Combination of Vinyl, Phenyl and Carbonyl Ligands in Ruthenium(II) Complexes: a Route to Vinyl Ketones

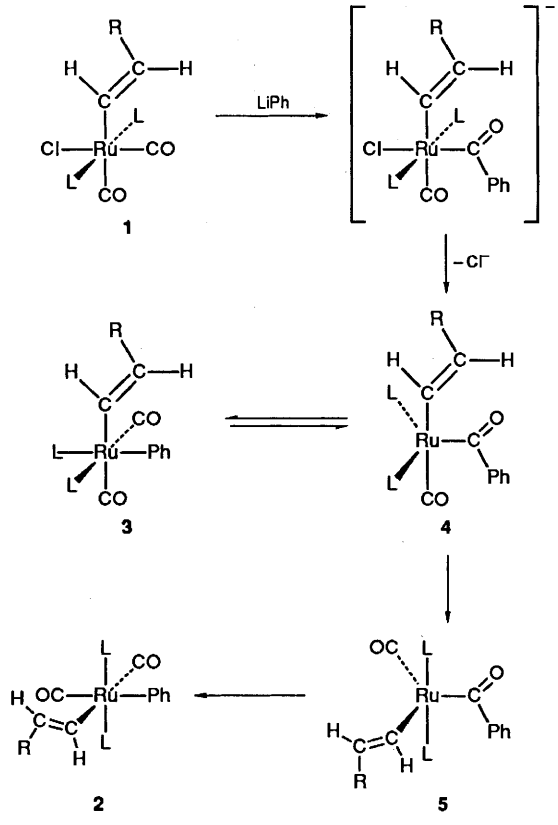
Barbara Chamberlain and Roger J. Mawby*
Department of Chemistry, University of York, York YO1 5DD, UK

Conversion of chloride complexes $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ (R = CMe_3 or Ph) into the corresponding phenyl complexes $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ by low-temperature treatment with LiPh is accompanied by a change in the ligand arrangement around the metal. At 20 °C the products undergo two competing rearrangement processes, one a simple isomerisation back to a ligand arrangement analogous to that in $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ and the other a remarkably facile combination of phenyl, carbonyl and vinyl ligands to yield the ketone complexes $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHR)(PMe_2Ph)_2]$, from which the ketone may be liberated by treatment with Me_3CNC.

Alkyl[1–3] and aryl[4] complexes of ruthenium(II) readily undergo reactions in which the organic ligand combines with CO to give an acyl complex. Such reactions of transition-metal complexes have received much attention, not least because they model steps in catalytic processes such as alkene hydroformylation and methanol carbonylation. Our studies have also encompassed complexes $[Ru(CO)_2R(R')(PMe_2Ph)_2]$ containing two organic ligands (R, R′ = methyl or aryl), which yield acyl products $[Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2]$ on treatment with Me_3CNC. In $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ the methyl ligand reacts in preference to phenyl,[5] while in complexes containing two 4-substituted aryl ligands the ligand bearing the more electron-releasing substituent is the one which undergoes reaction.[6] In the absence of added Me_3CNC these complexes decompose intramolecularly in solution to yield ketones RCOR′: presumably initial formation of an acyl complex $[Ru(CO)(COR)R'(PMe_2Ph)_2]$ is followed by reductive elimination.[7]

Recently we have extended our studies of organoruthenium complexes to those containing vinyl ligands. Reactions involving combination of vinyl and carbonyl ligands have received much less attention than the corresponding reactions of alkyl complexes, but there have been a few reports in the literature. Thus, for example, Baird *et al.*[8] described the conversion of $[RhCl_2(CH{=}CH_2)(PPh_3)_2]$ into $[RhCl_2(COCH{=}CH_2)(PPh_3)_2]$ by treatment with CO, and Montoya *et al.*[9] have recently reported that the reactions of complexes $[Ru(CO)Cl(CH{=}CHR)(PPh_3)_2]$ (R = CMe_3, Ph, *etc.*) with an excess of Me_3CNC yield acyl complexes $[Ru(COCH{=}CHR)(CNCMe_3)_3(PPh_3)_2]Cl$. Reger *et al.*[10,11] reported that conversion of $[Fe(CO)\{C(CH_2OMe){=}CMe_2\}(\eta^5\text{-}C_5H_5)\{P(OPh)_3\}]$ into $[Fe(CO)\{COC(CH_2OMe){=}CMe_2\}(\eta^5\text{-}C_5H_5)\{P(OPh)_3\}]$ under CO can be catalysed by an oxidising agent such as $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ or a Lewis acid ($AlCl_3$, $AlBr_3$, *etc.*). In some instances reaction sequences have been described in which combination of a vinyl ligand and CO appears to be a likely step: thus, for example, treatment of $[Ni(CMe{=}CMePh)Br(PPh_3)_2]$ with CO in methanol yields $PhCMe{=}CMeCO_2Me$, presumably *via* the acyl complex $[Ni(COCMe{=}CMePh)Br(PPh_3)_2]$.[12]

