I. SYNTHESIS AND CHARACTERIZATION OF THE NEW CYCLOPENTADIENYL VANADIUM TRICARBONYL HYDRIDE AND METHYL ANIONS AND THEIR REACTIONS WITH ORGANIC SUBSTRATES

II. MONOMERIC ORGANOMETALLIC DIANIONS

Thesis by

Robert James Kinney

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

California Institute of Technology
Pasadena, California
1978
(Submitted December 6, 1977)

ACKNOWLEDGMENTS

My thanks go to Robert Bergman for his patience and for allowing me to make my own mistakes. To the members of the Bergman Group go my thanks for their suggestions and criticisms.

I would also like to acknowledge financial support from the National Science Foundation and the California Institute of Technology.

Old man of the Chemistry Lab,
Don't live in the horrors of yesterday
Nor in the hopes and fears of tomorrow.

Come out just for today
And let all your lights shine,
Just for now, this moment,
Don't hold back.

Each day is a rebeginning.
Don't get hung up on what happened,
What wouldcould have been,
Or on what will happen or will be.
Or else you'll lose now.

Bernadine Hillseth

To Bernie, a friend

ABSTRACT

The new anionic cyclopentadienyl vanadium tricarbonyl complexes, $(\eta^5C_5H_5)V(CO)_3R^-$, $(R = H, CH_3)$, have been isolated as the phosphineminium salts. $(\eta^5C_5H_5)V(CO)_3H^-$ reacts with alkyl (primary, secondary, and tertiary), vinyl and aryl bromides at room temperature in THF to replace bromine with hydrogen. A gem-dibromocyclopropane was reduced to the mono-bromide, and acid chlorides were converted to aldehydes with $(\eta^5C_5H_5)V(CO)_3H^-$. Primary alkyl iodides react more rapidly than the bromides and aklyl chlorides do not react at all. Alkyl tosylates react much slower than the corresponding bromides. Carbon radicals and $(\eta^5C_5H_5)V(CO)_3Br^-$ as the kinetic organometallic product imply a radical chain mechanism for these reactions.

The reactions of $(\eta^5C_5H_5)V(CO)_3CH_3^-$ and alkylbromides and acyl chlorides do not produce new carbon-carbon bonds.

Attempts to prepare the dianious $RM(CO)_3^{2-}$, M = Cr,Mo; R = norbornadiene and M = Mo; R = cyclooctatetraene were not successful.

TABLE OF CONTENTS

PART I

PART II

PROPOSITIONS

INTRODUCTION

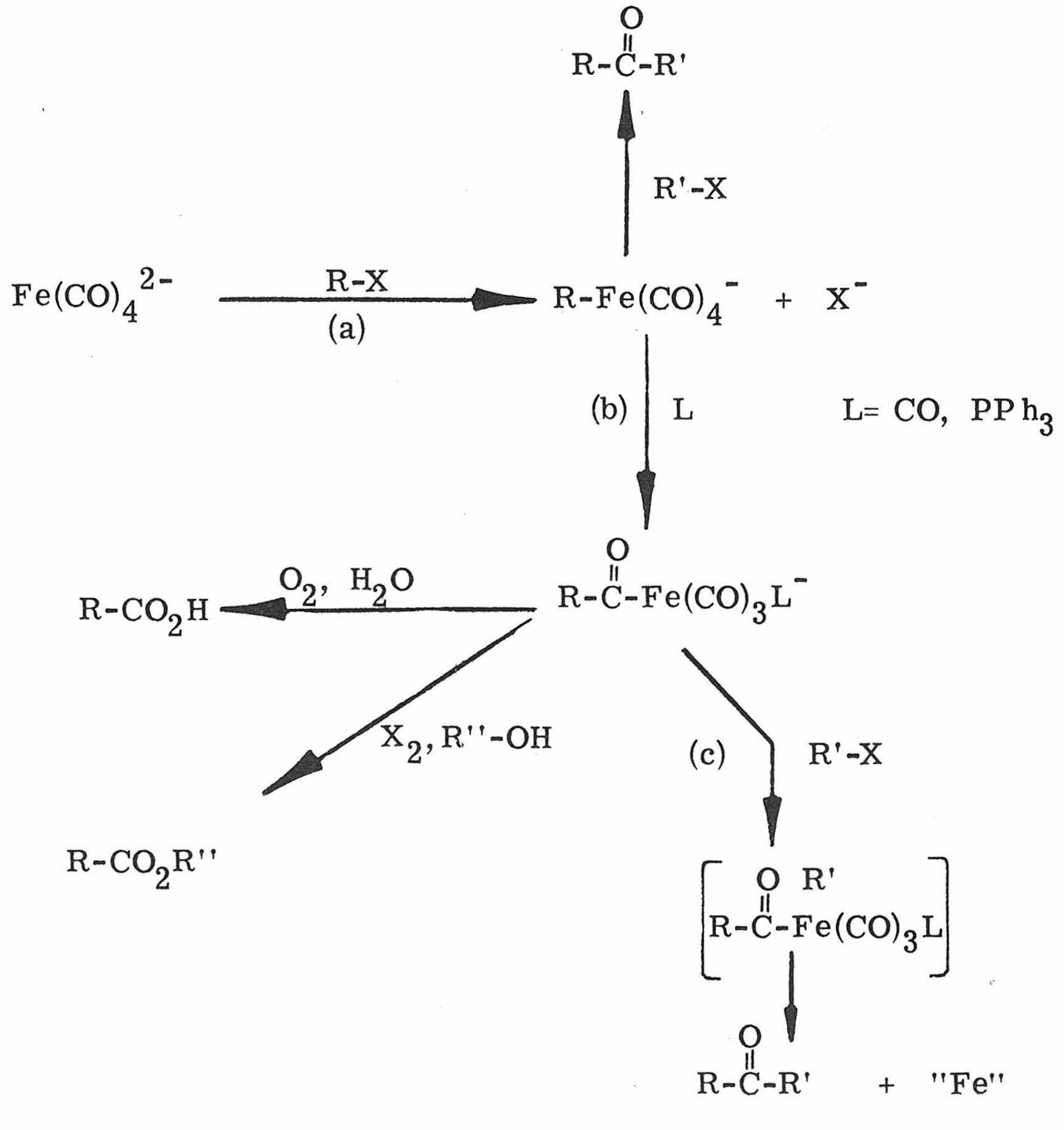
We report here the preparation of the new cyclopentadienyl vanadium tricarbonyl hydride and methyl anions, $(\eta^5C_5H_5)V(CO)_3R^-$, $(R = H,CH_3)$. These anions were prepared from the reactions of $(\eta^5C_5H_5)V(CO)_3^{2-}$. Their reactions with organic substrates are described.

The dianionic organometallic complex tetracarbonyl ferrate (-II), $Fe(CO)_4^{2-}$, has been shown by Collman (1a) to undergo a unique series of reactions with organic halides and tosylates to produce carbonyl compounds.

The overall reaction (Scheme I1) occurs by a series of individual steps [1b] starting with nucleophilic displacement [2] of halide or tosylate by iron (step a), to form the anionic iron-alkyl, $Fe(CO)_4R^-$. Alkyl migration [2] to one of the carbon monoxide ligands (step b) and coordination of the new ligand L generates the anionic iron acyl complex, $(CO)_3LFe\overset{O}{\overset{\|}{C}}R^-$. Reaction of this anion with a second mole of alkyl halide (step c) leads to ketones, presumably by a second nucleophilic displacement at carbon to produce the iron-alkyl-acyl complex $(CO)_3LFe(R')(\overset{O}{\overset{\|}{C}}R)$. Reductive elimination from this complex yields the observed ketones. The iron-acyl complex may be treated with acid to yield aldehydes [3a], oxygen and water to yield carboxylic acids [3b], and halogens with alcohols and amines to yield esters and amides [3b].

When the iron-alkyl complex is treated with alkyl halides, the product is still the corresponding ketone. The alkyl migration to carbon monoxide must be much faster than the direct reductive elimination of

SCHEME I1


R-C(=O)-R'
R'-X
Fe(CO)4 2-
R-X
(a)
R-Fe(CO)4 -
+ X-
(b)
L
L= CO, PPh3
R-C(=O)-Fe(CO)3L-
O2, H2O
R-CO2H
X2, R''-OH
R-CO2R''
(c)
R'-X
[R-C(=O)-Fe(CO)3L R']
R-C(=O)-R'
+ "Fe"

the two alkyl groups from the presumed bis-alkyl complex, $R_2Fe(CO)_4$.

This sequence makes $Fe(CO)_4^{2-}$ a useful synthetic reagent for introducing a carbonyl functionality into an organic molecule from organic halide precursors. Particularly useful is the preparation of unsymmetrical ketones [1]. However, since $Fe(CO)_4^{2-}$ is a relatively strong base (pk_b approximately that of OH^- [4]), the reactions with secondary and tertiary halides lead to large amounts of elimination products. Also, the migration step fails for alkyl groups with alpha electronegative groups. And finally, the second alkylation (step c) can only be carried out with very active alkylating reagents, usually primary iodides.

This sequence of reactions to form two new carbon-carbon bonds has been well documented only for $Fe(CO)_4^{2-}$. The other known dianionic organometallic complexes do not readily undergo these similar reactions.

The reactivity of $Os(CO)_4^{2-}$ is quite different from that of $Fe(CO)_4^{2-}$ [5]. Unlike the corresponding iron complex, dimethyl osmium tetracarbonyl is very stable. Decomposition at 160°C gives predominantly methane. With excess ligand added, the decomposition pathway changes, and acetone does become the major product. It is clear, though, that a change in metal changes the available reaction pathways [6].

No reactions of $Ru(CO)_4^{2-}$ with organic halides to form ruthenium-carbon bonds have been reported. The only nucleophilic reactions of $Ru(CO)_4^{2-}$ which have been reported are at tin and lead, to give cis-$(Me_3Sn)_2Ru(CO)_4$, trans-$(Ph_3Sn)_2Ru(CO)_4$, trans-$[(PhCH_2)_3Sn]_2$-$Ru(CO)_4$ and cis-$(Me_3Pb)_2Ru(CO)_4$ in low yields [7].

The pentacarbonyl dianions of chromium, molybdenum and tungsten have also been prepared [5], but they have quite different reactivity patterns than that described for $Fe(CO)_4^{2-}$. These complexes are strong nucleophiles, but interestingly they prefer to undergo what is equivalent to two nucleophilic displacements at the same carbon atom, instead of at two separate carbons. For example, the reaction of $Cr(CO)_5^{2-}$ with Me_2NCHCl_2 leads to the hexacoordinate chromium carbene complex, $(CO)_5CrCHNMe_2$, instead of the heptacoordinate complex, $(CO)_5Cr(CHClNMe_2)_2$ [8]. Chromium's reluctance to be seven coordinate probably prevents the bis alkyl complex from forming [5].

Curiously, no reports of the mono-alkyl chromium anions, $(CO)_5CrR^-$, are available [5], although the acyl anion $(CO)_5Cr(\overset{O}{\overset{\|}{C}}R)^-$ can be prepared from $Cr(CO)_6$ and lithium alkyls [9]. The reactions of this complex with strong alkylating agents do not alkylate at the metal but at the acyl oxygen [9], to form metal carbene complexes. The reactivity pattern for the molybdenum and tungsten pentacarbonyl dianions are similar to chromium [9].

Cyclopentadienyl vanadium tricarbonyl $(\eta^5C_5H_5)V(CO)_3^{2-}$ is the only other known monomeric, dianionic transition metal complex [10]. Its only reported reaction, prior to this work, was with aqueous HCl, to form hydrogen and the coordinatively unsaturated vanadium dimer $(\eta^5C_5H_5)_2V_2(CO)_5$ [10].

A comparison of the reactions of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with alkylating agents and those of the other dianions was of interest to us. $(\eta^5C_5H_5)V(CO)_3^{2-}$ is the only one of these dianions with ligands other than carbon monoxide [11]. Also, the very different electronic configuration (i.e., d^6 for vanadium and d^{10} for iron) for the metals in these complexes might lead to different reactions.

In particular, the mechanism of metal carbon bond formation could be very different. It has been shown that $Fe(CO)_4^{2-}$ [1b] and other organometallic transition metal complexes [12a,b] react with organic halides and tosylates by nucleophilic displacement (Sn2), with inversion at carbon, to form a metal carbon bond. Some complexes [12c,d] react with alkyl halides by electron transfer, with carbon radical intermediates prior to metal carbon bond formation. There appears to be a very small energetic difference between these two mechanisms, since the same complex may react with different organic halides by different mechanisms [12c].

Instead of alkylation and metal-carbon bond formation, all of the dianions, $M(CO)_4^{2-}$, M = Fe,Ru,Os, and $M(CO)_5^{2-}$, M = Cr,W, can be protonated with acids varying in strength from water to acetic acid [5,13] to form the mono-anionic hydrides, $HM(CO)_4^-$ and $HM(CO)_5^-$.

Even after protonation, the iron atom is nucleophilic enough that $HFe(CO)_4^-$ reacts with electrophilic carbon centers, such as alkyl halides and tosylates. New carbon-hydrogen bonds are formed by what has been suggested to be [14a] alkylation of the metal, and reductive elimination of the alkyl group and hydrogen. This mechanism is consistent with the observed inversion at carbon [14a], as it is likely the metal alkylation goes with inversion [14b], and the reductive elimination with retention [14a]. Interestingly, no alkyl migration to carbon monoxide was observed in the reactions of $HFe(CO)_4^-$ with alkyl halides [14a]. Likewise, in the reactions of $Fe(CO)_4R^-$ with acid, no alkyl migration was observed, in contrast to the reactions of $Fe(CO)_4R^-$ with alkyl halides [1]. Reductive elimination of carbon and hydrogen is faster than alkyl migration, and reductive elimination of two alkyl carbons is slower at this iron center.

$HCr(CO)_5^-$ and $HW(CO)_5^-$ are less basic than $HFe(CO)_4^-$ and appear to be less nucleophilic. No reactions of metal alkylation of $HM(CO)_5^-$, M = Cr,W, have been reported [5]. Because alkylation would generate a heptacoordinate chromium or tungsten complex, nucleophilic displacement by the $HM(CO)_5^-$ complexes may be very difficult.

Alternative mechanisms for the reaction $HM(CO)_5^-$ complexes with alkyl halides might be electron transfer [12c,d], or homolytic metal-hydrogen bond cleavage and halogen atom abstraction by the resultant metal radical, as in the reactions of tin hydrides [15].

The new anionic hydride, $(\eta^5C_5H_5)V(CO)_3H^-$, has been prepared and its reactions with organic halides and tosylates were investigated.

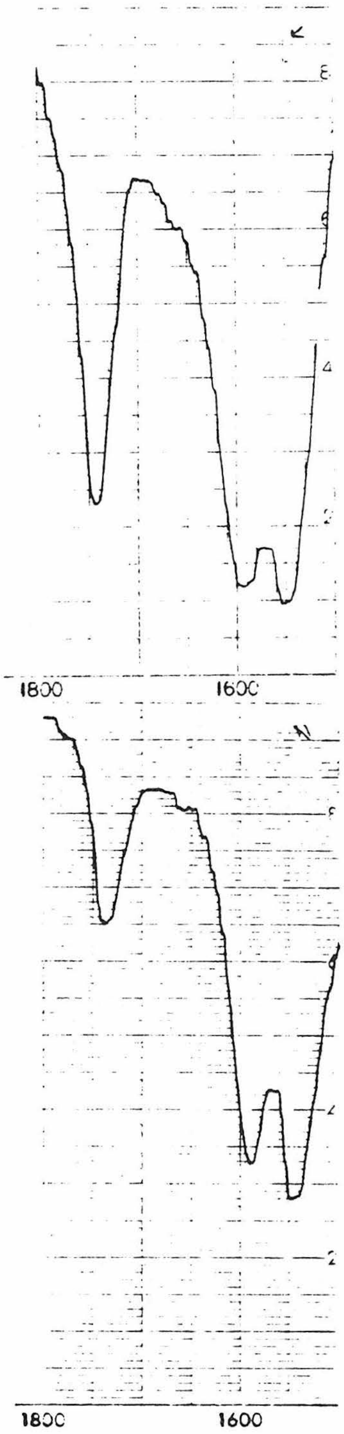
Results and Discussion

Preparation of $Na_2[\eta^5C_5H_5)V(CO)_3]\cdot THF$ from $(\eta^5C_5H_5)V(CO)_4$. The di-sodium salt of the dianion $(\eta^5C_5H_5)V(CO)_3^{2-}$, 1, was previously prepared by the reduction of $(\eta^5C_5H_5)V(CO)_4$, 2, with sodium metal in liquid ammonia [16] (Scheme IA). 1 was characterized by the nujol mull infrared spectrum of the cesium salt, Cs_2-1, which showed carbonyl absorption at 1742 and 1645 cm^{-1}. Later, the sodium salt, Na_2-1, was reported as the product of the reduction of 2 with sodium amalgam in tetrahydrofuran (THF), though no information concerning the characterization of this product was given [17]. It has also been noted that hexamethylphosphoramide (HMPA) solutions of 1 could be generated by adding 2 to sodium metal dissolved in HMPA (Scheme IB). The IR spectrum of these solutions showed carbonyl absorptions at 1742, 1619 and 1573 cm^{-1} [18].

We have found that when 2 was treated with sodium amalgam or sodium dispersion in THF, a yellow precipitate, characterized as Na_2-1$\cdot$THF, was formed quantitatively. The IR spectrum of this precipitate as a KBr pellet or as a nujol mull showed carbonyl absorptions at 1742, 1590 and 1550 cm^{-1} (Figure 1). The absorption at 1742 corresponded directly to those for 1 in HMPA solutions and CS_2-1. But the bands at 1590 and 1550 cm^{-1} for Na_2-1$\cdot$THF from our reactions were considerably lower in energy than the absorptions for 1 in HMPA and for Cs_2-1. This splitting of the lower energy absorption for Cs_2-1 into two absorptions for Na_2-1$\cdot$THF was likely due to ion pairing of the sodium, but not the cesium, cations to the carbonyl oxygens of 1 [19]. This ion pairing reduces the expected [20] C_{3V} symmetry of 1, causing the lower energy E

Figure 1

Infrared Spectra of $Na_2(\eta^5C_5H_5)V(CO)_3$ THF



a) KBr Pellet

b) Nujol Mull

SCHEME I

A)
$$\begin{tikzcd}
\mathrm{CpV(CO)_4} + \mathrm{Na} \arrow[r, "\text{Liq. } \mathrm{NH_3}"] & \mathrm{CpV(CO)_3}^{2-} + 2\mathrm{Na} \arrow[d, "2\mathrm{CsI}"] \\
 & \mathrm{Cs_2CpV(CO)_3} + 2\mathrm{I}^{-}
\end{tikzcd}$$

B)
$$\mathrm{CpV(CO)_4} + \mathrm{Na} \xrightarrow{\text{HMPA}} \mathrm{CpV(CO)_3}^{2-} + 2\mathrm{Na}^{+}$$

C)
$$\mathrm{CpV(CO)_4} + \left\{\begin{matrix}\mathrm{Na/Hg} \\ \text{or} \\ \mathrm{Na}\end{matrix}\right\} \xrightarrow{\text{THF}} \mathrm{Na_2CpV(CO)_3}\cdot\mathrm{THF}$$

$\mathrm{Cp} = (\eta^5\mathrm{C_5H_5})$

band to split into two nondegenerate absorptions. The shift to lower energy for these absorptions in Na_2-1·THF compared to HMPA solutions of 1 was probably due to stronger ion pairing in the solid than in solution.

The NMR spectrum of Na_2-1·THF in HMPA showed a single cyclopentadienide absorption at δ4.32 PPM (s,5H) and absorptions for the methylene protons of THF. Integration of these signals indicated there was one molecule of THF for each cyclopentadienide molecule, and therefore the product from the sodium amalgam reduction in THF was actually the mono-solvated salt.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)_3]^+[\eta^5C_5H_5)V(CO)_3H]^-$ *from* $Na_2[\eta^5C_5H_5)V(CO)_3]$*·THF.* $[(C_6H_5)_3PNP(C_6H_5)_3]^+[(\eta^5C_5H_5)V(CO)_3H]^-$, PPN^+-3, was prepared from Na_2-1·THF by protonation of 1 with water [21], to generate a solution of Na-3. Exchange of PPN^+ for sodium cation and precipitation with petroleum ether led to the isolation of the air sensitive, red-brown solid, PPN^+-3.

The IR spectrum of PPN^+-3 showed carbonyl absorptions at 1890 and 1780 cm^{-1} as the THF, HMPA and acetonitrile solutions and as a nujol mull and a KBr pellet (Figure 2). The two carbonyl absorptions for 3 are consistent with either local C_{3V} symmetry for the vanadium tricarbonyl fragment with the hydride ligand located on the C_{3V} axis, or with a square pyramidal structure with the three carbon monoxide and the hydride ligands occupying the basal sites [Figure 3]. The two lower energy carbonyl absorptions predicted for the Cs symmetry structure are not resolved.

Figure 2

Infrared Spectrum of $(C_6H_5)_3PNP(C_6H_5)_3$ $[(\eta^5C_5H_5)V(CO)_3H]^-$ in THF

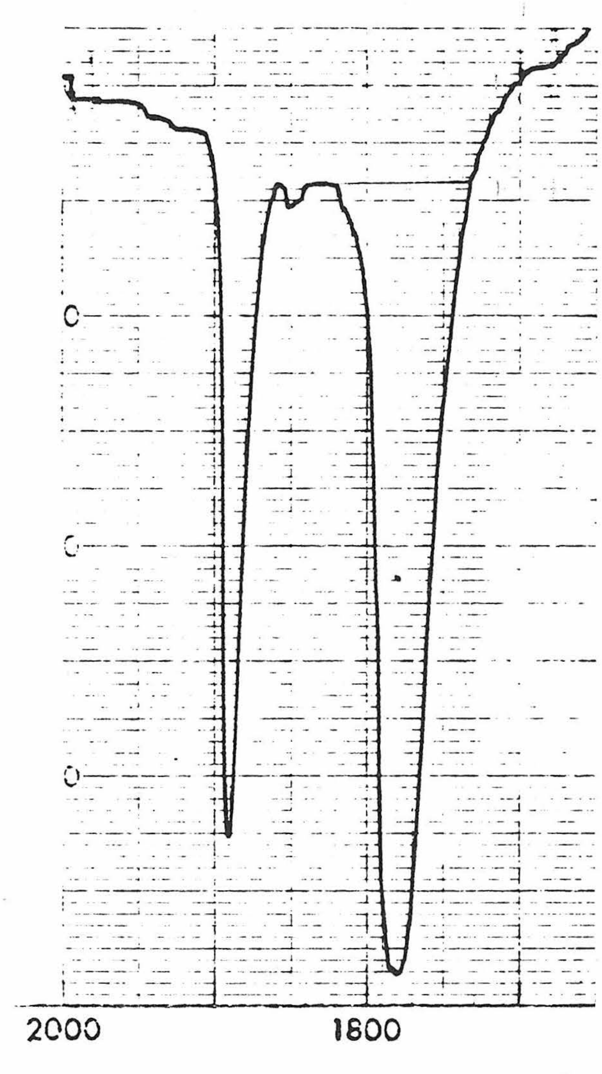


Figure 3

Possible Structures for $[(\eta^5C_5H_5)V(CO)_3H]^-$

C_{3v} C_s

It has been concluded, based on the width at half height of the lower energy carbonyl absorption in the IR spectrum, and on NMR spectral data, that the structure of $(\eta^5C_5H_5)W(CO)_3H$ is square pyramidal [22]. Analogously, the width at half height for the 1780 cm^{-1} absorption for 3 was great enough to conclude that this absorption could actually be two non-resolved bands. Also, other compounds with the $(\eta^5C_5H_5)V(CO)_3R$ formula, $(R=CH_3^-, P(C_6H_5)_3, P(n\text{-}C_4H_9)_3, Br^-, Cl^-)$ had three carbonyl stretches in their IR spectra, which indicated that these compounds had square pyramidal structures, and that it was therefore possible that 3 had a similar structure. Particularly interesting was the IR spectrum of $(\eta^5C_5H_5)V(CO)_3\ P(C_6H_5)_3$, which had three carbonyl absorptions in hexane but only two in THF.

However, other observations [23] about the site preference for hydride ligands in five coordinate complexes indicated that the hydride preferred to coordinate in an axial position compared with a basal position of a square pyramidal structure. Likewise, the ligand $Sn(C_6H_5)_3^-$ also showed a preference to coordinate in an axial position [23], and the complex $(\eta^5C_5H_5)V(CO)_3\ Sn(C_6H_5)_3^-$ contained only two carbonyl absorptions in its IR spectrum, consistent with a C_{3V} structure. It appeared then, that the IR spectra of 3 and $(\eta^5C_5H_5)V(CO)_3\ Sn(C_6H_5)_3^-$ were consistent with the observed preference for H^- and $Sn(C_6H_5)_3^-$ to coordinate in an axial position. Therefore, it was not possible to assign conclusively the structure of 3 from the IR data.

Single crystals of sufficient quality to carry out an x-ray crystallographic analysis of PPN^+-3 were not obtained. Though it was not likely that the exact position of the hydride ligand could have been determined, the positions of the carbon monoxide ligands may have distinguished between a C_{3V} or a Cs structure for 3.

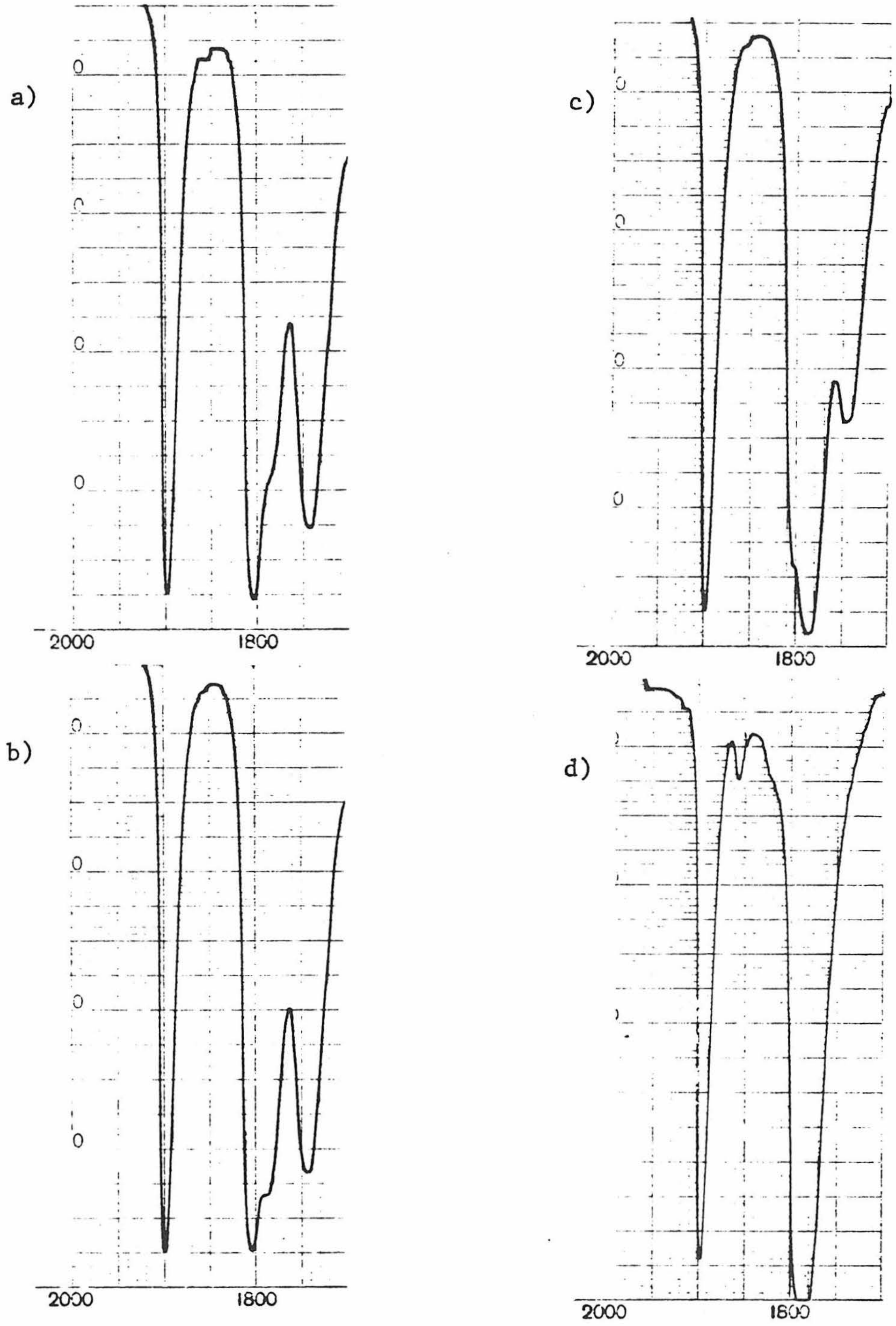
No IR absorption for the vanadium-hydrogen stretch was identified. The IR spectra of the KBr pellets of $PPN^+[(\eta^5C_5H_5)V(CO)_3D]^-$, PPN^+-3-D, and PPN^+-3 showed exactly the same absorptions between 4000 and 300 cm^{-1}.

The IR spectrum of solutions of Na-3 indicated significant ion pairing. When one equivalent of water was added to a slurry of Na_2-1·THF to produce Na-3, the IR spectrum of the solution showed carbonyl absorptions at 1890, 1795, 1780(sh) and 1735 cm^{-1}. The four carbonyl absorptions indicated more than one vanadium species in solution. The IR spectrum of this solution changed as limiting amounts of PPN^+Cl^- were added (Figure 4). The carbonyl absorptions at 1795 and 1735 cm^{-1} were reduced in intensity as the absorption at 1780 cm^{-1} increased. The IR spectrum of the final solution showed two carbonyl absorptions at 1890 and 1780 cm^{-1}, identical to the spectrum of isolated PPN^+-3 dissolved in THF.

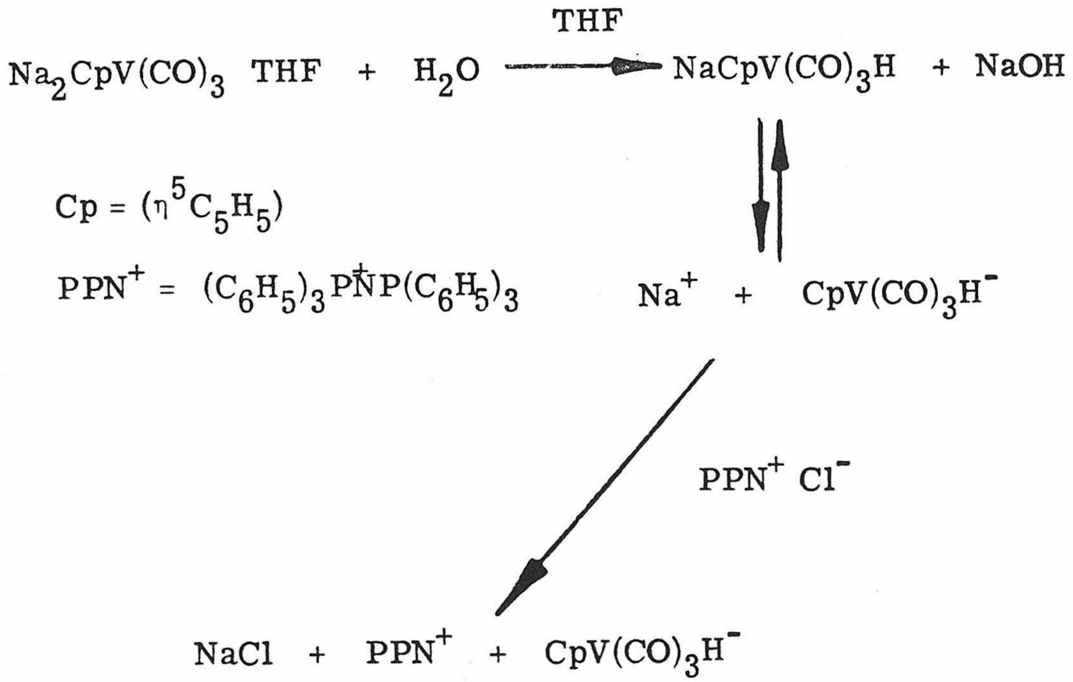
These changes in the IR spectrum of this solution are consistent with the reactions shown in Scheme II [24].

Figure 4

Addition of Limiting Amounts of PPN^+Cl^- to a Solution of $Na[(\eta^5C_5H_5)V(CO)_3H]$



SCHEME II



The carbonyl absorptions at 1890 and 1780 cm^{-1} in the IR spectrum of the solution of Na_2-1·THF and water, Figure 4a, by analogy to [24], corresponded to a solvent separated ion-pair of Na^+, and the bands at 1795 and 1735 cm^{-1} were from a more intimate ion-pair [24]. The intimate ion-paired species must also have had a carbonyl absorption at 1890 cm^{-1}, since the position and intensity of this absorption did not change in these IR spectra [25].

As PPN^+Cl^- was added, the sodium cation was irreversibly removed from solution as NaCl, and left only PPN^+ and 3, so that the IR spectrum was identical to isolated PPN^+-3 in THF (Figure 4d).

The NMR spectrum of PPN^+-3 in d_8-THF showed resonances at δ7.55 PPM (m,30H,PPN^+), δ4.60 PPM (s,5H,$\eta^5C_5H_5$) and δ-6.10 PPM (s,1H,hydride).

The resonance at δ-6.10 was very broad. The width at half-height was greater than one PPM at room temperature, but the signal sharpened to 0.43 PPM wide at half-height at -50°C (Figure 5). This temperature dependence for the hydride absorption was similar to that attributed to quadrupole coupling between vanadium nuclei and hydride ligands in other vanadium hydride complexes [26].

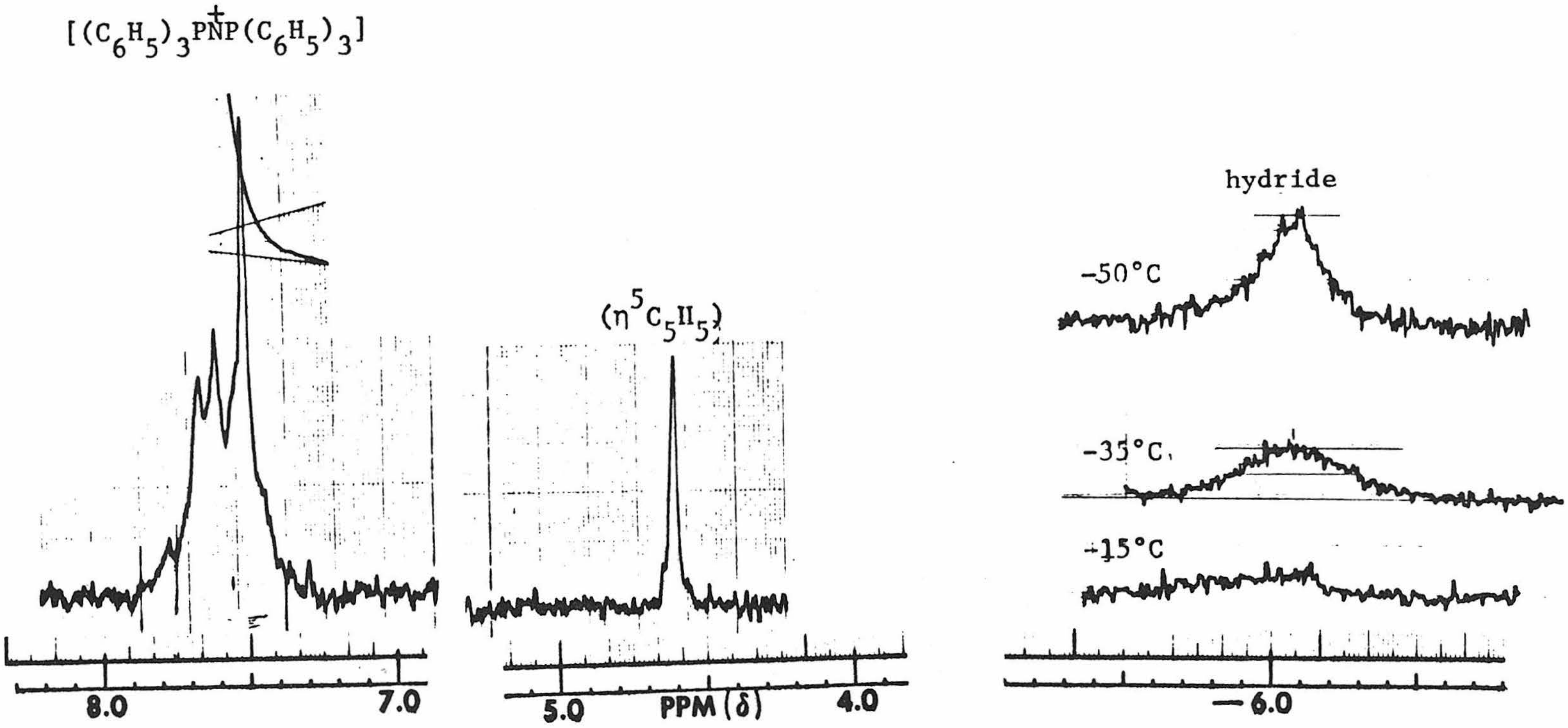
Reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl halides. Organic Products. The reactions of $[(\eta^5C_5H_5)V(CO)_3H]^-$, **3**, with alkyl halides proceeded with overall exchange of the halogen of the alkyl halide by the hydrogen of **3**, forming the corresponding alkane and the new vanadium complex, $PPN^+[(\eta^5C_5H_5)V(CO)_3Br]^-$, PPN^+-**4** (equation 1). The hydrogen in the alkane was shown to come exclusively from **3** by treating $[(\eta^5C_5H_5)V(CO)_3D]^-$ in h_8-THF and $[(\eta^5C_5H_5)V(CO)_3H]^-$ in d_8-THF with 1-bromooctane. Only $C_8H_{17}D$ and C_8H_{18} were observed, respectively (Scheme III).

$$(\eta^5C_5H_5)V(CO)_3H^- + RBr \longrightarrow (\eta^5C_5H_5)V(CO)_3Br^- + R\text{-}H \qquad (1)$$

THF solutions of PPN^+-**3** at room temperature reacted with equimolar quantities of primary, secondary and tertiary alkyl bromides, vinyl and aryl bromides and gem-dibromocyclopropanes. Reaction times, products and yields for individual reactions of alkyl chlorides, bromides and iodides are shown in Table I. The order of reactivity was iodides > bromides > chlorides, with only the most reactive chlorides, such as benzyl chloride, reacting at room temperature.

