REACTIVITY PATTERNS OF TRANSITION METAL HYDRIDES AND ALKYLS

Thesis by

William Davidson Jones II

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1979

(Submitted May 18, 1979)

Acknowledgements

This thesis is dedicated to my parents for allowing me to make the decision to do what I wanted and for making it possible to accomplish my objective, and to my wife and best friend, Heather, for standing beside me and helping me through my graduate school career.

I also wish to express gratitude for financial support from the Meridian Hunt Bennett Fellowship Fund, 1978-79.

ABSTRACT

The complex PPN$^+$ CpV(CO)$_3$H $^-$ (Cp=η^5-C$_5$H$_5$) has been prepared in 70% yield by sodium reduction of CpV(CO)$_4$ followed by protonation of the resulting dianion [CpV(CO)$_3$]$^{2-}$ with water and cation exchange with PPN$^+$Cl$^-$. The physical properties and chemical reactions of PPN$^+$CpV(CO)$_3$H$^-$ have been investigated. The sodium salt of CpV(CO)$_3$H$^-$ is contact ion-paired in the solid state and in THF; dissociation of solvent-separated pairs occurs on conversion to the PPN$^+$ salt or dissolution in polar solvents such as HMPA. PPN$^+$ CpV(CO)$_3$H$^-$ reacts with a wide range of organic halides, resulting in substitution of the halogen atom by the hydrogen of CpV(CO)$_3$H$^-$. The organometallic products of these reactions are the vanadium halides PPN$^+$[CpV(CO)$_3$X]$^-$. In some cases a second organometallic product is observed; this material is the binuclear bridging hydride PPN$^+$ [CpV(CO)$_3$]$_2$ H$^-$, and it is formed by reaction of the kinetic product CpV(CO)$_3$X$^-$ with starting CpV(CO)$_3$H$^-$ present in the reduction solutions. Irradiation of CpV(CO)$_4$ in the presence of CpV(CO)$_3$H$^-$ provides an alternate route to bridging hydride [CpV(CO)$_3$]$_2$ H$^-$. Competition experiments against PPh$_3$ have shown that CpV(CO)$_3$H$^-$ reacts more rapidly than the phosphine with transient, coordinatively unsaturated CpV(CO)$_3$, but thermodynamically PPh$_3$ is the better ligand. The borohydride salt PPN$^+$[CpV(CO)$_3$BH$_4$]$^-$ has also been prepared, by treating $CpV(CO)_4$ with $NaBH_4$ and by treating $CpV(CO)_3H^-$ with $BH_3 \cdot THF$. The mechanism of the reaction between $CpV(CO)_3H^-$ and organic halides has been investigated in detail, and compared in several cases with halide reductions carried out using tri-n-butyltin hydride. Relative reactivity, stereochemistry, cyclization and trapping studies demonstrate that in almost all cases, the reduction reaction proceeds via free radical intermediates. As in the R_3SnH case, these intermediates are generated in a chain process, and are trapped by hydrogen transfer from $CpV(CO)_3H^-$. The absolute rate constant for this transfer step can be estimated to be ca. $2 \times 10^7\ M^{-1}\ sec^{-1}$, nearly an order of magnitude larger than the rate constant for hydrogen transfer from tri-n-butyltin hydride. Reduction of cyclopropylcarbinyl bromide appears to be exceptional, and probably proceeds by a two-electron mechanism.

Sodium amalgam reduction of $CpRh(CO)_2$ or a mixture of $CpRh(CO)_2$ and $CpCo(CO)_2$ affords two new anions, $PPN^+[Cp_2Rh_3(CO)_4]^-$ and $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$. The latter compound appears to be physically and chemically similar to the known $PPN^+[Cp_2Co_2(CO)_2]^{\dot{-}}$, whereas the former posesses the same substructure bridged by a $Rh(CO)_2$ unit. Both anions react with CH_3I producing acetone via $CpRh(CO)(CH_3)_2$ or $CpCo(CO)(CH_3)_2$. In addition, the compounds $Cp_2RhCo(CO)_2R_2$ ($R=CH_3, CH_2CF_3$) are formed upon alkylation of $[Cp_2RhCo(CO)_2]^{\dot{-}}$

and are observed to decompose to $CpRh(CO)(CH_2CF_3)_2$ and $CpCo(CO)(CH_2CF_3)_2$.

$CpMo(CO)_3H$ (**1**) has been found to react with $CpMo(CO)_3R$ ($R=CH_3, C_2H_5, CH_2C_6H_5$; **2a**,**2b**,**2c**) at 25-50°C to quantitativly produce aldehyde RCHO and the dimers $[CpMo(CO)_3]_2$ and $[CpMo(CO)_2]_2$. Evidence is presented indicating that aldehyde formation occurs by insertion of CO into the Mo-R bond followed by hydride transfer by **1** forming an intermediate acyl hydride. The intermediate acyl $CpMo(CO)_2(COR)$ also reacts with ethylene and $CpMo(CO)_3H$ producing ketones $R-\overset{O}{\overset{\|}{C}}-C_2H_5$. A mechanism is proposed for these reactions and a comparison with the cobalt analogues in the hydroformylation process discussed.

The reactions of $PPN^+CpV(CO)_3H^-$ with some transition metal carbonyls, alkyl and acyls are studied. In almost all cases substitution of hydride (H^-) for CO is observed. The chemistry of $CpMo(CO)_3H$ with similar compounds is also examined and compared with that of $CpV(CO)_3H^-$. In general, $CpV(CO)_3H^-$ appears to transfer a hydrogen atom to the metal radical anion formed in an electron transfer process, whereas $CpMo(CO)_3H$ transfers hydride in a 2-electron process to a vacant coordination site. The chemical consequences are that $CpV(CO)_3H^-$ generally reacts with metal alkyls to give alkanes via. intermediate alkyl hydride species whereas $CpMo(CO)_3H$ reacts with metal alkyls to produce aldehyde, via. an intermediate acyl hydride species.

Table of Contents

I. The Reduction of Alkyl Halides by $[(Ph_3P)_2N]^+[CpV(CO)_3H]^-$.

II. The Reduction and Alkylation of $CpCo(CO)_2$ and $CpRh(CO)_2$.

III. The Reactions of $CpMo(CO)_3H$ with $CpMo(CO)_3R$ and Ethylene

IV. The Reactions of Two Isoelectronic Transition Metal Hydrides with Transition Metal Carbonyls, Alkyls, and Acyls.

Table of Contents (cont.)

Chapter I

The Reduction of Alkyl Halides by $[(Ph_3P)_2N]^+ [CpV(CO)_3H]^-$

Results and Discussion

Properites and Reactions of PPN^+ $[CpV(CO)_3H]^-$, PPN^+-**1**

Almost two decades ago, E. O. Fischer reported[1] the reduction of $CpV(CO)_4$, **2**, with sodium metal in liquid ammonia forming the tight ion pair $Na_2CpV(CO)_3$, **3**. **3**, upon treatment with aqueous HCl and extraction with hexane yielded the dimer $Cp_2V_2(CO)_5$.

We have found that in THF **3** may be treated with water rather than HCl to obtain the mono-protonated species $Na^+[CpV(CO)_3H]^-$. The IR spectrum of this new anionic vanadium hydride[3] in THF indicates that it consists of a tight ion pair in equilibrium with a solvent separated or free ion pair[4] (Scheme I). If one equivalent of $[(\phi_3P)_2N]^+Cl^-$ (PPN^+Cl^-) is added in small portions, the ν_{CO} bands at 1792 and 1732 cm^{-1} attributable to the tight ion paired complex are observed to collapse into the ν_{CO} band at 1775 cm^{-1}, while the band at 1887cm^{-1} remains unchanged (Fig. 1). **1** may exist in THF solution either as free ions or as a solvent separated ion pair.[5,6]

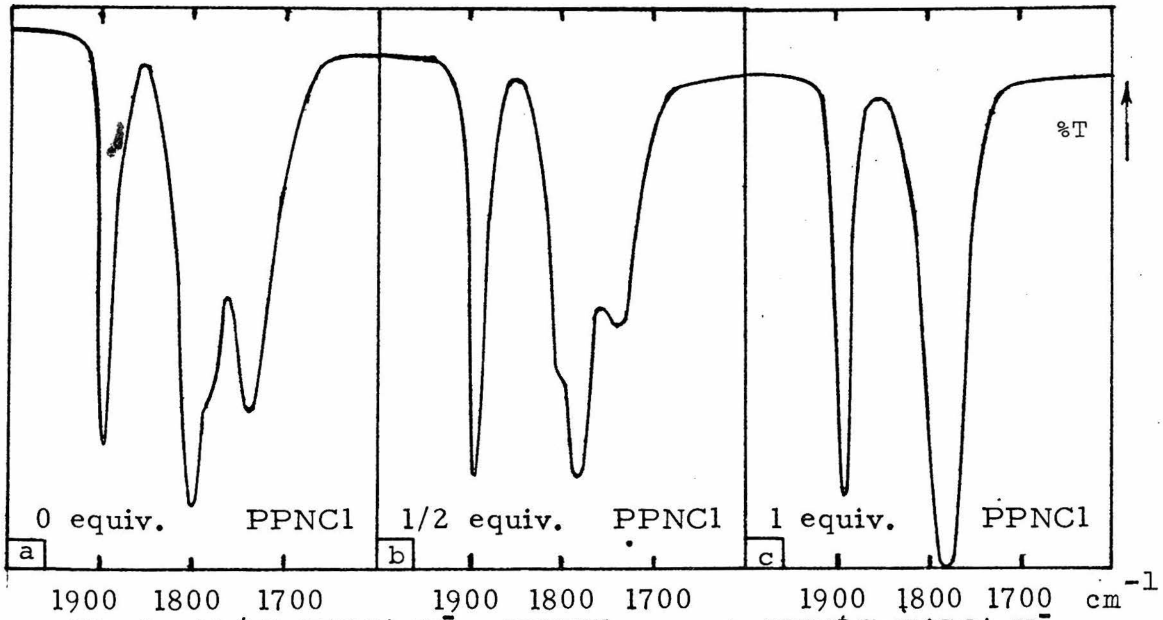


Fig. 1- $Na^+ CpV(CO)_3H^- + PPNCl \longrightarrow PPN^+ CpV(CO)_3H^-$

Scheme I

$$\begin{tikzcd}
Na^{+}CpV(CO)_3H^{-} \arrow[r, shift left, ""] & Na^{+}\cdots THF\cdots CpV(CO)_3H^{-} \arrow[l, shift left] \arrow[r, "PPN^{+}Cl^{-}"] \arrow[d, shift right] & PPN^{+}\cdots THF\cdots CpV(CO)_3H^{-} + NaCl\downarrow \arrow[d, shift right] \\
 & Na^{+}\parallel CpV(CO)_3H^{-} \arrow[u, shift right] & PPN^{+}\parallel CpV(CO)_3H^{-} \arrow[u, shift right]
\end{tikzcd}$$

An IR spectrum similar to that in Fig. 1c is also obtained upon formation of $Na^{+}[CpV(CO)_3H]^{-}$ in HMPA, or upon addition of 18-crown-6 to a THF solution of $Na^{+}[CpV(CO)_3H]^{-}$.

The PPN^{+} salt of 1 may be isolated by adding $PPN^{+}Cl^{-}$ to a solution of $Na^{+}[CpV(CO)_3H]^{-}$ and precipitating the yellow product with n-hexane. The NMR spectrum of this hydride in d_8-THF shows a complex pattern at δ 7.6 ppm due to the PPN^{+} protons and a sharp singlet at δ 4.60 ppm attributable to the C_5H_5 protons with the relative areas of 30:5. The hydridic hydrogen appears at δ -6.72 ppm as a broad low intensity peak with a width of ~1ppm.[8]

Reduction of 1-bromoctane: Addition of 1 equivalent of 1-bromooctane to a THF solution of 1 (0.10 M) results after several hours in the formation of n-octane in ~90% yield (eqn. 1). Reduction of 1-bromoctane with $PPN^{+}[CpV(CO)_3D]^{-}$[9] in d_0-THF or with 1 in d_8-THF gives only d_1-octane or d_0-octane, respectively, indicating that the vanadium hydride is the proton source.

$$PPN^{+}\ CpV(CO)_3H^{-} + RBr \xrightarrow{THF} PPN^{+}\ CpV(CO)_3Br^{-} + RH \qquad (1)$$

The primary organometallic product of the reaction is the expected $PPN^{+}[CpV(CO)_3Br]^{-}$, 4, which may be isolated from the reaction mixture by precipitation with n-hexane. This dark green compound may also be prepared by irradiating a THF solution of 2 and $PPN^{+}Br^{-}$ or $Na^{+}Br^{-}$ while purging with nitrogen to remove liberated CO and precipitating the air sensitive product with hexane.

(*Anal*. Calcd. for $C_{44}H_{35}BrNO_3P_2V$: C, 64.58; H, 4.28; N, 1.71; Br, 9.77. Found: C, 64.50; H, 4.76; N, 1.70; Br, 9.60). The IR spectrum of this vanadium halide in THF shows three ν_{co} bands at 1941 (m), 1847 (s), and 1804 (m) and a singlet in the NMR for the C_5H_5 protons at δ 4.83 ppm.

The reduction of an alkyl bromide by 1 may be followed by monitoring the changes in the IR (Fig. 2) or NMR (Fig. 3) spectrum. The IR spectrum shows the disappearance of the ν_{co} bands of 1 at 1887 and 1775 cm^{-1} with the simultaneous growth of bands at 1941, 1847, and 1804 cm^{-1} of 4. The color of the solution is observed to change from yellow to dark green.

Fig. 2- $CpV(CO)_3H^- \ (1) + RX \longrightarrow CpV(CO)_3X^- \ (4)$

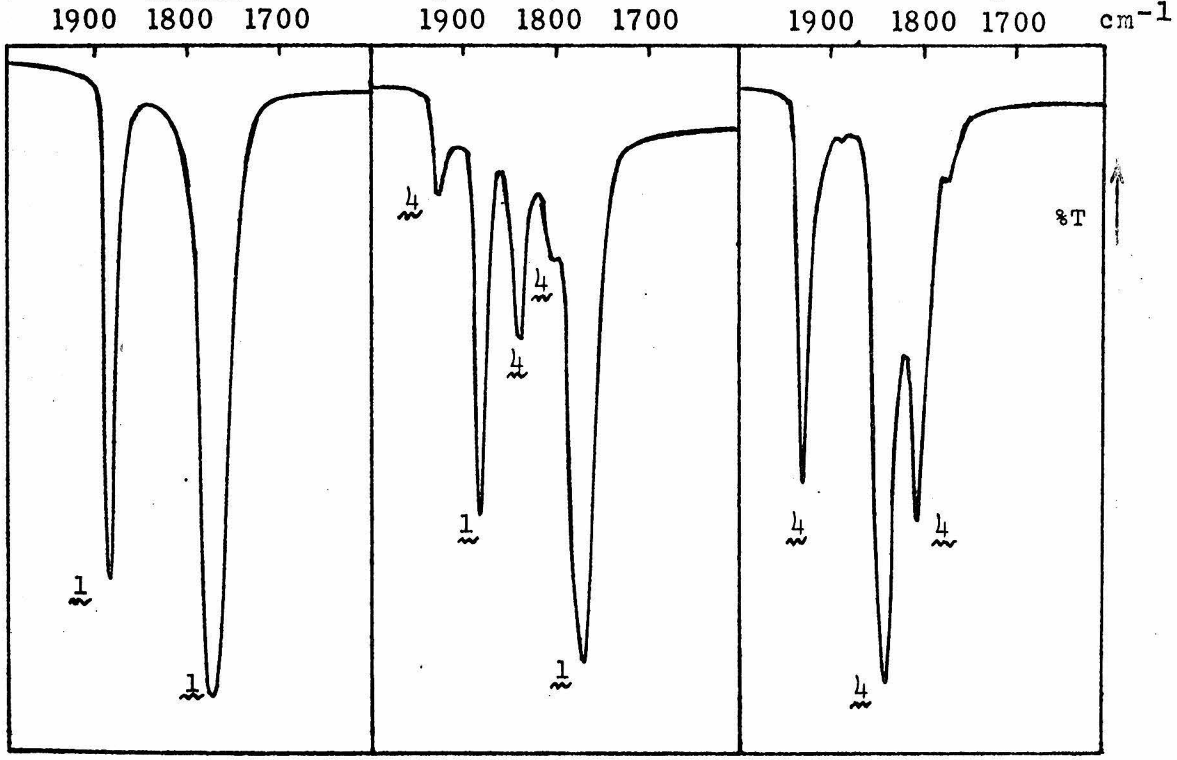
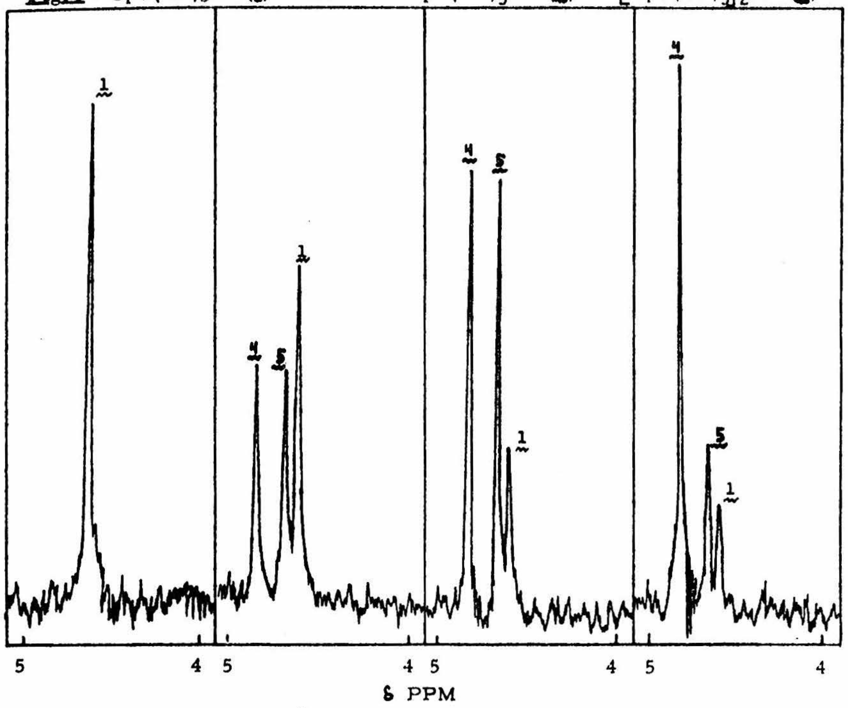
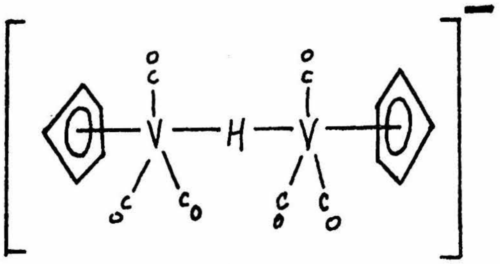


Fig. 3- $CpV(CO)_3H^-$ (1) + RX $\longrightarrow$ $CpV(CO)_3X^-$ (4) + $[CpV(CO)_3]_2H^-$ (5)



However, the C_5H_5 region of the NMR (δ 4-6 ppm) shows the formation of two organometallic products as 1 is consumed; 4 at δ 4.83 ppm and a new material which we believe to be a hydrogen bridged dimer, $PPN^+[CpV(CO)_3]_2H^-$, 5, at δ 4.65 ppm (singlet) (*vide infra*).



5

The C_5H_5 resonance of 1 at δ 5.60 ppm is found to disappear at at a rate faster than the octyl bromide triplet at δ 3.40 ppm and an insufficient amount of 4 is observed compared to the amount of octyl bromide consumed. Furthermore, the quantity of **5** observed (based on 5 C_5H_5 protons per equivalent) is equal to the amount of missing **4** plus **1**. Therefore, **5** appears to be a 1:1 adduct formed by the reaction of remaining **1** with newly formed **4**. Indeed, an NMR signal is observed at δ 4.65 ppm upon mixing THF solutions of **1** and **4**, suggesting the reaction in equation 2.

$$\underset{\mathbf{4}}{CpV(CO)_3Br^-} \rightleftharpoons CpV(CO)_3 + Br^- \underset{\mathbf{1}}{\xrightleftharpoons{CpV(CO)_3H^-}} \underset{\mathbf{5}}{[CpV(CO)_3]_2H^-} \qquad (2)$$

5 may be prepared <u>in situ</u> by a variety of methods, but isolation attempts at 25°C have been unsuccessful. If a THF solution of **2** and **1** is irradiated while purging with nitrogen, IR bands due to **5** at 1855 and 1814 cm^{-1} are observed to grow in while bands of **2** and **1** diminish[10] (Fig. 4). The formation of **5** probably occurs via the photodissociation of CO from **2** to yield a coordinatively unsaturated intermediate followed by hydridic attack at the vacant site by **1**.

This ability of a metal hydride to act as a ligand has been suggested previously by Kaesz, Bau, and Churchill.[11] The changes in the NMR spectrum as the photolysis proceeds are also consistent with this formulation.

5 has also been formed by the reduction of $Cp_2V_2(CO)_5$ in THF solution with Na/Hg amalgam followed by treatment with H_2O, PPN^+Cl and CO. An oxidation of **1** by $AgClO_4$ also yields **5**.

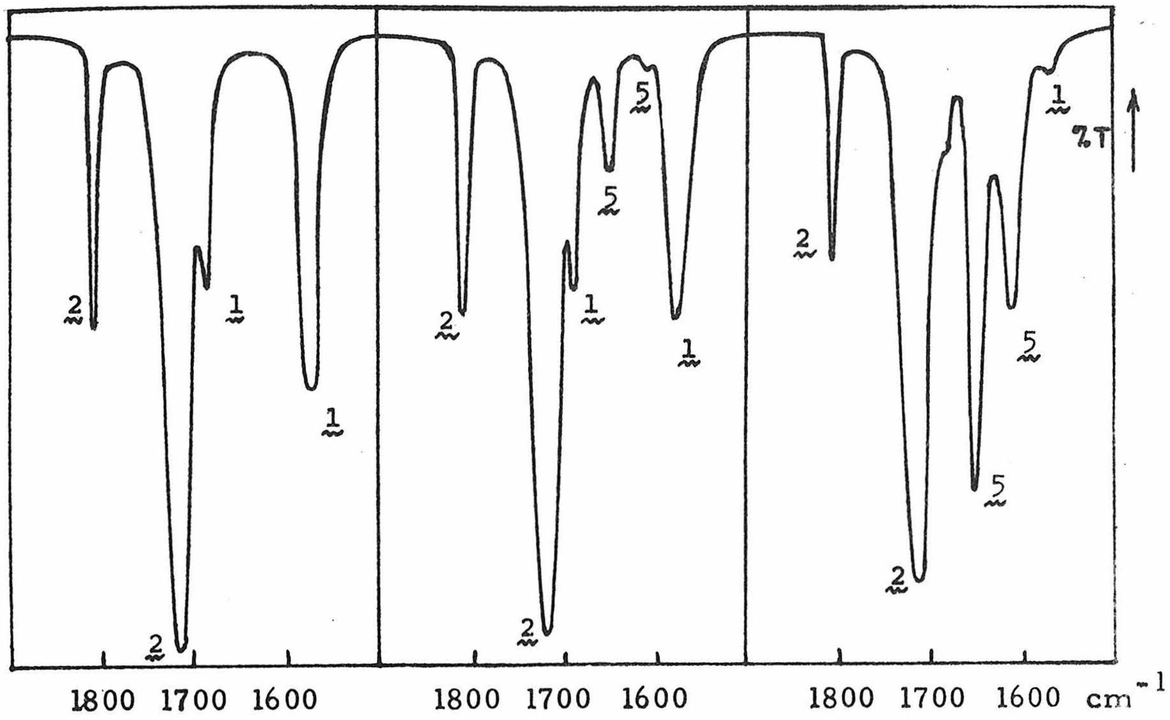


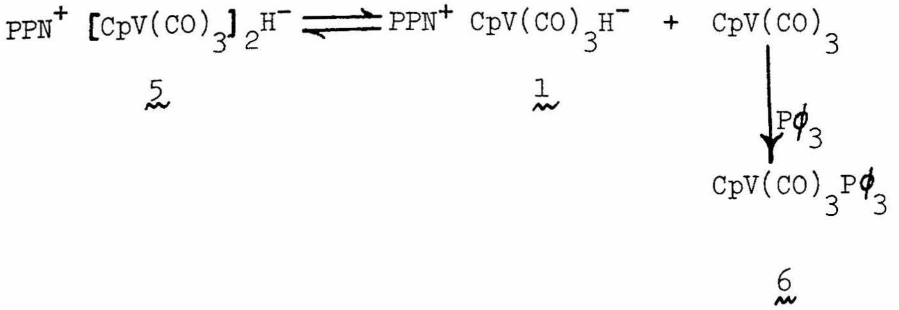
Fig. 4 $CpV(CO)_4 + CpV(CO)_3H^- \xrightarrow{h\nu} [CpV(CO)_3]_2H^-$

2 1 5

We propose a symmetrical bridging hydride structure with equivalent Cp rings for the intermediate 5, analogous to the isoelectronic tungsten complex reported by Davison and Wilkinson.[12] Both compounds show 2 IR bands in the ν_{co} region consistent with a D_{3h} or D_{3d} structure for the bridging hydride. Other similar transition metal bridging hydrides are also known.[13]

5 dissociates slowly ($\tau_{1/2}$ = 6 hrs. at 25°C) in solution to form 1 and "$CpV(CO)_3$" which may be scavenged by $P\phi_3$ (eqn. 3) forming the known[14] $CpV(CO)_3P\phi_3$, 6,. In stoiciometric reductions of alkyl bromides by 1 the consumption of the latter in forming 5 limits the rate of the reaction, in which case the slow dissociation of 5 becomes the

rate determining step.



$$\begin{array}{ccccc} \mathrm{PPN^{+}\,[CpV(CO)_3]_2H^{-}} & \rightleftharpoons & \mathrm{PPN^{+}\,CpV(CO)_3H^{-}} & + & \mathrm{CpV(CO)_3} \\ \mathbf{5} & & \mathbf{1} & & \downarrow{\scriptstyle \mathrm{P}\phi_3} \\ & & & & \mathrm{CpV(CO)_3P\phi_3} \\ & & & & \mathbf{6} \end{array} \qquad (3)$$

This argument is supported by the observation that no **5** is seen in the case of a reactive bromide (e.g., benzyl bromide), in which the reduction is complete within one minute and both **1** and **4** are not present for an appreciable length of time. However, if only 1/2 equivalent of benzyl bromide is added an almost quantitative yield of **5** is observed by NMR. Addition of a second 1/2 equivalent of benzyl bromide results in the disappearance of **5** over 2 hours with the formation of one equivalent of **4**, demonstrating the slow dissociation of **5** into **1** and coordinatively unsaturated $\mathrm{CpV(CO)_3}$.

Reduction of 1-iodooctane:

The reduction of 1-iodooctane (0.1 M) by **1** (0.1 M) is complete within 2 minutes and produces a quantitative yield of octane. However, $\mathrm{PPN^{+}[CpV(CO)_3I]^{-}}$, **7**, is the only organometallic product observed[15] and has spectral properties similar to those of **4** (IR: ν_{co} = 1936 (m), 1846 (s), 1806 (m), NMR: multiplet δ 7.55 ppm (30 H), singlet δ 4.86 (5 H)). The lack of formation of **5** indicates that the rate of reaction of **1** with 1-iodooctane to form **7** is faster than the rate of reaction of **1** with **7**.

Reduction of Acid Chlorides:

The reduction of heptanoic acid chloride with one equivalent of

1 occurs instantaneously with a quantitative yield of heptanal and $PPN^+[CpV(CO)_3Cl]^-$ (IR: ν_{co} = 1942 (m), 1844 (s), 1802 (m); NMR: multiplet δ7.55 ppm (30 H), singlet δ4.83 ppm (5 H)).[15] **1** reduces other acid chlorides to aldehydes in high yield with no further reduction to the alcohol.

Competitive Rate Studies:

1 reduces a host of organic halides including primary, secondary, tertiary, vinylic, and aryl centers as given in Table I. Iodides are reduced much more quickly than bromides, while chlorides (except for cyclopropylcarbinylchloride and benzyl chloride) and tosylates (except for methyl tosylate and cyclopropylcarbinyltosylate) do not react at all at 25°C.

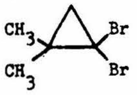
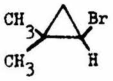
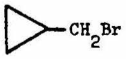
The relative reactivity of primary, secondary, and tertiary bromides was determined by reducing a mixture of 1-bromopentane, 2-bromohexane, and 2-bromo-2-methylpropane (0.5 M) with a deficiency of **1** (0.1 M). The product solution was analyzed to determine the ratio of pentane to hexane to 2-methylpropane, which gives the relative rates of reduction of primary, secondary, and tertiary centers, as 12:1:5, respectively.

A similar reduction of a mixture of 1-bromopentane, 1-bromohexane and 1-bromo- 2,2-dimethylpropane provided pentane, hexane, and 2,2-dimethylpropane in a 44:43:1 ratio. These results together suggest that there are two important effects in the reduction of alkyl halides; a steric effect that allows unhindered primary halides to be reduced more quickly than secondary or tertiary, and a smaller electronic effect that allows tertiary halides to be reduced more quickly than secondary.

Mechanism of Reduction of Alkyl Halides:

One can imagine several possible mechanisms for the reduction of alkyl halides by **1**, including: 1) S_N2 or nucleophilic attack on carbon (oxidative addition), followed by reductive elimination of product, 2) an outer sphere electron transfer process, and 3) a radical chain process.

Table I. Reduction of alkyl halides by $PPN^+ CpV(CO)_3H^-$

Alkyl Halide	Product	Reaction Time	Yield (%)[a]
1-bromooctane	octane	4 hrs.	75
1-iodooctane	octane	0.5 hrs.	97
1-bromohexane	hexane	7 hrs.	73
2-iodooctane	octane	1 hr.	97
bromocyclohexane	cyclohexane	10 hrs.	65
		0.5 hrs.[b]	95
$C_6H_{13}COCl$	$C_6H_{13}CHO$	0.1 hr.	100
$(CH_3)_3CBr$	$(CH_3)_3CH$	12 hrs.	100
$C_6H_5CH_2Br$	$C_6H_5CH_3$	0.5 hr.	90
$(-)$-$C_6H_5CH(Br)(CH_3)$	$(\pm)$-$C_6H_5CHD(CH_3)$	0.5 hr.	64[c]
$C_4H_9CHBrCH_2Br$	$C_4H_9{=}CH_2$	2.5 hrs.	100
C_6H_5Br	C_6H_6	8.5 hrs.	43
$C_6H_5CH{=}CHBr$	$C_6H_5CH{=}CH_2$	5. hrs.	46
cis- or trans- $CH_3CH_2CH{=}(Br)CH_2CH_3$	cis-3-hexene trans-3-hexene	260 hrs. 260 hrs.	30[d] 70[d]
6-bromo-1-hexene	1-hexene	17 hrs.	80
	methylcyclopentane	17 hrs.	6.8
	methylcyclopropane	2 hrs.	32
cyclohexenone	no reaction	1 hr.	--
$C_6H_{13}CO_2CH_3$	no reaction	12 hrs.	--

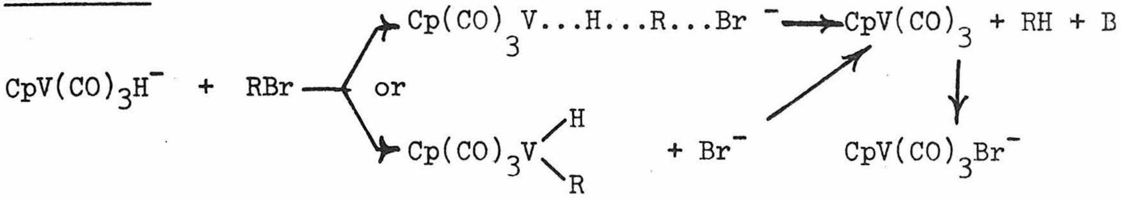
---

a - Yields determined by integration of NMR and VPC peaks.
b - No further reduction even after 24 hours.
c - Isolated yield (preparative VPC).
d - Corrected for unreacted starting material.

Nucleophilic Attack (Oxidative Addition)

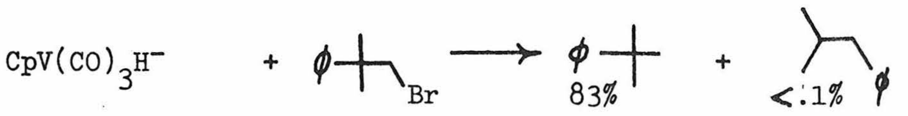
A possible mechanism to account for the observed reaction would be a nucleophilic attack by 1 upon the halide carbon, either by the hydride ligand or the metal, forming an alkane plus a coordinatively unsaturated CpV(CO)$_3$ intermediate in the case of the former or a metal alkyl hydride that could reductively eliminate alkane and a CpV(CO)$_3$ fragment in the case of the latter (Scheme II). This CpV(CO)$_3$ fragment could then react with the free halide ion to form the primary organometallic product (4 or 7).

Scheme II



We have been able to rule out these mechanisms on the basis of two observations: 1) The reduction of optically active (-)-α- bromoethyl-benzene with PPN$^+$[CpV(CO)$_3$D]$^-$ yields racemic α-deterioethylbenzene,[16] whereas the mechanism(s) depicted in Scheme II would predict a clean inversion in stereochemistry, and 2) the CpV(CO)$_3$ fragment cannot be trapped with a ligand to form a CpV(CO)$_3$L with up to a 35-fold excess of PR$_3$ (R=ϕ, CH$_3$) or with CH$_3$CN (used as solvent). In both of these competition experiments PPN$^+$[CpV(CO)$_3$X]$^-$ (X = halogen) is formed as the kinetic product which then is slowly substituted by PR$_3$ or CH$_3$CN.[17] Control experiments performed by irradition of a THF solution of CpV(CO)$_4$, Pϕ_3, and Na$^+$X$^-$ in a 1:2:2 ratio show CpV(CO)$_3$Pϕ_3,6, being formed 10:1 over the halide[19], demonstrating that **6** is the kinetic product formed in the competition between $P\phi_3$ and halide ion for a $CpV(CO)_3$ fragment.

This mechanism is also unlikely in view of the observation that tertiary, vinylic and benzylic centers are reduced as well as primary and secondary centers. We have also been able to rule out the intermediacy of carbonium ions. Reduction of neophyl bromide with **1** produces t-butyl-benzene with only traces (< 0.17) of isobutyl-benzene, the latter being expected as the product of a carbonium ion rearrangement (eqn. 4).



(4)

Electron Transfer

Another possible reaction mechanism is an outer sphere electron transfer from **1** to R-Br, forming $CpV(CO)_3H^{\cdot}$, and an intermediate free alkyl radical capable of abstracting a hydrogen from the $CpV(CO)_3H^{\cdot}$ species (Scheme III). However, this mechanism predicts the formation of a $CpV(CO)_3$ intermediate that would have to find a bromide ion in solution to form **4**. The competition experiments involving PR_3 and CH_3CN described previously allow this intermediate and consequently this mechanism to be ruled out.

Scheme III:

$$CpV(CO)_3H^- + R\text{-}Br \longrightarrow CpV(CO)_3H^{\cdot} + R^{\cdot} + Br^-$$

$$CpV(CO)_3H^{\cdot} + {}^{\cdot}R \longrightarrow CpV(CO)_3 + R - H$$

$$CpV(CO)_3 + Br^- \longrightarrow CpV(CO)_3Br^-$$

The possibility of formation of intermediate carbanions has also been examined by the reduction of 1-bromodecane in a THF/CD_3OD solution (4:1,V:V) with 1. The hydrocarbon produced is d_o-decane (~95%), whereas an intermediate carbanion would be expected to accept a deuterium from the CD_3OD, producing d_1-decane.

Radical Chain

The mechanism that we propose for the reduction of alkyl halides by 1 is a radical chain process similar to that observed for $(n\text{-}C_4H_9)_3SnH$. An advantageous radical initiator starts the chain by abstraction of a hydrogen atom from 1, forming a vanadium radical anion species. Subsequent halogen abstraction from R-X (X = Br,I) produces a free alkyl radical and the observed organometallic product 4 directly, without the intermediacy of a coordinatively unsaturated intermediate. Propagation of the chain occurs by abstraction of a hydrogen atom from 1 by the free alkyl radical (Scheme IV).

Scheme IV

$$\mathrm{CpV(CO)_3H^-} \xrightarrow{\mathrm{I^\cdot}} \mathrm{CpV(CO)_3}^{\dot{-}}$$

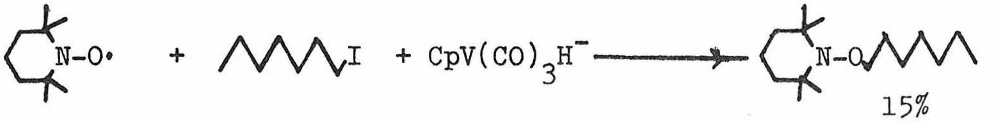
$$\mathrm{CpV(CO)_3}^{\dot{-}} + \mathrm{R - X} \longrightarrow \mathrm{CpV(CO)_3X^-} + \mathrm{R^\cdot}$$

$$\mathrm{R\cdot} + \mathrm{CpV(CO)_3H^-} \longrightarrow \mathrm{CpV(CO)_3}^{\dot{-}} + \mathrm{R\text{-}H}$$

Reduction of 1,2-dibromohexane with 1 produces 1-hexene as the only product. If either <u>cis</u>- or <u>trans</u>-3-bromo-3-hexene is reduced the same ratio of <u>cis</u> to <u>trans</u>-3-hexene is found in both reactions (1:2.3, respectively). Reduction of 1,1-dibromocyclopropane proceeds only to bromocyclopropane with no further reduction to cyclopropane. These observations are consistent with the formation of alkyl radicals, as have been reported in other systems.[22]

The intermediate free alkyl radicals may be scavenged using

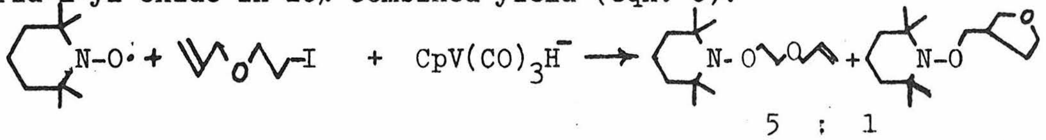
2,2,6,6-tetramethylpiperidoxyl (TMPO) as a trapping agent.[21,23,24] Addition of a mixture of 1-iodoheptane and TMPO to a THF solution of 1 (5:2:1 ratio)produces a 15% yield of O-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide (eqn. 5).



(5)

TMPO reacts quickly with 1, yet enough reduction occurs to produce some free radicals.

Similarly, addition of a mixture of 2-allyloxyethyl iodide and TMPO to a CH_3CN solution of 1 (1:4:1 ratio) produces a 5:1 ratio of O-allyloxyethyl-2,2,6,6-tetramethylpiperid-1-yl oxide to the cyclized product O-3-tetrahydrofurylmethyl -2,2,6,6-tetramethylpiperid-1-yl oxide in 20% combined yield (eqn. 6).



(6)

We have been unable to trap the intermediate free radicals using oxygen as a scavenger. Addition of benzyl bromide to a THF solution of 1 while purging with oxygen produced no benzyl alcohol after work-up. Although 1 is oxidized by oxygen within 30 seconds of purging, benzyl bromide reacts with 1 upon mixing, implying that either the vanadium hydride is a better proton donor than O_2 is a scavenger, or that all of the oxygen in solution reacts with 1 before it can scavenge an alkyl radical.

Radical Rearrangements

We have also demonstrated the intermediacy of free alkyl radicals by examining substrates whose radicals are capable of undergoing intramolecular rearrangements at rates competitive with hydrogen abstraction. Several such alkyl radicals are known to undergo isomerization, ring openings, and cyclizations. The alkyl halides used in this investigation and their rearrangement products are listed in Table II. The competition by alkyl radical between rearrangement and hydrogen abstraction from **1** is indicated in Scheme V.

Scheme V

$$\begin{tikzcd} {} \arrow[r] & R\cdot \arrow[r, "k_r"] \arrow[d, "k_H[1]"] & R'\cdot \arrow[d, "k_H[1]"] \\ & R-H & R'-H \end{tikzcd}$$

If an excess of **1** over RX is employed in the reductions[25], then the ratio $\frac{[RH]}{[R'H]}$ is given by equation 7 as has been noted by Beckwith, et al.[26]

$$\frac{[RH]}{[R'H]} = \frac{k_H}{k_r}\,[CpV(CO)_3H^-] \qquad (7)$$

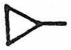
Plots of $[RH]/[R'H]$ vs. $PPN^+ [CpV(CO)_3H]^-$ concentration for the reductions of  and  give the expected straight lines as shown in Figs. 5 and 6, respectively.

TABLE II

Radical Rearrangements with 1[a]

Reactants			Products		
Substrate	Conc. (M)	PPNCpV(CO)$_3$H$^-$ Conc. (M)	Unrearranged(M)	Rearranged(M)	$\frac{\text{rearranged(M)}}{\text{unrearranged(M)}}$
	0.0050	0.0200	 (0.0039)	 (0.0000)	0
	0.0192	0.0770	 (0.0184)	 (0.0005)	0.027
	0.0200	0.1620	 (0.0195)	 (0.0005)	0.026
		0.0810	(0.0178)	(0.0008)	0.075
		0.0405	(0.0184)	(0.0022)	0.120
	0.0200	0.1640^b	 (0.0107)^b	 (0.0074)^b	0.69^b
		0.0820^b	(0.0085)^b	(0.0096)^b	1.13^b
		0.0410^b	(0.0051)^b	(0.0127)^b	2.49^b
		0.0809	(0.010)^c	(-0.010)^c	1.0^c
		0.1500	(0.008)^c	(0.012)^c	0.6^c

TABLE II (cont.)

