Intercalation of Catalytically Active Metal Complexes in Mica-Type Silicates. Rhodium Hydrogenation Catalysts

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Abstract: Cationic hydrogenation catalyst precursors of the type RhL_n^+ (L = triphenylphosphine; $n = 2, 3$) have been intercalated in a swelling mica-type silicate (hectorite) by the reaction of triphenylphosphine with $Rh_2(CH_3CO_2)_{4-x}{}^{x+}$ ($x = 1, 2$) ions on the interlamellar cation exchange sites of the layered silicate. The reduction in methanol of a terminal olefin (1-hexene) with the intercalated complexes occurs without isomerization, whereas extensive isomerization to internal olefins is observed with the analogous catalyst system in homogeneous solution. The difference in specificity between the intercalated and homogeneous catalyst systems is accounted for in terms of the position of an equilibrium, previously proposed by Schrock and Osborn, between catalytically active dihydride and monohydride rhodium complexes: $RhH_2L_n^+ \rightleftarrows RhHL_n + H^+$. The dihydride is a good terminal olefin 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 Brønsted acidity that is believed to arise from the dissociation of hydrated Na^+ ions which are also present on the interlamellar surfaces. A dramatic enhancement in substrate selectivity is observed for reduction of alkynes to cis olefins with the intercalated catalyst. The initial rates of reduction of relatively small alkynes (1-hexyne, 2-hexyne) in interlayers swelled with methanol to an average thickness of 7.7 Å ($= \Delta d_{001}$) are comparable to those observed with the homogeneous catalyst. With larger alkynes, such as diphenylacetylene, the intercalated rates may be up to 100 times lower than 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 ratios of intercalated to homogeneous rates for the reduction of 2-decyne are 0.85 and 0.02, respectively, with CH_2Cl_2 ($\Delta d_{001} = 10.0$ Å) and C_6H_6 ($\Delta d_{001} = 5.7$ Å) 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 C≡C bond is oriented perpendicular to the silicate sheets.

Introduction

The swelling mica-type silicates generally referred to as smectites have layer lattice structures in which two-dimensional silicate sheets approximately 9.6 Å thick are separated by interlayer cations.[1] The interlayer alkali metal or alkaline earth cations found in the native minerals or their synthetic analogues can be replaced by simple ion-exchange methods with almost any desired cation, including transition-metal ions, carbonium ions, and even protonated proteins. Moreover, the thickness of the interlayer region occupied by the exchange cations can be varied by the adsorption of polar solvents on the large internal surface area (~750 m^2/g).

Electron spin resonance studies[2,3] have shown that simple intercalated ions, such as hydrated Cu^{2+} and Mn^{2+}, tumble rapidly in a solution-like environment when the interlayers are swollen by water to a thickness of 10–12 Å. Rapid tumbling has also been observed for organic nitroxide spin probes in swollen smectite systems.[4] These observations suggested to us that it should be possible to carry out metal complex catalyzed reactions in the intracrystal space of the minerals. The results described in earlier communications[5,6] have indicated that cationic rhodium triphenylphosphine complexes can indeed be electrostatically intercalated in at least two smectites, namely, hectorite and montmorillonite, while at the same time retaining their solution-like properties as catalyst precursors for olefin hydrogenation.

In any particular solvent-swollen system, the interlayers hosting the metal complex catalyst are more or less of uniform thickness and polarity. Therefore, the possibility exists for selective substrate absorption and reaction based on size, shape, or polarity. In addition, preferred orientations of the intercalated complex under certain conditions of swelling may cause its substrate selectivity to differ from the selectivity of the same catalyst in homogeneous solution or from the selectivity of related complexes covalently bonded to the surfaces 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. The object of the present work, therefore, was to investigate the potential effects of intercalation on the substrate selectivity of cationic rhodium phosphine catalyst precursors in the hydrogenation of olefins and acetylenes.

Results and Discussion

Homogeneous Catalyst System. The cationic metal complex catalyst system selected for this investigation is one that Legzdins et al.[7,8] originally developed for the purpose of hydrogenating olefins that are soluble only in polar media. 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_3) and molecular hydrogen. The product of the protonation reaction was believed to be the solvated $Rh_2{}^{4+}$ ion, which reacted with PPh_3 to form cationic Rh(I) catalyst precursors 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[9] have noted that $Rh_2{}^{4+}$ as prepared by inner-sphere reduction of $Rh^{III}(H_2O)_5Cl^{2+}$ with $Cr^{2+}(aq)$ has chemical and physical properties different from those claimed for $Rh_2{}^{4+}$ by Legzdins et al. 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.

