regenerated by such redox treatment, a path not available to the carbonyl catalysts.

The shapes of the CO adsorption isotherms for all of the carbonyl-derived catalysts are quite similar to those shown in Figure 4 for $Fe(CO)_5/Al_2O_3$. If the catalysts are only activated at moderate temperatures, the chemisorption continues to rather high pressures, suggesting weaker bonding than for either the carbonyls after high-temperature activation or traditional Fe/Al_2O_3, both of which become saturated at $\lesssim 20$ torr.[3] Surprisingly, after a redox treatment the shape of the isotherm for the 4.6% Fe catalyst resembles that of the original carbonyl catalyst.

The evolution of about 1 H_2/Fe when the complexes are activated at high temperatures requires that essentially all of the Fe interacts with the surface even at elevated temperatures. This is also consistent with the dramatically different TPDE spectra given by the supported and unsupported complexes and the absence of an Fe mirror for the supported complexes. Thus, even though most of the Fe is no longer zerovalent, it is still highly "dispersed". It is possible that supporting carbonyls on materials which cannot oxidize the metal (as a dehydroxylated Al_2O_3[4]) will lead to even higher dispersions by allowing more extensive decarbonylation without oxidation.

Summary. From the foregoing it is clear that the information supplied by TPDE can be invaluable for the designed synthesis of catalysts of supported metals. The technique gives a handle on the development of potential catalytically active sites (coordinative unsaturation) as well as the temperatures and methodology to be used to retain the metals in the low-valent and highly dispersed state. However, it is also clear that the systems are complex, and additional characterization will be necessary to answer some of the residual questions. The use of IR spectroscopy to study some of the specific systems indicated by the TPDE experiments appears particularly promising.

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; Al_2O_3, 1344-28-1.

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Utilization of a Cationic Ligand for the Intercalation of Catalytically Active Rhodium Complexes in Swelling, Layer-Lattice Silicates

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Triphenylphosphine and the positively charged phosphonium phosphine ligand $Ph_2PCH_2CH_2P^+Ph_2CH_2Ph$ (abbreviated P-P$^+$) have been shown to react with $[RhCl(COD)]_2$ to give mixed-ligand cationic analogues of Wilkinson-type complexes. The positive charge carried by the phosphonium phosphine ligand allows the complexes to be electrostatically bound between the negatively charged sheets of the swelling, layer-lattice silicate mineral hectorite. The catalyst system derived from a 1:1:1 P-P$^+$:PPh_3:Rh reaction ratio is active for the hydrogenation of 1-hexene under homogeneous-solution conditions when intercalated in the intracrystal space of the layered silicate. The activity of the intercalated catalyst is about twice that of the homogeneous catalyst in methanol. ^{31}P NMR studies indicate that the phosphonium phosphine ligand is qualitatively similar to triphenylphosphine in its reactivity toward $[RhCl(COD)]_2$. However, the reaction of P-P$^+$ and $[RhCl(COD)]_2$ at 2:1 and 3:1 P-P$^+$:Rh ratios generates complexes which are inactive as olefin hydrogenation catalysts. The inactivity of these latter systems is attributed to steric crowding at the rhodium center by two or more of the bulky positively charged ligands. $RhCl(COD)(P\text{-}P^+)$, a cationic analogue of $RhCl(COD)(PPh_3)$, has been isolated as the BF_4^- salt by reaction of P-P$^+$ and $[RhCl(COD)]_2$ in stoichiometric amounts.

Introduction

It has been demonstrated recently that cationic metal-complex catalysts can be intercalated between the negatively charged sheets of swelling, micalike layered silicates.[2] For example, $Rh(PPh_3)_x^+$ complexes were shown to be active for the hydrogenation of alkenes and alkynes in the intracrystal space of the mineral hectorite. The $Rh(PPh_3)_x^+$/hectorite system exhibited much larger specificity for hydrogenation of terminal olefins vs. internal olefins in methanol than did the solution catalyst.[3] The activity of the mineral-bound catalyst was about 10 times less than that of the homogeneous catalyst for the hydrogenation of 1-hexene, while the activity of this catalyst supported on a cation-exchange resin was approximately 40 times less.[3] In contrast, the activity of $Rh(PPh_3)_x^+$/hectorite for reduction of 1-hexyne was comparable to that of the solution catalyst. One might infer from these

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results that, although the catalyst behaves as it would in solution for reduction of 1-hexyne, selective steric and adsorptive effects imposed by the support alter the reactivity for olefin hydrogenation.

These preliminary studies on catalysts electrostatically bound in the solvent-swollen space of layer-lattice silicates have illustrated the attractiveness of the approach. The ion-exchange method of catalyst immobilization on layered silicates is simple when compared to the multistep procedures for covalent attachment of complexes to polymer or amorphous metal oxide supports. Moreover, the catalysts exhibit potentially controllable selectivity effects when exchanged into the structures of these ubiquitous minerals. Under some conditions, however, the layer silicate systems can exhibit undesirable properties. For example, desorption of a catalytically active, presumably uncharged species occurs during reactions when certain silicate-supported cationic complexes are employed as hydrogenation[4,5] or hydroformylation[6] catalysts. In addition, the lack of numerous, well-studied, cationic homogeneous catalysts limits the range and type of complexes that might be supported.

This study investigates the possibility that positively charged ligands might be employed to produce active cationic transition-metal catalysts—analogous to well-known, otherwise neutral, homogeneous catalysts—capable of electrostatic attachment to anionic supports. Wilkinson's olefin hydrogenation catalyst, $RhCl(PPh_3)_x$, has been studied relatively well, both in homogeneous solution[7] and in supported environments.[8] The complex does not dissociate chloride to any observable extent in most solvent systems. It was felt that substitution of a cationic ligand for triphenylphosphine in this catalyst would afford a cationic complex with catalytic properties similar to those of the neutral species. There have been a few reports of the syntheses and properties of some cationic complexes employing positively charged phosphine ligands, but none of these complexes were tested as catalysts.[9] The tetrafluoroborate salt of the ligand 1-(diphenylphosphino)-2-(benzyldiphenylphosphonio)ethane (abbreviated $P\text{-}P^+$) was chosen for this study for its ease of preparation and for its spectroscopic similarity to PPh_3 in transition-metal complexes.[9a]

Results and Discussion

The Cationic Ligand. The BF_4^- salt of $P\text{-}P^+$ was prepared from the reaction of the known bromide salt with tetrafluoroborate anion exchange resin under oxygen-free conditions. Tetrafluoroborate anion was used instead of bromide ion to avoid halide exchange and/or coordination of the bromide ion with the metal. The preparation of $P\text{-}P^+Br$ from the stoichiometric addition of benzyl bromide to 1,2-bis(diphenylphosphino)ethane was conducted in benzene to facilitate the precipitation of the cation, and air was excluded from the reaction mixture to prevent the formation of an oxide impurity. $P\text{-}P^+BF_4$ is soluble in methylene chloride, chloroform, dimethyl sulfoxide, and *N*,*N*-dimethylformamide, partially soluble in methanol, ethanol, acetonitrile, and pyridine, and insoluble in water, acetone, ethers, and nonpolar solvents such as benzene, hexane, and carbon tetrachloride.

