The Stereochemistry of Alkyne Insertion into Ru–H and Ru–Cl Bonds

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Proton-coupled ^{13}C NMR studies of vinyl complexes obtained by insertion of $MeO_2CC{\equiv}CCO_2Me$ into the Ru–H bond of $[Ru(CO)_2Cl(H)L_2]$ (L = PMe_2Ph or $AsMe_2Ph$) or one Ru–H bond of $[Ru(CO)_2H_2L_2]$ have shown that the reactions involve *trans* addition of Ru–H to the alkyne. For the PMe_2Ph complexes, selective deuteriation was required to simplify the spectra. In contrast, $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ reacts by *cis* addition of Ru–H to the alkyne. Carbonyl substitution in $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_2]$ by PMe_2Ph leaves the geometry of the vinyl ligand unchanged, so that two (non-interconverting) isomers of $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_3]$ can be obtained. Whereas *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ combines with $MeO_2CC{\equiv}CCO_2Me$ by *cis* addition of Ru–Cl to the alkyne, $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ apparently reacts by *trans* addition, yielding $[Ru(CO)\{C(CO_2Me){=}C(COOMe)Cl\}Cl(PMe_2Ph)_2]$. Since, however, both reactions appear to involve the same ruthenium intermediate, $[Ru(CO)Cl_2(PMe_2Ph)_2]$, it is possible that the direction of addition is the same in both cases, but that the vinyl ligand can isomerize.

Recently we described reactions of hydride complexes of ruthenium(II) with alkynes, which resulted in the formation of vinyl and alkynyl complexes.[1] The reactions of $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ with alkynes $RC{\equiv}CH$ (R = CMe_3 or Ph) yielded the vinyl complexes $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ for which the value of the coupling constant $|^3J(H\text{–}H)|$ between the two vinyl protons clearly indicated that *cis* addition of Ru–H to the alkyne had occurred.[1] This is compatible with a conventional mechanism involving initial co-ordination of the alkyne to the metal (probably by replacement of a carbonyl ligand) followed by *cis* addition of Ru–H to the alkyne *via* a planar four-centre transition state.[2]

There are, however, clear-cut instances of *trans* addition of metal–hydrogen bonds to alkynes in cases where the alkyne contains electron-withdrawing substituents. Thus, for example, Herberich *et al.*[3] have shown that the product of the reaction of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with $MeO_2CC{\equiv}CCO_2Me$, $[Mo(\eta^5\text{-}C_5H_5)_2\{C(CO_2Me){=}C(CO_2Me)H\}H]$, has the ester groups *trans*, not (as originally reported[4]) *cis*. Similarly, Clark *et al.*[5] have reported that, under appropriate conditions, the reaction between $[PtCl(H)(PEt_3)_2]$ and $MeO_2CC{\equiv}CCO_2Me$ involves *trans* rather than *cis* addition of Pt–H to the alkyne, and Jones *et al.*[6] obtained a mixture of *cis*- and *trans*-addition products on treating $[Rh(\eta^5\text{-}C_5Me_5)Me(H)(PMe_3)]$ with the same alkyne. Herberich and Barlage[7] showed that a *trans*-addition product was formed in the reaction between $[Re(\eta^5\text{-}C_5H_5)_2H]$ and $NCC{\equiv}CCN$, although subsequent irradiation caused partial rearrangement to the *cis* product. Nakamura and Otsuka[8] used ^{19}F NMR spectroscopy to establish that all three complexes, $[Re(\eta^5\text{-}C_5H_5)_2H]$, $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2H_2]$, reacted with $F_3CC{\equiv}CCF_3$ by *trans* addition.

We observed[1] that the reaction of $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ with $MeO_2CC{\equiv}CCO_2Me$, which yields $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_2]$ **1**, is far more rapid than those with $RC{\equiv}CH$ (R = CMe_3 or Ph). Moreover, $[Ru(CO)_2H_2(PMe_2Ph)_2]$, which reacts slowly with the latter alkynes to yield $[Ru(CO)_2(C{\equiv}CR)H(PMe_2Ph)_2]$ by way of the ruthenium(0) species $[Ru(CO)_2(PMe_2Ph)_2]$, undergoes a much faster reaction with $MeO_2CC{\equiv}CCO_2Me$ to yield $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)H\}H(PMe_2Ph)_2]$ **2**, as a mixture of isomers or conformers (major component **2′** and minor component **2″**). These changes in reaction rate and pathway led us to suspect that the mechanism of Ru–H addition to $MeO_2CC{\equiv}CCO_2Me$ differed from that for the other alkynes, and hence that the geometry of addition might also be different.

The absence of a hydrogen atom on the α-carbon of the ligand $C(CO_2Me){=}C(CO_2Me)H$ makes it impossible to determine the stereochemistry of addition by measurement of $|^3J(H\text{–}H)|$, but Herberich and Barlage[7] have proposed a method which relies upon measurement of the coupling constant $|^3J(C\text{–}H)|$ between the hydrogen on the β-carbon atom and the carbonyl carbon atom in the α-CO_2Me substituent. They quote values of 8.5–10 Hz for *cis*-$|^3J(C\text{–}H)|$, corresponding to *trans* addition of the metal–hydrogen bond to the alkyne, and 14–16 Hz for *trans*-$|^3J(C\text{–}H)|$ (*cis* addition to the alkyne). The difficulty of applying this technique to complexes such as **1** and **2** lies in the complexity of the proton-coupled ^{13}C NMR spectra, particularly in the case of **2**, where two species, **2′** and **2″**, are present in solution and the α-CO_2Me resonance for each is split by the CO_2Me methyl protons, the ^{31}P nuclei in the PMe_2Ph ligands and the hydride ligand. Simplification can, however, be achieved by replacing appropriate hydrogens by deuterium or phosphorus by arsenic.

This paper demonstrates that closely related hydride complexes of ruthenium react with $MeO_2CC{\equiv}CCO_2Me$ to give vinyl products with different stereochemistries, and that the vinyl ligand appears to retain its stereochemistry in subsequent reactions of the complexes. Reactions involving both *cis* and *trans* addition of Ru–Cl to the alkyne are also discussed.

Results and Discussion

Details of the IR and $^{31}P\text{-}\{^1H\}$ NMR spectra of undeuteriated complexes are given in Table 1, and the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are summarized in Tables 2 and 3 respectively. Key features of the spectra of the deuteriated complexes are presented in the text.

