

is not identical with transport experiments A and C can be attributed to incomplete removal of Ag^+ or to leaks in the membrane that may have developed during the exchange processes.

At this time, it is not possible to assign the factors responsible for the enhanced fluxes of olefins through the Ag^+ form membranes unambiguously. If facilitated transport, which requires that the $\text{Ag}(\text{olefin})^+$ complex is mobile within the membrane, is the dominant factor, Noble has shown that the facilitation factor, assuming reaction equilibrium and no mass transport resistance at the decane/Nafion interfaces, should be¹⁸

$$F = 1 + \frac{\alpha K_D}{(1 + K_D)} \quad \text{where } K_D = K_{\text{eq}} C_{\text{olefin}}(x=0) \quad \text{and}$$

$$\alpha = \frac{D_{\text{complex}} C_{\text{Ag}^+}(\text{total})}{D_{\text{olefin}} C_{\text{olefin}}(x=0)}$$

We note that since the solubility of olefins in the aqueous membrane phase is low, the value of K_D in our system, ca. 2×10^{-4} is orders of magnitude lower than the theoretically predicted optimal values.¹⁹ This implies that still greater facilitation factors may be achieved by increasing either the complex formation constant or the solubility of the permeate in the membrane phase. We are presently exploring these possibilities as well as attempting to ascertain the factors responsible for the enhanced fluxes.

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Novel Diamagnetic and Paramagnetic Hydrides of Vanadium(II)

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Apart from V(I) complexes like $[\text{CpVH}(\text{CO})_3]^{-1}$ and $\text{HV}(\text{C}-\text{O})_4(\text{PP})$ (PP = chelating diphosphine),² very few vanadium hydride species are known which are as follows: one V(III) compound, $(\text{C}_5\text{Me}_5)_2\text{VH}$, and its CO adduct³ and two dimeric species, $[\text{CpV}(\mu\text{-H})]_2(\mu\text{-C}_6\text{H}_6)^4$ and $\text{V}_2\text{H}_4\text{Zn}_2(\text{BH}_4)_2(\text{PPh}_2\text{Me})_4$.⁵ Here

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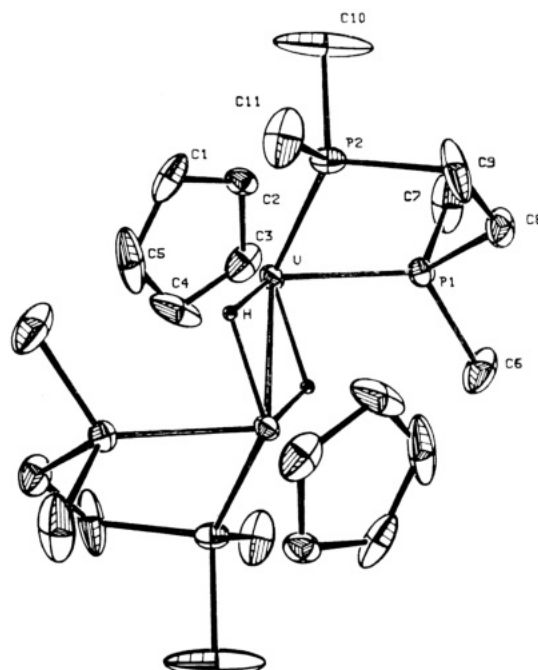
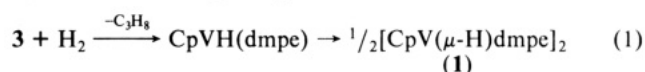


