$\Delta S_b^\ddagger = -20$ to $+26$ cal/(mol K)].[2] For discussion purposes, rate parameters for the decarboxylation of the $Co(en)(CO_3)(H_2O)_2^+$ and a few related complexes are presented in Table IV. Within the limits of experimental uncertainty, the parameters for the $Co(en)(CO_3)(H_2O)_2^+$ complex are identical with those of the (carbonato)bis(alkylamine) complexes $Co(en)_2CO_3^+$, $Co(pn)_2CO_3^+$, and $Co(tn)_2CO_3^+$. This implies that the ring-opening mechanistic step is not much affected by the replacement of the nitrogen donor atoms of simple alkylamines by the oxygen donor atoms of simple ligands. If this implication is correct, then it is possible to rationalize the other entries in Table IV. The $Rh(en)_2(CO_3)^+$ complex is considerably less reactive than $Co(en)(CO_3)(H_2O)_2^+$ or the carbonato bis(alkylamine) complexes because of the enhanced strength of the metal–oxygen bond in the rhodium complex. The $Co(py)_2CO_3(H_2O)_2^+$ ion is less reactive than the corresponding ethylenediamine complex because amine ligands with π systems tend to decarboxylate at very slow rates.[2] For the $Co(py)_2(CO_3)_2^-$ complex, the reduced rates expected by the presence of ligand pyridine are offset by the enhancement due to a negative charge on the complex and the possible straining of the metal–oxygen bond that is related to the presence of two carbonate chelate rings and two bulky pyridine molecules.

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Registry No. $K[Co(en)(CO_3)_2]$, 54992-64-2; $Na[Co(en)(CO_3)_2]$, 85995-30-8.

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Metal Complex Catalysts Interlayered in Smectite Clay. Hydroformylation of 1-Hexene with Rhodium Complexes Ion Exchanged into Hectorite

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The cationic hydroformylation catalyst precursor $Rh(COD)(PPh_3)_2^+$, where COD = 1,5-cyclooctadiene, readily intercalates into the swelling layered silicate clay mineral hectorite by replacement of Na^+ ions initially present on the interlamellar surfaces. Under hydroformylation conditions, however, the active rhodium complex desorbs from the clay interlayers due to the formation of neutral $RhH(CO)_x(PPh_3)_2$ ($x = 1, 2$) species. Rhodium complexes containing the positively charged phosphinophosphonium ligand $Ph_2P(CH_2)_2{}^+PPh_2(CH_2Ph)$, abbreviated $P-P^+$, are shown to be much more suitable for catalyst intercalation. $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and $Rh(COD)^+$ all form cationic complexes with $P-P^+$ which bind to the clay interlayers and catalyze the hydroformylation of 1-hexene at 100 °C and 600 psi CO/H_2 when acetone is the solvating medium. Under these conditions, >95% of the 1-hexene is hydroformylated in the clay interlayers. The ratios of normal- to branched-chain aldehydes (n/b) are somewhat higher for the intercalated catalysts (2.4–3.0) than for the homogeneous catalysts under analogous conditions (1.5–2.1). In addition, the intercalated catalyst tends to lower the extent of 1-hexene isomerization relative to homogeneous solution. Spatial factors may influence the relative stabilities of primary and secondary metal alkyls formed as intermediates in the restricted interlayer regions of the layered silicate. The polarity of the solvating medium is important in promoting hydroformylation in the interlayer regions of the intercalated clay catalysts. No hydroformylation activity is observed for the intercalated catalyst in benzene, since this solvent fails to swell the hectorite interlayers and provide access to the metal centers. Solvation by DMF causes extensive dissociation of $Rh-(P-P^+)$ bonds in the clay interlayers and loss of a neutral rhodium carbonyl to solution.

