Alkene Complexes of Ruthenium(0): Crystal Structures, Isomerism and Fluxionality†

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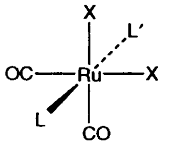
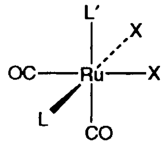
The ligand arrangements in alkene complexes [Ru(CO)$_2$(alkene)LL′] [alkene = *E*- or *Z*-MeO$_2$CCH=CHCO$_2$Me, L = L′ = PMe$_2$Ph or AsMe$_2$Ph, or L = PMe$_2$Ph, L′ = P(OMe)$_3$; alkene = H$_2$C=CH$_2$, H$_2$C=CHCO$_2$Me, *E*-NCCH=CHCN, *Z*-MeO$_2$CCH=CClCO$_2$Me, or *E*- or *Z*-MeO$_2$CCH=CPhCO$_2$Me, L = L′ = PMe$_2$Ph] have been determined by IR and NMR spectroscopy and, in two instances, by X-ray crystallography. Three types of arrangement have been identified: their relative stabilities are discussed in terms of steric interactions between the alkene substituents and the ligands L and L′. Variable-temperature NMR studies on [Ru(CO)$_2$(*E*-MeO$_2$CCH=CHCO$_2$Me)(PMe$_2$Ph)$_2$] have revealed that the complex is fluxional but that the fluxional motion is restricted by these same interactions. With *Z*-MeO$_2$CCH=CHCO$_2$Me, complex formation is accompanied by alkene isomerisation: deuterium labelling experiments have thrown light on the mechanism of isomerisation.

Alkene complexes of the transition metals are of fundamental importance as intermediates in the catalytic conversion of alkenes to a range of products. In the case of ruthenium, such complexes have been proposed as intermediates in hydrogenation, isomerisation and hydroformylation reactions.[1] Previously[2] we described the reactions of the dihydride complex *cis*-[Ru(CO)$_2$H$_2$(PMe$_2$Ph)$_2$] **1** with simple alkenes RCH=CH$_2$ (R = H, alkyl or PhCH$_2$) in which the alkene was hydrogenated or isomerised {the prefixes *cis* and all-*cis* are used to identify two ligand arrangements, shown below, for complexes [Ru(CO)$_2$X$_2$(L)L′], where X represents hydrogen or halogen and L and L′ are Group V ligands}. In the case of the reaction of **1** with ethene, the ruthenium was recovered as the alkene complex [Ru(CO)$_2$(C$_2$H$_4$)(PMe$_2$Ph)$_2$] **2**. This work prompted a study of the reactions of **1**, the related dihydride complex [Ru(CO)$_2$H$_2$(AsMe$_2$Ph)$_2$] **3**, which exists in solution as a mixture of *cis* and all-*cis* isomers, and a new complex *cis*-[Ru(CO)$_2$H$_2$(PMe$_2$Ph){P(OMe)$_3$}] **4**, with a series of alkenes containing electron-withdrawing groups, and of the stereochemistry and fluxional behaviour of the resulting alkene complexes.



cis



all-*cis*

Results and Discussion

The preparations of complexes **1** and **3** have been reported previously.[2] Complex **4** was obtained from *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph){P(OMe)$_3$}][3] by a similar procedure. Although **4** could not be induced to crystallise, NMR spectra (see Experimental section) indicated that it was free from impurities. For new alkene complexes, ^{31}P NMR and IR data are presented in Table 1, whilst ^{1}H and ^{13}C NMR data can be found in Tables 2 and 3 respectively. All ^{31}P and ^{13}C spectra were recorded with broad-band proton decoupling. The structures assigned to the alkene complexes are shown in Scheme 1.

Reactions with E-MeO$_2$CCH=CHCO$_2$Me.—When a C$_6$D$_6$ solution of **1** was treated with an excess of the alkene, a slow effervescence was observed. After a few days, **1** had been completely converted into a new alkene complex [Ru(CO)$_2$(*E*-MeO$_2$CCH=CHCO$_2$Me)(PMe$_2$Ph)$_2$] **5** and a small amount of the saturated diester MeO$_2$CCH$_2$CH$_2$CO$_2$Me had also been formed. The ambient-temperature ^{31}P NMR spectrum of **5** consisted of a slightly broadened singlet (see later), while the ^{1}H spectrum included a singlet due to the methyl ester protons and resonances of relative intensity 1:3:3 assigned respectively to the co-ordinated alkene protons and the two sets of protons in the diastereotopic PMe$_2$Ph groups. All three resonances were second-order patterns typical of spin systems X$_n$AA′X′$_n$ in which $|J(AA')|$ and $|J(AX) - J(AX')|$ are fairly similar in magnitude.[4] In contrast, the alkene protons in [Ru(CO)$_2$(C$_2$H$_4$)(PMe$_2$Ph)$_2$] **2** give rise to a triplet, whilst the PMe$_2$Ph methyl protons give one resonance, a 'virtual' triplet, indicating that $|^2J(PP)|$ is appreciably larger than $|^2J(PH) - {}^4J(PH)|$.[2,4] The ^{13}C NMR spectrum of **5** confirmed the formulation of the complex: again, second-order patterns were observed for the resonances due to the co-ordinated alkene carbon atoms and those for the methyl carbons and the phenyl *ipso* carbons in the PMe$_2$Ph ligands.

Evidently, the values of $|^2J(PP)|$ for **2** and **5** differ appreciably, suggesting that the complexes have different geometries. Five-co-ordinate complexes of d^8 transition-metal atoms normally adopt a trigonal-bipyramidal ligand arrangement, with the C=C bond of the alkene ligand lying in the equatorial plane.[5] Bray and Mawby[2] assigned this geometry to complex **2**, with the PMe$_2$Ph ligands occupying the axial positions: typically values of $|^2J(PP)|$ are very large for ruthenium complexes in which the P–Ru–P angle is close to 180°. Given that $|^2J(PP)|$ was evidently appreciably smaller for **5** than for **2**, we concluded that the PMe$_2$Ph ligands occupied equatorial positions in **5**, and this ligand arrangement was confirmed for **5** in the solid state by X-ray crystallography (see below).

The NMR spectrum of **5** was temperature dependent. At 209 K and 36.2 MHz, the ^{31}P spectrum of a C$_6$D$_5$CD$_3$ solution of the complex contained two singlet resonances, at δ 2.4 and 5.2, in an approximate intensity ratio of 4:1, implying that **5** exists in solution in two isomeric forms, **5a** and **5b**. As

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 ^{31}P-{^{1}H} NMR[a] and IR data[b] for new alkene complexes

Complex	δ, multiplicity	Assignment	$\lvert ^2J(PP)\rvert$/Hz	$\nu_{C\equiv O}$/cm^{-1}	$\nu_{C=O}$/cm^{-1}
5	2.9, s[c,d]	PMe_2Ph	—	1950	1690
6	160.1, d[c]	$P(OMe)_3$	7.9	2050[e]	1672
	0.5, d[c]	PMe_2Ph	7.9	1984	
7	—	—	—	2016	1675
				1940	
8	1.9, d[c]	PMe_2Ph	32.2	2025	1740
	−3.4, d[c]	PMe_2Ph	32.2	1938	1685
9	0.9, s[c]	PMe_2Ph	—	*f*	*f*
10	—	—	—	2018	1730
				1940	1680
11a	159.3, d	$P(OMe)_3$	49.1	*f*	*f*
	14.2, d	PMe_2Ph	49.1		
11b	140.8, d	$P(OMe)_3$	44.4		
	−1.1, d	PMe_2Ph	44.4		
12	11.1, d	PMe_2Ph	268	1968[g]	1690[g]
	8.8, d	PMe_2Ph	268	1910[g]	
13	2.5, d	PMe_2Ph	32.2	2018[g]	1690[g]
	−6.3, d	PMe_2Ph	32.2	1938[g]	
14	1.7, s	PMe_2Ph	—	2008	2205[h]
				1942	
15	0.0, d	PMe_2Ph	17.6	2050[e,g]	*f*
	−0.3, d	PMe_2Ph	17.6	1975[g]	
16	0.5, d	PMe_2Ph	16.0	2045[e]	1670
	−2.2, d	PMe_2Ph	16.0	1962	
17	−0.6, d	PMe_2Ph	21.1	2050[e,g]	1700[g]
	−0.8, d	PMe_2Ph	21.1	1960[g]	

[a] In C_6D_6 solution at 301 K and 121.49 MHz unless stated otherwise; s = singlet, d = doublet. [b] In $CHCl_3$ solution. All bands are strong unless stated otherwise. [c] Spectrum recorded at 36.2 MHz. [d] In $CDCl_3$ solution. [e] Weak band. [f] Spectrum not recorded. [g] Spectrum recorded in heptane solution. [h] $\nu_{C\equiv N}$.

the temperature was raised, these resonances broadened and coalesced, giving a single peak which became a sharp singlet at 343 K. The amount of the minor species present at low temperature varied appreciably with solvent: much less was present in C_6H_5Cl than in $C_6D_5CD_3$, and none could be detected in $CDCl_3$. At 209 K and 89.5 MHz, the ^{1}H NMR spectrum of **5** in $C_6D_5CD_3$ contained two singlets (intensity ratio 4:1) assigned to the methyl ester protons in **5a** and **5b** respectively. The resonances due to the PMe_2Ph methyl protons in **5a** appeared as one broad doublet, which presumably obscured the weaker resonance(s) for **5b**. A second-order pattern [$\lvert ^3J(PH) + {}^3J(PH)\rvert = 3.5$ Hz] was observed for the alkene protons in **5a**, but the corresponding resonance for **5b** could not be detected. With increasing temperature, the two methyl ester proton resonances coalesced, and those for the PMe_2Ph methyl protons changed in appearance to the second-order multiplets described above. The resonance for the alkene protons broadened slightly and then resharpened.

We concluded that **5a** possesses the structure adopted by **5** in the solid state, but that **5b** has a ligand arrangement similar to **2**. Evidence for this conclusion came from the change in appearance of the resonances for the PMe_2Ph methyl protons with temperature, which indicates that **5a** must have a value of $\lvert ^2J(PP)\rvert$ much smaller than that for **5** at the high-temperature limit. The latter value is an averaged figure for **5a** and **5b**, and it follows that $\lvert ^2J(PP)\rvert$ for **5b** must be very large, corresponding to a mutually *trans* arrangement of the PMe_2Ph ligands. A similar interconversion of isomers has been proposed for [Ru(CO)$_2$(*E*-NCCH=CHCN)(PPh$_3$)$_2$].[6]

It is intriguing that the motion which rapidly interconverts **5a** and **5b** at 343 K does not reduce the resonance for the alkene protons to a simple triplet and therefore cannot be scrambling the ends of the alkene with respect to the phosphorus nuclei. This can be explained by invoking a restricted version of the mechanism in which alkene rotation is coupled to a Berry pseudorotation[7] involving the other four ligands. In this process (see Scheme 2), the CO_2Me substituents in the alkene are unable, for steric reasons, to pass the PMe_2Ph ligands as the alkene rotates. Inspection of the solid-state structure of **5** and comparison with that of [Ru(CO)$_2$(*E*-NCCH=CHCN)(PMe$_2$Ph)$_2$] (see later) confirms that when the PMe_2Ph ligands occupy axial positions they are in severe steric conflict with the alkene CO_2Me substituents.

