Preparation, Isomerization, and Reactions of Hydride Complexes of Ruthenium(II)

Joanne M. Bray and Roger J. Mawby *
Department of Chemistry, The University of York, York YO1 5DD

Hydride complexes $[Ru(CO)_2XHL_2]$ (X = H or Cl, L = PMe_2Ph or $AsMe_2Ph$) and their deuteride analogues have been prepared. The complex $[Ru(CO)_2H_2(AsMe_2Ph)_2]$ exists in solution as an equilibrium mixture of isomers. The dideuteride $[Ru(CO)_2D_2(PMe_2Ph)_2]$ exchanges with H_2 in solution: no $[Ru(CO)_2DH(PMe_2Ph)_2]$ is formed, suggesting that exchange occurs *via* $[Ru(CO)_2(PMe_2Ph)_2]$. Exchange also occurs with ethene and propene: here $[Ru(CO)_2DH(PMe_2Ph)_2]$ *is* observed. Ethene is hydrogenated by $[Ru(CO)_2H_2L_2]$, with formation of ethane and complexes $[Ru(CO)_2(C_2H_4)L_2]$, which are reconverted to $[Ru(CO)_2H_2L_2]$ by H_2. The terminal alkenes 1-hexene and 3-phenylpropene are isomerized by $[Ru(CO)_2H_2L_2]$: for L = $AsMe_2Ph$, a little hydrogenation of 3-phenylpropene also occurs.

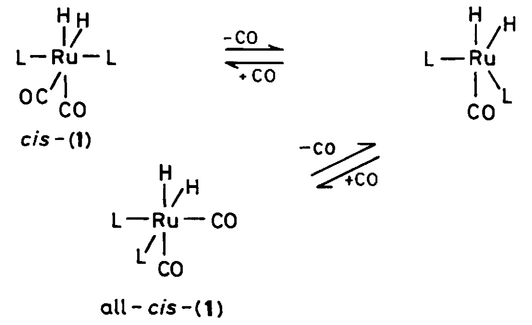
We have recently described a process in which complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ (R,R′ = alkyl or aryl) break down in $CHCl_3$ solution to yield ketones RCOR′.[1] In the case of diaryl complexes $[Ru(CO)_2(C_6H_4X\text{-}4)(C_6H_4Y\text{-}4)(PMe_2Ph)_2]$ (X = Y = Cl; X = Y = Me; X = Cl, Y = Me), *ortho*-metallated products $[Ru(CO)\{C_6H_3XC(O)C_6H_4Y\}Cl(PMe_2Ph)_2]$ were also obtained, and we proposed that these were formed by oxidative addition of the ketone to ruthenium(0), giving hydride complexes $[Ru(CO)\{C_6H_3XC(O)C_6H_4Y\}H(PMe_2Ph)_2]$ which then reacted with the $CHCl_3$. In $CDCl_3$ solution, the $CDHCl_2$ formed in this reaction was detected by n.m.r. spectroscopy.[2]

We were unable to confirm the presence of intermediate hydride complexes in the reaction mixtures, and this prompted us to attempt the preparation of hydride complexes of the general type $[Ru(CO)_2XH(PMe_2Ph)_2]$ (X = alkyl, aryl, halogen, or hydrogen) so that we could study their properties. We were also interested in the possibility of generating the dialkyl complexes $[Ru(CO)_2(CH_2CH_2R)_2(PMe_2Ph)_2]$ from $[Ru(CO)_2H_2(PMe_2Ph)_2]$ and alkenes, $RCH{=}CH_2$, and hence establishing a route from the alkenes to ketones, $(RCH_2CH_2)_2CO$, and this paper includes preliminary studies of the reactions of $[Ru(CO)_2H_2(PMe_2Ph)_2]$ with alkenes under mild conditions. The study was extended to include $[Ru(CO)_2H_2(AsMe_2Ph)_2]$ and some related complexes.

Results and Discussion

Preparation and Characterization of Complexes.—Details of the ^1H and ^2H n.m.r. spectra of all new complexes, together with their formulae, are given in Table 1. Infrared and $^{31}P\text{-}\{^1H\}$ n.m.r. data appear in Table 2, and details of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of selected complexes in Table 3.