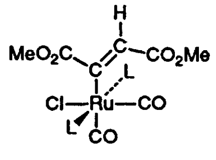
Treatment of $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ with $CD_3O_2CC{\equiv}CCO_2CD_3$ in C_6D_6 solution led to the rapid formation of $[Ru(CO)_2\{C(CO_2CD_3){=}C(CO_2CD_3)H\}Cl(PMe_2Ph)_2]$ $[^2H_6]$**1**. The $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra of $[^2H_6]$**1** were identical with those of complex **1** apart from the absence of the CO_2Me proton resonances. The $^{13}C\text{-}\{^1H\}$ NMR spectrum was also unchanged except for the splitting of the CO_2CD_3

Table 1 Infrared[a] and ^{31}P-{^{1}H} NMR[b] spectra of complexes

Complex	ν(C–O)/cm^{-1}	δ
1 $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_2]$	2056 1985	−0.5 (s)
2 $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}H(PMe_2Ph)_2]$[c]	2035 1975	4.7 (s) (**2′**) 6.0 (s) (**2″**)
3 $[Ru(CO)\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_3]$	1940	−6.1 (t)[d] −9.3 (d)[d]
4 $[Ru(CO)\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_3]$	1939	−1.4 (d)[e] −11.2 (t)[e]
5 $[Ru(CO)\{C(CO_2Me)=C(COOMe)H\}Cl(PMe_2Ph)_2]$	1952	4.6 (s)
6 $[Ru(CO)_2\{C(CO_2Me)=C(COO)H\}(PMe_2Ph)_2]$	2055 1985	2.4 (s)
8 $[Ru(CO)\{C(CO_2Me)=C(COOMe)Cl\}Cl(PMe_2Ph)_2]$	1960	16.9 (d)[f] 2.3 (d)[f]
9 $[Ru(CO)\{C(CO_2Me)=C(COOMe)Cl\}Cl(PMe_2Ph)_2]$[g]	1956	5.3 (s)

[a] In $CHCl_3$ solution unless stated otherwise. Only bands for the carbonyl ligands are listed. [b] In C_6D_6 solution unless stated otherwise. [c] Infrared spectrum in heptane solution. [d] $|^2J(P–P)|$ = 25.0 Hz. [e] $|^2J(P–P)|$ = 25.2 Hz. [f] $|^2J(P–P)|$ = 23.0 Hz. [g] ^{31}P-{^{1}H} NMR spectrum in $CDCl_3$ solution.

resonances by the deuterium nuclei. In the proton-coupled ^{13}C NMR spectrum the resonances for the CO_2CD_3 carbon atoms were doublets of triplets at δ 169.7 and 178.5 (the triplet splittings being due to the ^{31}P nuclei). For the former resonance the doublet splitting was 2.1 Hz: the small value indicates[7] that this is a geminal coupling $|^2J(C–H)|$ and that the resonance is due to β-CO_2CD_3. For the latter resonance, due to α-CO_2CD_3, $|^3J(C–H)|$ was 9.5 Hz, showing that the α-carboxylate group and the β-hydrogen are mutually *cis* and that complex **1** is formed by *trans* addition of Ru–H to the alkyne. Other resonances showing splittings by the β-hydrogen were those for the α- and β-vinyl carbon atoms and, more surprisingly, that at δ 194.7 [$|^4J(C–H)|$ = 3.7 Hz] assigned to the carbonyl ligand *trans* to the vinyl ligand. The structure of **1** is shown below, where L = PMe_2Ph.

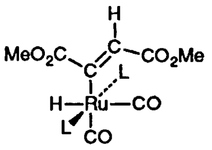


1

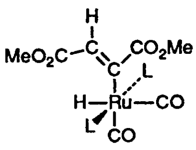
The reaction between $[Ru(CO)_2Cl(H)(AsMe_2Ph)_2]$ and $MeO_2CC{\equiv}CCO_2Me$ was also investigated by NMR spectroscopy, using C_6D_6 as solvent. A single product, **1a**, was formed and, apart from the absence of splittings by ^{31}P nuclei, the ^{1}H and ^{13}C-{^{1}H} NMR spectra were very similar to those for **1**. Thus **1a** was assumed to be $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}Cl(AsMe_2Ph)_2]$. Due to the absence of ^{31}P splittings, the proton-coupled ^{13}C NMR spectrum of **1a** could be interpreted without recourse to deuteriation. The resonances for α- and β-CO_2Me were doublets of quartets at δ 179.0 and 169.5, respectively. The latter showed a small doublet splitting [$|^2J(C–H)|$ = 2.8 Hz] characteristic of a geminal coupling, while for the former $|^3J(C–H)|$ was 9.4 Hz, again showing that the Ru–H bond had added *trans* to the alkyne. As in **1**, one of the carbonyl ligand resonances (δ 194.9) was split by the β-hydrogen in the vinyl ligand [$|^4J(C–H)|$ = 3.6 Hz].

Complex **2**, $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}H(PMe_2Ph)_2]$, may be prepared either from $[Ru(CO)_2H_2(PMe_2Ph)_2]$ and $MeO_2CC{\equiv}CCO_2Me$ or by the reaction of complex **1** with $NaBH_4$: both routes yield **2′** and **2″** in the same proportions. In order to achieve maximum simplification of the proton-coupled ^{13}C NMR spectrum, we treated [$^2H_6$]**1** with $NaBD_4$ in EtOD, obtaining the two forms of $[Ru(CO)_2\{C(CO_2CD_3)=C(CO_2CD_3)H\}D(PMe_2Ph)_2]$, [$^2H_7$]**2**. The chemical shifts for the ^{31}P nuclei (δ 4.7 [$^2H_7$]**2′** and 6.1 [$^2H_7$]**2″**) were virtually identical with those for **2′** and **2″**, but the resonances showed triplet splittings [$|^2J(P–D)|$ = 3.1 and 2.7 Hz, respectively] due to the deuteride ligand. Given that γ_D/γ_H = 0.153, these values agree with those of 22.3 and 20.1 Hz for $|^2J(P–H)|$ obtained from the ^{1}H NMR spectrum of **2′** and **2″**. All the expected resonances were observed in the ^{1}H NMR spectrum of [$^2H_7$]**2**.

In the proton-coupled ^{13}C NMR spectrum of [$^2H_7$]**2**, the resonances for α-CO_2CD_3 were doublets of triplets at δ 181.0 [$^2H_7$]**2′** and 181.4 [$^2H_7$]**2″**. For both, the doublet splitting $|^3J(C–H)|$ was 10.4 Hz. This established that in both **2′** and **2″** the α-carboxylate group and the β-hydrogen in the vinyl ligand are mutually *cis*, and hence (*i*) the stereochemistry of the vinyl ligand is unaltered when **1** is converted into **2** and (*ii*) the Ru–H bond in $[Ru(CO)_2H_2(PMe_2Ph)_2]$ adds *trans* to $MeO_2CC{\equiv}CCO_2Me$. Evidently **2′** and **2″** are conformers rather than geometrical isomers. Likely structures, consistent with the observation that each contains two equivalent PMe_2Ph ligands, are shown below, where L = PMe_2Ph. The decision as to which structure represents which conformer is based on the observation of long-range coupling [$|^4J(H–H)|$ = 1.4 Hz] between the hydride ligand and the vinyl proton for **2′** but not for **2″**. In the conformation assigned to **2′** the bonds between the two nuclei lie in the 'W' conformation which has been found to give rise to long-range coupling in organic[9] and organometallic[10] species.