The proton-decoupled ^{31}P NMR spectrum of $P\text{-}P^+BF_4$ consists of two doublets (Figure 1A). The doublet at +12.1 ppm upfield from 85% phosphoric acid is assigned to the trivalent phosphorus atom. The chemical shift of the phosphine is assigned this value since it compares well with the +12.5 ppm chemical shift for 1,2-(diphenylphosphino)ethane.[10] The doublet at −27.1 ppm is assigned to the quaternized phosphorus. The spin–spin coupling between the two phosphorus centers, $^3J_{PP^+}$, is 46 Hz.

The oxide $Ph_2POCH_2CH_2P^+Ph_2CH_2Ph$, which forms during the preparation of $P\text{-}P^+BF_4$ when dioxygen is present, is characterized by its intense absorption at 1190 cm^{-1} due to P=O stretching vibrations. The ^{31}P NMR spectrum of this impurity exhibits two doublets ($^3J_{PP^+}$ = 48 Hz) at −27.3 and −34.2 ppm.

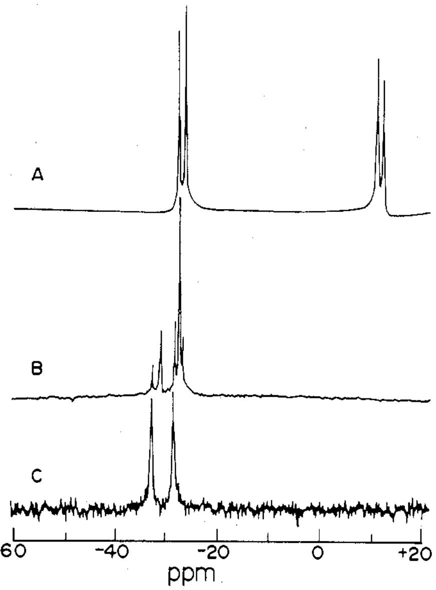

Figure 1. The ^{31}P NMR spectra (28 °C) of (A) $(Ph_2PCH_2CH_2PPh_2CH_2Ph)BF_4$, (B) $[RhCl(COD)(P\text{-}P^+)]BF_4$, and (C) $RhCl(COD)(PPh_3)$ in CH_2Cl_2. Chemical shifts are relative to external 85% H_3PO_4.

Homogeneous Catalysts. Benzene is generally the solvent of choice for Wilkinson-type catalysts, but methanol was chosen for this study because the cationic ligand is not soluble in nonpolar solvents. Methanol is also capable of swelling hectorite interlayers, thus providing a more solution-like environment for mineral-bound complexes.

Wilkinson's catalyst has not been employed for the hydrogenation of olefins in methanol previously due to its low solubility in this solvent. As a result it was necessary to investigate the catalytic behavior of a Wilkinson catalyst, as generated from $[RhCl(COD)]_2$ in methanol, in order that a meaningful comparison of this catalyst might be made with those incorporating $P\text{-}P^+$.

The effect of the PPh_3:Rh ratio on catalytic activity was studied for the $[RhCl(COD)]_2\text{–}PPh_3$ system in methanol. It was assumed, on the basis of previous work with analogous systems,[7] that the combination of stock solutions of $[RhCl(COD)]_2$ and PPh_3, followed by addition of hydrogen, would reduce COD to cyclooctane via rhodium hydride intermediates prior to formation of the desired Wilkinson-type catalyst, according to reaction 1.

$$^1/_2[RhCl(COD)]_2 + x(PPh_3) + 3H_2 \rightarrow RhH_2Cl(PPh_3)_x + C_8H_{16} \quad (1)$$

The rates for 1-hexene hydrogenation in systems employing PPh_3:Rh ratios from 0:1 to 4:1 are presented in Table I. The rates were followed as the number of catalyst turnovers increased from 100 to 900 mol of substrate reacted/mol of Rh. These results complement the findings of other workers in this area.[7] A 2:1 PPh_3:Rh ratio produces the most active catalyst, favoring coordinatively unsaturated intermediates such as $RhCl(PPh_3)_2$ and $RhH_2Cl(PPh_3)_2$. Increasing the PPh_3:Rh ratio results in less loss of catalyst activity with increasing catalyst turnover, but it also induces lower rates due to the competition of excess PPh_3 with substrate for coordination sites at the metal center. The loss of activity at PPh_3:Rh ratios lower than 2:1 was at one time attributed to the formation of catalytically inactive dimeric species,[7] $[RhCl(PPh_3)_2]_2$, but Tolman has recently shown that the dimer is a good catalyst

Table I. Rates after Various Catalyst Turnovers for Hydrogenation of 1-Hexene with Homogeneous and Hectorite-Supported Mixed Phosphine-Rhodium(I) Chloride Complexes[a]

	rates, mL of H_2/min (mmol of Rh)$^{-1}$								
	no. of catalyst turnovers[b]								
catalyst system P-P$^+$:PPh_3:Rh	100	200	300	400	500	600	700	800	900
0:0:1	no reaction–Rh(0) forms within 1-2 h								
0:1:1	30	20	reaction ceases						
0:2:1	540	530	460	370	280	220	150	100	50
0:3:1	240	210	230	220	220	200	200	150	130
0:4:1	130	120	120	110	100	90	90	80	90
1:0:1	no reaction								
2:0:1	no reaction								
3:0:1	no reaction								
1:1:1	100	90	100	90	80	80	70	60	60
2:1:1	70	100	120	120	60	20			
1:2:1	400	350	330	310	300	290	260	240	220
2:2:1	210	240	250	270	270	290	270	260	250
2:0:1/Hect	no reaction								
3:0:1/Hect	no reaction								
1:1:1/Hect	150	180	190	190	150	190	140	100	70
0:2:1/Hect[c]	530	490	500	460	410	340	120	50	

[a] Reaction conditions are as follows: 30 mL of 1.0 M 1-hexene in methanol; 0.020 mmol of rhodium; 25 °C; total pressure 740 torr; 1-hexene:Rh = 1500:1. [b] The number of catalyst turnovers is defined as the total moles of substrate hydrogenated per mole of rhodium catalyst. [c] Extensive rhodium desorption was observed for this system.

for olefin hydrogenation.[7c] Rhodium complexes containing less than two phosphines either may be unable to activate molecular hydrogen or may form tightly bound olefin complexes which are incapable of reductive elimination under hydrogenation conditions. $[RhCl(COD)]_2$, in the absence of PPh_3, is not a catalyst, but it is slowly reduced under hydrogenation conditions to rhodium(0), an excellent olefin hydrogenation catalyst.