We were interested in the possibility of synthesising ruthenium(II) complexes containing both a vinyl and a phenyl ligand. On the basis of the behaviour of complexes $[Ru(CO)_2R(R')(PMe_2Ph)_2]$ (R, R′ = methyl or aryl),[7] we anticipated that vinyl complexes $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ might prove to be useful intermediates in a route to vinyl ketones $PhCOCH{=}CHR$. At least one precedent for such a reaction exists: Hart and Schwartz[13] have reported that they obtained the ketone $MeCO[C(CO_2Me){=}CH(CO_2Me)]$ by carbonylation of $[Rh(CO)\{C(CO_2Me){=}CH(CO_2Me)\}Me(I)(PPh_3)_2]$.



Scheme 1

Results

Details of the $^{31}P\text{-}\{^1H\}$, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of new compounds are given in Tables 1, 2 and 3 respectively. Unless indicated otherwise, all ^{31}P and ^{13}C NMR spectra referred to in the text were recorded with complete proton decoupling.

Treatment of $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ with alkynes $RC{\equiv}CH$ (R = Ph or Me_3C) yields vinyl complexes $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ of structure **1** (see Scheme 1, where

Table 1 Phosphorus-31 NMR spectral data for the compounds*

Compound	R = CMe_3	R = Ph
$[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$, isomer **3**	−2.1 (d, 26.8 Hz) −9.6 (d, 26.8 Hz)	−1.9 (d, 26.1 Hz) −10.0 (d, 26.1 Hz)
$[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$, isomer **2**	2.6 (s)	1.9 (s)
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHR)(PMe_2Ph)_2]$	9.0 (d, 9.9 Hz) 2.9 (d, 9.9 Hz)	7.3 (d, 4.2 Hz) 5.7 (d, 4.2 Hz)

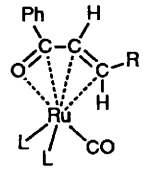
* In C_6D_6 solution. Spectra were proton-decoupled. Shift values are given on the δ scale, relative to H_3PO_4 (contained in a capillary within the NMR tube).

L = PMe_2Ph) by *cis* addition of Ru–H to the alkyne.[14] We anticipated that these complexes would react with LiPh to yield products $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ with an analogous ligand arrangement around the metal (*i.e.* structure **2** in Scheme 1). In the event, a ^{31}P NMR spectrum of a C_6D_6 solution of the crude product from the reaction of $[Ru(CO)_2(CH{=}CHCMe_3)Cl(PMe_2Ph)_2]$ with LiPh revealed the presence of two complexes, together with a little $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$.[15]

When both the reaction and the preliminary work-up were carried out at low temperature, and the ^{31}P NMR spectrum of the product was recorded in C_6D_6 solution at 10 °C, it showed that {apart from a small amount of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$} only one product had been formed, and that this was neither of the two complexes obtained from the initial experiment. The complex was too short-lived for elemental analysis, but low-temperature ^{31}P, ^1H and ^{13}C NMR spectra showed it to be the expected product, namely $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, but with an unexpected ligand arrangement, shown as **3** in Scheme 1, where L = PMe_2Ph. The resonances for the α- and β-carbon atoms of the vinyl ligand and for C^1 in the phenyl ligand were each split by the two inequivalent ^{31}P nuclei. A distortionless enhancement of polarisation transfer (DEPT) experiment provided a clear distinction between the phenyl C^1 resonance and the two vinyl resonances, and the very different sizes of the two doublet splittings for the former resonance [$|^2J(P\text{–}C)|$ = 61.8 and 15.6 Hz] showed that the phenyl ligand was *trans* to one of the PMe_2Ph ligands. In contrast, the two values of $|^2J(P\text{–}C)|$ for the vinyl α-carbon were more similar in magnitude (16.3 and 12.7 Hz), showing that the vinyl ligand was *cis* to both PMe_2Ph ligands. Confirmation of the ligand arrangement around the metal came from the values of $|^2J(P\text{–}C)|$ for the carbonyl ligands. The figure of 17.6 Hz for $|^3J(H\text{–}H)|$, the coupling constant between the two vinyl protons, indicated that the stereochemistry of the vinyl ligand had not altered in the reaction.[14]