Figure 5

NMR Spectrum of $[(C_6H_5)_3\overset{+}{P}NP(C_6H_5)_3]$ $[(\eta^5C_5H_5)V(CO)_3H]^-$



SCHEME III

$$CpV(CO)_3H^- \quad + \quad n\text{-}C_8H_{17}Br \xrightarrow{d_8\text{-THF}} CpV(CO)_3Br^- \quad + \quad C_8H_{18}$$

$$CpV(CO)_3D^- \quad + \quad n\text{-}C_8H_{17}Br \xrightarrow{h_8\text{-THF}} Cp(CO)_3Br^- \quad + \quad C_8H_{17}D$$

TABLE I

Reactions of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ with Organic Substrates in THF(a)

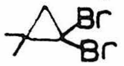
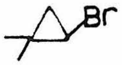
Substrate	Product	Reaction Time (hours)	Yield (%)(b)
n-$C_8H_{17}I$	n-C_8H_{18}	0.5	94
n-$C_8H_{17}Br$	n-C_8H_{18}	4.0	75
n-$C_8H_{17}Cl$	No reaction	1.5 (50°C)	-
n-$C_6H_{13}Br$	n-C_6H_{14}	7.0	73
Cyclo-$C_6H_{11}Br$	Cyclo-C_6H_{12}(c)	10.0	65
		0.5	95
	No reaction	24.0	-
$(CH_3)_3CBr$	$(CH_3)_3CH$(d)	12.0	100
$C_6H_5CH_2Br$	$C_6H_5CH_3$	< 0.5	90
$C_6H_5CH_2Cl$	$C_6H_5CH_3$	1.5	(e)
$C_6H_5CH{=}CHBr$	$C_6H_5CH{=}CH_2$	5.0	46(f)
C_6H_5Br	C_6H_6	8.5	43
$C_6H_{13}COCl$	$C_6H_{13}CHO$	< 0.1	100(g)
C_6H_5COCl	C_6H_5CHO	< 0.1	40(36)(h)

TABLE I (continued)

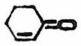
Substrate	Product	Reaction Time (hours)	Yield (%)(b)
$C_{11}H_{23}COCl$	$C_{11}H_{23}CHO$	< 0.1	(7)(i)
	- (j)	-	-
$CH_3O\overset{O}{\overset{\parallel}{C}}CH_2CH_2COCl$	$CH_3O\overset{O}{\overset{\parallel}{C}}CH_2CH_2CHO$(k)	-	-
$C_6H_5CH{=}CHCOCl$	-(ℓ)	-	-
$C_6H_5CH_2COCl$	$C_6H_5CH_2CHO$(m)	-	-
$C_4H_9CHBrCH_2Br$	$C_4H_9CH\ CH_2$(n)	2.0	99
d,ℓ-$C_2H_5CHBrCHBrC_2H_5$(o,p)	cis-$C_2H_5CH{=}CHC_2H_5$	1.0	(97)(r)
meso-$C_2H_5CHBrCHBrC_2H_5$(o,q)	trans-$C_2H_5CH{=}CHC_2H_5$	1.0	(99)(r)
1-Bromo-Adamantane	Adamantane	5.0(70°C)	60(s)
(-)$C_6H_5\overset{Br}{\overset{\mid}{C}}HCH_3$ (t)	(±)-$C_6H_5CH(D)CH_3$	0.25	64(u)
	 	17.5	99 (87)(v) (13)
	No reaction	1.0	-
$C_6H_{13}\overset{O}{\overset{\parallel}{C}}OCH_3$	No reaction	12.0	-
n-$C_7H_{15}O\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-(C_6H_4)CH_3$	n-C_7H_{16}	6.0(60°)	47

TABLE I (continued)

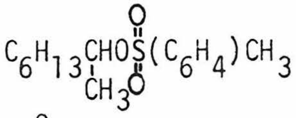
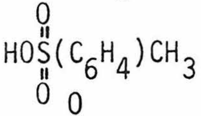
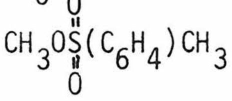
Substrate	Product	Reaction Time (hours)	Yield (%)[(b)]
 $C_6H_{13}\underset{CH_3}{CH}O\overset{O}{\underset{O}{S}}(C_6H_4)CH_3$	No reaction	36.0	-
 $HO\overset{O}{\underset{O}{S}}(C_6H_4)CH_3$	H_2(w)	-	-
 $CH_3O\overset{O}{\underset{O}{S}}(C_6H_4)CH_3$	CH_4(x)	-	-

TABLE I (continued)

(a) All reactions were carried out with equimolar quantities of $\mathrm{PPN^+}$-3 and organic substrates at 25°C unless stated otherwise.

(b) Yields were determined by gas chromatographic analysis peak area integration, or NMR integration unless otherwise noted.

(c) No cyclohexene could be detected by gas chromatography.

(d) No isobutene could be detected by NMR.

(e) Reaction monitored by NMR spectra to approximately one half-life.

(f) When cis-β-bromostyrene was reacted with $\mathrm{PPN^+}$-3D and the organic products vacuum transferred from the reaction mixture, the styrene obtained was 70% cis and 30% trans by NMR integration.

(g) Volatile material vacuum transferred from reaction mixture immediately after addition of acid chloride.

(h) The product was isolated as the 1,2-dianilinoethane adduct.

(i) Isolated as the 2,4-dinitrophenylhydrazine adduct.

(j) An immediate reaction occurred with $\mathrm{PPN^+}$-3, but no absorption for any aldehydes were observed in the IR spectrum.

(k) Product identified only by aldehyde NMR signal at δ9.85 PPM.

(ℓ) No aldehyde signal present in the IR spectrum of the reaction mixture.

(m) The product was identified by the IR spectrum of the reaction solution only. The aldehyde carbonyl absorption was no longer present in the IR spectrum 2 hours after the reaction.

(n) No hexane or monobromohexanes were formed as indicated by gas chromatographic analysis. The reaction was carried out with a molar ratio of $\mathrm{PPN^+}$-3 to $\mathrm{C_4H_9CHBrCH_2Br}$ of 2.6:1.

(o) The dibromides were analyzed by gas chromatography on a 10% DEGS chrom PNAW 10' x 3/8" glass column.

(p) Greater than 97% d,ℓ isomer. $\mathrm{PPN^+}$-3:dibromide; > 2:1.

(q) Greater than 99% meso isomer. $\mathrm{PPN^+}$-3:dibromide; 2.9:1.

(r) The hexenes were analyzed on a $\mathrm{AgNO_3}$, chromsorb P column. Relative yield of the given isomer. The total yield was not calculated. See reaction of 1,2-dibromohexane.

(s) Product isolated as an impure oil.

(t) 75% optically pure. $\mathrm{PPN^+[(\eta^5C_5H_5)V(CO)_3D]^-}$ was used in this reaction.

(u) Product isolated by preparative gas chromatography.

(v) This was the ratio at the end of the reaction. The ratio varies during the reaction.

(w) Assumed product.

(x) Identified by NMR.

It should be noted that alkyl-p-toluenesulfonates reacted much more slowly than the corresponding bromides. Also, the reactions of 3 with secondary and tertiary bromides showed no elimination products. The reactions of 3 with vinyl and aryl bromides and the gem-dibromocyclopropane were particularly noteworthy, since simple nucleophilic displacements do not usually occur readily at these carbon centers.

Reactions of $[(\eta^5C_5H_5)V(CO)_3H]^-$ with acyl chlorides. The reactions of PPN^+-3 with aliphatic acyl chlorides were instantaneous, and again led to exchange of halogen and hydrogen atoms, to yield the corresponding aldehydes and the new vanadium complex, $PPN^+[(\eta^5C_5H_5)V(CO)_3Cl]^-$, PPN^+-5 (equation 2). The aldehydes were identified by IR and NMR spectroscopy and by gas chromatography. No over reduction of the aldehydes to the alcohols was observed.

$$(\eta^5C_5H_5)V(CO)_3H^- + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow (\eta^5C_5H_5)V(CO)_3Cl^- + R-\overset{O}{\overset{\|}{C}}-H \qquad (2)$$

The reaction of 3 with heptanoyl chloride was shown to be quantitative by gas chromatographic analysis of the volatile fraction of the reaction solution. However, the aldehydes were not stable to the final reaction solution. In the reaction of 3 with phenylacetyl chloride, the carbonyl absorption in the IR spectrum for phenylacetaldehyde was gone two hours after the initial reaction was complete. Dodecanal persisted in the final reaction solution for over 6.5 hours, though the carbonyl absorption in the IR spectrum decreased in intensity over that period.

Because of this limited stability of the aldehydes in the final reaction mixture, and the presence of the unstable metal complex, 4, no satisfactory, general procedure for isolating the product aldehydes has been developed. Methods investigated for isolation of the aldehydes from these reactions included direct vacuum transfer of volatile aldehydes from the reaction solution, separation of vanadium and organic products respectively into aqueous and organic phases, column chromatography of the reaction solution, and precipitation of the vanadium products from the reaction solution and subsequent formation of aldehyde derivatives.

The best yield of isolated aldehydes was a 32% yield of 1,2,3-triphenyltetrahydroimidazole from the reaction of $\underset{\sim}{3}$ with benzoyl chloride. 1,2-dianilinoethane was added to the reaction after precipitation of PPN^+-$\underset{\sim}{4}$.

The IR spectra of the reaction solutions of p-nitrobenzoylchloride and cinnamoyl chloride with $\underset{\sim}{3}$ showed no aldehyde carbonyl absorptions. 3-carbomethoxypropanol was formed from the corresponding acid chloride, as evidenced by the aldehyde proton resonance in the NMR spectrum of the reaction solution.

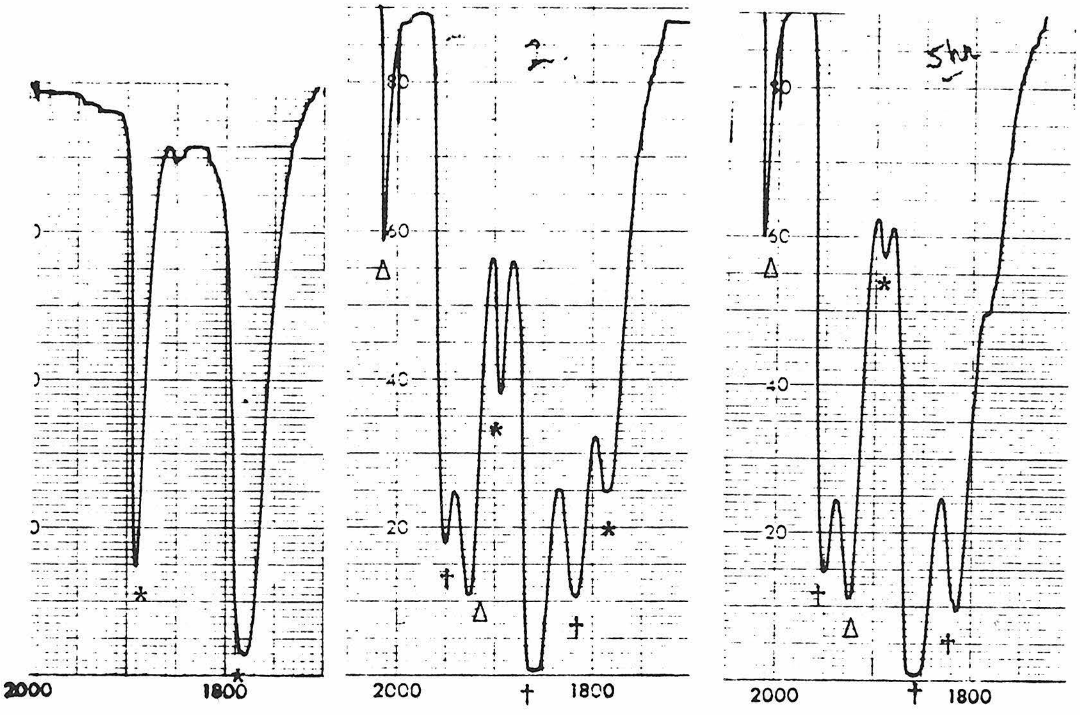
Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl halides. Organometallic Products. Treatment of $\underset{\sim}{3}$ with an equimolar amount of 1-bromohexane gave a solution whose IR spectrum showed new carbonyl absorptions at 2030, 1945, 1930, 1850 and 1810 cm^{-1} (Figure 6). The absorptions at 2030 and 1930 cm^{-1} corresponded to $(\eta^5C_5H_5)V(CO)_4$ [27], and the bands at 1945, 1850 and 1810 cm^{-1} were from the new, air sensitive vanadium carbonyl compound, $PPN^+[(\eta^5C_5H_5)V(CO)_3Br]^-$, PPN^+-$\underset{\sim}{4}$ (Scheme IV).

PPN^+-$\underset{\sim}{4}$ was identified as a product of the reactions of $\underset{\sim}{3}$ and alkyl bromides by a comparison of the carbonyl absorptions and NMR

Figure 6

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ and n-C_6H_{13}-Br

Infrared Spectra



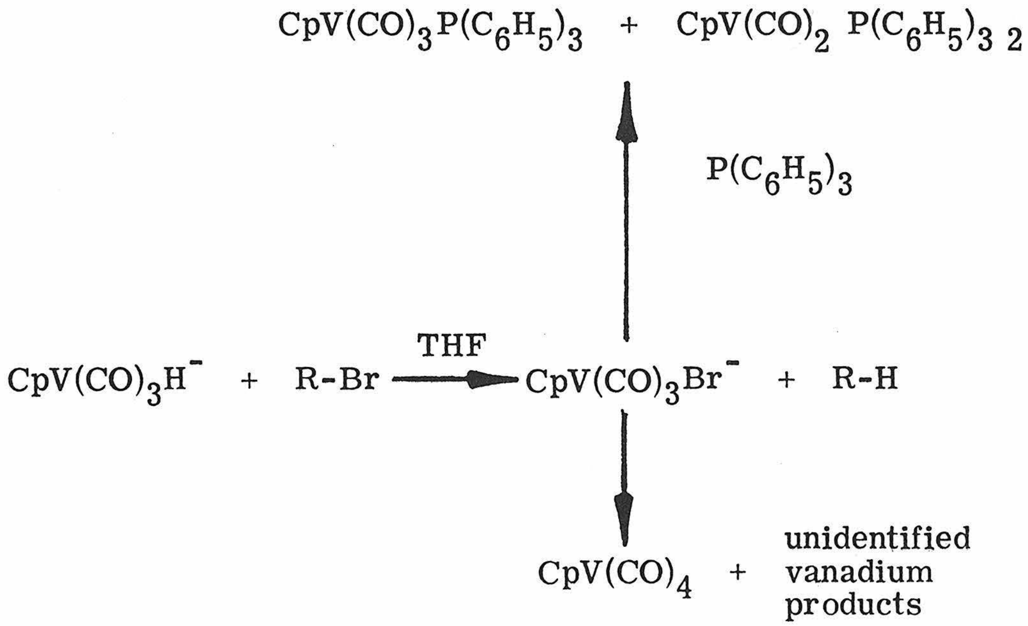
a) Start b) 2 Hours c) 5 Hours

* $[(\eta^5C_5H_5)V(CO)_3H]^-$

† $[(\eta^5C_5H_5)V(CO)_3Br]^-$

Δ $[(\eta^5C_5H_5)V(CO)_4$

SCHEME IV


$CpV(CO)_3P(C_6H_5)_3$ + $CpV(CO)_2\ P(C_6H_5)_{3\ 2}$
$P(C_6H_5)_3$
$CpV(CO)_3H^-$ + R-Br
THF
$CpV(CO)_3Br^-$ + R-H
$CpV(CO)_4$ + unidentified vanadium products

cyclopentadienide resonance of PPN$^+$-**4** which was isolated from the photolyses of PPN$^+$Br$^-$ and $(\eta^5C_5H_5)V(CO)_4$ [28]. The green solid isolated from the photolysis reaction was characterized by elemental analysis.

PPN$^+$-**4** was unstable in solution and decomposed, giving a low yield of $(\eta^5C_5H_5)V(CO)_4$, **2**, as the only identifiable vanadium carbonyl product (Scheme IV). This accounted for the detection of **2** in the reaction solutions of **3** and alkyl bromides.

The NMR spectra of the reaction solution of **3** and a molar excess of 1-bromooctane showed two new cyclopentadienide resonances, one at δ4.76 PPM, which corresponded to PPN$^+$-**4**, and the other at δ4.67 PPM (Figure 7). The NMR spectrum indicated there were actually two vanadium cyclopentadienide products, whereas the carbonyl absorptions in the IR spectrum of the reaction solutions appeared to be accounted for by PPN$^+$**4** only.

When all of **3** had reacted, the absorption at δ4.67 PPM decreased in intensity, and the absorption for **4** at δ4.76 PPM increased in intensity. The second vanadium product was converted into PPN$^+$-**4** in the presence of excess 1-bromooctane.

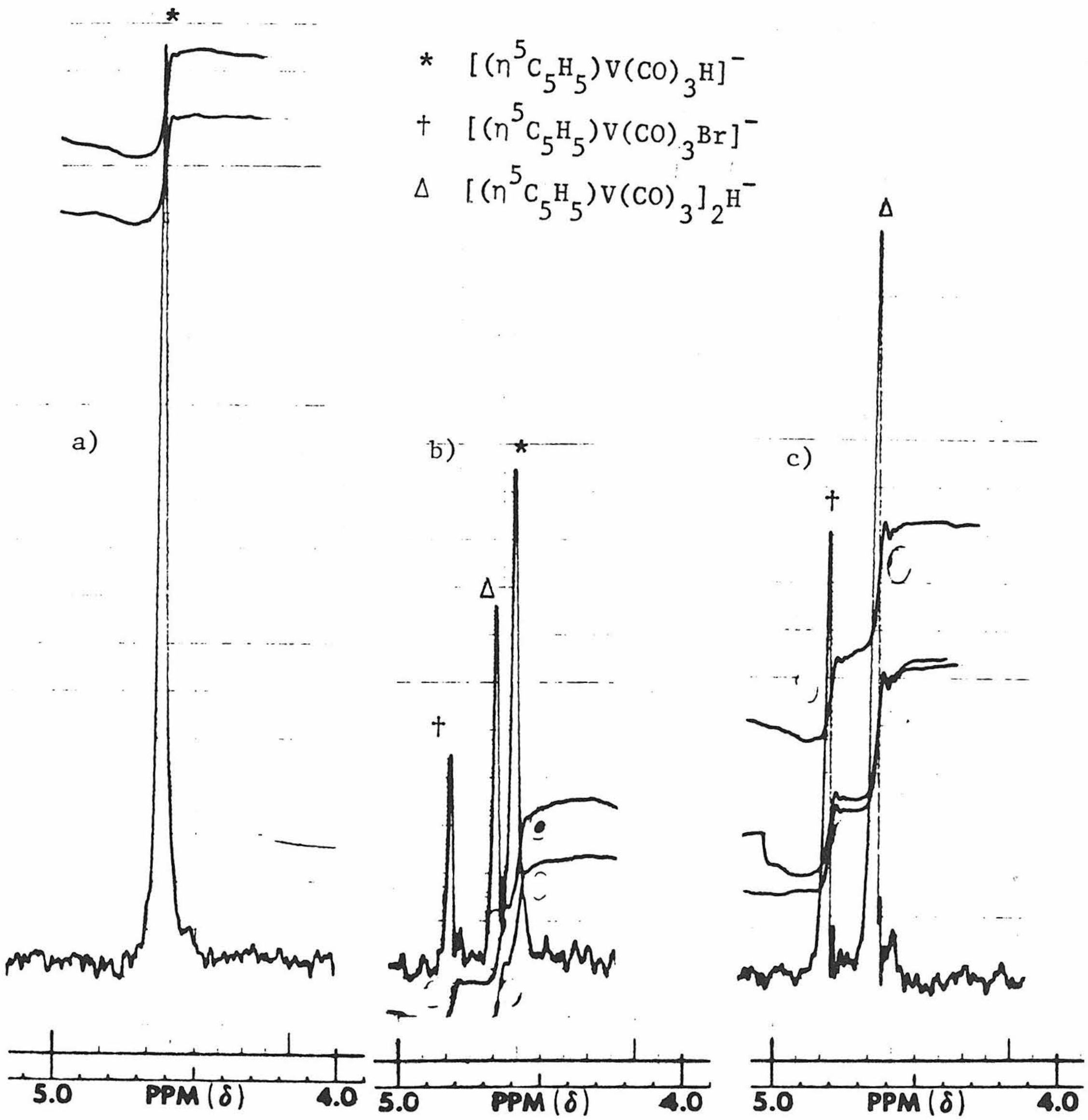
The vanadium carbonyl compound responsible for the δ4.67 PPM cyclopentadienide resonance was not isolated as the pure material. IR and NMR spectroscopic data, and the preparation of this compound in solution by other reactions [29], indicated that it was the vanadium hydride bridged dimer, $[(\eta^5C_5H_5)V(CO)_3]_2H^-$, **6** [30].

The IR spectrum of solutions containing **6**, but not **4**, showed carbonyl absorptions at 1857 and 1817 cm^{-1}. The bands overlapped the carbonyl absorptions for 4. This explained the presence of only three

Figure 7

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ and $n\text{-}C_8H_{17}\text{-}Br$

NMR Spectra



carbonyl absorptions in the IR spectra of the reaction solutions of 3 and alkyl bromides.

The IR spectrum of 6 was obtained by reacting 3 with one-half equivalent of 1-bromooctane. When all of the 1-bromooctane had reacted, the NMR spectrum showed cyclopentadienide resonances at δ4.76 PPM from 4, δ4.67 PPM from 6, and at δ4.60 PPM from 3 (Figure 8). In the presence of excess 3 and the absence of alkyl bromide, 6 was not converted to 4. After 18.5 hours 4 had decomposed to give a solution with cyclopentadienide resonances for 6, 3, and 2. The IR spectrum of this solution showed carbonyl absorptions at 2030 and 1930 cm^{-1} which corresponded to 2 and at 1890 and 1780 cm^{-1} from 3. The additional carbonyl absorptions at 1857 and 1817 cm^{-1} were due to 6 in the solution. Two carbonyl bands would be consistent with either D_{3h} or D_{3d} symmetry for the carbonyl ligands in 6.

No NMR signal for the bridging hydride ligand of 6 was observed at room temperature. This was probably the result of quadrupole coupling from the vanadium nuclei [26].

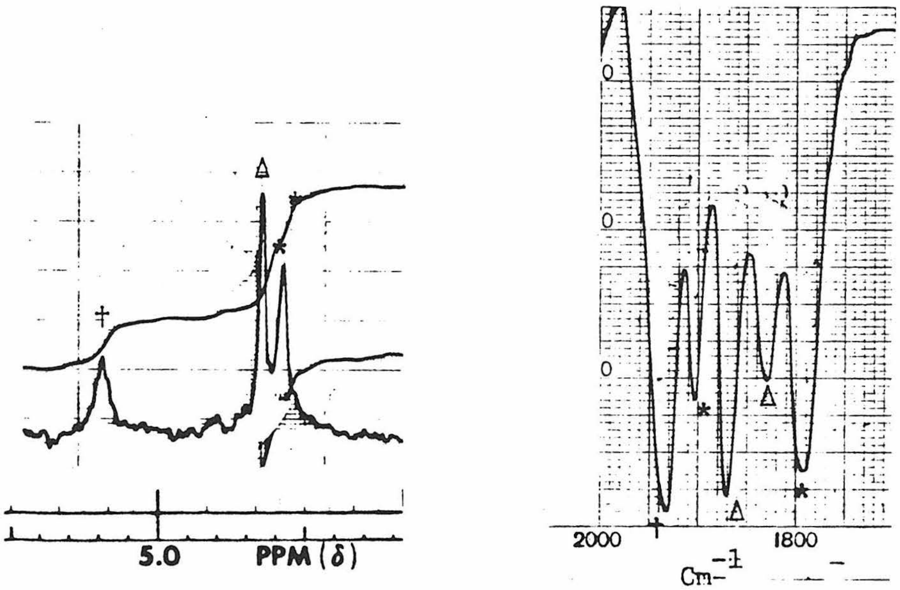
Solutions of 6, without 4, were also generated from the reactions of 3 with p-toluenesulfonic acid, galvinoxyl radical and silver (I). The IR and NMR spectra of these reaction solutions corresponded to those for 6 formed by the reaction of 3 with alkyl bromides.

Additional support for the formulation of 6 as a hydride bridged vanadium dimer came from the reaction of 3 with p-toluenesulfonic acid. In this reaction only one-half molar equivalent of acid was required to react with one molar equivalent of 3. Since 6 was the only cyclopentadienide containing product of this reaction, it must have contained the

Figure 8

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ and one-half equivalent of $n\text{-}C_8H_{17}\text{-}Br$

NMR and Infrared Spectra



* $[(\eta^5C_5H_5)V(CO)_3H]^-$

Δ $[(\eta^5C_5H_5)V(CO)_3]_2H^-$

† $[(\eta^5C_5H_5)V(CO)_4$

elements of the coordinatively unsaturated vanadium species $(\eta^5C_5H_5)V(CO)_3$, 7, [27] and 3. It was assumed that 7 was the initial product of 3 and p-toluenesulfonic acid, since the other product was hydrogen gas [28]. 6 would then have been formed by the reaction of 7 and 3 (Scheme V). The observation that 3 was regenerated when 6 decomposed was also consistent with 6 containing the molecular fragment, 3.

When 3 was added slowly to a solution of p-toluenesulfonic acid and a large molar excess of triphenylphosphine, no 6 was observed in the reaction solution. Only $(\eta^5C_5H_5)V(CO)_3\ P(C_6H_5)_3$ [31] was produced, as indicated by the IR spectrum of the reaction solution.

6 was also formed from the reaction of 4 and 3, by the formal displacement of bromide ion of 4 by 3 (Scheme V).

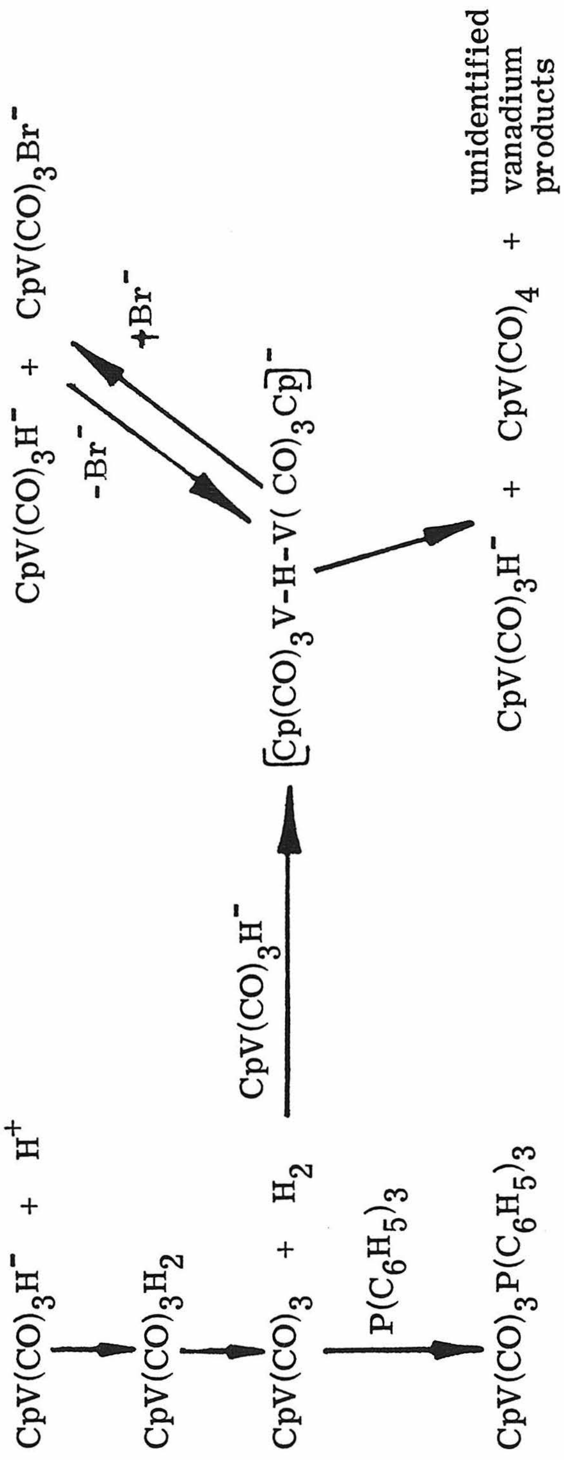
Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl bromides. Mechanistic considerations.

Organic intermediates. The similarity of the rates of reaction of $(\eta^5C_5H_5)V(CO)_3H^-$, 3, with primary, secondary, and tertiary bromides, and the reaction of 3 with vinyl and aryl bromides suggested that these reactions proceeded through carbon radicals.

Schemes VIA and VIB show possible mechanisms for carbon radical formation in these reactions. In scheme VIA carbon radicals are formed by a radical chain similar to the mechanism of the reactions of tin hydrides with alkyl halides [32]. Carbon radical formation in Scheme VIB occurs by electron transfer, analogous to the reactions of one electron reducing agent with alkyl halides [33].

The rapid reaction of 3 with gem-dibromocyclopropane also suggested the presence of carbon radicals in these reactions. The absence

SCHEME V


CpV(CO)3H- + H+
CpV(CO)3H2
CpV(CO)3 + H2
P(C6H5)3
CpV(CO)3P(C6H5)3
CpV(CO)3H-
[Cp(CO)3V-H-V(CO)3Cp]-
CpV(CO)3H- + CpV(CO)3Br-
-Br-
+Br-
CpV(CO)3H- + CpV(CO)4 + unidentified vanadium products

SCHEME VI

A) Radical Chain

$$CpV(CO)_3H^- + In^\cdot \longrightarrow Cpv(CO)_3^{\dot{-}} + InH$$

$$CpV(CO)_3^{\dot{-}} + R\text{-}Br \longrightarrow CpV(CO)_3Br^- + R^\cdot$$

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

B) Electron Transfer

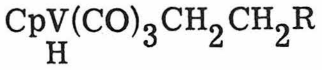
$$CpV(CO)_3H^- + R\text{-}Br \longrightarrow CpV(CO)_3H^\cdot + R^\cdot + Br^-$$

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

$$\begin{aligned} CpV(CO)_3 \; &+ Br^- \longrightarrow CpV(CO)_3Br^- \\ &+ (L) \longrightarrow (CpV(CO)_3L) \end{aligned}$$

C) Nucleophilic Displacement

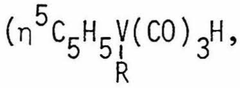
$$CpV(CO)_3H^- + R\text{-}CH_2CH_2\text{-}Br \longrightarrow$$



$$Cp\underset{H}{V}(CO)_3CH_2CH_2R$$

$$CpV(CO)_3CH_2CH_2R \begin{cases} \longrightarrow CpV(CO)_3 + R\text{-}H \\ \longrightarrow CpV(CO)_3H_2 + R\text{-}CH{=}CH_2 \end{cases}$$

$Cp = (\eta^5C_5H_5)$

of alkene products from the reactions of 3 and alkyl bromides (even tertiary bromides) suggested that a vanadium alkyl complex,  $(\eta^5C_5H_5\underset{R}{V}(CO)_3H$, was not an intermediate. Such a complex could be expected to undergo β-elimination, if R contained β hydrogens, to yield alkenes or reductive elimination to yield alkanes (Scheme VIC).

The formation of carbon radicals in the reactions of 3 with alkyl bromides was also supported by the products of the reactions of 3 with vicinal dibromides and 6-bromo-1-hexene, and the reaction of $(\eta^5C_5H_5)$-$V(CO)_3D^-$, 3-D, with (-)-1-phenylethylbromide.

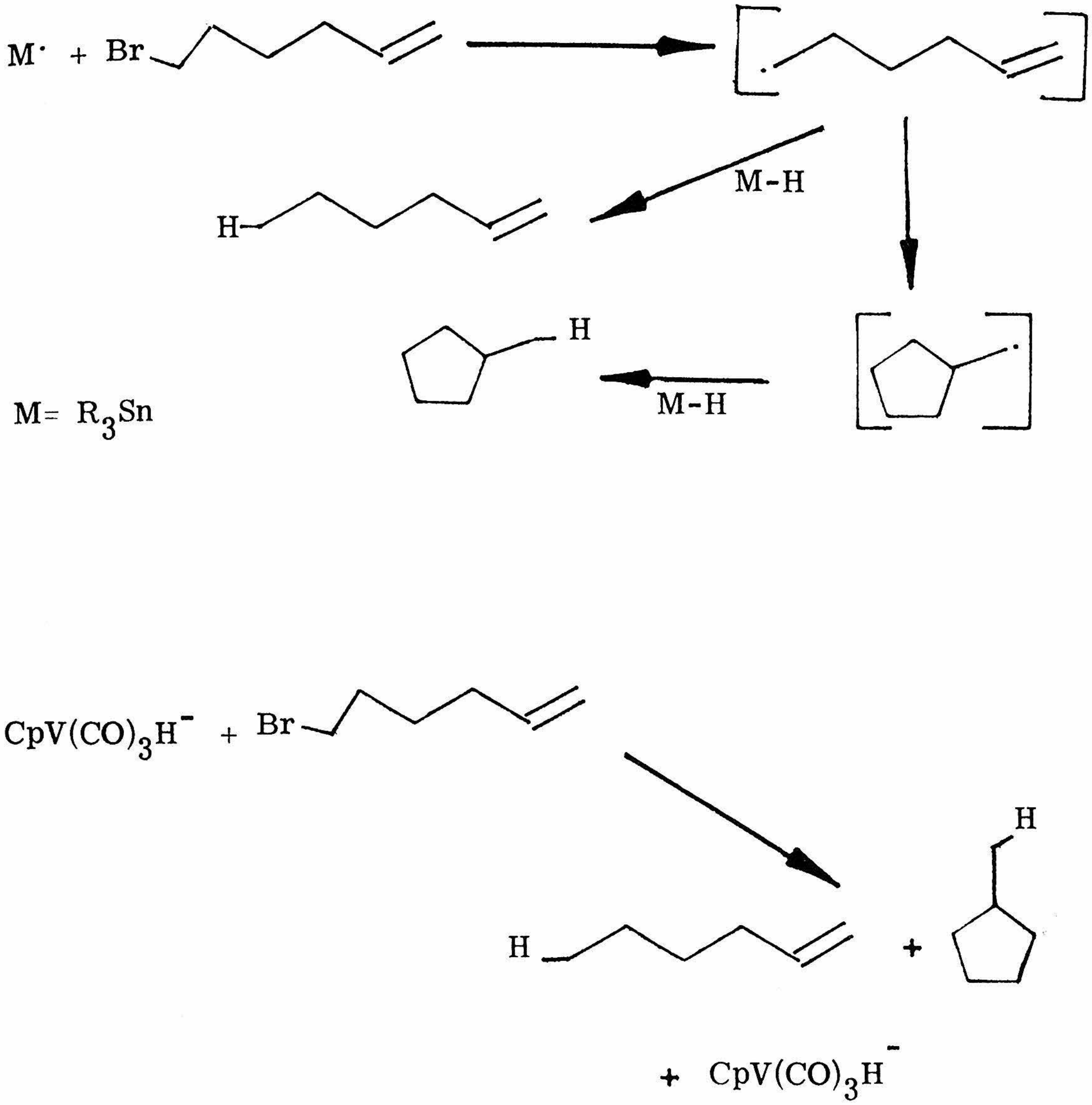
The reactions of chromous ion [33] and tin hydrides [32] with vicinal dibromides, which have been shown to proceed by halogen atom abstraction and carbon radical formation, produce the corresponding alkenes. Likewise, the reaction of 3 with 1,2-dibromohexane and meso- and d,ℓ-3,4-dibromohexane gave only alkene products (Table I).