Our ^1H NMR studies of the protonation of Rh_2OAc_4 by HBF_4 in methanol under the conditions used by Legzdins et al. show that ca. 30% of the acetate ligands react to form methyl acetate. The remaining acetates are distributed be-

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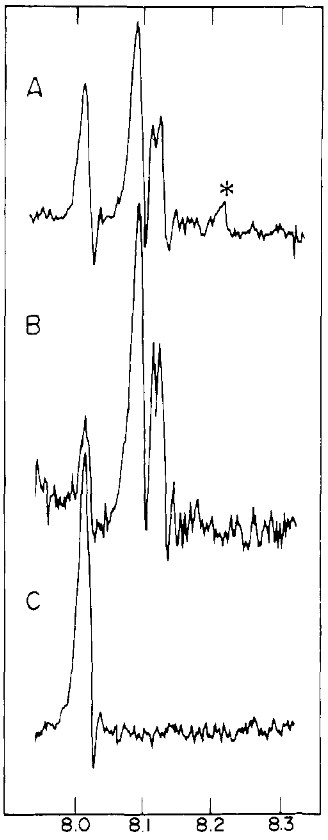

Figure 1. Acetate methyl proton resonance lines of (A) 0.008 M $Rh_2(OAc)_4$ after reaction at 60 °C for 41 h with 0.032 M HBF_4 in methanol, (B) solution A after partial vacuum distillation of solvent and methyl acetate, (C) solution B after addition of 3.0 mol of PPh_3 per mol of rhodium. The line marked by an asterisk is a spinning sideband of a solvent resonance.

tween $Rh_2(OAc)_3^+$ and $Rh_2(OAc)_2^{2+}$ complexes which are present in a 3:1 molar ratio. Figure 1A illustrates the acetate methyl resonances of $Rh_2(OAc)_4$ after reaction with HBF_4 in methanol. The line at τ 8.01 is assigned to methyl acetate, and the remaining lines are assigned to the $Rh_2(OAc)_{4-x}^{x+}$ (x = 1, 2) complexes. The line assignments are verified in part by the observation that the τ 8.01 line decreases in intensity upon partial vacuum distillation, whereas the remaining three lines do not change in relative intensity (Figure 1B). The addition of PPh_3 to the $Rh_2(OAc)_{4-x}^{x+}$ solution at PPh_3:Rh = 3:1 results in the loss of all coordinated acetate and a concomitant increase in the methyl acetate concentration (Figure 1C). Therefore, the transformation of Rh in the reaction system of Legzdins et al. is better described according to the equation:

$$Rh_2(OAc)_4 \xrightarrow[MeOH]{HBF_4} Rh_2(OAc)_{4-x}^{x+} \xrightarrow{n\text{-}PPh_3} Rh(PPh_3)_n^+ \quad (x = 1, 2) \tag{1}$$

It is presumed, based on analogies to the recent work of Schrock and Osborn[10] (vide infra), that the addition of H_2 to $Rh(PPh_3)_n^+$ forms a dihydride, which may exist in equilibrium with a monohydride:

$$RhH_2(PPh_3)_n^+ \rightleftarrows RhH(PPh_3)_n + H^+ \quad (n = 2 \text{ or } 3) \tag{2}$$

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

Intercalation Reactions. A schematic representation of the silicate sheets and interlayer exchange cations of hectorite is provided in Figure 2. The green $Rh_2(OAc)_{4-x}^{x+}$ (x = 1, 2) complexes prepared by protonation of $Rh_2(OAc)_4$ readily displace the interlayer Na^+ ions of the mineral in methanol suspension. Loadings corresponding from 0.7 to 20% of the exchange capacity of the mineral (~73 mequiv/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 anhydrous unit cell formula of the mineral ($Na_{0.66}[Mg_{5.34}, Li_{0.66}](Si_{8.00})O_{20}(OH,F)_4$) and the a and b cell parameters (5.25 × 9.18 Å), the average distance between exchange ions is ~8.7 Å. When 20% of the exchange sites are populated by rhodium, the average Rh-Rh distance is ~20 Å, which should allow ample surface area for formation of $Rh(PPh_3)_n^+$ complexes.

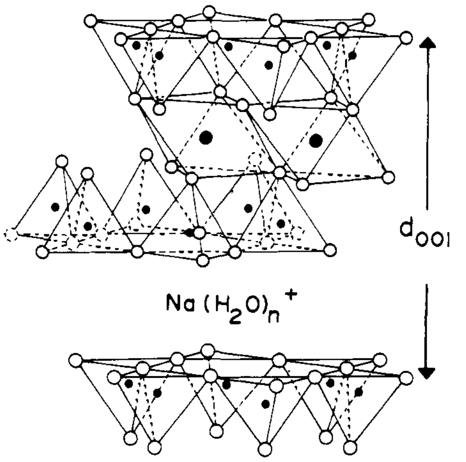

Figure 2. Schematic representation of the structure of hectorite. Oxygen atoms of the silicate sheet are represented by open circles. The upper and lower layers of tetrahedral holes are occupied mainly by silicon. Magnesium and lithium occupy the central layer of octahedral holes. The interlayer exchange ions are mainly solvated Na^+ ions. d_{001} defines the 001 basal spacing.

