

Reactions of Hydride Complexes of Ruthenium(II) with Alkynes

Joanne M. Bray and Roger J. Mawby*

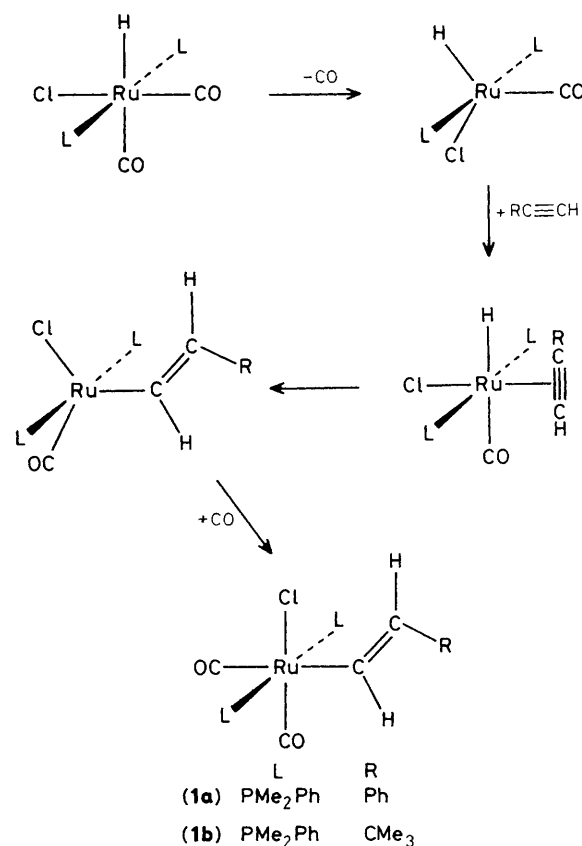
Department of Chemistry, University of York, York YO1 5DD

The complex $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ reacts with alkynes $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{H}$, $\text{R}' = \text{Ph}$ or CMe_3 ; $\text{R} = \text{R}' = \text{CO}_2\text{Me}$) to yield vinyl complexes $[\text{Ru}(\text{CO})_2(\text{CR}=\text{CHR}')\text{Cl}(\text{PMe}_2\text{Ph})_2]$. Addition of $\text{Ru}-\text{H}$ across the alkyne triple bond is *cis* for $\text{HC}\equiv\text{CPh}$ and $\text{HC}\equiv\text{CCMe}_3$, but may be *trans* for $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$. The dihydride $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ hydrogenates alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$ or CMe_3) to $\text{H}_2\text{C}=\text{CHR}$ and $\text{PhC}\equiv\text{CPh}$ to *cis*- $\text{PhCH}=\text{CHPh}$, with the accompanying formation of alkynyl complexes $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CR})\text{H}(\text{PMe}_2\text{Ph})_2]$ and the alkyne complex $[\text{Ru}(\text{CO})_2(\text{PhC}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$ respectively. The reaction sequence is believed to involve rate-determining formation of vinyl hydride complexes by *cis* addition of $\text{Ru}-\text{H}$ to the alkyne, followed by rapid alkene elimination and reaction of $[\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ with a second molecule of alkyne. With $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$, the complexes $[\text{Ru}(\text{CO})_2\text{H}_2\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or AsMe_2Ph) form long-lived vinyl hydride complexes $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{HL}_2]$ which exist in solution as mixtures of conformers.

Recently we described the reactions of complexes $[\text{Ru}(\text{CO})_2\text{H}_2\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or AsMe_2Ph) with ethene and some substituted alkenes.¹ We found that these complexes hydrogenated ethene and isomerized terminal alkenes, and from these observations and the results of deuterium-labelling experiments it appeared that both hydrogenation and isomerization occurred *via* intermediate complexes $[\text{Ru}(\text{CO})_2\text{R}(\text{H})\text{L}_2]$ containing both a hydride ligand and an alkyl ligand R . We were, however, unable to observe such species in solution, and attempts to obtain $[\text{Ru}(\text{CO})_2\text{R}(\text{H})(\text{PMe}_2\text{Ph})_2]$ ($\text{R} = \text{Me}$ or Ph) by treating $[\text{Ru}(\text{CO})_2\text{R}(\text{Cl})(\text{PMe}_2\text{Ph})_2]$ with NaBH_4 yielded only $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ and the hydrocarbon RH .¹