Treatment of an ethanol suspension of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$[3] with an excess of $NaBH_4$ yielded an oil which was shown by n.m.r. and i.r. spectroscopy to consist of a single compound $[Ru(CO)_2H_2(PMe_2Ph)_2]$ (**1a**), of structure *cis*-(**1**) (see Scheme, where L = PMe_2Ph). A ^1H n.m.r. spectrum of (**1a**), recorded at 400 MHz, revealed a broadening and lowering of the central component of the 'triplet' resonance for the PMe_2Ph methyl protons, indicating that this is not truly a limiting case of 'virtual coupling'.[4,5] There was also evidence of long-range coupling between methyl protons and hydride ligands, most clearly seen as a small triplet splitting of each of the outer peaks in the methyl proton triplet, and confirmed by decoupling experiments. In the ^{13}C n.m.r. spectrum, the size of $|^2J(P\text{–}C)|$ for the carbonyl ligands (9.0 Hz) clearly indicated that the carbonyl ligands were *cis* to the PMe_2Ph ligands[6] [a figure of *ca.* 100 Hz is typical for ruthenium(II) complexes containing mutually *trans* CO and PMe_2Ph ligands[7]]. The strong i.r. bands at 2 010 and 1 965 cm^{-1} were assigned to C–O stretching modes, and the weaker band at 1 920 cm^{-1} to a Ru–H mode. Failure to observe a second such band could be due to its being obscured by a C–O band or to near-degeneracy of symmetric and antisymmetric Ru–H modes. Cotton *et al.*[8] failed to observe Ru–H bands for $[Ru(CO)_2H_2(PPh_3)_2]$ and $[Ru(CO)_2H_2(PEt_3)_2]$, but L'Eplattenier and Calderazzo[9] claimed to have observed Ru–H bands at 1 878 and 1 823 cm^{-1} for $[Ru(CO)_2H_2(PPh_3)_2]$ in a halocarbon mull.



Scheme. (**1a**), L = PMe_2Ph; (**1b**), L = $AsMe_2Ph$

Treatment of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $NaBD_4$ in EtOD yielded $[Ru(CO)_2D_2(PMe_2Ph)_2]$ (**2a**). The observed value for $|^2J(P\text{–}D)|$ (3.9 Hz) agreed with the figure of 25.9 Hz for $|^2J(P\text{–}H)|$ in (**1a**) (γ_D/γ_H = 0.153). The C–O stretching bands for (**2a**) were at significantly lower energy than those for (**1a**), presumably because strong mixing of C–O and Ru–H modes increases the energy of the former for (**1a**), whereas one would expect less mixing of the more widely separated C–O and Ru–D modes for (**2a**).[10] We were unable to identify the Ru–D bands for (**2a**) with certainty.

The reaction between *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$[11] and $NaBH_4$ yielded a product (**1b**) which was an oil at room temperature. The ^1H and ^{13}C n.m.r. spectra of (**1b**) showed it to exist in C_6D_6 solution as a mixture of isomers of structures *cis*-(**1**) and all-*cis*-(**1**) (see Scheme, where L = $AsMe_2Ph$). Decoupling experiments confirmed the coupling between the inequivalent hydride ligands in all-*cis*-(**1b**). As in the case of (**1a**), both isomers of (**1b**) exhibited slight long-range coupling

Table 1. Proton and ^2H n.m.r. spectra of complexes[a]