Treatment of the green $Rh_2(OAc)_{4-x}^{x+}$ hectorite with methanolic solution of PPh_3 affords yellow-orange $Rh(PPh_3)_n^+$-hectorite. Evidence for the loss of coordinated acetate in the intercalated state is provided by infrared spectroscopy. Figure 3A shows the 1800-1200-cm^{-1} spectrum of Na^+ hectorite solvated by methanol. Replacement of 10% of the Na^+ ions by $Rh_2(OAc)_{4-x}^{x+}$ ions gives spectrum 3B, in which the bands at 1575 and 1453 cm^{-1} are assigned to the symmetric and antisymmetric vibrations of coordinated acetate.[11,12] Upon the addition of PPh_3 to $Rh_2(OAc)_{4-x}^{x+}$-hectorite at a PPh_3 to Rh ratio of 3:1, the acetate bands are replaced by two new bands at 1485 and 1439 cm^{-1}. These latter bands are assigned to the in-plane deformations of the phenyl ring of PPh_3.[13]

All of the bound PPh_3 in $Rh(PPh_3)_n^+$-hectorite is coordinated to rhodium as Na^+-hectorite physisorbs negligible quantities of the ligand. The average number of PPh_3 ligands per rhodium increases with increasing initial concentration of ligand in solution. As can be seen from the data in Table I, at the concentrations of PPh_3 employed a total of 3 and 9 mol of PPh_3 per mol of rhodium are needed to achieve 2:1 and 3:1 PPh_3 to Rh ratios, respectively, in the intercalated state. Apparently, some rhodium centers are more accessible than others for reaction with PPh_3. The difference in accessibility may be related to nonuniform swelling of the interlayers by methanol (vide infra). It is noteworthy that we found no spectroscopic evidence for the formation of $POPh_3$ in the reduction of $Rh_2(OAc)_{4-x}^{x+}$- to $Rh(PPh_3)_n^+$-hectorite even though Mitchell et al.[14] have observed the oxide in the reduction of protonated $Rh_2(OAc)_4$ to $Rh(PPh_3)_3(OAc)$ in homogeneous solution. However, we do observe the sharp absorption bands of $POPh_3$ (259, 265, and 272 nm) when the reduction is carried

Table I. Average Compositions of $Rh(PPh_3)_n{}^+$-Hectorite Complexes Prepared by Reaction of $Rh_2(OAc)_{4-x}{}^{x+}$-Hectorite and PPh_3 in Methanol[a]

initial PPh_3 concn, mmol/L	total PPh_3/Rh ratio	final PPh_3 concn, mmol/L	PPh_3/Rh for intercalated complex
1.0	1.5	0.15	1.3
1.5	2.3	0.37	1.7
2.0	3.0	0.73	1.9
3.0	4.5	1.5	2.2
4.0	6.0	2.2	2.7
6.0	9.0	4.0	3.0

[a] In each reaction 0.20 g of $Rh_2OAc_{4-x}{}^{x+}$-hectorite containing 0.86 wt % Rh was suspended in 25 mL of solution. Filtrates were analyzed spectroscopically for PPh_3 after a reaction time of 20 min at 25 °C.

out in the presence of trace amounts of oxygen. Thus, it is likely that the solvent, rather than PPh_3, is the reducing agent in the conversion of Rh(II) to Rh(I), though no attempt has been made to identify the oxidation product.

Olefin Reductions. $Rh(PPh_3)_n{}^+$-hectorite is prepared as a catalyst precursor for reduction of 1-hexene by adding enough PPh_3 to a methanol slurry of $Rh_2(OAc)_{4-x}{}^{x+}$-hectorite so that the average value of n for the surface complexes is in the range 2.0-3.0 (cf. Table I). A preliminary study of the effects of catalyst loading on the rate of reduction of 1.0 M 1-hexene in methanol showed that the turnover frequency or rate per mmol of rhodium remained constant over the range 0.06-0.7 wt %. At loadings above 0.7 wt %, the turnover frequency decreased with increasing loading. Thus, all subsequent reactions were carried out at 0.72 ± 0.04 wt % loading. At this loading ~10% of the Na^+ exchange ions have been replaced by rhodium complex. Based on the estimated size of a $Rh(PPh_3)_2{}^+$ complex (160 Å^2), at least 25% of the total surface area is occupied by the complex ion. The size of individual hectorite platelets is <2000 Å, with the average size probably somewhere between 500 and 1000 Å, as judged from sedimentation rates. Simple geometric considerations indicate that relatively rapid diffusion of reactants and products must occur 30-70 Å into the interlayer regions, even when the complex catalyst is localized to surface regions near the platelet edges. The decrease in rate beyond 0.7% loading may indicate an increased tendency toward segregation of the Na^+ and metal complex ions into different interlayers. Interlayers which are covered with a complete monolayer of metal complex should be more susceptible to diffusion limitations.

The reduction of 1-hexene with $Rh(PPh_3)_n{}^+$-hectorite is preceded by a brief induction period, probably because some time is needed for the concentration of olefin to build up on the interlamellar surfaces 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 ~16 mL 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 occurs over the observed range of substrate hydrogenation (60%).

The performance of $Rh(PPh_3)_n{}^+$-hectorite as a catalyst precursor for hydrogenation of 1-hexene is compared in Table IIA with the behavior of homogeneous $Rh(PPh_3)_n{}^+$ complexes as precursor for reduction of the same substrate under analogous reaction conditions. It is seen 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 more than two times lower than 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_3 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 IIB show that the homogeneous catalyst is much less active for hydrogenation of 2-hexene than 1-hexene, the initial rates differing by more than a factor of 10. On the other hand, the intercalated complexes show even lower activity for hydrogenation of 2-hexene (Table IIB), 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 olefins is enhanced by intercalation. The low activity of the intercalated complex toward 2-hexene is not due to inhibitive complexation effects 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.

