parameters for both structures (31 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975), and references cited therein.

(2) For some recent examples see R. J. Klinger, W. Butter, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975); F. A. Cotton, M. W. Extine, and R. H. Niswander, *Inorg. Chem.*, **17**, 692 (1978); W. I. Bailey, Jr., M. H. Chisholm, F. A. Cotton, C. A. Murillo, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 802 (1978); M. H. Chisholm, R. L. Kelly, F. A. Cotton, and M. W. Extine, *ibid.*, **100**, 2256 (1978).

(3) J. San Filippo, Jr., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, **13**, 2121 (1974); J. San Filippo, Jr., *Inorg. Chem.*, **11**, 3140 (1972).

(4) This composition is attained for the compound only after removal of solvent and drying in vacuo. Anal. Calcd for $Mo_2Cl_4(P(C_6H_5)_3)_2(CH_3OH)_2$: Mo, 20.80; Cl, 15.37; C, 49.48; H, 4.15. Found: Mo, 20.54; Cl, 15.42; C, 50.34; H, 4.45.

(5) The crystal structure analysis revealed three sites occupied by unbound solvent molecules, but less than full occupation of these sites makes n = 2.2.

(6) The crystals were found to be triclinic, $P\bar{1}$, $Z = 1$, $a = 11.547$ (6) Å, $b = 12.152$ (5) Å, $c = 9.458$ (4) Å, $\alpha = 103.87$ (5)°, $\beta = 112.47$ (4)°, $\gamma = 104.33$ (5)°. At the present stage of refinement all nonhydrogen atoms have been located and full-matrix least-squares refinement including anisotropic temperature factors has resulted in conventional descrepancy indices of $R = 0.066$ and $R_w = 0.087$. No attempt has been made to locate H atom positions.

(7) F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).

(8) J. A. Potenza, R. J. Johnson, and J. San Filippo, Jr., *Inorg. Chem.*, **15**, 2215 (1976).

(9) J. V. Brencic and P. Segedin, *Z. Anorg. Allg. Chem.*, **423**, 266 (1976).

(10) Other important bond distances and angles found in the molecule are Mo-Cl (av), 2.404 (2) Å; Mo-P, 2.539 (3) Å; Mo-Mo-Cl (av), 107.20 (6)°; Mo-Mo-P, 97.58 (6); Mo-Mo-O, 113.70 (16)°.

(11) Anal. Calcd for $MoCl_2(P(C_6H_5)_3)$: Mo, 22.36; Cl, 16.52. Found: Mo, 22.60; Cl, 17.30.

(12) Refinement of the structure of $Mo_4Cl_8(P(C_4H_9)_3)_4$ is still incomplete, but all nonhydrogen atom positions have been determined and the basic structural unit $Mo_4Cl_8P_4$ is the same in all essential features as that determined for $Mo_4Cl_8(P(C_2H_5)_3)_4$. Crystals of the latter grown from benzene were found to be monoclinic, $a = 14.274$ (2) Å, $b = 12.564$ (1) Å, $c = 14.427$ (2) Å, $\beta = 122.80$ (1)°, $P2_1/c$, $Z = 2$. Using 2378 data of limited quality with intensities $I > 3\sigma(I)$ the refinement has converged with $R = 0.126$ and $R_w = 0.158$. In the final refinement cycles anisotropic temperature factors were included for all nonhydrogen atoms except for the four C atoms of two ethyl groups, which had unusually large temperature factors.

(13) Other important distances and angles in the $Mo_4Cl_8(PEt_3)_4$ molecule follow: Mo(1)-Cl(1), 2.425 (5); Mo(2)-Cl(2), 2.421 (6); Mo(1)-Cl(3′), 2.381 (6); Mo(1)-Cl(4′), 2.427 (6); Mo(2)-Cl(3), 2.373 (5); Mo(2)-Cl(4), 2.422 (5); Mo(1)-P(1), 2.558 (6); Mo(2)-P(2), 2.556 (7) Å; Mo(1)-Mo(2)-Mo(1′), 90.6 (1)°; Mo(2)-Mo(1)-Mo(2′), 89.4°.

(14) The Mo-Mo single bond distance is known to vary markedly depending on the nature of all ligands present, from a minimum value of about 2.5 Å to a maximum of about 3.2 Å; ref 16.

(15) Representative of compounds having Mo-Mo triple bonds unsupported by any bridging ligands are $Mo_2(NMe_2)_6$ (ref 17), $Mo_2(CH_2SiMe_3)_6$ (ref 18), and $Mo_2(OSiMe_3)_6(NHMe_2)_2$ (ref 19), with Mo-Mo bond distances of 2.211 (2), 2.167, and 2.242 (1) Å, respectively. The comparison of distances in $Mo_4Cl_8(PEt_3)_4$ and $Mo_2(OSiMe_3)_6(NHMe_2)_2$ is especially pertinent because in both cases the Mo atoms are coordinated to four ligands.

(16) F. A. Cotton, *J. Less-Common Met.*, **54**, 3 (1977).

(17) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).

(18) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

(19) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978).

(20) In support of this is the loss of the band at 558 nm giving rise to the blue color of the dimer and assigned as the $\delta \rightarrow \delta^*$ transition; in the yellow tetramer strong bands are observed at 420 nm (ϵ 2.2×10^3) and 308 (1.7×10^4).

(21) Anal. Calcd for $MoCl_2(CH_3OH)$: Mo, 48.24; Cl, 35.7; C, 6.03; H, 2.01. Found: Mo, 48.2; Cl, 34.6; C, 6.08; H, 2.09.

Synthesis and Reactions of (η^5-Cyclopentadienyl)tricarbonylhydridovanadate. A Comparative Mechanistic Study of Its Organic Halide Reduction Reactions with Those of Tri-*n*-butyltin Hydride

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Abstract: The complex $PPN^+[CpV(CO)_3H]^-$ (PPN-**3**; Cp ≡ η^5-C_5H_5) has been prepared in 70% yield by sodium reduction of $CpV(CO)_4$ (**1**) followed by protonation of the resulting dianion $[CpV(CO)_3]^{2-}$ (**2**) with water and cation exchange with PPN^+Cl^-. The physical properties and chemical reactions of **3** have been investigated. The sodium salt of **3** is contact ion paired in the solid state and in THF; dissociation of solvent-separated pairs occurs on conversion to the PPN^+ salt or dissolution in polar solvents such as HMPA. Treatment of dianion **2** with methyl iodide gives the related salt $PPN^+[CpV(CO)_3CH_3]^-$, which may also be isolated and characterized. Hydride **3** reacts with a wide range of organic halides, resulting in substitution of the halogen atom by the hydrogen of **3**. The organometallic products of these reactions are the vanadium halides $PPN^+[CpV(CO)_3X]^-$ (**8**). In some cases a second organometallic product is observed; this material is the binuclear bridging hydride $PPN^+[CpV(CO)_3]_2H^-$ (**10**), and it is formed by reaction of the kinetic product **8** with starting **3** present in the reduction solutions. Irradiation of **1** in the presence of **3** provides an alternate route to bridging hydride **10**. Competition experiments against PPh_3 have shown that **3** reacts more rapidly than the phosphine with transient, coordinatively unsaturated $CpV(CO)_3$, but thermodynamically PPh_3 is the better ligand. The borohydride salt $PPN^+[CpV(CO)_2BH_4]^-$ has also been prepared, by treating **1** with $NaBH_4$ and by treating hydride **3** with BH_3·THF. The mechanism of the reaction between **3** and organic halides has been investigated in detail, and compared in several cases with halide reductions carried out using tri-*n*-butyltin hydride. Relative reactivity, stereochemistry, cyclization, and trapping studies demonstrate that in almost all cases, the reduction reaction proceeds via free-radical intermediates. As in the R_3SnH case, these intermediates are generated in a chain process, and are trapped by hydrogen transfer from **3**. The absolute rate constant for this transfer step can be estimated to be 2×10^7 M^{-1} s^{-1}, nearly an order of magnitude larger than the rate constant for hydrogen transfer from tri-*n*-butyltin hydride. Reduction of cyclopropylcarbinyl bromide appears to be exceptional, and probably proceeds by a two-electron mechanism.

Organotransition metal hydrides are not, in general, very "hydridic". Such complexes often suffer proton and hydrogen atom abstraction, and participate easily in insertion reactions involving M-H addition across carbon-carbon double and

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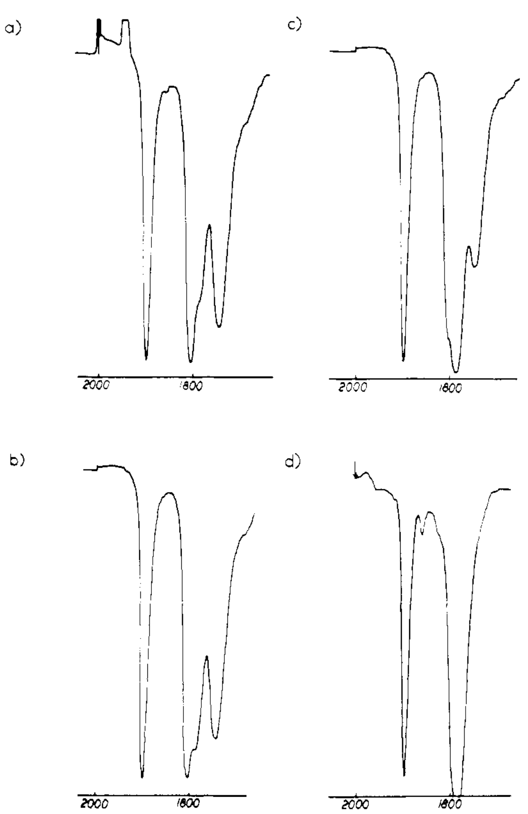


Figure 1. IR spectra of solutions formed upon addition of sequential amounts of PPN^+Cl^- to $Na[(\eta^5\text{-}C_5H_5)V(CO)_3H]$ in THF.

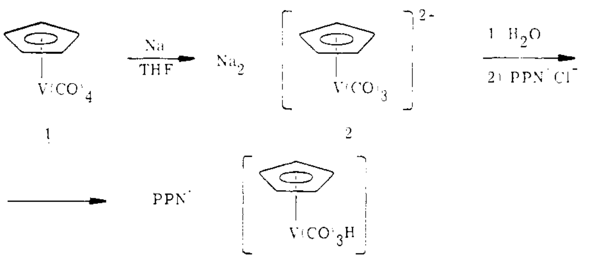
triple bonds. However, direct *nucleophilic* transfer of hydride from transition metals to electrophilic carbon centers, such as those in carbonyl compounds and alkyl halides, seems to be a relatively rare event, especially for uncharged hydrides.[2] One might expect an exception to this general situation to involve metal hydrides which are negatively charged (and are, in addition, in relatively low oxidation states). Such systems (e.g., $HFe(CO)_4^-$, $HCr(CO)_{10}^-$, $HFe_2(CO)_8^-$, "CuH_2^-") do appear to react more generally with electrophilic species.[3,4] The possibility that highly reduced, anionic metal systems might be useful in developing new hydride- and alkyl-transfer reactions has prompted us to initiate a number of studies aimed at preparing such materials and investigating their chemistry. The present paper describes the preparation of a new anionic hydride in the vanadium series, a survey of its organometallic chemistry and reactions with organic halides, and a detailed study of the mechanism of the halide replacement reaction. As will be seen, this anionic hydride does transfer hydrogen to electrophiles relatively efficiently, but the process involves a mechanism which is considerably more complicated than simple hydride transfer.[5]

Synthesis, Properties, and Reactions of Anionic Vanadium Complexes

Preparation of $[(Ph_3P)_2N]^+[CpV(CO)_3H]^-$ from $Na_2^+[CpV(CO)_3]^{2-}\cdot THF$. Ion-Pairing Studies. The disodium salt of the dianion $CpV(CO)_3^{2-}$, **2** ($Cp \equiv \eta^5\text{-}C_5H_5$), was previously prepared by the reduction of $CpV(CO)_4$ (**1**) with sodium metal in liquid ammonia[6] or sodium amalgam in tetrahydrofuran (THF).[7] It has also been noted[8] that hexamethylphosphoramide (HMPA) solutions of **1** may be generated by adding **1** to sodium metal dissolved in HMPA. The IR spectrum of these solutions showed carbonyl absorptions at 1742, 1619, and 1573 cm^{-1}.