By using [Ru(CO)$_2$H$_2$(PMe$_2$Ph){P(OMe)$_3$}] **4** in place of **1** in the reaction with *E*-MeO$_2$CCH=CHCO$_2$Me, it was possible to synthesise [Ru(CO)$_2$(*E*-MeO$_2$CCH=CHCO$_2$Me)(PMe$_2$Ph){P(OMe)$_3$}] **6** for which $\lvert ^2J(PP)\rvert$ could be measured directly. The value obtained, 7.9 Hz, showed that the two phosphorus ligands could not both occupy axial positions. Furthermore the resonances in the ^{13}C NMR spectrum for the carbonyl ligands showed couplings to ^{31}P which were too small for a structure containing one axial CO and one axial phosphorus ligand. We concluded that **6** was isostructural with **5a**. Unlike **5**, complex **6** appeared to exist in solution in a single form: even at 199 K, the ^{31}P NMR spectrum of a C_6H_5Cl–$C_6D_5CD_3$ solution of **6** contained no additional resonances attributable to a second isomer.

The ligand arrangements in **2**, **5** and **6** were also reflected in the IR spectra of the complexes. The spectrum of **2** contained two bands due to C≡O stretching modes. From the relative intensities of these bands, using the method of Beck *et al.*,[8] the value calculated for the OC–Ru–CO angle was 120°, the expected figure for two equatorial ligands in a trigonal-bipyramidal complex. The spectrum of **6** in $CHCl_3$ contained two bands, but one was much weaker than the other, while only one band was observed for **5**, indicating OC–Ru–CO angles much closer to 180° for both complexes.

The reaction of **3** with an excess of *E*-MeO$_2$CCH=CHCO$_2$Me was considerably slower than that of **1** with the same alkene, and was accompanied by more hydrogenation of the alkene. Only one ruthenium complex, assigned the formula [Ru(CO)$_2$(*E*-MeO$_2$CCH=CHCO$_2$Me)(AsMe$_2$Ph)$_2$] **7** on the basis of spectroscopic evidence, was formed: its limited stability prevented us from isolating it in a pure state. The ^{1}H and ^{13}C NMR spectra of **7** demonstrated the inequivalence of the two ends of the alkene, suggesting a trigonal-bipyramidal structure

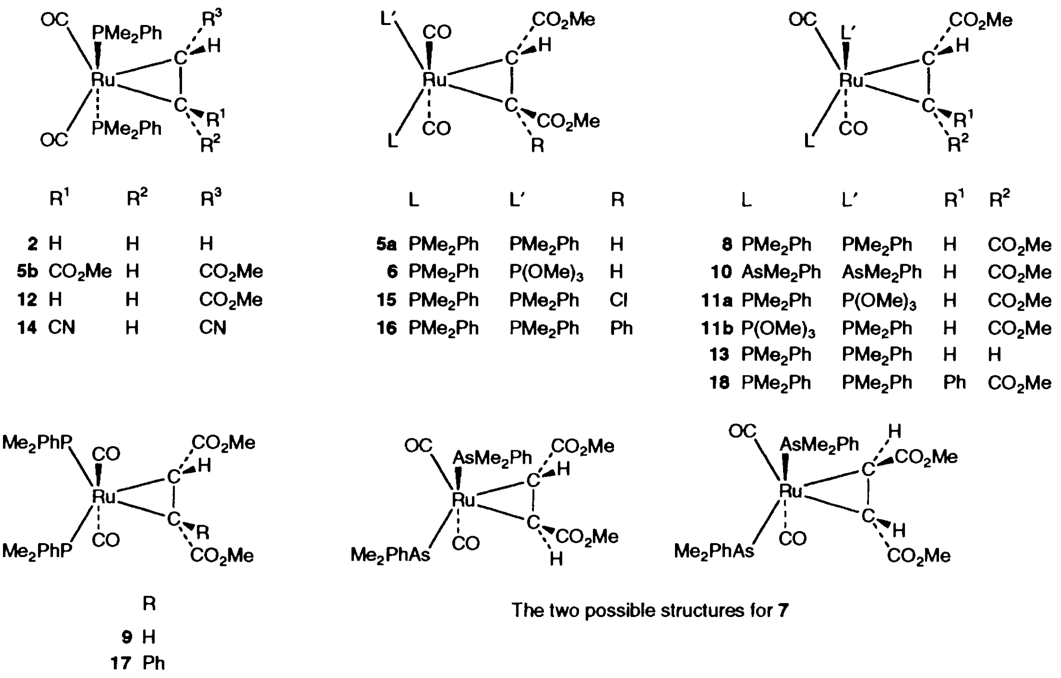
Table 2 ^{1}H NMR data[a] for new alkene complexes

Complex	δ, multiplicity (intensity)	Assignment	Coupling constant/Hz	Assignment
5	3.54, s(6)[b]	CO_2Me	—	—
	3.20, m(2)[b]	C=CH	3.2	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
	1.70, m(6)[b]	PMe_2Ph	8.1	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
	1.66, m(6)[b]	PMe_2Ph	8.0	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
6	3.87, ddd(1)	C=CH	8.8	$\lvert {}^3J(\mathrm{HH}) \rvert$
			5.1	$\lvert {}^3J(\mathrm{PH}) \rvert$
			1.3	$\lvert {}^3J(\mathrm{PH}) \rvert$
	3.60, ddd(1)	C=CH	8.8	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.6	$\lvert {}^3J(\mathrm{PH}) \rvert$
			1.6	$\lvert {}^3J(\mathrm{PH}) \rvert$
	3.46, s(6)	CO_2Me	—	—
	3.33, d(9)	$P(OMe)_3$	12.2	$\lvert {}^3J(\mathrm{PH}) \rvert$
	1.68, d(3)	PMe_2Ph	8.8	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.63, d(3)	PMe_2Ph	8.7	$\lvert {}^2J(\mathrm{PH}) \rvert$
7	4.37, d(1)	C=CH	9.1	$\lvert {}^3J(\mathrm{HH}) \rvert$
	3.46, s(6)	CO_2Me	—	—
	3.41, d(1)	C=CH	9.1	$\lvert {}^3J(\mathrm{HH}) \rvert$
	1.26, s(3)	AsMe_2Ph	—	—
	1.21, s(3)	AsMe_2Ph	—	—
	1.14, s(3)	AsMe_2Ph	—	—
	1.07, s(3)	AsMe_2Ph	—	—
8	3.69, s(3)[b,c]	CO_2Me	—	—
	3.67, s(3)[b,c]	CO_2Me	—	—
	2.34, ddd(1)[b,c]	C=CH	9.4	$\lvert {}^3J(\mathrm{HH}) \rvert$
			9.4	$\lvert {}^3J(\mathrm{PH}) \rvert$
			4.3	$\lvert {}^3J(\mathrm{PH}) \rvert$
	2.10, ddd(1)[b,c]	C=CH	9.4	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.2	$\lvert {}^3J(\mathrm{PH}) \rvert$
			3.4	$\lvert {}^3J(\mathrm{PH}) \rvert$
	1.68, d(3)[b,c]	PMe_2Ph	7.9	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.65, d(3)[b,c]	PMe_2Ph	7.7	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.26, d(3)[b,c]	PMe_2Ph	8.0	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.17, d(3)[b,c]	PMe_2Ph	8.0	$\lvert {}^2J(\mathrm{PH}) \rvert$
9	3.62, s(6)[b,c]	CO_2Me	—	—
	2.74, d(2)[b,c]	C=CH	1.9	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
	1.73, m(3)[b,c]	PMe_2Ph	6.5	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
	1.66, m(3)[b,c]	PMe_2Ph	6.5	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
10	3.63, s(3)	CO_2Me	—	—
	3.58, s(3)	CO_2Me	—	—
	2.94, d(1)	C=CH	8.2	$\lvert {}^3J(\mathrm{HH}) \rvert$
	2.55, d(1)	C=CH	8.2	$\lvert {}^3J(\mathrm{HH}) \rvert$
	1.39, s(3)	AsMe_2Ph	—	—
	1.32, s(3)	AsMe_2Ph	—	—
	0.80, s(3)	AsMe_2Ph	—	—
	0.74, s(3)	AsMe_2Ph	—	—
11a, 11b	3.02, d(3)	$P(OMe)_3$	10.9	$\lvert {}^3J(\mathrm{PH}) \rvert$
	2.78, ddd(1)	C=CH	9.4	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.7	$\lvert {}^3J(\mathrm{PH}) \rvert$
			6.4	$\lvert {}^3J(\mathrm{PH}) \rvert$
	2.37, ddd(1)	C=CH	9.6	$\lvert {}^3J(\mathrm{HH}) \rvert$
			8.4	$\lvert {}^3J(\mathrm{PH}) \rvert$
			5.9	$\lvert {}^3J(\mathrm{PH}) \rvert$
	2.21, ddd(1)	C=CH	9.6	$\lvert {}^3J(\mathrm{HH}) \rvert$
			8.2	$\lvert {}^3J(\mathrm{PH}) \rvert$
			4.4	$\lvert {}^3J(\mathrm{PH}) \rvert$
	1.71, d(3)	PMe_2Ph	8.7	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.60, d(3)	PMe_2Ph	8.8	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.23, d(3)	PMe_2Ph	8.6	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.15, d(3)	PMe_2Ph	8.7	$\lvert {}^2J(\mathrm{PH}) \rvert$
12	3.25, s(3)[c]	CO_2Me	—	—
	2.46, ddt(1)[c]	C=CH	9.9	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.9	$\lvert {}^3J(\mathrm{HH}) \rvert$
			6.0	$\lvert {}^3J(\mathrm{PH}) \rvert$, $\lvert {}^3J(\mathrm{PH}) \rvert$
	2.09, ddt(1)[c]	C=CH	9.9	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.1	$\lvert {}^3J(\mathrm{PH}) \rvert$, $\lvert {}^3J(\mathrm{PH}) \rvert$
			3.2	$\lvert {}^2J(\mathrm{HH}) \rvert$
	1.55, br(6)[d]	PMe_2Ph	5.6	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.54, br(6)[d]	PMe_2Ph	5.2	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.38, ddt(1)[c]	C=CH	7.9	$\lvert {}^3J(\mathrm{HH}) \rvert$
			6.1	$\lvert {}^3J(\mathrm{PH}) \rvert$, $\lvert {}^3J(\mathrm{PH}) \rvert$
			3.2	$\lvert {}^2J(\mathrm{HH}) \rvert$
	1.37, br(3)[d]	PMe_2Ph	6.1	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.21, br(3)[d]	PMe_2Ph	5.1	$\lvert {}^2J(\mathrm{PH}) \rvert$