The formation of the 5-hexenyl radical from 6-bromo-1-hexene by halogen atom abstraction with tin hydride led to the formation of both 1-hexene and methylcyclopentane [34]. When 3 was reacted with 6-bromo-1-hexene, both 1-hexene and methylcyclopentane were produced, indicating that the 5-hexenyl radical was formed in the reaction (Scheme VII).

The reaction of 3-D with (-)-1-phenlethyl bromide produced completely racemized α-deuterioethylbenzene, indicating the presence of a planear carbon intermediate. This intermediate was most likely the carbon radical [35].

The evidence for formation of carbon radicals in these reactions is consistent with Schemes VIA or VIB, but not with Scheme VIC.

SCHEME VII



Organometallic intermediates. The important differences between the mechanisms outlined in Scheme VIA and VIB are the initial reactions between **3** and alkyl bromides, leading to formation of carbon radicals, and the formation of the coordinatively unsaturated vanadium intermediate, $(\eta^5C_5H_5)V(CO)_3$, **7**, formed only in Scheme VIB. The direct electron transfer mechanism, Scheme VIB, causes homolytic cleavage of the carbon halogen bond. The carbon radical formed abstracts a hydrogen atom from the oxidized species, $(\eta^5C_5H_5)V(CO)_3H^{\dot{-}}$, to yield the alkane and the coordinatively unsaturated species **7**. If this coordinatively unsaturated species is generated in the reactions of **3** and alkyl bromides, then in the presence of some added ligand, L, $(\eta^5C_5H_5)V(CO)_3L$ [28] would be expected as one of the vanadium products.

The radical chain mechanism, Scheme VIA, which is analogous to the mechanism established for the reduction of alkyl bromides with tin hydrides [32],is initiated by hydrogen atom abstraction from **3**. The vanadium radical, $C_pV(CO)_3^{\dot{-}}$, possibly formed by a small amount of some initiator always present in the reactions, abstracts a halogen atom, leaving a carbon radical to carry the chain by abstracting a hydrogen atom from a second molecule of **3**. In this sequence of reactions the halogen atom is transferred directly into the coordination sphere of vanadium and the coordinatively unsaturated species, **7**, is not formed. Therefore, in contrast to the electron transfer mechanism, Scheme VIB, the radical chain mechanism of Scheme VIA predicts that if the reaction of **3** and alkyl bromides is carried out in the presence of an added ligand, L, the initial organometallic product would still be only $(\eta^5C_5H_5)V(CO)_3Br^-$, **4**.

The initial organometallic product of the reaction of 3 with benzyl bromide, with a five-fold molar excess of triphenylphosphine added, was 4. No $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$, 8 was detected by IR analysis of the reaction solution immediately after benzylbromide was added to a THF solution of 3. 8 was thermodynamically more stable than 4, and the triphenylphosphine displaced the bromide ion of 4 after a few hours.

The photolysis of 2 in the presence of triphenylphosphine and PPN^+Br^- [28] gave mostly 8 with only a small amount of 4 [29]. The reaction of 3 with p-toluenesulfonic acid in the presence of triphenylphosphine and lithium bromide produced only 8. 4 was produced in the reaction of 3 and p-toluenesulfonic acid, with only lithium bromide added, confirming that bromide ion can trap 7 in the absence of triphenylphosphine.

The intermediate vanadium complex formed in the photolysis of 2 [28] and in the reaction of 3 with acid [27] reacted more rapidly with triphenylphosphine to form 8 than with bromide ion to form 4. But the reaction of 3 and benzylbromide with triphenylphosphine added produced only 4, initially.

Therefore, the same vanadium intermediate was not formed in all of these reactions. It was concluded that the coordinatively unsaturated species, 7, was not formed in the reaction of 3 and benzyl bromide, since it was more likely to be the intermediate in the photolysis [28] of 2 and the reaction of 3 with acid [27].

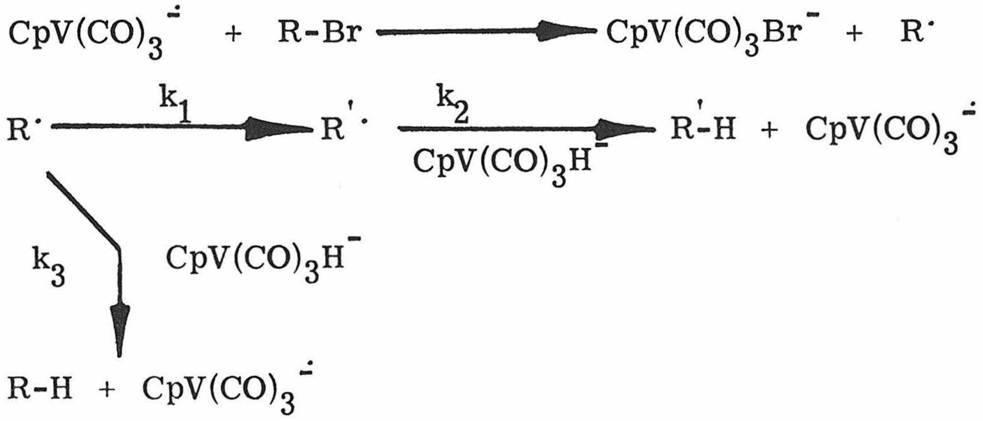
The specific formation of 4 in the reaction of 3 with benzyl bromide, and the absence of the coordinatively unsaturated species, 7, in this reaction is consistent with the radical chain mechanism, Scheme VIA, but not with Scheme VIB.

Further attempts to demonstrate the radical chain nature of these reactions by inhibition or initiation of the radical chain were not successful. The rate of disappearance of 3 in the reaction with 1-bromooctane did not change when the reaction was carried out in the presence of duroquinone or 2,4,6-tri-t-butyl phenol, nor when the reaction mixture was photolyzed with ultraviolet light in the presence or absence of azobisisobutyronitrile (AIBN).

Additional evidence for a radical chain mechanism might also be obtained from the rearrangement of an appropriate carbon radical. Consideration of the radical chain mechanism, Scheme VIA, showed that if radical $R^{\cdot}$ could rearrange to $R'^{\cdot}$ before hydrogen atom abstraction from 3, then the ratio of non-rearranged to rearranged product (R—H/R'—H) would be a linear function of the initial concentration of 3 (if that concentration does not change significantly during a reaction, Scheme VIII). A plot of R—H/R'—H vs. the initial concentration of 3 should have a slope of the rate constant ratio k_3/k_1.

The reactions of 3 and 6-bromo-1 hexene, with varying initial concentrations of 3, did not show a measurable variation in the ratio of 1-hexene and methylcyclopentane. The rate of cyclization of 5-hexenyl radical [34b] was so slow compared with the hydrogen atom abstraction from $(\eta^5C_5H_5)V(CO)_3H^-$ [36] that only a small amount of

SCHEME VIII



$$\mathrm{CpV(CO)_3}^{\dot{-}} + \mathrm{R\text{-}Br} \longrightarrow \mathrm{CpV(CO)_3Br^-} + \mathrm{R^{\cdot}}$$

$$\mathrm{R^{\cdot}} \xrightarrow{k_1} \mathrm{R'^{\cdot}} \xrightarrow[\mathrm{CpV(CO)_3H^-}]{k_2} \mathrm{R'\text{-}H} + \mathrm{CpV(CO)_3}^{\dot{-}}$$

$$\mathrm{R^{\cdot}} \xrightarrow[\mathrm{CpV(CO)_3H^-}]{k_3} \mathrm{R\text{-}H} + \mathrm{CpV(CO)_3}^{\dot{-}}$$

$$\frac{d[\mathrm{R\text{-}H}]}{dt} = k_3[\mathrm{R^{\cdot}}][\mathrm{CpV(CO)_3H^-}] \qquad \frac{d[\mathrm{R'\text{-}H}]}{dt} = k_1[\mathrm{R^{\cdot}}]$$

$$\frac{d[\mathrm{R\text{-}H}]}{d[\mathrm{R'\text{-}H}]} = \frac{k_3[\mathrm{CpV(CO)_3H^-}]}{k_1} \quad ; \quad \frac{[\mathrm{R\text{-}H}]}{[\mathrm{R'\text{-}H}]} = \frac{k_3[\mathrm{CpV(CO)_3H^-}]}{k_1}$$

methycyclopentane was formed. Small changes in the already small quantity of methycyclopentane produced could not be accurately measured.

However, the observed decrease in the 1-hexene to methylcyclopentane ratio during a single reaction was consistent with Scheme VIII. As the concentration of $(\eta^5C_5H_5)V(CO)_3H^-$ decreased during the reaction, the rate of bimolecular hydrogen abstraction by the non-rearranged, 5-hexenyl radical decreased relative to the unimolecular rearrangement, allowing more rearranged cyclopentymethyl radical to form. Therefore the total percentage of rearranged product, methylcyclopentane, increased as the reaction proceeded (Table II).

A carbon radical with a rearrangement rate faster than that of the 5-hexenyl radical is required to demonstrate conclusively the linear dependence of the non-rearranged to rearranged product ratio of the initial concentration of 3 [37].

Even though the rate of the reaction of 3 with alkyl bromides was not affected by radical inhibitors or initiators, the formation of carbon radicals and the absence of the coordinatively unsaturated vanadium carbonyl species, 7, in these reactions are best described by the radical chain mechanism, Scheme VIA.

The failure of radical initiators and inhibitors to affect the rate of these reactions implies that the proposed radical chain process must be very efficient. There must always be at least some small amount of initiator in these reactions, since added initiator did not increase the rate of the reaction. And, once the chains are started, the chain carrying steps (particularly hydrogen atom abstraction from 3 by carbon radicals) must be very efficient [37], since added carbon radical inhibitors did not affect the rate of the reaction.

Mechanistic Considerations: Secondary Organometallic Products

The formation of $[(\eta^5C_5H_5)V(CO)_3]_2H^-$, 6, in the reactions of 3 with alkyl bromides must be considered with regard to the radical chain mechanism, which accounts only for 4 as product. The appearance of 6 in these reactions implies that it must be a secondary product, formed from other vanadium compounds in solution.

When THF solutions of 4 and 3 were added together, 6 was formed immediately, as indicated from the NMR spectrum of the solution. The formation of 6 as a secondary product from 4 and 3 was also consistent with the observation that the ratio of 4:6 varies with the alkyl bromide used in the reaction with 3, such that the faster the reaction of 3 and alkyl bromide, the greater the 4:6 ratio (Figure 9). When 3 was removed from solution by the reaction with alkyl bromides, less 3 was available to react with 4 to form 6.

The ratio of 4 to 6 produced in these reactions varies not only with the alkyl bromide used, but also with the procedure followed to carry out the reaction. For the reaction of 3 with benzylbromide, when one equivalent of benzylbromide, as the neat liquid, was added to a solution of 3 in a single aliquot, only a very small amount of 6 was formed (Figure 9a). However, if small aliquots (less than one equivalent) of benzylbromide were successively added to a solution of 3, then much larger amounts of 6 were formed (Figure 10). This also indicated that 6 was formed by a secondary reaction of 3 and 4.

When small aliquots of benzylbromide were added to 3, after the fast reaction between 3 and benzylbromide, there were still large amounts

Figure 9

Reactions of $[(\eta^5C_5H_5)V(CO)_3H]^-$ with Organic Halides:
Variation in the ratio of $[(\eta^5C_5H_5)V(CO)_3]_2H^-$
and $[(\eta^5C_5H_5)V(CO)_3Br]^-$ produced.

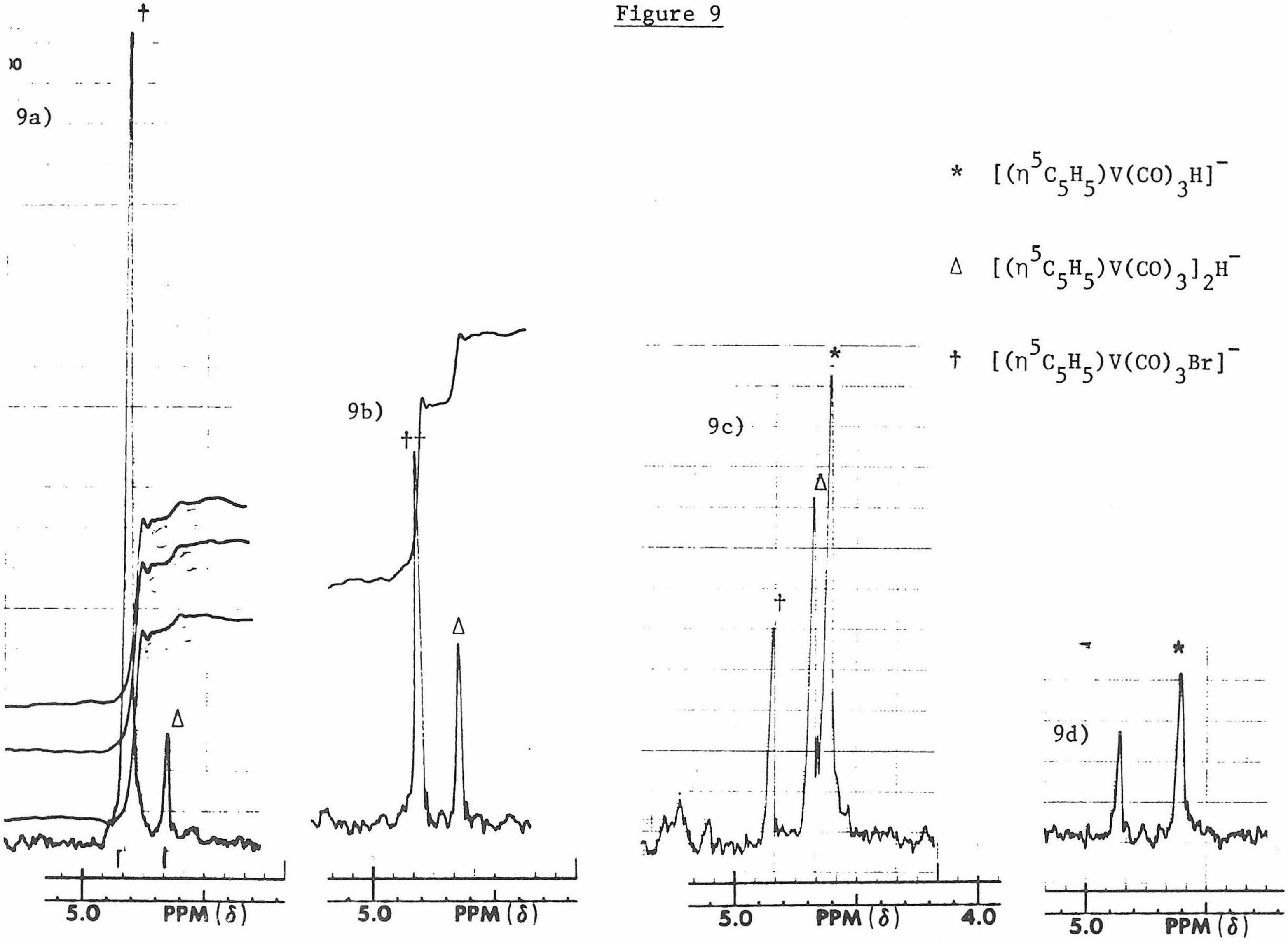
9a) Benzyl Bromide

9b) t-Butyl Bromide

9c) β-Bromostyrene

9d) Phenylacetyl Chloride
($[(\eta^5C_5H_5)V(CO)_3Cl]^-$ is the only product)

Figure 9



* $[(\eta^5 C_5H_5)V(CO)_3H]^-$

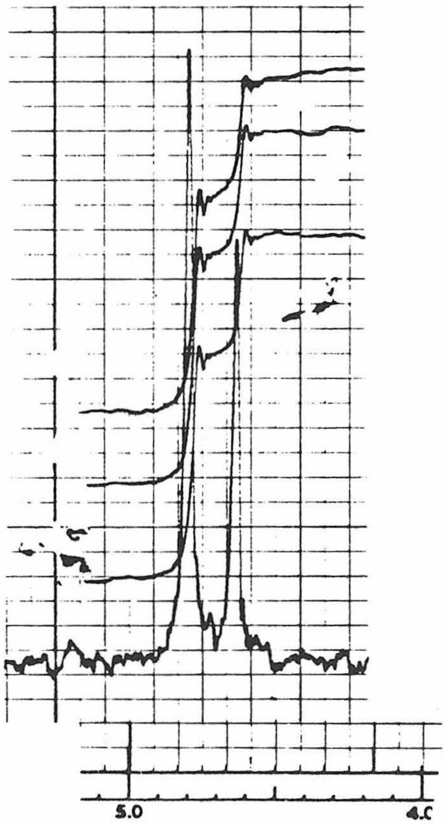
Δ $[(\eta^5 C_5H_5)V(CO)_3]_2H^-$

† $[(\eta^5 C_5H_5)V(CO)_3Br]^-$

Figure 10

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ and 0.82 Equivalents of $C_6H_5CH_2Br$ Added in Small Aliquots

NMR Spectra



Δ $[(\eta^5C_5H_5)V(CO)_3]_2H^-$

† $[(\eta^5C_5H_5)V(CO)_3Br]^-$

of 3 present in solution to react with 4 to form 6. But when one equivalent of benzylbromide was added all at once, 3 was used up quickly by the reaction with benzylbromide, and little 3 was left to react with 4 to give 6.

In addition to the formation of 6 in the reactions of 3 and alkyl bromides, when 3 was reacted with 1-bromooctane in the presence of triphenylphosphine, the final reaction solution contained $(\eta^4C_5H_5)V(CO)_3P(C_6H_5)_3$. However, the IR spectrum of the reaction solution also showed carbonyl absorptions at ∿1870 and 1780 cm^{-1}, and the NMR spectrum showed a cyclopentadienide absorption at δ4.28 (t, J = 3.0 Hz) which corresponded to $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$, 9 [17,38].

In this reaction, the kinetic product 4 was not observed, since the displacement of Br^- by triphenylphosphine on 4 was faster than the reaction of 3 and 1-bromooctane. However, 9 was not the result of carbon monoxide displacement in $[(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3]$, 8, by triphenylphosphine. The displacement of carbon monoxide in 8 by triphenylphosphine did occur, but much too slowly to account for 9 in the reaction of 3 and 1-bromooctane. When 4 or 6 were reacted with triphenylphosphine, both 8 and 9 were formed.

Formation of 9 in the reaction of triphenylphosphine with 6 implied that a carbon monoxide ligand was displaced by triphenylphosphine at one vanadium atom and then a second triphenylphosphine displaced $(\eta^5C_5H_5)V(CO)_3H^-$ from the same vanadium (Scheme IX). The direct displacement of $(\eta^5C_5H_5)V(CO)_3H^-$ from 6 by triphenylphosphine must occur, since 8 was also formed. Scheme IX was analogous to the reaction of triphenyl-

SCHEME IX

A) $$[Cp(CO)_3V\text{-}H\text{-}V(CO)_3Cp]^- + P(C_6H_5)_3 \longrightarrow [Cp(CO)_3V\text{-}H\text{-}V\ P(C_6H_5)_3\ (CO)_2Cp]^- + CO$$

$$[Cp(CO)_3V\text{-}H\text{-}V\ P(C_6H_5)_3(CO)_2Cp]^- + P(C_6H_5)_3$$

$$\longrightarrow Cp(CO)_3V\text{-}H^- + CpV\ P(C_6H_5)_{3\ 2}(CO)_2$$

$$[Cp(CO)_3V\text{-}H\text{-}V(CO)_3Cp]^- + P(C_6H_5)_3$$

$$\longrightarrow Cp(CO)_3V\text{-}H^- + CpV\ P(C_6H_5)_3(CO)_3$$

B) $$CpV(CO)_3Br^- + P(C_6H_5)_3 \longrightarrow CpV(CO)_2\ P(C_6H_5)_3\,Br^- + CO$$

$$CpV(CO)_2\ P(C_6H_5)_3\ Br^- + P(C_6H_5)_3 \longrightarrow CpV(CO)_2\ P(C_6H_5)_{3\ 2} + Br^-$$

$$CpV(CO)_3Br^- + P(C_6H_5)_3 \longrightarrow CpV(CO)_3\ P(C_6H_5)_3 + Br^-$$

phosphine with $[Cr(CO)_5]_2H^-$, except that no mono-triphenylphosphine complex, $Cr(CO)_5P(C_6H_5)_3$ was formed from $[Cr(CO)_5]_2H^-$ [30].

Presumably, the formation of **9** in the reaction of triphenylphosphine and **4** occurred by displacement of carbon monoxide by triphenylphosphine to form $(\eta^4C_5H_5)V(CO)_2P(C_6H_5)_3(Br^-)$. Then a second molecule of triphenylphosphine displaced Br^-, to form **9** (Scheme IX).

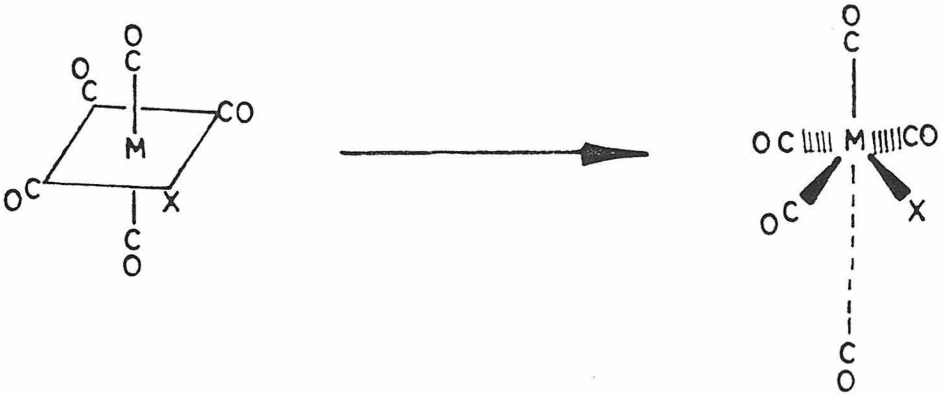
This apparent preference for displacement of carbon monoxide on $(\eta^5C_5H_5)V(CO)_3Br^-$, **4**, and $[\eta^5(C_5H_5)V(CO)_3]_2H^-$, **6**, by triphenylphosphine was quite unexpected. And, the substitution reactions on **4** and **6** proceed more rapidly than with $(\eta^5C_5H_5)V(CO)_4$, **2**. It was shown [38] that phosphine substitution on **2** proceeded by dissociation of carbon monoxide and it was therefore likely that substitution on **4** and **6** proceeded by a similar dissociative mechanism. It might have been expected that the total negative charges on **4** and **6** would have stabilized the carbon monoxide ligands to dissociation, as compared to **2**, by increased π bonding from the metal. This, of course, was not what was observed.

Brown [23] has noted a similar effect for the substituted carbonyl complexes, $M(CO)_5X$, where M = Cr, Mo, W, Mn, Re and X = Cl^-, Br^-, I^-, $P(C_6H_5)_3$, NC_5H_5. These complexes undergo carbon monoxide substitution (the carbon monoxides cis to X were substituted preferentially) by a dissociative mechanism at a greater rate than the corresponding $M(CO)_6$ complexes. Again, it might have been expected that the substituted complexes $M(CO)_5X$ would have substituted more slowly, since for X equal to the above ligands, X was more sigma donating and less π accepting than carbon monoxide. Each of these differences in bonding appeared to put more electron density on the metal, so that the carbon monoxide ligands in $M(CO)_5X$ would have been stabilized to dissociation, as compared to $M(CO)_6$.

Ground state effects (i.e., changes in cis M-C bond lengths or shifts in $\nu_{C\equiv O}$) did not appear to account for the cis labilization of carbon monoxide in $M(CO)_5X$ complexes [23]. Brown [23] proposed a transition state/intermediate stabilization [39] effect to rationalize the observed increase in labilization of the carbon monoxide ligands cis to X in $M(CO)_5X$.

The dissociative loss of a ligand from an octahedral complex must proceed through a structure which has some square pyramidal character as the ligand begins to leave the coordination sphere of the metal. Those ligands ,which help stabilize five coordinate square pyramidal structures relative to the stabilization by a carbon monoxide ligand, should make loss of carbon monoxide from $M(CO)_5X$ faster than from $M(CO)_6$.

Those ligands X, (X = Cl^-, Br^-, $P(C_6H_5)_3$, NC_5H_5) which do show large carbon monoxide labilization effects in $M(CO)_5X$, do stabilize five coordinate square pyramidal structures more than carbon monoxide (i.e., $M(CO)_4X$ is more stable than $M(CO)_5$) [40,23]. These ligands also show a preference for the basal site over the axial site in a square pyramid [40]. The basal site preference for X in $M(CO)_4X$ accounts for the cis labilization, since loss of carbon monoxide cis to X allows X to occupy a basal site in $M(CO)_4X$ without major ligand rearrangements, equation 3.



(3)

It is possible that similar transition state stabilization for loss of carbon monoxide is occurring in the substituted complexes $(\eta^5C_5H_5)V(CO)_3X$, where X = Cl^-, Br^-, $(\eta^5C_5H_5)V(CO)_3H^-$, $P(C_6H_5)_3$.

Preparation of $[(\eta^5C_5H_5)V(CO)_3R]^-$, ($R = CH_3$, C_8H_{17}) from $Na_2(\eta^5C_5H_5)V(CO)_3 \cdot THF$

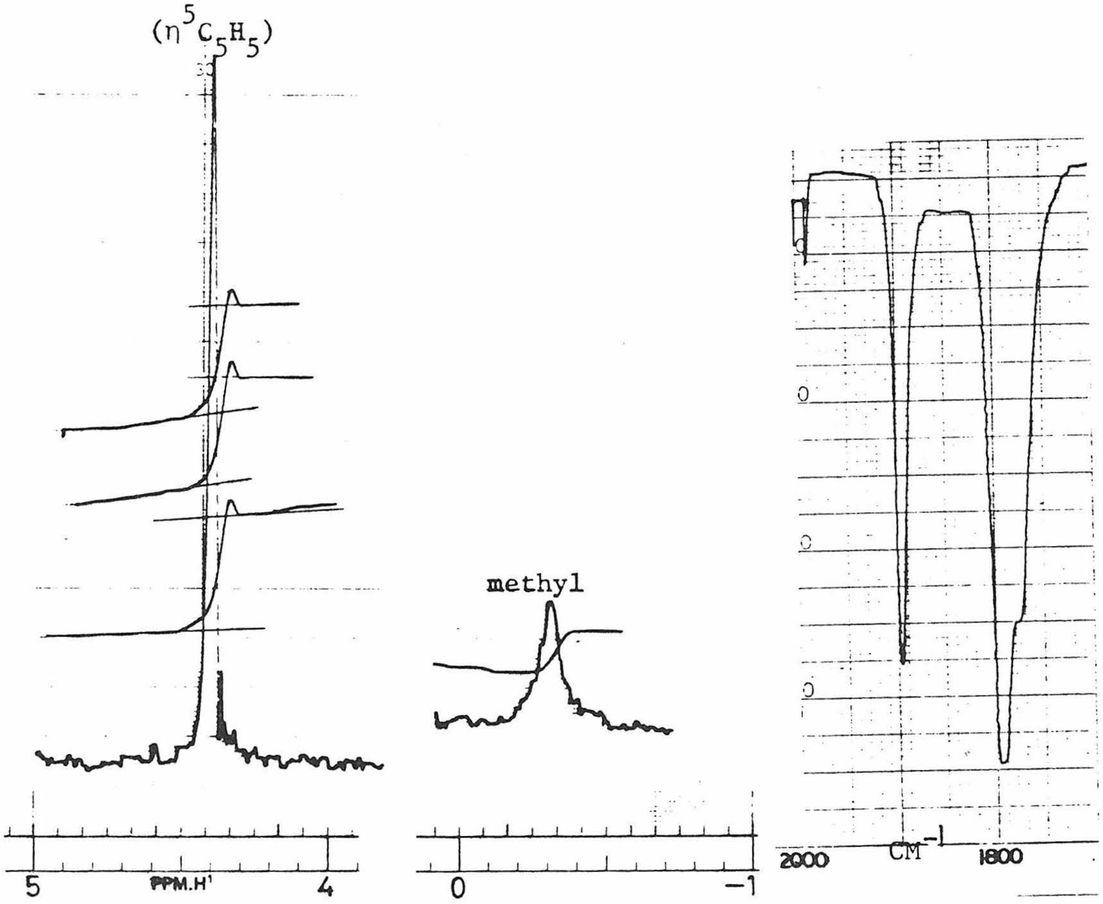
Treatment of a THF slurry of Na_2-**1**·THF with HMPA generated a homogeneous [18b] red-brown solution. Addition of one molar equivalent of methyl-p-toluenesulfonate and exchange of the sodium cation by PPN^+ led to a brick-red solid which was characterized by elemental analysis as $PPN^+[(\eta^5C_5H_5)V(CO)_3CH_3]^-$, PPN^+-**10**. In THF slurries without HMPA added, this reaction did not yield **10**. The IR spectrum of these reaction solutions showed carbonyl absorptions for **3**, and when benzyl bromide was added to the reaction solutions only small amounts of toluene (the product from **3** and benzyl bromide) were obtained. No ethylbenzene from an analogous reaction of **10** and benzyl bromide was detected.

The IR spectrum of PPN^+-**10** in THF showed carbonyl absorptions at 1895, 1795 and 1775 (shoulder) cm^{-1}. The NMR spectrum on d_8-THF, in addition to the large absorption for PPN^+, showed a cyclopentadienide resonance at δ4.43 PPM, and a slightly broadened signal (4 Hz at half height) at δ-0.33 PPM for the methyl ligand.(Figure 11). PPN^+-**10** was air sensitive, both as a powder and as a THF solution.

When an HMPA solution of Na_2-**1**·THF was treated with one equivalent of 1-bromooctane, the cyclopentadienide resonance at δ4.32 PPM for **1** disappeared and a new large absorption at δ4.42 PPM appeared along with a small absorption at δ4.55 PPM which was due to **3**. The absorption at δ4.42 PPM was presumed to be from $[(\eta^5C_5H_5)V(CO)_3(C_8H_{17})]^-$, although this material was not isolated. The similarity of the chemical shift of the new cyclopentadienide resonance in this reaction to that for **10** implied that **1** had been alkylated by 1-bromooctane. The IR spectrum of the solution was very similar to those of **3** and **10**, with carbonyl absorptions at 1895 and 1790 cm^{-1}. This compound decomposed over a period of approximately 100 hours at room temperature, as indicated by the decrease in intensity of the δ4.42 PPM absorption in the NMR spectrum of the solution. At the end of this period the δ4.42 PPM signal was almost completely gone. However, there was no concomitant increase in intensity of any new cyclopentadienide resonances in the NMR spectrum. Most significantly, **3** was not produced during the decomposition, as might have been expected if the decomposition of $[(\eta^5C_5H_5)V(CO)_3(C_8H_{17})]^-$ occurred by β-elimination.

Figure 11

NMR and Infrared Spectra of $[(C_6H_5)_3PNP(C_6H_5)_3][(\eta^5C_5H_5)V(CO)_3CH_3]$



The reaction of 1 with neopentyl chloride or neopentyl-p-toluenesulfonate was complete within fifteen minutes. This was comparable to the reactivity of $Na_2Fe(CO)_4$ [24] with these same substrates. However, these reactions were not investigated in detail, because no vanadium products were observed in these reactions. The NMR spectra of the reaction solutions showed only the disappearance of the cyclopentadienide resonance for 1, but no new absorptions appeared .

Reactions of $[(\eta^5C_5H_5)V(CO)_3]^{2-}$ with secondary alkylating agents

The reactions of Na_2-1·THF in HMPA with 2-iodopropane and with bromocyclopentane were completed in a few minutes, but no new characterizable vanadium products were formed, as indicated by the absence of any cyclopentadienide resonances in the NMR of the reaction solutions.

However, when an HMPA solution of Na_2-1·THF was added to 2-octyl-p-toluenesulfonate, the NMR spectrum showed a single new cyclopentadienide absorption which corresponded to 3. 3 could have resulted from either the formation of the vanadium alkyl complex, $(\eta^5C_5H_5)V(CO)_3[CH(CH_3)C_6H_{13}]^-$ and β-hydrogen elimination, or by direct proton abstraction from the β-position of 2-octyl-p-toluenesulfonate.

There was no indication of a vanadium alkyl complex in this reaction. However, at lower temperatures if β-elimination is slowed, then the vanadium alkyl complex might be observed.

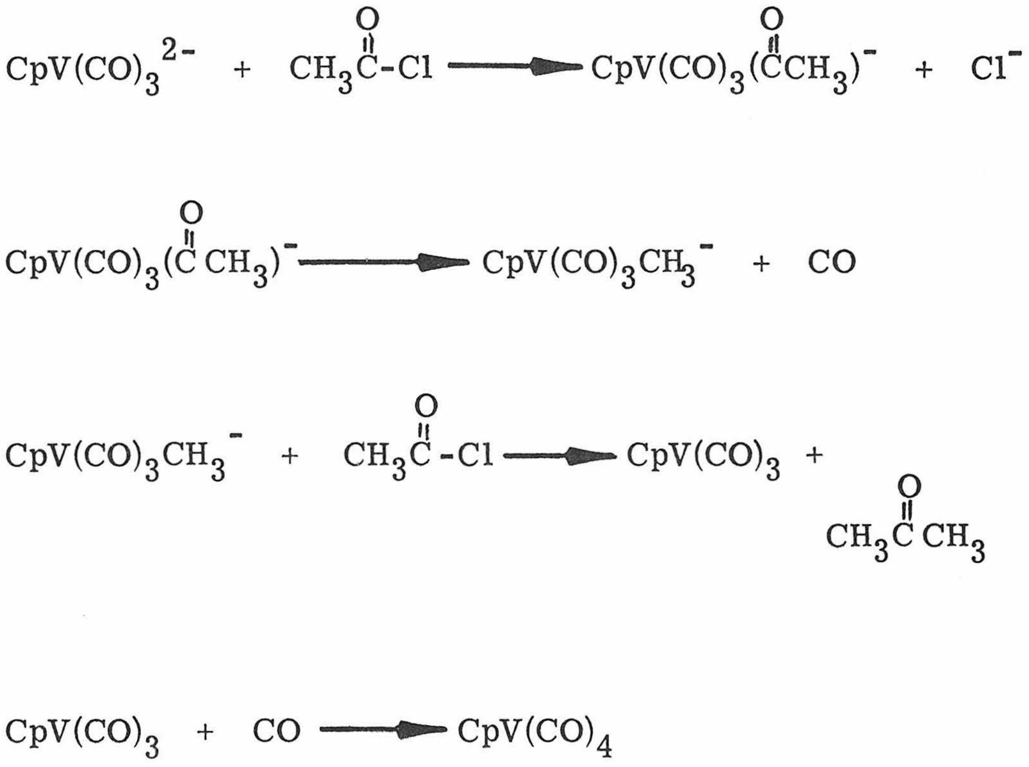
Reaction of $[(\eta^5C_5H_5)V(CO)_3]^{2-}$ with acetyl chloride

Attempts to form the vanadium-acyl anion complex $[(\eta^5C_5H_5)V(CO)_3$-$(\overset{O}{\overset{\|}{C}}CH_3)]^-$, 11 by the reaction of 1 and acetyl chloride in HMPA gave solutions which, from their IR spectra, contained only $[(\eta^5C_5H_5)V(CO)_4]$, **2**. It did not seem likely that **11** was formed in this reaction. The formation of **2** from **11** required the overall loss of a methyl anion. One possible pathway for this to have occurred would be the loss of carbon monoxide and de-insertion of the methyl group (Scheme X), to form the known vanadium-methyl anion $(\eta^5C_5H_5)V(CO)_3CH_3^-$, **10**. The de-insertion was thermodynamically favored, since the reverse reaction, the insertion of the methyl ligand into a carbon monoxide of **10**,did not proceed, even in the presence of excess triphenylphosphine. In order to form **2**, **10** would then have had to lose a methyl anion and add a carbon monoxide. This might have occurred by the reaction of **10** with a second molecule of acetyl chloride to form acetone and the coordinatively unsaturated species, $(\eta^5C_5H_5)V(CO)_3$, **7**, which could have coordinated a free carbon monoxide, present from the decomposition of another molecule of **7**. **10** did react with acetyl chloride when solutions of each in THF were added together, but no **2** was formed. Therefore, loss of methyl anion from **11** does not appear to have occurred by the formation of **10**.

