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# INTERCALATION OF RHODIUM COMPLEX HYDROGENATION CATALYSTS AND ORGANO-SILANES IN LAYERED SILICATES

Ву

Rasik Haridas Raythatha

#### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

#### ABSTRACT

# INTERCALATION OF RHODIUM COMPLEX HYDROGENATION CATALYSTS AND ORGANO-SILANES IN LAYERED SILICATES

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Catalytically active rhodium complexes have been intercalated in interlayer regions of hectorite, a swelling micatype layered silicate.

The calionic hydrogenation catalyst precursor,  $[Rh(NBD)-(dppe)]^+$  (NBD = norbornadiene, dppe = 1,2-bis(diphenylphosphino)ethane) has been used for the hydrogenation of 1,3-butadiene and two of its methylated derivatives, 2methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene under intercalated and homogeneous conditions in methanol, acetone and benzene medium. The rates of hydrogen addition are solvent dependent, and the solvation effect on hydrogen addition is especially pronounced with the intercalated catalyst relative to the homogeneous catalysts. The rates of hydrogen addition with the intercalated catalyst range from  $10^{-5}$  to 0.83 relative to the homogeneous catalyst. With the homogeneous catalysts, the product distribution is essentially independent of solvent. The thermodynamically stable 1,4-hydrogen addition products are the major products with homogeneous catalysts, whereas a significant enhancement in the synthetically important 1,2- addition products is observed with the intercalated catalysts. The yields of 1,2-addition products are consistently higher in methanol than in acetone, where the interlayers are more constricted. The observed effect of catalyst intercalation on rates of reduction and product distribution may be linked to the swelling properties of [Rh(NBD)(dppe)]<sup>+</sup>.

The hydrogenation catalyst precursors of the types  $RhL_{n}^{+}$  (L = triphenylphosphine, n = 2,3) also have been intercalated in hectorite by the reaction of triphenylphosphine with intercalated  $Rh_2(CH_3CO_2)_{4-x}^{x+}$  (x = 1,2) or by using  $[Rh(NBD)(PPh_3)_2]^+$  ions as a precursor. The reduction of 1-hexene with the intercalated complexes occurs without isomerization up to 60% conversion of substrate, whereas extensive isomerization to internal olefin is observed with the analogous catalyst system in homogeneous solution. The difference in specificity between the intercalated and homogeneous catalyst system is accounted for in terms of an equilibrium between catalytically active dihydride and monohydride rhodium complexes:  $RhH_{2}L_{n}^{+} \ddagger RhHL_{n} + H^{+}$ . The dihydride is a good hydrogenation catalyst but a poor isomerization catalyst, whereas the monohydride is both a good hydrogenation and isomerization catalyst. Relative to

homogeneous solution, the dihydride is favored in the intercalated state because of a surface Brönsted acidity that is believed to arise from the dissociation of hydrated Na<sup>+</sup> ions that are also present on the interlamellar surfaces. However, the surface Brönsted acidity is dependent on surface composition. The effect of surface composition is demonstrated in part by the dependence of product distribution upon the initial composition of substrate and the amount of water present in the solvent.

 $Rh(PPh_3)_n^+$  complexes are also catalysts for the reduction of alkynes to the corresponding cis-olefins. The initial rates of reduction of relatively small alkynes (1-hexyne, 2-hexyne) in the interlayers swelled with methanol are comparable to those observed with the homogeneous catalyst. With larger alkynes, such as diphenylacetylene, the intercalated rate may be one hundredth that of the homogeneous rates. The spatial requirements of the substrate in the swelled interlayers are important in determining its reactivity with the intercalated catalyst. For example, the ratio of intercalated to homogeneous rates for the reduction of 2-decyne are 0.85 and 0.02, respectively, with  $CH_2Cl_2$  and  $C_6H_6$  as the swelling solvent. A binding model is proposed for the intercalated substrate-catalyst complex in which the spatial requirements of the substrate are determined by the minimum distance it must span when the coordinated CEC bond is oriented perpendicular to the silicate sheets.

The intercalation of silanes containing chloro, amino, vinyl and epoxide functional groups in the interlayers of Na-montmorillonite leads to the swelling of the interlayer region in the range of 2.8 - 5.9 Å. These expanded phases are stable at least to 200°C for the chloro silane intercalates and in the range of 240-330°C for silanes containing amino, vinyl and epoxide functional groups. Qualitative studies indicate cation exchange capacities of these materials to be comparable to those of Na-montmorillonite.

.

## TO MY FAMILY

.

Mom, Dad

Sulu, Bholen, Raju, Babu

Anju and Anilbhai

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#### INTRODUCTION

#### A. Foundation, Homogeneous and Heterogeneous Catalysts

In the past thirty years, the industrial application of processes catalyzed by soluble transition metal compounds has grown in significance. Some twenty or more processes use such catalysts to produce various organic chemicals. A few of the large scale industrial processes are the carbonylation of methanol to acetic acid which uses a rhodium catalyst with a methyl iodide promoter at low pressure, <sup>1,2</sup> L-DOPA synthesis by asymmetric hydrogenation (Monsanto Process) where a cationic rhodium complex is used as the catalyst,<sup>3</sup> a two stage aqueous oxidation of ethylene to acetaldehyde with palladium salts (Wacker process), 4-6 the manufacture of phenol from toluene by the oxidation of toluene over cobalt and copper salts with magnesium compounds as promoters (Dow-Toluene process),<sup>6</sup> the production of vinyl acetate 6,7 and substituted vinyl acetate<sup>8</sup> from olefins and acetic acid over palladium and copper salts, hydrocyanation of butadiene for the production of adiponitrile (DuPont process)<sup>5,9</sup> with nickel catalysts, and propylene oxidation over molybdenum salts for the production of propylene oxide.<sup>10,11</sup> Despite this impressive growth, homogeneous catalysts are less widely

used than heterogeneous catalysts in chemical industries. Nevertheless, homogeneous catalysts demonstrate great selectivity and economic efficiency in some reactions.

The growth in the application of homogeneous catalysis has been followed by a rapid development of organo-transition metal chemistry. The remarkable growth of organometallic chemistry and the need to understand catalytic processes have had a synergistic effect on the development and mechanistic studies of these systems.<sup>12</sup>

The most commonly used homogeneous catalysts are transition metal complexes. Catalysis with these compounds offers a number of distinct advantages over traditional homogeneous catalysts. In a sufficiently dilute solution, all the molecules of homogeneous catalysts are available for the catalytic reaction. Heterogeneous catalysis reactions occur at the interfaces of solid-liquid or solid-gas phases: all of the atoms or molecules not present at the surface are not accessible and remain unused. As a result, homogeneous catalysts allow easier interpretation of kinetics studies. Since homogeneous catalysts often have a definite stoichiometry and structure and since powerful spectroscopic methods of solution analysis exist for proper characterization, the homogeneous catalysts can be prepared so that batch to batch performance of these catalysts is totally reproducible. In contrast, the structure of the surface of a heterogeneous catalysts is dependent upon both its

method of preparation and its history subsequent to the preparation. Despite recent understanding and development in the field of surface characterization, <sup>13</sup> our understanding of the exact nature of chemisorption-catalysis mechanisms is limited. Therefore, heterogeneous catalysts are not easy to reproduce, because the local environment of the surface structure is easily altered by slight change in the catalyst preparation and the reaction conditions. Homogeneous catalysts will generally have only one type of active site. Consequently, homogeneous catalysts are more specific and easier to design for specific application. In addition, the electronic nature of the metal center and the steric requirements of the active site can be selectively modified through ligand substitution or variation of the solvent system. In contrast, heterogeneous catalysts, where several types of active sites may be present, often possess lower specificity and are more difficult to modify.

In principle, homogeneous catalysts appears highly efficient and attractive. However, from a practical viewpoint, homogeneous catalysts suffer from three major technical problems. The major disadvantage of homogeneous catalysts is the problem of separating the catalysts from the products at the end of the reaction. It is possible that both products and reactants can be distilled away below the decomposition point of the catalyst.<sup>1,2</sup> However, distillation is inevitably an endothermic process, and

distillation is very expensive. Unless distillation is very efficient, it will result in a loss of catalyst and/ or contamination of the products. Also, distillation without destroying the catalyst may be impossible in the case of reactions which leave behind high-boiling side products. The extraction of catalyst by ion exchange or solvent extraction technique face similar problems. Even if the separation is achieved efficiently, the cost of the resulting process may be prohibitive in commercial applications.

Limited thermal stability is a second problem facing homogeneous catalysts. Even though homogeneous catalysts are very efficient under mild reaction conditions, it is sometimes desirable for kinetics reasons to carry out the reaction at an elevated temperature. Homogeneous catalysts, particularly organometallic compounds, exhibit poor thermal stability relative to heterogeneous catalysts. Hence, the ability to increase reaction rates by increasing temperature is often limited in this system.

A third problem for many homogeneous catalysts is their limited solubility in suitable solvents. Often they are soluble and active in only a limited range of solvents. The solubility limitation also may limit the number of possible substrates that are suitable for reaction with a given catalyst system.

#### B. Supported Metal Complexes and Recent Developments

A number of papers have discussed in great detail the general concept of supported metal complexes, the efforts to combine the best virtues of homogeneous catalysts and heterogeneous catalysts have received considerable attention.<sup>14</sup> The basic approach in this field has been to develop methods by which the solubility problems of homogeneous catalysts can be alleviated along with the problem of separation. Efficient catalyst separation in homogeneous systems has been achieved by using (1) catalysts bound to soluble high-molecular weight polymers<sup>15</sup>, (2) transition metal complexes dissolved in low-melting tetraalkylammonium salts of  $SnCl_3$  and  $GeCl_3$  anions,<sup>16</sup> and (3) in biphasicsolvent systems.<sup>17</sup> However, the most profound technique in this regard has been the attachment of soluble transition metal complexes to a variety of chemically inert, insoluble supports. The immobilization of the homogeneous catalysts on a solid support offers ease of separation, mechanical and thermal stability, efficiency in multistep or batch processes, and phase flexibility commonly associated with homogeneous catalysts. In addition, supported systems can allow a greater degree of selectivity, efficiency, reaction control and reproducibility usually associated with their homogeneous counterparts. There may be other advantages experienced on heterogenizing transition metal complex catalysts to a support. In certain

cases the support even enhances the activity and specificity of the catalysts by inhibiting the number of unwanted side reactions. Catalyst immobilization may also inhibit deactivation of the catalyst by preventing formation of inactive dimer or polymer species.<sup>18</sup> Catalyst immobilization also may allow substrate selectivity to be based on molecular size restrictions<sup>19</sup> or dipolar factors.<sup>20</sup>

The choice of the supporting materials depends on the catalyst under study. From a chemical stand-point, the factors to consider are the inertness of the support to the reagents, the mobilities of the attached species and the polarity of the support relative to the reactants and products. The important engineering considerations are the porosity of support, the surface area, the heat transfer properties and the mechanical and thermal stability.

A number of materials have been used as catalyst carriers, which are compiled in Table 1.

Amorphous inorganic metal oxides and organic polymers have practically dominated the field. In general, inorganic materials have better mechanical and thermal stabilities than organic supports. However, the synthetic approaches to organic polymers provide a greater range of surface functionality, pore size, and surface area, than the most inorganic carriers. A wide variety of techniques have been used to affix soluble catalysts to various supports, from simple physisorption to complex functionalization of

Inorganic	Organic
Silica	Polystyrene, polyamines,
Zeolites	polyvinyls, polyallyls
Glass	polybutadienes, poly amino-
Metal Oxides	acids, urethanes, acrylic polymers
Graphite	cellulose, agarose, nylon,
Clays	allyl chloride, cross-linked
Zirconium Phosphate	dextrans.
Biphasic: Polysiloxanes	s, silica coated with phosphinated

Table 1. Materials Used as Homogeneous Catalyst Support.

Part of the listing is taken from Hartley, F. R.; Vezey, P. N., <u>Advan</u>. <u>Organometal</u>. <u>Chem</u>. 1277, <u>15</u>, 189.

the surface with ligands capable of complexing metal center. A partial list of these methods is compiled in Table 2. Many of these methods, which are a consequence of the three dimensional nature of the polymer, have no counterparts in homogeneous catalysts. When a soluble catalyst is attached to an insoluble support, the complex becomes heterogeneous at the bulk level, but it is essentially identical to the soluble analog on a molecular level. Thus, each catalyst site has a molecularity identical to that of its closest neighbors. The molecular nature of these

se studime Metal Complex Catalysts to Supports, and Their

J.	Physisorption and Ion-Exchange		
<b>.</b> Ф	Silica + HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> + supported liquid phase catalysts	Hydroformylation	21
	Silica + RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> /BBP + supported liquid phase catalysts	Hydrogenation	22a
	Alumina + Co <sub>2</sub> (CO) <sub>6</sub> (PBu <sub>3</sub> ) <sub>2</sub> + supported liquid phase catalysts	Hydroformylation Isomerization	22b
Ф	2 P)-Cl <sup>-</sup> + Na <sub>2</sub> [MoO <sub>4</sub> (Ox) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] + P) <sub>2</sub> [MoO <sub>4</sub> (Ox) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2-</sup> + 2NaCl	Epoxidation	23
U	Na-montmorillonite + [Rh(NBD)L <sub>n</sub> ] <sup>+</sup> + [Rh(NBD)L <sub>n</sub> ] <sup>+</sup> -montmorillonite + Na <sup>+</sup>	Asymmetric Hydrogenation	24
<b>d</b> .	$P)-SO_{3} + Rh_{2}(OAc)_{4-x}^{x+} + PPh_{3} \rightarrow [Rh(PPh_{3})_{n}][P)-SO_{3}]$	Hydrogenation	25
e •	2 P)-S0 <sup>7</sup> + [M(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> + [M(NH <sub>2</sub> )][P)-S0 <sub>2</sub> ] <sub>3</sub>		
f.	Na <sup>+</sup> -h <sup>5</sup> ctorite <sup>7</sup> Kh <sub>2</sub> (OAc) <sup>x+</sup> + PPh <sub>3</sub> + [Rh(PPh <sub>3</sub> ) <sub>n</sub> ] <sup>+</sup> -hectorite	Hydrogenation	27

Selected Methods of Binding Metal Complex Catalysts to Supports, and Their Application in Chemical Reactions. Table 2.

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<b>5</b> 0	Na <sup>+</sup> -hectorite + [Rh(NBD)(diphos)] <sup>+</sup> + [Rh(NBD)(diphos)] <sup>+</sup> -hectorite	Selective Hydrogenation	28
Ч	Na <sup>+</sup> -hectorite + P-P <sup>+</sup> + [Rh(COE)Cl] <sub>2</sub> + PPh <sub>3</sub> + [Rh(COE)P -P <sup>+</sup> (PPh <sub>3</sub> ) <sub>n</sub> -hectorite	Hydrogenation	29
•	Na-X-zeolite + RhCl <sub>3</sub> → RhCl <sub>3</sub> -X-zeolite	Carbonylation	30
•	$[Cu(NH_3)_4]^{2+} + Na-Y-zeolite + [Cu(NH_3)_4]^{2+} - Y-zeolite + Na^+$	Nitric oxide reduction	31a
	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> or [Rh(NH <sub>3</sub> ) <sub>5</sub> OH] <sup>+</sup> + → Na-X-zeolite	Hydroformylation	31b
	$[Ru(NH_3)_6]^{2+}$ or $[Rh(NH_3)_5OH]^{-}X-zeolite$ +		
х	Na'-Y-zeolite + Co <sup>-'</sup> + NH <sub>3</sub> + NO + [Co(NH <sub>3</sub> ) <sub>n</sub> NO] <sup>2+</sup> -Y-zeolite	Oxidation	32
	$Na^{+}-Y-zeolite + [Rh(NH3)6]3+ + CO + H2 + Rhx(CO)y-Y-zeolite$	Hydroformylation	33
	Na <sup>+</sup> -zeolite + M <sub>x</sub> (CO) <sub>y</sub> + M <sub>x</sub> (CO) <sub>y</sub> -zeolite (M = Fe, Os, Rh)	Water Gas Shift	34

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<mark>-</mark>	<pre>Inorganic metal oxides + M<sub>x</sub>(CO)<sub>y</sub> + organic solvent M<sub>x</sub>(CO)<sub>y</sub>-inorganic metal oxide (M = Ir, Ru, Rh, Os) (M = Ir, Ru, Rh, Os)</pre>	Isomerization Hydrogenolysis Hydrogenation	35
2.	Supported Functional Group Reactions: Excludin	<u>ng Phosphine Groups)</u>	
а.	P)-CH <sub>2</sub> -C <sub>5</sub> H <sub>5</sub> + Co <sub>2</sub> (CO) <sub>8</sub> + P)-CH <sub>2</sub> -C <sub>5</sub> H <sub>5</sub> - Co(CO) <sub>2</sub>		
	P)-CH <sub>2</sub> -C <sub>5</sub> H <sub>5</sub> + [Rh(CO) <sub>2</sub> C1] <sub>2</sub> + P)-CH <sub>2</sub> -C <sub>E</sub> H <sub>5</sub> - Rh(CO) <sub>2</sub>		36
þ.	S1)-OH + $MR_n$ + S1)-OM $R_{n-1}$ + RH		14d,37c,d
	S1)-OH = S1)-O + MR = S1)-O S1)-OH = S1)-O S1)-OH = S1)-O		37b
	S1)-OH + $Zr(C_{3H_5})_{4}$ + [S1)-O]_n-Zr $(C_{3H_5})_{4-n}$ + $nC_{3H_6}$	Polymerization	37a
с С	P)- $c_{6}H_{4}$ - $c_{H_{2}}N(c_{H_{3}})_{2}$ + $H_{2}$ 0 + $Rh_{6}(c_{0})_{16}$ +	Water Gas Shift	38
	P)- $c_{6}H_{4}$ - $cH_{2}N(cH_{3})_{2}$ -H[ $Rh_{x}(co)_{y}$ ] <sup>2</sup> P)- $c_{6}H_{4}$ - $cH_{2}N(cH_{3})_{2}$ -H $Rh_{x}(co)_{y}$	Reaction	

d.	<pre>4 P)-NH<sub>2</sub> + 2CuCl<sub>2</sub> + (P)-NH<sub>2</sub>)<sub>2</sub>CuCl-μCl<sub>2</sub>μ'-CuCl(NH<sub>2</sub>-(P)<sub>2</sub></pre>	Dioxygen reduction	39
<b>.</b>	$P)-C_{6}H_{4}Br + NI(PPh_{3})_{4} + [P)-C_{6}H_{4}]NI(PPh_{3})_{2}Br + 2PPh_{3}$		4 0
f.	S1)-O-S1(Me) <sub>2</sub> -CH <sub>2</sub> -O-C <sub>6</sub> H <sub>5</sub> OH + Mo(CO) <sub>6</sub> + S1)-O-S1(Me) <sub>2</sub> -CH <sub>2</sub> -O-C <sub>6</sub> H <sub>5</sub> OH-Mo(CO) <sub>6</sub>	Metathesis	Γħ
<b>ы</b>	S1)-OH + RhCl <sub>3</sub> + S1)-O-RhCl <sub>x-n</sub> + $nHCl$	Codimerization	43
h.	$P)-C_{6}H_{4}-Sn(CH_{3})_{3} + WCl_{6} + P)-C_{6}H_{4}-Sn(CH_{3})_{n}Wcl_{m} + CH_{4}$	Metathesis	42
• +1	S1)-O-S1-(CH <sub>2</sub> ) <sub>x</sub> Y + MY <sub>n</sub> R <sub>m</sub> + [S1)-O-S1-(CH <sub>2</sub> ) <sub>x</sub> Y]MX <sub>n</sub> R <sub>m</sub> (Y = -CH, -NR <sub>2</sub> , -C <sub>5</sub> H <sub>4</sub> , -SH, -C <sub>5</sub> H <sub>4</sub> N, -CH(COCH <sub>3</sub> ) <sub>2</sub> )	Hydrogenation Hydroformylation	• † †
• ۳۰۵	S1)-OH + [X <sub>3</sub> S1(CH <sub>2</sub> ) <sub>x</sub> PPh <sub>2</sub> ]ML <sub>n</sub> → [S1)-O-S1-(CH <sub>2</sub> ) <sub>x</sub> PPh <sub>2</sub> ]ML <sub>n</sub> + HX	Hydrogenation	45
a	<u>Reactions with Phosphinated Supports</u> Reactions of metal halides with support.		
	$s)-PPh_2 + MX_n + s)-PPh_2MX_n$	Hydrogenation	46

Table 2. Continued.

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48 49 47 Hydroformylation Hydrogenation Hydrogenation Substitution of a ligand from the metal complex. n S)-PPh<sub>2</sub> + Nico<sub>4</sub> + [S)-PPh<sub>2</sub>]<sub>n</sub>Ni(CO)<sub>4-n</sub> 3 S)-PPh<sub>2</sub> + Rh<sub>6</sub>(CO)<sub>16</sub> + Rh<sub>6</sub>(CO)<sub>13</sub>-(S)-PPh<sub>2</sub>)<sub>3</sub> + 3CO P)-PPh<sub>2</sub> + RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> → P)-PPh<sub>2</sub>RhH(CO)(PPh<sub>3</sub>)<sub>2</sub> þ.

20,54a,b 52,22a 50 53 51 Hydrogenation Hydrogenation Dimerization ↑ 2P)-CH2Ph2 + Rh(PPh3)2COC1 +
(P)-CH2Ph2)2RhCOC1  $(P)-PR_2)_2$  + Rh(NBD)acac + H<sup>+</sup> (P)-PR\_2)\_2Rh(NBD)<sup>+</sup> + acacH<sup>+</sup> 2S)-PPh<sub>2</sub> + 1/2 [Rh(COE)<sub>2</sub>C1]<sub>2</sub> s)-PPh<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>3</sub> + PPh<sub>3</sub>  $[Rh(S)-PPh_2)_2C1] + 2C0E$  $S)-PPh_2 + Rhacac(CO)_2 +$  $(S)-PPh_2 + Pd(PPh_3)_4 +$ 

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Hydroformy lation Oligomerization

Rhacac(S)-PPh<sub>2</sub>) + CO
	S)-PPh <sub>2</sub> + [Rh(1,5 Hexadiene)L <sub>2</sub> ] +	Asymmetric	56
	[Rh(1,5-Hexadiene) (S)-PPh <sub>2</sub> )] + 2L	Hydrogenation	
c	зехе[ато] широционо[4]-и до ехес[]		
•			
	2S)-PPh <sub>2</sub> + [Rh(cOD)c1] <sub>2</sub> + [Rh(cOD)c1(S)-PPh <sub>2</sub> ) <sub>2</sub> ]		45a <b>,</b> 57
	2S)-PPh <sub>2</sub> + [RhCl(CO) <sub>2</sub> ] <sub>2</sub> + RhCl(CO) <sub>2</sub> (S)-PPh <sub>2</sub> ) <sub>2</sub>	Hydroformylation	45a <b>,</b> 58
	P)-PPh <sub>2</sub> + (Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> C1] + [Rh(C <sub>2</sub> H <sub>4</sub> )C1(S)-PPh <sub>2</sub> ) <sub>2</sub> ]	Hydrogenation	59

Table 2. Continued.

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catalysts, therefore, offers greater uniformity and reproducibility than traditional heterogeneous catalysts. Supported catalysts are usually less active than their homogeneous analogs. The physisorption of metal complexes on solid supports suffer a major disadvantage, because catalyst desorption during reaction may occur mainly when reaction involves solid-liquid phases. On the other hand, covalently and electrostatically bound complexes desorb less readily. Covalently bound metal complexes may be leached out of the support if the covalent bonding is weak, or if the surface link is chemically degraded in the presence of solvent or excess free ligands. Electrostatic bonding on the other hand is strong. However, electrostatically bound complexes may be displaced by charged species formed in the reaction. The optimum catalytic activity of supported catalysts is expected under nearly solution like conditions. Often, the degree of freedom experienced by molecular catalysts in solution is decreased upon their immobilization. The loss of rotational and/or translational degrees of freedom of these complexes can result in loss of catalytic activity in the bound form relative to homogeneous conditions. The effect may be profound, especially for complexes covalently bound to the support by ligands of short chain length, where close proximity of the support can sterically interact strongly with the active species. The reduced degree of translational motion can actually be desirable, particularly when

catalyst deactivation can occur by dimerization or polymerization. In order to attain or closely mimic solution activity it is desirable, if not essential, that the metal complexes at least maintain their vibrational and rotational degree of freedom. A covalent linkage to a surface will always exert restrictions on rotational motions of molecules. However, ions electrostatically bound to support can exist in an almost solution like environment, even when in close proximity of support. Even though the ion exchange techniques appear to be very promising for catalyst immobilization, the main problem is the availability of catalytically active charged species which can be electrostatically bound to an appropriate support material.