Table 2 (*continued*)

Complex	δ, multiplicity (intensity)	Assignment	Coupling constant/Hz	Assignment
13	3.57, s(3)^c	CO$_2$Me	—	—
	3.19, dddd(1)^c	C=CH	9.6	$\lvert {}^3J(\mathrm{HH}) \rvert$
			5.0	$\lvert {}^3J(\mathrm{PH}) \rvert$
			4.8	$\lvert {}^3J(\mathrm{PH}) \rvert$
			3.5	$\lvert {}^2J(\mathrm{HH}) \rvert$
	2.27, dddd(1)^c	C=CH	9.6	$\lvert {}^3J(\mathrm{HH}) \rvert$
			7.7	$\lvert {}^3J(\mathrm{HH}) \rvert$
			6.0	$\lvert {}^3J(\mathrm{PH}) \rvert$
			3.2	$\lvert {}^3J(\mathrm{PH}) \rvert$
	1.51, obscured^c	C=CH	—	—
	1.50, d(3)^c	P*Me*$_2$Ph	7.3	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.37, d(3)^c	P*Me*$_2$Ph	7.3	$\lvert {}^2J(\mathrm{PH}) \rvert$
	0.82, d(3)^c	P*Me*$_2$Ph	8.1	$\lvert {}^2J(\mathrm{PH}) \rvert$
	0.77, d(3)^c	P*Me*$_2$Ph	7.3	$\lvert {}^2J(\mathrm{PH}) \rvert$
14	1.89, t(3)^b	P*Me*$_2$Ph	6.3	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
	1.87, t(3)^b	P*Me*$_2$Ph	6.6	$\lvert {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) \rvert$
	1.22, t(3)^b	C=CH	15.2	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
15	3.96, m(1)	C=CH	2.2	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
	3.52, s(3)	CO$_2$Me	—	—
	3.41, s(3)	CO$_2$Me	—	—
	1.57, d(3)	P*Me*$_2$Ph	8.1	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.51, d(3)	P*Me*$_2$Ph	8.2	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.29, d(3)	P*Me*$_2$Ph	8.5	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.26, d(3)	P*Me*$_2$Ph	8.3	$\lvert {}^2J(\mathrm{PH}) \rvert$
16	4.14, d(3)	C=CH	0.7	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
	3.39, s(3)	CO$_2$Me	—	—
	3.36, s(3)	CO$_2$Me	—	—
	1.52, d(3)	P*Me*$_2$Ph	7.5	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.52, d(3)	P*Me*$_2$Ph	8.4	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.39, d(6)	P*Me*$_2$Ph	8.2	$\lvert {}^2J(\mathrm{PH}) \rvert$
17	3.87, m(1)	C=CH	1.9	$\lvert {}^3J(\mathrm{PH}) + {}^3J(\mathrm{PH}) \rvert$
	3.63, s(3)	CO$_2$Me	—	—
	3.56, s(3)	CO$_2$Me	—	—
	1.73, d(3)	P*Me*$_2$Ph	8.1	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.41, d(3)	P*Me*$_2$Ph	7.6	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.38, d(3)	P*Me*$_2$Ph	7.4	$\lvert {}^2J(\mathrm{PH}) \rvert$
	1.34, d(3)	P*Me*$_2$Ph	7.4	$\lvert {}^2J(\mathrm{PH}) \rvert$

[a] In C_6D_6 solution at 301 K and 300.13 MHz unless stated otherwise; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] In $CDCl_3$ solution. [c] Spectrum recorded at 360 MHz. [d] In $C_6D_5CD_3$ solution at 267 K.



	R^1	R^2	R^3
2	H	H	H
5b	CO$_2$Me	H	CO$_2$Me
12	H	H	CO$_2$Me
14	CN	H	CN

	L	L′	R
5a	PMe$_2$Ph	PMe$_2$Ph	H
6	PMe$_2$Ph	P(OMe)$_3$	H
15	PMe$_2$Ph	PMe$_2$Ph	Cl
16	PMe$_2$Ph	PMe$_2$Ph	Ph

	L	L′	R^1	R^2
8	PMe$_2$Ph	PMe$_2$Ph	H	CO$_2$Me
10	AsMe$_2$Ph	AsMe$_2$Ph	H	CO$_2$Me
11a	PMe$_2$Ph	P(OMe)$_3$	H	CO$_2$Me
11b	P(OMe)$_3$	PMe$_2$Ph	H	CO$_2$Me
13	PMe$_2$Ph	PMe$_2$Ph	H	H
18	PMe$_2$Ph	PMe$_2$Ph	Ph	CO$_2$Me

	R
9	H
17	Ph

The two possible structures for **7**

Scheme 1 Structures of alkene complexes

Table 3 $^{13}C-\{^1H\}$ NMR data[a] for new alkene complexes

Complex	δ, multiplicity	Assignment	Coupling constant/Hz	Assignment
5	202.4, t[b,c]	Ru–*C*O	15.6	$\|^2J(\mathrm{PC})\|$
	178.2, s[b,c]	*C*O$_2$Me	—	—
	50.2, s[b,c]	CO$_2$*Me*	—	—
	29.8, m[b,c]	*C*=*C*	8.0	$\|^2J(\mathrm{PC}) + {}^2J(\mathrm{PC})\|$
	19.8, m[b,c]	P*Me*$_2$Ph	29.3	$\|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})\|$
	19.2, m[b,c]	P*Me*$_2$Ph	29.3	$\|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})\|$
6	200.8, dd	Ru–CO	21.9	$\|^2J(\mathrm{PC})\|$
			13.2	$\|^2J(\mathrm{PC})\|$
	200.7, dd	Ru–CO	19.2	$\|^2J(\mathrm{PC})\|$
			14.7	$\|^2J(\mathrm{PC})\|$
	178.1, dd	*C*O$_2$Me	3.1	$\|^3J(\mathrm{PC})\|$
			1.9	$\|^3J(\mathrm{PC})\|$
	177.6, dd	*C*O$_2$Me	4.4	$\|^3J(\mathrm{PC})\|$
			2.3	$\|^3J(\mathrm{PC})\|$
	51.5, s	CO$_2$*Me*	—	—
	51.4, s	CO$_2$*Me*	—	—
	50.3, d	P(OMe)$_3$	4.6	$\|^2J(\mathrm{PC})\|$
	30.4, dd	C=*C*	14.9	$\|^2J(\mathrm{PC})\|$
			4.6	$\|^2J(\mathrm{PC})\|$
	30.2, m	C=*C*	—	—
	19.7, d	P*Me*$_2$Ph	28.2	$\|^1J(\mathrm{PC})\|$
	19.5, d	P*Me*$_2$Ph	28.1	$\|^1J(\mathrm{PC})\|$
7	206.0, s	Ru–CO	—	—
	198.7, s	Ru–CO	—	—
	179.0, s	*C*O$_2$Me	—	—
	177.3, s	*C*O$_2$Me	—	—
	50.7, s	CO$_2$*Me*	—	—
	50.0, s	CO$_2$*Me*	—	—
	34.4, s	C=*C*	—	—
	32.1, s	C=*C*	—	—
	14.4, s	As*Me*$_2$Ph	—	—
	13.9, s	As*Me*$_2$Ph	—	—
	11.2, s	As*Me*$_2$Ph	—	—
8	206.1, dd[b]	Ru–CO	19.4	$\|^2J(\mathrm{PC})\|$
			3.5	$\|^2J(\mathrm{PC})\|$
	199.0, dd[b]	Ru–CO	96.8	$\|^2J(\mathrm{PC})\|$
			11.5	$\|^2J(\mathrm{PC})\|$
	176.5, t[b]	*C*O$_2$Me	2.5	$\|^3J(\mathrm{PC})\|$, $\|^3J(\mathrm{PC})\|$
	176.4, t[b]	*C*O$_2$Me	3.0	$\|^3J(\mathrm{PC})\|$, $\|^3J(\mathrm{PC})\|$
	51.4, s[b]	CO$_2$*Me*	—	—
	50.7, s[b]	CO$_2$*Me*	—	—
	37.6, dd[b]	C=*C*	19.1	$\|^2J(\mathrm{PC})\|$
			4.1	$\|^2J(\mathrm{PC})\|$
	36.8, t[b]	C=*C*	4.6	$\|^2J(\mathrm{PC})\|$, $\|^2J(\mathrm{PC})\|$
	20.5, d[b]	P*Me*$_2$Ph	25.9	$\|^1J(\mathrm{PC})\|$
	19.2, dd[b]	P*Me*$_2$Ph	26.4	$\|^1J(\mathrm{PC})\|$
			2.3	$\|^3J(\mathrm{PC})\|$
	15.4, dd[b]	P*Me*$_2$Ph	27.5	$\|^1J(\mathrm{PC})\|$
			3.6	$\|^3J(\mathrm{PC})\|$
	13.7, dd[b]	P*Me*$_2$Ph	28.4	$\|^1J(\mathrm{PC})\|$
			2.7	$\|^3J(\mathrm{PC})\|$
9	51.1, s[b]	CO$_2$*Me*	—	—
	32.0, t[b]	C=*C*	11.0	$\|^2J(\mathrm{PC}) + {}^2J(\mathrm{PC})\|$
10	205.9, s	Ru–*C*O	—	—
	198.7, s	Ru–*C*O	—	—
	176.4, s	*C*O$_2$Me	—	—
	176.1, s	*C*O$_2$Me	—	—
	51.3, s	CO$_2$*Me*	—	—
	50.7, s	CO$_2$*Me*	—	—
	37.4, s	C=*C*	—	—
	33.6, s	C=*C*	—	—
	15.3, s	As*Me*$_2$Ph	—	—
	14.1, s	As*Me*$_2$Ph	—	—
	10.7, s	As*Me*$_2$Ph	—	—
	9.0, s	As*Me*$_2$Ph	—	—
11a, 11b	205.0, dd[d]	Ru–CO	25.0	$\|^2J(\mathrm{PC})\|$
			2.8	$\|^2J(\mathrm{PC})\|$
	204.9, dd[e]	Ru–CO	17.3	$\|^2J(\mathrm{PC})\|$
			3.5	$\|^2J(\mathrm{PC})\|$
	199.0, dd[d]	Ru–CO	137.3	$\|^2J(\mathrm{PC})\|$
			10.8	$\|^2J(\mathrm{PC})\|$
	197.0, dd[e]	Ru–CO	93.7	$\|^2J(\mathrm{PC})\|$
			16.7	$\|^2J(\mathrm{PC})\|$

