Alkyne Insertion into Ruthenium–Carbon Bonds: Formation and Ring-closing Reactions of Vinyl Complexes

Joseph R. Crook
Department of Chemistry, Western Washington University, Bellingham, WA 98225, U.S.A.
Barbara Chamberlain and Roger J. Mawby *
Department of Chemistry, The University of York, York YO1 5DD

Compounds $[Ru(CO)_2(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ [(**1a**), X = H; (**1b**), X = Cl; (**1c**), X = Me; (**1d**), X = OMe] react with $MeO_2CC{\equiv}CCO_2Me$ to yield vinyl complexes $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)(C_6H_4X\text{-}4)\}Cl(PMe_2Ph)_2]$ (**2a**)—(**2d**). The mechanism of formation appears to involve CO substitution by the alkyne, combination of alkyne and aryl ligands, and finally re-entry of CO. Thermal decomposition of (**2a**)—(**2d**) yields products $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)(C_6H_3X)\}(PMe_2Ph)_2]$ (**3a**)—(**3d**), complexes (**4a**)—(**4d**) whose structure is either $[Ru(CO)_2\{C(CO_2Me){=}C(COO)(C_6H_4X\text{-}4)\}(PMe_2Ph)_2]$ or $[Ru(CO)_2\{C(COO){=}C(CO_2Me)(C_6H_4X\text{-}4)\}(PMe_2Ph)_2]$, alkenes $CH(CO_2Me){=}C(CO_2Me)(C_6H_4X\text{-}4)$ (**5a**)—(**5d**), and *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$. Complex (**3a**) is also obtained from $[Ru(CO)_2(Me)Ph(PMe_2Ph)_2]$ and $MeO_2CC{\equiv}CCO_2Me$, while the reaction of $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ with $MeO_2CC{\equiv}CCO_2Me$ yields $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Me\}Me(PMe_2Ph)_2]$ (**6**).

Some time ago we described reactions involving the insertion of alkynes into metal–chlorine bonds of ruthenium(II) complexes.[1] Alkynes are also known to insert into transition metal–alkyl and aryl bonds. Thus $[Ni(Ph)Br(PPh_3)_2]$ has been shown to react with $MeC{\equiv}CMe$ to yield $[Ni(CMe{=}CMePh)Br(PPh_3)_2]$,[2] while $[Ni(CPh{=}CMePh)(acac)(PPh_3)]$ (acac = acetylacetonate) has been obtained from $[NiMe(acac)PPh_3]$ and $PhC{\equiv}CPh$.[3] Insertion of $CF_3C{\equiv}CCF_3$ into the metal–methyl bond in the complexes *trans*-$[Pt(Me)X(PMe_2Ph)_2]$ (X = Cl, Br, or I) has been reported,[4] and there are other examples of the insertion of this alkyne and of $MeO_2CC{\equiv}CCO_2Me$ into platinum–methyl bonds.[5,6]

In this paper, we report on a study of the reactions of a variety of organo-ruthenium(II) complexes with the alkyne $MeO_2CC{\equiv}CCO_2Me$. Several of the complexes used contained both a chloride ligand and an organic ligand, allowing us to determine whether alkyne insertion occurred preferentially into the Ru–Cl or Ru–C bond.

Results and Discussion

Details of the i.r., ^1H n.m.r., and ^{13}C n.m.r. spectra of the products of the reactions described below are given in Tables 1, 2, and 3, respectively. A list of the formulae of the products and of the numbers assigned to them is given in Table 1.

Reactions of the Complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ *with* $MeO_2CC{\equiv}CCO_2Me$.—When a $CHCl_3$ solution of $[Ru(CO)_2PhCl(PMe_2Ph)_2]$ (**1a**) (see Scheme 1; X = H) was warmed with an excess of $MeO_2CC{\equiv}CCO_2Me$ at 323 K, a slow reaction occurred. After several days the solvent was removed, and column chromatography of the residue followed by recrystallization yielded complex (**2a**) in high yield. Elemental analysis showed that (**2a**) contained the two reactants in a 1 : 1 ratio. From n.m.r.† and i.r. spectra it was clear that (**2a**), like (**1a**), contained a pair of mutually *trans* PMe_2Ph ligands and two mutually *cis* and inequivalent carbonyl ligands. We concluded that the alkyne had been inserted into either the metal–chlorine or the metal–phenyl bond of (**1a**).

For (**1a**), the resonance for the phenyl carbon atom attached to the metal (readily identified from a ^{13}C n.m.r. spectrum recorded under conditions of weak noise decoupling) was at δ 157.1 p.p.m., and had a coupling constant to ^{31}P of 15 Hz.[9] For (**2a**), the resonance for the corresponding atom was a triplet at δ 143.1 p.p.m., with a coupling constant to ^{31}P of only 1.1 Hz. We therefore concluded that the alkyne had become inserted into the ruthenium–phenyl bond. The vinylic carbon atoms in the ligand $-C(CO_2Me){=}C(CO_2Me)Ph$ were also coupled to the phosphorus nuclei [$|^2J(P\text{–}C)| = 13.3$, $|^3J(P\text{–}C)| = 3.7$ Hz], and the resonance for one carboxylate carbon atom showed a triplet splitting of 2.1 Hz. The proposed structure for (**2a**) is shown as (**2**) in Scheme 1, where X = H.

