acid at the cobalt-bound nitrogen would result in weakening of that cobalt-nitrogen bond and would facilitate loss of amidine. Under similar reactions, however, the cobalt-carbon bond of **5** would remain largely unaffected.

Conclusions

This work demonstrates that carbene or ylide complexes of Co(III) are stable, isolable species even in the presence of a trans methyl group. However, a route for the conversion of the amidine ligands into the isomeric carbene ligands has not been found with these cobalt complexes. The transformation of N bound to C bound imidazole or formamidine probably depends strongly on the activation of the C-H bond involved. In the known cases in which this isomerism occurs, it may be that a key isomerization step involves transfer of a proton from the imidazole carbon to the filled d orbitals of ruthenium. Evidence for electrophilic attack on the filled d orbitals of ruthenium has been presented;[29] similar attack is expected to be much less significant for cobalt(III) which would have a much reduced radial extention for its filled d orbitals.

Acknowledgments. This work was supported by Grant GM 18357 from the National Institutes of Health.

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Catalytic Hydrogenation Using Cationic Rhodium Complexes. I. Evolution of the Catalytic System and the Hydrogenation of Olefins

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Abstract: Homogeneous hydrogenation catalysts are prepared in situ by reductive elimination of a diene from a class of precursors of the type $[Rh(diene)L_n]^+A^-$ (L = tertiary phosphine or arsine, or phosphite, n = 2 or 3; L_2 = chelating phosphine or arsine; A^- = ClO_4^-, BF_4^-, or PF_6^-), on reaction with molecular hydrogen in polar solvents (S = acetone, tetrahydrofuran, or 2-methoxyethanol). We present evidence for two metal-hydride complexes, $[RhH_2L_nS_x]^+$ and $RhHL_nS_y$, in solution. The equilibrium between the two is sensitive to the nature of L and S and can be shifted by addition of acid or base. They are active catalysts in two of three basic catalytic cycles. The neutral monohydride is a powerful hydrogenation catalyst but also concomitantly isomerizes olefins (path A). Path B involves the cationic dihydride, which is a moderately active hydrogenation catalyst but a poor isomerization catalyst. Path C involves the cationic complex $[Rh(olefin)L_n]^+$ and probably occupies a minor catalytic role for weakly coordinating olefins. This system may serve as a model for homogeneous hydrogenation with cationic catalysts in general. Elucidation of its essential features led to its use to selectively reduce alkynes to cis olefins and chelating dienes to monoenes to be described in Parts II and III, respectively.

Interest in catalytic hydrogenation using soluble transition metal complexes continues to be intense.[2a] Unfortunately, relatively few homogeneous hydrogenation catalysts[2b] are commonly used by the practicing organic chemist since most, if not all, suffer, to varying degrees, from one or more of the following disadvantages: (i) they function satisfactorily only under conditions too vigorous or inconvenient for practical, routine applications; (ii) they cannot be greatly modified by altering the ligands to give, for example, regio- or stereoselectivity; and (iii) they usually reduce

only olefinic or acetylenic functional groups, the latter nonselectively.

We briefly described[3] a series of hydrogenation catalysts derived from cationic complexes of the type $[Rh(diene)L_n]^+$ (**1**: diene = norbornadiene (NBD, **1a**), or 1,5-cyclooctadiene (COD, **1b**); L = neutral donor ligand; n = 2 or 3).[4] More extensive studies, concluded in 1971,[5] showed that these catalysts are efficient at 25° and 1 atm of H_2, easy to make, comprise a fairly large class since L can vary widely, and are versatile and of general preparative utility. For example, some will reduce alkynes *specifically* to cis olefins, chelating dienes specifically to monoenes and ketones to alcohols.[6] Since our original communications,[3,6] others have used these, or closely similar catalysts, to hydrogenate olefins,[7] dienes,[7c] alkynes,[8] imines,[7a] and ketones,[7a,9] and to hydrosilate ketones.[10] Cationic catalysts bound to polymers function similarly.[11] Many of these catalysts contain optically active ligands and thus hydrogenate unsaturates asymmetrically. The most dramatic example of asymmetric olefin hydrogenation is the synthesis of optically active amino acids (in *up to 95%* enantiomeric excess)[7b] such as L-Dopa on a commercial scale.

Elucidation of the scope and at least the gross mechanistic details of hydrogenation of unsaturated carbon-carbon bonds using catalysts prepared from **1** therefore would be valuable. We propose to do this in three parts. This, the first, will describe catalyst precursors, catalytic principles, isolation of catalytically active complexes, and how a study of olefin isomerization led to discovery of the essential features of the hydrogenation mechanism. The second[12a] will describe selective hydrogenation of alkynes to cis olefins and the third,[12b] selective hydrogenation of diolefins to monoolefins.

Results and Discussion

Catalyst Precursors and Catalytic Principles. We previously described the preparation and some properties of the catalyst precursors, $[Rh(diene)L_n]^+A^-$ (**1**: A^- is a poorly or noncoordinating counterion like PF_6^-, BF_4^-, or ClO_4^-).[4] They are yellow or orange, crystalline, relatively stable to air, and soluble in polar organic solvents like tetrahydrofuran, acetone, or alcohols. L is most often a tertiary phosphine or arsine (n = 2 or 3) or a chelating diphosphine.

In solution **1** reacts readily with molecular hydrogen (1 atm, 25°). The diene is reduced ultimately to the alkane (quantitatively by GLC) and catalytically active complexes thereby generated in situ. This "reductive elimination" of diene[13] offers several notable advantages over previous, often fortuitous, methods of generating catalysts.[2a,14] In particular (i) **1** can be prepared simply and L can vary widely, a considerable advantage over systems where often only one representative catalyst precursor can be isolated; (ii) the diene is completely eliminated from any subsequent reaction scheme since the final product, an alkane, has, as yet, no known coordination chemistry; (iii) even when **1** is formally coordinatively saturated (i.e., $[Rh(NBD)L_3]^+$), reductive elimination yields a Rh(I) species with at least the minimum number of sites (three) necessary to bind hydrogen and the substrate to be hydrogenated; (iv) though neutral catalysts sometimes dimerize to relatively inactive species (e.g., $2Rh(PPh_3)_2Cl(S) \rightarrow [Rh(PPh_3)_2Cl]_2$, see ref 2a), the fact that catalysts described here are positively charged and do not contain potentially bridging ligands such as halide severely limits this possibility.

Any of the species, **1** (e.g., diene = 1,3-cyclohexadiene, norbornadiene (NBD), 1,3-butadiene, or 1,5-cyclooctadiene (COD)), will yield catalytically active solutions under hydrogen. However, the rate of reductive elimination varies markedly. For example, $[Rh(NBD)(PPh_3)_2]^+$ reacts with hydrogen as much as 10^2 times more rapidly than $[Rh(COD)(PPh_3)_2]^+$. Nevertheless, with time each gives the same catalytic species in situ. Since $[Rh(NBD)L_n]^+$ (**1a**, n = 2 or 3) species are most easily accessible and react most rapidly with hydrogen, we use them almost exclusively as precursors to catalytically active species prepared in situ by the reductive elimination process. Perchlorate, BF_4^-, or PF_6^- salts are all equally suitable but $[B(C_6H_5)_4]^-$ salts are not.[15]

The reaction of $[Rh(NBD)L_2]^+$ with hydrogen most likely yields a short-lived intermediate, $[Rh(NBD)L_2H_2]^+$. Rapid hdride transfer then yields norbornene which may or may not dissociate from incipient $[Rh(norbornene)L_2S_x]^+$ before it is reduced to norbornane.[16] Whether hydrides transfer stepwise or simultaneously is not important in this context nor need we know at this time if H_2 attacks $[Rh(norbornene)L_2S_x]^+$ or if norbornene dissociates and attacks a metal hydride (vide infra and Part III).

That $[Rh(NBD)L_3]^+$ reacts with hydrogen is somewhat unusual since it is formally five-coordinate and coordinatively saturated. Presumably NBD or L must dissociate before hydrogen can attack. NMR evidence indicates that added $PPhMe_2$ exchanges rapidly with coordinated $PPhMe_2$ in $[Rh(NBD)(PPhMe_2)_3]^+$ while added NBD does not alter the spectrum. This evidence is not conclusive but suggests that L rather than one arm of the chelating NBD ligand dissociates prior to attack by hydrogen on what is then $[Rh(NBD)L_2]^+$.

The reductive elimination principle would seem applicable to closely related diene complexes such as $Rh(NBD)(PPh_3)Cl$. Peculiarly, however, $Rh(NBD)(PPh_3)Cl$ does not react readily with molecular hydrogen under mild conditions. (This is why $Rh(PPh_3)_3Cl$ will not catalytically reduce NBD efficiently.[2a]) We have found that $[Rh(NBD)(bipy)]^+$ also does not react readily with molecular hydrogen. Clearly therefore we understand little about the factors which determine whether a given diene complex will react readily. So far **1** and analogous Ir complexes[3] where L is a phosphine or arsine comprise by far the largest family of complexes where the diene can be reductively eliminated under mild conditions. The next largest family is probably complexes of the type, $RhR(diene)L_2$ (vide infra).