We have confirmed that when **1** is treated with sodium amalgam or sodium dispersion in THF, a yellow precipitate,

Scheme I



which we have characterized as the THF solvate of Na_2-**2**, is formed quantitatively. This material is soluble only in very polar solvents (e.g., HMPA) and reacts rapidly with even traces of water or air. The IR spectrum of the precipitate as a KBr pellet or as a Nujol mull showed carbonyl absorptions at 1742, 1590, and 1550 cm^{-1}. The absorption at 1742 cm^{-1} corresponded directly to that observed for **2** in HMPA solution and reported[7] for Cs_2-**2**. However, the bands at 1590 and 1550 cm^{-1} for Na_2-**2**·THF from our reactions were considerably lower in energy than the absorptions for **2** in HMPA and for Cs_2-**2**. This splitting of the lower energy absorption for Cs_2-**2** into two absorptions for Na_2-**2**·THF was likely due to tight ion pairing of the sodium cations to the carbonyl oxygens of **2**.[9]

The (previously unreported) NMR spectrum of Na_2-**2**·THF in HMPA showed a single cyclopentadienide absorption at δ 4.32 ppm (s, 5 H) and absorptions for the methylene protons of THF. Integration of these signals indicated that there was one molecule of THF per each cyclopentadienide moiety.

$[(Ph_3P)_2N]^+[CpV(CO)_3H]^-$ (PPN^+-**3**) was prepared from Na_2-**2**·THF by protonation with water, to generate a THF solution of Na-**3**. Exchange of PPN^+ for sodium cation and precipitation with petroleum ether led to the isolation of the air-sensitive, yellow solid, PPN^+-**3**.

The IR spectrum of PPN^+-**3** showed only two carbonyl absorptions at 1890 and 1780 cm^{-1} in THF, HMPA, and acetonitrile solutions and as a Nujol mull and a KBr pellet. Although such a simple spectrum could be consistent with local C_{3v} symmetry, we feel that it is more likely that two bands are accidentally unresolved, and the structure of **3** is most likely analogous to that of the isoelectronic $CpW(CO)_3H$, which has been assigned a square pyramidal configuration on the basis of NMR investigations.[10] No IR absorption for the vanadium–hydrogen stretch was identified. The IR spectra of KBr pellets of $PPN^+[CpV(CO)_3D]^-$ (PPN^+-**3-D**) and PPN^+-**3** were superimposable between 4000 and 300 cm^{-1}.

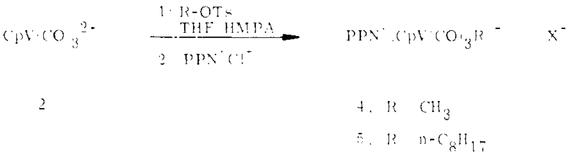
The IR spectra of solutions of Na-**3** indicated significant ion pairing. When 1 equiv of water was added to a slurry of Na_2-**2**·THF to produce Na-**3**, the IR spectrum of the solution showed carbonyl absorptions at 1890, 1795, 1780 (sh), and 1735 cm^{-1}. The four carbonyl absorptions indicated more than one vanadium species in solution. The IR spectrum of this solution changed as limiting amounts of PPN^+Cl^- were added (Figure 1). 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 with the spectrum of isolated PPN^+-**3** dissolved in THF.

We assign the carbonyl absorptions at 1890 and 1780 cm^{-1} in the IR spectrum to a solvent-separated ion pair, and the bands at 1795 and 1735 cm^{-1} to an intimate ion pair.[9,11,12] 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. As PPN^+Cl^- was added, the sodium cation was irreversibly removed from solution as NaCl, leaving only PPN^+-**3**.

The NMR spectrum of PPN^+-**3** in THF-d_8 showed resonances at δ 7.55 (m, 30 H, PPN^+), 4.57 (s, 5 H, Cp), and

−6.10 ppm (s, 1 H, hydride). The resonance at δ −6.10 was very broad. The width at half-height was greater than 1 ppm at room temperature, but the signal sharpened to 0.43 ppm at half-height at −50 °C. This temperature dependence is similar to that attributed to quadrupole coupling between vanadium nuclei and hydride ligands in other vanadium hydride complexes.[13]

Preparation of [CpV(CO)$_3$(*n*-alkyl)]$^-$ Complexes. Although this paper is concerned primarily with the preparation and reactions of hydride **3**, we have also carried out some preliminary experiments aimed at preparing related *n*-alkyl complexes. Alkylation of dianion **2** was achieved by carrying it out in THF with a small amount of HMPA added, sufficient to solubilize the dianion. The methyl derivative **4** was obtained by addition of PPN$^+$Cl$^-$ and precipitation with petroleum ether, and characterized on the basis of spectral and analytical data.



$$CpV(CO)_3^{2-} \xrightarrow[2)\ PPN^+Cl^-]{1)\ R\text{-}OTs,\ THF/HMPA} PPN^+[CpV(CO)_3R]^- \quad X^-$$

2

4, R = CH$_3$

5, R = n-C$_8$H$_{17}$

The IR spectrum of PPN$^+$-**4** in THF showed carbonyl absorptions at 1895, 1795, and 1775 (shoulder) cm^{-1}. The NMR spectrum in THF-d_8, in addition to the large absorption for PPN$^+$, showed a cyclopentadienide resonance at δ 4.43 ppm, and a slightly broadened signal (4 Hz at half-height) at δ −0.33 ppm for the methyl ligand. PPN$^+$-**4** was air sensitive, both as a powder and in THF solution.

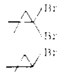
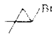
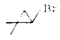
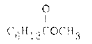
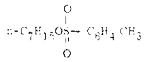
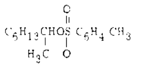
When an HMPA solution of Na$_2$-**2**·THF was treated with 1 equiv of 1-bromooctane, the cyclopentadienide resonance at δ 4.32 ppm for **2** disappeared and a new large absorption at δ 4.42 ppm appeared along with a small absorption at δ 4.55 ppm due to **3**. The similarity of the chemical shift of the new cyclopentadienide resonance in this reaction to that for **4** implied that **2** had been alkylated by 1-bromooctane, to give [CpV(CO)$_3$(C$_8$H$_{17}$)]$^-$ (**5**). The IR spectrum of the solution was very similar to those of **3** and **4**, with carbonyl absorptions at 1895 and 1790 cm^{-1}. This compound decomposed at room temperature, as indicated by the decrease in intensity of the δ 4.42 absorption in the NMR spectrum of the solution, and we were not able to isolate it in pure form. 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 decomposition of [CpV(CO)$_3$(C$_8$H$_{17}$)]$^-$ occurred by β-elimination.

Reactions of CpV(CO)$_3$H$^-$ with Halides. Organic Products. The reactions of CpV(CO)$_3$H$^-$ (**3**) with alkyl halides proceeded with complete substitution of the halogen of the alkyl halide by the hydrogen of **3**, forming the corresponding alkane (the organometallic products formed in this reaction are discussed in the following section). The hydrogen in the alkane was shown to come from **3** by treating [CpV(CO)$_3$D]$^-$ in THF-h_8 and [CpV(CO)$_3$H]$^-$ in THF-d_8 with 1-bromooctane. C$_8$H$_{17}$D and C$_8$H$_{18}$ were observed, respectively.

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.

It should be noted that alkyl *p*-toluenesulfonates react much more slowly than the corresponding bromides, and elevated temperatures are required to effect some conversion to alkane. Also, the reactions of **3** with secondary and tertiary bromides showed no elimination products.

Table I. Reactions of PPN$^+$[(η^5-C$_5$H$_5$)V(CO)$_3$H]$^-$ with Organic Substrates in THF^a at 25 °C

Substrate	Product	Reaction Time (hours)	Yield (%)^b
n-C$_8$H$_{17}$I	n-C$_8$H$_8$	0.5	94
n-C$_8$H$_{17}$Br	n-C$_8$H$_{18}$	4.0	77
n-C$_8$H$_{17}$Cl	No reaction	1.5 (50 °C)	--
n-C$_6$H$_{13}$Br	n-C$_6$H$_{14}$	7.0	73
Cyclo-C$_6$H$_{11}$Br	Cyclo-C$_6$H$_{12}$	10.0	65
		0.5	97
	No reaction	24.0	--
(CH$_3$)$_3$CBr	(CH$_3$)$_3$CH	12.0	100
C$_6$H$_5$CH$_2$Br	C$_6$H$_5$CH$_3$	< 0.5	60
C$_6$H$_5$CH=CHBr	C$_6$H$_5$CH=CH$_2$	5.0	40
C$_6$H$_5$Br	C$_6$H$_6$	6.5	44
C$_6$H$_{13}$COCl	C$_6$H$_{13}$CHO	< 0.1	100^c
C$_6$H$_5$COCl	C$_6$H$_5$CHO	0.1	40 (30)^d
C$_6$H$_5$CH$_2$COCl	C$_6$H$_5$CH$_2$CHO	< 0.1	67
C$_4$H$_9$CHBrCH$_2$Br	C$_4$H$_9$CH=CH$_2$	2.0	56^e
CH$_3$CH$_2$CH=C(Br)CH$_2$CH$_3$	3-hexene	260	100^f
1-Bromo-Adamantane	Adamantane	5.0 (70 °C)	66^g
C$_6$H$_5$CH(CH$_3$)Br	C$_6$H$_5$CH(D)CH$_3$	0.25	64^h
	No reaction	1.0	--
 $C_6H_{13}\overset{O}{\overset{\vert}{C}}OCH_3$	No reaction	12.0	--
 $n\text{-}C_7H_{15}O\overset{O}{\underset{O}{S}}\text{—}C_6H_4CH_3$	n-C$_7$H$_{16}$	6.0 (60 °C)	47
 $C_6H_{13}\underset{H_3C}{CH}O\overset{O}{\underset{O}{S}}C_6H_4CH_3$	No reaction	36.0	--

[a] All reactions were carried out with equimolar quantities of PPN$^+$-**3** and organic substrate at 25°C unless stated otherwise. [b] Yields were determined by gas chromatographic peak area integration or NMR integration unless otherwise noted. [c] Volatile material vacuum transferred from reaction mixture immediately after addition of acid chloride. [d] Yield of isolated product, obtained as the 1,2-dianilinoethane adduct. [e] No hexane or monobromohexanes were formed as indicated by gas chromatographic analysis. The reaction was carried out with a molar ratio of PPN$^+$-**3** to C$_4$H$_9$CHBrCH$_2$Br of 2.1:1. [f] Corrected for unreacted starting material; reaction carried to ca. 25% completion. [g] Product isolated as an impure oil. PPN$^+$[(η^5-C$_5$H$_5$)V(CO)$_3$D]$^-$ was used in this reaction. [h] Product isolated by preparative gas chromatography. Reaction run with optically active bromide; see text for details.

Reaction of PPN$^+$-**3** with acyl chlorides was instantaneous, and again led to exchange of halogen and hydrogen atoms, to yield the corresponding aldehydes. The aldehydes were identified by IR and NMR spectroscopy and by gas chromatography. No overreduction of the aldehydes to alcohols was observed. 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 indefinitely 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 2 h after the initial reaction was complete. Dodecanal persisted in the final reaction solution for over 6.5 h, 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, no satisfactory general procedure for isolating the product aldehydes has yet been developed, although in some cases moderate yields of aldehyde derivatives may be obtained on workup (see Table I).

Reaction of $CpV(CO)_3H^-$ with Halides. Organometallic Products. Treatment of **3** with an equimolar amount of alkyl halide (e.g., 1-bromohexane) in THF gave, in addition to *n*-alkane, a solution whose IR spectrum showed new carbonyl absorptions at 2008, 1948, 1915, 1855, and 1810 cm^{-1}. The absorptions at 2008 and 1915 cm^{-1} corresponded to $CpV(CO)_4$. Upon standing for several days, the bands at 1948, 1855, and 1810 cm^{-1} slowly diminished in intensity, along with a moderate increase in the $CpV(CO)_4$ absorptions. The primary product of the reaction therefore appeared to be an unstable vanadium carbonyl complex which exhibited three new IR absorptions, and slowly decomposed to give a low yield of $CpV(CO)_4$.

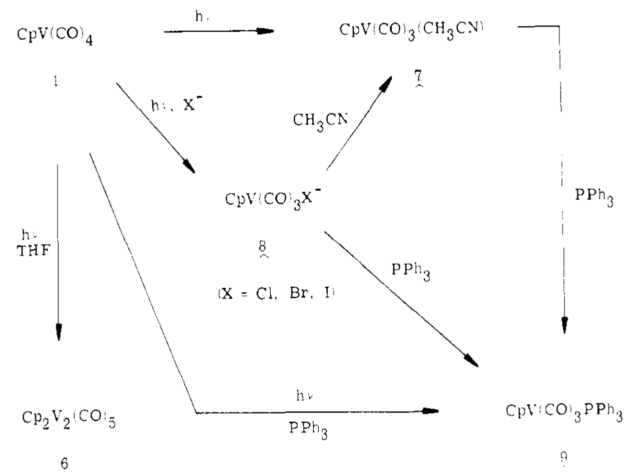
Monitoring the reaction by NMR indicated that the situation was more complicated than the IR experiment suggested. Reaction of **3** with 1-bromoalkanes (e.g., 1-bromooctane) showed *two* new Cp resonances, one at δ 4.83 (to which we will refer temporarily as compound A) and the other at δ 4.67 ppm (compound B), in addition to the characteristically broadened absorption for $CpV(CO)_4$ at δ 5.22 ppm. Upon standing for long periods of time, both A and B gradually disappeared, and an increased amount of tetracarbonyl was observed. The relative amounts of the products A and B varied from reaction to reaction. The amount of B was maximized when reaction between **3** and the halide had a reasonable half-life, or when the organic halide was added slowly to the vanadium hydride in THF. In the latter case, less than 1 equiv of bromide was required to consume all the vanadium hydride. When no halide was present in solution, some **3** reappeared, as well as $CpV(CO)_4$, upon decomposition. In the case of rapid reactions, such as between **3** and acid chlorides, little B was formed.