Complex	Formula	δ/p.p.m.	Assignment	Coupling constant (Hz)	Assignment
(1a)	$[Ru(CO)_2H_2(PMe_2Ph)_2]$	1.58 (t, 12)[b]	PMe_2Ph	6.7	$\|^2J(P-H) + {}^4J(P-H)\|$
		−7.01 (t, 2)[b]	RuH	25.9	$\|^2J(P-H)\|$
cis-**(1b)**	$[Ru(CO)_2H_2(AsMe_2Ph)_2]$	1.45 (s, 12)	$AsMe_2Ph$		
		−7.29 (s, 2)	RuH		
all-*cis*-**(1b)**	$[Ru(CO)_2H_2(AsMe_2Ph)_2]$	1.19 (s, 3)	$AsMe_2Ph$		
		1.15 (s, 6)[c]	$AsMe_2Ph$		
		1.12 (s, 3)	$AsMe_2Ph$		
		−6.74 (d, 1)	RuH	5.9	$\|^2J(H-H)\|$
		−8.56 (d, 1)	RuH	5.9	$\|^2J(H-H)\|$
(2a)	$[Ru(CO)_2D_2(PMe_2Ph)_2]$	−7.01 (t)	RuD	3.9	$\|^2J(P-D)\|$
cis-**(2b)**	$[Ru(CO)_2D_2(AsMe_2Ph)_2]$	−7.29 (s)	RuD		
all-*cis*-**(2b)**	$[Ru(CO)_2D_2(AsMe_2Ph)_2]$	−6.74 (s, 1)[d]	RuD		
		−8.56 (s, 1)[d]	RuD		
(3a)	$[Ru(CO)_2ClH(PMe_2Ph)_2]$	1.72 (t, 6)	PMe_2Ph	7.5	$\|^2J(P-H) + {}^4J(P-H)\|$
		1.68 (t, 6)	PMe_2Ph	7.5	$\|^2J(P-H) + {}^4J(P-H)\|$
		−5.25 (t, 1)	RuH	23.1	$\|^2J(P-H)\|$
(3b)	$[Ru(CO)_2ClH(AsMe_2Ph)_2]$	1.56 (s, 6)	$AsMe_2Ph$		
		1.55 (s, 6)	$AsMe_2Ph$		
		−5.04 (s, 1)	RuH		
(4a)	$[Ru(CO)_2ClD(PMe_2Ph)_2]$	−5.25 (t)	RuD	3.5	$\|^2J(P-D)\|$
(4b)	$[Ru(CO)_2ClD(AsMe_2Ph)_2]$	−5.04 (s)	RuD		
(5a)	$[Ru(CO)ClH(PMe_2Ph)_3]$	1.70 (t, 12)[c]	PMe_2Ph	6.6	$\|^2J(P-H) + {}^4J(P-H)\|$
		1.09 (d, 6)	PMe_2Ph	7.0	$\|^2J(P-H)\|$
		−6.56 (dt, 1)	RuH	114.3, 26.6	$\|^2J(P-H)\|$, $\|^2J(P-H)\|$
(6a)	$[Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$	1.33 (t, 12)	PMe_2Ph	6.2	$\|^2J(P-H) + {}^4J(P-H)\|$
		1.35 (t, 4)	C_2H_4	6.4	$\|^3J(P-H)\|$
(6b)	$[Ru(CO)_2(C_2H_4)(AsMe_2Ph)_2]$	1.10 (s, 12)	$AsMe_2Ph$		
		1.42 (s, 4)	C_2H_4		

[a] In C_6D_6 solution. Phenyl proton resonances have been omitted. Chemical shifts for methyl proton resonances for deuteride complexes were the same as for the corresponding hydride complexes. ^2H Spectra are proton-decoupled. [b] A spectrum recorded at 400 MHz detected a small long-range coupling: $|^4J(H-H)| = 0.5$ Hz. [c] Two superimposed resonances. [d] Value of $|^2J(D-D)|$ too small to give a detectable splitting.

between methyl protons and hydride ligands: although this was not enough to cause detectable splittings, irradiation in the methyl proton region significantly sharpened the hydride resonances. The i.r. spectrum of **(1b)** was too complicated for detailed interpretation.

Even at 313 K, interconversion of the two isomers of **(1b)** was not fast enough to cause significant broadening of the hydride resonances. In the reaction with ethene described below, the ratio of the concentrations of the two isomers remained constant throughout, but in the much more rapid reaction with $MeO_2CC{\equiv}CCO_2Me$ (currently under study) it is clear that *cis*-**(1b)** reacts preferentially with the alkyne. Addition of a small quantity of alkyne causes an immediate decrease in the concentration of *cis*-**(1b)**, and then the equilibrium between *cis*-**(1b)** and all-*cis*-**(1b)** is re-established. {If, like **(1b)**, **(1a)** exists in solution as a mixture of *cis* and all-*cis* isomers, the equilibrium must be heavily in favour of the *cis* version. We attempted the preparation of **(1a)** from all-*cis*- (as opposed to *cis*-) $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$,[3] but again obtained only the *cis* isomer.}

Table 2. Infrared[a] and ^{31}P n.m.r.[b] spectra of complexes

Complex	I.r. bands/(cm^{-1})	δ/p.p.m.
(1a)	2 010, 1 965, 1 920	12.1
(1b)	2 040, 2 010, 1 960, 1 920	
(2a)	2 000, 1 940	12.3[c]
(2b)	2 010, 1 945	
(3a)	2 045, 1 965	4.5
(3b)	2 045, 1 965	
(4a)	2 040, 1 965	4.5[d]
(4b)	2 040, 1 960	
(5a)	1 925, 1 865[e]	3.0,[f] −10.8[g]
(6a)	[h]	12.5[i]

[a] In CH_2Cl_2 solution except where stated otherwise. Only bands in the C–O and Ru–H stretching region are listed. [b] In C_6D_6 solution. Spectra are proton-decoupled, and resonances are singlets except where stated otherwise. [c] 1:2:3:2:1 quintet; $|^2J(P-D)| = 3.9$ Hz. [d] 1:1:1 triplet; $|^2J(P-D)| = 3.5$ Hz. [e] In C_6H_6 solution. [f] Doublet; $|^2J(P-P)| = 20.5$ Hz. [g] Triplet; $|^2J(P-P)| = 20.5$ Hz. [h] Spectrum not recorded. [i] Broad singlet.