Reactants			Products		
Substrate	Conc. (M)	PPNCpV(CO)$_3$H$^-$ Conc. (M)	Unrearranged(M).	Rearranged(M)	rearranged(M) / unrearranged(M)
	0.0200	0.081	 (0.0099)	 (0.102)	1.03
	0.0200	0.1600	 (0.0008)	 (0.0142)	17.7
		0.0800	(0.0003)	(0.0142)	47.3
	0.0200	0.1600	 (0.0047)^d	 (0.0007)^d	0.15^d
		0.1600	(0.0106)	(0.0070)	0.66
		0.0400	(0.0043)^d	(0.0013)^d	0.30^d
		0.0400	(0.0062)	(0.0106)	1.71

---

[a] all product yields >85% as determined by gas chromatography with internal standard. All reactions in THF at 25°C except as noted. [b] CH_3CN solvent [c] determined by NMR integration of $-CH_3$ resonances of products in d_8THF. [d] values at 30% completion

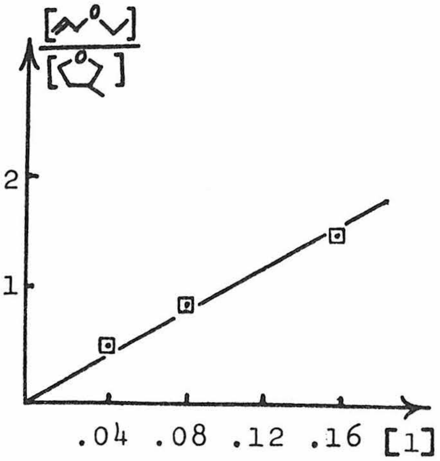


Fig.5 Plot of eqn. 7 for 

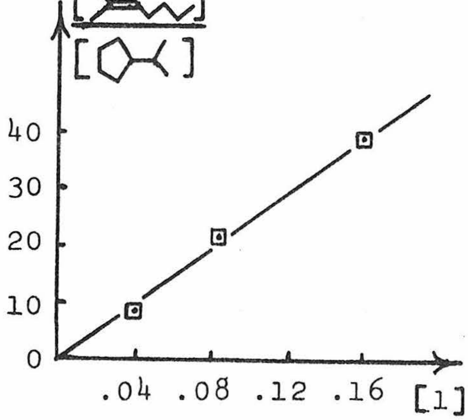
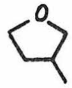


Fig.6 Plot of eqn. 7 for 

Also within experimental error the ratio of  to  is independent of halogen (Br or I), solvent (THF or CH_3CN) and of % completion (Fig.7), as predicted for the radical chain mechanism in Scheme IV.

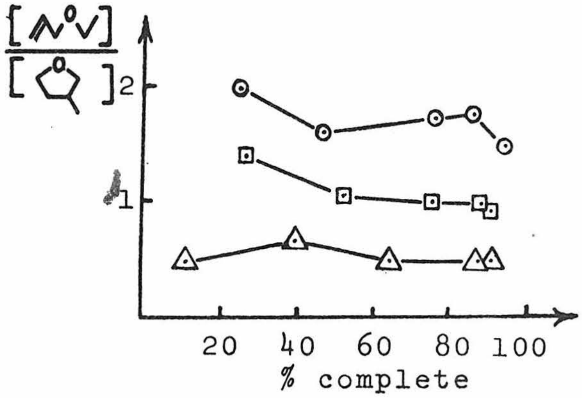


Fig.7 Product ratio in the reduction of  by 1 vs. % completion.
[RX] =0.02 M
[1]= 0.04 M(△), 0.08 M(⊡), 0.16 M(⊙)

If the rate constant for cyclization of the allylethyl ether radical is assumed to be $1.2x10^6$ sec^{-1} [27], then a value for k_H of $1.5x10^7$ $M^{-1}sec^{-1}$ can be calculated from the data in Table II and equation 7. This rate constant for abstraction of a hydrogen atom from 1 by a free alkyl radical is about 12 times that for abstraction from $(n\text{-}C_4H_9)_3SnH$.[30]

Deuterium Isotope Effect:

Reduction of 1-bromodecane (0.027 M) with a 52/48 mixture of $PPN^+[CpV(CO)_3D]^-/PPN^+[CpV(CO)_3H]^-$ (0.14M each) produced 58.3% d_1-decane and 41.7% d_o-decane, corresponding to a primary deuterium isotope effect of $k_H/k_D = 1.28$. This extremely low value compared with that for $(n\text{-}C_4H_9)_3SnH$ (k_H/k_D=2.7)[30] indicates that the vanadium-hydrogen bond is very weak, thereby accounting for the rapid hydrogen abstraction rate constant.

Effects of Initiators + Inhibitors:

Our attempts to inhibit this radical chain have been unsuccessful, since many commonly used inhibitors react with **1**. Addition of galvinoxyl[30,31] to a solution of **1** produces an immediate deep purple color associated with the galvinoxyl anion. Oxygen [31,32] reacts with radicals at a diffusion controlled rate, yet addition of 10 mole percent oxygen to a solution of 1-bromooctane and **1** has no noticable effect upon the rate of reduction. Also, addition of either o,o, p-tri-t-butylphenol[31] or duroquinone[30,31,33] to a reduction solution of **1** and 1-bromooctane has no effect upon the rate of reduction compared to an identical reduction with no inhibitors.

Irradiation of a solution of **1** and 1-bromooctane produces no enhancement of the rate of reduction, with or without added azobisisobutonitrile.[31,33,34] Our inability to initiate or inhibit these reactions suggests that short chain lengths are involved or that initiation occurs easily enough that termination of many of the chains does not alter the observed properties of the reaction.[35]

Reduction of cyclopropylcarbinyl derivatives:

We have examined the reduction of cyclopropylcarbinyl iodide bromide, chloride and tosylate and have found anomalous behavior to the mechanism proposed in Scheme II. Using a value of $1.4\mathrm{x}10^{8}$ sec^{-1} for the rate constant for ring opening of the cyclopropylcarbinyl radical[36] at 25°C and a value of $1.2\mathrm{x}10^{7}$ M^{-1} sec^{-1} for the rate constant for hydrogen abstraction from **1**, one would predict 1% methylcyclopropane to be observed in the reduction of cyclopropylcarbinyl halides. Indeed, reduction of cyclopropylcarbinyl iodide (0.02M) with **1** (0.08M) gives all 1-butene (98%) and little methylcyclopropane (2%).

However, reaction of cyclopropylcarbinyl bromide (0.02M) with **1** produces more methylcyclopropane (30-50%) than in the iodide case (Table II). Abstraction of hydrogen from **1** by cyclopropylcarbinyl radicals would require a hydrogen transfer rate of ~10^{8} M^{-1} sec^{-1} in order to account for the observed product ratio, an order of magnitude higher than the rate determined using other radical rearrangements. Furthermore, the ratio of 1-butene to methylcyclopropane was roughly independent of the concentration of **1** (Fig. 8) and suggested that a different mechanism was (also) occurring.

The inconsistency was clarified by the observation that cyclopropylcarbinyl tosylate reacts with **1** to produce exclusively methylcyclopropane with an overall rate constant for reaction approximately 0.2 times that for the corresponding bromide. Therefore we propose that cyclopropylcarbinyl bromide is being reduced by two different mechanisms: 1) a radical chain mechanism (Scheme IV) that produces almost all 1-butene, and 2) an oxidative addition/reductive elimination mechanism producing exclusively methylcyclopropane (Scheme VI).

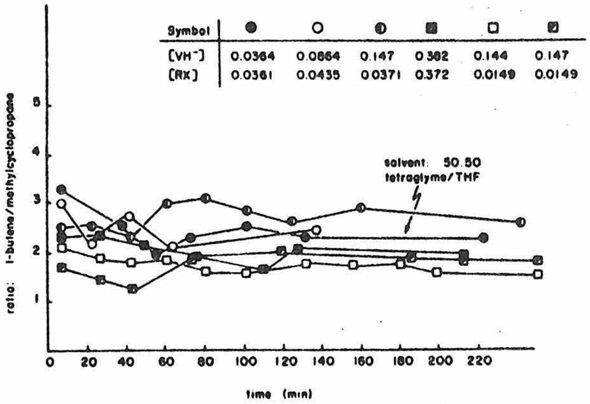
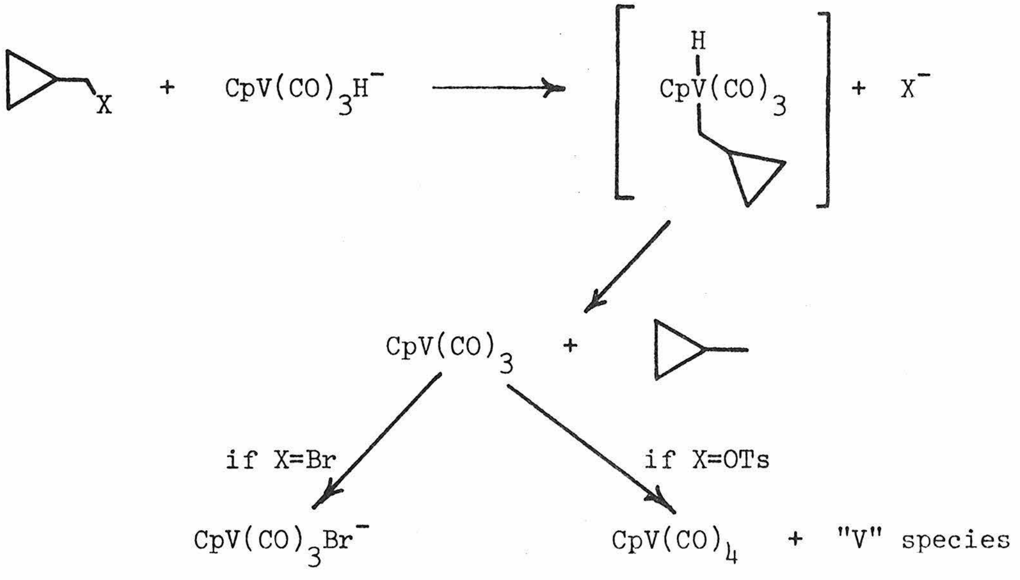


Figure 8. Ratio of 1-butene to methylcyclopropane formed on reduction of cyclopropylcarbinyl bromide by $CpV(CO)_3H^-$ in THF under varying concentration conditions, displayed as a function of reaction time (concentrations given in mol L^{-1}).

Scheme VI



In the reduction of cyclopropylcarbinyl bromide by **1** the overall rate of production of 1-butene by the radical chain process must be approximately twice the rate of production of methylcyclopropane by the oxidative addition/reductive elimination process. Yet in the reduction of cyclopropylcarbinyl iodide, the radical chain reaction dominates completely any nucleophilic process. A similar observation has been made for the alkylation of $[CpFe(CO)_2]^-$ by cyclopropylcarbinyl derivatives.[37] We suspected that reduction of cyclopropylcarbinyl chloride with **1**, if possible, would produce entirely methylcyclopropane Indeed, the reduction proceeds very slowly (7% product after 4 days) to yield exclusively methylcyclopropane.

The question as to why cyclopropylcarbinyl derivatives are capable of undergoing nucleophilic displacements whereas other primary bromides, chlorides, and tosylates are not can be answered if one considers the relative rates of solvolysis of cyclopropylcarbinyl tosylate vs. isobutyl tosylate. Roberts has found[38] that due to stabilization of the intermediate carbonium ion by the cyclopropane ring, cyclopropylcarbinyl tosylate is hydrolyzed at a relative rate of 10^6 times faster than its isobutane isomer. This tremendous rate enhancement for a carbonium ion intermediate could be reflected by a substantial increase in the rate of nucleophillic attack at the cyclopropyl carbinyl center relative to a primary center due to stabilization of the slight positive charge that would build up at the α-carbon during substitution. We propose that cyclopropyl carbinyl centers can undergo nucleophilic attack by **1** because their $\Delta G^{\ddagger}$ for substitution is substantially lower in energy than the $\Delta G^{\ddagger}$ for substitution at a primary center.

The only other system for which we have evidence of nucleophilic attack is for CH_3X derivatives (X=I,Br,OTs). As a probe for the amount of $S_N{}^2$ component in these reductions in THF solution we have used a 4-fold excess of $P\phi_3$ to trap any coordinatively unsaturated $CpV(CO)_3$ intermediate produced by nucleophilic attack on CH_3X. The radical chain component to the mechanism is measured by the amount of $[CpV(CO)_3X]^-$ formed, the relative quantities of the latter and $CpV(CO)_3P\phi_3$, **6**, being determined by their ν_{CO} IR absorptions 1940 and 1950 cm^{-1}, respectively.

Reduction of CH_3I by **1** in the presence of excess $P\phi_3$ occurs upon mixing, producing **7** in 10-fold excess over **6**. Then **7** is slowly ($T_{1/2} \approx 3$ hrs.) observed to be substituted by $P\phi_3$ forming **6**.

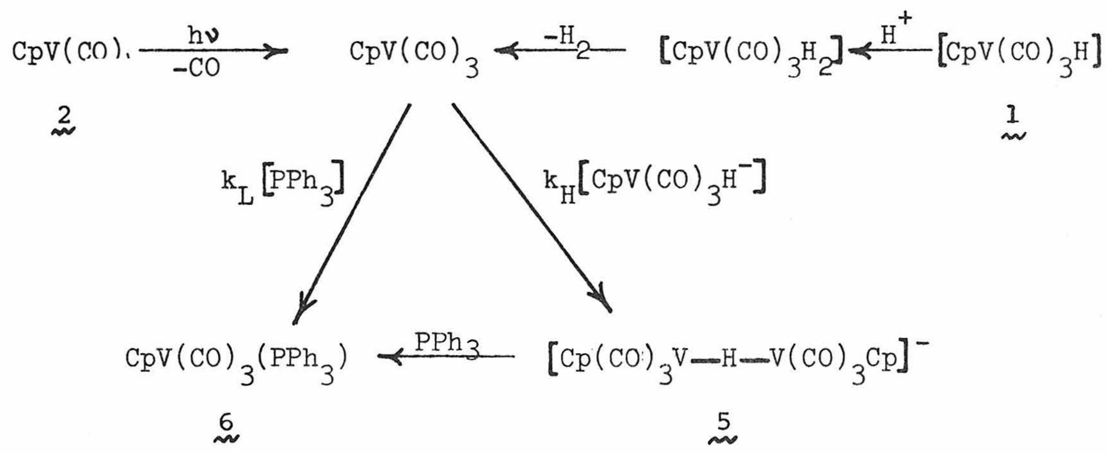
However, reduction of CH_3Br under identical conditions occurs within 30 seconds and produces an approximately 60/40 mixture of **6** and **4**, respectively. Slowly ($T_{1/2} \approx 3$ hrs.) the halide complex **4** is converted to the phosphine complex **6**, indicating that the **6** initially observed was the <u>kinetic</u> product of the reaction, presumably formed from the reaction of $P\phi_3$ with $CpV(CO)_3$. Therefore, CH_3Br also appears to react with **1** by two mechanisms, a radical chain and a nucleophilic process.

In support of the existence of an S_n2 component to the reduction of CH_3Br is the observation that CH_3OTs reacts with **1** to produce CH_4, yet n-heptyl tosylate produces no heptane after several days in solution with **1** at 25°C. As CH_3X has no electronic stabilization of an S_n2 transition state, we propose that reaction occurs due to the tremendous decrease in steric hindrance at the methyl center. Apparently even primary tosylates are too hindered to undergo S_n2 displacement by the bulky $[CpV(CO)_3H]^-$ nucleophilic.

Metal Hydrides As Ligands. Evaluation of Kinetic and Thermodynamic Ligating Ability of $[CpV(CO)_3H]^-$. The photochemical synthesis of 5 from 1 and 2 is analogous to the photochemistry outlined in Scheme II, except that the ligand entering the vanadium coordination sphere is a molecule of 1, rather than phosphine, halide, or acetonitrile. Although a few other bridging hydrides are known,[12,13] and ligating strengths of conventional ligands have been discussed at some length,[39] to our knowledge there has been only scant discussion of the relative ability of a metal hydride to act as a ligand in the coordination sphere of a second metal.[11] Our interest in this problem was stimulated by the observation, reported above, that irradiation of 2 in the presence of 1 led only to bridging hydride 5 --that is, formation of dimer $Cp_2V_2(CO)_5$ was completely suppressed by the presence of 1. It was also spurred by indirect evidence recently obtained by Norton and co-workers[40] that a rapid reaction between an osmium hydride and an unsaturated osmium complex plays an important role in the binuclear reductive elimination of methane from $(CO)_4Os(CH_3)(H)$.

Because phosphines have played a central role in determination of relative ligating abilities,[39] we decided to attempt to compare the affinities of 1 and PPh_3 for the $CpV(CO)_3$ fragment. Our first experiment involved preparing a THF solution of 5 by irradiating 2 in the presence of 1. We then added PPh_3, which (at a moderate rate) completely converted the bridging hydride to equimolar amounts of $[CpV(CO)_3H]^-$ and $CpV(CO)_3PPh_3$ (this incidentally provided additional confirmation for the empirical formula of 5). This experiment demonstrated that PPh_3 is clearly a thermodynamically better ligand for vanadium than is 1. *However, the kinetic ligating ability of these ligands does not follow the same trend.* Thus, we irradiated 2 (0.60M) in the presence of equimolar quantities (0.12 M each) of PPN^+ $[CpV(CO)_3H]^-$ and PPh_3, and examined (cf. Scheme IV) the kinetic ratio of 6 to 5 at early reaction times. The precision of this experiment was affected somewhat by the thermal reaction between 5 and PPh_3; However, it is clear that 1 enters the coordination sphere of vanadium *more rapidly* than PPh_3. By extrapolating to t = 0, we were able to determine from the kinetic product ratio that k_H/k_L (Scheme VII) is at least 2:1. Thus, there is some (as yet unexplained) property of hydride 1 which allows it to enter the vanadium coordination sphere more rapidly than phosphine, despite

Scheme VII



the fact that the thermodynamic affinity of vanadium for phosphine is larger.

It is possible, of course, that the photochemical replacement reaction takes place by a mechanism not involving $CpV(CO)_3$ (despite much indirect evidence to the contrary).[41] In order to check this possibility, we carried out a competition experiment on $CpV(CO)_3$ generated in a completely independent reaction. We chose the protonation of **3**, a reaction which presumably[2] first forms $CpV(CO)_3H_2$; this transient dihydride loses H_2, giving $CpV(CO)_3$ which in the absence of external ligand forms $Cp_2V_2(CO)_5$. Thus, 0.12 M$[CpV(CO)_3H]^-$ was treated with one-tenth equivalent of TsOH in the presence of 0.10 M PPh_3. As in the irradiation, no $Cp_2V_2(CO)_5$ dimer was observed, but a mixture of **6** and **5** was formed instead (again, this was slowly converted to pure **6**). The initial **5**/**6** ratio observed was 1.9:1, which is satisfyingly close to that seen in the photochemical reaction, considering the complicating thermal reaction and the difference in reaction conditions employed. This provides support for the quantitative reliability of the kinetic trapping ratio, as well as for the postulate that $CpV(CO)_3$ or a reactive analog of this species, such as $CpV(CO)_3THF$, is the intermediate in both reactions.

Preparation of PPN^+ $[CpV(CO)_3BH_4]^-$. The hydride-as-ligand experiments outlined above, as well as syntheses of transition metal borohydride complexes which have appeared in the literature recently, stimulated us to investigate the possibility of carrying out replacement reactions on $CpV(CO)_4$ with borohydride as the entering ligand. We therefore prepared[42] $PPN^+BH_4^-$, and irradiated $CpV(CO)_4$ in a THF solution of this material. Analysis of the reaction solution by IR showed that both hydride **3** and a new complex were formed. The new material has IR absorptions in the carbonyl region at 1835 and 1721 cm^{-1}, and absorptions characteristic of metal-bound BH_4^- at 2360 cm^{-1} (KBr pellet). In the NMR, this complex has a Cp signal at δ 4.14 ppm, and (as in the case of similar complexes[42]) coupling to boron and vanadium renders the boron-bound hydrogen signals too broad to be observed at room temperature.

The new complex proved to be difficult to separate from hydride **1**, and so in an alternative method of synthesis, pure PPN^+-**1** was treated with BH_3-THF. This produced the new material in a clean reaction, and it was isolated as green crystals and characterized as $PPN^+ [CpV(CO)_2BH_4]^-$ (**8**) on the basis of its spectral characteristics and elemental analysis.

Control experiments demonstrated that **8** was not the source of hydride **1** observed in the photochemical reaction; **1** is therefore produced in a direct reaction between **2** and $PPN^+BH_4^-$. We suggest pathways outlined in Scheme VIII are those responsible for the complexes formed in the reactions discussed here.

Scheme VIII

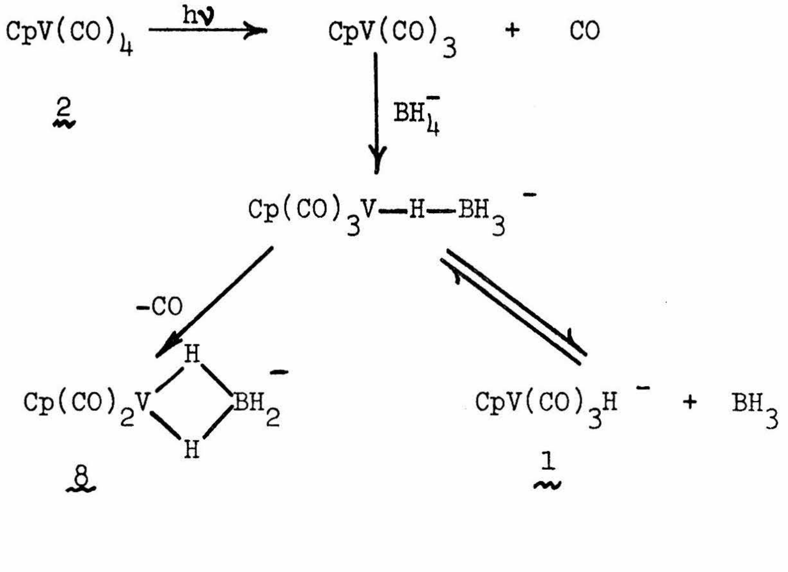


Table III

Spectral data on cyclopentadienyl vanadium compounds

Compound	IR (ν_{CO}) in THF	NMR[a] in d_8-THF
Li^+-$CpV(CO)_3Cl^-$	1941, 1849, 1814 cm^{-1}	4.80 ppm
PPN^+-$CpV(CO)_3Cl^-$	1942, 1844, 1802	4.83
Li^+-$CpV(CO)_3Br^-$	1941, 1847, 1806	4.88
PPN^+-$CpV(CO)_3Br^-$	1941, 1847, 1804	4.83
Na^+-$CpV(CO)_3I^-$	1936, 1846, 1806	4.86
PPN^+-$CpV(CO)_3I^-$	1938, 1848, 1810	4.80
$CpV(CO)_4$	2008, 1915	5.22
$Cp_2V_2(CO)_5$	1995, 1942, 1893, 1861, 1818	5.08
Na^+-$CpV(CO)_3H^-$	1889, 1792, 1778(sh), 1732	4.73
PPN^+-$CpV(CO)_3H^-$	1887, 1775	4.60, -6.72[b]
$Na_2CpV(CO)_3$	1733, 1595, 1530[c]	----
PPN^+-$[CpV(CO)_3]_2H^-$	1855, 1814	4.65
$CpV(CO)_3P\phi_3$	1950, 1870(sh), 1856	4.86(doublet),7.46[d]
$CpV(CO)_3(CH_3CN)$	1968, 1866, 1843(sh)[e]	5.08
$PPN^+CpV(CO)_2(BH_4)^-$	1846, 1735	4.14

---

a-All singlets unless other wise noted. (Cp resonances)
b-hydridic resonance (broad)
c-KBr pellet
d-$P\phi_3$ proton resonances
e-CH_3CN solvent

Experimental

General. All reactions of $CpV(CO)_4$, $Na_2CpV(CO)_3\cdot THF$, and $PPN^+[CpV(CO)_3R]^-$, R = H, X^-, were carried out in a Vacuum Atmospheres Corporation drybox, with continuously circulating nitrogen, or in serum capped reaction vessels which were prepared in the drybox. Reagents were added to the serum capped reaction vessels by syringe techniques. All other synthetic reactions were carried out under normal atmosphere conditions.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian A60A, EM390, or HR-220 MHz spectrometer. All chemical shifts are relative to internal tetramethylsilane, unless otherwise stated. The low temperature NMR spectra were recorded on a Varian 56/60 MHz instrument in NMR tubes sealed under vacuum. NMR spectra of oxygen sensitive solutions were recorded in NMR tubes which were loaded in the drybox and stoppered with regular NMR tube caps wrapped with parafilm, or rubber septa. Additional reagents were added through the septa by syringe.

Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrophotometer. Solution spectra were recorded on 0.1 mm sodium chloride cells which were loaded in the drybox and stoppered with solid teflon plugs. KBr pellets were prepared in the drybox, but no precautions were taken to prevent contact with the atmosphere when they were removed from the drybox. Nujol mull spectra were recorded between sodium chloride plates in a holder sealed from the atmosphere by rubber O-rings.

Gas chromatographic analyses were carried out on either a Hewlett-

Packard 5750 or a Varian Associates Model 90-P instrument. Peak area integrations were performed by multiplying the peak widths at half-height by the peak heights, by cutting out and weighing the peaks, or by electronic integration. Optical rotations were measured on a Perkin-Elmer 141 polarimeter, and melting points were obtained with a Thomas Hoover capillary melting point apparatus. Melting points were uncorrected. Irradiations were carried out with a 500 W high pressure Hg lamp (Osram HBO500W/2), in an Oriel Corp. focused beam lamp housing.

Elemental analyses were performed by Galbraith and Schwarzkopf Laboratories and Dornis u. Kolbe Mikoanalytischer Laboratorium.

Tetrahydrofuran (THF), diethyl ether, benzene, petroleum ether and hexane used in the drybox were purified by vacuum transfer from sodium-benzophenone ketyl. Prior to vacuum transfer from sodium-benzophenone ketyl, petroleum ether and hexane were stirred repeatedly over concentrated sulfuric acid until the sulfuric acid did not become colored. Then they were stirred with saturated potassium permanganate in 10M sulfuric acid overnight, washed with water and dried over calcium chloride. Hexamethylphosphoramide (HMPA) was purified by the literature procedure.[43] All other liquid substrates were degassed by freeze-pump-thaw cycles before being used in the drybox.

$CpV(CO)_4$ was purchased from Ventron or Strem Chemical Companies and purified by sublimation at 0.25 mm Hg and 80°C. Commercial triphenylphosphine was recrystallized once from benzene, once from absolute methanol, and dried under vacuum (5 mmHg) at 65°C for 7 hours. Other phosphines were commercial samples purified by distillation. Sodium dispersion and lithium dispersion (Lithcoa Co.) were commercial samples and sodium amalgam was prepared by a published procedure.[44]

Commercially available alkyl halides were obtained from Aldrich Chemical Co. or Chemical Samples Co. Samples of meso- and d,ℓ -3,4-dibromohexane,[45] 1,1-dibromo-2,2-dimethylcyclopropane,[46] 1-bromo-2,2-dimethylcyclopropane,[46] cis- and trans-3-bromo-3-hexene,[47] cyclopropylcarbinyl bromide[48] and tosylate,[49] and benzyl chloroformate[50] were prepared according to literature procedures. All other alkyl halides were commercial samples. They were washed with aqueous thiosulfate to remove halogen, washed with water, dried over sodium sulfate, and distilled before being degassed.

Dodecanoyl chloride, heptanoyl chloride, and cinnamoyl chloride were prepared from either the corresponding acids or their sodium salts by published procedures.[51] Benzoyl chloride, phenylacetyl chloride and 3-carbomethoxypropionyl chloride were commerical samples which were distilled and degassed.

Neopentyl-p-toluenesulfonate, n-heptyl-p-toluenesulfonate, 2-octyl-p-toluenesulfonate, n-octyl- trifluoromethylsulfonate, methyl heptanoate, and phosphiniminium bromide were all prepared by literature procedures.[51-53]

All other organic substrates were commercial samples used without purification.

Preparation of $Na_2CpV(CO)_3\cdot THF$ from $CpV(CO)_4$. Method A. Titration of sodium dispersion with a solution of $CpV(CO)_4$. Approximately 0.5 grams of 40% sodium dispersion in 400 ml of THF was titrated with a solution of $CpV(CO)_4$, 1.664 g (7.3 mmol) in 90 ml of THF . The $CpV(CO)_4$ solution was added dropwise to the sodium dispersion over a period of 10 hrs. The sodium dispersion suspension was initially grey, but shortly after addition of $CpV(CO)_4$ the solution began to turn yellow, and a yellow precipitate formed. Near the end of the addition, the solution turned a light orange-brown. Small amounts of sodium dispersion were added to the solution to reduce the excess $CpV(CO)_4$. When all of the $CpV(CO)_4$ solution had been added, and the reaction mixture remained a light orange-brown, the reaction mixture was filtered. The yellow precipitate was washed with THF until the IR spectrum of the wash solution showed no $CpV(CO)_4$. Then the precipitate was washed with petroleum ether and dried in the drybox. 1.364 g (4.3 mmol) of $Na_2CpV(CO)_3 \cdot THF$ (59% yield) was obtained.

Method B. Reduction of $CpV(CO)_4$ with sodium amalgam. 2.42 g (10.6 mmol) of $CpV(CO)_4$ was dissolved in 75 ml of THF, and 75 g of sodium amalgam (.0072 g Na/g amalgam) as added. The solution was stirred for 21.5 hr. The yellow precipitate which formed was collected, washed first with THF and then with petroleum ether, and dried at room temperature in the drybox. 3.310 g (10.4 mmol) of $Na_2CpV(CO)_3 \cdot THF$ was collected (98 % yield). NMR (HMPA): δ 4.32 (s, 5H, Cp); IR (KBr, Nujol): 1742, 1590 cm^{-1}; (HMPA): 1745, 1620, 1570 cm^{-1}; (Lit.) (HMPA): 1742, 1619, 1573 cm^{-1};[54] 1748,1645 cm^{-1}; $Cs_2CpV(CO)_3$, Nujol[1].

Addition of water to a THF slurry of $Na_2CpV(CO)_3 \cdot THF$: 0.2544 g (1.03 mmol) of $Na_2CpV(CO)_3 \cdot THF$ was slurried in 30 ml of THF and 20 ml (1.11 mmol) of water was added. The $Na_2CpV(CO)_3$ dissolved to give a greenish-yellow solution. 0.6586 g (1.14 mmol) of PPN^+Cl^-

was added as the solid, andthe solution turned dark red-brown and a white precipitate formed. The solution was filtered, and petroleum ether (30-60°C) was added slowly until a reddish-orange precipitate formed. The precipitate was collected and reprecipitated from THF-petroleum ether. This gave 0.4152 g (0.56 mmol) of $PPN^+ [CpV(CO)_3H]^-$ (70% yield), mp 201°C (decomp.). NMR (d_8-THF): δ 7.55 (m, 30H, PPN^+), δ 4.57 (s, 5H, Cp), δ-6.10 (broad signal, 1 H, hydride); IR (THF, HMPA, KBr pellet, nujol mull) ν_{CO}: 1890, 1780 cm^{-1}.

Anal. Calcd for $C_{44}H_{36}NO_3P_2V$: C, 71.44; H, 4.91; P, 8.36; V, 6.88; N, 1.89. Found: C, 70.72; H, 4.87; P, 8.46; V, 6.89; N, 1.96.

The preparation of $PPN^+ [CpV(CO)_3D]^-$ from $Na_2CpV(CO)_3 \cdot THF$ was analogous to the preparation of $PPN^+[CpV(CO)_3H]^-$, with deuterium oxide substituted for water.

Reactions of $CpV(CO)_3H^-$ with alkyl halides. General Method. The reactions of $CpV(CO)_3H^-$ with alkyl halides were carried out by two different procedures. Equimolar quantities were mixed and stored in the drybox, and the reaction solutions were removed from the drybox after a specific period and analyzed. Alternatively, a solution of $CpV(CO)_3H^-$ was prepared in the drybox in a serum capped flask, and the alkyl halide was added by syringe after the flask was removed from the drybox. Aliquots were then removed from the reaction solution and analyzed by gas chromatography. Examples of these reaction procedures are given below.

Reaction of **3** with benzoyl chloride. 0.651 g (0.88 mmol) of $PPN^+ [CpV(CO)_3H]^-$ was dissolved in 12 ml of THF and 0.120 g (0.85 mmol) of benzoyl chloride was added from a 250 μl syringe. After 1 min, 25 ml of petroleum ether was added. The green precipitate which formed was collected. The light green filtrate was taken from the drybox, and the solvent was removed by roto-evaporation. 5.0 ml of 1,2-dianilinoethane reagent (0.53 g 1,2-dianilinoethane and 0.5 ml 50% acetic acid in 10 ml of methanol) was added to the residue. The solution was heated on a steam bath for 5 min and upon cooling to room temperature a white precipitate formed. 0.1516 g (61%) of crude product was obtained. 0.0838 g (31%) of pure 1,2,3-triphenyl-tetrahydroimidazole was collected after recrystallization from CH_2Cl_2: hexane. HMR ($CDCl_3$): δ 7.13 (m,10H, phenyl),δ6.57 (m, 5H, phenyl), (s, 1H, methine),δ3.72 (m, 4H, methylene); mp: 135 - 136°C.

<u>Preparation of $PPN^+ [CpV(CO)_3Br]^-$ from $PPN^+ [CpV(CO)_3H]^-$ and benzyl bromide.</u> 0.392 g (.530 mmol) of $PPN^+ [CpV(CO)_3H]^-$ was dissolved in 15 ml of THF and 0.090 g (0.526 mmol) of benzylbromide was added. The solution immediately turned a dark green color, and a dark green precipitate formed when 25 ml of petroleum ether was added. 0.389 g of precipitate was collected. This was reprecipitated from 10 ml of THF by adding 8 ml of petroleum ether. 0.322 g (0.393 mmol) of $PPN^+[CpV(CO)_3Br]^-$ was collected (74%).

<u>Preparation of $PPN^+ [CpV(CO)_3Br]^-$ from $CpV(CO)_4$.</u> 0.0526 g (0.230 mmol) $CpV(CO)_4$ and 0.0865 g PPN^+Br^- were added to 5 ml of THF. Not all the PPN^+Br^- dissolved. This solution was irradiated with a 1000 watt Hg/Xe lamp through pyrex while cooling the reaction vessel externally with water and purging the solution with nitrogen. After 0.5 hr the infrared spectrum of the reaction solution showed

bands at 1948, 1855, 1810 cm^{-1}. Petroleum ether was added to a portion of the reaction solution until a green precipitate formed. This precipitate was collected and dried. NMR (d_8-THF): δ 4.83 (s, 5H, Cp); IR (THF): 1945, 1855, 1810 cm^{-1}; mp: 190°C (decomp).

Anal. calcd for $C_{44}H_{35}BrNO_3P_2V$: C, 64.58; H, 4.28; N, 1.71; Br, 9.77. Found: C, 64.50; H, 4.76; N. 1.70; Br, 9.60.

Reaction of $CpV(CO)_3H^-$ with one-half equivalent of 1-bromooctane. 0.0487 g (0.066 mmol) of PPN^+ $[CpV(CO)_3H]^-$ was dissolved in 0.350 ml of d_8-THF in an NMR tube with a serum cap and 5.7 μl (.033 mmol) of 1-bromooctane was added from a 10μl syringe. The progress of the reaction was monitored by recording the NMR spectrum of the reaction solution at various times. Two new cyclopentadienide resonances were observed initially. After 4.5 hr the reaction between $CpV(CO)_3H^-$ and 1-bromooctane was complete, as indicated by the absence of the signal for the alpha methylene proton of 1-bromooctane in the NMR spectrum. At this time the δ 4.67 ppm resonance was the most intense absorption in the spectrum.

After 18.5 hr the cyclopentadienide resonance at δ 4.83 ppm was absent from the NMR spectrum of the reaction solution, but the resonance at δ 4.67 ppm was still present, along with the resonance from $CpV(CO)_3H^-$ and a small broad absorption from $CpV(CO)_4$ at δ 5.22 ppm.

The IR spectrum of the reaction solution at this time showed carbonyl absorptions at 2008, 1915, 1890, 1857, 1817, and 1780 cm^{-1}. The absorptions at 2008 and 1915 cm^{-1} correspond to $CpV(CO)_4$, the absorptions at 1890 and 1780 cm^{-1} correspond to $CpV(CO)_3H^-$, and the absorptions at 1857 and 1817 cm^{-1} to $[CpV(CO)_3]_2H^-$.

Preparation of solutions of $CpV(CO)_3(CH_3CN)$. Reaction with PPh_3. A solution of 27 mg (0.12 mmol) $CpV(CO)_4$ in 5 ml CH_3CN was irradiated for 10 min while purging with nitrogen. IR analysis of 0.1 ml aliquots of this solution removed during the course of the irradiation showed the disappearance of the carbonyl IR bands of $CpV(CO)_4$ and the appearance of new bands at 1968, 1866, and 1843 (sh) cm^{-1} attributable to $CpV(CO)_3(CH_3CN)$.

A similarly prepared solution of $CpV(CO)_3(CD_3CN)$ (0.063 mmol) in CD_3CN was treated with an excess of PPh_3 (o.31 mmol). Observation of the Cp region of the ^{1}NMR showed the complete conversion of $CpV(CO)_3(CD_3CN)$ (δ 5.08 ppm, singlet) into $CpV(CO)_3PPh_3$ (δ 4.86 ppm, doublet) after 15 min.

Preparation of $Cp_2V_2(CO)_5$ by irradiation of $CpV(CO)_4$. A 0.15 M solution of $CpV(CO)_4$ in THF was irradiated for 2 hr while purging with nitrogen. The THF was removed (30°C, 0.1 mm) and the remaining solids taken up in 2 ml hexane and passed through a 2 cm x 10 cm silica gel chromatography column using hexane as eluent. The first yellow band contained unreacted $CpV(CO)_4$ (33%); the second green band yielded [2] $Cp_2V_2(CO)_5$ (10%) upon removal of the hexane (25°C, 0.1 mm). IR (THF) ν_{CO}: 1995, 1942, 1893, 1861, 1818 cm^{-1}; ^{1}H NMR: δ 5.08 (singlet) ppm.

Halide reduction experiments with isotopic tracer. A solution of PPN^+ $[CpV(CO)_3D]^-$ was prepared as described above for the corresponding hydride, except that D_2O was used as the proton source. A solution of 0.058 mmol of the deuteride in 1 ml THF was allowed to react with 0.059 mmol 1-bromooctane, and the resulting n-octane examined after 8 hr by direct GC-mass spectroscopic analysis of the reaction solution. This analysis showed that the octane produced in the reaction was extensively monodeuterated (90% d_1, 10% d_0). A similar reduction and analysis, employing $PPN^+ [CpV(CO)_3H]^-$ and 1-bromooctane in THF-d_8, gave protiated n-octane (99% d_0, 1% d_1).

Photochemical formation of $PPN^+[CpV(CO)_3]_2H^-$ and its reaction with PPh_3. A solution of 40 mg (0.18 mmol) $CpV(CO)_4$ and 35 mg (0.047 mmol) $PPN^+CpV(CO)_3H^-$ in 1 ml d_8-THF was irradiated for 6 min while purging with nitrogen. An NMR spectrum of the solution showed the equimolar disappearance of the Cp resonances of $CpV(CO)_4$ (δ 5.22 ppm) and $PPN^+CpV(CO)_3H^-$ (δ 4.57 ppm) and the stoichiometric formation of the single Cp absorption at δ 4.67 ppm due to $PPN^+ [CpV(CO)_3]_2H^-$. Treatment of this solution with 26 mg (0.099 mmol) PPh_3 produced $CpV(CO)_3PPh_3$ (δ 4.86 ppm, doublet) and $PPN^+CpV(CO)_3H^-$ in essentially quantitative yield by NMR integration over the next few hours.

Competition between PPh_3 and $CpV(CO)_3H^-$ for "$CpV(CO)_3$". (a) Photochemical experiment. 75 mg (0.10 mmol) $PPN^+[CpV(CO)_3H]^-$, 26 mg (0.10 mmol) PPh_3 and 115 mg (0.51 mmol) $CpV(CO)_4$ were dissolved in 0.85 ml d_8-THF in an NMR tube. The tube was irradiated for 15 sec at room temperature, and cooled to -78°C to slow the subsequent thermal reaction between the bridging hydride and PPh_3. Observation by NMR and integration of the appropriate Cp resonances showed a ratio of $[CpV(CO)_3]_2H^-$ to $CpV(CO)_3PPh_3$ of 2.8 ± 0.5. Allowing this solution to stand resulted in complete conversion of the bridging hydride to phosphine complex.

(b) Protonation experiment. To a solution of 27 mg (0.10 mmol) PPh_3 and 90 mg (0.12 mmol) PPN^+ $CpV(CO)_3H^-$ in 0.8 ml THF-d_8 was added 2.2 mg (0.012 mmol) p-toluenesulfonic acid$\cdot H_2O$ in 0.2 ml THF-d_8. An NMR spectrum recorded 1 min later showed a ratio of **5** to **6** of 1.9 ± 0.5 by integration of Cp resonances. Once again, allowing this mixture to stand resulted in complete conversion to the phosphine complex.

Preparation of $PPN^+CpV(CO)_2BH_4^-$. (a) From $PPN^+CpV(CO)_3H^-$ and $BH_3\cdot THF$. 1.35 ml of 1 M $BH_3\cdot THF$ (1.35 mmol) was added to 25 ml THF containing 200 mg (0.27 mmol) $PPN^+CpV(CO)_3H^-$ in a stoppered flask and stirred for 4 hr. Upon addition of 35 ml hexane a green oil separated that solidified after standing overnight. The solid was collected by filtration, dissolved in 10 ml THF, filtered, and crystallized by adding 20 ml diethyl ether. A second recrystallization yielded 100 mg (51%) of pure $PPN^+CpV(CO)_2BH_4^-$. IR (THF) ν_{CO}: 1846, 1735, cm^{-1}; (KBr pellet) ν_{BH}: 2360 cm^{-1}; ν_{CO}: 1835, 1721 cm^{-1}; NMR (d_8-THF): δ 4.14 (singlet, 5H), δ 7.52 (multiplet, 30H) ppm.

Anal. calcd for $C_{43}H_{39}BNO_2P_2V$: C, 71.19; H, 5.42; N, 1.93. Found: C, 70.80; H, 5.64; N, 2.00.