In this paper we report the reactions of hydride complexes of ruthenium(II) with alkynes. Although many studies have been made of reactions between alkynes and complexes containing a single hydride ligand, less attention has been paid to complexes with two such ligands, despite the wider range of possible reactions opened up by the presence of two metal-hydrogen bonds. Nakamura and Otsuka² studied the reactions of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ and $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$, and $\text{PhC}\equiv\text{CPh}$, and this work has since been extended by Scordia *et al.*³ and by Herberich and Barlage.⁴ Wailes *et al.*⁵ investigated reactions between $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ and alkyl-substituted alkynes, and more recently Roddick *et al.*⁶ have reported on the reaction between $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ and $\text{HC}\equiv\text{CCMe}_3$. Longato and Bresadola⁷ have described the reactions between iridium(III) complexes $[\text{Ir}(\text{CO})(7\text{-Ph-1,7-C}_2\text{B}_{10}\text{H}_{10})\text{H}_2(\text{NCR})(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$ or Ph) and a range of alkynes, and in a recent paper Clark *et al.*⁸ reported on reactions between complexes $[\text{PtH}_2\text{L}_2]$ ($\text{L} =$ tertiary phosphine) and activated alkynes. Yamazaki and Aoki⁹ obtained $[\text{Ru}(\text{CO})\{\text{CH}=\text{C}(\text{CO}_2\text{Me})\text{CH}=\text{C}(\text{CO}_2\text{Me})\text{C}\equiv\text{CHC}(\text{O})\text{OMe}\}(\text{PPh}_3)_2]$ by heating $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$ with $\text{HC}\equiv\text{CCO}_2\text{Me}$, but our intention was to study the reactions of complexes $[\text{Ru}(\text{CO})_2\text{H}_2\text{L}_2]$ with alkynes $\text{RC}\equiv\text{CR}'$ under mild conditions. Assuming that these reactions followed the same pattern as those with alkenes, intermediates $[\text{Ru}(\text{CO})_2(\text{CR}=\text{CHR}')\text{HL}_2]$ would be formed, and we hoped that these would be sufficiently long-lived to be detectable.

In the event, we found that the nature of the organoruthenium products of the reactions between $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ and alkynes varied according to the alkyne used, and in an



Scheme 1.

attempt to establish a pattern for these reactions we also studied those between $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ and the same alkynes. The results of the latter reactions are reported first.

Results and Discussion

Details of the ^1H , $^{13}\text{C}\{-^1\text{H}\}$, and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of new complexes are given in Tables 1, 2, and 3 respectively.

Table 1. Proton n.m.r. spectra of complexes^a

Complex	δ /p.p.m.	Assignment	Coupling constants/Hz	Assignment
(1a)	8.17 (dt, 1)	RuCH=CH	18.0, 3.5	$^3J(\text{H-H})$, $^3J(\text{P-H})$
	6.76 (dt, 1)	RuCH=CH	18.0, 2.6	$^3J(\text{H-H})$, $^4J(\text{P-H})$
	1.56 (t, 6)	PMe ₂ Ph	7.5	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.46 (t, 6)	PMe ₂ Ph	7.9	$^2J(\text{P-H}) + ^4J(\text{P-H})$
(1b)	6.87 (dt) ^b	RuCH=CH	17.6, 3.3	$^3J(\text{H-H})$, $^3J(\text{P-H})$
	5.71 (dt, 1)	RuCH=CH	17.6, 2.4	$^3J(\text{H-H})$, $^4J(\text{P-H})$
	1.62 (t, 6)	PMe ₂ Ph	7.9	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.54 (t, 6)	PMe ₂ Ph	7.5	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.15 (s, 9)	CMe ₃		
(2)	6.80 (t, 1)	RuC=CH	2.8	$^4J(\text{P-H})$
	3.69 (s, 3)	CO ₂ Me		
	3.42 (s, 3)	CO ₂ Me		
	1.82 (t, 6)	PMe ₂ Ph	8.8	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.79 (t, 6)	PMe ₂ Ph	7.9	$^2J(\text{P-H}) + ^4J(\text{P-H})$
(3a)	1.77 (t, 6)	PMe ₂ Ph	7.5	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.73 (t, 6)	PMe ₂ Ph	7.0	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	-6.30 (t, 1)	RuH	23.5	$^2J(\text{P-H})$
(3b)	1.81 (t, 6)	PMe ₂ Ph	7.5	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.77 (t, 6)	PMe ₂ Ph	7.0	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.39 (s, 9)	CMe ₃		
	-6.41 (t, 1)	RuH	24.2	$^2J(\text{P-H})$
(4a)	1.86 (t, 6)	PMe ₂ Ph	8.1	$^2J(\text{P-H}) + ^4J(\text{P-H})$
	1.85 (t, 6)	PMe ₂ Ph	7.9	$^2J(\text{P-H}) + ^4J(\text{P-H})$
(5)	1.12 (t)	PMe ₂ Ph	6.6	$^2J(\text{P-H}) + ^4J(\text{P-H})$
(6)	6.73 (t, 1)	RuC=CH	3.2	$^4J(\text{P-H})$
	3.54 (s, 3)	CO ₂ Me		
	3.46 (s, 3)	CO ₂ Me		
	-6.17 (t, 1)	RuH	20.1	$^2J(\text{P-H})$
(6')	6.79 (dt, 1)	RuC=CH	1.4, 3.4	$^4J(\text{H-H})$, $^4J(\text{P-H})$
	3.51 (s, 3)	CO ₂ Me		
	3.49 (s, 3)	CO ₂ Me		
	-5.41 (t, 1)	RuH	22.3	$^2J(\text{P-H})$
(7), (7') ^c	3.49 (s)	CO ₂ Me		
	3.46 (s) ^d	CO ₂ Me		
	3.43 (s)	CO ₂ Me		
	-5.57 (s)	RuH		
	-6.16 (s)	RuH		

^a In C₆D₆ solution. Phenyl proton resonances have been omitted. ^b Partly obscured by phenyl proton resonances. ^c Vinyl proton resonances obscured and AsMe₂Ph resonances poorly resolved. ^d Two coincident resonances.