It seemed more likely that the reaction of **1** and acetyl chloride occurred by electron transfer, which generated the coordinatively unsaturated species, **7**, and coordinated to free carbon monoxide in solution. The reaction of **1** with silver perchlorate produced **2**, along with some **3**. This reaction most certainly occurred by electron transfer to generate **7**, which was coordinated by free carbon monoxide.

The reactions of **1** and alkylating agents did not form the stable vanadium-alkyl compounds $(\eta^5C_5H_5)V(CO)_3R^-$, except for R equals methyl and

SCHEME X



$$CpV(CO)_3^{2-} + CH_3\overset{O}{\overset{\|}{C}}\text{-}Cl \longrightarrow CpV(CO)_3(\overset{O}{\overset{\|}{C}}CH_3)^- + Cl^-$$

$$CpV(CO)_3(\overset{O}{\overset{\|}{C}}CH_3)^- \longrightarrow CpV(CO)_3CH_3^- + CO$$

$$CpV(CO)_3CH_3^- + CH_3\overset{O}{\overset{\|}{C}}\text{-}Cl \longrightarrow CpV(CO)_3 + CH_3\overset{O}{\overset{\|}{C}}CH_3$$

$$CpV(CO)_3 + CO \longrightarrow CpV(CO)_4$$

some primary alkyl groups. Nor did it appear that the anionic vanadium-acyl complex, $(\eta^5C_5H_5)V(CO)_3(\overset{O}{\overset{\|}{C}}CH_3)^-$, was formed.

Reactions of $[\eta^5C_5H_5)V(CO)_3CH_3]^-$ with alkyl halides and alkyl-p-toluenesulfonates

$[(\eta^5C_5H_5)V(CO)_3CH_3]^-$, 10, does not react with alkyl halides and alkyl-p-toluenesulfonates to give products analogous to the products from the reaction of $(\eta^5C_5H_5)V(CO)_3H^-$, 3, with the same substrates. It was anticipated that carbon-carbon bonds, instead of carbon-hydrogen bonds as with 3, might have been formed from the reaction of 10 and alkylating agents (equation 4).

$$(\eta^5C_5H_5)V(CO)_3CH_3^- + R\text{—}X \longrightarrow (\eta^5C_5H_5)V(CO)_3X^- + R\text{—}CH_3 \tag{4}$$

When 10 was reacted with acetyl chloride, benzyl bromide, ethyl iodide or methyl-p-toluensulfonate, no vanadium products could be identified in the product solutions. No organic products corresponding to halide or p-toluenesulfonate replacement by a methyl group were produced.

No new carbonyl absorptions were observed in the IR spectra of the reaction solutions of 10 with acetyl chloride or ethyl iodide. The reaction with acetyl chloride was complete in a few minutes, while the carbonyl absorptions for 10 were absent from the ethyl iodide reaction solution after 14 hours.

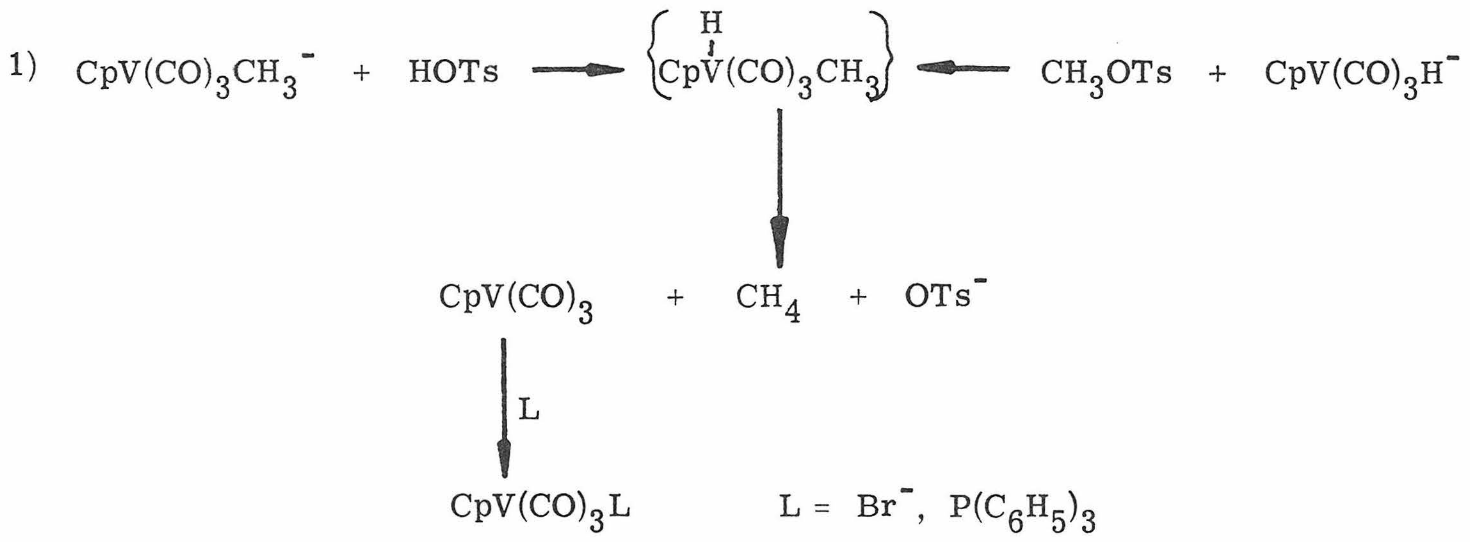
NMR spectra of the reaction solution of 10 and methyl-p-toluenesulfonate showed decreases in the intensity for the cyclopentadienide resonance and methyl resonance from 10. The sulfonate methyl resonance from methyl-p-toluenesulfonate also decreased in intensity, but no new cyclopentadienide resonances, nor any absorption corresponding to ethane, appeared in any of the spectra.

When benzyl bromide was added to a THF solution of **10**, the solution changed color from reddish-brown to black, indicating that **10** had reacted, but no ethyl benzene was identified by gas chromatographic analysis of the volatile fraction of the reaction solution.

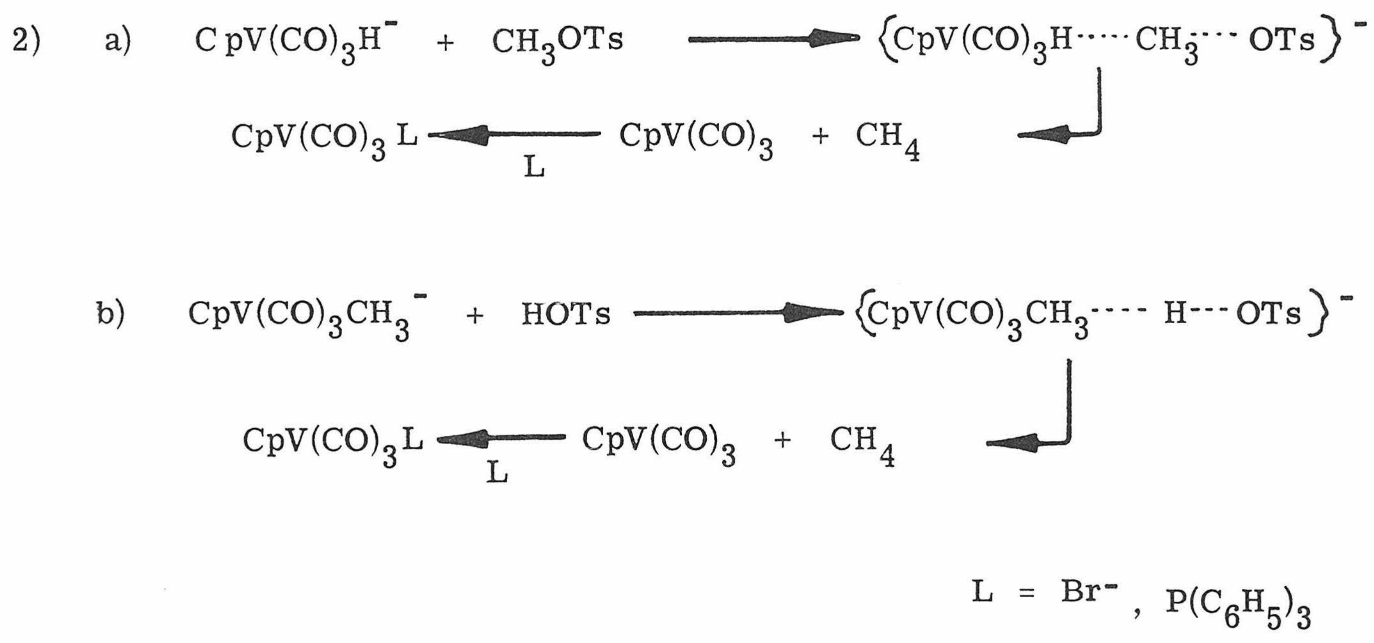
Possible formation of the vanadium methyl hydride complex, $[(\eta^5C_5H_5)V(CO)_3(CH_3)H]$

The reaction of **10** with p-toluenesulfonic acid was of interest because protonation at the vanadium would lead to the vanadium methyl hydride complex, $[\eta^5C_5H_5)V(CO)_3(CH_3)H]$, **12**. Formation of **12** is of interest because of recent work on the reductive eliminations from metal alkyl hydrides [42], and because it was suspected that **12** or other vanadium alkyl hydrides may have been formed when **3** was reacted with alkyl-p-toluenesulfonates rather than alkyl bromides. The reactions of **3** with alkyl p-toluenesulfonates are much slower than with the corresponding alkyl bromides (Table I). It was suspected that the reactions of **3** and alkyl-p-toluenesulfonates might therefore be occurring by alkylation of the metal hydride, and reductive elimination to form alkane. If this were the case then the reaction of **10** with p-toluenesulfonic acid, and **3** and alkyl-p-toluenesulfonates could both produce a vanadium alkyl hydride intermediate, Scheme XI . Reductive elimination would leave the coordinatively unsaturated species $(\eta^5C_5H_5)V(CO)_3$, **7**, which could be trapped by added ligands, L. This would be different from the reaction of $(\eta^5C_5H_5)V(CO)_3H^-$, **3**, with alkyl bromides where **7** was not formed. Therefore the reactions of **10** with p-toluenesulfonic acid and **3** with methyl-p-toluenesulfonate were carried out in the presence of the

SCHEME XI


1)
$CpV(CO)_3CH_3^-$ + HOTs
$\left\{ \overset{H}{CpV}(CO)_3CH_3 \right\}$
CH_3OTs + $CpV(CO)_3H^-$
$CpV(CO)_3$ + CH_4 + OTs^-
L
$CpV(CO)_3L$
$L = Br^-,\ P(C_6H_5)_3$

SCHEME XI (cont.)



added ligands, bromide ion and triphenylphosphine.

When **10** was reacted with p-toluenesulfonic acid, HOTs, in the presence of lithium bromide or triphenylphosphine, methane and $(\eta^5C_5H_5)V(CO)_3Br^-$, **4**, or $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$, **8** were formed, respectively. Likewise **4** or **8** was formed, along with some $[(\eta^5C_5H_5)$-$V(CO)_3]_2H^-$, **6**, when **3** was reacted with methyl-p-toluenesulfonate, CH_3OTs in the presence of the same ligands, respectively.

The formation of **4**, **8**, and **6** in these reactions was consistent with **7** as an intermediate in these reactions. In addition, when **10** was reacted with HOTs in the presence of both lithium bromide and triphenylphosphine, no **4** was produced, as indicated by the lack of a carbonyl absorption at 1810 cm^{-1} in the IR spectrum of the reaction solution. From the carbonyl absorptions in the IR spectrum of the reaction solution, **8** and a small amount of $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ were produced in the reaction. This was consistent with other experiments that **7** reacts more rapidly with triphenylphosphine than it does with bromide ion [29].

The formation of **7** was consistent with, but did not require, the formation of **12** as an intermediate in these reactions. It was possible that **7** was formed by direct hydride transfer to methyl in the reaction of **3** with CH_3OTs, and by direct protonation of the methyl ligand of **10** in the reaction of **10** with HOTs (Scheme XI). Both of the alternative reactions would produce **7**.

Therefore, without direct evidence, it cannot be concluded with certainty that **12** was an intermediate in these reactions [42b].

Experimental

General Methods

All reactions of $(\eta^5C_5H_5)V(CO)_4$, $Na_2(\eta^5C_5H_5)V(CO)_3 \cdot THF$, and $PPN^+[(\eta^5C_5H_5)V(CO)_3R]^-$, R = H, CH_3, 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.

Nuclear Magnetic Resonance (NMR) spectra were recorded on either a Varian A60A, T60, EM390, or HR-220 MHz spectrophotometer. 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 plastic NMR tube caps wrapped with parafilm, or rubber septums. Additional reagents were added through the rubber septums by syringe.

Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrophotometer. Solution spectra were recorded in 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-heights 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.

Elemental analyses were performed by Galbraith Laboratories [44], Schwarzkopf [45], or Dornis V. Kolbe Mikoanalytischer Laboratorium [46].

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 10% sulfuric acid over night, washed with water and dried over calcium chloride. Hexamethylphosphoramide (HMPA) was purified by the literature procedure [47]. All other liquid substrates were degassed by freeze-pump-thaw cycles before being used in the drybox.

$(\eta^5C_5H_5)V(CO)_4$ was purchased from Ventron or Strem Chemical Company and was purified by sublimation at 0.25 mm Hg and 80°C. Commercial triphenylphosphine was recrystallized once from benzene, once from absolute methanol, and was dried under vacuum ($\sim$ 5 mm Hg) 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 [48].

Samples of meso- and d,ℓ-3,4-dibromohexane [49], 1,1-dibromo-2,2-dimethylcyclopropane [50], and 1-bromo-2,2-dimethylcyclopropane [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 [52]. Benzoyl chloride, phenylacetyl chloride and 3-carbomethoxypropionyl chloride were commercial samples which were distilled and degassed.

Neopentyl-p-toluensulfonate [52], n-heptyl-p-toluenesulfonate [52], 2-octyl-p-toluenesulfonate [52], n-octyl-trifluoromethylsulfonate [53], methyl heptanoate [52], and phosphineminium bromide[54] were all prepared by literature procedures.

All other organic substrates were commercial samples without purification.

Preparation of Silver Nitrate GPC Column [55]

20 g of silver nitrate was added to 20 ml of glycerin and stirred for 30 min. The solution was centrifuged and 9 ml of the supernatant was added to 18 g of chromsorb P (100-200 mesh) and 100 ml of absolute ethanol. The alcohol was removed from the slurry by roto-evaporation

and the remaining solid was dried at ∿0.5 mm Hg at room temperature over night. The material was resieved (100-150 mesh) and packed in a 16' x 1/8" analytical stainless steel column. The column was conditioned by running a flow of helium through it for 3 hours. The column was never heated above 60°C.

Preparation of 1,2-dibromohexane from 1-hexene

11.5 g (.137 mol) of 1-hexene was dissolved in 75 ml of carbon tetrachloride in a three-neck flask fitted with a dropping funnel, thermometer, and ground glass stopper. The solution was cooled to 5°C and a solution of 5.5 ml (0.268 mol) of bromine in 15 ml of CCl_4 was added dropwise at such a rate that the temperature of the reaction solution did not rise above 8°C.

When all of the bromine was added, the solution was allowed to warm to room temperature and the solvent was removed by roto-evaporation. The reddish brown oil which remained was washed twice with equal volumes of 5% sodium bicarbonate solution. The residue was only slightly yellow and was dried over night with sodium sulfate. The crude product was distilled at 13 mm Hg and 85°C to yield 13.5 g (56%) of 1,2-dibromohexane.

Preparation of $Na_2(\eta^5C_5H_5)V(CO)_3 \cdot THF$ from $(\eta^5C_5H_5)V(CO)_4$ [16,17].

Method A. Titration of sodium dispersion with a solution of $(\eta^5C_5H_5)V(CO)_4$.

Approximately 0.5 grams of 40% sodium dispersion in 400 ml of THF was titrated with a solution of $(\eta^5C_5H_5)V(CO)_4$ [1.664 grams (7.3

mmol) in 90 ml of THF]. The $(\eta^5C_5H_5)V(CO)_4$ solution was added dropwise to the sodium dispersion over a period of ten hours. The sodium dispersion suspension was initially grey, but shortly after addition of $(\eta^5C_5H_5)V(CO)_4$ 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 $(\eta^5C_5H_5)V(CO)_4$. When all of the $(\eta^5C_5H_5)V(CO)_4$ 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 $(\eta^5C_5H_5)V(CO)_4$. Then the precipitate was washed with petroleum ether and dried in the drybox. 1.365 grams (4.3 mmol) of $Na_2(\eta^5C_5H_5V(CO)_3\cdot THF$ (59% yield) was obtained.

Method B. Reduction of $(\eta^5C_5H_5)V(CO)_4$ with sodium amalgam.

2.42 g (10.6 mmol) of $(\eta^5C_5H_5)V(CO)_4$ was dissolved in 75 ml of THF, and 75 g of sodium amalgam (.0072 g Na/g amalgam) was added. The solution was stirred for 21.5 hours. 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 $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ was collected (98% yield).

NMR: (HMPA) 4.32 (S,5H,$(\eta^5C_5H_5)$

IR: 1742, 1590, 1550 cm^{-1}; KBr, Nujol
1745, 1620, 1570 cm^{-1}; HMPA

IR(Lit.): 1742, 1619, 1573 cm^{-1} HMPA [18]
1748, 1645 cm^{-1}; $Cs_2(\eta^5C_5H_5)V(CO)_3$, Nujol [16].

Other preparations of $(\eta^5C_5H_5)V(CO)_3^{2-}$. Reduction of $(\eta^5C_5H_5)V(CO)_4$ with lithium dispersion

0.474 g (0.207 mmol) of $(\eta^5C_5H_5)V(CO)_4$ was dissolved in 20 ml of THF. This was added to 0.11 g of 30% lithium dispersion. After 5.5 hours the IR spectrum of the reaction mixture showed carbonyl absorptions at 1720, 1595 and 1540 cm^{-1}, corresponding to Li_2 $(\eta^5C_5H_5)V(CO)_3$ by analogy to the IR spectrum of Na_2 $(\eta^5C_5H_5)V(CO)_3 \cdot THF$ in HMPA [18].

The reaction mixture was filtered and an orange precipitate was collected. The orange precipitate turned black while setting in the dry-box over night.

Reaction of PPN^+ $(\eta^5C_5H_5)V(CO)_3Br^-$ with lithium aluminum hydride

$PPN^+[(\eta^5C_5H_5)V(CO)_3Br^-]$ was dissolved in THF and a slight excess of lithium aluminum hydride (LAH) was added. The solution changed color from dark green to dark brown. The IR spectrum of the solution showed no carbonyl absorptions at 1722, 1595 or 1540 cm^{-1}.

Reaction of $(\eta^5C_5H_5V(CO)_4$ with lithium aluminum hydride

$(\eta^5C_5H_5)V(CO)_4$ was dissolved in THF and an excess of LAH was added. The solution changed color from light reddish-brown to dark brown. The IR spectrum of the reaction mixture showed carbonyl absorptions at 1895 (w), 1810 (w), 1722 (s), 1595 (s) and 1540 cm^{-1}. The 1722, 1595 and 1540 cm^{-1} absorptions corresponded to $Li_2(\eta^5C_5H_5)V(CO)_4$ in solution.

Reaction of $(\eta^5C_5H_5)V(CO)_4$ with other hydride reducing agents

Treatment of $(\eta^5C_5H_5)V(CO)_4$ in THF with sodium hydride, lithium hydride, and sodium borohydride gave no reaction at room temperature.

Photolysis of the solution with sodium borohydride produced a solution with carbonyl absorptions at 1890 and 1780 cm^{-1} in the IR spectra. These absorptions were due to $(\eta^5C_5H_5)V(CO)_3H^-$.

Reaction of PPN$^+$ $(\eta^5C_5H_5)V(CO)_3Cl^-$ with sodium amalgam

When a THF solution of PPN$^+$ $(\eta^5C_5H_5V(CO)_3Cl^-$ was treated with sodium amalgam, a deep red-brown precipitate was formed. This precipitate was insoluble in organic solvents and was not identified.

Reaction of $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)$ with sodium dispersion

0.0625 g (0.135 mmol) of $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$ was dissolved in 10 ml of THF and sodium dispersion was added from the tip of a pipette. After one hour the solution had changed color from orange-brown to light brown, and a yellow precipitate had formed. 0.0237 g of material was collected by filtration, and its nujol mull IR spectrum showed carbonyl absorptions at 1740, 1585 and 1550 cm^{-1} for $(\eta^5C_5H_5)V(CO)_3^{2-}$.

Preparation of PPN$^+$$[\eta^5C_5H_5)V(CO)_3H]^-$ from $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$

Method A. Addition of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot$ THF to water.

0.075 g (0.235 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ was dissolved in 2 ml of water. A light greenish-yellow solution resulted. An excess of solid PPN$^+$Cl$^-$ was quickly added, and a reddish-orange precipitate formed. This precipitate was collected by filtration, dissolved in a minimum amount of THF, and precipitated by adding petroleum ether. The precipitate was collected, washed with petroleum ether, and dried in the drybox. 0.069 g (.094 mmol) of PPN$^+$$[\eta^5C_5H_5)V(CO)_3H\ ]^-$ was collected (40% yield).

Method B. Addition of water to a THF slurry of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot$ THF

0.2544 grams (1.03 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot$THF was slurried in 30 ml of THF and 20 μl (1.11 mmol) of water was added. The $Na_2(\eta^5C_5H_5)V(CO)_3$ dissolved to give a greenish-yellow solution. 0.6585 grams (1.14 mmol) of PPN^+Cl^- was added as the solid, and the solution turned dark red-brown and a white precipitate formed. The solution was filtered, and petroleum ether (30-60°) was added slowly until a reddish-orange precipitate formed. The precipitate was collected and reprecipitated from THF-petroleum ether. This gave 0.4152 grams (0.56 mmol) of $PPN^+[\eta^5C_5H_5)V(CO)_3H]$ (70% yield).

NMR(d_8-THF): δ7.55 (m,30H,PPN^+); δ4.60 (S,5H,($\eta^5C_5H_5$);
δ-6.10 (broad signal 1H, hydride)

IR(THF,HMPA,KBr pellet, nujol mull): $\nu_{C\equiv O}$, 1890, 1780 cm^{-1}.

Elemental Analysis: Calc. P8.36 V 6.88 N 1.89
Found P8.46 V 6.89 N 1.96

M.P. 201°C (decomposition)

Preparation of $PPN^+[(\eta^5C_5H_5)V(CO)_3D]^-$ from $Na_2(\eta^5C_5H_5)V(CO)_3\cdot$THF

The preparation of $PPN^+[(\eta^5C_5H_5)V(CO)_3D]^-$ from $Na_2(\eta^5C_5H_5)V(CO)_3\cdot$THF was analagous to the preparation of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$, with deuterium oxide substituted for water. Method A was preferable for preparing $(\eta^5C_5H_5V(CO)_3D^-$ because it yielded an isotopically pure product, whereas Method B gave a product which was only 60% isotopically pure.

Reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl halides

General Method

The reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl halides were carried out by two different procedures. Equimolar quantities were mixed and stored in the drybox, the reaction solutions were removed from the drybox after a specified period and analyzed. Or, a solution of $(\eta^5C_5H_5)V(CO)_3H^-$ 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 monitored by IR spectroscopy

$(\eta^5C_5H_5)V(CO)_3H^-$ was generated in solution by adding excess PPN^+Cl^- to a slurry of 0.0754 g (0.237 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ in 2.0 ml of THF. The color changed from yellow to dark brown. The solution was filtered, and the filtrate reduced in volume by vacuum transferring solvent from the solution. 44 μl (0.312 mmol) of n-hexyl bromide was added to the solution, and the infrared spectrum of the reaction solution recorded at various times during the reaction (Figure 6). The infrared spectra showed the appearance of five new carbonyl absorptions at 2030, 1945, 1930, 1850, and 1810 cm^{-1}.

Reaction monitored by NMR spectroscopy

0.0299g (0.0405 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ were dissolved in 350 μl of d_8-THF in the drybox. The NMR tube was removed from the drybox and 21 μl of n-octylbromide was syringed into the NMR tube. The NMR spectrum of the reaction mixture was recorded at various times during the reaction (Figure 7). The NMR spectra showed the appearance of two new vanadium cyclopentadienide signals at δ4.67 PPM and at δ4.80 PPM.

NMR spectra of reaction mixtures of $(\eta^6C_5H_5)V(CO)_3H^-$ and benzyl bromide, phenylacetylchloride, β-bromostyrene, and t-butyl bromide

When $(\eta^5C_5H_5)V(CO)_3H^-$ was reacted with equimolar quantities of benzyl bromide, β-bromostyrene and t-butyl bromide, the same two new vanadium cyclopentadienide resonances appeared in the NMR spectra of the reaction mixtures at δ4.67 PPM and at δ4.80 PPM (Figure 9). However, for the reaction of phenylacetyl chloride with $(\eta^5C_5H_5)V(CO)_3H^-$ only a single new vanadium cyclopentadienide resonance appeared at δ4.85 PPM.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with 1-bromoadamantane

0.2568 g (0.348 mmol) of PPN^+ $(\eta^5C_5H_5)V(CO)_3H^-$ and .0750 g (0.348 mmol) of 1-bromoadamantane were dissolved in 10 ml of THF in a serum capped flask. After 65 hours at room temperature only a small amount of $(\eta^5C_5H_5)V(CO)_3Br^-$ had formed, as indicated by the IR spectrum of the reaction mixture. The reaction mixture was heated to 70°C for 5 hours. At the end of this period no 1-bromoadamantane was present in the reaction as determined by GC analysis.

The THF was then removed from the reaction mixture by roto-evaporation, and the residue was extracted with benzene, filtered, and the benzene removed by roto-evaporation. 0.0557 g of a dark brown solid remained. This residue was again taken up in benzene, and GC analysis showed the same new peak which had appeared in the original reaction mixture.

After setting overnight, a dark brown solid had precipitated. The solution was filtered and the light yellow filtrate was roto-evaporated to dryness. The residue was taken up in pentane, filtered, and a slightly yellow filtrate was collected. When the pentane was removed by evaporation, 0.0289 g (60%) of an amorphous solid was collected.

NMR (CCl_4): 1.77 PPM (s, methine); δ1.75 PPM (s, methylene)

Lit: 1.80 PPM (s, methine); δ1.77 PPM (s, methylene).
(Sadtler NMR Spectra Index, NMR #835)

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with 6-bromo-1-hexene

7 μl (.052 mmol) of 6-bromo-1-hexene was added to a solution of PPN^+ $(\eta^5C_5H_5)V(CO)_3H^-$ (.054 g, .068 mmol) in 1.0 ml of THF in a round bottom flask stoppered with a serum cap. The progress of the reaction was monitored by gas chromatographic analysis of aliquots of the reaction mixture. The analyses were carried out with a 20' x 1/8" 25% STAP CHROM-WAWDMCS column, 100-200 mesh, with the injector at 115°C, the column at 62.5°C and the flame ionization detector at 230°C. Results of the GC analyses are shown in Table II. The products, 1-hexene and methylcyclopentane were identified by co-injection with authentic samples. No cyclohexane was detected. The combined yield of 1-hexene and methylcyclopentane was 99%.

TABLE II

GC Analysis of Reaction Solution of $(\eta^5C_5H_5)V(CO)_3H^-$ and 6-Bromo-1-Hexene

Time (Hrs)	Relative Area		
	1-Hexene	Methylcyclopentane	Methylcyclopentane / Total Product
0.5	.282	-	-
2.5	.476	.017	.034
4.0	.473	.030	.059
6.25	.542	.055	.092
17.0	.546	.085	.135

Reaction of $(\eta^5C_5H_5)V(CO)_3D^-$ with (-)-1-phenylethyl bromide

0.820 g (1.11 mmol) of PPN^+ $(\eta^5C_5H_5)V(CO)_3D^-$ was dissolved in 2.0 ml of THF in a septum stoppered flask. 0.150 ml of (-)-1-phenylethyl bromide (75% optically pure) 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 minutes 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 PNAW 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 $(\eta^5C_5H_5)V(CO)_3D^-$ and (-)-1-phenylethyl bromide had proceeded with complete inversion or retention would have been 0.030°, well within the detection limits of the polarimeter.

Calculation of Theoretical Rotation:

α_{589} = $[\alpha]^{24}_{589}$ x (optical purity of (-)-1-phenylethyl bromide) x (isotopic purity of α-deuterioethylbenzene) x (dilution fraction with racemic α-deuterioethylbenzene).

$[\alpha]^{24}_{589}$ = +0.730°; (+)-α-deuterioethylbenzene as the neat liquid [56].

$$\alpha_{589} = (0.730°) \times (0.75) \times (0.60) \times (72/(720+72)) = 0.030°.$$

Preparation of d,ℓ-α-deuterioethylbenzene from d,ℓ-1-phenylethyl bromide

d,ℓ-α-deuterioethylbenzene was used as the solvent for the optical rotation measurements of the α-deuterioethylbenzene obtained from the reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ and (-)-1-phenylethyl bromide.

A 250 ml three-necked flask, fitted with a dropping funnel, a reflex condensor and a nitrogen inlet was purged with nitrogen and charged with 75 ml of THF (purified by vacuum transfer from sodium-benzophenone ketyl) and 0.56 g (0.0135 mol) of lithium aluminum deuteride (LAD). The solution was heated to reflux, and a solution of 5.0 g (.027 mol) of d,ℓ-1-phenylethyl bromide in 30 ml of THF was added over a period of one hour. The solution was then refluxed for twelve hours.

At the end of this period the excess LAD was distroyed by adding a 2:3 H_2O:THF mixture, with cooling, and then the reaction solution was poured onto 100 ml of ice water which contained 20 ml of concentrated H_2SO_4. The aqueous solution was extracted with (3 x 75) ml of petroleum ether and the organic phase was washed successively with (2 x 100) ml water, (2 x 20) ml 85% phosphoric acid, (2 x 50) ml water, 100 ml sodium carbonate solution, and (2 x 100) ml of water. The organic phase was dried over calcium chloride and the petroleum ether was removed under reduced pressure. The crude product, which contained considerable starting material, was distilled at 28 mm Hg and 43-45°C. From this distillate, 0.9 ml of d,ℓ-α-deuterioethylbenzene was collected by preparative gas chromatography on a 10' x 3/8" 10% Degs 60/80 Chrom P NAW glass column, (27% yield). The d,ℓ-α-deuterioethylbenzene showed no optical rotation as the neat liquid.

NMR (CCl_4): δ7.0 PPM (S, 5H, phenyl); δ2.48 PPM (q of t, 1H, $J_{HH} = 8H_z$, $J_{HD} = 2H_z$, methine) δ1.10 PPM (d of t, 3H, $J_{HH} = 8H_z$, $J_{HD} = 1.5\ H_z$, methyl)

Preparation of d,ℓ-1-phenylethyl bromide from d,ℓ-1-phenylethyl alcohol [57]

20.0 g (0.164 mol) of d,ℓ-1-phenylethyl alcohol 27.5g (0.348 mol) of pyridine and 100 ml of diethyl ether were added to a 1000 ml three-necked flask, fitted with a nitrogen inlet, a dropping funnel, and a ground glass stopper. The flask was purged with nitrogen and cooled to -30°C in a dry ice/acetone bath. 48.5 g (0.179 mol) of phosphorus tribromide (PBr_3) in 100 ml of diethyl ether was added from the dropping funnel over a period of 35 minutes. The bath temperature was maintained between -35° and -30°C.

After all the PBr_3 was added, the dry ice acetone bath was removed and the reaction mixture was held at 0-5°C in an ice bath for 5 hours. 100 ml of ice water was then added to destroy the excess PBr_3. The ether layer was collected and washed successively with 100 ml ice water, 100 ml 85% phosphoric acid, 100 ml ice water, 150 ml saturated sodium bicarbonate solution, and finally twice with 100 ml ice water. The ether layer was dried with magnesium sulfate and fractional distillation of the crude product (40-42°C at 1.4 mm Hg) gave 15.6 grams of d,ℓ-1- phenylethyl bromide (52% yield) contaminated with less than 5% of the starting alcohol.

NMR (CCl_4): δ7.28 PPM (m, 5H, phenyl); δ5.09 PPM (q, 1H, methine);
δ1.82 PPM (d, 3H, methyl)

Preparation of (-)-1-phenylethyl bromide from (+)-1-phenylethyl alcohol

5.0 g (.041 mol) of (+)-1-phenylethyl alcohol (α_{589} = 42.50°, neat liquid, d = 1.0001, 97% optically pure), 6.9 g pyridine and 25 ml of diethyl ether were added to a nitrogen purged 3-necked flask fitted with a dropping funnel and a ground glass stopper. The mixture was cooled to -35°C and a solution of 12.2 g (0.045 mol) of PBr_3 in 20 ml of diethyl ether was added over a period of 50 minutes. The reaction solution was then warmed to between 0 and 5°C for 6.5 hours. The excess PBr_3 was destroyed by adding ice water and the reaction solution was poured into 50 ml of ice water. The ether layer was collected and washed with (2 x 30) ml 85% phosphoric acid, 40 ml water, 40 ml saturated sodium bicarbonate solution and (2 x 40) ml water. The ether layer was dried over magnesium sulfate for 1 hour in the refrigerator and the ether was removed by rotoevaporation. Approximately 2 ml of oil remained. This was fractionally distilled at 0.6 mm Hg with the distillation flask held at 65°C. Fractions #1 and #2 distilled at 34°C and fraction #3 distilled at 36-37°C.

Optical rotations of the three fractions:

#1 α_{589} = -1.028°; -1.030°, c = 0.0237 g/2 ml $CHCl_3$
α_{365} = -4.55°
#2 α_{589} = -1.086; -1.087°, c - 0.0261 g/2 ml $CHCl_3$

#3 α_{589} = -1.673 , 0.0335 g/2 ml $CHCl_3$

Optical purity = 100%[α_{589}/(g/m$CHCl_3$)(1)] / -111.5°

$[\alpha]_{589}$ = -111.5° taken from references (58,59).

Optical purities: Fraction #1 = 78%

#2 = 75%

#3 = 89%

Fractions 2 and 3 contained no (-)-1-phenylethyl alcohol as indicated by their NMR spectra.

Preparation of (-)-α-deuterioethylbenzene from (-)-1-phenylethyl bromide

Fraction #3 (∿ 0.3 ml, 1.2 mmol) of (-)-1-phenylethylbromide, prepared previously, was added to 1.0 ml of THF and was dropped slowly from a dropping funnel into a solution of 0.2 g (4.76 mmol) of LAD in 2.0 ml THF at reflux. After 24 hours the excess LAD was destroyed by adding 0.5 ml water in 2.0 ml THF. The reaction mixture was then added to 5 ml concentrated H_2SO_4 in 20 ml water, and the solution was extracted with 50 ml of diethyl ether. The organic phase was washed successively with (2 x 25) ml water, 20 ml 85% phosphoric acid, 25 ml water, 20 ml saturated sodium bicarbonate solution, and finally with (2 x 20) ml water. The ether layer was dried over calcium chloride and the ether was removed at room temperature under reduced pressure. The residue (∿ 80 μl) was purified as before by preparative gas chromatography. 0.0192 g of α-deuterioethylbenzene was collected (15% yield). A solution of this α-deuterioethylbenzene (0.0192 g/0.850 ml $CHCl_3$) showed

α_{589}^{RT} = -0.010° and α_{365}^{RT} = -0.033°.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with acid chlorides. Identification of products

7.1 μl (0.046 mmol) of heptanoylchloride was added to 0.0339 g (0.046 mmol) of $PPN^+(\eta^5C_5H_5)V(CO)_3H^-$ in 0.5 ml of THF. The solution immediately changed color from red-orange to dark green. The volatile material was removed by vacuum transfer at room temperature. The IR spectrum of the volatile material showed a carbonyl absorption at 1725 cm^{-1}, and the NMR spectrum contained a triplet at 9.42 PPM (J = 1.5 Hz). GC analysis showed the product to be heptanal by co-injection. Quantitative GC analysis of other reaction solutions of heptanoyl chloride and $(\eta^5C_5H_5)V(CO)_3H^-$ showed the yield to be 100%.