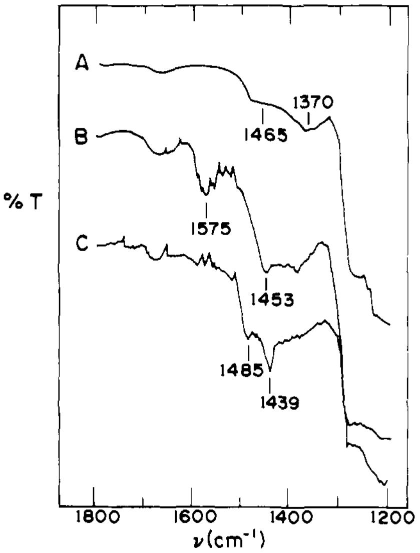

Figure 3. Infrared spectra (1800-1200 cm^{-1}) of methanol-solvated hectorites: (A) Na^+-hectorite, (B) $Rh_2(OAc)_{4-x}{}^{x+}$-hectorite, (C) $Rh(PPh_3)_x{}^+$-hectorite. The rhodium loadings used to obtain spectra B and C (0.76 wt %) correspond to ~10% of the cation exchange capacity of the mineral.

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 the equilibrium between the catalytically active dihydride and monohydride complexes proposed in eq 2. Schrock and Osborn[10] have shown that an equilibrium mixture of $RhH_2L_n{}^+$ and $RhHL_n$ complexes results from the hydrogenation of $Rh(diene)L_n{}^+$ catalyst precursors, where L is a tertiary phosphine and n = 2 or 3. The presence of a Brønsted acid favors the almost colorless cationic dihydride complexes, which catalyze the hydrogenation of terminal olefins with little or no isomerization. The neutral, deep yellow, monohydride complexes, which can be generated in the presence of a sterically hindered base such as NEt_3, are even better hydrogenation catalysts, but they are also good isomerization catalysts. The hydrogenation properties of the homogeneous $Rh(PPh_3)_n{}^+$ precursors formed from $Rh_2(OAc)_{4-x}{}^{x+}$ and PPh_3 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

Table II. Catalytic Hydrogenation of 1-Hexene and 2-Hexene in Methanol with Intercalated and Homogeneous $Rh(PPh_3)_n^+$ Complexes[a]

A. 1-Hexene

catalyst system	PPh_3/Rh	catalyst turnovers[b]	rate[c]	% isomerization[d]
$Rh(PPh_3)_n^+$-hectorite[e]	4.0	100 (5%)[f]	16	<1
		500 (25%)	16	<1
		1000 (50%)	16	<1
		1200 (60%)	13	<1
	6.0	100 (5%)	17	<1
		500 (25%)	16	<1
		1000 (50%)	17	<1
		1200 (60%)	15	<1
homogeneous soln	2.0	100 (5%)	180	
		250 (13%)	140	14
		600 (30%)	44	51
		750 (37%)	~6	58
	4.0	100 (5%)	200	
		480 (24%)	190	14
		850 (43%)	130	23
		1000 (50%)	54	30
		1200 (60%)	~7	34
homogeneous soln (0.07 M $HClO_4$)	4.0	100 (5%)	240	<1
		500 (25%)	150	<1
		900 (45%)	120	2
		1200 (60%)	48	5
		1600 (80%)	~3	18
homogeneous soln (0.07 M NEt_3)	4.0	100 (5%)	260	2
		400 (20%)	150	6
		500 (25%)	28	65
		600 (30%)	~5	69

B. 2-Hexene[g]

catalyst system	PPh_3/Rh	catalyst turnovers	rate
$Rh(PPh_3)_n^+$-hectorite	4.0	<20 (<1%)	<0.2
	6.0	<20 (<1%)	<0.2
homogeneous soln	2.0	100 (5%)	15
	4.0	200 (10%)	11
		700 (35%)	~5
homogeneous soln (0.07 M $HClO_4$)	4.0	100 (5%)	~1.0

[a] Initial substrate concentration is 1.0 M in methanol; initial substrate to Rh ratio is 2000:1; temperature, 25 °C. [b] Defined as moles of substrate hydrogenated per mol of Rh. [c] Rate of hydrogen uptake, mL H_2 min^{-1} (mmol $Rh)^{-1}$. [d] Fraction of total 1-hexene isomerized to 2- and 3-hexenes. [e] Rhodium loading is 0.72 ± 0.04 wt %. [f] Values in parentheses give the fraction of total substrate that was hydrogenated. [g] Hydrogenation data for 2-hexenes were obtained for a cis-trans mixture.

