Preparation, Structure, and Reactions of Alkenyl Complexes of Ruthenium(II) †

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Complexes *trans*-$[Ru(CO)_2Cl_2L_2]$ (L = PMe_2Ph or $AsMe_2Ph$) react with alkynes $RO_2CC\equiv CCO_2R$ (R = Me or Et) to yield alkenyl complexes $[Ru(CO)_2\{C(CO_2R)=C(CO_2R)Cl\}ClL_2]$. From the structure of $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$, as determined by *X*-ray diffraction, and from kinetic evidence, it would appear that alkyne complexes $[Ru(CO)(RO_2CC\equiv CCO_2R)Cl_2L_2]$ are formed initially, and that the alkyne then undergoes intramolecular nucleophilic attack by a chloride ligand. Unlike the methyl and σ-allyl complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$, which react with PMe_2Ph to form acyl complexes $[Ru(CO)(COR)Cl(PMe_2Ph)_3]$ (R = Me or C_3H_5), the complex $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ undergoes carbonyl substitution to yield $[Ru(CO)\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_3]$. Neither $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ nor the corresponding complex containing a weakly bound ClO_4 ligand in place of chloride reacts with further molecules of alkyne.

In recent papers [1,2] we have shown that ethene complexes of ruthenium(II), $[Ru(CO)(C_2H_4)X_2L_2]$ (X = halogen, L = PMe_2Ph or $AsMe_2Ph$), may be prepared by treatment of *trans*-$[Ru(CO)_2X_2L_2]$ with ethene in solution, and that the ethene ligand in such complexes is susceptible to nucleophilic attack. We decided to determine whether alkyne complexes of ruthenium(II) could be prepared in a similar manner, with the aim of investigating the reactivity of the co-ordinated alkynes.

Results and Discussion

Details of the i.r. and ^1H n.m.r. spectra of all new complexes are given in Table 1, and Table 2 contains details of the ^{13}C n.m.r. spectra of the complexes.

Formation of Complexes.—The reaction of equimolar quantities of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $MeO_2CC\equiv CCO_2Me$ in propanone at 313 K yielded a product, complex (1a), whose i.r. spectrum in $CHCl_3$ solution contained strong bands at 2 058 and 1 986 cm^{-1}. It was at first assumed that one of these bands was due to the C–O stretching mode of a carbonyl ligand, and the other to the triple-bond stretching vibration of the co-ordinated alkyne. For free $MeO_2CC\equiv CCO_2Me$ the $C\equiv C$ stretching frequency is 2 256 cm^{-1}, but the value is always markedly decreased on complex formation.[3] Analytical data for complex (1a) were in reasonable agreement with the figures expected for an alkyne complex of formula $[Ru(CO)(MeO_2CC\equiv CCO_2Me)Cl_2(PMe_2Ph)_2]$, but the ^{13}C n.m.r. spectrum was more complicated than had been expected and could only be reconciled with the above formula by assuming a marked degree of asymmetry in the bonding between metal and alkyne. An *X*-ray investigation of the structure of (1a), aimed at detecting this asymmetry, instead showed that the complex was actually $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ (see below).

Related complexes $[Ru(CO)_2\{C(CO_2R)=C(CO_2R)Cl\}ClL_2]$ [(1b; R = Me, L = $AsMe_2Ph$), (1c; R = Et, L = PMe_2Ph), and (1d; R = Et, L = $AsMe_2Ph$)] were prepared in a similar manner, but treatment of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with other alkynes ($PhC\equiv CPh$, $EtC\equiv CEt$, $PhCOC\equiv CCOPh$, or $HC\equiv CCO_2Et$) simply resulted either in isomerization of the ruthenium complex or in loss of CO to form $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$.

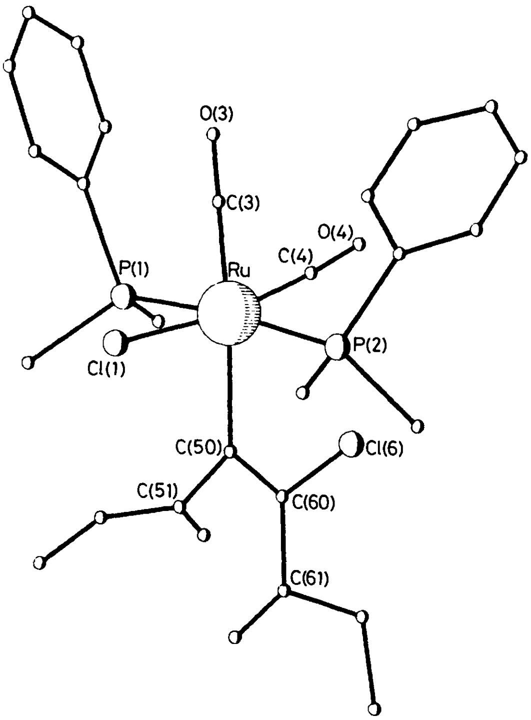

Figure. Structure of complex (1a) in the solid state

Crystal Structure of Complex (1a).—The structure consists of discrete molecules occupying general positions in the space group $P\bar{1}$. Atomic co-ordinates are listed in Table 3, selected bond lengths and angles in Table 4.

