N^{\bullet}]$, substituting eq. (1) and (4) into eq. (2);

$$\left(\frac{[C]}{[T]} \right)_{obs} = \frac{k_{-1}([C]/[T])_{eq}}{k_{-1} + k_2[N^{\bullet}]} \quad (5)$$

solving for k_{-1} ;

$$k_{-1} = \frac{k_2[N^{\bullet}]}{(([C]/[T])_{eq}/([C]/[T])_{obs}) - 1} \quad (6)$$

using eq (4) and solving for k_1

$$k_1 = k_{-1}([C]/[T])_{eq} \quad (7)$$

A similar analysis may be employed for the opposite isomer. However, the ratios $([C]/[T])_{obs}$ and $([T]/[C])_{obs}$ from *Z*- and *E*-alkenes will not necessarily be the same, and must be distinguished.

The ratio $([C]/[T])_{eq}$, on the other hand, must of necessity be identical starting from either vinyl fluoride isomer. This ratio can be evaluated by either of two methods. The first involves reducing the concentration of sodium naphthalenide until further dilution leads to no change in the ratio $([C]/[T])$ observed, always maintaining an excess of reducing agent. If this does not slow the rate of reduction sufficiently, then a change in either the metal cation or the aromatic radical anion is capable of changing k_2 by orders of magnitude.^{11,12} In particular, a change to either potassium naphthalenide or sodium

SCHEME II

anthracenide should work. It should be noted that the $([C]/[T])_{eq}$ is independent of the rate constant k_2 and the reducing agent, in must merely be established that equilibrium has been established between the two interconverting isomers.

THE EXPERIMENT

All reactions must be carried out under an inert atmosphere. The sodium naphthalenide can be prepared by depositing a sodium mirror on the wall of a flask, then transferring in the solution of naphthalene in DME. The solutions can be titrated with H_2O to determine their molarity.¹¹ Addition of the vinyl fluoride in DME solution to the filtered solutions of sodium naphthalenide can be done either by syringe or through a break seal as described by Garst,¹¹ a syringe pump may be particularly useful in this addition. All reactions should be carried out with a 5-10 fold excess of reducing agent, so that the concentration can be known accurately. Reactions of alkyl fluorides typically have half-lives of 3-5 minutes. The E- and Z-alkenes can be analyzed satisfactorily on a number of vapor phase chromatography (VPC) columns without workup. The column employed by Sargent and Browne was an $AgNO_3$ /glycerine column. Yields can be measured by addition of alkanes as internal standards and comparisons of output integrations after establishing molar resonance factors with known samples.

The synthesis of the vinyl fluorides required by this proposal can be achieved by one of two possible synthetic routes (Scheme III). The E- and Z-vinyl fluorides can be separated by

SCHEME III

column chromatography,¹³ or by preparative VPC techniques. Vinyl halides form peroxides easily and therefore the compounds should be chromatographed through alumina prior to use. NMR, IR, and mass spectral data should be sufficient in assigning the structures of the various isomers. However, if these methods do not suffice, then treatment of the pure isomers with *t*-butyllithium at -120°C followed by quenching with a proton source will allow correlation with the corresponding hydrocarbons.¹⁶

DISCUSSION

There are a number of assumptions inherent in this proposal. First, it is assumed that the mechanism for the reduction of vinyl fluorides by sodium naphthalenide is the same as for alkyl fluorides. Most importantly, it is assumed that the rate of reduction of the vinyl radical to the vinyl carbanion occurs at the same rate as was measured for alkyl radicals. There is no way that the validity of this assumption can be tested directly; however, considering the almost diffusion controlled rate of this process this assumption does not seem very drastic.

Secondly, it is assumed that the reduction of the cis- and trans-vinyl radicals proceeds at the same rate. That is, that there is no steric barrier like that which was encountered for hydrogen abstraction. The results of Sargent and Browne are encouraging in this regard. Furthermore, a comparison of $([T]/[C])_{eq}$ obtained for compound **1a,b** and **3a,b** should indicate if any significant steric barrier exists.