When the C_6D_6 solution of isomer **3** of $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$ was allowed to stand at 20 °C the complex was completely converted into the two species obtained from the original experiment. The two products were separated by column chromatography and fully characterised. Both yielded elemental analysis results consistent with the same formula, $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, as that assigned to **3**, the kinetic product of the reaction. One was shown by NMR spectroscopy to be the isomer of the complex with structure **2**, containing equivalent PMe_2Ph ligands and showing the expected triplet splittings by the ^{31}P nuclei of the resonances for the two inequivalent carbonyl ligands, the α- and β-carbon atoms of the vinyl ligand, and C^1 of the phenyl ligand. The value of the coupling constant between the two vinyl protons (17.5 Hz) was virtually unchanged by the isomerisation.

The other product proved to be the ruthenium(0) ketone complex $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$, with the ketone co-ordinated to the metal through the two vinyl carbon atoms and the carbon and oxygen of the carbonyl group



(see below, where R = CMe_3 and L = PMe_2Ph). Unusual features of its NMR spectra included the small value for $|^2J(P\text{–}P)|$ (9.9 Hz) and a chemical shift of δ 2.12 for one of the vinyl protons. The ^{13}C resonance for the remaining carbonyl ligand was at δ 209.1, whereas that for the carbonyl group now incorporated into the ketone ligand was at δ 138.8. The true nature of the complex was evident from the close ^1H and ^{13}C NMR similarities with complexes $[Fe(CO)_2(\eta^4\text{-}MeCOCH{=}CHPh)(PMe_2Ph)]$ and $[Fe(CO)(\eta^4\text{-}MeCOCH{=}CHPh)(PMe_2Ph)_2]$, obtained by irradiation of $[Fe(CO)_4(PMe_2Ph)]$ or $[Fe(CO)_3(PMe_2Ph)_2]$ in the presence of the ketone MeCOCH=CHPh.[16,17] The structure of $[Fe(CO)_2(\eta^4\text{-}MeCOCH{=}CHPh)(PMe_2Ph)]$ was confirmed by X-ray diffraction.[16]

For $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$ the value of the coupling constant $|^3J(H\text{–}H)|$ between the two vinyl protons is only 8.2 Hz, as opposed to 17.6 and 17.5 Hz for the two isomers of $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$. This does not, however, signify a change in the geometry of the vinyl group, since $|^3J(H\text{–}H)|$ for the corresponding protons in $[Fe(CO)_2(\eta^4\text{-}MeCOCH{=}CHPh)(PMe_2Ph)]$, where the vinyl protons are known to be *trans* to one another, is only 8.5 Hz, as opposed to 17 Hz for free MeCOCH=CHPh.[16] We were able to liberate $PhCOCH{=}CHCMe_3$ from $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$ by treating a C_6D_6 solution of the complex with Me_3CNC. The free ketone was characterised by ^1H and ^{13}C NMR spectroscopy and by mass spectrometry: the value for the coupling constant $|^3J(H\text{–}H)|$ was 15.7 Hz.

Similar results were obtained on treating $[Ru(CO)_2(CH{=}CHPh)Cl(PMe_2Ph)_2]$ with LiPh at low temperature. Again the initial product was the isomer of $[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$ of structure **3**. When warmed in C_6D_6 solution to 20 °C this rearranged to a mixture of isomer **2** of $[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$ and the ketone complex $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHPh)(PMe_2Ph)_2]$. The proportion of the two products was, however, markedly different from that in the case of $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, with more of isomer **2** of the vinyl complex being formed and less of the η^4-ketone complex.

