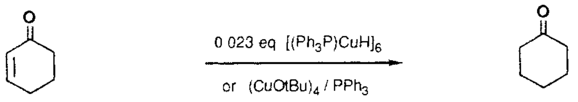
sentative examples and experimental conditions are given in Table I.[18] Notably, the reaction is quite stereoselective (entries 4–6), affording major products deriving from hydride delivery to the least hindered face of the substrate. The observed selectivities are superior to hydrosilation, catalytic hydrogenation, and reductions with the previously reported hydrido "ate" complexes on closely related substrates.[20] Isolated double bonds, carbonyl groups, and a variety of typical oxygenated functionality are not reduced under the reaction conditions.

Reactions run in the presence of chlorotrimethylsilane afford the corresponding silyl enol ether products in high yield (entries 2 and 9), although some 1,4-reduced untrapped material can be detected spectroscopically for substrates other than cyclohexenone itself.[21] Improved procedures for this reaction and extension to other common electrophiles are under investigation.[22]

The reported high yield synthesis of $[(Ph_3P)CuH]_6$ from $(CuOtBu)_4$ and Ph_3P under hydrogen[7] led us to propose that an intermediate copper(I) enolate in the conjugate hydride reduction would react with hydrogen in an analogous fashion. Slow (<1 turnover/hour) conversion of cyclohexenone to cyclohexanone is observed under 80 psi of H_2 by using a catalytic amount either of complex **1** or $(CuOtBu)_4/PPh_3$ (eq 1). Faster conversion is obtained at higher H_2 pressures (≥200 psi), but surprisingly the reaction proceeds exclusively to cyclohexanol. The nature of the active species and full definition of the reaction parameters and scope of this catalytic process are currently under investigation.



(1)

Extension of both the stoichiometric and catalytic reactions to other unsaturated functionality and to alkyne hydrometalation is in progress. Investigation into the preparation of other hydridic copper(I) complexes is also underway, in an effort to develop a general solution to the problem of effecting hydride reductions catalytically.

Acknowledgment. We thank Professors David R. Williams and Raymond L. Funk for generously providing samples of substrates **8** and **9**, respectively, and Professor William R. Roush for helpful discussion. Financial support (to J.M.S.) from a PPG Industries Foundation Grant of Research Corporation, BRSG Grant S07 RR07031 from the Biomedical Research Support Grant Program of the National Institutes of Health, and National Institutes of Health no. GM38068-01 is gratefully acknowledged.

Supplementary Material Available: Listing of references for product characterization for entries 5, 6, and 9–11 (products of entries 1–4, 7, 8, and 12 are commercial materials) (1 page). Ordering information is given on any current masthead page.

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[18] Representative experimental procedure, for Wieland–Miescher ketone **5** (entry 6): $[(Ph_3P)CuH]_6$ (1.61 g, 0.82 mmol), weighed under inert atmosphere, and **5** (0.400 g, 2.24 mmol) were added to a 100-mL, two-necked flask under positive N_2 pressure. Deoxygenated benzene (60 mL) containing 100 μL of H_2O (deoxygenated by nitrogen purge for 10 min) was added via cannula, and the resultant red solution was allowed to stir at room temperature until starting material had been consumed by TLC analysis (8 h). The cloudy red-brown reaction mixture was opened to air, and stirring was continued for 1 h, during which time copper-containing decomposition products precipitated. Filtration through Celite and removal of the solvent in vacuo gave crude product which was purified by flash chromatography.[19]

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[20] Reaction of 3,5-dimethylcyclohexenone with Boeckman's hydrido cuprate (sixfold excess, 10% HMPA in THF) gave a 9:1 ratio favoring the cis product,[2a] and catalytic hydrogenation (H_2, 5% Pd/C, C_6H_6) gave in our hands ~15:1 ratio favoring cis. With Δ^4-9-methyloctalone, both Boeckman's[2a] and Masamune's[2b] "ate" complexes gave a 7:3 ratio favoring the cis product. Surprisingly, Keinan's hydrosilation on 4-cholesten-3-one favored the trans product in a 60:40 ratio.[5]

[21] With 4-phenyl-3-buten-2-one and several other substrates, reaction in the presence of chlorotrimethylsilane gives varying amounts (2–10%) of reduced untrapped products. As with added H_2O, complete suppression of undesired side reactions is observed in these experiments.

[22] Reductive alkylation experiments on cyclohexenone using MeI as the electrophile give 2-methylcyclohexanone; however, the copper(I) hydride reacts competitively, requiring an excess of reagent.