Zeolites, layered silicates and layered zirconium phosphates are among the few inorganic supports that are capable of electrostatically binding cationic metal complexes. Naturally these materials are very attractive as catalyst supports for the reason discussed earlier (<u>vide</u> <u>supra</u>). Zeolite materials, though thermally stable, suffer from a few limitations: (1) the ion exchange charge sites may not be uniform and can lead to variation in local catalyst environments, like those of heterogeneous catalysts. (2) The zeolites are limited to reactions of small molecules, because most of the pore openings are small. (3) The three dimensional alumino-silicate frame-work of zeolites is rigid and does not allow the possibility of altering

selectivity through solvent effects. The zirconium phosphates are promising; however, their surface areas and cation exchange capacities limit their application.

Pinnavaia and coworkers<sup>27</sup> have recently demonstrated that cationic metal complex catalysts can be intercalated between negatively charged sheets of mica-type layered In highly swelled systems, the metal complex silicates. catalysts intercalated between the layered silicate sheets are almost in a solution-like environment. For example, Rh(I)-triphenyl-phosphine, $[Rh(PPh_3)_x]^+$  bound in the clay mineral hectorite was shown to hydrogenate alkenes and alkynes catalytically in the intracrystal region at ambient conditions. A suspension of the supported catalysts in methanol exhibited much higher specificity towards hydrogenation of 1-hexene than the homogeneous catalysts. Even though the catalytic activity of  $[Rh(PPh_3)_{r}]^{+}$ -hectorite for the hydrogenation of 1-hexene was nearly ten times lower than the homogeneous catalysts, the intercalated catalysts were nearly twice as active than similar catalysts supported on organic polymers. The catalytic activity of  $[Rh(PPh_3)_r]^+$ hectorite towards alkyne hydrogenation was almost equal to that of the homogeneous catalyst. The difference in activity of  $[Rh(PPh_3)_{y}]^+$ -hectorite for the hydrogenation of 1-hexene and 1-hexyne may be due to the selective steric and adsorptive effects imposed by the support on the coordination behavior of the substrates.

Although a direct comparison between the polymer supported and layered silicate supported catalyst cannot be made due to their structural differences, the greater reaction activity of the hectorite supported catalyst may be due to the greater accessibility of the catalyst in the interlayer regions of the mineral.

The success of these preliminary studies has illustrated the feasibility of carrying out catalytic reactions in the interlamellar regions of layered silicates and has prompted more intensive research in the field.<sup>60</sup> A number of catalytic reactions are being explored by using layer silicate supported catalysts. For example, the hydroformylation of 1-hexene with  $[Rh(COD)(P-P^+)]^+$ -hectorite<sup>61</sup> show increased specificity towards the formation of normal aldehydes relative to homogeneous solution. The optical yields obtained in the asymmetric hydrogenation of prochiro amino acid precursors with layer silicate supported rhodium complex catalysts were almost identical to the yields obtained with the homogeneous catalysts.<sup>62</sup> The substitution of positively charged ligands for neutral ligand in rhodium complexes can eliminate the possible desorption of active species from the layered silicate support.<sup>29</sup>

# C. The Properties of Clay Minerals and Their Structural Aspects

The layer silicates, hectorite and montmorillonite, described in this dissertation are a smectite mineral, a class of naturally occurring clay minerals. Clay materials generally are defined in soil science and geology as any finely divided materials with particle size less than  $2\mu$ . However, the term clay mineral refers to specific silicate minerals of defined stoichiometry and crystalline structure with particle size less than  $2\mu$ .

These minerals have unique properties associated with their two-dimensional structure.<sup>63</sup> These properties, along with their vast natural abundance, are the main reasons for their attractiveness as catalyst supports. The major building blocks of silicate minerals are silica tetrahedra and octahedra of alumina or magnesia. The framework of smectite layered silicates is composed of alternating arrays of interlayer cations and negatively charged silicate sheets, a schematic diagram of the structure is illustrated in Figure 1. All smectites including hectorite and montmorillonite have a 2:1 layer structure. The 2:1 notation refers to a structure in which two arrays of silica tetrahedra sandwich an array of either magnesia or alumina octahedra. The octahedral layer of hectorite is mainly composed of magnesia octahedra, whereas the octahedral layer of montmorillonite is composed of alumina octahedra. The resulting



- Schematic representation of the structure of Figure 1. smectite.
- **O** Oxygen Hydroxyls

Aluminum, Magnesium, Iron • Silicon, Occasionally Aluminum

silicate sheets have four distinct layers of oxygen: two oxygen layers are shared by both the octahedral layers and the tetrahedral layers of silica. In the tetrahedral sheets three of the four oxygen atoms of each tetrahedron are shared by three neighboring tetrahedra. The fourth oxygen atom is shared with the octahedral sheet. This results roughly in hexagonal holes in the tetrahedral sheets formed by rings of six oxygen atoms. The hydroxy groups, which are present to fulfill the charge neutrality, replace oxygen atoms located within the hexagonal cavity in the octahedral sheet. In montmorillonite only two thirds of the octahedral holes are filled with aluminum and magnesium cations; the remaining holes are vaccant. In hectorite all of the octahedral centers are occupied by magnesium and lithium cations. The schematic representation of smectite is provided in Figure 1.

The isomorphous substitution of  $Mg^{2+}$  for  $Al^{3+}$  in the octahedral layers of montmorillonite and the replacement of  $Mg^{2+}$  by Li<sup>+</sup> in hectorite results in a net negative charge on the oxygen framework. The charge for hectorite and montmorillonite is in the range of 0.5 - 1.0 charge per unit cell. Charge neutrality is achieved by the presence of an array of hydrated cations (sodium) between these layers. The idealized unit cell formula for hectorite and montmorillonite are,

 $Na_{0.67}[Mg_{5.33}, Li_{0.67}]$  (Si<sub>8.00</sub>) O<sub>20</sub> (OH,F)<sub>4</sub>; and

 $Na_{0.67}[A1_{3.33}, Mg_{0.67}]$  (Si<sub>8.00</sub>)  $O_{20}$  (OH)<sub>4</sub>, respectively. Note that some replacement of OH by F occurs in hectorite. The stacking of silicate sheets results in a crystalline layer structure. The alternate arrays of silicate sheet and hydrated cations are repeated in the crystallographic c-dimension. The adsorption of polar solvents between interlayers can result in considerable swelling of the Van Olphen $^{64}$  points out several factors that interlayers. influence the one-dimensional swelling. The swelling depends on a combination of the solvation energy of the cations, the energy of adsorption of solvent into the intracrystalline space, and the electrostatic energy between the charged species. The solvent polarity determines whether cation solvation energy or surface solvation is the predominant force in the swelling process. As a consequence of interlayer swelling, the interlayer alkali metal or alkaline earth cations can readily be reached and replaced by simple ion exchange methods with almost any desired cations, including transition metal ions, carbonium ions and even protonated proteins.

Electron spin resonance studies<sup>65</sup> have shown that simple ions, such as hydrated  $Cu^{2+}$  and  $Mn^{2+}$ , tumble rapidly in a solution-like environment when the interlayers are swollen to a thickness of 10-12 Å. The rapid tumbling has also been observed for organic nitroxide spin probes in the swollen smectite systems.<sup>66</sup> These observations provided

the bases for metal complex catalyzed reactions in the intracrystal space of the minerals. In the highly swelled interlayers, cationic organometallic catalysts exhibiting solution-like mobility should not lose appreciable activity compared to their homogeneous counterparts. In addition, these solvated interlayer ions should be readily available for the reagent molecules from bulk solution.

The internal surface area of hectorite and montmorillonite ( $\sqrt{750}$  m<sup>2</sup>/g) is greater than the surface area of amorphous metal oxides. The theoretical surface area is calculated from the unit cell dimensions 9.18 x 5.25  $\AA$ and taking unit cell weight to be 760 g/mole. For example, the surface area of various types of silica are typically in the range of 200-500  $m^2/g$ .<sup>67</sup> The surface area of most commonly used polymer, Amberlite XAD-2, is 120 m<sup>2</sup>/g.<sup>68</sup> Considering, the cation exchange capacity (CEC) of hectorite (70 meg/100g) and montmorillonite (83 meg/100g), one can estimate that  $\sim 80$  Å<sup>2</sup> is available for monovalent interlayer cations. This large area allows even large cations enough space to exist on the surface without charge interaction or steric constraint. Commercially available ion exchange resins offer no more than 16  $Å^2$ per exchange ion. Zeolite type X and type Y can provide large surface area in the supercage cavity of the zeolitic framework. However, zeolites are restricted to complexes of relatively small size due to their small pore openings  $(\sim 6-12 \text{ Å})$ . Complexes such as rhodium triphenylphosphine

would be much too large to exchange into Y-type zeolites.<sup>32</sup>

Smectites have been employed for many years as effective heterogeneous catalysts for a number of reactions. Early catalysts for the cracking of petroleum feed stock to valuable products were made from acid treated montmorillonite clays.<sup>69</sup> Theng has discussed extensively the organic-clay reactions and has reviewed the use of clay in the petroleum industry as cracking catalysts and as polymerization catalysts.<sup>70</sup> The active sites are of the Bronsted and Lewis acid type. The incorporation of various metals in synthetic mica-montmorillonite has shown that hydrocracking reactions with this material compare favorably with Pd-zeolite. The substitution of bivalent metal ions (for example Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup>) in the vaccant holes of Gibbsite octahedral layer results in metal substituted synthetic mica-montmorillonite. A synthetic montmorillonite with Ni(II) in the octahedral layer may be used as a light petroleum hydrogenation catalyst, as well as a Fischer-Tropsch catalyst.<sup>60a</sup> The presence of nickel increases the surface acidity and hence the activity of these catalysts. The catalysts are also active for hydroisomerization and oligomerization of light hydrocarbon fraction.<sup>60a</sup>

Metal ions intercalated in smectite can induce other types of reactions. For example, dimerization of anisole to 4,4'-dimethoxy biphenyl was reported to occur with Cu<sup>2+</sup>hectorite.<sup>71</sup> The interlayer regions of smectite often alter

the reactivities and stabilities of transition metal complexes.  $Cu^{2+}$ -arene complexes, not found in homogeneous conditions, are found and stabilized in smectites.<sup>72</sup>

The versatility of clay minerals and the ability of environment in interlayers to play constructive and advantageous roles in transition metal complex chemistry are some of the many reasons why clay minerals are being investigated as homogeneous catalyst supports.

# D. <u>Cationic Rhodium Complexes and Rationale for Their Use</u> as Hydrogenation Catalysts

The current literature on rhodium metal chemistry deals mostly with the synthesis of rhodium complexes and the catalytic properties they possess. Many rhodium complexes with phosphine, arsine and stibine ligands are active catalysts for a variety of homogeneous reactions. For example, Wilkinson's catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub>, is an active catalyst for hydrogenation and hydroformylation reactions.<sup>73</sup> Cationic complexes of the type  $[Rh(NH_3)_5OH]^{2+}$  have been shown to be an active hydrogenation catalyst.<sup>74</sup> Cationic rhodium complexes with nitrosyl ligands, for example,  $[Rh(NO)_2(PPh_3)_2]^+$  was proposed to catalyze the reaction<sup>75</sup>

 $CO + 2NO + N_2O + CO_2$ .

Schrock and  $Osborn^{76}$  have reported the preparation of

a number of rhodium (I) and rhodium (III) cationic complexes that function as catalyst precursors. The cationic complexes were prepared by the addition of a bidentate or monodentate phosphine ligand to a solution of [Rh(NBD)C1], in the presence of suitable anions. These complexes, upon passing hydrogen in solution, produced very active hydrogenation catalysts. These catalysts show significant specificity for hydrogenation of terminal olefins, for hydrogenation of alkynes to cis-olefins, and for conversion of dienes to monoolefins.<sup>77</sup> The specificity and reaction activities were dramatically altered under various reaction conditions. The substitution of a more basic ligand  $PMe_3$ or PPhMe<sub>2</sub> for PPh<sub>3</sub> in [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> a catalyst precursor, rapidly increased the hydrogenation and isomerization of terminal alkenes to internal alkenes. Crabtree<sup>78</sup> was able to reduce 1-alkenes and 1-alkynes selectively with similar cationic rhodium complexes, [Rh(COD)(PPh<sub>3</sub>)(Py)]<sup>+</sup> and [Rh(OCOPh)(COD)(PPh<sub>3</sub>)<sub>2</sub>].

In their elaborate study of reaction mechanism for the hydrogenation reactions with cationic rhodium complex catalysts, Schrock and Osborn<sup>77</sup> have proposed three mechanistic possibilities depending upon reaction conditions, and the nature of the ligands and the substrates. The details of these reaction mechanisms and their implications will be discussed later.

It is especially noteworthy that the catalytic species  $[Rh(PPh_3)_2]^+$ , which is proposed to occur upon reductive

elimination of coordinated diene from  $[Rh(NBD)(PPh_3)_2]^+$ -PF<sub>6</sub> solution, may be analogous to  $[Rh(PPh_3)_x]^+$  (x = 2,3) produced from the addition of triphenylphosphine to a solution of  $Rh_2(OAc)_4$  in the presence of a non-complexing acid.

It is of interest to investigate the behavior of these catalysts, in the hydrogenation of various substrates in homogeneous solution and in the intracrystal space of hectorite.

# E. <u>Research Objective: Studies of Hydrogenation Reactions</u> <u>With Rhodium Complex Catalysts Supported on Layered</u> <u>Silicate</u>

In any particular solvent swollen system, the interlayers hosting the metal complex catalyst are of more or less uniform thickness and polarity. Therefore, the possibility exists for selective substrate adsorption and reaction based on size, shape or polarity. In addition, the preferred orientations of the intercalated complex under certain conditions of swelling may cause the substrate selectivity to differ from the selectivity of the same catalyst in homogeneous solution or from selectivity of related complexes covalently bonded to the surface of amorphous polymers or inorganic oxides. The electric field gradient imposed by the silicate sheets may also influence substrate selectivity through selective polarization of bonds. Some of these fundamental factors are apparently responsible for the difference between homogeneous and intercalated catalysts in the hydrogenation of alkenes and alkynes.<sup>79,27a</sup>

One of the objectives of the present study has been to investigate the effect of intercalation on the substrate selectivity of cationic rhodium phosphine catalyst precursor in the hydrogenation of olefins and alkynes.

The layer silicates have the potential capabilities of affecting substrate selectivity based on molecular size or polarity. Therefore, a second objective of this dissertation has been to examine the effect of intercalation on the properties of  $[Rh(NBD)(Dppe)]^+$  as a catalyst precursor for the overall 1,2 and 1,4 addition of hydrogen to 1,3-butadienes. The reaction system was selected in part because the distribution of monoolefin products is kinetically regulated by the reaction pathways of a common intermediate. Under homogeneous conditions the thermodynamically more stable internal olefin products (1,4 addition) are favored over synthetically more desirable terminal olefin product (1,2 addition). Thus it was of interest to determine the effects of catalyst intercalation on product distribution, as well as on the rates of reaction.

The layer silicate possess Brönsted acidity. The origin of Brönsted acidity is proposed to arise from the hydrolysis of water present in the coordination sphere of

the interlayer cations.<sup>80</sup> Thus, whenever a protonic equilibrium is involved between catalytically active cationic species in the catalytic reactions, 77a,81 this equilibrium would be influenced by surface acidity. Recently, it has been demonstrated that catalytically active  $RhH_{2}L_{n}^{+}$  is preferred in the interlayers of hectorite over neutral  $RhHL_n$  (L = tertiaryphosphine, n = 2,3), which is in dissociative equilibrium with  $RhH_{2}L_{n}^{+}$ . The shift in the proton equilibrium may alter the specificity of the catalyst for 1-hexene hydrogenation. The observed specificity for 1hexene hydrogenation can be linked to the surface acidity and the role played by surface composition. The surface acidity is partially dependent upon surface adsorption and the nature of interlayer solvent.<sup>80</sup> It is possible that a continuous change in the surface composition during any given reaction can dramatically change the surface acidity. Therefore the intention of a third part of this dissertation has been to show that such dynamic processes may play a significant role in the hydrogenation of 1-hexene with a rhodium complex catalyst precursor [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> supported in the interlayers of hectorite.

### F. Pillaring Reactions of Layered Silicates

Ordinarily, the naturally occurring smectites are not suitable as general adsorbents and for catalytic applications because the silicate sheets collapse upon one another, as solvent is removed at elevated temperatures. Attempts to overcome this practical problem has created a considerable interest in introducing various pillaring species into the interlamellar regions of the swelling clays, so that internal surface is available for adsorption and catalysis even in the absence of swelling solvents.<sup>82</sup>

Organic materials have been quite successfully used to keep silicate layers apart at low to moderate temperatures but which fail in the temperature range of 250-500°C. For example, the exchange of protonated 1,4-diazabicyclo[2,2,2]octane(triethyldiamine) with interlayer cations of smectite produce  $d_{001}$  interlayer spacings of 14.2 Å.<sup>83</sup> The incorporation of the same cations in the interlayers of H<sup>+</sup>montmorillonite show markedly higher catalytic activity for esterification of carboxylic acids compared to ordinary alkyl-ammonium exchanged montmorillonite.<sup>84</sup>

As an alternate to organic materials, the inorganic molecular props are relatively stable in the temperature range 200-500°C and can produce higher interlayer spacings. For example, polymeric aluminum hydroxide cations, on intercalation in the interlayers of smectites form a stable phase of 18 Å d<sub>CO1</sub> spacings at 500°C.<sup>85</sup> The intercalation of  $[Si(acac)_3]^+$  in hectorite, subsequently followed by calcination at 500°C was suggested to form silica imbedded in the interlayers. The resulting hectorite containing array of silica in interlayers, retain its large surface area and the  $d_{001}$  spacings was 12.6 Å after calcination at 500°C.<sup>86</sup> Pillered clay minerals are prepared by introducing large cationic transition metal complexes, for example, Fe(Phen)<sub>3</sub><sup>2+</sup> and Cu(Bipy)<sub>3</sub><sup>2+</sup>.<sup>87</sup>

These layered silicates in the presence of props can exhibit properties like those of two-dimensional molecular sieves. It should be possible to carry out gas phase reactions and catalysis at high temperature by using these high temperature phase clay minerals.

The synthesis of interlayer silica, by incorporation of Si(acac)<sub>3</sub><sup>+</sup> cations and subsequent calcination, has prompted other workers to apply new methods to synthesize interlayer inorganic oxides and chemical props. It is known that coupling reagents such as chlorosilanes can bind to the edges of clay minerals.<sup>88</sup> Recently, incorporation of these silane coupling agents between the layers of silicic acid in DMSO or DMF solution has led to a new thermally stable material.<sup>89</sup> The chlorosilanes are known to hydrolyze in the interlayer and form expanded phases of 17 Å, which adsorbed aliphatic amine molecules. However, these phases were not stable beyond 60°C.<sup>90</sup> The hydrolysis of silanes appears to be a result of interlayer water, and the interlayer materials have been proposed to be of the siloxane type.

The last part of this dissertation has involved the preparation and characterization of thermally stable expanded

phase montmorillonite by utilizing various organo-silanes. The purpose of this investigation is twofold. First, to prepare an interlayer organo-silicone material that acts as chemical props at higher temperature. Second, to functionalize the internal surface with silane coupling agents, which probably involves coupling of the -OH group of Gibbsite layer. The functionalization of the internal surface should permit immobilization of otherwise neutral complex catalysts in the interlayer of silicates, while retaining the usual cation exchange sites for exchange with cationic metal complex catalysts. This type of system would be novel and may allow for the design of multi-functional catalysts.

#### EXPERIMENTAL

### A. Materials

All solvents used in syntheses and hydrogenation reactions were reagent grade. Spectrograde solvents were used in NMR and UV-Visible studies. The solvents were degassed by standard freeze-vacuum-thaw cycles prior to storing in sealed bottles in the glove box. Rhodium trichloride trihydrate (RhCl<sub>3</sub>·3H<sub>2</sub>O), purchased from Englehard Industries, was used without further treatment.

Natural sodium hectorite in spray dried form was obtained from Baroid Division of National Lead Industries. Generally, ion exchange reactions were carried out with the natural mineral. However, a small amount of  $CaCO_3$ present in the native mineral was removed prior to its use in infrared absorption measurements by washing 4.0 g of the mineral two times with 100 mL of 0.1M NaHSO<sub>4</sub>, and then washing it free of sulfate with deionized water. Na<sup>+</sup>-montmorillonite was obtained from the Source Clay Mineral Repository. The mineral was sedimented and saturated with Na<sup>+</sup> ions by adding an excess sodium chloride. The fraction containing particles less than  $2\mu$  was collected, centrifuged and dialyzed until free of excess sodium chloride and then freeze dried. Ion exchange of

Na<sup>+</sup> in the native minerals with 1.0  $\underline{M}$  Cu(NO<sub>3</sub>)<sub>2</sub> and subsequent analysis of the minerals for copper indicated the cation exchange capacities (CEC) were 70 meq/100g and 83 meq/100 g for hectorite and montmorillonite, respectively.

Methanol used as a solvent in the hydrogenation reactions was purchased from Matheson, Coleman and Bell containing 0.1 or 0.2% water. Higher percentages of water in methanol required for some reactions were achieved by addition of a calculated amount of deionized water. The exact percent of water in the methanol was determined by the Karl-Fischer method. Acetone, benzene, DMSO and pdioxane were purchased from Fischer-Scientific Co. pdioxane was dried and distilled over Na metal.

Most of the substrate used in this study decompose slowly when exposed to the atmosphere, and only traces of impurities are necessary to poison the catalysts. Therefore it was necessary to purify the substrate immediately before use. 1-hexene (Pfaltz-Bauer, Inc.) was shaken with aliquots of an acidified solution of  $FeSO_4$  until the red color of Fe(III) was no longer produced, dried over anhydrous  $CaSO_4$ , and distilled over sodium under argon. A cis-trans mixture of 2-hexene (Aldrich Chemical Co., Inc.) was shaken with and distilled from a mixture of NaBH<sub>4</sub> and ethyldiglyme. 1-hexyne, 2-hexyne, 3-hexyne and 2decyne (Farchan Division, Story Chemical Corp.) were

distilled over activated Al<sub>2</sub>O<sub>3</sub> under an argon atmosphere. The chromatographic grade alumina 80-200 mesh (Matheson, Coleman and Bell), was activated by heating to 300°C for 24 hrs. and then allowing it to cool under argon. 2,3-Dimethyl-1,3-butadiene and 2-methyl-1,3-butadiene (Chemical Samples Co.) were freshly distilled under an argon atmosphere. Fresh stock solutions of 1,3-butadiene (Pfaltz-Bauer, Inc.) were prepared by dissolving the gas in the desired, degassed solvents and determining the concentration based on the mass increase. Bicyclo(2,2,1)hepta-2,5diene (Aldrich Chemical Co., Inc.) was stored overnight over activated alumina, degassed and freshly distilled under argon prior to use in syntheses. The hydrogenation products expected in the catalytic studies were obtained in pure form from the respective companies which supplied substrates. They were used as received as standard references in GLC to identify the retention time of the products.

Triphenylphosphine (Aldrich Chemical Co.) and bis-(diphenylphosphino)ethane (Pressure Chemical Co.) showed no observable oxide impurities by  $^{31}$ P NMR or by UV-visible spectroscopy, and were used as purchased. Except for (CH<sub>3</sub>)<sub>3</sub>SiCl and (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> (Aldrich Chemical Co.) all other silanes used in the pillaring reactions were obtained from Dow-Corning Corp. They were handled in a dry, inert atmosphere to avoid possible hydrolysis.

Bottled hydrogen was purified by passage through a

column of reduced BASF catalyst R3-11 at 110°C and then through a bed of aquasorb (Mallinkrodt) or a 4 Å molecular sieve. Bottled argon and nitrogen were purified by the same technique. Elemental and water analysis was done by Gailbraith Inc.