The stereochemistry of the molecule is depicted in the Figure. The feature of major interest is the alkenyl ligand, which is arranged so that C(50), C(51), C(60), Cl(6), and C(61) are essentially coplanar with the metal, the chloride ligand, and the two carbonyl ligands. This orientation allows maximum overlap of the π system of the carbon–carbon double bond with the appropriate metal *d* orbital. Comparison of the Ru(1)–C(50) bond with those between ruthenium and sp^2-hybridized carbon atoms in other structures reveals that the length [2.16(2) Å] is similar to that of the ruthenium–naphthyl bond [2.16(1) Å] in $[Ru(C_{10}H_7)H(Me_2PCH_2CH_2PMe_2)_2]$,[4] but significantly greater than those to the alkenyl ligands in the

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† *Supplementary data available* (No. SUP 23485, 22 pp.): complete bond lengths and angles, structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared [a] and ^{1}H n.m.r. spectra [b] of complexes

Complex	ν(C–O)/cm^{-1}	δ/p.p.m.	Assignment
(1a)	2 058	3.73 (s, 3)	CO_2Me
	1 986	3.72 (s, 3)	CO_2Me
		1.95 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.92 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
(1b)	2 052	3.73 (s, 3)	CO_2Me
	1 980	3.69 (s, 3)	CO_2Me
		1.85 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.82 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
(1c)	2 058	4.33 (q, 2)	$\mathit{CH}_2\mathrm{CH}_3$
	1 980	4.26 (q, 2)	$\mathit{CH}_2\mathrm{CH}_3$
		2.01 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.97 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.31 (t, 6) [c]	$\mathrm{CH}_2\mathit{CH}_3$
(1d)	2 058	4.18 (q, 4) [c]	$\mathit{CH}_2\mathrm{CH}_3$
	1 983	1.90 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.86 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.27 (t, 3)	$\mathrm{CH}_2\mathit{CH}_3$
		1.26 (t, 3)	$\mathrm{CH}_2\mathit{CH}_3$
(2a)	1 940	3.86 (s, 3)	CO_2Me
		3.75 (s, 3)	CO_2Me
		1.80 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.79 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.25 (d, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
(2b)	1 939	3.84 (s, 3)	CO_2Me
		3.74 (s, 3)	CO_2Me
		1.67 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.66 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.12 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
(3a)	2 075	3.79 (s, 3)	CO_2Me
	2 000	3.74 (s, 3)	CO_2Me
		1.98 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.96 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
(3b)	2 070	3.78 (s, 3)	CO_2Me
	1 995	3.76 (s, 3)	CO_2Me
		1.94 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.90 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
(3c)	2 077	4.24 (q, 2)	$\mathit{CH}_2\mathrm{CH}_3$
	2 007	4.16 (q, 2)	$\mathit{CH}_2\mathrm{CH}_3$
		2.01 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.97 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.30 (t, 6) [c]	$\mathrm{CH}_2\mathit{CH}_3$
(4a)	2 058	3.82 (s, 3)	CO_2Me
	2 004	3.81 (s, 3)	CO_2Me
		1.94 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.90 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.50 (d, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
(5a)	2 072	3.79 (s, 3)	CO_2Me
	1 990	3.76 (s, 3)	CO_2Me
		2.00 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
		1.95 (t, 6)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$
(5b)	2 064	3.76 (s, 3)	CO_2Me
	1 990	3.71 (s, 3)	CO_2Me
		1.89 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$
		1.87 (s, 6)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$

[a] In $CHCl_3$ solution. Only C–O stretching bands for the carbonyl ligands are listed. [b] In $CDCl_3$ solution. Resonances due to phenyl protons are not included. Multiplicities and relative areas of resonances are given in parentheses after the chemical-shift values: s = singlet, d = doublet, t = triplet, and q = quartet. [c] Accidental superimposition of two resonances.

complexes $[Ru\{CH{=}C(CO_2Bu)Me\}H(PPh_3)_3]$ [2.061(10) Å] [5] and $[Ru\{\eta^5\text{-}C_5H_4C(CF_3)_2OH\}\{C(CO_2Me){=}C(CO_2Me)H\}(PPh_3)]$ [2.035(4) Å].[6] The comparison with the latter two complexes is not entirely fair, however, since in each case the alkenyl ligand is bidentate, and greater delocalization is achieved by co-ordination of the carbonyl oxygen atom in the terminal carboxylate group to the metal. This also has the effect of holding the oxygen atoms of the carboxylate group in the same plane as the carbon–carbon double bond and the metal. In complex (1a) the alkenyl ligand is unidentate, and the oxygen atoms in the carboxylate groups are twisted out of the plane of the metal and the carbon–carbon double bond, presumably because of steric interactions within the molecule.

Rather surprisingly [in view of the claim [5] that the alkenyl ligand has a large ' *trans* influence ' in ruthenium(II) complexes], the difference between the Ru–C bond lengths to the two carbonyl ligands in complex (1a) is not large enough to be significant. It is possible, however, that the Ru(1)–C(4) bond is lengthened by the steric interaction between this carbonyl ligand and the alkenyl ligand, which is reflected in the C(4)–Ru(1)–C(50) bond angle of 101.0(8)° (*cf.* the regular octahedral angle of 90°).

Spectra of Complexes.—Following the elucidation of the true structure of (1a), it was realized that the two strong bands at *ca.* 2 000 cm^{-1} in the i.r. spectra of complexes (1a)—(1d) were both due to the C–O stretching modes of the carbonyl ligands. The ^{1}H n.m.r. spectra of the complexes were as expected, except that in some instances the differences in chemical shift between corresponding protons in the two CO_2R groups were too small to detect.

In the ^{13}C n.m.r. spectra of the complexes we were initially unable to detect the resonance for the alkenyl carbon atom not directly attached to the metal. Weak noise decoupling, by removing the cluster of resonances for the hydrogen-bearing carbon atoms in the phenyl substituents, revealed the missing resonance. In the case of complexes (1a) and (1c), the resonance exhibited a triplet splitting due to coupling to the two ^{31}P nuclei, as did those for the three carbon atoms directly attached to the metal and that for the carboxyl carbon atom in the CO_2R group nearer to the metal.

