A $^{31}P\{^1H\}$ NMR Study of the Reactions of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with Unsymmetrical, Bidentate Ligands and Hydrogen

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Summary

$[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ reacts with $Ph_2PCH_2CH_2OMe$ (PC_2O), $Ph_2P(CH_2)_3NMe_2$ (PC_3N), PBu^nPh_2 or PPh_3 to give $[Rh(cod)L_2]Cl$ (L = PC_2O, PC_3N, PBu^nPh_2, PPh_3). In the presence of hydrogen, $[Rh(cod)L_2]Cl$ is converted to $[RhClH_2L_3]$. In contrast, $[Rh(cod)(PC_2O)_2]BPh_4$ reacts with H_2 to give $[RhH_2(PC_2O)_2S_2]BPh_4$ (S = solvent). With $Ph_2PCH_2CH_2NMe_2$ (PC_2N) or $Ph_2PCH_2CH_2SMe$ (PC_2S), $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ reacts to form the chelate complexes *cis*-$[Rh(PC_2N)_2]^+$ or *cis*-$[Rh(PC_2S)_2]^+$, neither of which reacts with hydrogen under ambient conditions. The products of the reactions are characterized *in situ* by $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Hydrogenation reactions catalyzed by rhodium phosphine complexes have been studied extensively [1–3]. A key step in such reactions is dissociation of a phosphine ligand to generate a coordinatively unsaturated (or solvent-associated) species, as demonstrated by kinetic [4] and spectroscopic [5] studies of Wilkinson's catalyst, $[RhCl(PPh_3)_3]$. Schrock and Osborn have shown [6] that cationic rhodium complexes, $[Rh(diene)L_2]^+$, with non-coordinating anions are catalyst precursors for olefin hydrogenation. In polar solvents these complexes react with hydrogen, by reduction of the diene, to give the solvent-associated species $[RhH_2L_2S_2]^+$ (S = solvent), from which solvent displacement by the olefin occurs readily.

Since these solvent-associated complexes are quite unstable, it seemed to us that more stable analogues might be formed with unsymmetrical, bidentate ligands. One end of the ligand would coordinate weakly, and thus be similar to a solvent molecule, but the chelate effect would confer additional stability on the complex. We report here a $^{31}P\{^1H\}$ NMR study of the reactions of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with $Ph_2PCH_2CH_2OMe$ (PC_2O), $Ph_2P(CH_2)_nNMe_2$ (n = 2, PC_2N; n = 3, PC_3N) and $Ph_2PCH_2CH_2SMe$ (PC_2S), and the interactions of the products with hydrogen.

Results and Discussion

When $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ is treated with 4 molar equivalents of PC_2O in acetone or acetonitrile solution, a deep orange color develops, and the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at δ(P) 25.6 with ^1J(Rh, P) = 149 Hz. (With less than 4 equivalents of PC_2O the same species is formed, but some $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ remains.) This complex is identified as $[Rh(cod)(PC_2O)_2]Cl$, by comparison of its NMR parameters with those of $[Rh(cod)(PPh_3)_2]Cl$ prepared analogously here, and those of $[Rh(nbd)(PPh_3)_2]ClO_4$, reported elsewhere [7]. When the reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with PC_2O or PPh_3 is performed in the presence of $NaBPh_4$, identical $^{31}P\{^1H\}$ NMR spectra are obtained, suggesting that in $[Rh(cod)L_2]Cl$ (L = PC_2O, PPh_3) no interaction exists between the chloride ion and the square planar rhodium(I) cation. In $[Rh(cod)(PC_2O)_2]^+$ the PC_2O ligand is coordinated through phosphorus only.

When hydrogen is introduced into an acetone solution of $[Rh(cod)(PC_2O)_2]Cl$ at ambient temperature, the solution becomes lighter in color and conversion to a single PC_2O-containing species occurs. The latter exhibits a doublet of doublets at δ(P) 25.5 and doublet of triplets at δ(P) 9.0 in its $^{31}P\{^1H\}$ NMR spectrum, and the smaller ^1J(Rh, P) values are indicative of formation of a rhodium(III) complex [5, 8]. The ^1H NMR spectrum of this complex at −40 °C contains two broad hydride resonances at δ(H) −15.2 and −7.6 (d, ^2J(P, H) 157 Hz). The complex is identified as $[RhClH_2(PC_2O)_3]$, by comparison of its ^1H and $^{31}P\{^1H\}$ NMR parameters with those of $[RhClH_2(PPh_3)_3]$ formed by addition of H_2 to Wilkinson's catalyst [5]. The complex $[RhClH_2(PC_2O)_3]$ exists as the single isomer **1**. On standing at ambient temperature $[RhClH_2(PC_2O)_3]$ slowly loses H_2 to give the PC_2O analogue of Wilkinson's catalyst (Table I). In contrast, addition

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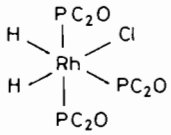
TABLE I. $^{31}P\{^1H\}$ NMR Parameters for Rhodium Complexes Containing Phosphine Ligands