It was felt that the positively charged phosphine ligand could be substituted for PPh_3 in the in situ generation of a cationic catalyst system. However, the combination of various quantities P-P$^+BF_4^-$ and $[RhCl(COD)]_2$, followed by exposure of the resulting solutions to hydrogen, does not produce species capable of acting as catalysts for the reduction of 1-hexene. As shown in Table I, the systems derived from P-P$^+$:Rh ratios of 1:1, 2:1, and 3:1 were all inactive. The cationic ligand might be expected to be more basic than PPh_3. Wilkinson has found that ligands of much higher basicity than PPh_3 generally afford less active hydrogenation catalysts.[7f] In fact, at a phosphine:Rh ratio of 2:1, the PEt_3 system shows very little activity. However, PPh_2Et, which should have nearly the same electronic properties as the cationic ligand, is highly active. At a phosphine:Rh ratio of 2:1, the PPh_2Et system is only 10% less active than the PPh_3 system. As a result, electronic effects alone cannot explain why P-P$^+$ is a poorer ligand for olefin hydrogenation than PPh_3.

The primary difference between P-P$^+$ and PPh_3 is one of steric bulk. PPh_3 is generally considered to be quite bulky, but comparison of space-filling models of the two ligands indicates that, although there are certain possible conformations about the ethylene bridge of P-P$^+$ that allow ligand cone angles that are approximately the same as those for PPh_3, most configurations of the cationic ligand should be much more bulky than PPh_3. Tolman has enumerated some of the effects on the activity and selectivity of homogeneous catalysts as the size of the substituents on phosphorus ligands increases.[11] In general, smaller ligands in competition for coordination sites with the bulky ligands are usually bound preferentially, and less crowded isomers are favored if the possibility of different isomers exists. Further, both increases in the rates of phosphorus-ligand dissociative reactions and decreases in rates of associative ones are observed as the ligand size increases. If the phosphorus ligands are particularly bulky, they can often interfere with or prevent the coordination of other ligands which would normally be strongly bound, for example, CO, O_2, or C_2H_4. This is especially true if there are two or more larger ligands in the coordination sphere of the metal. All of these effects, in combination with the electronic requirements of the system, contribute to the reactivity patterns of homogeneous catalysts.

The yellow 2:0:1 and 3:0:1 systems defined in Table I do lighten in color on exposure to hydrogen, suggesting the formation of rhodium(III) dihydride complexes. However, the 2:0:1 and 3:0:1 catalysts must be so crowded at the metal center that coordination by olefin, followed by metal alkyl formation and reductive elimination of product, is sterically hindered. The inactivity of the 1:0:1 system is not surprising in view of the behavior of the 0:1:1 catalyst.

Mixed-Ligand Reactions. A combination of the cationic ligand with a less bulky phosphine ligand should reduce the steric crowding at the metal center sufficiently to produce an active hydrogenation catalyst. A 1:1:1 ratio of P-P$^+$:PPh_3:Rh affords a catalyst of good longevity but of much lower activity than the analogous 0:2:1 catalyst (Table I). The lower activity of this system can be attributed to the steric and electronic effects discussed earlier.

The fact that neither the 0:1:1 nor the 1:0:1 systems are particularly active catalysts is indicative of the participation of both the positively charged ligand and triphenylphosphine in the 1:1:1 catalyst system. Ligand redistribution reactions that would allow the formation of the highly active $RhH_2Cl(PPh_3)_2$ intermediate probably does occur to some extent, but this species cannot be solely responsible for the observed activity, since the activity of the 1:1:1 system does not parallel that of the 0:2:1 system. It is noteworthy in this regard that Crabtree and co-workers have observed that the isolable mixed-ligand complexes $[Rh(COD)LL']^+$ are the only detectable species at equilibrium in solutions prepared by ligand exchange of $[Rh(COD)L_2]^+$ and $[Rh(COD)L_2']^+$ complexes.[12]

The 2:1:1, 1:2:1, and 2:2:1 ratios of P-P$^+$, PPh_3, and Rh also afford active homogeneous catalysts (Table I). Small differences in reactivity exist between the 1:1:1 and 2:1:1 reaction systems, whereas a significant increase in reactivity is observed in passing from the 1:1:1 to 1:2:1 system. These observations suggest that the bulky P-P$^+$ ligand does not compete well with PPh_3 for coordination positions on Rh. The 1:2:1 catalyst system is nearly as active as the 0:2:1 catalyst and more active than the 0:3:1 system. The major species in solution no doubt resemble those of the 0:2:1 catalyst, the cationic ligand

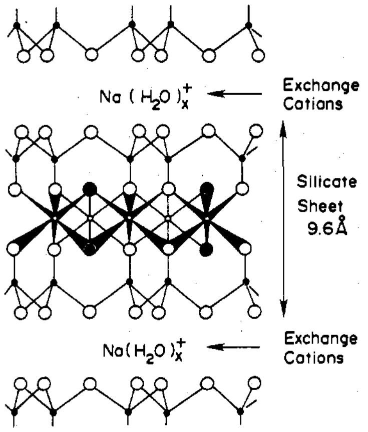

Figure 2. Schematic representation of hectorite, $Na_{0.66}[Li_{0.66}Mg_{5.34}](Si_{8.00})O_{20}(OH,F)_4$. View is down the *a* axis. Key: (O) oxygen; (●) hydroxyl or fluorine; (•) Si in tetrahedal positions; (∘) Li or Mg in octahedral positions.

competing only moderately well compared to PPh_3 for olefin coordination sites on the metal. The 2:2:1 catalyst is simply an extension of the 1:2:1 system in which an additional 1 mol of $P\text{-}P^+$ has been added. The 2:2:1 catalyst is much more active than the analogous 0:4:1 system, again indicating that $P\text{-}P^+$ is less able to compete for coordination sites than PPh_3 due to its large steric bulk.

Hectorite-Supported Catalysts. The homogeneous catalyst employing a $P\text{-}P^+$:PPh_3:Rh ratio of 1:1:1 appeared to be best suited for support by cation exchange within the intracrystal space of the mineral hectorite. The 1:0:1, 2:0:1, and 3:0:1 systems failed to function, the 2:1:1 system offers no advantage in activity, and the 1:2:1 and 2:2:1 systems probably contain too high a concentration of neutrally charged species. It was felt that generation of the hydride of the homogeneous catalyst prior to exchange with hectorite would allow a more meaningful comparison between the homogeneous and heterogeneous systems, since the nature of the reduction of the COD precursors might be altered within the mineral environment. Methanol was used as the solvent system to maintain consistency between the heterogeneous and homogeneous catalyst environments.