2′



2″

As in the case of complex [$^2H_6$]**1**, the resonances for one carbonyl ligand (δ 201.4 [$^2H_7$]**2′** and 200.7 [$^2H_7$]**2″**) showed doublet splittings [$|^4J(C–H)|$ = 2.5 and 2.0 Hz, respectively] caused by the vinyl proton, and these resonances were assigned to the carbonyl *trans* to the vinyl ligand. In both the ^{13}C-{^{1}H} and ^{13}C NMR spectra, the resonances for the other carbonyl were split by the deuteride ligand.

The reaction between $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ and $MeO_2CC{\equiv}CCO_2Me$ was also investigated, and the product, $[Ru(CO)\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_3]$ **3**, was isolated and characterized. The ^{31}P-{^{1}H} NMR spectrum of **3** was distorted by second-order effects but was successfully simulated. The pattern of resonances in both the ^{31}P-{^{1}H} and ^{1}H NMR spectra indicated that the three PMe_2Ph ligands were in the *mer* arrangement. The positions of the remaining ligands were

Table 2 Proton NMR spectra of complexes [a]

Complex	δ	Assignment	Coupling constants/Hz	Assignment
1	6.79 (t, 1)	β-H	3.0	$\lvert {}^4J(P-H) \rvert$
	3.67 (s, 3)	CO_2Me		
	3.42 (s, 3)	CO_2Me		
	1.82 (t, 6)	PMe_2Ph	8.7	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.80 (t, 6)	PMe_2Ph	8.2	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
1a	6.73 (s, 1)	β-H		
	3.62 (s, 1)	CO_2Me		
	3.34 (s, 1)	CO_2Me		
	1.75 (s, 6)	$AsMe_2Ph$		
	1.71 (s, 6)	$AsMe_2Ph$		
2	6.78 (dt, 1)	β-H (**2′**)	1.4, 3.4	$\lvert {}^4J(H-H) \rvert$, $\lvert {}^4J(P-H) \rvert$
	6.72 (t, 1)	β-H (**2″**)	3.2	$\lvert {}^4J(P-H) \rvert$
	3.52 (s, 3)	CO_2Me (**2″**)		
	3.49 (s, 3)	CO_2Me (**2′**)		
	3.47 (s, 3)	CO_2Me (**2′**)		
	3.24 (s, 3)	CO_2Me (**2″**)		
	ca. 1.7[b]	PMe_2Ph		
	−5.41 (t, 1)	RuH (**2′**)	22.3	$\lvert {}^2J(P-H) \rvert$
	−6.17 (t, 1)	RuH (**2″**)	20.1	$\lvert {}^2J(P-H) \rvert$
3	7.57 (dt, 1)	β-H	6.1, 2.4	$\lvert {}^4J(P-H) \rvert$, $\lvert {}^4J(P-H) \rvert$
	3.98 (s, 3)	CO_2Me		
	3.50 (s, 3)	CO_2Me		
	1.66 (t, 12)[c]	PMe_2Ph	8.2	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.00 (d, 6)	PMe_2Ph	8.0	$\lvert {}^2J(P-H) \rvert$
4	6.72 (dt, 1)	β-H	8.7, 3.0	$\lvert {}^4J(P-H) \rvert$, $\lvert {}^4J(P-H) \rvert$
	3.67 (s, 3)	CO_2Me		
	3.49 (s, 3)	CO_2Me		
	1.89 (t, 6)	PMe_2Ph	8.4	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.76 (t, 6)	PMe_2Ph	8.3	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.15 (d, 6)	PMe_2Ph	8.0	$\lvert {}^2J(P-H) \rvert$
5	6.30 (t, 1)	β-H	1.5	$\lvert {}^4J(P-H) \rvert$
	3.49 (s, 3)	CO_2Me		
	2.78 (s, 3)	CO_2Me		
	1.72 (t, 6)	PMe_2Ph	7.8	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.53 (t, 6)	PMe_2Ph	6.9	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
6	7.19 (t, 1)	β-H	2.9	$\lvert {}^4J(P-H) \rvert$
	3.45 (s, 3)	CO_2Me		
	1.37 (t, 6)	PMe_2Ph	7.6	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.30 (t, 6)	PMe_2Ph	8.1	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
8[d]	3.95 (s, 3)	CO_2Me		
	3.89 (s, 3)	CO_2Me		
	1.72 (d, 3)	PMe_2Ph	9.1	$\lvert {}^2J(P-H) \rvert$
	1.70 (d, 3)	PMe_2Ph	8.6	$\lvert {}^2J(P-H) \rvert$
	1.45 (d, 3)	PMe_2Ph	9.7	$\lvert {}^2J(P-H) \rvert$
	1.37 (d, 3)	PMe_2Ph	9.8	$\lvert {}^2J(P-H) \rvert$
9[d]	3.84 (s, 3)	CO_2Me		
	3.10 (s, 3)	CO_2Me		
	1.85 (t, 6)	PMe_2Ph	8.0	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$
	1.79 (t, 6)	PMe_2Ph	8.0	$\lvert {}^2J(P-H) + {}^4J(P-H) \rvert$

[a] In C_6D_6 solution unless stated otherwise. Resonances due to phenyl protons are not included. [b] Overlapping resonances. [c] Accidental coincidence of two resonances. [d] In $CDCl_3$ solution.

established by the ^{13}C-$\{^1H\}$ NMR spectrum, which contained doublet of triplets resonances for the carbonyl ligand and the α-carbon in the vinyl ligand. For the former, the values of $\lvert {}^2J(P-C) \rvert$ were 13.9 and 11.8 Hz, respectively, indicating that this ligand is *cis* to all three PMe_2Ph ligands; for the latter the values were 71.0 and 13.4 Hz, confirming that the vinyl ligand is *trans* to the unique PMe_2Ph ligand. One surprising feature of the ^1H NMR spectrum of complex **3** was a doubling of the $CO_2\mathit{Me}$ resonances, with strong singlets at δ 3.98 and 3.50 and weaker ones (about one-quarter intensity) at δ 4.02 and 3.52. No other resonance showed this effect, so if it indicates the presence in solution of two conformers of **3**, it seems likely that they differ only as a result of restricted rotation of one or both CO_2Me groups about their bonds to the rest of the vinyl ligand.