Complex	δ(P)[a]	^1J(Rh, P) (Hz)	^2J(P, P) (Hz)
$[Rh(cod)(PPh_3)_2]^+$	27.1 d[b]	147	
$[Rh(cod)(PC_2O)_2]^+$	25.6 d	149	
$[Rh(cod)(PC_2N)]^+$	41.4 d[b]	161	
cis-$[Rh(PC_2N)_2]^+$	56.5 d[b]	180	
cis-$[Rh(PC_2S)_2]^+$	63.8 d[b]	161	
$[RhCl(PPh_3)_3]$	31.1 dd	144	37
	47.9 dt	190	
$[RhCl(PC_2O)_3]$	28.6 dd	138	40
	43.5 dt	185	
$[RhClH_2(PPh_3)_3]$	40.2 dd	114	18
	20.6 dt	90	
$[RhClH_2(PC_2O)_3]$	25.5 dd	110	20
	9.0 dt	90	
$[RhClH_2(PC_3N)_3]$	31.9 dd	111	21
	13.0 dt	93	
$[RhClH_2(PBu^nPh_2)_3]$	31.2 dd	112	20
	13.6 dt	93	
$[RhH_2(PPh_3)_2(acetone)_2]^+$	37.6 d	112	
$[RhH_2(PC_2O)_2(acetone)_2]^+$	28.9 d	110	

[a]Recorded in acetone solution at ambient temperature, except where stated. Chemical shifts are in ppm relative to external 85% H_3PO_4. [b]Recorded in acetonitrile solution at ambient temperature.



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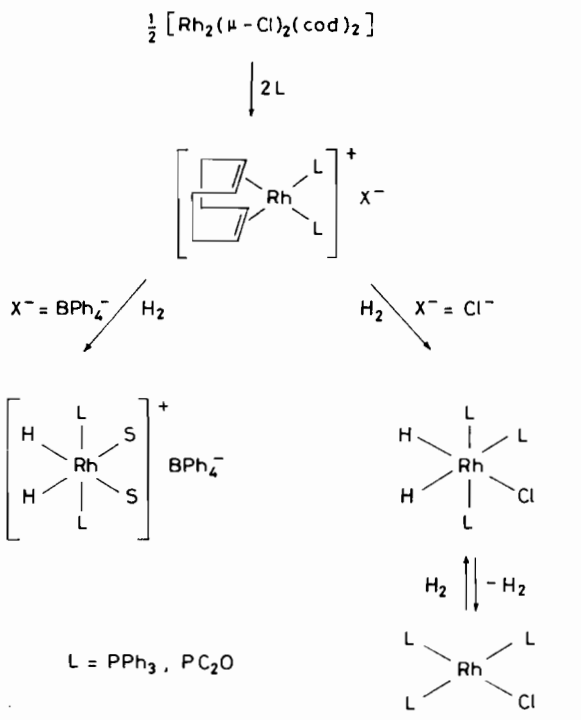
of H_2 to an acetone solution of $[Rh(cod)(PC_2O)_2]BPh_4$ results in the formation of an unstable complex which is presumed to be $[RhH_2(PC_2O)_2(acetone)_2]BPh_4$ (Table I) [6], since the value of δ(P) is much smaller than would be expected for a complex with chelated PC_2O [9].

A consideration of the stoichiometry of the reaction of $[Rh(cod)(PC_2O)_2]Cl$ with H_2 reveals that only two-thirds of the rhodium present may be accounted for by $[RhClH_2(PC_2O)_3]$, whereas the remainder must be in a form which contains no PC_2O. The reaction does not appear to involve decomposition to rhodium metal, so the remaining rhodium may be in the form of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$. The mechanism of this reaction is unclear, but it is obviously initiated by addition of H_2 to the $[Rh(cod)(PC_2O)_2]^+$ cation. Related ligand rearrangement reactions occur when platinum(II) complexes are treated with $SnCl_2$ [10–12].

In order to determine whether the ether function is important in facilitating the ligand rearrangement described above, we investigated the analogous reaction with PBu^nPh_2. The n-butyl group is the same size as the ether-containing chain in PC_2O. Treatment of an acetone solution of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with 4 molar equivalents of PBu^nPh_2, followed by the addition of H_2, results in the formation of $[RhClH_2(PBu^nPh_2)_3]$ as the only phosphorus-containing species in solution. In fact, similar reactions with PPh_3 or PC_3N proceed analogously (Table I). Thus it is clear that the presence of the ether function in PC_2O, or the amine in PC_3N, is unnecessary for the ligand rearrangement reaction to occur following the addition of H_2 to $[Rh(cod)L_2]Cl$. It is also apparent that this reaction is favored over chelation of PC_2O or PC_3N upon removal of the diene by hydrogenation.