Mechanism of Formation of the Complexes.—From the structure of complex (1a) (see Figure) it can be seen that the ruthenium and chlorine have added across the triple bond of the alkyne in *cis* fashion. This suggested that the alkenyl ligand was formed either by direct insertion of $MeO_2CC{\equiv}CCO_2Me$ into a metal–chlorine bond or by initial formation of an alkyne complex followed by intramolecular rearrangement. Initial co-ordination of the alkyne to the metal would be expected to involve displacement of one of the ligands in *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, the likeliest candidate (in view of other known reactions of the complex [7]) being a carbonyl ligand. Strong evidence for the formation of an intermediate alkyne complex by displacement of a carbonyl ligand was provided by the fact that there was *no* apparent reaction when *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ was treated with $MeO_2CC{\equiv}CCO_2Me$ at 313 K in CO-saturated propanone solution {a separate check showed that (1a) was not reconverted into *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ under these conditions}. Such inhibition by CO would not be expected if the formation of complex (1a) involved direct insertion of alkyne into a ruthenium–chlorine bond or initial displacement of a chloride or PMe_2Ph ligand by alkyne. Thus we believe the mechanism of formation of complexes (1a)—(1d) to be as shown in Scheme 1. The ligand arrangement around the

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

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
(1a)	195.6 (t)	CO	12.7	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	193.4 (t)	CO	9.8	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	177.7 (t)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$	13.7	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	174.0 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.7 (t)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$	2.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$
	128.6 (t) [b]	$\mathit{C}\mathrm{(CO_2Me)Cl}$	4.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$
	52.8 (s)	$\mathrm{CO_2}\mathit{Me}$		
	50.2 (s)	$\mathrm{CO_2}\mathit{Me}$		
	14.1 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	32.2	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
	13.1 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.3	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
(1b)	195.0 (s)	CO		
	193.6 (s)	CO		
	175.1 (s)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$		
	174.3 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.7 (s)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$		
	129.2 (s) [b]	$\mathit{C}\mathrm{(CO_2Me)Cl}$		
	52.7 (s)	$\mathrm{CO_2}\mathit{Me}$		
	50.3 (s)	$\mathrm{CO_2}\mathit{Me}$		
	10.6 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	10.0 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
(1c)	195.7 (t)	CO	12.7	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	193.4 (t)	CO	9.5	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	175.6 (t)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Et)}$	13.7	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	173.4 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Et)Cl}$		
	161.3 (t)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Et)}$	2.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$
	129.1 (t) [b]	$\mathit{C}\mathrm{(CO_2Et)Cl}$	4.8	$\lvert {}^3J(\mathrm{P-C}) \rvert$
	61.7 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	59.2 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	14.4 (s)	$\mathrm{CH_2}\mathit{C}\mathrm{H_3}$		
	14.1 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	33.7	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
	14.1 (s)	$\mathrm{CH_2}\mathit{C}\mathrm{H_3}$		
	13.2 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	34.2	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
(1d)	195.0 (s)	CO		
	193.5 (s)	CO		
	173.8 (s)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Et)}$		
	173.2 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Et)Cl}$		
	161.2 (s)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Et)}$		
	129.5 (s) [b]	$\mathit{C}\mathrm{(CO_2Et)Cl}$		
	61.6 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	59.2 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	14.4 (s)	$\mathrm{CH_2}\mathit{C}\mathrm{H_3}$		
	14.2 (s)	$\mathrm{CH_2}\mathit{C}\mathrm{H_3}$		
	10.6 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	10.0 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
(2a)	202.9 (dt)	CO	12.7, 14.6	$\lvert {}^2J(\mathrm{P-C}) \rvert$, $\lvert {}^2J(\mathrm{P-C}) \rvert$
	185.0 (dt)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$	71.3, 14.3	$\lvert {}^2J(\mathrm{P-C}) \rvert$, $\lvert {}^2J(\mathrm{P-C}) \rvert$
	175.0 (d)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$	3.9	$\lvert {}^4J(\mathrm{P-C}) \rvert$
	161.3 (dt)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$	5.9, 2.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$, $\lvert {}^3J(\mathrm{P-C}) \rvert$
	128.1 (dt) [b]	$\mathit{C}\mathrm{(CO_2Me)Cl}$	4.0, 4.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$, $\lvert {}^3J(\mathrm{P-C}) \rvert$
	52.5 (s)	$\mathrm{CO_2}\mathit{Me}$		
	49.9 (s)	$\mathrm{CO_2}\mathit{Me}$		
	19.0 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.2	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
	14.9 (d)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	28.3	$\lvert {}^1J(\mathrm{P-C}) \rvert$
	11.1 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	29.3	$\lvert {}^1J(\mathrm{P-C}) + {}^3J(\mathrm{P-C}) \rvert$
(2b)	201.7 (s)	CO		
	181.7 (s)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$		
	174.8 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.0 (s)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$		
	127.9 (s) [b]	$\mathit{C}\mathrm{(CO_2Me)Cl}$		
	52.5 (s)	$\mathrm{CO_2}\mathit{Me}$		
	50.1 (s)	$\mathrm{CO_2}\mathit{Me}$		
	13.9 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	10.6 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	6.9 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
(3a) [c]	196.7 (t)	CO	13.7	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	191.5 (t)	CO	9.0	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	175.9 (t)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$	13.5	$\lvert {}^2J(\mathrm{P-C}) \rvert$
	173.2 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.2 (t)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$	2.0	$\lvert {}^3J(\mathrm{P-C}) \rvert$