A sample of $[Ru(CO)\{C(CO_2CD_3){=}C(CO_2CD_3)H\}Cl(PMe_2Ph)_3]$, $[^2H_6]$**3**, was prepared from $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ and $CD_3O_2CC{\equiv}CCO_2CD_3$. In the proton-coupled ^{13}C NMR spectrum of $[^2H_6]$**3**, the resonance at δ 164.0 for β-CO_2CD_3 showed the expected small geminal splitting $[\lvert {}^2J(C-H) \rvert = 2.0$ Hz$]$ by the β-hydrogen, but for the α-CO_2CD_3 resonance at δ 180.4 the value of $\lvert {}^3J(C-H) \rvert$ was 14.8 Hz, indicating that the Ru–H bond in $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ adds *cis* to $MeO_2CC{\equiv}CCO_2Me$, and that **3** has the structure shown below, where L = PMe_2Ph.

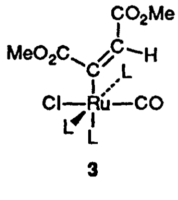


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Table 3 Carbon-13 NMR spectra of complexes [a]

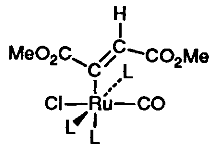
Complex	δ	Assignment	Coupling constants/Hz	Assignment
1	195.7 (t)	RuCO	12.4	$\lvert ^2J(\mathrm{P-C})\rvert$
	194.7 (t)	RuCO	9.5	$\lvert ^2J(\mathrm{P-C})\rvert$
	182.4 (t)	$\mathrm{Ru}C{=}\mathrm{C}$	14.0	$\lvert ^2J(\mathrm{P-C})\rvert$
	178.5 (t)	α-$C\mathrm{O_2Me}$	1.4	$\lvert ^3J(\mathrm{P-C})\rvert$
	169.7 (t)	β-$C\mathrm{O_2Me}$	1.7	$\lvert ^4J(\mathrm{P-C})\rvert$
	127.3 (t)	$\mathrm{RuC}{=}C$	3.9	$\lvert ^3J(\mathrm{P-C})\rvert$
	50.6 (t)	$\mathrm{CO_2}Me$		
	49.8 (s)	$\mathrm{CO_2}Me$		
	14.5 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	33.2	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	13.2 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	32.6	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
1a	195.5 (s)	RuCO		
	194.9 (s)	RuCO		
	181.2 (s)	$\mathrm{Ru}C{=}\mathrm{C}$		
	179.0 (s)	α-$C\mathrm{O_2Me}$		
	169.5 (s)	β-$C\mathrm{O_2Me}$		
	129.1 (s)	$\mathrm{RuC}{=}C$		
	50.7 (s)	$\mathrm{CO_2}Me$		
	50.0 (s)	$\mathrm{CO_2}Me$		
	11.3 (s)	$\mathrm{As}Me_2\mathrm{Ph}$		
	10.2 (s)	$\mathrm{As}Me_2\mathrm{Ph}$		
2	201.4 (t)	RuCO (**2′**)	11.5	$\lvert ^2J(\mathrm{P-C})\rvert$
	200.7 (t)	RuCO (**2″**)	11.5	$\lvert ^2J(\mathrm{P-C})\rvert$
	197.5 (t)	RuCO	11.0	$\lvert ^2J(\mathrm{P-C})\rvert$
	197.3 (t)	RuCO	11.0	$\lvert ^2J(\mathrm{P-C})\rvert$
	181.4 (t)	α-$C\mathrm{O_2Me}$ (**2″**)	<2.0	$\lvert ^3J(\mathrm{P-C})\rvert$
	181.0 (t)	α-$C\mathrm{O_2Me}$ (**2″**)	<2.0	$\lvert ^3J(\mathrm{P-C})\rvert$
	179.4 (t)	$\mathrm{Ru}C{=}\mathrm{C}$ (**2″**)	15.6	$\lvert ^2J(\mathrm{P-C})\rvert$
	174.0 (t)	$\mathrm{Ru}C{=}\mathrm{C}$ (**2′**)	15.5	$\lvert ^2J(\mathrm{P-C})\rvert$
	170.3 (t)	β-$C\mathrm{O_2Me}$ (**2′**)	1.7	$\lvert ^4J(\mathrm{P-C})\rvert$
	170.1 (t)	β-$C\mathrm{O_2Me}$ (**2″**)	2.0	$\lvert ^4J(\mathrm{P-C})\rvert$
	128.9 (t)	$\mathrm{RuC}{=}C$ (**2′**)	4.8	$\lvert ^3J(\mathrm{P-C})\rvert$
	126.1 (t)	$\mathrm{RuC}{=}C$ (**2″**)	4.2	$\lvert ^3J(\mathrm{P-C})\rvert$
	50.5 (s)	$\mathrm{CO_2}Me$ (**2″**)		
	50.4 (s)	$\mathrm{CO_2}Me$ (**2′**)		
	50.4 (s)	$\mathrm{CO_2}Me$ (**2″**)		
	50.3 (s)	$\mathrm{CO_2}Me$ (**2′**)		
	19.9 (t)	$\mathrm{P}Me_2\mathrm{Ph}$ (**2′**)	34.6	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	19.2 (t)	$\mathrm{P}Me_2\mathrm{Ph}$ (**2″**)	33.4	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	18.8 (t)	$\mathrm{P}Me_2\mathrm{Ph}$ (**2″**)	31.5	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	17.6 (t)	$\mathrm{P}Me_2\mathrm{Ph}$ (**2′**)	31.7	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
3	202.3 (dt)	RuCO	13.9, 11.8	$\lvert ^2J(\mathrm{P-C})\rvert$, $\lvert ^2J(\mathrm{P-C})\rvert$
	182.9 (dt)	$\mathrm{Ru}C{=}\mathrm{C}$	71.0, 13.4	$\lvert ^2J(\mathrm{P-C})\rvert$, $\lvert ^2J(\mathrm{P-C})\rvert$
	180.4 (s)	α-$C\mathrm{O_2Me}$		
	164.0 (dt)	β-$C\mathrm{O_2Me}$	8.2, 1.8	$\lvert ^4J(\mathrm{P-C})\rvert$, $\lvert ^4J(\mathrm{P-C})\rvert$
	125.2 (t)	$\mathrm{RuC}{=}C$	3.2	$\lvert ^3J(\mathrm{P-C})\rvert$
	50.3 (s)	$\mathrm{CO_2}Me$		
	50.2 (s)	$\mathrm{CO_2}Me$		
	16.2 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	34.3	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	16.1 (d)	$\mathrm{P}Me_2\mathrm{Ph}$	25.0	$\lvert ^1J(\mathrm{P-C})\rvert$
	14.6 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	29.6	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
4	202.8 (dt)	RuCO	11.7, 14.5	$\lvert ^2J(\mathrm{P-C})\rvert$, $\lvert ^2J(\mathrm{P-C})\rvert$
	187.2 (dt)	$\mathrm{Ru}C{=}\mathrm{C}$	77.0, 14.7	$\lvert ^2J(\mathrm{P-C})\rvert$, $\lvert ^2J(\mathrm{P-C})\rvert$
	179.5 (d)	α-$C\mathrm{O_2Me}$	6.2	$\lvert ^3J(\mathrm{P-C})\rvert$
	170.3 (d)	β-$C\mathrm{O_2Me}$	3.4	$\lvert ^4J(\mathrm{P-C})\rvert$
	127.4 (br)	$\mathrm{RuC}{=}C$		
	49.4 (s)	$\mathrm{CO_2}Me$		
	48.9 (s)	$\mathrm{CO_2}Me$		
	19.8 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	32.6	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	15.2 (d)	$\mathrm{P}Me_2\mathrm{Ph}$	26.2	$\lvert ^1J(\mathrm{P-C})\rvert$
	11.9 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	28.4	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
5	217.1 (t)	$\mathrm{Ru}C{=}\mathrm{C}$	9.5	$\lvert ^2J(\mathrm{P-C})\rvert$
	204.7 (t)	RuCO	15.0	$\lvert ^2J(\mathrm{P-C})\rvert$
	179.2 (s)	α-$C\mathrm{O_2Me}$		
	174.6 (s)	β-$C\mathrm{O_2Me}$		
	119.6 (t)	$\mathrm{RuC}{=}C$	2.0	$\lvert ^3J(\mathrm{P-C})\rvert$
	52.7 (s)	$\mathrm{CO_2}Me$		
	51.0 (s)	$\mathrm{CO_2}Me$		
	13.6 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	30.8	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$
	13.1 (t)	$\mathrm{P}Me_2\mathrm{Ph}$	31.6	$\lvert ^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C})\rvert$

