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The Hydrogenation in Methanol Solution of the Complexes $RhCl(CO)\{PPh_2[(CH_2)_nCH{=}CH_2]\}_2$ and $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CHCH_3)]_2$.[†]

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Abstract

The complexes $RhCl(CO)\{PPh_2[(CH_2)_nCH{=}CH_2]\}_2$ and $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$ add hydrogen in methanol solution saturating the olefin and forming $RhCl(CO)\{PPh_2[(CH_2)_{n+1}CH_3]\}_2$, n = 0–3. The reaction does not proceed in non-protic solvents. Carbon monoxide inhibits the reaction, whereas excess ligand (for n = 2) becomes catalytically saturated. The rate of the reaction depends largely on steric factors and follows the order $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2 \sim RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH{=}CH_2)]_2$. Deuteration experiments show that scrambling does occur and a mechanism for the hydrogenation is proposed. Isomerisation for n = 3 occurs at higher temperatures giving the *cis*-olefinphosphine complex $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$.

Introduction

During recent years, there has been considerable research into the synthesis, characterization and reactions of unsaturated tertiary

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[†] No reprints available.

phosphine and arsine complexes of rhodium(I) and iridium(I)[1-26]. Typical ligands include the *o*-styryl types $P(o\text{-}CH_2{=}CHC_6H_4)_3$[4,5,9], $P(o\text{-}CH_2{=}CHC_6H_4)_2Ph$[9], $P(o\text{-}CH_2{=}CHC_6H_4)Ph_2$[6,7,13,14,22,24]; the more flexible ligands $PPh_{3-x}[(CH_2)_nCH{=}CH_2]_x$, x = 1, 2 or 3 and n = 0-3 [2,3, 12,15,16,17,18]; and diphosphine and diarsine ligands such as $o\text{-}Ph_2P(C_6H_4CH{=}CHC_6H_4)PPh_2\text{-}o$[1,8,20], $Ph_2PCH_2CH_2CH{=}CHCH_2CH_2PPh_2$[19,25] $Ph_2AsCH_2CH_2CH{=}CHCH_2CH_2AsPh_2$[25], and ${}^tBu_2PCH_2CH_2CH{=}CHCH_2CH_2PBu_2{}^t$[22]. Since the metal-olefin bond in most cases studied is quite stable, such complexes could serve as model complexes for the intermediates in various homogeneous catalytic reactions involving transition metal compounds particularly for homogeneous hydrogenation, isomerisation, and hydroformylation reactions. We have previously reported, in a communication, the initial results of our study into the hydrogenation and isomerisation of the olefin part of the ligands of unsaturated tertiary phosphine complexes of rhodium(I)[2]. It has also been reported[18] by us that the complex $RhCl(mbp)_2$, mbp = but-e-enyldiphenylphosphine, $PPh_2(CH_2CH_2CH{=}CH_2)$, reacts with hydrogen gas at one atmosphere and -5°C in methanol to form the dimeric complex $Rh_2Cl_2[PPh_2(CH_2CH_2CH_2CH_3)]_2$. Since then Bennett and Hann have reported a similar metal-promoted hydrogenation of $[Rh(spp)_2]BPh_4$ spp = (*o*-vinylphenyl)diphenylphosphine, $o\text{-}CH_2{=}CHC_6H_4PPh_2$, to give $Rh(\eta^6\text{-}C_6H_5BPh_3)(\eta^2\text{-}o\text{-}CH_2{=}CHC_6H_4PPh_2)$ plus (*o*-ethylphenyl)diphenylphosphine. This reaction of Bennett and Hann's refutes the earlier work of Brookes' on the same reaction in which he claims to obtain $Rh(\eta^6\text{-}C_6H_5BPh_3)(o\text{-}C_2H_5C_6H_4PPh_2)_2$[14]. We now wish to report in detail our study into the hydrogenation and isomerisation of the series of complexes $RhCl(CO)L_2$ where $L = PPh_2[(CH_2)_nCH{=}CH_2]$, n = 0-3 and $L = PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)$.

