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Intramolecular combination of vinyl, aryl and carbonyl ligands in ruthenium(II) complexes: a mechanistic study

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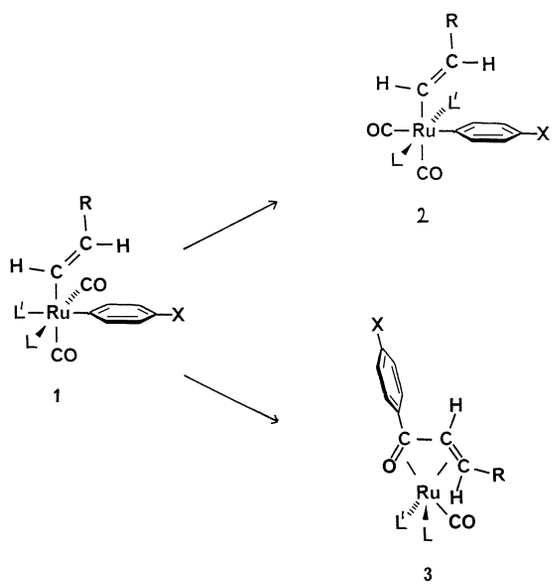
Complexes $[Ru(CO)_2(CH=CHR)(C_6H_4X\text{-}4)L(L')]$ [R = Ph, CMe_3, H, Me or OEt; X = H, Cl or OMe; L = L′ = PMe_2Ph, PMe_3, $P(OMe)_2Ph$ or PPh_3; L = PMe_3, L′ = PPh_3] underwent competing isomerisation reactions, one an intramolecular construction of a vinyl aryl ketone which remains co-ordinated, the other a simple redistribution of the ligands around the metal. Product ratios are determined by kinetic rather than thermodynamic factors. For a sequence of complexes with L = L′ = PMe_2Ph, electron-releasing substituents on the vinyl ligand favour formation of ketone complexes, whereas similar substituents on the phenyl ligand have the reverse effect. Increasing the reaction temperature disfavours ketone complex formation. Mechanisms involving initial migration of either the vinyl or the aryl ligand are discussed on the basis of these results and a complementary study involving trapping of the likely acyl intermediates.

The construction of organic molecules within the co-ordination sphere of a transition metal, particularly in cases where the product remains bound to the metal and available for further reaction, raises interesting possibilities for organic synthesis. In a recent paper[1] we reported that complexes $[Ru(CO)_2(CH=CHR)(C_6H_4X\text{-}4)L(L')]$ **1** (R = Ph or CMe_3, X = H, L = L′ = PMe_2Ph) underwent two competing rearrangements, shown in Scheme 1. One simply involved a redistribution of the ligands around the metal to give another isomer, **2**, of $[Ru(CO)_2(CH=CHR)(C_6H_4X\text{-}4)L(L')]$, but the other yielded products believed on the basis of elemental analysis and NMR evidence to be vinyl ketone complexes $[Ru(CO)\{\eta^4\text{-}RCH=CHC(C_6H_4X\text{-}4)=O\}L(L')]$ **3**, formed by combination of vinyl, aryl and carbonyl ligands. This has since been confirmed by an X-ray study of $[Ru(CO)\{\eta^4\text{-}PhCH=CHC(Ph)=O\}(PMe_2Ph)_2]$,[2] and the structure of a related iron complex (prepared from a preformed vinyl ketone) has also been reported.[3]

Since conversion of complex **2** into **3** is (see later) extremely slow even on heating, it is clearly of value to maximise the yield of **3** obtained in the initial rearrangement of **1**. In this paper we report on a study of the factors which determine the relative amounts of **2** and **3** formed in individual cases, and the possible mechanisms for conversion of **1** into **2** and **3**.



Scheme 1 Competing rearrangements of complexes **1**

Results and Discussion

The ^{31}P NMR and (where recorded) IR spectral data for new complexes are collected in Table 1, ^1H and ^{13}C NMR data for selected complexes in Tables 2 and 3 respectively. Unless indicated otherwise, all ^{31}P and ^{13}C NMR spectra were recorded with full proton decoupling.