Reaction of *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ with $NaBD_4$ gave $[Ru(CO)_2D_2(AsMe_2Ph)_2]$ **(2b)**, again as a mixture of *cis* and all-*cis* isomers. In the ^2H spectrum, the doublet splittings expected for all-*cis*-**(2b)** were too small to detect [since $|^2J(H-H)|$ for **(1b)** is 5.9 Hz, predicted $|^2J(D-D)|$ for **(2b)** is 0.14 Hz]. Evidently the C–O stretching bands of the two isomers were superimposed, since only two bands were observed in the i.r. spectrum.

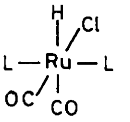
By carrying out the reaction of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with a smaller quantity of $NaBH_4$ and for a shorter period, it was possible to obtain the monohydride complex $[Ru(CO)_2ClH(PMe_2Ph)_2]$ **(3a)**. This was isolated as a solid and fully characterized. From n.m.r. spectra, **(3a)** was assigned structure (3), where L = PMe_2Ph. An Ru–H band was not observed in the i.r. spectrum of **(3a)**: presumably it was masked by one of the C–O bands. James *et al.*[12] were similarly unable to detect the Ru–H band for $[Ru(CO)_2ClH(PPh_3)_2]$ in CH_2Cl_2 solution, but Gill *et al.*[6] did observe a shoulder on the lower energy C–O band in the spectrum of $[Ru(CO)_2ClH\{PPr^n_2(Bu^t)\}_2]$.[6]

The method used to obtain **(3a)** was also successfully applied to the preparation of $[Ru(CO)_2ClH(AsMe_2Ph)_2]$ **(3b)**. This too was a solid, and was fully characterized. Unlike **(1b)**, it existed in solution as a single isomer, probably [given the spectroscopic similarities with **(3a)**] of structure (3), where L = $AsMe_2Ph$.

Table 3. Carbon-13 n.m.r. spectra of complexes[a]

Complex	δ/p.p.m.	Assignment	Coupling constant (Hz)	Assignment
(1a)	202.8 (t)	CO	8.9	$|{}^2J(\mathrm{P{-}C})|$
	25.3 (t)	PMe_2Ph	33.7	$|{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$
cis-**(1b)**[b]	19.6 (s)	$AsMe_2Ph$		
all-*cis*-**(1b)**[b]	19.0 (s)	$AsMe_2Ph$		
	17.9 (s)	$AsMe_2Ph$		
	17.2 (s)	$AsMe_2Ph$		
	16.7 (s)	$AsMe_2Ph$		
(3a)	199.5 (t)	CO	11.9	$|{}^2J(\mathrm{P{-}C})|$
	193.7 (t)	CO	8.2	$|{}^2J(\mathrm{P{-}C})|$
	18.2 (t)	PMe_2Ph	34.8	$|{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$
	17.3 (t)	PMe_2Ph	32.0	$|{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$
(5a)	203.7 (dt)	CO	13.5, 9.7	$|{}^2J(\mathrm{P{-}C})|, |{}^2J(\mathrm{P{-}C})|$
	21.1 (dt)	PMe_2Ph	3.1, 33.5	$|{}^3J(\mathrm{P{-}C})|, |{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$
	17.6 (dt)	PMe_2Ph	2.7, 31.3	$|{}^3J(\mathrm{P{-}C})|, |{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$
	15.3 (d)	PMe_2Ph	20.3	$|{}^1J(\mathrm{P{-}C})|$
(6a)	210.4 (t)	CO	14.2	$|{}^2J(\mathrm{P{-}C})|$
	26.2 (t)	C_2H_4	2.7	$|{}^2J(\mathrm{P{-}C})|$
	18.2 (t)	PMe_2Ph	30.2	$|{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})|$

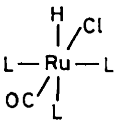
[a] In C_6D_6 solution. Spectra are proton-decoupled, and phenyl carbon resonances have been omitted. [b] Carbonyl resonances not identified (accumulation time limited by poor stability of complex).