Table III. Hydrogen Uptake Rates for Reduction of 1-, 2-, and 3-Hexyne with Intercalated and Homogeneous Rhodium Triphenylphosphine Catalyst Prescursors[a]

	$PPh_3/Rh = 3$		$PPh_3/Rh = 6$	
catalyst turnovers	intercalated	homogeneous	intercalated	homogeneous
	A. 1-Hexyne			
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
	B. 2-Hexyne			
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
	C. 3-Hexyne			
100	330	1100	360	1800
250	370	1100	350	1700
500	380	1100	330	1700
750	370	980	330	1700
1000	340	800	310	1600
1250	280	490	270	1500
1500	190			1400

[a] Initial substrate concentration is 1.0 M; initial substrate to Rh ratio is 2000:1; temperature, 25 °C. Rates are reported as mL H_2 min^{-1} (mmol $Rh)^{-1}$. Rhodium loading of the intercalated catalysts is 0.72 ±0.04 wt %.

data in Table IIA, the extent of isomerization of 1-hexene under homogeneous hydrogenation conditions is dramatically reduced in the presence of 0.07 M $HClO_4$ and greatly enhanced in 0.07 M NEt_3 relative to neutral methanol solution. Moreover, in the presence of 0.07 M $HClO_4$ a cis-trans mixture of 2-hexene is very slowly reduced by $Rh(PPh_3)_n^+$ precursors at a total PPh_3 to Rh ratio of 4:1 (cf. Table IIB), 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 NEt_3. The desorption of a yellow rhodium phosphine complex also occurs in the presence of NEt_3, but the desorption rate is sufficiently low to allow the observation of surface isomerizaton 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 $Rh(PPh_3)_n^+$ precursors in the presence of NEt_3.

The surface Brønsted acidity of swelling layered silicates arises mainly from the hydrolysis of the interlayer exchange cations.[15,16] In the system investigated here, the principal exchange ion is Na^+, and its hydrolysis, due to the presence of small amounts (~0.2 wt %) of water in methanol, probably determines the surface acidity. Although hydrated Na^+ is very weakly acidic in solution, its activity is greatly increased on layered silicate surfaces. For example, hydrated Na^+ on montmorillonite, a layered silicate closely related to hectorite, is sufficiently acidic to react with *meso*-tetraphenylporphyrin in acetone to give small but detectable amounts of surface-bound diprotonated *meso*-tetraphenylporphyrin dication.[17]

Alkyne Reactions. $Rh(PPh_3)_n^+$ complexes are also catalyst precursors for the reduction of alkynes to the corresponding cis olefins. The stereoselectivity of the reaction via a monohydride or dihydride mechanism has been discussed previously by Schrock and Osborn.[18] Typical hydrogen uptake rates for reduction of 1-, 2-, and 3-hexyne under homogeneous and intercalated catalyst conditions are compared in Table III.

The data for 1-hexyne (Table IIIA) 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. 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 systems is more clearly illustrated by the hydrogen uptake plots shown in Figure 4. Upon the addition of fresh substrate at the times indicated in the figure, the activity of the homogeneous

Table IV. Initial Hydrogen Uptake Rates for Reduction of Alkynes in Methanol with Intercalated and Homogeneous Rhodium Triphenylphosphine Catalyst Precursors[a]

substrate	rate, mL H_2 min^{-1} (mmol Rh)$^{-1}$ intercalated	homogeneous	R_I/R_H[b]
1-hexyne	2100	2100	1.0
2-hexyne	2200	2400	0.92
2-decyne	1200	2500	0.48
3-hexyne	360	1800	0.20
PhC≡CPh	<1	100	<0.01

[a] The reaction conditions are the same as those given in Table III except that $PPh_3/Rh = 6.0$ in all cases. [b] Ratio of intercalated to homogeneous rates.

system is 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 precursors by relatively acidic terminal alkynes has been observed independently by Schrock and Osborn.[18] These workers suggested one possible mechanism for inactivation for the formation of complexes containing Rh—C≡CR bonds. Whatever the mechanisms of inactivation may be, it is significantly inhibited by intercalation of the catalyst in layered silicates.

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 IIIB), but in the case of 3-hexyne as substrate the initial intercalated rates are three to five times lower than the homogeneous rates (Table IIIC). 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 IV. 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. This also means 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 substrates is sufficiently large. For example, the relative rates for 2-hexyne and 3-hexyne reduction are 6:1 for the intercalated catalyst and only 1.3:1 for the homogeneous catalyst. Even for the sterically similar substrates 2-hexyne and 2-decyne, intercalation enhances the selectivity of the metal complex by almost a factor of 2.