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constants/Hz	Assignment
6	199.7 (t)	$\mathrm{Ru}\mathit{C}\mathrm{O}$	11.8	$\lvert {}^2J(\mathrm{P{-}C})\rvert$
	194.6 (t)	$\mathrm{Ru}\mathit{C}\mathrm{O}$	9.5	$\lvert {}^2J(\mathrm{P{-}C})\rvert$
	181.6 (s)	$\alpha\text{-}\mathit{C}\mathrm{O_2Me}$		
	176.2 (t)	$\mathrm{Ru}\mathit{C}\mathrm{{=}C}$	14.2	$\lvert {}^2J(\mathrm{P{-}C})\rvert$
	174.3 (s)	$\mathrm{RuO}\mathit{C}$		
	137.3 (t)	$\mathrm{RuC{=}}\mathit{C}$	5.2	$\lvert {}^3J(\mathrm{P{-}C})\rvert$
	51.1 (s)	$\mathrm{CO_2}\mathit{Me}$		
	13.0 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.9	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
	11.6 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	34.3	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
8[b,c]	204.2 (dd)	$\mathrm{Ru}\mathit{C}\mathrm{{=}C}$	73.1, 10.2	$\lvert {}^2J(\mathrm{P{-}C})\rvert, \lvert {}^2J(\mathrm{P{-}C})\rvert$
	203.3 (dd)	$\mathrm{Ru}\mathit{C}\mathrm{O}$	17.0, 13.1	$\lvert {}^2J(\mathrm{P{-}C})\rvert, \lvert {}^2J(\mathrm{P{-}C})\rvert$
	177.1 (d)	$\alpha\text{-}\mathit{C}\mathrm{O_2Me}$	7.0	$\lvert {}^3J(\mathrm{P{-}C})\rvert$
	174.3 (s)	$\beta\text{-}\mathit{C}\mathrm{O_2Me}$		
	54.9 (s)	$\mathrm{CO_2}\mathit{Me}$		
	51.7 (s)	$\mathrm{CO_2}\mathit{Me}$		
	16.7 (dd)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	30.6, 1.4	$\lvert {}^1J(\mathrm{P{-}C})\rvert, \lvert {}^3J(\mathrm{P{-}C})\rvert$
	16.2 (dd)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	29.8, 1.3	$\lvert {}^1J(\mathrm{P{-}C})\rvert, \lvert {}^3J(\mathrm{P{-}C})\rvert$
	15.5 (d)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	30.9	$\lvert {}^1J(\mathrm{P{-}C})\rvert$
	12.6 (d)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	26.2	$\lvert {}^1J(\mathrm{P{-}C})\rvert$
9[b]	202.9 (t)	$\mathrm{Ru}\mathit{C}\mathrm{O}$	9.5	$\lvert {}^2J(\mathrm{P{-}C})\rvert$
	202.9 (t)	$\mathrm{Ru}\mathit{C}\mathrm{{=}C}$	14.7	$\lvert {}^2J(\mathrm{P{-}C})\rvert$
	173.9 (s)	$\mathit{C}\mathrm{O_2Me}$		
	173.4 (s)	$\mathit{C}\mathrm{O_2Me}$		
	128.6 (t)	$\mathrm{RuC{=}}\mathit{C}$	9.3	$\lvert {}^3J(\mathrm{P{-}C})\rvert$
	54.2 (s)	$\mathrm{CO_2}\mathit{Me}$		
	51.3 (s)	$\mathrm{CO_2}\mathit{Me}$		
	13.8 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.5	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
	12.8 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	32.4	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$

[a] In C_6D_6 solution unless stated otherwise. Resonances due to phenyl carbon atoms omitted. [b] In $CDCl_3$ solution. [c] Resonance for RuC=*C* obscured.