Experimental

The ligands diphenylvinylphosphine[27], allyldiphenylphosphine[28], but-3-enyldiphenylphosphine[29] and pent-4-enyldiphenylphosphine[29] were prepared by the standard literature method by reacting chlorodiphenylphosphine with the Grignard of the corresponding haloalkene and vacuum distilling out the product. All phosphines were stored under nitrogen until used. Chlorodiphenylphosphine and allyl chloride were obtained from Aldrich Chemical Company; vinyl chloride, hydrogen, deuterium and carbon monoxide were purchased from the Matheson Company; 5-bromopent-1-ene and 4-bromobut-1-ene were obtained from Pierce Chemical Company. Di-μ-chlorotetracarbonyldirhodium(I)[30] was prepared by the literature method. All chemicals were reagent grade and were used without further purification. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory; Elback über Engelskirchen, West Germany, and by Huffman Laboratories Inc., Wheatridge, Colorado.

Infrared spectra were recorded using Perkin-Elmer 137, 137G or 621 spectrometers while the ^{1}H NMR spectra were obtained on a Varian HA100 spectrometer operated in the field sweep mode using internal TMS as the lock signal. Spectra were integrated on two to five samples and the average taken. The integrals of the methyl and methylene protons of the hydrogenated and deuterated samples were calculated with respect to the phenyl protons. Mass spectra of the complexes were recorded using a Varian MAT CH-7 instrument operating under the same conditions for each complex using a normal solid sample probe. As the intensities of the parent (complex) ion were quite low, the phosphine peaks in the mass spectrum were analysed to determine the amount of deuterium added.

Preparation of Complexes

The compounds *trans*-$RhCl(CO)\{PPh_2[(CH_2)_nCH=CH_2]\}_2$, n = 0, 1 or 3 were prepared by the same method as *trans*-$RhCl(CO)[PPh_2(CH_2CH_2CH=CH_2)]_2$[15] from $Rh_2Cl_2(CO)_4$ and an excess of the corresponding ligand. The preparative conditions and yields are given below. The analyses are given in Table 1.

Complex	Solvent	% Yield
$RhCl(CO)[PPh_2(CH=CH_2)]_2$	ether	82

TABLE 1

Analytical Data for the Rhodium(I) Complexes

Complex	Found			Calculated		
	C	H	Cl	C	H	Cl
$RhCl(CO)[PPh_2(CH{=}CH_2)]_2$	58.8	4.38	6.8	58.9	4.41	6.0
$RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2$	61.0	5.37	5.8	60.1	4.85	5.7
$RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2$	62.5	5.48	5.0	62.4	5.64	5.3
$RhCl(CO)[PPh_2(CH_2CH_2CH_3)]_2$	59.6	5.90	5.6	59.7	5.46	5.7

$RhCl(CO[PPh_2(CH_2CH=CH_2)]_2$	ether	95
$RhCl(CO)[PPh_2(CH_2CH_2CH_2CH=CH_2)]_2$	petroleum ether/ether	71

Preparation of Carbonylchlorobis[cis-pent-3-enyldiphenylphosphine]-rhodium(I), $RhCl(CO)[PPh_2\{CH_2CH_2CH\overset{c}{=}CHCH_3\}]_2$.

A solution of 0.13g of carbonylchlorobis(pent-4-enyldiphenylphosphine)rhodium(I), $RhCl(CO)[PPh_2(CH_2CH_2CH_2CH=CH_2)]_2$ in 80ml of methanol was refluxed for 5h. The methanol was removed by vacuum and the product (as an oil) was characterized by infrared and ^1H NMR spectroscopy. The same isomerisation occurred in refluxing benzene. For reactions, the isomerised complex was prepared *in situ*.

Hydrogenation and Deuteration Reactions.

An excess of hydrogen or deuterium was bubbled slowly through a deaerated methanolic solution of each compound. The final product was crystallised from methanol for the reaction of *trans*-$RhCl(CO)\{PPh_2$-$[(CH_2)_nCH=CH_2]\}_2$ where n = 0, 1 or 2, and obtained as an oil for n = 3 and for the product of the reaction with *trans*-$RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3]_2$. The products were characterised by infrared and ^1H NMR spectroscopy. One product, *trans*-$RhCl(CO)[PPh_2(CH_2CH_2CH_3)]_2$ was analysed (Table 1) and the analysis was found to be satisfactory.