#### B. Syntheses

All syntheses were carried out under an inert atmosphere either in the dry box or on a vacuum line.

### 1. [Rh(NBD)C1]<sub>2</sub>

Bis(norbornadiene)- $\mu$ , $\mu$ '-dichlorodirhodium, a starting material used in the syntheses of subsequent cationic complexes, was prepared by the reaction of RhCl<sub>3</sub>·3H<sub>2</sub>O and norbornadiene in ethanol solution according to the method of Abel <u>et al.</u><sup>91</sup> The yellow crystalline complex decomposed above 240°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.91(t), 3.83(m), 1.16(t). The melting point and proton NMR spectrum agree well with literature values.<sup>92</sup>

### 2. Rh(NBD)acac

(Acetylacetonato)norbornadienerhodium(I) was obtained by reaction of  $[Rh(NBD)Cl]_2$  and acetylacetone by a method analogous to that for the preparation of  $Rh(C_2H_4)_2$ acac by Cramer.<sup>93</sup> A mixture of 0.62g (0.14 mmole) of  $[Rh(NBD)Cl]_2$ , 10 mL of diethyl ether and 0.27 mL (0.027 mmole) acetylacetone was chilled to  $-80^{\circ}$ C and a solution of 0.45 g potassium hydroxide in 1.5 mL of water was added dropwise. The mixture was warmed to 0°C with shaking and 7 mL more diethyl ether was added. This mixture was stirred at 0°C for half an hour. The ether layer was separated, filtered, and chilled to  $-80^{\circ}$ C. The Rh(NBD)acac separated as a fine yellow crystalline compound. The evaporation of some of the filtrate and then allowing it to cool to  $-80^{\circ}$ C provided an additional amount of the acetylacetone complex. M.P. 177-178°C.

# 3. [Rh(NBD)(diphos)]ClO<sub>4</sub>

Norbornadienebis(diphenylphosphino)ethanerhodium(I) perchlorate was prepared in a nitrogen filled glove box by reaction of the acetylacetone complex, Rh(NBD)acac, with diphos in the presence of  $HClO_4$  according to the method of Schrock and Osborn.<sup>76</sup> The orange crystals decompose above 212°C. The proton and phosphorus NMR spectra of the product were in good agreement with the previously reported spectra.<sup>76</sup> <sup>1</sup>H NMR ( $CD_2Cl_2$ ) 5.34 (4,olefin), 4.33 (2,methine), 1.84 (2,methylene), 2.37 (4,  $PCH_2CH_2P$ ). <sup>31</sup>P NMR ( $CH_2Cl_2$ ) -55.8 (d,  $J_{Rh-P}$  = 159 Hz). IR (KBr) 1439s, 1485s Cm<sup>-1</sup> (C=C), 1100s Cm<sup>-1</sup> ClO<sub>4</sub>  $\lambda_{max}$  = 473 nm.

### 4. [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>

The hexafluorophosphate salt of the norbornadienebis-(triphenylphosphine)rhodium(I) cation was prepared by reaction of  $[Rh(NBD)Cl]_2$  with triphenylphosphine in the presence of KPF<sub>6</sub> according to the method of Schrock and Osborn.<sup>76</sup> The bright orange crystals decompose above 190°C. The proton and phosphorus NMR spectra were in good agreement with those reported in the literature.<sup>76</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.56 (4,olefin), 4.02 (2,methaine). <sup>31</sup>P NMR -28.3 ppm (d, J<sub>Rh-P</sub> = 154 Hz). IR (KBr) 1439s, 1485s cm<sup>-1</sup> (C=C),  $\lambda_{max}$  = 446 nm.

# 5. <u>Rh<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)</u><sub>4</sub>

Rhodium(II) acetate dimer was prepared by reaction of  $RhCl_3 \cdot 3H_2O$ , sodium acetate and acetic acid in hot ethanol according to the procedure described by Wilkinson and co-workers.<sup>25b</sup> The product was recrystallized from methanol and recovered as the methanol adduct  $Rh_2(CH_3CO_2)_42CH_3OH$ . The dark green crystals were stable to at least 240°C. The electronic spectrum of the complex in methanol ( $\lambda_{max}$  = 586 and 445 nm) was also similar to the spectrum of the reported complex in ethanol ( $\lambda_{max}$  = 590 and 446 nm).

### 6. Protonation of Rhodium Acetate

The protonation of rhodium acetate was undertaken in an inert atmosphere to ensure a product uncontaminated by oxygen. The protonating solution contained 0.66 mL (4.9 mmole) of aqueous 48% tetrafluoroboric acid (J. T. Baker Co.) in 150 mL of methanol. The methanolic solution was deoxygenated by flushing with dry nitrogen for at least 20 min. and mixed with 0.60 g (1.2 mmole) of  $Rh_2(CH_3CO_2)_{\mu}$ . The mixture was heated to 60°C in an oil bath 2CH<sub>2</sub>OH. and stirred until the green solid dissolved (approximately two days). A small amount of insoluble black material (possibly rhodium metal) was removed from solution by filtra-The concentration of rhodium in the green solution tion. was 0.008 M. The electronic spectrum exhibited bands at 610, 423 and 250 nm, in favorable agreement with the band assignment made by Wilson and Taube for  $Rh_2(CH_3CO_2)_3^+$ and  $Rh_2(CH_3CO_2)_2^{2+}$ . <sup>1</sup>H NMR spectra showed the presence of a methyl acetate resonance at  $\tau$  8.01 and 6.39. Lines at  $\tau$  8.09, 8.11 and 8.12 were assigned to bridging acetate in  $Rh_2(CH_3CO_2)_3^+$  and  $Rh_2(CH_3CO_2)_2^{2+}$ . Specific chemical shift assignments for  $Rh_2(CH_3CO_2)_2^{2+}$ , which may exist as <u>cis</u> and <u>trans</u> isomers, and  $Rh_2(CH_3CO_2)_3^+$  could not be made because of insufficient spectral resolution.

### 7. [Rh(NBD)(diphos)]<sup>+</sup>-hectorite

Na<sup>+</sup>-hectorite (100 mg, 0.07 meq) was stirred for 30 min in 5 mL of acetone or methanol, and then [Rh(NBD)-(diphos)]ClO<sub>4</sub> (18.5 mg, 0.027 meq) in 5 mL of the same solvent was added. Stirring was continued for 10 min and the yellowish orange intercalate was filtered and washed several times with 5 mL portions of solvent to ensure complete removal of unexchanged rhodium complex. Elemental analysis indicated 1.62 wt % Rh. IR (mull), 1439s, 1485  $cm^{-1}$  (C=C).  $\lambda_{max}$  (mull) = 465 nm.

# 8. [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>-hectorite

Na-hectorite (0.2 g, 0.14 meq) was stirred for 30 min, in 5 mL methanol and then 14.5 mg  $[Rh(NBD)(PPh_3)_2]PF_6$ (0.015 meq) in 5 mL of the same solvent was added. Stirring was continued for ten more minutes and the yellow orange intercalate was filtered and washed at least three times with 5 mL portion of solvent to ensure complete removal of unexchanged rhodium complex. Elemental analysis indicated 0.72 ± 0.02 wt % Rh. IR (mull) 1439s, 1485s cm<sup>-1</sup> (C=C)  $\lambda_{max}$  (mull) = 464 nm.

# 9. $\frac{\text{Rh}_2(\text{CH}_3\text{CO}_2)_{4-x}^{x+}-\text{hectorite}}{4-x}$

In a typical experiment 0.20 g Na-hectorite was stirred with 1.0 mL of the protonated rhodium acetate stock solution,

diluted to 4 mL with methanol. The slurry was stirred for 1-2 min, the liquid was removed by filtration, and the mineral was washed five to six times with 2 mL portion of MeOH and finally dried by suction. Rhodium analysis of several samples prepared by this procedure gave an average composition of  $0.72 \pm 0.04\%$  rhodium by weight.

# 10. <u>Catalyst Precursors from Protonated Rhodium(II)-</u> Acetate

Homogeneous solutions of the catalyst precursor were prepared under oxygen free conditions by treating 0.92 mL of the protonated rhodium acetate solution (0.015 mmole of Rh) with the desired amount of 0.05 M triphenylphosphine solution and diluting the mixture to 25 mL with solvent. Samples of supported catalyst were prepared by treating freshly prepared rhodium exchanged hectorite containing 0.015-0.30 mmole of Rh with 0.05  $\underline{M}$  PPh<sub>3</sub> to obtain the desired PPh3:Rh ratio. The slurry was then diluted to 25 mL with solvent. Treatment of the green rhodium exchanged hectorite with PPh<sub>3</sub> gave an immediate color change to a dark red-brown color which gradually lightened to a yelloworange color upon standing for several minutes. Analogous color changes occur with the preparation of homogeneous catalyst solutions, except that they occur much more rapidly.

#### C. Hydrogenation Reactions

All hydrogenation reactions were carried out at ambient conditions and at constant pressure. The catalyst solutions or suspensions were prepared in a nitrogen filled glove box placed in a specially designed flat bottom, hour glass-shaped flask (Figure 2). This design is effective in minimizing "creeping" of the finely divided mineralsupported catalyst up the walls of the flask during the course of the reaction. Also the flask provides flexibility of inert atmosphere transfer of substrate and removal of the reaction mixture. In a typical experiment, the flask was charged with 0.015 mmol of Rhodium catalyst precursor, and the flask was attached to a standard hydrogenation apparatus equipped with glass vacuum manifold, gas inlet valve, gas buret, mercury leveling bulb and mercury manometer (Figure 3). First, the entire assembly, except the hydrogenation flask, was evacuated and purged with pure dry hydrogen. The cycle was repeated three times. The reaction flask was then evacuated momentarily (sufficient to induce solvent bubble) and then pressurized with hydrogen. A one hour prehydrogenation period preceded the injection of freshly distilled substrate. In each case enough solvent was added so that the desired molarity of the substrate can be achieved, while keeping the total volume constant. Following the injection of substrate, the mercury manometer



- Figure 2. Reaction flask used to minimize creeping of finely divided intercalated catalyst.
  - (A) Serum cap for admitting substrate by syringe.
  - (B) Magnetic stirring bar.
  - (C) Reaction chamber, 6 (diameter) x 2 cm.



was at once adjusted to atmospheric pressure by means of the mercury leveling bulb and manifold vent. The initial buret reading was recorded and the timer was started. The rate of hydrogen uptake was monitored by observing the change in the volume, with time, necessary to maintain a constant pressure of 1 atm. Fresh hydrogen was added and the buret and manometer were reset each time approximately 50 mL hydrogen was consumed. The time lapsed and the amount of hydrogen that should have been consumed during this resetting process were taken into account and necessary correction to the total amount of hydrogen taken up was applied before the next reading was obtained. The hydrogenation rates were measured as mL H2/min/mmol Rh. The percent of the substrate converted into products were determined by removing a fraction of reaction solution at a regular interval of time, and its analysis by gas-liquid chromatography. After each run with intercalation catalyst, the catalyst was filtered off and the clear filtrate was checked for hydrogenation activity to ensure that the observed rates were due only to immobilized catalysts.

### D. Pillaring Reaction of Layer Silicate with Organo-Silanes

1. Pretreatment of Na<sup>+</sup>-montmorillonite

The interlayer water of Na<sup>+</sup>-montmorillonite was removed by dehydration at 180°C in a vacuum for 24 hrs. The

dehydrated Na<sup>+</sup>-montmorillonite was reswelled with DMSO, by suspending 2.0 g Na<sup>+</sup>-montmorillonite in 50 mL DMSO for at least 18 hrs. The DMSO swelled Na<sup>+</sup>-montmorillonite was filtered and washed thoroughly with p-dioxane to ensure removal of excess DMSO, and finally dried under vacuum at  $25^{\circ}$ C, (d<sub>001</sub> = 13.8 Å). IR (KBr) 2800-2900 cm<sup>-1</sup> (C-H stretch), 1400 cm<sup>-1</sup> (C-H bend).

### 2. Silane/Na<sup>+</sup>-montmorillonite

In a typical synthesis, a mixture of 0.2 g (0.16 meq) pretreated Na<sup>+</sup>-montmorillonite and 20 mL of p-dioxane was mildly refluxed under an inert atmosphere with continuous stirring for 30 min. 1 mL of silane was then injected into the mixture and was refluxed for 24 hrs. Silane/Na<sup>+</sup>montmorillonite was removed by filtration and washed several times with 5 mL portions of dry p-dioxane to remove excess silanes and was finally dried under vacuum at 25°C.

### E. Physical Methods

### 1. X-ray Diffraction Study

X-ray basal spacings were determined with a Philips X-ray diffractometer or on Siemens Crystalloflex-4 both equipped with Ni filtered CuKa radiation. The film samples were prepared by allowing a suspension of the mineral in a

desired solvent to evaporate on microscope slide and monitoring the diffraction through 2° to 22° of 20. Basal spacings of fully solvated and swelled minerals were obtained by first forming a thin film of mineral on a  $1 \times 1$ in. white, porous fire clay material in place of microscope slide. This sample was then suspended under solvent and allowed to equilibrate for 30 min. The solvent adsorbed in the pores of fire clay material allow it to function as a solvent reservoir and prevented the film from drying during the X-ray diffraction measurements. This is a very convenient method to determine basal spacing of the mineral wetted with a solvent which is very vola-In case of air sensitive compounds the sample was tile. wrapped with a thin polyethylene sheet which also helped to minimize evaporation of solvent. In a blank experiment, no diffraction patterns from microscope slide or fire-clay material was observed in the scanning range of interest. The peak positions in the angle  $2\theta$  were converted to d spacings with a standard chart, (CuK $\alpha$   $\lambda$  = 1.5405 Å).

### 2. Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer Model 457 gratting spectrophotometer. The samples were prepared by using a KBr matrix or mulling the sample in fluorolube and placing the mulls between CsI disks. Mulls of oxygensensitive samples were prepared in a nitrogen filled

glove box just prior to measurement.

### 3. Magnetic Resonance Spectroscopy

The proton magnetic resonance spectra of rhodium complexes at 60 MHz were obtained with a Varian Associates T6055 analytical spectrometer. All spectra were recorded in the normal mode at a radio field frequency strength well below the level required to produce saturation. Chemical shifts are reported in  $\delta$  units. Tetramethylsilane was generally used as internal reference.

Proton decoupled  $^{31}$ P NMR spectra were recorded on a Bruker HFX-10 spectrometer operated at 36.44 MHz. All samples were prepared in a glove box by using degassed, spectroscopic grade methylene chloride, caping the tubes and sealing them with a few turns of plastic tape. A solution of 85% H<sub>3</sub>PO<sub>4</sub> was used as an external reference.

### 4. UV-Visible Spectra

Electronic spectra were recorded on a Varian Associates Model Cary-17 spectrophotometer. Spectra of mineral samples were prepared by mulling in mineral oil and placing the mull between silica disks. A mull sample of native mineral was placed in the reference beam to reduce the effect of scattering. Spectra of solutions were obtained using matched 1 cm path-length quartz cells.

### 5. Thermal Analysis

Enthalpic processes occurring in silane/montmorillonites were recorded with a DuPont 990 thermal analyzer. The analyzer was operated in differential scanning calorimetry mode. The samples were prepared by using non-hermitic, high thermal conductive aluminum pans and covers. DuPont thermal analyzer grade aluminum oxide was used as a reference. Most of the scans were carried out at a constant heating rate of 5°/min in the range of 25° to 500°C.

### 6. Gas Chromatography

Gas phase chromatography of products were performed with Varian Associates Model 90P or 920 single column chromatograph equipped with a thermal conductivity detector. The columns were 10 ft × 1/8 in. 10% UCW-98 (Hewlett-Packard) on 80-100 mesh chromosorb-W, 10 ft × 1/8 in. 10% AgNO<sub>3</sub> in propylene glycol on 80-100 mesh chromosorb-W, 6 ft × 3/16 in.  $\beta$ , $\beta$ ' oxydipropionitrile on 80-100 mesh chromosorb-W and 6 ft × 3/16 in. Durapak (Waters Associates), n-octane/ porasil-C 100/200.

Typically the columns were operated at 30°C with helium as the carrier gas at a flow rate of 35 ml/min. Injector and detector temperatures were 140° and 170°C respectively. The identity of reaction products was confirmed by comparing their retention times with chemically pure authentic samples.
### RESULTS AND DISCUSSION

The catalytic hydrogenation of conjugated 1,3-butadienes was undertaken with [Rh(NBD)(diphos)]<sup>+</sup> as a catalyst precursor under homogeneous conditions and after intercalation in the interlayers of hectorite. The actual catalyst species is proposed to form upon passing hydrogen into the solution of the catalyst precursor in a polar solvent.<sup>77a</sup> Three solvents, acetone, methanol and benzene were used to determine the effect of solvation on the rates of reaction and the product distributions.

Sodium ions in the interlayers of hectorite are readily replaced with [Rh(NBD)(diphos)]<sup>+</sup> cations. The cation exchange capacity of the mineral is 70 meq/100 g. Elemental analysis gave 1.62% Rh, which corresponds to replacement of 22% of the Na<sup>+</sup> ions. The internal surface area covered by the cationic rhodium complexes is 50-60% of the total available area. The remaining interlayer surface area is occupied by sodium ions and solvent. The low loading of complex cation indicates that only a partial monolayer of rhodium complex cation is present in the interlayer regions of the mineral.

The intercalated rhodium complexes were characterized by IR spectroscopy. The infrared spectrum of pure

Rh(NBD)(diphos)<sup>+</sup> exhibits characteristic bands at 1485 and 1439  $\rm cm^{-1}$  which may be assigned to a phenyl group in plane deformation vibration,  $9^4$  (Figure 4A). The IR spectrum of [Rh(NBD)(diphos)]<sup>+</sup>-hectorite in fluorolube mull also exhibits the bands at 1485 and 1439  $\text{cm}^{-1}$ . The IR scan of the intercalated rhodium complex was limited to the 1800-1200  $\rm cm^{-1}$  region because the other regions of the spectrum were dominated by the characteristic IR absorptions of the layered silicate frame work (vSi-0, vAl-0, vO-H),<sup>95</sup> Figure 4B,C. Another indication of the retention of chemical and structural constitution of the metal complex upon intercalation was provided by an electronic spectral study. The absorption observed at 472 nm for the complex in  $CH_2Cl_2$ solution was observed at 466 nm for the intercalated rhodium complex, where the sample was prepared in mull. This band is assigned to a ligand  $\rightarrow$  metal transition.<sup>60c</sup> The small deviation in the  $\lambda_{max}$  between the homogeneous and intercalated rhodium complex can be attributed to the change in solvation environment. The ultra violet  $n-\pi^*$  transitions<sup>96</sup> also are observed for the intercalated complexes, Table 3. Thus, the spectral studies indicate that Rh(NBD)(diphos)<sup>+</sup> retains its constitution in the intercalated state.

The intercalation of  $[Rh(NBD)(diphos)]^+$  in the interlamellar space of Na<sup>+</sup>-hectorite results in an increase in  $d_{001}$  spacing from 12.6 to 18.4 Å, (Figure 5). The increase in spacing most probably is determined by the size of the

	System	Solvent	Band Positions in nm
a.	[Rh(NBD)(diphos)]ClO <sub>4</sub>	CH2C12	472s, 332s, 270s
b.	[Rh(NBD)(diphos)] <sup>+</sup> - hectorite	(mull)	465b <b>,</b> 272b
c.	[Rh(PPh <sub>3</sub> ) <sub>n</sub> ]BF <sub>4</sub>	Methanol	350, 272s, 266s
d.	[Rh(PPh <sub>3</sub> ) <sub>n</sub> ] <sup>+</sup> - hectorite	(mull)	276m
e.	[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	CH <sub>2</sub> Cl <sub>2</sub>	446m, 353b, 271s
f.	[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> - hectorite	(mull)	464m, 355b, 272m

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Table 3. UV-Visible Spectroscopy Data for Cationic Rhodium Complexes and Na-Hectorite Partially Exchanged With These Complexes.

Mull samples were prepared using mineral oil.



- Figure 4. Infrared spectra of Na-Hectorite, [Rh(NBD)-(Diphos)]<sup>+</sup>-hectorite and [Rh(NBD)(Diphos)]-Cl0<sub>4</sub> in the region 1800-1200 cm<sup>-1</sup>.
  - (A) [Rh(NBD)(Diphos)]ClO<sub>4</sub> (B) [Rh(NBD)(Diphos)]<sup>+</sup>-Hectorite
  - (C) Na-Hectorite

- (A) Na-Hectorite (B) [Rh(NBD)(Diphos)]<sup>+</sup>-Hectorite (Dry)
- (C) [Rh(NBD)(Diphos)]<sup>+</sup>-Hectorite Methanol Solvated
- (D) [Rh(NBD)(Diphos)]<sup>+</sup>-Hectorite Acetone Solvated



Figure 5. X-ray diffraction patterns for Na<sup>+</sup>-hectorite partially exchanged with [Rh(NBD)(Diphos)]<sup>+</sup> cations in different solvation conditions. diphos ligand. In the absence of interlayer swelling solvent, the  $\Delta d_{001}$  basal spacing, defined as  $d_{001}$ -thickness of a silicate sheet (9.6 Å), is 8.8 Å (<u>cf</u>., Figure 5). In the presence of a swelling solvent, the interlayers swell to a considerable extent, (Figure 5, Table 4). There is no apparent relationship between solvent polarity and interlayer swelling. However, both the solvation energy of surface and the solvation energy of the cationic complex should contribute to the increase in  $\Delta d_{001}$ .

## A. Hydrogenation of 1,3-Butadienes

#### 1. Homogeneous Hydrogenation

The result for the homogeneous hydrogenation of 1,3butadiene and two of its methylated derivatives, isoprene and 2,3-dimethyl-1,3-butadiene, in methanol, acetone and benzene with [Rh(NBD)(diphos)]<sup>+</sup> as a catalyst precursor are provided in Table 5.

The addition of substrate to a light yellow solution of catalyst was followed by a rapid hydrogen uptake and a color change in the solution to orange. As can be observed from a typical plot of hydrogen uptake <u>vs</u> time (Figure 6A), the rates of hydrogen uptake remained constant until 60-80% conversion of the diolefins to monoolefins. A typical plot for the mole percent composition <u>vs</u> time for reduction of isoprene is provided in Figure 6B. It was

Table 4. 001 X-ray Basal Spacings of Na<sup>+</sup>-Hectorite and Na<sup>+</sup>-Hectorite Partially Exchanged With [Rh(NBD)-(diphos)]<sup>+</sup>.<sup>a</sup>

Mineral	d <sub>001</sub> , Å	۵d <sub>001</sub> , ۸
Na <sup>+</sup> -hectorite	12.6	3.0
[Rh(NBD)(diphos)] <sup>+</sup> - hectorite (dry)	18.4	8.8
[Rh(NBD)(diphos)] <sup>+</sup> -hectorite (acetone solvated)	24.5	14.9
[Rh(NBD)(diphos)] <sup>+</sup> -hectorite (methanol solvated)	21.5	11.9
<pre>[Rh(NBD)(diphos)]<sup>+</sup>-hectorite (benzene solvated)</pre>	18.4	8.8

<sup>a</sup>The percent exchange was 22  $\pm$  1% in all cases.

Table 5.	Homogeneo cursor. <sup>a</sup>	us Hydro	genation of	Butadie	nes with Rh	(NBD)(dppe)	as Catalyst Pre-
Diene	Solvent	Diene Conc. $(\underline{M})$	D1ene/Rh	Rate <sup>b</sup>		Products (	g) c
	Acet.	0.30	280	30		30	
Ţ	МеОН	0.30	280	58		33	67
/	c <sub>6</sub> H6	0.30	590	1030		33	67
	Acet.	0.50	500	760			6 8 1 8
ſ	MeOH	0.50	500	1070	14 14		6 80
/	c <sub>6</sub> H6	0.50	500	870	14		7 79 79
	Acet.	0.50	500	780			+ +
	МеОН	0.30	250	1330		20	80
/	c <sub>6</sub> H <sub>6</sub>	1.00	1050	1000		19	81

+

Table 5. Continued.

Footnotes:

<sup>a</sup>All reactions were carried out at  $25^{\circ}$  and 740 torr.

b<sub>Rates</sub> expressed as mL/min/mmol Rh.

<sup>c</sup>Product analysis was determined after >98% conversion to monoolefin.