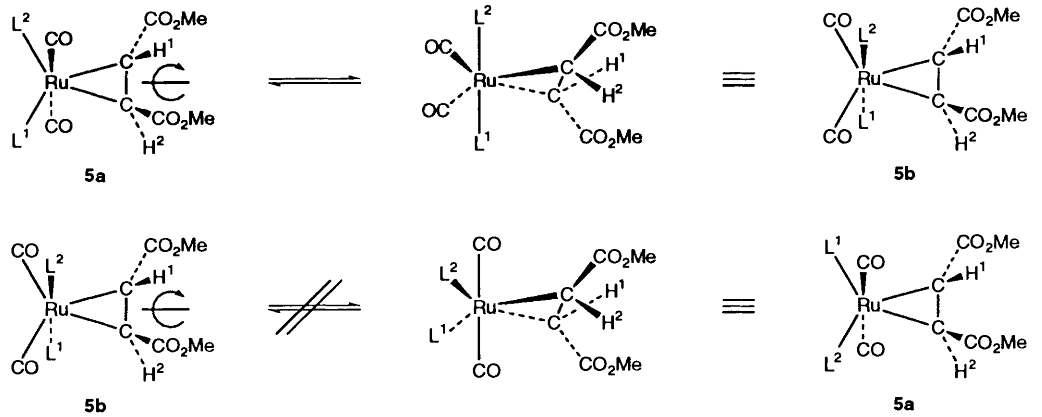
Table 3 (*continued*)

Complex	δ, multiplicity	Assignment	Coupling constant/Hz	Assignment
11a, 11b	176.6–176.0, m	*C*O$_2$Me	—	—
	175.9, dd	*C*O$_2$Me	4.9	$\lvert ^3J(PC)\rvert$
			2.7	$\lvert ^3J(PC)\rvert$
	52.2, d	P(OMe)$_3$	6.3	$\lvert ^2J(PC)\rvert$
	51.5–50.5	P(OMe)$_3$, *C*O$_2$Me		
	38.8, dd^e	C=*C*	34.3	$\lvert ^2J(PC)\rvert$
			3.6	$\lvert ^2J(PC)\rvert$
	36.9, t^d	C=*C*	5.3	$\lvert ^2J(PC)\rvert$, $\lvert ^2J(PC)\rvert$
	32.3, dd^d	C=*C*	29.6	$\lvert ^2J(PC)\rvert$
			4.6	$\lvert ^2J(PC)\rvert$
	30.8, dd^e	C=*C*	13.9	$\lvert ^2J(PC)\rvert$
			5.2	$\lvert ^2J(PC)\rvert$
	20.5, d	P*Me*$_2$Ph	28.0	$\lvert ^1J(PC)\rvert$
	18.4, d	P*Me*$_2$Ph	26.2	$\lvert ^1J(PC)\rvert$
	17.1, d	P*Me*$_2$Ph	30.1	$\lvert ^1J(PC)\rvert$
	14.8, d	P*Me*$_2$Ph	29.1	$\lvert ^1J(PC)\rvert$
12	208.3, t^f	Ru–CO	13.6	$\lvert ^2J(PC)\rvert$
	206.0, t^f	Ru–CO	14.7	$\lvert ^2J(PC)\rvert$
	178.8, t^f	*C*O$_2$Me	3.1	$\lvert ^3J(PC)\rvert$
	50.1, s^f	CO$_2$*Me*	—	—
	33.8, br s^f	*C*=C	—	—
	27.9, br^f	*C*=C	—	—
	18–17.0, br^f	P*Me*$_2$Ph	—	—
13	209.6, dd^f	Ru–CO	20.8	$\lvert ^2J(PC)\rvert$
			4.3	$\lvert ^2J(PC)\rvert$
	201.1, dd^f	Ru–CO	94.8	$\lvert ^2J(PC)\rvert$
			9.3	$\lvert ^2J(PC)\rvert$
	177.9, d^f	*C*O$_2$Me	3.3	$\lvert ^3J(PC)\rvert$
	49.7, s^f	CO$_2$*Me*	—	—
	21.0, d	P*Me*$_2$Ph	24.7	$\lvert ^1J(PC)\rvert$
	18.7, d	P*Me*$_2$Ph	27.9	$\lvert ^1J(PC)\rvert$
	15.7, d	P*Me*$_2$Ph	27.6	$\lvert ^1J(PC)\rvert$
	14.1, d	P*Me*$_2$Ph	28.7	$\lvert ^1J(PC)\rvert$
14	202.6, t	Ru–CO	13.6	$\lvert ^2J(PC)\rvert$
	127.2, t	CN	9.2	$\lvert ^3J(PC) + {}^3J(PC)\rvert$
	18.7, t	P*Me*$_2$Ph	34.3	$\lvert ^1J(PC) + {}^3J(PC)\rvert$
	11.7, t	*C*=C	8.4	$\lvert ^2J(PC) + {}^2J(PC)\rvert$
	11.0, t	P*Me*$_2$Ph	31.1	$\lvert ^1J(PC) + {}^3J(PC)\rvert$
15	202.6, dd	Ru–CO	15.9	$\lvert ^2J(PC)\rvert$
			14.6	$\lvert ^2J(PC)\rvert$
	200.4, t	Ru–CO	16.0	$\lvert ^2J(PC)\rvert$, $\lvert ^2J(PC)\rvert$
	175.7, d	*C*O$_2$Me	2.9	$\lvert ^3J(PC)\rvert$
	175.0, t	*C*O$_2$Me	2.2	$\lvert ^3J(PC)\rvert$, $\lvert ^3J(PC)\rvert$
	58.6, dd	Cl*C*=C	20.8	$\lvert ^2J(PC)\rvert$
			4.8	$\lvert ^2J(PC)\rvert$
	51.1, s	CO$_2$*Me*	—	—
	50.5, s	CO$_2$*Me*	—	—
	30.8, dd	H*C*=C	13.5	$\lvert ^2J(PC)\rvert$
			3.8	$\lvert ^2J(PC)\rvert$
	19.4, dd	P*Me*$_2$Ph	27.1	$\lvert ^1J(PC)\rvert$
			2.6	$\lvert ^3J(PC)\rvert$
	18.9, dd	P*Me*$_2$Ph	26.7	$\lvert ^1J(PC)\rvert$
			2.1	$\lvert ^3J(PC)\rvert$
	18.5, dd	P*Me*$_2$Ph	27.2	$\lvert ^1J(PC)\rvert$
			2.2	$\lvert ^3J(PC)\rvert$
	18.2, dd	P*Me*$_2$Ph	28.0	$\lvert ^1J(PC)\rvert$
			2.1	$\lvert ^3J(PC)\rvert$
16	203.7, t	Ru–CO	15.6	$\lvert ^2J(PC)\rvert$, $\lvert ^2J(PC)\rvert$
	202.6, t	Ru–CO	15.2	$\lvert ^2J(PC)\rvert$, $\lvert ^2J(PC)\rvert$
	177.2, d	*C*O$_2$Me	3.3	$\lvert ^3J(PC)\rvert$
	176.9, dd	*C*O$_2$Me	3.9	$\lvert ^3J(PC)\rvert$
			1.1	$\lvert ^3J(PC)\rvert$
	57.7, dd	Ph*C*=C	15.8	$\lvert ^2J(PC)\rvert$
			4.5	$\lvert ^2J(PC)\rvert$
	50.8, s	CO$_2$*Me*	—	—
	49.9, s	CO$_2$*Me*	—	—
	34.0, dd	H*C*=C	13.9	$\lvert ^2J(PC)\rvert$
			4.0	$\lvert ^2J(PC)\rvert$
	20.0, d	P*Me*$_2$Ph	28.8	$\lvert ^1J(PC)\rvert$
	19.4, d	P*Me*$_2$Ph	27.0	$\lvert ^1J(PC)\rvert$
	19.2, d	P*Me*$_2$Ph	29.0	$\lvert ^1J(PC)\rvert$
	18.5, d	P*Me*$_2$Ph	27.9	$\lvert ^1J(PC)\rvert$

Table 3 (*continued*)

Complex	δ, multiplicity	Assignment	Coupling constant/Hz	Assignment
17	203.8, t	Ru–CO	15.3	$|^2J(PC)|$, $|^2J(PC)|$
	202.8, dd	Ru–CO	16.3	$|^2J(PC)|$
			15.2	$|^2J(PC)|$
	177.8, s	CO_2Me	—	—
	176.4, s	CO_2Me	—	—
	60.3, d	$\mathrm{Ph}\mathit{C}{=}\mathrm{C}$	18.7	$|^2J(PC)|$
	52.5, s	$\mathrm{CO_2}\mathit{Me}$	—	—
	50.4, s	$\mathrm{CO_2}\mathit{Me}$	—	—
	29.2, d	$\mathrm{H}\mathit{C}{=}\mathrm{C}$	11.5	$|^2J(PC)|$
	19.5, dd	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	24.9	$|^1J(PC)|$
			8.2	$|^3J(PC)|$
	19.4, dd	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	24.0	$|^1J(PC)|$
			7.0	$|^3J(PC)|$
	18.8, dd	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	24.0	$|^1J(PC)|$
			3.4	$|^3J(PC)|$
	18.4, dd	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	25.0	$|^1J(PC)|$
			4.5	$|^3J(PC)|$

[a] In C_6D_6 solution at 301 K and 75.5 MHz unless stated otherwise; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] Spectrum recorded at 22.5 MHz. [c] In $CDCl_3$ solution. [d] Resonance assigned to **11a**. [e] Resonance assigned to **11b**. [f] In $C_6D_5CD_3$ solution at 267 K.



Scheme 2 Mechanism for the restricted interconversion of **5a** and **5b**

in which the remaining equatorial positions were occupied by one $AsMe_2Ph$ and one CO ligand (the two possibilities are shown in Scheme 1). Such a geometry, in which the two carbonyl ligands (one axial, one equatorial) would be at about 90° to each other, would also be compatible with the IR spectrum of the complex, which contained two C≡O stretching bands of similar intensity. We found no evidence to indicate that **7** is fluxional.