Discussion

It is intriguing that the isomer of the complexes $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ which is the kinetic product of the reactions between $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ (R = CMe_3 or Ph) and LiPh has a ligand arrangement **3** which

Table 2 Proton NMR spectral data for the compounds[a]

Compound	δ	Assignment	Coupling constant/Hz	Assignment
$[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, isomer **3**	6.71 (ddd, 1)	$CH{=}CHCMe_3$	18.1	$\|^3J(P-H)\|$
			17.6	$\|^3J(H-H)\|$
			4.8	$\|^3J(P-H)\|$
	5.94 (dd, 1)	$CH{=}CHCMe_3$	17.6	$\|^3J(H-H)\|$
			2.5	$\|^4J(P-H)\|$
	1.26 (s, 9)	$CH{=}CHCMe_3$		
	1.18 (d, 3)	PMe_2Ph	7.6	$\|^2J(P-H)\|$
	1.06 (d, 3)	PMe_2Ph	8.5	$\|^2J(P-H)\|$
	1.04 (d, 3)	PMe_2Ph	7.4	$\|^2J(P-H)\|$
	1.01 (d, 3)	PMe_2Ph	7.7	$\|^2J(P-H)\|$
$[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, isomer **2**	6.58 (dt, 1)	$CH{=}CHCMe_3$	17.5	$\|^3J(H-H)\|$
			4.7	$\|^3J(P-H)\|$
	5.86 (dt, 1)	$CH{=}CHCMe_3$	17.5	$\|^3J(H-H)\|$
			2.1	$\|^4J(P-H)\|$
	1.32 (t, 6)	PMe_2Ph	7.2	$\|^2J(P-H) + {}^4J(P-H)\|$
	1.22 (s, 9)	$CH{=}CHCMe_3$		
	1.15 (t, 6)	PMe_2Ph	7.4	$\|^2J(P-H) + {}^4J(P-H)\|$
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$	5.76 (ddd, 1)	$PhCOCH{=}CHCMe_3$	8.2	$\|^3J(H-H)\|$
			2.7	$\|^3J(P-H)\|$
			1.1	$\|^3J(P-H)\|$
	2.12 (ddd, 1)	$PhCOCH{=}CHCMe_3$	8.2	$\|^3J(H-H)\|$
			7.4	$\|^3J(P-H)\|$
			5.9	$\|^3J(P-H)\|$
	1.71 (d, 3)	PMe_2Ph	8.6	$\|^2J(P-H)\|$
	1.61 (d, 3)	PMe_2Ph	8.3	$\|^2J(P-H)\|$
	1.21 (s, 9)	$PhCOCH{=}CHCMe_3$		
	0.97 (d, 3)	PMe_2Ph	8.5	$\|^2J(P-H)\|$
	0.95 (d, 3)	PMe_2Ph	7.8	$\|^2J(P-H)\|$
$[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$, isomer **3**[b]	1.08 (d, 3)	PMe_2Ph	7.8	$\|^2J(P-H)\|$
	1.04 (d, 3)	PMe_2Ph	8.9	$\|^2J(P-H)\|$
	1.01 (d, 3)	PMe_2Ph	8.2	$\|^2J(P-H)\|$
	0.96 (d, 3)	PMe_2Ph	7.5	$\|^2J(P-H)\|$
$[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$, isomer **2**	7.94 (dt, 1)	$CH{=}CHPh$	18.0	$\|^3J(H-H)\|$
			4.6	$\|^3J(P-H)\|$
	6.93 (dt, 1)	$CH{=}CHPh$	18.0	$\|^3J(H-H)\|$
			2.1	$\|^4J(P-H)\|$
	1.23 (t, 6)	PMe_2Ph	7.1	$\|^2J(P-H) + {}^4J(P-H)\|$
	1.11 (t, 6)	PMe_2Ph	7.1	$\|^2J(P-H) + {}^4J(P-H)\|$
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHPh)(PMe_2Ph)_2]$	6.03 (dd, 1)	$PhCOCH{=}CHPh$	7.5	$\|^3J(H-H)\|$
			2.4	$\|^3J(P-H)\|$
	2.88 (ddd, 1)	$PhCOCH{=}CHPh$	7.5	$\|^3J(H-H)\|$
			4.8	$\|^3J(P-H)\|$
			4.5	$\|^3J(P-H)\|$
	1.63 (d)	PMe_2Ph	8.8	$\|^2J(P-H)\|$
	1.25 (d)	PMe_2Ph	8.3	$\|^2J(P-H)\|$
	0.98 (d)	PMe_2Ph	8.2	$\|^2J(P-H)\|$
	0.84 (d)	PMe_2Ph	8.2	$\|^2J(P-H)\|$
$PhCOCH{=}CHCMe_3$[c]	7.06 (d)	$PhCOCH{=}CHCMe_3$	15.7	$\|^3J(H-H)\|$
	6.78 (d)	$PhCOCH{=}CHCMe_3$	15.7	$\|^3J(H-H)\|$
	1.16 (s)	$PhCOCH{=}CHCMe_3$		