Figure 6. (A) Hydrogen uptake plot for the reduction of isoprene in acetone and methanol under homogeneous conditions with [Rh(NBD)(Diphos)]<sup>+</sup> catalyst precursor. (B) Plot of percent composition with time for the reduction of isoprene in acetone under homogeneous conditions with [Rh(NBD)-(Diphos)]<sup>+</sup> complex. observed that the distribution of monoolefins was independent of conversion over the range 10-98%, indicating that the products resulted directly from the overall 1,2 and 1,4 addition of hydrogen to the diene. No alkane formation or isomerization of terminal olefin was observed until all of the substrate diene was consumed. These latter results are consistent with those observed earlier by Schrock and Osborn.<sup>77c</sup>

The rates of hydrogen uptake are solvent dependent. 1,3-Butadiene and isoprene both exhibit high hydrogen uptake rates in each solvent, whereas with 2,3-dimethyl-1,3-butadiene, the rates in methanol and acetone are more than an order of magnitude lower than in benzene. Thus solvation effects can influence reaction rates, at least in case of most highly substituted butadiene derivatives. With all three substrates, the rates of diene hydrogenation are consistently higher in methanol than in acetone. The variation in the rates of diene hydrogenation upon changing solvents was also reported by Schrock and Osborn.77a At present, the solvation properties of homogeneous catalysts are not well understood. Since the catalyst is cationic, the more polar solvent (methanol) should be a better sol-However, the rates of diene hydrogenation are both vent. solvent and substrate dependent, which indicates that the interaction of intermediates or transition states with solvents should be considered for judicious evaluation of

solvent effects.

The monoolefin products are essentially quantitative > 98%. Regardless of the effect of solvent on the absolute rates of reaction, the product distributions are essentially solvent independent, with the internal olefin products (1,4-addition) being strongly favored. The 1,2-addition products of isoprene generally favors the hydrogenation of the double bond containing the sterically less crowded carbon atoms. Hence, the yield of 2-methyl-l-butene is approximately two times that of 3-methyl-l-butene. Although the hydrogenation products of 1,3-butadiene, cis and trans-2-butene, could not be completely resolved by GLC, a partial separation indicated that cis-2-butene was the predominant product. Exclusively cis- olefin was reported as a product by Schrock and Osborn<sup>77c</sup> for the hydrogenation of 2,4-hexadiene. These latter results indicate that the reduction of the conjugated diene is occurring mostly by cisoid coordination to the metal center.<sup>97a</sup>

# 2. Intercalation Catalysts

Table 6 summarizes the results obtained with the intercalation catalyst under conditions identical to those used to investigate the homogeneous reactions. As in the case of homogeneous reactions, the rates of hydrogen uptake were linear up to 60-80% conversion. A 5 min induction period preceded the reduction of 2,3-dimethyl-1,3-butadiene in

Diene	Solvent	Rațe <sup>b</sup>	Prod	ucts (%) <sup>C</sup>	
	,		Ň	$\setminus$ /	$\overline{ \setminus / }$
// \\	Acetone	25	/	45	/ <sub>55</sub> \
	Methanol	4.4		60	40
	Benzene	<0.01			
$\mathbf{N}$			\ \		<b>\</b>
// \\	N		$\parallel \wedge \mid$	/ \\	
	Acetone	300	24	10	66
	Methanol	126	28	16	56
	Benzene	<0.01			
	<b>N</b>		$\parallel $		
•	Acetone	430	32		68
	Methanol	370	39		61
	Benzene	<0.01			

Table 6.	Hydrogenation	of	Butadienes	with	[Rh(NBD)(Dppe)] <sup>+</sup>
	Intercalated i	n I	Hectorite. <sup>a</sup>		

<sup>a</sup>Reaction conditions are identical to those described for analogous Homogeneous Reactions.

<sup>b</sup>MLH<sub>2</sub>/min/mmole Rh.

 $^{\rm C}{\rm Product}$  analysis after <98% conversion.

acetone, and a somewhat longer induction period ( $\sim 25$  min) was observed for this substrate in methanol. None of the other substrates showed an induction period with intercalated catalyst in these two solvents. Typical plots of % composition <u>vs</u> time, for the reduction of isoprene in methanol and acetone are provided in Figure 7.

Pronounced solvent effects on the rates of hydrogenation are observed for each substrate. Essentially no reaction occurs in benzene, even though, this solvent gives uniformly high rates for all three substrates under homogeneous conditions. In addition, the intercalated rates are consistently higher in acetone than in methanol, which is the reverse order of solvent activity found under homogeneous conditions.

Except for 2,3-dimethyl-1,3-butadiene reduction in methanol, overall 1,4 addition is favored over 1,2 addition, but the yields of 1,2 addition products are significantly (almost two times) higher for the intercalation catalyst compared with the homogeneous catalysts. The intercalation catalyst provides consistently higher yields of terminal olefins in methanol than in acetone medium. In contrast, the product distributions are virtually identical in these two solvents under homogeneous reaction conditions.

To obtain an indication of the swelling properties of [Rh(NBD)(dppe)]<sup>+</sup> intercalated hectorite, X-ray powder



Figure 7. Typical percent composition plots for the hydrogenation of isoprene with [Rh(NBD)(Diphos)]+- hectorite (A) in acetone medium (B) in methanol medium.

diffraction measurements were carried out under conditions where the interlayers were solvated by the three solvents used in the catalytic studies. In all cases only one or two orders of 001 reflection were observed, Figure 5, indicating that the interlayers are interstratified. That is, some layers have spacings which are larger or smaller than the value indicated by the first order reflection. The interstratification can be caused by non uniform charge distribution among silicate sheets and by the preferential segregation of Na<sup>+</sup> and [Rh(NBD)(dppe)]<sup>+</sup> ions. Nevertheless, the observed reflections provide a gualitative indication of the extent of interlayer swelling. The position of the first order reflections were as follows: 24.5 Å (acetone), 21.5 Å (methanol), 18.4 Å (benzene). Virtually no swelling occurs with benzene, because the same reflection is observed when no solvent occupies the interlayer regions. Both acetone and methanol, however, swell the interlayer region, with the former solvent being the better swelling agent. Substrate may also play a role in the swelling, as indicated by the induction periods for 2,3-dimethyl-1,3butadiene. However, since the induction period is much shorter with acetone than with methanol, the nature of the solvent probably plays the dominant role in determining the extent of swelling.

The effect of catalyst intercalation on the hydrogenation of butadienes are best compared relative to the homogeneous solution. Relative rates and selectivity towards

1,2 addition are provided in Table 7.

The difference in relative rates for the three different solvent systems can be related to the extent of interlayer swelling. In the case of benzene, the interlayers are not swollen nor sufficiently mobile to permit ready access to the metal centers by even the smallest substrate; consequently, the rates are more than  $10^5$ times lower than in homogeneous solution. However, the relative rates increase greatly when the interlayers are swelled by acetone and methanol beyond the dimensions of the unsolvated intercalate. As the swelling of interlayers becomes larger, the interlayer environment approach that of homogeneous conditions. The interlayer swelling was highest in acetone, consequently, rates of butadiene reduction are faster in acetone than in methanol or benzene mediums.

The size of the substrate molecule relative to the extent of interlayer swelling seems to play some role in determining the differences in relative rates for the methanol- and acetone-solvated systems. The relative rate for 2,3-dimethyl-1,3-butadiene reduction decreases by a factor of ten upon replacing acetone with the poorer swelling solvent methanol, whereas for 1,3-butadiene the relative rates differ by only a factor of two for these two solvents. Thus the smaller substrate has better accessibility to the metal centers.

Diene	Solvent	Relative Rate <sup>a</sup>	Relative Selectivity <sup>b</sup>
	Acetone	0.83	1.5
	Methanol	0.08	1.8
// \\	Benzene	<10 <sup>-5</sup>	
$\mathbf{x}$	Acetone	0.39	1.8
	Methanol	0.12	2.3
// \\	Benzene	<10 <sup>-5</sup>	
	Acetone	0.55	1.6
	Methanol	0.28	2.3
// \\	Benzene	<10 <sup>-5</sup>	·

Table 7.	Relative Rates	and	Selectivity	Towards	1,2	Addi-
	tion Products.					

<sup>a</sup>Intercalated Rate/Homogeneous Rate.

b% Intercalated 1,2 Addition Product/% Homogeneous 1,2 Addition Product.

Substrate size, however, is not the only factor influencing relative rates. Although the relative rates increase with decreasing substrate size when the reaction is carried out in methanol solvated interlayers, no correlation exists between size and relative rate when the interlayers are solvated by acetone. It appears that the spatial requirements of the substrate are important when the extent of swelling is more nearly comparable to the size of the substrate (as with methanol) but other effects, such as differences in solvation between the intercalated and homogeneous states, begin to dominate when the swelling is larger and the interlayer adopt more solution-like character. The potential importance of solvation effects under homogeneous conditions is clearly illustrated by the large difference in absolute rates for 2,3-dimethy1-1,3-butadiene reduction (cf., Table 5) in benzene and methanol or acetone.

The effect of catalyst intercalation on monoolefin product distribution though modest in absolute terms, is significant. Depending upon the substrate and solvent, the yields of 1,2 addition products for the intercalation catalyst are 150 to 230% higher than those under homogeneous conditions. The increase in the fraction of terminal olefin products in the case of 2,3-dimethyl-1,3butadiene are comparable to those induced for this substrate in homogeneous solution when the diphosphine ligand at the rhodium center is replaced by diarsine ligand.<sup>77c</sup>

It is noteworthy that in absolute as well as in relative terms, the 1,2 addition products obtained with the intercalated catalyst are higher in methanol than in acetone. These results indicate that the product distribution with the intercalated catalyst is partially influenced by steric factors and partially by the electronic effect of the charged silicate sheets. Since the product distribution under homogeneous conditions is remarkably independent of solvent polarity ( $\underline{cf}$ ., Table 5), it is unlikely that changes in solvation under intercalated conditions are responsible for the increased yields of terminal olefins.

The hydrogenation of 2,3-dimethyl-l-butene and 2,3dimethyl-2-butene with homogeneous and with intercalated [Rh(NBD)(dppe)]<sup>+</sup>-catalyst precursor in methanol showed no observable isomerization (Table 8). The rates of alkene reduction were almost 1/25 that of the rates of diene reduction, which indicate that the quantitative formation of monoolefin by reduction of diolefin is related to the relative preference of substrate coordination.

The origin of the catalytic activity of cationic rhodium complexes has been discussed by Schrock and Osborn.<sup>77</sup> The mechanism of conjugated diene reduction with [Rh(NBD)-(dppe)]<sup>+</sup> as the catalyst precursor has been shown to involve a coordinately unsaturated pathway in which the diene adds to the metal center before oxidative addition of hydrogen.

Three mechanisms proposed by Schrock and Osborn $^{77}$  for

Table 8. Hydrogenation of 2,3-dimethyl-l-butene and 2,3dimethyl-2-butene in Methanol Under Homogeneous and Intercalated Conditions with [Rh(NBD)(Diphos)] +-Catalyst Precursor.<sup>a</sup>

Substrate	System	Rate <sup>b</sup>	% Isomerization
	Homogeneous	∿2	0
$\succ$	Intercalated	<0.2	0
$\succ$	Homogeneous	<0.2	0

<sup>a</sup>Substrate/Rh = 150, <sup>b</sup>mL H<sub>2</sub> min<sup>-1</sup>(mmol Rh)<sup>-1</sup>. All reactions were carried out at 25°C.

the hydrogenation of olefins, alkynes and diolefins with rhodium complexes are reproduced in Figure 8. The unsaturated pathway (path C in Figure 8) is believed to operate for 1.3-diene reduction. Little is known regarding the structure of the  $[RhH(R)(dppe)]^+$  intermediate which precedes the reductive elimination of the olefin, but  $\eta^3$ -allyl species (1) has been proposed for the homogeneous catalytic reduction of 1,3-dienes.<sup>97</sup> The transfer of hydrogen to the « carbon would lead to overall 1.4 addition, whereas overall 1,2 addition would result from hydrogen transfer to the  $\gamma$  position. A facile  $\eta^3$  to  $\eta^1$ arrangement ( $\pi$ -allyl to  $\sigma$ -alkenyl), analogous to that proposed for syn-anti interchange of  $n^3$ -allyl complexes,  $9^8$ could precede the hydrogen transfer step. In this latter case, the distribution of monoolefine products would be determined by the relative energies of  $n^1$  species 2 and 3, Figure 9.

The reaction mechanism of conjugated diene hydrogenation with the intercalated catalyst, based on the catalyst characterization and reaction pattern, should be similar to that of the homogeneous catalyst. Since the product distribution is determined by the changes occurring at the  $[RhH(R)(dppe)]^+$  stage, the intercalation of the catalyst in hectorite can influence the migration step of second hydrogen in the  $\eta^3$ -allyl intermediate or it may influence the relative energies of the  $\eta^1$  intermediates.







Figure 9. Probable structure of the intermediate [RhH(dppe)]<sup>+</sup>.

Whatever the precise mechanistic details may be, catalyst intercalation decreases the difference in activation free energy for the two transition states which lead to 1,2 and 1,4 addition. For all three substrates investigated, the tendency toward 1,2 addition product is consistently higher for the more constricted methanolsolvated intercalate than for the acetone solvated intermediate. Whether the effect of catalyst intercalation on the distribution of kinetically regulated products result from spatial factors or from polarization effects induced by the charged silicate sheets cannot be determined at this Since the intercalation catalyst is interstratified time. and not uniformly swollen by acetone or methanol, it is possible that only a fraction of the interlayers have the proper spacing or charge density to influence product distribution. Interstratification in hectorite and other naturally occuring layered silicates result in part from non-uniform charge distribution on the silicate sheets.<sup>99</sup> A layered silicate intercalation catalyst with a more uniform charge distribution may lead to more dramatic effects on product distribution.

# B. Hydrogenation of Monoolefins

The cationic metal complex catalyst system selected for the investigation of monoolefin hydrogenation, with layer silicate intercalation catalyst, is one that Legzdins

et al.<sup>25</sup> originally developed for the purpose of hydrogenating olefins that are soluble only in polar media. As discussed earlier in the experimental section, the preparative reaction scheme involved the protonation of rhodium (II) acetate dimer,  $Rh_2(OAC)_4$ , with  $HBF_4$  in methanol, followed by reaction of the protonated product with triphenylphosphine (PPh<sub>3</sub>) and molecular hydrogen. The product of the protonation reaction was believed to be solvated  $Rh_2^{4+}$ ion, which reacted with PPh<sub>3</sub> to form a cationic Rh(I)catalyst precursor of the type  $Rh(PPh_3)_n^+$ . Evidence for cationic complexes was provided in part by the isolation of  $Rh(PPh_3)_3BF_4$  and by the observation that the complexes bind to cation exchange resins and retain their catalytic properties in the resin bound environment.

More recently, Wilson and Taube<sup>100</sup> have noted that  $Rh_2^{4+}$  as prepared by inner-sphere reduction of  $Rh^{(III)}$ -  $(H_2O)_5Cl$  with  $Cr^{2+}$  (aq) has chemical and physical properties different from those claimed for  $Rh_2^{4+}$  by Legzdins <u>et al</u>.<sup>25</sup> This prompted Wilson and Taube to reinvestigate by column chromatography the protonation of  $Rh_2(OAc)_4$  by strong, noncomplexing acids. Their results indicated that protonation of the complex is incomplete, with  $Rh_2(OAc)_3^+$  and  $Rh_2(OAc)_2^{2+}$  being formed in relative amounts that depend on reaction conditions. Neither the triply charged species  $Rh_2(OAc)^{3+}$  nor  $Rh_2^{4+}$  was observed as a reaction product. Based on <sup>1</sup>H NMR studies of the protonation of  $Rh_2(OAc)_4$  by HBF<sub>4</sub> in methanol under the conditions used by Legzdins et al., Hoffman has shown that 30% of the acetate ligands reacted to form methyl acetate.<sup>101</sup> The remaining acetates are distributed between  $Rh_2(OAc)_3^+$  and  $Rh_2(OAc)_2^{2+}$  complexes which are present in 3:1 molar ratio. The addition of PPh<sub>3</sub> to  $Rh_2(OAc)_{4-x}^{x+}$  solution at PPh<sub>3</sub>:Rh = 3:1 results in the loss of all coordinated acetate which can be observed by NMR and IR spectroscopy. Therefore, the transformation of Rh in the reaction system of Legzdins <u>et al</u>. is better described according to the equation:

$$Rh_{2}(OAc)_{4} \stackrel{HBF_{4}}{\rightarrow} Rh_{2}(OAc)_{4-x}^{x+} \stackrel{nPPh_{3}}{\rightarrow} Rh(PPh_{3})_{n}^{+}$$
(1)  
(x=1,2)

It is presumed, based on the analogies to the recent work of Schrock and Osborn<sup>77</sup> (vide infra), that the addition of  $H_2$  to Rh(PPh<sub>3</sub>)<sup>+</sup><sub>n</sub> forms a dihydride, which may exist in equilibrium with a monohydride:

$$RhH_2(PPh_3)_n^{\dagger} \ddagger RhH(PPh_3)_n + H^{\dagger}$$
(2)

These complexes will later be shown to be the most likely species responsible for the observed catalytic activity.

The green  $\operatorname{Rh}_2(\operatorname{OAc})_{4-x}^{x+}$  (x=1,2) complexes, readily displace the interlayer Na<sup>+</sup> ions of the mineral hectorite in methanol suspension. Loadings corresponding to 0.7 to 20%

of the exchange capacity of the mineral ( 73 meq/100 g) could be achieved by adjusting the concentration of  $Rh_2$ - $(OAc)_{4-x}^{x+}$  in contact with the mineral phase. Based on the idealized unit cell formula of the mineral  $[Na_{0.66} (Mg_{5.34}, Li_{0.66}) (Si_{8.0}) O_{20} (OH,F)_4]$  and the a and b cell parameters  $(5.25 \times 9.18 \text{ Å})$ , the average Rh-Rh distance is 20 Å, which should allow ample surface area for formation of  $Rh(PPh_3)_n^+$ complexes (the size of  $Rh(PPh_3)_n^+$  where n = 2 is 12 x 13.5 Å).

The treatment of the green  $\operatorname{Rh}_2(\operatorname{OAc})_{4-x}^{x+}$ -hectorite with methanolic solution of PPh<sub>3</sub> affords yellow-orange  $\operatorname{Rh}(\operatorname{PPh}_3)_n^+$ hectorite. Evidence for the loss of coordinated acetate in the intercalated state is provided by IR spectroscopy. Figure 10 shows the 1800-1200 cm<sup>-1</sup> IR spectrum of Na<sup>+</sup>hectorite solvated by methanol. The replacement of 10% of the Na<sup>+</sup> ions by  $\operatorname{Rh}_2(\operatorname{OAc})_{4-x}^{x+}$  ions gives spectrum 10B in which the bands at 1575 and 1453 cm<sup>-1</sup> are assigned to the symmetric and antisymmetric vibration of coordinated acetate.<sup>102</sup> Upon the addition of PPh<sub>3</sub> to  $\operatorname{Rh}_2(\operatorname{OAc})_{4-x}^{x+}$ hectorite at PPh<sub>3</sub> to Rh ratio of 3:1, the acetate bands are replaced by two new bands at 1485 and 1439 cm<sup>-1</sup>. These latter bands are assigned to the in plane deformation of phenyl rings of PPh<sub>3</sub>.



Figure 10. Infrared spectra (1800-1200 cm<sup>-1</sup>) of methanolsolvated hectorites. (A) Na<sup>+</sup>-hectorite. (B)  $Rh_2(OAc)_{4-x}^{x+}$ -hectorite. (C)  $Rh(PPh_3)_x^{+}$ -hectorite. The rhodium loadings used to obtain spectra B and C (0.76 wt %) correspond to  $\sim 10\%$  of the cation exchange capacity of the mineral.

### 1. Olefin Reduction

 $\operatorname{Rh}(\operatorname{PPh}_3)_n^+$ -hectorite was prepared as a catalyst precursor for the reduction of 1-hexene by adding enough  $\operatorname{Ph}_3$ to a methanol slurry of  $\operatorname{Rh}_2(\operatorname{OAc})_{4-x}^{x+}$ -hectorite so that the average value of n for the surface complex is in the range 2.0-3.0.<sup>27c</sup> A preliminary study of the effect of catalyst loading on the rate of reduction of 1.0 <u>M</u> 1-hexene in methanol showed that the turnover frequency or rate per mmole of rhodium remained constant over the range 0.06-0.7 wt %. At loading above 0.7 wt % the turnover frequency decreased with increasing loading. Thus all reactions were carried out at 0.72 ± 0.04 wt % loading. At this loading v10% of the Na<sup>+</sup> exchange ions have been replaced by rhodium complex. Based on the estimated size of a  $\operatorname{Rh}(\operatorname{PPh}_3)_2^+$ complex (v160 Å<sup>2</sup>, from CPK molecular model), at least 25% of the total surface area is occupied by the complex ion.

The reduction of 1-hexene with  $[Rh(PPh_3)_n]^+$ -hectorite is preceded by a very brief induction period, probably because some time is needed for the concentration of olefin to build up on the interlamellar surface of the mineral. After 100 catalyst turnovers (defined as the moles of substrate hydrogenated per mol of rhodium) the rate of hydrogen uptake achieves a constant value of  $\sim 16$  mL  $H_2 \min^{-1} (mmol Rh)^{-1}$  and remains near this value up to 1200 catalyst turnovers. The constant rate of reaction with increasing substrate conversion may indicate that

physical adsorption forces maintain a constant surface concentration of 1-hexene over the range of solution concentrations examined (1.0-0.40 M), significantly, no observable isomerization of 1-hexene to 2-hexene occur over the observed range of substrate hydrogenation (60%).

The performance of  $Rh(PPh_3)_n^+$ -hectorite as a catalyst precursor for the hydrogenation of 1-hexene is compared in Table 9, with the behavior of homogeneous  $Rh(PPh_3)_n^+$ complexes as precursor for the reduction of the same substrate under analogous reaction conditions. It is observed that at  $PPh_3/Rh = 2.0$ , the homogeneous complex exhibits a much larger initial rate of hydrogenation than the intercalated complex. However, the rate drops off dramatically as the extent of hydrogenation increases. By the time 750 hydrogenation turnovers have been achieved, the rate is less than half of that observed for the intercalated catalyst after 1200 hydrogenation turnovers. Moreover, extensive isomerization of 1-hexene to 2-hexene accompanies the hydrogenation reaction. For example, at 95% conversion of the substrate, 37% of it is hydrogenated and 58% is isomerized. Increasing the PPh, to Rh ratio to 4:1 inhibits the isomerization, but after 94% conversion, the extent of isomerization (34%) is still significant relative to the extent of hydrogenation (60%). The data in Table 9B show that the homogeneous catalyst is much less active for hydrogenation of 2-hexene than 1-hexene, the

Table 9. Catal and H	ytic Hydrog omogeneous	enation of l- Rh(PPh <sub>3</sub> )n <sup>+</sup> Co	Hexene and 2-Hexene mplexes. <sup>a</sup>	in Methanol	. with Intercalated
		(A)	1-Hexene		
Catalyst Syst	еш	PPh3/Rh	Catalyst <sub>b</sub> Turnovers <sup>b</sup>	Rate <sup>c</sup>	% Isomerization <sup>d</sup>
Rh(PPh <sub>3</sub> ) <sup>+</sup> -Hecto	rlte <sup>e</sup>	μ.0	100(5%) <sup>f</sup> 500(25%) 1000(50%) 1200(60%)	16 16 13	, ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^
		6.0	100(5%) 500(25%) 1000(50%) 1200(60%)	17 16 17	↓ ↓ ↓ ↓ ↓ ↓
Homogeneous Sol	n.	2.0	100(5%) 250(13%) 600(30%) 750(37%)	140 140 26	14 51 58
		0.4	100(5%) 480(24%) 850(43%) 1000(50%) 1200(60%)	200 190 54 ~7	14 30 34 84

Catalyst System	PPh <sub>3</sub> /Rh	Catalyst <sub>b</sub> Turnovers	Rate <sup>c</sup>	g Isomerization <sup>d</sup>
Homogeneous Solution (0.07 <u>M</u> HClO <sub>4</sub> )	۲°0	100(5%) 500(25%) 900(45%) 1200(60%) 1600(80%)	240 150 48 ~3	ц ү ү ү <del>ү</del> 81
Homogeneous Solution (0.07 <u>M</u> NEt <sub>3</sub> )	4.0	100(5%) 400(20%) 500(25%) 600(30%)	260 28 28	00205 000
	(B)	2-Hexene <sup>g</sup>		
Catalyst System	PPh3/Rh		Catalyst Turnover	s
Rh(PPh <sub>3</sub> ) <mark>+</mark> Hectorite	4.0 6.0		<20 (<1%) <20 (<1%)	<0.2<0.2
Homogeneous Solution	2.0		100 (5%) 200 (10% 700 (35%)	ч г С Г С
Homogeneous Solution (0.07 <u>M</u> HClO <sub>4</sub> )	4.0		100 (5%)	0.1~

Table 9. Continued.