Catalytic Hydrogenation of Olefins—Some Preliminary Observations. To prepare a catalytically active solution one dissolves $[Rh(NBD)L_n]^+$ (**1a**, n = 2 or 3) in an appropriate solvent (acetone, 2-methoxyethanol, tetrahydrofuran, etc.) under molecular hydrogen. (We should note immediately that acetonitrile is an inappropriate solvent for use in catalytic hydrogenation systems; vide infra.) The color of **1a** fades as hydrogen reduces NBD; for example, an orange acetone solution of $[Rh(NBD)(PPh_3)_2]^+PF_6^-$ becomes colorless in a few seconds. When the color change is less dramatic, complete reduction of the diene can be determined by GLC analysis. A drawing of the hydrogenation apparatus and details of the method can be found in the Experimental Section. A typical run employed 0.053 mmol of **1a**, 10.0 ml of purified solvent, and 1.0 ml of purified olefin, at constant temperature (30°) and constant total pressure (1 atm).

Injection of olefin (1-hexene or *cis*-2-hexene) into solutions of **1a** after stirring 10 min under hydrogen leads to a rapid uptake of hydrogen, the rate of which depends on the nature of L, the solvent, and the olefin. Uptake data alone provide insufficient information about the catalytic process since the olefin can also isomerize to one which is hydrogenated less readily. Therefore quantitative GLC analysis was carried out consistently (see Experimental Section). We should repeat that we are interested only in the semiquantitative or gross mechanistic features of the catalytic system.

Table I. The Catalytic Hydrogenation of 1-Hexene and *cis*-2-Hexene

Catalyst precursor	(a) 1-Hexene Concn (mM)	Solvent[a]	k_h[b]	k_i[c]
$[Rh(NBD)(PPh_3)_2]^+$	5.3	2ME	~1	*d*
$[Rh(NBD)(PPhMe_2)_3]^+$	5.3	2ME	3.6	8.4 (65% trans)
$[Rh(NBD)(P(OPh)_3)_2]^+$	5.3	THF	1.3	2.6
$[Rh(NBD)(PPh_3)_2]^+$	5.3	Acet	~0.1	*d*
$[Rh(NBD)(PPh_2Me)_2]^+$	3.7	Acet	3.0	4.5 (60% trans)
$[Rh(NBD)(PPhMe_2)_3]^+$	3.5	Acet	6.0	6.0 (60% trans)

Catalyst precursor	(b) *cis*-2-Hexene Concn (mM)	Solvent	$(k_h + k_i)$[e]
$[Rh(NBD)(PPh_3)_2]^+$	5.3	2ME	~0.1[f]
$[Rh(NBD)(PPh_2Me)_2]^+$	5.3	2ME	1.0
$[Rh(NBD)(PPhMe_2)_3]^+$	5.2	2ME	2.0
$[Rh(NBD)(PPh_2Me)_2]^+$	5.3	Acet	2.0
$[Rh(NBD)(PPh_2OMe)_2]^+$	5.3	Acet	3.5
$[Rh(NBD)(PPhMe_2)_2]^+$	5.3	Acet	5.0
$[Rh(NBD)(PPhMe_2)_3]^+$	5.3	Acet	5.5

[a] Key: 2ME = 2-methoxyethanol; acet = acetone; THF = tetrahydrofuran. [b] k_h is the initial rate constant ($\times 10^{+4}$ in units of s^{-1}) for the appearance of hexane. [c] k_i is the rate constant ($\times 10^{+4}$ in units of s^{-1}) for appearance of *cis*- and *trans*-2-hexene; the percent trans in the mixture, if measured, is listed within the parentheses and did not vary more than ±5% up to 90% 1-hexene consumption. [d] Not measured. [e] Separation of the two rates was not feasible due to concomitant hydrogenation of the *trans*-2- and -3-hexenes; units as in (*b*). [f] This is the initial k_h only.

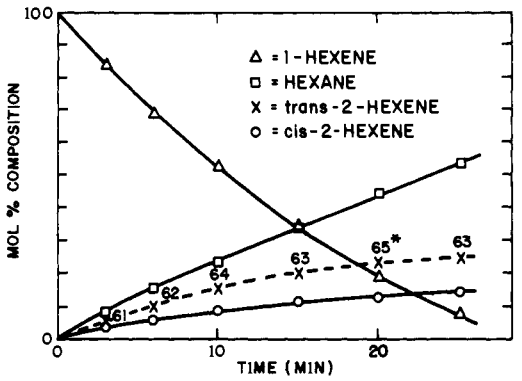


Figure 1. The catalytic hydrogenation of 1-hexene with $[Rh(NBD)(PPhMe_2)_3]^+$ (3.5 mM) in acetone. (* numbers refer to percent trans in the isomeric 2-hexene mixture.)

Therefore we have calculated and listed rate constants for the purpose of comparison only. As will be evident later, determining their mechanistic significance will require further careful and more detailed studies.

Tables Ia and b list some representative results, and Figure 1 shows a typical reaction profile. (In order to simplify discussion we will omit results for catalysts containing arsine or chelating phosphines. These will find use in later studies; see Parts II and III.) Though the system is clearly complicated by large and variable amounts of olefin isomerization in addition to hydrogenation, we can discern two general trends. (i) 1-Hexene usually disappears more rapidly than 2-hexene (at least initially) in comparable systems; that is, *comparatively*, 1-hexene is more rapidly hydrogenated and isomerized than *cis*-2-hexene. This is also true in a *competitive* sense; that is, *cis*- and *trans*-2-hexene formed during the reduction of 1-hexene are not reduced or isomerized until the concentration of 1-hexene is very low. (ii) Catalysts which contain more basic phosphines (e.g., $PPhMe_2$) appear to hydrogenate olefins more rapidly, but, unfortunately, they also isomerize olefins more rapidly. Furthermore, though a change in solvent appreciably alters the rates of both processes (to different extents), isomerization is always a major side reaction under these conditions (but vide infra).

Since isomerization often greatly hampers the utility of a hydrogenation catalyst, its persistence when either L or S is varied is problematic. Therefore further studies were aimed at elucidating the origin of isomerization in order to eliminate it if possible. Before continuing in this vein, however, we will first describe the isolation of one catalytically active species which is present under catalytic conditions.

Identification of Cationic Dihydrides. The orange color of $[Rh(NBD)L_2]^+A^-$ (L = PPh_3 or PPh_2Cy (Cy = C_6H_{11}); A = PF_6^-, BF_4^-, or ClO_4^-) in solvent S (S = acetone, ethanol, or acetonitrile) fades to very pale yellow when hydrogen is bubbled through for several minutes. Norbornane is present in quantitative yield at this stage according to GLC analysis. On addition of diethyl ether the white dihydride complexes,[3] $[RhH_2L_2S_2]^+A^-$ or $[RhH_2L_2(S_1)(S_2)]^+A^-$ (in a mixed solvent), crystallize from solution.[17] We could not isolate analogous complexes where L = $PPhMe_2$ or PPh_2Me even though the color of $[Rh(NBD)L_2]^+A^-$ lightens considerably and norbornane is produced quantitatively. However, on addition of more strongly coordinating ligands (L_2) such as selected tertiary phosphines, tertiary arsines, or bipyridyl, dihydrides of the type $[RhH_2(L_1)_2(L_2)_2]^+A^-$ can be isolated where L_1 = $PPhMe_2$, PPh_2Me, $AsPh_3$ as well as when L_1 = PPh_3 or PPh_2Cy. We have already described four members of this class (L_1 = L_2 = $PPhMe_2$, PMe_3, or $AsPhMe_2$; L_1 = PPh_3, L_2 = $AsPhMe_2$).[4] We will not discuss these and the strictly analogous complexes, $[RhH_2L_2(bpy)]^+A^-$ (see Experimental Section, L = PPh_3, PPh_2Me, or $AsPh_3$). We are more interested in solvated dihydride species since they are most likely present to a greater or lesser extent in all solutions of $[Rh(NBD)L_2]^+$ after reaction with hydrogen. Though $[RhH_2L_3S]^+$ species have not been isolated, one might reasonably presume by analogy that they are present in solution after reaction of $[Rh(NBD)L_3]^+$ with hydrogen.

Table II lists the isolated complexes and the infrared and ^1H NMR data which support their formulation.