Introduction

Earlier reports from our laboratory[1-3] have demonstrated that metal complex catalysts can be immobilized by intercalation in swelling layered silicate clay minerals such as montmorillonite and hectorite. Under appropriate conditions of swelling by adsorbed solvents, the interlayers occupied by the intercalant are accessible to substrates, and catalytic hydrogenation reactions analogous to those that occur in homogeneous solution can be accomplished in the solid state. Since these intercalated layered silicate intercalation catalysts are ordered in the 00*l* direction and since the degree of swelling can be controlled within rather narrow limits, they offer the potential for influencing catalyst selectivity based on the spatial requirements of substrate–metal complex intermediates formed in the restricted interlamellar space.[1]

The objective of the present study was to examine the properties of clay-intercalated hydroformylation catalysts. Most hydroformylation catalyst precursors are neutral species[4-6] that can be immobilized on polymer[7-9] and inorganic oxide[10,11] supports by covalent attachment mechanisms. However, the mechanism of catalyst intercalation in layered silicates involves an exchange reaction of Na^+ ions that normally occupy the solvated interlayer regions:

$$\overline{\underline{\mathrm{Na^+(solv)}}} + \mathrm{ML}_n^+ \xrightleftharpoons{\text{solvent}} \overline{\underline{\mathrm{ML}_n^+(\mathrm{solv})}} + \mathrm{Na^+} \qquad (1)$$

where the lines represent the negatively charged silicate layers and ML_n^+ is the catalyst precursor. Therefore, a positively charged precursor is required for catalyst immobilization in layered silicates.

Cationic complexes of the type $Rh(diene)(PPh_3)_2^+$ have been reported by Oro et al.[12,13] to have hydroformylation activity

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Table I. Homogeneous Hydroformylation of 1-Hexene with $[Rh(COD)(PPh_3)_2]PF_6$ as the Catalyst Precursor[a]

run	PPh_3 added, mol/mol of Rh	solvent	reacn temp, °C	reacn time, h	% conversion	product distribution, %: heptanal	2-methylhexanal	2-hexene	*n*/*b*
1	0	acetone	25	48	10	75	25		3.0
2	0	DMF	25	48	70	76	24		3.2
3	0	DMF (NEt_3)[b]	25	24	100	78	22		3.5
4	0	DMF ($HClO_4$)[c]	25	24	0				
5	0	acetone	100	1.0	100	52	24	24[d]	2.2
6	2	acetone	100	1.0	100	59	26	15	2.3
7	8	acetone	100	1.0	100	66	22	12	3.0

[a] Initial 1-hexene concentration is 1.0 M; CO/H_2 = 1; total pressure = 1 atm (for reactions at 25 °C) or 600 psi (at 100 °C). [b] In this run 3 mol of NEt_3 was added per mol of Rh. [c] In this run 1 mol of $HClO_4$ was added per mol of Rh. [d] trans/cis = 2.5.

under relatively mild conditions of temperature and pressure. Moreover, the infrared spectra of the intermediates formed under hydroformylation conditions were reported to be characteristic of cationic species.[13] These complexes were selected initially as promising candidates for intercalation in layered silicates, but the results obtained in the present study along with those reported recently by Crabtree and Felkin[14] suggest the catalytically active species to be electrically neutral. Consequently, the rhodium readily desorbs from the clay interlayers. However, the results reported here show in part that hydroformylation catalysts can be intercalated in a layered silicate clay by replacing the neutral phosphine ligands in certain rhodium catalysts precursors with a positively charged phosphine ligand.

Results and Discussion

Homogeneous $Rh(COD)(PPh_3)_2^+$. Table I lists the results for the homogeneous hydroformylation of 1-hexene under batch reaction conditions with $Rh(COD)(PPh_3)_2^+$ as the catalyst precursor. The conversion of 1-hexene at 25 °C is appreciably lower in acetone than in DMF, but the distribution of normal- and branched-chain aldehyde products ($n/b \simeq 3.1$) is the same for the two solvents (runs 1, 2). It is especially noteworthy that the addition of NEt_3 to the reaction mixture in DMF at 25 °C increases the reaction rate without influencing the aldehyde distribution (run 3), whereas the addition of $HClO_4$ greatly depresses the reaction (run 4). The addition of 2 mol of NEt_3 to the solution containing 1 mol of $HClO_4$ restores the catalytic activity.

Although no significant isomerization or hydrogenation of 1-hexene is observed under hydroformylation conditions at 25 °C, extensive isomerization occurs at 100 °C, along with a decrease in the *n*/*b* value (run 5). The addition of excess PPh_3 decreases the extent of isomerization and increases the *n*/*b* values (runs 6, 7).