Having discovered that complexes **2**, **5a** and **7** each possessed a different ligand arrangement, we wished to obtain further evidence as to the factors affecting the relative stabilities of these arrangements. To do this, we attempted to prepare complexes with related alkenes.

Reactions with Z-$MeO_2CCH{=}CHCO_2Me$.—We anticipated that the result of treating an excess of *Z*-$MeO_2CCH{=}CHCO_2Me$ with **1** might be (*a*) alkene complex formation, (*b*) hydrogenation to the saturated diester, or (*c*) isomerisation to the thermodynamically preferred *E* isomer. In the event, all three occurred. Gentle effervescence from the solution was observed and some of the alkene (certainly more than one mole per mole of ruthenium complex) was converted into its *E* isomer, while a little was hydrogenated to $MeO_2CCH_2CH_2CO_2Me$. The fate of the *Z*-$MeO_2CCH{=}CHCO_2Me$ depended to some extent on the molar ratio of alkene to ruthenium complex. If the excess of alkene was small, all the free *Z* isomer disappeared, but if a larger excess was used some *Z* isomer remained at the end of the reaction. The rate of the *Z* ⟶ *E* isomerisation was clearly linked to the concentration of **1**: isomerisation ceased when no **1** remained in the solution. The mechanism of this isomerisation will be discussed later.

Complex **1** was converted into three species. One was **5**, the complex of *E*-$MeO_2CCH{=}CHCO_2Me$ described above. Complex **5** was not observed in the early stages of the reaction, and, as the initial excess of *Z*-$MeO_2CCH{=}CHCO_2Me$ over **1** was increased, so the concentration of **5** relative to the other products decreased. The other two complexes, **8** and **9**, both formed from the start of the reaction, were assumed to contain the *Z* isomer of the alkene: neither had been observed in the reaction of **1** with *E*-$MeO_2CCH{=}CHCO_2Me$. The major product, **8**, was obtained relatively pure (although still contaminated with a small amount of **5**) by column chromatography, and was assigned the formula $[Ru(CO)_2(Z\text{-}MeO_2CCH{=}CHCO_2Me)(PMe_2Ph)_2]$ and the structure shown in Scheme 1. The presence of two inequivalent phosphine ligands, each containing two inequivalent methyl groups, was confirmed by ^{31}P, ^1H and ^{13}C NMR spectroscopy, and the value of $|^2J(PP)|$, 32.2 Hz, showed that the two ligands were not mutually *trans*. Similarly, evidence for the presence of two inequivalent carbonyl ligands came from the ^{13}C spectrum: from the values of $|^2J(PC)|$ it was evident that one carbonyl ligand was *trans* to one of the phosphines. The IR spectrum of a $CHCl_3$ solution of **8** contained two bands of similar intensity attributable to C≡O stretching modes of the carbonyl ligands.

Broad-band and selective ^{31}P decoupling experiments were of considerable assistance in analysing the ^1H NMR spectrum of **8**, and in particular the complex splitting patterns for the two inequivalent alkene protons. This inequivalence of the two ends of the alkene was also reflected in the resonances for the $-CO_2Me$ substituents and the alkene carbons, where the two values of $|^2J(PC)|$ were 19.1 and 4.1 Hz for one atom but almost identical (at *ca.* 4.6 Hz) for the other. If the structure of **8** is visualised as an octahedron in which each alkene carbon occupies a separate co-ordination site, each can be regarded as being '*trans*' to one of the other two equatorial ligands and '*cis*' to the other. We assume that the 19.1 Hz coupling represents $|^2J(PC)|$ for the mutually '*trans*' alkene carbon and PMe_2Ph ligand. A further indication of the inequivalence of the two ends of the alkene is the appearance in the IR spectrum of two C=O stretching bands for the $-CO_2Me$ groups, at 1740 and 1685 cm^{-1}. Grevels *et al.*[9] made a similar observation for the complexes $[M(CO)_4(Z\text{-}MeO_2CCH{=}CHCO_2Me)]$ (M = Fe or Ru), and concluded that the groups must adopt markedly different conformations in the molecule.

In assigning a structure to **8**, we have assumed that the axial PMe_2Ph is *anti* to the $-CO_2Me$ groups on the alkene, as is the case for the anhydride group in $[Os(CO)_2\{\overline{CH{=}CHC(O)OC}(O)\}(PPh_3)_2]$.[10] Clearly **8** is not fluxional on the NMR time-scale: even the restricted movement exhibited by **5** cannot be occurring since this would interchange the ends of the alkene, the two phosphine ligands and the two carbonyl ligands.

Complex **9** could not be isolated from the reaction mixture, and indeed its concentration decreased after reaching a maximum in the early stages of the reaction. It was characterised by a singlet in the ^{31}P NMR spectrum, and selective ^{31}P decoupling of the ^1H spectrum of the reaction mixture enabled us to identify two resonances for the PMe_2Ph methyl groups in **9**. Each was a second-order pattern indicative of a spin system $X_3AA'X'_3$ in which the value of $|J(AA')|$ is small compared to $|J(AX) - J(AX')|$. We concluded that both phosphine ligands in **9** occupied equatorial positions. The selective decoupling also allowed us to identify a doublet resonance for the two (equivalent) alkene protons and hence, by integration, a singlet for the six equivalent $-CO_2Me$ protons. We have therefore assigned the structure shown in Scheme 1 to **9**. Its disappearance from the reaction mixture is presumably due to its conversion into either **5** or **8**: precedents for both types of rearrangement can be found in analogous systems.[11,12]

The reaction of **3** with $Z\text{-}MeO_2CCH{=}CHCO_2Me$ was slower than the corresponding reaction of **1**, and resulted in significantly more isomerisation and hydrogenation of the alkene. The NMR spectra of the reaction mixture indicated the formation of two ruthenium complexes: the minor product was **7** (see above), whilst the ^1H and ^{13}C NMR spectra of the major product, **10**, closely resembled those of **8** (apart from the absence of splittings by phosphorus nuclei). Complex **10** was therefore assigned the formula $[Ru(CO)_2(Z\text{-}MeO_2CCH{=}CHCO_2Me)(AsMe_2Ph)_2]$ and assumed to be isostructural with **8**.

Treatment of **4** with an excess of $Z\text{-}MeO_2CCH{=}CHCO_2Me$ yielded some $E\text{-}MeO_2CCH{=}CHCO_2Me$ and $MeO_2CCH_2CH_2CO_2Me$ in addition to four ruthenium complexes, formed in approximate proportions of 1:1:4:4, which we could not separate from each other. One of the minor products was complex **6**, while the other, characterised by doublets with $|^2J(PP)| = 8.7$ Hz at δ −0.2 and 159.9 in the ^{31}P NMR spectrum, was tentatively identified as an isomer of $[Ru(CO)_2(Z\text{-}MeO_2CCH{=}CHCO_2Me)(PMe_2Ph)\{P(OMe)_3\}]$ with a structure analogous to **9**. The major products, **11a** and **11b**, possessed fairly similar ^{31}P NMR spectra but with slightly different values, 49.1 and 44.4 Hz, for $|^2J(PP)|$. Neither complex was formed in the reaction of **4** with the *E* isomer of the alkene, and we concluded that they were isomers of $[Ru(CO)_2(Z\text{-}MeO_2CCH{=}CHCO_2Me)(PMe_2Ph)\{P(OMe)_3\}]$ with the structures shown in Scheme 1. Evidence in support of these structures came from the ^{13}C NMR spectrum, in which the four major resonances in the region characteristic of carbonyl ligands were all doublets of doublets. For two of the four, the two doublet splittings were of very different magnitudes: comparison with the spectra of complexes already discussed enabled us to assign the resonance at δ 199.0 $[|^2J(PC)| = 137.3$ and 10.8 Hz$]$ to the carbonyl ligand *trans* to $P(OMe)_3$ in **11a** and that at δ 197.0 $[|^2J(PC)| = 93.7$ and 16.7 Hz$]$ to the ligand *trans* to PMe_2Ph in **11b**. Other resonances in the ^1H and ^{13}C NMR spectra of the reaction mixture assigned to **11a** and **11b** included those for the phosphine methyl groups and most of the alkene $-CH{=}CH-$ resonances. These exhibited chemical shifts and coupling constants to ^{31}P similar to those for **8**. Like **8** and **10**, **11a** and **11b** were not fluxional on the NMR time-scale.

We had established that the complexes of the *Z* isomer of $MeO_2CCH{=}CHCO_2Me$ exhibited a different pattern of ligand arrangements from those of the *E* isomer, with a shift towards the arrangement in which one Group 15 ligand occupied an axial position and the other an equatorial position. This shift was clearly a result of the differing steric interactions between the two alkene isomers and the other ligands. In later sections we will explore further the effects of altering the alkene substituents.

Mechanisms of the Reactions with $Z\text{-}MeO_2CCH{=}CHCO_2Me$.—It seems probable that the complexes $[Ru(CO)_2(alkene)L_2]$ are formed by reaction of the appropriate alkene with the 16-electron species $[Ru(CO)_2L_2]$. Such species can be formed by direct elimination of dihydrogen from $[Ru(CO)_2H_2L_2]$: evidence for this comes from the direct conversion of $[Ru(CO)_2D_2(PMe_2Ph)_2]$ into $[Ru(CO)_2H_2(PMe_2Ph)_2]$ on treatment with H_2, with no intermediate formation of $[Ru(CO)_2D(H)(PMe_2Ph)_2]$,[2] and from the gas evolution observed on treatment of the dihydride complexes with either isomer of $MeO_2CCH{=}CHCO_2Me$. An alternative route to $[Ru(CO)_2L_2]$ involves the reaction of $[Ru(CO)_2H_2L_2]$ with the alkene RCH=CHR to yield an alkyl hydride complex $[Ru(CO)_2(CHRCH_2R)(H)L_2]$, which then eliminates alkane. Bray and Mawby[2] proposed this route to account for the formation of ethane as well as $[Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$ in the reaction of **1** with C_2H_4, and we found that in the reaction of $[Ru(CO)_2D_2(PMe_2Ph)_2]$ **1-D₂** with $Z\text{-}MeO_2CCH{=}CHCO_2Me$ the small amount of saturated diester formed contained deuterium in the methylene groups.