(3)

(3a), L = PMe_2Ph

(3b), L = $AsMe_2Ph$



(5)

(5a), L = PMe_2Ph

Corresponding deuteride complexes $[Ru(CO)_2ClD(PMe_2Ph)_2]$ **(4a)** and $[Ru(CO)_2ClD(AsMe_2Ph)_2]$ **(4b)** were also synthesized.

Treatment of $[Ru(CO)_2PhCl(PMe_2Ph)_2]$[13] with $NaBH_4$ in ethanol yielded not the desired $[Ru(CO)_2PhH(PMe_2Ph)_2]$ but complex **(1a)**. The experiment was repeated, and the solvent and all volatile materials were removed under reduced pressure and analysed by gas chromatography, confirming that benzene had been formed in the reaction. In order to show that this came from the phenyl rather than from a PMe_2Ph ligand, the experiment was repeated using $[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$.[14] Complex **(1a)** was again formed, together with PhOMe: *no* benzene was detected. Complex **(1a)** was also obtained when $[Ru(CO)_2MeCl(PMe_2Ph)_2]$[13] was treated with $NaBH_4$.

Reactions of the Complexes.—All the complexes reacted quickly in benzene solution with CCl_4 or $CHCl_3$ to give *cis*-$[Ru(CO)_2Cl_2L_2]$ (L = PMe_2Ph or $AsMe_2Ph$), so our failure to observe the proposed hydride intermediates in the conversion of complexes $[Ru(CO)_2(C_6H_4X\text{-}4)(C_6H_4Y\text{-}4)(PMe_2Ph)_2]$ into $[Ru(CO)\{C_6H_3XC(O)C_6H_4Y\}Cl(PMe_2Ph)_2]$ in $CHCl_3$ solution[2] was not surprising. The all-*cis* isomer of $[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ was *not* observed in the reaction of **(1b)** with $CHCl_3$. Reactions of the complexes with CH_2Cl_2 were shown by n.m.r. spectroscopy to be considerably slower, making it possible to use this solvent to obtain i.r. spectra. In the reactions of complexes **(1a)**, **(1b)**, **(2a)**, and **(2b)** with CH_2Cl_2, i.r. bands attributable to **(3a)**, **(3b)**, **(4a)**, and **(4b)**, respectively, were observed during the conversion into *cis*-$[Ru(CO)_2Cl_2L_2]$ (L = PMe_2Ph or $AsMe_2Ph$).

Complex **(1a)** failed to react with either CO or PMe_2Ph to give a formyl complex $[Ru(CO)(CHO)HL(PMe_2Ph)_2]$ (L = CO or PMe_2Ph), nor did it undergo carbonyl substitution by PMe_2Ph to give $[Ru(CO)H_2(PMe_2Ph)_3]$. In this respect it mirrored the complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$ (R = alkyl or aryl), whose inability to undergo substitution of CO by PMe_2Ph we have attributed to the unwillingness of the metal to accept a fifth strongly σ-donating ligand.[15] In contrast, **(3a)**, which contains only three such ligands, reacted with PMe_2Ph to yield $[Ru(CO)ClH(PMe_2Ph)_3]$ **(5a)**. N.m.r. spectra of **(5a)** established that it possessed structure **(5)**, where L = PMe_2Ph, so that the reaction involved substitution of the carbonyl ligand *trans* to hydride. Complex **(5a)** was also obtained by treating $[Ru(CO)Cl_2(PMe_2Ph)_3]$[3] with $NaBH_4$: again, the reluctance of the metal to accept a fifth σ-donor ligand was demonstrated by the non-formation of $[Ru(CO)H_2(PMe_2Ph)_3]$ even when a large excess of $NaBH_4$ was used.

Complex **(2a)**, when dissolved in C_6H_6, did not undergo exchange of deuterium with the solvent. When, however, the solution was treated with H_2, the ^{31}P n.m.r. spectrum changed slowly from the quintet pattern for **(2a)** to the singlet resonance characteristic of **(1a)**. The rate of hydrogen/deuterium exchange was markedly increased by u.v. irradiation of the solution. At no stage was the characteristic 1:1:1 triplet resonance for $[Ru(CO)_2DH(PMe_2Ph)_2]$ (see below) observed. Thus it seemed more likely that D_2 was eliminated {giving $[Ru(CO)_2(PMe_2Ph)_2]$} before H_2 was added than that oxidative addition of H_2 to give a ruthenium(IV) species preceded reductive elimination.