In acetonitrile solution, somewhat different results were observed. If the reaction was monitored several minutes after the reactants were mixed, a third new material was formed (compound C), which had IR absorptions at 1968, 1866, and 1843 (sh) cm^{-1} and an NMR Cp signal at δ 5.08 ppm. However, formation of this material, which is red in color, is preceded by a brief flash of green-brown, which changes to red moments after reaction has commenced (this phenomenon is best observed with substrates such as alkyl iodides or acid chlorides, which react immediately upon mixing). Adding the halide to a solution of hydride in an IR cell and monitoring the reaction immediately shows that the primary (green-brown) product of reaction is in fact complex A, which is rapidly converted to C in acetonitrile.

Identification of A as Halide Complex $CpV(CO)_3X^-$. It seemed likely that the complexes discussed above were products formed by trapping coordinatively unsaturated $CpV(CO)_3$, a possible primary product of the replacement reaction. We therefore investigated photochemical substitution reactions of $CpV(CO)_4$ with various ligands present in the reaction medium, as a possible way of preparing these materials independently.[14]

We first examined the possibility of producing solvent complexes. Irradiation of $CpV(CO)_4$ in acetonitrile did indeed lead to a solvent complex, which was too reactive to isolate. However, its composition could be assigned as $CpV(CO)_3(CH_3CN)$ on the basis of spectral data, and by its conversion to the known complex[14] $CpV(CO)_3PPh_3$ by treatment with triphenylphosphine. The acetonitrile complex is identical with complex C, described above. In THF, no solvent complex was observed; irradiation of **2** gave only $Cp_2V_2(CO)_5$ (**6**), the dimer which had been previously observed to be formed upon protonation of dianion **2** with mineral acid.[7,15] However, irradiation of **1** in THF in the presence of PPN^+Br^- gave complex A. Furthermore, irradiation in the presence of $[N\text{-}Et_4]^+Br^-$ in CH_2Cl_2 also gave a complex with the same IR and NMR absorptions as A. These materials could be isolated and were shown by standard analytical procedures to be salts of $CpV(CO)_3Br^-$. In a similar way, salts of $CpV(CO)_3Cl^-$ and $CpV(CO)_3I^-$ were prepared and isolated, and identified as organometallic products of chloride and iodide replacement reactions (cf. Scheme II).

Scheme II

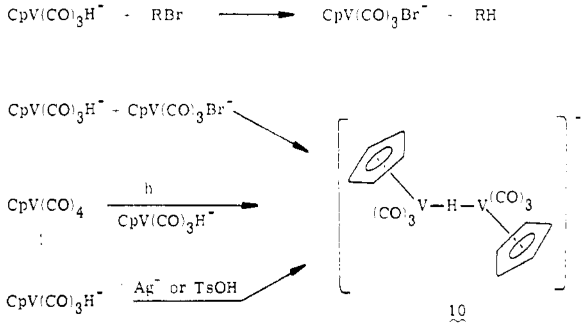


Identification of Complex B as $[(CpV(CO)_3)_2H]^-$. Complex B, the other organometallic product observed in variable amounts in the replacement reaction, was extremely reactive. Attempted isolation by removal of solvent gave tetracarbonyl **1** and appeared also to regenerate some hydride **3**. In addition, reasonable yields of B were obtained by treating **3** with *p*-toluenesulfonic acid (TsOH), galvinoxyl, or silver ion. The fact that only 0.5 equiv of TsOH was required to convert **3** completely to B suggested that the new complex was a dimer formed by reaction of hydride **3** with unsaturated $CpV(CO)_3$; i.e., it was the bridging dimer $[Cp(CO)_3V\text{-}H\text{-}V(CO)_3Cp]^-$ (**10**). This assumption was again confirmed by photochemistry: irradiation of $CpV(CO)_4$ in the presence of $CpV(CO)_3H^-$ led to a quantitative yield of complex B. Furthermore, reaction of equimolar quantities of $CpV(CO)_3Br^-$ and **3** also led to a quantitative yield of the bridging dimer. These experiments showed that complex B had only two carbonyl IR bands (1857 and 1817 cm^{-1}). These bands are very similar to two of those exhibited by halide complex **6**, which explained why only three IR bands were observed in solutions containing both **6** and B. Reexamination of the replacement reaction spectra confirmed that reaction of the vanadium bromide with vanadium hydride **3** was the source of **10** observed.

Because of its extreme sensitivity, we can only speculate about the geometric structure of **10**. Its two IR bands are consistent with a highly symmetrical structure such as D_{3d} or D_{3h} but, as with hydride **3**, a less symmetrical structure having degenerate IR bands is likely. The large number of $CpML_4$ complexes which have square pyramidal structures (including dimers similar to **10**, but without hydrogen bridges)[16] suggests that a double square pyramid having a linear V-H-V bridge (Scheme III) may be the best guess for the structure.

Metal Hydrides as Ligands. Evaluation of Kinetic and Thermodynamic Ligating Ability of $[CpV(CO)_3H]^-$. The photochemical synthesis of **10** from **1** and **3** is analogous to the photochemistry outlined in Scheme II, except that the ligand entering the vanadium coordination sphere is a molecule of **3**, rather than phosphine, halide, or acetonitrile. Although a few other bridging hydrides are known,[17] and ligating strengths of conventional ligands have been discussed at some length,[18] to our knowledge there has been only scant discussion of the

Scheme III

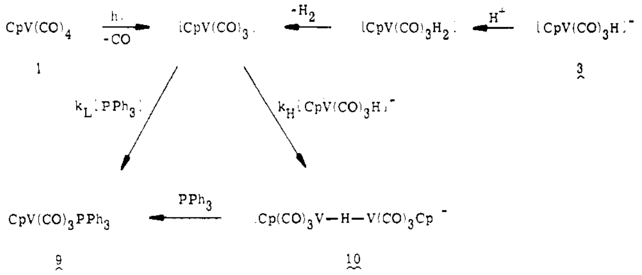


relative ability of a metal hydride to act as a ligand in the coordination sphere of a second metal.[19] Our interest in this problem was stimulated by the observation, reported above, that irradiation of **1** in the presence of **3** led only to bridging hydride **10**—that is, formation of dimer **6** was completely suppressed by the presence of **3**. It was also spurred by indirect evidence recently obtained by Norton and co-workers[20] that a rapid reaction between an osmium hydride and an unsaturated osmium complex plays an important role in the binuclear reductive elimination of methane from $(CO)_4Os(CH_3)(H)$.

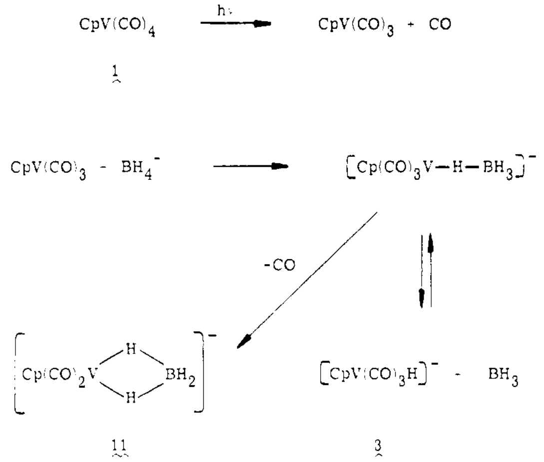
Because phosphines have played a central role in determination of relative ligating abilities,[18] we decided to attempt to compare the affinities of **3** and PPh_3 for the $CpV(CO)_3$ fragment. Our first experiment involved preparing a THF solution of **10** by irradiating **1** in the presence of **3**. We then added PPh_3, which (at a moderate rate) completely converted the bridging hydride to equimolar amounts of $CpV(CO)_3H^-$ and $CpV(CO)_3PPh_3$ (this incidentally provided additional confirmation for the empirical formula of **10**). This experiment demonstrated that PPh_3 is clearly a thermodynamically better ligand for vanadium than is **3**. *However, the kinetic ligating ability of these ligands does not follow the same trend.* Thus, we irradiated **1** (0.60 M) in the presence of equimolar quantities (0.12 M each) of $PPN^+[CpV(CO)_3H]^-$ and PPh_3, and examined (cf. Scheme IV) the kinetic ratio of **9** to **10** at early reaction times. The precision of this experiment was affected somewhat by the thermal reaction between **10** and PPh_3; however, it is clear that **3** enters the coordination sphere of vanadium *more rapidly* than PPh_3. By extrapolating to $t = 0$, we were able to determine from the kinetic product ratio that k_H/k_L (Scheme IV) is at least 2:1. Thus, there is some (as yet unexplained) property of hydride **3** which allows it to enter the vanadium coordination sphere more rapidly than phosphine, despite the fact that the thermodynamic affinity of vanadium for phosphine is larger.

It is possible, of course, that the photochemical replacement reaction takes place by a mechanism not involving $CpV(CO)_3$ (despite much indirect evidence to the contrary).[14] In order to check this possibility, we carried out a competition experiment on $CpV(CO)_3$ generated in a completely independent reaction. We chose the protonation of **3**, a reaction which presumably[15] first forms $CpV(CO)_3H_2$; this transient dihydride loses H_2, giving $CpV(CO)_3$, which in the absence of external ligand forms **6**. Thus, 0.12 M $CpV(CO)_3H^-$ was treated with 0.1 equiv of TsOH in the presence of 0.10 M PPh_3. As in the irradiation, no dimer **6** was observed, but a mixture of **9** and **10** was formed instead (again, this was slowly converted to pure **9**). The initial **10**/**9** ratio observed was 1.9:1, which is satisfyingly close to that seen in the photochemical reaction, considering the complicating thermal reaction and the difference in reaction conditions employed. This provides support for the quantitative reliability of the kinetic trapping ratio, as well as for the postulate that $CpV(CO)_3$ [or a reactive analogue of this species, such as $CpV(CO)_3THF$] is the intermediate in both reactions.

Scheme IV



Scheme V



Preparation of $PPN^+[CpV(CO)_3BH_4]^-$. The hydride as ligand experiments outlined above, as well as syntheses of transition metal borohydride complexes which have appeared in the literature recently, stimulated us to investigate the possibility of carrying out replacement reactions on $CpV(CO)_4$ with borohydride as the entering ligand. We therefore prepared[21] $PPN^+BH_4^-$, and irradiated $CpV(CO)_4$ in a THF solution of this material. Analysis of the reaction solution by IR showed that both hydride **3** and a new complex were formed. The new material has IR absorptions in the carbonyl region at 1835 and 1721 cm^{-1}, and absorptions characteristic of metal-bound BH_4^- at 2360 cm^{-1} (KBr pellet). In the NMR, this complex has a Cp signal at δ 4.14 ppm, and (as in the case of similar complexes[21]) coupling to boron and vanadium renders the boron-bound hydrogen signals too broad to be observed at room temperature.

The new complex proved to be difficult to separate from hydride **3**, and so in an alternative method of synthesis, pure PPN^+-**3** was treated with BH_3-THF. This produced the new material in a clean reaction, and it was isolated as green crystals and characterized as $PPN^+[CpV(CO)_2BH_4]^-$ (**11**) on the basis of its spectral characteristics and elemental analysis.

Control experiments demonstrated that **11** was not the source of hydride **3** observed in the photochemical reaction; **3** is therefore produced in a direct reaction between **1** and $PPN^+BH_4^-$. We suggest that pathways outlined in Scheme V are those responsible for the complexes formed in the reactions discussed here.