Table 9. Continued.

Footnotes:

<sup>a</sup>Initial substrate concentration is 1.0  $\underline{M}$  in methanol; initial substrate to Rh ratio is 2000:1; temperature, 25°C.

<sup>b</sup>Defined as moles of substrate hydrogenated per mole of Rh.

<sup>c</sup>Rate of hydrogen uptake, mL H<sub>2</sub>/min/mmol Rh.

<sup>d</sup>Fraction of total l-hexene isomerized to 2- and 3-hexenes.

<sup>e</sup>Rhodium loading is 0.72±.04 wt%.

 $^{
m f}$ Values in parenthesis give the fraction of total substrate that was hydrogenated.  $^{g}$ Hydrogenation data for 2-hexenes were obtained for a <u>cis-trans</u> mixture. initial rates differing by more than a factor of 10. On the other hand, the intercalated complex shows even lower activity for hydrogenation of 2-hexene (Table 9B), relative to 1-hexene. Thus not only does intercalation lead to a dramatic reduction in isomerization during the hydrogenation of a terminal olefin, but also the selectivity of the catalyst for reduction of terminal olefins over internal olefin is enhanced by intercalation. The low activity of the intercalated complex toward 2-hexene is not due to inhibitive complexation effect by the internal olefin since  $Rh(PPh_3)_n^+$ -hectorite can be used to selectively hydrogenate 1-hexene in an equal molar mixture of 1- and 2-hexene.

The difference between intercalated and homogeneous  $Rh(PPh_3)_n^+$  catalyst precursors for olefin hydrogenation may be related to a difference in the position of equilibrium between catalytically active dihydride and monohydride complexes proposed in equation 2. Schrock and Osborn<sup>77</sup> have shown that an equilibrium mixture of  $RhH_2L_n^+$  and  $RhHL_n$  complexes results from the hydrogenation of  $Rh-(diene)L_n^+$  catalyst precursor, where L is a tertiaryphosphine and n = 2 or 3. The hydrogenation of olefin occurs by two different paths (<u>cf</u>. Figure 8). The presence of a Brönsted acid favors the almost colorless cationic di-hydride complexes, which catalyze the hydrogenation of the terminal olefin with little or no isomerization. The neutral deep yellow, monohydride complex which can be generated in

the presence of a sterically hindered base such as NEt<sub>3</sub>, is even a better hydrogenation catalyst, but it also is a good isomerization catalyst. The hydrogenation properties of homogeneous  $Rh(PPh_3)_n^+$  precursors formed from  $Rh_2(OAc)_{x-4}^{x+}$ and PPh3 in the present study are qualitatively identical with those exhibited by the Schrock and Osborn catalysts under acidic and basic conditions. As is shown by the data in Table 9A, the extent of isomerization of 1-hexene under homogeneous hydrogenation conditions is dramatically reduced in the presence of 0.07  $\underline{M}$  HClO<sub>4</sub> and greatly enhanced in 0.07  $\underline{M}$  NEt<sub>3</sub> relative to methanol solution in the absence of acid or base. Moreover, in the presence of 0.07 <u>M</u> HClO<sub> $\mu$ </sub> a <u>cis-trans</u> mixture of 2-hexene is very slowly reduced by  $Rh(PPh_3)_n^+$  precursor at a total PPh<sub>3</sub> to Rh ratio of 4:1 (Table 9B), suggesting that the  $RhH_2(PPh_3)_n^+$  species show a marked preference for reduction of terminal olefins over internal olefins. Thus the catalytic behavior of the intercalated complexes most likely is determined by a surface acidity effect which favors the formation of surface  $RhH_2(PPh_3)_n^+$  over  $RhH(PPh_3)_n$  species. The existence of a surface equilibrium is verified in part by the isomerization of 1-hexene with the intercalated catalyst in the presence of NEt3. The desorption of a yellow rhodium phosphine complex also occurs in the presence of NEt3, but the desorption rate is sufficiently low to allow the observation of surface isomerization of 1-hexene to 2-hexene in the
initial stages of reaction. The desorption product is most likely a neutral  $RhH(PPh_3)_n$  species, because it exhibits the same hydrogenation and isomerization properties as  $Rh(PPh_3)_n^+$  precursor in the presence of NEt<sub>3</sub>.

The surface Bronsted acidity of swelling layered silicate arises mainly from the hydrolysis of the interlayer exchange cations.<sup>80</sup> In the system investigated here, the principal exchange ion is Na<sup>+</sup>, and its hydrolysis, due to the presence of small amounts ( $\sim 0.2$  wt %) of water in methanol, probably determines the surface acidity. The second factor which may have affected the equilibrium in Equation 2 in interlayers of hectorite could be the intrinsic preference of cationic rhodium dihydride complexes over proton which has small charge to radius ratio.

## C. <u>Olefin Reduction with [Rh(NBD)(PPh3)2]</u> Catalyst Precursor

The surface composition can dramatically alter the surface acidity. Variation in the surface acidity at various stages of dehydration for Ca-montmorillonite were shown to be remarkable.<sup>80b</sup> It has been observed in the hydrogenation of 1.0 M l-hexene with  $Rh(PPh_3)_n^+$ -hectorite (<u>cf</u>. Table 9) that after  $\sim 60\%$  conversion of the substrate a rapid isomerization of terminal alkene to internal alkene was initiated. This latter result indicates that the surface composition and hence surface acidity must have changed with 60% conversion of substrate.

Evidence that surface acidity changes with surface composition was obtained by varying the initial concentration of substrate, and wt % water of methanol in the hydrogenation of 1-hexene. The initial concentration of substrate was such that it compared closely to the concentration of substrate that should be present at different percent conversion in the hydrogenation of 1-hexene (1.0  $\underline{M}$ ) with  $Rh(PPh_3)_n^+$ -hectorite precursor.

The catalyst precursor chosen for these studies were  $[Rh(NBD)(PPh_3)_2]^+$  and  $[Rh(NBD)(diphos)]^+$ , previously reported by Schrock and Osborn.<sup>77</sup> The reaction conditions were identical to those used for the  $Rh(PPh_3)_n^+$ -catalyst precursor in the hydrogenation of 1-hexene.

The results for 1-hexene hydrogenation with  $[Rh(NBD)-(PPh_3)_2]^+$ -hectorite as a catalyst precursor in methanol (0.2 wt % water) solution are provided in Table 10. Practically no induction periods were observed. The rates of hydrogen uptake remain constant over 50-60% hydrogenation of 1-hexene initially present in the solution. The absolute rates of hydrogenation increased uniformly from ~150 to 650 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> when the initial concentration of 1-hexene was increased from 0.1 <u>M</u> to 1.2 <u>M</u>. It is possible that rapid mass transfer of substrate from solution into interlayers of hectorite is favored at higher initial concentrations of substrate, consequently a steady increase in the hydrogen uptake is expected. However, at concentrations

[l-Hexene] <u>M</u>	l-Hexene/Rh	Catalyst Turnover <sup>b</sup>	Rate <sup>C</sup>	% Isomeri- zation <sup>d</sup>
0.1	100	20(20%) <sup>e</sup> 40(40%) 70(70%) 80(80%)	155 153 130 91	2 6 14 17
0.4	400	40(10%) 100(25%) 200(50%) 265(65%) 286(70%)	323 370 387 359 180	3 16 26 23 20
0.6	600	60(10%) 140(23%) 220(37%) 305(50%) 362(60%) 372(62%)	503 529 504 478 180 88	9 29 37 39 39 39
0.7	700	100(14%) 220(32%) 350(50%) 420(60%)	670 542 390 368	<1 <1 4 15
0.8	800	118(15%) 286(36%) 395(49%) 510(64%)	851 854 841 757	<1 <1 <1 8
1.0	1000	110(11%) 310(31%) 495(50%) 600(60%)	543 549 546 230	<1 6 17 20
1.2	1200	120(10%) 385(32%) 515(43%) 725(60%) 770(64%)	658 674 697 675 606	<1 15 19 23 22

Table 10.	Catalytic Hydrogenation of 1-Hexene in Methanol
	(0.2% H <sub>2</sub> O), [Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> -hectorite as
	Catalyst Precursor.a

<sup>a</sup>Rhodium loading was  $0.72\pm0.04$  wt%. <sup>b</sup>Defined as moles of substrate hydrogenated per mole of Rh. <sup>c</sup>Rate of hydrogen uptake, mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup>. <sup>d</sup>Fraction of total 1-hexene isomerized to internal alkene. <sup>e</sup>Values in parentheses give the fraction of total substrate that was hydrogenated.

beyond 0.8 M 1-hexene other factors start dominating the The composition of the reaction solutions were reaction. monitored over 5-100% conversion of substrate. It is especially noteworthy that the isomerization of 1-hexene to internal alkene was significantly dependent upon the initial concentration of 1-hexene. At initial concentrations of 1-hexene, in the range of 0.1 M - 0.6 M, isomerization was observed concomitantly with the hydrogenation of 1-hexene. For example, at 50% conversion, almost 20 and 30% of 1hexene was converted to 2-hexene when the concentration of the substrate was 0.4 and 0.6 M, respectively. The plots of percent composition with respect to time are presented in Figures 11-14. Upon increasing the initial concentration of 1-hexene to 0.7 M and beyond a dramatic shift in product formation was observed. Unlike the low initial concentration of substrate, no immediate isomerization of 1-hexene to 2-hexene was observed. For example, at 50% conversion nearly all of the substrate was reduced to hexane for solutions containing 0.7 and 0.8 M 1-hexene. Similar reaction patterns were observed if the initial concentration of 1hexene was increased to 1.0 or 1.2 M. However, at 50% conversion of the substrate about 10-14% isomerization was observed (Figures 13B, 14A). These observations indicate in part the importance of initial surface composition and suggest that surface composition alters the hydrogenation reaction of 1-hexene. Consequently, the equilibrium between



Figure 11. The hydrogenation of 1-hexene (A) 0.1 <u>M</u> (B) 0.4 <u>M</u> with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite in methanol (0.2 wt % H<sub>2</sub>O).



Figure 12. The hydrogenation of 1-hexene (A) 0.6  $\underline{M}$ , (B) 0.7  $\underline{M}$  with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite in methanol (0.2 wt % H<sub>2</sub>0).



Figure 13. The hydrogenation of 1-hexene (A) 0.8  $\underline{M}$ , (B) 1.0  $\underline{M}$  with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite in methanol (0.2 wt % H<sub>2</sub>O).



Figure 14. (A) The hydrogenation of 1-hexene, 1.2 <u>M</u> in methanol (0.2 wt %  $H_2^{(0)}$ ) with  $[Rh(NBD)(PPh_3)_2^+$ hectorite. (B) The hydrogenation of 1-hexene, 0.1 <u>M</u>, under homogeneous conditions with  $[Rh(NBD)(PPh_3)_2]^+$  in methanol (0.2 wt %  $H_2^{(0)}$ ).  $RhH_2(PPh_3)_2^+$  and  $RhH(PPh_3)_2$  on the surface of hectorite is a dynamic process, which also varies with the surface composition.

The rapid decline in the isomerization of 1-hexene upon increasing the 1-hexene concentration from 0.6 to 0.7 <u>M</u> and beyond indicates that there probably is a hysteresis involved which is related to the amount of 1-hexene adsorbed on the surface <u>vs</u> bulk concentration of 1-hexene. It is unlikely that a diffusion controlled induction period is involved before isomerization of 1-hexene occurs when the initial concentration of 1-hexene is greater than 0.7 <u>M</u>. The catalyst is filtered at the end of the reaction and recharged with fresh 0.8 <u>M</u> 1-hexene, an identical reaction pattern was observed. Also, in the case of 0.8 <u>M</u> 1-hexene, if the reaction is stopped at 50% conversion, and the catalyst is filtered and recycled with 0.6 <u>M</u> 1-hexene as a substrate, an immediate isomerization was observed.

The similarity in the hydrogenation reaction of 1-hexene with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite and  $Rh(PPh_3)_n^+$ -hectorite precursors suggest that catalytic species obtained from both systems should be almost identical. However, the reaction rates observed with  $Rh(PPh_3)_n^+$ -hectorite are much lower than those obtained with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite. The reason for the low rates with  $Rh(PPh_3)_n^+$ -hectorite is the presence of excess free triphenylphosphine in solution, which can compete with substrate for coordination sites.

Also excess ligand may limit the pore opening upon physical adsorption on the surface of hectorite. The effect of free triphenylphosphine on the rate of 1-hexene hydrogenation was independently verified by carrying out the hydrogenation of 1.0 <u>M</u> 1-hexene with the  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite precursor and excess triphenylphosphine so that PPh\_3:Rh = 6:1. The rate of 1-hexene reduction in this condition was ^17 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup>, which is nearly 1/200f that in the absence of free triphenylphosphine.

In contrast to  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite as a catalyst precursor, the hydrogenation of 1-hexene with homogeneous  $[Rh(NBD)(PPh_3)_2]^+$  catalyst precursor occurs with extensive isomerization of substrate to internal alkene.

The homogeneous hydrogenation of 1-hexene at various initial concentrations of substrate with the  $[Rh(NBD)(PPh_3)_2]^+$ catalyst precursor in methanol (0.2 wt % water) is presented in Table 11. The initial rates of hydrogen uptake increased from  $\sim 64$  to 340 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> upon increasing the initial concentration of 1-hexene from 0.1 <u>M</u> to 1.0 <u>M</u>, respectively. The rate of hydrogen uptake, however, declines rapidly with increasing conversion of substrate. For example, at 0.6 <u>M</u> 1-hexene the initial rate of hydrogen uptake was 315 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> and then decreased to  $\sim 85$  mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> within 200 catalyst turnovers. The homogeneous hydrogenation of 1-hexene with  $[Fh(NBD)(PPh_3)_2]^+$  catalyst precursor was accompanied by

[1-Hexene] <u>M</u>	l-Hexene/Rh	Catalyst Turnover <sup>b</sup>	Rate <sup>C</sup>	% Isomeriza- tion
0.1	100	10(10%) <sup>e</sup>	57	18
		16(16%)	48	37
		23(23%)	27	59
		25(25%)	13	60
0.6	600	60(10%)	301	16
		150(25%)	247	39
		200(33%)	85	57
		205(34%)	61	59
1.0	1000	50(5%)	296	7
		156(16%)	133	32
		248(25%)	71	51
		320(32%)	47	60

Table ll.	Catalytic Hydrogenation of 1-Hexene in Methanol
	(0.2 wt % Water) Under Homogeneous Conditions
	With [Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> -Catalyst Precursor. <sup>a</sup>

<sup>a</sup>Rhodium loading was 0.72±0.04 wt %.

<sup>b</sup>Defined as moles of substrate hydrogenated per mol of Rh. <sup>c</sup>Rate of hydrogen uptake, mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup>.

<sup>d</sup>Fraction of total 1-hexene isomerized to internal alkene.

<sup>e</sup>Values in parentheses give the fraction of total substrate that was hydrogenated.

extensive isomerization to 2-hexene. As an example, in the hydrogenation of 0.6  $\underline{M}$  l-hexene, at 90% conversion of the substrate, 32% was hydrogenated and 58% was isomerized to internal alkene. Significantly, the percent composition with time in the homogeneous condition is virtually independent of initial concentration of l-hexene, Figures 14B, 15.

The latter results suggest that in the absence of surface acidity a rapid equilibrium between rhodium dihydride and rhodium monohydride complexes can occur. The rapid decline in the homogeneous hydrogenation rate may be related to the fact that extensive isomerization of 1-hexene produces 2-hexene which is reduced at a much lower rate. This phenomenon is very similar to the one observed in the homogeneous hydrogenation of 1-hexene with  $Rh(PPh_3)_n^+$ hectorite precursor.

## 1. The Effect of Water Content of Methanol on the Hydrogenation of 1-Hexene with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> Catalyst Precursor

The surface acidity of smectite minerals are reported to depend upon the amount of interlayer water, which was reported to increase upon removal of interlayer water.<sup>80</sup>

Therefore, to obtain an indication of the effect of surface acidity on the equilibrium between rhodium dihydride and rhodium monohydride complexes, the hydrogenation of



Figure 15. The hydrogenation of 1-hexene (A) 0.6  $\underline{M}$ , (B) 1.0 M, under homogeneous conditions with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in methanol (0.2 wt % H<sub>2</sub>O).

1-hexene was carried out with the homogeneous and intercalated  $[Rh(NBD)(PPh_3)_2]^+$  catalyst precursors in methanol solution containing 0.1, 0.2, 0.5 and 1.0 wt % water. The initial concentration of 1-hexene in each case was maintained at 0.8 <u>M</u>. This concentration was chosen in part because a minimum amount of isomerization of 1-hexene was observed when the water content is 0.2 wt %. Any dependence of product distribution on water content may be linked to the change in surface composition and, hence, surface acidity.

The results of these experiments for the hydrogenation of 1-hexene is provided in Table 12. At a water content 0.1 wt % in methanol, the rate and product distributions are similar to those obtained when water content of methanol was 0.2 wt %. However, when the water content was increased to 0.5 and 1.0 wt %, a significant reduction in the rates of hydrogen uptake was observed. For example, the rate of 1-hexene hydrogenation was 85 mL  $\rm H_{2}\ min^{-1}\ (mmol\ Rh)^{-1}$ at 1.0 wt % water in methanol and  $\sim$ 530 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> when the water content was 0.1 wt %. Also, the isomerization of substrate to internal alkene accompanied hydrogenation. At 50% conversion of substrate, 25% of the substrate was hydrogenated and 25% was isomerized to 2hexene when the water content of the solution was 1.0% (Figure 16,17). Once all of the substrate was consumed, some desorption of rhodium complex (<5%) was observed, when the water content was 0.5 and 1.0 wt %.

Catalyst Sys	% Water in tem Methanol	Catalyst Turnover	Rate	% Isomeri- zation
[Rh(NBD)(PPh <sub>3</sub> Hectorite	) <sub>2</sub> ] <b>+-</b> 0.1	40( 5%) 200(25%) 320(40%) 400(50%) 455(57%) 480(60%)	593 553 548 536 242 117	<1 <1 <1 10 15 16
	0.5	40( 5%) 120(15%) 200(25%) 280(35%) 320(40%)	79 82 60 35 24	3 11 20 31 34
	0.2	118(15%) 286(36%) 395(49%) 510(64%)	851 854 841 757	<1 <1 <1 8
	1.0	40( 5%) 130(16%) 200(32%) 255(32%) 330(41%)	90 77 59 40 11	6 19 25 29 31
Homogeneous	0.2*	50( 5%) 156(16%) 248(25%) 320(32%)	296 133 71 47	7 32 51 60
	0.5	62( 8%) 120(15%) 200(25%) 320(40%) 400(50%)	304 248 187 124 76	23 26 42 44 43

Table 12. Catalytic Hydrogenation of 1-Hexene, 0.8 M Under Intercalated and Homogeneous Conditions with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>-Catalyst Precursor in Methanol Containing Varying Amounts of Water.<sup>a</sup>,<sup>b</sup>

Table 12. Continued.

Catalyst System	% Water in Methanol	Catalyst Turnover	Rate	% Isomeri- zation
Homogeneous	1.0	70(9%) 125(18%) 200(25%) 320(40%) 380(48%)	255 221 172 82 41	15 27 48 45 45

 $a_{1-\text{Hexene/Rh}} = 800.$ 

<sup>b</sup>Catalyst loading in each case 0.72±0.04 wt % Rh.

\* 1-Hexene/Rh in this case was 1000. All other conditions are the same as Table 10.



Figure 16. The hydrogenation of 1-hexene, 0.8 M, with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite in methanol containing (A) 0.1 wt % H<sub>2</sub>O (B) 0.5 wt % H<sub>2</sub>O.



Figure 17. The hydrogenation of 1-hexene, 0.8  $\underline{M}$ , with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>-hectorite in methanol containing 1.0 wt  $\frac{1}{3}$  water. Varying the amount of water present in methanol appears to have very little effect on the performance of the homogeneous catalyst until almost 75 to 80% conversion of substrate, at which point an increase in the hydrogenation rate of 2-hexene was observed (Figure 18). The increase in the hydrogenation rate may be related to a solvation effect. The solvation of the cationic rhodium complex should differ in methanol with low or high water content.

The hydrogenation product, hexane, apparently has little effect on the surface acidity. When the hydrogenation of  $0.8 \ M$  and  $0.6 \ M$  l-hexene in methanol (0.2 wt % water) was carried out with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite in the presence of  $0.2 \ M$  hexane (Table 13), a brief 10 min induction period preceded the hydrogen uptake and the rates of hydrogenation were low. However, no difference was observed in the product distribution relative to the results obtained in the absence of added hexane (<u>cf</u>., Table 10). Hexane appears to have little tendency to remain in the interlayers long enough to significantly influence surface acidity.

The hydrogenation of 0.6 <u>M</u> 1-hexene with  $[Rh(NBD)-(PPh_3)_2]^+$ -hectorite in the presence of 0.2 <u>M</u> 2-hexene (another product), (Table 13), was preceded by a somewhat longer ( $\sim$ 20 min) induction period. Even though, only 17% of the 1-hexene was isomerized to 2-hexene at 50% conversion, the isomerization still accompanies the hydrogenation from the beginning. The reason for the somewhat longer induction



Figure 18. The hydrogenation of 1-hexene, 0.8 <u>M</u>, with [Rh(NBD)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex under homogeneous conditions in methanol containing (A) 0.5 wt % H<sub>2</sub>O (B) 1.0 wt % H<sub>2</sub>O.

ראר) ( אח ( אח ( אשט ) ( איז	n3)2] -catalys	Precursor.			
Catalyst System	Solvent	[1-Hexene] <sup>a</sup> <u>M</u>	Catalyst <sup>b</sup> Turnover	Rate <sup>c</sup>	% Isomeri- zation <sup>d</sup> ,e
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> - Hectorite <sup>f</sup>	Methanol <sup>g</sup> + 0.2 <u>M</u> 2-hexene	0.6 (600)	10(2%) <sup>h</sup> 65(11%) 162(27%) 240(40%) 330(55%) 400(67%)	1120 1030 1030 1030 1030	1221 2001 2001 2001
	Methanol + 0.2 <u>M</u> Hexane	0.8 (800)	24(3%) 56(8%) 136(17%) 230(29%) 315(39%) 400(50%)	108 1959 1958 1949	33122212 331222 331222
	Methanol + 0.2 <u>M</u> Hexane	0.6 (600)	92(15%) 202(34%) 250(42%) 300(50%)	449 464 812 812	០ ឆ ហ ហ ហ ល ហ ហ
	Hexane	0.8 (800)	24(3%) 54(7%) 122(15%) 200(25%) 255(32%)	3337 119 19 19	300 300 300 300 300 300 300 300 300 300
Homogeneous	Hexane	0.8 (800)	24(3%) 90(11%)	ى ھ	: :

Catalytic Hydrogenation of l-Hexene with Intercalated and Homogeneous Table 13.

Table 13. Continued.

Footnotes:

 $^{
m h}$ Values in parentheses give the fraction of total substrate that was hydrogenated. <sup>b</sup>Defined as moles of substrate hydrogenated per mol of Rh. <sup>d</sup>Fraction of total 1-hexene isomerized to internal alkene. <sup>a</sup>Values in parentheses give the 1-hexene/Rh ratio. <sup>c</sup>Rate of hydrogen uptake, mL H<sub>2</sub>/min/mmol Rh.  $^{\rm g}$  water content of methanol was 0.2 wt m g. fRhodium loading is  $0.72\pm0.02$  wt % Rh. <sup>e</sup>Values are after normalization.

period may be related to the kinetics of 1-hexene coordination with metal center.