[a] In C_6D_6 solution, except where stated otherwise. Resonances due to phenyl protons have been omitted. [b] Vinyl proton resonances obscured by phenyl protons. [c] In $CDCl_3$ solution.

differs from that of the starting materials **1**, whereas the thermodynamically preferred isomer of $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ **2** has a ligand arrangement analogous to **1**. Reactions of related ruthenium(II) complexes with LiPh appear to proceed by nucleophilic attack on a carbonyl ligand rather than by a direct substitution at the metal,[15] and it seems likely that the same is true here (see Scheme 1). Dissociation of the chloride ligand then occurs, followed by breakdown of the benzoyl ligand into separate phenyl and carbonyl ligands. Formation of **3** rather than **2** implies that the preferred geometry for the benzoyl complex $[Ru(CO)(CH{=}CHR)(COPh)(PMe_2Ph)_2]$ which is the immediate precursor of **3** must be either a trigonal bipyramid with the two PMe_2Ph ligands in equatorial positions (**4** in Scheme 1) or a square pyramid with mutually *cis* PMe_2Ph ligands. The same intermediate may be involved in the isomerisation of **3** to **2**: the mechanism shown in Scheme 1 involves interconversion of trigonal-bipyramidal intermediates **4** and **5** by the Berry[18] mechanism, but a mechanism involving two square-pyramidal intermediates can also be envisaged. Species **4** could also be an intermediate on the route to the ketone complexes $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHR)(PMe_2Ph)_2]$, but a mechanism involving initial combination of vinyl and carbonyl ligands to give $[Ru(CO)(COCH{=}CHR)Ph(PMe_2Ph)_2]$ is equally plausible.

We have previously used the reaction of complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ (R = methyl or aryl) with LiPh as a means of obtaining products $[Ru(CO)_2R(Ph)(PMe_2Ph)_2]$: in these reactions the starting materials and products possessed analogous ligand arrangements with mutually *trans* PMe_2Ph ligands and *cis* carbonyl ligands.[15] In view of the results reported above, we repeated the reaction of $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ with LiPh, using the same

Table 3 Carbon-13 NMR spectral data for the compounds[a]