The reactions of the substituted phenyl complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ [X = Cl, (**1b**); X = Me, (**1c**); X = OMe, (**1d**)] with $MeO_2CC{\equiv}CCO_2Me$ similarly yielded products shown by elemental analysis and spectroscopic evidence to be of the type $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)(C_6H_4X\text{-}4)\}Cl(PMe_2Ph)_2]$ (**2b**)—(**2d**).

Mechanism of Formation of Complexes (**2a**)—(**2d**).—A possible mechanism for the formation of complexes (**2a**)—(**2d**) is shown in Scheme 1. Evidence for an initial dissociation of CO was provided by the fact that there was *no* reaction between (**1c**) and $MeO_2CC{\equiv}CCO_2Me$ in CO-saturated $CHCl_3$ solution at 323 K. In reactions of (**1a**) with phosphorus ligands L, the ligand L enters *trans* to the phenyl ligand,[9] but in the case of the reaction with $MeO_2CC{\equiv}CCO_2Me$ we assume that the alkyne must enter *cis* to the phenyl ligand. A precedent for this variation in the stereochemistry of carbonyl-substitution reactions of ruthenium(II) complexes according to the nature of the incoming ligand is provided by the reactions of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.[10] In the kinetic products, $[Ru(CO)Cl_2L(PMe_2Ph)_2]$, of reactions of this complex with

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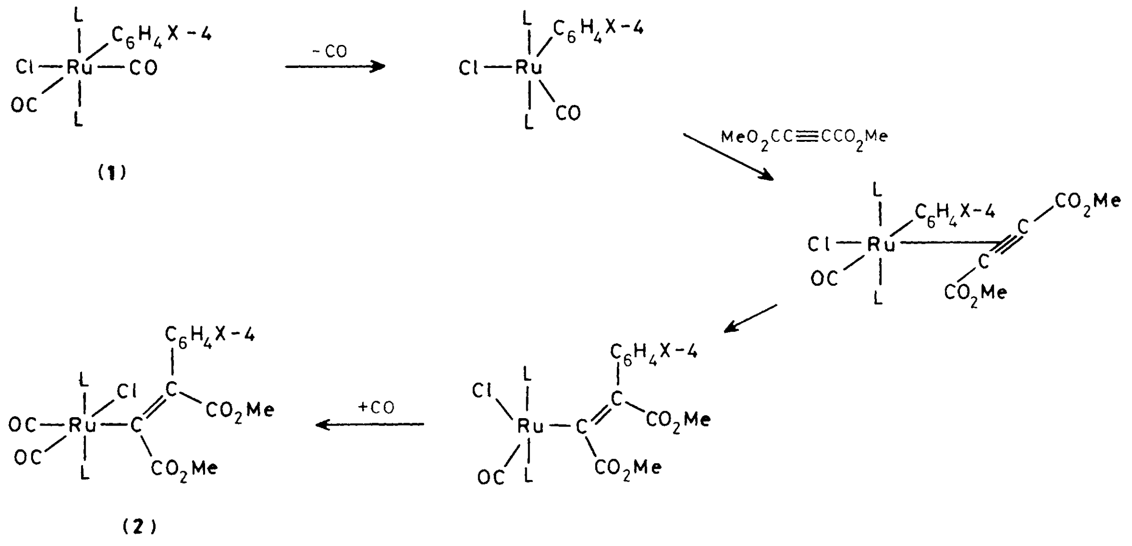
† The ways in which phosphorus ligands may be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[7,8]

Table 1. Infrared spectra of compounds[a]

	Compound	$\nu(C\equiv O)/cm^{-1}$	$\nu(C=O)/cm^{-1}$ [b]
(2a)	$[(Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Ph\}Cl(PMe_2Ph)_2]$	2 054 1 986	1 700
(2b)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4Cl\text{-}4)\}Cl(PMe_2Ph)_2]$	2 053 1 985	1 695
(2c)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4Me\text{-}4)\}Cl(PMe_2Ph)_2]$	2 054 1 986	1 700
(2d)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4OMe\text{-}4)\}Cl(PMe_2Ph)_2]$	2 053 1 983	1 701
(3a)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4)\}(PMe_2Ph)_2]$	2 028 1 968	1 691
(3b)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_3Cl)\}(PMe_2Ph)_2]$	2 028 1 973	1 691
(3c)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_3Me)\}(PMe_2Ph)_2]$	2 028 1 965	1 692
(3d)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_3OMe)\}(PMe_2Ph)_2]$	2 024 1 963	1 688
(4a)	$[Ru(CO)_2\{C(CO_2Me)=C(COO)Ph\}(PMe_2Ph)_2]$	2 052 1 981	1 694
(4b)	$[Ru(CO)_2\{C(CO_2Me)=C(COO)(C_6H_4Cl\text{-}4)\}(PMe_2Ph)_2]$	2 048 1 979	1 694
(4c)	$[Ru(CO)_2\{C(CO_2Me)=C(COO)(C_6H_4Me\text{-}4)\}(PMe_2Ph)_2]$	2 052 1 980	1 695
(4d)	$[Ru(CO)_2\{C(CO_2Me)=C(COO)(C_6H_4OMe\text{-}4)\}(PMe_2Ph)_2]$	2 049 1 979	1 693
(5a)	$CH(CO_2Me)=C(CO_2Me)Ph$		1 736[c]
(5b)	$CH(CO_2Me)=C(CO_2Me)(C_6H_4Cl\text{-}4)$		1 731[c]
(5c)	$CH(CO_2Me)=C(CO_2Me)(C_6H_4Me\text{-}4)$		1 730[c]
(5d)	$CH(CO_2Me)=C(CO_2Me)(C_6H_4OMe\text{-}4)$		1 726[c]
(6)	$[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Me\}Me(PMe_2Ph)_2]$	2 014 1 948	1 688