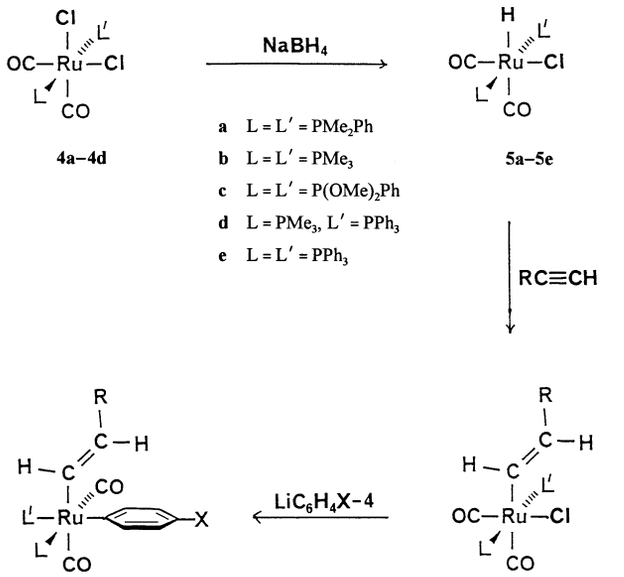
Synthesis of complexes $[Ru(CO)_2(CH=CHR)(C_6H_4X\text{-}4)L(L')]$, isomer 1

The route to these complexes is outlined in Scheme 2, which also lists and labels the complexes according to the nature of R, X, L and L′.

Of the starting materials $[Ru(CO)_2Cl_2L(L')]$ **4a**–**4d**, **4a** was prepared by the method of Jenkins *et al.*[4] as modified by Barnard *et al.*,[5] and **4b** was obtained in the same way. Complex **4c** was synthesized by heating $[\{Ru(CO)_2Cl_2\}_n]$ with $P(OMe)_2Ph$ in methanol, and **4d** by treating $[\{Ru(CO)_2Cl_2(PMe_3)\}_2]$, a by-product in the synthesis of **4b**, with PPh_3 in propanone.

Brief treatment with $NaBH_4$ in ethanol (or, for solubility reasons, a mixture of ethanol and benzene) converted each of the complexes **4a**–**4d** into $[Ru(CO)_2Cl(H)L(L')]$ **5a**–**5d**. The complex $[Ru(CO)_2Cl(D)(PMe_2Ph)_2]$, $[^2H_1]$**5a** and its PMe_3 analogue $[^2H_1]$**5b** were prepared as described by Bray and Mawby.[6] Like the previously characterised **5a**, complexes **5b** and **5c** exhibited singlet ^{31}P NMR spectra, and the ^1H resonance for the hydride ligand and the ^{13}C resonances for the two (inequivalent) carbonyl ligands were all triplets, establishing the stereochemistry. For **5d**, which contained two different phosphorus ligands, the ^{31}P NMR spectrum showed two doublets with a very large value for $|^2J(PP)|$ (278.5) Hz, characteristic of mutually *trans* phosphorus ligands.[7] Complex **5e**, $[Ru(CO)_2Cl(H)(PPh_3)_2]$, was obtained by treating $[Ru(CO)Cl(H)(PPh_3)_3]$ with CO, as described by Geoffroy and Bradley.[8]

Of the complexes $[Ru(CO)_2(CH=CHR)Cl(L)L']$ **6**, Bray and Mawby[9] have previously characterised **6aa** and **6ab**, the



1aaa L = L′ = PMe_2Ph, R = Ph, X = H
1aba L = L′ = PMe_2Ph, R = CMe_3, X = H
1abb L = L′ = PMe_2Ph, R = CMe_3, X = Cl
1abc L = L′ = PMe_2Ph, R = CMe_3, X = Me
1abd L = L′ = PMe_2Ph, R = CMe_3, X = OMe
1aca L = L′ = PMe_2Ph, R = H, X = H
1ada L = L′ = PMe_2Ph, R = Me, X = H
1aea L = L′ = PMe_2Ph, R = OEt, X = H
1bba L = L′ = PMe_3, R = CMe_3, X = H
1bbb L = L′ = PMe_3, R = CMe_3, X = Cl
1bbd L = L′ = PMe_3, R = CMe_3, X = OMe
1cba L = L′ = $P(OMe)_2Ph$, R = CMe_3, X = H
1dba L = PMe_3, L′ = PPh_3, R = CMe_3, X = H
1eba L = L′ = PPh_3, R = CMe_3, X = H