Compound	δ	Assignment	Coupling constant/Hz	Assignment
$[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, isomer **3**	201.6 (dd)	CO	97.5	*trans*-$\lvert^2J$(P–C)$\rvert$
			8.3	*cis*-$\lvert^2J$(P–C)$\rvert$
	200.1 (dd)	CO	13.3	*cis*-$\lvert^2J$(P–C)$\rvert$
			7.2	*cis*-$\lvert^2J$(P–C)$\rvert$
	154.6 (dd)	RuPh, C^1	61.8	*trans*-$\lvert^2J$(P–C)$\rvert$
			15.6	*cis*-$\lvert^2J$(P–C)$\rvert$
	150.7 (dd)	$CH{=}CHCMe_3$	5.4	*cis*-$\lvert^3J$(P–C)$\rvert$
			3.7	*cis*-$\lvert^3J$(P–C)$\rvert$
	141.7 (dd)	$CH{=}CHCMe_3$	16.3	*cis*-$\lvert^2J$(P–C)$\rvert$
			12.7	*cis*-$\lvert^2J$(P–C)$\rvert$
	36.6 (d)	$CH{=}CHCMe_3$	1.5	*cis*-$\lvert^4J$(P–C)$\rvert$
	30.4 (s)	$CH{=}CHCMe_3$		
	16.9 (d)	PMe_2Ph	26.8	$\lvert^1J$(P–C)$\rvert$
	15.9 (d)	PMe_2Ph	31.3	$\lvert^1J$(P–C)$\rvert$
	14.7 (d)	PMe_2Ph	25.0	$\lvert^1J$(P–C)$\rvert$
	10.9 (d)	PMe_2Ph	30.0	$\lvert^1J$(P–C)$\rvert$
$[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, isomer **2**	199.9 (t)	CO	9.4	$\lvert^2J$(P–C)$\rvert$
	198.7 (t)	CO	9.4	$\lvert^2J$(P–C)$\rvert$
	160.7 (t)	RuPh, C^1	15.8	$\lvert^2J$(P–C)$\rvert$
	154.1 (t)	$CH{=}CHCMe_3$	4.9	$\lvert^3J$(P–C)$\rvert$
	144.7 (t)	$CH{=}CHCMe_3$	15.9	$\lvert^2J$(P–C)$\rvert$
	36.7 (s)	$CH{=}CHCMe_3$		
	30.5 (s)	$CH{=}CHCMe_3$		
	14.5 (t)	PMe_2Ph	32.9	$\lvert^1J$(P–C) + ^3J(P–C)$\rvert$
	13.9 (t)	PMe_2Ph	33.2	$\lvert^1J$(P–C) + ^3J(P–C)$\rvert$
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$	209.1 (dd)	CO	14.9	$\lvert^2J$(P–C)$\rvert$
			11.6	$\lvert^2J$(P–C)$\rvert$
	138.8 (d)[b]	$PhCOCH{=}CHCMe_3$	3.3	$\lvert^2J$(P–C)$\rvert$
	132.4 (s)[c]	$PhCOCH{=}CHCMe_3$, C^1		
	76.9 (s)	$PhCOCH{=}CHCMe_3$		
	68.8 (d)	$PhCOCH{=}CHCMe_3$	33.1	$\lvert^2J$(P–C)$\rvert$
	33.7 (d)	$PhCOCH{=}CHCMe_3$	1.9	$\lvert^3J$(P–C)$\rvert$
	33.0 (s)[c]	$PhCOCH{=}CHCMe_3$		
	18.9 (d)[b]	PMe_2Ph	25.2	$\lvert^1J$(P–C)$\rvert$
	18.6 (d)[b]	PMe_2Ph	26.4	$\lvert^1J$(P–C)$\rvert$
	16.0 (d)[b]	PMe_2Ph	22.0	$\lvert^1J$(P–C)$\rvert$
	15.3 (d)[b]	PMe_2Ph	21.5	$\lvert^1J$(P–C)$\rvert$
$[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$,[d] isomer **3**	201.1 (dd)	CO	97.1	*trans*-$\lvert^2J$(P–C)$\rvert$
			7.9	*cis*-$\lvert^2J$(P–C)$\rvert$
	200.3 (dd)	CO	14.0	*cis*-$\lvert^2J$(P–C)$\rvert$
			7.5	*cis*-$\lvert^2J$(P–C)$\rvert$
	157.1 (dd)	$CH{=}CHPh$	16.9	*cis*-$\lvert^2J$(P–C)$\rvert$
			12.8	*cis*-$\lvert^2J$(P–C)$\rvert$
	153.5 (dd)	RuPh, C^1	60.8	*trans*-$\lvert^2J$(P–C)$\rvert$
			15.7	*cis*-$\lvert^2J$(P–C)$\rvert$
	140.6 (dd)	$CH{=}CHPh$	6.0	*cis*-$\lvert^3J$(P–C)$\rvert$
			4.2	*cis*-$\lvert^3J$(P–C)$\rvert$
	17.0 (d)	PMe_2Ph	26.2	$\lvert^1J$(P–C)$\rvert$
	16.0 (d)	PMe_2Ph	31.6	$\lvert^1J$(P–C)$\rvert$
	15.7 (d)	PMe_2Ph	25.1	$\lvert^1J$(P–C)$\rvert$
	11.4 (d)	PMe_2Ph	30.2	$\lvert^1J$(P–C)$\rvert$
$[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$, isomer **2**	199.5 (t)	CO	9.1	$\lvert^2J$(P–C)$\rvert$
	199.0 (t)	CO	9.5	$\lvert^2J$(P–C)$\rvert$
	160.6 (t)	$CH{=}CHPh$	16.5	$\lvert^2J$(P–C)$\rvert$
	160.1 (t)	RuPh, C^1	15.1	$\lvert^2J$(P–C)$\rvert$
	144.3 (t)	$CH{=}CHPh$	3.4	$\lvert^3J$(P–C)$\rvert$
	142.6 (t)	$CH{=}CHPh$, C^1	2.2	$\lvert^4J$(P–C)$\rvert$
	14.9 (t)	PMe_2Ph	32.9	$\lvert^1J$(P–C) + ^3J(P–C)$\rvert$
	14.1 (t)	PMe_2Ph	33.0	$\lvert^1J$(P–C) + ^3J(P–C)$\rvert$
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHPh)(PMe_2Ph)_2]$	207.1 (dd)	CO	16.0	$\lvert^2J$(P–C)$\rvert$
			11.8	$\lvert^2J$(P–C)$\rvert$
	146.4 (d)	$PhCOCH{=}CHPh$, C^1	3.9	$\lvert^3J$(P–C)$\rvert$
	138.6 (d)	$PhCOCH{=}CHPh$	2.6	$\lvert^2J$(P–C)$\rvert$
	132.1 (s)[c]	$PhCOCH{=}CHPh$, C^1		
	77.6 (s)	$PhCOCH{=}CHPh$		
	54.0 (d)	$PhCOCH{=}CHPh$	28.6	$\lvert^2J$(P–C)$\rvert$
	17.2 (d)	PMe_2Ph	28.0	$\lvert^1J$(P–C)$\rvert$
	17.1 (d)	PMe_2Ph	27.5	$\lvert^1J$(P–C)$\rvert$
	16.5 (d)	PMe_2Ph	24.3	$\lvert^1J$(P–C)$\rvert$
	15.5 (d)	PMe_2Ph	23.7	$\lvert^1J$(P–C)$\rvert$