All isolated $[RhH_2L_2S_2]^+$ species exhibit solid-state infrared spectra characteristic of cis hydride ligands and cis, bound solvents. In the acetone adducts, $\nu_{C=O}$ is generally lower than the free value by ca. 50 cm^{-1}, consistent with "end-on" bonding to the metal via the oxygen lone pair of electrons (in the BF_3-acetone adduct, $\Delta\nu_{C=O} = -60$ cm^{-1}; ref 18). The ν_{O-H} for bound ethanol consistently occurs at ca. 3400 cm^{-1} for the perchlorate salts but at somewhat

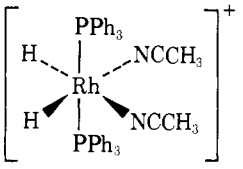
Table II. Infrared and ^{1}H NMR Data for the $[RhH_2L_2S_2]^+$ Species[a]

	Compound	Ir (Nujol) in cm^{-1}	^{1}H NMR (CH_2Cl_2, 35 °C, 100 MHz), shift (τ), J (Hz)
2a	$[RhH_2(PPh_3)_2(EtOH)_2]^+ClO_4^-$	(ν_{M-H}) 2140 w, 2190 w (ν_{O-H}) 3410 m, br	32.31 (dt, J_{H-Rh} = 27 ± 1, J_{H-PP} = 16 ± 1) ~9.3 (-CH_3), ~6.9 (-CH_2-), ~7.3 (O-H)
2b	$[RhH_2(PPh_3)_2(EtOH)(acetone)]^+ClO_4^-$	(ν_{M-H}) 2135 w, 2190 w (ν_{O-H}) 3410 m, br ($\nu_{C=O}$) 1675 s (ν_{M-D}) 1585 w, 1544 w	31.69 (dt, J_{H-Rh} = 26 ± 1, J_{H-PP} = 16.0 ± 0.5) ~9.4 (-CH_3), ~7.1 (-CH_2-), ~7.1 (O-H) ~8.4 (acetone)
2c	$[RhH_2(PPh_3)_2(CH_3CN)_2]^+ClO_4^-$	(ν_{M-H}) 2100 w, 2150 w ($\nu_{C\equiv N}$) 2280 w, 2310 w	27.07 (dt, J_{H-Rh} = 17.0 ± 0.5, J_{H-PP} = 13.0 ± 0.5) 8.41 (CH_3CN)
2d	$[RhH_2(PPh_2Cy)_2(acetone)_2]^+PF_6^-$	(ν_{M-H}) 2115 m, 2140 m, sh ($\nu_{C=O}$) 1677 s	7.88 (acetone)
2e	$[RhH_2(PPh_2Cy)_2(CH_3CN)_2]^+PF_6^-$	(ν_{M-H}) 2080 m, br, 2120 m, sh ($\nu_{C\equiv N}$) 2275 w, 2310 w	27.91 (dt, J_{H-Rh} = 17.5 ± 0.5, J_{H-PP} = 13.0 ± 0.5) 8.42 (CH_3CN)

[a] See Experimental Section for $[RhH_2(AsPh_3)_2S_2]^+$; phenyl and C_6H_{11} (Cy) proton resonances are omitted: w = weak, m = medium, s = strong, sh = shoulder.

higher frequencies for the hexafluorophosphate salts. Since perchlorate ion can hydrogen bond to ethanol, this mode is not a good measure of the degree of bonding of the ethanol to the metal. The two $\nu_{C\equiv N}$ absorptions are always at higher frequencies than for free CH_3CN (ca. 2150 cm^{-1}). The quality of solution infrared spectra in dichloromethane is generally poor except for $[RhH_2(PPh_3)_2(CH_3CN)_2]^+$ (**2c**) where two ν_{M-H} and two $\nu_{C\equiv N}$ absorptions are observed at approximately the same positions as in the solid-state spectrum. Addition of acetonitrile to dichloromethane solutions of $[RhH_2(PPh_3)_2S_2]^+$ (**2a** or **2b**, S = acetone or ethanol) yields a spectrum identical with that of **2c**; displaced acetone or ethanol absorb in positions characteristic of the uncoordinated molecules.

The ^{1}H NMR spectrum of **2c** in dichloromethane is consistent with the structure shown below. In the presence of 1



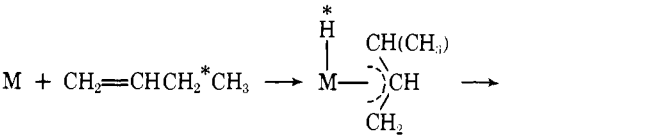
2c

mol of added acetonitrile the two broad resonances found at ca. τ 8.1 and 8.4 indicate an intermediate rate of exchange between free and coordinated acetonitrile on the NMR time scale (at 100 MHz and 37°, $1/\tau \approx 2\pi(\nu_a - \nu_b) = 190$ s^{-1}; ref 19). The solvents in **2a** (**2b**) are significantly more labile and exchange much more readily than acetonitrile. At −90 °C *both* free and coordinated solvent (acetone and/or ethanol) and *two* poorly resolved hydride resonances (at τ 30.5 and 31.8) are observed. At 35 °C the averaged solvent resonances are sharp and upfield of the corresponding positions of signals expected for noncoordinated solvent; addition of S at 35° shifts the sharp, averaged resonances toward the position expected for noncoordinated solvent. Addition of 2 mol of acetonitrile generates a spectrum of **2c** plus acetone and/or ethanol.

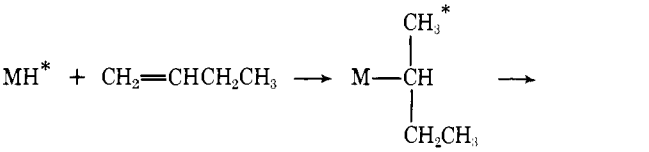
Clearly acetonitrile binds strongly to the metal. In fact, if cationic dihydrides are active olefin hydrogenation catalysts, acetonitrile must compete well with an olefin like 1-hexene for the metal coordination sites since, in acetonitrile, olefins are not hydrogenated at a noticeable rate under standard conditions (vide supra) with (e.g.) $[Rh(NBD)(PPh_3)_2]^+$ as the catalyst precursor.

The precise nature of the species responsible for the observed low temperature spectra of **2a** (**2b**) in dichloromethane cannot be stated at this time. However, the general features of their spectra at 25° (cf. **2c**) allow several observations to be made in relation to their possible use as hydrogenation catalysts. The weakly coordinating solvents trans to the hydride ligands exchange rapidly; an unsaturated substrate could therefore readily gain access to the metal's coordination sphere. Coupling of the hydride ligands to phosphorus (J_{H-PP} = ca. 16 Hz) indicates that triphenylphosphine does not rapidly dissociate and recombine with the metal. Finally, since ^{103}Rh-H coupling is maintained, deprotonation of **2a** (**2b**) or loss of molecular hydrogen is not rapid on the NMR time scale at 35° (in CH_2Cl_2).

The Origin of Olefin Isomerization. Two catalytic pathways to olefin isomerization are well established (eq 1 and 2 with 1-butene as an example; M = metal; ancillary ligands are omitted).[20] Few bona fide examples of monoolefin isom-



$$M + CH_3{}^*CH{=}CHCH_3 \quad (1)$$



$$MH + CH_3{}^*CH{=}CHCH_3 \quad (2)$$

erization by the "π-allyl mechanism" (eq 1) are known. The far more prominent pathway is via a reversible olefin "insertion" into a metal-hydride bond (eq 2).[21] Olefin isomerization involving a dihydride species would be a variation of eq 2.

Though we have fairly well established that solvated, cationic, dihydride complexes are present in solution under catalytic conditions, we decided to first test a second species which could be formed by a well-known process in homogeneous hydrogenation, loss of molecular hydrogen (eq 3).

$$\underset{\mathbf{2}}{[RhH_2L_nS_x]^+} \xrightarrow{-H_2} \underset{\mathbf{3}}{[RhL_nS_y]^+} \quad (3)$$

In order to assess the magnitude of isomerization with **3**, it was necessary to generate a representative unambiguously. $[Rh(P(OPh)_3)_2S_x]^+$ could be prepared in situ by a known method (eq 4)[22] and was employed in the first experiment.

$$[Rh(P(OPh)_3)_2Cl]_2 + AgPF_6 \xrightarrow[THF]{-AgCl} [Rh(P(OPh)_3)_2S_x]^+PF_6^- \quad (4)$$

Stirring 1-hexene in a solution prepared as in eq 4 for 2 days produced only 2.6% *trans*-2-hexene and 4.6% *cis*-2-

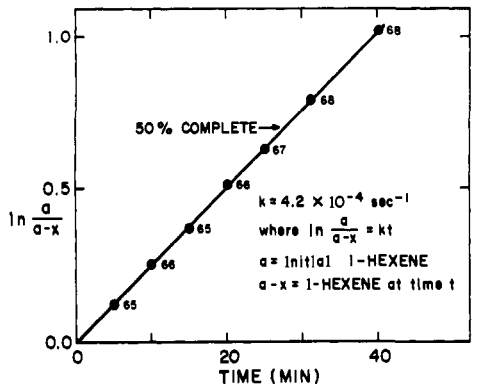


Figure 2. The isomerization of 1-hexene by a 5.3 mM acetone solution of $[Rh(NBD)(PPhMe_2)_3]^+$ after exposure to and subsequent removal of hydrogen—a first-order plot for the disappearance of 1-hexene. Numbers next to points refer to the percent trans in the isomeric mixture of 2-hexenes.

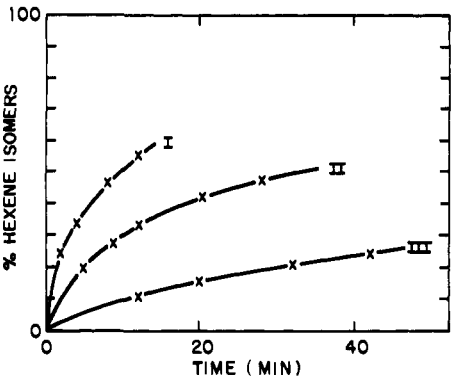


Figure 3. The isomerization of *cis*-2-hexene by prepared catalytic solutions after removal of hydrogen: I = 6.2 mM $[Rh(NBD)(PMe_3)_3]^+PF_6^-$ in acetone; II = 5.3 mM $[Rh(NBD)(PPhMe_2)_2]^+PF_6^-$ in acetone; III = 4.7 mM $[Rh(NBD)(PPh_2Me)_2^+PF_6^-$ in acetone.

hexene with 93% of the 1-hexene remaining. Clearly olefin isomerization by **3** contributes little toward the total isomerization observed under hydrogenation conditions (see Table Ia).