Table 2 (*continued*)

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
	52.9 (s)	$\mathrm{CO_2}\mathit{Me}$		
	51.2 (s)	$\mathrm{CO_2}\mathit{Me}$		
	13.8 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	36.0	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
	12.6 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	30.0	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
(3b)	196.0 (s)	CO		
	191.7 (s)	CO		
	174.1 (s)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$		
	173.4 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.0 (s)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$		
	129.3 (s)	$\mathit{C}\mathrm{(CO_2Me)Cl}$		
	52.9 (s)	$\mathrm{CO_2}\mathit{Me}$		
	51.2 (s)	$\mathrm{CO_2}\mathit{Me}$		
	10.5 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	10.3 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
(3c) [c]	196.8 (t)	CO	13.5	$\lvert {}^2J(\mathrm{P{-}C}) \rvert$
	191.7 (t)	CO	9.0	$\lvert {}^2J(\mathrm{P{-}C}) \rvert$
	174.0 (t)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Et)}$	13.5	$\lvert {}^2J(\mathrm{P{-}C}) \rvert$
	172.8 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Et)Cl}$		
	160.8 (t)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Et)}$	1.5	$\lvert {}^3J(\mathrm{P{-}C}) \rvert$
	61.9 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	60.6 (s)	$\mathit{C}\mathrm{H_2CH_3}$		
	14.2 (s) [d]	$\mathrm{CH_2}\mathit{C}\mathrm{H_3}$		
	13.9 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	36.2	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
	13.7 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.0	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
(5a) [c]	196.8 (dt)	CO	5.9, 14.0	$\lvert {}^3J(\mathrm{P{-}C}) \rvert, \lvert {}^2J(\mathrm{P{-}C}) \rvert$
	191.4 (dt)	CO	2.0, 9.0	$\lvert {}^3J(\mathrm{P{-}C}) \rvert, \lvert {}^2J(\mathrm{P{-}C}) \rvert$
	178.3 (dt)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$	2.0, 14.2	$\lvert {}^3J(\mathrm{P{-}C}) \rvert, \lvert {}^2J(\mathrm{P{-}C}) \rvert$
	173.3 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.2 (t)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$	2.5	$\lvert {}^3J(\mathrm{P{-}C}) \rvert$
	52.9 (s)	$\mathrm{CO_2}\mathit{Me}$		
	50.7 (s)	$\mathrm{CO_2}\mathit{Me}$		
	13.7 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	34.2	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
	12.3 (t)	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	31.2	$\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$
(5b) [c]	196.3 (d)	CO	6.0	$\lvert {}^3J(\mathrm{P{-}C}) \rvert$
	191.7 (d)	CO	*e*	$\lvert {}^3J(\mathrm{P{-}C}) \rvert$
	176.2 (d)	$\mathrm{Ru}\mathit{C}\mathrm{(CO_2Me)}$	2.0	$\lvert {}^3J(\mathrm{P{-}C}) \rvert$
	173.5 (s)	$\mathrm{C(}\mathit{C}\mathrm{O_2Me)Cl}$		
	161.0 (s)	$\mathrm{RuC(}\mathit{C}\mathrm{O_2Me)}$		
	52.8 (s)	$\mathrm{CO_2}\mathit{Me}$		
	50.8 (s)	$\mathrm{CO_2}\mathit{Me}$		
	10.4 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		
	9.8 (s)	$\mathrm{As}\mathit{Me}_2\mathrm{Ph}$		

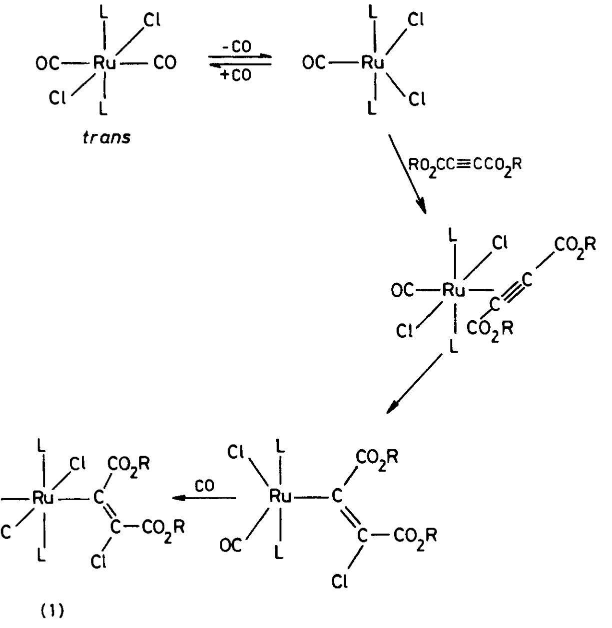
[a] Spectra were recorded on $CDCl_3$ solutions of the complexes. Resonances due to phenyl carbon atoms are not included. Multiplicities are given in parentheses after the chemical-shift values: dt = doublet of triplets. [b] Obscured by phenyl carbon resonances, but identified under conditions of weak noise decoupling. [c] Resonance for the alkenyl carbon atom not directly attached to the metal obscured by phenyl carbon resonances. [d] Accidental superimposition of two resonances. [e] Too small for accurate measurement.