The intercalated catalysts can be used even when the solubility of the metal complex prohibits its use under homogeneous reaction conditions. For example, the hydrogenation of 1-hexene (0.8 M) with  $[Rh(NBD)(PPh_3)_2]^+$ -hectorite can be carried out in hexane as a solvent. However, the rate of hydrogenation was very low (Table 13). To carry out the same reaction under homogeneous conditions in hexane is not practicable due to the negligible solubility of the cationic rhodium complex in hexane.

## 2. <u>Hydrogenation of 1-Hexene with [Rh(NBD)(Diphos)]</u><sup>+</sup> <u>Catalyst Precursor</u>

Additional evidence that changes in surface composition are responsible for the observed differences in the reactivity of the homogeneous and intercalated catalysts was obtained by substituting the monodentate triphenylphosphine ligands in the catalyst precursor with a bidentate ligand, bis(diphenylphosphino)ethane. The replacement of the monodentate ligands by a bidentate ligand in the rhodium complex forces both phosphorus atoms to occupy <u>cis</u> positions. Consequently, the hydrogenation mechanism differs significantly from that of the hydride mechanism.<sup>77</sup> It is proposed that in the presence of a bidentate ligand, the equilibrium between dihydride and monohydride rhodium complexes does

not occur. Hence, a change in surface composition with variation in initial concentration of substrate should not effect the product formation in hydrogenation of 1hexene.

The results of 1-hexene hydrogenation with  $[Rh(NBD)-(diphos)]^+$  under homogeneous and intercalated catalyst precursor are provided in Table 14. In homogeneous solution, an extensive and very rapid isomerization of substrate to 2-hexene was observed. For example, at 80% conversion of substrate, 68% was converted to 2-hexene and 12% was hydrogenated to hexane. The initially high rate of 233 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> drops off rapidly to 76 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup> within 60 turnover of catalyst. It is significant that the initial rates of hydrogen uptake or 1-hexene isomerization are almost independent of the initial solution composition (Figure 19, 20).

Table 14 contains the results of 1-hexene hydrogenation with  $[Rh(NBD)(diphos)]^+$ -hectorite as the catalyst precursor. In each case a brief, 10 min, induction period preceded hydrogen uptake. The initial rates of hydrogen uptake were slow, but the rate attained an optimum value within 20% conversion of substrate and remained constant until almost all the substrate was converted to products. For example at 0.4 <u>M</u> initial concentration of 1-hexene the optimum rate of hydrogen uptake was 14 mL H<sub>2</sub> min<sup>-1</sup> (mmol Rh)<sup>-1</sup>. The optimum rates of 1-hexene hydrogenation increased from 14

Homo- Precur-
<pre>in Methanol (0.2 wt % H<sub>2</sub>O) Under with [Rh(NBD)(diphos)]+2catalyst</pre>
Catalytic Hydrogenation of l-Hexene geneous and Intercalated Conditions sor.
Table 14.

Catalyst System	[1-Hexene] <sup>a</sup> <u>M</u>	Catalyst Turnover <sup>b</sup>	Rate <sup>c</sup>	% Isomeri- zation <sup>d</sup>
[Rh(NBD)(diphos)] <sup>+</sup> - Homogeneous Solution	0.4 (400)	24( 6%) <sup>f</sup> 40(10%) 80(20%) 112(28%) 150(38%)	143 120 28 88 88	20 65 72 62
	0.8 (800)	40(5%) 123(15%) 200(25%) 274(34%) 320(40%)	ト 50 15 50 75 50 75 50 75 50 75 50 75 50 75 50 75 50 75 50 75 50 75 75 75 75 75 75 75 75 75 75 75 75 75	20 667 80
	1.2 (1200)	74( 6%) 169(14%) 250(21%) 345(29%) 435(36%) 505(42%)	246 936 947 1122 1122	19 718 64 78
[Rh(NBD)(diphos)] <sup>+</sup> - Hectorite <sup>e</sup>	0.4 (400)	20(5%) 80(20%) 112(28%) 144(36%) 180(45%)	чччч 04 РРИ	11 22 45 7 54

Continued.	
14.	
Table	

Catalyst System	[1-Hexene] <sup>a</sup> <u>M</u>	Catalyst Turnover <sup>b</sup>	Rate <sup>c</sup>	% Isomeri- zation <sup>d</sup>
[Rh(NBD)(diphos)] <sup>+</sup> - Hectorite <sup>e</sup>	0.8 (800)	25(3%) 95(12%) 154(19%) 240(30%) 300(38%) 340(43%)	12 22 122 192	±030080
	1.2 (1200)	60(5%) 225(12%) 350(29%) 453(38%) 515(43%) 542(45%)	чч <i>с</i> мен 4 <i>0</i> 007600	лч 847 170 89 4 17 60
allo 100 dr noront horses	hovere/Dh			

Values in parentheses give 1-hexene/Rh.

<sup>b</sup>Defined as moles of substrate hydrogenated per mole of Rh.

<sup>c</sup>Rate of hydrogen uptake mL H<sub>2</sub> min/mmol Rh.

<sup>d</sup>Fraction of total 1-hexene isomerized to internal alkene.

<sup>e</sup>Rhodium loading was 0.72±0.04 wt %.

 $^{
m f}$ Values in parentheses give the fraction of total substrate that was hydrogenated.



Figure 19. The hydrogenation of 1-hexene, (A) 0.4 M, (B) 0.8 M, under homogeneous conditions with [Rh(NBD)(Diphos)]<sup>+</sup> complex in methanol, (0.2 wt % water).



Figure 20. (A) The hydrogenation of 1-hexene, 1.2 M, with [Rh(NBD)(Diphos)]<sup>+</sup> under homogeneous conditions in methanol (0.2 wt % H<sub>2</sub>O). (B) The hydrogenation of 1-hexene, 0.4 M, with [Rh(NBD)-(Diphos)]<sup>+</sup>-hectorite in methanol (0.2 wt % H<sub>2</sub>O).

to 22 and 39 mL  $H_2 \min^{-1} (mmol Rh)^{-1}$  upon increasing the initial concentration of 1-hexene from 0.4 to 0.8 and 1.2 <u>M</u> respectively. The rate dependence on concentration may be accounted for by the mass action on the transfer of substrate from solution to the interlayer region of the mineral. It is noteworthy that the intercalation of the catalyst has significantly reduced the isomerization of substrate to 2-hexene. For example, at 50% conversion of 0.4 <u>M</u> 1-hexene, 28% was isomerized to 2-hexene and 22% was hydrogenated to hexane. The product distribution is almost independent of the amount of 1-hexene initially present in solution (Figure 20B, 21). Relative to homogeneous reaction, the hydrogenation of 2-hexene with the intercalated catalyst is much slower.

The effect of catalyst intercalation is most evident in the hydrogenation of 1-hexene with  $[Rh(NBD)(PPh_3)_2]^+$ as a catalyst precursor. The difference observed between the intercalated and homogeneous catalysts, most likely is related to the effect of silicate surface composition on the equilibrium between  $RhH_2(PPh_3)_2^+$  and  $RhH(PPh_3)_2$ . The effect of catalyst intercalation on this equilibrium is mostly due to the surface Brönsted acidity and its variation with interlayer composition.

The surface Brönsted acidity of layered silicate arises mainly from the hydrolysis of interlayer exchange cations. The principal exchange ion of the layered silicate, in





this study, is Na<sup>+</sup> and its hydrolysis is due to the presence of small amount of water in methanol. Although the hydrated Na<sup>+</sup> ion is very weakly acidic in solution, its activity is greatly enhanced on negatively charged layered silicate surfaces. The surface acidity is proposed to depend upon the nature of the cation and the charge on the silicate sheets. Also, the surface acidity of the hydrated cations is greatly affected by the amount of water present in the interlayer regions. For example, if the amount of interlayer water is reduced in the presence of a given cation, enhanced surface acidity is observed. The increase in surface acidity is manifested by an increase in  $NH_{\mu}^{+}$  formation when the mineral exposed to NH<sub>3</sub> vapor.<sup>80b</sup> The polarizing effect of the exchangeable cation increases as the number of coordinated water molecules around it decreases upon dehydration. When a great deal of water is present, the polarization forces of the exchangeable cations may be distributed among a large number of water molecules, and the acidity of such a system might approach that of the ions in an aqueous solution. However, as the water content is decreased polarization forces become more concentrated on the fewer remaining water molecules, causing an increase in hydrolysis and in their proton donating abilities.<sup>80b</sup>

The differences observed in the catalytic activity of homogeneous and intercalated  $[Rh(NBD)(PPh_3)_2]^+$  catalyst precursor can best be deduced by comparing the product

distribution at 50 and 90% conversion of 1-hexene, (Table 15).

Regardless of the initial concentration of substrate, the percent hydrogenation at 50 and 90% conversion are consistently higher under intercalated catalyst conditions than under homogeneous conditions. Therefore, based on reaction mechanism proposed by Schrock and Osborn,<sup>77</sup> the catalytic hydrogenation catalyst probably occurs by the reaction of substrate with  $[RhH_2(PPh_3)_2]^+$ .

The dramatic dependence of product distribution, at 50% conversion of substrate, on initial concentration of 1hexene indicates that the equilibrium that affects the intercalation catalyst, takes place immediately upon the addition of substrate to the reaction system. The absence of an induction period precludes the diffusion of substrate in the interlayers as an important factor.

It is possible that at higher initial concentrations of 1-hexene ( $\geq 0.7 \text{ M}$ ) the intercalated catalyst experiences dielectric effect that is significantly different than at lower concentration ( $\leq 0.6 \text{ M}$ ) of substrate. The dielectric effect may change considerably along with the consumption of substrate.

As discussed earlier, the surface acidity and the equilibrium between  $[RhH_2(PPh_3)_2]^+$  and  $RhH(PPh_3)_2$  may depend on surface composition. The origin of the dielectric effect and the position of the dihydride-monohydride

Table 15. Product L and Inter wt % H <sub>2</sub> 0)	istribution fo calated [Rh(NB	r the Hydrogena D)(PPh <sub>3</sub> ) <sub>2</sub> ]+-Cata	tion of l-Hex alyst Precurs	ene with Homoge or in Methanol	neous (0.2
		50% Convei	rsion	90% Conve	rsion
System	[l-hexene] <u>M</u>	% Hydrogena- tion	% Isomeri- zation	% Hydrogena- tion	% Isomeri- zation
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> -	0.1	84	16	80	20
hectorite	0.4	60	40	72	28
	0.6	4 4	56	58	42
	0.7	96	<b>4</b>	1 t	26
	0.8	96	4~	79	21
	1.0	75	25	73	27
	1.2	70	30	73	27
Homogeneous Solution	0.1	30	70	32	68
	0.6	38	62	39	61
	1.0	32	68	33	67

equilibrium may be related to the adsorption of substrate in the interlayers. The adsorption of 1-hexene on the interlayer surface should replace some of the interlayer water and solvent. The replacement of some of the solvent and water molecules can lead to higher polarization of the remaining molecules by interlayer cations, and thus enhance surface acidity. However, as the substrate is consumed the above process may be reversed, allowing formation of  $RhH(PPh_3)_2$  which can initiate the immediate isomerization of 1-hexene to internal alkene.

At higher initial concentrations between 0.7 and 1.2 M 1-hexene the polarization forces in interlayers may be such that [RhH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> is primarily preferred in the interlayer regions. Consequently, very little isomerization of substrate occurs until 50% conversion. At 50% conversion of 0.8 - 1.2 M l-hexene, the effective concentration of 1-hexene in solution should be 0.4 - 0.6 M. At this point the isomerization was observed. As a result, significant internal alkene was observed at 90% conver-The hydrogenation of 1-hexene at concentrations sion. between 0.1 and 0.6 M is accompanied by isomerization of substrate to internal alkene. The product distribution at 90% conversion indicates that the rates of isomerization in all cases are significant. These facts suggest that the isomerization occurs with a catalyst species which is identical to that of homogeneous solution, most probably

the neutral RhH(PPh<sub>3</sub>)<sub>2</sub> species.

A comparison of the percent composition at 50 and 90% conversion of 1-hexene under homogeneous conditions with that of intercalated catalyst, at various initial concentration, indicated that in the absence of strong polarization effects (surface acidity) the product distribution remains essentially identical in each case (Table 15). It appears that under homogeneous conditions an immediate equilibrium between  $[RhH_2(PPh_3)_2]^+$  and  $RhH(PPh_3)_2$  must occur so that the catalytically more active neutral  $RhH(PPh_3)_2$  complex determines the solution products. Consequently, isomerization of substrate is nearly twice that of hydrogenation.

Strong support in favor of surface acidity effects in reaction of 1-hexene was provided by the effect of water present in methanol under intercalated catalyst. Increasing the amount of water in the interlayers (0.5 - 1.0 wt %)water in methanol) caused isomerization of 0.8 M 1-hexene even at the beginning stages of reaction. As a result, at 50% conversion of substrate the percent of both isomerization and hydrogenation products in solution were almost identical (Table 16). This indicates that even at higher concentration of 1-hexene (0.8 M) the effective surface acidity is determined by water molecules in the interlayers. However, at low water content (0.1 and 0.2 wt %) the surface acidity is mainly determined by adsorption of 1-hexene on the surface and by the percent conversion

Table 16. Product D1 Intercalat Varying Am	stribution ed [Rh(NBD ounts of W	for the Hydrog )(PPh <sub>3</sub> ) <sub>2</sub> ]+-Cata ater.	cenation of 1- ilyst Precurso	Hexene with Hom r in Methanol C	ogeneous and ontaining
		50% Conv	rersion	90% Conve	rsion
System	% Water	% Hydrogena- tion	% Isomeri- zation	% Hydrogena- tion	% Isomeri- zation
[Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> -	0.1	96	7	76	24
hectorite	0.2	96	ħ	79	21
	0.5	56	t1 t1	69	31
	1.0	50	50	66	34
Homogeneous Solution	0.2*	32	68	33	67
	0.5	35	65	52	48
	1.0	34	66	50	50
<sup>a</sup> In all cases initial	concentrat	tion of 1-hexen	le was 0.8 <u>M</u> .		
* In this case initial	concentra	tion of l-hexen	ie was 1.0 $\underline{M}$ .		

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of substrate.

The linearity of hydrogen uptake and the absence of any dependence of OOl X-ray basal spacing on 1-hexene concentration, in the hydrogenation of 1-hexene with  $[Rh(NBD)-(PPh_3)_2]^+$ -hectorite, suggest that the effect of intercalation on catalyst is most probably a consequence of surface composition and not of any apparent phase change during reaction.

The results of 1-hexene hydrogenation with homogeneous and intercalated [Rh(NBD)(diphos)]<sup>+</sup> catalyst precursor suggest that the hydrogenation of the terminal alkene with this catalyst is occurring by a mechanism which is different from the mechanism which operates with  $RhH_2(PPh_3)_2^+$ or RhH(PPh3)2. The reaction mechanism for the hydrogenation of olefin by [Rh(NBD)(diphos)]<sup>+</sup> catalyst precursor is expected to follow the coordinatively unsaturated pathway as proposed by Schrock and Osborn.<sup>77</sup> According to this pathway the olefin coordinates to [Rh(diphos)]<sup>+</sup> prior to the oxidative addition of the hydrogen molecule. In this situation almost no or very little isomerization of terminal alkene is expected. However, the extensive isomerization of substrate observed in homogeneous solution as well as with the intercalated catalyst suggest that [RhH(diphos)]<sup>2+</sup> is the most likely catalytically active species present in solution. According to Halpern <u>et al</u>.<sup>103</sup> [RhH(diphos)]<sup>2+</sup> can occur on oxidative addition of one hydrogen to

[Rh(diphos)]<sup>+</sup> prior to olefin coordination to the rhodium center. The formation of [RhH(diphos)]<sup>2+</sup> may be responsible for the isomerization of the olefin by a mechanism analogous to that proposed for RhH(PPh3)2. Schrock and Osborn have shown that the rates of homogeneous hydrogenation of diolefins with [Rh(NBD)(diphos)]<sup>+</sup> were apparently not affected by addition of acid or base, which substantiated the unsaturated path mechanism proposed to explain hydrogenation of diolefins. It was expected that if unsaturated pathway is acting in the hydrogenation of 1hexene with [Rh(NBD)(dppe)]<sup>+</sup> then the addition of a small amount of acid or base should have very little effect on the performance of catalyst in homogeneous solution. However, the homogeneous hydrogenation of 1-hexene with  $[Rh(NBD)(diphos)]^+$  in the presence of 0.07 <u>M</u> HClO<sub>1</sub> or 0.07 <u>M</u> NEt<sub>3</sub> occurs at lower rate of hydrogen uptake and with decreased isomerization. If [RhH(diphos)]<sup>2+</sup> is presumed to be an active species, then the presence of  $HClO_4$  should inhibit the formation of RhH(diphos)<sup>2+</sup>. Therefore a lower rate of 1-hexene hydrogenation as well as a lower rate of isomerization is expected. However, the effect of triethylamine, which should actually enhance both the formation of [RhH(diphos)]<sup>2+</sup> and isomerization is not expected.

It is possible that the difference observed for the hydrogenation of 1-hexene with [Rh(NBD)(diphos)]<sup>+</sup> under homogeneous and intercalated conditions most probably is a

combination of electronic effect due to the negatively charged silicate layers and a steric effect due to the constrained interlayer environment.

These studies strongly indicate that the effect of catalyst intercalation on the catalytic activity of  $[Rh(NBD)-(PPh_3)_2]^+$ , arises mainly from surface composition and surface acidity effect. However, an intrinsic stabilization of rhodium dihydride complexes in the interlayers can also play some role. It is possible that mineral prefers binding cationic rhodium dihydride complex over the dis-sociation product proton as shown in Equation 3.



The stabilization of the rhodium dihydride complex would be aided by the presence of surface Brönsted acidity. The equilibrium constant between  $[RhH_2(PPh_3)_2]^+$  and  $RhH(PPh_3)_2$  in interlayers of hectorite cannot be determined due to the limitation of present techniques. However, these studies have indicated that the role played by surface compositions is very critical whenever protonic equilibria are involved in the given reaction. Whether the effect is solely a result of surface acidity or some synergistic contribution from electronic as well as steric effects needs further exploration.

## D. Alkyne Hydrogenation

 $Rh(PPh_3)_n^+$  complexes are also catalyst precursors for the reduction of alkynes to the corresponding <u>cis</u> olefins. The stereoselectivity of the reaction via a monohydride or dihydride mechanism has been discussed by Schrock and Osborn.<sup>77c</sup> Typical hydrogen uptake rates for reduction of 1-, 2-, and 3-hexyne under homogeneous and intercalated conditions are compared in Table 17.

The data for 1-hexyne (Table 17A) show that at  $PPh_3$ : Rh = 3:1 the activity of the homogeneous catalyst decreases rapidly with increasing substrate conversion. For example, the rate approaches zero after only 1000 catalyst turnovers or 50% conversion. The longevity of the homogeneous catalyst, however, is greatly improved by increasing the  $PPh_3$ :Rh ratio to 6:1. These results are similar to the results for hydrogenation of 1-hexene with  $[Rh(PPh_3)_n]^+$ 

		l-Hexyne	, //	
	<sup>PPn</sup> 3/1	n = 3	<sup>PPn</sup> 3/1	n = 0
Catalyst Turnovers	Inter- calated	Homo- geneous	Inter- calated	Homo- geneous
100	1400	1200	2100	2100
250	1300	1000	2000	2100
500	1100	630	1700	1900
750	900	310	-1600	1800
1000	830	70	1500	1700
1250	750	0	1400	1700
1500	630		1200	1600

Table 17. Hydrogen Uptake Rates for Reduction of 1-, 2-, and 3-Hexyne with Intercalated and Homogeneous Rhodium Triphenylphosphine Catalyst Precursors.<sup>a</sup>

Β.	2-Hexyne
-	

	PPh <sub>3</sub> /I	Rh = 3	PPh <sub>3</sub> /H	Rh = 6
Catalyst Turnover	Inter- calated	Homo- geneous	Inter- calated	Homo- geneous
100	2200	1700	2200	2400
250	2100	1800	2000	2300
500	1900	1800	1900	2400
750	1800	1700	1700	2400
1000	1700	1600	1600	2400
1250	1500	1500	1600	2300
1500	1200	1300	1300	1600

Table 17. Continued.

	С.	3-Hexyne		
	PPh3/I	Rh = 3	PPh3/1	Rh = 6
Catalyst Turnovers	Inter- calated	Homo- geneous	Inter- calated	Homo- geneous
100	330	1100	360	1800
250	370	1100	350	1700
500	380	1100	330	1700
750	370	980	330	1700
1000	340	800	310	160 <b>0</b>
1250	280	490	270	1500
1500	190			1400

<sup>a</sup>Initial substrate concentration is 1.0 <u>M</u>; initial substrate to Rh ratio is 2000:1; temperature,  $25^{\circ}\overline{\text{C}}$ . Rates are reported as mL H<sub>2</sub>/min/mmol Rh. Rhodium loading of the intercalated catalysts is  $0.72\pm0.04$  wt %.

complexes. The isomerization of 1-hexene was decreased and the rate remained constant over 50% conversion of substrate when the PPh, to Rh ratio was 6:1. In contrast to the behavior of the homogeneous catalyst system, the intercalated system at  $PPh_3:Rh = 3:1$  retains significant activity even after 1500 turnovers. The difference in performance between the homogeneous and intercalated system is more clearly illustrated by the hydrogen uptake plots shown in Figure 22. Upon the addition of fresh substrate at the times indicated in Figure 22, the activity of the homogeneous catalyst was not restored, whereas the initial rate for the intercalated system returns to about 70% of its original value. It is unlikely that the difference in longevity is due to a difference in reactivity toward trace amounts of oxygen or other oxidants, because the homogeneous and intercalated catalysts both undergo deactivation instantaneously when oxygen or unpurified substrate is deliberately added to the reaction systems. Moreover, an analogous inactivation of homogeneous  $RhL_n^+$  catalyst precursor by relatively acidic terminal alkynes has been observed independently by Schrock and Osborn.<sup>77c</sup> These workers suggested one possible mechanism for inactivation for the formation of complexes containing Rh-CECR bonds. Whatever the mechanisms of inactivation may be, it is significantly inhibited by the intercalation of the catalyst in layered silicates.



Figure 22. Hydrogen uptake plots for reduction in methanol of 1-hexyne to 1-hexene with homogeneous and intercalated rhodium triphenylphosphine complexes. The arrows indicate the times at which fresh substrate was added. In both catalyst systems the initial substrate concentration is 1.0 M, the substrate to rhodium ratio is 2000:1, the total PPh<sub>3</sub> to Rh ratio is 3:1 and the temperature range is 25°C.

The initial rates of hydrogen uptake for the reduction of 2-hexyne with the intercalated complex are similar to those observed for the homogeneous catalyst (Table 17B), but in the case of 3-hexyne as substrate the initial intercalated rates are three to five times lower than the homogeneous rates (Table 17C). These results for 3-hexyne suggest that spatial factors may be important in determining the activity of the intercalated catalyst. The importance of spatial factors is further indicated when the initial rates for reduction of 1-, 2-, and 3-hexyne, along with those for reduction of 2-decyne and diphenylacetylene, are compared for the homogeneous and intercalated catalyst systems. These comparisons are made in Table 18. It is seen that the ratio of intercalated to homogeneous initial rates  $R_{I}/R_{H}$ , ranges from 1.0 for 1-hexyne to <0.01 for diphenylacetylene. These also mean that the substrate selectivity of the active rhodium hydride species can be dramatically altered by intercalation between silicate sheets, provided that the difference in the size of the substrate is sufficiently large. For example, the relative rates for 2-hexyne and 3-hexyne reduction are 6:1 for the intercalation catalyst and only 1.3:1 for the homogeneous catalyst. Even for the sterically similar substrate 2hexyne and 2-decyne, intercalation enhances the selectivity of metal complexes by almost a factor of 2.