Approximately 14% of the exchangeable Na^+ ions in the interlayers of hectorite were replaced by cationic rhodium complexes derived from the 1:1:1 reaction system. On the basis of the unit-cell dimensions of $RhCl(PPh_3)_3$,[14] each bound complex is expected to occupy ~360 $Å^2$ of surface. If one also considers the theoretical surface area of the mineral (~760 m^2/g),[15] then the maximum possible catalyst loading under monolayer conditions would be 18 mequiv/100 g or 25% of the total cation-exchange capacity. At the loading employed, the average distance between rhodium centers should be ~25 Å. Figure 2 illustrates the hectorite structure.

As may be seen in Table I, the 1:1:1 catalyst when electrostatically bound in hectorite (1:1:1/Hect) is an active catalyst for the hydrogenation of 1-hexene. Wilkinson-type catalysts normally exhibit decreased activity when immobilized on polymer or silica supports,[8,16] but in the case of hectorite the solution-like environment expected within the interlayers should allow the catalyst to approximate its behavior in homogeneous solution. In fact, the intercalated system is almost twice as active as the homogeneous system. The fact that the rates of the heterogeneous and homogeneous 1:1:1 systems parallel one another suggests that the species responsible for catalytic activity in both systems are probably very similar in composition. It is noteworthy that the composition of the supported 1:1:1 catalyst as determined by chemical analysis gave a Rh:P:Cl ratio of 1.00:3.17:0.76, as expected for the overall composition of the homogeneous catalyst. No coloration of the solution phase due to catalyst desorption was observed during the course of the reaction. Independent tests for olefin hydrogenation activity of filtrates taken from the reactions after 50% and 80% hydrogenation gave negative results.

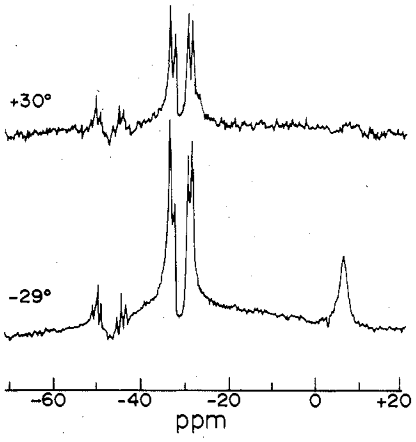

Figure 3. The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 to 0.03 M $RhCl(COD)(PPh_3)$ in CH_2Cl_2.

As was the case for the 2:0:1 and 3:0:1 homogeneous systems, both the 2:0:1/Hect and 3:0:1/Hect systems are inactive as catalysts for olefin hydrogenation. The neutral complexes derived from reaction of $[RhCl(COD)]_2$ and triphenylphosphine (for example, the 0:2:1 reaction system) also bind to hectorite, but in these cases the binding occurs through a physisorption mechanism. Consequently, much of the bound rhodium is desorbed readily upon suspension of the mineral in the hydrogenation solvent.

^{31}P NMR Studies. A phosphorus-31 NMR study was undertaken in an effort to better understand the nature of the homogeneous catalysts. Of particular interest were those catalysts derived from 0:2:1 and 1:1:1 $P\text{-}P^+$:PPh_3:Rh reaction ratios. The 0:2:1 catalyst is generated by the sequential addition of PPh_3 and H_2 to $[RhCl(COD)]_2$. It was felt that ^{31}P NMR analysis of these steps would allow characterization of the catalyst precursors and the major components of the catalyst solution. CH_2Cl_2 was used as the solvent in these studies since good spectra could not be obtained with methanol due to the limited solubility of $[RhCl(COD)]_2$ and most other catalyst precursors in that solvent.

The interaction of 2 equiv of PPh_3 with $[RhCl(COD)]_2$ is known to result in chloride-bridge cleavage and the formation of 2 equiv of $RhCl(COD)(PPh_3)$.[17,18] The phosphorus chemical shift for $RhCl(COD)(PPh_3)$ at +28 °C is −30.6 ppm and J_{PRh} = 151 Hz (see Figure 1C).

The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 to $RhCl(COD)(PPh_3)$ are reproduced in Figure 3. The doublet of triplets at $\delta_{P_c} = 47.8$ ($J_{P_cRh} = 193$ Hz, $J_{P_cP_t} = 39$ Hz) and the doublet of doublets at $\delta_{P_t} = 31.2$ ($J_{P_tRh} = 146$ Hz) are characteristic of $RhCl(PPh_3)_3$ (lit.[7c] $\delta_{P_c} = -48.9$, $\delta_{P_t} = -32.2$, $J_{P_cRh} = 146$ Hz). P_c is the phosphorus cis to the two trans phosphines, P_t, in the roughly square-planar complex. The distortion in the intensities of the doublet of doublets at −29 °C is attributed to overlap of the resonances due to an equilibrium concentration of $RhCl(COD)(PPh_3)$. The resonance at $\delta P = +7.1$ may be attributed to free PPh_3 (lit.[7c] $\delta_P = \sim+6$). The same spectral features were observed for the PPh_3–$RhCl(COD)(PPh_3)$ reaction system when toluene was used as the solvent.

The presence of $RhCl(PPh_3)_3$ in the PPh_3–$RhCl(COD)(PPh_3)$ system was a somewhat surprising result. Previously reported proton NMR studies have shown that $RhClL_3$

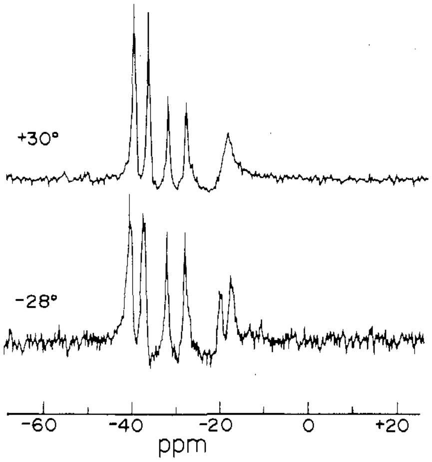

Figure 4. The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 and excess H_2 to $RhCl(COD)(PPh_3)$, 0.03 M in CH_2Cl_2.

complexes are produced on addition of L to RhCl(COD)L, where L equals the more basic, less bulky ligands PPh_2Me, $PPhMe_2$, and PBu_3,[19] presumably according to the eq 2 and 3, where COD* represents monodentate 1,5-cyclooctadiene.

$$RhCl(COD)L + L \rightleftharpoons RhCl(COD)L_2 \rightleftharpoons RhCl(COD^*)L_2 \quad (2)$$

$$RhCl(COD^*)L_2 + L \rightleftharpoons RhCl(COD^*)L_3 \rightleftharpoons RhClL_3 + COD \quad (3)$$