Intercalated $Rh(COD)(PPh_3)_2^+$. Excess $Rh(COD)(PPh_3)_2^+$ in acetone readily exchanges at 25 °C with Na^+–hectorite to form a $Rh(COD)(PPh_3)_3^+$–hectorite intercalated complex in which ~22% of the Na^+ exchange ions are replaced by the rhodium complex. The exchange limit of ~22% is consistent with the value expected for monolayer formation by the rhodium complex on the interlamellar surfaces of the mineral. On the basis of the difference between the thickness of the silicate sheets (9.6 Å) and the observed 001 X-ray reflection (17.7 Å), we estimate the average thickness of the interlayers to be 8.1 Å, which agrees well with the value expected from molecular models for a monolayer. Solvating the interlayers with liquid acetone causes them to expand to ~12.5 Å. A schematic representation of the hectorite structue is given in Figure 1.

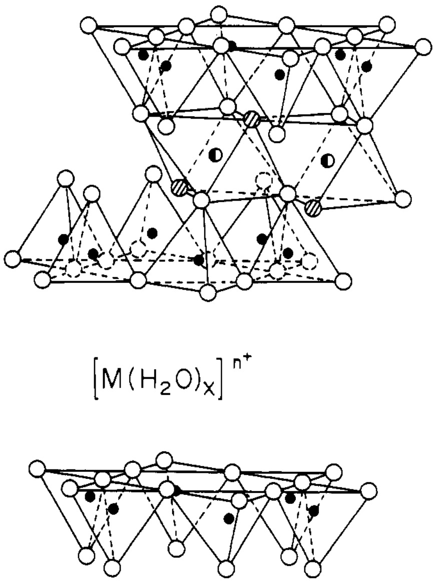

Figure 1. Schematic representation of the hectorite structure: (○) oxygen; (●) hydroxyls; (●) silicon in tetrahedral holes; (◐) Mg^{2+} or Li^+ in octahedral holes. $[M(H_2O)_x^{n+}]$ represents the interlamellar exchange cations, usually hydrated Na^+.

$Rh(COD)(PPh_3)_2^+$–hectorite at the 5% exchange level is active for the hydroformylation of 1-hexene, but extensive rhodium desorption occurs under hydroformylation conditions. Almost all of the catalysis takes place in homogeneous solution. Since electrical neutrality must be maintained in the silicate structure, the complex that desorbs from the negatively charged silicate surfaces clearly cannot be cationic. Significantly, the desorbed rhodium complex is more active than the species formed from $Rh(COD)(PPh_3)_2^+$ in homogeneous solutions. The desorbed complex in DMF, for example, undergoes ~250 catalyst turnovers in 24 h at 25 °C ($n/b \simeq 3$), whereas only ~50 turnovers occur in 48 h with $Rh(COD)(PPh_3)_2^+$ as the catalyst precursor.

Recently, Crabtree and Felkin[14] have found that the hydroformylation of 1-hexene in benzene with $Rh(COD)(PPh_3)_2^+$ in the presence of NEt_3 as a base and 1 mol of PPh_3 gave reaction rates and *n*/*b* product ratios identical with those obtained with an authentic sample of $RhH(CO)(PPh_3)_3$. Moreover, they were able to isolate the latter compound from the reaction mixture in high yield. On the basis of the results by Crabtree and Felkin, together with our findings on the behavior of homogeneous and intercalated $Rh(COD)(PPh_3)_2^+$, it is likely that the active species is a neutral monohydride, whch may exist in equilibrium with $Rh(PPh_3)_2(CO)_x^+$ species:

$$\mathrm{Rh(COD)(PPh_3)_2^+} \xrightarrow{\mathrm{CO/H_2}} \underset{x\,=\,1,\,2,\,3}{\mathrm{Rh(CO)_x(PPh_3)_2^+}} \xrightleftharpoons{\mathrm{H_2}} \mathrm{H^+} + \underset{x\,=\,1,\,2}{\mathrm{HRh(CO)_x(PPh_3)_2}} \quad (2)$$