There remains the question of the mechanism of alkene isomerisation. Bray and Mawby[2] proposed that isomerisation of terminal alkenes $RCH{=}CH_2$ (R = alkyl) occurred by way of alkyl hydride intermediates, and supported this by demonstrating that when **1-D₂** was treated with ethene stepwise H–D exchange between complex and alkene occurred more rapidly than formation of **2**. In support of this mechanism, we found that **1-D₂** isomerised *Z*-PhCH=CHPh to its *E* form with accompanying H–D exchange between metal and alkene. In contrast, however, when **1-D₂** was treated with $Z\text{-}MeO_2CCH{=}CHCO_2Me$ the rearrangement to the *E* isomer was not accompanied by H–D exchange. By monitoring the ^2H NMR spectrum of the reaction mixture, we detected the release of D_2 into the solution from **1-D₂** and also (as mentioned above) deuterium incorporation into the saturated diester, but there was no evidence for the incorporation of deuterium into either isomer of the alkene or for the formation of **1-D₁** or **1-D₀**.

Since, in the reaction with **1**, conversion of free $Z\text{-}MeO_2CCH{=}CHCO_2Me$ into its *E* isomer ceases when **1** is no longer present, the complexes $[Ru(CO)_2(alkene)(PMe_2Ph)_2]$ cannot be active isomerisation catalysts. Given the absence of H–D exchange, it may well be that the active species is the 16-electron ruthenium(0) complex $[Ru(CO)_2(PMe_2Ph)_2]$. There are other examples of 16-electron d^8 transition-metal complexes acting as catalysts for alkene isomerisation.[13] Given that the mechanism evidently applies only to an alkene containing strongly electron-withdrawing substituents, it may well involve a reversible one-electron reduction of the alkene by the metal and isomerisation of the carbon skeleton of the resulting radical anion. Mechanisms involving the one-electron oxidation of transition-metal complexes by alkenes[14] and alkynes[15] containing electron-withdrawing substituents have been proposed elsewhere. Support for the view that the active species is $[Ru(CO)_2(PMe_2Ph)_2]$ was provided by the reaction between an excess of *Z*-$MeO_2CCH{=}CHCO_2Me$ and $[Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$ **2**. In **2** the bond to the ethene ligand is very labile, and the complex effectively acts as a source of $[Ru(CO)_2(PMe_2Ph)_2]$.[2,16] Over a period of 20 min, during which **2** was converted into the three complexes **5**, **7** and **8** produced in the reaction of the same alkene with $[Ru(CO)_2H_2(PMe_2Ph)_2]$, a considerable amount of free *E*-$MeO_2CCH{=}CHCO_2Me$ was produced, but thereafter no further isomerisation of the free *Z* alkene occurred.

Reaction of **1** *with* $H_2C{=}CHCO_2Me$.—The contrast between the behaviour of **1** towards C_2H_4 and the two isomers of $MeO_2CCH{=}CHCO_2Me$ led us to study the reaction with $H_2C{=}CHCO_2Me$. The reaction, slow in C_6D_6 solution at room temperature but more rapid at 315 K, yielded two complexes, **12** and **13**, believed to be isomers of $[Ru(CO)_2(H_2C{=}CHCO_2Me)(PMe_2Ph)_2]$, in a ratio (little affected by temperature) of *ca.* 3:1. When **1-D$_2$** was used in place of **1**, there was no H–D exchange between the alkene and ruthenium, and **12** and **13** were again obtained. In addition, reaction between **2** and $H_2C{=}CHCO_2Me$ yielded the same products in the same proportions. We concluded that the route from **1** to **12** and **13** involved initial loss of H_2 followed by addition of the alkene to $[Ru(CO)_2(PMe_2Ph)_2]$.

The two complexes were separated from the excess of alkene, but could not be separated from each other, and spectra were recorded on the mixture of the two. In the ^{31}P NMR spectrum, the major product, **12**, was represented by a slightly broadened AB pattern with a value for $|^2J(PP)|$ of 268 Hz: the breadth of the peaks did not alter significantly as the temperature was lowered. Clearly the structure of **12** is analogous to that of **2**, the inequivalence between the two phosphorus nuclei resulting from the unsymmetrical nature of the alkene. In the ^1H NMR spectrum of the mixture, the resonances for the PMe_2Ph methyl protons in **12** were broad, whereas those for the alkene protons were sharp. Selective ^{31}P and ^1H decoupling experiments enabled us to pick out and analyse the resonances for each of the alkene protons. Resonances for **12** in the ^{13}C NMR spectrum of the mixture were rather broad at ambient temperature but somewhat sharper at 267 K in $C_6D_5CD_3$ solution, allowing the signals (both triplets) for the two inequivalent carbonyl ligands to be identified.

At ambient temperature, all the resonances associated with the minor product, **13**, were sharp. The value of the coupling constant between the two (inequivalent) ^{31}P nuclei was identical with that for **8**, and the values of $|^2J(PC)|$ for the (also inequivalent) carbonyl ligands were very similar to those for **8**. We concluded that **13** and **8** were isostructural. Selective ^{31}P decoupling experiments made it possible to assign the four resonances for the PMe_2Ph methyl protons and the three for the alkene protons. In the structure shown for **13**, we have assumed that the CO_2Me group is positioned *anti* to the axial phosphine ligand to minimise steric interactions.

If the breadth of some of the resonances for **12** in the ambient temperature NMR spectra of the mixture is indicative of some type of fluxional motion, it is clear that the motion does not involve interconversion of **12** and **13**. As the temperature of the solution was raised, however, the resonances for both **12** and **13** in the ^{31}P NMR spectrum of the mixture broadened considerably, but due to decomposition we were unable to obtain a limiting high-temperature spectrum.

Reaction of **1** *with E*-$NCCH{=}CHCN$.—Addition of an excess of *E*-$NCCH{=}CHCN$ to a C_6D_6 solution of **1** resulted in a very slow effervescence and separation of a red oil (assumed to be polymerised alkene), with the formation of one ruthenium complex which was isolated and fully characterised as $[Ru(CO)_2(E\text{-}NCCH{=}CHCN)(PMe_2Ph)_2]$ **14**. A singlet resonance in the ^{31}P NMR spectrum showed the PMe_2Ph ligands to be equivalent, and the observation of two 'virtual' triplet resonances for the methyl protons indicated that these ligands were mutually *trans*. These results, and the observation of triplet resonances for the (equivalent) carbonyl ligands and the (also equivalent) alkene carbon atoms, suggested that **14** was isostructural with **2**, and this was confirmed by an X-ray investigation of the structure of **14** (see below).

Reactions of **1** *and* **2** *with Other Alkenes*.—Complex **1** also reacted slowly with *Z*-$MeO_2CCH{=}CClCO_2Me$[17] and with *E*- and *Z*-$MeO_2CCH{=}CPhCO_2Me$,[18,19] but the products of these reactions could be obtained much more quickly using **2** in place of **1**. On the basis of IR and NMR evidence, the products of the reactions with *Z*-$MeO_2CCH{=}CClCO_2Me$ and *E*-$MeO_2CCH{=}CPhCO_2Me$, **15** and **16** respectively, were assigned structures analogous to that of **5a**. The ^{31}P NMR spectra of **15** and **16** both showed second-order character as a result of the small chemical shift differences between the coupled phosphorus nuclei. Nevertheless we were able to simulate the spectra and obtain precise chemical shifts. Neither spectrum was temperature dependent, so neither **15** nor **16** undergoes a rapid isomerisation similar to the **5a** $\rightleftharpoons$ **5b** rearrangement discussed earlier. The second-order nature of the ^{31}P spectra caused the resonances for the alkene protons, which were coupled to the ^{31}P nuclei, to alter significantly in appearance with field strength.

The reaction with *Z*-$MeO_2CCH{=}CPhCO_2Me$ gave a complex, **17**, which appeared to be isostructural with **9**. Neither **1** nor **2** brought about isomerisation of this alkene. Complex **17** slowly came into equilibrium with a second complex, **18**, not well characterised but assigned a structure analogous to those of **8** and **13** on the basis of similarities in ^{31}P chemical shifts and values of $|^2J(PP)|$. This interconversion of isomers parallels that proposed earlier for **9** and **8**.

Structures of Complexes **5** *and* **14**.—The crystal structures of **5** and **14**, together with the atom numbering schemes, are shown in Figs. 1 and 2 respectively. Atomic coordinates are listed in Tables 4 and 5 respectively. Table 6 contains selected