6aa L = L′ = PMe_2Ph, R = Ph
6ab L = L′ = PMe_2Ph, R = CMe_3
6ac L = L′ = PMe_2Ph, R = H
6ad L = L′ = PMe_2Ph, R = Me
6ae L = L′ = PMe_2Ph, R = OEt
6bb L = L′ = PMe_3, R = CMe_3
6cb L = L′ = $P(OMe)_2Ph$, R = CMe_3
6db L = PMe_3, L′ = PPh_3, R = CMe_3
6eb L = L′ = PPh_3, R = CMe_3

Scheme 2 Synthetic route to complexes **1**: in **1aea** and **6ae R** is *cis*, not *trans*, to Ru; **1eba** is not observed, the product being **2eba**

products of reaction of **5a** with PhC≡CH and Me_3CC≡CH respectively. Complexes **6bb**, **6cb**, **6db** and **6eb** were formed by heating **5b**, **5c**, **5d** and **5e**, respectively, with Me_3CC≡CH in C_6D_6. For **6bb** and **6cb** the ligand arrangements were established by the singlet ^{31}P resonances and the two triplet ^{13}C resonances for the carbonyl ligands. For each complex, doublet of triplets resonances were observed for the vinyl protons, and the values for $|^3J(HH)|$, 17.6 and 17.4 Hz respectively, confirmed that (as in the case of **6aa** and **6ab**) the vinyl ligand had been formed by *cis* addition of RuH to the alkyne. The assignments of the α- and β-proton resonances, initially based on the assumption that $|^3J(PH)|$ would be larger than $|^4J(PH)|$, were confirmed for **6aa**, **6ab** and **6bb** by preparing the vinyl complexes [$^2H_1$]**6aa**, [$^2H_1$]**6ab** and [$^2H_1$]**6bb** from [$^2H_1$]**5a**, [$^2H_1$]**5b** and the appropriate alkynes. Complex **6eb** has previously been reported by Loumrhari *et al.*[10]

For complex **6db**, also, both vinyl protons exhibited doublet of triplets resonances: the doublet splitting [$|^3J(HH)| = 17.4$ Hz] confirmed that *cis* addition of RuH to the alkyne had occurred, while the fact that triplet splittings were observed indicated that the values of $|^3J(PH)|$ were virtually identical for coupling to PMe_3 and to PPh_3, and that the same was true for $|^4J(PH)|$. Differences were, however, observed for coupling of the α-carbon in the vinyl ligand to the two phosphorus ligands, and also for the carbon in one of the two carbonyl ligands.

Complex **6ac** was obtained by treating a C_6D_6 solution of **5a** with ethyne for several hours. The vinyl-proton resonances were assigned on the basis of the coupling constants between them [*trans*-$|^3J(HH)| = 19.2$, *cis*-$|^3J(HH)| = 11.4$, *gem*-$|^2J(HH)| =$