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Table II. Hydroformylation of 1-Hexene with the $[RhCl(COD)]_2$ + $P\text{-}P^+$ Precursor System[a]

run	solvent	$P\text{-}P^+$ added, mol/mol of Rh	reacn time, h	% conversion	product distribution, %: heptanal	2-methylhexanal	2-hexene	other	*n*/*b*
				(A) Homogeneous Catalyst[b]					
8	acetone	2	3	100	45	26	25	4[c]	1.5
9	acetone	4	4	97	55	22	23		2.5
10	acetone	10	4	76	61	18	21		3.4
11	DMF	2	2	100	52	22	9	10[d]	1.8
12	C_6H_6	2	2	70	29	14	57		2.0
				(B) Intercalated Catalyst[e]					
13	acetone	2	12	80	53	22	25		2.4
14	acetone	4	18	87	63	23	8	6[d]	2.8
15[f]	DMF	2	24	22	42	45	2	11[d]	0.9
16	C_6H_6	2	18	0					

[a] Initial 1-hexene concentration is 0.4 M; 100 °C; 600 psi; $CO/H_2 = 1$. [b] 1-Hexene/Rh = 200. [c] 2-Ethylpentanal. [d] Unidentified product. [e] 1-Hexene/Rh = 1300; Rh loading, 0.32 wt %. [f] Rhodium desorption was observed in this run (see text).

The formation of $Rh(CO)_x(PPh_3)_2^+$ species from $Rh(diene)(PPh_3)_2^+$ and CO/H_2 has been established previously by Schrock and Osborn.[15]

The equilibrium proposed in eq 2 is supported by the observed acid–base dependence of the homogeneous catalyst. This equilibrium also accounts for the desorption of rhodium from the intercalated catalyst under hydroformylation conditions without loss of electrical neutrality in the silicate structure:

$$\overline{\underline{Rh(COD)(PPh_3)_2{}^+}} \xrightarrow{CO/H_2} \overline{\underline{H^+}} + HRh(CO)_x(PPh_3)_2(soln) \quad (3)$$

Since the silicate surface is acting as a base in eq 3, the mineral plays the same role as NEt_3 in homogeneous solution. Consequently, the activity of the desorbed catalyst is greater than the activity of the catalyst formed directly from $Rh(COD)(PPh_3)_2^+$ in homogeneous solution.

Utilization of a Positively Charged Ligand. In an attempt to limit the desorption of rhodium from the interlayers of hectorite, we considered replacing the neutral PPh_3 ligands on rhodium with the positively charged phosphinophosphonium ligand $Ph_2P(CH_2)_2{}^+PPh_2(CH_2Ph)$, abbreviated $P\text{-}P^+$. This approach should allow formation of a rhodium monohydride complex in the clay interlayers, but the complex should remain electrostatically bonded to the surface due to the positive charge retained by the ligand.

Following the earlier work of Wilkinson and his co-workers,[16,17] we expect to form $P\text{-}P^+$ analogues of $HRh(CO)_x(PPh_3)_2$ species by the reaction of $[RhCl(COD)]_2$ with $P\text{-}P^+$ under hydroformylation conditions:

$$[RhCl(COD)]_2 \xrightarrow{P\text{-}P^+} RhCl(COD)(P\text{-}P^+) \quad (4)$$

$$RhCl(COD)(P\text{-}P^+) \xrightarrow[2.\ CO/H_2\ (1\ atm,\ 25\ °C)]{1.\ P\text{-}P^+} RhCl(CO)(P\text{-}P^+)_2 \quad (5)$$

$$RhCl(CO)(P\text{-}P^+)_2 \xrightarrow{CO/H_2\ (37\ atm,\ 100\ °C)} RhH(CO)_x(P\text{-}P^+)_2 + HCl \quad (6)$$