Condensed Phase Facilitated Transport of Olefins through an Ion Exchange Membrane

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While numerous biological processes utilize membranes that contain transporting agents (carriers) to separate molecular and ionic permeates,[1] the potential of synthetic membranes for separations in commercial processes has not been fully realized.[2] In principal, the phenomenon of facilitated transport (FT) in membranes, which relies on the reversible formation of a permeate: carrier complex, can provide selective and efficient separations. However, development of useful membrane separation technologies requires the discovery of systems wherein selective complexation reactions can be used to achieve enhanced transport rates for specific permeates through stable membrane structures. Recently, membranes and thin films derived from ion exchange materials, such as Nafion,[3] have received considerable attention with respect to their structural, physical, and chemical properties.[4-10] In particular, ion and electron transport have been studied extensively. Far less is known about transport processes involving neutrals, even though it is the rates of these processes which ultimately will be important for many applications.

Herein we report the facilitated transport of 1-hexene and 1,5-hexadiene between two decane phases separated by thin, hydrated Nafion membranes (ca. 25 μm). The flux of olefin across the membranes is enhanced by factors of several hundred when silver ions are exchanged for sodium ions. The fact that olefin transport is caused by Ag^+ incorporation is demonstrated by monitoring the ion-exchange process with transmission Fourier transform infrared spectroscopy (FTIR). While FT of gaseous permeates such as ethylene and carbon dioxide by ions has been reported,[11] this work describes stable membrane transport for molecules with low volatility from a condensed matrix.

The Nafion membranes used in this study are an experimental material, NE111, and were provided by Dr. Louis L. Burton.[12]

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[3] Nafion is the registered trademark of E.I. du Pont de Nemours & Co.

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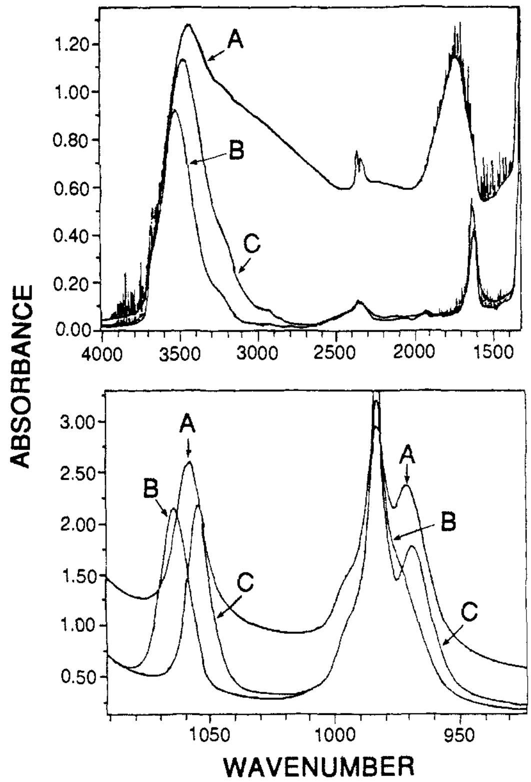

Figure 1. Portions of FTIR spectra obtained for 25-μm Nafion membranes: curve A, H^+ form as received; curve B, hydrated Na^+ form; curve C: hydrated Ag^+ form.

These membranes, which are 25-μm thick as received in the H^+ form, were converted to the Na^+ form by gentle stirring in an aqueous solution of NaOH (1 M) for 24 h. Conversion to the Ag^+ form was accomplished by stirring in a solution of $AgNO_3$ (1 M) for 24 h. The infrared spectroscopy of 175-μm Nafion 117 membranes has been studied extensively with use of reflection techniques.[13] Due to the thinness of 25-μm Nafion NE111, it was possible to obtain FTIR spectra of solvated membranes in the transmission mode after each exchange process and transport experiment. Figure 1 contains portions of FTIR spectra for the 25-μm membranes in the H^+ form, Na^+ form, and Ag^+ form. These spectra are very similar to published spectra for 175-μm membranes.[13] Of particular interest are the bands at ca. 1050 and 975 cm^{-1} which have been assigned to the symmetric stretching of the $-SO_3^-$ group and the $-COC-$ groups in the pendant side chains, respectively. The position and shapes of these bands are sensitive to the identity of the cation and to the hydration of the membrane. Clearly, there are sufficient changes in the FTIR spectrum to allow the ion exchange process to be monitored.