Discussion

Properties of $RhCl(CO)[PPh_2(CH_2CH_2CH=CH_2)]_2$

The compound $RhCl(CO)[PPh_2(CH_2CH_2CH=CH_2)]_2$ is a yellow crystalline solid which readily dissolves in non-protic solvents such as methylene chloride, chloroform or benzene forming yellow solutions, and is moderately soluble in protic solvents such as methanol (*ca.* 15mM) and ethanol (*ca.* 13mM) forming colourless and pale yellow solutions respectively. The vinyl, allyl and pentenyl complexes, $RhCl(CO)\{PPh_2[(CH_2)_nCH=CH_2]\}_2$, n = 0, 1 or 3, and $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$ display a similar solubility in non-protic solvents but are somewhat less soluble in methanol. In a chloroform solution (19.7mM), the compound RhCl(CO)-

$[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ has an apparent molecular weight of 600 whereas under the same conditions in a methanol solution (7.4 mM), the compound has an apparent molecular weight of 378 as determined by vapour pressure osmometry. The calculated value for the molecular weight is 647. In chloroform (3.35 mM) the compound $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ is a non-electrolyte (molecular conductivity = 0.04 ohm^{-1} mol^{-1}), but in methanol (3.64 mM) the results are consistent with the compound being 1:1 electrolyte (molecular conductivity = 64.0 ohm^{-1} cm^2 mol^{-1}). The molecular conductivity of a 5.32 mM solution of tetra-n-butylammonium iodide solution in methanol was 77.8 ohm^{-1} cm^2 mol^{-1}. These results are consistent with the observed infrared and ^1H NMR results. In the solid state (KBr) in the infrared spectrum, the compound $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ has a single carbonyl stretching band at 1950 cm^{-1}, and in a non-protic solvent (methylene chloride) it again has a single carbonyl band at 1972 cm^{-1}, while in a protic solvent (methanol) it has two carbonyl bands at 2004 cm^{-1} and at 1968 cm^{-1} in the approximate ratio of 1:2. The reaction of $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ with sodium tetra-

TABLE 2

Reaction Conditions for the Hydrogenation and Deuteration

of

$RhCl(CO)\{PPh_2[(CH_2)_nCH{=}CH_2]\}$, n = 0, 1, 2 or 3

and

$RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$

Complex	Time	Temperature
$RhCl(CO)[PPh_2(CH{=}CH_2)]_2$	12h	64°C
$RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2$	3h	64°C
$RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$	1h	ambient
$RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2$	5h	ambient
$RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$	5h	ambient

phenylborate in methanol gives the five-coordinate cationic complex $\{\overline{\mathrm{Rh}(\mathrm{CO})[\mathrm{PPh_2}(\mathrm{CH_2CH_2CH}}{=}\mathrm{CH_2})]_2\}\mathrm{BPh_4}$ in which both olefins are coordinated to the rhodium centre; and it has a single carbonyl resonance at 2001 cm^{-1} in the solid state (KBr) and at 2028 cm^{-1} in solution (methylene chloride) [18]. The ^1H NMR spectrum of the butenyl compound in d-chloroform shows olefinic resonances in the normal position at 4.20, 5.06 and 5.10τ (Table 3). In the ^1H NMR spectrum of the butenyl compound in d_4-methanol, there are no resonances assignable to uncoordinated olefin, and the upfield peaks are broad and somewhat obscured by the residual proton peaks of the methyl resonance of the solvent. Therefore it is apparent that there is an equilibrium between $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ and $\{Rh(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2\}^+$ in methanol, and that at least one of the olefinic groups is bonded to the rhodium centre and that there is probably an equilibrium between bonded and uncoordinated olefins (See Scheme 1). Such equilibria between bonded and unbonded olefins in rhodium compounds are quite common e.g. $\overline{\mathrm{RhCl}[\mathrm{PPh_2}(\mathrm{CH_2CH_2CH}}{=}\mathrm{CH_2})]_2$, whose crystal structure has been determined[17], exhibits similar fluxional behaviour[18].

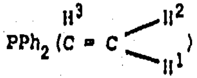
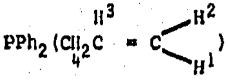
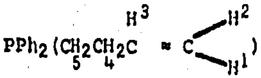
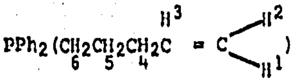
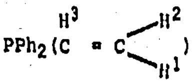
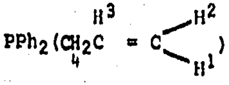
The Hydrogenation Reaction.