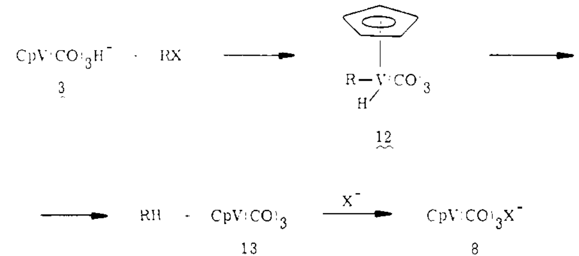
Mechanism of the Halide Replacement Reaction

Stoichiometry, Kinetics, and Relative Reactivity Studies. As outlined above, the reaction between hydride **3** and organic

$$\underset{\mathbf{3}}{CpV(CO)_3H^-} + RX \longrightarrow \underset{\substack{\mathbf{8a},\ X = Cl \\ \mathbf{8b},\ X = Br \\ \mathbf{8c},\ X = I}}{CpV(CO)_3X^-} + RH \qquad (1)$$

$$\underset{\mathbf{8}}{CpV(CO)_3X^-} + \underset{\mathbf{3}}{CpV(CO)_3H^-} \longrightarrow \underset{\mathbf{10}}{[CpV(CO)_3]_2H^-} + X^- \qquad (2)$$

Scheme VI

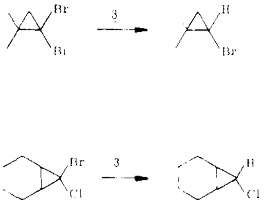


halides (cf. Table I) involves interchange of hydrogen and halogen atoms between carbon and vanadium (eq 1), and the initial organometallic product of the reaction is the anionic vanadium halide **8.** Experiments carried out with CpV(CO)$_3$D$^-$ (**3**-*d*), prepared from dianion **2** and D$_2$O, gave exclusively R–D, demonstrating that the hydrogen appearing in the product is in fact the one originally attached to vanadium. In the case of relatively slow reactions, or when a deficiency of organic halide is used, reaction between **8** and starting hydride, leading to bridging hydride **10,** is observed.

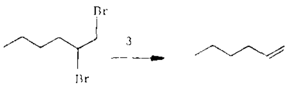
By monitoring reactions by IR and NMR, qualitative information on the relative reactivity of several organic substrates was obtained (cf. Table I). Iodides in general react very rapidly, and bromides less rapidly [a typical alkyl bromide (at ca. 0.1 M) requires 3–4 h to undergo complete reduction at room temperature in THF]. Chlorides are very unreactive, only activated chlorides (e.g., benzylic) giving any reduction product at all. Carbon substrate reactivity at first seemed consistent with an alkylation–reductive elimination mechanism (Scheme VI)—e.g., benzylic and acid halides react immediately, whereas alkyl halides require longer periods (3–12 h) to undergo complete reaction.[22] However, the absence of β-elimination products (even with tertiary bromides),[23] and the fact that vinyl and aryl bromides could be reduced to the corresponding alkenes (albeit somewhat slowly), raised doubts about mechanisms which involve initial alkylation at the metal, and suggested strongly that organic *radicals* were being formed in the rate-determining step of the reduction.

In order to quantify the relative reactivity of primary, secondary, and tertiary halides, we carried out competition studies on a mixture of 1-bromopentane, 2-bromohexane, and 2-bromo-2-methylpropane (each 0.5 M), which were subjected to reduction using a deficiency of hydride **3** (0.1 M). Analysis of the resulting solution by gas chromatography showed an *n*-pentane:*n*-hexane:2-methylpropane distribution of 12:1:5, which provides a reasonable idea of the relative rates of reaction at primary, secondary, and tertiary centers. The comparable reactivity of the three substrates, as well as the minimum in reactivity shown by the secondary system, once again did not seem characteristic of a process involving rate-determining alkylation. An estimate of both chain-length and steric effects on the reaction rate was obtained by carrying out a similar competition study on a mixture of *n*-pentyl, *n*-hexyl, and neopentyl bromides. The corresponding hydrocarbon products were formed in the ratio 1:1:0.02.

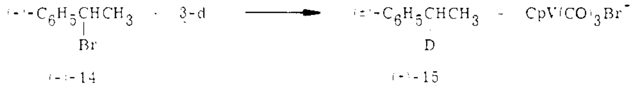
The hypothesis that the critical intermediates in these reactions are organic radicals is further supported by experiments on other types of substrates. In reduction of *gem*-dihalocyclopropanes, replacement of one halogen atom is very rapid, and attack at the second is extremely slow. This behavior is reminiscent of that observed in trialkyltin hydride reductions (except that the difference in rates is larger in the vanadium case), which are known to take place by free radical chain mechanisms.[24] Despite the fact that primary bromides react readily at room temperature, *p*-toluenesulfonates (which have comparable reactivity to bromides in most alkylation reactions) are completely inert, and can only be forced to react slowly upon heating to 60–70 °C. 1,2-Dibromoalkanes are quantitatively debrominated, rather than reduced, an observation which again has precedent in other radical processes.[25]



$C_6H_{13}OTs \xrightarrow{3}$ N.R.

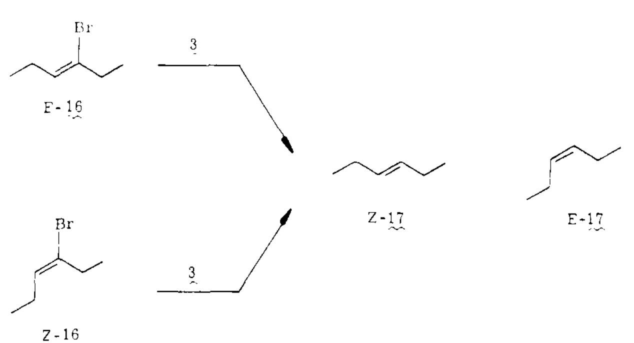


Stereochemistry. The stereochemistry of the replacement reaction is also consistent with the intervention of radicals. In order to investigate the stereochemistry at a saturated carbon center, we decided to attempt the reduction of optically active α-bromoethylbenzene (**14**) with the vanadium deuteride **3**-*d*. The active bromide was prepared by literature methods[26] and treated with **3**-*d*, and the hydrocarbon (**15**) was purified by



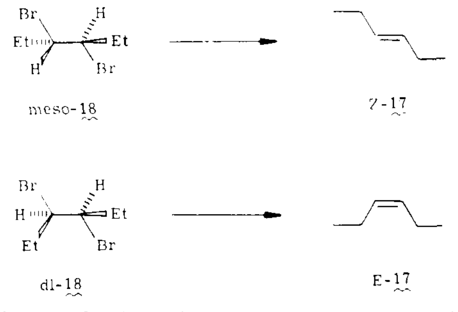
$(-)\text{-}C_6H_5\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + \textbf{3}\text{-d} \longrightarrow (\pm)\text{-}C_6H_5\underset{\displaystyle D}{C}HCH_3 + CpV(CO)_3Br^-$

(−)-14 (±)-15

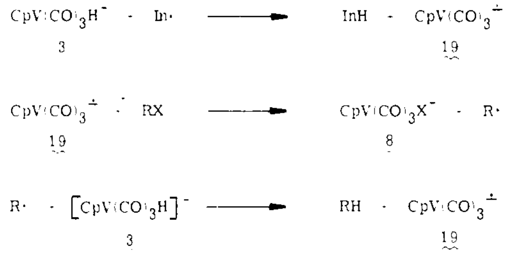


preparative gas chromatography. The hydrocarbon isolated had no detectable rotation. After correction for the partial optical purity of the starting halide[26b] and percent deuterium content of the product, and estimation of our limits of detection of optical activity (ca. 0.005° at λ_{365}), we are able to say that the reaction proceeds with at least 85% (and probably complete) loss of stereochemistry at carbon.

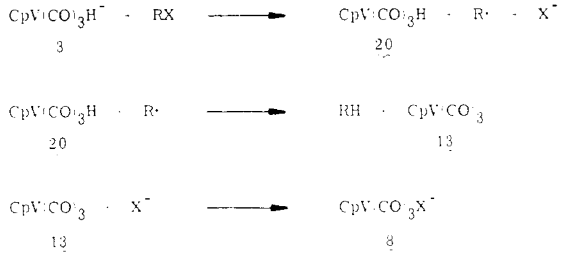
Experiments with the stereoisomeric 3-hexenyl halides, which may be analyzed more precisely using gas chromatographic techniques, showed that stereochemical scrambling is also observed when the replacement is carried out at a vinyl center. Pure (*E*)- and (*Z*)-3-bromohexenes were prepared and purified by gas chromatography, and treated with **3.** Although the reaction was slow, reduction did occur at room temperature, and the product observed from each stereoisomer was a 70:30 mixture of (*E*)- and (*Z*)-3-hexenes (**17**). Monitoring the reaction by gas chromatography showed that no *E–Z* isomerization of the starting halides occurred during the reaction. In debromination of *vic*-dibromoalkanes, the halogens are removed in a stereospecific trans elimination, again in agreement with similar observations in other radical reactions.[25]



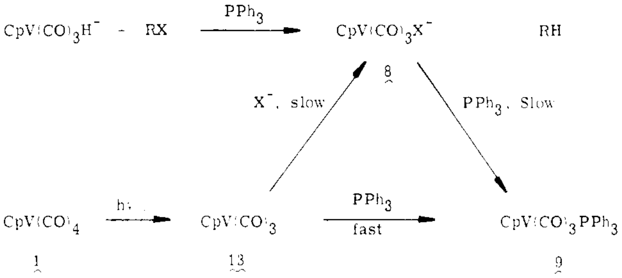
Scheme VII



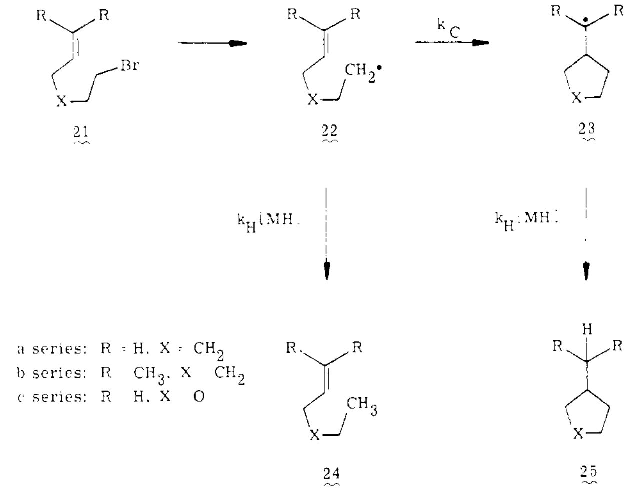
Scheme VIII



Scheme IX



Scheme X



Thus, *meso*-3,4-dibromohexane is debrominated stereospecifically to *trans*-3-hexene, and the corresponding *dl* diastereomer gives only (*E*)-3-hexene.

Mechanism of Radical Formation. Although the experiments described above are most consistent with the intervention of radical intermediates in these reactions, they provide little information as to how the radicals are formed. The two most likely mechanisms for this process are outlined in Schemes VII and VIII. The first is a direct analogy to the chain mechanism established for R_3SnH reactions. The process is initiated by adventitious abstraction of a hydrogen atom from **3**, giving the 17-electron "six-coordinate" vanadium radical anion **19**. This species should have a powerful affinity for one-electron ligands, and would be expected to rapidly abstract halogen from organic halides. This generates **8** directly, along with an alkyl radical, which propagates the chain by abstracting a hydrogen atom from another molecule of **3**. Termination would presumably involve occasional encounters between two radicals, or (relatively slow) reaction of R· with solvent. The chains must be long enough in this mechanism that only extremely small amounts of solvent-reduced and radical-radical products are formed.

The other reasonable mechanism[27] is the "outer sphere" electron transfer mechanism shown in Scheme VIII. Here the reaction is initiated by electron transfer, giving neutral, 17-electron vanadium hydride **20** and an organic halide radical anion, which (if it has any lifetime at all) rapidly dissociates to R· and X^-. The organic radical then abstracts a hydrogen atom from **20**, leaving coordinatively unsaturated fragment **13** (cf. the alkylation/reductive elimination mechanism, Scheme VI). This species is scavenged by halide ion, giving **8**.

A critical difference between these mechanisms is the intervention of **13**. This species is involved in the alkylation (Scheme VI) and electron transfer mechanisms, but is avoided in the radical chain mechanism. We decided to test for the intervention of **13** by carrying out the reduction in the presence of an excess of PPh_3, assuming that **13**, if present, would be diverted to the known[14] (and relatively stable) complex $CpV(CO)_3PPh_3$ (**9**). Reduction of several of the halides studied here does in fact give **9** as the final organometallic product. However, this complex is not the first-formed (kinetic) product of the reduction. Thus, treating benzyl bromide with 1 equiv of **3** in the presence of a large excess of PPh_3, and monitoring the reaction by NMR or IR, shows that the only detectable initial product of the reaction is the vanadium halide **8**, which (as discussed in a preceding section) undergoes slow conversion to **9** in the presence of phosphine (Scheme IX). One would expect that **13**, if formed, would be trapped faster by phosphine than Br^-, and therefore this experiment rules out the intervention of **13**. As a check on the relative rate of reaction of **13** with PPh_3 and Br^-, we irradiated $CpV(CO)_4$ in the presence of roughly equimolar quantities of the two ligands. As expected, the major product of this reaction was **9** (in a control experiment, the bromide **8** did not undergo photoconversion to **9** at a rapid rate). We therefore conclude that the bromine atom is transferred directly from carbon to vanadium in the reduction, and the chain mechanism (Scheme VII) is the most reasonable way of accounting for this fact.