Table 1 Phosphorus-31 NMR[a] and IR data[b] for new complexes

Complex	δ	Assignment	$\|^2J(PP)\|$/Hz	$\tilde{\nu}$(C≡O)/cm^{-1}
5b[c]	−6.2 (s)	PMe_3	—	2040
				1960
5c[c]	162.7 (s)	$P(OMe)_2Ph$	—	2065
				2000
5d[d]	35.8 (d)	PPh_3	278.5	
	−2.0 (d)	PMe_3	278.5	
6ac	−1.0 (s)	PMe_2Ph	—	2042
				1970
6ad	−0.5 (s)	PMe_2Ph	—	2040
				1970
6ae	0.2 (s)	PMe_2Ph	—	2045
				1970
6bb[e]	−9.0 (s)	PMe_3	—	2034
				1959
6cb	164.8 (s)	$P(OMe)_2Ph$	—	2050
				1990
1abb[d]	−2.7 (d)	PMe_2Ph	27.5	
	−9.6 (d)	PMe_2Ph	27.5	
1abc[d]	−3.0 (d)	PMe_2Ph	26.6	
	−9.2 (d)	PMe_2Ph	26.6	
1abd[d]	−3.1 (d)	PMe_2Ph	26.4	
	−9.1 (d)	PMe_2Ph	26.4	
1aca[d]	−2.5 (d)	PMe_2Ph	26.4	
	−9.5 (d)	PMe_2Ph	26.4	
1ada[d]	−2.2 (d)	PMe_2Ph	26.6	
	−9.0 (d)	PMe_2Ph	26.6	
1aea[d]	−2.2 (d)	PMe_2Ph	26.1	
	−8.6 (d)	PMe_2Ph	26.1	
1bba[d]	−11.4 (d)	PMe_3	29.0	
	−20.0 (d)	PMe_3	29.0	
1bbb[d,f]	−11.5 (d)	PMe_3	29.8	
	−19.1 (d)	PMe_3	29.8	
1bbd[d,f]	−10.5 (d)	PMe_3	28.6	
	−18.9 (d)	PMe_3	28.6	
1cba[d]	166.9 (d)	$P(OMe)_2Ph$	36.5	
	163.9 (d)	$P(OMe)_2Ph$	36.5	
1dba[d]	28.7 (d)	PPh_3	26.0	
	−15.4 (d)	PMe_3	26.0	
2abb[d]	0.9 (s)	PMe_2Ph	—	
2abc[d]	1.6 (s)	PMe_2Ph	—	
2abd[d]	1.6 (s)	PMe_2Ph	—	
2aca	1.8 (s)	PMe_2Ph	—	2015
				1955
2ada[d]	2.3 (s)	PMe_2Ph	—	
2aea	2.8 (s)	PMe_2Ph	—	2040
				1960
2bba	−9.2 (s)	PMe_3	—	2005
				1940
2bbb[d,f]	−9.3 (s)	PMe_3	—	
2bbd[d,f]	−8.4 (s)	PMe_3	—	
2dba[d]	29.7 (d)	PPh_3	282.6	
	−5.1 (d)	PMe_3	282.6	
2eba[d]	28.2 (s)	PPh_3	—	
3abb[d]	8.0 (d)	PMe_2Ph	10.4	
	1.8 (d)	PMe_2Ph	10.4	
3abc[d]	7.9 (d)	PMe_2Ph	10.1	
	1.8 (d)	PMe_2Ph	10.1	
3abd[d]	8.0 (d)	PMe_2Ph	11.9	
	1.9 (d)	PMe_2Ph	11.9	
3aca[d]	11.3 (d)	PMe_2Ph	13.2	
	2.1 (d)	PMe_2Ph	13.2	
3ada[d]	9.1 (d)	PMe_2Ph	9.0	
	1.2 (d)	PMe_2Ph	9.0	
3bba[d]	0.0 (d)	PMe_3	8.9	
	−8.5 (d)	PMe_3	8.9	
3bbb[d,f]	−1.2 (d)	PMe_3	17.9	
	−8.2 (d)	PMe_3	17.9	
3bbd[d,f]	0.5 (d)	PMe_3	8.2	
	−7.5 (d)	PMe_3	8.2	
3cba[d]	176.2 (d)	$P(OMe)_2Ph$	15.6	
	165.9 (d)	$P(OMe)_2Ph$	15.6	
3dba[d]	39.9 (d)	PPh_3	9.0	
	−5.1 (d)	PMe_3	9.0	

[a] In C_6D_6 solution unless stated otherwise. [b] In $CHCl_3$ solution unless stated otherwise. Only bands for the carbonyl ligands are listed. [c] Infrared spectrum in heptane solution. [d] Infrared spectrum not recorded. [e] ^{31}P NMR spectrum in $CDCl_3$ solution. [f] ^{31}P NMR spectrum in $C_6D_5CD_3$ solution.