Evidently the closely related complexes $[\mathrm{Ru(CO)_2Cl(H)(PMe_2Ph)_2}]$ and $[\mathrm{Ru(CO)Cl(H)(PMe_2Ph)_3}]$ react with $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ to give products, **1** and **3**, in which the vinyl ligand has different geometries. We wished to discover whether conversion of **1** into $[\mathrm{Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_3}]$ would be accompanied by a change in the geometry of the vinyl ligand. In fact the reaction of **1** with $\mathrm{PMe_2Ph}$ at 40 °C in C_6D_6 yielded three products, **4**, **5** and **6**, which were separated by column chromatography and characterized. Complexes **5** and **6**, which were also obtained when **1** was heated on its own at 40 °C in C_6D_6, will be discussed later. Complex **4** gave elemental analysis figures compatible with the desired formula, $[\mathrm{Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_3}]$, but it was *not* identical with **3**, although it resembled **3** in that the three $\mathrm{PMe_2Ph}$ ligands were in a *mer* arrangement, the carbonyl ligand was *cis* to all three and the vinyl ligand was *trans* to the unique $\mathrm{PMe_2Ph}$ ligand. A sample of $[^2H_6]$**4** was obtained by treating $[^2H_6]$**1** with $\mathrm{PMe_2Ph}$, and the proton-coupled ^{13}C NMR spectrum revealed that $\lvert {}^3J(\mathrm{C{-}H})\rvert$ for the α-*C*O$_2$Me was 8.4 Hz, as opposed to 14.8 Hz in the case of $[^2H_6]$**3**. Thus the structure of **4** is as shown below, where L = $\mathrm{PMe_2Ph}$. Evidently the geometry of the vinyl ligand does not alter during the reaction of **1** with $\mathrm{PMe_2Ph}$, and the fact that **4** does not rearrange to **3** under the conditions of the reaction indicates that it cannot be an intermediate in the formation of **3** from $[\mathrm{Ru(CO)Cl(H)(PMe_2Ph)_3}]$ and $\mathrm{MeO_2CC{\equiv}CCO_2Me}$.



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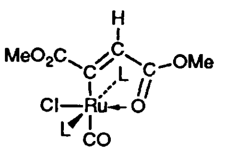

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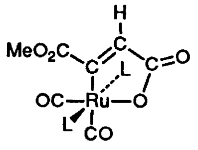


6

Analysis figures for complex **5** suggested the formula $[\mathrm{Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_2}]$, implying that it is formed by loss of a carbonyl ligand from **1**. Spectroscopic data confirmed the presence of equivalent and mutually *trans* $\mathrm{PMe_2Ph}$ ligands and a single carbonyl ligand. Although five-co-ordinate vinyl complexes of ruthenium(II) are known,[11,12] it seems more likely that in the conversion of **1** to **5** the loss of a carbonyl ligand is followed by co-ordination of the conveniently placed β-CO$_2$Me carbonyl oxygen, giving **5** the structure shown below, where L = $\mathrm{PMe_2Ph}$, or a similar structure with the positions of the carbonyl and chloride ligands reversed. An unusual feature of the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **5** is the high chemical shift (δ 217.1) for the α-carbon in the vinyl ligand. Other complexes[13–15] containing five-membered ring systems M–C=C–C=O show the same effect, with chemical shifts ranging from δ 198.8 for $[\mathrm{Ir\{CH{=}CHC(O)Me\}Cl(H)\{P(CHMe_2)_3\}_2}]$[13] to δ 263.7 for $[\mathrm{Cr(CO)_2(\eta^5\text{-}C_5Me_5)\{CH{=}CHC(O)Me\}}]$.[15] Remembering that chemical shifts for carbene carbon atoms in metal complexes are very high (typically[16] δ 270–360), the values may reflect significant contributions to the bonding from the canonical structure M=C–C=C–O.

Complex **6** could not be obtained in crystalline form. Spectroscopic evidence established the presence of two mutually *trans* $\mathrm{PMe_2Ph}$ ligands and two mutually *cis* and inequivalent carbonyl ligands. All of the expected resonances for the vinyl ligand $\mathrm{C(CO_2Me){=}C(CO_2Me)H}$ were identified in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra, except that there was only *one* resonance in each spectrum attributable to a CO$_2$Me methyl group. In view of the strong similarities between the spectra of **6** and those of $[Ru(CO)_2\{C(CO_2Me){=}C(COO)Ph\}(PMe_2Ph)_2]$,[17] we concluded that **6** was probably $[Ru(CO)_2\{C(CO_2Me){=}C(COO)H\}(PMe_2Ph)_2]$ (see structure above, where L = PMe_2Ph), formed by elimination of MeCl from **1**.

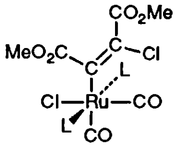
Just as Ru–H bonds may add either *cis* or *trans* to $MeO_2CC{\equiv}CCO_2Me$, so the same appears to be true of Ru–Cl bonds. We have shown[18] that the reaction between *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and the alkyne involves *cis* addition, yielding $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ of structure **7** (see below, where L = PMe_2Ph). The results of treating $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$[19] with $MeO_2CC{\equiv}CCO_2Me$ were, however, quite different. Ethene was slowly liberated, and two new complexes, **8** and **9**, were obtained. These were separated by column chromatography, but complete purification of **8** was hampered by its slow conversion to **9**, of which it appears to be an isomer. Elemental analysis of **9** gave results which agreed with the formula $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$, and spectroscopic data confirmed the presence of mutually *trans* PMe_2Ph ligands, a single carbonyl and the vinyl ligand. As in the case of the closely related complex **5**, however, it seems likely that the vinyl ligand is bidentate, as shown below or with the positions of the carbonyl and chloride ligands reversed. In support of this formulation, the chemical shift for the α-carbon atom in the vinyl ligand is δ 202.9 as opposed to 177.7 for complex **7**.

If complex **8** is indeed an isomer of **9**, its structure must be as shown below (or with the positions of the carbonyl ligand and the phosphine *trans* to the CO_2Me group interchanged). The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows the two PMe_2Ph ligands to be inequivalent and the value for $|^2J(P\text{–}P)|$, 23.0 Hz, is typical for mutually *cis* PMe_2Ph ligands in a ruthenium(II) complex. From the $^{13}C\text{-}\{^1H\}$ spectrum it is evident that the carbonyl ligand is *cis* to both PMe_2Ph ligands and that the α-carbon in the vinyl ligand is *trans* to one PMe_2Ph and *cis* to the other. Again the chemical shift for this atom is unusually high (δ 204.2), in keeping with the presence of the $Ru\text{–}C{=}C\text{–}C{=}O$ ring system.