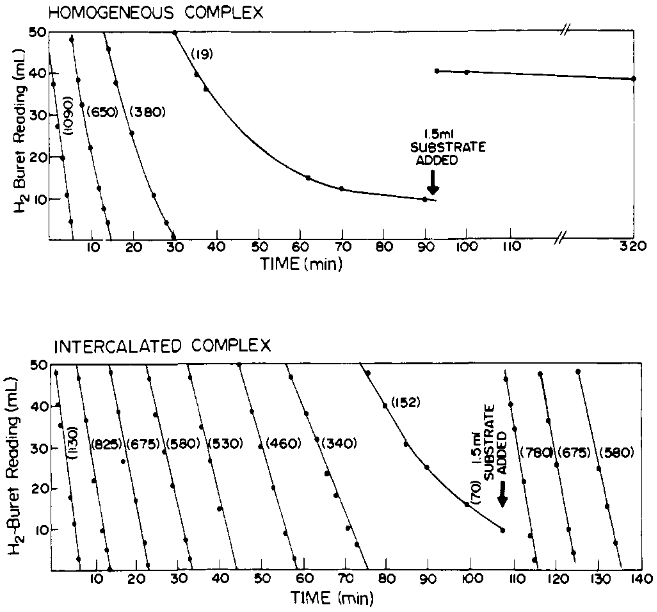

Figure 4. Hydrogen uptake plots for reduction in methanol of 1-hexyne to *cis*-1-hexene with homogeneous and intercalated rhodium triphenylphosphine complexes. The arrows indicate the times at which fresh substrate was added. In both catalyst systems the initial substrate concentration is 1.0 M, the substrate to rhodium ratio is 2000:1, the total PPh_3:Rh ratio is 3:1, and the temperature is 25 °C.

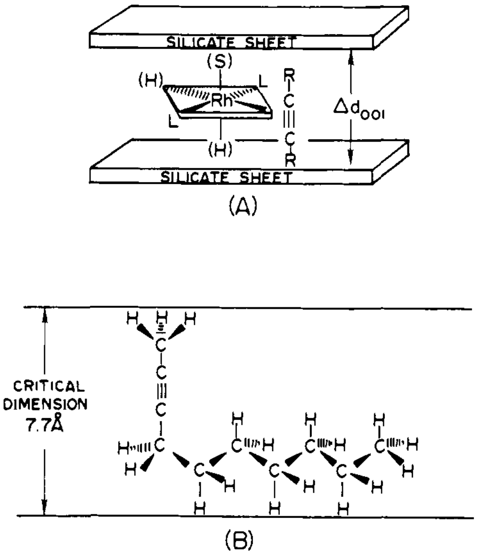

Figure 5. (A) Proposed orientation of the alkyne-rhodium triphenylphosphine complex between the silicate sheets of hectorite prior to hydrogen transfer. The Δd_{001}, which is obtained by subtracting the thickness of the silicate sheet (~9.6 Å) from the observed 001 X-ray reflection, is a measure of the interlayer thickness. (B) The critical dimension of 2-decyne, defined as the minimum distance which must be spanned by the molecule when the C≡C axis is perpendicular to the silicate sheets.

The origin of the 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 methanol-solvated $Rh(PPh_3)_n^+$-hectorite at 0.72 wt % Rh loading corresponds to a spacing of 17.3 Å. Since the silicate sheets are 9.6 Å thick, the average Δd_{001} value, which is a measure of the thickness of the interlayer region occupied by the complex, is 7.7 Å. Schrock and Osborn have suggested on the basis of NMR evidence a trans phosphine ligand geometry for $RhH_2(PPh_3)_2S_2^+$ (S = CH_3CN). Based on differences in reactivity toward H_2 of bis(phosphine)rhodium complexes containing monodentate and bidentate phosphine ligands, Halpern et al.[19] have also suggested a trans phosphine geometry for $RhH_2L_2S_2^+$ complexes. The Δd_{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≡C axis is most likely perpendicular to the phosphine-rhodium axis and, hence, perpendicular to the silicate sheets as schematically illustrated in Figure 5A. Unfavorable interactions between the alkyl groups of the substrate and the silicate oxygens could inhibit this spatial arrangement when the 001 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

Table V. Initial Rates of Hydrogen Uptake for Reduction of 2-Decyne to *cis*-2-Decene in Different Solvents with Intercalated and Homogeneous Catalysts[a]

solvent	rate, mL min^{-1} (mmol Rh)$^{-1}$ intercalated	homogeneous	R_I/R_H	Δd_{001}, Å
CH_2Cl_2[b]	2800	3300	0.85	10.0
MeOH	1200	2800	0.43	7.7
Et_2O/MeOH (3:1 v/v)	660	2800	0.24	6.7
C_6H_6[b]	20	1000	0.02	5.7

[a] For reaction conditions see footnote *a*, Table III. $PPh_3/Rh = 6:1$. [b] These solvents contain 7% methanol by volume.

Table VI. Critical Dimensions of Selected Substrates[a]

substrate	critical dimension, Å	substrate	critical dimension, Å
1-hexyne	7.0	$C_6H_5C{\equiv}CC_6H_5$	13.8
2-hexyne	7.7	1-hexene	5.3
3-hexyne	8.8	*cis*-2-hexene	5.8

[a] Estimated from space-filling models.

is perpendicular to the silicate sheets. Figure 5B illustrates the critical dimension of 2-decyne (7.7 Å), as estimated from space-filling models. This value requires a gauche conformation about the C_4–C_5 bond rather than the more spatially demanding anti conformation preferred by the free molecule.