Table 3. Atomic co-ordinates for complex (1a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.725 4(2)	0.617 1(2)	0.750 5(1)	C(28)	1.081(2)	0.871(3)	0.722(1)
P(1)	0.524 9(6)	0.431 7(6)	0.704 3(3)	Cl(1)	0.518 8(5)	0.771 1(5)	0.767 0(3)
P(2)	0.930 3(6)	0.826 3(6)	0.786 6(3)	C(3)	0.705(3)	0.582(3)	0.853(1)
C(11)	0.448(2)	0.312(2)	0.780(1)	O(3)	0.694(2)	0.562(2)	0.915(1)
C(12)	0.360(2)	0.373(3)	0.832(2)	C(4)	0.875(2)	0.502(2)	0.756(1)
C(13)	0.310(3)	0.286(3)	0.890(2)	O(4)	0.962(2)	0.427(2)	0.763(1)
C(14)	0.342(3)	0.150(3)	0.901(1)	C(50)	0.730(2)	0.704(2)	0.637(1)
C(15)	0.430(3)	0.090(3)	0.852(2)	C(51)	0.639(3)	0.825(3)	0.618(1)
C(16)	0.484(2)	0.175(2)	0.794(1)	O(50)	0.687(2)	0.950(2)	0.631(1)
C(17)	0.348(2)	0.481(3)	0.650(2)	O(52)	0.491(2)	0.768(1)	0.586(1)
C(18)	0.586(3)	0.310(2)	0.639(1)	C(53)	0.382(3)	0.870(3)	0.571(2)
C(21)	1.044(2)	0.795(2)	0.874(1)	C(60)	0.825(2)	0.675(2)	0.582(1)
C(22)	1.185(2)	0.740(2)	0.882(1)	Cl(6)	0.951 2(6)	0.548 7(6)	0.595 9(3)
C(23)	1.265(3)	0.715(2)	0.949(1)	C(61)	0.831(3)	0.757(2)	0.511(1)
C(24)	1.209(4)	0.752(3)	1.012(1)	O(60)	0.741(2)	0.826(2)	0.484(1)
C(25)	1.067(3)	0.802(2)	1.008(2)	O(62)	0.975(2)	0.755(2)	0.485(1)
C(26)	0.984(3)	0.826(2)	0.942(1)	C(63)	1.000(4)	0.843(3)	0.418(2)
C(27)	0.870(2)	1.000(2)	0.796(1)				

Table 4. Selected bond lengths (Å) and angles (°) for complex (1a)

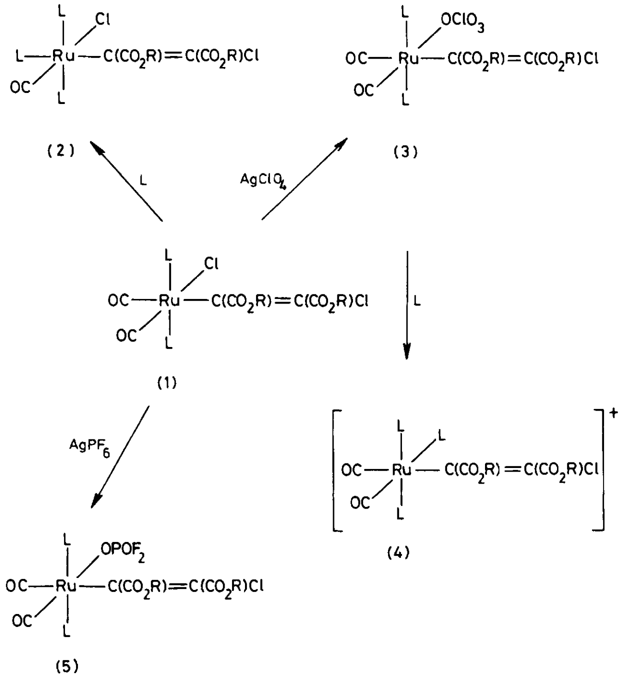
Ru(1)-P(1)	2.386(5)	C(3)-O(3)	1.14(3)
Ru(1)-P(2)	2.389(5)	C(4)-O(4)	1.10(3)
Ru(1)-C(3)	1.91(2)	C(50)-C(51)	1.49(3)
Ru(1)-C(4)	1.87(2)	C(50)-C(60)	1.41(3)
Ru(1)-Cl(1)	2.447(6)	C(60)-C(61)	1.49(3)
Ru(1)-C(50)	2.16(2)	C(60)-Cl(6)	1.73(2)
P(1)-Ru(1)-P(2)	175.4(2)	C(3)-Ru(1)-Cl(1)	81.9(8)
C(3)-Ru(1)-C(50)	171.4(10)	C(4)-Ru(1)-C(50)	101.0(8)
C(4)-Ru(1)-Cl(1)	169.0(7)	Cl(1)-Ru(1)-C(50)	89.9(6)
P(1)-Ru(1)-C(3)	93.9(7)	Ru(1)-C(3)-O(3)	177.1(21)
P(1)-Ru(1)-C(4)	89.3(6)	Ru(1)-C(4)-O(4)	176.3(19)
P(1)-Ru(1)-Cl(1)	89.5(2)	Ru(1)-C(50)-C(51)	114.7(15)
P(1)-Ru(1)-C(50)	88.4(5)	Ru(1)-C(50)-C(60)	129.9(14)
P(2)-Ru(1)-C(3)	90.6(7)	C(50)-C(60)-C(61)	122.1(19)
P(2)-Ru(1)-C(4)	90.5(6)	C(50)-C(60)-Cl(6)	122.4(16)
P(2)-Ru(1)-Cl(1)	91.6(2)	C(51)-C(50)-C(60)	114.5(18)
P(2)-Ru(1)-C(50)	87.2(5)	Cl(6)-C(60)-C(61)	115.4(17)
C(3)-Ru(1)-C(4)	87.3(10)		



Scheme 1.

metal in the intermediate alkyne complexes is, of course, uncertain, but the orientation shown for the alkyne would avoid steric interactions with the relatively bulky ligands L and facilitate intramolecular attack by the neighbouring chloride ligand. Finally the vacant co-ordination site is filled by the CO lost in the first step.