Figure 1. Molecular structure of $[\text{CpV}(\mu\text{-H})\text{dmpe}]_2$ (1). Selected structural parameters: $\text{V}-\text{V}' = 2.701$ (1) Å, $\text{V}-\text{H} = 1.64$ (4) Å, $\text{V}-\text{H}' = 1.72$ (4) Å, $\angle \text{H}-\text{V}-\text{H}' = 73$. (2)°, $\angle \text{V}-\text{H}-\text{V}' = 107$. (2)°, $\angle \text{P}(1)-\text{V}-\text{P}(2) = 78.40$ (3)°, $\angle \text{CT}-\text{V}-\text{P}(1) = 115.41$ (2)°, $\angle \text{CT}-\text{V}-\text{P}(2) = 115.69$ (2)°, $\angle \text{CT}-\text{V}-\text{H} = 119$. (2)°. Prime denotes symmetry related atom; CT is Cp centroid.

we wish to report two new vanadium(II) hydride species, diamagnetic $[\text{CpV}(\mu\text{-H})\text{dmpe}]_2$ (1) (dmpe = 1,2-bis(dimethylphosphino)ethane) and paramagnetic $[\text{CpVH}(\text{dmpe})]_2(\mu\text{-dmpe})$ (2), produced in the reaction of the V(II) alkyl complex $\text{CpV}(\text{-}n\text{-Pr})\text{dmpe}$ (3) with molecular hydrogen.

When molecular hydrogen (1 atm) is admitted to a dark brown solution of 3 in toluene at 0 °C, the solution turns red in several hours and a small amount of grey precipitate is formed. A Toepler pump experiment indicated that 1 mol of H_2 per mol of V was consumed and 1 mol of propane per mol of V was produced. After filtration, red crystals could be obtained from the liquid by cooling. This compound is diamagnetic (by NMR⁷) and was shown by X-ray analysis⁸ to be the dimeric $[\text{CpV}(\mu\text{-H})\text{dmpe}]_2$ (1, Figure 1), formed according to eq 1.



The molecule is centrosymmetric and consists of a planar V_2H_2 unit with two $\eta^5\text{-Cp}$ and two $\eta^2\text{-dmpe}$ ligands in a trans arrangement. A $\text{V}-\text{V}'$ distance of 2.701 (1) Å is found. EHMO calculations on $\text{CpV}(\eta^2\text{-BH}_4)(\text{PH}_3)_2$ have indicated that the d^3 metal center, in such a coordination geometry, has a preference for the low-spin ($S = 1/2$) state.⁶ Thus 1 can be considered to consist of two low-spin d^3 centers forming a single metal-metal bond. This is in accordance with both the observed intermetal

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(7) ^1H NMR (300 MHz, $\text{THF}-d_6$, 20 °C) of 1: 4.13 ppm (s, 10 H, Cp), 2.49 ppm (br m, 4 H, P-CH₂), 2.05 ppm (br m, 4 H, P-CH₂), 1.40 ppm (s, 12 H, P-Me), 0.64 ppm (s, 12 H, P-Me), -15.9 ppm (very br, $\Delta\nu_{1/2} = 630$ Hz, 2 H, V-H).

(8) 1 crystallizes in the monoclinic space group $P2_1/n$, $a = 10.128$ (2) Å, $b = 8.511$ (5) Å, $c = 15.458$ (2) Å, $\beta = 100.48$ (1)° (130 K), $Z = 2$. Reflections (2056) with $1^\circ \leq \theta \leq 27^\circ$ were considered observed. All atoms were located from the Fourier difference map. The V-bound hydrogen atoms were refined isotropically, and the other hydrogen atoms were constrained at 0.95 Å from their corresponding C atoms in the final refinement cycles: $R = 0.039$, $R_w = 0.042$ ($w = 1$).