However, proton NMR studies of the addition of 1 equiv of PPh_3 to $RhCl(COD)(PPh_3)$ in $CHCl_3$ have not provided any evidence for $RhCl(PPh_3)_3$ formation. The previously observed temperature dependence of the COD vinyl proton resonances from −60 to 0 °C has been attributed to a phosphine-exchange process involving a pentacoordinate intermediate:[18,19]

$$RhCl(COD)(PPh_3) + PPh_3 \rightleftharpoons [RhCl(COD)(PPh_3)_2] \quad (4)$$

The ^{31}P NMR spectra in Figure 3 indicate that equilibrium 5 operates when 1 mol of PPh_3 is added to $RhCl(COD)(PPh_3)$.

$$RhCl(COD)(PPh_3) + 2PPh_3 \rightleftharpoons RhCl(PPh_3)_3 + COD \quad (5)$$

Dissociation of the cis phosphine ligand in $RhCl(PPh_3)_3$ is slow at 30 °C, because the low-field doublet of triplets does not broaden or collapse. However, free PPh_3 is apparently in rapid thermal equilibrium with a second species since the line near 7.1 ppm weakens and broadens at 30 °C. This line broadening may be the result of ligand exchange with $RhCl(COD)(PPh_3)$ via the same mechanism which has been proposed for vinyl-group interchange in $RhCl(COD)(PPh_3)$ in presence of free PPh_3 (cf. eq 4). However, the expected concomitant broadening of the $RhCl(COD)(PPh_3)$ doublet cannot be ascertained, as these lines are obscured by the cis phosphine lines of $RhCl(PPh_3)_3$. Phosphine-ligand exchange according to equilibrium 6 is unlikely. Although bis(diene) analogues

$$RhCl(COD)(PPh_3) + COD \rightleftharpoons RhCl(COD)_2 + PPh_3 \quad (6)$$

of $RhCl(COD)_2$ have been observed previously with norbornadiene[20] and butadiene,[21] $RhCl(COD)_2$ itself is not known. Moreover, the addition of 1 mol of COD to $RhCl(COD)(PPh_3)$ produces no observable change in the ^{31}P NMR spectrum of the complex between −80 and 30 °C.

The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of hydrogen to the $RhCl(COD)(PPh_3)$–PPh_3 system are reproduced in Figure 4. The −28 °C spectrum may be characterized in the following way. The downfield incompletely resolved doublet of doublets at $\delta_{P_t} = -40.1$ ($J_{P_tRh} = 115$ Hz, $J_{P_tP_c} = 18$ Hz) and the upfield unresolved doublet of triplets at $\delta_{P_c} = -19.4$ ($J_{P_cRh} = 90$ Hz) are characteristic of $RhH_2Cl(PPh_3)_3$ (lit.[7c] δ_{P_t}(in CH_2Cl_2) = −40.3, $J_{P_tRh} = 114$ Hz, $J_{P_tPc} = 18$ Hz, $\delta_{P_c} = -20.7$ ppm, $J_{P_cRh} = 90$ Hz). Apparently, hydrogen adds directly to $RhCl(PPh_3)_3$ to form $RhH_2Cl(PPh_3)_3$. The temperature dependence of the spectrum of $RhH_2Cl(PPh_3)_3$ is well-known.[7c] The line broadening and loss of coupling at 30 °C are due to exchange of the labile cis phosphine ligands. The doublet centered at $\delta_P = -30.6$ ($J_{PRh} = 151$ Hz) is characteristic of $RhCl(COD)(PPh_3)$. $RhCl(COD)(PPh_3)$ appears to be less active toward the addition of molecular hydrogen than the analogous iridium complex. According to Gargano et al.,[22] 2 equiv of H_2 reacts with 2 equiv of $IrCl(COD)(PPh_3)$ to produce cyclooctene and the chloride-bridged species $Ir_2H_2Cl_2(COD)(PPh_3)_2$. The possibility that the analogous rhodium complex, $Rh_2H_2Cl_2(COD)(PPh_3)_2$ (or the simpler dihydride, $RhH_2Cl(COD)(PPh_3)$), has the same ^{31}P chemical shift and coupling constant as $RhCl(COD)(PPh_3)$ is remote but cannot be ruled out.

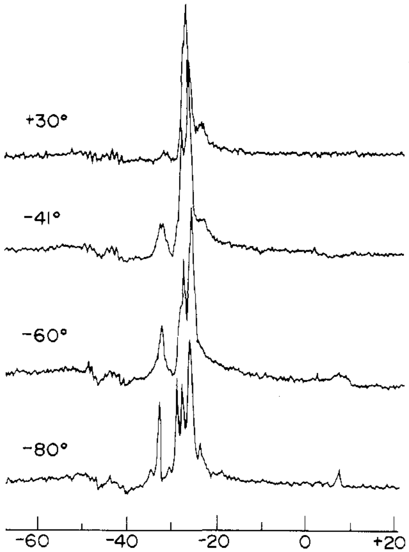

Figure 5. The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 to 0.03 M $[RhCl(COD)(P\text{-}P^+)]BF_4$ in CH_2Cl_2.

A ^{31}P NMR study of the 1:1:1 catalyst system was undertaken in order that a comparison might be made with the analogous 0:2:1 catalyst system just described. The 1:1:1 catalyst is generated by the sequential addition of $P\text{-}P^+BF_4$, PPh_3, and H_2 to $[RhCl(COD)]_2$.

The addition of 2 equiv of $P\text{-}P^+$ to $[RhCl(COD)]_2$ produces $RhCl(COD)(P\text{-}P^+)$, which is analogous to $RhCl(COD)(PPh_3)$. The ^{31}P NMR spectrum of $[RhCl(COD)(P\text{-}P^+)]BF_4$ is reproduced in Figure 1B. The five-line pattern is readily interpreted as an ABX splitting pattern in which the coupling between Rh and P^+ is relatively small compared with J_{PRh} and J_{PP^+}. The spectrum was submitted to the ABX spectral analysis technique outlined by Becker,[23] with the following results: $\delta_P = -29.5$, $\delta_P = -27.3$, $J_{PRh} = +149$ Hz, $J_{PP^+} = +54$ Hz, $J_{P^+Rh} = +7$ Hz. The chemical shift of the phosphine phosphorus atom is very close to that of PPh_3 for the analogous uncharged complex, and the J_{PRh} values for the respective complexes are nearly identical. Although $P\text{-}P^+$ is expected to be more basic and, for certain conformations about the ethylene bridge, possess greater steric bulk than PPh_3, it may be inferred from the ^{31}P NMR data that, at least for RhCl(COD)L complexes, the cationic ligand interacts with the rhodium center to much the same degree.