Other alkenyl complexes of ruthenium, for example [Ru(η^5-C_5H_5){C(CF_3)=C(CF_3)H}(PPh_3)$_2$], have been obtained by interaction of alkynes with hydrido-complexes of ruthenium(II).[8] Again it was proposed that the reactions proceeded by way of intermediate alkyne complexes {in this instance [Ru(η^5-C_5H_5)(F_3CC≡CCF_3)H(PPh_3)]}, but the subsequent rearrangement was depicted as occurring by way of σ-alkyne complexes in which the carbon atom not attached to the metal carried a negative charge. Proton transfer from metal to carbon then yielded the product alkenyl complexes. It seems unlikely that formation of the chloroalkenyl complexes (1a)—(1d) involves attack by Cl^+ on the co-ordinated alkyne, and we feel that the rearrangements are best regarded as instances of intramolecular *nucleophilic* attack on the alkyne by Cl^-.



Scheme 2.

Reactions of the Complexes.—The complexes [Ru(CO)$_2${C(CO_2R)=C(CO_2R)Cl}Cl(PMe_2Ph)$_2$] can be regarded as members of the same family as [Ru(CO)$_2$Me(Cl)(PMe_2Ph)$_2$] and the σ-allyl complex [Ru(CO)$_2$(σ-C_3H_5)Cl(PMe_2Ph)$_2$]. The latter two complexes readily react with PMe_2Ph to form acyl complexes {[Ru(CO)(COMe)Cl(PMe_2Ph)$_3$] and [Ru(CO)(COC_3H_5)Cl(PMe_2Ph)$_3$] respectively},[9,10] the reactions involving intramolecular combination of alkyl (or allyl) and carbonyl ligands, with PMe_2Ph then occupying the vacant co-ordination site. The methyl complex also reacts with CO to form [Ru(CO)$_2$(COMe)Cl(PMe_2Ph)$_2$].[9] In contrast, complex (1a) failed to react with CO, and reacted with PMe_2Ph to yield the carbonyl substitution product [Ru(CO){C(CO_2Me)=C(CO_2Me)Cl}Cl(PMe_2Ph)$_3$] (2a) rather than an acyl complex. The pattern of resonances for the methyl protons and carbon atoms in the three PMe_2Ph ligands established that these were arranged in the *mer* fashion,* and the very large doublet splitting of the resonance for the metal-bonded carbon atom in the alkenyl ligand [$|^2J(P-C)| = 71.3$ Hz] made it clear that this ligand lay *trans* to the unique PMe_2Ph ligand. (Indeed the resonances for *all* the carbon atoms in the alkenyl ligand other than those in the methyl substituents were split to a significant extent by the ^{31}P nucleus in this PMe_2Ph ligand.) Thus conversion of (1a) into (2a) involves substitution of the carbonyl ligand *trans* to the alkenyl group (see Scheme 2). In a similar manner, complex (1b) was found to react with $AsMe_2Ph$ to yield [Ru(CO){C(CO_2Me)=C(CO_2Me)Cl}Cl($AsMe_2Ph$)$_3$] (2b).

The failure of the alkenyl complexes to form acyl species may indicate that the Ru–C bond to the alkenyl ligand is stronger than those to methyl and σ-allyl ligands. This may be due to some measure of delocalization between the appropri-

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* The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[11,12]

Table 5. Analytical data

Complex	Found (%)		Calculated (%)	
	C	H	C	H
(1a)	44.6	4.40	44.6	4.35
(1b)	39.3	3.85	39.25	3.85
(1c)	46.45	4.90	46.3	4.80
(1d)	40.95	4.35	40.95	4.25
(2a)	49.45	5.30	49.2	5.20
(2b)	42.05	4.40	41.9	4.45
(3a)	40.65	4.20	40.55	3.95
(3b)	36.25	3.55	36.1	3.55
(3c)	42.25	4.50	42.3	4.35
(4a)	45.45	4.70	45.3	4.65
(5a)	40.55	3.85	40.5	3.95
(5b)	35.75	3.45	36.05	3.55

ate metal *d* orbital and the π system of the alkenyl ligand (such delocalization is not possible for the σ-allyl ligand because of the methylene group between metal and double bond).

Maitlis[13] has proposed that the reactions of chloro-complexes of palladium(II) with alkynes also involve initial formation of alkyne complexes followed by *cis* addition of palladium and chlorine across the triple bond. In the case of the palladium(II) systems, however, these alkenyl complexes are not observed because they react rapidly with more alkyne to give butadienyl complexes, which *have* in some instances been isolated and characterized.[14] Further reaction may then occur to give a variety of organic products and/or palladium complexes. Since, in the case of the ruthenium complexes, we had been able to isolate and characterize the products of reaction with a *single* molecule of alkyne, we were particularly interested to determine how these alkenyl complexes would react with further molecules of alkyne.

Complex (1a) failed to react with $MeO_2CC{\equiv}CCO_2Me$ in chlorobenzene at room temperature. Some form of reaction appeared to occur at 358 K, but a ^1H n.m.r. spectrum recorded after several hours revealed that the quantity of free $MeO_2CC{\equiv}CCO_2Me$ had actually *increased*, and that some of the alkenyl complex had been converted into all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.[7] When the reaction was repeated in the absence of added $MeO_2CC{\equiv}CCO_2Me$, alkyne was again slowly liberated and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ formed. Ultimately all the alkenyl complex decomposed, and the all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ underwent the expected rearrangement to its more stable *cis* isomer. Since *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ is known to rearrange to its all-*cis* isomer and ultimately to the *cis* isomer on heating in solution,[7] the mechanism of decomposition of complex (1a) may simply be the reverse of that shown for its formation in Scheme 1. Reaction of (1a) with an alkyne bearing electron-releasing substituents, $EtC{\equiv}CEt$, was similarly unsuccessful.