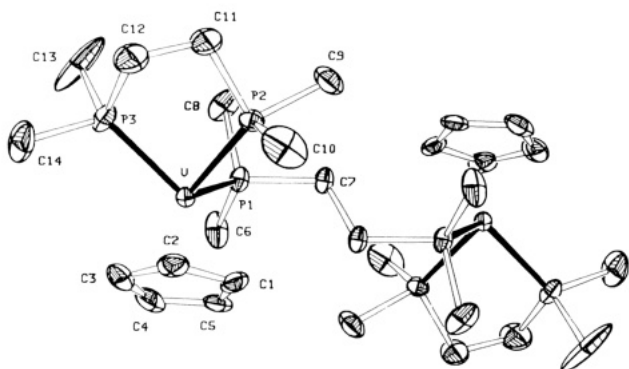


Figure 2. Molecular structure of $[\text{CpV}(\text{H})\text{dmpe}]_2(\mu\text{-dmpe})$ (**2**). Selected structural parameters: $\text{V-P}(1) = 2.369$ (1) Å, $\text{V-P}(2) = \text{V-P}(3) = 2.378$ (1) Å, $\angle\text{P}(1)\text{-V-P}(2) = 95.00$ (4)°, $\angle\text{P}(1)\text{-V-P}(3) = 117.40$ (5)°, $\angle\text{P}(2)\text{-V-P}(3) = 79.02$ (4)°.

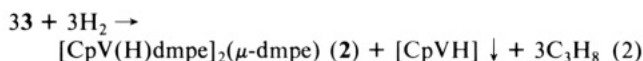
distance (which is too long for a triple bond, characteristically 2.2–2.4 Å⁹) and the diamagnetism of **1**. The V–H distances (1.64 (4) and 1.72 (4) Å) and the nonbonding separation of the H atoms of 2.01 (5) Å are similar to those found in $[\text{CpV}(\mu\text{-H})]_2(\mu\text{-C}_6\text{H}_6)$,⁴ but the latter compound contains a puckered V_2H_2 ring with multiple metal–metal bond character ($\text{V-V} = 2.425$ (1) Å).

1 was isolated in 30% yield, but it is not the only product formed. From the mother liquor another compound can be obtained as orange-brown crystals from pentane or diethyl ether in 10–20% yield. This product is paramagnetic (by NMR), while the IR spectrum indicates the presence of a terminal hydride, with $\nu_{\text{V-H}} = 1560$ cm⁻¹ ($\nu_{\text{V-D}} = 1105$ cm⁻¹ in the D_2 reaction product, $\nu_{\text{V-H}}/\nu_{\text{V-D}} = 1.412$).

X-ray diffraction¹⁰ revealed that the compound is the dimeric $[\text{CpV}(\text{H})\text{dmpe}]_2(\mu\text{-dmpe})$ (**2**, Figure 2). Unfortunately, the positions of the hydride ligands could not be determined unequivocally from the Fourier difference map. However, a substantial asymmetry in the P–V–P angles can be seen ($\text{P}(2)\text{-V-P}(3) = 79.02$ (4)°, $\text{P}(1)\text{-V-P}(2) = 95.00$ (4)°, $\text{P}(1)\text{-V-P}(3) = 117.40$ (5)°), leaving room for the hydride ligand in the sector of the metal between $\text{P}(1)$ and $\text{P}(3)$.

As no metal–metal contacts are present in the structure, the vanadium atoms should behave like two isolated 17-electron low-spin ($S = 1/2$) d^3 centers. Indeed **2** is ESR active and in solution exhibits a complicated hyperfine splitting pattern with $g = 2.0003$. Replacing the hydride by a deuteride simplifies the solution ESR spectra considerably.¹¹ A comparison of these two ESR spectra indicates that the unpaired electron on each vanadium center in **2** interacts with one hydride ligand, $a(^1\text{H}) = 15.5$ G.¹² Simulation of the spectrum of **2-d**₂ confirmed additional interactions of the unpaired electron with the vanadium nucleus, $a(^{51}\text{V}) = 57.4$ G, and with three nonequivalent phosphorus nuclei, $a(^{31}\text{P}) = 30.5, 33.5$, and 36.0 G. The extensive delocalization of the unpaired electron, resultant in low spin-orbit coupling, is in accordance with the relatively large g value.