The hydrogenation product of 2-hexyne reduction

Table 18. Initial Hydrogen Uptake Rates for Reduction of Alkynes in Methanol with Intercalated and Homogeneous Rhodium Triphenylphosphine Catalyst Precursors.<sup>a</sup>

	Rate,	mL H <sub>2</sub> /min/mmol Rr	1 . h
Substrate	Intercalated	Homogeneous	R <sub>I</sub> /R <sub>H</sub> °
l-hexyne	2100	2100	1.0
2 <b>-</b> hexyne	2200	2400	0.92
2-decyne	1200	2500	0.48
3-hexyne	360	1800	0.20
PhC≡CPh	< 1	100	<0.01

<sup>a</sup>The reaction conditions are the same as those given in Table 17 except that PPh<sub>3</sub>/Rh = 6.0 in all cases.

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<sup>b</sup>Ratio of intercalated to homogeneous rates.

monitored over 98% conversion of substrate was exclusively  $\underline{cis}$ -2-hexene, for both the homogeneous and intercalated catalyst systems, as long as the substrate was present in solution. Once all the substrate was consumed, then a slow isomerization of  $\underline{cis}$ -2-hexene to  $\underline{trans}$ -2-hexene was observed.

The origin of substrate selectivity enhancement effect appears to be related to the orientation and spatial requirements of the substrate-rhodium complex in the intercalated state. The observed 001 X-ray reflection of methanolsolvated [Rh(PPh3)]<sup>+</sup>-hectorite at 0.72 wt % of Rh loading corresponds to a spacing of 17.3 Å. Since the silicate sheets are 9.6 Å thick, the average  $\Delta d_{001}$  value, which is a measure of the thickness of the interlayer region occupied by the complex, is 7.7 Å. Schrock and  $Osborn^{77}$ have suggested on the basis of NMR evidence a trans phosphine geometry for  $[RhH_2(PPh_3)_2S_2]^+$  (S =  $CH_3CN$ ). Based on difference in reactivity toward  $H_2$  of bis(phosphine)rhodium complexes containing monodentate and bidentate phosphine ligands, Halpern et al.<sup>103</sup> have also suggested a <u>trans</u> phosphine geometry for  $[RhH_2L_2S_2]^+$  complexes. The  $\Delta d_{001}$  value of 7.7 Å for the swelled intercalation complex means that the axis defined by a trans pair of phosphine ligands and the Rh atom is parallel or nearly parallel to the silicate sheets. When the substrate binds to the hydrogenated complex, by replacing

coordinated solvent, the  $-C \equiv C$ -axis is most likely perpendicular to the phosphine-rhodium axis and, hence, perpendicular to the silicate sheets as schematically illustrated in Figure 23. Unfavorable interaction between the alkyl groups of the substrate and the silicate oxygens could inhibit this spatial arrangement when the OOl spacing is less than the "critical" dimension of the substrate. The critical dimension is defined here as the minimum distance that must be spanned by the substrate when the unsaturated bond axis is perpendicular to the silicate sheets. Figure 23B illustrates the critical dimension of 2-decyne (7.7 Å), as estimated from space-filling models.

A precise, controlled relationship between  $\Delta d_{001}$ and the reactivity of the intercalated complex toward a given substrate cannot be expected, because the spacings between the silicate sheets are not rigorously regular. That is the solvated intercalate is interstratified with some spacings larger and smaller than the average value indicated by the 001 X-ray reflection.<sup>99,104</sup> Nevertheless, relative to homogeneous solution rates, the rates of reduction of a substrate with the intercalated complex should decrease with decreasing  $\Delta d_{001}$  in the region where  $\Delta d_{001}$  is near the critical dimension of the substrate. Such behavior is observed for reduction of 2-decyne by  $Rh(PPh_3)_n^+$ -hectorite swelled to various degrees by different solvents. As can be seen by the data presented





Figure 23. (A) Proposed orientation of the alkyne-rhodium triphenylphosphine complex between the silicate sheets of hectorite prior to hydrogen transfer. (B) The critical dimension of 2-decyne, defined as the minimum distance which must be spanned by the molecule when CEC axis is perpendicular to the silicate sheets. in Table 19, the initial  $R_I/R_H$  values range from 0.85 with  $CH_2Cl_2$  as the solvating molecule ( $\Delta d_{001} = 10.0$  Å) to 0.02 with benzene ( $\Delta d_{001} = 5.7$  Å).

Table 20 lists the critical dimensions of other substrates used in this study. It is noteworthy that the critical dimension of 2-decyne and 2-hexyne are the same (7.7  $^{\circ}_{\rm A}$ ), yet, as pointed out earlier, their initial reduction rates with methanol-solvated  $Rh(PPh_3)_n^+$ -hectorite ( $\Delta d_{001}$ = 7.7 Å) differ by a factor of almost 2. Apparently, conformational differences in the alkyl groups of the alkynes can influence the actual distance spanned by the coordinated substrate in the interlayer space of the sili-The other point to be noted is that the critical cate. dimensions of 1-hexene and 2-hexene are considerably smaller than those of the corresponding alkynes, yet the initial  $R_T/R_H$  values are <0.1 for the olefins (<u>cf</u>., absolute rates in Table 9) and near unity for the alkynes (<u>cf.</u>, Table 18). It is possible that the alkynes are more strongly physisorbed than the olefins, thus giving rise to a higher substrate concentration in the interlayers of the intercalate.

## E. Properties of Silane-Montmorillonite

The treatment of DMSO solvated Na-montmorillonite with  $(CH_3)_3SiCl$  and  $(CH_3)_2SiCl_2$  in p-dioxane provided dark gray products, whereas the treatment with silanes containing vinyl, amino or epoxide functional groups gave dark to pale

Rate, mL/min/mmol Rh				
Solvent	Intercalated	Homogeneous	<sup>R</sup> ı∕ <sup>R</sup> H	∆d <sub>001</sub> (Å)
CH2C12 <sup>b</sup>	2800	3300	0.85	10.0
МеОН	1200	2800	0.43	7.7
Et <sub>2</sub> 0/MeOH (3:l v/v)	660	2800	0.24	6.7
C <sub>6</sub> H <sub>6</sub> b	20	1000	0.02	5.7

Table 19. Initial Rates of Hydrogen Uptake for Reduction of 2-Decyne to <u>cis</u>-2-Decene in Different Solvents with Intercalated and Homogeneous Catalysts.<sup>a</sup>

<sup>a</sup>For reaction conditions see footnote <u>a</u> in Table 17. PPh<sub>3</sub>/Rh = 6:1.

 $^{\rm b}{\rm These}$  solvents contain 7% methanol by volume.

Substrate	Critical Dimension, Å
l-hexyne	7.0
2-hexyne	7.7
3-hexyne	8.8
°6 <sup>H</sup> 5 <sup>C≡CC</sup> 6 <sup>H</sup> 5	13.8
l-hexene	5.3
<u>cis</u> -2-hexene	5.8

Table 20. Critical Dimensions of Selected Substrates.<sup>a</sup>

<sup>a</sup>Estimated from space filling models.

yellow products. The presence or absence of intercalated silane was determined by comparing OOl X-ray basal spacings of montmorillonite before and after reaction at 25°C and at 150°C for 24 hrs. The X-ray basal spacing data are presented in Table 21. In all cases only first order reflections were observed, which indicate that the interlayers are interstratified. The OOl basal spacings recorded after drying the samples at 25°C does not provide sufficient information to indicate that silanes are present in the interlayer regions of the silicate, because the basal spacings observed for silane-montmorillonite are very close to that of Na-montmorillonite solvated with DMSO. However, basal spacings for Q1-6011 and Z-6040-Montmorillonite are nearly an angstrom unit larger than that of Na-montmorillonite solvated with DMSO. The latter results indicate the presence of silanes in the interlayer of montmorillonite. It also suggests that the silanes are actually involved in the swelling process so that the interlayer region expands beyond the dimension of the solvent swollen system.

The important difference in OOl basal spacings were observed for the samples and dried at 25°C and 150°C for 24 hrs. It is especially noteworthy that the DMSO solvated interlayers collapsed to  $\Delta d_{001} = 1.8$  Å upon drying at 150°C, whereas the  $\Delta d_{001}$  for the silane-montmorillonites were in the range of 2.8 - 5.9 Å. The decrease in  $\Delta d_{001}$ 

	d <sub>00</sub>	Adaaa at Å	
Silane	25°C	150°C	150°C
None (Dehydrated)	9.6		
None (DMSO Solvated) <sup>a</sup>	13.8	11.4	1.8
(CH <sub>3</sub> ) <sub>3</sub> SiCl-	14.0	12.4	2.8
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> -	13.5	12.8	3.2
Q1-6011- <sup>b</sup>	15.8	15.5	5.9
z-6020- <sup>b</sup>	13.8	12.6	3.0
z-6040- <sup>b</sup>	14.7	14.2	4.6
(MeO) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> -	14.0	13.6	4.0

Table 21. 001 Basal Spacings of Na<sup>+</sup>/Silane-Montmorillonite.

<sup>a</sup>Washed free of excess DMSO by p-dioxane.

<sup>b</sup>Q1-6011 = (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, Z-6020 = (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH-(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, Z-6040 = (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>CH - CH<sub>2</sub>.

in the case of DMSO solvated Na-montmorillonite should be due to the migration of solvent molecules out of the interlayers. The retention of the expanded interlayer spacings of silane-montmorillonite at 150°C suggest that the silanes are actually in the interlayer regions of the silicate. The basal spacing data indicate that the swelling of the interlayers may partially be related to the chain length of the silanes. The swelling with the short chain silanes is better than with silanes of long chain length. For example,  $\Delta d_{001}$  for Q1-6011-montmorillonite is 2.9 Å than Z-6020-montmorillonite (Table 21). The exact correlation between the chain length and OOl basal spacings cannot be established, because the conformational interaction of the alkyl groups and functional groups with the silicate sheets may also play some role. However, the size of functional groups on silicon atom appear to have even greater role on interlayer swelling. For example, replacing the silane containing methoxy groups (Z-6020) with a silane containing ethoxy group (Q1-6011) leads to an increase of 2.9  ${\rm \AA}$ in  $\Delta d_{001}$ . The results of the X-ray diffraction studies indicate that the intercalated silanes are in monolayer form, because the mean  $\Delta d_{001}$  value for the silanes studied is 3.9 Å; which corresponds to the thickness of one  $-SiR_3$ group.<sup>90</sup>

It is possible that the differences observed in the Xray basal spacings upon intercalation of different silanes

are related to the preferential orientation of the silanes. In the presence of the solvent molecules (silanemontmorillonite dried at 25°C) the silane orientation may not be very critical for the interlayer swelling. However, as the solvent is removed at 150°C, then the orientation of the silane in the interlayer should determine the interlayer swelling. The interstratification observed may be the result of non-uniform orientation of the silanes within the same layer.

The presence of silanes in the interlayer of silicate was also confirmed by infrared spectroscopy. The data obtained from these studies are reported in Table 22. The bands observed around 2900 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> are assigned to the stretching and deformation vibration of alkyl groups. The band observed around 1255 cm<sup>-1</sup> is assigned to the Si-C stretching vibration. It is noteworthy that except for a small loss in the band intensities, no changes in the position or the number of the IR bands were caused by drying the samples at  $150^{\circ}$ C.

The results of the X-ray and infrared studies confirm that the silanes are indeed in the interlayer regions of montmorillonite.

The thermal stabilities of silane-montmorillonites have been determined by differential scanning calorimetry. The results are provided in Table 23. The typical DSC plot observed for chloro-silane- and amino-silane-montmorillonite is provided in Figure 24. In all cases the

Montmorillonite	νC – Η	vSi – C	νN – Η
(CH <sub>3</sub> ) <sub>3</sub> SiCl-	2900b, 1450b (2910b,1450b)	1255s ()	
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> -	2920m, 1450b (2930b,1435b)	1260s (1265m)	
Q1-6011 -	2920s, 1440m (2930s, 1450b)	1255s ()	3240b (3230b)
Z-6020 -	2910b, 1455m (2920b, 1450b)	1255s (1260b)	3360 <b>s</b> (3360b)
Z-6040 -	2920b, 1450b (2930b,	1260s (1260m)	
(MeO) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> -	2915m, 1440b (2920b, 1445b)	1255b ()	

Table 22. Infrared Spectroscopy Study of Silane-Montmorillonite.<sup>a</sup>,<sup>b</sup>

<sup>a</sup>IR frequencies are expressed in wave number cm<sup>-1</sup>.

<sup>b</sup>Values in parentheses are for the samples after drying at 150°C for 12 hours.

Silane	Temperature of Thermal Transition °C
None (Dehydrated)	ll0 (very weak)
None (DMSO Solvated) <sup>a</sup>	105 (very weak)
(CH <sub>3</sub> ) <sub>3</sub> SiCl-	110, 205, 265
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> -	130, 215, 275
Z-6020-	100, 240*
Z-6040-	110, 295*
Q1-6011-	125, 330*
(EtO) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> -	140, 285*

Table 23. Enthalpic Transitions with Temperature for Na<sup>+</sup>/ Silane-Montmorillonite.

<sup>a</sup>Washed with p-dioxane to remove excess DMSO.

\* Exothermic transition.



Figure 24. Differential scanning calorimetry curve for (A) Z-6020-Montmorillonite (B) (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>-Montmorillonite in the range 25-300°C.

endothermic transition occurring between 100-140°C is assigned to the removal of solvent from the interlayers. A similar transition was observed at 105°C for Na-montmorillonite solvated with DMSO and washed with p-dioxane. When the same sample was scanned a second time over the same temperature range, the transition at 105°C disappeared, indicating that the solvent was removed on the first scan. The weak endothermic transition observed at 110°C for dehydrated Na-montmorillonite is due to the presence of very small quantities of residual water in the interlayers. The presence of water was detected by IR spectroscopy. The band at 1620 cm<sup>-1</sup> was assigned to the deformation vibration mode of the water molecule.

It is noteworthy that the first enthalpic transition . of these silane-montmorillonites, which is assigned to thermal migration of solvent out of interlayers, is dependent upon the nature of intercalated silanes. Since there is no correlation between the first enthalpic transition and  $\Delta d_{001}$  (<u>cf</u>. Table 21), it is unlikely that the diffusion of solvent out of the interlayers is totally dependent upon the interlayer swelling. It is possible that even at high interlayer spacings, the pore size may be small so that solvent diffusion is relatively slow. For example, intercalation of Q1-6011 in montmorillonite gives  $\Delta d_{001} = 5.9$  Å, but the first transition occurs at relatively higher temperature (125°C) than the other silane-montmorillonites.

It is possible that the lyophilic properties of the silanemontmorillonite surfaces differ considerably with each silane. De La Cruz <u>et al</u>.<sup>90</sup> have proposed that the capacity to absorb hydrocarbons between the silicate sheets may be due to a modification of the interlamellar surface of the silicate as a result of the interaction of chlorosilanes with  $\equiv$ Si-OH of the silicate.

The endothermic transitions at 205 and 265°C for  $(CH_3)_3$ SiCl- and at 215 and 275°C for  $(CH_3)_2$ SiCl<sub>2</sub>-montmorillonite could possibly be due to the stepwise dissociation of Cl and alkyl groups or thermal rearrangement followed by decomposition of the organic counterpart of the silanes. These results along with X-ray diffraction data suggest that the decrease in interlayer swelling with increasing temperature is associated with these enthalpic transitions.

The exothermic transitions occurring in the region  $240-330^{\circ}$ C with the other intercalates, Z6020-, Z6040-, Q1-6011-, and (EtO)<sub>3</sub>SiCH<sub>2</sub>CH = CH<sub>2</sub>-montmorillonite (Table 23) should be due to the dissociation and/or decomposition of the organic counterparts of the silanes.

The high thermal stability of the intercalates indicate that the interlayer swelling should be stable to temperatures slightly below the transition temperature. The thermal stability and the high interlayer swelling should allow access to the large internal surface area of the silicate for catalysis or selective molecular adsorption.

The qualitative study of the expanded phase silanemontmorillonites has shown considerable cation exchange capacity with  $Cu^{2+}$  and large  $Fe(Phen)_3^{2+}$  ions. The cation exchange occurring with  $Fe(Phen)_3^{2+}$  suggest that there should be some pores large enough to allow this bulky cation into the interlayers of the silicate. The result of cation exchange reactions indicate the possibility of developing bifunctional catalysts, where the neutral catalysts can be bound to the intercalated ligand silane and the cationic complex catalyst can exchange with Na<sup>+</sup> of silicate.

#### CONCLUSION

The results of this research project elucidate some of the fundamental factors that affect the catalytic activity of metal complex catalysts upon their intercalation in layered silicates.

The hydrogenation of 1,3-butadiene and two of its methyl derivatives with  $[Rh(NBD)(dppe)]^+$  under homogeneous and intercalated conditions demonstrates the effect of interlayer environment on catalytic activity. Swelling of the interlayers beyond the dimensions of the simple intercalate ( $\Delta d_{001} = 8.8$  Å) is essential for the reaction to occur in the interlamellar regions of hectorite. The difference observed in the distribution of 1,2- addition products for the homogeneous and intercalated catalysts indicate that the specificity of the metal complex catalyst can be modified by intercalation.

The hydrogenation of monoolefins with  $Rh(PPh_3)_n^+$  catalyst precursor suggests the potential of catalyst intercalation in inhibiting the isomerization of substrate and allowing greater catalyst specificity. The changes in catalyst specificity caused by intercalation can be accounted for by the shift in an equilibrium between dihydride and monohydride rhodium complexes. The presence of surface Brönsted acidity favors the dihydride complex. The surface Brönsted

acidity is dependent upon a number of factors. The forces that most affect the surface Brönsted acidity are the amount of substrate adsorbed and the amount of interlayer water. The results show that the surface acidity effect can be more important than spatial factors in determining the specificity of a layered silicate intercalation catalyst.

The differences observed in the relative rates of alkyne reduction with  $Rh(PPh_3)_x^+$  catalyst precursor under homogeneous and intercalated conditions show that the enhanced specificity of the intercalated catalyst is related to the molecular size of the substrate. The spatial factors especially are important when the molecular size of the substrate is greater than the interlayer swelling of a layered silicate. Most probably, spatial factors also affect the hydrogenation of 2,3-dimethyl-1,3-butadiene with  $[Rh(NBD)(dppe)]^+$  under intercalated state.

The intercalation of organo-silane in the interlayers of smectite provides a new and promising method of obtaining thermally stable expanded interlayers. These materials may prove to be very useful for the immobilization of neutral or moisture sensitive catalysts by reaction with the intercalated ligand silanes. It may be feasible to prepare a bifunctional catalyst system by anchoring a neutral metal complex catalyst using an intercalated ligand silane and a second, cationic catalyst by ion exchange with the available interlayer cations. The lyophilic nature of silane smectite may permit development of a material which can provide selective adsorption properties.

This research has demonstrated some of the attractive features of layered silicate as a catalyst support. In most cases the effect of catalyst intercalation has been significant. The enhanced specificity demonstrated by catalyst intercalation suggest that layered silicates are very attractive supports for catalyst immobilization.

## APPENDIX

## LIST OF ABBREVIATIONS AND SYMBOLS

acac	acetylacetone
Acet.	acetone .
aq	aqueous
BBP	benzylbutylphthalate
bipy	2,2'-bipyridyl
Bu	Butyl
CEC	cation exchange capacity
COD	l,5 cyclooctadiene
COE	cyclooctene
diphos or dppe	l,2-bis(diphenylphosphino)ethane
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
ESR	electron spin resonance
Et	ethyl
EtO	ethoxy
GLC	gas liquid chromatography
IR	infra red
L	general neutral ligand
Μ	general metal center
Me	methyl
MeOH	methanol
mL	milliliter
MeO	methoxy
M	molar
NBD	norbornadiene
NMR	nuclear magnetic resonance
NEtz	triethylamine

.

OAc	acetate
-OH	hydroxyl group
OX	oxalate
ol	olefin
P)-	polymer for catalyst support
Ph	phenyl
PPh <sub>3</sub>	triphenylphosphine
PPh <sub>2</sub> Me	diphenylmethylphosphine
PPhMe <sub>2</sub>	phenyldimethylphosphine
Phen	l,10-phenanthrolin
P-P <sup>+</sup>	l-diphenylphosphino-2-benzyldiphenyl- phosphonium ethane
Ру	pyridine
Q1-6011	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>
R	alkyl- or aryl-
R <sub>I</sub>	rate intercalated
R <sub>H</sub>	rate homogeneous
S	solvent
S)-	catalyst support
THF	tetrahydrofuran
VV	ultra violet
V	volume
wt.	weight
x	usually halogen
Z6020	$(MeO)_{3}Si(CH_{2})_{3}NH(CH_{2})_{2}NH_{2}$
Z6040	(MeO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> CH - O CH <sub>2</sub>

# BIBLIOGRAPHY

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#### BIBLIOGRAPHY

- Roth, J. F., Craddock, J. H., Hershman, A., Paulik, F. E., <u>Chemtech</u>, 1977, 600.
- Paulik, F. E., Hershman, A., Knox, W. R., Roth, J. F., <u>U.S. Patent</u>, 1273, 3,769,329.
- 3. (a) Knowles, W. S., Sabacky, M. J.; Vineyard, B. D., <u>Chemtech</u>, 1972, 590.
  (b) Knowles, W. S., Sabacky, M. J., Vineyard, B. D., <u>Adv. Chem. Ser</u>., 1974, 132, 275.
  (c) Knowles, W. S., Sabacky, M. J., <u>U.S. Patent</u>, 1974, 3,849,480.
- Schmidt, J., Hafner, W., Jira, R., Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H., <u>Angew. Chem</u>., 1959, <u>71</u>, 176.
- 5. Parshall, G. W., <u>J. Mol. Catal</u>., <u>1978</u>, <u>4</u>, 243.
- 6. Szonyi, G., <u>Advan. Chem. Ser</u>., <u>1968</u>, <u>70</u>, 53.
- 7. Bond, G. C., <u>Advan. Chem. Ser</u>., <u>1968</u>, <u>70</u>, 25.
- 8. Schultz, R. G., Gross, D. E., <u>Advan. Chem. Ser</u>., <u>1968</u>, <u>70</u>, 97.
- 9. Chemical and Engineering News, 1971, April 26, 30.
- Sheng, M. N.; Zajackek, J. G., <u>Advan. Chem. Ser</u>., 1273, <u>76</u>, 99.
- 11. Stobaugh, R. B.; Calarco, V. A.; Morris, R. A.; Stroud L. W., <u>Hydrocarbon Process</u>, 1273, <u>52</u>, 99.
- 12. (a) Collman, J. P., <u>Acc. Chem. Res</u>., <u>1968</u>, <u>1</u>, 136.
  - (b) Cramer, R., <u>Acc. Chem. Res</u>., <u>1968</u>, <u>1</u>, 186.
  - (c) Halpern, J., <u>Advan. Chem. Ser</u>., 1968, <u>70</u>, 1.
- 13. (a) Madix, R. J., <u>Catal. Rev.-Sci. Eng</u>., <u>1977</u>, <u>15</u>, 293.
  (b) Thomas, J. M.; Lambert, R. M., Eds., "Characteriza-tion of Catalysts", John Wiley & Sons, Inc., NY, <u>1980</u>.

13. (c) Somorjai, G. A., "Chemistry in Two Dimension: Surfaces", Cornell University Press, 1981. (d) Adamson, A. W., "Physical Chemistry of Surfaces", 3rd Ed., John Wiley & Sons., Inc., New York, NY 1976. (e) Rhodin, T. N.; Ertl, G., Eds., "The Nature of the Surface Chemical Bond", North-Holland Publication Co., New York, 1972. (a) Whitehurst, D. D. <u>Chemtech</u>, 1980, 44. 14. (b) Grubbs, R. H., <u>Chemtech</u>, 1977, 512. (c) Hartley, F. R.; Vezey, P. N., Adv. Organomet. <u>Chem</u>., 1977, 15, 189. (d) Yermakov, Yu. I. Catal. Rev.-Sci. Eng., 1976, 13, 77. (e) Bailar, J. C., Jr., <u>Catal. Rev.-Sci. Eng</u>., <u>1974</u>, 10,17. (f) Heinemann, H., <u>Chemtech</u>, 1971, 288. Pitmann, C. U., Jr., Evans, G. O., Chemtech, 1973, (g) 560. (h) Michalska, Z. M.; Webster, D. E., Chemtech, 1975, 118. (i) <u>J. Molecular Catalysis</u>, 1981, <u>11</u>, 143-397. Bayer, E.; Schurig, V., <u>Chemtech</u>, 1976, 212. 15. Parshall, G. W., J. Am. Chem. Soc., 1972, 94, 8716. 16. 17. Dror, Y.; Manassen, J., <u>J. Mol. Catal.</u>, <u>1977</u>, <u>2</u>, 219. Bond, W. D., Jr.; Brubaker, C. H., Jr.; Chandrashekharan, E. S.; Gibbons, S.; Grubbs, R. H.; Kroll, L. C., J. 18. <u>Am. Chem. Soc., 1975, 97, 2128.</u> Grubbs, R. H.; Kroll, L. C., J. Am. Chem. Soc., 1971, 19. <u>93</u>, 3062. Dumont, W.; Paulin, J. C.; Dang, T. P.; Kagan, H. B., 20. J. Am. Chem. Soc., 1973, 95, 8295. (a) Hjortkjaer, J.; Scurrell, M. S.; Simonsen, P., 21. J. Mol. Catal., 1272, 6, 405. (b) Gerritsen, L. A.; Van Meerker, A.; Vreugdenhill, M. H.; Scholten, J. J. F., <u>J. Mol. Catal</u>., 1980, <u>9</u>, 139 and 157. (a) Rony, P. R.; Roth, J. F., <u>J. Mol. Catal</u>., 1975/76, 22. <u>1</u>, 13.