Reactions of [Ru(CO)₂Cl(H)(PMe₂Ph)₂] with Alkynes.—Equimolar quantities of [Ru(CO)₂Cl(H)(PMe₂Ph)₂] and HC≡CPh reacted slowly in C₆D₆ to give a single product, **(1a)**, identified on the basis of analytical and spectroscopic evidence as [Ru(CO)₂(CH=CHPh)Cl(PMe₂Ph)₂] (see Scheme 1). The mutually *trans* positioning of the PMe₂Ph ligands was established by the ¹H and ¹³C n.m.r. spectra.* From the value of $^3J(\text{H-H})$ for the alkene hydrogens in the vinyl (alkenyl) ligand (18.0 Hz), we concluded that these atoms were *trans* to each other [typically $^3J(\text{H-H})$ is between 18 and 21 Hz for mutually *trans* hydrogens in a ligand of the type -CH=CHR^{5,6,12} but only 12–14 Hz for mutually *cis* hydrogens,^{3,12} while $^2J(\text{H-H})$ in the grouping -CR=CH₂ is normally only 2–5 Hz^{3,13}].

A similar reaction between [Ru(CO)₂Cl(H)(PMe₂Ph)₂] and HC≡CCMe₃ yielded [Ru(CO)₂(CH=CHCMe₃)Cl(PMe₂Ph)₂], **(1b)**. The chemical shifts for the vinyl protons and carbon atoms differed significantly from those for **(1a)**, but the splitting patterns and coupling constants were similar for the two complexes. We concluded that both complexes resulted from *cis* addition of Ru-H across the alkyne triple bond, and that the substituted carbon in the alkyne became the β carbon in the vinyl ligand.

A possible mechanism for the formation of complexes **(1a)** and **(1b)** is shown in Scheme 1. A key step is the carbonyl substitution which allows the introduction of the alkyne *cis* to the hydride ligand. The ease of carbonyl substitution in [Ru(CO)₂Cl(H)(PMe₂Ph)₂] has been demonstrated by its reaction with PMe₂Ph, but in this instance the PMe₂Ph ligand enters *trans* to hydride.¹ We have, however, observed a similar variation in the geometry of carbonyl substitution reactions of *trans*-[Ru(CO)₂Cl₂(PMe₂Ph)₂]: here the kinetic products [Ru-

* The ways in which phosphorus ligands may be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.^{10,11}

Table 2. Carbon-13 n.m.r. spectra of complexes^a

Complex	δ /p.p.m.	Assignment	Coupling constant/ Hz ^b	Complex	δ /p.p.m.	Assignment	Coupling constant/ Hz ^b
(1a)	198.9 (t)	CO	11.9	(3b)	115.9 (t)	RuC \equiv C	2.3
	193.9 (t)	CO	9.0		88.5 (t)	RuC \equiv C	22.0
	189.4 (t)	RuC=C	15.6		33.5 (s)	CMe ₃	
	141.6 (t)	RuC=C	2.7		28.3 (s)	CMe ₃	
	13.9 (t)	PMe ₂ Ph	34.8		19.0 (t)	PMe ₂ Ph	35.7
	12.1 (t)	PMe ₂ Ph	33.0		18.4 (t)	PMe ₂ Ph	33.9
(1b)	199.2 (t)	CO	11.9	(4a)	195.5 (t)	CO	11.4
	193.8 (t)	CO	9.6		193.3 (t)	CO	10.1
	149.3 (t)	RuC=C	4.6		113.6 (s)	RuC \equiv C	
	145.4 (t)	RuCCO ₂ Me	15.1		112.1 (t)	RuC \equiv C	20.1
	36.5 (s)	RuC=CCO ₂ Me			14.3 (t)	PMe ₂ Ph	35.7
	30.3 (s)	CO ₂ Me			13.9 (t)	PMe ₂ Ph	33.8
	13.5 (t)	CO ₂ Me	33.9	(5)	209.6 (t)	CO	12.8
	11.7 (t)	PMe ₂ Ph	30.2		136.0 (t)	PhC \equiv CPh, C ¹	3.7
		PMe ₂ Ph			113.6 (t)	PhC \equiv CPh	5.0
(2) ^c	195.8 (t)	CO	12.4		17.2 (t)	PMe ₂ Ph	29.3
	193.4 (t)	CO	15.2	(6), (6') ^e	203.5 (t)	CO	15.4
	182.7 (t)	RuC=C	13.7		201.8 (t)	CO	11.6
	178.5 (s)	RuCCO ₂ Me			200.7 (t)	CO	11.6
	169.8 (s)	RuC=CCO ₂ Me			197.5 (t)	CO	11.0
	50.6 (s)	CO ₂ Me			179.2 (t) ^d	RuC=C	14.8
	49.8 (s)	CO ₂ Me			177.8 (s) ^e	RuCCO ₂ Me	
	14.6 (t)	PMe ₂ Ph	30.2		173.5 (t) ^f	RuC=C	15.4
	13.2 (t)	PMe ₂ Ph	29.3		170.3 (t) ^f	RuC=CCO ₂ Me	4.8
					170.1 (t) ^d	RuC=CCO ₂ Me	4.4
(3a)	199.7 (t)	CO	10.5		50.5 (s) ^e	CO ₂ Me	
	196.5 (t)	CO	8.5		50.3 (s)	CO ₂ Me	
	113.6 (s)	RuC \equiv C			50.0 (s)	CO ₂ Me	
	111.7 (t)	RuC \equiv C	22.0		20.0 (t) ^d	PMe ₂ Ph	34.8
	20.3 (t)	PMe ₂ Ph	34.8		19.6 (t) ^f	PMe ₂ Ph	29.5
	19.6 (t)	PMe ₂ Ph	33.9		18.9 (t) ^f	PMe ₂ Ph	31.3
(3b)	198.4 (t)	CO	10.1		17.6 (t) ^d	PMe ₂ Ph	31.1
	196.9 (t)	CO	16.0				