Cyclization Studies. Estimation of the Hydrogen Transfer Rate Constant. A critical test of a mechanism such as that outlined in Scheme VII involves the examination of substrates which should generate radicals that might rearrange or cyclize. If the rate of rearrangement is competitive with that of destruction of the initially formed radical, the ratio of rearranged to unrearranged products should depend linearly upon the concentration of trapping reagent, and the relative rate constants associated with these processes can be determined. Classic experiments of this type[28] (cf. Scheme X) typically involve 5-hexenyl radical (**22a**), which cyclizes specifically and irreversibly (and with an absolute rate constant[28d] $k_C \simeq 1.0 \times 10^5\ s^{-1}$) to cyclopentylmethyl radical (**23a**). We were surprised to find, however (cf. Table II), that neither 6-bromo-1-hexene (**21a**) nor its dimethyl derivative **21b** gave proportions of cyclization product large enough to analyze reliably. We achieved more success with 2-allyloxyethyl bromide (**21c**). Although the rate of cyclization of the derived radical **22c** has not been measured, experiments carried out on closely related systems indicate that replacement of CH_2 by O at C-4 increases the rate of cyclization by about an order of magnitude.[29] In this system we were able to obtain comparable percentages of **24** and **25**. As shown in Table II, the **24c**/**25c** ratio shows an approximately linear dependence on the concentration of vanadium hydride.

Because cyclic ether **25c** is so similar in chemical character

Table II. Cyclization of Unsaturated Halides (at 25 °C) Induced by $CpV(CO)_3H^-$ and $(n\text{-}Bu)_3SnH$

substrate	concn, M	hydride	concn, M	solvent	ratio of products (cyc/uncyc)[a]
$CH_2{=}CH(CH_2)_4Br$	0.019	V	0.077	THF	0.027
$Me_2C{=}CH(CH_2)_4Br$	0.02	V	0.162	THF	0.026
			0.081	THF	0.075
			0.040	THF	0.120
	0.24	Sn	0.30	C_6H_6	1.70
$CH_2{=}CHCH_2OCH_2CH_2Br$	0.02	V	0.164	CH_3CN	0.69
			0.082	CH_3CN	1.13
			0.041	CH_3CN	2.49
			0.081	THF-d_8	1.0[b]
			0.150	THF-d_8	0.6[b]
	0.08	Sn	3.8	none	0.5
$CH_2{=}CHCH_2OCH_2CH_2I$	0.02	V	0.081	CH_3CN	1.03
	0.02	Sn	0.08	CH_3CN	18.6

[a] Determined by gas chromatography vs. internal standard, except where indicated; all total yields ~85%. [b] Determined by NMR integration of CH_3 resonances in products.

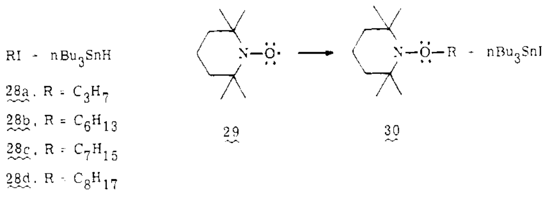
to THF, it was not possible to carefully measure the **24c**/**25c** ratio in that solvent by gas chromatography. We therefore carried out the cyclization study described above in acetonitrile solution. All indications are that the mechanism of the reduction reaction is the same in THF and acetonitrile. However, in order to assure ourselves that the **24c**/**25c** ratio is dependent on [**3**] in THF, we carried out the reaction of **21c** with **3** at two different concentrations of **3** in THF-d_8, and estimated the ratio of products by ^1H NMR. The amounts of **24** and **25** cannot be quantified as precisely as in the acetonitrile experiments, but the experiment again demonstrated a clear dependence of the **24c**/**25c** ratio on the concentration of **3**.

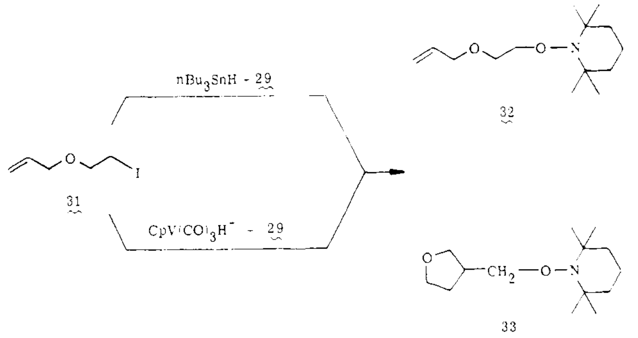
In the process of searching for a rapidly cyclizing radical, we also examined the reduction of 6-bromo-2-heptyne (**26**). As in the case of the hexenyl system, this substrate gave only small amounts of cyclized product. Interestingly, although the vanadium bromide was once again the kinetic product of the reaction, it was transformed slowly during the reaction to a new species, identified as the π complex $CpV(CO)_2$[2-heptyne] (**27**).[30]

Knowledge of the rate constant for rearrangement of radical **22c** would allow us to calculate the absolute rate constant for transfer of hydrogen from **3** to the radical. As indicated above, this rate constant has not been measured. However, we were able to obtain a close estimate of k_H in the following manner. We first examined the tri-*n*-butyltin hydride reduction of bromo ether **21c** at 0.08 M concentration of hydride in acetonitrile. This gave a **25c**/**24c** ratio of 18.6. Assuming that the reaction between **22c** and R_3SnH takes place with approximately the same rate constant in acetonitrile and cyclohexane (ca. 1×10^6 M^{-1} s^{-1}), we estimate that the rate constant k_C (Scheme X) is 1.2×10^6 s^{-1}. This then requires that k_H for the reaction of **3** with *n*-alkyl radicals is about 2×10^7 s^{-1}, more than an order of magnitude larger than that measured[24c,d] for Bu_3SnH.

Radical Trapping Experiments. Another critical test for radical intermediates in chemical reactions involves the inhibition or acceleration of the reaction by nonstoichiometric amounts of additives, and the trapping of radicals by stoichiometric amounts of radical scavengers or "traps". Inhibition and acceleration experiments were somewhat difficult to carry out in our system, because many species used for this purpose (e.g., galvinoxyl, nitroxides) are oxidizing agents and rapidly destroy the vanadium hydride. Milder inhibitors such as duroquinone had no effect on the reaction rate. However, we had somewhat better luck with highly reactive radical traps such as nitroxyls.[31]

Once again model experiments were run initially with trialkyltin hydride and (for reasons outlined below) iodides rather than bromides. Thus, treatment of iodides **28a–d** with Bu_3SnH in the presence of 0.1 M nitroxide **29** produced adducts **30a–d.** In the case of **30c,** the adduct was synthesized independently by the Grignard route[31] to confirm conventional





spectral characterization. Tin hydride reduction of iodide **31** was also examined, and gave both uncyclized and cyclized adducts **32** and **33.**

Difficulties in carrying out similar experiments in our vanadium system were once again caused by the tendency of **29** to cause irreversible decomposition of **3.** For this reason we were not able to carry out trapping studies on primary bromides, which react more slowly than **3** is oxidized. However, iodides are reduced much more rapidly; thus it was found possible to mix solutions of **29** and **28c** without reaction, and then rapidly add a solution of **3.** Under these conditions, the **3** + **28d** reaction and oxidation of **3** occurred at competitive rates, and a moderate yield of **30c** was detected. Similarly, reaction of **31** with **3** in the presence of **29** gave both **32** and **33.**

An Anomalous Case: Cyclopropylcarbinyl Bromide. During our search for a radical which would rearrange in competition with hydrogen transfer from **3**, we carried out a number of experiments on cyclopropylcarbinyl bromide (**34a**). The cyclopropylcarbinyl radical (**35**) rearranges irreversibly to the 3-buten-1-yl radical (**36**) with a rate that has been measured directly at low temperature; extrapolation gives $k_{25} = 1 \times 10^8$ s^{-1} for this process.[32] If this radical were an intermediate in the reduction of the corresponding bromide by **3,** under our

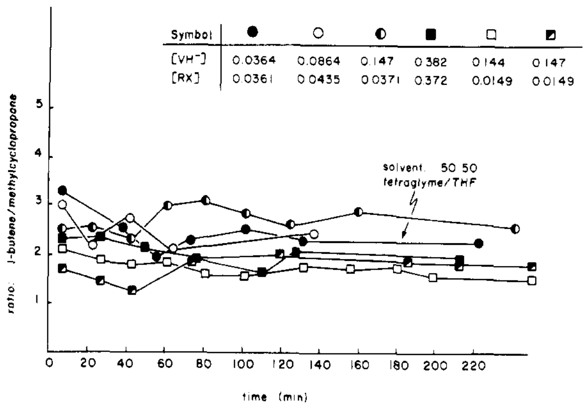
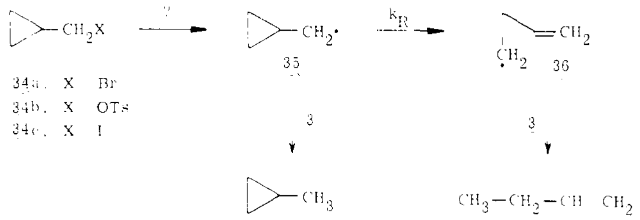


Figure 2. Ratio of 1-butene to methylcyclopropane formed on reduction of cyclopropylcarbinyl bromide by CpV(CO)$_3$H$^-$ in THF under varying concentration conditions, displayed as a function of reaction time (concentrations given in mol L^{-1}).

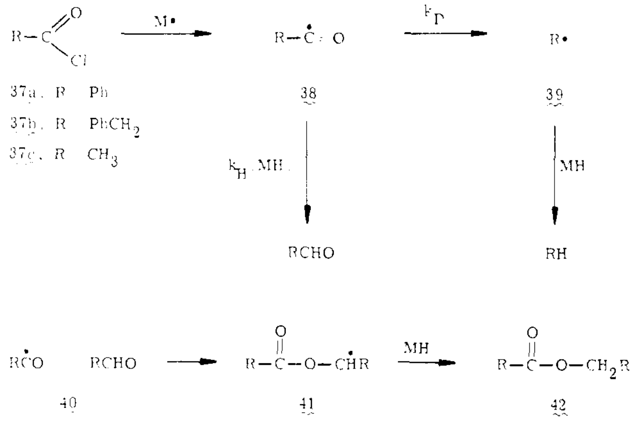
standard conditions little ring-closed product should be observed. However, substantial amounts of methylcyclopropane were formed in this reaction. Furthermore, although some dependence of product ratio on the concentration of **3** was observed, it was minimal compared with that expected on the basis of the chain mechanism, and in fact the variation within each run was comparable to that observed between runs (see Figure 2).



In order to assure ourselves that the methylcyclopropane/1-butene ratio is in fact dependent upon the hydride concentration in a known free-radical reaction, we once again carried out a parallel study with tri-*n*-butyltin hydride. As expected, the rapid rate of rearrangement of **35** made it difficult to capture this radical before extensive isomerization to **36** had occurred, and 1-butene was always the major product of the reaction. With the cyclopropylcarbinyl bromide concentration (THF solution) at 0.037 M, and the R$_3$SnH concentration at 0.15 M, less than 0.5% methylcyclopropane was observed. However, raising the concentration of tin hydride to 0.74 M produced detectable amounts of the ring-closed product (1-butene/methylcyclopropane = 90). Using Carlsson and Ingold's rearrangement rate constant $k_R = 1 \times 10^8\ s^{-1}$, we calculated from this ratio that k_H (the hydrogen transfer rate constant) = $1.5 \times 10^6\ M^{-1}\ s^{-1}$, in excellent agreement with the absolute values Ingold has determined[24c] for this type of reaction in cyclohexane solvent. Reduction of 0.037 M cyclopropylcarbinyl bromide in neat (3.8 M) tin hydride further lowered the methylcyclopropane/1-butene ratio to 11. Neat hydride is a medium of higher viscosity than THF; if we assume that k_R is viscosity independent, this value indicates that k_H has dropped somewhat, to $1.1 \times 10^6\ M^{-1}\ s^{-1}$. This trend again is in good agreement with the magnitude of the viscosity effect observed by Ingold.[24c]

Thus in both a qualitative and quantitative sense, the reaction of **34a** with tri-*n*-butyltin hydride exhibits behavior completely consistent with expectations based on the radical chain mechanism. This reinforces our conclusion that the mechanism of reduction of **34a** by CpV(CO)$_3$H$^-$ differs somehow from the chain process. That this difference is due to the onset of a direct-displacement pathway was suggested by experiments on the corresponding tosylate (**34b**). Unlike ordinary *n*-alkyl tosylates, which are completely stable to **3**, **34b** is reduced at rates comparable to those of the corresponding bromide. Significantly, the major product of this reduction is methylcyclopropane (95%). Reduction of the corresponding iodide (**34c**), however, gives 95% 1-butene. We therefore believe that **34c** is reduced by the chain mechanism, but tosylate **34b** is reduced by a two-electron process (perhaps alkylation/reductive elimination) that avoids free-radical intermediates. The displacement reactivity at the halide-bearing carbon in **34a** is known to be very much enhanced by the adjacent cyclopropyl ring. However, the cyclopropyl ring does not stabilize an adjacent radical greatly. Thus relative to "normal" *n*-alkyl systems, the two-electron process is much accelerated, but bromine atom abstraction by a vanadium radical is not, and in **34a** the two processes become competitive.