Evidently $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$, unlike *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, reacts with $MeO_2CC{\equiv}CCO_2Me$ to give a *trans*-addition product. The other intriguing feature of the reaction is that **8** is formed at all, given that **9** is clearly more stable than **8** and resembles $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ in containing mutually *trans* PMe_2Ph ligands. A clue to the reason for the formation of **8** is provided by the appearance and subsequent disappearance of the dimeric species $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$ of structure **10**[20] during the reaction. A reasonable mechanism for the formation of **8** and **9** would involve initial dissociation of C_2H_4 from $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ and (reversible) dimerization of the fragment $[Ru(CO)Cl_2(PMe_2Ph)_2]$ evidently competes with its reaction with the alkyne. The formation of both **8** and **10** implies that the preferred structure for $[Ru(CO)Cl_2(PMe_2Ph)_2]$ is either a trigonal bipyramid with equatorial rather than axial PMe_2Ph ligands or a square pyramid in which these ligands are mutually *cis*.[20]

Conclusion

The rapidity of the reactions between $MeO_2CC{\equiv}CCO_2Me$ and the ruthenium hydride complexes, particularly $[Ru(CO)_2H_2(PMe_2Ph)_2]$, is at odds with a mechanism involving initial ligand substitution to yield an η^2-alkyne complex. Study of the exchange of the carbonyl ligands in $[Ru(CO)_2H_2(PMe_3)_2]$ with ^{13}CO has demonstrated[21] that any dissociation of the carbonyl ligands must be extremely slow at ambient temperature, and conversion of $[Ru(CO)_2D_2(PMe_2Ph)_2]$ into $[Ru(CO)_2H_2(PMe_2Ph)_2]$ by treatment with H_2 is also slow.[22] There is no evidence to indicate that the PMe_2Ph ligands in the dihydride complex are labile.



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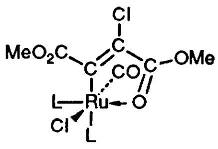

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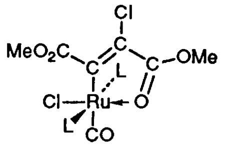

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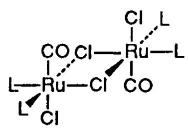
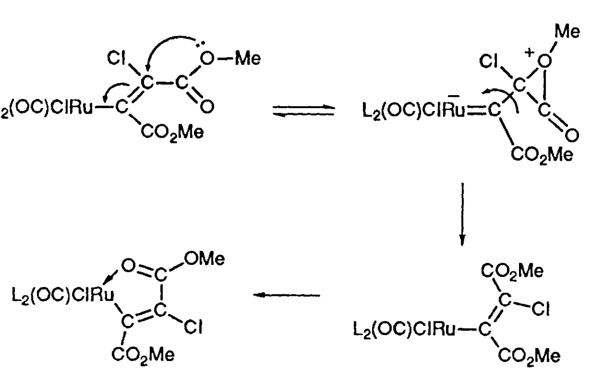


10

A more likely mechanism for these reactions is that suggested by Clark *et al.*[5] and Jones *et al.*,[6] which involves an initial one-electron reduction of the alkyne by the metal complex followed by proton transfer, yielding a five-co-ordinate ruthenium(I) species and the vinyl radical $^{\bullet}C(CO_2Me){=}C(CO_2Me)H$ which combine in the final step. There appears to be some debate as to whether vinyl radicals adopt a Y shape or exist in two isomeric forms separated by a low energy barrier.[23,24]

In either case, the possibility arises of metal attack to give complexes containing vinyl groups in which the CO_2R substituents are either *cis* or *trans*,[6] and the surprising feature of these reactions is not that products with both stereochemistries are obtained but that each of the ruthenium complexes investigated gives a single isomer of the product rather than a mixture of isomers. Steric factors may play a role in determining stereochemistry. If $\cdot C(CO_2Me){=}C(CO_2Me)H$ does exist as a rapidly equilibrating pair of isomers, the equilibrium may well favour the less crowded isomer in which the CO_2Me groups are mutually *trans*, but attack by the ruthenium on this isomer will be disfavoured by the fact that the CO_2Me substituent on the β carbon of the vinyl radical is on the side of the radical that the metal is attacking. The greater the crowding around the metal, the more severe this problem will become, so it is reasonable that the only complex studied which contains three bulky Group 15 ligands rather than two should also be the only one which yields a product in which the β-CO_2Me substituent is *trans*, not *cis*, to the metal. Similar considerations apply if the radical is Y-shaped: attack on one side leads to the development of an unfavourable interaction between the two CO_2Me substituents, whereas attack on the other is hindered by interaction between the β-CO_2Me substituent and the other ligands on the metal.

It is intriguing that the geometry of Ru–Cl addition to $MeO_2CC{\equiv}CCO_2Me$ appears to be different for *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$. The reaction with *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ requires conditions similar to those used to bring about carbonyl substitution reactions of the complex[20] and is inhibited by CO.[18] These observations, coupled with the formation of a *cis*-addition product, point to initial carbonyl substitution to yield $[Ru(CO)(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)Cl_2(PMe_2Ph)_2]$, four-centre rearrangement to $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$, and rapid attack by CO to give $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$. The ethene ligand in $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ is extremely labile,[25] and this fact, coupled with the formation of $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$ as an intermediate in the reaction with $MeO_2CC{\equiv}CCO_2Me$, suggests that $[Ru(CO)(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)Cl_2(PMe_2Ph)_2]$ is again formed and presumably rearranges by *cis* addition to give $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$. Unlike CO, ethene does not recombine with this species, and it seems most likely that the vinyl ligand now isomerizes. The key to the ready isomerization in this instance is probably the fact that the five-co-ordinate



Scheme 1

$[Ru(CO)\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ is a 16-electron species. Huggins and Bergman[26] have suggested that the isomerization of vinyl complexes of nickel may occur by way of zwitterionic carbene complexes and, as shown in Scheme 1, $[Ru(CO)\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ could rearrange in this manner *via* an 18-electron intermediate. Once rearrangement has occurred, the β-CO_2Me substituent can chelate to the metal. In the reaction between *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $MeO_2CC\equiv CCO_2Me$, the recombination of the five-co-ordinate intermediate with CO is presumably too rapid to allow the rearrangement to occur.

Experimental

Complexes were prepared and purified using dry, oxygen-free solvents. Reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin Elmer PE257 spectrometer, and NMR spectra on either a JEOL FX90Q or a Bruker MSL300 spectrometer.

The syntheses of *cis,mer*-$[Ru(CO)Cl_2(PMe_2Ph)_3]$,[20] $[Ru(CO)_2Cl(H)L_2]$ (L = PMe_2Ph or $AsMe_2Ph$),[22] $[Ru(CO)_2H_2(PMe_2Ph)_2]$,[22] $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$[20] and $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}X(PMe_2Ph)_2]$ (X = Cl or H)[1] have been described in previous papers.