[a] In $CHCl_3$ solution. [b] All spectra included bands at *ca.* 1 600 cm^{-1}, possibly also due to C=O stretching modes. [c] Broad band with signs of fine structure.



Scheme 1. L = PMe_2Ph; (**1a**), (**2a**), X = H; (**1b**), (**2b**), X = Cl; (**1c**), (**2c**), X = Me; (**1d**), (**2d**), X = OMe

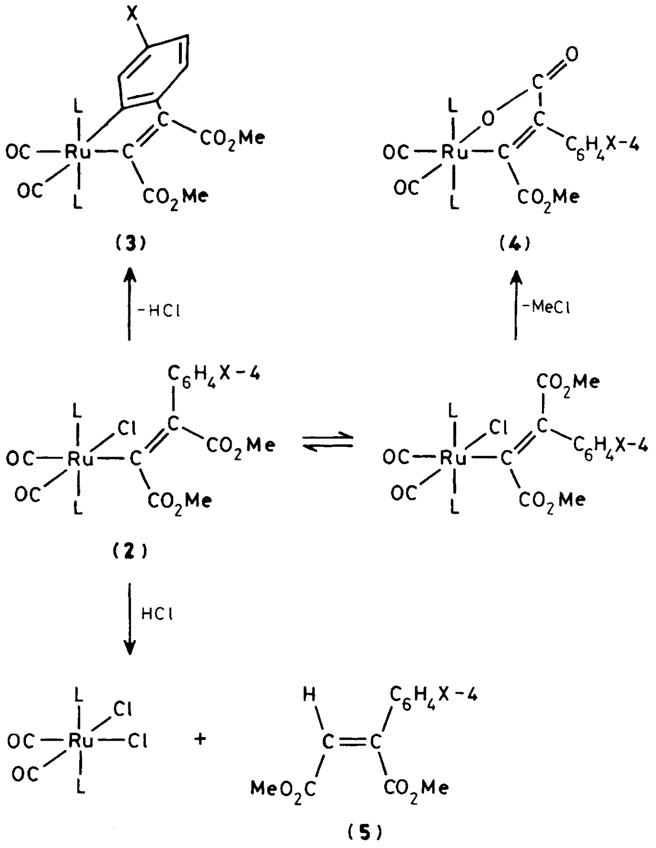
phosphorus ligands, the ligand L is *trans* to CO, but in the complex $[Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_2]$ obtained from the reaction with ethene the ethene ligand is *trans* to chloride, possibly because the *trans*-labilizing effect of CO is too great to allow a stable metal–ethene bond to be formed *trans* to CO.[10] Similar considerations may result in the geometry shown for the proposed intermediates $[Ru(CO)(MeO_2CC\equiv CCO_2Me)(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ in Scheme 1. An attempt to detect the intermediate with X = H by carrying out the reaction between (**1a**) and $MeO_2CC\equiv CCO_2Me$ with a slow stream of N_2 passing through the solution to remove CO was unsuccessful. Conversion of (**1a**) into (**2a**) still occurred in high yield, suggesting that the lifetime of a free CO molecule is extremely short.

Intramolecular rearrangement of these intermediates should result in a *cis* addition of the metal–aryl bond across the alkyne triple bond, as has been shown to be the case for alkyne insertion into a metal–chlorine bond of *trans*-$[Ru(CO)_2Cl_2$-

Table 2. Proton n.m.r. spectra of compounds[a]

Compound	P*Me*$_2$Ph[b]	CO$_2$Me[c]	Other resonances[c]	Assign-ment
(2a)	2.06	3.81		
	1.92	3.53		
(2b)	2.03	3.82		
	1.91	3.54		
(2c)	2.04	3.81	2.11	4-Me
	1.92	3.55		
(2d)	2.04	3.81	3.57	4-MeO
	1.92	3.55		
(3a)[d]	1.54	3.77	7.59 (ddd)	H^6
	1.35	3.73	7.30 (dddt)	H^3
			7.00 (dddt)	H^5
			6.85 (dt)	H^4
(3b)	1.57	3.76		
	1.38	3.74		
(3c)	1.55	3.77	2.22	4-Me
	1.34	3.73		
(3d)	1.56	3.77	3.72	4-MeO
	1.37	3.73		
(4a)	1.87	3.60		
	1.72			
(4b)	1.86	3.62		
	1.72			
(4c)	1.87	3.62	2.30	4-Me
	1.71			
(4d)	1.86	3.62	3.78	4-MeO
	1.71			
(5a)		3.94	6.32	CH
		3.78		
(5b)		3.94	6.29	CH
		3.79		
(5c)		3.93	6.28	CH
		3.67	2.35	4-Me
(5d)		3.95	6.24	CH
		3.78	3.84	4-MeO
(6)	1.73	3.62	1.80 (t)[e]	CMe
	1.69	3.59	−0.60 (t)[f]	RuMe