The ability of $P\text{-}P^+$ to substitute for PPh_3 at rhodium centers has been verified, in part, by the previously reported[2] isolation of $RhCl(COD)(P\text{-}P^+)$ according to eq 4. The analogy between $P\text{-}P^+$ and PPh_3 was further demonstrated in the present work by the isolation of $[RhCl(CO)(P\text{-}P^+)_2][BF_4^-]_2$ as an acetone solvate from the reaction of $[RhCl(COD)]_2$ and $P\text{-}P^+$ under hydroformylation conditions when the pressure was reduced to 1 atm. The ^{31}P NMR spectrum in perdeuterioacetone at −30 °C contained two resonances at −31.5 (phosphine) and −29.0 ppm (phosphonium) with $J_{Rh\text{-}P} = 125$ and $J_{P\text{-}P+} = 31$ Hz. The chemical shift and Rh–P coupling constant for the coordinated phosphorus agree well with those reported for the neutral analogue *trans*-$RhCl(CO)(PPh_3)_2$ (−29.1 ppm, 124 Hz).[18,19] The CO stretching frequency for $RhCl(CO)(P\text{-}P^+)_2$ (1975 cm^{-1}) and $RhCl(CO)(PPh_3)_2$ (1962 cm^{-1})[18] also are in good agreement.

Table IIA lists the results for the homogeneous hydroformylation of 1-hexene at 100 °C with the $[RhCl(COD)]_2$ + $P\text{-}P^+$ precursor system. As is observed for the analogous PPh_3 system,[17] the *n*/*b* aldehyde product ratio in acetone increases with increasing $P\text{-}P^+/Rh$ (runs 8–10). However, the extent of 1-hexene isomerization shows little or no dependence on $P\text{-}P^+/Rh$. The presence of chlororhodium complexes under hydroformylation conditions may play a role in olefin isomerization. At $P\text{-}P^+/Rh = 2$ the extent of isomerization is significantly decreased when acetone is replaced with DMF as the solvent (run 11) and greatly increased when the solvent is benzene (run 12). Essentially no solvent dependence is observed for the *n*/*b* aldehyde ratio. It may be that the chlororhodium species responsible for substrate isomerization are in equilibrium with the hydridorhodium hydroformylation catalyst and that the position of the equilibrium is solvent dependent. The probable importance of chloride in olefin isomerization also is suggested by the results for the $Rh(COD)^+\text{–}(P\text{-}P^+)$ precursor system described later.

The precursors formed in the $[RhCl(COD)]_2$ + $P\text{-}P^+$ system under hydroformylation conditions readily intercalate into Na^+-hectorite. The results for the intercalated catalyst are given in Table IIB. With acetone as the swelling solvent, the *n*/*b* aldehyde product ratios obtained with the intercalated catalyst (runs 13, 14) are slightly higher than those obtained for the homogeneous catalyst (runs 8, 9). Also, catalyst intercalation results in a reduction in the rate of reaction and in the extent of substrate isomerization (at least at $P\text{-}P^+/Rh = 4$) relative to homogeneous solution.

The filtrate from run 13 showed no observable catalytic activity for 1-hexene hydroformylation (<3% conversion after 18 h). Therefore, the products obtained for the intercalated catalyst were formed almost exclusively (>95%) on the clay surfaces. That reaction occurs in the clay interlayers and not at external surface sites is verified by the absence of catalytic activity for the intercalated catalyst in benzene (compare run 16 with run 12). The latter solvent fails to swell the clay interlayers. The 00*l* X-ray spacing of the benzene-solvated clay is the same as the vacuum-dried intercalate (18.4 Å). In

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Table III. Hydroformylation of 1-Hexene in Acetone with the $[Rh(CO)_2Cl]_2$ + P-P$^+$ Precursor System[a]

run	P-P$^+$ added, mol/mol of Rh	reacn time, h	% conversion	product distribution, %: heptanal	product distribution, %: 2-methylhexanal	product distribution, %: 2-hexene	n/b
(A) Homogeneous Catalyst[b]							
17	3	2	100	54	26	20	2.1
(B) Intercalated Catalyst[c]							
18	3	18	75	71	23	6	3.1

[a] Initial hexene concentration is 0.4 M; 100 °C; 600 psi; CO/H$_2$ = 1. [b] 1-Hexene/Rh = 570. [c] 1-Hexene/Rh ≃ 1000.