It seemed possible that the failure of (1a) to react with alkynes to give butadienyl complexes might be due to stereochemical factors. Assuming that such reactions would require prior co-ordination of a further molecule of alkyne to the metal, the results of the reaction of complex (1a) with PMe_2Ph (see above) indicated that the alkyne would replace the carbonyl ligand *trans* to the alkenyl group, making intramolecular combination of alkyne and alkenyl ligand impossible. We attempted to overcome this problem by using silver ion to remove the chloride ligand in (1a), so that it might then be possible to introduce an alkyne *cis* to the alkenyl ligand.

When complex (1a) was treated with $AgClO_4$ in propanone solution a precipitate of AgCl was rapidly formed. After filtration, the desired product $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}(ClO_4)(PMe_2Ph)_2]$ (3a) was obtained from the filtrate. The close similarity between the spectra of (3a) and (1a) suggested that the ClO_4^- anion was actually co-ordinated to the metal in the position previously occupied by the chloride ligand (see Scheme 2). The related complexes $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}(ClO_4)(AsMe_2Ph)_2]$ and $[Ru(CO)_2\{C(CO_2Et){=}C(CO_2Et)Cl\}(ClO_4)(PMe_2Ph)_2]$, (3b) and (3c) respectively, were prepared in the same way.

The extreme ease of displacement of the ClO_4^- ligand from its co-ordination site was shown by the rapid reaction of complex (3a) with PMe_2Ph in propanone solution at room temperature. The product, (4a), shown by elemental analysis to be $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}(PMe_2Ph)_3]ClO_4$, was not sufficiently long-lived in solution for a satisfactory ^{13}C n.m.r. spectrum to be obtained, but the i.r. and ^1H n.m.r. spectra were sufficient to confirm that the PMe_2Ph ligand had entered, as desired, *cis* to the alkenyl ligand. Unfortunately (3a) and $MeO_2CC{\equiv}CCO_2Me$ failed to react at room temperature, and the effect of heat, as in the case of complex (1a), was to *increase* the concentration of free alkyne in the solution. When (3a) was heated on its own in $CDCl_3$ solution, alkyne was liberated and a new ruthenium complex, probably $[Ru(CO)_2Cl(ClO_4)(PMe_2Ph)_2]$, was formed. In fact the only result of introducing the ClO_4^- ligand *cis* to the alkenyl group was that the release of alkyne from complex (3a) appeared to occur under rather milder conditions than those required in the case of (1a), presumably because the easy loss of the ClO_4^- ligand provides a lower-energy pathway for the rearrangement involved in the decomposition.

One unexpected result of the experiments in removing the chloride ligand from complexes (1a) and (1b) came when they were treated with $AgPF_6$ instead of $AgClO_4$. Elemental analysis figures for the products, (5a) and (5b), were not in particularly good agreement with those expected for $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}(PF_6)L_2]$, and in both cases agreement was markedly better if the products were formulated as $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}(PO_2F_2)L_2]$. Presumably traces of water in the solvent caused partial hydrolysis of the PF_6^- anion during the reactions. There are precedents for such behaviour: the reaction of $[Mn(CO)_5Br]$ with $AgPF_6$ in CH_2Cl_2 has been reported to give $[Mn(CO)_5(PO_2F_2)]$,[15] and the complex $[Ru(\eta^6\text{-}C_6Me_6)(OCMe_2)_3][PF_6]_2$ is readily hydrolysed to yield $[Ru_2(\eta^6\text{-}C_6Me_6)_2(\mu\text{-}PO_2F_2)_3]PF_6$.[16] Although the ^1H n.m.r. spectra of complexes (5a) and (5b) contained no unusual features, the resonances for the three carbon atoms directly attached to the metal in (5a) were doublets of triplets, not triplets as in the case of (3a). Similarly, the corresponding resonances for (5b) were doublets, not singlets as in (3b). We assumed that the extra doublet splittings were due to either phosphorus or fluorine in the $PO_2F_2^-$ anion, the implication being that this anion (like ClO_4^-) was actually co-ordinated to the metal. The ^{31}P and ^{19}F n.m.r. spectra of complex (5a) confirmed the presence of the $PO_2F_2^-$ anion: the resonance for the phosphorus nucleus was split into a triplet (confirming the presence of two fluorine nuclei), and the value of the coupling constant [$|^1J(P-F)| =$ 956 Hz] was characteristic of the $PO_2F_2^-$ anion, being close to the values for the free ion (952 Hz)[17] and the complex $[Mn(CO)_5(PO_2F_2)]$ (968 Hz).[15] The ^{19}F spectrum confirmed that the two fluorine nuclei were equivalent (and coupled only to the phosphorus nucleus within the $PO_2F_2^-$ ligand). We therefore concluded that the $PO_2F_2^-$ ligand was bonded to ruthenium through oxygen rather than fluorine, and that the extra doublet splittings were due to the phosphorus nucleus. The bonding is evidently reasonably strong, since the $PO_2F_2^-$ ligand could not be replaced by PMe_2Ph under the same mild conditions as those required to convert complex (3a) into (4a).