^a In C₆D₆ solution. Spectra are proton-decoupled. Except for compound (5), all phenyl carbon resonances have been omitted. ^b All to ³¹P. For PMe₂Ph methyl carbons, values listed are for ¹J(P-C) + ³J(P-C). ^c Resonances for RuC=C obscured by phenyl carbon resonances. ^d Resonance assigned to compound (6). ^e Two coincident resonances. ^f Resonance assigned to compound (6').

Table 3. Phosphorus-31 n.m.r. spectra of complexes*

Complex	δ /p.p.m.
(1a)	-0.6
(1b)	-1.3
(2)	-0.6
(3a)	5.7
(3b)	6.0
(4a)	-0.3
(5)	8.8
(6)	6.1
(6')	4.8

* In C₆D₆ solution. Spectra were proton-decoupled, and all resonances were singlets. Chemical shifts are given relative to H₃PO₄ (contained in a capillary within the n.m.r. tube).

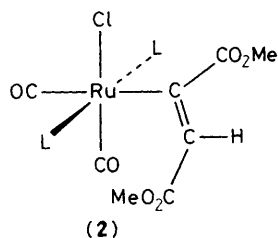
(CO)Cl₂L(PMe₂Ph)₂] of reactions with phosphorus ligands L have L *trans* to CO, whereas for L = C₂H₄ the product obtained has the ethene ligand *trans* to chloride,¹⁴ as is the alkyne ligand in the intermediate in Scheme 1.

No reaction was observed when [Ru(CO)₂Cl(H)(PMe₂Ph)₂] was treated with PhC \equiv CPh in C₆D₆ solution, but with MeO₂CC \equiv CCO₂Me a rapid reaction occurred. Again a single product, (2), was obtained. The ¹³C n.m.r. spectrum of (2) fairly closely resembled that of [Ru(CO)₂{C(CO₂Me)=C(CO₂Me)-Cl}Cl(PMe₂Ph)₂], obtained from the reaction of *trans*-

[Ru(CO)₂Cl₂(PMe₂Ph)₂] with MeO₂CC \equiv CCO₂Me.¹⁵ It was, however, clear that (2) was [Ru(CO)₂{C(CO₂Me)=CH(CO₂Me)}Cl(PMe₂Ph)₂] rather than [Ru(CO)₂{C(CO₂Me)=CCl(CO₂Me)}H(PMe₂Ph)₂], since its ¹H n.m.r. spectrum contained no hydride ligand resonance but included a triplet at δ 6.80, attributable to a vinyl proton.

In this instance, the absence of a hydrogen atom on the α carbon of the vinyl ligand made it impossible to use the size of ³J(H-H) as a guide to the stereochemistry of the addition, although by analogy with the reactions of [Ru(CO)₂Cl(H)(PMe₂Ph)₂] with HC \equiv CPh and HC \equiv CCMe₃ and of *trans*-[Ru(CO)₂Cl₂(PMe₂Ph)₂] with MeO₂CC \equiv CCO₂Me¹⁵ one might assume that *cis* addition of Ru-H across the triple bond occurred. Torres *et al.*,¹⁶ who investigated the reactions of [Ru(CO)Cl(H)(PPh₃)₃] with alkynes, used the value of ³J(H-H) to demonstrate that *cis* addition occurred for HC \equiv CR, where R = CO₂Me, CO₂Et, or COMe, and assumed that the same would be the case for the alkyne MeO₂CC \equiv CCO₂Me. There are, however, clear-cut instances of *trans* addition of metal-hydrogen bonds to activated alkynes,^{8,17} and in a recent paper Herberich and Barlage⁴ have suggested that in vinyl ligands -C(CO₂Me)=CH(CO₂Me) and -C(CN)=CH(CN) the value of the coupling constant ³J(C-H) between the hydrogen on the β -carbon atom and the -CO₂Me or -CN carbon attached to the α -carbon atom may be used as a guide to stereochemistry. They quote values of 8.5–10 Hz for *cis*-

$^3J(\text{C-H})$ (i.e. for *trans* addition to the alkyne) and 14–16 Hz for *trans*- $^3J(\text{C-H})$ (i.e. *cis* addition to the alkyne). In the proton-coupled ^{13}C n.m.r. spectrum of compound (2) the resonance for the carboxylate carbon of the $-\text{CO}_2\text{Me}$ substituent on the α -carbon atom was a complex multiplet, but it was clear that the splitting pattern did not include a doublet splitting of 14 Hz or more. Thus it is quite possible that (2), unlike (1a) and (1b), is formed by *trans* addition of Ru–H across the alkyne triple bond, giving it the structure shown below, where $\text{L} = \text{PMe}_2\text{Ph}$.