However, when the above solution was exposed to molecular hydrogen, 1-hexene (70% of the total initially present) isomerized extensively in 2 h. The active isomerization catalyst must therefore be generated *in the presence of molecular hydrogen.* Furthermore, subsequent removal of gaseous hydrogen from above the solution by flushing the apparatus with nitrogen[23] yielded a solution which still isomerized olefins rapidly. In fact, rapid isomerization is found for all catalyst solutions (generated by usual reductive elimination methods) after the gaseous hydrogen is removed. Isomerization of 1-hexene by a catalyst thus derived (L = $PPhMe_2$) is shown in Figure 2. The rate of isomerization is first order with respect to 1-hexene. Isomerization of *cis*-2-hexene by a series of similarly prepared catalysts is shown in Figure 3. Here it should be noted that the rate of isomerization decreases in the sequence, L = PMe_3 > $PPhMe_2$ > PPh_2Me.

Deuterium labeling experiments provided crucial clues.[24] (i) Hydrogen and deuterium scramble *in the absence* of olefin (eq 5).

$$[Rh(NBD)(P(OPh)_3)_2]^+PF_6^- + H_2/D_2\ (\sim 1{:}1) \xrightarrow[THF]{17\ h} 40\%\ HD \quad (5)$$

(ii) Hydrogen from water or 1-hexene exchanges with molecular deuterium (eq 6 and 7).

$$[Rh(NBD)(PPhMe_2)_2]^+ClO_4^- + D_2 \xrightarrow[4{:}1\ THF{:}H_2O]{24\ h} 73\%\ H_2,\ 23\%\ HD,\ 4\%\ D_2\ (\text{ref } 25) \quad (6)$$

$$[Rh(NBD)(P(OPh)_3)_2]^+PF_6^- + D_2 + \text{1-hexene} \xrightarrow[\text{in THF}]{18\ h} 19\%\ H_2,\ 34\%\ HD,\ 47\%\ D_2 + \text{a 1:1 mixture of hexane and 2- and 3-hexenes} \quad (7)$$

(iii) Ortho hydrogens on $P(OPh)_3$ also exchange[26] with molecular deuterium (eq 8) but even complete ortho-hydrogen exchange cannot account for the results shown in eq 6 and 7.[27]

$$[Rh(NBD)(P(OPh)_3)_2]^+BF_4^- + D_2 \xrightarrow[THF]{17\ h} 2\%\ H_2,\ 18\%\ HD,\ 80\%\ D_2 \quad (8)$$

Behavior observed in the above experiments is characteristic of group 8 monohydride complexes. For example, $RhH(CO)(PPh_3)_3$,[28a,b] $IrH(CO)_2(PPh_3)_2$,[28c] $RuHCl(PPh_3)_3$,[28d] and $RuH(NO)(PPh_3)_3$,[28e] among others, catalyze H_2/D_2 exchange. Also, the corresponding deuteride complex in each case will exchange D in the presence of an olefin to yield the corresponding hydride complex. Finally, note that $RuH(NO)(PPh_3)_3$ is an extremely active olefin isomerization catalyst.[28e] Notably, none of these observations is consistent with the behavior of known d^6 dihydride species such as $RhH_2Cl(PPh_3)_2$.[28f]

Monohydride species in these catalytic systems can clearly arise by deprotonation of the cationic dihydride species[29] (eq 9).

$$[RhH_2L_nS_x]^+ \rightleftharpoons RhHL_nS_y + H^+ \quad (9)$$
$$\mathbf{2} \qquad\qquad \mathbf{4}$$

The following three experiments test this hypothesis (catalyst = 0.05 mmol in 10 ml of acetone). (i) $[Rh(NBD)(PPhMe_2)_3]^+$ was treated with molecular hydrogen and 1.8 mol of $HClO_4$ (70% aqueous; relative to Rh). After flushing with N_2, 1-hexene was injected. After 1 h less than 1% isomerization had occurred. In an identical system in the absence of acid, isomerization was 50% complete in ca. 30 min (see Figure 2). (ii) $[Rh(NBD)(PPhMe_2)_3]^+$ was treated as in (i) substituting 1.0 mol of NEt_3 per Rh for $HClO_4$. Under these conditions 1-hexene isomerized extremely rapidly with a half-life of ca. 2 min (compare with Figure 3). (iii) $[Rh(NBD)(P(OPh)_3)_2]^+$ was treated with H_2 in the presence of 3.3 mol of $HClO_4$ per Rh. One hour after injecting 1-hexene the solution contained 96% 1-hexene, 2% *cis*-2-hexene, 1.5% *trans*-2-hexene, and ca. 0.5% hexane. Note that in the absence of $HClO_4$, hydrogenation and isomerization (~30:70) occurred very rapidly (vide supra).

The above observations can be explained readily. (i) reversible protonation/deprotonation (eq 9) undoubtedly occurs in solution (cf. $[RhH_2[P(OPh)_3]_4]^+$ + base → $Rh[C_6H_4OP(OPh)_2][P(OPh_3)]_3 + H_2$; ref 31); (ii) the monohydride[32] (**4**) is an extremely active isomerization and hydrogenation catalyst; and (iii) the cationic dihydride (**2**) is a considerably less active, possible inactive, isomerization catalyst and—at least when $L_2 = 2P(OPh)_3$—a poor hydrogenation catalyst.

Deprotonation of neutral or cationic transition metal hydrides per se, of course, is not new.[33] What is new, we believe, is recognition that an equilibrium (eq 9) can exist in a cationic hydrogenation catalyst system and that one can control its position and thereby drastically alter the overall

results. We might go further and suggest that eq 9 is fundamentally important in hydrogenation systems where cationic dihydride (or monohydride) catalysts are believed present. These observations also indicate that protonation of neutral monohydride complexes may lead to catalytically distinct systems.

Further Studies of Solution Equilibria. Isolation of a monohydride from a cationic dihydride by addition of base (eq 10, route 1) provides further evidence for solution behavior as in eq 9.

$$[Rh(NBD)(PPh_3)_2]^+ \text{ (in acetone)} \xrightarrow[2.\ NEt_3]{1.\ 3PPh_3,\ H_2} RhH(PPh_3)_4 \text{ (80\% yield)} \quad (10)$$

The physical and chemical properties, infrared spectrum, and ^1H NMR spectrum of $RhH(PPh_3)_4$ thus obtained are identical with those reported elsewhere.[34] Another route to $RhH(PPh_3)_4$ is shown in eq 11 (route 2).[35]

$$Rh(NBD)(CH_3)(PPh_3)_2 \text{ (in benzene)} \xrightarrow[2.\ H_2]{1.\ \text{excess } PPh_3} RhH(PPh_3)_4 \quad (11)$$

In the absence of added triphenylphosphine both routes (in acetone) give rise to deep red-brown solutions whose electronic spectra—though somewhat featureless—are essentially identical. We might presume these solutions contain solvated monohydride species of the type, $RhH(PPh_3)_2S_x$. This hypothesis seems reasonable since the red-brown solutions generated by either route show essentially identical catalytic activity. Similar observations were made where L = PPh_2Me; i.e., the catalytic activities of $RhH(PPh_2Me)_2S_x$ prepared by either method are essentially identical.

A comparison of the catalytic activity of $RhH(PPh_2Me)_2S_y$ and $[RhH_2(PPh_2Me)_2S_x]^+$ is shown in Figures 4a-c. Figure 4a shows the activity of $RhH(PPh_2Me)_2S_y$ (via route 2); 4b shows the activity of the catalyst solution generated by the reductive elimination process (the solution will contain both the monohydride and cationic dihydride species); the solution whose activity is shown in 4c contains the highest concentration of the cationic dihydride species (since $HClO_4$ has been added). The results show that the rate of 1-hexene *hydrogenation* decreases in the order 4a > 4b > 4c. However, and significantly, the rate of 1-hexene *isomerization* decreases considerably more steeply from 4a to 4c.[36] These results complement the conclusions of the previous section: (i) $[RhH_2(PPh_2Me)_2S_x]^+$ is a less efficient hydrogenation catalyst than $RhH(PPh_2Me)_2S_y$ but (ii) it is a *much* less efficient isomerization catalyst.

A general mechanistic scheme which can qualitatively account for these observations is presented in Scheme I.[37] There are three possible paths by which an olefin can be hydrogenated. Path A involves a monohydride catalyst which will extensively isomerize as well as hydrogenate olefins. In path B the cationic dihydride is the active catalyst, and will, in general, hydrogenate olefins less efficiently; possibly only limited isomerization may be involved. Path B is, of course, strictly analogous to the proposed mechanism involving $Rh(PPh_3)_3Cl$.[28f] Path C involves direct hydrogenation of $[RhL_2(ol)S_x]^+$ (ol = olefin). It may operate to some extent since the mode of production of the catalysts is via direct hydrogenation of a diolefin complex, $[Rh(diene)L_n]^+$. Note that the proposed intermediate alkyl-hydride complex, $[RhH(R)L_nS_x]^+$, is common to both B and C. This species probably eliminates alkane so rapidly that extensive isomerization should not be observed for either path B or path C (vide infra).