The reaction of hydrogen with the compounds $RhCl(CO)\{PPh_2[(CH_2)_nCH{=}CH_2]\}_2$, n = 0 - 3, and with $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$ in methanol under the conditions listed in Table 2 yields the compounds $RhCl(CO)\text{-}\{PPh_2[(CH_2)_{n+1}CH_3]\}_2$ in which the olefin has been saturated. Although no accurate rates were measured, it was obvious that the rate depended greatly on the size of the chelate ring formed in the reaction. The reaction of $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ with hydrogen proceeded very quickly at room temperature, whereas $RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2$ and $RhCl(CO)[PPh_2(CH{=}CH_2)]_2$ needed refluxing conditions for the reaction to proceed at any comparable rate. The relative rates of reaction were $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2 \sim RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2 > RhCl(CO)[PPh_2(CH{=}CH_2)]_2$. Upon repeating the reactions with deuterium,

(Continued on p. 395)

TABLE 3

^1H NMR Data for the Ligands and Complexes Studied in the Hydrogenation Reactions

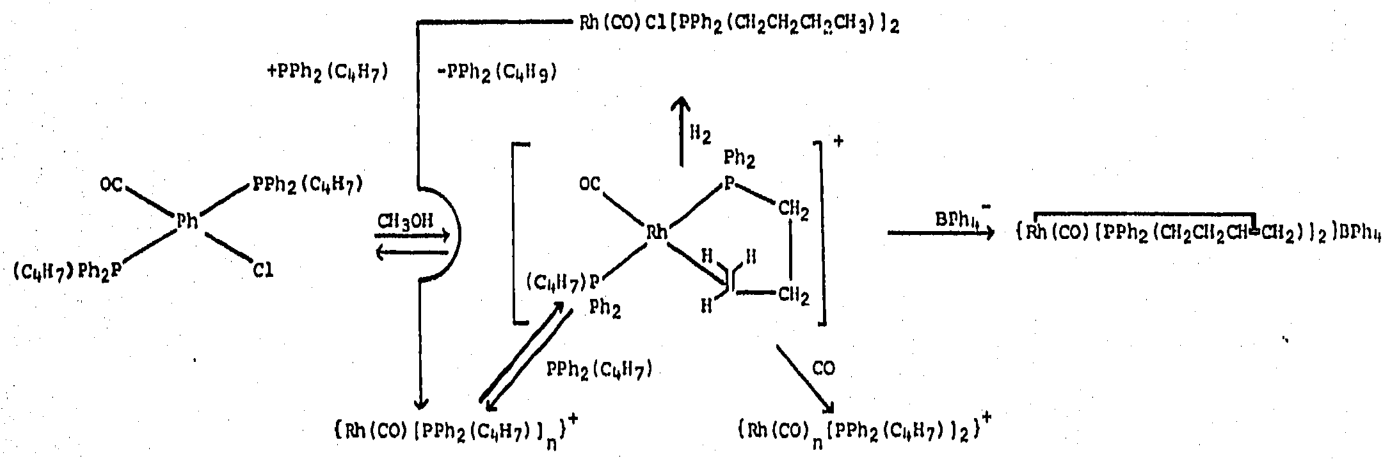
	Chemical Shifts[a]						Coupling Constants[b]		
	H_1	H_2	H_3	H_4	H_5	H_6	*J(cis)*	*J(trans)*	Other
Ligand									
 $PPh_2(\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	4.37	4.11	3.34				12.0	18.0	$J(P\text{-}H_1)$ = 14.0 $J(P\text{-}H_2)$ = 31.0 $J(P\text{-}H_3)$ = 12.0
 $PPh_2(\underset{4}{CH_2}\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	5.10	5.09	4.26	7.29			9.8	17.7	$J(P\text{-}H_1)$ = 0.7 $J(P\text{-}H_2)$ = 0.7 $J(P\text{-}H_3)$ = 6.1 $J(P\text{-}H_4)$ = 0.5
 $PPh_2(\underset{5}{CH_2}\underset{4}{CH_2}\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	5.16	5.11	4.19	7.9	7.9		10.0	17.0	
 $PPh_2(\underset{6}{CH_2}\underset{5}{CH_2}\underset{4}{CH_2}\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	5.10	5.16	4.38	8.0	8.50	8.0	11.0	17.0	
Complex RhCl(CO)(Ligand)$_2$									
 $PPh_2(\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	4.38	3.88	c				12.0	18.0	$J(P\text{-}H_1)$ = 11.0 $J(P\text{-}H_2)$ = 18.0
 $PPh_2(\underset{4}{CH_2}\overset{H^3}{C}=C\genfrac{}{}{0pt}{}{H^2}{H^1})$	5.07	4.98	3.95	6.55			11.0	17.0	$J(P\text{-}H_4)$ = 0.5