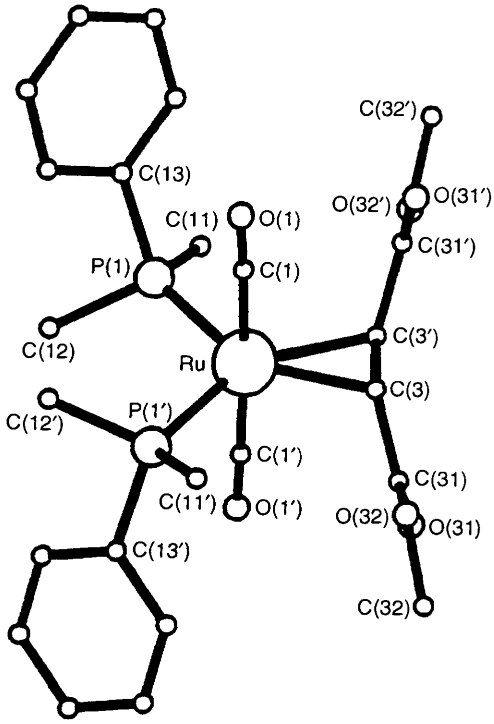


Fig. 1 Crystal structure of complex **5**

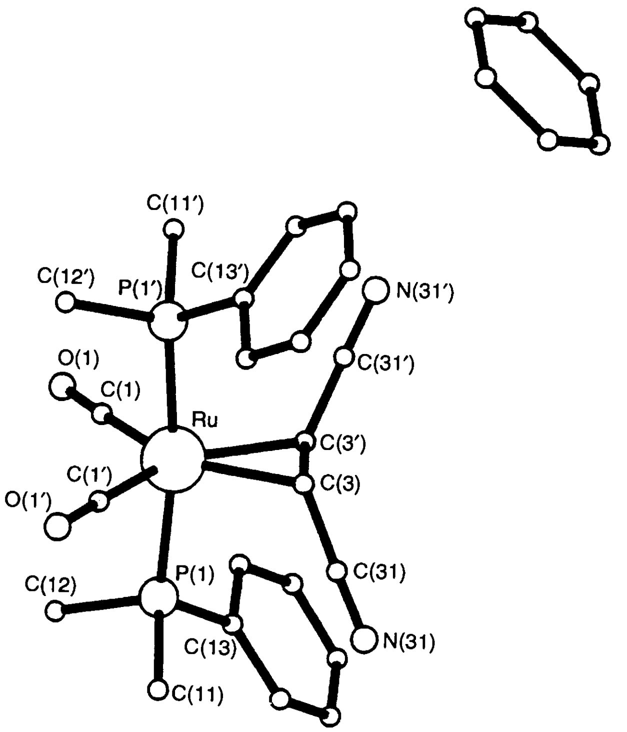


Fig. 2 Crystal structure of complex **14**

Table 4 Fractional atomic coordinates for complex **5**

Atom	*x*	*y*	*z*
Ru	0.5000(0)	0.5223(1)	0.2500(0)
P(1)	0.3757(1)	0.3674(1)	0.1906(1)
C(11)	0.2460(3)	0.4444(5)	0.1685(2)
H(111)	0.2487(3)	0.5496(5)	0.1469(2)
H(112)	0.2160(3)	0.4572(5)	0.2095(2)
H(113)	0.1965(3)	0.3720(5)	0.1362(2)
C(12)	0.3489(4)	0.1944(5)	0.2252(2)
H(121)	0.4199(4)	0.1341(5)	0.2410(2)
H(122)	0.2957(4)	0.1309(5)	0.1908(2)
H(123)	0.3152(4)	0.2162(5)	0.2640(2)
C(13)	0.4009(3)	0.3116(3)	0.1166(1)
C(14)	0.4602(3)	0.1876(3)	0.1136(1)
C(15)	0.4862(3)	0.1509(3)	0.0581(1)
C(16)	0.4528(3)	0.2383(3)	0.0056(1)
C(17)	0.3935(3)	0.3623(3)	0.0086(1)
C(18)	0.3675(3)	0.3989(3)	0.0641(1)
H(141)	0.4860(3)	0.1200(3)	0.1543(1)
H(151)	0.5321(3)	0.0549(3)	0.0558(1)
H(161)	0.4729(3)	0.2099(3)	−0.0374(1)
H(171)	0.3677(3)	0.4299(3)	−0.0321(1)
H(181)	0.3216(3)	0.4949(3)	0.0665(1)
C(1)	0.5744(2)	0.5185(4)	0.1853(2)
O(1)	0.6191(2)	0.5127(3)	0.1476(1)
C(3)	0.5523(2)	0.7475(3)	0.2685(1)
C(31)	0.5739(3)	0.7899(3)	0.3337(2)
H(31)	0.6053(29)	0.7665(43)	0.2513(18)
O(31)	0.5120(2)	0.8128(3)	0.3648(1)
O(32)	0.6766(2)	0.8032(4)	0.3574(1)
C(32)	0.7091(4)	0.8373(7)	0.4223(2)
H(321)	0.7922(4)	0.8451(7)	0.4356(2)
H(322)	0.6837(4)	0.7524(7)	0.4490(2)
H(333)	0.6758(4)	0.9402(7)	0.4312(2)

bond lengths and Table 7 bond angles for both complexes. In both structures, the asymmetric unit consists of half of the molecule (the other half being generated by rotation about a two-fold axis), but for **14** it also contains half a benzene molecule (the other half being generated by inversion). The closest contact between **14** and the benzene molecule is 3.89 Å [C(15)···C(21)]. Each complex has an approximately trigonal-bipyramidal ligand arrangement, with the alkene in an equatorial position and the C=C bond lying approximately in the equatorial plane, but the complexes differ in the arrangement of carbonyl and phosphine ligands.

Table 5 Fractional atomic coordinates for complex **14**

Atom	*x*	*y*	*z*
Ru	0.5000(0)	0.0000(1)	0.2500(0)
P(1)	0.4022(1)	−0.0220(1)	0.3020(1)
C(11)	0.3147(2)	−0.0168(8)	0.2473(3)
H(111)	0.3088(2)	0.1097(8)	0.2197(3)
H(112)	0.2737(2)	−0.0238(8)	0.2749(3)
H(113)	0.3095(2)	−0.1334(8)	0.2148(3)
C(12)	0.3991(3)	−0.2436(5)	0.3424(2)
H(121)	0.4488(3)	−0.2651(5)	0.3771(2)
H(122)	0.3913(3)	−0.3532(5)	0.3070(2)
H(123)	0.3556(3)	−0.2436(5)	0.3671(2)
C(13)	0.3987(2)	0.1395(4)	0.3675(1)
C(14)	0.3396(2)	0.2462(6)	0.3698(2)
H(141)	0.2937(2)	0.2454(6)	0.3298(2)
C(15)	0.3400(3)	0.3556(6)	0.4230(3)
H(151)	0.2928(3)	0.4333(6)	0.4257(3)
C(16)	0.3984(3)	0.3656(6)	0.4724(2)
H(161)	0.3980(3)	0.4542(6)	0.5133(2)
C(17)	0.4575(3)	0.2653(6)	0.4705(2)
H(171)	0.5040(3)	0.2745(6)	0.5097(2)
C(18)	0.4587(2)	0.1508(5)	0.4183(2)
H(181)	0.5058(2)	0.0708(5)	0.4170(2)
C(1)	0.5515(2)	−0.1581(5)	0.3160(2)
O(1)	0.5823(2)	−0.2454(6)	0.3572(2)
C(3)	0.4752(1)	0.2808(4)	0.2178(1)
H(31)	0.4922(18)	0.3097(49)	0.1738(10)
C(31)	0.4056(2)	0.3593(4)	0.2148(1)
N(31)	0.3510(2)	0.4230(6)	0.2122(2)
C(21)	−0.2982(3)	0.8860(8)	0.0043(2)
H(211)	−0.3342(22)	1.0014(47)	−0.0017(34)
C(22)	−0.3091(3)	0.7755(7)	−0.0502(2)
H(221)	−0.3549(17)	0.7823(69)	−0.0905(16)
C(23)	−0.2610(3)	0.6398(7)	−0.0539(2)
H(231)	−0.2701(40)	0.5789(105)	−0.1015(18)

Table 6 Selected bond lengths (Å) for complexes **5** and **14**

	5	**14**
Ru–P(1)	2.337(1)	2.383(1)
P(1)–C(11)	1.824(4)	1.820(5)
P(1)–C(12)	1.832(4)	1.827(4)
P(1)–C(13)	1.820(3)	1.829(3)
Ru–C(1)	1.926(3)	1.907(4)
C(1)–O(1)	1.136(4)	1.134(5)
Ru–C(3)	2.186(3)	2.164(3)
C(3)–C(3′)	1.442(6)	1.484(6)
C(3)–C(31)	1.456(4)	1.440(4)
C(3)–H(31)	0.896(39)	1.076(10)
C(31)–O(31)	1.213(4)	—
C(31)–O(32)	1.351(4)	—
O(32)–C(32)	1.435(5)	—
C(31)–N(31)	—	1.136(4)

The Ru–P bond length in **5** [2.337(1) Å] is close to that in other ruthenium(0) complexes containing PMe_2Ph in an equatorial position:[20] in **14** the bond length is slightly greater [2.383(1) Å] and in fact close to those for ruthenium(II) complexes containing a pair of mutually *trans* PMe_2Ph ligands.[21] The Ru–CO bond lengths are similar for the two complexes, as are the lengths of the Ru–C bonds to the alkene carbon atoms: in both cases the values are close to those for related complexes.[10,22,23] The bond angles between the two axial ligands are not far removed from 180° [177.9(1)° for C(1′)–Ru–C(1) in **5**; 172.3(1)° for P(1′)–Ru–P(1) in **14**], but

Table 7 Selected bond angles (°) for complexes **5** and **14**

	5	**14**
P(1′)–Ru–P(1)	105.2(1)	172.3(1)
C(1)–Ru–P(1)	89.6(1)	87.4(1)
C(1′)–Ru–P(1)	89.2(1)	88.0(1)
C(3)–Ru–P(1)	146.2(1)	93.9(1)
C(3′)–Ru–P(1)	108.4(1)	93.3(1)
C(3)–Ru–C(1)	87.6(1)	146.9(2)
C(1′)–Ru–C(1)	177.9(1)	106.2(2)
C(3′)–Ru–C(1)	94.3(1)	106.8(2)
C(11)–P(1)–Ru	114.7(1)	114.5(2)
C(12)–P(1)–Ru	118.2(1)	112.8(2)
C(13)–P(1)–Ru	114.8(1)	118.3(1)
C(11)–P(1)–C(12)	100.4(2)	101.3(3)
C(11)–P(1)–C(13)	103.5(2)	106.7(2)
C(12)–P(1)–C(13)	103.2(2)	101.2(2)
O(1)–C(1)–Ru	178.3(3)	176.8(4)
C(31)–C(3)–Ru	114.6(2)	121.5(2)
C(3′)–C(3)–Ru	70.7(2)	69.9(2)
H(31)–C(3)–Ru	110.6(25)	111.6(20)
H(31)–C(3)–C(3′)	120.8(25)	122.9(20)
H(31)–C(3)–C(31)	112.3(25)	110.0(20)
C(31)–C(3)–C(3′)	120.1(3)	116.3(4)
C(3)–Ru–C(3′)	38.5(2)	40.1(2)
O(31)–C(31)–C(3)	127.5(3)	—
O(32)–C(31)–C(3)	110.7(3)	—
O(31)–C(31)–O(32)	121.9(3)	—
C(32)–O(32)–C(31)	116.5(4)	—
N(31)–C(31)–C(3)	—	179.2(4)

those between the two other equatorial ligands are midway between the 120° expected for trigonal-bipyramidal geometry and the 90° for an octahedral structure (considering the alkene as a bidentate ligand): the values are 105.2(1)° for P(1′)–Ru–P(1) in **5** and 106.2(2)° for C(1′)–Ru–C(1) in **14**. This compression of the bond angle between the other equatorial ligands is a feature of all five-co-ordinate alkene complexes of d^8 metals, and the values are close to those for several other complexes.[22,23]

A degree of deformation of the alkene on co-ordination, towards a metallacyclopropane-like geometry, is expected from the Dewar–Chatt–Duncanson[24] model for bonding in alkene complexes, and it corresponds to a partial oxidation of the metal by the alkene. The extent to which this occurs can be gauged from the increase in the alkene C=C bond length and from the bending of the alkene substituents backwards out of the plane. The length of the C=C bond in **5** is similar to those reported for other complexes of alkenes containing two carboxylate substituents[25] whilst the bond in **14** is slightly longer than those for related complexes of the same alkene.[26] The bending back of the alkene substituents has been quantified by Ittel and Ibers[5] in terms of two angles designated as α and β. For both complexes, these are respectively the angle between the normals to the two C(3)–C(31)–H(31) planes and the angle the C=C vector makes with the normal to the C(3)–C(31)–H(31) plane. For **5**, α = 51° and β = 64°, while for **14**, α = 62° and β = 58°: these values imply that **14** has more ruthenacyclopropane character than **5**. One other feature of interest in the structures lies in the extent to which the alkene C=C bond is twisted out of the equatorial plane by interactions between the alkene substituents and the other ligands: this angle of twist is 9.9° for **5** but only 0.4° for **14**.