Thirdly, it is assumed that the vinyl carbanions are

stable to cis/trans isomerization under reaction conditions. There is good evidence for this stability.¹⁷ In particular, the two electron reduction of vinyl chlorides by Na/NH₃ goes with at least 96% retention of stereochemistry.¹⁸

Most importantly there is the steady state assumption. This, however, can be tested. A plot of k_{-1} vs $[N^{\bullet}]$ should yield a straight line with a slope of zero. This lack of a concentration dependence will work both to confirm the correctness of the steady state assumption and the kinetic analysis derived from it, but also indirectly it will confirm the mechanism in Scheme II.

In conclusion it is proposed to measure the absolute rate constant for the cis-trans isomerization of vinyl radicals by using a steady state analysis on the reduction of vinyl fluorides by sodium naphthalenide. The rate of reduction of the vinyl radical isomers to the stable vinyl carbanions is assumed to be $1.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, the value obtained for the reduction of alkyl radicals to carbanions by sodium naphthalenide.

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THE STUDY OF CATIONIC BISPHOSPHINE METHYLNICKEL(II) AND PLATINUM(II) COMPLEXES: THE SEARCH FOR EVIDENCE OF AN α -HYDRIDE MIGRATION PROCESS.

INTRODUCTION

The process of α -hydride migration is represented in equation (1). Evidence for this reaction only exists for a few

metal complexes.¹⁻⁵ The most convincing evidence exists for multiply alkylated complexes of Cr, Nb, and Ta (MR_n , $n \geq 3$), and in a report by Green and Cooper in which a tungsten hydrido-carbene complex was trapped with $\text{P}(\text{CH}_3)_2\text{Ph}$.¹ This reaction is presented in Scheme I.

The complex 2 was isolated from the reaction of the alkene complex 1 with $\text{P}(\text{CH}_3)_2\text{Ph}$ at room temperature. Upon heating to 50°C in acetone for 1 1/2 hours this complex was converted with loss of ethene to a second product 5 in about 70% yield. Complex 5 exhibits an IR absorption at 1938 cm^{-1} , and ^1H NMR absorptions at δ 1.16 and -12.11 ppm (ratio 2:1) which led to the structural assignment shown in Scheme I. Heating 5 for an additional 8 days at 70°C led to a 50:50 mixture of 5 and 6.¹

These observations led Green and Cooper to conclude that they had observed the equilibrium $3 \rightleftharpoons 4$, an α -hydride migration process. The kinetic product of the reaction is attack of phosphine at carbon to give 5, the thermodynamic product being attack at tungsten leading to 6.

SCHEME I

THE PROPOSAL

It is proposed to look for evidence of an α -hydride migration process in the reactions of complexes of the type $[(L)_2M(R)(\text{solvent})]^+PF_6^-$ (7: M = Ni, Pt; R = $-CH_3$, $-CH_2Ph$; L = bulky phosphite ligand). The complex $[(L)_2Pt(CH_3)(\text{acetone})]^+PF_6^-$ (L = $P(CH_3)_2Ph$) has been prepared by Chisholm and Clark.⁶ It is stable at room temperature, but decomposes upon heating. The acetone ligand can be displaced easily to form π -complexes with a number of alkynes. The chemistry of these methylplatinum(alkyne) complexes has been extensively studied.^{6,7}

The complexes 7 will be prepared at low temperature,^{6,8,9} then allowed to react with a number of "trapping" reagents at room temperature or below. The preparation of these complexes and two different approaches to trapping an intermediate hydrido-carbene complex 8 are summarized in Scheme II.