Isolation of aldehydes from reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ and acid chlorides

Heptanal. 0.5592 g (0.76 mmol) of $PPN^+(\eta^5C_5H_5)V(CO)_3H^-$ was dissolved in 30 ml of THF and 110 μl of heptanoylchloride was added from a syringe. The reaction mixture was removed from the drybox and the volatile material removed by vacuum transfer at room temperature. 50 ml of diethyl ether was added to the THF solution which vacuum transferred, and this was extracted twice with 100 ml of H_2O. The remaining ether phase was dried with sodium sulfate and the ether was removed by rotoevaporation. 30 μl of 90% pure heptanal was recovered and identified by IR and NMR spectroscopy and GC analysis (∿ 30% yield).

Another reaction using a mixed solvent (3:1 THF-diethyl ether) and an identical work-up as above gave a 46% yield of impure aldehyde.

Preparation of the 2,4-dinitrophenylhydrazine derivative of dodecanal. 0.2581 g (0.35 mmol) of PPN^+ $(\eta^5C_5H_5)V(CO)_3H^-$ was dissolved in approximately 20 ml of THF with 0.092 g (0.35 mmol) of triphenylphosphine and 80 µl (0.34 mmol) of dodecanoyl chloride was added. 70 ml of pentane was added to the reaction mixture and a green precipitate formed. The reaction mixture was extracted with 50 ml distilled water. Some of the pentane was then removed by roto-evaporation, and a brown precipitate formed. This was collected, but a KBr pellet infrared spectrum showed no carbonyl absorption. The remaining solvent was removed from the supernatant, and a brown oil remained. 2,4-dinitrophenylhydrazine reagent was added to this oil and a yellowish-orange precipitate formed. 0.0086 g of the 2,4 dinitrophenylhydrazine of dodecanal was obtained (7% yield, M.P. 99-100°C.)

Column chromatography of the reaction solution of $(\eta^5C_5H_5)V(CO)_3H^-$ and dodecanoyl chloride

0.2222 g (0.30 mmol) of PPN^+ $[\eta^5(C_5H_5)V(CO)_3H]$ was dissolved in 10 ml of THF and 70 µl dodecanoyl chloride was added. The reaction mixture was immediately chromatographed outside the drybox, on a grade III alumina column prepared with THF. The column was eluted with THF. A wide yellow band, eluted with the solvent, was collected and the THF removed by roto-evaporation. The residue was extracted with pentane, and a light yellow filtrate was obtained when the solution was filtered. The pentane was removed by roto-evaporation to yield .070 g of a brown solid. This material was chromatographed again on a grade III alumina column, eluting first with pentane to yield a yellow band, and then with

THF to give a fraction which yielded .041 g of a yellow oil. This oil had only a very small amount of dodecanal as indicated by TLC. The exact yield of dodecanal was not determined.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with dodecanoyl chloride and dimethylphenylphosphine

0.1583 g (0.21 mmol) of PPN^+ $(\eta^5C_5H_5)V(CO)_3H^-$ and 100 μl of dimethylphenylphosphine were dissolved in 15 ml of THF and 45 μl (0.19 mmol) of dodecanoyl chloride was added. The solution began to turn dark green but very quickly changed to bright orange and a brown precipitate formed. The IR spectrum of the reaction mixture showed strong carbonyl absorptions at 1940, 1845, 1765 cm^{-1} and a weak absorption of 1720 cm^{-1}. The 1720 cm^{-1} absorption is assigned to dodecanal, and the other absorptions to $(\eta^5C_5H_5)V(CO)_3\ P(C_6H_5)(CH_3)_2$.

The solution was filtered and the THF was removed by rotoevaporation to yield a dark brown residue. This was taken up in pentane but TLC of this reddish-orange solution showed no dodecanal.

Preparation of the 1,2-dianilinoethane derivative of benzaldehyde

0.651 g (0.88 mmol) of PPN^+ $(\eta^5C_5H_5)V(CO)_3H^-$ 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 one minute, 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 rotoevaporation. 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 minutes and upon cooling to room temperature a white precipitate formed. 0.1516 g (61%) of crude product was obtained. 0.0838 g of pure 1,2,3-triphenyl-tetrahydroimidazole was collected after recrystallization from CH_2Cl_2:hexane (32% yield).

NMR ($CDCl_3$): 7.13 (m, 10H, phenyl); 6.57 (m, 5H, phenyl);
5.90 (s, 1H, methine); 3.72 (m, 4H, methylene).

M.P. 135-136°C Lit. 137°C [43]

Preparation of $PPN^+ [(\eta^5C_5H_5)V(CO)_3Br]^-$ from $PPN^+ [(\eta^5C_5H_5)V(CO)_3H]$ and benzyl bromide

0.392 g (.530 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]$ 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 $PPN^+[(\eta^5C_5H_5)V(CO)_3Br]$ was collected (74% yield).

Preparation of $PPN^+[(\eta^5C_5H_5)V(CO)_3Br]^-$ from $(\eta^5C_5H_5)V(CO)_4$

0.0526 g (0.230 mmol) $(\eta^5C_5H_5)V(CO)_4$ and 0.0865 g PPN^+Br^- were added to 5 ml of THF. Not all the PPN^+Br^- dissolved. This solution was photolyzed with a 1000 watt Hg/Xe lamp through pyrex while cooling the reaction vessel externally with water. After 2.25 hours the infrared spectrum of the reaction solution showed bands at 2030, 1945, 1930, 1850, 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): δ4.80 (S, 5H, ($\eta^5C_5H_5$)).

IR (THF): 1945, 1850, 1810 cm^{-1}.

MP 190°C (decomposition)

Elemental Analysis, Calc: C64.58 H 4.28 N 1.71 Br 9.77

Found: C64.50 H 4.76 N 1.70 Br 9.60

Reaction of ($\eta^5C_5H_5$)V(CO)$_3$H$^-$ with limiting amounts of benzylbromide

0.0383 g (0.051 mmol) of PPN$^+$[($\eta^5C_5H_5$)V(CO)$_3$H]$^-$ was dissolved in 0.30 ml of d_8-THF in an NMR tube stoppered with a serum cap. 1.5 μl aliquots (0.0126 mmol) of benzylbromide was added from a 10 μl syringe. The NMR spectrum of the reaction solution was recorded after the addition of each aliquot. Only 5.1 μl (0.042 mmol) of benzylbromide was added before the signal for ($\eta^5C_5H_5$)V(CO)$_3$H$^-$ was completely gone. This was only 0.83 equivalents of benzylbromode which reacted with one equivalent of ($\eta^4C_5H_5$)V(CO)$_3$H$^-$.

The NMR spectra of this reaction solution showed the same new cyclopentadienide resonances that appeared in the NMR spectrum of the reaction solution when one equivalent of benzylbromide was added to ($\eta^5C_5H_5$)V(CO)$_3$H$^-$ in a single aliquot. However, the new resonances appeared in different ratios in the spectra of these reaction solutions. Compare Figure 9a and Figure 10.

Reaction of ($\eta^5C_5H_5$)V(CO)$_3$H$^-$ with p-toluene-sulfonic acid

A solution of PPN$^+$[($\eta^5C_5H_5$)V(CO)$_3$H]$^-$, 0.054 g (0.073 mmol) in 0.350 ml of d_8-THF was prepared in an NMR tube stoppered with a rubber septum. 25 μl of a 2.03 M solution of p-toluenesulfonic acid was added from a 50 μl syringe. The only new cyclopentadienide resonance in the NMR spectra (Figure 12) was at δ4.67 PPM. This was the same chemical shift for one of the new cyclopentadienide resonances in the reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with alkyl bromides.

The cyclopentadienide resonance for $(\eta^5C_5H_5)V(CO)_3H^-$ was absent from the NMR spectrum of the reaction solution after addition of only 0.69 molar equivalents of p-toluenesulfonic acid. After 18 hours the NMR spectrum of the reaction solution showed cyclopentadienide resonances at δ5.14 PPM from $(\eta^5C_5H_5)V(CO)_4$, δ4.67 PPM from the product of the original reaction, and at 4.60 PPM from $(\eta^5C_5H_5)V(CO)_3H^-$.

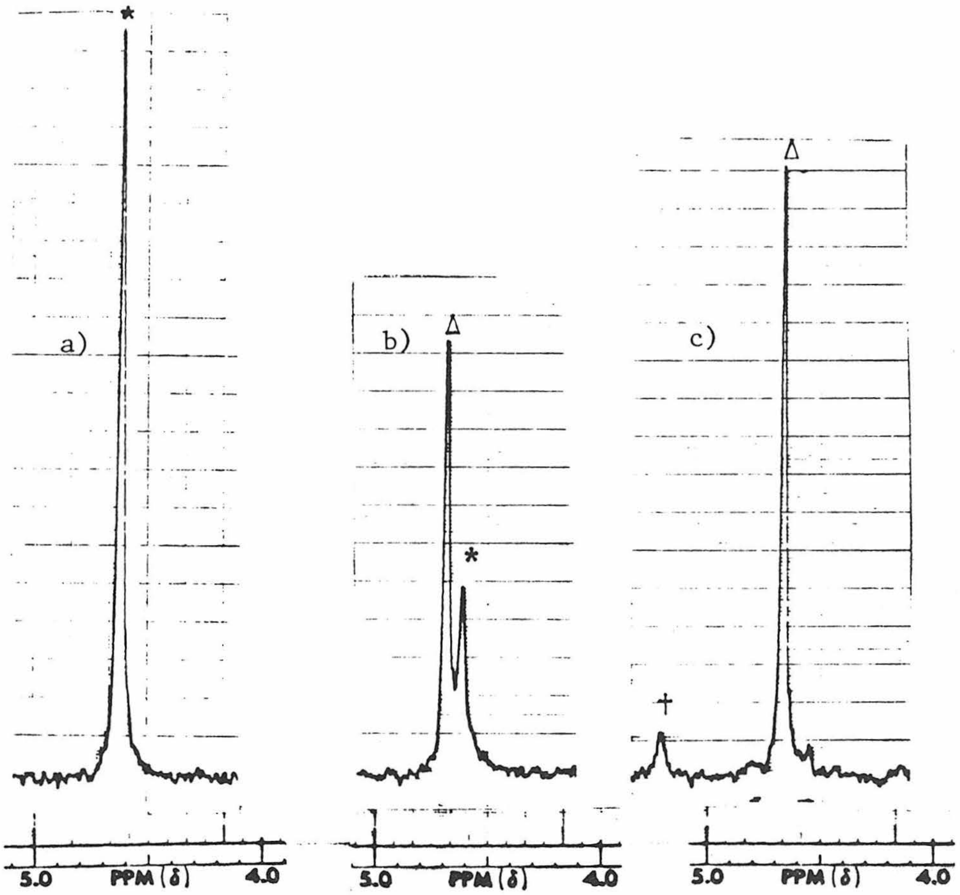
Reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ with galvinoxyl radical and with silver perchlorate gave solutions whose NMR spectra also showed a new cyclopentadienide resonance at δ4.67 PPM.

Reaction of $(\eta^5C_5H_5)V(CO)_3Br^-$ and $(\eta^5C_5H_5)V(CO)_3H^-$

0.0343 g (0.0464 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ and 0.0186 g (0.0228 mmol) of $PPN^+(\eta^5C_5H_5)V(CO)_3Br^-$ were weighed into an NMR tube, and 0.350 ml of d_8-THF was added. The NMR spectrum of the solution was recorded within 5 minutes after addition of the THF. The NMR spectrum showed cyclopentadienide absorptions at δ4.60 from $(\eta^5C_5H_5)V(CO)_3H^-$, δ4.67 and δ4.82 from $(\eta^5C_5H_5)V(CO)_3Br^-$ (Figure 13). The absorption at δ4.67 PPM was the same as that observed in the reactions of $(\eta^5C_5H_5)V(CO)_3H^-$ and alkylbromides.

Figure 12

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ with p-Toluenesulfonic Acid



* $[(\eta^5C_5H_5)V(CO)_3H]^-$

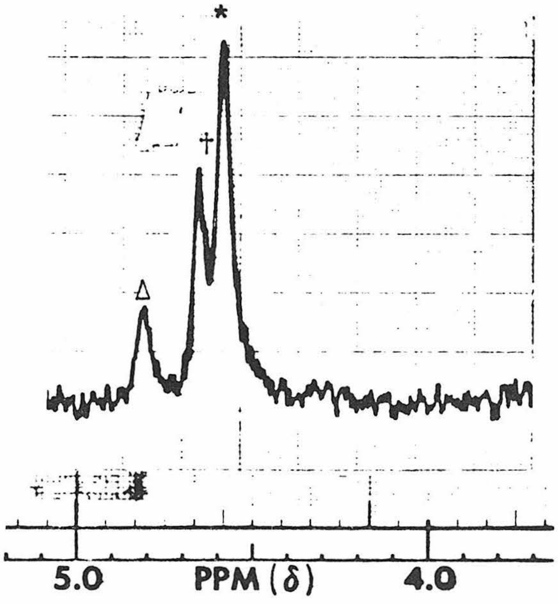
Δ $[(\eta^5C_5H_5)V(CO)_3]_2H^-$

† $[(\eta^5C_5H_5)V(CO)_4$

Figure 13

Reaction of $[(\eta^5C_5H_5)V(CO)_3H]^-$ and $[(\eta^5C_5H_5)V(CO)_3Br]^-$

NMR Spectrum



* $[(\eta^5C_5H_5)V(CO)_3H]^-$

† $[(\eta^5C_5H_5)V(CO)_3]_2H^-$

Δ $[(\eta^5C_5H_5)V(CO)_3Br]^-$

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with one-half equivalent of 1-bromooctane

0.0487 g (0.066 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H^-$ 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 10 µl 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 (Figure 8). After 4.5 hours the reaction between $(\eta^5C_5H_5)V(CO)_3H^-$ 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 δ4.67 PPM resonance was the most intense absorption in the spectrum.

After 18.5 hours the cyclopentadienide resonance at δ4.80 PPM was absent from the NMR spectrum of the reaction solution, but the resonance at δ4.67 PPM was still present, along with the resonance from $(\eta^5C_5H_5)V(CO)_3H^-$ and a small broad absorption from $(\eta^5C_5H_5)V(CO)_4$ at δ5.14 PPM.

The IR spectrum of the reaction solution at this time showed carbonyl absorptions at 2030, 1930, 1890, 1857, 1817, and 1780 cm^{-1} (Figure 8). The absorptions at 2030 and 1930 cm^{-1} correspond to $(\eta^5C_5H_5)V(CO)_4$ and the absorptions at 1890 and 1780 cm^{-1} correspond to $(\eta^5C_5H_5)V(CO)_3H^-$. Therefore, the carbonyl absorptions at 1857 and 1817 cm^{-1} must be from the same vanadium complex that has the δ4.67 PPM resonance in the NMR spectrum.

Attempted isolation of $PPN^+[(\eta^5C_5H_5)V(CO)_3]_2H^-$

0.2736 g (0.371 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ was dissolved in 3 ml of THF, and a solution of 0.0604 g (0.291 mmol) of anhydrous silver perchlorate in 1.0 ml of THF was added by syringe. The color of the solution changed from reddish-orange to a very dark green. A dark grey solid precipitated. This was silver metal. The solution was filtered and the IR spectrum of the filtrate showed carbonyl absorptions at 2030 and 1930 cm^{-1} from $(\eta^5C_5H_5)V(CO)_4$ and at 1855 and 1817 cm^{-1}. There were no carbonyl absorptions corresponding to $(\eta^5C_5H_5)V(CO)_3H^-$. Petroleum ether was added to the filtrate until a sticky precipitate formed. The solution was filtered and the IR spectrum of the filtrate showed carbonyl absorptions for $(\eta^5C_5H_5)V(CO)_4$ only. The precipitate was redissolved in THF, and the IR spectrum had strong carbonyl absorptions at 1855 and 1817 cm^{-1}, with weak absorptions at 1890 and 1780 cm^{-1} which indicated that $(\eta^5C_5H_5)V(CO)_3H^-$ was now present in solution.

When the THF was removed by vacuum transfer and the residue was redissolved in THF, the IR spectrum of the solution showed strong carbonyl absorptions at 1890 and 1780 cm^{-1} for $(\eta^5C_5H_5)V(CO)_3H^-$, and only a very weak absorption at 1855 cm^{-1}. Some $(\eta^5C_5H_5)V(CO)_4$ was also present in solution. Therefore, $PPN^+[(\eta^5C_5H_5)V(CO)_3]_2H^-$ was not stable enough to isolate it as the pure solid by this procedure.

Reaction of $[(\eta^5C_5H_5)V(CO)_3]_2H^-$ with triphenylphosphine

0.118 g (0.160 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ was dissolved in 3.0 ml of THF, and 19 μl of a p-toluenesulfonic acid solution (0.230 g/ 2.0 ml THF; 0.08 mmol) was added. 0.200 g (0.763 mmol) of triphenylphosphine was added to the solution.

After 5 hours the IR spectrum of the reaction solution showed carbonyl absorptions at 1960, 1890, 1860 and 1780 cm^{-1}, and the NMR spectrum showed cyclpentadienide resonances at δ4.78 PPM (d, J= 2.0 Hz), δ4.60 PPM (s) and δ4.28 PPM (t, J = 3.0 Hz) (Figure 14). The NMR resonances corresponded to $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$, $(\eta^5C_5H_5)V(CO)_3H^-$ and what was assumed to be $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$, respectively. The carbonyl absorptions in the IR spectrum were assigned as follows: 1960 and 1860 cm^{-1}, $(\eta^5C_5H_5)V(CO)_3H^-$. $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ was reported to have carbonyl absorptions at δ1870 and δ1780 cm^{-1} [38] so that it was not evident from the IR spectrum that $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ was present. $[(\eta^5C_5H_5)V(CO)_3H^-$ was removed from the solution by the following procedure.

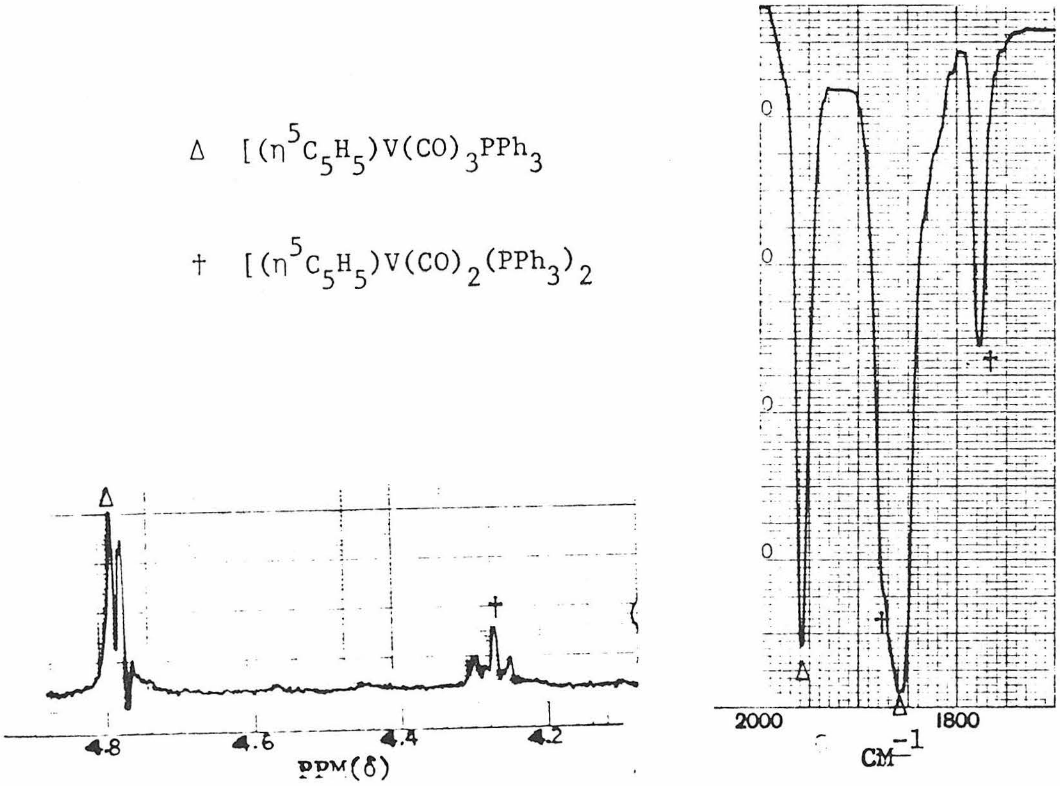
The THF was removed at room temperature under reduced pressure, and the oily residue was extracted with d_6-benzene. $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ was not soluble in benzene. The solution was filtered and a brown solid was collected. The IR spectrum of the reddish-brown filtrate showed carbonyl absorptions at 1960, 1860, and 1780 cm^{-1}. The absence of an 1890 cm^{-1} absorption indicated that $[(\eta^5C_5H_5)V(CO)_3H]^-$ was not present in this solution. Strangely, the NMR spectrum showed only a single doublet at δ4.64 PPM (J = 2.0 Hz). The 1780 cm^{-1} absorption in the IR spectrum implied that $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ was present, but the expected triplet for the cyclopentadienide resonance was not observed in the NMR spectrum. However, when the benzene was removed from the solution, and the residue was redissolved in d_8-THF, then the resonances at δ4.78 PPM (d,J = 2.0 Hz) and at δ4.28 PPM (t, 3.0 Hz), as observed

Figure 14

Reaction of $[(\eta^5C_5H_5)V(CO)_3]_2H^-$ and PPh_3

Δ $[(\eta^5C_5H_5)V(CO)_3PPh_3$

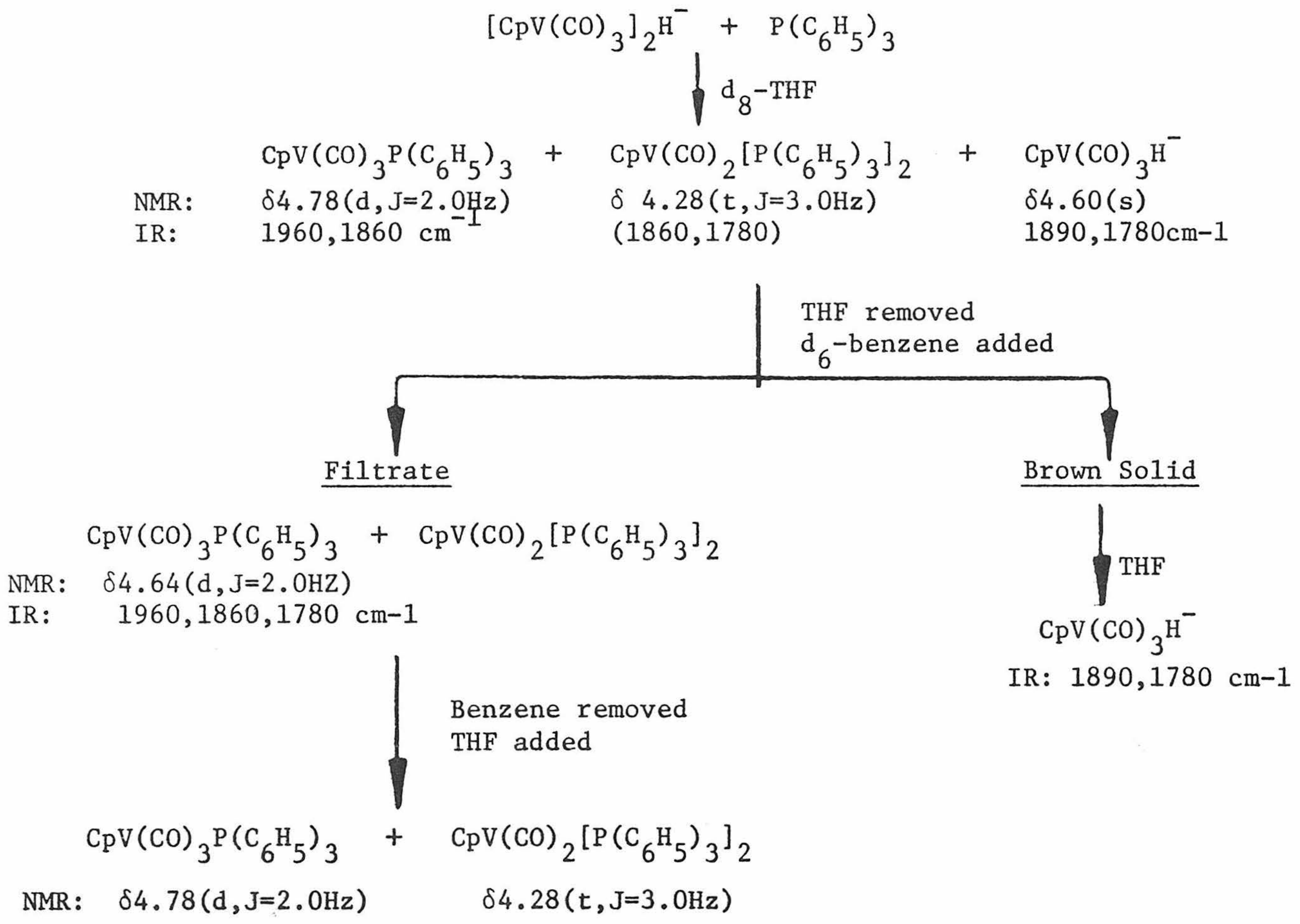
† $[(\eta^5C_5H_5)V(CO)_2(PPh_3)_2$



a) d_8-THF solution of residue from bezene extract.

b) Benzene extract of reaction residue.

SCHEME XIII


$[CpV(CO)_3]_2H^-$ + $P(C_6H_5)_3$
d_8-THF
$CpV(CO)_3P(C_6H_5)_3$ + $CpV(CO)_2[P(C_6H_5)_3]_2$ + $CpV(CO)_3H^-$
NMR: δ4.78(d,J=2.0Hz) δ 4.28(t,J=3.0Hz) δ4.60(s)
IR: 1960,1860 cm^{-1} (1860,1780) 1890,1780cm-1
THF removed
d_6-benzene added
Filtrate
Brown Solid
$CpV(CO)_3P(C_6H_5)_3$ + $CpV(CO)_2[P(C_6H_5)_3]_2$
NMR: δ4.64(d,J=2.0HZ)
IR: 1960,1860,1780 cm-1
THF
$CpV(CO)_3H^-$
IR: 1890,1780 cm-1
Benzene removed
THF added
$CpV(CO)_3P(C_6H_5)_3$ + $CpV(CO)_2[P(C_6H_5)_3]_2$
NMR: δ4.78(d,J=2.0Hz) δ4.28(t,J=3.0Hz)

in the NMR spectrum of the original reaction solution, were present.

Therefore it was concluded that both $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$ and $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ were products of the reaction of triphenylphosphine and $[(\eta^5C_5H_5)V(CO)_3]_2H^-$ (see Scheme XIII).

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ 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 $PPN^+(\eta^5C_5H_5)V(CO)_3H^-$ was added dropwise over a period of five minutes. The solution turned green as the $(\eta^5C_5H_5)V(CO)_3H^-$ was added. An IR spectrum of the reaction solution after all of the $(\eta^5C_5H_5)V(CO)_3H^-$ solution had been added, showed carbonyl absorptions at 1940, 1845, and 1805 cm^{-1} only. This corresponded to $(\eta^5C_5H_5)V(CO)_3Br^-$.

The NMR spectra of the reaction solution of $(\eta^5C_5H_5)V(CO)_3H^-$ and benzyl bromide with triphenylphospine showed cyclopentadienide absorptions for $(\eta^5C_5H_5)V(CO)_3Br^-$, $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$ and $[(\eta^5C_5H_5)V(CO)_3]_2H^-$. The major product was $(\eta^5C_5H_5V(CO)_3Br^-$.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with p-toluenesulfonic acid and triphenylphosphine: Inverse addition

0.80 ml (0.055 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H\ ]^-$ (0.120 g/2.0 ml THF) was added drop-by-drop from a syringe to a solution of 0.152 g (0.882 mmol of p-toluenesulfonic acid and 0.092 g (0.351 mmol) of triphenylphopshine in 2.0 ml THF. A localized green area developed where the $(\eta^5C_5H_5)V(CO)_3H^-$ contacted the p-toluenesulfonic acid solution. There was an immediate color change from green to light red-orange. The

IR spectrum of the reaction solution after all of the $(\eta^5C_5H_5)V(CO)_3H^-$ had been added showed carbonyl absorptions at 1955 and 1860 cm^{-1}, which corresponded to $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with p-toluenesulfonic acid and triphenylphosphine

56.3 μl of a 0.236 M solution of p-toluenesulfonic acid was added from a 10 μl syringe to a solution of 0.057 g (0.077 mmol) of PPN* $[(\eta^5C_5H_5)V(CO)_3H^-]$ and 0.025 g (.099 mmol) of triphenylphosphine. The solution immediately changed color from reddish-brown to dark green. The IR spectrum immediately after the addition showed carbonyl absorptions at 1955, 1860, and 1817 cm^{-1}. The absorptions at 1955 and 1860 cm^{-1} corresponded to $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$ and the absorption at 1817 cm^{-1} indicated that $[(\eta^5C_5H_5)V(CO)_3]_2H^-$ was formed. $[(\eta^5C_5H_5)V(CO)_3]_2H^-$ also has a carbonyl absorption at approximately 1860 cm^{-1}.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with p-toluenesulfonic acid and lithium bromide

0.091 g (0.123 mmol) of $PPN^+[(\eta^5C_5H_5)V(CO)_3H^-]$ and 0.070 g (.806 mmol) of lithium bromide were dissolved in 3.0 ml of THF, and 1.23 ml (.094 g/5 ml; 0.123 mmol) of a p-toluenesulfonic acid solution was added dropwise from a syringe. An immediate reaction occurred and the reaction mixture turned green. An IR spectrum of the reaction mixture showed carbonyl absorptions at 1940, 1845, 1805 cm^{-1}, which corresponded to $(\eta^5C_5H_5)V(CO)_3Br^-$.

Reaction of $(\eta^5C_5H_5)V(CO)_3H^-$ with methyl-p-toluenesulfonate and triphenylphosphine

When 0.8 ml (0.55 mmol) of a $PPN^+[\eta^5C_5H_5)V(CO)_3H]^-$ solution (0.102g/ 2.0 ml THF) was added to a solution of 0.188 g (1.00 mmol) methyl-p-toluenesulfonate and 0.124 g (0.473 mmol) of triphenylphosphine, the IR spectrum of the reaction mixture showed carbonyl absorptions at 1950, 1890, 1855, 1815, 1780 cm^{-1} during the reaction, and at 1955, 1860, and 1780 cm^{-1} when the reaction was complete, as indicated by the disappearance of the 1890 cm^{-1} absorption for $(\eta^5C_5H_5)V(CO)_3H^-$.

The carbonyl absorption in the IR spectrum of the final reaction solution indicated that $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$ and $(\eta^5C_5H_5)V(CO)_2[P(C_6H_5)_3]_2$ were present.

Preparation of $PPN^+[(\eta^5C_5H_5)V(CO)_3CH_3]^-$ from $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ and methyl-p-toluenesulfonate

0.780 g (2.45 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ was slurried in 30 ml THF, and 5.0 ml HMPA was added. A dark red-brown solution resulted. A small amount of grey solid did not dissolve. 0.590 (3.17 mmol) of methyl-p-toluenesulfonate in 10 ml of THF was added from a dropping funnel, and a grey precipitate formed. The solution was stirred for fifteen minutes and filtered. 1.81 g (3.17 mmol) of PPN^+Cl^- was added to the filtrate as the solid. A white precipitate formed and the solution was filtered again. 40 ml of petroleum ether was added to the filtrate in 10 ml portions. 1.536 g of a brick red precipitate was formed and was collected. This was purified by dissolving it in 30 ml of THF, filtering the solution and adding three 10 ml portions of diethyl ether. Each portion was carefully layered on top of the THF solution and allowed to diffuse into the THF before the next portion was added. 1.10 g of a $PPN^+[(\eta^5C_5H_5)V(CO)_3H]^-$ precipitated and was collected (64% yield).

NMR (d_8-THF): δ7.75 (m, 30H, PPN^+); δ4.43 (s, 5H, $(\eta^5C_5H_5)$);
δ-0.33 (S, 3H, methyl).
IR(THF): 1895, 1795, 1775 (sh) cm^{-1}.
M.P. 157°C (decomposition)
Elemental analysis: Calc: C, 71.71; H, 5.08; P, 8.22 V, 6.76
Found: C, 71.38; H, 5.32; P, 8.43; V, 6.82.

Reaction of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with 1-bromooctane in HMPA

0.055 g (0.172 mmol) of $Na_2\ (\eta^5C_5H_5)V(CO)_3\cdot THF$ was dissolved in 0.5 ml of HMPA in an NMR tube stoppered with a rubber septum. The NMR spectrum of the solution showed a single cyclopentadienide resonance at δ4.32 PPM. 9.0 μl (0.056 mmol) of 1-bromooctane was added to the solution. After 50 minutes the NMR spectrum of the solution showed a small cyclopentadienide absorption for $(\eta^5C_5H_5)V(CO)_3H^-$ at δ4.55 PPM, and a new signal at δ4.42 PPM. A signal for the starting material at δ4.32 PPM was still present in the spectrum. Two more 9.0 μl aliquots of 1-bromooctane were added to the reaction solution. After these additions, the cyclopentadienide signal for the starting material was absent from the NMR spectrum of the reaction solution and the new signal at δ4.42 PPM had increased in intensity. The δ4.42 absorption was assumed to be from $(\eta^5C_5H_5)V(CO)_3(C_8H_{17})^-$ in solution, based on the previous preparation of $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$.

$(\eta^5C_5H_5)V(CO)_3(C_8H_{17})^-$ was not isolated, but it was quite stable in HMPA solution. After 8 hours, there was only a very small decrease in the intensity of the cyclopentadienide signal at δ4.42 PPM in the NMR spectrum. After approximately 100 hours, the signal was nearly gone, but there was no concomitant increase in any other cyclopentadienide resonances in the NMR spectrum.

Reactions of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with secondary alkyl halides

The reactions of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ with 2-iodopropane and bromocyclopentane were carried out similarly to the reaction with 1-bromooctane. The reactions with 2-iodopropane and bromocyclopentane were very fast, but gave no new vanadium products. The cyclopentadienide resonance for $(\eta^5C_5H_5)V(CO)_3^{2-}$ in the NMR spectra of the reaction solution disappeared during the reactions, but no new cyclopentadienide resonances appeared. The organic products were not identified.

Reaction of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with 2-octyl-p-toluenesulfonate

When a solution of 0.164 g (0.458 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ in 2.0 ml of HMPA was added to a 0.152 g (0.532 mmol) of 2-octyl-p-toluenesulfonate in 1.0 ml of HMPA, a reaction occurred immediately. The NMR spectrum of the reaction solution showed a single cyclopentadienide resonance at δ4.56 PPM, which corresponded to $(\eta^5C_5H_5)V(CO)_3H^-$.

Reaction of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with acetyl chloride

0.100 g (0.314 mmol) of $Na_2(\eta^5C_5H_5)V(CO)_3\cdot THF$ was slurried in 2.4 ml THF, and 0.6 ml HMPA was added. A red-brown homogeneous solution resulted. 30 μl (0.406 mmol) of acetyl chloride was added. The reaction solution immediately changed color to dark brown, and the IR spectrum of the reaction solution showed carbonyl absorptions at 2030, 1930, and

1800 cm^{-1}. The 2030 and 1930 cm^{-1} absorptions corresponded to $(\eta^5C_5H_5)V(CO)_4$.

Reaction of $(\eta^5C_5H_5)V(CO)_3^{2-}$ with anhydrous silver perchlorate

0.0882 g (0.358 mmol) of Na_2 $(\eta^5C_5H_5)V(CO)_3$·THF was slurried in 6 ml of THF and aliquots of a 0.437M THF solution of silver perchlorate were added. After 0.36 molar equivalents of silver perchlorate had been added, the IR spectrum of the reaction solution showed carbonyl absorption at 2030 and 1930 cm^{-1} corresponding to $(\eta^5C_5H_5)V(CO)_4$, and at 1890, 1855, 1795, 1780 (sh) and 1735 cm^{-1}, which indicated Na $[(\eta^5C_5H_5)V(CO)_3H]$ was present. After the addition of 0.73 mole equivalents of silver perchlorate and an excess of PPN^+Cl^- the IR spectrum showed carbonyl absorptions for $(\eta^5C_5H_5V(CO)_4$ and $(\eta^5C_5H_5)V(CO)_3H^-$.

Reaction of $(\eta^5C_5H_5)V(CO)_3CH_3^-$ with acetyl chloride

0.031 g (0.041 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3(CH_3)]^-$ and 0.050 g (0.190 mmol) of triphenylphosphine were dissolved in 2.2 ml of THF, and 3.0 μl (0.040 mmol) of acetyl chloride was added from a 10 μl syringe. There was an immediate color change from reddish-brown to black. The IR spectrum of the reaction mixture showed no carbonyl absorptions. No attempts were made to identify the organic products.