Rationalisation of the Geometries of the Complexes.—Work by Rossi and Hoffmann[27] suggests that the geometry adopted by complexes **2** and **14** should be favoured because it places the best σ-donor ligands in the axial positions and the best π acceptors in the equatorial plane, and it is interesting that the same geometry is adopted by complexes of two alkenes as different (from an electronic viewpoint) as C_2H_4 and NCCH=CHCN.

The steric interaction between an axial phosphine ligand and an alkene CO_2Me substituent *syn* to such a ligand clearly destabilises this structure, and for alkenes containing one or more such substituents ligand arrangements with one or both phosphines in the equatorial plane become realistic alternatives. The low-temperature NMR studies on [Ru(CO)$_2$(*E*-MeO$_2$CCH=CHCO$_2$Me)(PMe$_2$Ph)$_2$] suggested the presence of an isomer of structure **5b** as a minor component, so the positioning of a CO_2Me substituent *syn* to an axial phosphine is evidently not impossible, but for complexes of this alkene there is clearly some degree of preference for placing the phosphines in equatorial positions (**5a** and **6**). In the case of **7** it is perhaps unexpected that only one AsMe$_2$Ph ligand lies in the equatorial plane, but presumably the greater bond lengths to arsenic (as compared to those to phosphorus) reduce the interations between the substituents on an AsMe$_2$Ph ligand and those on other ligands (arsine or alkene). This is certainly implied by the fact that *cis* and all-*cis* isomers of [Ru(CO)$_2$H$_2$(AsMe$_2$Ph)$_2$] **3** exist in equilibrium with one another in solution, whereas [Ru(CO)$_2$H$_2$(PMe$_2$Ph)$_2$] **1** exists only as the *cis* isomer.[2]

For complexes of *Z*-MeO$_2$CCH=CHCO$_2$Me, a geometry analogous to **2** places two CO_2Me substituents *syn* to an axial PMe$_2$Ph, and is not observed. With a single axial phosphine ligand, as in the case of **8** and **11**, the CO_2Me substituents can be placed *anti* to the phosphine, but the crowding caused by the mutually *cis* positioning of the phosphines in **8** clearly makes the energy difference between **8** and **9** relatively small. For the complexes of *Z*-MeO$_2$CCH=CClCO$_2$Me and *E*- and *Z*-MeO$_2$CCH=CPhCO$_2$Me the increase in the number of sterically demanding substituents on the alkene completely rules out the positioning of either phosphine ligand in an axial position.

Recently Burrell *et al.*[10] have proposed that in complexes of the type [Ru(CO)(alkene)(PPh$_3$)$_2$L] [alkene = C_2F_4 or (O)CCH=CHC(O)O; L = CO or CNC$_6$H$_4$Me-4] the ligand arrangement is determined by the extent to which the alkene behaves as a π acceptor. Since we have found that complexes of C_2H_4 and NCCH=CHCN adopt the same structure, whereas complexes of the *E*- and *Z*-isomers of MeO$_2$CCH=CHCO$_2$Me adopt different structures, our results offer little support to this proposal.

Experimental

Details of techniques used and of NMR and IR spectrometers have been given previously.[2,16]

Preparations.—*Complex* **4**. A mixture of *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph){P(OMe)$_3$}] (0.22 g) and NaBH$_4$ (0.25 g) was stirred in ethanol (15 cm^3) for 16 h. Removal of the ethanol under reduced pressure and extraction of **4** from the residue with benzene was followed by removal of the benzene, again under reduced pressure. Complex **4** was obtained as a brown oil. NMR spectra (C$_6$D$_6$ solution): ^{1}H (300 MHz), δ 3.45 [d, $|^3J(PH)|$ = 5.8, P(OMe)$_3$], 1.58 [dd, $|^2J(PH)|$ = 8.6, $|^4J(PH)|$ = 2.8, P*Me*$_2$Ph], −6.40 [dd, $|^2J(PH)|$ = 25.5 and 22.8, RuH]; ^{31}P-{^{1}H} (36 MHz), δ 168.2 [d, $|^2J(PP)|$ = 340.0, P(OMe)$_3$], 9.5 [d, $|^2J(PP)|$ = 340.0 Hz, PMe$_2$Ph]. IR spectrum (CH$_2$Cl$_2$ solution): $\nu_{C=O}$ 2025, 1978 cm^{-1}.

Complex **5**. A C$_6$D$_6$ (0.3 cm^3) solution of **1** (0.05 g) in an NMR tube was treated with *E*-MeO$_2$CCH=CHCO$_2$Me (0.03 g). After 2 d at ambient temperature (or 5 h at 313 K) the C$_6$D$_6$ was removed under a stream of N$_2$ and the residue treated with ethanol (5 cm^3). After filtration of the ethanol extract, slow evaporation of the filtrate gave yellow crystals of **5** which could be recrystallised from hot ethanol (Found: C, 50.05; H, 5.20. Calc. for $C_{24}H_{30}O_6P_2Ru$: C, 49.90; H, 5.25%).

Complexes **6** *and* **7**. These were prepared from **4** and **3** respectively by the method used to obtain **5** from **1** (Found for **6**: C, 40.25; H, 5.20. Calc. for $C_{19}H_{28}O_9P_2Ru$: C, 40.50; H, 5.00%). Complex **7** could not be obtained in crystalline form.

Complexes **8–13**. These complexes were all obtained from **1**, **3** or **4** by the method described for complex **5**, but using the alkenes *Z*-$MeO_2CCH{=}CHCO_2Me$ (**8–11**) or $H_2C{=}CHCO_2Me$ (**12** and **13**). The products were isolated as yellow oils which could not be induced to crystallise even after column chromatography on neutral alumina.

Complex **14**. To a solution of **1** (0.05 g) in C_6D_6 (0.3 cm^3) in an NMR tube was added *E*-NCCH=CHCN (0.014 g). A dark red oil was slowly formed, and the solution darkened. After 4 d the reaction mixture was subjected to column chromatography on neutral alumina. Elution with $CHCl_3$ carried the desired product in the first fraction {decomposition on the column produced a little *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ in later fractions}. Evaporation of the $CHCl_3$ yielded **14** as a colourless crystalline solid (Found: C, 51.75; H, 4.70. Calc. for $C_{22}H_{24}N_2O_2P_2Ru$: C, 51.65; H, 4.75%). Recrystallisation from benzene gave crystals of $[Ru(CO)_2(E\text{-}NCCH{=}CHCN)(PMe_2Ph)_2]\cdot C_6H_6$.

Complex **15**. This complex could be obtained directly from **1** but was best prepared *via* **2**. Ethene was passed for a few hours through a solution of **1** (0.05g) in heptane (10 cm^3), and the reaction was monitored by IR spectroscopy. When **1** had been completely converted into **2**, the ethene flow was stopped and *Z*-$MeO_2CCH{=}CClCO_2Me$ (0.03 g) was added. After 1 h the solvent was removed under reduced pressure. The residue was triturated with ethanol, yielding **15** which could be obtained as yellow prisms by recrystallisation from ethanol (Found: C, 47.30; H, 4.65. Calc. for $C_{24}H_{29}ClO_6P_2Ru$: C, 47.10; H, 4.80%).

Complexes **16** and **17**. These were prepared from the appropriate alkenes in the same way as **15**, and were obtained as yellow oils which could not be induced to crystallise.

Crystal-structure Determination of **5**.—The crystal used, of dimensions 1.0 × 0.7 × 0.2 mm, was obtained by recrystallisation from ethanol, and was mounted in a capillary tube.

Crystal data. $C_{24}H_{30}O_6P_2Ru$, $M = 577.5$, monoclinic, space group $C2/c$, $a = 13.338$, $b = 9.162$, $c = 22.143$ Å, $\beta = 103.685°$, $U = 2629.12$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1183.98$, $\mu(\text{Mo-K}\alpha) = 6.66$ cm^{-1}, $\lambda = 0.71069$ Å, final $R = 0.0361$, $R' = 0.0367$.

Preliminary precession photographs showed the crystal to be monoclinic. Intensity data were collected on an upgraded Hilger and Watts four-circle diffractometer. Accurate cell dimensions were obtained from 30 centred reflections. Intensities of 2754 independent reflections were measured for $2\theta < 54°$ in an ω–2θ scan mode. Absorption corrections were applied using the empirical method of North *et al.*[28] and Lorentz-polarisation corrections were applied. The structure was partially solved, with location of the ruthenium and phosphorus atoms and the carbonyl groups, using MULTAN 85.[29] The remaining atoms were located by subsequent Fourier difference maps using SHELX 76.[30] The measurement of four standard reflections every 200 reflections showed no signs of decay.

The final structure was refined using conventional Fourier synthesis in SHELX 76 and based on 2519 reflections with $I > 2\sigma(I)$ and 145 variable parameters. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The phosphine phenyl ring, C(13)–C(18), was constrained to be a regular hexagon, C(17) and C(18) showing high thermal parameters. Most hydrogen atoms were included in the refinement with constraints on bond lengths, angles and thermal parameters. The alkene hydrogen atom, H(31), was located from a Fourier difference map. The weighting scheme used was $w = 4.2320/[\sigma^2(F_o) + 0.000\,560|F_o|^2]$.

Crystal-structure Determination of **14**.—The crystal used, of dimensions 0.8 × 0.4 × 0.2 mm, was obtained by recrystallisation from benzene, and was mounted in a capillary tube under an atmosphere of benzene vapour.

Crystal data. $C_{22}H_{24}N_2O_2P_2Ru\cdot C_6H_6$, $M = 589.5$, monoclinic, space group $C2/c$, $a = 19.200$, $b = 7.241$, $c = 21.218$ Å, $\beta = 102.760°$, $U = 2877.03$ Å^3, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $F(000) = 1207.98$, $\mu(\text{Mo-K}\alpha) = 6.02$ cm^{-1}, $\lambda = 0.7107$ Å, final $R = 0.0401$, $R' = 0.0468$.

The methods used have been described for **5** above. Accurate cell dimensions were obtained from 24 centred reflections. Intensities of 2802 unique reflections were measured. The ruthenium and phosphorus positions were obtained from a Patterson synthesis. The remaining atoms were located by subsequent Fourier difference syntheses. The measurement of four standard reflections every 200 reflections showed no signs of decay.

In the final structure refinement, using 2559 reflections with $I > 2\sigma(I)$ and 177 variable parameters, non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included with constraints on bond lengths, angles and thermal parameters. The weighting scheme used was $w = 2.5889/[\sigma^2(F_o) + 0.000\,470|F_o|^2]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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