A precise "on–off" switching type of relationship between Δd_{001} and the reactivity of the intercalated complex toward a given substrate cannot be expected, because the spacings between the silicate sheets are not rigorosuly 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.[20-23] Nevertheless, relative to homogeneous solution rates, the rates of reduction of a substrate with the intercalated complex should decrease with decreasing Δd_{001} in the region where Δd_{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 in Table V, the initial R_I/R_H values range from 0.85 with CH_2Cl_2 as the solvating molecule (Δd_{001} = 10.0 Å) to 0.02 with benzene (Δd_{001} = 5.7 Å).

Table VI lists the critical dimensions of other substrates used in this study. It is noteworthy that the critical dimensions of 2-decyne and 2-hexyne are the same (7.7 Å), yet, as pointed out earlier, their initial reduction rates with methanol-solvated $Rh(PPh_3)_n{}^+$-hectorite (Δd_{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 silicate. The other point to be noted is that the critical dimensions of 1- and 2-hexene are considerably smaller than those of the corresponding alkynes, yet the initial R_I/R_H values are <0.1 for the olefins (cf. absolute rates in Table II) and near unity for the alkynes (cf. Table IV). 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. Studies of the physisorption of alkynes and olefins on layered silicate surfaces would be of interest.

Catalyst Desorption. Finally, it must be pointed out that a small, but detectable, amount of metal complex is desorbed from the intercalated catalyst during the course of reaction. For example, after approximately 4000 catalyst turnovers in the hydrogenation of 2-hexyne, approximately 5% of the initial total activity is observed in the solution phase. Since the intercalated and homogeneous rates are comparable for this substrate, about 5% of the metal complex is lost to solution. In general, the intercalated cations in layered silicates can only be replaced by ion exchange with other cations, because electrical neutrality of the structure must be maintained. Therefore, metal complex desorption is not expected in catalyzed reactions in which the reactants and products are electrically neutral, such as those observed here. However, a reasonable mechanism for desorption is possible based on the equilibrium defined by eq 2, in which the dihydride complex can dissociate to give H^+ on the exchange sites of the silicate and the neutral monohydride can be desorbed into solution. Support for this mechanism is provided by the observation that the extent of rhodium desorption is greatly increased in the presence of triethylamine (vide supra).

The loss of precious metal complex would be a serious disadvantage in any large-scale application of intercalation catalysts. We have recently demonstrated, however, that the neutral PPh_3 ligands on a rhodium hydrogenation catalyst can be replaced by a positively charged ligand such as $Ph_2P(CH_2)_2P^+Ph_2CH_2Ph$.[24] The replacement of neutral ligands by positively charged ligands would permit proton dissociation of the dihydride while retaining positive charge on the complex. Positively charged ligands should also provide a route to cationic analogues of neutral metal complex catalysts that would be suitable for intercalation in layered silicate structures.

Experimental Section

Materials. Rhodium(II) acetate dimer was prepared by reaction of $RhCl_3$, sodium acetate, and acetic acid in hot ethanol according to the procedure described by Wilkinson and co-workers.[8] The product was recrystallized from methanol and recovered as the methanol adduct $Rh_2(CH_3CO_2)_4{\cdot}2(CH_3OH)$. Natural sodium hectorite in the spray-dried form was obtained from Baroid Division of NL Industries. The 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 0.1 M $NaHSO_4$, and then washing it free of sulfate with distilled water. All solvents were reagent grade and were deoxygenated before use by bubbling a stream of dry argon or nitrogen through them for at least 30 min. 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 (Mallinckrodt) or activated 4A molecular sieves. Most of the substrates 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 substrates immediately before use. Technical grade 1-hexene (Pfaltz and Bauer) 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) was shaken with and distilled from a mixture of $NaBH_4$ and ethyldiglyme. 1-Hexyne, 2-hexyne, 3-hexyne, and 2-decyne (Farchan Division, Story Chemical Corp.) were distilled over activated Al_2O_3 under an argon atmosphere. The chromatographic grade alumina, 80–200 mesh (Matheson Coleman and Bell), was activated by heating to 300 °C for 24 h and then allowing it to cool under argon. Triphenylphosphine (Aldrich) showed no observable oxide impurity by ^{31}P NMR and was used as purchased.

Protonation of Rhodium Acetate. Protonation of rhodium acetate was undertaken in a nitrogen-filled glovebox to ensure a product uncontaminated by free or bound oxygen. The protonating solution of 0.66 mL (4.9 mmol) of aqueous 48% tetrafluoroboric acid (J. T. Baker) in 150 mL of methanol was deoxygenated by flushing with dry nitrogen for at least 20 min. The solution and 0.60 g (1.2 mmol) of $Rh_2(CH_3CO_2)_4{\cdot}2CH_3OH$ were mixed and heated to 60 °C in an oil bath and stirred until the green solid dissolved (approximately 2 days). A small amount of insoluble black material (possibly rhodium metal) was removed from the solution by filtration. After a reaction time of 41 h, one solution exhibited bands at 610, 425, and 250 nm, in favorable agreement with the band assignments made by Wilson and Taube[9] for $Rh_2(OAc)_3{}^+$ and $Rh_2(OAc)_2{}^{2+}$. ^1H NMR spectra showed the presence of methyl acetate resonances at τ 8.01 and 6.39. Lines at τ 8.09, 8.11, and 8.12 were assigned to bridging acetates in $Rh_2(OAc)_3^+$ and $Rh_2(OAc)_2^{2+}$. Approximately 30% of the total acetate was converted to methyl acetate. Specific chemical shift assignments for $Rh_2(OAc)_2^{2+}$, which may exist as cis and trans isomers, and $Rh_2(OAc)_3^+$ could not be made because of insufficient spectral resolution.