Flux measurements were made by using a two-compartment cell arranged vertically and separated by the membrane which was held in place with o-rings and a clamp. The surface area of the membrane exposed to the solution was 1.8 cm^2. Both compartments of the cell contained decane (20 mL) that had been saturated with water and were mechanically stirred to provide efficient mass transport to and from the membrane. The lower compartment contained either 1-hexene or 1,5-hexadiene (0.1 M). After the cell was assembled, aliquots (1 μL) of the solution were removed periodically with a syringe from the upper compartment and analyzed for olefin by gas chromatography.[14]

Figure 2 contains plots of the concentration of olefin in the upper compartment as a function of time after the cell was assembled.

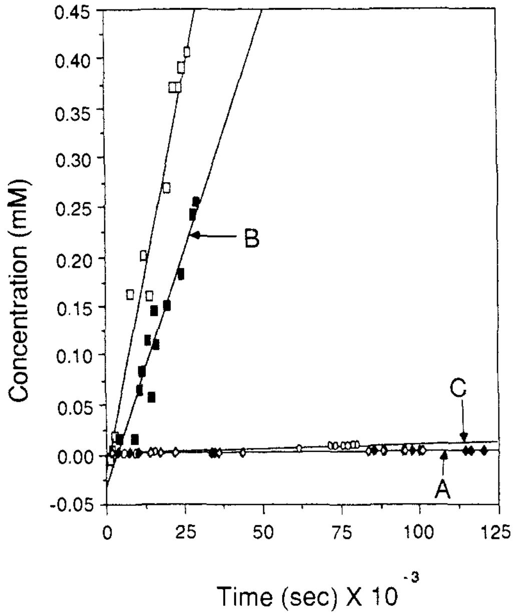

Figure 2. Facilitated transport of 1-hexene and 1,5-hexadiene across 25-μm Nafion NE111 membranes. Ordinate is the concentration of olefin determined in the upper compartment of the transport cell: open and filled diamonds, 1,5-hexadiene and 1-hexene, respectively, through initial hydrated Na^+ form; open and filled squares, through hydrated Ag^+ form; open circles, 1-hexene through hydrated Na^+ form after treatment with $Na_2S_2O_3$ (see text). Solid lines represent linear regression.

For membranes in the Na^+ form, the flux of olefin across the membrane was quite low but stable for over 2 days. Transport rates were much higher for the membranes in the Ag^+ form. In both cases, linearity of the plots indicates a constant flux of olefin across the membrane which can be readily calculated from the slopes. For the data presented in Figure 2, $J_{Na^+,hexene} = 2.4 \times 10^{-13}$, $J_{Ag^+,hexene} = 1.1 \times 10^{-10}$, $J_{Na^+,hexadiene} = 4.0 \times 10^{-13}$, and $J_{Ag^+,hexadiene} = 1.8 \times 10^{-10}$ (all J's in mol cm^{-2} s^{-1}).

We attribute the enhanced olefin flux for the Ag^+ form of the membrane to the reversible complexation of the olefins with silver ion

$$Ag^+ + \text{olefin} \rightleftharpoons Ag(\text{olefin})^+$$

Formation constants for these complexes have been reported for 1-hexene ($K = 860$ M^{-1}) and 1,5-hexadiene ($K = 1850$ M^{-1}) in 1 M aqueous $AgNO_3$.[15] The enhanced fluxes could be due to facilitated transport associated with the mobility of the $Ag(\text{olefin})^+$ complex or to a "hopping" mechanism in which olefin molecules exchange between cation sites. Regardless of the mechanism, facilitation factors, F, can be calculated as the ratio of the olefin flux for the Ag^+ form to the flux for the Na^+ form.[16] From the data in Figure 2, $F_{hexene} = 460$ and $F_{hexadiene} = 450$.[17]

Figure 2 also demonstrates that the enhanced fluxes attributed to incorporation of Ag^+ in the membrane is reversible. Curve A represents transport of 1-hexene for a membrane in the Na^+ form. This same membrane was converted to the Ag^+ form and used to obtain the data for curve B. After this data was obtained, the membrane was returned to the Na^+ form by stirring in a 1 M solution of $Na_2S_2O_3$, and the data represented by curve C was obtained. FTIR spectra of the membrane prior to each transport experiment were recorded. For transport experiments A and C, the spectra were identical with those reported here for the hydrated Na^+ form of the membrane (Figure 1, curve B). For experiment B the spectrum obtained was that of the Ag^+ form (Figure 1, curve C). The fact that the flux for the Na^+ form of the membrane

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(17) Due to the low fluxes involved, there is significant error associated with measurement of olefin fluxes for the Na^+ forms of the membranes. Therefore, the facilitation factors are only accurate to within a factor of 2–3.