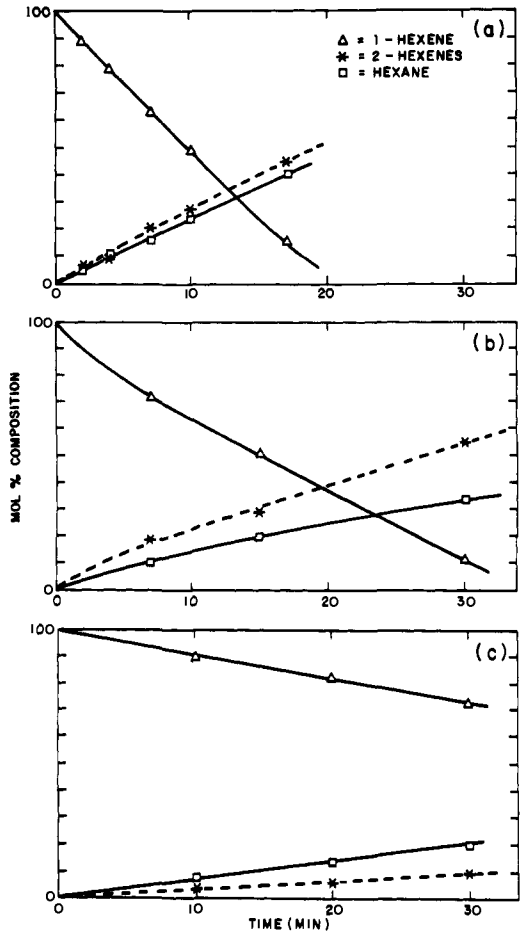
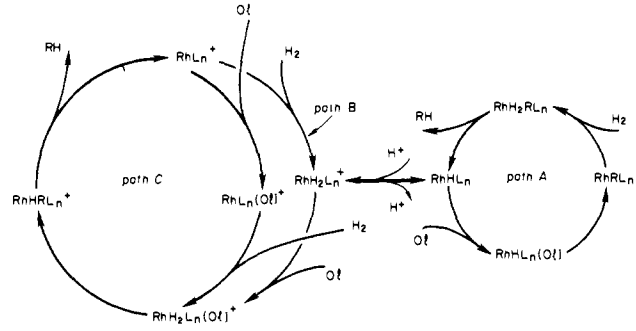


Figure 4. The hydrogenation of 1-hexene in acetone: (a) 3.7 mM $Rh(CH_3)(NBD)(PPh_2Me)$; (b) 3.7 mM $[Rh(NBD)(PPh_2Me)_2]^+PF_6^-$; (c) 5.3 mM $[Rh(NBD)(PPh_2Me)_2]^+PF_6^-$ in the presence of 2.2 mol of $HClO_4$.

Scheme I. Pathways for Olefin Hydrogenation and Isomerization (n = 2 or 3, Ol = olefin, R = alkyl, RH = alkane, L = a ligand, e.g., $PPhMe_2$; S_x and S_y omitted).



This scheme suggests that in order to hydrogenate an olefin without concomitant isomerization, path A must be repressed. This can best be achieved by protonation of $RhHL_nS_x$, i.e., by hydrogenation under acidic conditions. Protonation should be easier when L is more basic (e.g., L = PMe_3 or $PPhMe_2$) since other studies have shown that a metal protonates more readily as the donor properties of its ligands increase.[33,38]

Catalytic Hydrogenation of Olefins under Acidic Conditions. Considerations of the previous section indicate that hydrogenation with minimal concomitant isomerization is best accomplished under acidic conditions and that the most favorable catalysts should be those containing more basic phosphine ligands. This is borne out by the experimental re-

Table III. Summary of the Catalytic Activity of $[RhH_2L_nS_x]^+$ toward 1-Hexene[a]

Catalyst precursor	Concn (mM)	Solvent	H^+ (mol)	Result
$[Rh(NBD)(P(OPh)_3)_2]^+$	5.0	THF	3.0	97% 1-hexene after 60 min[b]
$[Rh(NBD)(PPh_3)_2]^+$	5.3	Acet	2.1	$k = 1.0 \times 10^{-4}$, 70% isom, 40% trans
	5.3	2ME	1.3	$k = 8.3 \times 10^{-5}$, 19% isom, 70% trans
$[Rh(NBD)(PPh_2Me)_2]^+$	5.3	Acet	2.0	$k = 1.8 \times 10^{-4}$, 30% isom, 50% trans
	5.3	2ME	1.3	$k = 8.2 \times 10^{-4}$, 80% isom, 80% trans
	5.3	2ME	2.5	$k = 6.4 \times 10^{-4}$, 70% isom, 80% trans
$[Rh(NBD)(PPhMe_2)_2]^+$	5.3	2ME	1.6	$k = 7.5 \times 10^{-5}$, 14% isom, 50% trans
$[Rh(NBD)(PPhMe_2)_3]^+$	5.3	Acet	4.0	94% 1-hexene after 66 min[c]
	5.3	THF	2.2	98% 1-hexene after 45 min[d]
	5.3	2ME	1.4	$k = 1.4 \times 10^{-4}$, 3% isom, 75% trans[e]
$[Rh(NBD)(PMe_3)_3]^+$	5.3	2ME	1.6	$k = 1.1 \times 10^{-4}$, 8% isom, 50% trans

[a] Nomenclature as in Table I; conditions as given in the text; H^+ as a 70% aqueous solution of $HClO_4$; k is the first-order rate constant (s^{-1}) for the disappearance of olefin due to hydrogenation *and* isomerization (95% 1-hexene remaining after 60 min corresponds to $k = 1.3 \times 10^{-5}$); percent isomerization is relative to the sum of all products while percent trans is relative to the isomeric mixture of 2-hexenes—both are constant up to ca. 90% consumption of 1-hexene. [b] A trace of hexane, 1% *trans*-2-hexene, 2% *cis*-2-hexene. [c] 3.5% hexane, 2.5% isomers. [d] 2% hexane, negligible isomerization. [e] In the absence of acid with catalyst concentration = 3.5 mM, $k = 1.7 \times 10^{-3}$ with 70% isomerization (65% *trans*-2-hexene).

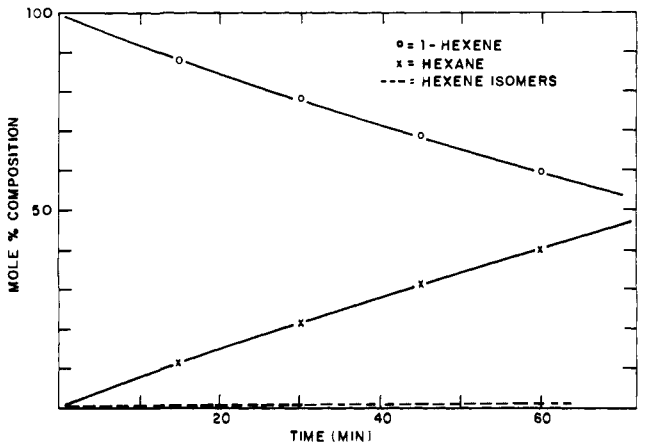


Figure 5. The catalytic hydrogenation of 1-hexene with $[Rh(NBD)(PPhMe_2)_3]^+$ (5.3 mM) in the presence of 1.4 mol of $HClO_4$ per Rh in 2-methoxyethanol.

sults presented in Table III and Figure 5. For example, using $[Rh(NBD)(PPhMe_2)_3]^+$ as the catalyst precursor in the presence of 1.4 mol of $HClO_4$, smooth hydrogenation of 1-hexene takes place with very little isomerization (~3% at t = 60 min, Figure 5). With catalysts containing less basic phosphines even comparatively large amounts of acid will not prevent extensive olefin isomerization since, presumably, substantial monohydride remains.

The last two experiments (Table III) suggest a subtle complication. Though less $RhH(PMe_3)_3S_y$ than $RhH(PPhMe_2)_3S_y$ presumably remains in identical systems under acidic conditions, the former may isomerize olefins much more efficiently than the latter. Since the rate of hydrogenation by $[RhH_2(PMe_3)_3S_x]^+$ is roughly comparable to that by $[RhH_2(PPhMe_2)_3S_x]^+$, more isomerization occurs relative to hydrogenation when L = PMe_3 (see following section).

All data are consistent with the postulate that olefin isomerization by $[RhH_2L_nS_x]^+$ is insignificant. In that case, an interesting conclusion can be drawn on more careful inspection of the hydride transfer steps. (Analogous arguments apply to the Wilkinson catalyst intermediate, $Rh(PPh_3)_2H_2Cl$.)[28f,37c] The olefin is proposed to enter the coordination sphere by displacing a solvent. The olefin would then be cis to one hydride but trans to the other. If the cis hydride migrates to the olefin and the stereochemistry does not change further, the resultant alkyl-hydride intermediate would have trans stereochemistry. This stereochemistry would not permit facile reductive elimination of RH in the next step. Consequently either the first hydride migration is accompanied by stereochemical rearrangement (e.g., via a trigonal bipyramidal geometry with R and H both equatorial) or rapid rearrangement must occur after this migration. Certainly the sterochemical change must be reasonably rapid so that reductive elimination can be facile and reverse reactions (which lead to isomerization) not competitive.