$PPh_2(\underset{5}{CH_2}\underset{4}{CH_2}\overset{H^3}{C}=C\begin{smallmatrix}H^2\\H^1\end{smallmatrix})$	5.06	5.10	4.20	7.54	7.38		11.0	17.0	
$PPh_2(\underset{6}{CH_2}\underset{5}{CH_2}\underset{4}{CH_2}\overset{H^3}{C}=C\begin{smallmatrix}H^2\\H^1\end{smallmatrix})$	5.05	5.12	4.30	7.86	8.26	7.48	11.0	17.0	
$PPh_2(\underset{2}{CH_2}\underset{1}{CH_3})$	8.81	7.44							J(P-H_1) = 16.0 J(P-H_2) = 4.0
$PPh_2(\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_3})$	9.00	8.36	7.48						J(P-H_3) = 4.0
$PPh_2(\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_3})$	9.25	8.50	8.36	7.50					J(P-H_4) = 4.0
$PPh_2(\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_3})$	9.19	8.67	8.50	8.36	7.47				J(P-H_5) = 4.0

a Measured at 100 MHz; chemical shifts in ppm relative to internal TMS, τ = 10.0.

b Coupling constants in Hz.

c obscured by phenyl protons.



Scheme 1

Equilibria involving $Rh(CO)Cl[PPh_2(C_4H_7)]_2$ in Methanol Solution.

The Effect of Other Ligands on the Hydrogenation Reaction.

it was found that 2.0 deuterium atoms per ligand were added. The amount of deuterium added was determined from accurate mass spectral data. No hydrogenation of the ligands in methanol in the absence of the metal complexes took place, and no incorporation of deuterium was observed when hydrogenation took place in d_1-methanol. No hydrogenation was observed on attempting the reaction of $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ in the non-protic solvents benzene, chloroform or ether. This is in agreement with Wilkinson and co-worker's observation that although

TABLE 4

Added Deuterium Distribution from ^1H NMR

and

Mass Spectral Results

Compound	Total[a] Deuterium Added	Internal[b] Carbon	External[b] Carbon
$RhCl(CO)[PPh_2(CH{=}CH_2)]_2$	2.00	0.94	1.06
$RhCl(CO)[PPh_2(CH_2CH{=}CH_2)]_2$	2.05	0.79	1.21
$RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$	1.99	0.75	1.25
$RhCl(CO)[PPh_2(CH_2CH_2CH{=}CHCH_3)]_2$	2.0[c]	1.04	0.96
$RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2$	2.04	0.45	1.55
$RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ + excess $PPh_2(CH_2CH_2CH{=}CH_2)$	2.0[c]	0.76	1.24
$PPh_2(CH_2CH_2CH{=}CH_2)$	0.0	0.0	0.0
$PPh_2(CH{=}CH_2)$	0.0	0.0	0.0

[a] Mass Spectral Results.

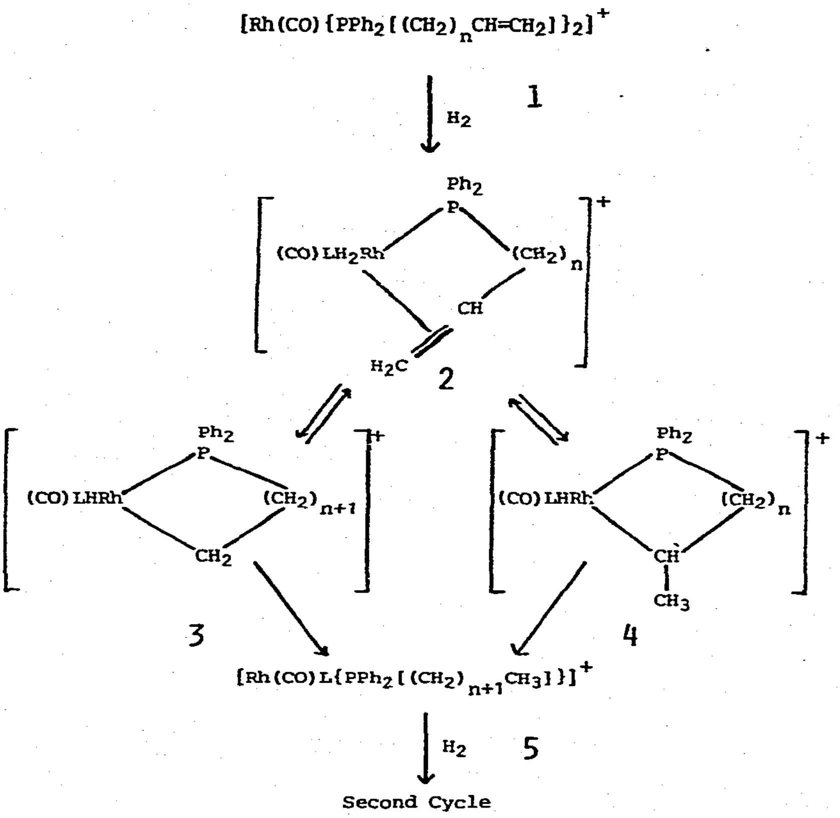
[b] Number of deuterium atoms added per mole of ligand; ^1H NMR values normalised to 2.0 deuterium atoms.