The mechanism of formation of **2** is unclear. Apparently, parallel with the reaction sequence in eq 1, some disproportionation occurs according to eq 2, where $[\text{CpVH}]$ may be identified with the poorly soluble gray powder that is also observed in the reaction mixture.



Once formed, the hydrido-bridged dimer **1** is fairly unreactive. For instance, it cannot be broken up into monomeric units by Lewis bases like THF or PMe_3 . Pure **1** does not catalyze the hydrogenation and isomerization of 1-hexene at ambient conditions, whereas **3**, dissolved in 1-hexene under 1 atm of H_2 , does.⁶ Apparently it is necessary to trap the monomeric hydrido species immediately after hydrogenolysis of the V–C bond.

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Registry No. **1**, 111635-25-7; **2**, 111717-72-7; **3**, 110174-52-2; 1-hexene, 592-41-6.

Supplementary Material Available: Observed and calculated ESR spectra of **2-d**₂, tables of crystallographic data and positional and thermal parameters, and lists of interatomic distances and angles for **1** and **2** (13 pages); listings of observed and calculated structure factors for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

Stereochemistry of the Thermal Isomerization of Bicyclo[3.2.0]hept-2-ene to Bicyclo[2.2.1]hept-2-ene

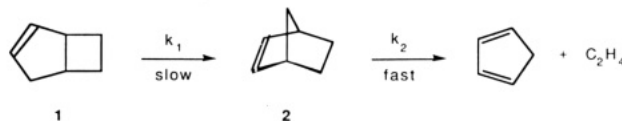
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Sigmatropic [1,3] CHD-carbon migrations of unsubstituted bicyclic hydrocarbons constrained to isomerize suprafacially may provide stereochemical information sensitive to reaction mechanistic course and dynamics. Totally stereoselective inversion is consistent with an allowed, orbital symmetry controlled process,¹ while participation of both inversion and retention modes implicates competitive paths,² either parallel concerted processes with opposite stereochemistry³ or the partitioning of a short-lived biradical intermediate. To know the stereochemical features of CHD-carbon shifts as a function of bicyclic system could provide grounds for distinguishing among these subtle but mechanistically significant alternatives.

Such stereochemical information has been gained for only one system: bicyclo[2.1.1]hex-2-ene labeled with deuterium at C5 gives 6-deuteriobicyclo[3.1.0]hex-2-ene with high but not complete stereoselectivity favoring inversion. At 197 °C in isooctane solution the retention component is 6.9%.²

We have followed the stereochemical course of the bicyclo[3.2.0]hept-2-ene (**1**) to bicyclo[2.2.1]hept-2-ene (**2**) isomerization.⁴ Stereochemical assessment of this isomerization is experimentally challenging since the product **2** reacts further to give cyclopentadiene and ethene. At 276 °C, the maximum concentration of **2** to be expected is only 1–2%.^{4,5}



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(10) **2** crystallizes in the monoclinic space group $P2_1/n$, $a = 8.429$ (2) Å, $b = 24.053$ (4) Å, $c = 9.468$ (5) Å, $\beta = 110.16$ (4)° (130 K), $Z = 2$. Reflections (2548) with $1^\circ \leq \theta \leq 26^\circ$ were considered observed. Nonmetal bound hydrogen atoms were located from the Fourier difference map and constrained at 0.95 Å from their corresponding carbon atoms in the final refinement cycles with use of isotropic fixed thermal parameters: $R = 0.042$, $R_w = 0.055$ ($w = 1$).

(11) In general $a(^2\text{H})$ is 1–2 G, which remains unresolved in the spectrum.

(12) The only $a(^1\text{H})$ observed so far in a vanadium system is 14.6 G in the reaction mixture of Cp_2V with HSnEt_3 : Razuvaev, G. A.; Abakumov, G. A.; Gladyshev, E. N.; Fokeev, A. P.; Cherkasov, V. S. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 135.

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