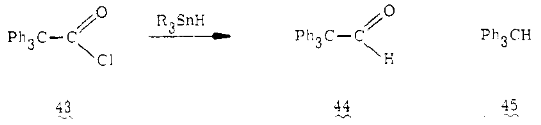
Scheme XI



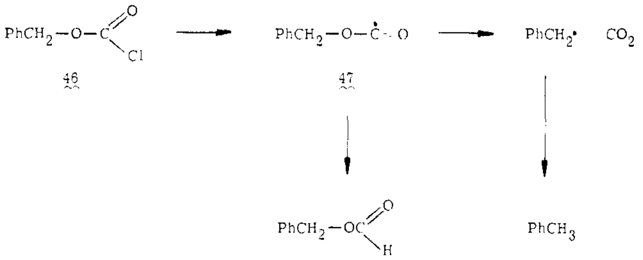
It may be that acid chloride reduction will also fall into the "anomalous" category. Unfortunately, the available data on acyl radical behavior seem to be somewhat contradictory, and so it is not clear how acyl halides should behave upon reduction by vanadium hydride. Briefly, the situation is the following. Ordinary acyl radicals (e.g., phenyl, alkyl) decarbonylate relatively slowly;[33] it is thus understandable that CpV(CO)$_3$H$^-$ reduces benzoyl chloride to benzaldehyde, and *n*-heptanoyl chloride to *n*-heptaldehyde, rather than leading to the products of decarbonylation and reduction (benzene and *n*-heptane, respectively). According to a number of absolute rate studies in the literature, however,[33] there appears to be a dramatic substituent effect on acyl radical decarbonylation rate; thus, for example, phenylacetyl radical (**38b**) decarbonylates 10^6 times faster than acetyl (**38c**). The corresponding absolute rates are somewhat uncertain, but Ingold and coworkers have estimated[34] the rate constant for decarbonylation of **38b** to be $5 \times 10^7\ s^{-1}$ at 25 °C.

If one accepts this value for the rate of decarbonylation, the reported behavior of the corresponding acid chloride in the presence of tri-*n*-butyltin hydride is somewhat curious. The tin hydride reduction of acid chlorides typically gives both aldehyde and ester (**42**) products. The mechanism of this reaction has been studied in detail, and Kuivila and Walsh have concluded that both products are derived from acyl radicals.[35] These authors report good yields of aldehyde and ester from phenylacetyl chloride (**37b**), a result which requires that **38b** live long enough to undergo extensive reduction and attack on aldehyde (both of which are bimolecular reactions), at concentrations near 0.6 M. If we *assume* that the hydrogen transfer rate constant (k_H in Scheme XI) is the same as that measured for alkyl radicals[23c] (ca. $1 \times 10^6\ M^{-1}\ s^{-1}$); and conservatively estimate that the RCHO/RH ratio in this experiment is at least 10, we conclude that the decarbonylation rate constant k_D can be no larger than $6 \times 10^4\ s^{-1}$. This contrasts sharply with the absolute rate estimate mentioned above.

In an effort to promote decarbonylation, Kuivila and Walsh examined the reduction of triphenylacetyl chloride (**43**); the



corresponding radical should decarbonylate even more rapidly than **38b.** However, only 10% triphenylmethane (**45**) was observed, and a 90% yield of triphenylacetaldehyde (**44**) was isolated.[35a] Similarly,[35,36] reduction of benzyl chloroformate (**46**) gave substantial amounts of formate ester (as well as some hydrocarbon).



In light of these results, and our finding that **3** is an order of magnitude more effective as a hydrogen donor than is tri-*n*-butyltin hydride, it is perhaps not surprising that neither toluene nor ester is formed in the reduction of **37b** by **3.** We also find that only benzyl formate is formed on reaction of **3** with **46.** Given the apparent longevity of acyl radicals in the tin hydride reduction, it seems most reasonable to assume for the present that such radicals are also involved in reduction of acyl halides by **3.** It should be kept in mind, however, that neither the tin nor vanadium reaction appears to be consistent with current estimates of absolute rate constants. Either (a) the absolute rate for transfer of hydrogen from metal hydride to acyl radicals is much more rapid than the corresponding transfer to alkyl radicals, (b) room temperature decarbonylation rates for acyl radicals are considerably lower than current estimates indicate, or (c) *both* the tin and vanadium hydride reactions avoid radical mechanisms in the acyl chloride case.

Experimental Section

General. All reactions of CpV(CO)$_4$, Na$_2$CpV(CO)$_3$·THF, and PPN$^+$[CpV(CO)$_3$R]$^-$, R = H, CH$_3$, were carried out in a Vacuum Atmospheres Corp. drybox, with continuously circulating nitrogen, or in serum capped reaction vessels which were prepared in the drybox. Reagents were added to the serum capped reaction vessels by syringe techniques. All other synthetic reactions were carried out under normal atmosphere conditions.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian A-60A, 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 septa. Additional reagents were added through the septa by syringe.

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

Gas chromatographic analyses were carried out on either a Hewlett-Packard 5750 or a Varian Associates Model 90-P instrument. Peak area integrations were performed by multiplying the peak widths at half-height by the peak heights, by cutting out and weighing the peaks, or by electronic integration. Optical rotations were measured on a Perkin-Elmer 141 polarimeter, and melting points were obtained with a Thomas-Hoover capillary melting point apparatus. Melting points were uncorrected. Irradiations were carried out with a 500-W high-pressure Hg lamp (Osram HB0500W/2), in an Oriel Corp. focused beam lamp housing.

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

Tetrahydrofuran (THF), diethyl ether, benzene, petroleum ether, and hexane used in the drybox were purified by vacuum transfer from sodium benzophenone ketyl. Prior to vacuum transfer from sodium benzophenone ketyl, petroleum ether and hexane were stirred repeatedly over concentrated sulfuric acid until the sulfuric acid did not become colored. Then they were stirred with saturated potassium permanganate in 10% sulfuric acid overnight, washed with water, and dried over calcium chloride. Hexamethylphosphoramide (HMPA) was purified by the literature procedure.[37] All other liquid substrates were degassed by freeze-pump-thaw cycles before being used in the drybox.

CpV(CO)$_4$ was purchased from Ventron or Strem Chemical Co. and purified by sublimation at 0.25 mmHg and 80 °C. Commercial triphenylphosphine was recrystallized once from benzene and once from absolute methanol and dried under vacuum (~5 mmHg) at 65 °C for 7 h. 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.[38]

Commercially available alkyl halides were obtained from Aldrich Chemical Co. or Chemical Samples Co. Samples of *meso-* and *dl-*3,4-dibromohexane,[39] 1,1-dibromo-2,2-dimethylcyclopropane,[40] 1-bromo-2,2-dimethylcyclopropane,[40] *cis-* and *trans-*3-bromo-3-hexene,[41] cyclopropylcarbinyl bromide[42] and tosylate,[43] and benzyl chloroformate[44] 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.[45] Benzoyl chloride, phenylacetyl chloride, and 3-carbomethoxypropinonyl chloride were commercial samples which were distilled and degassed.

Neopentyl *p*-toluenesulfonate, *n*-heptyl *p*-toluenesulfonate, 2-octyl *p*-toluenesulfonate, *n*-octyl trifluoromethylsulfonate, methyl heptanoate, and phosphiniminium bromide were all prepared by literature procedures.[45-47]

All other organic substrates were commercial samples used without purification.

Preparation of Na$_2$CpV(CO)$_3$·THF from CpV(CO)$_4$. Method A. Titration of Sodium Dispersion with a Solution of CpV(CO)$_4$. Approximately 0.5 g of 40% sodium dispersion in 400 mL of THF was titrated with a solution of CpV(CO)$_4$ [1.664 g (7.3 mmol) in 90 mL of THF]. The Cp(CO)$_4$ solution was added dropwise to the sodium dispersion over a period of 10 h. The sodium dispersion suspension was initially gray, but shortly after addition of CpV(CO)$_4$ the solution began to turn yellow, and a yellow precipitate formed. Near the end of the addition, the solution turned a light orange-brown. Small amounts of sodium dispersion were added to the solution to reduce the excess CpV(CO)$_4$. When all of the CpV(CO)$_4$ solution had been added, and the reaction mixture remained a light orange-brown, the reaction mixture was filtered. The yellow precipitate was washed with THF until the IR spectrum of the wash solution showed no CpV(CO)$_4$. Then the precipitate was washed with petroleum ether and dried in the drybox; 1.364 g (4.3 mmol) of Na$_2$CpV(CO)$_3$·THF (59% yield) was obtained.

Method B. Reduction of CpV(CO)$_4$ with Sodium Amalgam. CpV(CO)$_4$ (2.42 g, 10.6 mmol) was dissolved in 75 mL of THF, and 75 g of sodium amalgam (0.0072 g Na/g amalgam) was added. The solution was stirred for 21.5 h. The yellow precipitate which formed was collected, washed first with THF and then with petroleum ether, and dried at room temperature in the drybox, and 3.310 g (10.4 mmol) of Na$_2$CpV(CO)$_3$·THF was collected (98% yield): NMR (HMPA) δ 4.32 (s, 5 H, Cp); IR (KBr, Nujol) 1742, 1590, 1550 cm^{-1}; (HMPA) 1745, 1620, 1570 cm^{-1}; (lit.) (HMPA) 1742, 1619, 1573 cm^{-1};[8] 1748, 1645 cm^{-1}; $Cs_2CpV(CO)_3$, Nujol.[6]

Preparation of $PPN^+[CpV(CO)_3H]^-$ from $Na_2CpV(CO)_3{\cdot}THF$. $Na_2CpV(CO)_3{\cdot}THF$ (0.2544 g, 1.03 mmol) was slurried in 30 mL of THF and 20 μL (1.11 mmol) of water was added. The $Na_2CpV(CO)_3$ dissolved to give a greenish-yellow solution; 0.6585 g (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 (bp 30-60 °C) was added slowly until a reddish-orange precipitate formed. The precipitate was collected and reprecipitated from THF-petroleum ether. This gave 0.4152 g (0.56 mmol) of $PPN^+[CpV(CO)_3H]^-$ (70% yield): mp 201 °C dec; NMR (THF-d_8) δ 7.55 (m, 30 H, PPN^+), 4.57 (s, 5 H, Cp), −6.10 (broad signal ^1H, hydride); IR (THF, HMPA, KBr pellet, Nujol mull) ν_{CO} 1890, 1780 cm^{-1}.

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

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

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

Reaction of 3 with Benzoyl Chloride. $PPN^+[CpV(CO)_3H]^-$ (0.651 g, 0.88 mmol) was dissolved in 12 mL of THF and 0.120 g (0.85 mmol) of benzoyl chloride was added from a 250-μL syringe. After 1 min, 25 mL of petroleum ether was added. The green precipitate which formed was collected. The light green filtrate was taken from the drybox, the solvent was removed by rotoevaporation, and 5.0 mL of 1,2-dianilinoethane reagent (0.53 g of 1,2-dianilinoethane and 0.5 mL of 50% acetic acid in 10 mL of methanol) was added to the residue. The solution was heated on a steam bath for 5 min and upon cooling to room temperature a white precipitate formed; 0.1516 g (61%) of crude product was obtained. Pure 1,2,3-triphenyltetrahydroimidazole (0.0838 g, 31%) was collected after recrystallization from CH_2Cl_2/hexane: NMR ($CDCl_3$) δ 7.13 (m, 10 H, phenyl), 6.57 (m, 5 H, phenyl), 590 (s, 1 H, methine), 3.72 (m, 4 H, methylene); mp 135-136 °C (lit.[29] 137 °C).

Preparation of $PPN^+[CpV(CO)_3Br]^-$ from $PPN^+[CpV(CO)_3H]^-$ and Benzyl Bromide. $PPN^+[CpV(CO)_3H]^-$ (0.392 g, 0.530 mmol) was dissolved in 15 mL of THF and 0.090 g (0.526 mmol) of benzyl bromide was added. The solution immediately turned a dark green color, and a dark green precipitate formed when 25 mL of petroleum ether was added; 0.389 g of precipitate was collected. This was reprecipitated from 10 mL of THF by adding 8 mL of petroleum ether; 0.322 g (0.393 mmol) of $PPN^+[CpV(CO)_3Br]^-$ was collected (74%).