The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 to

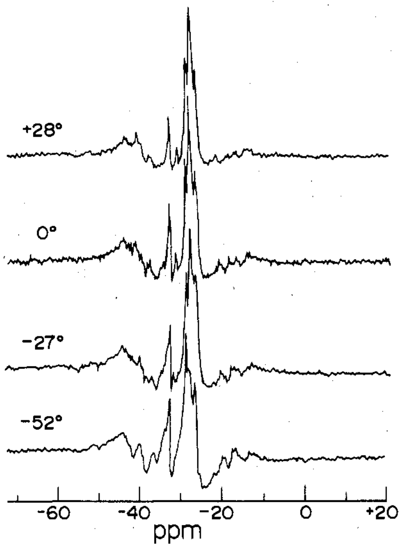

Figure 6. The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of 1 equiv of PPh_3 and excess H_2 to 0.03 M $[RhCl(COD)(P\text{-}P^+)]BF_4$ in CH_2Cl_2.

$[RhCl(COD)(P\text{-}P^+)]BF_4$ are reproduced in Figure 5. The spectra are too complex to allow direct assignment of the lines because of the formation of mixed-ligand complexes and the severe overlap of the lines due to phosphine and phosphonium resonances. However, certain major features of the spectra deserve comment. The larger peaks near −27 ppm are in the region expected for the phosphonium-group resonances of the cationic ligand. The two multiplets found between −40 and −50 ppm are reminiscent of the doublet of triplets found at $\delta_{P_c} = -47.8$ for the $RhCl(COD)(PPh_3)$–PPh_3 system and are indicative of tris(phosphine) complexes of the type $RhCl(PPh_3)_x(P\text{-}P^+)_{3-x}$.

The resonances between −20 and −35 ppm, aside from those due to the phosphonium group, are found where the trans phosphines of $RhClL_3$ complexes should resonate, as well as the phosphine resonances due to $RhCl(COD)L$ complexes. As in the case of the spectra for the $RhCl(COD)(PPh_3)$–PPh_3 system, the $[RhCl(COD)(P\text{-}P^+)]BF_4$–$PPh_3$ system shows the presence of free phosphine as the temperature is lowered, although this occurs at much lower temperature. It may be inferred from these generalizations that the $[RhCl(COD)(P\text{-}P^+)]BF_4$–$PPh_3$ and $RhCl(COD)(PPh_3)$–PPh_3 systems are similar in their tendency to form tris(phosphine) complexes.

The temperature-dependent ^{31}P NMR spectra of the solution resulting from the addition of hydrogen to the $[RhCl(COD)(P\text{-}P^+)]BF_4$–$PPh_3$ system are reproduced in Figure 6. The large central peaks near −27 ppm may be attributed to the phosphonium group of the cationic ligand. The broad multiplets near −41 ppm as well as those near −19 ppm are indicative of the presence of RhH_2ClL_3 complexes, where L is PPh_3 and/or $P\text{-}P^+BF_4$. There are also lines centered about −30 ppm which may be due to $RhCl(COD)L$ complexes.

The catalysis data discussed earlier showed that the 2:0:1 $P\text{-}P^+$:PPh_3:Rh system is inactive for homogeneous 1-hexene hydrogenation, whereas the analogous 0:2:1 system is highly active. The complexes formed in the former system bind electrostatically to hectorite, whereas the species formed in the latter system bind only weakly through physisorption forces to the silicate surfaces. These chemical facts, together with the ^{31}P NMR data, imply that the tris(phosphine) complexes formed in the 1:1:1 reaction system lie strongly in the direction of the mixed-ligand species $RhClH_2(PPh_3)_x(P\text{-}P^+)_{3-x}$ with $x = 1$ or 2 rather than in the direction of parent complexes with $x = 0$ or 3. This would also be consistent with Crabtree's observation[12] that mixed-ligand complexes are strongly favored over the parent complexes in the $Rh(COD)L_2^+$–$Rh(COD)L'_2{}^+$ ligand-exchange system. It is presumed that the active species in the 1:1:1 system under hydrogenation conditions are analogous to the coordinately unsaturated complexes normally proposed for Wilkinson-catalyst systems (e.g., $RhClH_2L_2$).

Conclusion

The ^{31}P NMR studies show that both $RhCl(COD)(PPh_3)$ and $RhCl(COD)(P\text{-}P^+)$ react with PPh_3 to form tris(phosphine) complexes. A significant equilibrium concentration of the tris species is formed in solution even when the overall phosphine to rhodium ratio is 2:1. The tris complexes oxidatively add H_2 and function as olefin hydrogenation catalyst precursors. The mixed-ligand, cationic hydride complexes derived from the 1:1:1 $P\text{-}P^+$:PPh_3:Rh system under hydrogenation conditions readily intercalate into the hectorite structure through an electrostatic binding mechanism. Moreover, the activities of the complexes in the solution and intercalated states are comparable, further confirming the similarities between the constitution of the complexes in the two phases. It is concluded, therefore, that positively charged ligands can be effectively used to replace neutral ligands in homogeneous catalysts and thereby convert neutral catalysts into cationic catalysts capable of binding to anionic solid supports. The particular positively charged ligand investigated here apparently has too large a cone angle to permit catalytic activity when all of the neutral phosphine ligands in a Wilkinson-type system are replaced. However, it should be possible to design aprotic, positively charged ligands in which the cone angle should not be restrictive. Experiments intended to achieve this are currently under investigation.

Experimental Section

Materials. Sodium hectorite (B1-26) with a particle size <0.2 μm was obtained from the Baroid Division of the National Lead Co. in the precentrifuged and spray-dried form. The idealized, anhydrous unit-cell formula is $Na_{0.66}[Li_{0.66}Mg_{5.34}](Si_{8.00})O_{20}(OH,F)_4$,[15] and the experimentally determined cation-exchange capacity is 73 mequiv/100 g.[13] The small amount of $CaCO_3$ impurity associated with this mineral was not removed prior to use. $[RhCl(COD)]_2$ was obtained from Strem Chemicals, Inc. $RhCl(COD)(PPh_3)$ was prepared from $[RhCl(COD)]_2$ and PPh_3 without modification of the Chatt and Venanzi procedure.[17] ^1H NMR: $\delta_{H_{vinyl}}$ 5.52 (s), 3.10 (s).

$(Ph_2PCH_2CH_2PPh_2CH_2Ph)Br$. 1-(Diphenylphosphine)-2-(benzyldiphenylphosphino)ethane bromide ($P\text{-}P^+Br$) was synthesized from diphos and benzyl bromide by a modification of Quagliano's method.[9a] In a nitrogen-filled glovebox, 6.1 mL (0.025 mol) of benzyl bromide was added, dropwise, over a period of 10 min, to a stirred solution of 10.0 g (0.025 mol) of diphos in about 250 mL of dry, degassed benzene or toluene. The reaction flask was stoppered and allowed to stand overnight. The resulting microcrystalline powder was filtered from the solution, slurried, and washed twice with 60 mL of benzene (or toluene). The soluble portion was taken up in 250 mL of degassed methanol, and the insoluble dicationic salt was filtered on a fine frit. The methanol solution was reduced to one-eighth the original volume, and the resulting white crystals were collected and dried on a fritted filter (mp 224–247 °C). Anal. Calcd for $C_{33}H_{31}BrP_2$: C, 69.60; H, 5.49; P, 10.88. Found: C, 69.43; H, 5.48; P, 11.08.