[c] Determined by ^1H NMR integration.

$RhCl(PPh_3)_3$ readily activates molecular hydrogen in benzene, the corresponding carbonyl complex, *trans*-$RhCl(CO)(PPh_3)_2$ does not[31]. Also in these non-protic solvents, the olefin is not coordinated to the rhodium centre as determined by ^1H NMR.

In the original paper on the homogeneous hydrogenation of olefins using $RhCl(PPh_3)_3$, it was suggested that the intermediate consisted of a *cis*-dihydride complex with both hydrogens *cis* to the olefin giving rise to a simultaneous addition to the olefin[31]. Since then several authors have indicated that a two step mechanism is more likely [32] since scrambling does occur. Our work substantiates this latter viewpoint since we do observe scrambling in our system (See Table 4), and the extent of the scrambling depends on the size of the chelated intermediate. The fact that there is an uneven distribution of deuterium atoms between the internal and external carbon atoms of the olefin is consistent with the reversible metal-hydride-olefin complex and metal-alkyl complex reaction (See Scheme 2). Such a reversible mechanism has recently been shown to exist in the complex $[HMo(C_2H_4)_2(Ph_2PCH_2CH_2PPh_2)_2]^+$[33]. It has also been shown that ligands such as tri-n-propylphosphine and tri-n-butylphosphine in the platinum complexes $Pt_2Cl_4L_2$, undergo a hydrogen-deuterium exchange reaction involving presumably a metal-hydride-alkyl intermediate. The exchange in this reaction is controlled by steric requirements of the ligand and the most favoured intermediate involves a 5-membered chelate ring[34]. We are able to say that such an equilibrium between the saturated phosphine complexes, $RhCl(CO)[PPh_2[(CH)_{n+1}-CH_3]]_2$ and a metal-alkyl-hydride species does not exist in our system since only 2.0 deuteriums per ligand are incorporated, although the activation of alkyl groups on rhodium is well known, and the dehydrogenation of alkyl groups has been reported[19,20,22].

Effect of Temperature. Upon attempting to hydrogenate $RhCl(CO)-[PPh_2(CH_2CH_2CH{=}CH_2)]_2$ in methanol at lower temperatures between -5°C to -15°C, the reaction is completely inhibited. It is suggested that



Scheme 2

Proposed Mechanism for the Hydrogenation of $Rh(CO)Cl\{PPh_2[(CH_2)_nCH{=}CH_2]\}_2$ in Methanol, $n = 0{-}3$

the proposed equilibrium between bonded and uncoordinated olefin has been shifted to the completely bonded species which could not activate molecular hydrogen.

Effect of Added Ligand. In the presence of excess carbon monoxide the hydrogenation of $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)_2]$ in methanol is completely inhibited and only the original complex is isolated.

However, when an excess of the ligand, $PPh_2(CH_2CH_2CH{=}CH_2)$, is added to the complex $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$, the colour changes immediately from colourless to yellow, suggesting the formation of the complexes $\{Rh(CO)[PPh_2(CH_2CH_2CH{=}CH_2)_2]_n\}^+$, $2 \leq n \leq 4$. The complex $[Ir(CO)(PPh_3)_4]^+$ has been prepared in methanol by this method[35]. When hydrogen or deuterium is admitted to the solution, the olefin of both the free ligand and complexed ligand become hydrogenated or deuterated respectively (See Scheme 1). In the deuteration experiment 2.0 atoms of deuterium are added per mole of ligand and the distribution is the same as in the case without excess ligand (Table 4). This indicates that the same mechanism is operative where excess ligand is present, and it indicates that an equilibrium is present between the complexes $\{RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_n\}^+$, $2 < n < 4$. The reaction was complete within one hour at room temperature and one atmosphere of hydrogen. It should be noted that Wilkinson's catalyst, $RhCl(PPh_3)_3$, is inhibited by excess triphenylphosphine, but Wilkinson's catalyst was used in a non-protic solvent such as benzene.