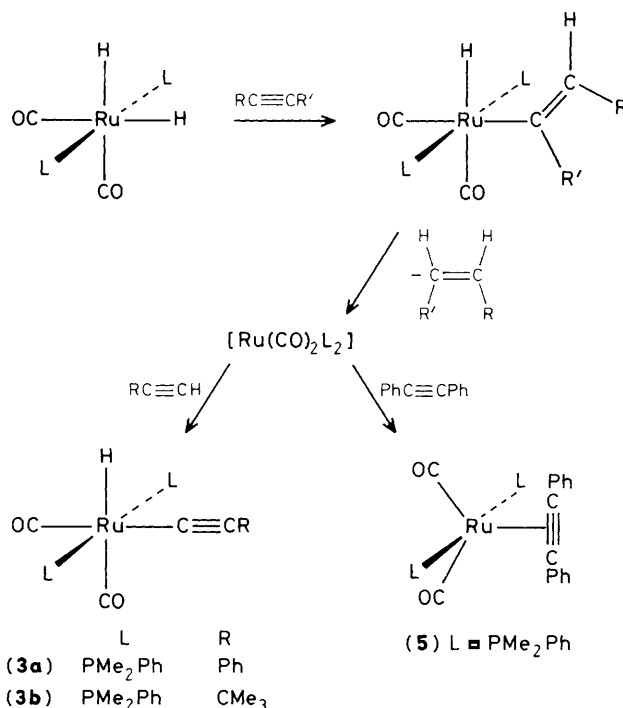


The equivalence of the two PMe_2Ph ligands in complexes (1a), (1b), and (2) indicates that the vinyl ligand must either lie in the plane of the carbonyl and chloride ligands, as has been shown to be the case for the carbon skeleton of the vinyl ligand in $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CCl}(\text{CO}_2\text{Me})\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$,¹⁵ or must rotate (or at least oscillate) about the Ru–C bond at a rate which is rapid on the n.m.r. time-scale. The planar orientation may be adopted because it maximizes the overlap between the π system of the C=C bond and the one ruthenium d orbital which is not shared with the carbonyl ligand *cis* to the vinyl group.

Reactions of Complexes $[\text{Ru}(\text{CO})_2\text{H}_2\text{L}_2]$ with Alkynes.—Treatment of a C_6D_6 solution of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ with a small quantity of $\text{HC}\equiv\text{CPh}$ resulted in conversion of some of the $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ into a new ruthenium complex (3a). Subsequent additions of $\text{HC}\equiv\text{CPh}$ eventually caused complete conversion into (3a). The reaction was monitored by ^{31}P n.m.r. spectroscopy, and no phosphorus-containing species other than $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ and (3a) could be detected at any stage. Proton n.m.r. spectra indicated that the formation of (3a) was accompanied by the appearance of $\text{H}_2\text{C}=\text{CHPh}$. We were unable to isolate (3a) in solid form, but identified it on the basis of spectroscopic evidence as the alkynyl complex $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})\text{H}(\text{PMe}_2\text{Ph})_2]$ (see Scheme 2). Triplet and singlet resonances, at δ 111.7 and 113.6 p.p.m. respectively, in the ^{13}C n.m.r. spectrum were attributed to the α - and β -carbon atoms of the alkynyl ligand. The fact that both resonances also appeared in a spectrum recorded under conditions of low-power noise decoupling confirmed that the carbon atoms responsible for them had no attached hydrogen atoms.

Complex (3a) reacted slowly with CCl_4 in C_6D_6 solution to yield a product (4a), $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})\text{Cl}(\text{PMe}_2\text{Ph})_2]$, which was isolated and fully characterized. Apart from the absence of a hydride ligand resonance, the n.m.r. spectra of (4a) closely resembled those of (3a).

The reaction of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ with $\text{HC}\equiv\text{CCMe}_3$ was similarly studied by addition of successive small amounts of the alkyne. Again only one new complex, (3b), was formed, and the reaction also yielded the alkene $\text{H}_2\text{C}=\text{CHCMe}_3$. From the similarities between the ^1H and ^{13}C n.m.r. spectra of (3a) and (3b) we concluded that (3b) was $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CCMe}_3)\text{H}(\text{PMe}_2\text{Ph})_2]$. A ^{13}C n.m.r. spectrum recorded with full proton coupling showed that both α - and β -carbon nuclei in the alkynyl ligand were coupled to the hydride ligand [$^2J(\text{C-H}) = 6.1$, $^3J(\text{C-H}) = 3.7$ Hz]. It is intriguing to note that the resonance for the α -carbon atom in the alkynyl ligand in (3a), (4a), and (3b) appears at δ 111.7, 112.1, and 88.5 p.p.m. respectively, whereas



Scheme 2.