At present we cannot satisfactorily explain solvent effects (Table III). Clearly the equilibria in Scheme I will be very sensitive to solvent, and, moreover, olefin must displace solvent in all proposed hydrogenation paths. However, the marked rate differences on changing from 2-methoxyethanol to acetone are unexpected.

Further Considerations. No quantitative data concerning the equilibria presented in Scheme I have been obtained. Indeed the complexity and extent of the proposed equilibria make such data difficult and time consuming to obtain. Since we now have a working knowledge of the catalytic process the cost at this time would not be justified. However, in retrospect we can now make several observations.

In principle, the position of the dihydride-monohydride equilibrium (eq 9) could be determined spectroscopically. However, visible-uv spectroscopy has not been useful because the spectra of the species involved are generally featureless and closely similar. The ^1H NMR data presented earlier indicated the presence of only the dihydride species (for L = PPh_3, coordinated solvent = acetone or ethanol) with at most slow proton exchange on the NMR time scale; low standing concentrations of the monohydride (<10%) might have gone undetected. Furthermore, addition of phosphine or amine ligands under a hydrogen atmosphere gave only dihydride species in high yield. It must now be recognized, however, that addition of such donor ligands would shift the equilibrium in favor of the dihydride complex. In the same sense the equilibrium cannot be separated entirely from the conditions prevailing during catalysis since the presence of olefin will also affect its position (if the concentration of $[RhH_2L_nS_x]^+$ is reduced by olefin hydrogenation). Though species of the formulation $[RhL_n(ol)S_x]^+$ have not been isolated, the isolation of $[Rh(diene)L_2]^+$ (to be discussed in Part III) in good yield from solutions of $[RhH_2L_2S_x]^+$ (containing $RhHL_2S_x$) implies that this is the case (eq 12).

$$[Rh(diene)L_2]^+ \underset{-\text{alkene}}{\overset{+\,2\text{diene}}{\rightleftharpoons}} [RhH_2L_2S_x]^+ \overset{H^-}{\rightleftharpoons} RhHL_2S_x \quad (12)$$

We have so far said little about loss of molecular hydrogen from $[RhH_2L_nS_x]^+$ (**2**) to give $[RhL_nS_y]^+$ (**3**, eq 3). That **2** loses H_2 to some extent can be judged qualitatively by the catalyst solution's color. For example, a colorless THF solution of $[RhH_2(PPh_3)_2(THF)_2]^+$ becomes orange in a few minutes when hydrogen is removed in vacuo. The orange color must be due to a species which results from loss of molecular hydrogen since reexposure to hydrogen rapidly regenerates the colorless solution. This process can be repeated indefinitely and indicates a reversible equilibrium between **2** and **3**. However, at this stage, we have not been able to quantify this equilibrium in order to say how its position depends on L and S (however, vide infra).

The fact that catalyst solutions isomerize olefins in the absence of added acid after removal of hydrogen would seem to imply two things: (i) the loss of hydrogen from $[RhH_2L_nS_x]^+$ (**2**) and/or reprotonation of $RhHL_nS_y$ (**4**) are slow in the presence of monoolefins; and (ii) the rate of isomerization by **4** must be much more rapid than the rate of hydrogenation by residual **2**. An estimate of the hydrogenation activity of **2** relative to the isomerization activity of **4** for L = $PPhMe_2$ and n = 3 may be obtained from the following data (catalyst concentration = 5.3 mM, olefin = 1-hexene, k_h = first-order rate constant (s^{-1}) for hydrogenation, k_i = first-order rate constant (s^{-1}) for isomerization): (i) $k_h = 1.4 \times 10^{-4}$ in 2-methoxyethanol in the presence of acid (ca. 3% isomerization); (ii) $k_i = 7.0 \times 10^{-4}$ in 2-methoxyethanol in the absence of H_2; (iii) $k_i = 40 \times 10^{-4}$ in acetone in the presence of NEt_3 and absence of H_2. Comparison of (ii) and (iii) (assuming NEt_3 completely deprotonates **2**) implies that $[RhH_2(PPhMe_2)_3S_x]^+$ is ca. 20% dissociated (eq 13).

$$\underset{80\%}{[RhH_2(PPhMe_2)_3S_x]^+} \rightleftharpoons \underset{20\%}{RhH(PPhMe_2)_3S_x} + H^+ \quad (13)$$

If we assume eq 13 is not greatly altered in the absence of excess hydrogen then comparison of (i) and (ii) implies that $RhH(PPhMe_2)_3S_x$ *isomerizes* 1-hexene in 2-methoxyethanol *25 times more rapidly* than $[RhH_2(PPhMe_2)_3S_x]^+$ *hydrogenates* 1-hexene in the same solvent. (If NEt_3 does not completely deprotonate $[RhH_2(PPhMe_2)_3S_x]^+$ then the figure will be larger.) It is acceptable, therefore, that the rate of 1-hexene isomerization after removing hydrogen shows little or no deviation from first-order behavior (see Figure 2).[39,40]

Finally, it has been noted (see Figure 3) that isomerization activity in the absence of hydrogen increases when L varies in the order $PPh_2Me < PPhme_2 < PMe_e$. Since the basicity of **4** is also expected to increase in this order[33] than the increase in activity of **4** for olefin isomerization in the series L = PPh_2Me, $PPhMe_2$, PMe_3 must be quite pronounced.

Conclusions

The preferred conditions for hydrogenation of olefins without significant concomitant isomerization include approximately 1 mol of an acid of a noncoordinating anion per mole of catalyst precursor of the type $[Rh(NBD)L_n]^+$. Exposure to molecular hydrogen generates $[RhH_2L_nS_x]^+$. The most efficient catalysts involve basic phosphines (e.g., L = PMe_2Ph) as stabilizing ligands. They are comparable to Wilkinson's catalyst in activity but are soluble in polar solvents.

The uncharged species, $RhHL_nS_y$ (present under neutral or basic conditions), are considerably more efficient hydrogenation catalysts but also cause rapid isomerization of olefins. Such catalysts are thus useful when isomerization is not a problem.

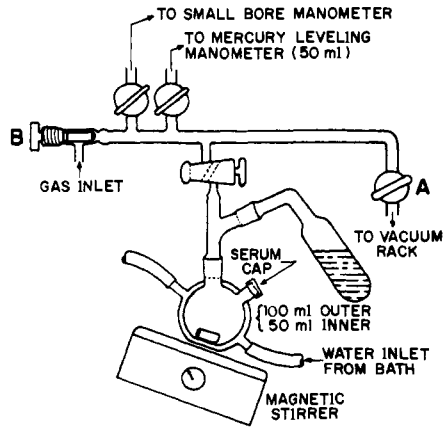


Figure 6. A schematic drawing of the catalytic hydrogenation apparatus.

Experimental Section

Catalyst precursors were prepared by previously described methods.[4,22a] $[Rh(NBD)Cl]_2$ and several of the cationic catalyst precursors are available commercially (Strem Chemicals). Here we describe a typical hydrogenation or isomerization experiment, product analysis, the preparation of isolable dihydride complexes which have not been previously described, and some special experiments and procedures.

A Description of the Catalytic System. The apparatus used for hydrogenation and isomerization studies is shown schematically in Figure 6. A typical experiment is described below. (i) The catalyst precursor was weighed out to ±0.1 mg and placed in the water-jacketed flask along with a Teflon-coated stirring bar. (Water at 30.0 ± 0.5 °C circulated continuously.) As a precaution, it is best to evacuate the apparatus at this point and flush with nitrogen while the side arm is removed to be filled with solvent. (ii) A measured volume of purified solvent was added to the detached side arm by syringe under nitrogen. The arm was replaced and frozen in liquid nitrogen. The apparatus was then evacuated via stopcock A. A was closed and hydrogen bled in through B while the solvent was thawed with warm water. (iii) The catalyst solution was prepared by rotating the side arm and stirring the solution for ca. 10 min under hydrogen. The total pressure within the apparatus was adjusted to 1 atm before injection of olefin. No attempt was made to compensate for the partial pressure of the solvent. If the experiment was to be performed in the absence of hydrogen (e.g., olefin isomerization), the apparatus was evacuated at this point to a total pressure of ca. 200 mm and refilled with N_2; the procedure was repeated twice more at 1-min intervals while vigorously stirring the solution. (iv) The substrate was introduced through the serum cap by syringe. If the object was to hydrogenate the olefin the total pressure was maintained at 1 atm with the leveling manometer and by periodic addition of H_2 via B. (v) Samples for GLC analysis were withdrawn at intervals by syringe and immediately quenched with a small amount of diphos (1,2-bisdiphenylphosphinoethane). The product, $[Rh(diphos)_2]^+$, has negligible hydrogenation or isomerization activity under these conditions. Larger samples could be distilled at atmospheric pressure without any detectable change in product distribution.