Complex **(1a)** reacted slowly with C_2H_4 (1 atm) at room temperature in C_6D_6 to give a product **(6a)**. Spectroscopic studies showed that the reaction was accompanied by ethane formation and that **(6a)** contained two equivalent PMe_2Ph ligands and also carbonyl ligands. Resonances for co-ordinated ethene were observed in the n.m.r. spectra: an INEPT experiment confirmed that the resonance in the ^{13}C spectrum was due to carbon atoms bearing two hydrogens. We were unable to isolate **(6a)**, and it decomposed quickly in solution when the free C_2H_4 was swept from the solution with N_2. When the solution was treated briefly with H_2 rather than N_2, the immediate disappearance of the resonance due to free C_2H_4 in the ^1H n.m.r. spectrum was followed by conversion of **(6a)** into

(**1a**) and the reappearance of the free ethene resonance. Thus it seemed reasonable to assume that (**6a**) was $[Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$, analogous to the complex $[Ru(CO)_2(C_2H_4)(PPh_3)_2]$ obtained by treating $[Ru(CO)_2(PPh_3)_3]$ with C_2H_4.[16]

The only feature casting doubt on this simple formulation of (**6a**) was the unusually broad resonance in the ^{31}P spectrum of the complex. In order to discover whether the shape of this resonance was temperature-dependent, we repeated the reaction between (**1a**) and C_2H_4 in PhCl solution, and then examined the variation in the spectrum of (**6a**) between 248 and 313 K. At both extremes a sharp singlet was observed, but between these temperatures the resonance broadened markedly, with signs of fine structure at around 300 K. In comparison, the resonance for (**1a**) in this solvent remained as a sharp singlet over the whole temperature range. Whatever the explanation of the temperature dependence of the ^{31}P spectrum of (**6a**), it is not the result of rapid and reversible ethene dissociation, because the ^{1}H resonances of free and co-ordinated ethene in the solution remained separate and sharp up to 313 K.

Complex (**2a**) reacted similarly with C_2H_4, but here hydrogenation of C_2H_4 and formation of (**6a**) were accompanied by fairly rapid exchange of deuterium and hydrogen between (**2a**) and C_2H_4. In the ^{31}P n.m.r. spectrum, the quintet at δ 12.3 for (**2a**) decreased in area, with initial growth and subsequent decay of a 1:1:1 triplet at δ 12.2 attributed to $[Ru(CO)_2DH(PMe_2Ph)_2]$ and the steady growth of the singlet at δ 12.1 characteristic of (**1a**).

Complex (**1b**) reacted more rapidly with C_2H_4 than did (**1a**). The ^{1}H n.m.r. spectrum of the reaction mixture indicated the presence of more than one product, but resonances attributable to a complex (**6b**), analogous to (**6a**), were observed. Again these resonances disappeared on purging the solution with H_2 or N_2, and the former caused the reappearance of resonances for (**1b**).

Complex (**1a**) did not appear to hydrogenate propene, but ^{31}P n.m.r. studies of a solution of (**2a**) containing propene again indicated that exchange of deuterium and hydrogen was occurring, with the formation of $[Ru(CO)_2DH(PMe_2Ph)_2]$ and then (**1a**). Both (**1a**) and (**1b**) catalysed the isomerization of 1-hexene to *trans*-2-hexene, without significant hydrogenation to hexane; similarly 3-phenylpropene was isomerized to 1-phenylpropene, but in the case of (**1b**) a small amount of the hydrogenation product 1-phenylpropane was also obtained. The presence of two hydride ligands appears to be important: any isomerization of 1-hexene and 3-phenylpropene by complex (**3a**) was very much slower than in the case of (**1a**). Isomerization of hexene by $[Ru(CO)_2H_2(PPh_3)_2]$ has been reported by Porta *et al.*[17]

Mechanisms of Formation and Reactions of the Complexes.— The complex *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ undergoes replacement of chloride ligands by bromide or iodide only under forcing conditions,[4] yet it readily reacts with LiR (R = alkyl or aryl)[15] and with $NaBH_4$ at room temperature. As we have suggested for the reactions with LiR,[15] the initial attack may be on a carbonyl ligand, yielding in this instance a formyl complex $[Ru(CO)(CHO)Cl_2(PMe_2Ph)_2]^-$ which then loses a chloride ligand and rearranges to (**3a**). Conversion of (**3a**) into (**1a**) can then occur by a similar sequence.