(b) From $PPN^+BH_4^-$ and $CpV(CO)_4$. A solution of 50 mg (0.22 mmol) $CpV(CO)_4$ and 121 mg (0.22 mmol) $PPN^+BH_4^-$ in 10 ml THF was irradiated while purging with nitrogen for 15 min and allowed to stand for 24 hr. An IR spectrum of 0.1 ml aliquot showed IR bands due to $CpV(CO)_4$ (2008, 1915 cm^{-1}), $PPN^+CpV(CO)_2BH_4^-$ (1846, 1735 cm^{-1}), and $PPN^+CpV(CO)_3H^-$ (1890, 1780 cm^{-1}). Precipitation with hexane provided a mixture of $PPN^+CpV(CO)_3H^-$ and $PPN^+CpV(CO)_2BH_4^-$ which could not be separated.

Competition between 1-bromopentane, 2-bromohexane, and 1-bromo-2-methylpropane for $PPN^+ [CpV(CO)_3H]^-$. 1.0 ml of a THF solution of 1-bromopentane, 2-bromohexane, and 1-bromo-2-methylpropane (0.5 M each) was added to a septum capped vial containing 75 mg (.10 mmol) $PPN^+ [CpV(CO)_3H]^-$, 1 μl aliquots were analyzed on a 25', 5% β,β'-ODPN column at 25°C using 2-methylpentane as an internal standard. The reaction was 80% complete after 2.5 hr; a 12:1:5 ratio of pentane:hexane:2-methylpropane was observed.

Reaction of $CpV(CO)_3D^-$ with (-) -1-phenylethyl bromide. 0.820 g (1.11 mmol) of $PPN^+ CpV(CO)_3D^-$ was dissolved in 2.0 ml of THF in a septum stoppered flask. 0.150 ml of (-) -1-phenylethyl bromide (75% optically pure)[55] was added from a 250 μl syringe. The color of the reaction solution changed from dark red-brown to deep green immediately, and the reaction solution warmed slightly. After 15 min a precipitate formed. The volatile material was vacuum transferred from the reaction mixture at room temperature, and a light yellow solution was collected. The α-deuterioethylbenzene from the volatile fraction was collected by preparative gas chromatography on a 10' x 3/8" 10% DEGS 60/80 Chrom P glass column and identified by mass spectrometry. Instrument conditions: Injector 150°C; column 100°C; detector 143°C; flow rate 30 ml/min. 0.0763 g of α-deuterioethylbenzene was collected (64% yield). There was less than 1% THF in this sample.

72 μl of this α-deuterioethylbenzene was dissolved in 720 μl of d,ℓ-α-deuterioethylbenzene. This mixture showed absolutely no optical rotation at 589 mμ or 365 mμ at room temperature in a 1 decimeter cell. The calculated rotation for the above solution, if the reaction of $CpV(CO)_3D^-$ and (-)-1-phenylethyl bromide had proceeded with complete inversion or retention, would have been[55] 0.030°C, well within the detection limits of the polarimeter.

Reaction of $CpV(CO)_3H^-$ with benzyl bromide and triphenylphosphine. 0.045 g (0.263 mmol) of benzyl bromide and 0.085 g (.324 mmol) of triphenylphosphine were added to 2.0 ml of THF. Then 0.8 ml of a THF solution of $PPN^+CpV(CO)_3H^-$ was added dropwise over a period of 5 min. The solution turned green as the $CpV(CO)_3H^-$ was added. An IR spectrum of the reaction solution after all of the $CpV(CO)_3H^-$ solution had been added, showed only $CpV(CO)_3Br^-$ carbonyl absorptions at 1940, 1845, and 1805 cm^{-1}.

Competition between PPh_3 and halide ion for "$CpV(CO)_3$". A THF solution of 40 mg (.18 mmol) $CpV(CO)_4$, 86 mg (.33 mmol) PPh_3 , and 48 mg (.32 mmol) NaI was irradiated under nitrogen purge for 15 min. An IR spectrum of a 0.1 ml aliquot showed ν_{CO} bands at 1950 and 1854 cm^{-1} due to $CpV(CO)_3PPh_3$ and only a very small band at 1806 cm^{-1} attributable to $CpV(CO)_3I^-$.

In a separate control experiment a solution of the vanadium halide (0.01 M) and PPh_3 (0.1 M) in THF was divided into two portions and one portion irradiated. The rate of substitution was slow, and was essentially the same for the two solutions.

Preparation of 7-bromo-2-methyl-2-heptene. 29.8 g (.29 mmol) dihydropyran was stirred with 1 ml 5 N HCl and 200 ml H_2O at 45°C for 1 hr and allowed to come to room temperature overnight. The aqueous solution was extracted with ether (3 x 150 ml) and the ether dried ($MgSO_4$) and removed (30 mm, 25°C). The remaining oil was vacuum distilled, discarding 1 ml of forerun, to yield 22 g (.18 mmol) 2-hydroxytetrahydropyran (bp 70-81°C, 0.1 mm).

Isopropyltriphenylphosphonium iodide was prepared by combining 21.6 g (.082 mmol) PPh_3 and 9.6 g (.057 mmol) 2-iodopropane in a 3-neck flask fitted with reflux condenser and heating with a steam bath under nitrogen for 20 hr. After cooling, the solid was crushed and the powder obtained washed with benzene (3 x 50 ml). Recrystallization from EtOH/Et_2O yielded 11.9 g (.028 mmol) of isopropyltriphenylphosphonium iodide, mp: 196.2-197.2°C (lit.[53] 195-196°C).

11.9 g (0.028 mmol) isopropyltriphenylphosphonium iodide was slurred in 150 ml ether under nitrogen, 19 ml of 1.45 M (.028 mmol) methyllithium added slowly, and the deep red solution stirred for 3 hr. 2.8 g (.028 mol) of 2-hydroxytetrahydropyran in 5 ml ether was added slowly, whereupon a white precipitate formed, After 6 hr the mixture was poured into 150 ml H_2O, filtered, and the remaining solids washed with ether (2 x 10 ml). The aqueous portion was washed with ether (2 x 50 ml) and the combined ether extracts dried ($MgSO_4$) and concentrated (25°C, 30 mm). The remaining oil was vacuum distilled to yield 1.38 g (.011 mol) 2-methyl-2-hepten-7-ol.[57]

Addition of 1.18 ml (.022 mol) Br_2 to 6.7 g (.022 mol) $P(OPh)_3$ in 10 ml anhydrous ether at 0°C under nitrogen produced white crystals of $Br_2P(OPh)_3$. The supernatant liquid was removed with a pipette and the solid washed with dry, nitrogen purged ether (2 x 20 ml). 1.38 g (.011 mol) 2-methyl-2-hepten-7-ol and 1.74 ml (.022 mol) pyridine (distilled from BaO) were added slowly to the cooled (0°C) salt with stirring and the mixture was worked up by adding 50 ml H_2O, extracting with ether (3 x 50 ml), and washing the ether with dilute HCl (2 x 25 ml) and dilute NaOH (2 x 25 ml). After drying ($MgSO_4$) and removing the ether (25°C, 30 mm), the remaining oil was vacuum distilled to yield 0.7 g (3.7 mmol) of 70% pure 7-bromo-2-methyl-2-heptene (bp 88-92°C, 0.1 mm). The bromide[58] was further purified by preparative gc on a 12' x 3/8" 4% SE-30 column at 120°C. NMR (CCl_4): δ 5.09 (m, 1H), δ3.34 (t, 2H), δ1.85 (m, 10H), δ1.68 (s, 3H), δ1.59 (s, 3H).

Reduction of 7-bromo-2-methyl-2-heptene with $PPN^+[CpV(CO)_3H]^-$. A 0.16 M solution of $PPN^+ [CpV(CO)_3H]^-$ in THF was prepared and portions diluted to give 0.08 M and 0.04 M solutions. To 1.00 ml of each of these solutions was added 3.35 μl (.02 mmol) 7-bromo-2-methyl-2-heptene and 1 μl aliquots analyzed by gas chromatography on a 25' 10% β,β' -ODPN column at 20°C using hexane as an internal standard. The 2-methyl-2-heptene/isopropylcyclopentane ratio was found to be 40, 22, and 8 for the 0.16 M, 0.08 M, and 0.04 M $PPN^+[CpV(CO)_3H]^-$ reactions, respectively.

Preparation of 2-allyloxyethyl bromide. 4.3 g (.19 mol) sodium was added in small pieces to 100 g ethylene glycol followed by 13.8 ml (.16 mol) allyl bromide. After standing overnight the solution was distilled to yield 11.5 g (.11 mol) of 85% pure 2-allyloxyethanol, bp 155-161°C (ethylene glycol impurity). The alcohol was mixed with 9 ml pyridine (distilled from BaO) and added slowly to 41 g (.122 mol) $Br_2P(OPh)_3$, prepared as described above. After 1 hr the reaction mixture was poured into 100 ml H_2O and extracted with ether (3 x 50 ml). The ether was washed with dilute NaOH (2 x 100 ml), dilute HCl (2 x 100 ml), and H_2O (2 x 100 ml). After drying ($MgSO_4$) and removing the ether (25°C, 30 mm), the remaining 30 ml oil was vacuum distilled (.1 mm) into three fractions: The first fraction (bp 28-29°C, 1 ml) contained 10% Et_2O, 10% 2-allyoxyethanol, and 80% 2-allyloxyethyl bromide; the second fraction (bp 29-40°C, 1 ml) contained 85% 2-allyloxyethyl bromide; the third fraction (bp 40-42°C, 4 ml) contained 40% 2-allyloxyethyl bromide and higher boiling impurities. Fractions one and two were combined and the bromide purified by preparative gas chromatography before use on a 12' x 3/8" 4% SE-30 column at 100°C. $d^{25} = 1.325$; NMR (CCl_4): δ 6.0-4.8 (m, 3H), δ3.58 (d,2H), δ3.22 (d, 2H), δ3.01 (d, 2H); IR (neat): $\nu_{C=C} = 1640$ (w), $\nu_{C-O} = 1100$(s) cm^{-1}; mass spectrum: parent ion 166/164 (Br isotope pattern), fragments 109/107, 85, 71,57, 41.

Anal. Calcd. for C_5H_9OBr: C, 36.59; H, 5.50. Found: C, 36.38, H, 5.43.

Preparation of 2-allyloxyethyl iodide. 1.1 g of 45% pure

(3.0 mmol) 2-allyloxyethyl bromide and 9.5 g (63 mmol) NaI were dissolved in 25 ml acetone and heated at reflux for 1 hr. The solution was filtered and the acetone removed (25°C, 30 mm). The remaining solid was taken up in 50 ml H_2O and 50 ml ether. The ether layer was washed with 5% sodium thiosulfate (1 x 20 ml), dilute HCl (2 x 50 ml), dilute NaOH (2 x 50 ml), and H_2O (2 x 50 ml). The ether was dried ($MgSO_4$) and removed (25°C, 30 mm), yielding 0.5 g (2.3 mmol) of 90% pure 2-allyloxyethyl iodide. The product was purified by preparative gas chromatography before use on a 12' x 3/8" 4% SE-30 column at 110°C. d^{25} = 1.60; NMR (CCl_4): δ 6.0-4.8 (m, 3H), δ3.93 (d, 2H), δ3.58 (t, 2H), δ 3.20 (t, 2H); IR (neat): $\nu_{C=C}$ = 1640(w), ν_{C-C} = 1100(s) cm^{-1}; mass spectrum: parent ion 212, fragments 184, 155, 127.

Anal. Calcd for C_5H_9OI: C, 28.32; H, 4.48. Found: C, 28.65, H, 4.21.

Reduction of 2-allyloxyethyl bromide and iodide. A 0.16 M solution of PPN^+ $[CpV(CO)_3H]^-$ in CH_3CN was prepared and portions diluted to make 0.08 M and 0.04 solutions. To 1.00 ml of each of these solutions was added 2.5 μl (.02 mmol) 2-allyloxyethyl bromide and 1 μl aliquots analyzed throughout the reaction on a 100' x 1/16" TCEP open tubular column at 60°C (injector at 50°C) using 1,2-dimethoxyethane as an internal standard. The ratio of allyl ethyl ether to 3-methyltetrahydrofuran was found to be 0.4, 0.88 and 1.44 in the 0.04 M, 0.08 M, and 0.16 M PPN^+ $[CpV(CO)_3H]^-$ reactions, respectively, and remained constant throughout the reduction.

A similar reduction in CH_3CN using 2.65 μl (.02 mmol) 2-allyloxyethyl iodide and 60 mg (.08 mmol) PPN^+ $[CpV(CO)_3H]^-$ in 1.00 ml

CH_3CN provided a 0.98 to 1 ratio of allyl ethyl ether to 3-methyltetrahydrofuran, essentially the same product ratio as found for the bromide.

Reductions of 1.25 μl (.02 mmol) 2-allyloxyethyl bromide with 0.50 ml of 0.08 M and 0.04 M PPN^+ $[CpV(CO)_3H]^-$ solutions in d_8-THF gave allyl ethyl ether/3-methyltetrahydrofuran ratios of roughly 1.5 and 1.0, respectively, by NMR integration of the methyl absorptions of the products.

Reduction of 2-allyloxyethyl iodide with Bu_3SnH. 2.65 μl (.02 mmol) 2-allyloxyethyl iodide was added to a solution of 21 μl (.08 mmol) Bu_3SnH in 1.00 ml CH_3CN. Gas chromatographic analysis of a 1μl aliquot after 30 min showed a 98% yield of products consisting of 19:1 ratio of 3-methyltetrahydrofuran to allyl ethyl ether.

Reduction of n-heptyl and 2-allyl-oxyethyl iodides with Bu_3SnH in the presence of 2,2,6,6-tetramethylpiperidoxyl. To 5 μl (0.3 M) alkyl iodide and 5 μl (.03 mmol) piperidoxyl in 0.5 ml benzene was added 10 μl (.04 mmol) Bu_3SnH, and 1 μl aliquots analyzed by gas chromatography on a 10' 10% SE-30 column at 200°C. 2,2,6,6-tetramethylpiperidoxyl, Bu_3SnI, and Bu_3SnH were identified by co-injection with authentic samples. In the n-heptyl iodide case one other product was observed (15% yield), which coinjected with an authentic sample (see below) of O-n-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide. In the case of 2-allyloxyethyl iodide, two adducts were formed, and sufficient quantities were collected by preparative gas chromatography (from a larger scale reaction) to obtain NMR and high resolution mass spectra. The products were identified as O-allyloxyethyl-2,2,6,6-tetramethylpiperid-1-yl oxide NMR(CCl_4): δ 5.0-6.0 (m, 3H), δ 3.88 (d,2H), 3.81 (d, 2H),δ3.45 (t, 2H),δ1.45 (s, 6H),δ1.15 (s, 6H),δ1.08 (s, 6H); high resolution mass spectrum (peak match): calcd. for $C_{14}H_{27}O_2N$, 241.207; found 241.2071 and O-3-tetrahydrofurylmethyl-2,2,6,6-tetramethylpiperid-1-yl oxide NMR (CCl_4): δ 3.4-3.8 (m, 6H),δ1.45 (s, 6H), 1.16 (s, 6H),δ1.09 (s, 6H); high resolution mass spectrum (peak match) calcd. for $C_{14}H_{27}O_2N$, 241.207; found 241.205 .

Reduction of 2-allyloxyethyl iodide with $PPN^+ [CpV(CO)_3H]^-$ in the presence of 2,2,6,6-tetramethylpiperidoxyl. 4 μl (.03 mmol) 2-allyloxyethyl iodide and 20 μl (.12 mmol) piperidoxyl in 0.5 ml CH_3CN were added to a solution of 28 mg (.038 mmol) $PPN^+ [CpV(CO)_3H]^-$ in 0.5 ml CH_3CN. A 1 μl aliquot was analyzed by gas chromatography on a 10' 10% SE-30 column at 200°C, and showed a 5:1 ratio of the two adducts isolated from the R_3SnH reduction (20% combined yield).

Reduction of n-heptyl iodide with $PPN^+ [CpV(CO)_3H]^-$ in the presence of 2,2,6,6-tetramethylpiperidoxyl. A mixture of 111 μl (.68 mmol) heptyl iodide and 46 μl (.27 mmol) piperidoxyl were added to a solution of 106 mg (.14 mmol) $PPN^+ [CpV(CO)_3H]^-$ in 1.0 ml THF. Gas chromatography analysis of a 1 μl aliquot on a 20' 5% SE-30 column at 200°C using pentane as an internal standard showed a 15% yield of a long retention time product that coinjected with an authentic sample (see below) of O-n-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide.

Preparation of O-n-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide. 0.01 mmol of n-heptyl magnesium iodide was prepared by treating 1.64 ml (.01 mol) n-heptyl iodide with 0.27 g (.011 mol) magnesium in 20 ml ether. Upon addition of 0.75 ml (.0044 mol) 2,2,6,6-tetramethylpiperidoxyl, two layers formed. After 30 min the ether layer was removed and the remaining liquid washed with 10 ml ether. The combined ether layers were washed with 20 ml H_2O, dried ($MgSO_4$), and concentrated (30°C, 30 mm). Gas chromatography analysis of a 1 μl aliquot on a 12' x 3/8" 4% SE-20 column at 180°C showed 60% tetradecane and 30% of the desired product. Purification by preparative gas chromatography yielded 0.3 g (1.2 mmol) O-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide. $d^{25} = 0.86$; NMR (CCl_4): δ3.68 (t, 2H), δ1.7 (m, 16H), δ1.10 (d, 22H), δ0.87 (s, 3H); IR (neat): CH_3 = 1467(m), ν_{C-O} = 1045 (m) cm^{-1}; mass spectrum: parent ion 255, fragments 240, 156.

Anal. calcd for $C_{16}H_{33}NO$: C, 75.23; H, 13.02: N, 5.48. Found: C, 75.36; H, 12.50: N, 5.78.

Reduction of cyclopropyl carbinyl tosylate with $PPN^+CpV(CO)_3H^-$. 4.1 μl (.02 mmol) cyclopropylcarbinyl tosylate was added to a solution of 64 mg (.086 mmol) $PPN^+ [CpV(CO)_3H]^-$ in 1.00 ml CH_3CN and 1 μl aliquots analyzed by gas chromatography on an 25' 5% β,β' -ODPN column at 25°C. After 2.5 days a 40% yield of methylcyclopropane was observed accompanied by only 2% 1-butene.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-78-08706) for the financial support.

References

1. E.O.Fischer & S.Vigoureux, *Chem. Berichte*, *91*, 2205 (1958).
2. E.O.Fischer & R.J.J.Schneider, *Angew. Chem. Internat. Edit.* *6*, 569 (1967); E.O.Fischer & R.J.J.Schneider, *Chem. Ber.*, *103*, 3684 (1970).
3. For other known vanadium hydrides see:
    - a) T.Kruck & H.U.Hempel, *Angew. Chem. Internat. Edit.*, *13*, 201 (1974).
    - b) F.Calderazzo, *Inorg. Chem.*, *5*, 429 (1966).
    - c) J.E.Ellis, R.A.Faltynek & S.G.Hentges, *J.Amer. Chem. Soc.*, *99*, 626 (1977).
    - d) J.E.Ellis & R.A.Faltynek, *Jour. Organometal. Chem.*, *93*, 205 (1975).
    - e) A.Davison & D.L.Reger, *Jour. Organometal. Chem.*, *23*, 491 (1970).
4. The effects of ion pairing on the IR spectra of other metal anions are examined in : M.Y.Darensbourg, D.J.Darensbourg, D.Burns & D.A.Drew, *J.Amer. Chem. Soc.*, *98*, 3127 (1976); C.D.Pribula and T.L.Brown, *J. Organometal. Chem.*, *71*, 215 (1974); J.P.Collman, J.N.Cause, & J.I.Brauman *J.Amer. Chem. Soc.*, *94*, 5905 (1972); M.Y.Darensbourg & D.Burns, *Inorg. Chem.*, *13*, 2970 (1974).
5. For examples of the effects of PPN$^+$ on ion pairing see: M.Y.Darensbourg, *J.Amer. Chem. Soc.*, *99*, 1647 (1977).
6. Conductivity measurements in THF suggest that **1** exists as a solvent separated ion pair with a dissociation constant[7]

of 10^{-4}M.

7. M.Y.Darensbourg, private communication.

8. The broadness of the hydridic signal is probably due to coupling with the ^{51}V nucleus (I = 7/2)

9. Prepared by addition of D_2O to $Na_2CpV(CO)_3$, followed by addition of PPNCl.

10. The irradiation of either **1** or **2** alone does not produce the IR bands or NMR signal attributable to **5**, although both compounds have photo-products of their own:
1 upon irradiation forms a compound with 2 IR bands (1835, 1750 cm^{-1}) and a singlet in the NMR (δ4.49 PPM);
2 upon irradiation forms $Cp_2V_2(CO)_5$.

11. H.D.Kaesz, R.Bau, and M.R.Churchill, *J.Amer. Chem. Soc.*, 89, 2775 (1967).

12. A.Davison, W.McFarlane, L.Pratt & G.Wilkinson, *J.Chem. Soc.*, *3653* (1962).

13. R.G.Hayter, *J.Amer. Chem. Soc.*, *88*, 4376 (1966); L.V.Handy, P.M.Treichel, L.F.Dahl & R.G.Hayter, *J.Amer. Chem. Soc.*, *88*, 366 (1966); U.A.Anders, W.A.G.Graham, *Chem. Comm.*, *499* (1966).

14. R.Tsumura & N.Hagihara, *Bull. Chem. Soc.Japan*, *38*, 1901 (1965).

15. Both $PPN^+[CpV(CO)_3I]^-$ and $PPN^+[CpV(CO)_3Cl]^-$ may be prepared and isolated by irradiation of a THF solution of **2** and PPN-I or PPN-Cl.

16. (+)- α-deuterioethylbenzene is stable towards isomer-

ization to the reaction conditions.

17. 7 is converted into $CpV(CO)_3(CH_3CN)$[18] in CH_3CN solvent with a half life of about 20 minutes. 4 is converted to $CpV(CO)_3(CH_3CN)$ with a half life of ~5 min.

18. Red $CpV(CO)_3(CH_3CN)$ is also formed upon irradiation of 2 in CH_3CN solvent (ν_{CO}= 1968(n), 1866(s),1843(sh)). Removal of solvent (25°C, 0.02 mm) provides green $Cp_2V_2(CO)_5$.

19. Separate control experiments demonstrated that irradiation of 4 in the presence of $P\phi_3$ did not accelerate the rate of substitution.

20. A similar test was used to rule out carbonium ion intermediates by Whitesides[21].

21. C.L.Hill & G.M.Whitesides, J.Amer. Chem. Soc., 96, 870 (1974).

22. Radical reactivity of:
    a) R-CHBr-CHBr-R: H.G.Kuivila, Acc. Chem. Res., 1, 299 (1968); D.M.Singleton & J.K.Kochi, J.Amer. Chem. Soc., 89, 6547 (1967).
    b) 2-bromo-2-butene: G.D.Sargent & M.W.Browne, J.Amer. Chem. Soc., 89, 2788 (1967).
    c) Dibromocyclopropane: H.G.Kuivila, Acc. Chem. Res., 1, 299 (1968).

23. Preparation of TMPO: T.Toda, E.Mori & K. Marayama, Bull. Chem. Soc. Japan, 45, 1904 (1972).

24. R.L.Willson, *Trans. Faraday Soc.*, *67*, 3008 (1971); M.S.Khloplyankina, A.L.Buchachenko, M.B.Neiman & A.G.Vasil'eva, *Kinet. Katal.*, *6*, 394 (1965); I.T.Browlie & K.U.Ingold, *Can. J. Chem.*, *45*, 2427 (1967).

25. Use of an excess of **1** also avoids complications in the kinetic analysis due to reaction of **1** with **4** or **7** to form **5**.

26. A.L.J.Beckwith & W.B.Gara, *J.Amer. Chem. Soc.*, *91*, 5691 (1969); A.L.J.Beckwith & G.Phillipou, *Aust. J. Chem.*, *29*, 123 (1976).

27. Beckwith has reported[28] that the reduction of 6-chloro-1-hexene with ϕ_3SnH gives methylcyclopentane and 1-hexene in a 0.26 to 1 ratio; a reduction of 2-chloroethyl allyl ether under identical conditions give 3-methyltetrahydrofuran and allyl ethyl ether in a 3.0:1 ratio implying an 11-12 fold increase in the cyclization rate constant. Using Ingolds's value[29] of $1 \times 10^5 \text{sec}^{-1}$ for the 6-hexenyl radical cyclization rate constant, the value for the rate of cyclization of the allyl ethyl ether radical may be approximated as $1.2 \times 10^6 \text{sec}^{-1}$.

28. A.L.J. Beckwith, I. Blair and G.Phillipou, *J. Amer. Chem. Soc.*, *96*, 1613 (1974).

29. K.U.Ingold, D.Cal, D.Griller and S.Husband, *J. Amer. Chem. Soc.*, *96*, 6355 (1974).

30. D.J.Carlsson and K.U.Ingold, *J. Amer. Chem. Soc.*, *90*, 7047 (1968).

31. J.K.Kochi, "Free Radicals", Vol. 1, Ch. 4, John Wiley & Sons, New York, 1973 .

32. G.E.Adams and R.L.Willson, *Trans. Faraday Soc.*, *65*, 2981 (1969).

33. K.G.Kuivila, *Acc. Chem. Res.*, *1*, 299 (1968).

34. C.Walling, J.H.Cooley, A.A.Ponaras and E.J.Racah, *J. Amer. Chem. Soc.*, *88*, 5361 (1966).

35. It is possible that the termination reactions themselves produce species capable of initiating the chain reaction, e.g.

$$2\ \mathrm{CpV(CO)_3}^{\dot{-}} \longrightarrow [\mathrm{CpV(CO)_3}]_2^{=}$$

$$[\mathrm{CpV(CO)_3}]_2^{=} + \mathrm{RX} \longrightarrow \mathrm{R}\cdot + \mathrm{X}^- + [\mathrm{CpV(CO)_3}]_2^{\dot{-}}$$

$$[\mathrm{CpV(CO)_3}]_2^{\dot{-}} \longrightarrow \mathrm{CpV(CO)_3} + \mathrm{CpV(CO)_3}^{\dot{-}}$$

A chain length of only 20 would decrease the yield of identifiable organometallic products by only 5% and would not be detected within experimental error.

36. B.Maillard, D.Forrest and K.U.Ingold, *J. Amer. Chem. Soc.*, *98*, 7024 (1976).

37. P.J.Krusic, P.J.Fagan and J.San Filippo, *J. Amer. Chem. Soc.*, *99*, 250 (1977).

38. D.D.Roberts, *J. Org. Chem.*, *29*, 294 (1964); S.Winstein and H.Marshall, *J. Amer. Chem. Soc.*, *74*, 1120 (1952).

39. See, for example, (a) C.A.Tolman, *J. Amer. Chem. Soc.*, *96*, 2780 (1974); (b) C.A.Tolman, A.D.English, and L.E.Manzer, *Inorg. Chem.*, *14*, 2353 (1975); (c) E.Koerner von Gustorf, M.C.Henry, and D.J.McAdoo, *Ann.*, *707*,190 (1967); (d) S.D.Ittel, *Inorg. Chem.*, *16*, 2589 (1977) and references cited there . (e) W.Partenheimer, *J. Amer. Chem. Soc.*,

98, 2779 (1976) and references cited there.

40. J.R.Norton, private communication; c.f. (a) J.Okrasinkski and J.R.Norton, J. Amer. Chem. Soc., 99, 295 (1977); (b) J.Evans and J.R.Norton, J. Amer. Chem. Soc., 96, 7577 (1974).

41. R. Tsumura and N.Hagihara, Bull. Chem. Soc. Japan, 38, 1901 (1965).

42. S.W.Kirtley, M.A.Andrews, R.Bau, G.W.Grynkewich, T.J.Marks, D.L.Tipton, and B.R.Whittlesey, J. Amer. Chem. Soc., 99, 7155 (1977), and references cited there.

43. J.E.Ellis, S.G.Hentges, D.G.Kalina, and G.P.Hagen, J. Organomet. Chem., 97, 79 (1975).

44. S.H.Babcock, Inorg. Synth., 1, 10 (1939).

45. H.H. Horhold, G.Drefall, and P.Hinderson, Z. Chem., 7, 459 (1967).

46. W.vonE.Doering and W.A.Henderson, Jr., J. Amer. Chem. Soc., 80, 5274 (1958).

47. W.E.Truce and J.J. Breiter, J. Amer. Chem. Soc., 84, 1623 (1962).

48. J.S.Meek and J.W.Rowe, J. Amer. Chem. Soc., 77, 6675 (1955).

49. G.G.Bergstrom and S.Siegel, J. Amer. Chem. Soc., 74, 145 (1952).

50. H.E.Carter, R.L.Frank, and H.W.Johnston, "Organic Syntheses", Coll. Vol. III, Wiley, New York, N.Y., 1955, p. 167.

51. M.Fieser and L.F.Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967.

52. C.D.Beard, K.Baum, and V.Grakaukas, J. Org. Chem., 38, 3675 (1975).

53. J.K.Ruff, Inorg. Synth., 15, 84 (1974).

54. J.E.Ellis, R.A.Faultynek,and S.G.Hentges, J. Organomet. Chem., 120, 389 (1976).

55. A.Streitwieser, J.R.Wolfe, and W.D.Schaeffer, Tetrahedron Lett.,

338, (1957); H.J.Dauben and L.L.McKoy, J. Amer. Chem. Soc., 81, 5404 (1959).

56. Wittig, Annal., 606, 1 (1957).

57. J.Colonge, G.Descotes, and G.Poilane, Bull. Soc. Chim. Fr., 408 (1959).

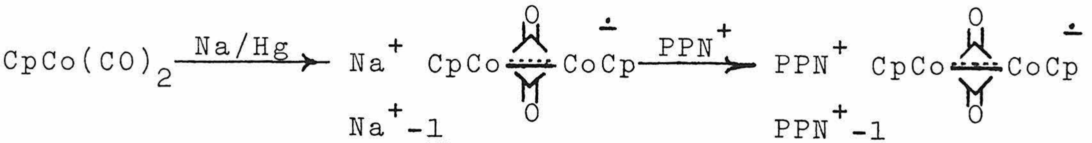
58. A.L.J.Beckwith, I.A.Blair, and G.Phillipou, Tetrahedron Lett., 2251 (1974).

Chapter II

The Reduction and Alkylation of $CpCo(CO)_2$ and $CpRh(CO)_2$.

Introduction

Our interest in studying binuclear reductive elimination processes led us to investigate the reduction of $CpCo(CO)_2$ with 0.65% Na/Hg in THF solution, which is known[1] to give a dimeric radical anion, Na^+-1 (eqn.1). The sodium ion may be exchanged for a bulkier bis-triphenylphosphiniminium cation, and the infrared spectrum shows a single ν_{co} absorption at 1690 cm^{-1}. A crystal structure confirmed a D_{2h} geometry.

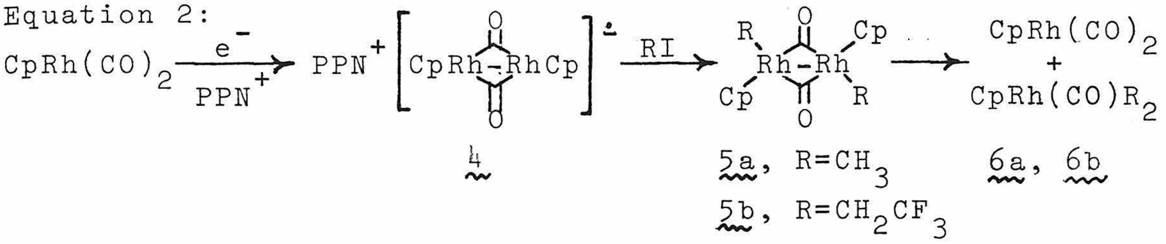


Na^+-1 PPN^+-1 (1)

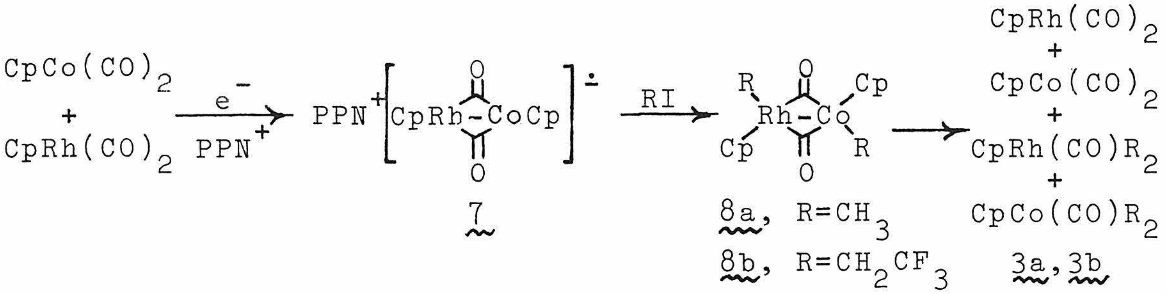
Alkylation of PPN^+-1 with CH_3I produces the dinuclear dimethyl complex[2], $[CpCo(CO)(CH_3)]_2$, 2a (NMR,IR:Table I). In the presence of CO this compound decomposes thermally to form acetone and $CpCo(CO)_2$ via the intermediate $CpCo(CO)(CH_3)_2$ complex,[2] 3a. Similarly, alkylation of PPN^+-1 with CF_3CH_2I produces[3] $[CpCo(CO)(CH_2CF_3)]_2$, 2b(^{1}H-NMR, ^{19}F-NMR,IR:Table I). However, this compound decomposes under CO to give only $CpCo(CO)(CH_2CF_3)_2$, 3b (^{1}H,^{19}F-NMR; Table I) and $CpCo(CO)_2$, with no further decomposition to ketone.

This chapter reports the analogous reduction and alkylation of $CpRh(CO)_2$ and the co-reduction of $CpRh(CO)_2$ and $CpCo(CO)_2$ as indicated in equations (2) and (3), respectively. We expected greater stability in the Rh-Co series of compounds 7 and 8 attributable to the added electostatic interaction between the metal centers due to their electronegativity differences.[5]

Equation 2:



Equation 3:



I. Reduction of $CpRh(CO)_2$.

The reduction of $CpRh(CO)_2$ has been reported by Knox[6] to give $[CpRh(CO)H]^-$. A single IR band was observed (1890 cm^{-1}, THF) and attributed to the carbonyl hydride product. We have repeated this reduction employing 0.3% Na/Hg amalgam and have found[7] that two products are formed. One product, $PPN^+[Rh(CO)_4]^-$, is isolated as a white powder in ~20% yield from the reduction solution. Its single IR band (1890 cm^{-1}) is the same as that reported by other workers[8] for $Rh(CO)_4^-$, indicating that this was the species observed by Knox.

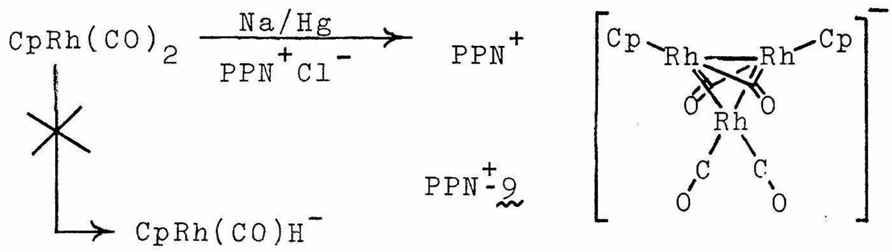
The other product is an anion which may be isolated in 40% yield (eqn.4), $PPN^+[Cp_2Rh_3(CO)_4]^-\cdot THF$, 9 (IR,NMR: Table I).

Table I

IR, ^{1}H-, and ^{19}F-NMR Spectral Data[4]

Compound	IR(THF)	^{1}H-NMR(PPM)[a]	^{19}F-NMR(PPM)[a]
$\mathrm{PPN^+[CpCo(CO)]_2^{\dot{-}}}$ (1)	1690 $\mathrm{cm^{-1}}$	—	—
$\mathrm{[CpCo(CO)(CH_3)]_2}$ (2a)	1820 $\mathrm{cm^{-1}}$	δ5.09(10H),δ-0.72(6H)	—
$\mathrm{[CpCo(CO)(CH_2CF_3)]_2}$ (2b)	1879,1847 $\mathrm{cm^{-1}}$	δ5.38(10H), δ0.26(4H,q,j=14.6hz)	δ-0.93(t,j=14.6hz)
$\mathrm{CpCo(CO)(CH_3)_2}$ (3a)	2010$\mathrm{cm^{-1}}$	δ4.44(5H),δ0.67(6H)[a]	—
		δ5.00(5H),δ0.42(6H)[b]	—
$\mathrm{CpCo(CO)(CH_2CF_3)_2}$ (3b)		δ4.30(5H),δ1.80,0.66(4H)[d]	δ-1.91(t,j=14.6hz)
$\mathrm{[CpRh(CO)(CH_2CF_3)]_2}$ (5b)		δ4.95(5H),δ2.86(q of d, j=14.6,4.0hz)	δ-4.20(t of d,j=14.6hz)
$\mathrm{CpRh(CO)(CH_3)_2}$ (6a)		δ4.88(5H), δ0.83(6H,d,j=3hz)	—
$\mathrm{CpRh(CO)(CH_2CF_3)_2}$ (6b)		δ4.63(5H),δ2.06,1.13(4H)[d]	δ-3.42(t of d,j=14.6,3.9hz)
$\mathrm{PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}}$ (7)	1690 $\mathrm{cm^{-1}}$	—	—
$\mathrm{Cp_2RhCo(CO)_2(CH_3)_2}$ (8a)	1862,1823 $\mathrm{cm^{-1}}$	δ5.24(5H),δ4.77(5H),δ0.43 (3H,d,j=3hz),δ-0.14(3H)	—
$\mathrm{CpRhCo(CO)_2(CH_2CF_3)_2}$ (8b)	1886,1847 $\mathrm{cm^{-1}}$	δ4.90(5H),δ4.50(5H),δ0.50 (2H,q,j=14.6),δ1.26(q of d, j=14.6,4.0hz)	δ-0.27(t,14.6hz), (t of d,j=4.8,14.6,3.9hz)
$\mathrm{PPN^+[Cp_2Rh_3(CO)_4]^-}$ (9)	1973,1910,1693$\mathrm{cm^{-1}}$	δ7.60(30H),δ5.20(10H)	—

a) C_6D_6 b) d_8-THF c) $(CD_3)_2CO$ d) see Fig. 8.



(4)

A crystal structure of compound 9 (Fig.1) shows two semi-triple bridging[7] CO molecules (Fig.2). Lists of atomic coordinates, thermal parameters, and bond angles and distances are provided in Appendix I.

The changes in the infrared spectrum of the reduction solution are shown in Fig.3. The immense extinction coefficient of $Rh(CO)_4^-$ dominates the ν_{CO} region. However, a second product may be observed with IR bands at 1973, 1910, 1750, 1693, and 1662 cm^{-1}(Na^+ salt). Addition of PPN^+Cl^- collapses the three lower energy bands into a single band at 1693 cm^{-1}, and is typical of the ion pairing effects reported for Na^+-1.

The formation of 9 as well as $Rh(CO)_4^-$ can be explained by the mechanism shown in Scheme I. Upon acceptance of an electron by $CpRh(CO)_2$, CO dissociation is competitive with loss of cyclopentadienyl anion. The product of the former, $CpRh(CO)^{\dot{-}}$, reacts with another molecule of $CpRh(CO)_2$ producing the expected radical anion, $[CpRh(CO)]_2^{\dot{-}}$, 4, but further reaction with $\cdot Rh(CO)_2$ produces the observed product, 9. $Rh(CO)_4^-$ is produced by the reduction and

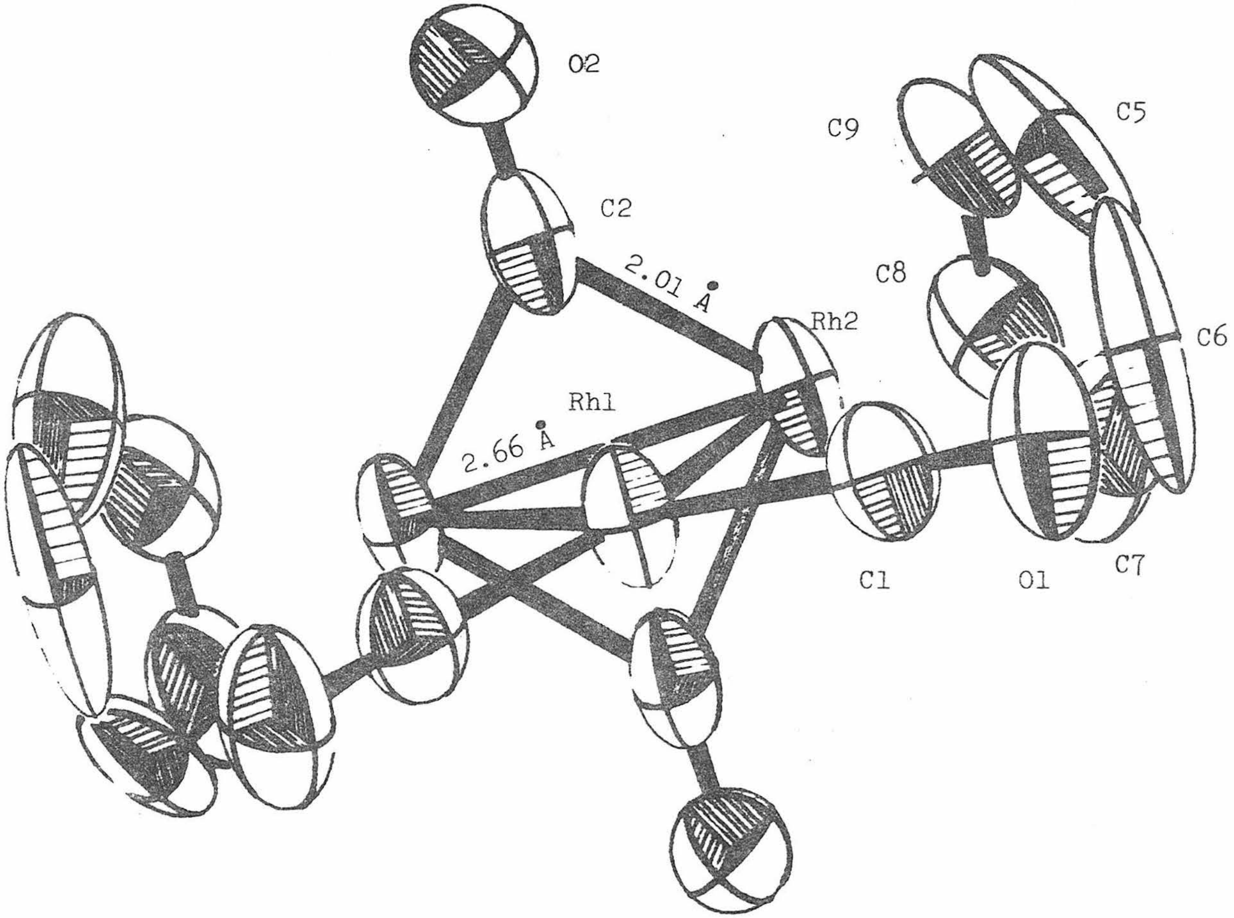


Figure 1. ORTEP drawing of $Cp_2Rh_3(CO)_4^-$. The ellipsoids represent 50% of the electron distribution.