Reaction of $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$ with methyl-p-toluenesulfonate

0.030 g (0.040 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3(CH_3)]^-$ was dissolved in 2.0 ml of THF, and 0.028 g (0.150 mmol) of methyl-p-toluenesulfonate was added as the solid. The carbonyl absorptions for $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$ were absent from the IR spectrum of the reaction solution after 44.5

hours, but no new carbonyl absorptions appeared.

The NMR spectra of a similar reaction solution showed the disappearance of the cyclopentadienide and methyl resonances for $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$. The methyl absorption from methyl-p-toluenesulfonate also decreased in intensity, but no new cyclopentadienide or methyl absorptions appeared in the NMR spectrum of the reaction solution. No absorptions for ethane were observed in any of the NMR spectra.

Reaction of $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$ and triphenylphosphine

0.050 g (0.19 mmol) of triphenylphosphine was added to a solution of 0.031 g (.041 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3CH_3^-]$ in 2.2 ml THF. The IR spectra of the reaction mixture showed no changes in the carbonyl absorptions after 18.5 hours.

Reaction of $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$ with benzyl bromide

9.4 μl (0.079 mmol) of benzyl bromide was added to 0.028 g (0.037 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3(CH_3)]^-$ in 1.0 ml of THF. After 4 hours the color of the solution had changed from red-brown to black. The volatile material from the reaction solution was vacuum transferred and analyzed by gas chromatography. No ethylbenzene was detected.

Reactions of $(\eta^5C_5H_5)V(CO)_3(CH_3)^-$ and p-toluenesulfonic acid

With Added Triphenylphosphine: 32 μl of a 0.236M THF solution of p-toluenesulfonic acid (0.044 mmol) was added to a solution of 0.033 g (.044 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3CH_3^-]$ and .030 g (0.14 mmol) of triphenylphosphine in 3.0 ml of THF. The solution immediately changed color from reddish brown to dark brown. The IR spectrum of the reaction solution showed new carbonyl absorptions at 1955 and 1860 cm^{-1} only, which corresponded to $(\eta^5C_5H_5)V(CO)_3P(C_6H_5)_3$.

With Added Lithium Bromide: 740 µl of a 0.110M solution of p-toluenesulfonic acid was added to a solution of 0.061 g (.081 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3CH_3^-]$ and 0.036 g (0.41 mmol) in 5.0 ml of THF. The solution changed color immediately from reddish-brown to dark brown. The IR spectrum showed new carbonyl absorptions at 1945, 1850, 1810 cm^{-1}.

With Added Triphenylphosphine and Lithium Bromide: When 172 µl of a 1.07M solution of p-toluenesulfonic acid was added to a solution of 0.081 g (0.108 mmol) of PPN^+ $[(\eta^5C_5H_5)V(CO)_3CH_3^-]$, 0.070 g (0.806 mmol) of lithium bromide and 0.151 g (0.576 mmol) of triphenylphosphine, there was an immediate color change from reddish-brown to dark brown. The IR spectrum of the reaction solution recorded within 15 minutes after the addition of the p-toluenesulfonic acid showed carbonyl absorptions at 1955, 1870 (sh), 1860, and 1780 cm^{-1}. There was no carbonyl absorption at 1810 cm^{-1} to indicate that $(\eta^5C_5H_5)V(CO)_3Br^-$ had been formed. The carbonyl absorptions at 1955 and 1860 cm^{-1} corresponded to $(\eta^5C_5H_5)V(CO)_3$-$P(C_6H_5)_3$, and the absorptions at 1870 and 1780 cm^{-1} to $(\eta^5C_5H_5)V(CO)_2$-$[P(C_6H_5)_3]_2$.

X-ray analysis of PPN^+ $[(\eta^5C_5H_5)V(CO)_3H^-$

Single crystals of PPN^+ $[(\eta^5C_5H_5)V(CO)_3H]^-$ were prepared by two methods. Petroleum ether was carefully layered onto a THF solution of PPN^+ $[(\eta^5C_5H_5)V(CO)_3H]^-$. This mixture was left at room temperature until the petroleum ether diffused into the THF solution. The dark brown precipitate was collected, washed quickly with THF and petroleum ether, and dried in the drybox.

Alternatively, PPN$^+$ [(η^5C$_5$H$_5$)V(CO)$_3$H] was precipitated from a THF solution at low temperatures. 0.122 g of PPN$^+$ [(η^5C$_5$H$_5$)V(CO)$_3$H] was added to 0.350 ml of d$_8$-THF in an NMR tube, and the NMR tube was sealed under vacuum. The THF was warmed slightly in order to dissolve all of the PPN$^+$ [(η^5C$_5$H$_5$)V(CO)$_3$H], and the NMR tube was stored at -50°C for two weeks. The precipitate which formed was collected as before. The crystals which were collected were air stable.

The crystals obtained from these procedures were multiple crystals, and intensity data for a complete structure were not collected. Oscillation photographs had m_x symmetry [61a], indicating that there was a mirror plane perpendicular to the rotation axis. First level Weissenberg photographs showed that the a and c axes were separated by 90°. Therefore the crystal system was orthorhombic.

First level Weissenberg pictures had systematic absences of h = 2n+1 and k = 2n+1 so that space group was P2$_1$2$_1$2$_1$ or P2$_1$2$_1$2 [61b]. From the oscillation photograph, b, the direct lattice repeat distance was 26.23Å [61c], and a = 19.59Å, c = 14.00Å from the zero level Weissenberg photograph. The unit cell volume was 7,193Å.

The calculated density, assuming eight molecules per unit, was 1.36 g/ml. This agreed with a density of 1.33 g/ml measured by floatation in CCl$_4$:hexane. Therefore there were two molecules of PPN$^+$ [(η^5C$_5$H$_5$)-V(CO)$_3$H]$^-$ and 102 nonhydrogen atoms per asymmetric unit.

References

1. a) J. P. Collman, *Acc. Chem. Res.* **8**, 342 (1975);
   b) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.* **99**, 2515 (1977).
2. It is assumed that the alkyl group migrates, as opposed to carbon monoxide insertion, as has been shown for $Mn(CO)_3CH_3$. K. Noack and F. Calderazzo, *J. Organomet. Chem.* **10**, 101 (1967).
3. a) M. P. Cooke, *J. Amer. Chem. Soc.* **92**, 6080 (1970);
   b) J. P. Collman, S. R. Winter, and R. G. Komota, *J. Amer. Chem. Soc.* **95**, 249 (1973).
4. W. Strohmeier and J. F. Guttenberger, *Ber.* **97**, 1256 (1964).
5. J. Ellis, *J. Organomet. Chem.* **86**, 1 (1975).
6. J. Evans, S. I. Okrasinki, A. J. Pribula, and J. R. Norton, *J. Amer. Chem. Soc.* **99**, 5835 (1977).
7. J. D. Cotton, S.A.R. Knox, and F.G.A. Stone, *J. Amer. Chem. Soc. A* 2758 (1968).
8. B. Centikaya, M. F. Lappert, and K. Turner, *J. Chem. Soc.*, 851 (1972).
9. E. O. Fischer, *Adv. Organomet. Chem.* **14**, 1 (1976).
10. E. O. Fischer, *Chem. Ber.* **103**, 3684 (1970).
11. Attempts to prepare the dianions $(\eta^5C_5H_5)CoCO^{2-}$ and $(\eta^5C_5H_5)Mn(CO)_2^{2-}$ have been unsuccessful. C. S. Ilenda, N. S. Schore, and R. G. Bergman, *J. Amer. Chem. Soc.* **98**, 255,256 (1976).
12. a) K.S.Y. Lau, P. K. Wong, and J. K. Stille, *J. Amer. Chem. Soc.* **98**, 5832 (1976); b) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.* **96**, 2815 (1974);

c) P. J. Krusic, P. J. Fagan, and J. San Filippo, Jr., *J. Amer. Chem. Soc.* **99**, 250 (1970); d) J. K. Stille and A. B. Cowell, *J. Organomet. Chem.* **124**, 253 (1977).

13. J. N. Cawse, PH.D. Thesis, Stanford University, California, 1973.

14. a) H. Alper, *Tetrahedron Lett.* **27**, 2257 (1975); b) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.* **93**, 1529 (1971).

15. H. G. Kuvilla, *Acc. Chem. Res.* **1**, 299 (1968).

16. E. O. Fischer and S. Vigoureux, *Chem. Ber.* **91**, 2205 (1958).

17. E. O. Fischer and R.J.J. Schneider, *Angew. Chem. Inter. Ed.* **6**, 569 (1967).

18. a) J. E. Ellis, R. A. Faltynek and S. G. Hentges, *J. Organomet. Chem.* **120**, 389 (1976); b) A very small amount of grey solid did not dissolve. This presumably was mercury from the sodium amalgam used in the preparation of Na_2-**1**·THF.

19. a) K. H. Powell and D. Jackson, *J. Amer. Chem. Soc.* **98**, 4443 (1976); b) M. Darensbourg, D. J. Darensbourg, D. Burns and D. A. Drew, *J. Amer. Chem. Soc.* **98**, 3127 (1976).

20. M. Elian and R. Hoffman, *Inorg. Chem.* **14**, 1056 (1975).

21. The reaction of Na_2-**1** with water to form **3** had previously been suggested, but the hydride product had not been isolated or characterized (see Ref. 16).

22. J. W. Faller, A. S. Anderson and Chin-Chun Chen, Chemm. Comm., 719 (1969).

23. J. D. Atwood and T. L. Brown, *J. Amer. Chem. Soc.* **98**, 3610 (1976).

24. A similar explanation has been given for the changes in the IR spectra of THF solutions of Na $(\eta^5C_5H_5)Fe(CO)_2$ when dibenzo-18-crown-6 was added [19].

25. The anion $[(CH_3)_3C_6H_3V(CO)_3]^-$ showed a similar cation dependence, such that the high energy carbonyl stretch was independent of the cation, but the lower energy absorptions changed position. $Na[(CH_3)_3C_6H_3V(CO)_3]$, $\nu_{C\equiv O}$ at 1837 (vs), 1761 (s), 1703 (s) cm^{-1} and $[(C_4H_9)_4N][(CH_3)_3C_6H_3V(CO)_3]$, $\nu_{C\equiv O}$ at 1838 (vs), 1753 (s) and 1733 (sh) cm^{-1}.

26. A. Davidson and R. L. Reger, *J. Organomet. Chem.* **23**, 491 (1970); b) J. E. Ellis and R. A. Faltynek, *J. Organomet. Chem.* **93**, 205 (1975); c) T. Kruck and H. U. Hempel, *Angew. Chem. Inter. Ed.* **13**, 201 (1974).

27. $(\eta^5C_5H_5)V(CO)_3$ has been proposed in the reaction of **1** with aqueous HCl. E. O. Fischer and R.J.J. Schneider, *Chem. Ber.* **103**, 3684 (1970).

28. Photochemical ligand substitutions occur very readily on $(\eta^5C_5H_5)V(CO)_4$. a) Ref. 16; b) M. Wrighton, *Chem. Rev.* **74**, 401 (1971).

29. W. D. Jones and R. G. Bergman, unpublished results.

30. The isoelectronic complex $[Cr(CO)_5]_2H^-$ is known. M. Darensbourg and N. Walker, *J. Organomet. Chem.* **117**, C68 (1976).

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

32. H. G. Kuvilla, Acc. Chem. Res. **1**, 299 (1968).

33. D. M. Singleton and J. K. Kochi, *J. Amer. Chem. Soc.* **89**, 6547 (1967).

34. a) C. A. Walling and J. H. Cooley, *J. Amer. Chem. Soc.* **88**, 5363 (1966); b) D. Lai, D. Griller, S. Husband and K. U. Ingold, *J. Amer. Chem. Soc.* **96**, 6355 (1974).

35. When **3** was reacted with neophyl bromide no carbonium ion rearranged product, 2-methylpropylbenzene was formed. W. D. Jones and R. G. Bergman, unpublished results.

36. The rate of hydrogen atom abstraction from $(\eta^5 C_5H_5)V(CO)_3H^-$ by carbon radicals has been estimated to be $\sim 2 \times 10^7 \text{ sec}^{-1}$, nearly an order of magnitude greater than tri-n-butyl tin hydride. W. D. Jones and R. G. Bergman, unpublished results.

37. W. D. Jones and R. G. Bergman have shown that for reduction of CH_2 $CHCH_2OCH_2CH_2Br$ with **3**, the ratio of ethyl allyl ether and 2-methyltetrahydrofuran produced does vary linearly with the concentration of **3**.

38. A dissociative mechanism has not been demonstrated for the displacement of carbon monoxide by triphenylphosphine on **4** and **6**. However, the thermal displacement of carbon monoxide by triphenylphosphine on $(\eta^5 C_5H_5)V(CO)_4$ has been shown to occur by dissociation of carbon monoxide. G. C. Faber and R. J. Angelici, *Inorg. Chem.* **9**, 1536 (1970).

39. The arguments used by Brown [8] can be applied to either a transition state or an assumed square pyramidal intermediate, formed from dissociative loss of carbon monoxide.

40. a) A. R. Rossi and R. Hoffman, *Inorg. Chem.* **14**, 365 (1975); b) J. K. Burdett, *Inorg Chem.* **14**, 375,391 (1975).

41. J. P. Collman, R. G. Finke, J. N. Cawse and J. I. Beauman, *J. Amer. Chem. Soc.* **99**, 2515 (1977).

42. a) S. J. Okrasinski and J. R. Norton, *J. Amer. Chem. Soc.* **99** 295 (1977); b) E. L. Muetterties and P. L. Watson, *J. Amer. Chem. Soc.* **98**, 4665 (1976).

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

44. Galbraith Laboratories, P. O. Box 4187, Knoxville, Tenn. 37921.

45. Schwarzkopf Microanalytical Laboratory, Inc., 56-19 37th Avenue, Woodside, New York 11377.

46. Dornis V. Kolbe Mikroanalytischer Laboratorium, 4330 Mulheim a.d. Ruhr 7, Hohenweg 17, West Germany.

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

48. S. H. Babcock in H. S. Booth (ed.) *Inorg. Synthesis* **1**, 10 (1939).

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

50. T. H. Morton, Ph.D. Dissertation, California Institute of Technology, 1972.

51. M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis", 1967, pp. 767, 1158.

52. *Ibid*, p. 1180.

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

54. J. K. Ruff in G. W. Parshall (ed.), *Inorg. Synthesis* **15**, 84 (1974).

55. M. E. Bednas and D. S. Russell, *Can. J. Chem.* **36**, 1272 (1958).

56. a) L. Verbit, Progress in Physical Organic Chemistry **7**, 51 (1970); b) d^{25}= 0.8712 g/ml for α-deuterioethylbenzene. H. J. Dauben Jr. and L. L. McCoy, *J. Amer. Chem. Soc.* **81**, 5404 (1959).

57. Hans-Werner Wanzlick and W. Lochel, *Jahrg.* **86**, 1463 (1953).

58. H.M.R. Hoffman and E. D. Hughes, *J. Chem. Soc.*, 1244 (1964).

59. K.S.Y. Lau, P. K. Wong and J. K. Stille, *J. Amer. Chem. Soc.* **98** 5832 (1975).

60. R. L. Burwell, Jr., A..D. Shields and H. Hart, *J. Amer. Chem. Soc.* 76, 908 (1954).

61. a) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination--A Practical Guide" (1968), p. 97; b) *Ibid*, p. 134; c) *Ibid*, p. 118.

62. Assistance from Dr. Neil Mandel is gratefully acknowledged.

63. The measured density of cyclobutenecarbonate was 1.474 g/ml.

Introduction:

Cyclopentadienyl vanadium tricarbonyl, $(\eta^5C_5H_5)V(CO)_3^{2-}$, is the only known monomeric dianionic organometallic complex with ligands other than carbon monoxide [14]. Attempts to prepare $(\eta^5C_5H_5)Mn(CO)_2^{2-}$ and $(\eta^5C_5H_5)CO(CO)^{2-}$ have not been successful [14]. These complexes may lack sufficient carbon monoxide ligands to stabilize, through π-bonding, the electron density on the metal.

It occurred to us that the two electron reduction of complexes of the general formula $RM(CO)_3L$, where R represents an organic π-electron system, and L is a 2 electron donor ligand, might loose L to form the dianions $RM(CO)_3^{2-}$. The π-accepting ability of R is important in these complexes. R should be a better π-acceptor than L, so that R is not lost during the reduction. It seems likely that the poorer π-acceptor ligands will be lost during the reduction reaction, and the better π-acceptors will remain on the metal to help stabilize the large amount of electron density at the metal center in the dianion.

For the Group VI metals, R must be a four electron ligand in order that $RM(CO)_3L$ satisfy the Effective Atomic Number Rule. Such four electron ligands could be dienes. Calculations [15] indicate that the most favorable bonding interaction for the $M(CO)_3L$ fragment, where L = CO, occurs with the cyclobutadiene ligand, though stable complexes with non-conjugated dienes are known [16].

If R is cyclooctatraene, initially a six electron ligand, $RM(CO)_3$, upon reduction, cyclooctatraene might change to a four electron ligand [17] in $RM(CO)_3^{2-}$.

We report here the reduction of the complexes $RM(CO)_3L$, where M = Cr, Mo; R = norbornadiene; L = CO, and M = Mo; R,L = cyclooctatetraene. Attempts to prepare complexes where R was a cyclobutadiene ligand were not successful.

Results and Discussion

Reductions of the complexes $RM(CO)_4$, where R equaled norbornadiene and cyclooctatetralene and M = Cr, Mo, to the corresponding dianions $RM(CO)_3^{2-}$, were not successful. The complexes for R equal 1,2,3,4-tetramethylcyclobutadiene, benzocyclobutadiene and cyclobutadiene could not be prepared.

Attempted preparation of 1,2,3,4-tetramethyl cyclobutadiene chromium tetracarbonyl

1,2,3,4-tetramethylcyclobutadiene chromium tetracarbonyl had been previously reported [1], but no experimental details were included. It was reported that a THF solution of $Cr(CO)_6$, treated with sodium amalgam and then with 1,2,3,4-tetramethyldichlorocyclobutene, gave low yields of the cyclobutadiene chromium tetracarbonyl. It was not determined by these workers [1] if the low yields were due to partial reduction of the $Cr(CO)_6$ (to form the presumed reactive species $Cr(CO)_5^{2-}$) or to the subsequent reaction with 1,2,3,4-tetramethyldichlorocyclobutene.

Therefore, disodium chromium pentacarbonyl was prepared [2] and isolated. Its reaction with 1,2,3,4-tetramethyldichlorocyclobutene in THF gave no cyclobutadiene chromium tetracarbonyl. The IR spectrum of the reaction mixture which resulted from the addition of one-half molar equivalent of disodium chromium pentacarbonyl to 1,2,3,4-tetramethyldichlorocyclobutene showed carbonyl absorptions at 2035 (very weak), 1940 (very strong) and 1900 cm^{-1}. The reported IR spectrum for tetramethylcyclobutadiene chromium tetracarbonyl had absorptions at 2039, 1949, and 1941 cm^{-1}, although the solvent was not specified [1]. After another one-half equivalent of disodium chromium pentacarbonyl was added to the reaction mixture, the IR spectrum showed no carbonyl absorptions above 2000 cm^{-1}, and strong absorptions at 1930 and 1870 cm^{-1}. The disappearance of the 2035 and 1940 cm^{-1} absorptions indicated that if any of the cyclobutadiene complex had been formed it was not stable to the reaction conditions. This reaction was not pursued because it appeared from the intensity of the 2035 cm^{-1} band that only very small quantities of the desired product were being formed.

Attempted preparation of cyclobutadiene chromium tetracarbonyl

Cyclobutadiene chromium tetracarbonyl had also been reported [1] but the yield was less than 1% when $Cr(CO)_6$ was photolyzed in the presence of 3,4-dichlorocyclobutene [3]. The reaction of $Cr(CO)_6$ with sodium amalgam in THF and subsequent treatment of that solution with 3,4-dichlorocyclobutene also gave low yields of cyclobutadiene chromium tetracarbonyl [3].

Because the published procedure for preparing 3,4-dichlorocyclobutene was very tedious [4], cyclobutene carbonate was used instead as a precursor for the cyclobutadiene ligand. Grubbs [5] used cyclobutene carbonate [6] and tetracarbonyl ferrate(-II) anion, $Fe(CO)_4^{2-}$, to prepare cyclobutadiene iron tricarbonyl. In the analogous manner, disodium chromium pentacarbonyl was added to a solution of cyclobutene carbonate at -78°C. The IR spectrum of the reaction solution recorded at -40°C showed that no chromium pentacarbonyl was present, nor was any cyclobutadiene chromium tetracarbonyl produced. The reported IR spectrum for the desired product had carbonyl absorptions at 2080 and 1970 cm^{-1}, but the

IR spectrum of the reaction solution had bands at neither of these positions.

Attempted preparation of benzocyclobutadiene chromium tetracarbonyl

The addition of disodium chromium pentacarbonyl to 3,4-dibromobenzocyclobutane gave a solution whose IR spectrum showed carbonyl absorptions at 2060 (very weak), 1975, 1945, 1925, 1898, and 1875 cm^{-1}. Three of these bands were similar to the reported carbonyl absorptions for benzocyclobutadiene chromium tetracarbonyl at 2080,, 1980, and 1945 cm^{-1} [3]. The absorptions at 1898 and 1875 cm^{-1} corresponded to $Cr_2(CO)_{10}^{2-}$ [10]. Attempts to isolate the product responsible for the 2060, 1975, and 1945 cm^{-1} absorptions by removing the reaction solvent and extracting the residue with petroleum ether and then diethyl ether led to decomposition. The only carbony absorption remaining in the IR spectrum of the diethyl ether extract was at 1990 cm^{-1} from $Cr(CO)_6$. If benzocyclobutadiene chromium tetracarbonyl was produced in the reaction, it was unstable to this isolation procedure.

When $Cr(CO)_6$ was photolyzed in the presence of 3,4-dibromocyclobutane, as reported by Pettit [3], no new signals appeared in the NMR spectrum of the reaction solution, which corresponded to the reported values for benzocyclobutadiene chromium tetracarbonyl.

The preparation of cyclobutadiene complexes was not pursued. The reported preparations and characterizations [2,3] of the above compounds were not particularly useful. The yields from the reported preparations were generally 10% or less and the spectroscopic data were reported without reference to the solvents used. The elemental analysis for cyclobutadiene chromium tetracarbonyl was reported not to be satisfactory, although it was stated that the mass spectrum was consistent with the proposed formula [3].

Only the reaction of disodium chromium pentacarbonyl with 3,4-dibromocyclobutane gave any indication that the desired cyclobutadiene complex might have been formed, although the spectroscopic data did not correspond exactly to the literature values.

Preparation and reduction of norbornadiene molybdenum tetracarbonyl and norbornadiene chromium tetracarbonyl

Another 4π-electron system capable of forming stable complexes with the $M(CO)_4$ fragment, M = Cr, Mo was norbornadiene [11]. The reduction of norbornadiene molybdenum tetracarbonyl and norbornadiene chromium tetracarbonyl with sodium amalgam or sodium dispersion led to decomposition of the starting complexes by loss of the norbornadiene ligand. The only new absorptions in the NMR spectra of these reaction solutions was non-coordinated norbornadiene. The IR spectra showed carbonyl absorptions which corresponded to $Mo_2(CO)_{10}^{2-}$ and $Cr_2(CO)_{10}^{2-}$ [10].

The loss of the norbornadiene ligand upon reduction of these complexes was not unreasonable. As electron density on the metal was increased by addition of electrons, the better π-back bonding ligands were held more strongly to help stabilize the electron density. The isolated olefins of norbornadiene were certainly weaker π-bonding ligands than carbon monoxide and so were lost from the complex during reduction. Formation of $Mo_2(CO)_{10}^{2-}$ and $Cr_2(CO)_{10}^{2-}$ was also consistent with the observation that these are the products when $Mo(CO)_6$ and $Cr(CO)_6$ are reduced with sodium amalgam in THF [10].

Experimental

Reaction of $Cr(CO)_5^{2-}$ with 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene

10 ml of a solution of 0.386 g (1.79 mmol) of disodium chromium pentacarbonyl in 20 ml of THF was added to a solution of 0.3 g (1.67 mmol) of 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene. The reaction mixture was kept at room temperature over night. The IR spectrum of the reaction mixture showed no disodium chromium pentacarbonyl to be present. A very weak absorption at 2035 cm^{-1} and strong absorptions at 1940 and 1900 cm^{-1} were present. The remaining 10 ml of disodium chromium pentacarbonyl solution was added to the reaction solution. The IR spectrum then showed no carbonyl absorptions above 2000 cm^{-1}. No 1,2,3,4-tetramethylcyclobutadiene chromium tetracarbonyl was indicated to be present from the IR spectrum.

Reaction of $Cr(CO)_5^{2-}$ with cyclobutene carbonate

A solution of 0.095 ml (1.18 mmol)[163] of cyclobutene carbonate in 10 ml of THF was placed in a 100 ml round bottom flask which was fitted with a pressure equalizing dropping funnel that contained a solution of 0.280 g (1.17 mmol) of disodium chromium pentacarbonyl in 20 ml of THF. The dropping funnel was stoppered with a straightbore stopcock and the apparatus was removed from the drybox and attached to an argon line with a bubbler. The cyclobutene carbonate solution was cooled to -78°C and the disodium chromium pentacarbonyl solution was added slowly over a forty-five minute period. When all of the disodium chromium pentacarbonyl solution had been added, the reaction solution was light orange. The THF was removed at -10°C under a dynamic vacuum, and the dark brown residue was transferred into the drybox.

The IR spectrum of a petroleum ether extract showed carbonyl absorptions at 1990, 1960, 1945 and 1915 cm^{-1}. The absence of an absorption at 2080 cm^{-1} indicated that no cyclobutadiene chromium tetracarbonyl was present.

The reaction was repeated and the IR spectrum of the reaction solution was recorded at -40°C. Carbonyl absorptions were observed at 1960, 1941, 1886, 1851, and 1801 cm^{-1}. None of these bands corresponded to disodium chromium pentacarbonyl or cyclobutadiene chromium tetracarbonyl.

Reaction of $Cr(CO)_5^{2-}$ with 3,4-dibromobenzocyclobutane

A solution 0.98 g (3.74 mmol) of 3,4-dibromobenzocyclobutane in 10 ml of THF was placed in a 100 ml round bottom flask which was fitted with a pressure equalizing dropping funnel containing 0.932 g (3.91 mmol) of disodium chromium pentacarbonyl in 20 ml of THF. The dropping funnel was fitted with a serum cap and the entire apparatus was removed from the drybox. The flask was cooled to -78°C while argon was bubbled into the solution. The disodium chromium pentacarbonyl was added to the flask from the dropping funnel over a period of one hour. The reaction mixture was allowed to warm to room temperature over a four hour period. While the solution was warming to room temperature a precipitate formed.

The reaction flask was transferred back into the drybox, the reaction solution was filtered, and the solvent was removed from the filtrate by vacuum transfer. The IR spectrum of the residue showed carbonyl absorptions at 2060 (very weak), 1975, 1945, 1925 (strong), 1898, and 1875 cm^{-1}. The IR spectrum of the diethyl ether extract of the residue from the above petroleum ether solution showed carbonyl absorptions at 2040 (very weak), 1990 (very strong) and 1930 cm^{-1}. After 24 hours the IR spectrum of the diethyl ether solution showed only a single carbonyl absorption at 1990 cm^{-1}. This corresponded to chromium hexacarbonyl.

None of these IR spectra indicate that benzocyclobutadiene chromium tetracarbonyl had been formed [1,3].

Preparation of disodium chromium pentacarbonyl

The following procedure was adapted from that of Ellis [2].

Two 3-necked, 500 ml round bottom flasks were fitted with dry ice condensers with drying tubes, and were connected to each other by a piece of vacuum tubing. Flask #1 was connected to a liquid ammonia tank. Flask #2 was stoppered with a ground glass stopper.

Flask #1 was flushed with nitrogen, and 1.0 gram of sodium metal was added. Then ∿200 ml of liquid ammonia was condensed into flask #1 by filling the condenser with dry ice/acetone, cooling the flask with a dry ice/acetone bath, and allowing gaseous ammonia from the tank to flow into flask #1. When the ammonia condensed on the sodium, a dark blue solution formed. After the ammonia was condensed into flask #1, flask #2 was flushed with nitrogen and 7.5 g (34 mmol) of chromium hexacarbonyl and 3.0 g (131 mmol) of freshly cut sodium metal were added. The dried ammonia in flask #1 was then transferred to flask #2 by opening the clamp on the vacuum tubing between the flasks, and condensing the ammonia into flask #2.

After the ammonia was transferred to flask #2, the clamp between flask #1 and flask #2 was replaced. The solution in flask #2 was allowed to stir at reflux for 3 hours. At the end of this period the solution was red-brown. The dry ice/acetone condenser was removed from flask #2, and a mercury bubbler was attached to the flask. The ammonia was allowed to evaporate slowly at room temperature. When the ammonia had evaporated and only a dark brown oil remained, the mercury bubbler was removed and the remaining ammonia was removed under vacuum ($\sim$ 0.25 mm Hg) at room temperature. When the ammonia was removed a light yellow solid remained. The flask was transferred into the drybox and the yellow solid was extracted with 150 ml of THF. The solution was filtered, and the THF was removed from the filtrate under vacuum at room temperature. The bright yellow solid which remained was dried under vacuum (0.25 mm Hg) at 45°C for 1.5 hours. 7.05 g (87% yield) of disodium chromium pentacarbonyl was collected.

Reduction of norbornadiene molybdenum tetracarbonyl and norbornadiene chromium tetracarbonyl

Norbornadiene molybdenum tetracarbonyl and norbornadiene chromium tetracarbonyl were prepared by literature procedures [11].

0.173 g (0.576 mmol) of norbornadiene molybdenum tetracarbonyl was dissolved in 5.0 ml of THF and 6.4 g (2.0 mmol of sodium) of sodium amalgam was added to the solution. The IR spectrum of the reaction mixture, after twelve hours at room temperature, showed carbonyl absorptions for norbornadiene molybdenum tetracarbonyl which were reduced in intensity from the starting reaction solution, but no new carbonyl absorptions were present. The NMR spectrum of a similar reaction mixture showed new absorptions at $\delta 6.68$ (t,4H) and $\delta 1.90$ (t,2H) for norbornadiene.

Reductions with sodium dispersion also caused the loss of the norbornadiene ligand from norbornadiene molybdenum tetracarbonyl as was indicated by the NMR spectra of the reaction solutions.

The reactions of norbornadiene chromium tetracarbonyl with sodium dispersion also yielded new absorptions for norbornadiene in the NMR spectra of the reaction solutions.

Pyrolysis of norbornadiene molybdenum tetracarbonyl

0.341 g (1.14 mmol) of norbornadiene molybdenum tetracarbonyl was placed in a 10 ml round bottom flask and the flask was evacuated. The flask was immersed in an oil bath and the temperature was increased slowly to a maximum of 200°C. The volatile products were trapped at -198°C.

The NMR and IR spectra of the volatile products showed only norbornadiene, molybdenum hexacarbonyl and norbornadiene molybdenum tetracarbonyl to be present.

Preparation of cyclooctatetraene molybdenum tricarbonyl

The procedure was analogous to that of King and Fronzaglia [12].

3.45 g (11.7 mmol) of tris-acetonitrile molybdenum tricarbonyl, 2.5 ml (22.0 mmol) of cyclooctatetraene, and 50 ml of hexane were placed in a 100 ml round bottom flask with a reflux condenser. The flask was removed from the drybox and heated at reflux for 31 hours. At the end of this period the solution was dark red-brown. The solution was filtered and the solvent removed from the filtrate at 0.5 mm Hg and room temperature. The residue was transferred into the drybox, extracted with 25 ml hexane, and filtered. An IR spectrum of the filtrate showed carbonyl absorptions at 2005, 1948, and 1917 cm^{-1}. The filtrate was cooled to -78°C and the solution was filtered under argon. 0.100 g of red-brown solid was collected. The IR spectrum of this material was identical to the original filtrate, and corresponded to the reported spectrum for cyclooctatetraene molybdenum tricarbonyl. See Table I for the carbonyl absorptions of cyclooctatetraene molybdenum tricarbonyl in various solvents.

IR spectrum of cyclooctatetrane molybdenum tricarbonyl in THF

0.008 g of cyclooctatetraene molybdenum tricarbonyl was dissolved in 1.0 ml of THF and the IR spectrum was recorded. Carbonyl absorptions occurred at 1992, 1922, 1895 and 1782 cm^{-1}. The THF was removed under vacuum at room temperature, and the residue was redissolved in petroleum ether. The IR spectrum showed carbonyl absorptions at 2005, 1950, 1918, and 1908 (sh) cm^{-1}, the same as cyclooctatetraene molybdenum tricarbonyl in hexane.

Reduction of cyclooctatetrane molybdenum tricarbonyl in diethyl ether

0.038 g (0.129 mmol) of cyclooctatetraene molybdenum tricarbonyl was dissolved in 8 ml of diethyl ether and 2.74 g (0.86 mmol sodium) of sodium amalgam was added. After 6.5 hours there were no changes in the infrared spectra of the reaction solution. The reaction mixture was decanted from the sodium amalgam, and an excess of sodium dispersion was added. After 16 hours the IR spectrum of the reaction mixture showed only two weak absorptions at 1940 and 1895. No other new carbonyl absorptions were present.

A precipitate had formed in the reaction mixture. This was collected and a portion redissolved in HMPA. The HMPA immediately turned blue, indicating there was some sodium dispersion in the precipitate. The IR spectrum of the HMPA solution had a sharp absorption at 1855 cm^{-1} and a very broad absorption centered at 1720 cm^{-1}.

TABLE I

Carbonyl Absorptions for Cyclooctatetraene Molybdenum in Various Solvents

Solvent	$\nu_{C\equiv O}(cm^{-1})$	$\nu_{C=C}(cm^{-1})$
cyclohexane	2006, 1945, 1916	1675 (13)
THF	1992, 1922, 1895, 1782	
diethyl ether	2005, 1938, 1906	1675
HMPA	1895, 1748	

<u>Reduction of cyclooctatetraene molybdenum tricarbonyl in THF</u>

0.022 g (0.075 mmol) of cyclooctatetraene molybdenum tricarbonyl was dissolved in 3 ml of THF and an excess of sodium amalgam (0.00034 mol sodium/g amalgam) was added to the solution. The IR spectrum of the reaction mixture after 19.5 hours showed carbonyl absorptions of 1902, 1860 and 1765 cm^{-1}. The IR spectrum of the reaction mixture did not change over the next 24 hours. The solution was decanted from the sodium amalgam and an excess of sodium dispersion was added. After 16 hours the IR spectrum of the reaction mixture still had not changed.

Reduction of 1,3-butadiene iron tricarbonyl

0.190 g (0.98 mmol) of 1,3-butadiene iron tricarbonyl was dissolved in 10 ml of THF, and less than one molar equivalent of sodium dispersion was added. There was an immediate color change from light yellow to dark red-brown. The IR spectrum of the reaction mixture showed carbonyl absorptions at 2045 and 1975 cm^{-1} for 1,3-butadiene iron tricarbonyl and new absorptions at 1932, 1880, 1850, 1800, and 1640 cm^{-1}.

When an excess of sodium dispersion was added, the IR spectrum of the reaction solution showed no carbonyl absorptions for the starting material and no additional new bands.

No products were isolated from the reaction mixture, nor were any of these new carbonyl absorptions assigned.

Preparation of cyclobutene carbonate

A photolysis cell, similar to that described by Bloomfield [7], was charged with 1200 ml of acetone which had been dried over 4A molecular sieves and fractionally distilled, and 10.0 g (0.108 mmol) of vinylene carbonate. The solution was purged with argon for 30 minutes, and then cooled to 0°C. The solution was saturated with acetylene.

Photolysis of the solution was carried out with a 450 watt Hanovia mercury vapor arc lamp, Model 679-A36, through a quartz immersion photolysis well.

The progress of the reaction was monitored by removing 5 ml samples from the photolysis cell with a syringe and needle, removing the solvent by roto-evaporation, dissolving the light brown residue in d_6-acetone, and recording the NMR spectrum.

The photolysis was discontinued after 14 hours when the amount of cyclobutene carbonate in the reaction mixture began to decrease. The solvent was removed by roto-evaporation, leaving 8.5 ml of a dark-brown oil. The residue was fractionally distilled. The first fraction distilled at 33-34°C (∿2 mm Hg) and the second at 86-89°C (1.8 mm Hg). The second fraction was redistilled to give 1.7 g (13% yield) of a light brown liquid, whose NMR spectrum corresponded to that reported for cyclobutene carbonate [5].

NMR (d_6-acetone): δ6.82 (m, 1H, vinyl); δ5.52 (m, 1H, methane)
Lit [5]: δ6.71 (m, 1H); δ5.48 (m, 1H).