[a] In CDCl$_3$ solution. Except for (**3a**), resonances due to aromatic ring protons have been omitted. [b] Triplet resonances: $|^2J(\text{P–H}) + {}^4J(\text{P–H})|$ = *ca.* 8 Hz. [c] Singlet resonances unless indicated otherwise. [d] Labelling for orthometallated ring protons is as for carbon atoms (see Table 3): $|J(\text{H}^3\text{–H}^4)| = |J(\text{H}^4\text{–H}^5)| = 7.2$, $|J(\text{H}^3\text{–H}^5)| = 1.3$, $|J(\text{H}^3\text{–H}^6)| = 0.4$, $|J(\text{H}^4\text{–H}^6)| = 1.4$, $|J(\text{H}^5\text{–H}^6)| = 7.8$, $|J(\text{H}^3\text{–P})| = 1.4$, $|J(\text{H}^5\text{–P})| = 1.0$ Hz. [e] $|^5J(\text{P–H})| = 1.8$ Hz. [f] $|^3J(\text{P–H})| = 7.0$ Hz.



Scheme 2. L = PMe$_2$Ph

(PMe$_2$Ph)$_2$],[1] and also for insertion into other metal–alkyl and –aryl bonds.[2,4,6] Interestingly, though, a study of the effect of heating complexes (**2a**)—(**2d**) in solution (see below) has revealed products apparently attributable to further reaction of both the *cis* and the *trans* form of the RuC(CO$_2$Me)=C(CO$_2$Me)(C$_6$H$_4$X-4) unit, suggesting that the two forms may interconvert in solution. Nevertheless it should be stressed that we obtained no direct evidence for the formation of more than one isomer of complexes (**2a**)—(**2d**) in the reactions of (**1a**)—(**1d**) with MeO$_2$CC≡CCO$_2$Me.

Decomposition of Complexes (**2a**)—(**2d**).—During purification of the complexes (**2a**)—(**2d**), it became evident that significant quantities of other materials were present in the crude products. We believed that these probably resulted from thermal decomposition of (**2a**)—(**2d**), and we therefore studied the effect of heat on solutions of the isolated complexes.

Complex (**2a**) decomposed slowly at 323 K in CHCl$_3$ solution. After 40 d none of the complex remained, and, when the residue was subjected to column chromatography, three ruthenium complexes, (**3a**), (**4a**), and the known species *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$],[10] were obtained, together with an organic product (**5a**). Like (**2a**), (**3a**) and (**4a**) possessed mutually *trans* PMe$_2$Ph ligands and mutually *cis* and inequivalent carbonyl ligands. The ^{1}H n.m.r. spectrum of (**3a**), however, contained a complex pattern of aromatic proton resonances, which were assigned by selective decoupling experiments at 360 MHz to the four hydrogens in an *ortho*-disubstituted benzene ring. In the ^{13}C n.m.r. spectrum, separate resonances were observed for all six ring carbons, and two of these (one, at δ 168.8 p.p.m., showing a triplet splitting of 13.3 Hz due to coupling to the phosphorus nuclei) appeared in a spectrum recorded under conditions of weak noise decoupling. We concluded that (**3a**) was the metallacycle [$\overline{\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})\text{=C}(\text{CO}_2\text{Me})(\text{C}}_6\text{H}_4)\}(\text{PMe}_2\text{Ph})_2$] (Scheme 2, X = H). Elemental analysis confirmed the formula of (**3a**). We presume that, as shown in Scheme 2, it is formed by elimination of HCl from (**2a**). The organic product (**5a**) was shown, by comparison of its mass spectrum and ^{1}H and ^{13}C n.m.r. spectra with those of an authentic sample, to be the alkene CH(CO$_2$Me)=C(CO$_2$Me)Ph with the structure shown in Scheme 2. In a separate experiment, we found that treatment of (**2a**) with HCl in CDCl$_3$ at 323 K resulted in formation of *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] and (**5a**), so, as indicated in Scheme 2, the HCl liberated in the formation of (**3a**) may be the cause of the production of *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] and some of (**5a**). The molar ratio in which (**5a**) and *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] were obtained in the decomposition of (**2a**), however, indicated that there might be another route to (**5a**) as well.