Bruce and Wallis¹⁸ have reported that this resonance is at *ca.* δ 230 p.p.m. for complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{PPh}_3)_2]$ ($\text{R} = \text{alkyl, aryl, or CO}_2\text{Me}$).

In order to determine whether the hydride ligand in complexes (3a) and (3b) originated from $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ or from the alkyne, we studied the reaction of $[\text{Ru}(\text{CO})_2\text{D}_2(\text{PMe}_2\text{Ph})_2]$ with $\text{HC}\equiv\text{CCMe}_3$. The product was shown to be $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CCMe}_3)\text{H}(\text{PMe}_2\text{Ph})_2]$ rather than $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CCMe}_3)\text{D}(\text{PMe}_2\text{Ph})_2]$ by the presence of a resonance for the hydride ligand in the ^1H n.m.r. spectrum and the absence of a deuterium splitting in the ^{31}P n.m.r. spectrum (in complexes containing mutually *cis* PMe_2Ph and deuteride ligands, there is significant coupling between ^{31}P and ^2H nuclei¹).

The complex $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ also reacted slowly with $\text{PhC}\equiv\text{CPh}$ in C_6D_6 solution. The reaction yielded *cis*- $\text{PhCH}=\text{CHPh}$, identified (using an authentic sample of *cis*- $\text{PhCH}=\text{CHPh}$ for purposes of comparison) by the singlet resonance for the alkene protons at δ 6.46 in the ^1H n.m.r. spectrum of the reaction mixture. Unfortunately, the corresponding resonance for any *trans*- $\text{PhCH}=\text{CHPh}$ that might have been present would have been obscured by resonances for the PMe_2Ph ligands. When organic products were separated from the ruthenium-containing materials by t.l.c., the main product was confirmed as *cis*- $\text{PhCH}=\text{CHPh}$. There was also a trace of a second organic compound, but the quantity present was insufficient for characterization.

The appearance of *cis*- $\text{PhCH}=\text{CHPh}$ was accompanied by the formation of a new complex, (5). Even when the alkyne was added in successive small quantities, (5) and residual $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ were the only ruthenium complexes observed. Complex (5) was identified on the basis of its n.m.r. and i.r. spectra as the alkynyl complex $[\text{Ru}(\text{CO})_2(\text{PhC}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$. The i.r. spectrum included a band at 1935 cm^{-1} , tentatively assigned as the $\text{C}\equiv\text{C}$ stretching mode of co-ordinated $\text{PhC}\equiv\text{CPh}$. Although the wavenumber of this mode for free $\text{PhC}\equiv\text{CPh}$ is 2223 cm^{-1} , a drop in stretching frequency of this magnitude commonly occurs when the alkyne is complexed.¹⁹ The formation of compound (5) and *cis*- $\text{PhCH}=\text{CHPh}$ parallels

the reaction of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ with $\text{PhC}\equiv\text{CPh}$, which yields $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PhC}\equiv\text{CPh})]$ and *cis*- $\text{PhCH}=\text{CHPh}$.² From the n.m.r. spectra of (5) it was evident that the alkyne ligand must either be positioned so as to preserve the symmetry of the rest of the molecule (perhaps as shown in Scheme 2) or be rotating rapidly about the metal-alkyne bond.

It seems probable (see Scheme 2) that (3a), (3b), and (5) are all formed by way of vinyl complexes $[\text{Ru}(\text{CO})_2(\text{CR}'=\text{CHR})\text{H}(\text{PMe}_2\text{Ph})_2]$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; $\text{R} = \text{CMe}_3$, $\text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{Ph}$), from which alkenes $\text{RCH}=\text{CHR}'$ are then eliminated. The assumption of a *cis* addition of Ru-H across the triple bond of the alkyne is in line with the reactions of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ with $\text{HC}\equiv\text{CPh}$ and $\text{HC}\equiv\text{CCMe}_3$ (see above) and with the formation of the *cis* isomer of $\text{PhCH}=\text{CHPh}$ in the reaction with $\text{PhC}\equiv\text{CPh}$. Alkene elimination leaves $[\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, which undergoes oxidative addition with $\text{HC}\equiv\text{CPh}$ and $\text{HC}\equiv\text{CCMe}_3$ to give (3a) and (3b), but simply forms the alkyne complex (5) with $\text{PhC}\equiv\text{CPh}$. This reaction sequence is also compatible with the formation of deuterium-free (3b) on treating $[\text{Ru}(\text{CO})_2\text{D}_2(\text{PMe}_2\text{Ph})_2]$ with $\text{HC}\equiv\text{CCMe}_3$. The failure to observe any organoruthenium species other than (3a), (3b), and (5) in these reactions, even when insufficient alkyne was used, indicates that in every case the reductive elimination of alkene and subsequent reaction of $[\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ must be rapid by comparison with the formation of the intermediate vinyl complexes.

The reaction between $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ in C_6D_6 solution was virtually instantaneous at ambient temperature. Two ruthenium complexes, characterized by singlet resonances at δ 6.1 [complex (6)] and 4.8 p.p.m. [complex (6')] in the ^{31}P n.m.r. spectrum of the solution, were formed in unequal amounts. When the quantity of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ added was insufficient to react with all the $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$, (6) and (6') were still obtained in the same ratio: as successive portions of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ were added, the concentrations of (6) and (6') increased but the ratio did not vary, nor did it alter when the solution was left to stand once all the $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ had been consumed.