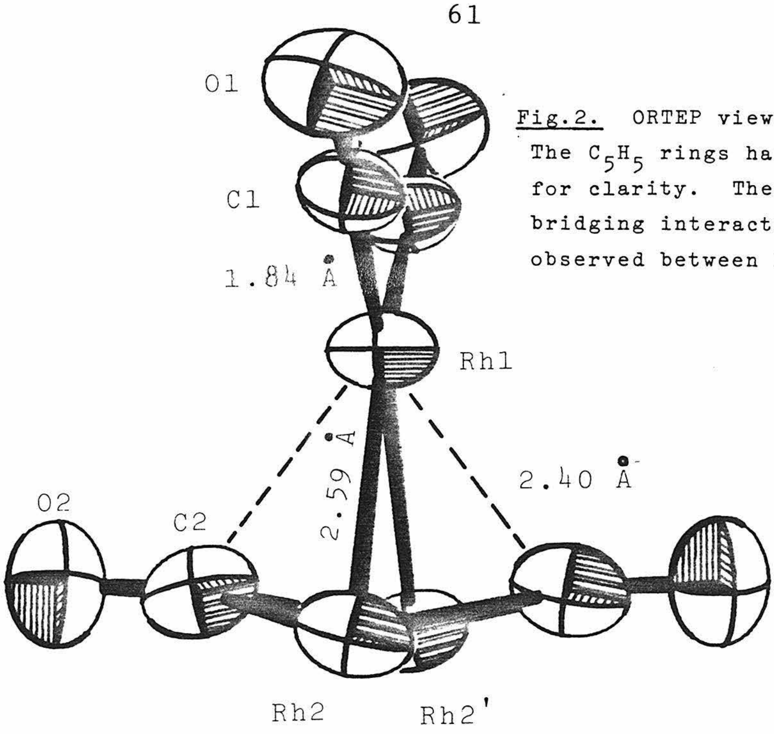


Fig.2. ORTEP view of $Cp_2Rh_3(CO)_4^-$. The C_5H_5 rings have been removed for clarity. The semi-triple bridging interaction may be observed between Rh1 and C2.

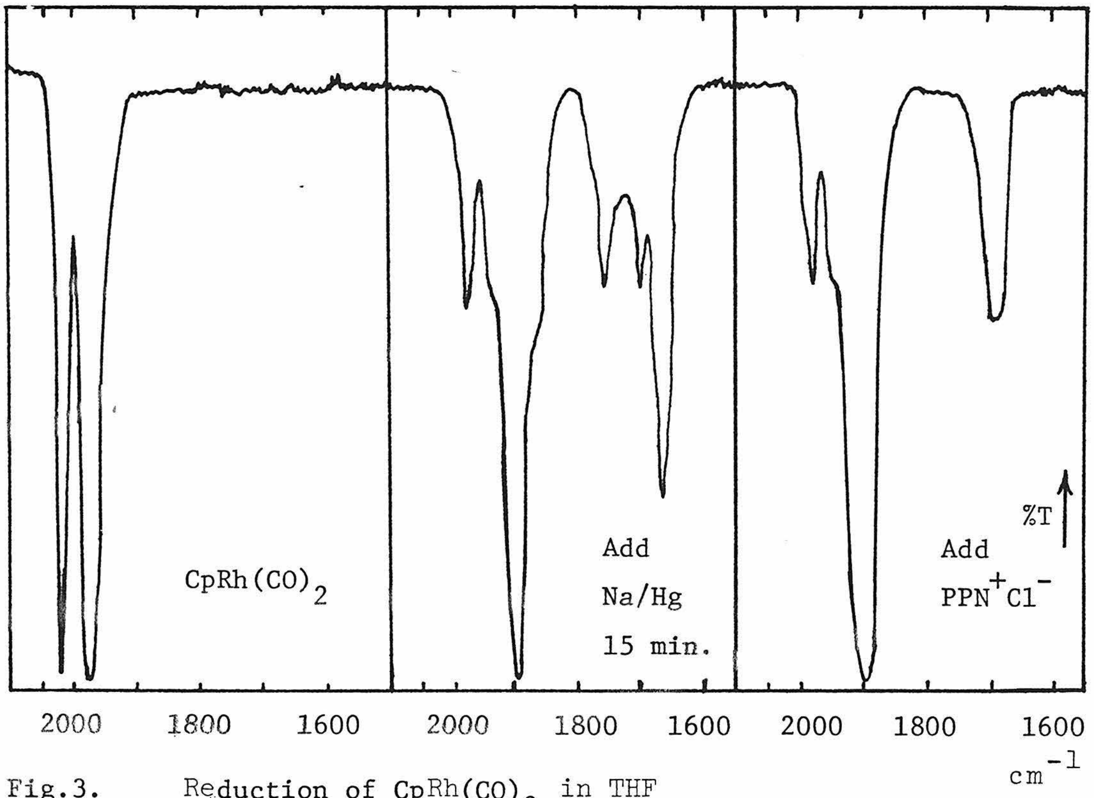
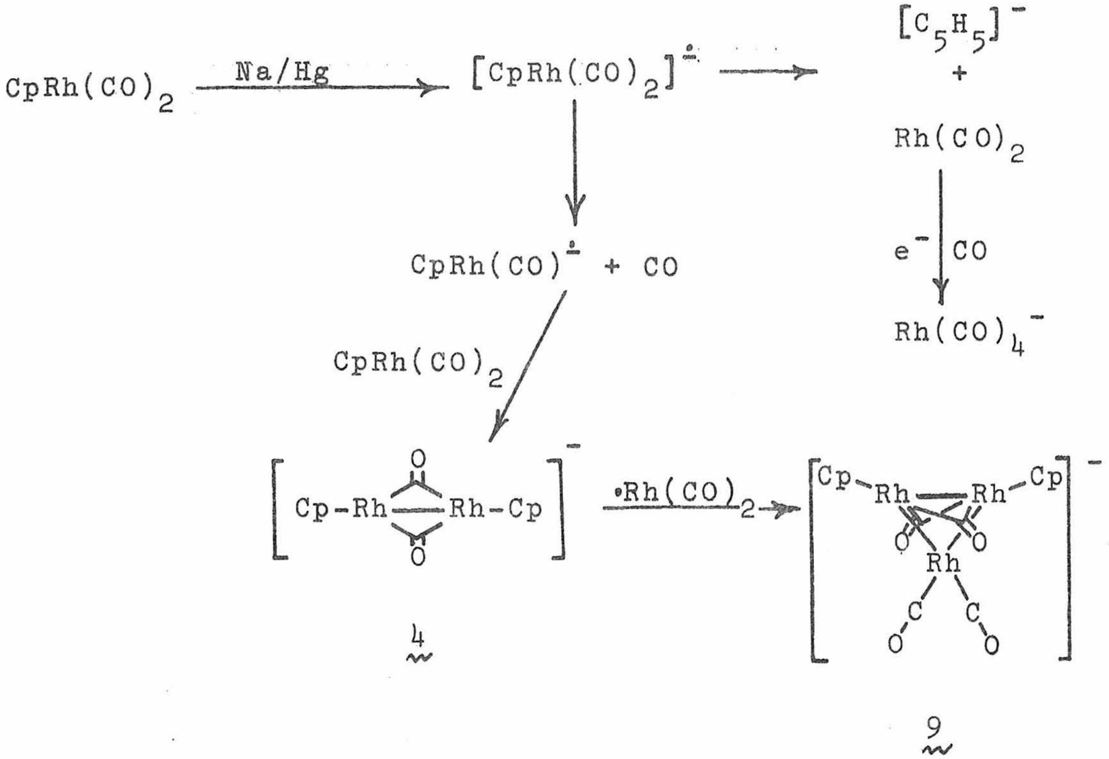


Fig.3. Reduction of $CpRh(CO)_2$ in THF

Scheme I



carbonylation of $\cdot$Rh(CO)$_2$.

Alkylation of 9 in d_8-THF with an excess of CH_3I produces an unisolated compound with a new Cp resonance (δ5.45 PPM) and a new methyl doublet (δ1.48 PPM), consistent with the compound CpRh(CO)$(CH_3)_2$, 6a (30% yield,NMR). 6a decomposes slowly to give a quantitive yield of acetone ($\tau_{1/2}$=12hrs.).

II. Co-reduction of $CpCo(CO)_2$ and $CpRh(CO)_2$.

As the reduction of $CpCo(CO)_2$ followed by alkylation with CH_3I led to the product **2a** which formed acetone via a mononuclear species, and the reduction and alkylation of $CpRh(CO)_2$ also led to ketone via a mononuclear species, we decided to synthesize and alkylate the heteronuclear compound $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$, PPN^+-**7**. The cobalt-rhodium bond is expected to be stronger than the cobalt-cobalt bond in **2a** or **2b** due to an added ionic contribution to the bond strength resulting from their electronegativity difference, perhaps allowing binuclear processes to dominate the reaction path.

We wish to report now that PPN^+-**7** has been prepared by reducing a 1:1.1 mixture of $CpCo(CO)_2$ and $CpRh(CO)_2$ followed by cation exchange with PPN^+Cl^- (IR: 1690 cm^{-1}) This compound displays an eight line ESR signal in solution, due to coupling with a single cobalt nucleus (I=7/2) (Fig. 4); the coupling with rhodium (I=1/2) is not observed. The asymmetry may be due to anisotropic tumbling, as the moments of inertia of this molecule are quite different. A single crystal ESR shows two different g values upon rotation of the crystal by 90° ($g_{\parallel}$=2.148, $g_{\perp}$=2.236)

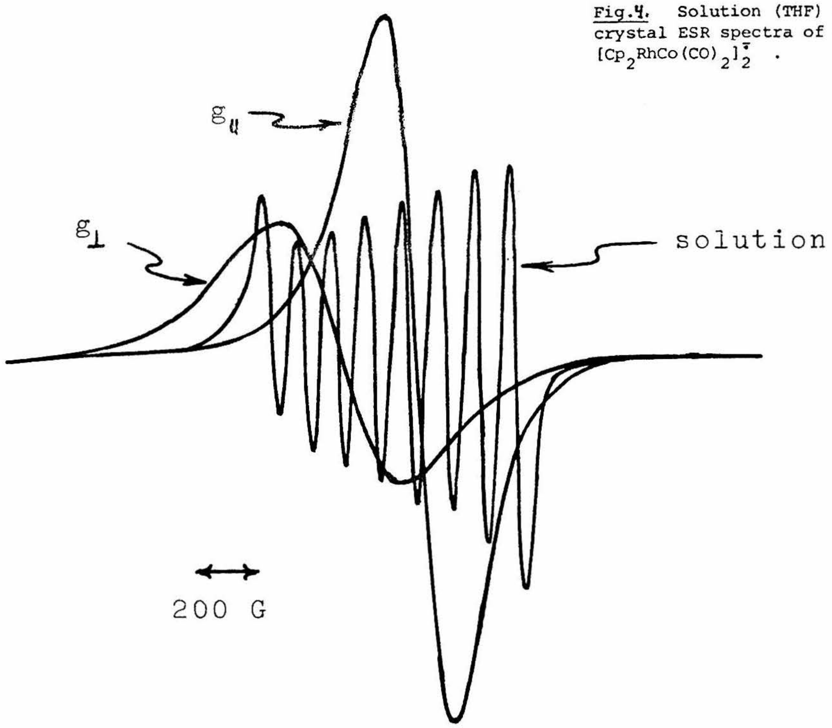


Fig.4. Solution (THF) and single crystal ESR spectra of PPN^+ $[Cp_2RhCo(CO)_2]_2^{\overset{\bullet}{-}}$.

This compound may also be alkylated with CH_3I to form $Cp_2RhCo(CO)_2(CH_3)_2$, **8a**, which may be purified by chromatography on silica gel with hexane (27% isolated yield, ^{1}H-NMR, IR: Table I). The decomposition of **8a** is easily followed by NMR slowly giving acetone in 26% yield ($t_{\frac{1}{2}}$ =25 hrs.) via. the mononuclear complex, $CpCo(CO)(CH_3)_2$, (15% by NMR: δ 4.44 PPM, 5H, s; δ 0.67 PPM, 6H, s). $CpRh(CO)Me_2$ is also observed (60%, δ 4.88 PPM, δ 0.3 PPM).

Similarly, alkylation of **6** with CF_3CH_2I followed by a fast chromatography gives $Cp_2RhCo(CO)_2(CH_2CF_3)_2$, **8b** (eqn.3). (17% isolated yield) The infrared spectrum of **8b** in THF solution shows carbonyl bands at 1886(w) and 1847 (m)cm^{-1}, suggesting a structure analogous to 2b. The ^{1}H-NMR of 8b shows two singlets at δ4.90 PPM and δ4.50 PPM attributable to the two C_5H_5 resonances (5H). The $-CH_2-$ resonances (2H) appear as a quartet (δ 0.50 PPM) and a quartet of doublets (δ 1.26 PPM). ^{19}F-NMR shows a triplet (δ -0.27 PPM) and a triplet of doublets (δ -1.65 PPM) in a 1:1 ratio.

At 25°C in THF solution 8b quickly(15 min.) exchanges metals to form the known 3, $Cp_2Co_2(CO)_2(CH_2CF_3)_2$ and the previously unavailable $Cp_2Rh_2(CO)_2(CH_2CF_3)_2$, 5b, both observable by NMR. The mononuclear complexes $CpM(CO)(CH_2CF_3)_2$ are also observed to form more slowly[9] (Figs. 5,6).

Upon standing under CO, spectra show the decomposition to a mixture of $CpCo(CO)_2$ (δ 4.41 PPM) and $CpRh(CO)_2$ (δ4.86 PPM) (~4:1), and 3b and 6b (~1:6). The latter two compounds were not isolated and display rather complex ^{1}H-NMR methylene resonances in the region δ 1-2 PPM as the protons are diastereotopic and are split by both fluorine and/or rhodium (Fig.7). The observed spectrum for the methylene hydrogens of 3b and 6b arising from the decomposition of 8b is shown in Fig. 8. A simulated spectrum for 6b is shown for comparison[10], showing complete resolution of all couplings.

The scrambling of metal atoms observed for 8b may be explained on the basis of symmetrical cleavage of the metal-metal bond as indicated in Scheme II. The formation

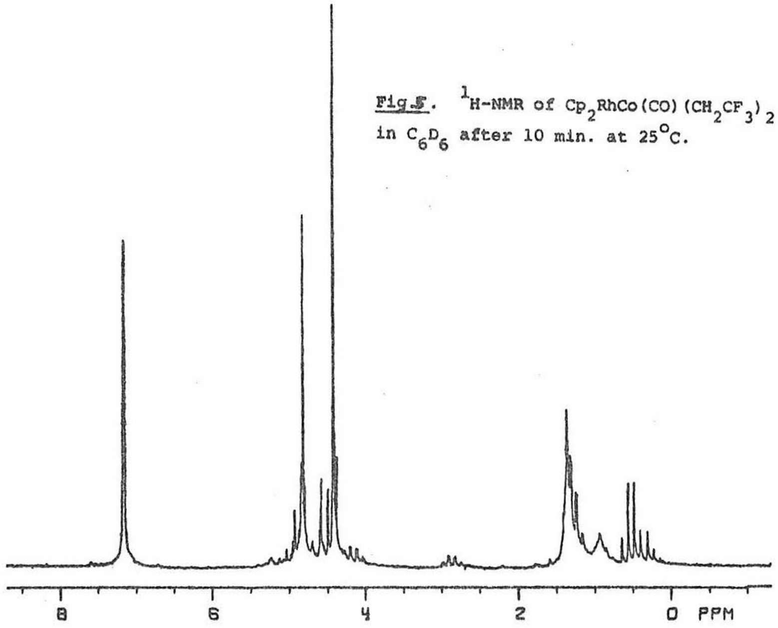


Fig.5. ^{1}H-NMR of $Cp_2RhCo(CO)(CH_2CF_3)_2$ in C_6D_6 after 10 min. at 25°C.

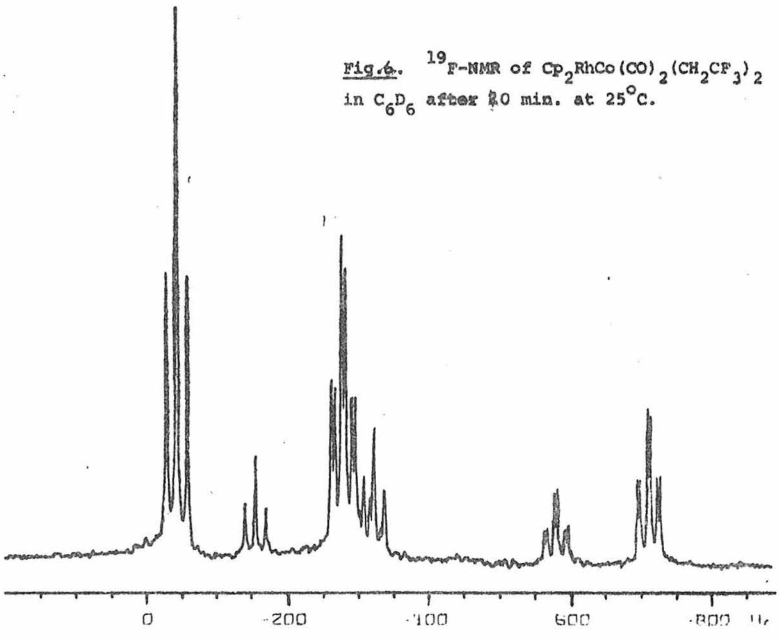


Fig.6. ^{19}F-NMR of $Cp_2RhCo(CO)_2(CH_2CF_3)_2$ in C_6D_6 after 20 min. at 25°C.

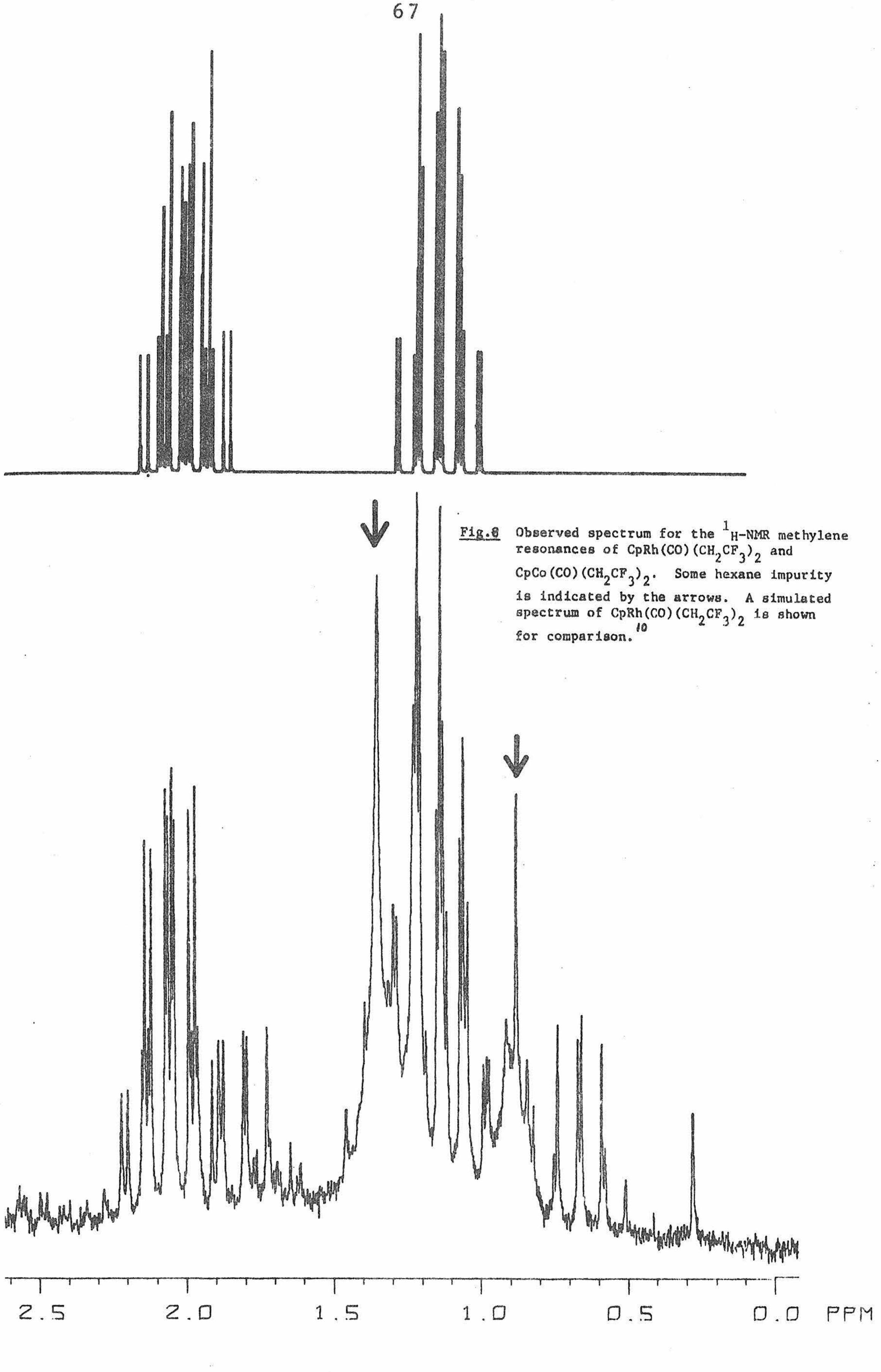
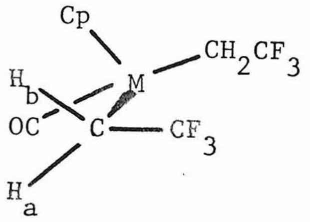


Fig.8 Observed spectrum for the ^{1}H-NMR methylene resonances of $CpRh(CO)(CH_2CF_3)_2$ and $CpCo(CO)(CH_2CF_3)_2$. Some hexane impurity is indicated by the arrows. A simulated spectrum of $CpRh(CO)(CH_2CF_3)_2$ is shown for comparison.[10]

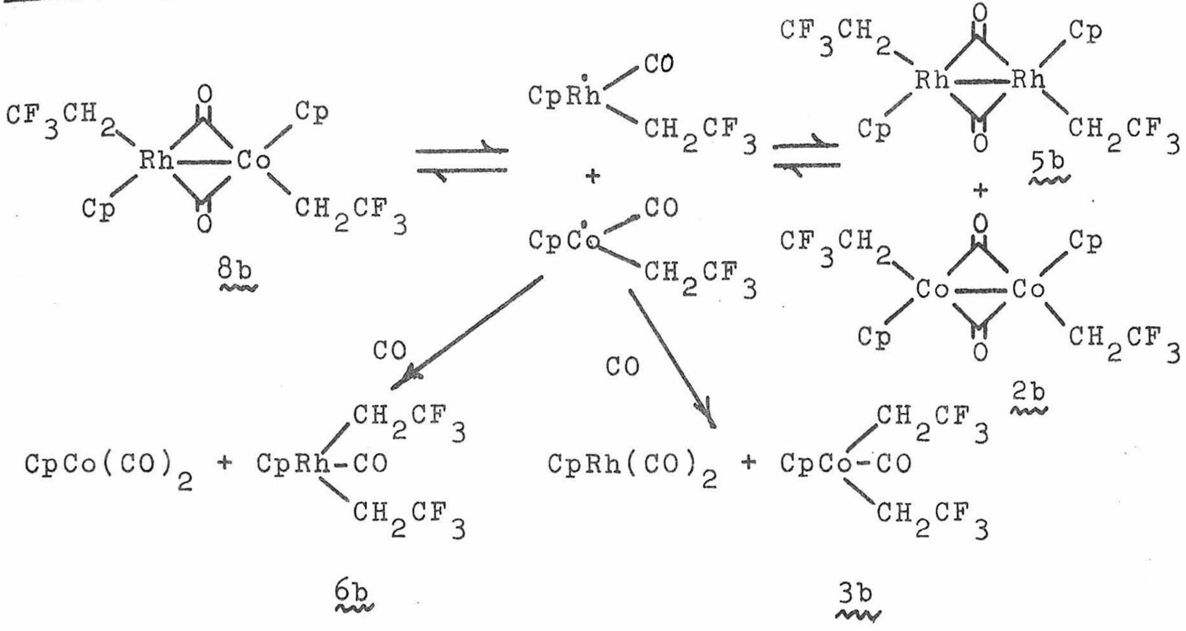
Fig.7. Compounds 3b & 6b showing diasteriotopic hydrogens (M=Rh,Co).



of metal radicals is supported by the observation that 3b has no NMR at 25°C; a single, broad ESR signal (g=2.114) is observed instead. Upon cooling to - 10°C a broad peak appears at δ5.38 PPM in the ^1H-NMR, and eventually (-50°C) a sharp C_5H_5 line is observed as well as the $-CH_2CF_3$ quartet (δ 0.26 PPM).[3] The dialkyl compounds 3b and 6b form through an alkyl transfer reaction.

Our expectation that the CoRh bond in 8 would be stronger than the Co-Co bond in 2 was borne out by the observation of a slower decomposition rate for 2, and by the observation of sharp NMR signals for 8 at 25°C. Unfortunately, no new binuclear chemistry was observed with this system. Rather, the predominant pathway in these systems is the formation of $CpM(CO)R_2$ which then proceeds to ketone.

Scheme II



Experimental

All solvents were distilled from Na/benzophenone/tetraglyme prior to use on a vacuum line or in a Vacuum Atmospheres glove box. $CpRh(CO)_2$ was prepared from $Na^+C_5H_5^-$ and $[Rh(CO)_2Cl]_2$[11] as described below. PPN^+Cl^- was obtained from Alfa Corporation and recrystallized from CH_2Cl_2/Et_2O before use. $CpCo(CO)_2$ was purchased from Alfa Corporation.

NMR spectra were recorded on a 180 MHz ^1H (169 MHz ^{19}F) NMR equipped with a Brucker superconducting magnet and a Nicolet Corporation Fourier Transform Computer package. IR spectra were recorded on a Perkin-Elmer 283 Infrared Spectrometer. Analyses were performed by Mr. V. Tashinian at the University of California, Berkeley, Analytical Laboratory.

Preparation of $CpRh(CO)_2$. The preparation is a modification of that reported[12] earlier. 3.0 g (34 mmol) $Na^+(C_5H_5)^-$ was added to a THF solution (65 ml) of $[Rh(CO)_2Cl]_2$ (3.36 g, 8.6 mmol) in the dry box. The THF was then removed (25°C, 10^{-2}mm) and the remaining solid treated with 100 ml H_2O, extracted with ether (3x75ml), and the ether dried ($MgSO_4$) and removed (20°C, 10^{-2}mm). The remaining oil was distilled under dynamic vacuum (10°C, 10^{-5}mm) to yield 2.57 g (66%) $CpRh(CO)_2$, >95% by NMR (C_6D_6): δ4.86 PPM. IR (THF): 2041, 1970 cm^{-1}.

Reduction of $CpRh(CO)_2$. 0.43 g (1.9 mmol) $CpRh(CO)_2$

was dissolved in 15 ml THF under N_2 and 12.5 g of 0.3% Na/Hg amalgam added. After 125 min. the solution was separated from the amalgam and 1.2 g PPN^+Cl^- added. The mixture was filtered to remove NaCl and an equal volume of hexane added. Filtration provided microcrystalline $PPN^+[Cp_2Rh_3(CO)_4]^-\cdot THF$ that was washed with hexane. This material was recrystallized from THF/hexane and dried in vacuum (25°C, 10^{-2}mm), yielding 0.34 g (38%) of product. Anal. calcd. for $C_{54}H_{48}P_2NO_3Rh_3$: 55.83%C, 4.16% H, 1.21% N; found: 55.04% C, 4.10% H, 1.37% N. Addition of more hexane precipitated white PPN^+ $Rh(CO)_4{}^-$(IR: 1890(S) cm^{-1}, NMR(d_8-THF): δ 7.53 PPM),20%.

Diffusion of hexane through a sintered glass frit into a THF solution of $PPN^+[Cp_2Rh_3(CO)_4]^-$ provided yellow-brown crystalline plates (0.1mm x 0.3mm x 0.4mm). A crystal was mounted in epoxy on a glass fiber and subjected to x-ray diffraction analysis using a Syntex $P2_1$ diffractometer employing the $\theta/2\theta$ scan method. 4624 reflections in a single quadrant were collected for $5^\circ < 2\theta < 50^\circ$. A Patterson map revealed the location of all three rhodium atoms; a subsequent Fourier map revealed all other non-hydrogen atoms in $PPN^+[Cp_2Rh_3(CO)_4]^-$. A difference Fourier map showed a single THF molecule situated in a crystal void (see Appendix I). Anisotropic least squares refinement of all non-hydrogen atoms led to the final discrepancy factors R_1=5.3%,

R_2=1.05% for the 2502 reflections with $F_{obs} > 3\sigma$.

Preparation of $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$. A THF solution (50ml) of 0.47 g (1.1 mmol) $CpRh(CO)_2$ and 0.35 g (1.9 mmol) $CpCo(CO)_2$ was treated with 41 g 0.3% Na/Hg amalgam. After 15 min., the solution was transferred via. cannula into a flask containing 1.7 g (3.0 mmol) PPN^+Cl^-. The solution was filtered to remove NaCl and 60 ml hexane added. This product was dissolved in 50 ml THF and 10 ml hexane added; cooling to -30°C provided crystalline $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$ (0.60 g, 32%). Anal. calcd. for $C_{48}H_{40}NO_2P_2RhCo$: 65.02%C, 4.55% H, 1.58%N; found: 64.56% C, 4.66%H, 1.50%N. IR (THF): 1690 cm^{-1}. Adding 15 ml more hexane produced 0.27 g(34%)$PPN^+[Cp_2Rh_3(CO)_4]^-$.

Reaction of $PPN^+[Cp_2Rh_3(CO)_4]^-$ with CH_3I. A solution of 38 mg (0.032 mmol) $PPN^+[Cp_2Rh_3(CO)_4]^-$ in 0.3 ml d_8-THF was treated with 4 ul (0.065 mmol) CH_3I in an NMR tube. A fast reaction ensued, showing the appearance of a doublet at δ 1.48 PPM (6H) and a singlet at δ 5.45 PPM (5H) attributable to $CpRh(CO)(CH_3)_2$. Acetone was observed to form slowly at 25°C by NMR (δ 2.03 PPM).

Reaction of $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$ with CH_3I. A solution of 0.80 g (1.0 mmol) $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$ in THF (50ml) was treated with 0.4 ml(6.4 mmol) CH_3I. The THF was removed (0°C, 10^{-2}mm) and the remaining solid taken up in benzene and quickly chromatographed on silica gel (2cm x 25 cm) using benzene as eluent. A preliminary yellow band ($CpM(CO)_2$, M=Co,Rh) was followed by a red-brown band of the product. Removal of solvent (0°C, 10^{-2}mm) provided 100 mg (27%) $Cp_2RhCo(CO)_2(CH_3)$. Sublimation (60°C, 10^{-4}mm) produced analytically pure product in low yield.[13]

Reaction of $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$ with CF_3CH_2I:

500 mg (0.56 mmol) $PPN^+[Cp_2RhCo(CO)_2]^{\dot{-}}$ was reacted with 2 ml(20 mmol) neat CF_3CH_2I. The excess CF_3CH_2I was removed (25°C, 10^{-2} mm) and the remaining solid chromatographed on silica gel (2 x 23cm) using hexane as eluent. A preliminary yellow band was followed by a red-brown band containing the product. The solvent was removed (10°C, 10^{-2}mm). This solid was rechromatographed (1 cm x 30 cm silica gel) using benzene as eluent. The brown fraction was collected and the solvent removed (10°C,10^{-2} mm), yielding 50 mg (17%) analytically pure $Cp_2RhCo(CO)_2(CH_2CF_3)_2$. IR(THF): 1886, 1847 cm^{-1}. Anal. Calcd. for $C_{16}H_{14}O_2RhCoF_6$: 37.38% C, 2.74%H; found: 37.63% C, 2.92%H. ^1H-NMR (C_6D_6): δ 4.90 PPM, 5H, s; δ 4.50, PPM, 5H, s; δ 1.26 PPM, 2H, t of d; j=14.6, 4hz; δ 0.50 PPM, 2H, q, j= 14.6hz. ^{19}F-NMR (C_6D_6): δ-0.27 PPM, t, j=14.6hz; δ-1.65 PPM, t of d, j=14.6, 4.8hz.

Decomposition of $Cp_2RhCo(CO)_2(CH_3)_2$. A solution containing 15 mg (0.040 mmol) $Cp_2RhCo(CO)_2(CH_3)_2$ in 0.5 ml C_6D_6 was prepared in an NMR tube attached to a ground glass joint. On a vacuum line the tube was sealed under a pressure of 620 mm CO. ^{1}H FT-NMR spectra were recorded as the tube was heated at 50°C for 2 hours. The NMR resonances of the starting material decreased as resonances attributable to $CpRh(CO)(CH_3)_2$ (δ4.88, δ0.83 PPM, d), $CpCo(CO)(CH_3)_2$ (δ4.44, δ0.67 PPM), $CpRh(CO)_2$ (δ4.87 PPM), $CpCo(CO)_2$ (δ4.41 PPM) and acetone (δ1.58 PPM) appeared.

Decomposition of $Cp_2RhCo(CO)_2(CH_2CF_3)_2$.

A solution of 20 mg (0.039 mmol) $Cp_2RhCo(CO)_2(CH_2CF_3)_2$ in 0.5 ml C_6D_6 was prepared in an NMR tube and the tube sealed under 600 mm CO. ^{1}H and ^{19}F FT NMR were recorded over the next hour. The initial ^{1}H spectrum showed resonances at δ4.90 (5H,s) and δ4.50 (5H,s) PPM, as well as a quartet (δ0.50 PPM) and a quartet of doublets (δ1.26 PPM) obscured by some hexane impurity. The ^{19}F-spectrum showed a large triplet (δ-0.27 PPM) and triplet of doublets (δ-1.65 PPM). Gated decoupling of each of these ^{19}F frequencies separately resulted in the collapse of the ^{1}H quartet and quartet of doublets, respectively, into singlets.

Within 1/2 hour new ^{19}F resonances appeared, attributable to $Cp_2Rh_2(CO)_2(CH_2CF_5)_2$ (δ-4.20 PPM, t of d), and $CpRh(CO)(CH_2CF_3)_2$ (δ-3.42 PPM, t of d), $CpCo(CO)(CH_2CF_3)_2$ (δ-1.91 PPM, t), and $Cp_2Co_2(CO)_2(CH_2CF_3)_2$ (δ-0.93 PPM, t). New ^{1}H Cp resonances appeared at δ4.95, δ5.38, δ4.30, and δ 4.63 PPM assignable to these compounds. Eventually (2hrs.) only the resonances of CpCo(CO)$(CH_2CF_3)_2$ (~15%) and CpRh(CO)$(CH_2CF_3)_2$ (~85%) remained (see Fig.8). ^1H resonances for $CpCo(CO)_2$ (80%, δ 4.41) and $CpRh(CO)_2$ (20%, δ 4.87 PPM) were also observed.

REFERENCES

1. N.E.Schore, C.S.Ilenda, and R.G.Bergman, J.Amer.Chem.Soc., 99, 1781(1977).
2. N.E.Schore, C.S.Ilenda, and R.G.Bergman, J.Amer.Chem.Soc., 98, 7438(1976).
3. M.A.White and R.G.Bergman, unpublished results.
4. All ^{1}H-NMR and ^{19}F-NMR were recorded by 180 Mhz FT-NMR in d_8-THF, C_6D_6, or acetone. Chemical shifts of ^{1}H-NMR were referenced to the residual α-protons of THF at δ 3.58 PPM or benzene at δ 7.15 PPM. ^{19}F-NMR were shifted -10.64159 Mhz relative to ^{1}H-NMR. All IR spectra were recorded in THF.
5. Pauling electronegativities: Co=1.8, Rh=2.2 .
6. R.Hill and S.A.R.Knox, J.Chem.Soc., Dalton Trans.,2622(1975).
7. W.D.Jones, M.A.White, and R.G.Bergman, J.Amer.Chem.Soc., 100, 6771(1978); for other semi-bridging structures, see: A.A.Hock and O.S.Mills, Acta Cryst.,A, 14, 139(1961); R.J.Doedens and L.F.Dahl, J.Amer.Chem.Soc., 88, 4847(1966); F.A.Cotton, and J.M.Troop, J.Amer.Chem.Soc., 96,1233(1974); H.B.Chin and R.Bau, J.Amer.Chem.Soc., 95, 5068(1973); M.R.Churchill and M.V.Veidis, J.Chem.Soc,A,2170(1971); D.B.Yawney, R.J.Doedens, Inorg.Chem., 11, 838(1971); A.A.Pasynskii, Yu.V.Sdripkin, I.L.Eremenkok V.T.Kalinnikov, G.G.Aleksandrov, and Yu.T.Struchkov, J.Organometal.Chem., 165, 49(1979).

8. P.Chini and S.Martinengo, Inorg.Chim.Acta, 3,21(1969).

9. Assignments were confirmed by ^{19}F decoupling.

10. Simulation parameters: δH_a=2.06PPM, δH_b=1.13PPM, j_{ab}= 14.2 hz, $j_{aF}=j_{bF}$=14.2 hz, j_{aRh}=5.0 hz, j_{bRh}=2.1 hz

11. Inorganic Synthesis, 8, 211 (1966).

12. R.S.Dickson and G.R.Tailby, Aust.J.Chem., 23, 1531(1970).

13. Anal.calcd. for $C_{14}H_{16}O_2RhCo$: 44.47% C, 4.27% H, 27.21% Rh, 15.59% Co; found; 44.71% C, 4.45% H, 26.3% Rh, 17.1% Co.

Chapter III

The Reactions of $CpMo(CO)_3H$ with $CpMo(CO)_3R$ and Ethylene.

Results and Discussion

The cobalt catalyzed hydroformylation of olefins is one of the most important uses of transition metal complexes to accomplish organic synthesis on an industrial scale and has been studied extensively by many workers.[1,2] Several studies have suggested that aldehyde formation in this process results from the direct reaction of $HCo(CO)_4$ with a cobalt acyl complex.[2] Others have proposed the interaction of H_2 with a cobalt complex generating aldehyde via. an intermediate cobalt acyl hydride.[1]

The more general question concerning the mechanism of reductive elimination of aldehydes and alkanes from hydrido metal acyls and alkyls and their relative stabilities bears directly upon the mechanism and products of the oxo-process. Several stable transition metal hydridoalkyls are known (e.g., $H(CH_3)Pt(PPh_3)_2$[3a], $H(CH_3)Os(CO)_4$[3b], $H(CH_3)Ni(PR_3)_2$[3c], $H(\text{i-butyl})Zr[C_5(CH_3)_5]_2$[3d], $H(\text{2-naphthyl})Fe(Me_2PCH_2CH_2PMe_2)_2$[3e], $H(CH_3)ZrCp_2$[3f], and $H(NCCH_2)Pt(PPh_3)_2$[3g]), but stable acyl hydrides are more rare and only a few such products have been reported.[4,5,25,26] Hydrido metal alkyls have been implicated as unstable intermediates in reductive elimination processes;[6] hydrido metal acyls have also been proposed in oxo-type processes,[2] in aldehyde decarbonylation reactions,[7] and in hydroacylation reactions.[4,8]

In our studies of the reactions of transition metal hydrides with metal alkyls and acyls, we have found that

$(C_5H_5)Mo(CO)_3H$, **1**, reacts stoichiometrically with complexes $(C_5H_5)Mo(CO)_3R$ ($R{=}CH_3$, C_2H_5, $CH_2C_6H_5$; **2a**, **2b**, **2c**) at 50°C to generate the corresponding aldehydes, RCHO, and the dimers[9] $[(C_5H_5)Mo(CO)_3]_2$ and $[(C_5H_5)Mo(CO)_2]_2$. The rate of reaction of **1** and **2b** in THF solution [13] was found to follow second order kinetics (first order in each reactant) with a rate constant $k = 4.0 \times 10^{-3}\ M^{-1}s^{-1}$ (Figs.1,2), indicating the molecularity shown in equation (1). The rate of

$$\mathrm{CpMo(CO)_3H} \quad + \quad \mathrm{CpMo(CO)_3R} \longrightarrow \mathrm{RCHO} + \tfrac{1}{2}\left\{\begin{array}{l}[\mathrm{CpMo(CO)_3}]_2\\ [\mathrm{CpMo(CO)_2}]_2\end{array}\right. \qquad (1)$$

1

2a, $R{=}CH_3$
2b, $R{=}CH_2CH_3$
2c, $R{=}CH_2C_6H_5$

reaction is faster in THF than in benzene(~10X) and follows the order $C_2H_5 > CH_3 > CH_2C_6H_5$ (Table I). No reaction is observed between **1** and **2a** after 7 days at 70°C in hexane solution.

When $(CH_3C_5H_4)Mo(CO)_3(CD_3)$ is heated at 50°C in d_8-THF with an equimolar amount of $(C_5H_5)Mo(CO)_3(CH_3)$ for 48 hrs. none of the crossover product $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ is observed by NMR[14], implying that the processes shown in equations (2), (3), and (4) are not occurring quickly with respect to aldehyde formation. Also, no crossover is observed upon addition of ½ equivalent of **1**; only acetaldehyde is observed by NMR[15].