Preparations.—$CD_3O_2CC\equiv CCO_2CD_3$. A solution of $HO_2CC\equiv CCO_2H$ (5.00 g) and D_2SO_4 (30 mm^3) in CD_3OD (10 cm^3) was heated under reflux for 16 h. After addition of water (10 cm^3), the product was extracted with Et_2O (5 × 10 cm^3). The extracts were combined, washed with water (5 × 10 cm^3) and dried over $MgSO_4$. Evaporation of the Et_2O under a stream of N_2 left $CD_3O_2CC\equiv CCO_2CD_3$ as a pale yellow liquid. A ^{13}C NMR spectrum of the product provided no evidence of the presence of impurities and the alkyne was used without further purification.

$[Ru(CO)_2\{C(CO_2CD_3)=C(CO_2CD_3)H\}Cl(PMe_2Ph)_2]$ $[^2H_6]$**1**. A solution of $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ (0.03 g) in C_6D_6 (0.3 cm^3) was treated with $CD_3O_2CC\equiv CCO_2CD_3$ (5 mm^3). The reaction was monitored by NMR spectroscopy and further small quantities of the alkyne were added at intervals until no $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ remained. The product was isolated as pale yellow crystals on removal of the solvent and addition of pentane (2 cm^3).

$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}Cl(AsMe_2Ph)_2]$ **1a**. This was prepared from $[Ru(CO)_2Cl(H)(AsMe_2Ph)_2]$ and $MeO_2CC\equiv CCO_2Me$ in C_6D_6 solution by the same technique as that described for $[^2H_6]$**1**, but was not isolated from solution.

$[Ru(CO)_2\{C(CO_2CD_3)=C(CO_2CD_3)H\}D(PMe_2Ph)_2]$ $[^2H_7]$**2**. A mixture of $[^2H_6]$**1** (0.02 g) and $NaBD_4$ (0.01 g) was stirred in EtOD (5 cm^3) for 5 min. The solvent was then removed under reduced pressure and the product extracted from the residue with C_6H_6 (5 cm^3). Removal of C_6H_6 under reduced pressure yielded $[^2H_7]$**2** as a yellow oil which could not be induced to crystallize.

$[Ru(CO)\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_3]$ **3**. The complex *cis,mer*-$[Ru(CO)Cl_2(PMe_2Ph)_3]$ (0.32 g) was stirred with $NaBH_4$ (0.20 g) in ethanol (20 cm^3) for 24 h. The solvent was removed under reduced pressure, and the ruthenium product extracted from the residue with C_6H_6 (5 cm^3). Removal of the C_6H_6 under reduced pressure left a yellow oil. This was treated with 2 cm^3 of a 1 : 1 mixture of ethanol and pentane and cooled to 0 °C. Slow concentration of the solution under a stream of nitrogen yielded colourless crystals of $[Ru(CO)Cl(H)(PMe_2Ph)_3]$.

A solution of $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ (0.2 g) in C_6D_6 (0.3 cm^3) was treated with $MeO_2CC\equiv CCO_2Me$ (63 mm^3), added in small portions. The reaction was monitored by NMR spectroscopy. When no $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ remained, the reaction mixture was subjected to column chromatography on neutral alumina. The column was eluted with Et_2O, CH_2Cl_2 and then $CHCl_3$. The $CHCl_3$ fraction was evaporated to dryness under reduced pressure, leaving **3**, which was solidified by treatment with a 1 : 1 : 1 mixture of EtOH, $CHCl_3$ and heptane and obtained as colourless crystals by recrystallization from EtOH (Found: C, 51.40; H, 5.45. Calc. for $C_{31}H_{40}ClO_5P_3Ru$: C, 51.65; H, 5.60%).

$[Ru(CO)\{C(CO_2CD_3)=C(CO_2CD_3)H\}Cl(PMe_2Ph)_3]$ $[^2H_6]$**3**. This was prepared in the same way as **3** from $[Ru(CO)Cl(H)(PMe_2Ph)_3]$ and $CD_3O_2CC\equiv CCO_2CD_3$.

Reaction of complex **1** *with* PMe_2Ph. A solution of complex **1** (0.10 g) and PMe_2Ph (20 mm^3) in C_6D_6 (0.3 cm^3) was heated at 40 °C. After 5 h, the ^1H NMR spectrum of the solution showed that none of complex **1** remained and the reaction mixture was subjected to column chromatography on neutral alumina. After successive elution with pentane, C_6H_6 and CH_2Cl_2, none of which removed ruthenium-containing products, elution with $CHCl_3$ removed all three products, **4**, **5** and **6**, and achieved reasonable separation of the three. Complex **4** was isolated as colourless crystals by removing solvent from the appropriate fraction under reduced pressure and treating the residue with EtOH (Found: C, 51.30; H, 5.70. Calc. for $C_{31}H_{40}ClO_5P_3Ru$: C, 51.55; H, 5.60%).

Complex **5** was obtained as yellow crystals by the same technique (Found: C, 47.60; H, 4.95. Calc. for $C_{23}H_{29}ClO_5P_2Ru$: C, 47.30; H, 5.00%). The complex was also prepared by heating **1** (0.05 g) in C_6D_6 (0.3 cm^3) at 50 °C for 5 h. The yellow solid remaining after removal of the C_6D_6 was recrystallized from ethanol.

Complex **6** was recovered from the appropriate $CHCl_3$ fraction, but could not be obtained in crystalline form.

$[Ru(CO)\{C(CO_2CD_3)=C(CO_2CD_3)H\}Cl(PMe_2Ph)_3]$ $[^2H_6]$**4**. This was prepared in the same way as **4** from $[^2H_6]$**1** and PMe_2Ph.

$[Ru(CO)\{C(CO_2Me)=C(COOMe)Cl\}Cl(PMe_2Ph)_2]$, **8** *and* **9**. The reaction of $[Ru(CO)(\eta^2\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ (0.02 g) and $MeO_2CC\equiv CCO_2Me$ (20 mm^3) in $CDCl_3$ (0.3 cm^3) at room temperature was monitored by ^1H NMR spectroscopy. When conversion to **8** and **9** was complete, the mixture of products was subjected to chromatography on acid-washed alumina. Following elution with pentane, C_6H_6, CH_2Cl_2 and $CHCl_3$, which removed only organic materials and a little $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, elution with Me_2CO yielded **8**. The slow conversion of **8** into **9** prevented us from isolating it in pure crystalline form.

Complex **9** was obtained by elution with EtOH. After removal of the solvent under reduced pressure, the oily residue was treated with a 1 : 1 mixture of methanol and heptane, yielding **9** as yellow crystals (Found: C, 44.85; H, 4.40. Calc. for $C_{23}H_{28}Cl_2O_5P_2Ru$: C, 44.65; H, 4.55%).

Acknowledgements

We thank the SERC and BP Chemicals for financial support through a CASE award to J. D. V., and Professor W. D. Jones for helpful discussions.

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Received 1st *April* 1992; *Paper* 2/01718K