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 $Ag(olefin)^+$ 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 be[18]

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

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

We note that since the solubility of olefins in the aqueous membrane phase is low, the value of K_D in our system, ca. $2 \times 10,^{-4}$ 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 $[CpVH(CO)_3]^{-1}$ and $HV(CO)_4(PP)$ (PP = chelating diphosphine),[2] very few vanadium hydride species are known which are as follows: one V(III) compound, $(C_5Me_5)_2VH$, and its CO adduct[3] and two dimeric species, $[CpV(\mu\text{-}H)]_2(\mu\text{-}C_6H_6)$[4] and $V_2H_4Zn_2(BH_4)_2(PPh_2Me)_4$.[5] Here we wish to report two new vanadium(II) hydride species, diamagnetic $[CpV(\mu\text{-}H)dmpe]_2$ (**1**) (dmpe = 1,2-bis(dimethylphosphino)ethane) and paramagnetic $[CpVH(dmpe)]_2(\mu\text{-}dmpe)$ (**2**), produced in the reaction of the V(II) alkyl complex CpV(n-Pr)dmpe[6] (**3**) with molecular hydrogen.

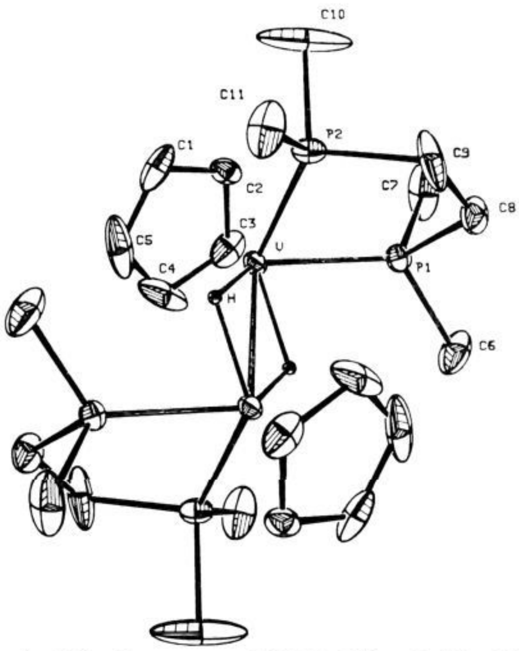

Figure 1. Molecular structure of $[CpV(\mu\text{-}H)dmpe]_2$ (**1**). Selected structural parameters: V–V′ = 2.701 (1) Å, V–H = 1.64 (4) Å, V–H′ = 1.72 (4) Å, ∠H–V–H′ = 73. (2)°, ∠V–H–V′ = 107. (2)°, ∠P(1)–V–P(2) = 78.40 (3)°, ∠CT–V–P(1) = 115.41 (2)°, ∠CT–V–P(2) = 115.69 (2)°, ∠CT–V–H = 119. (2)°. Prime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

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 NMR[7]) and was shown by X-ray analysis[8] to be the dimeric $[CpV(\mu\text{-}H)dmpe]_2$ (**1**, Figure 1), formed according to eq 1.

$$\mathbf{3} + H_2 \xrightarrow{-C_3H_8} CpVH(dmpe) \rightarrow {}^1/_2[CpV(\mu\text{-}H)dmpe]_2 \qquad (1)$$

(**1**)

The molecule is centrosymmetric and consists of a planar V_2H_2 unit with two η^5-Cp and two η^2-dmpe ligands in a trans arrangement. A V–V′ distance of 2.701 (1) Å is found. EHMO calculations on $CpV(\eta^2\text{-}BH_4)(PH_3)_2$ 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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(1) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.

(2) Many derivatives of this type have been described. See, for example: Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219 and references cited therein.

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(7) ^1H NMR (300 MHz, THF-d_8, 20 °C) of **1**: 4.13 ppm (s, 10 H, Cp), 2.49 ppm (br m, 4 H, P-CH_2), 2.05 ppm (br m, 4 H, P-CH_2), 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, β = 100.48 (1)° (130 K), Z = 2. Reflections (2056) with $1° \le \theta \le 27°$ 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).