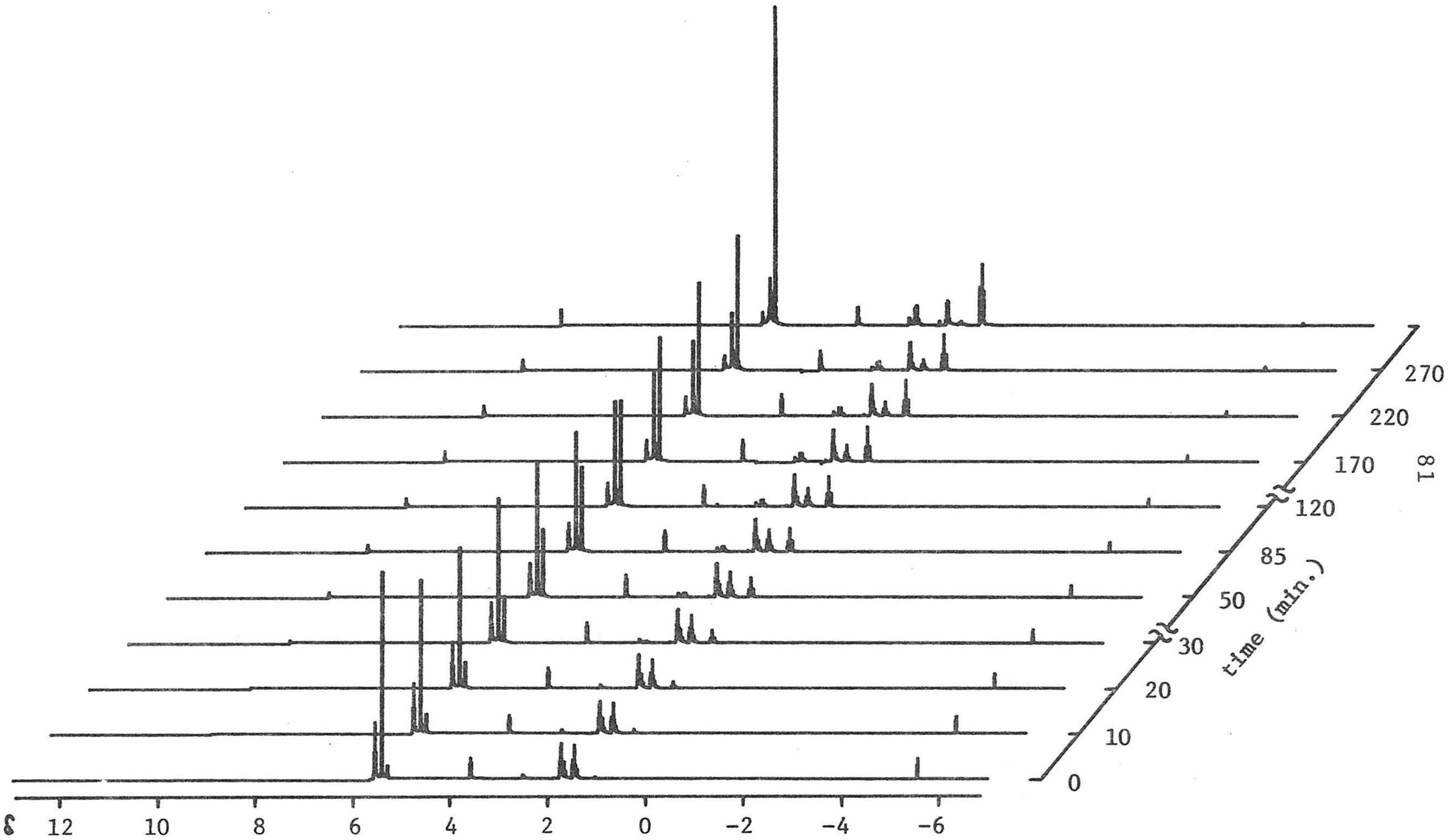


Figure 1. Reaction of CpMo(CO)$_3$H (0.12M) with CpMo(CO)$_3$(C$_2$H$_5$)(0.12M) at 25°C in d$_8$-THF solution. Elapsed time = 5.5hrs. Sweep width = δ+13 PPM to δ-7 PPM.

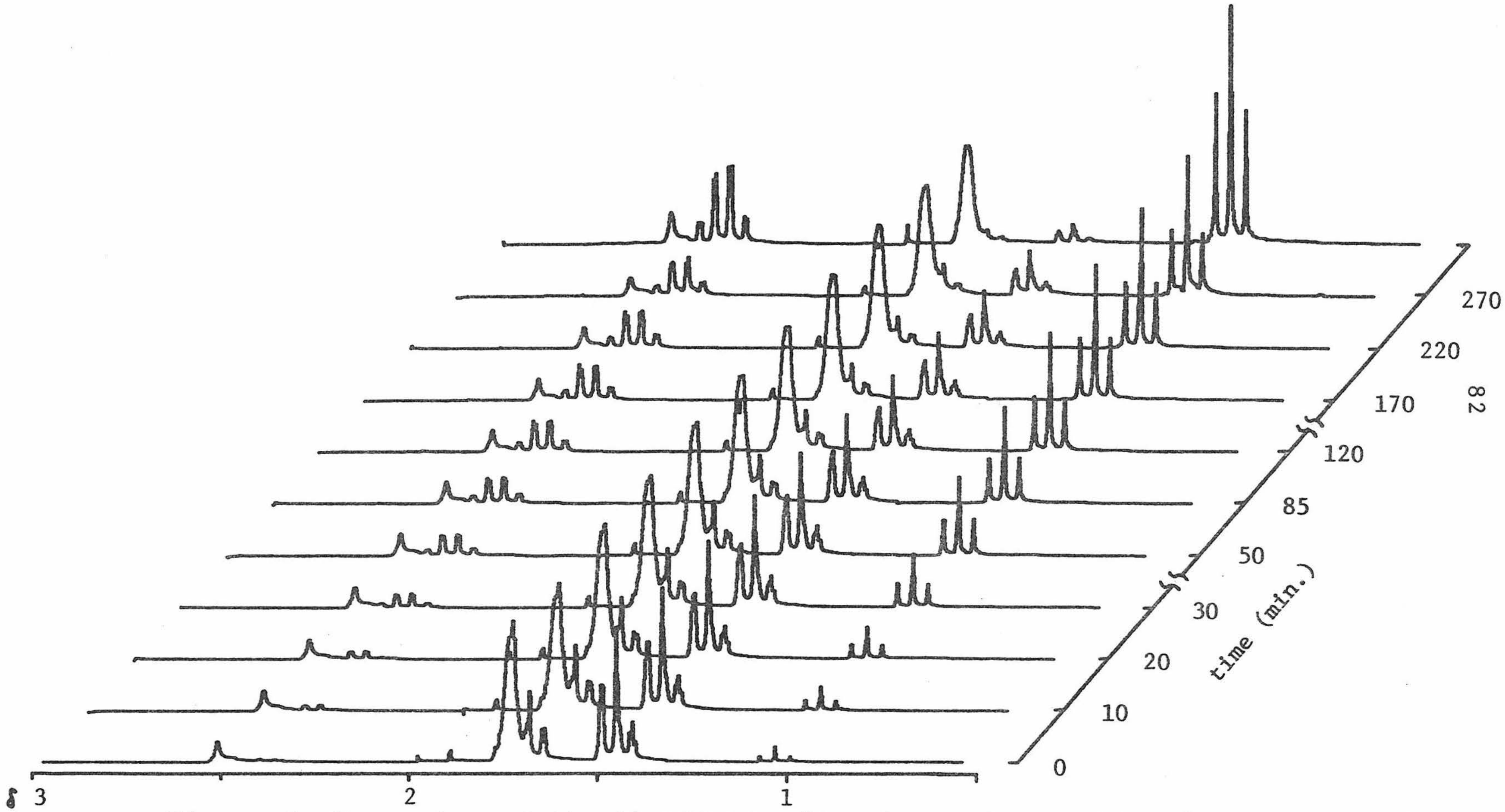


Figure 2. Expansion of the δ + 3 PPM to δ 0.5 PPM region of Fig. 1.

$$\mathrm{CpMo(CO)_3R} \rightleftharpoons \mathrm{Cp\dot{M}o(CO)_3} + \cdot\mathrm{R} \qquad (2)$$

$$\mathrm{CpMo(CO)_3R} \rightleftharpoons \mathrm{CpMo(CO)_2(COR)} \qquad (3)$$

$$\mathrm{CpMo(CO)_2(COR)} \rightleftharpoons \mathrm{Cp\dot{M}o(CO)_2} + \mathrm{R{-}\dot{C}{=}O} \qquad (4)$$

A similar result obtains upon heating a mixture of $(CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$ and $(C_5H_5)Mo(CO)_3(CH_2C_6H_5)$ at 50°C except that ~5% of the crossover product, $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$, is observed after 190 hrs.[16] However, no crossover is found if one heats a solution .1 M in each of $(CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$, $(C_5H_5)Mo(CO)_3(CH_2C_6H_5)$, and **1** for 70 hrs., and a 62% yield of aldehyde based on **1** is formed. A small amount of toluene was also identified in both reactions. Independent heating (50°C) of a solution of **2c** in d_8-THF showed a slow first order appearance[17a,c] of $C_6H_5CH_3$ ($k=2.58 \times 10^{-7}\ s^{-1}$). The rate of disappearance of **2c** was $5.05 \times 10^{-7} s^{-1}$, twice the rate of appearance of toluene. A similar decomposition of $(C_5H_5)Mo(CO)_3(CD_2C_6D_5)$ in d_8-THF yielded only $C_6D_5CD_2H$[17b,c]. These observations are best explained by the mechanism shown in Scheme I, which also accommodates reports by earlier workers.[18] No alkane is observed at 50°C when R= methyl or ethyl.

We believe these experiments rule out a radical process for the formation of aldehyde. Our observations are consistent with the mechanism shown in Scheme II, where a rate determining hydrogen transfer step (k_H) occurs after

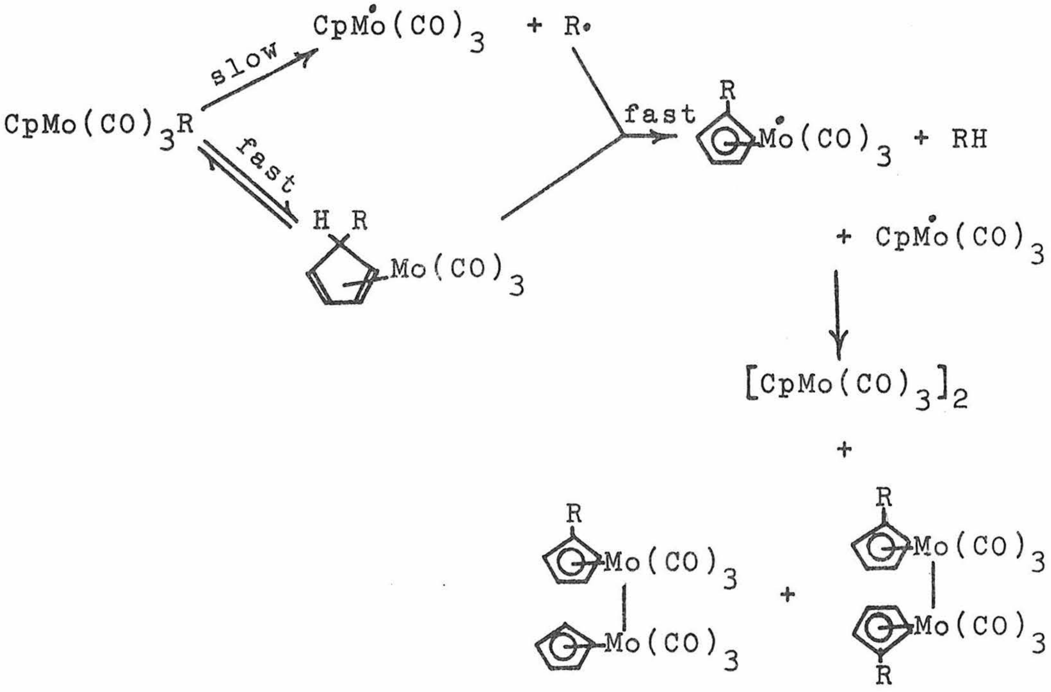
Table I

Second Order Rate Constants for the Reaction of $CpMo(CO)_3H$ with $CpMo(CO)_3R$

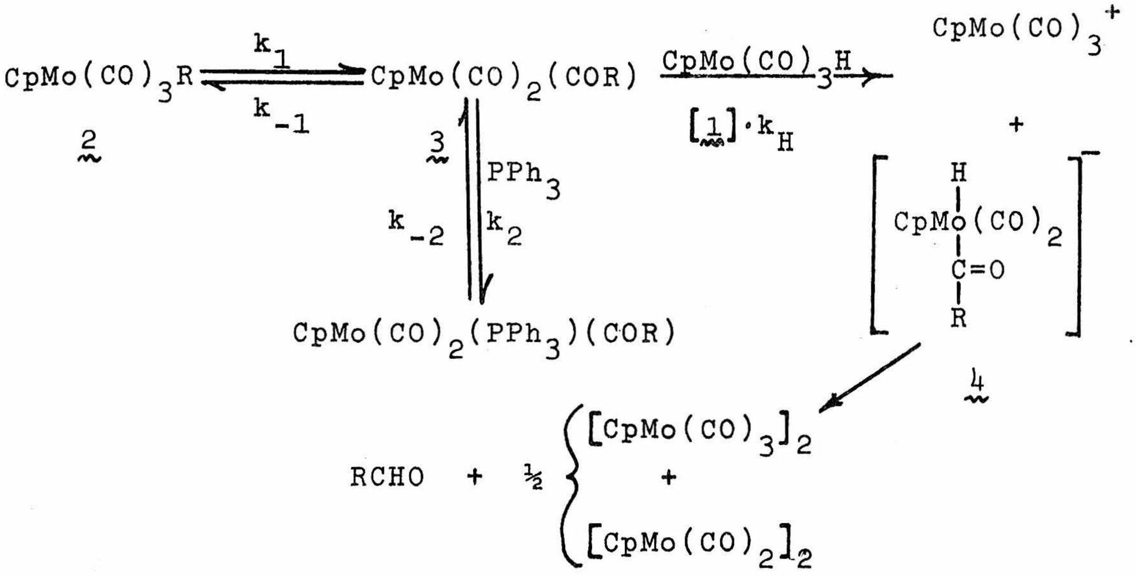
R	T(°C)	k $(M^{-1}s^{-1})(d_8\text{-THF})$
$-C_2H_5$	50	4.0×10^{-3}
$-CH_3$	50	2.5×10^{-4}
$-CH_2C_6H_5$	50	2.5×10^{-5}
$-C_2H_5$	25	8.5×10^{-4}
$-CH_3$ (*)	50	2.3×10^{-4}

(*) $(CH_3C_5H_4)Mo(CO)_3(CH_3)$

Scheme I



Scheme II



a fast pre-equilibrium between the coordinatively unsaturated molybdenum acyl complex **3** and the starting alkyl complex **2**. The lack of reactivity in hexane suggests the formation of an ionic intermediate such as **4**. We have not been able to trap any of the alternatively charged product $CpMo(CO)_3^-$ with a 10-fold excess of alkylating reagent such as CH_3I. The less acidic $CpMo(CO)_2(PMe_3)(H)$ reacts with **2b** at about the same rate as **1** ($k^{25^\circ C} = 2 \times 10^{-3}\ M^{-1}s^{-1}$), so that protonation of the acyl intermediate **3** by **1** appears less likely than hydride transfer. Also, no reaction occurs between **2a** and CH_3COOH in d_8-THF after 24 hrs. at 50°C.[19]

The intermediate $CpMo(CO)_2(COR)$ species **3** has also been formed by heating a solution of $CoMo(CO)_2(PPh_3)(COC_2H_5)$; in the presence of an excess of **1** aldehyde is formed, but traces of 2b are also observed (Figs. 3,4). Our measurements show that reaction of 2b with PPh_3 (Fig. 5) is slightly faster than with 1 ($k_2 > k_H$) and that formation of 2b from $CpMo(CO)_2(COCH_2CH_3)$ is competitive with aldehyde formation ($k_H[1] \cong k_{-1}$). We have observed no change in the rate of reaction of 1 with 2c when the reaction is carried out under 10 atm. CO.

Attempts to carry out this process catalytically have been unsuccessful. Heating a THF solution of ethylene (200 psi), CO (100 psi), and H_2 (800 psi) in the presence of $[CpMo(CO)_3]_2$ (0.004 mmols) produces no aldehyde after 72 hrs. at 100°C or after 24 hrs. at 155°C. The reaction (100°C, 10 atm.) of 1 with ethylene has been reported[21] to give 2b; we have repeated this reaction and have found that 2b is <u>not</u> formed. Rather, the major product is ethane and some (10%) diethyl ketone. We believe that 1 does react with C_2H_4 to give 2b, but in the presence of excess ethylene the coordinatively unsaturated acyl 3 is trapped as indicated in Scheme III and continues to form diethyl ketone.

Above 70°C the primary thermal process for 2b is loss of CO followed by attack by 1 to give ethane via. an intermediate hydrido metal alkyl complex. We have demonstrated this latter process by irradiating a d_8-THF solution of $CpMo(CO)_3(CH_3)$ (0.36 M) and $CpMo(CO)_3H$ (0.21 M)

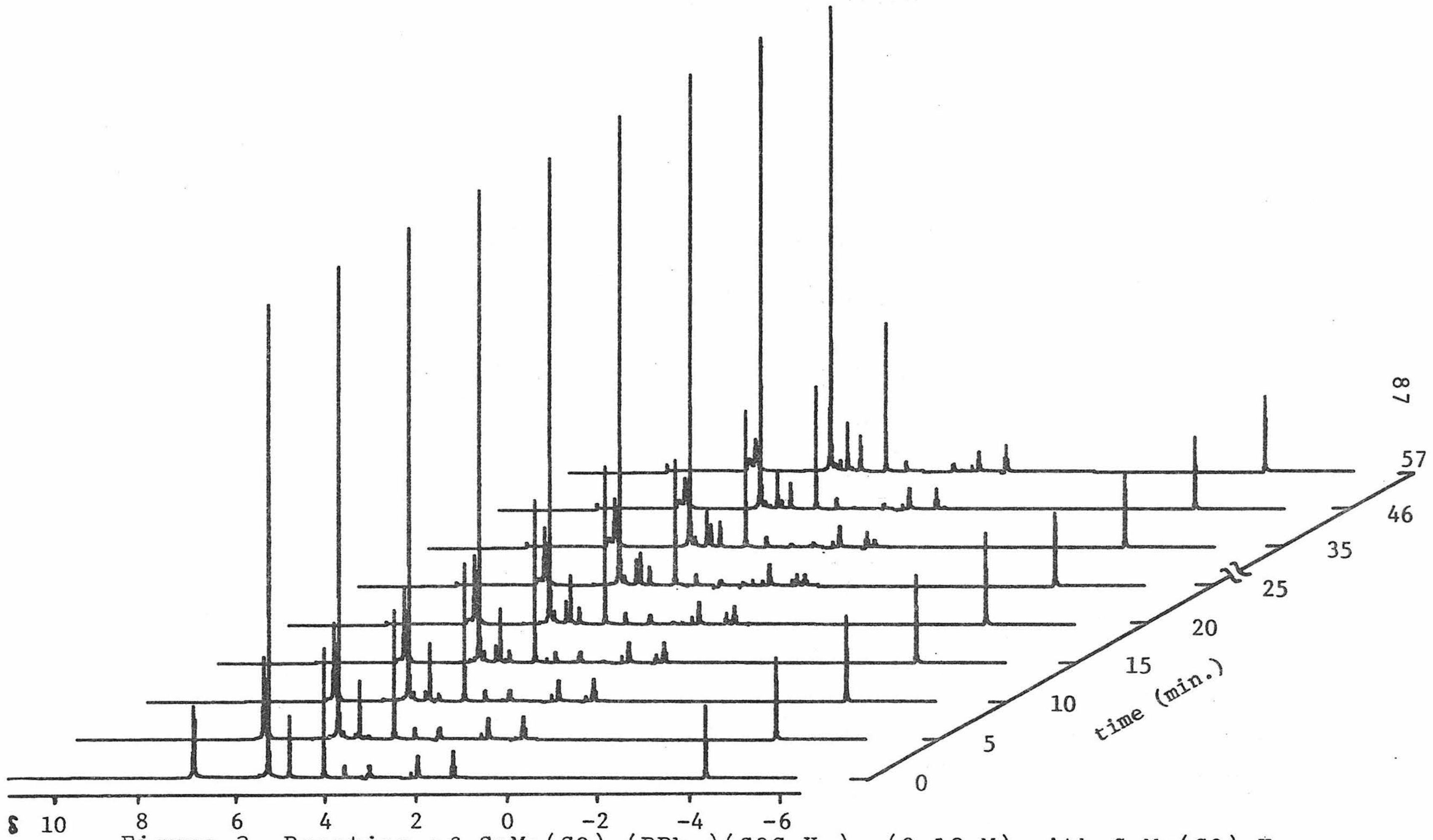


Figure 3. Reaction of $CpMo(CO)_2(PPh_3)(COC_2H_5)$ (0.12 M) with $CpMo(CO)_3H$ (1.0 M) at 50°C in d_8-THF solution, ferrocene added as internal standard. Elapsed time = 1 hr. Sweep width = δ +11 PPM to δ -7 PPM.

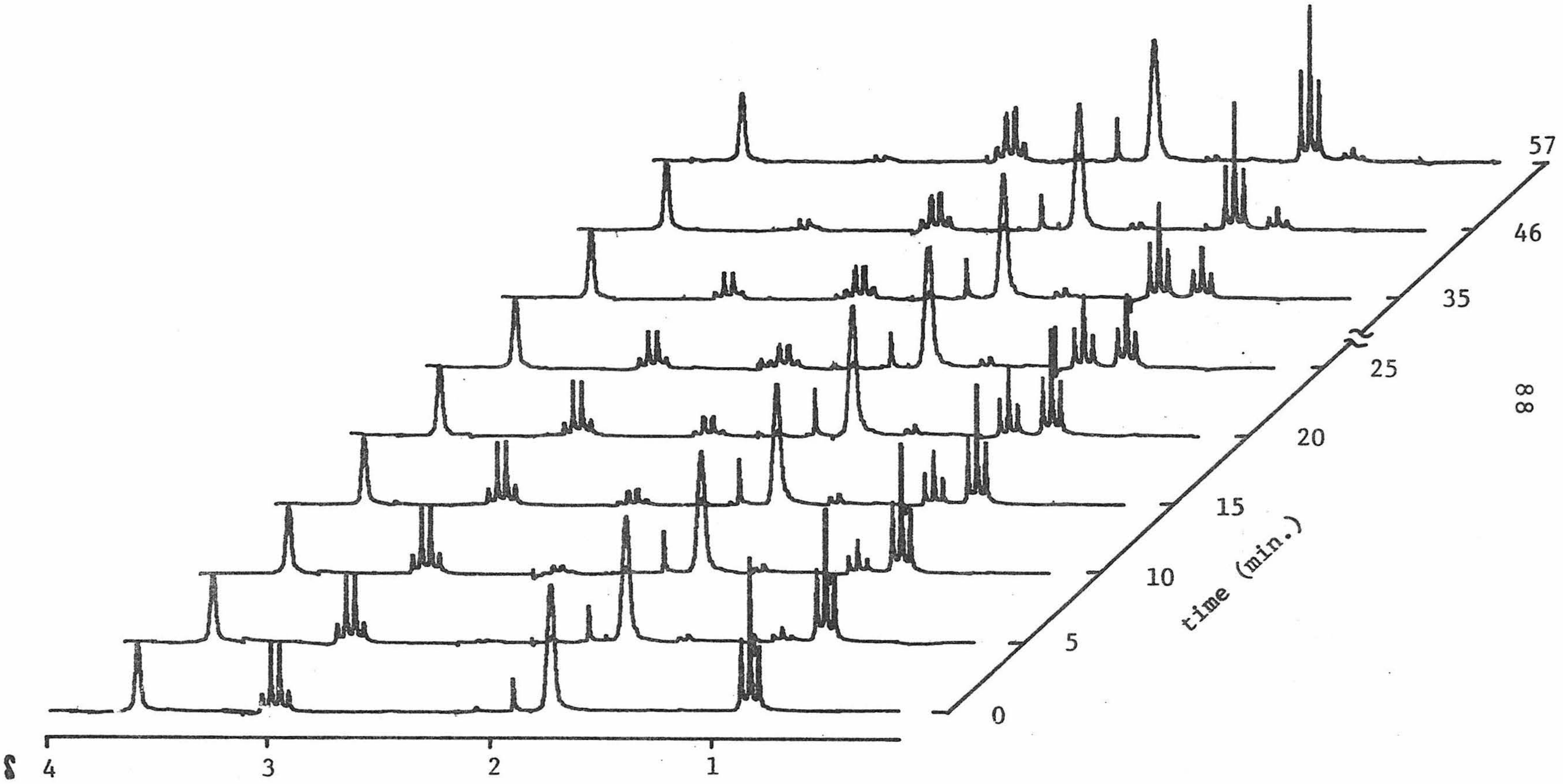


Figure 4. Expansion of the δ+4 PPM to δ 0 PPM region of Fig.3

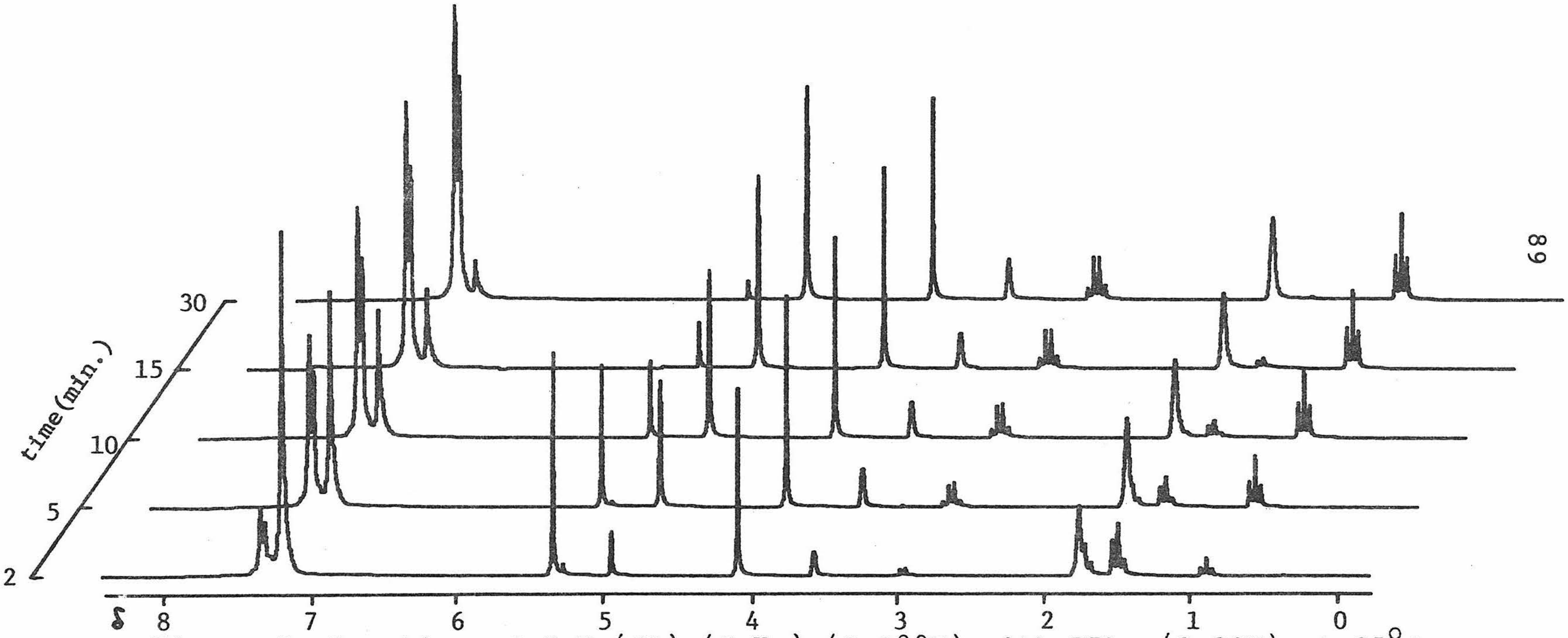
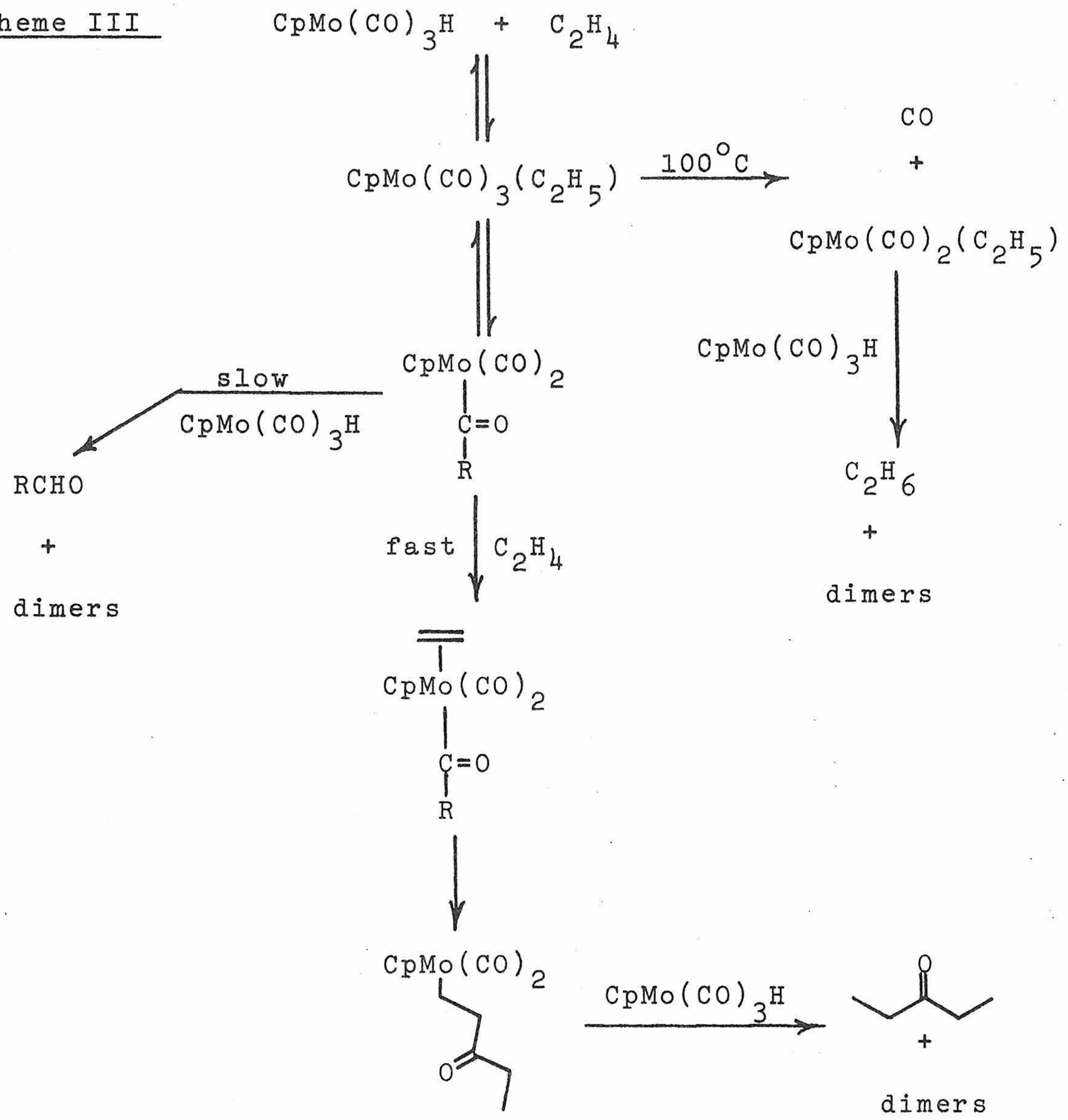


Figure 5. Reaction of $CpMo(CO)_3(C_2H_5)$ (0.088M) with PPh_3 (0.09M) at 25°C in d_8-THF solution, ferrocene added as internal standard. Elapsed time = 30 min. Sweep width = δ+8 PPM to δ 0 PPM.

Scheme III



The observed products are CH_4 (50%) and CH_3CHO (~5%). Irradiation of a d_8-THF solution of $CpMo(CO)_3(CH_3)$ and $(CH_3C_5H_4)Mo(CO)_3(CD_3)$ produces very little $(CH_3C_5H_4)Mo(CO)_3$-(CH_3) (2%) and no CH_4 ($<.5\%$) under similar conditions, indicating that metal-carbon homolysis is not a likely photochemical process.[27]

2a also reacts with ethylene at 100°C to produce methyl ethyl ketone in 50% yield. Traces of 1-buten-3-one are also observed (~5%). No acetone or diethyl ketone are formed. The methyl ethyl ketone is probably formed by the reaction of $CpMo(CO)_2(CH_2CH_2COCH_3)$ with **1** just as in the formation of diethyl ketone. We believe **1** arises from β-elimination in $CpMo(CO)_2(CH_2CH_2COCH_3)$, accounting for the observation of 1-butene-3-one. The low yield is due to a secondary reaction of the α,β-unsaturated ketone. Interestingly, no methane is detected. In the presence of added **1**, the yield of methyl ethyl ketone decreases drastically (to ~3%) as the ethane yield increases (~40%).

This system mimics the aldehyde forming step in the oxo-process with the $Co(CO)_4$ unit replaced by $CpMo(CO)_3$. The cyclopentadienyl molybdenum alkyl and acyl complexes are more stable, thus permitting easier study than in the cobalt system.

The insertion of olefins into the metal acyl bond has been previously observed by several workers in the cobalt carbonyl system[22,23]. It has been reported that if a limited amount of hydrogen is employed in the oxo-reaction the coordinatively unsaturated cobalt acyl reacts preferentially with olefin rather than hydrogen. The resulting 3-keto-1-pentylcobalt derivative then reacts with the small concentration of hydrogen present to produce dialkyl ketone.[22]

The molybdenum system mimics these reactions identically, including the decreased ketone yield with increasing hydride concentration, with only one exception: the active hydrogen source is $CpMo(CO)_3H$ and not H_2. A mixture of H_2, olefin, and $[CpMo(CO)_3]_2$ does not give any dialkyl ketone. The equivalent chemistry of both the molybdenum and cobalt systems also indicates that a metal hydride is the hydrogen transfer agent in the oxo-type processes as well.

Experimental. THF and benzene were distilled from Na/benzophenone prior to use. All manipulations were performed in a Vacuum Atmospheres Corp. Dry Box with a nitrogen atmosphere or on a high vacuum line. $[CpMo(CO)_3]_2$ and $[(CH_3C_5H_4)Mo(CO)_3]_2$ were obtained from Strem Chem. Co. or Alfa Corp. $CpMo(CO)_3H$ and $CpMo(CO)_3R$ were prepared from the dimer as previously described by Wilkinson.[10] The methyl-Cp derivatives were prepared analogously from the methyl-Cp dimer. Deuterated derivatives were prepared using CD_3I or $C_6D_5CD_2Br$. $CpMo(CO)_2(PPh_3)(COC_2H_5)$ was prepared as before.[24]

^{1}H-NMR spectra were recorded on a 180 MHz FT-NMR instrument equipped with a Bruecker superconducting magnet and a Nicolet 1180 FT-NMR computer.

Preparation of $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ and $(CH_3C_5H_4)Mo(CO)_3$-(CD_3). 0.75 g (1.5 mmol) $[(CH_3C_5H_4)Mo(CO)_3]_2$ was dissolved in 15 ml THF and stirred over 20 g 0.65% Na/Hg amalgam for 1 hr. The solution was decanted from the mercury and 0.25 ml CH_3I added (4.0 mmol). The THF was removed (25°C, 10^{-2}mm) and the product sublimed at 50°C (10^{-4}mm). Yield-0.35 g (45%) $(CH_3C_5H_4)Mo(CO)_3(CH_3)$. Anal. calcd. for $C_{10}H_{10}MoO_3$: 3.73% H, 43.45% C; found: 3.64% H, 43.22% C. NMR(d_8-THF): δ5.25 PPM, 4H, m; δ1.93 PPM, 3H, s; δ0.29 PPM, 3H, s.

Substitution of 0.3 ml CD_3I in place of CH_3I produced 0.52 g (60%) $(CH_3C_5H_4)Mo(CO)_3(CD_3)$, whose NMR was identical to that of $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ except for the absence of a methyl resonance at δ1.93 PPM.

Preparation of $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$ and $(CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$. 0.60 g (1.16 mmol) $[(CH_3C_5H_4)Mo(CO)_3]_2$ was reduced with 20 g 0.65% Na/Hg amalgam in 10 ml THF. 0.4 ml (2.53 mmol) $C_6H_5CH_2Br$ was added and the solution stirred for 30 min. The solvent was removed (25°C, 10^{-2}mm) and the solid chromatographed on silica gel (2cm x 10cm) using benzene as eluent. A yellow band was collected and the benzene removed (35°C, 10^{-2}mm), yielding 0.52 g (64%) $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$. NMR($d_8$-THF): δ7.12 PPM, 5H, m; δ5.20 PPM, 5H, s; δ2.82 PPM, 2H, s; δ1.96 PPM, 3H, s. Anal. calcd. for $C_{16}H_{14}MoO_3$: 54.87% C, 4.03% H; found: 54.66% C, 4.08% H.

Use of $C_6D_5CD_2Br$ (see below) (0.3 ml) in place of $C_6H_5CH_2Br$ produced $(CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$, m.p. 49-50°C, whose NMR was the same as that of $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$ except for the absence of the resonances at δ7.12 PPM and δ2.82 PPM.

Preparation of $C_6D_5CD_2Br$. 5 g (50 mmol) d_8-toluene (99.5%D) and 8.9 g (50 mmol) NBS were refluxed in 60 ml CCl_4 for 3 hrs. The solvent was removed (25°C, 20mm) and the remaining oil vacuum distilled (0.15mm, 50°C), yielding 6.7 g

(75%) $C_6D_5CD_2Br$. Mass spec.: m/e= 179/177 (Br isotope pattern), 98.

Reaction of $CpMo(CO)_3H$ with $CpMo(CO)_3(C_2H_5)$. 15 mg (0.061 mmol) $CpMo(CO)_3H$ and 17 mg (0.062 mmol) $CpMo(CO)_3(C_2H_5)$ were weighed into an NMR tube attached to a ground glass joint in the dry box and 0.51 ml d_8-THF introduced on a vacuum line. The tube was sealed under vacuum and FT-NMR recorded over the next 6 hrs. The product propionaldehyde was identified by its NMR resonances (δ9.68 PPM, $1H_a$, t, j_{ab}=1.7hz; δ2.38 PPM, $2H_b$, q of d, j_{bc}=7.3hz; δ1.04 PPM, $3H_c$, t). The dimers $[CpMo(CO)_3]_2$ and $[CpMo(CO)_2]_2$ were identified by comparison of their NMR resonances to those of authentic samples (δ5.40 PPM, δ5.27 PPM, respectively)

Reaction of $CpMo(CO)_3(CH_3)$, $(CH_3C_5H_4)Mo(CO)_3(CD_3)$, and $CpMo(CO)_3H$. 22 mg $CoMo(CO)_3H$ (0.089 mmol), 24 mg (0.092 mmol) $CpMo(CO)_3(CH_3)$, and 24 mg (0.086 mmol) $(CH_3C_5H_4)Mo(CO)_3(CD_3)$ were weighed into an NMR tube and 0.38 ml d_8-THF introduced on a vacuum line. The tube was sealed and heated to 50°C, and NMR spectra recorded over the next 12 hrs. 48% of the $CpMo(CO)_3(CH_3)$ was consumed vs. 41% of the $(CH_3C_5H_4)Mo(CO)_3(CD_3)$. No $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ was observed. An authentic mixture of the two compounds shows a 6 hz upfield shift for the methyl resonance of the methyl-Cp compound compared with the C_5H_5 compound.

A similar experiment with $R=CH_2C_6H_5$ and $CD_2C_6D_5$ also showed no crossover after 72 hrs, only benzaldehyde (62%, δ2.89 PPM, δ9.56 PPM) and toluene (25%, δ2.29 PPM) by NMR. Extended heating (192 hrs.) of only the benzyl compounds showed traces of the crossover product $(CH_3C_5H_4)Mo(CO)_3$-$(CH_2C_6H_5)$ by NMR, a new $-CH_2-$ resonance appearing ~12 hz upfield from the $CpMo(CO)_3(CH_2C_6H_5)$ methylene resonance. Toluene was also formed.

Thermolysis of $CpMo(CO)_3(CD_2C_6D_5)$ in d_8-THF. Heating a d_8-THF solution of $CpMo(CO)_3(CD_2C_6D_5)$ (0.23M) at 70°C for 7 days in a sealed NMR tube showed the formation of a quintet (δ2.27 PPM) in the NMR. The tube was broken open in air and the volatile contents vacuum distilled (30°C,10^{-2}mm) away from the molybedenum products. Preparative gas chromatography (¼"x10' 10% SE-30/Chrom P) produced a sample of toluene that showed a parent peak at m/e= 99, corresponding to $C_6D_5CD_2H$.

Reaction of $CpMo(CO)_3H$ with C_2H_4. A solution of 31 mg (0.126 mmol) $CpMo(CO)_3H$ in 0.4 ml d_8-THF was prepared in an NMR tube, 0.245 mmol C_2H_4 condensed into the tube on a vacuum line, and the tube sealed. The tube was heated to 100°C and NMR spectra recorded over the next 24 hrs. No propionaldehyde was observed; only ethane (36%) and diethyl ketone by NMR (15%; δ2.35 PPM, 4H, q; δ0.96 PPM, 6H, t). The tube was broken open in air and the contents vacuum distilled (30°C, 10^{-2}mm) into a -77°K receiving vessel.

1 ul aliquots were examined by gas chromatography (¼"x10' 20% Carbowax 20M/Chrom WAW), confirming the NMR product identification by co-injection with authentic samples.