BF_4^-/Resin. AG2-X8 Dowex anion exchange resin (50–100 mesh) was exchanged with two separate treatments of threefold excess of $NaBF_4$ in H_2O under oxygen-free conditions, washed with methanol, filtered, and degassed under high vacuum for 4 days.

$(Ph_2PCH_2{}^1CH_2{}^2PPh_2CH_2{}^3Ph)BF_4$. In a nitrogen-filled glovebox, 31 g (100 mequiv) of BF_4^-/resin was added to the filtered methanol solution obtained from a preparation of $P\text{-}P^+Br$. This was stirred 4 h and filtered. Then fresh BF_4^-/resin (31 g) was added to the solution. It was necessary to add additional methanol at this point. After an additional 4 h the procedure was repeated a third time. The solvent was reduced under vacuum to one-eighth the original volume. In the glovebox, the resulting white, needlelike crystals were collected on a frit and washed with benzene or toluene (mp 188–189 °C). ^1H NMR: δ_{H^1} 2.65 (ddt), δ_{H^2} 2.09 (dt), δ_{H^3} 4.37 (d), $J_{H^1H^2} = 10.6$, J_{H^1P}

≈ 6, $J_{\mathrm{H^1P^+}} \approx 3$, $J_{\mathrm{H^2P^+}} = 6.4$, $J_{\mathrm{H^3P^+}} = 14.5$ Hz. Anal. Calcd for $C_{33}H_{31}BF_4P_2$: C, 68.77; H, 5.42; P, 10.75; Br, 0.00. Found: C, 68.95; H, 5.57; P, 10.66; Br, <0.1.

$[RhCl(COD)(Ph_2PCH_2{}^1CH_2{}^2P^+Ph_2CH_2{}^3Ph)]BF_4$. In a nitrogen-filled glovebox, 1.636 g (2.84 mmol) of $P\text{-}P^+BF_4$ in 20 mL of dichloromethane was added to a stirred dichloromethane solution (20 mL) of 0.700 g (1.42 mmol) of $[RhCl(COD)]_2$, analogous to the Chatt and Venanzi preparation of $RhCl(COD)(PPh_3)$.[17] After the solution had been allowed to age 1 h, the solvent was removed under vacuum, and the complex was washed with two 20-mL portions of toluene, filtered, and washed quickly with 10 mL of methanol (mp 195–200 °C dec). ^{1}H NMR: $\delta_{\mathrm{H^1}}$ 3.72 (m), $\delta_{\mathrm{H^2}}$ ~2.1 (m), $\delta_{\mathrm{H^3}}$ 4.48 (d), $\delta_{\mathrm{H_{vinyl}}}$ 5.47 (s), 3.12 (s), $J_{\mathrm{H^3P^+}} = 14.0$ Hz. Anal. Calcd for $C_{41}H_{43}BClF_4P_2Rh$: C, 59.84; H, 5.27; P, 7.53. Found: C, 60.20; H, 5.34; P, 6.88.

Hydrogenation Studies. The rate of 1-hexene hydrogenation was determined with a volumetric hydrogenation apparatus at atmospheric pressure and ambient temperature (25 °C). The catalyst solutions or suspensions were placed in a flat-bottom, hourglass-shaped hydrogenation flask with lower reaction chamber dimensions 6 cm (diameter) × 2 cm. This design was especially effective in minimizing creeping of the finely divided supported catalyst up the wall of the flask. The reaction mixtures were vigorously stirred with a magnetic stirrer. The stirring was sufficiently fast to permit hydrogen uptake rates of >30 mL/min without the rates being limited by gas to liquid mass transfer. It is unlikely that at the catalyst loadings and reaction conditions employed that liquid to solid mass transfer has a significant effect on the rates for the supported catalysts, because the rates are comparable to those observed for the homogeneous catalysts. Turnover frequencies were determined by averaging the volume of hydrogen consumed over short time periods (5–15 min).

1-Hexene was purified before use by the following procedure. The olefin was shaken and extracted three times with an equal volume of acidified (pH 1), aqueous ferrous sulfate, dried over anhydrous, 12-mesh calcium chloride under nitrogen atmosphere for at least 2 h, and finally distilled immediately before use under argon over fresh sodium borohydride.

Homogeneous Catalysts. Homogeneous catalysts were prepared in situ in a nitrogen-filled glovebox immediately prior to use. Stock solutions of the catalyst components ($P\text{-}P^+BF_4$ in methanol, PPh_3 in methanol, and $[RhCl(COD)]_2$ in dichloromethane) were added to the hydrogenation flask. Sufficient methanol was added to make 26.25 mL total solution volume. The flask was sealed and attached to the hydrogenation apparatus, whereupon hydrogen was added and allowed to equilibrate with the catalyst solution 1 h prior to addition of 3.75 mL (0.03 mol) of 1-hexene. All homogeneous catalysts contained 0.02 mmol of rhodium(I), which results in a substrate to rhodium ratio of 1500:1.

Silicate-Supported Catalysts. The 1:1:1/Hect catalyst system was prepared by mixing in 20 mL of methanol, 2 mL (0.01 M) of $P\text{-}P^+BF_4$ in methanol, and 1 mL (0.01 M) of $[RhCl(COD)]_2$ stock solutions. After 10 min, 2 mL (0.01 M) of PPh_3 was added, and the mixture was stirred 30 min. The flask was attached to the hydrogenation apparatus, and hydrogen was added, with stirring, for 2.5 h. In the glovebox, the hydrogenated solution was added, with swirling, to 0.200 g (0.146 mequiv of Na^+) of hectorite which had been previously equilibrated with 10 mL of methanol for 30 min. After 5-min contact time, the mixture was filtered, and the mineral was washed four times with 15-mL aliquots of methanol. The mineral was placed in the hydrogenation flask with 25.25 mL of methanol and 1 mL of dichloromethane. The suspension was exposed to hydrogen 30 min prior to addition of 3.75 mL (0.03 mol) of 1-hexene. Analysis of the material prior to olefin hydrogenation yielded 0.88% Rh, 0.84% P, and 0.23% Cl, which corresponds to a Rh:P:Cl molar ratio of 1.00:3.17:0.76.

The 2:0:1, 3:0:1, and 0:2:1/Hect systems were prepared in a manner analogous to that described for the 1:1:1/Hect catalyst.