Table IV. Hydroformylation of 1-Hexene in Acetone with the Rh(COD)$^+$ + P-P$^+$ Precursor System[a]

run	P-P$^+$/Rh	reacn time, h	% conversion	product distribution, %: heptanal	product distribution, %: 2-methylhexanal	product distribution, %: 2-hexene	product distribution, %: other	n/b
(A) Homogeneous Catalyst[b]								
19	2	2	100	60	30	10		2.0
(B) Intercalated Catalyst[c]								
20	2	24	60	70	23	0	7	3.0

[a] Initial 1-hexene concentration is 0.4 M; 100 °C; 600 psi; CO/H$_2$O = 1. [b] 1-Hexene/Rh = 570. [c] 1-Hexene/Rh = 900; Rh loading = 0.47 wt %.

contrast, the 00*l* spacing with acetone as the solvating medium is 20.5 Å. Thus, the interlayers of the clay are not sufficiently swollen and accessible for reaction with substrate when benzene is the solvent, and reaction is inhibited.

Although the above results confirm the hydroformylation of 1-hexene in the clay interlayers when acetone is the solvating medium, we cannot claim the complete absence of rhodium desorption. In fact, the desorption of rhodium from the clay interlayers was observed directly in DMF under hydroformylation conditions. The filtrate from run 16, for example, was catalytically active. Also, the solution exhibited an IR band near 2000 cm^{-1}, which we attribute to a terminally coordinated carbonyl stretching vibration. A reasonable mechanism for the desorption of rhodium is shown in eq 7,

$$\overline{\underline{RhH(CO)_x(P\text{–}P^+)_2}} \underset{}{\overset{CO/H_2}{\rightleftarrows}} \overline{\underline{2P\text{–}P^+}} + \text{metal carbonyl (soln)} \quad (7)$$

where Rh–(P–P$^+$) ligand dissociation results in loss of a neutral rhodium carbonyl to solution and retention of P–P$^+$ ligand on the interlamellar surfaces of the clay. The equilibrium apparently is dependent on solvent polarity, because the filtrates from the acetone and benzene solvated reaction mixtures showed no catalytic activity or IR band at 2000 cm^{-1}.

In an alternative approach to the immobilization of a rhodium hydroformylation catalyst on the interlamellar surfaces of hectorite, we investigated briefly the $[Rh(CO)_2Cl]_2$ + P–P$^+$ precursor system. The reported reactions of $[Rh(CO)_2Cl]_2$ with phosphine ligands[20,21] suggest that facile splitting of the bridge bond should occur with P–P$^+$:

$$[Rh(CO)_2Cl]_2 + 2P\text{–}P^+ \rightarrow 2RhCl(CO)_2(P\text{–}P^+) \quad (8)$$

$$[Rh(CO)_2Cl]_2 + 4P\text{–}P^+ \rightarrow 2RhCl(CO)(P\text{–}P^+)_2 + 2CO \quad (9)$$

Thus, the catalytic properties of this precursor system should be analogous to those observed for the $[Rh(COD)Cl]_2$ + P–P$^+$ systems.

The results given in Table III for 1-hexene hydroformylation in acetone agree well with those obtained for the $[Rh(COD)Cl]_2$ + P–P$^+$ precursor system. As before, no catalytic activity or IR band at 2000 cm^{-1} was observed for the filtrate. Also, the extent of substrate isomerization is lower for the intercalated catalyst (run 18) than the homogeneous catalyst (run 17), and the yield of normal aldehyde again is slightly higher for the intercalated catalyst than for the homogeneous catalyst.

To further probe the role of chloride in substrate isomerization, we have examined the hydroformylation of 1-hexene in acetone with Rh(COD)$^+$ + P–P$^+$ as a catalyst precursor system. In this case, the catalyst system was generated in situ by reaction of $[Rh(COD)Cl]_2$ in acetone with AgBF$_4$ in the presence of [P–P$^+$]BF$_4$ according to eq 10. A catalytic in-

$$[Rh(COD)Cl]_2 + 2Ag^+ + 4P\text{–}P^+ \rightarrow 2[Rh(COD)(P\text{–}P^+)]^{3+} + 2AgCl \quad (10)$$

termediate analogous to that formed from Rh(COD)(PPh$_3$)$_2^+$ is expected under hydroformylation conditions (cf. eq 2), except that PPh$_3$ has been replaced by P–P$^+$. The data in Table IV for the homogeneous catalyst at P–P$^+$/Rh = 2 (run 19) indicate that the extent of isomerization is significantly lower than that of the corresponding chloride containing systems (cf. runs 8 and 17). Also, the extent of substrate isomerization is lower than the analogous chloride-free PPh$_3$ ligand system (cf. run 5), suggesting that the steric requirements of the phosphine ligand also influence the isomerization pathway. Although catalyst intercalation reduces the extent of isomerization (run 20), the advantage of lower isomerization is offset by the presence of an equivalent amount of an unidentified reaction product. Again, no catalytic activity or IR band at 2000 cm^{-1} was observed for the filtrate.