Comparison of ^{1}H and ^{13}C n.m.r. spectra indicated that the conversion of (**2a**) into (**4a**) involved loss of a methyl group from one of the –CO$_2$Me substituents. Elemental analysis confirmed this and showed that the chlorine atom in (**2a**) was also lost in the reaction. Thus it appeared that (**4a**) was

Table 3. Carbon-13 n.m.r. spectra (δ/p.p.m., J/Hz) of compounds[a]

Compound	CO	PMe_2Ph[b]	C=C	CO_2	CO_2Me	Aryl group[c]				
						C^1	C^2, C^6	C^3, C^5	C^4	X
(2a)	193.7 (10.1)	15.8 (33.0)	176.7 (13.3)	176.5	51.6	143.1 (1.1)	129.7	127.5	126.9	
	192.5 (11.9)	13.4 (32.0)	137.7 (3.7)	166.1 (2.1)	49.7					
(2b)	193.6 (10.5)	16.1 (33.9)	178.3 (13.5)	176.4	51.7	141.5	131.2	127.7	132.8	
	192.9 (11.5)	13.2 (33.0)	136.7 (3.7)	165.6 (2.0)	49.7					
(2c)	193.7 (10.1)	15.7 (33.9)	176.7 (14.0)	176.6	51.6	140.3	129.7	128.3	136.6	21.1
	192.5 (11.9)	13.5 (32.0)	137.6 (4.6)	166.3 (2.3)	49.7					
(2d)	193.8 (10.5)	15.8 (32.9)	177.3 (13.3)	176.6	51.6	135.9	130.8	113.0	158.7	55.0
	192.4 (11.9)	13.2 (32.0)	137.2 (3.7)	166.3 (2.3)	49.6					
(3a)	199.2 (11.0)	14.3 (32.0)	182.4 (13.3)	178.1	51.1	153.9	168.8 (13.3)	139.9	124.9	
	196.9 (8.7)	14.0 (34.8)	143.2 (4.1)	165.3 (2.3)	50.4		125.1	122.8		
(3b)	198.7 (10.5)	14.7 (33.0)	183.9 (12.8)	178.0	51.2	152.0	172.0 (13.7)	138.5 (1.8)	130.3	
	196.8 (9.2)	13.9 (33.0)	141.8 (3.7)	164.8 (2.3)	50.5		125.8	122.7		
(3c)	199.2 (10.5)	14.5 (33.9)	180.7 (13.3)	178.1	51.1	151.1	168.8 (13.7)	141.0 (2.7)	134.1	21.4
	196.9 (8.7)	13.7 (34.8)	143.2 (4.1)	165.5 (2.7)	50.4		124.4	123.4		
(3d)	199.1 (10.5)	14.5 (33.0)	178.1 (13.0)	178.1	51.2	147.2	171.4 (13.7)	125.4	156.6	54.9
	197.0 (9.1)	13.9 (33.8)	142.9 (4.1)	165.6 (2.3)	50.4		125.2	107.6		
(4a)	198.8 (11.5)	13.4 (31.2)	174.2 (13.3)	180.3 (1.8)	50.7	139.0 (1.8)	128.2	127.6	126.6	
	193.3 (9.6)	12.1 (31.2)	138.4 (5.5)	176.8						
(4b)	198.7 (11.0)	13.6 (32.0)	175.2 (13.3)	180.0 (1.8)	50.8	137.3 (1.8)	129.6	127.8	132.4	
	193.3 (10.1)	12.3 (32.0)	137.1 (5.5)	176.6						
(4c)	198.8 (11.4)	13.4 (32.0)	173.3 (13.7)	180.4	50.6	136.0	128.0	128.3	136.0	21.2
	193.3 (10.1)	12.1 (31.1)	138.2 (5.5)	176.8						
(4d)	198.9 (11.0)	13.5 (29.3)	172.6 (13.0)	180.5 (2.0)	50.7	131.8 (1.5)	129.4	113.2	158.3	55.2
	193.4 (10.0)	12.2 (29.3)	137.9 (5.5)	176.9						
(5a)			148.9	168.2	52.7	133.2	129.0	126.7	130.6	
			117.1	165.3	52.0					
(5b)			147.7	168.0	52.9	131.7	129.4	128.1	136.9	
			117.7	165.2	52.2					
(5c)			148.9	168.4	52.5	130.3	129.7	126.6	141.1	21.2
			115.8	165.5	51.8					
(6)[d]	201.3 (10.5)	15.5 (32.0)	177.5 (15.1)	177.1	51.2					
	196.1 (10.1)	14.4 (31.1)	131.0 (3.6)	166.6 (1.8)	49.1					

[a] In $CDCl_3$ solution. Except where indicated otherwise, figures in parentheses are values of $|J(P–C)|$ for triplet resonances; other resonances were singlets. PMe_2Ph phenyl resonances have been omitted. [b] Figures in parentheses are values of $|^1J(P–C) + {}^3J(P–C)|$. [c] C^1 is attached to C=C; for **(3a)**—**(3d)**, C^2 is attached to Ru. [d] RuMe at δ −8.1 (9.2); C=C*Me* at δ 22.7 p.p.m.