Experimental

Preparation of Complexes.—All preparative work was carried out under an atmosphere of dry nitrogen. Analytical data for the complexes, all of which were white, are given in Table 5. Details of the preparations of *trans*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] and *trans*-[Ru(CO)$_2$Cl$_2$(AsMe$_2$Ph)$_2$] have been given elsewhere.[2,7]

Complex (1a). A solution of *trans*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] (0.39 g) and MeO$_2$CC≡CCO$_2$Me (0.11 g) in propanone (50 cm^3) was heated at 313 K until i.r. spectra indicated that reaction was complete (*ca.* 48 h). The solvent was removed under reduced pressure and the residual oil was crystallized from ethanol. Complexes (1b)—(1d) were prepared in the same manner.

Complex (2a). A solution of complex (1a) (0.06 g) and PMe$_2$Ph (0.02 g) in propanone (5 cm^3) was stirred at 313 K for 72 h. The microcrystalline solid formed was filtered off and washed successively with propanone, ethanol, and light petroleum (b.p. 313—333 K). The same method was used to obtain (2b), but a longer reaction time (170 h) was required.

Complex (3a). A solution of complex (1a) (0.19 g) and AgClO$_4$ (0.06 g) in propanone (30 cm^3) was shaken in the absence of light for 0.1 h. The precipitate of AgCl was filtered off, and the solution evaporated to dryness under reduced pressure. The residual oil was crystallized from a mixture of benzene and light petroleum (b.p. 353—373 K). Complexes (3b) and (3c) were prepared in a similar manner.

Complex (4a). A solution of complex (3a) (0.13 g) in propanone (10 cm^3) was treated with PMe$_2$Ph (0.03 g). After 0.1 h, the solvent was removed under reduced pressure, and the residual solid was recrystallized from a mixture of benzene and propanone.

Complexes (5a) *and* (5b). These were prepared in the same way as (3a) and (3b), but using AgPF$_6$ in place of AgClO$_4$.

Crystal-structure Determination of Complex (1a).—The crystals for the structure determination were obtained from ethanol solution. Preliminary precession photographs showed the crystals to be triclinic and the space group was assumed to be $P\bar{1}$. A crystal of dimensions 0.22 × 0.10 × 0.33 mm was used in the structure determination.

Crystal data. $C_{24}H_{28}Cl_2O_6P_2Ru$, $M = 646.4$, $a = 8.603(3)$, $b = 9.366(4)$, $c = 17.987(6)$ Å, $\alpha = 89.04(4)$, $\beta = 96.96(4)$, $\gamma = 99.37(5)^\circ$, $U = 1\,419.4$ Å^3, $Z = 2$, $D_c = 1.51$ g cm^{-3}, $F(000) = 657.9$, $\mu(\text{Cu-}K_\alpha) = 75.54$ cm^{-1}, $\lambda = 1.5418$ Å.

Intensity data were collected on a Hilger and Watts computer-controlled four-circle diffractometer. The counts were recorded in 35 steps at intervals of $\theta = 0.02^\circ$, the count time per step being 1.0 s. The background on each side of the peak was estimated in a single step count of 3.5 s. Reflections were measured out to a maximum θ value of 57°. 2 687 Reflections were recorded. Of the 2 442 unique reflections, 908 with $I < 3\sigma(I)$ were classified as unobserved. Periodic checks on three reference reflections showed no significant change in intensities over the period of data collection.

Atom Ru(1) was located from the Ru(1)–Ru(1′) vectors in a Patterson map. A structure-factor calculation at this stage, using an isotropic thermal parameter for Ru(1), gave $R = 0.488$ for all the reflections. The remaining non-hydrogen atoms were located by successive electron-density syntheses; isotropic full-matrix least-squares refinement on the atomic parameters reduced R to 0.139. An absorption-correction curve was constructed from values for the mean ratio of F(obs.) to F(calc.) for φ values incremented from 0 to 180° in 5° steps and refined by successive calculations of the curve shape from corrected least-squares refinement. Correction of the data reduced R to 0.130.

Introduction of anisotropic thermal parameters for the Ru(1), P(1), P(2), Cl(1), and Cl(6) atoms reduced R to 0.115 after several further cycles. The positions of the hydrogen atoms were calculated from those of the appropriate carbon and phosphorus atoms, and their thermal parameters were refined in blocks. In the subsequent least-squares refinement the hydrogen atoms were allowed to move with their parent atoms. This procedure reduced R to 0.109. Finally, anisotropic least-squares refinement of the remaining non-hydrogen atoms reduced R to 0.097.

Details of spectroscopic instrumentation have been given elsewhere,[9] except for the ^{19}F and ^{31}P spectra, which were recorded on a JEOL FX90Q spectrometer. The SHELX 76 program system [18] was used for the structure refinement.

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References

1 L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby, and J. A. Ibers, *Inorg. Chem.*, 1978, **17**, 2932.

2 M. Stephenson and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1981, 2112.

2 S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, 1976, **14**, 245.

4 U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1971, 1118.

5 S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 3874.

6 N. V. Raghavan and R. E. Davis, *J. Cryst. Mol. Struct.*, 1975, **5**, 163.

7 C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953.

8 T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106.

9 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331.

10 C. F. J. Barnard, J. A. Daniels, P. R. Holland, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1980, 2418.

11 J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1787.

12 D. F. Gill, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 311.

13 P. M. Maitlis, *Acc. Chem. Res.*, 1976, **9**, 93.

14 E. A. Kelly, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 289.

15 F. L. Wimmer and M. R. Snow, *Aust. J. Chem.*, 1978, **31**, 267.

16 M. A. Bennett, T. W. Matheson, G. B. Robertson, W. L. Steffen, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 32.

17 M. Lustig and J. K. Ruff, *Inorg. Chem.*, 1967, **6**, 2115.

18 G. M. Sheldrick, SHELX 76, a program system for crystal structure determination, University of Cambridge, 1976.

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