Precautions. All solvents were freshly distilled under argon or nitrogen (acetone and acetonitrile from 4A molecular sieves, THF from $LiAlH_4$, and 2-methoxyethanol without additives). All solvents which rapidly yield peroxides on exposure to air (e.g., THF) were checked before use with SCN^-/Fe^{2+} in water. THF was checked for an impurity which usually was found in the first 10–15 ml of distillate by addition of $AgPF_6$; what is probably black or brown silver metal forms when it is present. All solvents were transferred directly by syringe from the distillation receivers to the hydrogenation apparatus.

All olefins were passed through Woelm neutral alumina before each run and stored for short periods of time under N_2. Freshly purified samples were randomly and periodically checked for peroxides with SCN^-/Fe^{2+} in water under N_2. Samples were injected into the catalyst solution by syringe.

Only new serum caps were used at pressures less than 1 atm.

After each run a new one was greased, wired into place, and not punctured with pressures less than ca. 1 atm within.

Product Analysis. Reaction products were analyzed quantitatively on a Hewlett-Packard 5750 dual column research chromatograph (thermal conductivity detector) using the following columns: 12 ft × ⅛ in. 10% UC-W98 on 80–100 Diatoport S (Hewlett-Packard); 10 ft × ⅛ in. 10% Carbowax on 80–100 Diatoport S; 15 ft × ⅛ in. 10% silver nitrate in polypropylene glycol on 80–100 Chromasorb W (Hewlett-Packard). Their widely varying characteristics allowed satisfactory analysis of any mixture encountered in these studies.

The percentage product composition was calculated as the ratio of each peak weight (cut out and weighed) to the total. Detector sensitivity was the same (±5%) per mole of C_6 hydrocarbon in any homologous series.

Products were identified either by GLC comparison with known samples or by standard spectroscopic means (primarily ^{1}H NMR) after preparative GLC separation. We purchased olefins from standard sources (Farchan, Chemical Samples, and Aldrich).

Preparation of $[RhH_2L_2S_2]^+$ (anion = PF_6^-, ClO_4^-, or BF_4^-). $[Rh(NBD)(PPh_3)_2]^+ClO_4^-$ (0.5 g) was placed in 5 ml of acetone and treated with H_2 (either bubbling through or by stirring under 1 atm) until the solution became yellow (ca. 30 min). Addition of 1 ml of ethanol followed by diethyl ether yielded $[RhH_2(PPh_3)_2(acetone)(ethanol)]^+ClO_4^-$. Addition of 1 ml of acetonitrile followed by diethyl ether yielded $[RhH_2(PPh_3)_2(CH_3CN)_2]^+ClO_4^-$. $[RhH_2(PPh_3)_2(ethanol)_2]^+ClO_4^-$ was similarly prepared in a mixture of dichloromethane and ethanol. The yields are ca. 80% and the products may be recrystallized from dichloromethane plus the appropriate solvent under hydrogen by the addition of diethyl ether.

Anal. (respectively) Calcd for $RhC_{41}H_{44}P_2ClO_6$: C, 59.10; H, 5.32. Found: C, 58.73; H, 5.09. Calcd for $RhC_{40}H_{38}P_2N_2ClO_4$: C, 59.24; H, 4.72; P, 7.64; N, 3.46. Found: C, 59.63; H, 4.85; P, 7.61; N, 3.59. Calcd for $RhC_{40}H_{46}P_2ClO_6$: C, 58.51; H, 5.49. Found: C, 58.47; H, 5.43.

$[RhH_2(PPh_2Cy)_2S_2]^+$. $AgPF_6$ (185 mg) in 4 ml of acetone was added to 170 mg $[Rh(NBD)Cl]_2$ in 10 ml of acetone under N_2. AgCl was filtered off after 5 min and 0.40 g of PPh_2Cy added followed by bubbling with H_2 for 5 min. A flocky, white precipitate of $[RhH_2(PPh_2Cy)_2(acetone)_2]^+PF_6^-$ rapidly formed and was filtered off, washed with diethyl ether, and air dried, yield 0.48 g. Dissolution in dichloromethane and addition of ca. 4 mol of acetonitrile yielded $[RhH_2(PPh_2Cy)_2(CH_3CN)_2]^+PF_6^-$ on addition of diethyl ether under H_2.

Anal. (respectively) Calcd for $RhC_{42}H_{56}P_3O_2F_6$: C, 55.32; H, 6.46. Found: C, 55.50; H, 6.55. Calcd for $RhC_{40}H_{50}N_2P_3F_6$: C, 55.18; H, 6.01. Found: C, 55.36; H, 6.07.

$[RhH_2(AsPh_3)_2S_2]^+$ $[Rh(NBD)(AsPh_3)_2]^+ClO_4^-$ (150 mg) in 3 ml of acetone and 1 drop of 70% aqueous perchloric acid was treated with H_2 for 10 min to yield a yellow solution. Diethyl ether (15 ml) was added followed by 1 drop (14 mg, ca. 2 mol per Rh) of acetonitrile. Crystals appeared on scratching with a pipette through which H_2 was bubbling continuously. Filtration yielded 70 mg of pale yellow crystals which could be recrystallized in moderate yield from acetone without change. The infrared spectrum of the product suggests that this product is a ca. 4:1 mixture of $[RhH_2(AsPh_3)_2(CH_3CN)_2]^+ClO_4^-$ (ν_{M-H} at 2130 and 2075 cm^{-1}; $\nu_{C\equiv N}$ at 2280 and 2315 cm^{-1}) and $[RhH_2(AsPh_3)_2(acetone)_2]^+ClO_4^-$ (ν_{M-H} at 2165 and 2105 cm^{-1}; $\nu_{C=O}$ at 1675 cm^{-1}).

Preparation of $[RhH_2L_2(bpy)]^+ClO_4^-$ (or PF_6^-). $[Rh(NBD)(PPh_3)_2]^+ClO_4^-$ (200 mg) was placed in 4 ml of acetone and treated with H_2 until the orange solution turned pale yellow. 2,2′-Dipyridyl (40 mg, 1.0 mol per Rh) was added and crystals formed immediately. The pale yellow product was filtered off and recrystallized from dichloromethane with diethyl ether, yield 190 mg (88%) of $[RhH_2(PPh_3)_2(bpy)]^+ClO_4^-$.

Preparations of $[RhH_2(PPh_2Me)_2(bpy)]^+PF_6^-$ and $[RhH_2(AsPh_3)_2(bpy)]^+ClO_4^-$ are entirely analogous.

Anal. Calcd for $RhC_{46}H_{40}P_2ClO_4$: C, 62.42; H, 4.56. Found: C, 62.14; H, 4.69. Calcd for $RhC_{36}H_{32}P_3N_2F_6$: C, 53.61; H, 4.50. Found: C, 54.00; H, 4.66. Calcd for $RhC_{46}H_{40}As_2ClO_4$: C, 56.78; H, 4.14; N, 2.88. Found: C, 55.84; H, 4.15; N, 3.14. ^{1}H NMR (τ, except phenyl, CH_2Cl_2): L = PPh_3, 25.66 (2, q, $J_{H-Rh} = J_{H-P}$ = 14.5 Hz); L = PPh_2Me, 26.10 (2, dt, J_{H-Rh} = 17.0, J_{H-P} = 16.0 Hz), 8.30 (6, poor t, J = 2.5 Hz). Ir (ν_{Rh-H}, cm^{-1}, Nujol): L = PPh_3, 2060 m, br; L = $PPhMe_2$, 2050 m, br; L = $AsPh_3$, 2070 m, 2030 m.

Preparation of Rh(NBD)(Me)$(PPh_3)_2$. $[Rh(NBD)Cl]_2$ (250 mg) was placed in 5 ml of degassed benzene (distilled from sodium) along with 570 mg of PPh_3. LiMe (0.75 ml, 2.3 M in diethyl ether) was then added under N_2 and the solution stirred for 10 min. After adding 10 ml of isopropyl alcohol the solution was cooled to 0°. Yellow crystals were filtered off under N_2, washed with a small amount of methanol, and dried under a flow of N_2, then in vacuo, yield 0.66 g (83%). Its variable temperature ^{1}H NMR spectrum was characteristic of five-coordinate Rh and Ir complexes of this variety.[41]

Preparation of Rh(NBD)(Me)$(PPh_2Me)_2$. Methyllithium (0.75 ml, 2.3 M in diethyl ether) was added to 290 mg of $[Rh(NBD)Cl]_2$ and 500 mg of $PPhMe_2$ in 10 ml of degassed, dry benzene under N_2. After stirring for 1 h, 5 ml of 1.0 M NH_4Cl solution in water was added followed by 15 ml of benzene. The benzene layer was decanted, dried with 4A molecular seives, and filtered. After adding 30 ml of degassed ethanol, the solution left at 0° overnight deposited 420 mg (46%) of yellow crystals. It was identified by comparison of its ^{1}H NMR spectrum with those of other Rh and Ir complexes of this variety.[41]

Experimental Observations and Procedures. Preparation of $RhH(PPh_3)_4$ from $[Rh(NBD)(PPh_3)_2]^+PF_6^-$. $[Rh(NBD)(PPh_3)_2]^+PF_6^-$ (500 mg) and 500 mg of PPh_3 were stirred for 1 h under H_2 in a mixture of 1 ml of ethanol and 9 ml of acetone. Triethylamine (80 μl, 1 mol per Rh) was added and yellow crystals formed rapidly. The solution was pumped free of H_2 and cooled to 0° under N_2. The product was filtered off after 15 min, washed with methanol, and dried under a flow of N_2: yield 525 mg (80%), ir (Nujol) 2150 cm^{-1} (ν_{M-H}). Dewhirst[34] observed ν_{M-H} at 2140 cm^{-1} for $RhH(PPh_3)_4$ prepared by another route.