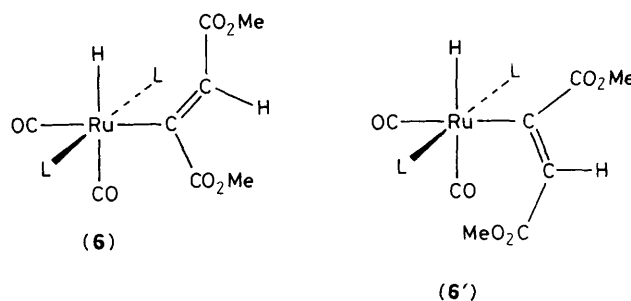
The ^1H n.m.r. spectrum of the mixture of (6) and (6') was recorded at 360 MHz. Two vinyl proton resonances, two hydride ligand resonances, and four resonances for CO_2Me protons were observed, and from the areas of these resonances and heteronuclear decoupling experiments it was possible to assign each resonance to a particular complex. Each vinyl proton resonance exhibited a triplet splitting due to the ^{31}P nuclei, but that for (6') also showed a doublet splitting. This persisted when the spectrum was recorded with ^{31}P decoupling, but was lost on irradiation at the centre of the hydride ligand resonance for (6'), showing that the hydride ligand and vinyl proton for (6') were coupled [$^4J(\text{H-H}) = 1.4$ Hz]: no such coupling was detected for (6). The hydride ligand resonance for (6') showed only the triplet splitting due to the ^{31}P nuclei, but each peak of the triplet was somewhat broadened {a similar broadening was noted for $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ and was shown to be due to weak coupling to the methyl protons of the PMe_2Ph ligands¹}, and this broadening presumably obscured the doublet splitting by the vinyl proton.

Extensive overlapping made the pattern of PMe_2Ph methyl proton resonances for the mixture of (6) and (6') difficult to interpret, but inspection of the corresponding resonances in the ^{13}C n.m.r. spectrum established that each species contained mutually *trans* PMe_2Ph ligands and that the Ru-P bonds did not lie in a plane of symmetry. Four resonances were observed in the region around δ 200 p.p.m., indicating that each complex contained two inequivalent carbonyl ligands.

We concluded that (6) and (6') were both $[\text{Ru}(\text{CO})_2\text{-}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{H}(\text{PMe}_2\text{Ph})_2]$, obtained by addition of one Ru-H bond across the triple bond of the alkyne,

and that they were either isomers resulting from different directions of addition or different conformers of a single species. As mentioned earlier, the reaction of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ yielded only *one* form of $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$, complex (2), and we decided to attempt the substitution of the chloride ligand in (2) by hydride, using NaBH_4 . If (6) and (6') were isomers formed by different modes of addition of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ to the alkyne, we anticipated that the reaction of (2) with NaBH_4 would yield only *one* of them; if they were merely conformers, we expected to obtain both. In the event, the reaction yielded (6) and (6') in the same ratio as that obtained by treating $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$. Similar pairs of conformers have been reported for complexes $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\{\text{C}(\text{CF}_3)=\text{CHR}\}\text{H}]$ ($\text{R} = \text{H}^3$ or CF_3^{20}) and for $[\text{M}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)_2(\text{CR}=\text{CHR})]$ ($\text{M} = \text{Nb}$ or Ta , $\text{R} = \text{CN}$ or CF_3).¹³

From the n.m.r. spectra of (6) and (6'), it was evident that in both conformers the vinyl ligand must lie in the plane at right angles to the Ru-P bonds, as it is known to do in $[\text{Ru}(\text{CO})_2\text{-}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{Cl}\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$.¹⁵ If the addition of Ru-H across the alkyne is *trans*, the structures are presumably as shown below, where $\text{L} = \text{PMe}_2\text{Ph}$, and the long-range coupling between the hydride ligand and vinyl proton observed for (6') may be attributable to the W conformation of



the bonds between the two. If the addition is *cis*, one conformer has the two hydrogens in close proximity, and the coupling could be due to a 'through space' interaction.

The complex $[\text{Ru}(\text{CO})_2\text{H}_2(\text{AsMe}_2\text{Ph})_2]$ was also found to react rapidly with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ in C_6D_6 solution. This complex exists in solution as an equilibrium mixture of isomers,¹ and the rapidity of the reaction made it possible to show that the isomer which reacted with the alkyne was the one which was isostructural with $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$. Two species, (7) and (7'), with singlet resonances at chemical shifts very similar to those of the hydride ligand resonances for (6) and (6'), were formed in the reaction. The resonances for the AsMe_2Ph methyl protons were not well resolved, but the pattern of resonances for the protons in the CO_2Me groups was again similar to that for (6) and (6'). We concluded that (7) and (7') were conformers of $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{H}(\text{AsMe}_2\text{Ph})_2]$.