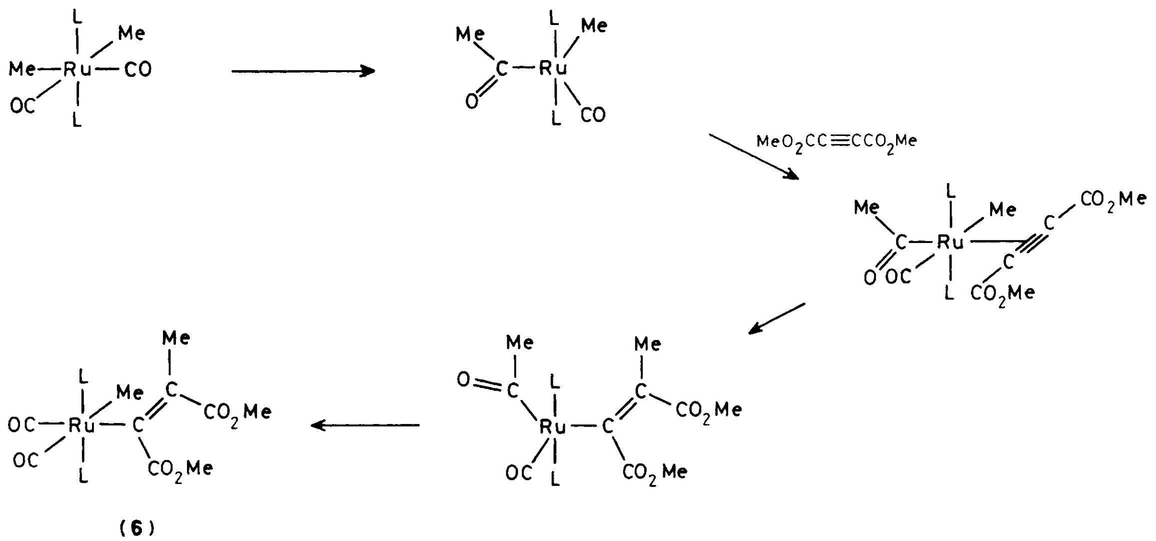
another metallacycle, formed by elimination of MeCl from **(2a)**. In Scheme 2 we have suggested that **(4a)** has the structure $[Ru(CO)_2\{C(CO_2Me)=C(COO)Ph\}(PMe_2Ph)_2]$ [**(4)**, X = H]. For **(4)** to be formed from **(2)**, it is necessary to assume that at 323 K **(2)** is in equilibrium with its isomer in which the two carboxylate groups are mutually *trans* (*i.e.* the species that would be formed by *trans* addition of Ru–Ph across the alkyne). Similar equilibria have been proposed in the case of the reaction of $[NiMe(acac)(PPh_3)]$ with PhC≡CPh,[3] and to rationalize the products obtained by insertion of $MeO_2CC≡CCO_2Me$ into the Pt–Me bond of a bis(1-pyrazolyl)borate complex of platinum(II).[6]

One odd feature of the conversion of **(2a)** into **(4a)** should, however, be mentioned. Comparison of ^{13}C n.m.r. spectra showed that the carboxylate group in **(2a)** involved in the reaction was the one whose carbon atom exhibited coupling to the phosphorus nuclei: arguably this should be the group attached to the α-carbon of the vinyl ligand. This would imply that **(4a)** was $[Ru(CO)_2\{C(COO)=C(CO_2Me)Ph\}(PMe_2Ph)_2]$; in that it contains a four-membered ring, this structure seems less likely than structure **(4)** in Scheme 2, but it can be formed directly from **(2a)**, avoiding the need to postulate an initial *cis* ⟶ *trans* isomerization.

The decompositions of complexes **(2b)**—**(2d)** appeared to follow the same pathways as those for **(2a)**. Ring closure by loss of HCl yielded the complexes $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_3X)\}(PMe_2Ph)_2]$ [X = Cl, **(3b)**; X = Me, **(3c)**; X = OMe, **(3d)**]. The alkenes $CH(CO_2Me)=C(CO_2Me)(C_6H_4X\text{-}4)$ **(5b)**—**(5d)** were obtained, together with *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, and loss of MeCl yielded the species $[Ru(CO)_2\{C(CO_2Me)=C(COO)(C_6H_4X\text{-}4)\}(PMe_2Ph)_2]$ **(4b)**—**(4d)**.

Reactions of Complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ *with* $MeO_2CC≡CCO_2Me$.—The complex $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ was found to react with $MeO_2CC≡CCO_2Me$ in $CHCl_3$ solution within a few days at room temperature to give the product $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Me\}Me(PMe_2Ph)_2]$ **(6)**, which was fully characterized. It was clear from the ^1H and ^{13}C n.m.r. spectra of **(6)** that one methyl ligand remained on the ruthenium: interestingly, a long-range coupling [$|^5J(P–H)|$ = 1.8 Hz] was detected between the phosphorus nuclei and the protons of the methyl group on the β-carbon atom of the vinyl ligand. A key feature of this reaction was that it resulted in insertion of the alkyne into a ruthenium–methyl bond, not into a ruthenium–acetyl bond. There are several recorded instances of reactions of alkynes with other complexes containing both methyl and carbonyl ligands which have yielded products of the latter type, indicating that combination of methyl and carbonyl ligands preceded the alkyne insertion.[11–15]

The complex $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ readily undergoes combination of methyl and carbonyl ligands, yielding acyl



Scheme 3. L = PMe$_2$Ph

products [Ru(CO)(COMe)(Me)L(PMe$_2$Ph)$_2$] when treated with ligands L = CO or CNCMe$_3$.[16] Indeed, as shown in Scheme 3, this is probably the means by which the alkyne is introduced into the co-ordination sphere of the metal, but it is then inserted into the remaining metal–methyl bond rather than into the metal–acetyl bond.