Table 3 (*continued*)

Compound	δ	Assignment	Coupling constant/Hz	Assignment
$PhCOCH{=}CHCMe_3$ [e]	192.4 (s)	$PhCOCH{=}CHCMe_3$		
	160.4 (s)	$PhCOCH{=}CHCMe_3$		
	138.9 (s)	$PhCOCH{=}CHCMe_3$, C^1		
	121.7 (s)	$PhCOCH{=}CHCMe_3$		
	34.9 (s)	$PhCOCH{=}CHCMe_3$		
	29.5 (s)	$PhCOCH{=}CHCMe_3$		

[a] In C_6D_6 solution, except where stated otherwise. Phenyl resonances for PMe_2Ph ligands have been omitted, as have those for C^{2-6} in other phenyl groups. [b] Evidence of an additional unresolved doublet splitting. [c] Evidence of an unresolved doublet splitting. [d] Resonance for C^1 in CH=CH*Ph* not definitely identified. [e] In $CDCl_3$ solution.

Table 4 Infrared * and analytical data

Compound	ν(C≡O)/cm^{-1}	Analysis (%) Found C	Found H	Calculated C	Calculated H
$[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$, isomer **2**	2015, 1960	59.60	6.10	60.70	6.45
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$	1905	61.45	6.70	60.70	6.45
$[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$, isomer **2**	2020, 1960	62.70	5.70	62.65	5.60
$[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHPh)(PMe_2Ph)_2]$	1915	62.40	5.75	62.65	5.60

* In $CHCl_3$ solution. Only bands in the C≡O stretching region are listed.

low-temperature conditions as those employed in the reactions between $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ and LiPh. A ^{31}P NMR spectrum of the product, recorded at 10 °C in C_6D_6 solution, revealed the presence of two species. One, characterised by a singlet at δ 2.4, was the already known isomer of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$:[15] the other, present in relatively small quantity, exhibited doublet resonances [$|^2J(P\text{–}P)| = 25.7$ Hz] at δ −3.9 and −10.2. The similarity in spectrum to isomer **3** of the complexes $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$, coupled with the fact that the doublet resonances fairly quickly disappeared (with intensification of the singlet resonance at δ 2.4) implied that the complex was the isomer of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ with a structure analogous to **3**. This does not, of course, prove that the only route from $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ and LiPh to the known isomer of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ is by way of the other isomer.