Formation of RH in the reactions of $[Ru(CO)_2RCl(PMe_2Ph)_2]$ (R = Ph, C_6H_4OMe-4, or Me) with $NaBH_4$ may involve reductive elimination from intermediates $[Ru(CO)_2RH(PMe_2Ph)_2]$. Although we obtained no evidence of the presence of such species, mononuclear ruthenium(II) complexes containing hydride and alkyl or aryl ligands have been reported by Chatt and Hayter,[18] and the complex $[RuMeH(PMe_3)_4]$ has been synthesized by Statler *et al.*[19] It is, however, still necessary to explain how (**1a**) is formed in these reactions. Simple H_2 addition to $[Ru(CO)_2(PMe_2Ph)_2]$ formed in the reductive elimination is an unsatisfactory explanation, since (**1a**) was formed in good yield however carefully the ethanol used as solvent was dried (to remove any water which could react with the $NaBH_4$ to produce the necessary H_2). A possible alternative would be that $[Ru(CO)_2(PMe_2Ph)_2]$ reacted with the solvent to yield $[Ru(CO)_2H(OEt)(PMe_2Ph)_2]$, and that this underwent β-hydrogen transfer to give (**1a**) and ethanal. There was g.c.–m.s. evidence for the presence of ethanal in the volatile reaction products.

The simplest mechanism for the reactions of (**1a**), (**1b**), (**2a**), and (**2b**) with alkenes would involve initial dissociation of a carbonyl ligand (assisted by the *trans*-labilizing effect of hydride[20]) to create a vacant co-ordination site for the alkene. This agrees with our finding that isomerization of hexene by (**1a**) was inhibited by CO but restored to its normal rate by purging the solution with N_2. A possible reaction sequence for (**1a**) and ethene is shown below, and it can be seen that similar sequences are compatible with the alkene isomerization and hydrogen/deuterium exchange results.

$$[Ru(CO)_2H_2(PMe_2Ph)_2] \rightleftharpoons [Ru(CO)H_2(PMe_2Ph)_2] + CO$$

$$[Ru(CO)H_2(PMe_2Ph)_2] + C_2H_4 \rightleftharpoons [Ru(CO)(C_2H_4)H_2(PMe_2Ph)_2]$$

$$[Ru(CO)(C_2H_4)H_2(PMe_2Ph)_2] \rightleftharpoons [Ru(CO)(C_2H_5)H(PMe_2Ph)_2]$$

$$[Ru(CO)(C_2H_5)H(PMe_2Ph)_2] + CO \rightleftharpoons [Ru(CO)_2(C_2H_5)H(PMe_2Ph)_2]$$

$$[Ru(CO)_2(C_2H_5)H(PMe_2Ph)_2] \longrightarrow [Ru(CO)_2(PMe_2Ph)_2] + C_2H_6$$

$$[Ru(CO)_2(PMe_2Ph)_2] + C_2H_4 \rightleftharpoons [Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$$

$$[Ru(CO)_2(PMe_2Ph)_2] + H_2 \rightleftharpoons [Ru(CO)_2H_2(PMe_2Ph)_2]$$

As the Scheme shows, carbonyl dissociation could also provide a pathway for the interconversion of *cis* and all-*cis* isomers of (**1b**) {as we have previously suggested for the rearrangement of all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ to its *cis* isomer[3]}.

Clearly there are other possible mechanisms. For example, a vacant site for alkene co-ordination could be generated by combination of hydride and carbonyl ligands to give a formyl group, and this would still leave a hydride ligand on the metal to combine with the alkene. Interconversion of *cis* and all-*cis* isomers of (**1b**) could also occur *via* five-co-ordinate $[Ru(CO)(CHO)H(PMe_2Ph)_2]$ or simply by hydride tunnelling, as has been suggested by Meakin *et al.*[21] in the case of complexes $[RuH_2L_4]$ (L = ligand containing a phosphorus donor atom).

Experimental

Complexes were prepared under an atmosphere of nitrogen, using dry, oxygen-free solvents. Details of the syntheses of the starting materials, *cis*- and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$,[3] *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$,[11] $[Ru(CO)_2(C_6H_4X$-$4)Cl(PMe_2Ph)_2]$ (X = H[13] or OMe[14]), $[Ru(CO)_2MeCl(PMe_2Ph)_2]$,[13] and $[Ru(CO)Cl_2(PMe_2Ph)_3]$,[3] have been given in earlier papers. Alkene isomerization and hydrogenation reactions and hydrogen/deuterium exchange reactions were carried out at ambient temperature and 1 atm pressure (*ca.* 10^5 Pa) in n.m.r. tubes fitted with gas-tight screw caps. Most n.m.r. spectra were recorded on a JEOL FX90Q spectrometer; a few ^{1}H spectra were run on a Bruker WH400 instrument. Infrared spectra were recorded on a Perkin-Elmer PE257 spectrometer.