Conclusions

The desorption of catalytically active intermediates from the charged surfaces of Rh(COD)(PPh$_3$)$_2^+$–hectorite under hydroformylation conditions, along with the observed acid–base dependence of Rh(COD)(PPh$_3$)$_2^+$ in the homogeneous hydroformylation of 1-hexene, suggests that neutral monohydride complexes of the type RhH(CO)$_x$(PPh$_3$)$_2$ (x = 1, 2) are the reactive intermediates. This conclusion is verified further by the isolation by Crabtree and Felkin[14] of RhH(CO)(PPh$_3$)$_3$ from a Rh(diene)(PPh$_3$)$_2$ precursor under hydroformylation conditions in the presence of PPh$_3$ and NEt$_3$.

Cationic analogues of the above monohydrides can be formed by the reaction of the positively charged P–P$^+$ ligand with $[Rh(diene)Cl]_2$, $[Rh(CO)_2Cl]_2$, or Rh(diene)$^+$ precursors under hydroformylation conditions. The analogies between P–P$^+$ and PPh$_3$ in the coordination chemistry of rhodium are

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supported by the isolation of $RhCl(CO)(P{-}P^+)_2$ hydroformylation a BF_4^- salt and by the previously reported isolation of a $RhCl(COD)(P{-}P^+)$ salt.[2] The cationic rhodium monohydride analogues containing $P{-}P^+$ are readily intercalated into hectorite. The choice of solvent, however, is crucial in promoting hydroformylation in the interlamellar regions of the intercalated clay catalysts. The solvent must be sufficiently polar to swell the interlayer regions of the clay (as with acetone, but not benzene), but not too polar (as with DMF) to promote extensive ligand dissociation and loss of neutral rhodium carbonyl to solution. Even in acetone, however, some loss of rhodium to solution can be anticipated due to ligand dissociation.

Finally, the tendency for the intercalated catalysts to increase the normal- to branched-chain aldehyde ratio and to decrease the extent of olefin isomerization relative to homogeneous solution suggests that the relative stabilities of primary and secondary metal alkyl intermediates may be influenced by the spatially restricted interlayer environment of the clay mineral.

Experimental Section

Materials. Sodium–hectorite was obtained from the Baroid Division of NL Industries in the precentrifuged and spray-dried form. The idealized, anhydrous unit cell formula is $Na_{0.66}[Li_{0.66}Mg_{5.34}](Si_{8.00})O_{20}(OH,F)_4$,[22] and the experimentally determined cation exchange capacity is 70 mequiv/100 g.[3] Methods described elsewhere were used to prepare $[RhCl(COD)]_2$,[23] $[Rh(CO)_2Cl]_2$,[24] and $[P{-}P^+]BF_4$.[2] $[Rh(COD)(PPh_3)_2]PF_6$ was prepared by reaction of $[RhCl(COD)]_2$, KPF_6, and PPh_3 according to the method of Schrock and Osborn.[15] The analogous $Rh(COD)^+{-}(P{-}P^+)$ precursor system was formed in situ by reaction of $[RhCl(COD)]_2$ and $AgBF_4$ in acetone in the presence of $[P{-}P^+]BF_4$.