Table 2 Proton NMR data[a] for new complexes

Complex	δ (multiplicity, intensity)	Assignment	Coupling constant/Hz	Assignment
5b	1.26 (t, 18)	PMe_3	7.5	$\|^2J(PH) + {}^4J(PH)\|$
	−5.59 (t, 1)	RuH	23.6	$\|^2J(PH)\|$
5c	3.64 (t, 6)	$P(OMe)_2Ph$	13.1	$\|^3J(PH) + {}^5J(PH)\|$
	3.31 (t, 6)	$P(OMe)_2Ph$	12.0	$\|^3J(PH) + {}^5J(PH)\|$
	−4.98 (t, 1)	RuH	17.0	$\|^2J(PH)\|$
5d	1.30 (dd, 9)	PMe_3	10.1	$\|^2J(PH)\|$
			1.9	$\|^4J(PH)\|$
	−4.78 (dd, 1)	RuH	24.0	$\|^2J(PH)\|$
			18.9	$\|^2J(PH)\|$
6ac	7.64 (ddt, 1)	$CH{=}CH_2$	19.2	$\|^3J(HH)\|$
			11.4	$\|^3J(HH)\|$
			3.4	$\|^3J(PH)\|$
	6.27 (ddt, 1)	$CH{=}CH_2$	11.4	$\|^3J(HH)\|$
			3.1	$\|^2J(HH)\|$
			2.7	$\|^4J(PH)\|$
	5.58 (ddt, 1)	$CH{=}CH_2$	19.2	$\|^3J(HH)\|$
			3.1	$\|^2J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.63 (t, 6)	PMe_2Ph	7.9	$\|^2J(PH) + {}^4J(PH)\|$
	1.55 (t, 6)	PMe_2Ph	7.7	$\|^2J(PH) + {}^4J(PH)\|$
6ad	6.93 (dtq, 1)	$CH{=}CHMe$	17.1	$\|^3J(HH)\|$
			3.4	$\|^3J(PH)\|$
			1.5	$\|^4J(HH)\|$
	5.67 (dtq, 1)	$CH{=}CHMe$	17.1	$\|^3J(HH)\|$
			6.0	$\|^3J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.96 (dtd, 3)	$CH{=}CHMe$	6.0	$\|^3J(HH)\|$
			3.0	$\|^5J(PH)\|$
			1.5	$\|^4J(HH)\|$
	1.59 (t, 6)	PMe_2Ph	7.7	$\|^2J(PH) + {}^4J(PH)\|$
	1.49 (t, 6)	PMe_2Ph	7.6	$\|^2J(PH) + {}^4J(PH)\|$
6ae	6.86 (dt, 1)	$CH{=}CHOEt$	6.4	$\|^3J(HH)\|$
			3.1	$\|^4J(PH)\|$
	5.49 (dt, 1)	$CH{=}CHOEt$	6.4	$\|^3J(HH)\|$
			3.2	$\|^3J(PH)\|$
	3.50 (t, 2)	OCH_2CH_3	7.0	$\|^3J(HH)\|$
	1.69 (t, 6)	PMe_2Ph	8.1	$\|^2J(PH) + {}^4J(PH)\|$
	1.64 (t, 6)	PMe_2Ph	7.7	$\|^2J(PH) + {}^4J(PH)\|$
	1.08 (q, 3)	OCH_2CH_3	7.0	$\|^3J(HH)\|$
6bb[b]	6.31 (dt, 1)	$CH{=}CHCMe_3$	17.6	$\|^3J(HH)\|$
			3.6	$\|^3J(PH)\|$
	5.54 (dt, 1)	$CH{=}CHCMe_3$	17.6	$\|^3J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.48 (t, 18)	PMe_3	7.5	$\|^2J(PH) + {}^4J(PH)\|$
	0.98 (s, 9)	CMe_3	—	—
6cb[b]	5.99 (dt, 1)	$CH{=}CHCMe_3$	17.4	$\|^3J(HH)\|$
			4.1	$\|^3J(PH)\|$
	5.28 (dt, 1)	$CH{=}CHCMe_3$	17.4	$\|^3J(HH)\|$
			2.0	$\|^4J(PH)\|$
	3.75 (t, 6)	$P(OMe)_2Ph$	11.5	$\|^3J(PH) + {}^5J(PH)\|$
	3.67 (t, 6)	$P(OMe)_2Ph$	11.1	$\|^3J(PH) + {}^5J(PH)\|$
	0.70 (s, 9)	CMe_3	—	—
6db[b]	6.42 (dt, 1)	$CH{=}CHCMe_3$	17.4	$\|^3J(HH)\|$
			3.6	$\|^3J(PH)\|$
	5.24 (dt, 1)	$CH{=}CHCMe_3$	17.4	$\|^3J(HH)\|$
			2.4	$\|^4J(PH)\|$
	1.53 (dd, 9)	PMe_3	10.0	$\|^2J(PH)\|$
			1.9	$\|^4J(PH)\|$
	0.76 (s, 9)	CMe_3	—	—
1abb	6.56 (ddd, 1)	$CH{=}CHCMe_3$	18.3	$\|^3J(PH)\|$
			17.6	$\|^3J(HH)\|$
			5.2	$\|^3J(PH)\|$
	5.84 (dd, 1)	$CH{=}CHCMe_3$	17.6	$\|^3J(HH)\|$
			2.5	$\|^4J(PH)\|$
	1.17 (s, 9)	CMe_3	—	—
1aca	7.58 (dddd, 1)	$CH{=}CH_2$	19.3	$\|^3J(HH)\|$
			18.2	$\|^3J(PH)\|$
			12.0	$\|^3J(HH)\|$
			4.4	$\|^3J(PH)\|$
	6.65 (dddd, 1)	$CH{=}CH_2$	12.0	$\|^3J(HH)\|$
			3.8	$\|^2J(HH)\|$
			2.9	$\|^4J(PH)\|$
			1.4	$\|^4J(PH)\|$
	5.87 (ddd, 1)	$CH{=}CH_2$	19.3	$\|^3J(HH)\|$
			3.8	$\|^2J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.30 (d, 3)	PMe_2Ph	6.4	$\|^2J(PH)\|$