Irradiation of $CpMo(CO)_3(CH_3)$ in the presence of $CpMo(CO)_3H$. A d_8-THF solution of $CpMo(CO)_3H$ (0.21 M) and $CpMo(CO)_3(CH_3)$ (0.36 M) was irradiated with a 500 W lamp for 5 min. NMR analysis showed a 25% disappearance of $CpMo(CO)_3(CH_3)$, a 15% yield of CH_4, and a trace of CH_3CHO (~1%). A similar irradiation of $CpMo(CO)_3(CH_3)$ (0.20M) and $(CH_3C_5H_4)Mo(CO)_3(CD_3)$ (0.19M) produced no methane and only ~2% $(CH_3C_5H_4)Mo(CO)_3(CH_3)$.

Reaction of $CpMo(CO)_3(PPh_3)(COCH_2CH_3)$ with $CpMo(CO)_3H$. 20.0 mg (0.0372 mmol) $CpMo(CO)_2(PPh_3)(COC_2H_5)$, 74.1 mg (0.301 mmol) $CpMo(CO)_3H$, and 11.1 mg (0.0597 mmol) ferrocene (internal standard) were weighed into an NMR tube and 0.55ml d_8-THF distilled in on a vacuum line. The tube was sealed and heated to 50°C in an NMR probe. NMR spectra recorded over the next hour showed the disappearance of $CpMo(CO)_2(PPh_3)(COCH_2CH_3)$ (δ7.42 PPM, 15H, m; δ4.97 PPM, 5H, s; δ2.95 PPM, 2H, q; δ0.82 PPM, 3H, t) and the appearance of CH_3CH_2CHO (δ2.35 PPM, 2H, q of d; δ1.01 PPM, 3H, t; δ9.67 PPM, 1H, t). $CpMo(CO)_3(C_2H_5)$ was observed at intermediate times in about 5% yield (δ5.30 PPM, 5H, s; δ1.44 PPM, 3H, t).

Reaction of $CpMo(CO)_3(CH_2C_6H_5)$ with $CpMo(CO)_3H$. A sealed NMR tube was prepared as described above containing 88 mg

(0.358 mmol) CpMo(CO)$_3$H, 15 mg (0.045 mmol) CpMo(CO)$_3$-(CH$_2$C$_6$H$_5$), and 12.3 mg (0.066 mmol) ferrocene in 0.43 ml d$_8$-THF. This solution was heated to 50°C in an NMR probe and the disappearance of CpMo(CO)$_3$(CH$_2$C$_6$H$_5$) monitored (δ7.16 PPM, 5H, m; δ5.29 PPM, 5H, s; δ2.89 PPM, 2H, s). Both benzaldehyde (δ9.63 PPM, 1H; other signals obscured by solvent and phenyl resonances) and toluene (δ2.29 PPM) were observed. The ratio of these two products changed from 6:1 to 3:1 over the course of the reaction.

Reaction of CpMo(CO)$_2$(PMe$_3$)(H) with CpMo(CO)$_3$(C$_2$H$_5$). 11 mg (0.037 mmol) CpMo(CO)$_2$(PMe$_3$)(H) and 8 mg CpMo(CO)$_3$-(C$_2$H$_5$) (0.029 mmol) were sealed in an NMR tube along with 0.42 ml d$_8$-THF. Reaction at 25°C showed the disappearance of CpMo(CO)$_3$(C$_2$H$_5$) and CpMo(CO)$_2$(PMe$_3$)(H) (cis/trans mixture, δ5.17 PPM, 5H, s; δ1.50 PPM, 9H, d, J$_{PH}$=9 hz; δ-6.00 PPM, 0.5H, sharp singlet(cis); δ-6.50 PPM, broad singlet, 0.5H (trans)). Propionaldehyde was the only product observed by NMR (δ9.68 PPM, 1H, t; δ2.38 PPM, 2H, q of d; δ1.04 PPM, 3H, t). The measured half life of this reaction was ~100 min., in comparison with the value of ~170 min. when CpMo(CO)$_3$H is employed at the concentration specified in the previously described experiment.

Reaction of CpMo(CO)$_3$(CH$_3$) with CH$_3$COOH). 25 mg (0.096 mmol) CpMo(CO)$_3$(CH$_3$) was dissolved in 0.32 ml d$_8$-THF in an NMR tube fitted with a rubber septum. 5.5 ul CH$_3$COOH

(0.096 mmol) was introduced with a syringe and the solution heated to 50^{o}C for 24 hrs. No changes were observed by NMR.

Reaction of $CpMo(CO)_3(CH_3)$ with ethylene. 35 mg (0.135 mmol) $CpMo(CO)_3(CH_3)$ was weighed into a medium wall NMR tube attached to a ground glass joint and 21.3 ml C_2H_4(215mm,25^{o}C) 0.245 mmol) condensed into the tube(-77^{o}K) on a vacuum line. 0.35 ml d_8-THF was also distilled in before sealing the tube. The solution was heated at 100^{o}C for 4 hrs. over which time the NMR resonances of $CpMo(CO)_3(CH_3)$ (δ5.41 PPM, δ0.36 PPM) were observed to diminish as resonances of $CH_3COCH_2CH_3$ (δ2.37 PPM, 4H, q, j=7.2hz; δ0.96 PPM, 6H, s; δ2.02 PPM, 3H, s) grew in (50% yield). No CH_4 was observed. The tube was broken open and the contents vacuum distilled into a -77^{o}K receiver. GC analysis of a 1 ul aliquot (¼"x10' 20% Carbowax 20M/Chrom WAW, 90^{o}C) showed a 55% yield of methyl ethyl ketone and a 5% yield of 1-buten-3-one using pentane as internal standard.

Reaction of $CpMo(CO)_3(CH_3)$, $CpMo(CO)_3H$, and ethylene. 15 mg (0.061 mmol) $CpMo(CO)_3H$ and 17 mg (0.065 mmol) $CpMo(CO)_3(CH_3)$ were weighed into a medium wall NMR tube attached to a ground glass joint and 21.3 ml (215mm, 25^{o}C, 0.245 mmol) ethylene plus 0.42 ml d_8-THF condensed into the tube on a vacuum line. The tube was sealed and heated to 70^{o}C for 3 hrs. An NMR spectrum showed ethane (δ0.47 PPM, 40%) and a mixture of other ethyl and methyl ketones.

No aldehyde resonances were found. The tube was broken open and the volatile products vacuum distilled (30°C,10^{-2}mm) into a -77°K receiver. GC analysis (¼"x10' 20% Carbowax 20M /Chrom WAW, 90°C) of a 1 ul aliquot showed small quantities of methyl ethyl ketone (3%), diethyl ketone (4%), and 1-buten-3-one (1%). (No acetone)

Reaction of $CpMo(CO)_3H$ with ethylene. 31 mg (0.126 mmol) $CpMo(CO)_3H$, 0.245 mmol C_2H_4, and 0.4 ml d_8-THF were sealed in a medium wall NMR tube as previously described. The tube was heated to 100°C for 24 hrs., at which time an NMR spectrum showed a quartet (δ2.35 PPM, 4H, j=7.5 hz) and a triplet (δ0.96 PPM, 6H, j=7.5 hz) attributable to diethyl ketone (~10%). No aldehyde resonances were observed, but ethane was formed (δ0.47PPM) in ~25% yield. The tube was broken open, the contents vacuum distilled (30°C,10^{-2}mm), and a 1 ul aliquot examined by GC (1/16"x100' open tubular TCEP column, 70°C) confirming the product as diethyl ketone by co-injection with an authentic sample.

Reaction of $CpMo(CO)_3(C_2H_5)$ with PPh_3. 13.1 mg (0.0478 mmol) $CpMo(CO)_3(C_2H_5)$, 12.8 mg (0.0487 mmol) PPh_3, and 3.1 mg ferrocene (internal standard) were weighed into an NMR tube and 0.54 ml d_8-THF distilled in on a vacuum line. The tube was sealed, warmed to 25°C in a water bath, and quickly transferred to the probe (25°C) of the NMR instrument. NMR spectra were recorded every 5 min., showing the rapid conversion of $CpMo(CO)_3(C_2H_5)$ (δ5.20 PPM, δ1.70 PPM, δ1.44 PPM) into $CpMo(CO)_2(PPh_3)(COCH_2CH_3)$ (δ7.42 PPM, 15H, m; δ4.97 PPM, 5H, s; δ2.95 PPM, 2H, q; δ0.80 PPM, 3H, t).

Reaction of $CpMo(CO)_3(CH_3)$ with C_2H_4 in the presence of 1-buten-3-one. 36 mg (0.138 mmol) $CpMo(CO)_3(CH_3)$ was weighed into an NMR tube fitted with a ground glass joint and 2.5 ul (0.030 mmol) 1-buten-3-one introduced with a syringe. The tube was quickly attached to a vacuum line, cooled to -77°K, and evacuated. The ethylene (0.25 mmol) and 0.42 ml d_8-THF were condensed in and the tube sealed. The tube was heated to 100°C and NMR spectra recorded over the next 18 hrs. In 1 hr., 46% of the $CpMo(CO)_3(CH_3)$ (δ0.36 PPM) was consumed and a 25% yield of 2-butanone (δ0.96 PPM, 3H, t; δ2.37 PPM, 4H, q; δ2.02 PPM, 3H, s) observed. 80% of the 2-buten-3-one had disappeared. In 6 hrs., the reaction was 95% complete and a 54% yield of 2-butanone was found. After 18 hrs. all $CpMo(CO)_3(CH_3)$ had been consumed and a 58% yield of 2-butanone was measured. The tube was broken open and the volatile contents vacuum distilled and analyzed by GC (10'x¼" 20% Carbowax 20M/Chrom WAW, 90°C). A 55% yield of 2-butanone was confirmed relative to added internal standard(pentane). Traces of 2-buten-3-one were found(<5%).

REFERENCES

1. N.H.Alemdoroglu, J.L.M.Penninger, and E.Oltay, Monatshefte fur Chemie, 107, 1153 (1976); P.S.Breslow and R.F.Heck, Chemistry and Industry, 467 (1960); W.Rupilius and M. Orchin, J.Org. Chem., 37, 936 (1972).

2. R.F.Heck and D.S.Breslow, J.Amer.Chem.Soc., 83, 4023 (1961); L.Kirsch and M.Orchin, J.Amer.Chem. Soc., 81, 4200 (1959); V.Yu Gankin, V.Congr. on Catal., 1, 25 (1972); V.Yu Gankin, V.L.Klimenko, V.A.Ribakov, and V.A.Divinin, Symp. on Hydrof., Veszprem 1972, p.32; V.Yu Gankin, V.A.Divinin, V.P.N.Norikov, V.A.Ribakov, and S.K.Skop, Kinetica i Katiliz, 14, 1149 (1973); R.Whyman, J. Organometall. Chem.,66,c23 (1974); L.Marko, G.Bor. G.Almasy, and P.Szabo, Brennstoff-Chem., 44, 184 (1963).

3.a)L.Abis, A.Sen, and J.Halpern, J.Amer. Chem. Soc., 100, 2915 (1978); b) S.J.Okrazinski, and J.R.Norton, J. Amer. Chem. Soc., 99, 295 (1977); c) K.Jonas and G.Wilke, Angew. Chem. Int. Ed. Engl., 8, 519 (1969); d) D.R. McAlister, D.K.Erwin, and J.E.Bercaw, J. Amer. Chem. Soc., 100, 5966 (1978); e) S.D.Ittel, C.A.Tolman, A.D.English, and J.P.Jesson, J.Amer. Chem. Soc., 98, 6073 (1976); f) R.C.Wailes and H.Weigold, J.Organometal. Chem., 24, 405 (1970); R. Ros, R.A.Michelin, R.B.Bataillard, and R.Roulet, J. Organometal. Chem., 161, 75 (1978).

4. J.W.Suggs, J.Amer. Chem. Soc., 100, 640 (1978).

5. T.B.Rauchfuss, *J.Amer. Chem. Soc.*, *101*, 1045 (1979).

6. E.L.Muetterties and P.L.Watson, *J.Amer. Chem. Soc.*, *98*, 4665, (1976); G.M.Whitesides, J.F.Gaasch, and E.R.Stedronsky, *J.Amer. Chem. Soc.*, *94*, 5258 (1972).

7. H.M.Walborsky and L.E.Allan, *J.Amer. Chem. Soc.*, *92*, 5465 (1971); M.C.Baird, C.J.Nyman, and G.Wilkinson, *J.Chem. Soc.*, *A*, 348 (1968).

8. K.Sakai, J.Ide, O.Oda, and N.Nakamura, *Tet. Lett.*, 1287 (1972); K.Sakai and O.Oda, *Tet. Lett.*, 4375 (1972); C.F.Lochow and R.G.Miller, *J.Amer. Chem. Soc.*, *98*, 1281 (1976).

9. All compounds prepared as previously described.[10,11,12] NMR data (d_8-THF): $(C_5H_5)Mo(CO)_3(CH_3)$: δ 5.41 PPM, 5 H, s; δ 0.36 PPM, 3 H, s; $(C_5H_5)Mo(CO)_3(CH_2CH_3)$: δ 5.30 PPM, 5 H, s; δ 1.70 PPM, 2 H, quart; δ 1.44 PPM, 3 H, t; $(C_5H_5)Mo(CO)_3(CH_2C_6H_5)$: δ 7.16 PPM, 5 H, m; δ 5.29 PPM, 5 H, s; δ 2.89 PPM, 2 H, s; $[(C_5H_5)Mo(CO)_3]_2$: δ 5.40 PPM, s; $[(C_5H_5)Mo(CO)_2]_2$: δ 5.27 PPM, s; $(C_5H_5)Mo(CO)_3H$: δ 5.52 PPM, 5 H, s; δ -5.59 PPM, 1 H, s.

10. T.S.Piper and G.Wilkinson, *J.Inorg. Nuc. Chem.*, *3*, 104 (1956).

11. D.S.Ginley, C.R.Bock, and M.S.Wrighton, *Inorg. Chim. Acta*, *23*, 85 (1977).

12. P.J.Craig and M.Green, *J.Chem. Soc.*, *A*, 1978(1968).

13. A d_8-THF solution of **1** and **2b** (0.16 M each) was monitored by 180 MHz FT-NMR. The rate calculation was based

upon the disappearance of hydride (δ -5.59 PPM) relative to internal standard (ferrocene).

14. $(CH_3C_5H_4)Mo(CO)_3(CH_3)$: δ 5.25 PPM, 4 H, m; δ 1.93 PPM, 3H , s; δ 0.29 PPM, 3 H, s.

15. The rate of reaction of $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ with **1** is essentially the same as **2a** with **1**.

16. $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$; δ 7.12 PPM, 5 H, m; δ 5.20 PPM, 4 H, m: δ 2.82 PPM, 2 H, s; δ 1.96 PPM, 3 H, s.

17. a) $C_6H_5CH_3$ identified by NMR (d_8-THF) in 40% yield: δ2.28 PPM, s; and mass spec.: m/e = 92. b) $C_6D_5CD_2H$ identified by NMR (d_8-THF) in 40% yield: δ 2.28 PPM, quint.; and mass spec.; m/e = 99. c) The other products observed by NMR are $[(C_5H_5)Mo(CO)_3]_2$, $(C_5H_5)(CO)_3$Mo--Mo$(CO)_3(C_5H_4CH_2C_6H_5)$,[18] and $[(C_5H_4CH_2C_6H_5)Mo(CO)_3]_2$.[18]

18. C.U.Pittman, Jr. and R.F.Felis, J.Organometall. Chem., 72, 399 (1974).

19. However, CF_3COOH reacts with $CpMo(CO)_3(CH_3)$ at 20°C to produce a quantitative yield of methane.[20]

20. R.L.Watson and R.G.Bergman, Jour.Amer.Chem.Soc., 101, (1979).

21. R.A.Schunn, Inorg.Chem., 9, 2567(1970).

22. J.H.Staib, W.R.F.Guyer, and O.C.Slotterbeck, U.S. Patent 2,864,864 (1958).

23. R.F.Heck, Acc. Chem. Res., 2, 10(1969); R.F.Heck, J. Amer. Chem. Soc., 85, 3381(1963); R.F.Heck, J. Amer. Chem. Soc., 85, 3116(1963).

24. F.P.Bibler, and A.Wojiciki, *Inorg. Chem.*, *5*, 889(1963).

25. C.A.Tolman, S.D.Ittel, A.D.English, and J.P.Jesson, *J.Amer. Chem. Soc.*, *101*, 1742 (1979).

26. S.G.Davies and M.L.H.Green, *J.Chem.Soc.*, *Dalton Trans.*, 1510(1978).

27. Rather, CO loss is the primary photoprocess, in accordance with the known photosubstitution chemistry of $CpMo(CO)_3(CH_3)$. See: H.G.Alt, *J.Organometal.Chem.*, *124*, 167(1977).

Chapter IV

The Reactions of Two Isoelectronic Transition Metal Hydrides with Transition Metal Carbonyls, Alkyls, and Acyls.

Introduction

The reactions of transition metal hydrides have been of interest to inorganic and organic chemists for many years. Several hydrides are believed to react with transition metal alkyls,[1] acyls,[2] and carbonyls[3] to give alkanes, aldehydes, and formyls. We wish to report upon the reactivity patterns of the anionic hydride $CpV(CO)_3H^-$, and to compare its reactivity to that of the isoelectronic $CpMo(CO)_3H$.

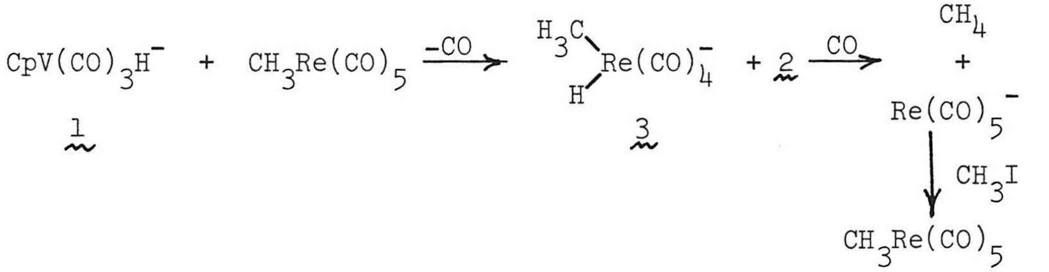
Results

1. PPN^+ $CpV(CO)_3H^-$ with Metal Carbonyls. PPN^+ $CpV(CO)_3H^-$, **1**, has been reported previously[4] to react with alkyl halides and acid chlorides to give alkanes and aldehydes respectively. We suspected that **1** might also reduce metal carbonyls and have found by monitoring the ^1H-NMR of d_8-THF solutions that **1** reacts with $Cr(CO)_6$ and $Fe(CO)_5$ at 25°C to give quantitative yields of $CpV(CO)_4$, **2**, and $HCr(CO)_5^-$ and $HFe(CO)_4^-$, respectively(eqn.1). Addition of 10 mole percent $Na_2CpV(CO)_3$ accelerates the rate of this reaction. $CpV(CO)_3H^-$ also undergoes a self-exchange reaction with $CpV(CO)_4$, as

$$\underset{\mathbf{1}}{CpV(CO)_3H^-} + M(CO)_n \rightleftharpoons \underset{\mathbf{2}}{CpV(CO)_4} + HM(CO)_{n-1}^- \qquad (1)$$

evidenced by the appearance of NMR signals of 2 and $(CH_3C_5H_4)V(CO)_3H^-$ upon mixing a solution of $(CH_3C_5H_4)V(CO)_4$ and 1. No bridging species such as $Cp(CO)_3V\text{-}H\text{-}M(CO)_{n-1}^-$ were observed in any of these reactions. While no thermal substitution occurs between PPh_3 and 2 in d_8-THF solution (0.1M each), addition of 1 (0.05 M) catalyzes this exchange.

2. PPN^+ $CpV(CO)_3H^-$ with Metal Alkyls. We have also investigated the reduction of some transition metal alkyls with 1 in d_8-THF solution. $(CH_3)Mn(CO)_5$ reacts immediately at 25°C to produce a trace of CH_4 (NMR, 5%) and intractable metal products. The isoelectronic $(CH_3)Re(CO)_5$ reacts at 50°C with 1 to form 2 and a new complex, $(H)(CH_3)Re(CO)_4^-$, 3, identified by ^1H-NMR (δ -0.65 PPM, 3H, d, j=3hz; δ -5.56 PPM, 1H, br). 3 decomposes slowly to form CH_4 and $Re(CO)_5^-$, which reacts with CH_3I to re-form $(CH_3)Re(CO)_5$ (eqn.2).



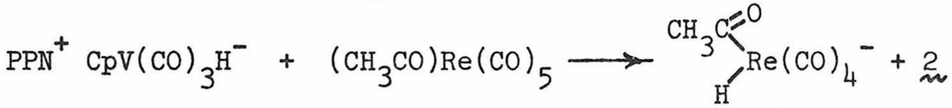
$$CpV(CO)_3H^- + CH_3Re(CO)_5 \xrightarrow{-CO} (H_3C)(H)Re(CO)_4^- + 2 \xrightarrow{CO} CH_4 + Re(CO)_5^- \xrightarrow{CH_3I} CH_3Re(CO)_5 \qquad (2)$$

1 3

No reaction occurs between $CpFe(CO)_2(CH_3)$ and 1 at 25°C. However, $CpMo(CO)_3(C_2H_5)$ reacts rapidly with 1 to produce ~30% yield (NMR) of propionaldehyde. No metal products were identified nor was any ethane found. Reaction with $\mathrm{CpCo(PPh_3)(CH_3)_2}$ produces ~ 2:1 mixture of methane and acetone by NMR. Metal products other than **2** could not be identified but presumably are cobalt clusters.[5]

3. $\mathrm{PPN^+\ CpV(CO)_3H^-}$ with Metal Acyls. We have examined the reaction of **1** with $\mathrm{CpFe(CO)(PPh_3)(COCH_3)}$ by ^{1}H-NMR; no reaction occurs at 25°C. However, in the presence of CO, a catalytic exchange of $\mathrm{PPh_3}$ for CO occurs, forming $\mathrm{CpFe(CO)_2(COCH_3)}$. Neither of these react with **1** upon heating for 24 hrs. at 65°C.

The reaction of **1** with $\mathrm{(CH_3CO)Re(CO)_5}$ at 50°C produces **2** and a compound with NMR resonances consistent with a new anionic acyl hydride, **4** (eqn.3). The rate of this reaction



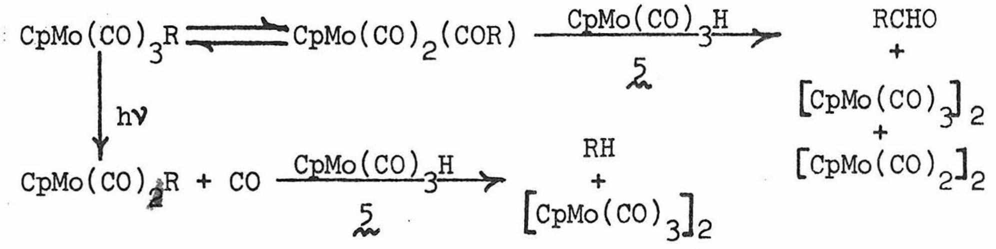
$$\mathrm{PPN^+\ CpV(CO)_3H^-} + \mathrm{(CH_3CO)Re(CO)_5} \longrightarrow \mathrm{(CH_3C{=}O)(H)Re(CO)_4^-} + \mathbf{2} \qquad (3)$$

1 **4**

is greatly accelerated by the addition of 10 mole percent of Na metal or $\mathrm{Na_2CpV(CO)_3}$. Addition of hexane to this solution produces only a dark brown oil that cannot be crystallized. Hexane washings of this oil contain yellow **2**, leaving behind impure $\mathrm{PPN^+\ [(H)(CH_3CO)Re(CO)_4]^-}$ (~90% pure). Further attempts to recrystallize this material have been unsuccessful.

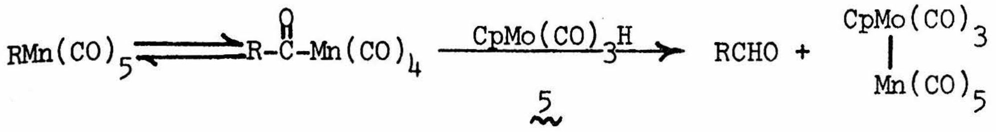
4. CpMo(CO)$_3$H with Metal Carbonyls. Reaction of CpMo(CO)$_3$H, **5**, with Fe(CO)$_5$ produces only decomposition upon heating to 70°C for 24 hrs. Reaction of **1** with Cr(CO)$_6$ at 70°C in d$_8$-THF produces no HCr(CO)$_5^-$. However, an NMR signal attributable to [CpMo(CO)$_3$]$_2$ is observed as well as a broad resonance at δ4.98 PPM (~62% of **5** still remained).

5. CpMo(CO)$_3$H with Metal Alkyls. In an earlier chapter we described the thermal reaction between **5** and CpMo(CO)$_3$R to give aldehyde and the metal dimers [CpMo(CO)$_3$]$_2$ and [CpMo(CO)$_2$]$_2$.[6] However, photolysis of a mixture of **5**(0.21M) and CpMo(CO)$_3$(CH$_3$) (0.36M) produces alkane as the sole product (~60% by NMR) and suggests the paths shown in equation 4. Irradiation of a mixture of CpMo(CO)$_3$(CH$_3$) and (CH$_3$C$_5$H$_4$)Mo(CO)$_3$(CD$_3$) (0.2M each) produces only 2% (CH$_3$C$_5$H$_4$)Mo(CO)$_3$(CH$_3$) and no methane under identical irradiation conditions and times.



(4)

This reaction pathway has been extended to the compounds RMn(CO)$_5$ (c.f., ref.3b). Reaction of **5** with (CH$_3$)Mn(CO)$_5$ at 25°C produces new NMR signals identical to those of authentic samples of the aldehyde CH_3CHO and the known[7] metal dimer $Cp(CO)_3Mo{-}Mn(CO)_5$ (eqn.5). No reaction occurs between **5** and $(CH_3)Re(CO)_5$ under similar conditions.



$$\mathrm{RMn(CO)_5} \rightleftharpoons \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}Mn(CO)_4} \xrightarrow[\mathbf{5}]{\mathrm{CpMo(CO)_3H}} \mathrm{RCHO} + \begin{array}{c}\mathrm{CpMo(CO)_3}\\ | \\ \mathrm{Mn(CO)_5}\end{array} \qquad (5)$$

Reactions of $CpMo(CO)_3H$ with Metal Acyls . In an earlier chapter we reported[6] the reaction of **5** with the transition metal acyl $CpMo(CO)_2(PPh_3)(COC_2H_5)$. At 50°C, propionaldehyde is the sole product. Phosphine substituted dimers are presumably also formed. Since the solution must be heated for reaction to occur, phosphine loss appears to be the rate determining step.

Discussion

The reactions of transition metal carbonyls with $CpV(CO)_3H^-$ show a consistent pattern of substitution of CO for hydride (Table I). The observation that the rate is accelerated by Na or $Na_2CpV(CO)_3$ suggests an outer sphere electron transfer chain mechanism, (Scheme I) with the $Na_2CpV(CO)_3$ acting as an initiator. Abstraction of a hydrogen atom from $CpV(CO)_3H^-$ occurs readily, as the V-H bond is very weak.[4] The observed products are not being formed by de-insertion of CO from the metal formyl compounds as the formyl complexes are stable for days at 25°C.[8]

Scheme I:

Initiation:

$$\left.\begin{matrix} CpV(CO)_3H^- \\ \text{or} \\ Na_2CpV(CO)_3 \\ \text{or} \\ Na \end{matrix}\right\} + M(CO)_n \longrightarrow \begin{matrix} M(CO)_{n-1}^{\dot{-}} \\ + \\ CO \end{matrix} + \left\{\begin{matrix} CpV(CO)_3H\cdot \\ \text{or} \\ CpV(CO)_3^{\dot{-}} \\ \text{or} \\ Na^+ \end{matrix}\right.$$

Propagation:

$$\left.\begin{matrix} CpV(CO)_3H^- \\ \text{or} \\ CpV(CO)_3H\cdot \end{matrix}\right\} + M(CO)_{n-1}^{\dot{-}} \longrightarrow HM(CO)_{n-1}^- + \left\{\begin{matrix} CpV(CO)_3^{\dot{-}} \\ \text{or} \\ CpV(CO)_3 \end{matrix}\right.$$

$$CpV(CO)_3^{\dot{-}} + M(CO)_n \longrightarrow CpV(CO)_3 + M(CO)_{n-1}^{\dot{-}} + CO$$

$$\begin{tikzcd} CpV(CO)_3 \arrow[r, "CO"] \arrow[dr, "PPh_3"'] & CpV(CO)_4 \\ & CpV(CO)_3(PPh_3) \end{tikzcd}$$

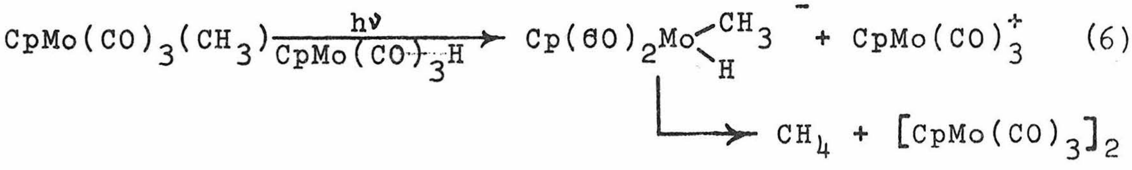
The catalytic substitution of PPh_3 in $CpV(CO)_4$ by **1** may also be accomodated with this mechanism. It is also possible for hydride-CO exchange to occur by a non-chain process through a pairwise electron-transfer followed by hydrogen abstraction from the resulting $CpV(CO)_3H\cdot$ (Scheme I). We do not believe the reactions proceed by inner sphere electron transfer because: 1) the parent carbonyls have no vacant coordination sites and are not thermally labile, 2) the reactions are too slow ($k \approx 10^{-4}-10^{-6}\ M^{-1}s^{-1}$), and 3) $CpMo(CO)_3H$ produces no new hydrides when reacted with $M(CO)_n$ species. The latter observation is consistent with a reduced metal species being needed as a reducing agent in electron transfer.

The reaction of **1** with $(CH_3)Re(CO)_5$ proceeds along the same pathway, exchange of hydride for CO. Subsequent methane formation occurs from the hydrido alkyl anion, $(H)(CH_3)Re(CO)_4^-$, which is isoelectronic with the osmium analog studied by Norton.[9] Interestingly, he has found that the osmium compound does not undergo simple reductive elimination but rather a binuclear elimination process. $(CH_3)Mn(CO)_5$ also reacts with **1** but no intermediates are observed and very little CH_4 is found.

The higher reactivity of **1** with $(CH_3)Mn(CO)_5$ compared with $(CH_3)Re(CO)_5$ suggested to us that a similar effect might be observed for the reactions with **5**. Thus, while no reaction occurred between $(CH_3)Re(CO)_5$ and **5** after 75 hrs., a smooth reaction forming acetaldehyde and $CpMo(CO)_3-Mn(CO)_5$

occurred between $(CH_3)Mn(CO)_5$ and **5**. The formation of a different organic product in this case demonstrates that a different intermediate is involved than when **1** is used as reducing agent. We believe that the latter reduction proceeds by electron transfer through $(H)(CH_3)Re(CO)_4^-$ whereas the reaction with **5** occurs by attack upon a vacant coordination site (by **5**) forming a $(H)(CH_3CO)Mn(CO)_4^-$ intermediate. Reductive elimination from this intermediate produces the observed product .

A similar determination of products by the coordination number of a reactive intermediate may be proposed for the reduction of $CpMo(CO)_3R$ by **1** or **5**. Thermally, both **1** and **5** react with $CpMo(CO)_3(C_2H_5)$ to give propionaldehyde, **1** reacting immediately, **5** more slowly ($k \sim 10^{-4} M^{-1} s^{-1}$).[6] The rate difference may be explained on the basis of the relative abilities of **1** and **5** to trap the coordinatively unsaturated acyl, $CpMo(CO)_2(COR)$, producing aldehyde via. an intermediate acyl hydride.[10] However, <u>irradiation</u> of a solution of **5** and $CpMo(CO)_3(CH_3)$ produces only methane. If the primary photoprocess of $CpMo(CO)_3(CH_3)$ is loss of CO, then an intermediate alkyl hydride might be formed; reductive elimination provides methane (eqn. 6).



$$CpMo(CO)_3(CH_3) \xrightarrow[CpMo(CO)_3H]{h\nu} \left[Cp(CO)_2Mo{<}^{CH_3}_{H}\right]^- + CpMo(CO)_3^+ \quad (6)$$
$$\longrightarrow CH_4 + [CpMo(CO)_3]_2$$

As irradiation of a mixture of $CpMo(CO)_3(CH_3)$ and $(CH_3C_5H_4)$-$Mo(CO)_3(CD_3)$ produces little $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ (2%) using identical irradiation times and concentrations as in the methane producing experiments, the quantum yield for molybdenum-methyl bond cleavage must be appreciably less than that for CO dissociation. Consequently, photolytic homolysis of the molybdenum-methyl bond is not occurring to any appreciable extent, and is not responsible for methane production.

Here, once again, is a system where an alkyl hydride gives alkane, whereas an acyl hydride gives aldehyde. These observations are exactly what one expects on the basis of the usual reductive elimination process. We have found no evidence that alkane formation occurs via. an intermediate acyl hydride.

The reaction of $(CH_3CO)Re(CO)_5$ with $\underset{\sim}{1}$ produces $(H)(CH_3CO)$-$Re(CO)_4^-$. This compound does not give acetaldehyde upon thermal decomposition or upon irradiation. Only traces of methane were found upon irradiation.

The reaction of $CpFe(CO)(PPh_3)(COCH_3)$ with $\underset{\sim}{1}$ is interesting in that although there is no evidence of any net chemistry occurring, a phosphine labilization by $\underset{\sim}{1}$ is actually taking place. While no reaction occurs between $CpFe(PPh_3)(CO)(COCH_3)$ and CO at 25°C for 15 hrs., addition of 8 mole percent $\underset{\sim}{1}$ causes a catalytic substitution of CO for PPh_3. Unfortunately, no exchange of hydride for CO or PPh_3 occurs. It is interesting that other preparations of

As irradiation of a mixture of $CpMo(CO)_3(CH_3)$ and $(CH_3C_5H_4)$-$Mo(CO)_3(CD_3)$ produces little $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ (2%) using identical irradiation times and concentrations as in the methane producing experiments, the quantum yield for molybdenum-methyl bond cleavage must be appreciably less than that for CO dissociation. Consequently, photolytic homolysis of the molybdenum-methyl bond is not occurring to any appreciable extent, and is not responsible for methane production.

Here, once again, is a system where an alkyl hydride gives alkane, whereas an acyl hydride gives aldehyde. These observations are exactly what one expects on the basis of the usual reductive elimination process. We have found no evidence that alkane formation occurs via. an intermediate acyl hydride.

The reaction of $(CH_3CO)Re(CO)_5$ with **1** produces $(H)(CH_3CO)$-$Re(CO)_4^-$. This compound does not give acetaldehyde upon thermal decomposition or upon irradiation. Only traces of methane were found upon irradiation.

The reaction of $CpFe(CO)(PPh_3)(COCH_3)$ with **1** is interesting in that although there is no evidence of any net chemistry occurring, a phosphine labilization by **1** is actually taking place. While no reaction occurs between $CpFe(PPh_3)(CO)(COCH_3)$ and CO at 25°C for 15 hrs., addition of 8 mole percent **1** causes a catalytic substitution of CO for PPh_3. Unfortunately, no exchange of hydride for CO or PPh_3 occurs. It is interesting that other preparations of

$CpFe(CO)_2(COCH_3)$ require treatment of $CpFe(CO)_2(CH_3)$ with high pressures (200 psi) and temperatures (125°C) of CO or by treatment of $CpFe(CO)_2^-$ with acetyl chloride and not by exchange of PPh_3 for CO in $CpFe(CO)(PPh_3)(COCH_3)$.[11]

The electron transfer process shown in Scheme II shows how this might occur; 16 electron intermediates that could de-insert CO are avoided. Apparently, the vanadium to iron hydrogen atom transfer is thermodynamically unfavorable in this system.

Scheme II:

$$
\begin{array}{l}
\mathrm{CpV(CO)_3H^-} + \mathrm{CpFe(CO)(PPh_3)(COCH_3)} \\
\qquad \updownarrow \\
\qquad \mathrm{CpV(CO)_3H\cdot} + \mathrm{CpFe(CO)(PPh_3)(COCH_3)^{\dot{-}}} \\
\qquad\qquad \updownarrow \; \mathrm{PPh_3} \\
\qquad\qquad \mathrm{CpV(CO)_3H\cdot} + \mathrm{CpFe(CO)(CHCH_3)^{\dot{-}}} \\
\qquad\qquad\qquad \mathrm{CO} \updownarrow \\
\qquad\qquad\qquad \mathrm{CpV(CO)_3H\cdot} + \mathrm{CpFe(CO)_2(COCH_3)^{\dot{-}}} \\
\qquad\qquad\qquad\qquad \updownarrow \\
\qquad\qquad\qquad\qquad \mathrm{CpV(CO)_3H^-} + \mathrm{CpFe(CO)_2(COCH_3)}
\end{array}
$$

The mechanism of reaction of $CpCo(PPh_3)(CH_3)_2$ with **1** to give CH_4 and acetone is not understood. Presumably, acetone is formed via. $CpCo(CO)(CH_3)_2$, and methane through a cobalt methyl hydride produced by phosphine-hydride exchange.

The above discussed reactions are summarized in Table I and show the greater reactivity of **1** compared to **5**. **1** also appears to react with metal carbonyls, alkyls, and acyls through a different mechanism (electron transfer) than **5** (hydrogen coordination at vacant site). Our studies suggest that examination of the reactions of two neutral transition metal hydrides in low oxidation states (+I) would prove interesting.

Table I

Summary of the Reactions of $CpMo(CO)_3H$ and $CpV(CO)_3H^-$ with Metal Carbonyls, Alkyls, and Acyls.

	Metal Hydride	
Substrate	$PPN^+CpV(CO)_3H^-$	$CpMo(CO)_3H$
$Fe(CO)_5$	$HFe(CO)_4^-$	a
$Cr(CO)_6$	$HCr(CO)_5^-$	a
$(CH_3C_5H_4)V(CO)_4$	$(CH_3C_5H_4)V(CO)_3H^-$	b
$CH_3Re(CO)_5$	$(H)(CH_3)Re(CO)_4^-$, CH_4	c
$CpMo(CO)_3R$	RCHO	RCHO RH^d
$CpFe(CO)_2(CH_3)$	c	b
$CpCo(PPh_3)(CH_3)_2$	CH_4 + acetone	b
$CpMo(CO)_2(PPh_3)(COCH_3)$	b	RCHO
$(CH_3CO)Re(CO)_5$	$(H)(CH_3CO)Re(CO)_4^-$	b

---

a) Reaction proceeded with decomposition. Metal products not identifiable. b) Not attempted c) No reaction d) Product observed upon irradiation e) CO substitution for phosphine occurs in the presence of added CO.

Experimental

All solvents were distilled from Na/benzophenone/tetraglyme prior to use and all manipulations performed either in a Vacuum Atmospheres Corporation dry lab or on a high vacuum line. CpV(CO)$_4$, Na(diglyme)$^+$ V(CO)$_6^-$, [CpMo(CO)$_3$]$_2$, Mn$_2$(CO)$_{10}$, Re$_2$(CO)$_{10}$, Cr(CO)$_6$, Fe(CO)$_5$ and [CpFe(CO)$_2$]$_2$ were obtained from Alfa Corporation or Strem Chemical Company PPN$^+$ CpV(CO)$_3$H$^-$,[4] CH$_3$Mn(CO)$_5$,[12] CH$_3$Re(CO)$_5$,[13] CpCo(PPh$_3$)(CH$_3$)$_2$,[14] CpMo(CO)$_2$(PPh$_3$)(COC$_2$H$_5$),[15] and CpFe(CO)(PPh$_3$)(CHOCH$_3$)[16] were prepared as previously described. CpMo(CO)$_3$H, CpMo(CO)$_3$R (R=CH$_3$, C$_2$H$_5$) and CpFe(CO)$_2$(CH$_3$) were prepared by the method of Piper and Wilkinson[17].

^{1}H-NMR spectra were recorded on a Varian EM-390 spectrometer. IR spectra were recorded on a PE-283 infrared spectrometer.

Preparation of (CH$_3$C$_5$H$_4$)V(CO)$_4$. 2.88g (0.125 mol) sodium and 10g methylcyclopentadiene monomer (0.125 mmol) were dissolved in 50 ml dimethoxyethane (DME). After stirring overnight, the solvent was removed (30°C, 10^{-2} mm) and the remaining solid recrystallized from THF/hexane at -30°C. 1.3g (11.8 mmol) of this Na$^+$(CH$_3$C$_5$H$_4$)$^-$ was dissolved in 30 ml THF and 3.55 g (13.4 mmol) HgCl$_2$, added. A solution of 5g (11.8 mmol) Na(DME)$_2^+$ V(CO)$_6^-$ in 10 ml THF was added slowly as the solution became red-orange. After 1 hr. the THF was removed (35°C, 10^{-2} mm) and the remaining material taken up in 50 ml H$_2$O plus 50 ml petroleum ether.

The H_2O layer was extracted with petroleum ether (2 x 25 ml) and the combined ether layers washed with water (2 x 50 ml) and dried ($MgSO_4$). The pet. ether was removed (25°, 20 mm) and the remaining oil chromatographed on a silica gel column (2 x 15 cm) using petroleum ether as eluent. The yellow fraction was collected, the solvent removed (25°C, 20 mm), and the remaining solid sublimed (50°C, 10^{-2}mm) to yield 200 mg (15%) $(CH_3C_5H_4)V(CO)_4$ NMR (d_8-THF): δ5.16 PPM 2H; δ5.05 PPM, 2H; δ2.01 PPM, 3H. Mass spectrum: m/e = 242, 214, 186, 158, 130, 51. Anal: Calcd. for $C_{10}H_7O_4V$: 49.61% C, 2.91% H; found: 49.38% C, 2.97%H.