^{31}P NMR Spectra. Fourier-transform, proton-decoupled phosphorus-31 NMR spectra were recorded on a Bruker HFX-10 spectrometer modified for multinuclear measurements. Spectra were obtained at 36.43 MHz. Chemical shifts were calculated relative to an 85% phosphoric acid external reference solution. Usually 2000 transients were taken to record each spectrum. The delay time of 0.5 s between transients is too short compared to typical ^{31}P spin–lattice relaxation times to allow anything other than qualitative interpretation of the spectra. Corrections for magnetic susceptibility differences were not made. In experiments where 1 atm of hydrogen pressure was required, the samples were prepared in the glovebox in 10-mm NMR tubes equipped with a female 14/35 Pyrex ground-joint stopper and one or two side arms. The tubes were attached to a hydrogenation line, and the pressure was monitored as a function of time, hydrogen being added as necessary, prior to conducting the NMR experiment. These latter tubes were not spun in the probe. Comparisons of the half-height line widths of a sample of $[Rh(COD)(PPh_3)_2]PF_6$ under spinning conditions showed no appreciable increase in line widths as a result of not spinning the sample.

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Registry No. $P\text{-}P^+Br^-$, 25004-99-3; $P\text{-}P^+BF_4$, 71243-21-5; $[RhCl(COD)(P\text{-}P^+)]BF_4$, 71250-43-6; $[RhCl(COD)]_2$, 12092-47-6; hectorite, 12173-47-6; PPh_3, 603-35-0; 1-hexene, 592-41-6; $Ph_2POCH_2CH_2P^+Ph_2CH_2Ph$, 71243-22-6.

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Empirical Force Field Calculations of Strain-Energy Contributions to the Thermodynamics of Complex Formation. 3. Chelate Effect in Complexes of Polyamines

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Empirical force field calculations are used to show that the steady decrease in enthalpy change on complex formation per nitrogen donor atom in complexes of polyamine ligands $H(NHCH_2CH_2)_xNH_2$, with Ni^{II} as x increases from 1 (en) to 4 (tetren), is due to cumulative ring strain. At the same time, this effect is partly offset by the increase in Ni–N bond strength in the absence of strain effects as the nitrogen donor changes from primary to secondary to tertiary. The opposing effects of cumulative ring strain and increasing bond strength of secondary relative to primary nitrogen donors coordinated to Ni^{II} produce a net decrease in ΔH on complex formation that almost exactly matches a term in ΔS present in the free energies of formation of the unidentate ammine complexes. This matching of terms makes analysis of the chelate effect in these polyamines appear much simpler than when the separate enthalpy and entropy contributions are examined.

Introduction

In the first two papers in this series[1,2] the difference in stability between analogous complexes of Ni^{II} containing on the one hand five-membered and on the other six-membered chelate rings formed with polyamine ligands was examined by means of semiempirical force field calculations. The program used for these calculations is that used by Snow,[3] and our modifications to it have also been described.[1,2] The program minimizes the conformational potential energy, U, of the molecule, taking into consideration contributions from bond-stretching, angle-bending, nonbonded, and torsional interactions. The necessary force constants have been tabulated in our first two papers.[1] The differences in stability between the five- and six-membered ring analogues is almost entirely an enthalpy effect,[4] which has been attributed to greater steric strain in the six-membered ring.[5,6] If it is assumed that the strain is an intramolecular phenomenon, so that solvent effects are not important, direct comparison should be possible of the difference in strain energy between the five- and six-membered ring analogues with the difference in their enthalpy changes on complex formation, ΔH, even though these have been measured in aqueous solution.[4] The conformational potential energy, U, must also be calculated for the free ligands, since these will not be the same and must contribute to the overall difference in ΔH. In Table I, only the difference in U for ethylenediamine (en) and 1,3-diaminopropane (pn) was calculated (0.37 kcal mol^{-1}),[7] and it was assumed that for other polyamine ligands, the effect of the addition of a methylene group to an ethylene bridge would also be to increase U by 0.37 kcal mol^{-1}. The comparison of the difference in ΔU and in ΔH for the five- and six-membered ring analogues is seen in Table I. The excellent agreement observed is highly encouraging, because Table I was regarded as a test of the usefulness of the type of calculations attempted here.

Table I. The Strain Energies, U, of Pairs of Otherwise Analogous Ni^{II} Complexes of Polyamines[a]

complex	U, kcal mol^{-1}	$-\Delta U_{5,6}$, kcal mol^{-1}	ΔH,[b] kcal mol^{-1}	$-\Delta(\Delta H)_{5,6}$, kcal mol^{-1}
$[Ni(en)(H_2O)_4]^{2+}$	1.14	1.53	−9.0	1.2
$[Ni(pn)(H_2O)_4]^{2+}$	3.04		−7.8	
$[Ni(en)_2(H_2O)_2]^{2+}$	3.35	3.07	−18.3	3.3
$[Ni(pn)_2(H_2O)_2]^{2+}$	7.16		−15.0	
$[Ni(en)_3]^{2+}$	4.57	7.44	−28.0	6.7
$[Ni(pn)_3]^{2+}$	13.12		−21.3	
$[Ni(dien)(H_2O)_3]^{2+}$	6.08	1.46	−11.9	1.3
$[Ni(dptn)(H_2O)_3]^{2+}$	8.28		−10.6	
$[Ni(dien)_2]^{2+}$	11.87	7.97	−25.3	7.7
$[Ni(dptn)_2]^{2+}$	21.32		−17.6	

[a] The polyamines are those in which the first member of the pair has all five-membered and the second member all six-membered chelate rings. The difference in U for each pair, $\Delta U_{5,6}$, is shown in the second column, corrected as described in the text for the extra strain induced in the free ligands by the presence of an extra methylene group in those forming six-membered rings. 0.37 kcal mol^{-1} is subtracted from U for the complex for each such extra methylene group. In the third column is shown ΔH for the formation of the complex in aqueous solution. The difference in ΔH for each pair must then be compared with $\Delta U_{5,6}$. [b] Reference 4.

In an examination of the chelate effect in complexes of polyamines, it had previously been noted[8] that the stability constants of the complexes of polyamines forming five-membered rings could be very simply related to the stability constants of the analogous ammonia complexes by eq 1. In

$$\log K_1(\text{polyamine}) = 1.152n \log K_1(NH_3) - \left(\sum_{i=1}^{n-1} i\right)\lambda + (n-1)\log 55.5 \quad (1)$$

eq 1, n is the number of nitrogen donor atoms, and the factor of 1.152, which is $pK_a(CH_3NH_2)/pK_a(NH_3)$, accounts for the inductive effect of the ethylene bridges. The $(n - 1) \log 55.5$ term corrects for the asymmetry of the standard reference state.[9] The term in λ, where λ is simply $\log K - \log K_{n+1}$, accounts for the steady decrease in $\log K_n(NH_3)$ as n increases. The term $\log \beta_n(NH_3)$ could just as well have been used in

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