The extremely facile rearrangement of isomer **3** of the complexes $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$ to the ketone complexes $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHR)(PMe_2Ph)_2]$ is in marked contrast to the relative inertness of the isomers of structure **2** which appear to be long-lived in C_6D_6 solution at room temperature. As mentioned earlier, complexes $[Ru(CO)_2R(R')(PMe_2Ph)_2]$ (R, R′ = methyl or aryl), which have structures analogous to isomer **2** of $[Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2]$, do form ketones RCOR′ in solution, but even on warming above room temperature the reactions are slow. Clearly there is a link between ligand arrangement and reactivity: it may be that the barrier to migration of the phenyl or vinyl ligand is lower in isomer **3** than in **2**, or simply that ketone formation is facilitated by the convenient *cis* positioning of all three component ligands in **3**.

Experimental

Complexes were prepared and purified using dry, oxygen-free solvents. Reactions were carried out under an atmosphere of dry nitrogen. The NMR spectra were recorded on JEOL FX90Q and Bruker MSL300 instruments: in some instances ^1H spectra were also recorded on a Bruker WH360 spectrometer with broad-band or selective decoupling of ^{31}P nuclei. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer: the data, together with elemental analysis figures, appear in Table 4.

The preparations of the vinyl complexes $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ (R = CMe_3 or Ph) have been described in a previous paper.[14]

Synthesis of Isomer **3** *of* $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$.—All operations were carried out at 0 °C. A stirred solution of $[Ru(CO)_2(CH{=}CHCMe_3)Cl(PMe_2Ph)_2]$ (0.15 g) in diethyl ether (25 cm^3) was treated with a freshly prepared solution (4 cm^3) of LiPh [from lithium (0.30 g) and bromobenzene (1 cm^3) in ether (25 cm^3)]. After 1 min a portion (0.5 cm^3) of the reaction mixture was removed and added to ice-cold water (1 cm^3) to destroy excess of LiPh. The IR spectrum of the ether solution was then checked to ensure that no $[Ru(CO)_2(CH{=}CHCMe_3)Cl(PMe_2Ph)_2]$ remained. The rest of the reaction mixture was then stirred with ice-cold water (4 cm^3). The aqueous phase was removed, and the ether solution was dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure, leaving a yellow oil.

The same method was used to obtain isomer **3** of $[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$ from $[Ru(CO)_2(CH{=}CHPh)Cl(PMe_2Ph)_2]$.

Conversion of Isomer **3** *of* $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$ *into Isomer* **2** *and* $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$.—The conversion was carried out at 20 °C in C_6D_6 solution (0.5 cm^3) and monitored by NMR spectroscopy. When the reaction was complete the solvent was removed under reduced pressure, and the residue dissolved in ether containing a small amount of benzene. The solution was subjected to chromatography on an alumina column packed in hexane. Elution with ether followed by removal of the solvent under reduced pressure yielded isomer **2** of $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PMe_2Ph)_2]$ contaminated with a little $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$, a by-product of the preparation of isomer **3**. Elution with ether containing a little ethanol then yielded $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$,

obtained as yellow crystals on removing the solvent under reduced pressure.

Further purification of isomer **2** was achieved by treatment with a little ethanol in which it dissolved, leaving insoluble $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$. After removal of the ethanol under reduced pressure, isomer **2** was dissolved in hexane containing a little ether and again subjected to chromatography on alumina. After initial elution with hexane, isomer **2** was removed by elution with hexane containing 10% of ether. Removal of the solvent under reduced pressure followed by crystallisation from a mixture of pentane and ethanol yielded colourless crystals.

Isomer **2** of $[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$ and $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHPh)(PMe_2Ph)_2]$ were obtained from isomer **3** of $[Ru(CO)_2(CH{=}CHPh)Ph(PMe_2Ph)_2]$ in the same way.

Liberation of $PhCOCH{=}CHCMe_3$ *from* $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$.—A solution of $[Ru(CO)(\eta^4\text{-}PhCOCH{=}CHCMe_3)(PMe_2Ph)_2]$ (0.04 g) in C_6D_6 (0.5 cm^3) was treated with Me_3CNC (2 mol per mol of ruthenium complex) at room temperature. After 3 d the C_6D_6 was removed by evaporation under a stream of nitrogen. The residue was dissolved in hexane containing 10% of ether and subjected to column chromatography on alumina. Elution with hexane–ether (70:30) removed the $PhCOCH{=}CHCMe_3$, leaving ruthenium-containing materials on the column. The ketone was obtained as a colourless oil on removing the solvent under a stream of nitrogen.

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