Isomerisation

Upon refluxing a solution of $RhCl(CO)[PPh_2(CH_2CH_2CH_2CH{=}CH_2)]_2$ in methanol or benzene for about 5h, it was found that the olefin had isomerised to give the complex $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]$ in which the olefin had the *cis*-configuration (by ^1H NMR). Such an isomerisation has been reported in the preparation of tetracarbonyl-[diphenyl-2-(prop-*cis*-1-enyl)phenylphosphine)molybdenum(o) whose structure has been confirmed by an X-ray analysis[36,37]. This isomerisation also occurs in the preparation of $Rh(\eta^6\text{-}C_6H_5BPh_3)$-$[\eta^2\text{-}PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]$[18]. We attempted to isomerise the ligand in the butenyl complex, $RhCl(CO)[PPh_2(CH_2CH_2CH{=}CH_2)]_2$, but only a mixture of compounds was isolated even after 88h of refluxing. The isomerisation is proposed to proceed via a π-allyl-hydride intermediate as has been suggested elsewhere[38].

Mechanism

A proposed mechanism for the hydrogenation of these complexes is given in Scheme 2. The factors affecting the deuterium distribution in the final products will depend on (a) the amount of alkene isomerisation (b) the Markownikov versus anti-Markownikov addition of Rh-H(D) to the ligand $PPh_2[(CH_2)_nCH=CH_2]$[39] (c) the degree of scrambling between H and D in transition states.

It has been shown that the rate of isomerisation is much slower than the hydrogenation reactions (see above). Both the butene and pentene complexes, $RhCl(CO)[PPh_2(CH_2CH_2CH=CH_2)]_2$ and $RhCl(CO)[PPh_2(CH_2CH_2CH_2CH=CH_2)]_2$, are hydrogenated at room temperature; whereas the isomerisation of the pentene complex only occurs at higher temperatures, and the isomerisation of the butene complex is only minimal even after prolonged refluxing. Therefore it is unlikely that isomerisation has much affect in determining the product distribution. However, once the alkyl intermediates 3 or 4 are formed, this could promote the isomerisation of the olefin particularly in the pentene case.

The factors influencing the addition of the Rh-H(D) to the ligand $PPh_2(CH_2CH_2CH=CH_2)$ will depend on the polarity of the Rh-H(D) bond and by the steric requirements of the ligand in forming the transition states 2, 3 or 4. Since all the complexes are essentially the same, the polarity of the Rh-H(D) should not change, and the addition should depend on the steric requirements of the ligand. Masters and coworkers have found that the most stable configuration for the intermediate in H(D) exchange with the phosphine complexes of platinum $Pt_2Cl_4L_2$, L = $P(C_3H_7)_3$ or $P(C_4H_9)_3$ involves a five membered ring system; and the stability of the intermediate follows the following ring size order, 5 > 6 > 4[34]. Using this argument, then the intermediate 4 would be preferred for the compounds $RhCl(CO)[PPh_2(CH_2CH_2CH_2CH=CH_2)]_2$, $RhCl(CO)[PPh_2(CH_2CH_2CH\overset{c}{=}CHCH_3)]_2$ and $RhCl(CO)[PPh_2(CH_2CH_2CH=CH_2)]_2$, and the intermediate 3 would be preferred for the compounds $RhCl(CO)[PPh_2(CH_2CH=CH_2)]_2$ and $RhCl(CO)[PPh_2(CH=CH_2)]_2$. We are unable to give any definitive answers to the proportion of intermediates 3 or 4 occurring in any particular case since we are unable to determine the degree of scrambling between H and D in the transition states; and our system is further complicated since we have two carbon sites for the initial addition of Rh-H(D) to the olefin.