Reaction of $PPN^+ CpV(CO)_3H^-$ with $(CH_3C_5H_4)V(CO)_4$. 31 mg (0.054 mmol) $(CH_3C_5H_4)V(CO)_4$ and 40 mg (0.054 mmol) $PPN^+CpV(CO)_3H^-$ were dissolved in 0.47 ml d_8-THF in an NMR tube . NMR spectra recorded over the next 12 hrs. showed the disappearance of $(CH_3C_5H_4)V(CO)_4$ and $CpV(CO)_3H^-$ (δ4.60 PPM) and the appearance of $CpV(CO)_4$ (δ 5.20 PPM) and $(CH_3C_5H_4)V(CO)_3H^-$ (δ4.58 PPM, 2H; δ4.42 PPM, 2H; δ1.86 PPM, 3H).

Reaction of $CpV(CO)_3H^-$ with $Fe(CO)_5$ and $Cr(CO)_6$. A similar reaction of 51 mg(0.069 mmol) $PPN^+CpV(CO)_3H^-$ with 9.3 ul (0.069 mmol) $Fe(CO)_5$ in 0.5 ml d_8-THF produces isolable crystals of $PPN^+HFe(CO)_4^-$ [18] upon standing for 12 hours. Anal.: Calcd. for $C_{40}H_{31}P_2NFeO_4$: 67.91%C, 4.42%H, 1.98%N; found: 67.51%C, 4.58%H, 1.94%N. No $(CHO)Fe(CO)_4^-$ is observed at any time during the reaction. Similarly,

$Cr(CO)_6$ (47 mg, 0.21 mmol) also reacts with $PPN^+CpV(CO)_3H^-$ 79 mg, 0.11 mmol) in d_8-THF (0.75 ml) to produce PPN^+ $HCr(CO)_5^-$ (not isolated) NMR: δ-6.88 PPM. IR(THF); 1938, 1881 cm^{-1}.

Reaction of $CpMo(CO)_3H$ with $Fe(CO)_5$ and $Cr(CO)_6$.

Identical reactions of $CpMo(CO)_3H$ (20 mg, 0.081 mmol) with $Cr(CO)_6$ (15 mg, 0.068 mmol) or $Fe(CO)_5$ (15 ul, 0.11 mmol) at 70°C in d_8-THF (0.4 ml) produced no new hydride resonances by NMR. Metal was observed to form on the walls of the tube, and all resonances were broadened. $[CpMo(CO)_3]_2$ was observed (δ 5.40 PPM) in the $Cr(CO)_6$ reaction.

Hydride Catalyzed Substitution of $CpV(CO)_4$ by L (L=PPh_3, PMe_3). 75 mg (0.10 mmol) $PPN^+CpV(CO)_3H^-$, 60 mg (0.23 mmol) PPh_3, and 58 mg (.25 mmol) $CpV(CO)_4$ were dissolved in 1.0 ml d_8-THF and the flask covered to exclude light. NMR spectra were recorded periodically and showed the conversion of $CpV(CO)_4$ into $CpV(CO)_3(PPh_3)$ (NMR; δ 4.73 PPM, d, j_{PH}=1.5hz) with no change in the $CpV(CO)_3H^-$ resonance ($\tau_{1/2}$= 1 hr.)

An identical reaction employing PMe_3 instead of PPh_3 showed a complete conversion to $CpV(CO)_3PMe_3$ in 15 min. (NMR: δ 4.90 PPM, 5H,d, j_{PH} =1.9hz; δ 1.44 PPM, 9H,d,j_{PH}= 8.7hz).

Reaction of PPN^+ $CpV(CO)_3H^-$ with $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$.

A d_8-THF solution (0.5 ml) of 61 mg (0.082 mmol) PPN^+ $CpV(CO)_3H^-$ was added to a d_8-THF solution (0.5 ml) of 18 mg (0.086 mmol) $CH_3Mn(CO)_5$ in an NMR tube. Although no immediate reaction occurred, the tube turned brown within 5 min. The ^{1}H-NMR showed the disappearance of $CpV(CO)_3H^-$ with the concurrent formation of $CpV(CO)_4$. Traces of CH_4 (~5%) were observed by NMR and by GC (9' x 1/16 Poropak Q, 80°C).

A similar reaction using 14.3 mg (0.042 mmol) CH_3-$Re(CO)_5$ and 30.4 mg (0.041 mmol) $PPN^+CpV(CO)_3H^-$ in 0.46 ml d_8-THF under 1 atm CO showed a slow reaction at 25°C forming methane. Heating this solution to 50°C resulted in a faster reaction rate ($\tau_{1/2} \approx 2$ hrs.) and an unisolated intermediate, **3**, believed to be $(CH_3)(H)Re(CO)_4^-$, was detected by NMR (δ -0.65 PPM, 3H,d,J_{H-H}=3hz; δ -5.56 PPM, 1H,br). Eventually all of the $CH_3Re(CO)_5$ disappeared and only the intermediate **3** (plus CH_4) was observed. As the intermediate **3** disappeared, the amount of methane was found to increase. A second intermediate "X" was also observed in ~10% yield (NMR; δ -0.30 PPM, 3H,s; δ -4.30 PPM, 1H,s) and is probably the trans isomer of **3**. This solution was treated with 5 ul CH_3I, and a large methyl resonance of $CH_3Re(CO)_5$ (δ -0.20 PPM) was observed.

Reaction of $PPN^+CpV(CO)_3H^-$ with $CpFe(CO)_2(CH_3)$.

17 mg (0.089 mmol) $CpFe(CO)_2(CH_3)$ and 60 mg (0.089 mmol) $PPN^+CpV(CO)_3H^-$ were dissolved in 0.87 ml d_8-THF. An NMR spectrum after 24 hrs. at 25°C showed no reaction.

Reaction of $PPN^+CpV(CO)_3H^-$ with $CpCo(PPh_3)(CH_3)_2$ + CO.

40 mg (0.054 mmol) $PPN^+CpV(CO)_3H^-$ and 19 mg (0.046 mmol) $CpCo(PPh_3)(CH_3)_2$ in d_8-THF solution (0.45 ml) were sealed

in an NMR tube under 600 mm CO(.054 mmol). NMR spectra recorded over the next 4 hrs. showed the formation of CH_4 (~50% yield) and acetone (~20% yield) as the $CpCo(PPh_3)(CH_3)_2$ (NMR: δ 4.41, 5H, s; δ 0.06 PPM, 6H,d,J_{PH}=6hz) disappeared.

Reaction of $PPN^+CpV(CO)_3H^-$ with $CpFe(CO)(PPh_3)(COCH_3)$ and CO. 26 mg (0.057 mmol) $CpFe(CO)(PPh_3)(COCH_3)$ and 44 mg (0.058 mmol) PPN^+ $CpV(CO)_3H^-$ were dissolved in 0.5 ml d_8-THF and sealed in a NMR tube under 600 mm CO(0.031 mmol). After 2 days at 25°C, NMR spectra showed the $CpV(CO)_3H^-$ was unchanged, whereas the $CpFe(CO)(PPh_3)(COCH)_3$ (NMR: δ4.38, 5H,d,J_{PH}=2hz;δ 2.28 PPM, 3H, s) had been 50% converted (100% yield based on CO) into $CpFe(CO)_2(COCH_3)$[11] (NMR:δ4.93 PPM, 5H, 2;δ2.50 PPM, 3H, s). The solution was heated to 65°C for 24 hrs., but no changes were observed by NMR.

Preparation of $(CH_3CO)Re(CO)_5$.

1 g (1.53 mmol) $Re_2(CO)_{10}$ was reduced with 1.5 ml 0.65% Na/Hg amalgam in 10 ml THF. The solution was decanted from the mercury and 0.22 ml (3.1 mmol) CH_3COCl added. After 15 min. the solvent was removed (0°C,10^{-3} mm) and the remaining solid sublimed to a -78°C probe, yielding 500 mg (44%) $(CH_3CO)Re(CO)_5$. NMR(d_8-THF): δ 2.47 PPM. IR (THF): 2125 (w), 2060(w), 2009 (s), 1996(sh), 1612(v) cm^{-1}. Anal. Calcd. for $C_7H_3ReO_6$: 22.77% C,0.82 %H; found: 22.56% C, 0.87% H.

Reaction of PPN^+ $CpV(CO)_3H^-$ with $(CH_3CO)Re(CO)_5$. 35 mg (0.047 mmol) $(CH_3CO)Re(CO)_5$ and 18 mg (0.049 mmol) $CpV(CO)_3H$ were sealed under vacuum in an NMR tube along with 0.4 ml d_8-THF. Upon heating the solution at 50°C, new singlets were observed to grow in slowly over 24 hrs. at δ 2.20 PPM (3H) and δ -4.38 PPM (1H) attributable to $(H)(CH_3CO)Re(CO)_4^-$. A quantitative yield of $CpV(CO)_4$ was also produced. Due to the long reaction time however, extensive decomposition occurred.

A similar solution was treated with 1 mg Na and heated at 50°C. NMR analysis showed a 50% yield of $(H)(CH_3CO)$-$Re(CO)_4^-$. Another solution of $(CH_3CO)Re(CO)_5$ and PPN^+ $CpV(CO)_3H^-$ was treated with 5 mg $Na_2CpV(CO)_3$. Quantitative yields of $(H)(CH_3CO)Re(CO)_4^-$ and $CpV(CO)_4$ were observed after 3 min. at 25°C. Irradiation of this solution resulted in decomposition with a trace of CH_4 being observed.

Attempts to isolate this material by precipitation with hexane or diethyl ether produced an oil. This oil could be washed with hexane to remove $CpV(CO)_4$ and redissolved in d_8-THF showing NMR resonances attributable to $PPN^+(H)(CH_3CO)Re(CO)_4^-$. An IR spectrum in THF showed several terminal CO bands in the 1850-1950 cm^{-1} region and an acyl band at 1580 cm^{-1}.

Reaction of $CpMo(CO)_3H$ with $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$. 27 mg (0.11 mmol) $CpMo(CO)_3H$ and 22 mg (0.11 mmol) CH_3Mn-$(CO)_5$ were dissolved in 0.48 ml d_8-THF in an NMR tube.

NMR spectra showed a complete reaction to form $CpMo(CO)_3$-$Mn(CO)_5$ (δ 5.49 PPM), $[CpMo(CO)_3]_2$ (δ5.40 PPM), $[CpMo(CO)_2]_2$ (δ5.27 PPM) and CH_3CHO (δ 2.07, 3H,d,j=3hz; 9.66 PPM, 1H, q; 50% yield). An equimolar mixture of $CpMo(CO)_3H$ (0.22M) and $CH_3Re(CO)_5$(.22M) in d_8-THF showed no reaction after 3 days at 25°C.

REFERENCES

1. K.I.Gell and J.Schwartz, J.Amer.Chem.Soc.,100, 3246 (1978); J.Chatt and R.G.Hayter, J.Chem. Soc., 6017 (1963); P.C.Wailes and H.Weigold, J.Organometal.Chem., 24, 405(1970); R.Renaut, G.Tainturier, and B.Gautheron, J.Organometal. Chem., 150, C9(1978); H.Werner and W.Hofmann, Angew.Chem.Int.Ed.Engl.,17, 464(1978).

2. W.Rupilius and M.Orchin, J.Org.Chem., 37, 936 (1972; D.S.Breslow and R.F.Heck, Chem.Ind.(London), 467(1960); N.H.Alemdaraglu, J.L.M.Penninger, and E.Oltay, Monatsh. Chem., 107, 1153(1976).

3.(a)C.P.Casey, M.Andrews, and J.E.Rinz, J.Amer.Chem.Soc., 101, 741(1979): C.P.Casey and S.M.Neumann, J.Amer.Chem. Soc., 98, 5395(1976); J.A.Gladysz and W.Tam, J.Amer. Chem. Soc., 100, 2545(1978); S.T.Winter, G.W.Cornett, E.A.Thompson, J.Organometal. Chem., 133, 339 (1977); C.P.Casey and S.M.Neumann, J.Amer.Chem.Soc., 100, 2544 (1978).

(b) W.Tam, W.K.Wong, and J.A.Gladysz, J.Amer.Chem.Soc., 101, 1591 (1979).

4. R.J.Kinney, W.D.Jones, and R.G.Bergman, J.Amer.Chem.Soc. 100, 635(1978); R.J.Kinney, W.D.Jones, and R.G.Bergman, J.Amer.Chem.Soc., 100, 7902(1978).

5. Cobalt clusters were also observed in the decompositon of $CpCo(CO)(CH_3)_2$ in the absence of CO. See: N.E.Schore, C.Ilenda, and R.G.Bergman, J.Amer.Chem.Soc.,

98,7436 (1976); K.P.C.Volhardt, J.E.Bercaw, and R.G.Bergman *J.Amer.Chem.Soc.*, *96*, 4998(1974); K.P.C.Volhardt, J.E.Bercaw, and R.G.Bergman, *J.Organometal.Chem.*, *97*, 283(1975).

6. R.G.Bergman and W.D.Jones, submitted for publication. See Chapter III, this work.

7. D.S.Ginley and M.S.Wrighton, *J.Amer.Chem.Soc.*, *97*,4908 (1975).

8. J.P.Collman and S.R.Winter, *J.Amer.Chem.Soc.*, *95*, 4089(1973).

9. S.J.Okrasinski and J.R.Norton, *J.Amer.Chem.Soc.*, *99*, 295 (1977).

10. The reaction of **1** with $CpMo(CO)_3R$ is anomalous in that hydride-CO exchange does not occur by the usual electron transfer process. Perhaps **1** coordinates to the vacant site of $CpMo(CO)_2(COR)$ in the same manner as **5**. Another possibility is that electron transfer to $CpMo(CO)_2(COR)$ occurs more readily than to $CpMo(CO)_3R$, and subsequent hydride abstraction produces an acyl hydride intermediate. A third pat way is direct hydride attack upon the acyl carbon.

11. T.H.Coffield, J.Kozikowski, and R.D.Clossen, Special Publication No.13, The Chemical Society, London, 1959, p.26.

12. R.D.Clossen, J.Kozikowski, and T.H.Coffield, *J.Org.Chem.*, *22*, 598(1957).

13. V.W.Hieber and G.Braun, Z.Naturforsch, 14B, 132(1959).

14. H.Yamizaki and N.Hagihara, J.Organometal. Chem., 21, 431(1970).

15. P.J.Craig and M.Green, J.Chem.Soc.,A,1978(1968); I.S.Butler, F.Balolo, and R.G.Pearson, Inorg. Chem., 6, 2074(1967).

16. J.P.Bibler and A.Wojiciki, Inorg. Chem., 5, 889(1966).

17. T.S.Piper and G.Wilkinson, J.Inorg.Nucl.Chem.,3, 104(1956)1

18. W.O.Siegl, J.Organometal.Chem.,92, 321(1975).

Chapter V

Propositions

Proposition I

Reductive Elimination in $H(CH_3)Os(CO)_4$

Reductive Elimination in $H(CH_3)Os(CO)_4$

The reductive elimination of alkanes from transition metal alkyl hydrides is a well known process, and few such stable species are known.[1,2] Some of these eliminations have been shown to occur through bimolecular intermediates.[3] Norton[4] has suggested that the decomposition of cis-$(CH_3)HOs(CO)_4$, 1a, occurs by a bimolecular process, a conclusion consistent with experimental observations but not necessarily indicated.

The net decomposition reaction is outlined in Scheme I. If a mixture of both cis-$(CH_3)DOs(CO)_4$, 1b, and $(CD_3)HOs(CO)_4$, 1c, is allowed to decompose all four possible crossover products are found (CH_4, CD_4, CHD_3, CDH_3). The reaction is not reversible as the decomposition of 1a in the presence of CD_4 yielded only CH_4. Norton claims these observations are indicative of a dinuclear elimination.[4]

Scheme I:

$$2\ (CH_3)HOs(CO)_4 \xrightarrow{k_o} CH_4 + H(CO)_4Os—Os(CO)_4(CH_3)$$

$$k_o = 1.38 \times 10^{-4}\ s^{-1}$$

The disappearance of 1a was found to be first order. Labled CO was found not to be incorporated into either the starting material or the dinuclear product, ruling out CO dissociation as a step in the reaction.[5]

An additional piece of evidince in Norton's mechanism is that the addition of excess PEt_3 prevents the binuclear products CH_4, CD_4, and $H(CO)_4Os—Os(CO)_4(CH_3)$ from forming in the decomposition of a mixture of 1b and 1c. The rate of the reaction is halved ($k_o = 6.4 \times 10^{-5}\ s^{-1}$) and is independent of the concentration of PEt_3 between a 7 and 110 -fold excess of ligand. The mechanism Norton proposes is shown in Scheme II.

Scheme II:

$$(CH_3)HOs(CO)_4 \xrightarrow{\text{slow}} \underset{\sim}{2}$$

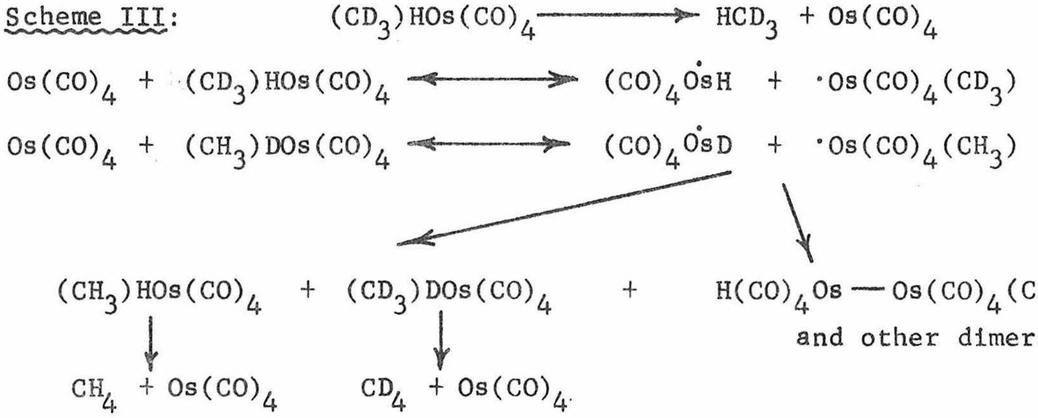
$$\underset{\sim}{2} + (CH_3)HOs(CO)_4 \xrightarrow{\text{fast}} CH_4 + H(CO)_4Os - Os(CO)_4(CH_3)$$

$$\underset{\sim}{2} + PEt_3 \xrightarrow{\text{faster}} CH_4 + (PEt_3)Os(CO)_4$$

The suggestion of an unsaturated acyl complex for the intermediate 2 allows for the formation of a binuclear species (possibly via. a hydrogen bridge) and the exclusion of its formation by PEt_3 coordination. Attempts to trap and observe the intermediate with PEt_3 and $P(OMe)_3$ have been unsuccessful. Norton does not indicate how the formation of the binuclear species results in scrambled methane evolution.

The experiments do not rule out the possibility that the formation of methane occurs by a simple reductive elimination from the mononuclear species 1a. The reaction would still be first order in the disappearance of 1a. The remaining $Os(CO)_4$ fragment could be responsible for the scrambling of labled 1b and 1c. Two possible scrambling mechanisms are shown in Schemes III and IV.

Scheme III:



$$(CD_3)HOs(CO)_4 \longrightarrow HCD_3 + Os(CO)_4$$

$$Os(CO)_4 + (CD_3)HOs(CO)_4 \longleftrightarrow (CO)_4\dot{O}sH + \cdot Os(CO)_4(CD_3)$$

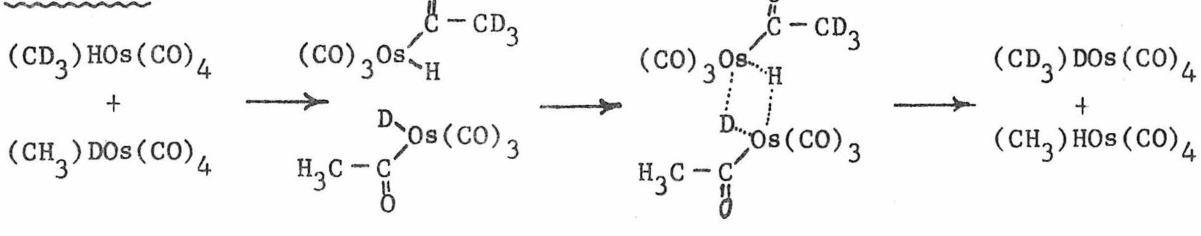
$$Os(CO)_4 + (CH_3)DOs(CO)_4 \longleftrightarrow (CO)_4\dot{O}sD + \cdot Os(CO)_4(CH_3)$$

$$(CH_3)HOs(CO)_4 + (CD_3)DOs(CO)_4 + H(CO)_4Os - Os(CO)_4(CH_3)$$

and other dimers

$$CH_4 + Os(CO)_4 \qquad CD_4 + Os(CO)_4$$

Scheme IV:



With both schemes the coordination of PEt_3 would prevent scrambling of methyl groups. The observed product of the elimination in the presence of PEt_3 , $(PEt_3)Os(CO)_4$, is formed from the reaction of PEt_3 with the coordinatively unsaturated $Os(CO)_4$.[7]

For the radical mechanism (Scheme III) PEt_3 coordination prevents the reaction of a second equivalent of 1a with the $Os(CO)_4$ intermediate, thereby lowering the rate at which starting material is consumed.[8] The observed dimeric product results from recombination of two of the radical species forming an Os—Os bond.

The second mechanism (Scheme IV) allows for scrambling through the acyl intermediate and would be inhibited by PEt_3 coordination. However, the observed rate of disappearance of 1a should not change unless the buildup of an intermediate is found.

There are several ways to test the involvement of $Os(CO)_4$ in a scrambling process. The easiest way is to add $Os(CO)_4$ to a mixture of 1b and 1c and see if the amounts of CH_4 and CD_4 are increased to their statistical percentages[9] (~ 25% neglecting isotope effects). The $Os(CO)_4$ could be generated by irradiation of $Os(CO)_5$[7] or $Os_3(CO)_{12}$,[10] or by addition of $LOs(CO)_4$ where L is labile under the reaction conditions (*e.g.*, CH_3CN or THF[11]). Control experiments would have to demonstrate that 1a is photo-inert with respect to scrambling.

Should $Os(CO)_4$ be present one would expect it to be trapped by a variety of ligands, such as phosphines, amines, cyanide, and ^{13}CO. The substituted products could easily be prepared and characterized separately from $Os(CO)_5$. The ligands would also have the effect of inhibiting the scrambling of methyl groups in 1b and 1c. The rate of reaction should be independent of the concentration and nature of the incoming ligand.[12]

If scrambling occurs prior to reductive elimination of methane, then an analysis of a mixture of 1b and 1c after 50% reaction should show the presence of $D(CD_3)Os(CO)_4$ and $H(CH_3)Os(CO)_4$. The former compound should be easily seen by mass spectrometry (the compound is a volatile liquid) and possibly by gas phase IR.[13] The NMR of the latter compound shows a quartet at 17.94 τ and a doublet at 10.00 τ in THF[15], and should be readily distinguishable from the NMR signals of 1b and 1c (deuterium decoupling simplifies interpretation).

It might be possible to scavenge any metal radical species using $Mn(CO)_5$ generated from $Mn_2(CO)_{10}$.[11] Other metal radicals might also be used as trapping agents, such as $Re_2(CO)_{10}$.

1. E.L.Muetterties & P.L.Watson, *J.Amer. Chem. Soc.*, *98*, 4665 (1976).
2. Stable methyl hydrides are discussed in:
   K.Jonas & G.Wilke, *Angew. Chem. Int. Ed. Engl.*, *8*, 519 (1969).
   J.Chatt & R.G.Hayter, *J.Chem. Soc.*, 6017 (1963).
   P.C.Wailes & H.Weigold, *J.Organometal. Chem.*, *24*, 405 (1970).
3. G.M.Whitesides, E.R.Stedronsky, C.P.Casey, and J.S.Filippo, *J.Amer. Chem. Soc.*, *92*, 1426 (1970); J.Schwartz & J.B.Cannon, *J.Amer. Chem. Soc.*, *96*, 2278 (1974); A.Tamiki & J.K.Kochi, *J.Organometal, Chem.*, *61*, 441, (1973).
4. S.J.Okrasinski & J.R.Norton, *J.Amer. Chem. Soc.*, *99*, 295 (1977).
5. This result is in direct contrast to the $H_2Os(CO)_4$ decomposition.[6]
6. J.E.Evans & J.R.Norton, *J.Amer. Chem. Soc.*, *96*, 7577 (1974).
7. F.Calderazzo & F.L'Eplattenier, *Inorg. Chem.*, 6, 1223 (1967).
8. The rate constant for the formation of the dimer product from the osmium radicals must be about the same as the rate of monomeric reductive elimination so that the addition of PEt_3 halves the rate.
9. Norton did not give the percentages of CH_4 and CD_4 in ref. 4.
10. S.A.R.Knox & F.G.A.Stone, *J.Chem. Soc.*, *A*, 3147 (1970).

11. M.Wrighton, Chem. Rev., 74, 401 (1974).

12. M.J.Mays, R.N.F.Simpson, & F.P.Stephanini, J.Chem. Soc. A, 3000 (1970).

13. $H_2Os(CO)_4$ and $D_2Os(CO)_4$ have IR bands different by 15 cm^{-1}.[14]

14. F.L'Eplattenier & F.Calderazzo, Inorg. Chem., 6, 2093 (1967).

15. F.L'Eplattenier, Inorg. Chem., 8, 965 (1969).

Proposition II

Hydrolysis of $Cl(PPh_3)_2Pt(COOR)$

Hydrolysis of $Cl(P\phi_3)_2Pt(COOR)$

The activation of CO by cationic transition metal complexes has been studied for many systems.[1] Some of these compounds react with water (hydroxide) directly to give CO_2 and the corresponding metal hydride, whereas some react with alcohols to form alkoxycarbonyl compounds.[2] $[PtCl(P\phi_3)_2(CO)]^+[BF_4]^-$ has been shown[3] to react with alcohols to form $PtCl(P\phi_3)_2(COOR)$ which then forms CO_2 and $PtCl(P\phi_3)_2H$ upon treatment with water.[4] A reasonable mechanism for this process has been suggested by Clark, Dixon, and Jacobs,[4] but other observations on CO activation in cationic metal carbonyls hint that another mechanism may be operative.

The mechanism of Clark, Dixon, and Jacobs[4] is shown in Scheme I. Alkoxide ion can reversibly dissociate from and attack the carbonyl carbon.[5] Added water (hydroxide) can then attack the carbonyl carbon to form the observed products, CO_2 and $PtCl(P\phi_3)_2H$.

Scheme I:

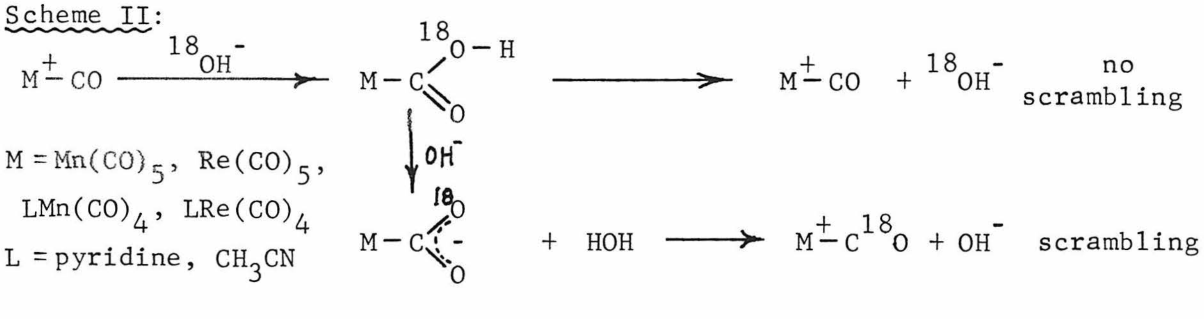
$$PtCl(P\phi_3)_2(COOR) + H_2O \longrightarrow \underset{+\ ROH}{[PtCl(P\phi_3)_2(CO)]^+} + OH^- \longrightarrow PtCl(P\phi_3)_2(COOH)$$

$$PtCl(P\phi_3)_2(COOH) \longrightarrow CO_2 + PtCl(P\phi_3)_2H$$

These suppositions are supported by the observations that: 1) $[PtCl(P\phi_3)_2(CO)]^+$ reacts with alcohols in a straightforward associative mechanism to form the alkoxycarbonyl, as shown by Byrd and Halpern,[3] and 2) $[PtCl(P\phi_3)_2(CO)]^+$ reacts with refluxing water to give CO_2 and $PtCl(P\phi_3)_2H$.

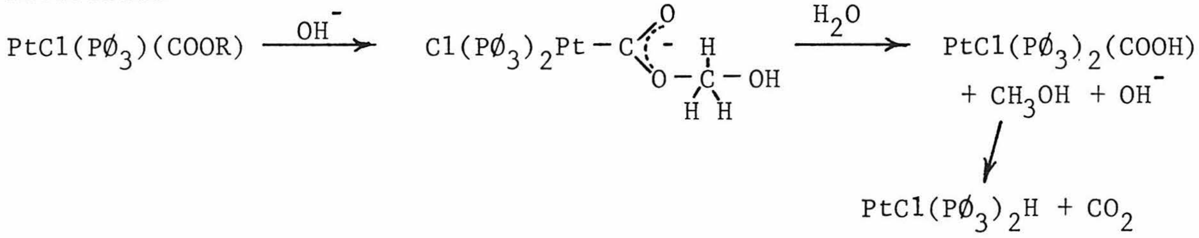
However, other cationic transition metal carbonyl complexes have been shown to exchange oxygen with added $H_2{}^{18}O$.[6,7,8] A reversible attack by $^{18}OH^-$ upon the carbonyl carbon would not result in oxygen exchange, whereas a separate attack by a second hydroxide to form a symmetric carboxylate species would result in scrambling (Scheme II).

Scheme II:



This suggests the possibility that the reaction of OH^- with $PtCl(PØ_3)_2(COOR)$ could proceed by an associative S_n2 attack upon the alkyl group. The carboxylate anion which formed could react with water and decarboxylate to form CO_2 and $PtCl(PØ_3)_2H$ (Scheme III).

Scheme III:



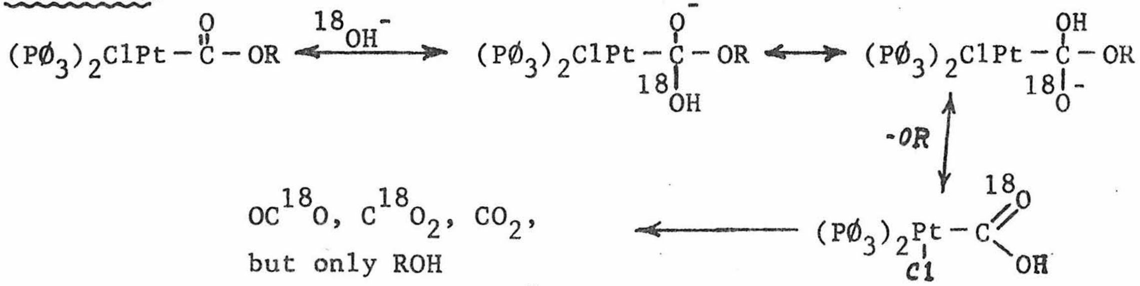
There are several methods for testing this possibility. The best way is to use an optically active alcohol.[9] The mechanism shown in Scheme I would result in retention of configuration whereas the mechanism shown in Scheme III predicts an inversion of configuration.

Another method involves reacting $PtCl(PØ_3)_2(COOR)$ with $H_2{}^{18}O$. If the mechanism shown in Scheme III is operative, then all of the label should be found in the alcohol, with none in the CO_2.[11] If the mechanism in Scheme I is occurring, then all of the label should be found in the CO_2 and not in the alcohol.

Another way to do this experiment would be to prepare $PtCl(P\emptyset_3)_2\text{-}\overset{O}{\overset{\|}{C}}-{}^{18}OR$ from $[PtCl(P\emptyset_3)_2(CO)]^+$ and $R-{}^{18}OH$. This alkoxycarbonyl when reacted with H_2O should show complementary results to the above experiment: labeled CO_2 implies Scheme III is operative; labeled ROH implies Scheme I is operative.

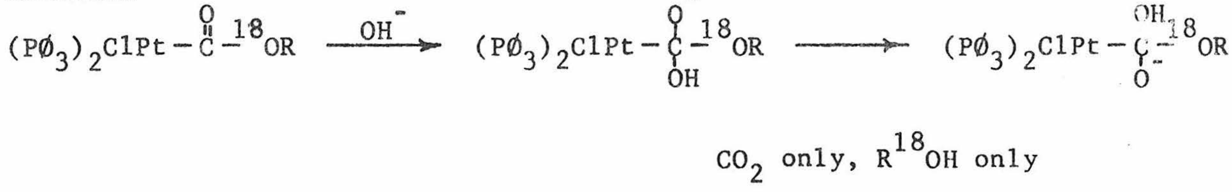
The above observations may be complicated if the mechanism in Scheme I is an associative process. The intermediate formed could undergo proton transfer[12] and scramble the labeled oxygen in the reaction of $PtCl(P\emptyset_3)_2(COOR)$ with $H_2{}^{18}O$, resulting in doubly labeled and unlabeled CO_2. However, this proton transfer would not scramble the oxygen of the alcohol, so that examination of its label incorporation would be meaningful (Scheme IV).

Scheme IV:



The reaction of $(P\emptyset_3)_2ClPt-\overset{O}{\overset{\|}{C}}-{}^{18}OR$ with H_2O avoids the oxygen scrambling problem. Proton transfer does not change the labeling of the starting material, so that only $OC^{18}O$ or $R^{18}OH$ should be observed (Scheme V).

Scheme V:



1. M.M.Taqui Khan & A.E.Martell, "Homogeneous Catalysis by Metal Complexes", Vol.1, Chptr.4, Academic Press, New York (1974), and references therein.
2. T.Kruck & M.Noack, Chem. Ber., 97, 1693 (1964); L.Malatesta, G.Caglio, & M.Angoletta, J.Chem. Soc., 6974 (1965); L.Malatesta, M.Angoletta, & G.Caglio, J. Chem. Soc., A, 1836 (1970); W.Hieber & V.Frey, Chem. Ber., 99, 2614 (1966).
3. J.E.Byrd & J.Halpern, J.Amer. Chem. Soc., 93, 1634 (1971).
4. H.C.Clark, K.R.Dixon, & W.J.Jacobs, J.Amer.Chem. Soc., 91, 1346 (1969).
5. $(P\phi_3)_2ClPt(COOR)$ Slowly exchanges with added R'OH.[4]
6. E.L.Muetterties, Inorg. Chem., 4, 1841 (1965).
7. D.J.Darensbourg & D.Drew, J.Amer.Chem. Soc., 98, 275 (1976).
8. W.Hieber & T.Kruck, Z.Naturforsch, 16b, 709 (1961).
9. Such as 1-deuterio-1-butanol.[10]
10. L.Verbict, Prog. Phys. Org. Chem., 7, 51 (1970).
11. Both compounds could be analyzed by mass spectrometry. CO_2 could be analyzed by gas phase IR.
12. M.L.Bender, J.Amer. Chem. Soc., 73. 1626 (1951).

Proposition III

Vibrationally Nonrandomized Decomposition of d_2-hexafluorobicyclopropane

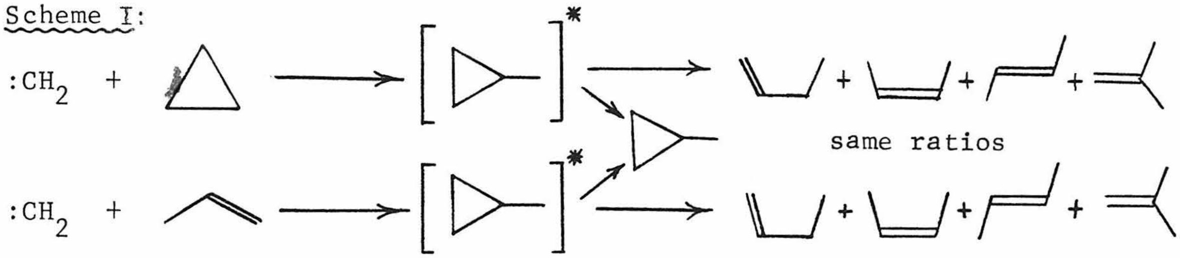
Vibrationally Nonrandomized Decomposition of d_2-hexafluorobicyclopropane

The generation of vibrationally "hot" molecules in the gas phase in exoergic chemical reactions has been a topic of concern recently. The randomization of energy in the various vibrational modes prior to unimolecular decomposition was predicted by RRKM theory.[1,2] Several investigators have tested this prediction on small molecules as described below with varying conclusions, resulting in confusion.

One attempt to look for non-randomization was examined in the shock-tube decomposition of SF_6 to SF_5 and F by Bott and Jacobs.[3] They found that the vibrational energy was distributed over six oscillators, in support of randomization prior to decomposition.

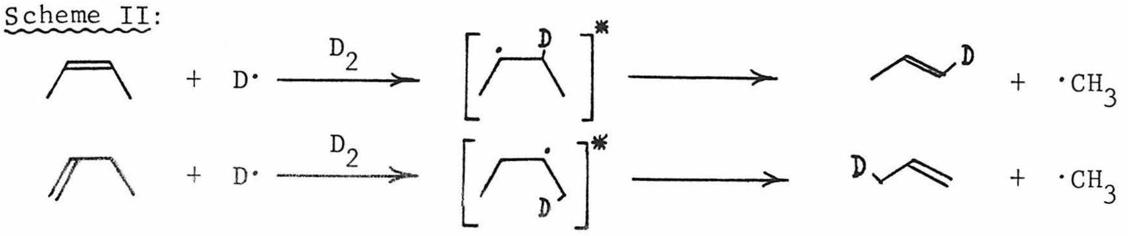
Butler and Kistiakowsky were able to demonstrate that hot methylcyclopropane formed from two independent routes in the gas phase decomposed to give the same distribution of butenes (Scheme I). The distribution was also independent of the source of methylene (ketene or diazomethane) and of the pressure over a 100-fold range. This observation supports the rapid randomization of vibrational energy in this molecule, as at higher pressures non-randomized processes are predicted to become more important.[4]

Scheme I:



A similar observation was found[5] in the similar rate of decomposition of sec-butyl radicals prepared from two different sources(Scheme II).

Scheme II:

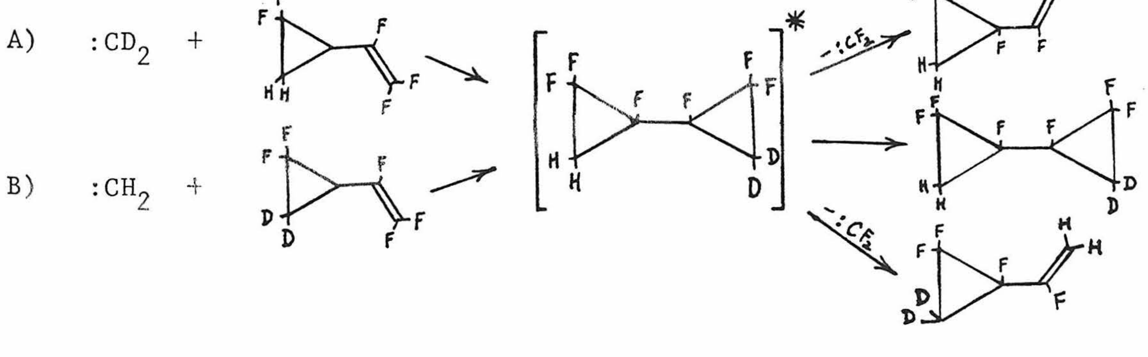


The value of the rate constant k was also independent of the pressure between 0.036 and 200 atm.[6] At the highest pressure collisions occur every 2 x 10^{-13} sec., demonstrating the alacrity of randomization.

Frey has reported[7] a non-randomized decomposition in the addition of methylene to isobutylene, forming hot 1,1-dimethylcyclopropane that decomposes to a mixture of butenes. The ratio of butene products was found to be significantly different than in the pyrolysis of 1,1-dimethylcyclopropane.

Other examples of randomized vibrational energy have appeared,[8] but recent reports by Rabinovitch, et.al., show a failure of intramolecular energy relaxation in a unimolecular decomposition.[9,10,11] The system chosen was d_2-hexafluorobicyclopropane (HBC) prepared by addition of $:CD_2$ or $:CH_2$(from irradiation of the corresponding ketene) to hexafluorovinylcyclopropane (HVC) or d_2-HVC, respectively. The vibrationally excited HBC^* formed initially decomposes to d_2-tetrafluorovinylcyclopropane or is collisionally deactivated (SchemeIII).

Scheme III:

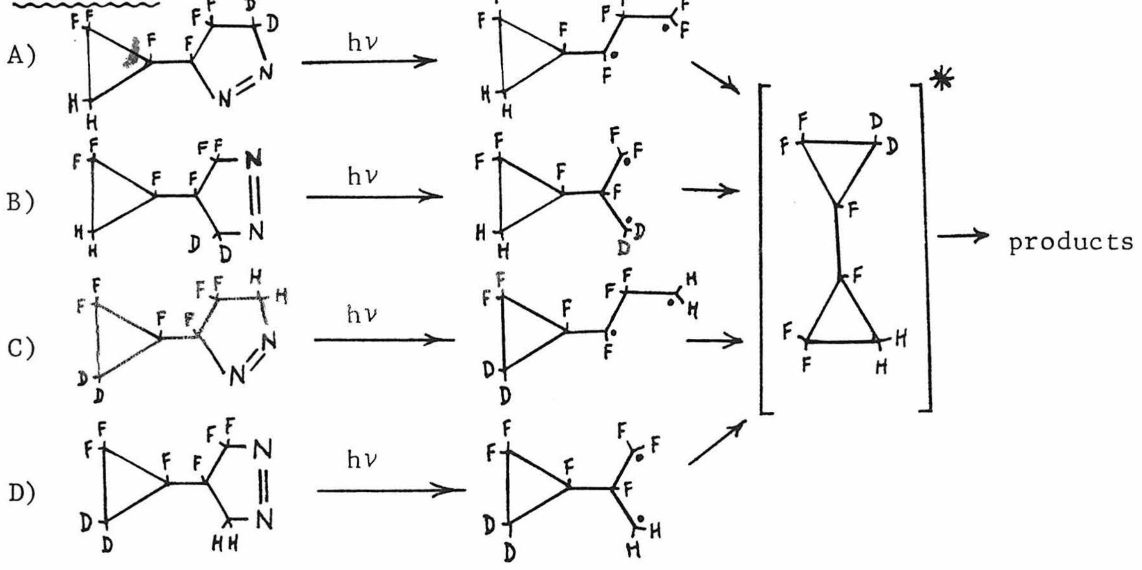


Rabinovitch observed an excess of the d_2-vinylic over h_2-vinylic product upon addition of $:CD_2$ to HVC and the reverse ratio upon addition of $:CH_2$ to d_2-HVC. These results are consistent with decomposition of the same cyclopropane ring formed by carbene addition to the HVC, indicating incomplete randomization. As the pressure was increased by addition of CO ($\sim$4 atm.) the ratio of non-randomized to randomized decomposition increases due to collisional quenching of randomized HBC*.