Preparation of $RhH(PPh_3)_4$ from Rh(NBD)(Me)$(PPh_3)_2$. Stirring 200 mg of $Rh(NBD)(Me)(PPh_3)_2$ and 200 mg of PPh_3 in benzene under hydrogen for 2 h gave a yellow precipitate. Ethanol (4 ml) and pentane (10 ml) were then added, and the solution was filtered. The yellow product was washed with acetone and air dried, yield 220 mg. Its infrared spectrum was identical with that of $RhH(PPh_3)_4$ prepared by the preceding method.

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References and Notes

(1) (a) Address correspondence to this author at Department of Chemistry, Massachusetts Institute of Technology 6-331, Cambridge, Mass. 02139. (b) Address correspondence to this author at Université Louis Pasteur, Institute de Chimie, Strasbourg, France.
(2) (a) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973. (b) "Catalyst" more often than not means catalyst precursor, i.e., an isolable complex which dissolves to give a catalytically active solution. In a general context it usually does not mean what it more accurately describes, the true, catalytically active species which forms in solution. Here we will try to always distinguish between catalyst precursor and active catalyst.
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(12) (a) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, following paper in this issue; (b) R. R. Schrock and J. A. Osborn, submitted for publication.
(13) A referee has suggested that "reductive elimination" is somewhat misleading since it has come to mean the reverse of an "oxidative addition" reaction. We concur but argue that (i) two steps of the overall process (transfer of two hydrides to a coordinated olefin bond) actually fit

the definition above and (ii) this description most accurately and concisely describes the overall process (the diene is reduced and thereby eliminated from the coordination sphere).
(14) (a) Another method of generating related Rh catalysts involves protonation of an acetate ligand in a neutral Rh(I) or Rh(II) complex.[7c,14b,c] Catalytic hydrogenation systems based on this method behave similarly in many respects to those based on the cationic complexes discussed here. (b) P. Legzdins, R. W. Mitchell, G. L. Rempel, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970). (c) R. W. Mitchell, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 846 (1973).
(15) (a) Tetraphenylborate ion can coordinate to the cation once the diene is removed.[15b] The resulting neutral species are relatively inactive under the mild conditions employed here. (b) R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970).
(16) We will write S_x (or S_y, etc.) in all formulas of nonisolated species which almost certainly contain "coordinatively labile" solvents, though the number, of course, is unknown.
(17) Formation of unstable dihydrides containing other bound solvents has been observed; e.g., $[RhH_2(PPh_3)_2(THF)_2]^+$ may be obtained as an unstable cream colored powder from concentrated THF solutions of $[Rh(NBD)(PPh_3)_2]^+$ under hydrogen. Metal–hydrogen stretching frequencies are evident in an infrared spectrum of this complex in Nujol but poorly resolved. The ease of isolation of $[RhH_2(PPh_3)_2S_2]^+$ appears to increase roughly in the order S = THF < ethanol ~ acetone < CH_3CN.
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(22) (a) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3089 (1971). (b) The existence of $[Rh(P(OPh)_3)_2S_x]^+$ may be shown by (e.g.) the essentially quantitative yield of $[Rh(NBD)(P(OPh)_3)_2]^+$ on addition of norbornadiene.[22a] Note that catalysts prepared from $[Rh(NBD)(P(OPh)_3)_2]^+$ isomerize olefins rapidly (see Table Ia).
(23) Flushing consisted of evacuation to ca. 200 mm total pressure followed by introduction of nitrogen to 1 atm; this was repeated three times.
(24) All experiments were conducted with 0.12 mmol of catalyst in 10 ml of solvent under ca. 200 ml of molecular hydrogen (deuterium).
(25) Complete equilibration of H_2O and D_2 would yield 93% H_2, 7% HD, and a trace of D_2.
(26) (a) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970); (b) *ibid.*, **8**, 113 (1975).
(27) The catalyst solution was taken to dryness, dissolved in dichloromethane, and stirred with KCN in water for 24 h. The dichloromethane solution was dried and taken to an oil in vacuo. A 220-MHz ^1H NMR spectrum (in C_6D_6) of the triphenyl phosphite thus isolated showed that 65% of the ortho-hydrogen atoms had been replaced by deuterium atoms. H in the gas is 70% of that which would be found on complete exchange of ortho-H with D.
(28) (a) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968); (b) C. O'Connor and G. Wilkinson, *ibid.*, 2665 (1968); (c) G. Yagupsky and G. Wilkinson, *ibid.*, 725 (1969); (d) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *ibid.*, 3143 (1968); (e) S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3068 (1971); (f) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966).
(29) A neutral monohydride species could conceivably be produced by other means such as ortho proton abstraction from the phenyl ring of L[26] or by some reaction involving the solvent. Though the former occurs in these systems (see eq 7) it is probably not a major source of monohydride since $[Rh(NBD)(PMe_3)_3]^+$ produces an effective olefin isomerization catalyst after exposure to hydrogen. (Proton abstraction from a alkyl group in a *nonbulky* phosphine[30] is extremely rare.[26]) The latter is also unlikely since isomerization is rapid in THF, a solvent which is normally inert. Also note that there is no induction period for isomerization or hydrogenation of 1-hexene or *cis*-2-hexene and the rate of isomerization of 1-hexene in the absence of hydrogen is first order with respect to the olefin (see Figure 2).
(30) See, however, J. M. Duff, B. E. Mann, B. L. Shaw, and B. Turtle, *J. Chem. Soc.*, 139 (1974), and references therein.
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(32) Possibly a trihydride (cf. $CoH_3(PPh_3)_3$) is present in solution but the catalytic chemistry almost certainly will arise from the monohydride.
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(35) An analogous reaction of this type has been reported for $Rh(COD)(C_6H_5)(PPh_3)_2$; M. Takesada, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **41**, 270 (1968). See also ref 2a, p 272.
(36) These results are best regarded as only semiquantitative since it would appear the behavior of 4b is not exactly that expected; i.e., it is not intermediate between 4a and 4c. Most likely 4a is not completely correct; a side reaction when the concentration of $RhH(PPh_2Me)_2S_x$ is high could alter the catalytic behavior.
(37) (a) We want to stress again that we are interested only in a broad mechanistic interpretation here. One could postulate an even more elaborate scheme involving less obvious, but not necessarily less important, kinetic intermediates (cf. the Wilkinson catalyst system[37b,c]). However, at this time and for our purpose, Scheme I is adequate. (b) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973). (c) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
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(39) Note that Figure 2 shows "hydrogen-free" olefin isomerization in acetone. In 2-methoxyethanol, where the rate of hydrogenation is only one-tenth as fast (Table III), the rate could conceivably deviate from first-order behavior.
(40) We suppose the forward step of eq 13 to be rapid even in the presence of olefin. However, we cannot be assured that $RhH(PPhMe_2)_3S_x$ can freely enter into the reverse in the presence of olefin, i.e., formation of a relatively stable metal alkyl, $RhR(PPhMe_2)_3S_x$, may slow the rate at which (13) is attained while still allowing rapid olefin isomerization.
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Catalytic Hydrogenation Using Cationic Rhodium Complexes. II. The Selective Hydrogenation of Alkynes to Cis Olefins

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Abstract: The cationic dihydride, $[RhH_2L_nS_x]^+$ and the neutral monhydride, $RhHL_nS_y$, which are present in equilibrium in solutions of $[Rh(NBD)L_n]^+A^-$ after exposure to molecular hydrogen, both catalyze the reduction of alkynes to cis olefins at comparable rates (n = 2 or 3, x and y unknown, A^- = (e.g.) PF_6^-, NBD = norbornadiene, S = (e.g.) acetone). When L is a more electron donating phosphine like $PPhMe_2$ (n = 2 or 3) and the alkyne is 2-hexyne the reduction is rapid and selective; after absorption of 1 mol of H_2 the solution contains ca. 99% *cis*-2-hexene. Employing $[RhH_2L_nS_x]^+$, the predominant catalytically active species in the presence of H^+A^-, isomerization of the olefin is negligible. In either case the reaction can be quenched at the endpoint and pure *cis*-2-hexene recovered by standard techniques. Selective reductions of several substituted alkynes have been equally successful. In one direct comparison, a system based on a cationic catalyst precursor was shown to be far superior to the Lindlar-type heterogeneous catalyst.

Several years ago we prepared a large class of complexes of the type $[Rh(diene)L_n]^+A^-$ (**1**; for example, diene = norbornadiene, L = $PPhMe_2$, n = 3, A^- = PF_6^-).[2] They react readily with molecular hydrogen to give the corresponding saturated hydrocarbon and solutions which contain active catalysts for the hydrogenation of olefins, alkynes, dienes, and ketones.[2a,d,3] The fact that one can vary L at will allowed close examination of how L influences the