Preparation of $PPN^+[CpV(CO)_3Br]^-$ from $CpV(CO)_4$. $CpV(CO)_4$ (0.0526 g, 0,230 mmol) and 0.0865 g of PPN^+Br^- were added to 5 mL of THF. Not all the PPN^+Br^- dissolved. This solution was irradiated with a 100-W Hg/Xe lamp through Pyrex while cooling the reaction vessel externally with water and purging the solution with nitrogen. After 0.5 h the infrared spectrum of the reaction solution showed bands at 1948, 1855, and 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 (THF-d_8) δ 4.83 (s, 5 H, Cp); IR (THF) 1945, 1855, 1810 cm^{-1}; mp 190 °C dec.

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

Reaction of $CpV(CO)_3H^-$ with 0.5 Equiv of 1-Bromooctane. $PPN^+[CpV(CO)_3H]^-$ (0.0487 g, 0.066 mmol) was dissolved in 0.350 mL of THF-d_8 in an NMR tube with a serum cap and 5.7 μL (0.033 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. After 4.5 h the reaction between $CpV(CO)_3H^-$ and 1-bromooctane was complete, as indicated by the absence of the signal for the α methylene proton of 1-bromooctane in the NMR spectrum. At this time the δ 4.67 ppm resonance was the most intense absorption in the spectrum.

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

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

Preparation of $PPN^+[CpV(CO)_3CH_3]^-$ from $Na_2CpV(CO)_3{\cdot}THF$ and Methyl *p*-Toluenesulfonate. $Na_2CpV(CO)_3{\cdot}THF$ (0.780 g, 2.45 mmol) was slurried in 30 mL of THF, and 5.0 mL of HMPA was added. A dark red-brown solution resulted. A small amount of gray solid did not dissolve. Methyl *p*-toluenesulfonate (0.590 g, 3.17 mmol) in 10 mL of THF was added from a dropping funnel, and a gray precipitate formed. The solution was stirred for 15 min and filtered. PPN^+Cl^- (1.81 g, 3.17 mmol) 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. A brick red precipitate (1.536 g) 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. $PPN^+[CpV(CO)_3CH_3]^-$ (1.10 g) precipitated and was collected (64% yield): NMR (THF-d_8) δ 7.75 (m, 30 H, PPN^+), 4.43 (s, 5 H, Cp), −0.33 (s, 3 H, methyl); IR (THF) 1895, 1795, 1775 (sh) cm^{-1}; mp 157 °C dec.

Anal. Calcd for $C_{45}H_{38}NO_3P_2V$: 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.

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

A similarly prepared solution of $CpV(CO)_3(CD_3CN)$ (0.063 mmol) in CD_3CN was treated with an excess of PPh_3 (0.31 mmol). Observation of the Cp region of the ^1H NMR showed the complete conversion of $CpV(CO)_3(CD_3CN)$ (δ 5.08 ppm, singlet) into $CpV(CO)_3PPh_3$ (δ 4.86 ppm, doublet) after 15 min.

Preparation of $Cp_2V_2(CO)_5$ by Irradiation of $CpV(CO)_4$. A 0.15 M solution of $CpV(CO)_4$ in THF was irradiated for 2 h while purging with nitrogen. The THF was removed (30 °C, 0.1 mm) and the remaining solids were taken up in 2 mL of hexane and passed through a 2 × 10 cm silica gel chromatography column using hexane as eluent. The first yellow band contained unreacted $CpV(CO)_4$ (33%); the second green band yielded[15] $Cp_2V_2(CO)_5$ (10%) upon removal of the hexane (25 °C, 0.1 mm). IR (THF) ν_{CO} 1995, 1942, 1893, 1861, 1818 cm^{-1}; ^1H NMR δ 5.08 ppm (singlet).

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

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

Competition between PPh_3 and $[CpV(CO)_3H]^-$ for "$CpV(CO)_3$".

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

B. Protonation Experiment. To a solution of 27 mg (0.10 mmol) of PPh_3 and 90 mg (0.12 mmol) of $PPN^+[CpV(CO)_3H]^-$ in 0.8 ml of THF-d_8 was added 2.2 mg (0.012 mmol) of *p*-toluenesulfonic acid hydrate in 0.2 mL of THF-d_8. An NMR spectrum recorded 1 min later showed a ratio of **10** to **9** of 1.9 ± 0.5 by integration of Cp resonances. Once again, allowing this mixture to stand resulted in complete conversion to the phosphine complex.

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

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

Competition between 1-Bromopentane, 2-Bromohexane, and 1-Bromo-2-methylpropane for $PPN^+[CpV(CO)_3H]^-$. A THF solution (1.0 mL) of 1-bromopentane, 2-bromohexane, and 1-bromo-2-methylpropane (0.5 M each) was added to a septum-capped vial containing 75 mg (0.10 mmol) of $PPN^+[CpV(CO)_3H]^-$. Aliquots (1 μL) were analyzed on a 25-ft, 5% β,β'-ODPN column at 25 °C using 2-methylpentane as an internal standard. The reaction was 80% complete after 2.5 h; a 12:1:5 ratio of pentane:hexane:2-methylpropane was observed.

Reaction of $CpV(CO)_3D^-$ with (−)-1-Phenylethyl Bromide. PPN^+ $CpV(CO)_3D^-$ (0.820 g, 1.11 mmol) was dissolved in 2.0 mL of THF in a septum-stoppered flask. (−)-1-Phenylethyl bromide (0.150 mL, 75% optically pure)[26] was added from a 250-μL syringe. The color of the reaction solution changed from dark red-brown to deep green immediately, and the reaction solution warmed slightly. After 15 min a precipitate formed. The volatile material was vacuum transferred from the reaction mixture at room temperature, and a light yellow solution was collected. The α-deuterioethylbenzene from the volatile fraction was collected by preparative gas chromatography on a 10 ft × 3/8 in. 10% DEGS 60/80 Chromosorb P NAW glass column and identified by mass spectrometry. Instrument conditions: injector 150 °C; column 100 °C; detector 143 °C; flow rate 30 mL/min. α-Deuterioethylbenzene was collected (0.0763 g, 64% yield). There was less than 1% THF in this sample.

This α-deuterioethylbenzene (72 μL) was dissolved in 720 μL of *dl*-α-deuterioethylbenzene. This mixture showed absolutely no optical rotation at 589 or 365 nm at room temperature in a 1-dm cell. The calculated rotation for the above solution, if the reaction of $CpV(CO)_3D^-$ and (−)-1-phenylethyl bromide had proceeded with complete inversion or retention, would have been[26] 0.030°, well within the detection limits of the polarimeter.

Reaction of $CpV(CO)_3H^-$ with Benzyl Bromide and Triphenylphosphine. Benzyl bromide (0.045 g, 0.263 mmol) and 0.085 g (0.324 mmol) of triphenylphosphine were added to 2.0 mL of THF. Then 0.8 mL of a THF solution of $PPN^+CpV(CO)_3H^-$ was added dropwise over a period of 5 min. The solution turned green as the $CpV(CO)_3H^-$ was added. An IR spectrum of the reaction solution after all of the $CpV(CO)_3H^-$ solution had been added showed only $CpV(CO)_3Br^-$ carbonyl absorptions at 1940, 1845, and 1805 cm^{-1}.

Competition between PPh_3 and Halide Ion for "$CpV(CO)_3$". A THF solution of 40 mg (0.18 mmol) of $CpV(CO)_4$, 86 mg (0.33 mmol) of PPh_3, and 48 mg (0.32 mmol) of NaI was irradiated under nitrogen purge for 15 min. An IR spectrum of a 0.1-μL aliquot showed ν_{CO} bands at 1950 and 1854 cm^{-1} due to $CpV(CO)_3PPh_3$ and only a very small band at 1806 cm^{-1} attributable to $CpV(CO)_3I^-$.

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

Preparation of 7-Bromo-2-methyl-2-heptene. Dihydropyran (29.8 g, 0.29 mmol) was stirred with 1 mL of 6 N HCl and 200 mL of H_2O at 45 °C for 1 h and allowed to come to room temperature overnight. The aqueous solution was extracted with ether (3 × 150 mL) and the ether dried ($MgSO_4$) and removed (30 mm, 25 °C). The remaining oil was vacuum distilled, discarding 1 mL of forerun, to yield 22 g (0.18 mmol) of 2-hydroxytetrahydropyran (bp 70–81 °C, 0.1 mm).

Isopropyltriphenylphosphonium iodide was prepared by combining 21.6 g (0.082 mmol) of PPh_3 and 9.6 g (0.057 mmol) of 2-iodopropane in a three-neck flask fitted with a reflux condenser and heating with a steam bath under nitrogen for 20 h. After cooling, the solid was crushed and the powder obtained washed with benzene (3 × 50 mL). Recrystallization from $EtOH/Et_2O$ yielded 11.9 g (0.028 mmol) of isopropyltriphenylphosphonium iodide, mp 196.2–197.2 °C (lit. 195–196 °C).

Isopropyltriphenylphosphonium iodide (11.9 g, 0.028 mmol) was slurried in 150 mL of ether under nitrogen, 19 mL of 1.45 M (0.028 mmol) methyllithium added slowly, and the deep red solution stirred for 3 h. 2-Hydroxytetrahydropyran (2.8 g, 0.028 mol) in 5 mL of ether was added slowly, whereupon a white precipitate formed. After 6 h the mixture was poured into 150 mL of H_2O and filtered, and the remaining solids were washed with ether (2 × 10 mL). The aqueous portion was washed with ether (2 × 50 mL) and the combined ether extracts were dried ($MgSO_4$) and concentrated (25 °C, 30 mm). The remaining oil was vacuum distilled to yield 1.38 g (0.011 mol) of 2-methyl-2-hepten-7-ol.[48]

Addition of 1.18 mL (0.022 mol) of Br_2 to 6.7 g (0.022 mol) of $P(OPh)_3$ in 10 mL of anhydrous ether at 0 °C under nitrogen produced white crystals of $Br_2P(OPh)_3$. The supernatant liquid was removed with a pipet and the solid washed with dry, nitrogen-purged ether (2 × 20 mL). 2-Methyl-2-hepten-7-ol (1.38 g, 0.011 mol) and 1.74 mL (0.022 mol) of pyridine (distilled from BaO) were added slowly to the cooled (0 °C) salt with stirring and the mixture was worked up by adding 50 mL of H_2O, extracting with ether (3 × 50 mL), and washing the ether with dilute HCl (2 × 25 mL) and dilute NaOH (2 × 25 mL). After the solution was dried ($MgSO_4$) and the ether removed (25 °C, 30 mm), the remaining oil was vacuum distilled to yield 0.7 g (3.7 mmol) of 70% pure 7-bromo-2-methyl-2-heptene (bp 88–92 °C, 0.1 mm). The bromide[49] was further purified by preparative GC on a 12 ft × 3/8 in. 4% SE-30 column at 120 °C: NMR (CCl_4) δ 5.09 (m, 1 H), 3.34 (t, 2 H), 1.85 (m, 10 H), 1.68 (s, 3 H), 1.49 (s, 3 H).

Reduction of 7-Bromo-2-methyl-2-heptene with $PPN^+[CpV(CO)_3H]^-$. A 0.16 M solution of $PPN^+[CpV(CO)_3H]^-$ in THF was prepared and portions were diluted to give 0.08 and 0.04 M solutions. To 1.00 mL of each of these solutions was added 3.35 μL (0.02 mmol) of 7-bromo-2-methyl-2-heptene and 1-μL aliquots were analyzed by gas chromatography on a 25-ft 10% β,β'-ODPN column at 20 °C using hexane as an internal standard. The 2-methyl-2-heptene/isopropylcyclopentane ratio was found to be 40, 22, and 8 for the 0.16, 0.08, and 0.04 M $PPN^+[CpV(CO)_3H]^-$ reactions, respectively.