The amount of nonrandom decomposition was assumed to be the same in both reactions A) and B) in Scheme III and could be a source of error on two counts: 1) the deuterated ring should show a slower decomposition rate due to secondary isotope effects, and 2) the $:CH_2$ and $:CD_2$ may bring different amounts of energy into the system.

A possible way to test Rabinovitch's results is to use a different source[12] for the two hot bicyclopropyl species. Two alternate routes are shown in Scheme IV. These systems have the advantages that:1) the

Scheme IV:



azo compounds can be decomposed by irradiation in the gas phase, 2) the diradicals produced should give the desired bicyclopropanes as major products,[12,14] 3) the absence of ketene precludes polymerization, and 4) the isotope effects should be reduced.

Routes B) and D) to the vibrationally excited species may be complicated by a secondary reaction. The biradical intermediate may lose $:CF_2$ directly and form d_2-HVC without going through the bicyclopropane intermediate. This side reaction would have the effect of indicating an even greater amount of non-randomization, and suggests that routes B) and D) are not suitable for preparation of d_2-HBC*.

A possible problem with the azo route to HBC* is that the product may not be highly excited enough to lose $:CF_2$. If the heats of formation of the azo starting material and of d_2-HBC were known, one could make a prediction. Also, if nitrogen carries off a significant amount of vibrational energy the remaining cyclopropane may be too deactivated to extrude $:CF_2$.

Should the d_2-HBC* formed by the azo route decompose as Rabinovitch observed, the same experiments could be performed; <u>i.e.</u>, a study of the pressure dependence of the amount of non-randomized vs. randomized d_2-HVC. Similar dependances would offer direct support to the incomplete intramolecular energy relaxation as proposed by Rabinovitch.

References

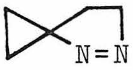
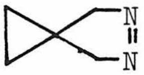
1. L. Kassel, "Kinetics of Homogenous Gas Reactions", Reinhold, New York (1932).
2. R.A. Marcus & O.K. Rice, J.Phys. Colloid Chem., 55, 894 (1951).
3. J.F.Bott & T.A.Jacobs, J.Chem. Phys., 50, 3850 (1969).
4. R.C.Baetzold & D.J.Wilson, J.Phys. Chem., 68, 3141 (1964).

   D.L. Bunker, J.Chem. Phys., 40, 1946 (1964).
5. R.E.Harrington & B.S.Rabinovitch J.Chem. Phys., 33, 1271 (1960).
6. D.W.Placzek, B.S.Rabinovitch & F.H.Dover, J.Chem. Phys., 44,279 (1966).

   I.Oref, D.Schuetzle, & B.S.Rabinovitch,J.Chem. Phys., 54, 575 (1971).
7. H.M.Frey, Trans. Faraday Soc., 56, 51 (1960). See also: H.M.Frey & G.B.Kistiakowsky, J.Amer. Chem. Soc., 79, 6373 (1957).
8. a) W.VonE.Doering, J.C.Gilbert, & P.A.Leermakers, Tetrahedron, 24, 6863 (1968).

   b) Review article: L.D.Spicer & B.S.Rabinovitch, Ann. Rev. Phys. Chem., 21, 349 (1970).
9. J.D.Rynbrandt & B.S.Rabinovitch, J.Chem. Phys., 54, 2275 (1971).
10. J.D.Rynbrandt & B.S.Rabinovitch, J.Phys. Chem., 75, 2164 (1971).
11. B.S.Rabinovitch, J.F.Meagher, K.J.Chao, & J.R.Barker,

J.Chem. Phys., *60*, 2932 (1974).

12. The similar compounds  and  have been shown to yield 99% spiropentane,[13] plus further decomposition products.

13. R.G.Bergman & K.Shen, unpublished results.

14. For references on cyclic trimethylene-azo decompositions see:

J.Kochi, "Free Radicals," Vol.1, Chptr.5, John Wiley & Sons, New York (1973).

Proposition IV

Isocyanide Insertion into Activated Aryl-Hydrogen Bonds

Isocyanide Insertion into Activated Aryl-Hydrogen Bonds

The activation of carbon-hydrogen bonds by transition metals has been the goal of many researchers, with limited success. While a few examples of alkyl-hydrogen bond activation have been reported[1], many examples of activation of aryl-hydrogen bonds are now known,[2] most of these involving only reversible insertion into the C-H bond.[3] Unfortunately, aryl substitution processes involving direct activation of an aryl-hydrogen bond by a transition metal (as opposed to activation of an attacking reagent[4]) are not used on an industrial scale, although such a process would be quite desirable.

Interception of an intermediate transition metal aryl (or alkyl) hydride by CO or some other insertion group also has the possibility of being catalytic in metal (eqn.1).

$$\mathrm{RH} + \mathrm{CO} \xrightarrow{[\mathrm{M}]} \mathrm{R{-}C}\begin{smallmatrix} \diagup \mathrm{H} \\ \diagdown\!\!\diagdown \mathrm{O} \end{smallmatrix} \qquad (1)$$

The hydroformylation reaction is an example of a catalytic system where CO insertion into a metal-alkyl bond is followed by reductive elimination from an acyl hydride intermediate, producing aldehyde products.[5] This process has not yet been reported to include insertion of CO into an aryl-hydrogen bond, perhaps because none of the compounds known to insert into aryl-hydrogen bonds possess CO as a ligand,[2] or due to the reluctance of CO to insert into metal-aryl bonds.

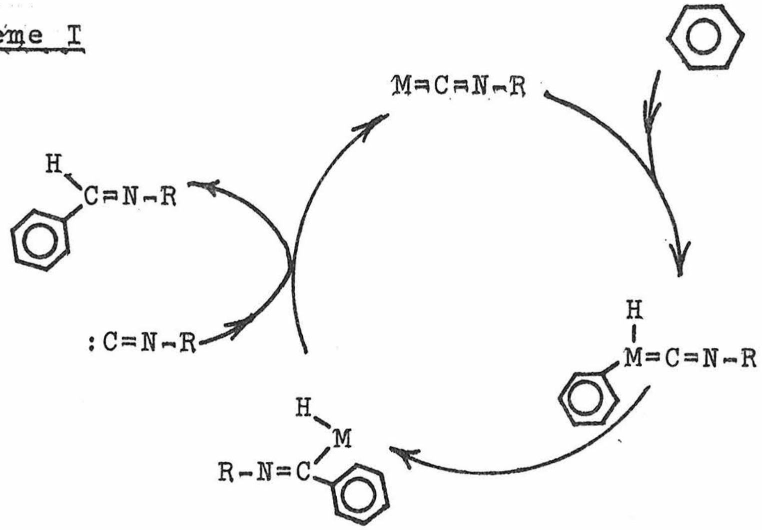
The functionally equivalent isocyanide ligand, :C=N-R, has also been reported to insert rapidly into metal-carbon bonds in the compounds $CpMo(CO)_3R$,[6] $CpFe(CO)_2R$ (with CO pressure)[7], and $CpNi(PPh_3)R$,[8] as well as in Pd[9] and Pt[10] -alkyl complexes. One of the alternate resonance forms of a transition metal isocyanide (eqn.2) increases negative charge on the metal center and might increase the metal's nucleophilic character towards arene C-H insertion (a requirement suggested by Parshall[1a]).

$$R-\overset{+}{N}-C-M^{-} \rightleftharpoons R-N=C=M \qquad (2)$$

The products of a reaction involving arene C-H activation followed by isonitrile insertion and reductive elimination are an imine and a coordinatively unsaturated metal complex. A catalytic cycle for this process is shown in Scheme I. The first two steps of the cycle are known,[2,6-11] whereas the reductive elimination of imine from the iminoacyl hydride complex has not been observed, but is not expected to be an unlikely process.

The feasibility of the iminoacyl hydride reductive elimination step could be investigated by protonating the known[12] compound $(C_5H_5)Mo(CO)_2(CH_3-C=NCH_3)$ with CF_3COOH,[13]

Scheme I



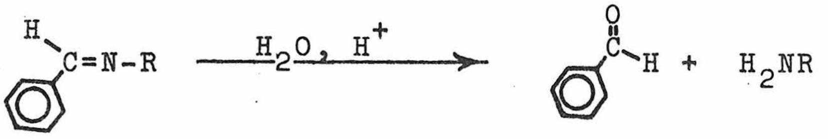
generating an iminoacyl hydride. The related compound $(C_5H_5)Mo(CO)_3(CH_3)$ protonates to give methane.[14] Similarly, hydridic reduction of $PdBr(PPh_3)(CR=NCH_3)$[9] might produce an iminoacyl hydride that could demonstrate this process.

The types of acyl C-H bonds activated include intramolecular reactions with the ligands PPh_3 (orthometalation)[15] and $R_2NCH_2C_6H_5$ (orthometalation),[16] and intermolecular reactions with benzene, toluene, and anthracene.[2] Metal complexes that intermolecularly activate arenes include $(C_5H_5)Rh(C_2H_4)_2$,[2a] $(CH_3PCH_2CH_2PCH_3)_2M(C_{10}H_7)H$ (M=Ru,Os),[2b] $(C_5H_5)_2MH_3$ (M=Nb,[2c] Ta[2f]), $ReH_7(PEt_2C_6H_5)_2$,[2d] $H_5Ta(CH_3PCH_2CH_2PCH_3)$,[2e] and $HIr[P(CH_3)_3]_2$.[2f]

Of these compounds, $(C_5H_5)Rh(C_2H_4)_2$, $(C_5H_5)NbH_3$, and $(C_5H_5)TaH_3$ are the most likely candidates to carry out the processes in Scheme I as they are more similar to the complexes known to insert isonitriles than the phosphine substituted compounds.[17] Of these three C_5H_5 compounds,

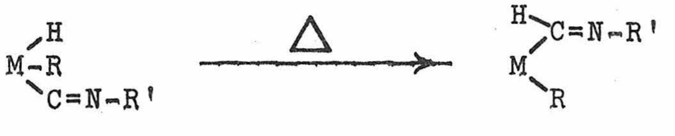
$(C_5H_5)NbH_3$ is the most active towards C_6H_6 - D_2 exchange and might be the best choice. $(C_5H_5)Rh(C_2H_4)_2$ has the advantage that no hydride ligands are present that could react with the starting isonitrile or the imine product.

The alkyl group of the isonitrile might also be "fine tuned" to increase insertion rates, just as the alkyl groups on phosphine ligands can be varied to affect reaction rates. Most literature reports[11] indicate that a bulky isonitrile increases isonitrile insertion products (with respect to CO insertion products). Hydrolysis of the imine product removes the isocyanide alkyl group, yet leaves a substituted benzene derivative, benzaldehyde (eqn.4).[18]



(4)

Insertion of isonitrile into the M-H bond instead of the M-acyl bond has also been observed,[19] but requires more severe reaction conditions (eqn.5). Consequently, this insertion is not expected to interfere with the catalytic cycle.



(5)

It should be noted that several transition metal compounds are known to effect just the opposite of equation 1, stoichiometric decarbonylation of aldehydes to produce arene and a metal carbonyl (eqn.6).[20] Since the thermodynamics of equation 1 favors aldehyde formation, the reason for this reversal must be attributable to the high stability of the metal carbonyl product. Isonitriles, being weaker π-acceptor ligands than CO with respect to transition metals,[11] should not suffer from de-insertion reactions analogous to equation 4 as the thermodynamics are probably unfavorable.

$$M + R\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \longrightarrow RH + M\text{-}CO \qquad (6)$$

REFERENCES

1. a) G.W.Parshall, *Acc.Chem.Res.*, *8*, 113(1975). (Review)
   b) A.J.Cheyney, B.E.Mann, B.L.Shaw, and R.M.Slade, *J.Chem.Soc.,Chem.Commun.*, 755(1974); J.Chatt and J.M. Davidson, *J.Chem.Soc.*, 843(1965); F.A.Cotton, B.A.Frenz, and D.L.Hunter, *J.Chem.Soc.,Chem.Commun.*, 755(1974); D.R.McAlister, D.K.Erwin, and J.E.Bercaw, *J.Amer.Chem.Soc.* *100*, 5966(1978); S.Trofimenko, *Inorg.Chem.*, *9*, 2493(1970); R.M.Laine, D.W.Thomas, L.W.Cary, and S.E.Buttrill, *J.Amer.Chem.Soc.*, *100*, 6527(1978).
2. a) L.P.Seiwell, *J.Amer.Chem.Soc.*, *96*, 7134(1974); b) J.Chatt and J.M.Davidson, *J.Chem.Soc.*, 843(1965); J.A.Gregory, S.D.Ibekwe, B.T.Kilbourn, and D.R.Rusell, *J.Chem.Soc.,A*, 1118(1971); c) F.N.Tebbe and G.W.Parshall, *J.Amer.Chem. Soc.*, *93*, 3793(1971); d) J.Chatt and R.S.Coffey, *J.Chem. Soc.,A*, 1963(1969); e) F.N.Tebbe, *J.Amer.Chem.Soc.*, *95*, 5823(1973); f) E.K.Barefield, G.W.Parshall, and F.N.Tebbe, *J.Amer.Chem.Soc.*, *92*, 5234(1970); g) D.E.Webster, *Adv.Organometal.Chem.*, *15*, 147(1977). (Review)
3. Chlorination of benzene and other alkanes has been reported using a Pt(IV)/Pt(II) catalyst with Cl_2. Also, a report of aromatic substitution has been observed with trialkyl aluminum.[1a]
4. For example, ferrous chloride catalyzes the electrophilic chlorination of benzene by activation of Cl_2 and not

the benzene C-H bonds. See: G.W.Parshall, Chem.Tech., 4, 445 (1974).

5. See, for example: D.S.Breslow and R.F.Heck, Chem.&Ind., 467 (1960).

6. Y.Yamamoto and H.Yamazaki, Bull.Chem.Soc.Jap.,43,143(1970); Y.Yamamoto and H.Yamazaki, J.Organometal.Chem., 24, 717 (1970).

7. Y.Yamamoto and H.Yamazaki, unpublished results.(See ref.11).

8. Y.Yamamoto, H.Yamazaki, and N.Hagihara, Bull.Chem.Soc.Jap., 43, 532(1968); J.Organometal.Chem., 18, 189(1969).

9. Y.Yamamoto and H.Yamazaki, Bull.Chem.Soc.Jap.,43,2653(1970).

10. P.M.Treichel and R.W.Hess, J.Amer.Chem.Soc., 92,4731(1970); Y.Yamamoto and H.Yamazaki, Bull.Chem.Soc.Jap., 44, 1873 (1971).

11. See: Y.Yamamoto and H.Yamazaki, Coord.Chem.Rev., 8, 225 (1972), and refs. therein.

12. R.D.Adams and D.F.Chodosh, J.Amer.Chem.Soc., 99,6544(1977).

13. Use of CF_3COOH as a universal proton source for use with transition metals by Gladysz. See: J.A.Gladysz, W.Tam, G.M.Williams, D.L.Johnson, and D.W.Parker, Inorg.Chem., 18, 1163(1979).

14. P.L.Watson and R.G.Bergman, J.Amer.Chem.Soc.,101,2055(1979).

15. See, for example: L.W.Gosser, Inorg.Chem.,14, 1453(1975); M.A.Bennett and D.L.Milner, J.Amer.Chem.Soc.,91, 6983 (1969); W.Keim, J.Organometal.Chem., 19, 161(1969);

G.W.Parshall, W.H.Knoth, and R.A.Schunn, J.Amer.Chem. Soc., 91, 4990(1969).

16.A.C.Cope and E.C.Friedlich, J.Amer.Chem.Soc.,90,909(1968).

17.However, it could also be argued that isonitrile ligands are more like phosphines in their π-acceptor capabilities so that replacement of a phosphine by isonitrile in phosphine containing compounds known to activate arenes would produce electronically similar complexes that could also activate arenes.

18.J.B.Hendrickson, D.J.Cram, and G.S.Hammond, "Organic Chemistry", McGraw Hill Book Co., New York, p.487(1970).

19.R.D.Adams and N.M.Golembeski, J.Amer.Chem.Soc., 100, 4622 (1978).

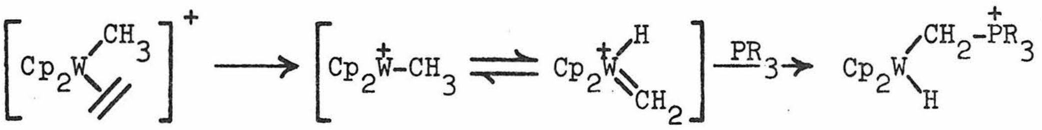
20.T.B.Rauchfuss, J.Amer.Chem.Soc.,100, 1045 (1979); J.W. Suggs, J.Amer.Chem.Soc., 100, 640(1978), and refs. therein.

Proposition V

The Mechanism of α-elimination in Ta(alkyl)$_5$

The Mechanism of α-elimination in Ta(alkyl)$_5$

The preparation and chemistry of transition metal alkyls has become an intricate part of the newly-fashioned field of organometallic chemistry. Many metal-alkyl compounds have been established to decompose by a common (yet poorly understood) process termed β-elimination, forming a metal hydride and an olefin.[1] Another process, metal-carbon bond homolysis, has also been shown to occur.[1,2] More recently, a new method of decomposition for metal-alkyl compounds containing no β-hydrogen atoms has been suggested by Green and Cooper[3], involving the elimination of an α-hydrogen atom forming a metal carbene hydride that was trapped as the PR_3 adduct (eqn.1).



(1)

Since this report, Schrock has found several examples of the α-elimination process in his study of the $M(CH_3)_5$,[4] $M(CH_2Ph)_5$,[4,5] and $M(CH_2CMe_3)_5$[6] (M=Nb,Ta) systems. The decomposition of $Ta(CD_3)_5$ in diethyl ether solution at 25°C shows the formation of 3.5 equivalents of CD_4, with little ethane (<1%) being observed, providing evidence for the absence of free methyl radicals formed by M-C homolysis.[7]

The decomposition of $Ta(CH_2C_6H_5)_5$ has also been alleged to decompose by a non-radical process.[5] Actually, a radical chain process such as that shown in Scheme I was found not to be the mechanism of toluene formation, as neither radical traps nor initiators had any effect upon the reaction rate, nor were any ESR signals observed. However, a crossover experiment provided conflicting results: decomposition of a mixture of $\mathrm{Ta(CH_2C_6H_5)_5}$ and $\mathrm{Ta(CD_2C_6H_5)_5}$ provided both $\mathrm{C_6H_5CH_3}$ and $\mathrm{C_6H_5CH_2D}$. Schrock explained this observation in terms of an independent ligand exchange reaction as opposed to reversible M-C cleavage.[5]

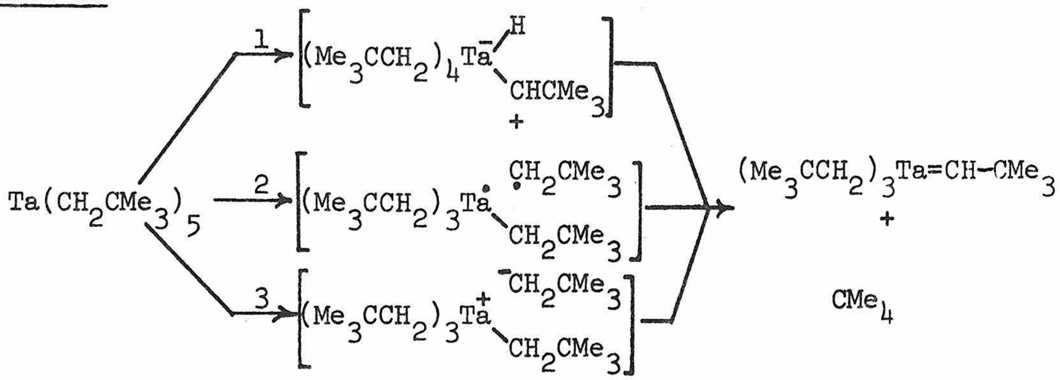
The decomposition of $\mathrm{Ta(CH_2CMe_3)_5}$ formed <u>in situ</u> by the reaction of $\mathrm{Ta(CH_2CMe_3)_4Cl}$ with $\mathrm{LiCH_2CMe_3}$ proceeded similarly, providing neopentane and $\mathrm{(Me_3CCH{=}Ta(CH_2CMe_3)_3}$. Labeling studies demonstrated the intramolecularity of the reaction. Three possible mechanisms for the formation of the neopentylidene were considered by Schrock:[6] 1) α-elimination (transfer of an α-hydrogen atom(hydride) to Ta), 2) α-abstraction (M-C bond cleavage followed by rapid abstraction of an α-hydrogen from an adjacent alkyl group), and 3) deprotonation (loss of $\mathrm{CH_3CCH_2^-}$ followed by rapid α-deprotonation of an adjacent alkyl group) (Scheme II). All three of these mechanisms accomplish the same transformation in the polyalkyl systems.

<u>Scheme I</u>

$$\mathrm{RCH_2^{\bullet}} + \mathrm{Ta(CH_2Ph)_5} \longrightarrow \mathrm{RCH_3} + \mathrm{Ta(CH_2Ph)_4(\dot{C}HPh)}$$

$$\mathrm{Ta(CH_2Ph)_4(\dot{C}HPh)} \longrightarrow \mathrm{RHC{=}Ta(CH_2Ph)_3} + \mathrm{RCH_2^{\bullet}}$$

Scheme II



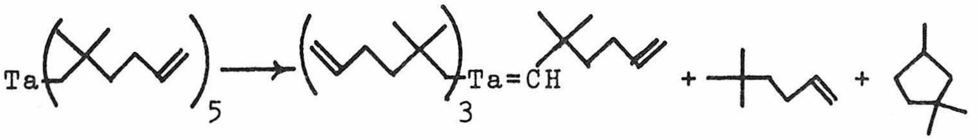
Schrock discounts the first mechanism on the basis that Ta(V) would prefer not to be formally negatively charged relative to a carbon ligand, so that this α-elimination process (1) is not occurring in these systems. However, both mechanisms 2 and 3 are plausible,[4,6a,6b] and cannot be distinguished between by his experiments. Mechanism 3 is preferred as it is known that $Cp_2M(CH_3)_2^+$ [9] (M=Mo,W) $CpTa(CHCMe_3)Cl_2(PMe_3)$ [10] may be deprotonated with $Ph_3P=CH_2$ to give $Cp_2M=CH_2(CH_3)$ and $CpTa\equiv CCMe_3)Cl(PMe_3)_2$, respectively.

No tests have been employed in this system to specifically detect short-lived radicals, thereby distinguishing between mechanisms 2 and 3 above. With the large number of radical rearrangements known, it ought to be possible to find one that rearranges quickly enough to demonstrate the presence of short-lived radicals, either caged or in solution (Scheme III).

The known rearrangement of the 1-hexenyl radical could be employed if the α-positions were blocked with methyl groups (eqn.2). However, the rearrangement rate of this radical is probably slow ($k \approx 1.0 \times 10^5 s^{-1}$)[11] compared with the expected lifetimes of the radicals in this system. The allyloxyethyl radical () cyclizes about 20 times faster[12] but still may not be fast enough.

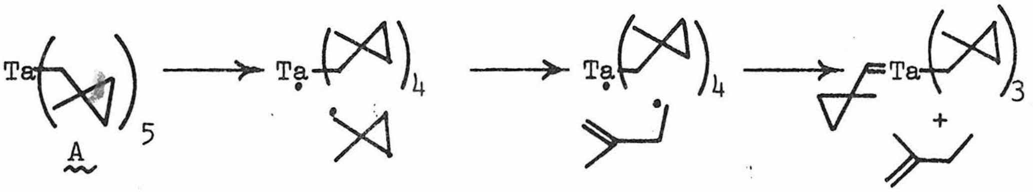
Scheme III

$$\begin{tikzcd}
TaR_5 \arrow[r] & \dot{Ta}R_4 + \cdot R \arrow[r, "k_r"] \arrow[d, "k_H"] & \dot{Ta}R_4 + \cdot R' \arrow[d, "k_H"] \\
 & R_3Ta{=}R(-H) + RH & R_3Ta{=}R(-H) + R'H
\end{tikzcd}$$



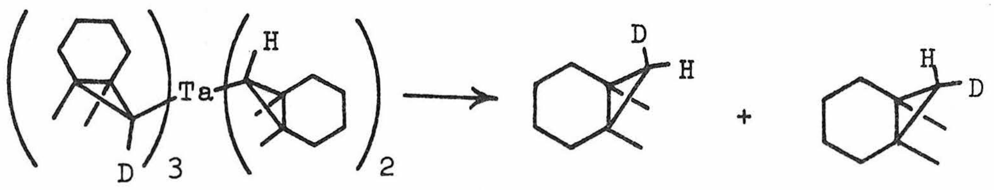
(2)

The most optimal compound for this study is perhaps the methylcyclopropylcarbinyl derivative, A (eqn.3). The framework of the methylcyclopropylcarbinyl ligand is identical to that of the neopentyl ligand so that steric differences would be minimized. The cyclopropyl carbinyl radical ring opens very rapidly ($k \approx 2 \times 10^8 s^{-1}$)[13] and would probably be fast enough for this experiment. The formation of 2-methyl-1-butene would indicate the intermediacy of radicals.



(3)

An even faster rearrangement[14] could be detected with the mixed compound **B**.[15] Mechanism 3 would produce only **D** as cyclopropyl anions have been demonstrated to be configurationally stable,[14,15] whereas mechanism 2 would produce a mixture of **C** and **D** due to the rapid interconversion of the cyclopropyl radical.



B **C** **D**

Although these experiments are rather difficult to perform, they would distinguish between two of the pathways of the α-elimination process. The increased understanding of the detailed mechanism, while not important in terms of the observed products, would add insight into one of the basic processes available to transition metal poly-alkyls.

REFERENCES

1. For a recent review see: a) P.J.Davidson, M.F.Lappert, and R.Pearce, *Chem.Rev.*, *76*, 219(1976); b) R.R.Schrock, and G.W.Parshall, *Chem.Rev.*, *76*, 243(1976).
2. J.Halpern, unpublished results.
3. N.J.Cooper and M.L.H.Green, *J.Chem.Soc.,Chem.Commun.,* 761 (1974).
4. R.R.Schrock, *J.Organometal.Chem.*, *122*, 209(1976).
5. V.Malatesta, K.U.Ingold, and R.R.Schrock, *J.Organometal. Chem.*, *152*, C53(1978).
6. a) R.R.Schrock, *J.Amer.Chem.Soc.*, *96*, 6796(1974); b) R.R. Schrock, *J.Amer.Chem.Soc.*, *100*, 3359(1978).
7. Diethyl ether is known[8] to readily donate a hydrogen atom to free methyl radicals.
8. A.F.Trotman-Dickenson, *Adv.Free Rad.Chem.*, *1*,1(1965).
9. R.R.Schrock and P.R.Sharp, *J.Amer.Chem.Soc.*, *100*,2389(1978).
10. S.J.McLain, C.D.Wood, L.W.Messerle, R.R.Schrock, F.J. Hollander, W.J.Youngs, and M.R.Churchill, *J.Amer.Chem. Soc.*, *100*, 5962(1978).
11. D.Lal, D.Griller, S.Husband, and K.U.Ingold, *J.Amer. Chem.Soc.*, *96*, 6355(1974).
12. A.L.J.Beckwith, I.Blair, and G.Phillipou, *J.Amer.Chem. Soc.*, *96*, 1613(1974).
13. R.J.Kinney, W.D.Jones, and R.G.Bergman, *J.Amer.Chem.Soc.*, *100*, 635(1978).

14.While the rate of isomerization of the cyclopropyl radical is not known exactly, it is believed to be an extremely fast process. See, for example: J.Jacobus and D.Pensak, *J.Chem.Soc.,Chem.Commun.*, 400(1969).

15.Such "mixed" ligand complexes can be prepared. See ref.6b.

16. M.J.S.Dewer and J.M.Harris, *J.Amer.Chem.Soc.*, **91**, 3652(1969).

APPENDIX I

CONTENTS

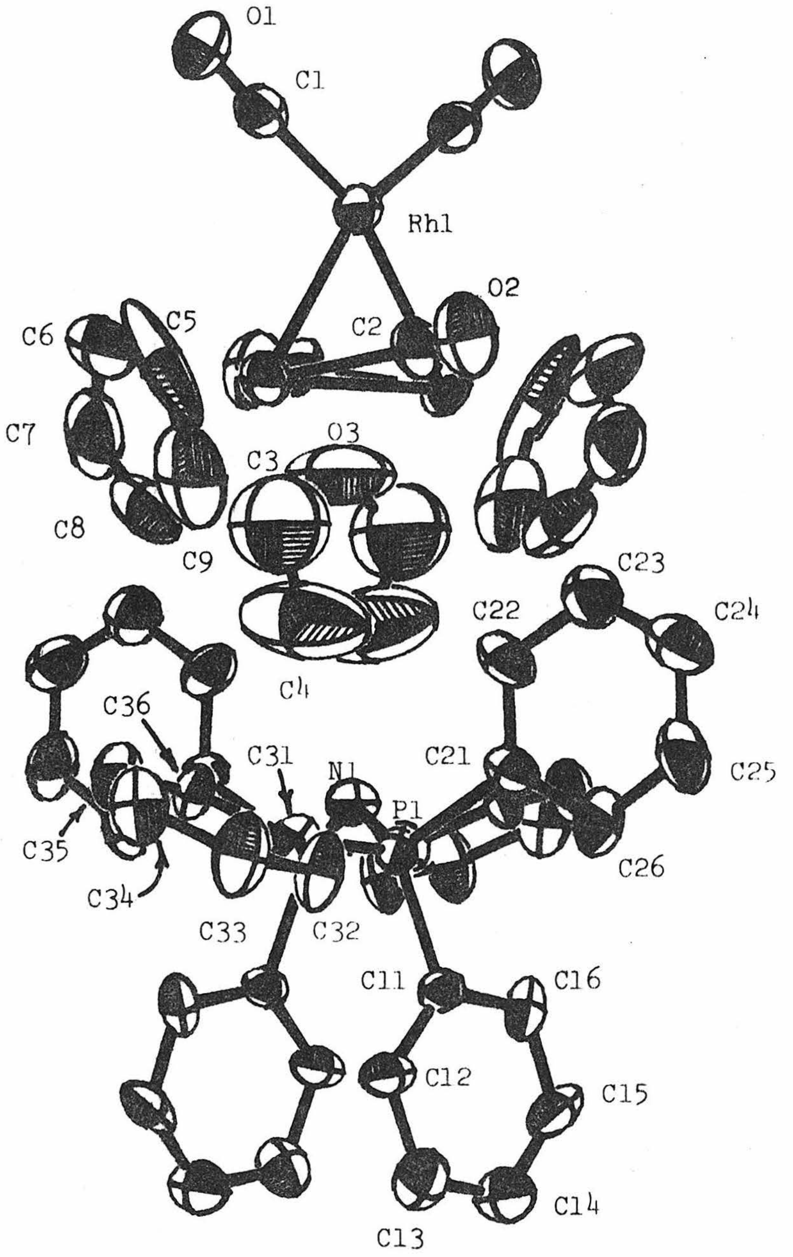


Figure 9. ORTEP drawing of two asymmetric units, related by a twofold axis, in $[(Ph_3P)_2N]^+[Cp_2Rh_3(CO)_4]^-$THF.

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

Metal to Metal Bonds

Rh1-Rh2	2.590
Rh2-Rh2	2.661

Metal To Carbon Bonds

Rh1-C1	1.843
Rh2-C2	2.005
Rh1-C2*	2.400
Rh2-C5	2.206
Rh2-C6	2.201
Rh2-C7	2.259
Rh2-C8	2.267
Rh2-C9	2.258
Rh2'-C2	2.010

Carbon to Oxygen Bonds

C1-O1	1.147
C2-O2	1.163
C3-O3	1.330

Carbon to Phosphorous Bonds

C11-P1	1.830
C21-P1	1.829
C31-P1	1.815

Nitrogen to Phosphorous Bonds

N1-P1	1.589

Carbon to Carbon Bonds

C5-C6	1.357
C6-C7	1.316
C7-C8	1.288
C8-C9	1.342

Carbon to Carbon Bonds (con'd)

C9-C5	1.432
C11-C12	1.380
C12-C13	1.393
C13-C14	1.380
C14-C15	1.368
C15-C16	1.374
C16-C11	1.402
C21-C22	1.373
C22-C23	1.389
C23-C24	1.364
C24-C25	1.360
C25-C26	1.387
C26-C21	1.395
C31-C32	1.376
C32-C33	1.377
C33-C34	1.381
C34-C35	1.356
C35-C36	1.383
C36-C31	1.411
C3-C4	1.355
C4-C4	1.401

Metal Cluster Bond Angles

Rh1-Rh2-Rh2	59.1
Rh2-Rh1-Rh2	61.8
Rh1-C1-O1	177.9
Rh2-C2-O2	138.4
Rh2'-C2-O2	136.8
CEN-C2-O2**	170.7
C5-C6-C7	111.5
C6-C7-C8	107.9
C7-C8-C9	111.7

Table 1. Continued

Metal Cluster Bond Angles (con'd)

C8-C9-C5	105.5
C9-C5-C6	103.3

Triphenylphosphiniminium Cation Bond Angles

P1-N1-P1	133.6
P1-C11-C12	122.1
P1-C11-C16	116.4
C11-C12-C13	118.8
C12-C13-C14	119.8
C13-C14-C15	120.7
C14-C15-C16	120.8
C15-C16-C11	118.6
C16-C11-C12	121.2
P1-C21-C22	118.3
P1-C21-C26	119.1
C21-C22-C23	117.6
C22-C23-C24	121.2
C23-C24-C25	120.3
C24-C25-C26	121.0
C25-C26-C21	117.4

Triphenylphosphiniminium Cation Bond Angles (con'd)

C26-C21-C22	122.4
P1-C31-C32	120.1
P1-C31-C36	118.4
C31-C32-C33	119.4
C32-C33-C34	119.6
C33-C34-C35	121.2
C34-C35-C36	121.1
C35-C36-C31	117.4
C36-C31-C32	121.4

Tetrahydrofuran Bond Angles

C3-O3-C3	113.7
O3-C3-C4	105.2
C3-C4-C4	107.5

Average estimated error in bond lengths ca. ± 0.008 Å.

*Semi-bonding interaction

**Center of Rh2-Rh2 bond

Table 2. Fractional Coordinates

BIS-CYCLOPENTADIENYLTRIRHUDIUMTETRACARBONYL ANION

DIRECT CELL PARAMETERS

A	B	C		ALPHA	BETA	GAMMA
12.134100	25.322800	15.706900		90.000	91.218	90.000
			COSINE	0.00000127	-0.02125357	0.00000127

	X	Y	Z	U11	U22	U33	U12	U13	U23
RH1	0(0)	14023(3)	25000(0)	717(8)	380(5)	397(5)	0(0)	202(5)	0(0)
N1	0(0)	43713(29)	25000(0)	271(54)	332(48)	484(52)	0(0)	-46(42)	0(0)
O41	50000(0)	25515(63)	25000(0)	2331(273)	625(119)	2378(254)	0(0)	267(204)	0(0)
C3	5690(72)	9479(29)	17045(49)	641(62)	430(45)	479(48)	22(47)	118(45)	72(41)
C5	19584(102)	22733(70)	9321(82)	931(98)	2763(182)	1068(104)	1197(118)	724(82)	1376(117)
C6	10551(153)	21525(44)	4468(69)	3122(219)	701(84)	823(86)	634(104)	1323(121)	316(64)
C7	3663(118)	25532(56)	3922(62)	1820(143)	1208(107)	561(71)	-664(104)	190(79)	129(73)
C8	7927(100)	29411(39)	8151(68)	928(94)	766(67)	849(82)	79(68)	290(71)	394(58)
C9	17748(112)	28123(61)	11655(66)	902(105)	1622(144)	815(76)	-436(102)	341(76)	280(92)
C11	39479(57)	3029(26)	18146(41)	397(46)	280(42)	382(39)	19(36)	-102(35)	31(33)
C12	34862(62)	7153(26)	22567(45)	488(53)	284(39)	530(50)	-11(38)	-51(41)	49(36)
C13	36697(68)	12301(32)	19805(49)	550(58)	603(56)	496(50)	47(46)	60(45)	78(42)
C14	43195(73)	13195(31)	12843(53)	699(68)	462(51)	655(59)	0(48)	-15(52)	33(44)
C15	47942(71)	9076(31)	8640(49)	625(63)	463(50)	534(52)	-58(47)	-92(47)	251(42)
C16	46164(63)	3951(31)	11129(42)	441(51)	670(57)	262(40)	-72(45)	-5(37)	77(38)
C21	17228(61)	42260(28)	36951(44)	421(49)	355(46)	466(45)	60(39)	53(38)	78(36)
C22	16265(67)	36862(31)	36544(49)	554(59)	488(53)	554(51)	151(45)	-24(44)	167(42)
C23	21497(75)	33923(33)	42908(54)	697(67)	600(58)	592(58)	-36(52)	-95(51)	47(48)
C24	27374(76)	36311(33)	49330(56)	705(71)	534(55)	707(61)	147(54)	89(53)	167(49)
C25	28197(75)	41665(36)	49640(51)	672(69)	830(69)	468(51)	129(58)	-182(48)	132(48)
C26	23177(66)	44805(32)	43450(49)	462(55)	729(58)	417(48)	21(47)	-215(42)	-89(44)
C31	21622(58)	45760(26)	19937(41)	262(45)	411(41)	381(40)	23(37)	-14(34)	-64(33)
C32	32308(63)	47326(33)	21614(45)	288(48)	929(67)	361(43)	-39(47)	105(37)	-135(43)
C33	40146(68)	46603(36)	15515(50)	428(58)	1034(74)	493(50)	-58(53)	-92(44)	-136(49)
C34	37176(68)	44335(35)	7807(51)	388(54)	888(67)	490(53)	62(50)	27(44)	27(48)
C35	26642(72)	42809(32)	6117(48)	566(61)	711(59)	408(48)	81(50)	78(45)	-78(43)
C36	18521(66)	43442(28)	12078(42)	610(58)	470(48)	271(40)	13(42)	-60(40)	-100(35)
O3	9264(56)	6534(23)	12288(35)	1184(59)	742(45)	534(38)	199(42)	272(38)	-114(33)
RH3	5112(6)	22800(3)	17590(4)	725(5)	461(4)	404(4)	72(4)	267(3)	86(3)
P1	11398(16)	46185(7)	28179(11)	339(12)	347(11)	255(10)	17(10)	-4(9)	-20(8)
C2	10692(79)	21519(31)	29552(48)	795(73)	568(58)	445(50)	20(53)	244(50)	114(42)
O2	19211(51)	21261(25)	33057(37)	596(45)	1073(56)	641(41)	-90(41)	40(35)	111(38)
C41	44203(151)	28386(60)	30405(91)	2865(239)	1747(146)	1907(152)	-40(172)	1126(149)	-51(131)
C42	45530(150)	33472(50)	28099(115)	2888(234)	1135(109)	3224(244)	-188(140)	1587(167)	-359(137)

	X	Y	Z	B
HS5	2657 (0)	2217 (0)	1208 (0)	3.45 (0.0)
HS6	1326 (0)	1797 (0)	343 (0)	3.45 (0.0)
HS7	-160 (0)	2349 (0)	43 (0)	3.45 (0.0)
HS8	139 (0)	3161 (0)	655 (0)	3.45 (0.0)
HS9	1930 (0)	3153 (0)	1437 (0)	3.45 (0.0)
HS11	4182 (0)	-62 (0)	1612 (0)	3.45 (0.0)
HS12	3244 (0)	393 (0)	2571 (0)	3.45 (0.0)
HS13	3181 (0)	1266 (0)	2483 (0)	3.45 (0.0)
HS14	4069 (0)	1673 (0)	1479 (0)	3.45 (0.0)
HS15	5049 (0)	1234 (0)	564 (0)	3.45 (0.0)
HS16	5102 (0)	359 (0)	613 (0)	3.45 (0.0)
HS21	1661 (0)	4622 (0)	3573 (0)	3.45 (0.0)
HS22	1184 (0)	3808 (0)	3140 (0)	3.45 (0.0)
HS23	1778 (0)	3130 (0)	3901 (0)	3.45 (0.0)
HS24	2797 (0)	3242 (0)	5051 (0)	3.45 (0.0)
HS25	3250 (0)	4033 (0)	5470 (0)	3.45 (0.0)
HS26	2685 (0)	4739 (0)	4729 (0)	3.45 (0.0)
HS31	1336 (0)	4498 (0)	2029 (0)	3.45 (0.0)
HS32	2826 (0)	4822 (0)	2691 (0)	3.45 (0.0)
HS33	4414 (0)	4833 (0)	2050 (0)	3.45 (0.0)
HS34	4527 (0)	4513 (0)	753 (0)	3.45 (0.0)
HS35	3077 (0)	4190 (0)	87 (0)	3.45 (0.0)
HS36	1441 (0)	4180 (0)	720 (0)	3.45 (0.0)
HS51	3608 (0)	2737 (0)	3001 (0)	10.00 (0.0)
HS61	4650 (0)	2760 (0)	3649 (0)	10.00 (0.0)
HS52	4850 (0)	3552 (0)	3322 (0)	10.00 (0.0)
HS62	3899 (0)	3508 (0)	2597 (0)	10.00 (0.0)
HS53	4488 (0)	2315 (0)	2167 (0)	10.00 (0.0)
HS63	5512 (0)	2315 (0)	2833 (0)	10.00 (0.0)

X, Y, AND Z COORDINATES OF ALL NON-HYDROGEN ATOMS HAVE BEEN MULTIPLIED BY 10**5.

COORDINATES OF HYDROGEN ATOMS HAVE BEEN MULTIPLIED BY 10**4.

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