- 22. (b) Rony, P. R.; Roth, J. F., <u>J. Catal</u>., <u>1969</u>, <u>14</u>, 142.
- Sobczak, J.; Zilkowski, J. J., <u>J. Mol. Catal</u>., 1977/78, <u>3</u>, 165.
- 24. (a) Mazzei, M.; Marconi, W.; Riocci, M., <u>J. Mol</u>. <u>Catal</u>., <u>1980</u>, 9, 381.
  (b) Chang, H. M.; Pinnavaia, T. J., Personal Communication.
- 25. (a) Legzdins, P.; Rampel, G. L.; Wilkinson, G., <u>Chem</u>. Commun., 1969, 825.
  (b) Legzdins, P.; Mitchell, R. W.; Rampel, G. L.; Ru dick, J. D.; Wilkinson, G., <u>J. Chem. Soc. (A)</u>, 1970, 3322.
- 26. Haag, W. O.; Whitehurst, D. D., <u>Belgian Patent</u>, 1969, 721, 686.
- 27. (a) Welty, P. K.; Pinnavaia, T. J., <u>J. Am. Chem. Soc.</u>, <u>1975</u>, <u>97</u>, 3819.
  (b) Pinnavaia, T. J.; Welty, P. K.; Hoffman, J. F., <u>Proc. Int. Clay. Conf</u>., Mexico City, <u>1975</u>, 373.
  (c) Pinnavaia, T. J.; Raythatha, R.; Lee, J. G. S.; Hollaran, L. J.; Hoffman, J. F., <u>J. Am. Chem. Soc</u>., <u>1979</u>, <u>101</u>, 6891.
- 28. Raythatha, R.; Pinnavaia, T. J., <u>J. Organomet. Chem.</u>, 1981, (in press).
- 29. Quayle, W. H.; Pinnavaia, T. J., <u>Inorg. Chem</u>., 1979, <u>18</u>, 2840.
- 30. (a) Andersson, S. L. T.; Scurrell, M. S., <u>J. Catal</u>. 1979, <u>59</u>, 340.
  (b) Scurrell, M. S.; Howe, R. F., <u>J. Mol. Catal</u>., 1980, <u>7</u>, 535.
- 31. (a) Oates, M. D.; Lunsford, J. H., <u>J. Mol. Catal.</u>, 1980, <u>9</u>, 91.
  (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Ganzerla, R.; Lenarda, M.; Graziani, M., <u>J. Organomet</u>. 1980, <u>190</u>, C-1.
- 32. Lunsford, J. H., <u>Catal. Rev.-Sci. Eng</u>., 1975, <u>12</u>, 137.
- 33. Mantovani, E.; Palladino, N.; Zanobi, A., <u>J. Mol. Catal.</u>, 1977/78, <u>3</u>, 285.

34. (a) Gellin, P.; Taarit, Y. B.; Naccache, C, J. Catal., 1272, 59, 357. (b) Ganzerla, R.; Lenarda, M.; Pinna, F.; Graziani,
M., J. Organomet. Chem., 1981, 208, C-43. Ikatchenko, D. B.; Coudurier, G.; Mozzanega, H.; (c) Tkatchenko, I., <u>J. Mol. Catal</u>. 1979, <u>6</u>, 293. (d) Primet, M.; Vedrine, J. C.; Naccache, C., J. Mol. Catal., 1978, 4, 411. (a) Foger, K.; Andersson, J. R., <u>J. Catal.</u>, <u>1979</u>, 35. <u>59</u>, 325. (b) Kuznetsov, V.; Bell, A. T.; Yermakov, Y. I., <u>J</u>. <u>Catal</u>., <u>1980</u>, <u>65</u>, 374. (c) Wong, N. W.; Watters, K. L.; Howe, R. F.; Cho-jnacki, T. P.; Fu, C. M.; Schneider, R. L., <u>J. Catal</u>., 1980, <u>66</u>, 424. (d) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderghi, G. M.; Ugo, R., <u>J. Organomet. Chem</u>., <u>1978</u>, <u>153</u>, 73. (e) Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R., J. Organomet. Chem., 1980, 192, C-31. (f) Lausarot, P. M.; Vaglio, G. A.; Valle, M., J. <u>Organomet. Chem.</u>, 1981, 204, 249. Chang, B. H.; Grubbs, R. H.; Brubaker, C. H., Jr., J. 36. Organomet. Chem., 1979, 172, 81. (a) Zakharov, V. A.; Dudchenko, V. K.; Paukshtis, 37. E. A.; Karakchiev, L. G.; Hermakov, Y. I., J. Mol. <u>Catal</u>., 1277, 2, 421. (b) Candin, J. P.; Thomas, H., Advan. Chem. Ser., 1274, <u>132</u>, 212. (c) Yermakov, Y. I.; Kuznetsov, B. N., J. Mol. Catal., 1980, <u>9</u>, 13. (d) Schwartz, J.; Ward, M. D., <u>J. Mol. Catal.</u>, 1980, 8, 465. 38. Ryan, R. C.; Wilemon, G. M.; Dalsanto, M. P.; Pittman, C. U., Jr., <u>J. Mol. Catal</u>., <u>1979</u>, <u>5</u>, 319. Schouten, A. J.; Challa, G., <u>J. Mol. Catal.</u>, <u>1980</u>, <u>9</u>, 39. 41. 40. Kawata, N.; Mizoroki, T.; Ozaki, A.; Ohkawara, M. <u>Chem. Lett.</u>, 1273, 1165.
- 41. Mortreux, A.; Delgrange, J. C.; Blanchard, M.; Lubochinsky, B., <u>J. Mol. Catal.</u>, <u>1977</u>, <u>2</u>, 73.
- 42. Grubbs, R. H.; Swetnick, S.; Su, S. C. H., <u>J. MO1</u>. Catal., <u>1977/78</u>, <u>3</u>, 11.
- 43. (a) Takahashi, N.; Okura, J.; Keii, T., <u>J. Mol. Catal.</u>, <u>1978</u>, <u>3</u>, 211.
  (b) Takahashi, N.; Okura, J.; Keii, T., <u>J. Mol. Catal.</u>, <u>1978</u>, <u>3</u>, 277.
- 44. (a) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKanzie, S.; Pitkethly, R. C.; Robinson, P. J., J. Organomet. Chem., 1975, 87, 203.
  (b) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKanzie, S.; Pithkethly, R. C.; Robinson, P. J., J. Catal., 1976, 43, 322.
  (c) Wild, F. R. W. P.; Gubitosa, G.; Brintzinger, H. H., J. Organomet. Chem., 1978, 148, 73.
- 45. (a) Boucher, L. J.; Oswald, A. A.; Murrell, L. L. <u>Preprints, Div. Petr. Chem., ACS</u>, Los Angeles, 1974, 162.
  (b) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKanzie, S.; Pitkethley, R. C.; Robinson, P. J., <u>J. Organomet. Chem.</u>, 1976, 107, 393.
  (c) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKanzie, S.; Pitkethly, R. C.; Robinson, P. J., <u>J. Organomet. Chem</u>., 1975, 87, 203.
- (a) Tarasawa, M.; Yamamoto, H.; Kaneda, K.; Imanaka, J.; Teranishi, S., <u>J. Catal</u>., <u>1979</u>, <u>57</u>, 315. 46. (b) Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S., J. Organomet. Chem., 1978, 162, 403. (c) Capka, M.; Svoboda, P.; Kraus, M.; Hetflejs, J. <u>Chem. Ind.</u>, 1972, 650. Bruner, H. S.; Bailar, J. C., Inorg. Chem., 1973, (d) <u>12</u>, 465. (e) Allum, K. B.; Hancock, R. D.; Howell, I. V., Pitkethly, R. C.; Robinson, P. J., J. Organomet. <u>Chem</u>., 1975, <u>87</u>, 189. 47. Smith, A. K.; Basset, J. M.; Maitilis, P. M., <u>J. Mol</u>. <u>Catal</u>., <u>1977</u>, <u>2</u>, 223.
- 48. (a) Jarrell, M. S.,; Gates, B. C., <u>J. Catal</u>., <u>1978</u>, <u>54</u>, 81.

- 48. (b) Bilhou, J. L.; Bougnol, V. B.; Graydon, W. F.; Basset, J. M.; Smith, A. K., <u>J. Mol. Catal.</u>, 1980, <u>8</u>, 411.
  (c) Knozinger, M.; Rumpf, H., <u>Inorg. Chim. Acta.</u>, 1978, <u>30</u>, 51.
  (d) Iwakate, K.; Dasgupta, S. R.; Schneider, R. L.; Smith, G. C.; Watters, K. L., <u>Inorg. Chim. Acta.</u>, 1975, 15, 191.
  (e) Knozinger, H.; Thornton, E. W.; Wolm, M., <u>J.</u> <u>Chem. Soc., FTR(I)</u>, 1972, <u>75</u>, 1888.
- 49. (a) Innorta, G.; Modelli, A.; Scagnolari, F.; Foffani, F., <u>J. Organomet. Chem</u>., <u>1980</u>, <u>185</u>, 403.
  (b) Grubbs, R. H.; Kroll, L. C., <u>J. Am. Chem. Soc.</u>, <u>1971</u>, <u>93</u>, 3062.
  (c) Pittman, C. U., Jr.; Smith, L. R.; Hanes, R. M., <u>J. Am. Chem. Soc</u>., <u>1975</u>, <u>97</u>, 1742.
  (d) Grubbs, R. H.; Kroll, L. C.; Sweet, E. M., <u>J. Macromol. Sci. Chem</u>., <u>1973</u>, <u>A7</u>, 1047.
  (e) Pittman, C. U., Jr.; Smith, L. R., <u>J. Am. Chem</u>. <u>Soc</u>., <u>1975</u>, <u>97</u>, 1749.
  (f) Bartholin, M.; Graillat, C.; Guyot, A., <u>J. Mol. Catal</u>., <u>1981</u>, <u>10</u>, 361.
- 50. Demunck, N. A.; Verbruggen, M. W.; Scholten, J. J. F., <u>J. Mol. Catal</u>., 1981, <u>10</u>, 313.
- 51. (a) Strukul, G.; Bonivento, M.; Graziani, M.; Cernia, E.; Palladino, N., <u>Inorg. Chim. Acta</u>, <u>1975</u>, <u>12</u>, 15.
  (b) Pinna, F.; Bonivento, M.; Strukul, G.; Graziani, M.; Cernia, E.; Palladino, N., <u>J. Mol. Catal</u>., <u>1975</u>,776, <u>1</u>, 309.
  (c) Strukul, G.; D'Olimpio, P.; Bonivento, M.; Pinna, F.; Graziani, M., <u>J. Mol. Catal</u>., <u>1977</u>, <u>2</u>, 179.
- 52. Herschcovitz, H.; Schmukler, G., <u>J. Inorg. Nucl. Chem</u>., <u>1979</u>, <u>41</u>, 687.
- 53. Pittman, C. U., Jr.; Quock, N., <u>J. Organomet. Chem.</u>, <u>1978</u>, <u>153</u>, 85.
- 54. (a) Conan, J.; Bertholin, M.; Guyot, A., <u>J. Mol. Catal.</u>, <u>1275/76</u>, <u>1</u>, 375.
  (b) Grubbs, R. H.; Sweet, E. M., <u>J. Mol. Catal.</u>, <u>1277/78</u>, <u>3</u>, 259.

- 55. Allum, K. G.; Hancock, R. D.; Howell, I. V.; Lester, T. E.; McKanzie, S.; Pitkethly, R. C.; Robinson, P. J., J. Organomet. Chem., 1975, 87, 203.
- 56. Kawabata, Y.; Tanaka, M.; Ogata, I., <u>Chem. Lett.</u>, 1976, 1213.
- 57. (a) Grubbs, R. H.; Gibbons, C.; Kroll, L. C.; Bonds, W. D., Jr.; Brubaker, C. H., Jr., <u>J. Am. Chem. Soc.</u>, <u>1973</u>, <u>95</u>, 2313.
  (b) Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N., <u>J. Am</u>. <u>Chem. Soc</u>., <u>1972</u>, <u>94</u>, 1789.
- 58. Haag, W. O.; Whitehurst, D. D., <u>Procd. Int. Cong.</u> <u>Catal</u>., <u>1972</u>, <u>5</u>, 465.
- 59. Lamalle, S.; Mortreux, A.; Evarard, M.; Petit, F.; Grimblet, J.; Bonnelle, J. P., <u>J. Mol. Catal</u>., 1979, <u>6</u>, 11.
- 60. (a) Swift, H. E. in "Advanced Materials in Catalysis", Burton, J. J.; Garten, R. L., Eds., Academic Press, New York, 1977, 209.
  (b) Barrer, R. M., "Zeolite and Clay Minerals as Sorbents and Molecular Sieves", Academic Press, New York, 1978, 405.
  (c) Raythatha, R. H., M. S. Thesis, Department of Chemistry, Michigan State University, 1978.
  (d) Quayle, W. H., Ph.D. Dissertation, Department of Chemistry, Michigan State University, 1978.
- 61. Farzaneh, F.; Pinnavaia, T. J., Unpublished results.
- 62. Chang, H. M.; Pinnavaia, T. J., Unpublished results.
- 63. Grim, R. E., "Clay Minerology", 2nd Ed., 1968, McGraw-Hill Book Co., New York.
- 64. Van Olphen, H., "An Introduction to Clay Colloid Chemistry", 1963, pp. 68-69, John Wiley & Sons, Inc., New York.
- 65. (a) McBride, M. B.; Pinnavaia, T. J.; Mortland, M. M., <u>J. Phys. Chem</u>., 1975, 79, 2430.
  (b) McBride, M. B.; Pinnavaia, T. J.; Mortland, M. M., <u>Amer. Minerals</u>, 1975, <u>60</u>, 66.

- 65. (c) McBride, M. B. in "Advanced Chemical Methods for Soil and Clay Minerals Research", Stucki, J. W.; Banwart, W. L., Eds., D. Reidel Publishing Company, 1980, 423.
  (d) Pinnavaia, T. J., in "Advanced Chemical Methods for Soil and Clay Minerals Research", Stucki, J. W.; Banwart, W. L., Eds., D. Reidel Publishing Company, 1980, 391.
- 66. McBride, M. B., Clay and Clay Minerals, 1977, 25, 6.
- 67. (a) Bartholin, M.; Graillat, Ch.; Guyot, A.; Coudurier, G.; Bandiera, J.; Naccache, C., <u>J. Mol. Catal.</u>, <u>1977/78</u>, <u>3</u>, 17.
  (b) Rony, P. R.; Roth, J. F., <u>J. Mol. Catal.</u>, <u>1975/</u> <u>76</u>, <u>1</u>, 12.
  (c) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKanzie, S.; Pitkethly, R. C.; Robinson, P. J., <u>J.</u> <u>Organomet. Chem.</u>, <u>1976</u>, <u>107</u>, 393.
- 68. Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J., <u>J. Organomet. Chem</u>., 1975, 87, 189.
- 69. (a) Granquist, W. T.; Pollack, S. S., <u>Am. Minerals</u>, <u>1967</u>, <u>52</u>, 212.
  (b) Hofmann, U., <u>Angew. Chem. Int. Ed</u>., <u>1968</u>, <u>7</u>, 681.
- 70. Theng, B. K. G. "The Chemistry of Clay-Organic Reactions", 1974, John Wiley & Sons, Inc., New York.
- 71. Fenn, D. B.; Mortland, M. M.; Pinnavaia, T. J., <u>Clays</u> and Clay Minerals, 1973, 21, 315.
- 72. Pinnavaia, T. J.; Mortland, M. M., <u>J. Phys. Chem</u>., <u>1971</u>, <u>75</u>, 3957.
- 73. (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G., <u>J. Chem. Soc.,(A)</u>, 1966, 1711.
  (b) James, B. R., <u>Advan. Organomet. Chem</u>., 1979, <u>17</u>, 319.
- 74. (a) Iguchi, M., <u>J. Chem. Soc., Japan</u>, <u>1232</u>, <u>60</u>, 1287.
  (b) Bhaduri, S.; Grundy, K.; Johnson, B. F. G., <u>J. Chem. Soc., Dalton</u>, <u>1277</u>, 2085.
  (c) Bhaduri, S.; Johnson, B. F. G., <u>Tran. Met. Chem</u>., <u>1278</u>, <u>3</u>, 156.

(d) Johnston, L. E.; Pafe, J. A., <u>Can. J. Chem</u>., 1969, 1278, <u>3</u>, 156.

- 75. (a) Reed, J.; Eisenberg, R., <u>Science</u>, 1974, <u>184</u>, 568.
  (b) Bhaduri, S.; Grundy, K.; Johnson, B. F. G., <u>J</u>. <u>Chem. Soc., Dalton</u>, 1977, 2085.
  (c) Bhaduri, S.; Johnson, B. F. G., <u>Tran. Met. Chem.</u>, 1978, <u>3</u>, 156.
- 76. Schrock, R. R.; Osborn, J. A., <u>J. Am. Chem. Soc</u>., <u>1971</u>, <u>91</u>, 2397.
- (a) Schrock, R. R.; Osborn, J. A., J. Am. Chem. Soc., 1976, 98, 2134.
  (b) Schrock, R. R.; Osborn, J. A., J. Am. Chem. Soc., 1976, 98, 2143.
  (c) Schrock, R. R.; Osborn, J. A., J. Am. Chem. Soc., 1976, 98, 4450.
- 78. Crabtree, R. H., <u>J. Chem. Soc.</u>, <u>Chem. Commun</u>., <u>1975</u>, 647.
- 79. This work.
- 80. (a) Mortland, M. M.; Fripiat, J. J.; Chaussidon, J.; Uytterhoven, J., <u>J. Phys. Chem</u>., <u>1963</u>, <u>67</u>, 248.
  (b) Mortland, M. M.; Raman, K. V., <u>Clays and Clay</u> <u>Minerals</u>, <u>1968</u>, <u>16</u>, 393.
- 81. Farzaneh, F., Ph.D. Dissertation, Department of Chemistry, Michigan State University, 1981.
- 82. (a) Berkheiser, V. E.; Mortland, M. M., <u>Clays and Clay</u> <u>Minerals</u>, <u>1977</u>, <u>25</u>, 105.
  (b) Barrer, R. M.; MacLeod, D. M., <u>Trans. Faraday</u> <u>Soc</u>., <u>1951</u>, <u>51</u>, 1290.
- 83. Mortland, M. M.; Berkheiser, V. E., <u>Clays and Clay</u> <u>Minerals</u>, <u>1977</u>, <u>24</u>, 60.
- 84. Shabtai, J.; Frydman, N.; Lazar, R., <u>Proc. 6th Int.</u> <u>Congr. Catal.</u>, <u>1977</u>, <u>2</u>, 660.
- 85. (a) Brindley, G. W.; Kao, C. C., <u>Clays and Clay Minerals</u>, <u>1980</u>, <u>28</u>, 435.
  (b) Shabtai, J., <u>U.S. Patent</u>, <u>1980</u>, 4,238,364.
  (c) Yamanaka, S.; Brindley, G. W., <u>Clays and Clay</u> <u>Minerals</u>, <u>1979</u>, <u>27</u>, 119.

- 86. Endo, T.; Pinnavaia, T. J.; Mortland, M. M., Clays and Clay Minerals, 1980, 28, 105.
- 87. (a) Traynor, M. F.; Mortland, M. M.; Pinnavaia, T. J., <u>Clays and Clay Minerals</u>, 1278, 26, 318.
  (b) Loeppert, R. H.; Mortland, M. M.; Pinnavaia, T. J., <u>Clays and Clay Minerals</u>, 1979, 27, 201.
  (c) Loeppert, R. H.; Raythatha, R. H.; Mortland, M. M.; Pinnavaia, T. J., Preprints, Catalysis Soc. 6th North American Meeting, Chicago, 1279, D-9.
- 88. (a) Zisman, W. A., <u>Ind. Eng. Chem. Prod. Res. Devep.</u>, <u>1969</u>, <u>8</u>, 98.
  (b) Plueddemann, E. P. in "Interfaces in Polymer Matrix Composities", <u>1974</u>, <u>6</u>, 173. Academic Press, New York.
- 89. Ruiz-Hitzky, E.; Rojo, J. M., <u>Nature</u>, <u>1980</u>, <u>287</u>, 28.
- 90. Aragon de la cruz, F.; Esteban, J.; Viton, C., Proc. Int. Clay Conf., Madrid, Spain, 1972, 705.
- 91. Abel, E. W.; Bennett, M. A.; Wilkinson, G., <u>J. Chem</u>. <u>Soc.</u>, <u>1959</u>, 3178.
- 92. Volger, H. C.; Hogeveen, H., <u>Rec. Trav. Chim</u>., <u>1267</u>, <u>86</u>, 1066.
- 93. Cramer, R., <u>J. Am. Chem. Soc.</u>, <u>1964</u>, <u>86</u>, 217.
- 94. Horn, H. G., Sommer, K., <u>Spectrochim. Acta, Part A.</u>, 1271, <u>27</u>, 1049.
- 95. Farmer, V. C. in "Data Handbook for Clay Materials and Other Non-Metallic Minerals", 1979, 285., Van Olphen, H.; Fripiat, J. J. Eds., Pergamon Press, New York.
- 96. Schindlbauer, H., Monat. Fur. Chem., 1963, 94, 100.
- 97. (a) Friedlin, L. Kh.; Litvin, E. F.; Topuridze, L. F., <u>Zh. Org. Chim.</u>, 1272, 669.
  (b) Rupilius, W.; Orchin, M., <u>J. Org. Chem</u>., 1971, <u>36</u>, 3604.
  (c) James, B. R. "Homogeneous Hydrogenation", John Wiley & Sons, Inc., New York, 1973, 116.
  (d) Pregaglia, G. F.; Ferrari, G. F.; Andreetta, A.; Capperella, G.; Genoni, F.; Ugo, R., <u>J. Organomet</u>. <u>Chem.</u>, 1974, 70, 89.

- 98. Vrieze, K., in "Dynamic Nuclear Magnetic Resonance Spectroscopy", Jackson, L. M.; Cotton, F. A., Eds., Academic Press, New York, 1975, 441.
- 99. Frey, E.; Legally, G., in "Developments in Sedimentology 27", <u>International Clay Conference</u>, 1978. Moorland, M. M.; Farmer, V. C., Eds., American Elesvier, New York, 1979, 131.
- 100. Wilson, C. R.; Taube, H., <u>Inorg. Chem.</u>, <u>1975</u>, <u>14</u>, 2276.
- 101. Hoffman, J. F., <u>Ph.D. Dissertation</u>, Department of Chemistry, Michigan State University, 1976.
- 102. (a) Mal'kova, T. A.; Shatranskii, V. M., <u>Zh, Norg</u>. <u>Khim</u>, 1974, <u>19</u>, 2501.
  (b) Kharitonov, Y. Y.; Mazo, G. Y.; Knyazeva, N. A., <u>Zh, Norg. Khim</u>., 1970, <u>15</u>, 1449.
- 103. Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J., <u>J. Am. Chem. Soc</u>., <u>1977</u>, <u>99</u>, 8055.
- 104. Hendricks, S. B.; Teller, E., <u>J. Chem. Phys</u>., 1942, <u>10</u>, 147.