Table 2 (*continued*)

Complex	δ (multiplicity, intensity)	Assignment	Coupling constant/Hz	Assignment
	1.14 (d, 3)	P*Me*$_2$Ph	7.9	$\|^2J(PH)\|$
	1.00 (d, 3)	P*Me*$_2$Ph	7.9	$\|^2J(PH)\|$
	0.95 (d, 3)	P*Me*$_2$Ph	7.6	$\|^2J(PH)\|$
1aea	7.02 (dd, 1)	CH=C*H*OEt	6.9	$\|^3J(HH)\|$
			3.4	$\|^4J(PH)\|$
	5.36 (ddd, 1)	C*H*=CHOEt	17.9	$\|^3J(PH)\|$
			6.9	$\|^3J(HH)\|$
			2.2	$\|^3J(PH)\|$
	3.63 (c, 2)[c]	OC*H*$_2$CH$_3$	—	—
	1.50 (d, 3)	P*Me*$_2$Ph	7.7	$\|^2J(PH)\|$
	1.19 (d, 3)	P*Me*$_2$Ph	8.2	$\|^2J(PH)\|$
	1.11 (t, 3)	OCH$_2$C*H*$_3$	7.0	$\|^3J(HH)\|$
	1.06 (d, 3)	P*Me*$_2$Ph	8.2	$\|^2J(PH)\|$
	0.97 (d, 3)	P*Me*$_2$Ph	8.5	$\|^2J(PH)\|$
1bba	6.50 (ddd, 1)	C*H*=CHCMe$_3$	18.7	$\|^3J(PH)\|$
			17.6	$\|^3J(HH)\|$
			4.4	$\|^3J(PH)\|$
	5.88 (dd, 1)	CH=C*H*CMe$_3$	17.6	$\|^3J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.20 (s, 9)	CMe$_3$	—	—
	0.97 (d, 9)	PMe$_3$	7.4	$\|^2J(PH)\|$
	0.74 (d, 9)	PMe$_3$	8.2	$\|^2J(PH)\|$
1bbb[d]	6.40 (ddd, 1)	C*H*=CHCMe$_3$	19.1	$\|^3J(PH)\|$
			17.6	$\|^3J(HH)\|$
			4.3	$\|^3J(PH)\|$
	5.81 (dd, 1)	CH=C*H*CMe$_3$	17.6	$\|^3J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.15 (s, 9)	CMe$_3$	—	—
	0.97 (d, 9)	PMe$_3$	7.6	$\|^2J(PH)\|$
	0.72 (d, 9)	PMe$_3$	8.6	$\|^2J(PH)\|$
1bbd[d]	6.51 (ddd, 1)	C*H*=CHCMe$_3$	19.1	$\|^3J(PH)\|$
			17.6	$\|^3J(HH)\|$
			3.8	$\|^3J(PH)\|$
	5.91 (dd, 1)	CH=C*H*CMe$_3$	17.6	$\|^3J(HH)\|$
			2.4	$\|^4J(PH)\|$
	1.24 (s, 9)	CMe$_3$	—	—
	0.96 (d, 9)	PMe$_3$	7.6	$\|^2J(PH)\|$
	0.74 (d, 9)	PMe$_3$	8.1	$\|^2J(PH)\|$
1cba	5.97 (ddd, 1)	C*H*=CHCMe$_3$	17.4	$\|^3J(PH)\|$
			17.4	$\|^3J(HH)\|$
			7.5	$\|^3J(PH)\|$
	5.77 (dd, 1)	CH=C*H*CMe$_3$	17.4	$\|^3J(HH)\|$
			1.6	$\|^4J(PH)\|$
	3.32 (d, 3)	P(O*Me*)$_2$Ph	11.2	$\|^3J(PH)\|$