Preparation of 2-Allyloxyethyl Bromide. Sodium (4.3 g, 0.19 mol) was added in small pieces to 100 g of ethylene glycol followed by 13.8 mL (0.16 mol) of allyl bromide. After standing overnight the solution was distilled to yield 11.5 g (0.11 mol) of 85% pure 2-allyloxyethanol, bp 155–161 °C (ethylene glycol impurity). The alcohol was mixed with 9 mL of pyridine (distilled from BaO) and added slowly to 41 g (0.122 mol) of $Br_2P(OPh)_3$, prepared as described above. After 1 h the reaction mixture was poured into 100 mL of H_2O and extracted with ether (3 × 50 mL). The ether was washed with dilute NaOH (2 × 100 mL), dilute HCl (2 × 100 mL), and H_2O (2 × 100 mL). After the solution was dried ($MgSO_4$) and the ether removed (25 °C, 30 mm), the remaining 30 mL of oil was vacuum distilled (0.1 mm) into three fractions. The first fraction (bp 28–29 °C, 1 mL) contained 10% Et_2O, 10% 2-allyloxyethanol, and 80% 2-allyloxyethyl bromide; the second fraction (bp 29–40 °C, 1 mL) contained 85% 2-allyloxyethyl bromide; the third fraction (bp 40–42 °C, 4 mL) contained 40% 2-allyloxyethyl bromide and higher boiling impurities. Fractions 1 and 2 were combined and the bromide was purified by preparative gas chromatography before use on a 12 × 3/8 in. 4% SE-30 column at 100 °C: d^{25} = 1.325; NMR (CCl_4) δ 6.0–4.8 (m, 3 H), 3.58 (d, 2 H), 3.22 (d, 2 H), 3.01 (d, 2 H); IR (neat) $\nu_{C=C}$ 1640 (w), ν_{C-O} 1100 (s) cm^{-1}; mass spectrum parent ion 166/164 (Br isotope pattern), fragments 109/107, 85, 71, 57, 41.

Anal. Calcd for C_5H_9OBr: C, 36.39; H, 5.50. Found: C, 36.38; H, 5.43.

Preparation of 2-Allyloxyethyl Iodide. 2-Allyloxyethyl bromide (45% pure, 1.1 g, 3.0 mmol) and 9.5 g (63 mmol) of NaI were dissolved in 25 mL of acetone and heated at reflux for 1 h. The solution was filtered and the acetone removed (25 °C, 30 mm). The remaining solid was taken up in 50 mL of H_2O and 50 mL of ether. The ether layer was washed with 5% sodium thiosulfate (1 × 20 mL), dilute HCl (2 × 50 mL), dilute NaOH (2 × 50 mL), and H_2O (2 × 50 mL). The ether was dried ($MgSO_4$) and removed (25 °C, 30 mm), yielding 0.5 g (2.3 mmol) of 90% pure 2-allyloxyethyl iodide. The product was purified by preparative gas chromatography before use on a 12 ft × $^3/_8$ in. 4% SE-30 column at 110 °C: d^{25} = 1.60; NMR (CCl_4) δ 6.0–4.8 (m, 3 H), 3.93 (d, 2 H), 3.58 (t, 2 H), 3.20 (t, 2 H); IR (neat) $\nu_{C=C}$ 1640 (w), ν_{C-O} 1100 (s) cm^{-1}; mass spectrum parent ion m/e 212, fragments 184, 155, 127.

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

Reduction of 2-Allyloxyethyl Bromide and Iodide. A 0.16 M solution of $PPN^+[CpV(CO)_3H]^-$ in CH_3CN was prepared and portions diluted to make 0.08 and 0.04 M solutions. To 1.00 mL of each of these solutions was added 2.5 μL (0.02 mmol) of 2-allyloxyethyl bromide and 1-μL aliquots were analyzed throughout the reaction on a 100 ft × $^1/_{16}$ in. TCEP open tubular column at 60 °C (injector at 50 °C) using 1,2-dimethoxyethane as an internal standard. The ratio of allyl ethyl ether to 3-methyltetrahydrofuran was found to be 0.4, 0.88, and 1.44 in the 0.16, 0.08, and 0.04 M $PPN^+[CpV(CO)_3H]^-$ reactions, respectively, and remained constant throughout the reduction.

A similar reduction in CH_3CN using 2.65 μL (0.02 mmol) of 2-allyloxyethyl iodide and 60 mg (0.08 mmol) of $PPN^+[CpV(CO)_3H]^-$ in 1.00 mL of CH_3CN provided a 0.98:1 ratio of allyl ethyl ether to 3-methyltetrahydrofuran, essentially the same product ratio as found for the bromide.

Reductions of 1.25 μL (0.02 mmol) of 2-allyloxyethyl bromide with 0.50 mL of 0.08 and 0.04 M $PPN^+[CpV(CO)_3H]^-$ solutions in THF-d_8 gave allyl ethyl ether/3-methyltetrahydrofuran ratios of roughly 1.0 and 1.5, respectively, by NMR integration of the methyl absorptions of the products.

Reduction of 2-Allyloxyethyl Iodide with Bu_3SnH. 2-Allyloxyethyl iodide (2.65 μL, 0.02 mmol) was added to a solution of 21 μL (0.08 mmol) of Bu_3SnH in 1.00 mL of CH_3CN. Gas chromatographic analysis of a 1-μL aliquot after 30 min showed a 98% yield of products consisting of a 19:1 ratio of 3-methyltetrahydrofuran to allyl ethyl ether.

Reduction of *n*-Heptyl and 2-Allyloxyethyl Iodides with Bu_3SnH in the Presence of 2,2,6,6-Tetramethylpiperidoxyl. To 5 μL (~0.3 M) of alkyl iodide and 5 μL (0.03 mmol) of piperidoxyl in 0.5 mL of benzene was added 10 μL (0.04 mmol) of Bu_3SnH, and 1-μL aliquots were analyzed by gas chromatography on a 10-ft 10% SE-30 column at 200 °C. 2,2,6,6-Tetramethylpiperidoxyl, Bu_3SnI, and Bu_3SnH were identified by coinjection with authentic samples. In the *n*-heptyl iodide case one other product was observed (15% yield), which coinjected with an authentic sample (see below) of *O*-*n*-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide. In the case of 2-allyloxyethyl iodide, two adducts were formed, and sufficient quantities were collected by preparative gas chromatography (from a larger scale reaction) to obtain NMR and high-resolution mass spectra. The products were identified as *O*-allyloxyethyl-2,2,6,6-tetramethylpiperid-1-yl oxide [NMR (CCl_4) δ 5.0–6.0 (m, 3 H), 3.88 (d, 2 H), 3.81 (d, 2 H), 3.45 (t, 2 H), 1.45 (s, 6 H), 1.15 (s, 6 H), 1.08 (s, 6 H); high-resolution mass spectrum (peak match), calcd for $C_{14}H_{27}O_2N$ 241.207, found 241.207] and *O*-3-tetrahydrofurylmethyl-2,2,6,6-tetramethylpiperid-1-yl oxide [NMR (CCl_4) δ 3.4–3.8 (m, 6 H), 1.43 (s, 6 H), 1.16 (s, 6 H), 1.09 (s, 6 H); high-resolution mass spectrum (peak match) calcd for $C_{14}H_{27}O_2N$ 241.207, found 241.205].

Reduction of 2-Allyloxyethyl Iodide with $PPN^+[CpV(CO)_3H]^-$ in the Presence of 2,2,6,6-Tetramethylpiperidoxyl. 2-Allyloxyethyl iodide (4 μL, 0.03 mmol) and 20 μL (0.12 mmol) of piperidoxyl in 0.5 mL of CH_3CN were added to a solution of 28 mg (0.038 mmol) of $PPN^+[CpV(CO)_3H]^-$ in 0.5 mL of CH_3CN. A 1-μL aliquot was analyzed by gas chromatography on a 10-ft 10% SE-30 column at 200 °C, and showed a 5:1 ratio of the two spin adducts isolated from the R_3SnH reduction (20% combined yield).

***Reduction of n-Heptyl Iodide with $PPN^+[CpV(CO)_3H]^-$ in the* Presence of 2,2,6,6-Tetramethylpiperidoxyl.** A mixture of 111 μL (0.68 mmol) of heptyl iodide and 46 μL (0.27 mmol) of piperidoxyl was added to a solution of 106 mg (0.14 mmol) of $PPN^+[CpV(CO)_3H]^-$ in 1.0 mL of THF. Gas chromatographic analysis of a 1-μL aliquot on a 20-ft 5% SE-30 column at 200 °C using pentane as an internal standard showed a 15% yield of a long retention time product that coinjected with an authentic sample (see below) of *O*-*n*-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide.

Preparation of *O*-*n*-Heptyl-2,2,6,6-tetramethylpiperid-1-yl Oxide. *n*-Heptylmagnesium iodide (0.01 mmol) was prepared by treating 1.64 mL (0.01 mol) of *n*-heptyl iodide with 0.27 g (0.011 mol) of magnesium in 20 mL of ether. Upon addition of 0.75 mL (0.0044 mol) of 2,2,6,6-tetramethylpiperidoxyl, two layers formed. After 30 min the ether layer was removed and the remaining liquid washed with 10 mL of ether. The combined ether layers were washed with 20 mL of H_2O, dried ($MgSO_4$), and concentrated (30 °C, 30 mm). Gas chromatographic analysis of a 1-μL aliquot on a 12 ft × $^3/_8$ in. 4% SE-20 column at 180 °C showed 60% tetradecane and 30% of the desired product. Purification by preparative gas chromatography yielded 0.3 g (1.2 mmol) of *O*-heptyl-2,2,6,6-tetramethylpiperid-1-yl oxide: d^{25} = 0.86; NMR (CCl_4) δ 3.68 (t, 2 H), 1.7 (m, 16 H), 1.10 (d, 12 H), 0.87 (s, 3 H); IR (neat) ν_{CH_3} 1467 (m), ν_{C-O} 1045 (m) cm^{-1}; mass spectrum parent ion 255, fragments 240, 156.

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

Reduction of Cyclopropylcarbinyl Tosylate with $PPN^+[CpV(CO)_3H]^-$. Cyclopropylcarbinyl tosylate (4.1 μL, 0.02 mmol) was added to a solution of 64 mg (0.086 mmol) of $PPN^+[CpV(CO)_3H]^-$ in 1.00 mL of CH_3CN and 1-μL aliquots were analyzed by gas chromatography on a 25-ft 5% β,β'-ODPN column at 25 °C. After 2.5 days a 40% yield of methylcyclopropane was observed accompanied by only 2% 1-butene.

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Structures of Butyl Ions Formed by Electron Impact Ionization of Isomeric Butyl Halides and Alkanes

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Abstract: Using a pulsed ion cyclotron resonance (ICR) spectrometer, it is demonstrated that at pressures of about 10^{-6} Torr and at observation times ranging from 10^{-3} to 0.5 s, isobutane, neopentane, 2,2-dimethylbutane, isobutyl halides, and *tert*-butyl halides form $C_4H_9^+$ ions having the tertiary structure. In *n*-alkanes, 2-methylbutane, 3-methylpentane, *n*-butyl halides, and *sec*-butyl halides, both *sec*-$C_4H_9^+$ and *t*-$C_4H_9^+$ ions are observed, the *sec*-$C_4H_9^+$ ions surviving without rearrangement for at least 0.1 s. However, in the case of the halides, a collision-induced isomerization of the *sec*-$C_4H_9^+$ to the *t*-$C_4H_9^+$ ions occurs. The efficiency of this process increases with the basicity of the alkyl halide. Radiolysis experiments carried out at atmospheric pressures indicate, in agreement with ICR and solution experiments, that at times as short as 10^{-10} s the majority of the *i*-$C_4H_9^+$ ions from isobutyl bromide rearrange to the *t*-$C_4H_9^+$ structure. On the other hand, in the radiolysis of both *n*-hexane and 3-methylpentane, the abundance of *t*-$C_4H_9^+$ relative to *sec*-$C_4H_9^+$ is substantially smaller than that observed in the ICR experiments, and decreases with decreasing collision interval. It is suggested that about 90% of the *i*-$C_4H_9^+$ can rearrange to *t*-$C_4H_9^+$ by simple 1,2-hydride shift without involving secondary or protonated methylcyclopropane structures as intermediates.

Introduction

More than a decade ago, Munson[1,2] demonstrated that *sec*-$C_4H_9^+$ and *t*-$C_4H_9^+$ ions can retain their structure in the ion source of a mass spectrometer for up to 10^{-6} s. In a more recent collisional activation study by Dymerski and McLafferty,[3] a similar conclusion was reached. In addition, the suggestion was made that *i*-$C_4H_9^+$ ions originating from the electron impact induced fragmentation of *i*-C_4H_9Br isomerize mainly to the *sec*-$C_4H_9^+$ structure within 10^{-6} s. As pointed out by these authors, solution isomerization studies[4] as well as the interpretation of isomerization mechanisms occurring in the radiolysis of alkanes[5] lead to a different conclusion, namely, that isobutyl ions rearrange mainly to the tertiary structure. A new attempt to identify the structures of butyl ions was made using a pulsed ion cyclotron resonance spectrometer (ICR) which permits the observation of ions at times as long as seconds after their formation. The approach was the same as that employed in a recent ICR examination of $C_7H_7^+$ structures.[6] A previous examination of the $C_4H_9^+$ structures[7] using an ICR operating in the continuous mode was thought to give inconclusive results because no distinction could be made between structurally different ions and structurally similar ions containing different amounts of internal energy. In order to circumvent internal energy effects, the present study mainly examines $C_4H_9^+$ ions which have undergone several unreactive collisions prior to reaction. In addition we report