The stability of complexes (6), (6'), (7), and (7') is in marked contrast to our failure to observe the related vinyl complexes postulated as intermediates in Scheme 2. The electron-withdrawing nature of the carboxylate substituents may result in a strengthening of the metal-vinyl bond by back donation from the appropriate metal *d* orbital. As discussed earlier in the paper, this back donation may also be responsible for the positioning of the vinyl ligand in the plane at right angles to the Ru-P bonds, and it could account for the energy barrier to interconversion of the pairs of conformers (although steric factors may be significant here too).

Experimental

Complexes were prepared and purified using dry, oxygen-free solvents. Except where stated otherwise, the light petroleum used had a boiling range of 313–333 K. Reactions were carried out in n.m.r. tubes under an atmosphere of dry nitrogen, and were monitored using a JEOL FX90Q n.m.r. spectrometer. Spectra of some reaction products were also recorded on Bruker WH360 and MSL 300 instruments. Infrared spectra were recorded on a Perkin-Elmer PE257 spectrometer.

The preparations of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$, $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$, and $[\text{Ru}(\text{CO})_2\text{H}_2(\text{AsMe}_2\text{Ph})_2]$ have been described in a previous paper.¹

Preparations.— $[\text{Ru}(\text{CO})_2(\text{CH}=\text{CHPh})\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (**1a**). To a solution of $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ (0.10 g) in C_6D_6 (0.3 cm^3) was added $\text{HC}\equiv\text{CPh}$ (30 mm^3). After 5 d, the solvent was removed by evaporation under a stream of N_2 , leaving a yellow oil. This was redissolved in a mixture of light petroleum (boiling range 353–373 K) and benzene (1:1, 10 cm^3), and ethanol (5 cm^3) was added. After slow evaporation of the solvent mixture under a stream of N_2 , a pale yellow powder was obtained. This was washed with light petroleum and dried *in vacuo* (Found: C, 54.65; H, 5.10. Calc. for $\text{C}_{26}\text{H}_{29}\text{ClO}_2\text{P}_2\text{Ru}$: C, 54.60; H, 5.10%). $\nu(\text{C}=\text{O})$ (CHCl_3) 2 030s and 1 965s cm^{-1} .

The complexes $[\text{Ru}(\text{CO})_2(\text{CH}=\text{CHCMe}_3)\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (**1b**), and $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (**2**), were prepared in the same way from $[\text{Ru}(\text{CO})_2\text{Cl}(\text{H})(\text{PMe}_2\text{Ph})_2]$ (0.05 g) and $\text{HC}\equiv\text{CCMe}_3$ or $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (13 mm^3), with reaction times of 48 and 0.5 h respectively, but could not be induced to crystallize.

$[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})\text{H}(\text{PMe}_2\text{Ph})_2]$, (**3a**). A solution of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ (ca. 0.04 g) in C_6D_6 (0.3 cm^3) was treated with successive 2- mm^3 portions of $\text{HC}\equiv\text{CPh}$ (each portion being added when the previous one had been completely consumed) until no $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ remained in the solution. The product was not isolated, but was converted into (**4a**) (see below). The same method was used to prepare $[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CCMe}_3)\text{H}(\text{PMe}_2\text{Ph})_2]$, (**3b**).

$[\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (**4a**). The C_6D_6 solution of compound (**3a**) (see above) was treated with CCl_4 (10 mm^3). When no (**3a**) remained, the C_6D_6 was removed under reduced pressure, and the residual powder was recrystallized from ethanol–light petroleum (2:1) (Found: C, 54.65; H, 4.50. Calc. for $\text{C}_{26}\text{H}_{27}\text{ClO}_2\text{P}_2\text{Ru}$: C, 54.80; H, 4.75%). $\nu(\text{C}=\text{O})$ (CH_2Cl_2) 2 050s and 1 985s cm^{-1} .

$[\text{Ru}(\text{CO})_2(\text{PhC}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$, (**5**). To a solution of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ (ca. 0.04 g) in C_6D_6 (0.3 cm^3) was added $\text{PhC}\equiv\text{CPh}$ (0.02 g), and the solution was shaken to ensure mixing. After 4 d all volatile material was removed under reduced pressure, leaving a yellow oil which could not be induced to solidify. $\nu(\text{C}=\text{O})$ (heptane) 1 965s and 1 920s cm^{-1} .

$[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{H}(\text{PMe}_2\text{Ph})_2]$, (**6**) and (**6'**). (a) Successive 2- mm^3 portions of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ were added to a solution of $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ (ca. 0.04 g) in

C_6D_6 (0.3 cm^3) until no $[\text{Ru}(\text{CO})_2\text{H}_2(\text{PMe}_2\text{Ph})_2]$ remained. The product, a mixture of conformers (**6**) and (**6'**), was obtained as a yellow oil by removing the solvent under reduced pressure, but attempts to crystallize the oil were unsuccessful.

(b) A mixture of $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$ (0.08 g) and NaBH_4 (0.05 g) in EtOH (5 cm^3) was stirred for 1 h. The solvent was removed under reduced pressure and the product extracted into benzene. Removal of the benzene yielded a mixture of (**6**) and (**6'**), again as an oil.

Method (a) was also used to obtain $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}\text{H}(\text{AsMe}_2\text{Ph})_2]$, (**7**) and (**7'**), from $[\text{Ru}(\text{CO})_2\text{H}_2(\text{AsMe}_2\text{Ph})_2]$ and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$.

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