Preparation of $(\eta^5C_5H_5)V(CO)_2[P(C_4H_9)_3]_2$ from $(\eta^5C_5H_5)V(CO)_4$

0.4336 g (1.9 mmol) of $(\eta^5C_5H_5)V(CO)_4$ and 0.860 g (4.28 mmol) of $P(C_4H_9)_3$ were dissolved in 25 ml of benzene in a pyrex flask fitted with a reflux condenser. The solution was photolyzed with a 1000 watt Hg/Xe lamp without external cooling of the reaction flask. The reaction progress was monitored by recording the IR spectrum of the reaction solution, and the photolysis was stopped after 3 hours when the carbonyl absorptions for $(\eta^5C_5H_5)V(CO)_2[P(C_4H_9)_3]_2$ no longer increased in intensity. There was still $(\eta^5C_5H_5)V(CO)_3[P(C_5H_9)_3]$ in solution, but no $(\eta^5C_5H_5)V(CO)_4$ remained.

The benzene was removed under reduced pressure, and the residue was chromatographed on Grade V alumina with hexane. A single red band was eluted. The IR spectrum showed carbonyl absorptions for both $(\eta^5C_5H_5)V(CO)_3[P(C_4H_9)_3]$ and $(\eta^5C_5H_5)V(CO)_2[P(C_4H_9)_3]_2$.

This mixture was rechromatographed on Grade III alumina with petroleum ether. A light red band, $(\eta^5C_5H_5)V(CO)_2[P(C_4H_9)_3]_2$, eluted first, and was followed by a yellow band of $(\eta^5C_5H_5)V(CO)_3[P(C_4H_9)_3]$.

Addition of sodium amalgam to a THF solution of $(\eta^5C_5H_5)V(CO)_2[P(C_4H_9)_3]_2$ gave no reaction.

References

1. R. G. Amiet, P. C. Reeves, and R. Pettit, *Chemm. Comm.*, 1208 (1967).
2. J. E. Ellis, S. G. Hedges, A. G. Kalina, and G. P. Hagen, *J. Organomet. Chem.* **97**, 79 (1975).
3. a) J. S. Ward and R. Pettit, *Chemm. Comm.*, 1419 (1970);
   b) Cyclobutadiene chromium tetracarbonyl reported in 3a was characterized by IR, NMR and Moss spectroscopy. Elemental analyses were not satisfactory. No solvents were reported for the IR and NMR data.
4. R. Pettit and J. Henry in R. Breslow (ed.), *Org. Syn.* **50**, 36 (1970).
5. a) R. H. Grubbs, *J. Amer. Chem. Soc.* **92**, 6693 (1970).
   b) Private communication from R. H. Grubbs to R. G. Bergman.
6. Cyclobutene carbonate was prepared by the method described by Grubbs [4] in a low temperature photolysis cell similar to the one described by Bloomfield [7].
7. J. J. Bloomfield and D. C. Owsley, *Organic Preparation and Procedure, Inc.* **3**, 6 (1971).
8. The 3,4-dibromobenzocyclobutane was a gracious gift of D. W. Brown, prepared by the method of Cava [9].
9. M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **79**, 1701 (1957).
10. a) R. G. Hayter, *J. Amer. Chem. Soc.* **88**, 4376 (1966); b) E. Lindner, H. Behrens, and S. Birkle, *J. Organomet. Chem.* **15**, 7516 (1968).
11. M. A. Bennet, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).
12. R. B. King and A. Fronzaglia, *Inorg. Chem.* **5**, 1837 (1966).
13. C. G. Kruter, A. Maasbal, F.A.L. Anet, and H. D. Kaesz, *J. Amer. Chem. Soc.* 88, 3444 (1966).

14. C. S. Ilenda, N. S. Schore, and R. G. Bergman, J. Amer. Chem. Soc. **98**, 255,256 (1976).

15. M. Elian and R. Hoffman, Inorg. Chem. **14**, 1056 (1975).

16. M. A. Bennett, L. Pratt, and G. Wilkinson, J. Chem. Soc., 2037 (1961).

17. H. D. Kaesz, S. Winstein, and C. G. Kreiter, J. Amer. Chem. Soc. 88, 1319 (1966).

Abstracts of Propositions

I. Stabilization of silicon-carbon double bonds in aromatic π-systems is considered. Preparations of sila-benzene transition metal complexes are proposed.

II. A study of the ligand substitution rates in the complexes $(\eta^5C_5H_5)V(CO)_3X^-$, where X= I^-, Br^-, Cl^-, NC_5H_5, PR_3, $(\eta^5C_5H_5)V(CO)_3H^-$, is proposed in order to evaluate the labilizing effects of the ligands, X.

III. A mechanistic study of the chemiluminescence in the oscillating reaction of horseradish peroxidase catalyzed oxidations is proposed.

IV. A test is described for distinguishing between a 1,3-hydrogen and a 1,3-carbon shift in a rearrangement of a 1,2-dimethylenecyclobutane ligand of a transition metal complex.

V. The possiblity of transition metal-silylene complexes as intermediates in the catalyzed addition of disilanes to acetylenes is discussed. The prepararion of transition metal-silylenes and a study of their reactions with acetylenes is described.

Proposition I

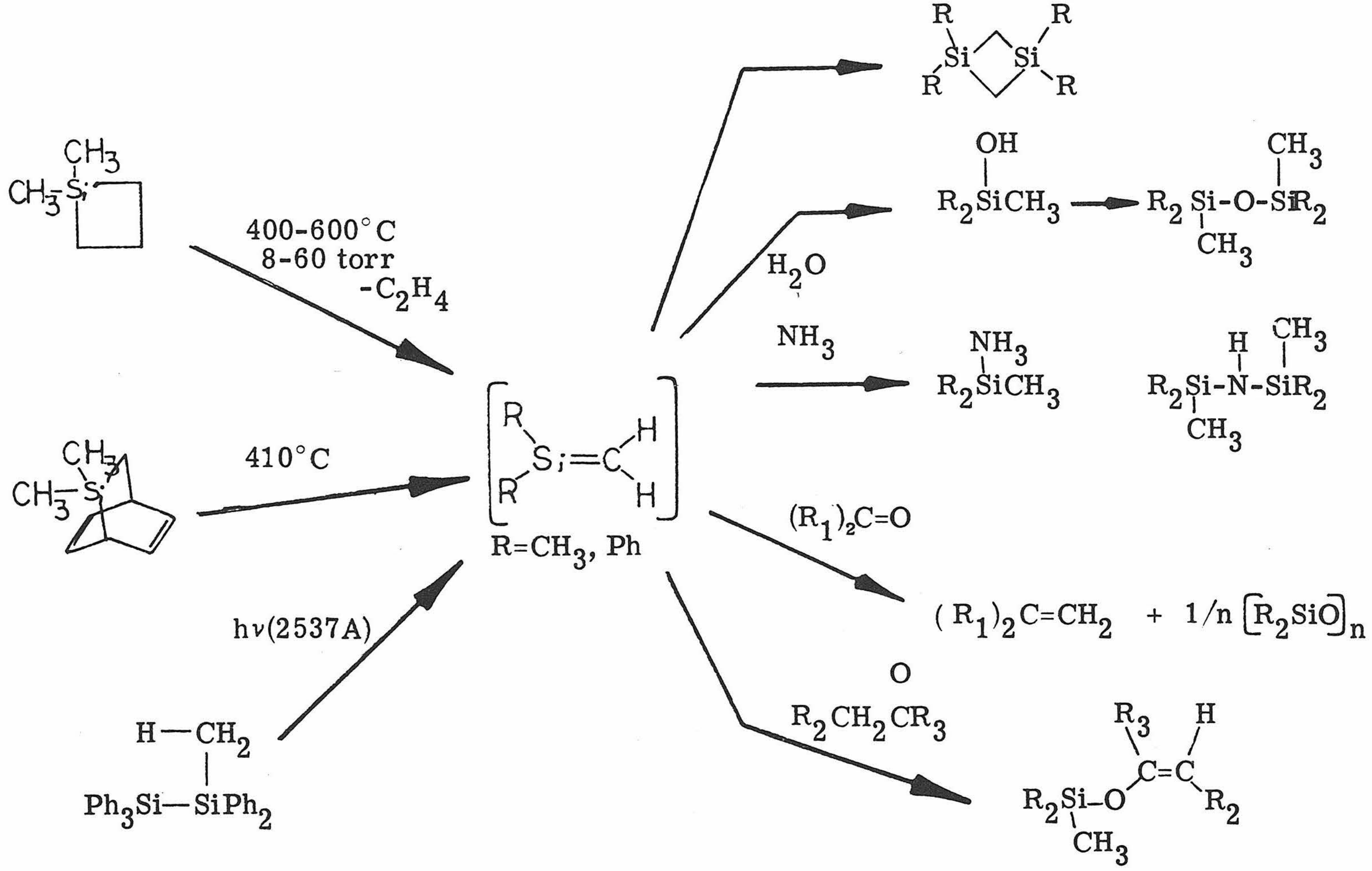
Preparation of Sila-Benzene Transition Metal Complexes

Early theoretical work (1) led to the formulation of the "chemical double bond rule", which stated that elements having a principal quantum number greater than two, should not form $(p-p)\pi$ bonds with themselves or with other elements. However, recent experimental work has produced several exceptions to this rule. Stable phosphorus-carbon, arsenic-carbon, antimony-carbon and bismuth-carbon double bonds have been prepared (2).

There has also been considerable interest in the preparation of silicon carbon double bonds (2), and in particular aromatic systems where a single carbon atom has been replaced by silicon (2,3). A number of methods for the generation of reactive silicon-carbon double bonds have been developed. Scheme I shows different silicon-carbon double bond precursors and the products obtained from the reactions of the reactive silaethylene (2). Chapman and Barton (4) and Chedekel (5) have recently presented spectroscopic evidence for the presence of 1,1,2-trimethylsilaethylene in inert matrices below 45 K.

Only recently has a compound with a stabilized silicon-carbon double bond been prepared. Two η^3-1-sila-propenyl tricarbonyl iron complexes have been prepared as shown in Scheme II (6). These complexes, though somewhat air sensitive were thermally stable to 80°C. The sturctures were assigned on the basis of spectroscopic data, with the important $\nu_{s=c}$ assigned to an absorption at 1315 cm^{-1} (6).

SCHEME I


400-600° C
8-60 torr
$-C_2H_4$
410° C
hν(2537A)
$H-CH_2$
$Ph_3Si-SiPh_2$
R=CH_3, Ph
H_2O
NH_3
$(R_1)_2C=O$
$R_2CH_2CR_3$
R_2SiCH_3
$R_2Si-O-SiR_2$
$R_2Si-N-SiR_2$
$(R_1)_2C=CH_2$ + 1/n $[R_2SiO]_n$
R_2Si-O

No direct evidence has been presented for existence of Silabenzene (Figure 1).

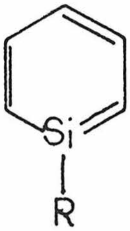
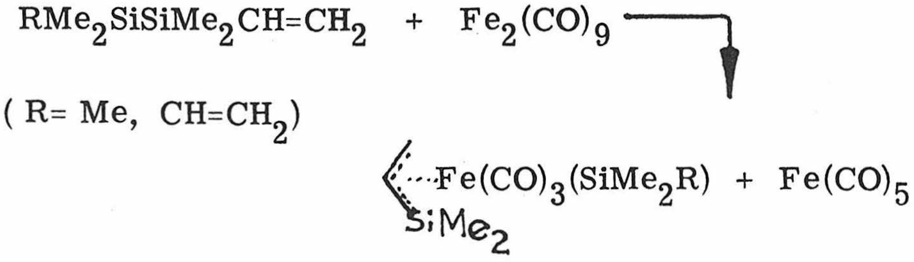


FIGURE 1

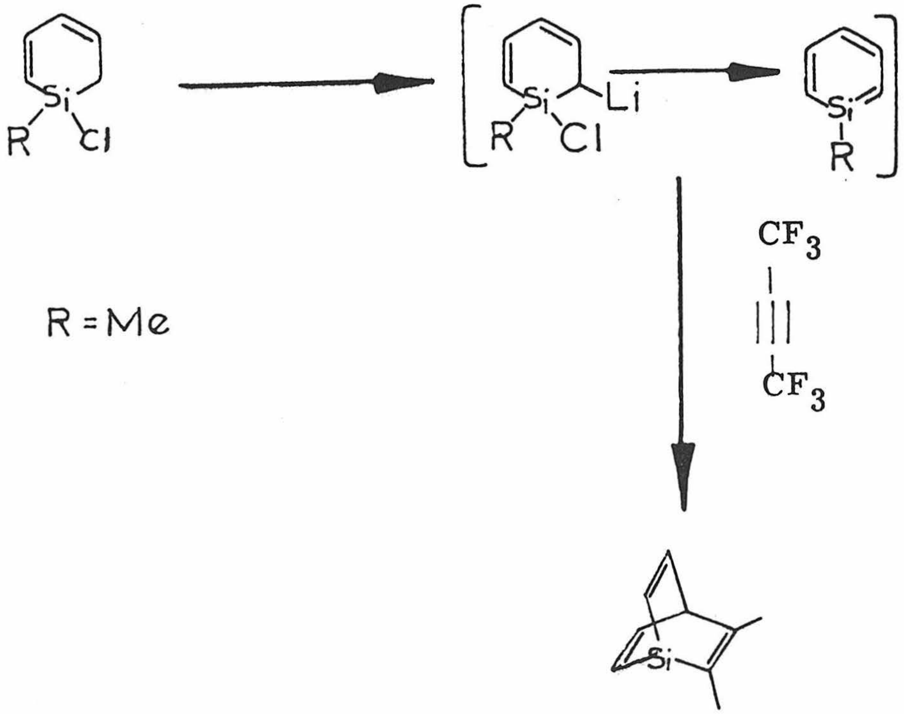
Barton has presented indirect evidence for the generation of silabenzene from the 1,2 elimination of lithium chloride from the silacyclohexadiene shown in Scheme III. However, the author admits that the observed product could have resulted from the reaction of the metalated intermediate and bis-trifluoromethylacetylene.

Considering that a large number of very stable Arene-transition metal complexes have been reported (7) it is proposed that transition metal complexes of sila-benzene be prepared. This method of stabilizing silicon-carbon bonds has been considered previously (6,8). Attempts to prepare silaethylene have not been successful (8), but η^3-silapropenyl iron compounds have been made (6). However, no reports of

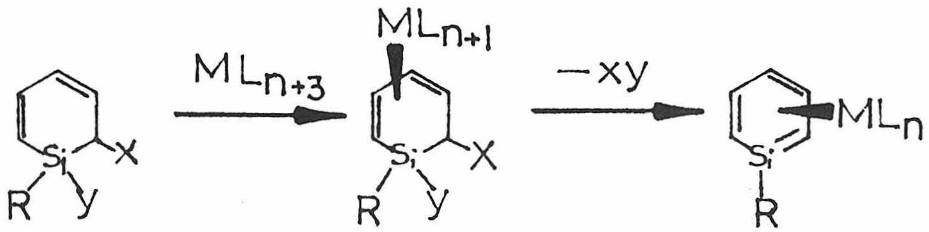
SCHEME II



SCHEME III



SCHEME IV



any sila-aromatic systems coordinated to transition metals could be found.

The general procedure proposed is preparation of transition metal complexes of 1-sila-cyclohexa-2,4-dienes (Scheme IV). A 1,2-elimination of X and Y will generate a sila-benzene which is already partially bound to the metal. The metal must only lose a ligand and form a π bond to the silicon-carbon double bond in order to form a sila-benzene complex.

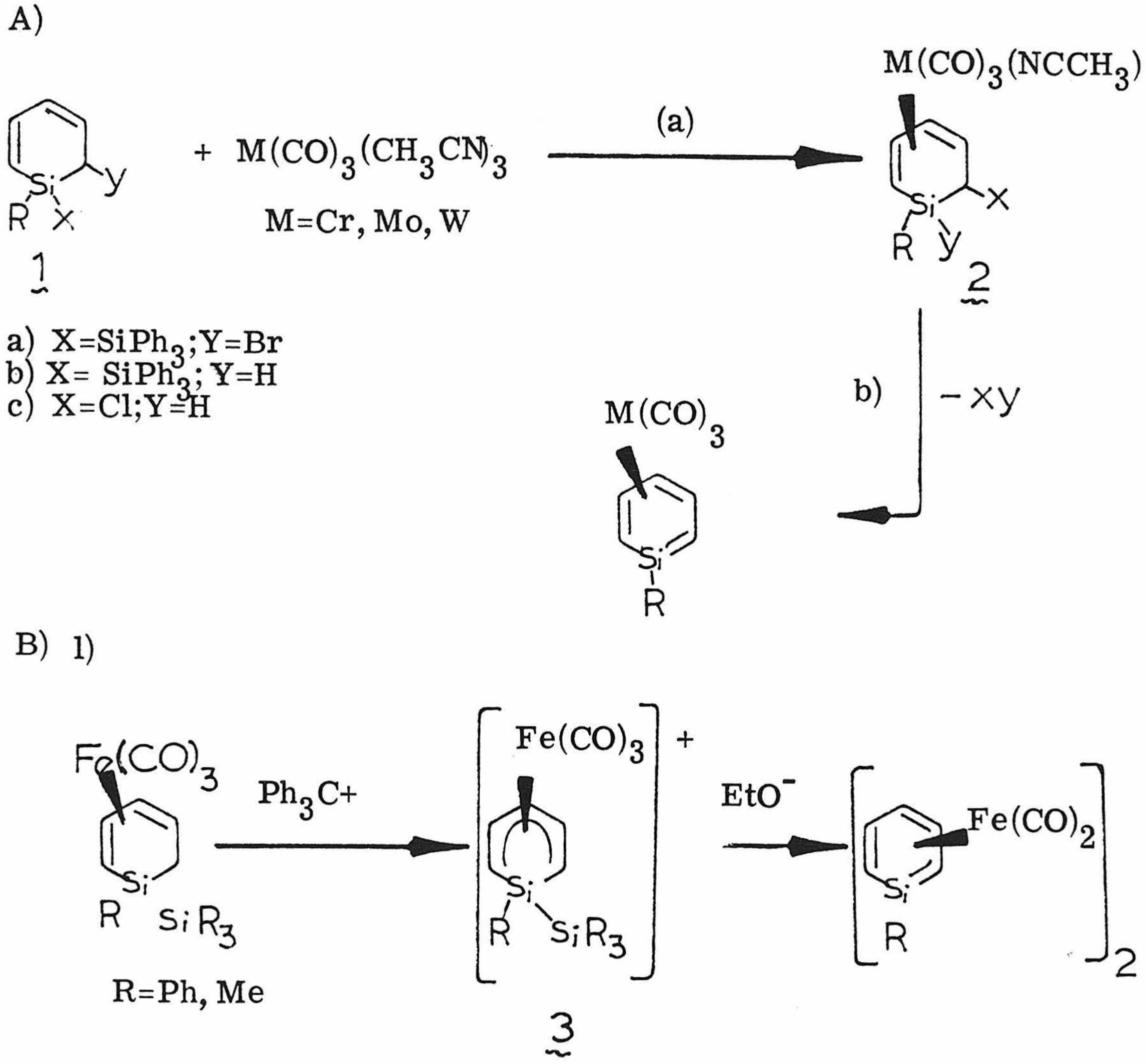
Some specific reaction sequences proposed for the preparation of sila-benzene complexes are shown in Scheme V.

Scheme VA shows the preparation of sila-benzene $M(CO)_3$ complexes, where M=Cr, Mo, W. The benzene analogues are well known, stable complexes. The tris-acetonitrile tricarbonyl complexes undergo facile ligand substitution (9), and should allow the diene system to coordinate to the metal readily (10).

The required 1,1-disubstituted-1-sila-cyclohexa-2,4-dienes, 1a-c (Scheme V) can be prepared from the 1,1-dichloro compound, which has been previously prepared (11). R_1 in 1a-c may be methyl or phenyl and could be introduced by displacement of chloride with methyl or phenyl lithium (11). The silicon substituent in 1a,b could be added by nucleophilic displacement at silicon by triphenylsilicon anion. Bromination of 1b to 1a can be carried out with n-bromosuccinimide (11).

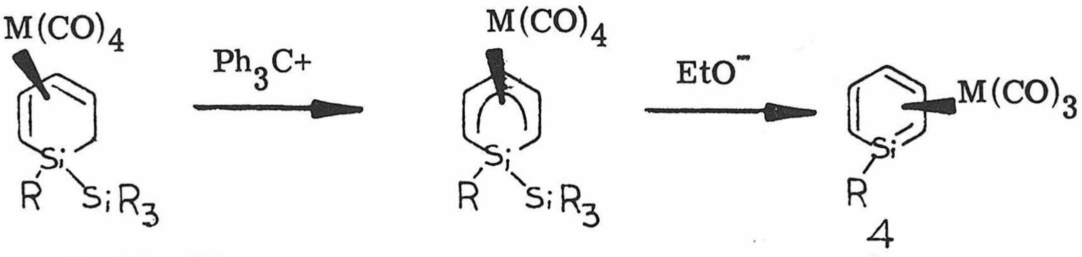
Formation of the diene complex 2 should occur readily by displacement of the acetonitrile ligands of $M(CH_3CN)_3(CO)_3$. All of the 1,2-eliminations of XY to form silicon-carbon double bonds are precedented

SCHEME V


A)
M(CO)3(NCCH3)
(a)
+ M(CO)3(CH3CN)3
M=Cr, Mo, W
Si
R
X
Y
1
2
a) X=SiPh3;Y=Br
b) X= SiPh3; Y=H
c) X=Cl;Y=H
b)
-XY
M(CO)3
B) 1)
Fe(CO)3
Ph3C+
Fe(CO)3 +
EtO-
Fe(CO)2
SiR3
R=Ph, Me
3
2

SCHEME V (cont)

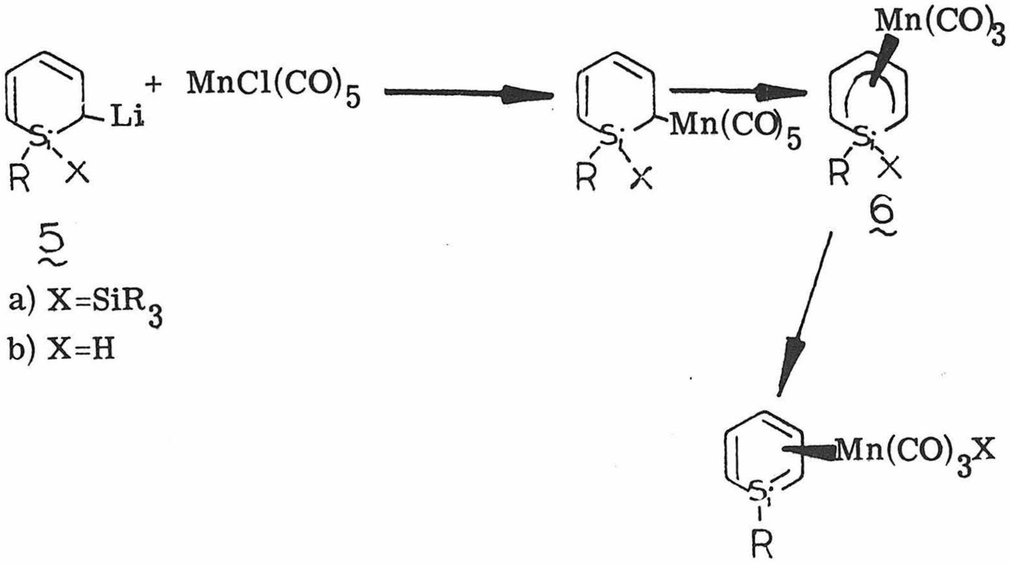
B) 2)



M=Cr, Mo, W

R=Ph, Me

C)



a) X=SiR$_3$

b) X=H

(2).

Scheme VB1 shows the sequential loss of X and Y to form the silicon-carbon double bond. Formation of cation 3, where the ring silicon is substituted with two methyl groups has been prepared (12). Generation of a silicon anion in the ring would leave a 6π electron system attached to the iron. The silicon anion could be generated by base cleavage of the silicon-silicon bond of 3 (13). Scheme VB2 shows the analogous reaction with the Group VI metals. The use of the Group VI metals would probably be favored here since the sila-benzene complexes would again be the analogues of the stable arene tricarbonyl complexes.

The reaction outlined in Scheme VC is very different than the other methods proposed. This scheme requires the generation of a carbanion alpha to silicon. Similar sila-cyclohexadiene anions have been prepared previously (14). Displacements by carbon anions at transition metals are well precedented (7). Formation of a metal carbon sigma bond and loss of two carbon monoxide ligands leads to 6 (15). Oxidative addition across a silicon-silicon, 6a, (6) or a silicon-hydrogen bond, 6b, (16) would produce sila-benzene bound to manganese.

References

1. a) K. S. Pitzer, J. Amer. Chem. Soc., 70, 2140 (1948); b) R. S. Mulliken, J. Amer. Chem. Soc., 72, 4493 (1950): 77, 884 (1955).
2. P. Jutzi, Angew. Chem. Internat. Ed., 14, 232 (1975).
3. a) T. J. Barton and E. Kline, J. Organomet. Chem., 42, C21 (1972); b) T. J. Barton and G. L. McIntosh, J. L. S. Chem. Comm., 861 (1972).
4. O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton and M. L. Tuney, J. Amer. Chem. Soc., 98, 7844 (1976).
5. M. R. Chedekel, M. Skoglund, R. L. Kreeger and H. Shechter. J. Amer. Chem. Soc., 98, 7846 (1976).
6. H. Sakarai, Y. Kamiyama and Y. Nakadaira. J. Amer. Chem. Soc., 98, 7453 (1976).
7. M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, Chapter 5.
8. a) J. E. Bulkowski, N. D. Miron, D. Sepalak and C. H. van Dyke. J. Organomet. Chem., 101, 267 (1974); b) W. Malisch and P. Panster. J. Organomet. Chem., 64, C5 (1974).
9. R. B. King and A. Fronzaglia, Inorg. Chem., 5, 1837 (1966).
10. E. W. Abel, T. Blackmore and R. J. Whitley, J. C. S. Dalton, 2484, (1976).
11. a) T. J. Barton and D. S. Banasiak, J. Chem. Soc., 99, 5199 (1977); b) R. Benkesec and R. F. Cunico, J. Organomet. Chem., 4, 285 (1965).
12. von Walter Fink. Helvetica Chimica Acta., 59, 276 (1976).

13. M. Kumada, K. Tamao, M. Ishikawa and M. Matsumo. *Chem. Comm.*, 614 (1968).

14. G. Markl and P. L. Mertz, *Tetrahedron Lett.*, 1303 (1971).

15. E. W. Abel and S. Moorhouse, *Angew. Chem. Int. Ed.*, *10*, 339 (1971).

16. M. S. Wrighton. *Chem. Rev.*, *74*, 401 (1974).

Proposition II

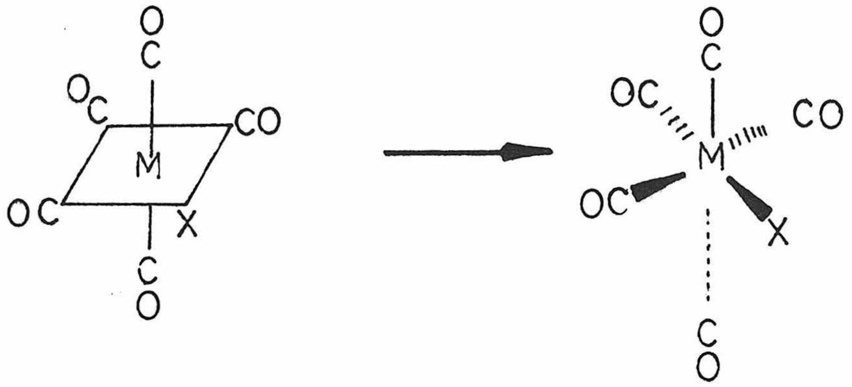
Investigation of Carbon Monoxide Labilization in $(\eta^5C_5H_5)V(CO)_3X$ Complexes.

Brown (1) has recently proposed a transition state/intermediate (2) stabilization effect for the observed (1,3) cis labilization of carbon monoxide in the substituted octahedral complexes, $M(CO)_5X$, where M = Cr, Mo, W, Mn, and X = I^-, Br^-, Cl^-, NC_5H_5, $Cr(CO)_5H^-$, PPh_3 etc. Carbon monoxide substitution by phosphines occurs more rapidly for $M(CO)_5X$ than for the corresponding unsubstituted complexes, $M(CO)_6$ (1). It has also been demonstrated that these substitution reactions proceed by a dissociative mechanism and that the carbon monoxides cis to X are substituted more rapidly than the trans CO (1).

The faster carbon monoxide dissociation in the $M(CO)_5X$ complexes is somewhat surprising. It might have been expected that substitution of better sigma bonding and poorer π-accepting ligands, as are most of the ligands, X, for a carbon monoxide ligand, would have allowed the remaining carbon monoxide ligands to bond more strongly to the metal, and decrease their rate of dissociation.

Instead, Brown (1) has proposed that X stabilizes the pentacoordinate transition state/intermediate (Figure 1) more than carbon monoxide, and X does so with a preference for the basal position. This preference for the basal position explains the labilization of the cis carbon monoxides, and is consistent with a site preference model established by calculations on the stability of $M(CO)_4X$ square pyramidal complexes (4). Those ligands, X, which show a preference for the basal site in a square pyramidal, $M(CO)_4X$, complex also show

FIGURE 1



cis labilization of carbon monoxide in $M(CO)_5X$ complexes. The ordering of ligands, according to increasing cis labilizing ability in octahedral complexes is: CO, H^-, $SnPh_3^-$, $M(CO)_n$ < $P(OPh)_3$ < PPh_3 < I^-, NC_5H_5 < Br^- < NCO^-, Cl, NO_3^- (1).

Recent observations (5) imply that similar transition state/intermediate stabilization effects may be important in the substitution of carbon monoxide by triphenylphosphine (PPh_3) in the structurally different complexes, $(\eta^5C_5H_5)V(CO)_3X$. The reactions of $CpV(CO)_3X$, X = Br^-, Cl^-, $CpV(CO)_3^-$, with triphenylphosphine produced both $CpV(CO)_3$ PPh_3 and $CpV(CO)_2(PPh_3)_2$ Cp = $(\eta^5-C_5H_5)$. It was shown (5) that phosphine substitution on $CpV(CO)_3PPh_3$ was too slow (6) to account for the formation of $CpV(CO)_2(PPh_3)_2$ in the former reactions.

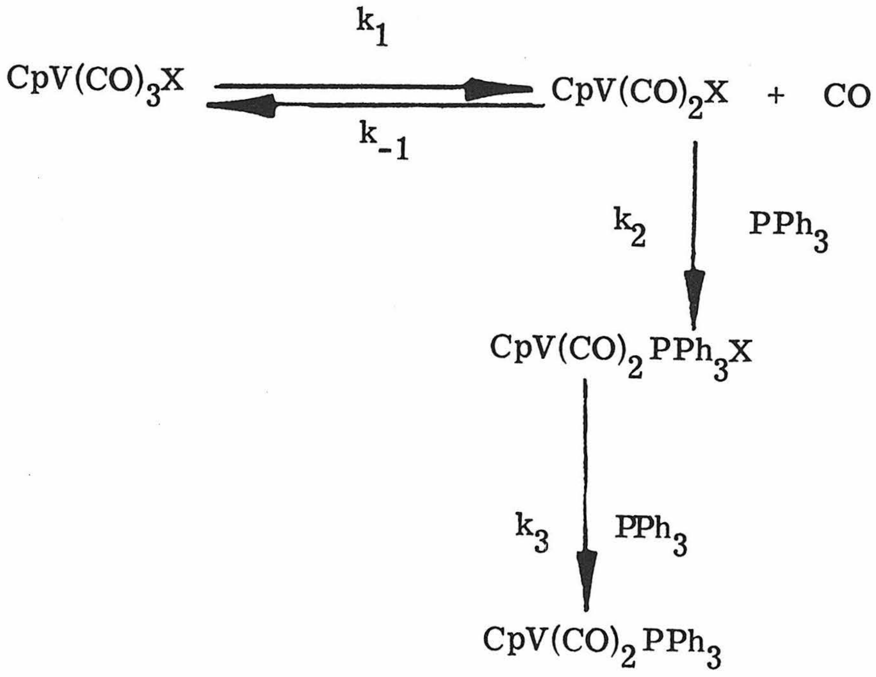
It can also be noted that the reactions of triphenylphosphine and $CpV(CO)_3X$ occur more rapidly than thermal substitution of triphenylphosphine on $CpV(CO)_4$ (7).

This increased reactivity of some substituted complexes, $CpV(CO)_3X$, over that of $CpV(CO)_4$ is similar to the octahedral $M(CO)_5X$ and $M(CO)_6$ complexes.

It is proposed that a detailed investigation of the reactions of phosphines with $CpV(CO)_3X$ complexes be undertaken. The phosphine dependence of the rate of formation of $CpV(CO)_2(PR_3)_2$ needs to be established. Based on an analogy to the carbon monoxide substitutions in $M(CO)_5X$, the reaction of $CpV(CO)_3X$ with phosphines is likely to be dissociative (Scheme I).

If the reaction does proceed by a dissociative mechanism, then at some high concentration of phosphine, the rate of phosphine

SCHEME I


k1
CpV(CO)3X
CpV(CO)2X + CO
k-1
k2
PPh3
CpV(CO)2PPh3X
k3
PPh3
CpV(CO)2PPh3

substitution (i.e. formation of $CpV(CO)_2(PPh_3)_2$ should become independent of phosphine concentration. In addition, the limiting rates should be the same for different phosphine ligands. Labelled carbon monoxide exchange should occur at this same limiting rate.

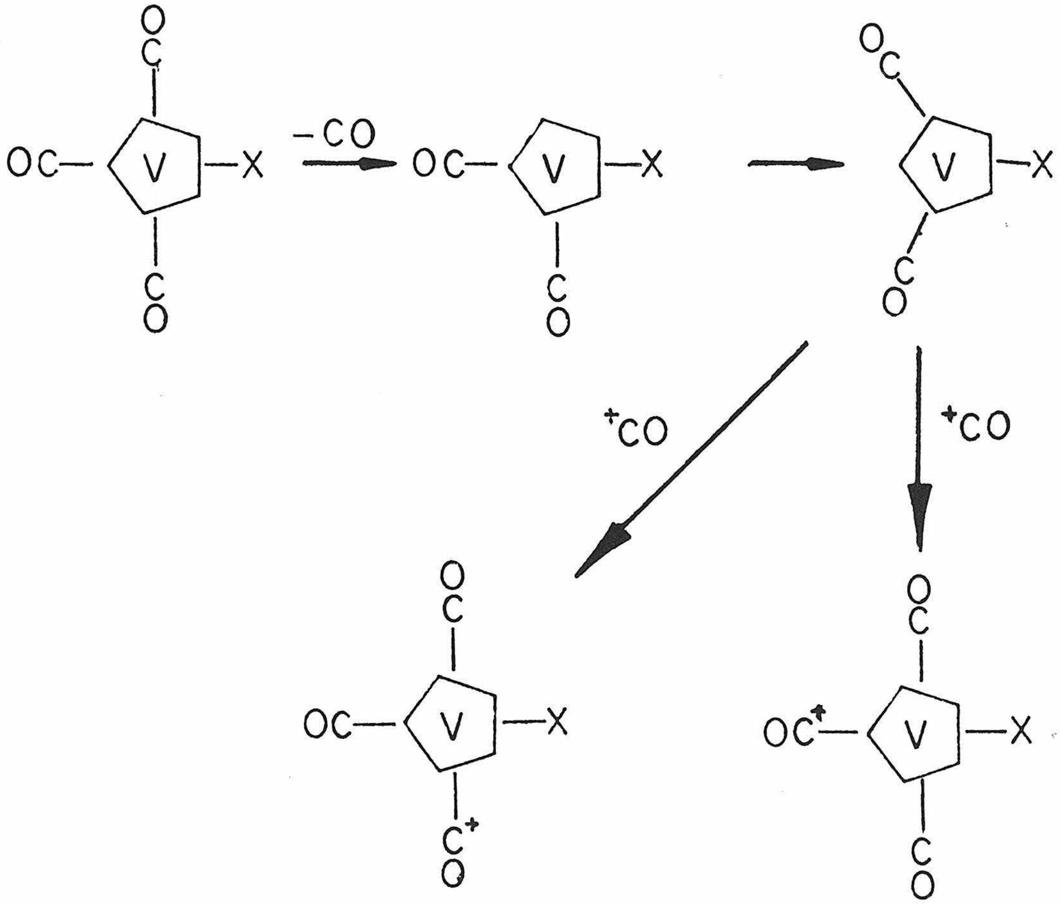
It would be of interest to establish the order of the rates of substitutions on $CpV(CO)_3X$ to determine if the labilization effects for X in the octahedral, $M(CO)_5X$ complexes can be extended to different coordination geometries. It may be that the labilizing effects of ligands, X, will be different in the different geometry of the $CpV(CO)_3X$ complexes (Scheme I).