By analogy to the results of Green and Cooper phosphines such as $P(CH_3)_2Ph$, $PPh_2(CH_3)$, or $P(CH_3)_3$ will be used in an effort to observe complex 9. This complex will be characterized by IR ($\nu(M-H)$), ^1H NMR ($M-H$, $M-CH_2P$), and by chemical trapping with dry DCl to give HD, $(CDH_2PR_3)^+$, and $L_2M(H)(Cl)$.¹⁰

Other attempts to confirm the existence of 8 are based upon the presently favored mechanism for the olefin metathesis reaction.¹¹ Treatment of 7- d_3 with ethene- d_0 can result in one of three possible reaction pathways.

(I) Reversible formation of a hydridometallocyclobutane complex

(II) results in no net reaction. Complex II is symmetrical and

SCHEME II

can reverse to ethene and **8** to give either $\text{CH}_2=\text{CH}_2$ and **8**-d₃, or $\text{CH}_2=\text{CD}_2$ and **8**-d₁. Detection of $\text{CH}_2=\text{CD}_2$ in the recovered ethene would confirm the existence of this pathway.

(2) The hydridometallobicyclobutane complex (**11**) could be isolated as a stable product. Complex **11** is a 16 electron Ni(II) or Pt(II) complex, normally a stable electron count for this oxidation state.

(3) Alternatively **11** could react to give other products by one of three pathways: a) reductive elimination to give cyclopropane, b) β -hydride elimination to give propene,^{11,12} c) α -hydride transfer to give a cationic propyl complex (**12**), and possibly polymerization by a repetition of this process. This propyl complex, if observed, will contain a mixture of propyl groups, $-\text{CH}_2\text{CH}_2\text{CD}_3$ and $-\text{CD}_2\text{CH}_2\text{CH}_2\text{D}$.

It cannot reasonably be predicted which of these pathways will be observed. However, with the exception of the polymerization of ethene each process will give products that are unique and will necessitate the postulate of **8** as an intermediate in their formation.

Alternative approaches involve starting with a cationic benzyl complex $[(\text{L})_2\text{M}(\text{CH}_2\text{Ph})(\text{acetone})]^+$ (**13**) and looking for formation of styrene and **7** in the reaction with ethene. Or conversely allowing the cationic methyl complex **7** to react with styrene and looking for the formation of **13** and ethene. In addition **13** may react with phosphines to form complexes of the type **9** more readily, because of stabilization of the resonance

structures for 8 that place the positive charge on carbon, increasing its electrophilicity.

DISCUSSION

Two characteristics of the system studied by Green and Cooper were recognized as being significant in the design of this proposal.

(1) The complex $[\text{Cp}_2\text{W}-\text{CH}_3]^+$ (3) is a 16 electron unsaturated complex, α -elimination gives $[\text{Cp}_2\text{W}(\text{H})=\text{CH}_2]^+$ (4) a saturated 18 electron complex. In addition this complex is a cation with strong π -acid ligands, the cyclopentadienyl ligands. These factors contribute to destabilize 3 with respect to 4.

(2) Green and Cooper observed a situation where $k_2 > k_3$ (Scheme I). Furthermore the thermodynamic equilibrium of 5 and 6 is roughly 50:50, thus this kinetic preference for attack at carbon (to give 5) is probably due to greater steric hindrance to attack at the metal center. In addition a resonance form for 4, $\text{Cp}_2\text{M}(\text{H})-\text{CH}_2^+$, places the positive charge on carbon, increasing its electrophilicity.

Consideration of these points led to the design of the present system. $[\text{L}_2\text{M}(\text{CH}_3)(\text{acetone})]^+$ can be considered an unsaturated 14 electron M(II) complex if the acetone ligand is ignored. The ligands L are to be strong π -acids to maximize destabilization of complex 7 relative to 8 (Scheme II), and bulky so as to favor nucleophilic attack at carbon rather than the metal.

In summary, it is proposed to study the reactions of

cationic methylnickel and methylplatinum complexes of the type $[(L)_2M(CH_3)(acetone)]^+PF_6^-$ with phosphines and alkenes. These reaction will be analyzed in an effort to gain evidence for the intermediacy of an α -hydride migration process.

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