The above reactions may be summarized as shown in Scheme 1. The direction of the reaction of $[Rh(cod)L_2]^+X^-$ with hydrogen does not depend on the nature of L, but does depend on the initially uncoordinated anion. Each reaction involves reduction of the diene and hence is irreversible. Where the anion is chloride there is clearly a link between the cationic rhodium(I) complexes prepared by Schrock and Osborn [6, 7] and Wilkinson's catalyst, *i.e.* both $[Rh(cod)L_2]Cl$ and $[RhClL_3]$ react with hydrogen to form $[RhClH_2L_3]$.

When $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ is treated with 2 molar equivalents of PC_2N in the presence of $NaBPh_4$ in acetonitrile solution the $^{31}P\{^1H\}$ NMR spectrum exhibits doublets at δ(P) 41.4, ^1J(Rh, P) 161 Hz, and δ(P) 56.5, ^1J(Rh, P) 180 Hz. The large downfield shifts are indicative of chelated PC_2N ligands [9]. Addition of 2 further equivalents of PC_2N causes complete conversion to the latter species, which is therefore identified as the *cis*-$[Rh(PC_2N)_2]^+$ cation. The *cis* geometry is inferred from the magnitude of



Scheme 1.

the one-bond coupling constant, which is considerably greater than those observed for [Rh(diphosphine)$_2$]$^+$ complexes which contain mutually *trans* phosphines [13]. The other species, which is observed only at PC_2N:Rh ratios less than 2, is believed to be [Rh(cod)(PC_2N)]$^+$. The formation of chelate complexes with PC_2N illustrates the greater nucleophilicity towards rhodium(I) of the amine compared with the ether function, and the easier formation of five-membered chelate rings compared with their six-membered counterparts.

The only phosphorus-containing product of the reaction of [Rh$_2$(μ-Cl)$_2$(cod)$_2$] with PC_2S in acetonitrile solution is *cis*-[Rh(PC_2S)$_2$]Cl, irrespective of the PC_2S:Rh ratio employed. The *cis*-[Rh(PC_2S)$_2$]$^+$ cation has been prepared previously [14], as well as analogous species with $Ph_2PCH_2CH_2SEt$ [14] and $Ph_2PCH_2CH_2SPh$ [14, 15]. Addition of H_2 to an acetonitrile solution of *cis*-[Rh(PC_2N)$_2$]$^+$, as its chloride or tetraphenylborate salt, or *cis*-[Rh(PC_2S)$_2$]Cl causes no change in the $^{31}P\{^1H\}$ NMR spectrum.

Solutions of the rhodium phosphine complexes are oxygen-sensitive, with the phosphine oxides being the ultimate products. It has been shown [14] that [Rh($Ph_2PCH_2CH_2SR$)$_2$]$^+$ (R = Me, Et, Ph) reacts with dioxygen to form adducts, which are believed to adopt trigonal bipyramidal geometries. We also find that when an acetonitrile solution of *cis*-[Rh(PC_2S)$_2$]Cl is exposed to air or dioxygen for a few minutes an intermediate complex is formed (δP 52.8 d, ^1J(Rh, P) 124 Hz), but extensive oxidation of PC_2S occurs also. Longer exposure to air causes complete conversion to the phosphine oxide (δ(P) 28.3).

Experimental

The ligands PC_2O, PC_2N, PC_3N and PC_2S were prepared as described previously [16]. Triphenylphosphine was obtained from SCM Specialty Chemicals. PBu^nPh_2 was prepared by reaction of PPh_3 with Li metal in THF solution, followed by addition of excess Bu^nCl; PBu^nPh_2 was obtained as a colorless oil in 46% yield by distillation under reduced pressure (boiling point 148 °C at 0.5 torr). [Rh$_2$(μ-Cl)$_2$(cod)$_2$] was prepared by an established method [17]. Acetone and acetonitrile were obtained from Fisher. Acetone was distilled immediately prior to use; acetonitrile was refluxed over P_2O_5, then distilled prior to use.

$^{31}P\{^1H\}$ NMR spectra were recorded on Varian XL-300 or JEOL FX-100 spectrometers at 121.4 and 40.3 MHz respectively. Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. The reactions were performed in 5 mm or 10 mm NMR tubes fitted with a valve containing an O-ring sealed PTFE piston with an axial bore, constructed by J. Young (London) and distributed by R. J. Brunfeldt, Bartlesville, Oklahoma. A typical procedure is outlined below.

Reaction of [Rh$_2$(μ-Cl)$_2$(cod)$_2$] with PC_2O

An acetone solution (3 ml) of PC_2O (60 mg, 0.25 mmol) was introduced into a 10 mm NMR tube. The tube was placed in a −78 °C slush bath, and [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (30 mg, 0.061 mmol) was added. The tube was attached to the vacuum line and deaerated by two freeze–pump–thaw cycles. The tube was then filled with argon, the valve was closed, and the contents were examined by $^{31}P\{^1H\}$ NMR spectroscopy. To introduce hydrogen, the solution was cooled to −78 °C and the tube was evacuated, then filled with hydrogen. The valve was closed, the solution was allowed to warm to ambient temperature, then the solution was examined spectroscopically.

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