The conditions necessary to obtain (**6**) were milder than those required to convert complexes (**1a**)—(**1d**) into (**2a**)—(**2d**), but even under more forcing conditions and using an excess of MeO$_2$CC≡CCO$_2$Me there was no further reaction involving the remaining methyl ligand in (**6**). Prolonged heating of a CDCl$_3$ solution of (**6**) at 323 K resulted in slow decomposition, but no evidence was obtained for the formation of ruthenium-containing products analogous to (**3a**)—(**3d**) and (**4a**)—(**4d**).

The complex [Ru(CO)$_2$(Me)Cl(PMe$_2$Ph)$_2$], which forms acetyl complexes at a much more rapid rate than does [Ru(CO)$_2$Me$_2$(PMe$_2$Ph)$_2$],[17] failed to yield an insertion product on treatment with MeO$_2$CC≡CCO$_2$Me. No reaction occurred under mild conditions, and decomposition resulted when more forcing conditions were used.

We were unable to isolate either [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)Me}Ph(PMe$_2$Ph)$_2$] or [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)Ph}Me(PMe$_2$Ph)$_2$] from the reaction of [Ru(CO)$_2$(Me)Ph(PMe$_2$Ph)$_2$] with MeO$_2$CC≡CCO$_2$Me in CHCl$_3$ solution. At the temperature (323 K) necessary to bring about reaction, [Ru(CO)$_2$(Me)Ph(PMe$_2$Ph)$_2$] is known to decompose to yield the ketone MeCOPh.[18] This mode of reaction persisted to some extent in the presence of MeO$_2$CC≡CCO$_2$Me. Nevertheless, despite the failure to detect either of the expected alkyne insertion products, we were able to isolate a significant quantity of (**3a**) from the reaction mixture. By analogy with the decomposition of complexes (**2a**)—(**2d**) to (**3a**)—(**3d**), (**3a**) would be a logical product of thermal decomposition of [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)Ph}Me(PMe$_2$Ph)$_2$], by the elimination of methane. Some of the hexa-substituted benzene derivative C$_6$(CO$_2$Me)$_6$ was also isolated from the reaction mixture and fully characterized, but no organoruthenium species which could be regarded as plausible intermediates in the trimerization of the alkyne were detected.

No alkyne insertion product was obtained from the reaction of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$] with MeO$_2$CC≡CCO$_2$Me in CHCl$_3$ solution at 323 K. This complex decomposes on heating in CHCl$_3$ solution in the absence of the alkyne to yield (4-MeC$_6$H$_4$)$_2$CO and the *ortho*-metallated product [Ru(CO){C$_6$H$_3$MeC(O)(C$_6$H$_4$Me)}Cl(PMe$_2$Ph)$_2$],[18] and both these species were among the products obtained in the presence of MeO$_2$CC≡CCO$_2$Me, as was C$_6$(CO$_2$Me)$_6$.

Table 4. Analytical data for ruthenium complexes

Complex	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H
(**2a**)	52.25	4.85	52.35	4.85
(**2b**)	50.00	4.35	49.85	4.45
(**2c**)	52.95	4.95	53.05	5.00
(**2d**)	51.45	4.90	51.85	4.90
(**3a**)	55.20	4.80	55.30	4.95
(**3b**)[a]	52.60	4.60	52.50	4.55
(**3c**)	55.65	5.15	55.95	5.15
(**3d**)	53.60	4.90	54.60	5.05
(**4a**)	54.85	5.05	54.65	4.75
(**4b**)[b]	51.50	4.25	51.85	4.35
(**4c**)	55.75	4.95	55.30	4.95
(**4d**)	53.95	4.95	53.95	4.85
(**6**)	51.30	5.65	51.55	5.65

[a] Cl: Found, 5.40. Calc., 5.15%. [b] Cl: Found, 5.45. Calc., 5.30%.

Conclusions

Our results indicate a clear preference for insertion into ruthenium–carbon rather than ruthenium–chlorine bonds, despite the fact that the latter process is feasible.[1] The chloride ligand is, however, readily eliminated as HCl or MeCl in the formation of metallacyclic products. The fact that insertion into a Ru–Me bond was achieved under milder conditions than those necessary for insertion into Ru–aryl bonds parallels the relative reactivity of ruthenium–methyl and –phenyl complexes towards CO,[19] but part of the reason for the greater reactivity of [Ru(CO)$_2$Me$_2$(PMe$_2$Ph)$_2$] may be the ease with which a co-ordination site can be freed for the attacking alkyne by combination of methyl and carbonyl ligands.