References

1. M.A. Bennett and P.A. Longstaff, *J.Amer.Chem.Soc.*, 91(1969)6226.
2. G.E. Hartwell and P.W. Clark, *Chem.Commun.*, (1970)1115.
3. P.W. Clark and G.E. Hartwell, *Inorg.Chem.*, 9(1970)1948.
4. D.I. Hall and R.S. Nyholm, *Chem.Commun.*, (1970)488.
5. C. Nave and M.R. Truter, *Chem.Commun.*, (1971)1253.
6. M.A. Bennett and E.J. Hann, *J.Organometal.Chem.*, 29(1971)C15.
7. M.A. Bennett, S.J. Gruber, E.J. Hann and R.S. Nyholm, *J.Organometal. Chem.*, 29(1971)C12.
8. M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, *Chem. Commun.*, (1972)1011.
9. D.I. Hall and R.S. Nyholm, *J.Chem.Soc.Dalton Trans.*, (1972)804.
10. M.A. Bennett, R.N. Johnson and I.B. Tomkins, *J.Organometal.Chem.*, 54(1973)C48.
11. M. Orrico Visscher, J.C. Huffman and W.E. Streib, *Inorg.Chem.*, 13(1974)792.
12. J.L.S. Curtis and G.E. Hartwell, *J.Chem.Soc.Dalton Trans.*, (1974) 1898.
13. P.R Brookes, *J.Organometal.Chem.*, 42(1972)459.
14. P.R. Brookes, *J.Organometal.Chem.*, 43(1972)415.
15. P.W. Clark and G.E. Hartwell, *J.Organometal.Chem.*, 96(1975)451.
16. P.W. Clark and G.E. Hartwell, *J.Organometal.Chem.*, 97(1975)117.
17. R.R. Ryan, R. Schaeffer, P. Clark and G.E. Hartwell, *Inorg.Chem.*, 14(1975)3039.
18. P.W. Clark and G.E. Hartwell, *J.Organometal.Chem.*, 102(1975)387.
19. P.W. Clark, *J.Organometal.Chem.*, 110(1976)C13.
20. M.A. Bennett and P.W. Clark, *J.Organometal.Chem.*, 110(1976)367.
21. M.A. Bennett, R.N. Johnson and I.B. Tomkins, *J.Organometal.Chem.*, 118(1976)205.

22. R. Mason, G. Scollary, B. Moyle and K.I. Hardcastle, *J.Organometal. Chem.*, 113(1976)C49.

23. M.A. Bennett, E.J. Hann and R.N. Johnson, *J.Organometal.Chem.*, 124(1977)189.

24. M.A. Bennett and E.J. Hann, *J.Organometal.Chem.*, 124(1977)213.

25. P.W. Clark, *J.Organometal.Chem.*, submitted for publication.

26. P.W. Clark and A.J. Jones, *J.Organometal.Chem.*, 122(1976)C41.

27. K.D. Berlin and G.B. Butler, *J.Org.Chem.*, 26(1961)2537.

28. L. Horner, P. Beck and H. Hoffman, *Chem.Ber.*, 92(1959)2068.

29. P.W. Clark, J.L.S. Curtis, P.E. Garrou and G.E. Hartwell, *Can.J.Chem.*, 52(1974)1714.

30. J.A. McCleverty and G. Wilkinson, *Inorg.Syn.*, 8(1966)211.

31. J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, *J.Chem.Soc.*, (1966)1711.

32. See for example J.G. Atkinson and M.O. Luke, *Can.J.Chem.*, 48(1970) 3580; J.F. Biellman and M.J. Jung, *J.Amer.Chem.Soc.*, 90(1968) 1673; A.S. Hussey and Y. Takeuchi, *J.Amer.Chem.Soc.*, 91(1969) 672; A.J. Odell, J.B. Richardson and W.R. Roper, *J.Catal.*, 8 (1967)393.

33. J.W. Byrne, H.U. Blaser and J.A. Osborn, *J.Amer.Chem.Soc.*, 97 (1975)3871.

34. A.A. Kiffen, C. Masters and L. Raynand, *J.C.S.Dalton*, (1975)853.

35. A.J. Deeming and B.L. Shaw, *J.Chem.Soc. A*, (1970)2705.

36. L.V. Interrante, M.A. Bennett and R.S. Nyholm, *Inorg.Chem.*, 5(1966)2212.

37. H. Luth, M.R. Truter and A. Robson, *J.Chem.Soc. A*, (1969)28.

38. J.F. Harrod and A.J. Chalk, *J.Amer.Chem.Soc.*, 88(1966)3491.

39. See for example D. Evans, J.A. Osborn and G. Wilkinson, *J.Chem.Soc.A.*, (1968)3133.