Preparation of $Rh_2(CH_3CO_2)_{4-x}{}^{x+}$-Hectorite. In a typical experiment, 0.20 g of natural 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 portions of MeOH and finally dried by suction. Rhodium analyses of several samples prepared by this procedure gave an average composition of 0.72 ± 0.04% rhodium by weight. Samples containing higher or lower loadings of rhodium were prepared by varying the concentration of $Rh_2(OAc)_{4-x}{}^{x+}$ and the mass of hectorite used in the exchange reaction.

Preparation of Rhodium Triphenylphosphine Catalyst Precursors. Homogeneous solutions of the catalyst precursor were prepared under oxygen-free conditions of treating 0.92 mL of the protonated rhodium acetate solution (0.015 mmol of Rh) with desired amounts of 0.05 M triphenylphosphine solution and diluting the mixture to 25 mL with solvent. Samples of the supported catalyst were prepared by treating freshly prepared rhodium-exchanged hectorite containing 0.015-0.030 mmol of Rh with 0.05 M PPh_3 to obtain the desired PPh_3:Rh ratio. The slurry was then diluted to 25 mL with solvent. Treatment of the green rhodium-exchanged hectorite with PPh_3 gave an immediate color change to a dark red-brown color which gradually lightened to a yellow-orange color upon standing for several minutes. Analogous color changes occur with the preparation of homogeneous catalyst solutions, except that they occur much more rapidly.

Reaction of Intercalated $Rh_2(OAc)_{4-x}{}^{x+}$ and PPh_3. The amount of PPh_3 that reacts with intercalated $Rh_2(OAc)_{4-x}{}^{x+}$ complexes was determined by monitoring the decrease in the absorbance of the 240-nm band of free phosphine ligand in the solution phase. Freshly prepared rhodium-exchanged hectorite (0.20 g, 0.86 wt % Rh) was suspended in 25-mL portions of methanol solutions of PPh_3. The PPh_3:Rh ratios were varied over the range 1.5-9.0. The slurries were filtered after a reaction time of 20 min, and the PPh_3 remaining in solution was analyzed spectroscopically.

Hydrogenation Reactions. The catalyst solution or suspensions were placed in a specially designed flat-bottom, hourglass-shaped flask (Figure 6). This design was especially effective in minimizing "creeping" of the finely divided mineral-supported catalyst up the walls of the flask during the course of the reaction. In a typical experiment, the flask was charged with 0.0075-0.015 mmol of rhodium catalyst precursor, and the flask was attached to a glass vacuum manifold equipped with gas inlets, gas buret, mercury leveling bulb, and mercury manometer. A stream of hydrogen was bubbled through the reaction vessel for at least 1 h before substrate addition. Enough solvent was added to the substrate to bring the initial substrate concentration to 1.0 M. The rate of hydrogen uptake was monitored by observing the change in volume necessary to maintain constant pressure of 1 atm.

Gas-phase chromatography of products was performed with a Varian Associates Model 90-P single-column chromatograph equipped with a thermal conductivity detector. The columns were a 5 ft × 0.25 in. 3% SE-30 oil on a diatomite CLQ-100/120 support, a 10 ft × 1/8 in. 10% UCW (Hewlett-Packard) on 80-100 mesh Chromosorb W, and a 10 ft × 1/8 in. 10% $AgNO_3$ in propylene glycol on 80-100 mesh Chromosorb W support.

Physical Measurements. X-ray basal spacings were determined with a Phillips X-ray diffractometer and Ni-filtered Cu Kα radiation. Film samples were prepared by allowing methanol suspensions to evaporate on microscope slides. Basal spacings of fully solvated and swelled minerals were obtained by placing the slides in a polyethylene bag containing methanol and then heat-sealing the bags. This technique was also used to prevent the samples from coming in contact with air. UV-visible spectra were recorded on a Varian Associates 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 hectorite was placed in the reference beam to reduce the effects of scattering. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Spectra in the region 1200-1800 cm^{-1} were obtained by mulling the samples in Fluorolube and placing the mulls between CsI disks. Multiple-scan, continuous-wave ^{1}H NMR spectra at 60 MHz were obtained with a Varian Associates 56/60 analytical spectrometer equipped with a Varian Associates C-1024 time-averaging computer.

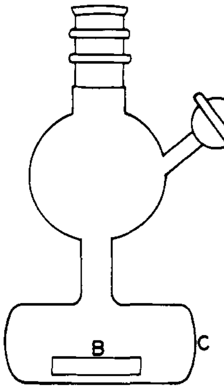

Figure 6. Reaction flask used to minimize creeping of finely divided intercalated catalyst: (A) serum cap for admitting substrates by syringe, (B) magnetic stirring bar, (C) reaction chamber, 6 (diameter) × 2 cm.

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