Experimental

Details of the preparations of all the parent ruthenium complexes [Ru(CO)$_2$(R)Cl(PMe$_2$Ph)$_2$)] and [Ru(CO)$_2$(R)R′-

$(PMe_2Ph)_2]$ (R,R′ = alkyl or aryl) have been given in earlier papers.[9,19,20] The light petroleum used in synthetic work had a boiling range of 313—333 K. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^1H and ^{13}C n.m.r. spectra on either a JEOL FX90Q or a Bruker WH360 spectrometer, and mass spectra on an AEI MS30 spectrometer. Unless indicated otherwise, products were colourless. Elemental analysis data for new compounds are given in Table 4.

Synthesis of Complex (**2a**).—A solution of complex (**1a**) (0.50 g) and $MeO_2CC{\equiv}CCO_2Me$ (0.23 cm^3) in $CHCl_3$ (5 cm^3) was kept in a closed flask at 323 K for 14 d. After removal of the solvent under reduced pressure, the crude product was extracted with light petroleum (3 × 3 cm^3) to remove unreacted alkyne. The residue was then treated with Et_2O (2 cm^3) and the minimum quantity of $CHCl_3$ (*ca.* 2 cm^3) required to dissolve all the material. The resulting solution was subjected to chromatography on an alumina column which had been packed using ethoxyethane. Elution was accomplished using mixtures of $CHCl_3$ and Et_2O containing an increasing proportion of $CHCl_3$. Early fractions contained small amounts of unreacted (**1a**) and also of products resulting from the decomposition of (**2a**) (see below). Complex (**2a**) was obtained from a fraction eluted with $CHCl_3$–Et_2O (30:70 v/v), and, after removal of eluant under reduced pressure, was recrystallized from hot ethanol (yield 80%). Later fractions contained a small amount of a further product of decomposition of (**2a**) (see below).

Complexes (**2b**)—(**2d**) were obtained from (**1b**)—(**1d**) by the same procedure, and in similar yield to that achieved for (**2a**).

Decomposition of Complex (**2a**).—A solution of (**2a**) (0.50 g) in $CHCl_3$ (5 cm^3) was heated at 323 K until the ^1H n.m.r. spectrum of the solution indicated that none of the starting material remained (*ca.* 40 d). After removal of the solvent under reduced pressure, the residue was subjected to chromatography under the same conditions as those described above. Early fractions, eluted using $CHCl_3$–Et_2O mixtures containing less than 10% of $CHCl_3$, contained (**3a**), (**5a**), and a small amount of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$. After removal of the eluant under reduced pressure, the alkene (**5a**) was separated from the solid components of the mixture by vacuum distillation on to a cold-finger at 353—373 K and 1 mmHg (*ca.* 133 Pa). The presence of some *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ in the residual solid was confirmed by i.r. and ^1H n.m.r. spectroscopy, but recrystallization of the solid from a mixture of EtOH and water gave (**3a**) uncontaminated by *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.

Later fractions, eluted with $CHCl_3$–Et_2O mixtures containing 50% or more of $CHCl_3$, contained complex (**4a**), which was purified by removal of the eluant under reduced pressure and recrystallization from a mixture of benzene and light petroleum.

The decomposition of complexes (**2b**)—(**2d**) and isolation of (**3b**)—(**3d**), (**4b**)—(**4d**), and (**5b**)—(**5d**) were carried out in the same way. Approximate molar yields, based on the quantities of (**2a**)—(**2d**) used, were (**3a**)—(**3d**) *ca.* 10%, (**4a**)—(**4d**) 40—50%, *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ *ca.* 10%, and (**5a**)—(**5d**) *ca.* 15%, but (**2b**) yielded less of (**4b**) (24%) and rather more (**3b**) (21%) and (**5b**) (25%).

Synthesis of Complex (**6**).—A solution of $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ (0.46 g) and $MeO_2CC{\equiv}CCO_2Me$ (0.18 cm^3) in $CHCl_3$ (5 cm^3) was allowed to stand at ambient temperature for 3 d. The solvent was then removed under reduced pressure, and the crude product was recrystallized from hot ethanol, giving light golden crystals (yield 65%).

Reaction of $[Ru(CO)_2(Me)Ph(PMe_2Ph)_2]$ *with* $MeO_2CC{\equiv}CCO_2Me$.—A solution of $[Ru(CO)_2(Me)Ph(PMe_2Ph)_2]$ (0.89 g) and $MeO_2CC{\equiv}CCO_2Me$ (0.52 cm^3) in $CHCl_3$ (5 cm^3) was kept at 323 K for 22 d. Removal of the solvent under reduced pressure was followed by extraction with light petroleum (3 × 3 cm^3). From this extract the ketone MeCOPh was obtained. Column chromatography of the residue on alumina yielded first unreacted $[Ru(CO)_2(Me)Ph(PMe_2Ph)_2]$ and then complex (**3a**) on elution with $CHCl_3$–Et_2O (10:90 v/v). No other ruthenium-containing products were identified, but the benzene derivative $C_6(CO_2Me)_6$ was obtained on elution with $CHCl_3$–Et_2O (30:70 v/v).

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