$[RhCl(CO)(P{-}P^+)_2][BF_4]_2 \cdot 3CH_3COCH_3$. Chlorocarbonylbis[benzyldiphenyl[2-(diphenylphosphino)ethyl]phosphorus(1+)]rhodium(I) tetrafluoroborate was isolated as an acetone solvate from the $[RhCl(COD)]_2 + P{-}P^+$ precursor system. In a nitrogen-filled glovebox $[RhCl(COD)]_2$ (0.1 mmol) in 10 mL of acetone was treated slowly with $[P{-}P^+]BF_4$ (0.2 mmol) in 10 mL of acetone with vigorous shaking for 30 min. The solution was transferred into a stainless steel autoclave, and the autoclave was pressurized to 600 psi by addition of 1:1 $CO{:}H_2$. The reaction mixture was heated at 100 °C for 1 h, and then it was cooled to room temperature. The pressure was reduced to 1 atm, and a yellow precipitate was obtained by the addition of pentane. The yellow precipitate was washed several times with pentane and dried under nitrogen. Chemical analysis and IR spectroscopy indicated the presence of acetone.

Anal. Calcd for $C_{76}H_{80}ClP_4Rh$: Rh, 6.90; P, 8.30; Cl, 2.40; C, 61.10; H, 5.36. Found: Rh, 6.70; P, 8.28; Cl, 2.50; C, 61.40; H, 5.31. IR (KBr) 1975 (s, C≡O) and 1700 (C=O acetone) cm^{-1}.

$[Rh(COD)(PPh_3)_2{}^+]$–Hectorite. Clay intercalated $Rh(COD)(PPh_3)_2{}^+$ for use in the catalytic studies was prepared in the following manner. Na^+–hectorite (0.2 g) was stirred for 30 min in 5 mL of acetone or DMF, and then $[Rh(COD)(PPh_3)_2]PF_6$ (14 mg, 0.016 meq) in 5 mL of the same solvent was added. Stiring was continued for 15 min and the yellowish intercalate was filtered and washed several times with 5-mL portions of solvent to ensure complete removal of unexchanged rhodium complex.

Hydroformylation Studies. 1-Hexene as substrate was hydroformylated under two different conditions of pressure and temperature: 1 atm, 25 °C, and 600 psi (37 atm), 100 °C. For reactions carried out at atmospheric pressure, the catalysts' components were added to the hydroformylation flask in a nitrogen-filled glovebox. The flask was sealed and attached to a manifold fitted with a mercury manometer for monitoring gas uptake. The entire assembly was evacuated and purged with CO/H_2 (1:1). After 15 min equilibration time, freshly distilled 1-hexene was added to the reaction flask. The reaction was stopped after 24 or 48 h, and the percent conversion of substrate was measured by GC analysis. The same general procedure was used for hydroformylation reactions at 1 atm pressure with $Rh(COD)(PPh_3)_2{}^+$–hectorite as the catalyst precursor.

The hydroformylation reactions at 500 psi and 100 °C were carried out by using a stainless steel autoclave apparatus. Homogeneous catalysts were prepared in a nitrogen-filled glovebox by adding the required amount of $[P{-}P^+]BF_4$ in 5 mL of solvent to a solution containing 0.014 mmol of the desired rhodium complex precursor in 5 mL of solvent. The solution was stirred for 30 min, and then it was transferred to the autoclave, followed by addition of 10 mL of solvent and 1 mL of 1-hexene. The metal complex species used for intercalation in hectorite were generated in acetone at 100 °C and 600 psi CO/H_2 (1:1) by reaction of 0.014 mmol of rhodium complex precursor and the appropriate amount of $P{-}P^+$ in 20 mL of acetone. After 1 h, the solution was cooled to room temperature and the pressure was decreased to 1 atm. The active precursor was then intercalated in 0.2 g of hectorite as explained previously for $Rh(COD)(PPh_3)_2{}^+$–hectorite. The yellow mineral was washed with acetone and dried under nitrogen. Chemical analysis of intercalated catalysts formed from the $[RhCl(COD)]_2 + 4P{-}P^+$ and $Rh(COD)^+ + 2P{-}P^+$ precursor systems indicated the Rh loading to be 0.32 and 0.47 wt %, respectively. These values correspond to replacement of 4.4% and 6.5% of the interlayer Na^+ ions or to approximately one-fifth and one-fourth of a rhodium complex monolayer, respectively.

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Registry No. $[RhCl(CO)(P{-}P^+)_2][BF_4]_2$, 86013-16-3; 1-hexene, 592-41-6.

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