Preparation of [Ru(CO)$_2$H$_2$(PMe$_2$Ph)$_2$] (**1a**).—A suspension of *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] (0.50 g) in ethanol (50 cm^3) was stirred with NaBH$_4$ (0.32 g) for 16 h. The solvent was removed under reduced pressure and the residue extracted into benzene. Removal of the benzene under reduced pressure left an oil which solidified at low temperatures but remelted on warming to room temperature. Complex (**1a**) was also obtained when all-*cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] was used in place of the *cis* isomer, and (**1b**) was synthesized from *cis*-[Ru(CO)$_2$Cl$_2$(AsMe$_2$Ph)$_2$] by the same technique. The corresponding deuteride complexes (**2a**) and (**2b**) were obtained using NaBD$_4$ in place of NaBH$_4$ and with EtOD as the solvent.

Preparation of [Ru(CO)$_2$ClH(PMe$_2$Ph)$_2$] (**3a**).—A suspension of *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] (0.50 g) in ethanol (15 cm^3) was stirred with NaBH$_4$ (0.16 g) for 0.1 h. The solution was then filtered to remove unreacted starting material, and the filtrate evaporated to dryness under reduced pressure. The product was purified by extraction into benzene: removal of the solvent under reduced pressure left white crystals (Found: C, 46.10; H, 5.05. Calc. for C$_{18}$H$_{23}$ClO$_2$P$_2$Ru: C, 46.00; H, 4.95%). Complex (**3b**) was prepared in the same way (Found: C, 38.95; H, 4.55. Calc. for C$_{18}$H$_{23}$As$_2$ClO$_2$Ru: C, 38.75; H, 4.15%). Complex (**4a**) was prepared using NaBD$_4$ and EtOD in place of NaBH$_4$ and EtOH (Found: C, 45.75; H + D, 5.05. Calc. for C$_{18}$H$_{22}$ClDO$_2$P$_2$Ru: C, 45.90; H + D, 5.15%), as was (**4b**).

Attempt to prepare [Ru(CO)$_2$PhH(PMe$_2$Ph)$_2$].—Treatment of [Ru(CO)$_2$PhCl(PMe$_2$Ph)$_2$] with NaBH$_4$, using the conditions described for the preparation of complex (**1a**), simply yielded (**1a**). An i.r. study of the reaction revealed that the only new bands appearing in the C–O and Ru–H stretching region were those for (**1a**). Similar results were obtained using [Ru(CO)$_2$(C$_6$H$_4$OMe-4)Cl(PMe$_2$Ph)$_2$] or [Ru(CO)$_2$MeCl(PMe$_2$Ph$_2$] in place of the phenyl complex.

Preparation of [Ru(CO)ClH(PMe$_2$Ph)$_3$] (**5a**).—The complex [Ru(CO)Cl$_2$(PMe$_2$Ph)$_3$] (0.20 g) and NaBH$_4$ (0.015 g) were stirred in ethanol (20 cm^3) for 24 h. The solvent was then removed under reduced pressure, and the product was extracted from the residue with benzene. Removal of the benzene under reduced pressure left white crystals, which were washed with light petroleum (Found: C, 51.85; H, 5.95. Calc. for C$_{25}$H$_{34}$ClOP$_3$Ru: C, 51.75; H, 5.90%). Complex (**5a**) was also obtained from the reaction of (**3a**) (0.050 g) with PMe$_2$Ph (0.015 g) in C$_6$D$_6$ (0.5 cm^3).

Preparation of [Ru(CO)$_2$(C$_2$H$_4$)(PMe$_2$Ph)$_2$] (**6a**).—A solution of (**1a**) (0.050 g) in C$_6$D$_6$ (0.5 cm^3) was saturated with ethene. The reaction was monitored by n.m.r. spectroscopy, and further ethene was added at intervals. Conversion into (**6a**) was essentially complete after 7 d. Attempts to remove the solvent or to expel excess ethene from the solution with N$_2$ caused decomposition. The same procedure was used to convert (**1b**) into (**6b**), with a reaction time of 19 h.

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