The effect of the ligand X = $CpV(CO)_3H^-$ is of particular interest. It has been proposed (5) that the complex $CpV(CO)_3X$, for X = $CpV(CO)_3H^-$ contains a hydride bridge.

It is intriguing that $CpV(CO)_3H\ CpV(CO)_3^-$ reacts readily with triphenylphosphine to give $CpV(CO)_3PPh_3$, $CpV(CO)_2(PPh_3)_2$ and $CpV(CO)_3H^-$, while the complex $CpV(CO)_3H^-$ does not react with PPh_3 at all (5). The hydride bridge and the terminal hydride ligands appear to have very different labilizing properties.

A study of the stereochemistry of labilization by the ligands X would also be of value, but it seems likely that this may not be possible. Carbon-13 labelled carbon monoxide exchange could be carried out with $CpV(CO)_3X$ complexes, but stereospecific incorporation would appear unlikely. Loss of carbon monoxide from $CpV(CO)_3X$ (Figure 2) would produce an intermediate with a T structure. The barrier to rearrangement to a pseudo-C_{3v} structure (Figure 2) is likely to be very low and once this occurs the stereochemistry of carbon monoxide

FIGURE 2



(View of complexes is along pseudo-C_5 axis) substitution is lost. Labelled carbon monoxide incorporation would yield a statistical distribution of label in the cis and trans positions.

References

1. J. D. Atwood and T. L. Brown, J. Amer. Chem. Soc., 98, 3160 (1976).
2. The effects attributed to X for stabilization of a pentacoordinate species are applicable whether they occur in the developing transition state or an intermediate.
3. M. Darensbourg and N. Walker. J. Organomet. Chem., 117, C68 (1976).
4. A. R. Rosse and R. Hoffman, Inorg. Chem., 14, 365 (1975).
5. R. Kinney, Ph.D. Thesis, California Institute of Technology, (1978).
6. Carbon monoxide substitution by triphenylphosphine does occur thermally at higher temperatures (7).
7. G. Faber and R. J. Angelici, Inorg. Chem., 9, 1586 (1970).

Proposition III

Chemiluminescence in Peroxidase Catalyzed Oscillating Reactions

First observed many years ago (1), closed chemical systems in which the concentrations of some chemical species vary periodically, repeatedly passing through local minima and maxima, have gained considerable attention and are now being investigated in greater detail (2).

Early work in this area focussed on the mathematical analysis of theoretical reaction schemes. The general conclusion was that oscillations could occur only in chemical systems that were far from equilibrium (3). The time dependent differential equations for some of the chemical species must be non-linear.

Two oscillating chemical reactions have recently been investigated in detail. The Belousow-Zhabotinsky reaction is the cerium catalyzed bromate oxidation of malonic acid and the Bray-Liebhafsky reaction consists of the iodate-iodine catalyzed decomposition of hydrogen peroxide (5). Both reactions proceed by radical and non-radical processes (2c). A generalized reaction scheme has been put forth to model these systems, but it cannot account for all of the features of both reactions.

A number of enzyme catalyzed reactions also show oscillations (6), and even bacterial cultures exhibit oscillations in some substrates. The importance of oscillating reactions in living systems seems clear, for such periodic processes as heartbeat, respiration and circadian rhythms are likely chemical in nature (2c). A better understanding of the mechanisms of oscillating reactions would lead to an increase in our knowledge about the basic chemical processes of life itself.

In view of the radical processes involved in the two reactions previously mentioned, a particularly interesting enzymatic system is the peroxidase catalyzed aerobic oxidation of nicotinamide adenine dinucleotide (NADH) (6).

Damped oscillations have been observed in this reaction (7), and organic radicals have been detected by electron paramagnetic resonance (EPR) when dihydroxyfumaric acid or indole-3-acetic acid (IAA) are used in place of NADH.

The presence of radicals in these peroxidase systems implies possible similarities to the Belosow-Zhabotinski and Bray-Liebhafsky reactions. However, little else seems to be known about the details of the mechanism of the peroxidase system. The most confusing aspect of the work presented thus far (6,8) is the role of the highly oxidized, oxyperoxidase species. The concentration of oxyperoxidase does oscillate in these reactions, but it may (8) or may not (6) be essential in the mechanism of the oscillations. In the aerobic oxidation of DHF by horse radish peroxidase (HRP), oxyperoxidase shows only very low amplitude oscillations (6). In another reaction (8), with nicotinamide adenosine dinucleotide phosphate (NADPH), the oscillations of oxyperoxidase are very strong.

An important feature of the DHF reaction is the oscillation of chemiluminescence during the oscillating phase, and also strong chemiluminescence near the end of the reaction. This latter chemiluminescence appear (6) to correspond to a sharp decrease in the concentration of oxyperoxidase.

It is proposed that the role of the oxyperoxidase in the chemiluminescent reaction be investigated. It would be valuable to establish the mechanism of the chemiluminescence. Establishing the chemical species involved in the chemiluminescence could lead to an understanding of the possible regulatory intermediates in the oscillations, even if oxyperoxidase is not directly involved in the oscillations.

It is also possible that more than one mechanism for chemiluminescence is operating since chemiluminescence occurs both during the oscillations in the reaction, and at the end of the reaction, after oscillations have stopped.

The specific chemiluminescing species needs to be identified since chemiluminescence intensity varies with the reductant (DHF, IAA or NADH) used. Considering an electron transfer mechanism for chemiluminescence proposed by Schuster (9) it is likely that some oxidized form of DHF, IAA or NADH is responsible for the chemiluminescence.

Identification of other substrates which lead to chemiluminescence in reactions with oxyperoxidase would be valuable in identifying the role oxyperoxidase plays in chemiluminescence. Schuster has observed chemiluminescence in the reactions of bis-acid peroxides with aromatic hydrocarbons. Such substrates could be used in reaction with oxyperoxidase, since oxyperoxidase may resemble bis-acid peroxides in its one electron oxidizing ability (8). Oxyperoxidase has been identified as the product of peroxidase (iron oxidation state is +3) and superoxide anion. Formally the iron is in a +6 oxidation state

(8), and would be expected to be a very powerful oxidizing agent.

The chemiluminescence in the oscillating reactions of HRP and DHF is also related to the variation in oxygen concentration (6). In particular, the final chemiluminescence seems to be at the least a response to a certain oxygen concentration in the reaction. It is also possible that other oxygen species such as superoxide anion or hydrogen peroxide, both apparently generated in the oscillating reaction, could be involved in electron transfer and chemiluminescence.

Oxyperoxidase can be prepared (8) independent of the other oxidation states of peroxidase so careful studies of its reactions with specific substrates can be conducted.

It is anticipated that a detailed understanding of the chemiluminescent steps in the oscillating reaction of HRP and DHF (or other substrates) will lead to identification of chemical species involved in the oscillations, particularly those which regulate the oscillations.

References

1. H. Degn, J. Chem. Educ., 49, 302 (1972) and references.
2. a) Faraday Symposia of the Chemical Society, No. 9, "Physical Chemistry of Oscillating Phenomena", 1974; b) R. M. Noyes and R. J. Field, Acc. Chem. Res., 10, 214 (1977); c) R. J. Field and R. M. Noyes, 10, 273 (1977).
3. J. Z. Hearon, Bull. Math. Biophys., 15, 21 (1953).
4. A. J. Lotka, J. Phys. Chem., 14, 271 (1910).
5. a) R. J. Field, E. Koros and R. M. Noyes, J. Amer. Chem. Soc., 94, 8649 (1972); b) R. M. Noyes, R. J. Field and E. Koros, J. Amer. Chem. Soc., 94, 1394 (1972); c) R. M. Noyes, R. J. Field and R. C. Thompson, J. Amer. Chem. Soc., 93, 7315 (1971); d) K. R. Sharma and R. M. Noyes, J. Amer. Chem. Soc., 98, 4345 (1976).
6. "Biological and Biochemical Oscillators," Ed. by B. Chance, E. K. Pye, A. K. Ghosh and B. Hess, Colloquium of the Johnson Research Foundation, 1973.
7. a) B. Chance, B. Scheoner and S. Elsaesser, J. Biol. Chem., 240, 3170 (1965); b) R. Frenkel, Biochem. Biophys. Res. Comm., 21, 497 (1965).
8. I. Yamayzki and K. Yotota, Mol. Cell. Biochem., 2, 39 (1973).
9. J. Koo and G. B. Schuster, J. Amer. Chem. Soc., 99, 6107 (1977).

Proposition IV

A Mechanistic Test for 1,3 Hydrogen vs. 1,3 Carbon Shift: The Thermal Rearrangement of a 1,2 Dimethylenecyclobutane Ligand.

The thermal rearrangement of a 1,2-dimethylenecyclobutane ligand is proposed which will differentiate between a 1,3 hydrogen or 1,3 carbon shift.

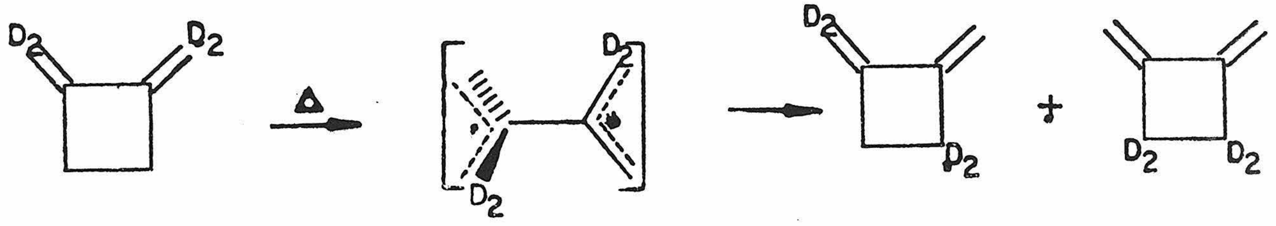
It has been shown (1) that 1,2 dimethylenecyclobutane, 1, rearranges by exchange of the ring methylene and exo-methylene carbon at 250°C in the gas phase (Scheme I).

Gajewski has demonstrated that the reaction proceeds by a biradical mechanism. The bis-allyl intermediate, 2, gives both 3 and 4 in the expected ratio of 2:1. A concerted Cope rearrangement would produce only 4. The ring opening reaction to generate 2, proceeds predominantly with conrotatory motion in 3,4-dimethyl-1,2-dimethylenecyclobutane, with the trans isomer rearranging 1.3 times as fast as the cis isomer (2).

Gajewski has also shown (3) that the 1,2-dimethylenecyclobutane iron tricarbonyl 5, undergoes rearrangement at 170°C in the gas phase. The method of analysis (4) used in identifying the rearranged products could not distinguish between a 1,3 carbon migration or a 1,3 hydrogen shift (3). (Scheme II). The analysis determined the number of deuterium atoms in the product molecules but not their positions. Both mechanisms have been proposed previously for transition metal catalyzed rearrangements (5,6). Stable σ-allyl-π allyl complexes, similar to, 6, (Scheme II) have even been isolated (7).

It would be valuable to establish which of these processes,

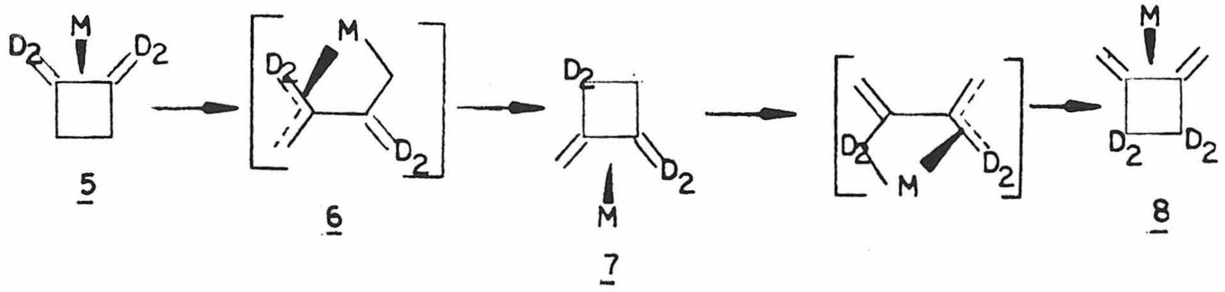
SCHEME I



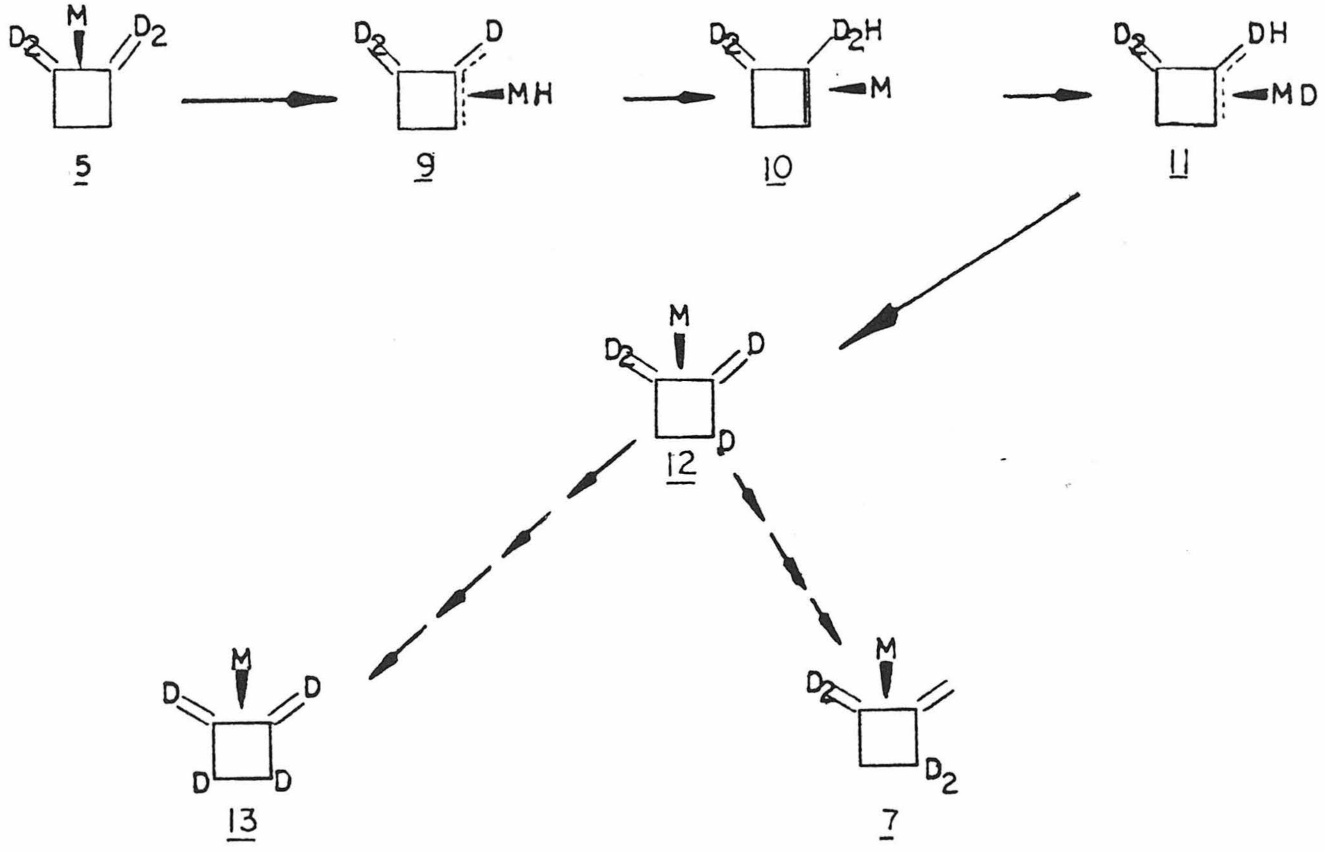
1 2 3 4

SCHEME II

1, 3 Carbon Migration



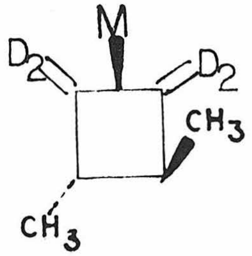
1, 3 Hydrogen Migration



$M = Fe(CO)_3$

1,3 hydrogen or 1,3-carbon migration is of lower energy. Since it seems likely that metal insertion into either the carbon-hydrogen or carbon-carbon bond is the rate determining step, this system also allows for a direct comparison of the activation energy for C-H and C-C bond cleavage. It must be realized, of course, that this particular carbon-carbon bond has considerable ring strain (8). However, it would still be useful to have this comparison as a guide for evaluating other reaction mechanisms.

In order to differentiate between these mechanisms, it is proposed that the double labeled compound 14 (9)



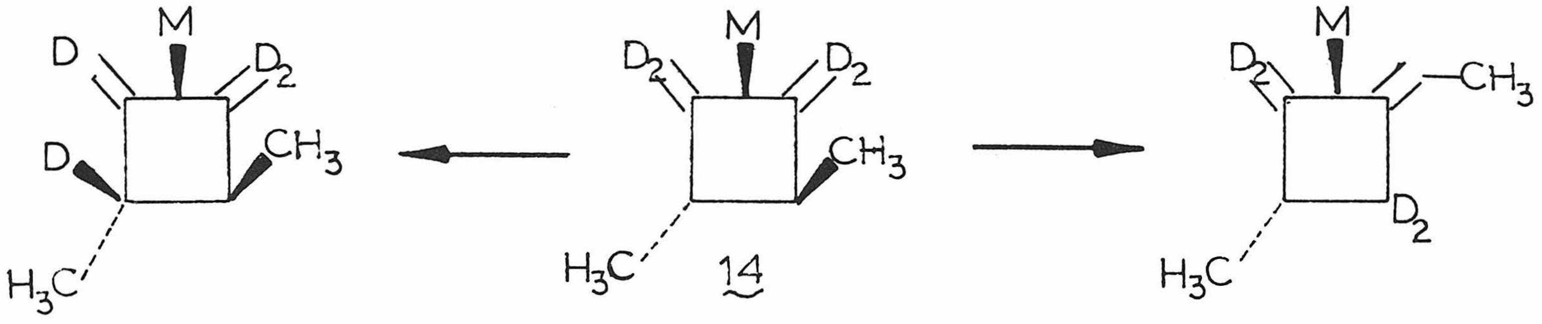
$M=Fe(CO)_3$

14

be pyrolyzed. A 1,3-hydrogen shift will exchange only deuterium and hydrogen between the exo and ring methylene positions, but the 1,3 carbon shift will exchange both deuterium and methyl groups between these two positions. The rearrangement of 14 can be followed by NMR spectroscopy to differentiate the two mechanisms (10). (Scheme III).

14 can be prepared by the reductive dimerization of diethyl ethylidenemalonate (13). Decarboxylation, reduction with lithium aluminum deuteride (14), and elimination (15) yields a mixture of cis and trans 3,4-dimethyl-1,2-dicarboethoxycyclobutanes. These isomers can be separated by preparative gas chromatography. The trans isomer

SCHEME III



14

1,3-Hydrogen Shift

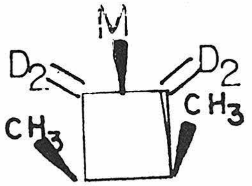
1,3-Carbon Shift

M=Fe(CO)$_3$

is required, since it assures a hydrogen endo to the metal in the iron tricarbonyl complex (17).

If the mechanism for rearrangement in 14 is a 1,3 hydrogen shift, it would be interesting to pyrolyze 15 to see if the mechanism would be changed to a 1,3 carbon shift when no endo hydrogens were present.

If the rearrangement of 14 proceeds by the 1,3 carbon shift, then the even more intriguing question of the stereochemistry of oxidative and addition may be investigated.



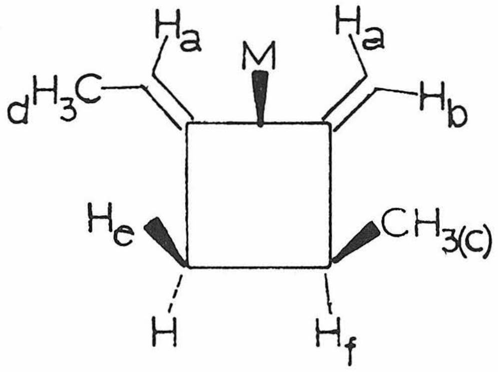
M=Fe(CO)$_3$

15

References

1. a) J. J. Gajewski and C. N. Shih, J. Amer. Chem. Soc., 89, 4532 (1967); W. Von E. Doering and W. B. Dolbier, J. Amer. Chem. Soc., 89, 4534 (1967).
2. J. J. Gajewski and C. N. Shih, J. Amer. Chem. Soc., 94, 1675 (1972).
3. J. J. Gajewski and C. N. Shih, Tetrahedron Letters, 3959 (1973).
4. The products were analyzed by oxidizing the recovered iron complexes to remove the cyclobutane ligand. Diels-Alder addition of dicarbomethoxyacetylene, and reduction with dichlorocyanoquinone gave labeled 3,4 dicarbomethoxybicyclo 4.2.0 octa-1,3,5-trienes which were analyzed by mass spectroscopy for their deuterium content.
5. T. H. Whitesides and J. P. Neilan, J. Amer. Chem. Soc., 98, 63 (1976).
6. V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and P. H. Williamson, J. Chem. Soc. Perkin II, 1, 4 (1975).
7. N. Yasudu, Y. Kai, N. Yasuoka and N. Kasai, J. Chem. Soc. Chem. Comm., 157 (1972); b) R. M. Moriarity, Chen-Lung Yeh and K. C. Ramey, J. Amer. Chem. Soc., 93, 6709 (1975); c) R. Aumann, Angew. Chem. Int. Ed., 10, 188 (1972).
8. The ring strain in cyclobutane is approximately 26 Kcal/mole.
9. 14 is only one of the enantiomers of this complex. A racemic mixture can be used in these experiments.

10. It will be necessary to distinguish the exo-methylene protons (H_a, H_b) and



the ring methylene protons (H_e, H_f) in the NMR spectra. These are well resolved (3). The chemical shifts of the exo-methylene methyl (H_d) and ring-methylene methyl groups are different in the uncomplexed cyclobutane are expected to so in the complex also (11). It appears from other diene-iron tricarbonyl complexes (12), that H_d and H_a, H_b will be resolved.

11. J. J. Gajewski and C. N. Shih, J. Amer. Chem. Soc., 91, 5900 (1969).

12. a) J. E. Mawer and R. Pettet, J. Amer. Chem. Soc., 85, 3955 (1963); b) J. E. Mawer, D. H. Gibson and R. Pettit, J. Amer. Chem. Soc., 85, 3959 (1963).

13. I. Vogel, J. Chem. Soc., 594, 1985 (1927).

14. J. J. Gajewski and C. N. Shih, J. Org. Chem., 37, 64 (1972).

15. Elimination is accomplished by converting the alcohol to the tosylate, displacement by iodide and treatment in potassium hydroxide (16).

16. E. A. Dorko, *J. Amer. Chem. Soc.*, *87*, 5518 (1967).

17. It is most likely (5) that the 1,3 hydrogen shift requires a hydrogen on the same side of the diene plane (endo) as the metal in order to occur.

Proposition V

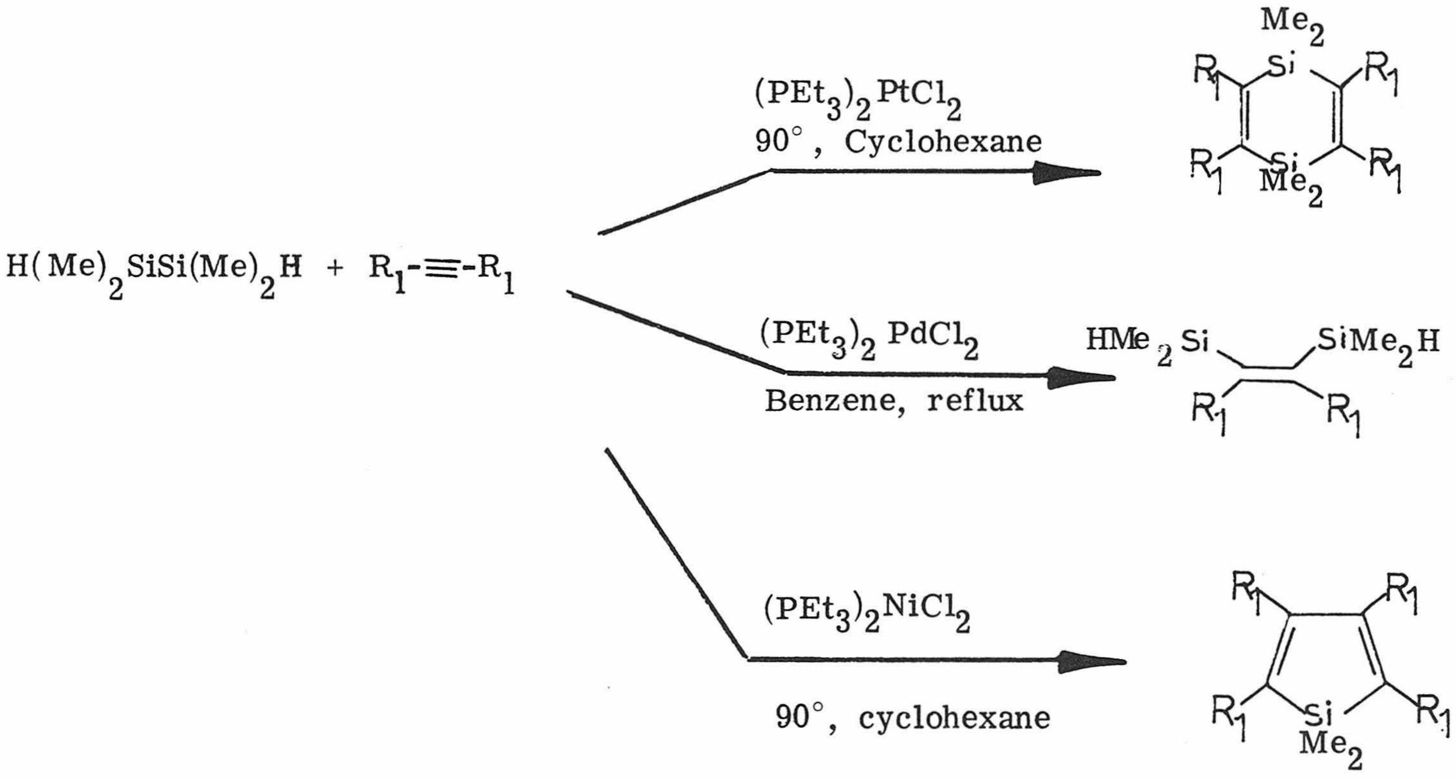
Metal Silylenes as Intermediates

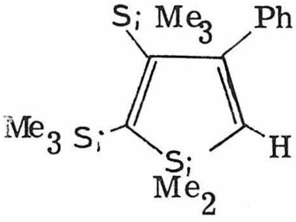
The reactions of symmetrical disalanes (HR_2SiSiR_2H) with acetylenes catalyzed by the transition metal complexes $(PEt_3)MCl_2$, M = Ni, Pd, Pt lead to the products shown in Scheme I(1). The platinum complex also catalyzes the polymerization of disilanes (1c) (Scheme II). It has been proposed that these reactions proceed by "silenoid" intermediates, which are most likely not "free silylenes" (2), but associated with the metals in some manner. This seems quite reasonable since each complex gives different products. The silylene species are probably formed by the reaction in Scheme III. Metal insertion into a silicon-hydron bond is well precedented (3). A 1,2-elimination of hydrogen from the metal and silicon could lead to a metal-silylene complex. This would be the most direct formation of a metal-silylene. However, other eliminations could occur, which would lead to a metal-silylene with the metal in other formal oxidation states (4).

It was proposed (1a) that the metal-silylene then reacts with acetylenes to form silacyclopropenes, which presumably are no longer associated with the metal. The observed products (Scheme I) certainly appear to be consistent with the reactions of silacyclopropenes (2,5), but it is odd that very different products are obtained from catalysis by different metals.

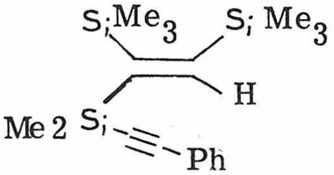
It has more recently been shown (5) that phenyl acetylene reacts with 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene (I) to give the products II and III in

SCHEME I


H(Me)$_2$SiSi(Me)$_2$H + R$_1$-≡-R$_1$
(PEt$_3$)$_2$PtCl$_2$
90°, Cyclohexane
(PEt$_3$)$_2$ PdCl$_2$
Benzene, reflux
(PEt$_3$)$_2$NiCl$_2$
90°, cyclohexane
Me$_2$
Si
R$_1$
HMe$_2$Si
SiMe$_2$H

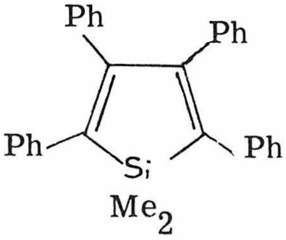


II



III

a 3:7 ratio. III was not reported at all in the palladuim catalyzed reaction with phenylacetylene (1a) (Scheme I). In addition, when I was reacted with $(PEt_3)_2PdCl_2$ with phenylacetylene at room temperature, the only product was 1,1-dimethyl-1-sila-2,3,4,5-tetraphenyl-cyclopenta-2,4-diene, IV.



IV

It would appear then that metal-silylene complexes are viable intermediates in the metal catalyzed reactions of disilanes with acetylenes. However, the reactions of these complexes with acetylenes probably do not give silacyclopropenes. The immediate reaction of I and $(PEt_3)_2PdCl_2$ to give IV, with the complete loss of bis-

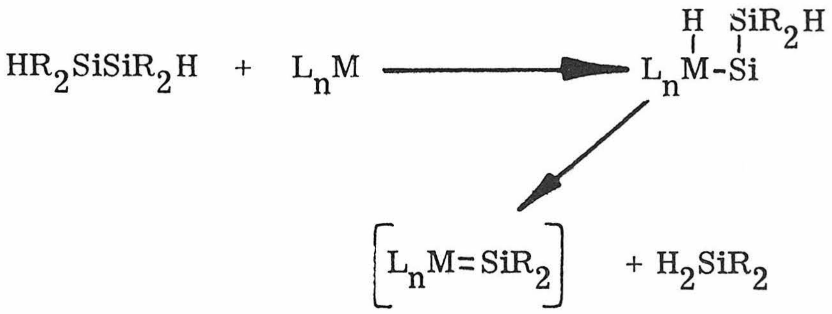
SCHEME II

$$R_3SiSiR_2X \xrightarrow[90^\circ,\ \text{cyclohexane}]{(PEt_3)_2PtCl_2} \Sigma R(SiR_2)_nX$$

X= H, and others(lc)

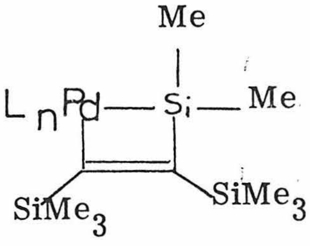
n=1, 2, 3, . . .

SCHEME III



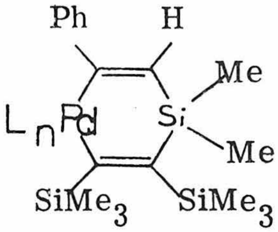
$$HR_2SiSiR_2H + L_nM \longrightarrow L_n\overset{H}{M}-\overset{SiR_2H}{Si} \longrightarrow \left[L_nM{=}SiR_2\right] + H_2SiR_2$$

(trimethylsilyl) acetylene implies a metal insertion into I, to form a metallo-silacyclobutene, V.



V

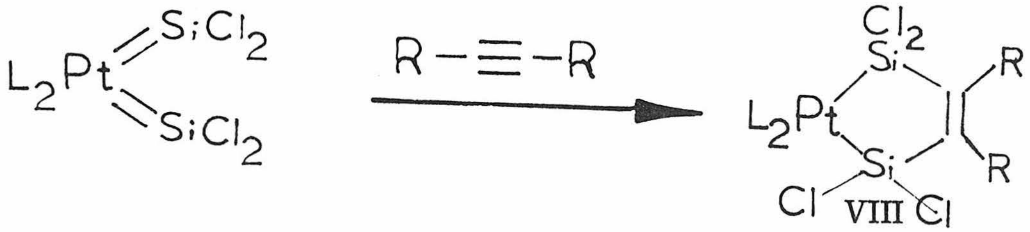
Loss of acetylene from V would leave a metal silylene. V might also react with a second molecule of acetylene to form VI. The formation of VI would have to be reversible, since the bis (trimethyl-silyl) acetylene doesn't appear in the final product IV.



VI

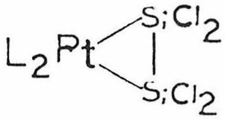
There appears to be reasonable evidence here for metal-silylenes as intermediates, but none have ever been detected in any of the reactions. Only a single report of a stable metal-silylene complex has been made (6). The bis-silylene platinum complex, VII, has been identified only by elemental analysis, infrared spectrum and its reaction with diphenylacetylene as shown in Scheme IV.

SCHEME IV



VIII

In this reaction the acetylene reacts to form a metalo-disila-cyclopentene VIII Scheme IV, rather than a metalo-sila-cyclobutene. It is quite possible that this compound is not a metal-silylene but a metalo-silacycle, IX.



IX

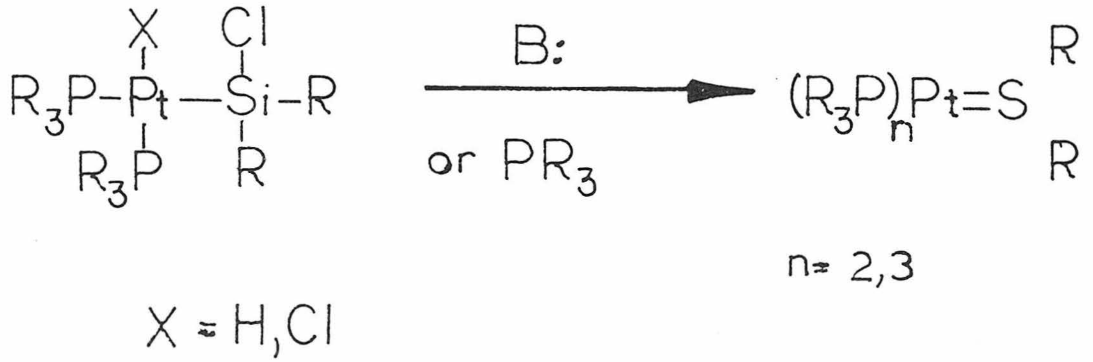
In view of this apparent lack of examples of metal-silylenes and the numerous implications in reactions, it is proposed that stable metal-silylenes be prepared and their reactions be investigated.

A possible route to metal-silylenes is shown in Scheme V. A base catalyzed elimination of Cl from X would leave a metal-silicon double bond. Compounds with the general formula, X, x=Cl, H are easily prepared from bis-phosphine platinum dichlorides (3) or platinum hydrogen chlorides (4) with diorgano-dichlorosilanes. For X=H, the reactions of tetrakis-phosphine platinum complexes with diorgano-chlorosilanes produce X (4).

The proposed 1,2 elimination appears to have occurred under more strenuous conditions where the assumed metal silylene dimerized (4). This base induced elimination should proceed under milder conditions (possibly even below room temperature) where dimerization may not occur. Strong amine bases could be used for the elimination of HCl, and trialkyl phosphines for the elimination of Cl_2 (6).

Substitution on the silicon may also influence the stability of the metal-silylene. Strong π-electron donating groups (i.e. p-dimethylaminophenyl, methoxy) would help stabilize the expected positive charge at silicon.

SCHEME V



References

1. a)H.Okinoshima, K. Yamamoto and M. Kumada, *J. Organomet. Chem.*, *86*, C27 (1975); b) K. Yamamoto, H. Okinoshima and K. Kumada, *J. Organomet. Chem.*, *27*, C31 (1971); c) K. Yamamoto, H. Okinoshima and K, Kumada, *J. Organomet. Chem.*, *23*, C7 (1970); d) H. Okinoshima, K. Yamamoto and K. Kumada, *J Amer. Chem. Soc.*, *94*, 9263 (1972).

2. W.H. Atwell and D. H. Weyenberg, *Angew. Chem. Int. Ed.*, *8*, 469 (1969).

3. J. E. Benthem, S Cradock and E.A.V. Ebsworth. *J. Chem. Soc.*,587 (1971).

4. J. Chatt, C. Eaborn and P.N. Kapoor, *J Chem. Soc.*, 881 (1970).

5. a) D. Seyferth, D.P. Duncan and S.C. Vick. *J. Organomet. Chem.*, *125*, C5 (1977).

6. G. Schmid and H. J. Balk, *Chem. Ber.*, *103*, 2240 (1970).