	3.28 (d, 3)	P(O*Me*)$_2$Ph	11.2	$\|^3J(PH)\|$
	3.04 (d, 3)	P(O*Me*)$_2$Ph	11.6	$\|^3J(PH)\|$
	2.95 (d, 3)	P(O*Me*)$_2$Ph	10.8	$\|^3J(PH)\|$
	0.95 (s, 9)	CMe$_3$	—	—
1dba[e]	5.45 (dd, 1)	CH=C*H*CMe$_3$	17.8	$\|^3J(HH)\|$
			2.0	$\|^4J(PH)\|$
	1.16 (s, 9)	CMe$_3$	—	—
	0.73 (d, 9)	PMe$_3$	8.3	$\|^2J(PH)\|$
2abb	6.40 (dt, 1)	C*H*=CHCMe$_3$	17.4	$\|^3J(HH)\|$
			4.8	$\|^3J(PH)\|$
	5.82 (dt, 1)	CH=C*H*CMe$_3$	17.4	$\|^3J(HH)\|$
			2.0	$\|^4J(PH)\|$
	1.25 (t, 6)	P*Me*$_2$Ph	7.2	$\|^2J(PH) + {}^4J(PH)\|$
	1.18 (s, 9)	CMe$_3$	—	—
	1.06 (t, 6)	P*Me*$_2$Ph	7.2	$\|^2J(PH) + {}^4J(PH)\|$
2abc	6.61 (dt, 1)	C*H*=CHCMe$_3$	17.7	$\|^3J(HH)\|$
			4.6	$\|^3J(PH)\|$
	5.85 (dt, 1)	CH=C*H*CMe$_3$	17.7	$\|^3J(HH)\|$
			2.0	$\|^4J(PH)\|$
	2.10 (s, 3)	C$_6$H$_4$*Me*	—	—
	1.33 (t, 6)	P*Me*$_2$Ph	7.4	$\|^2J(PH) + {}^4J(PH)\|$
	1.22 (s, 9)	CMe$_3$	—	—
	1.17 (t, 6)	P*Me*$_2$Ph	7.4	$\|^2J(PH) + {}^4J(PH)\|$
2abd	6.57 (dt, 1)	C*H*=CHCMe$_3$	17.4	$\|^3J(HH)\|$
			2.9	$\|^3J(PH)\|$
	5.85 (dt, 1)	CH=C*H*CMe$_3$	17.4	$\|^3J(HH)\|$
			2.1	$\|^4J(PH)\|$
	1.37 (t, 6)	P*Me*$_2$Ph	7.3	$\|^2J(PH) + {}^4J(PH)\|$
	1.20 (s, 9)	CMe$_3$	—	—
	1.16 (t, 6)	P*Me*$_2$Ph	7.2	$\|^2J(PH) + {}^4J(PH)\|$
2aca	7.42 (ddt, 1)	C*H*=CH$_2$	19.2	$\|^3J(HH)\|$
			11.9	$\|^3J(HH)\|$
			4.6	$\|^3J(PH)\|$

Table 2 (*continued*)

Complex	δ (multiplicity, intensity)	Assignment	Coupling constant/Hz	Assignment
	6.53 (ddt, 1)	CH=CH_2	11.9	$\|^3J(HH)\|$
			3.8	$\|^2J(HH)\|$
			2.4	$\|^4J(PH)\|$
	5.80 (ddt, 1)	CH=CH_2	19.2	$\|^3J(HH)\|$
			3.8	$\|^2J(HH)\|$
			2.0	$\|^4J(PH)\|$
	1.32 (t, 6)	PMe_2Ph	7.3	$\|^2J(PH) + {}^4J(PH)\|$
	1.11 (t, 6)	PMe_2Ph	7.3	$\|^2J(PH) + {}^4J(PH)\|$
2aea	6.92 (dt, 1)	CH=CHOEt	6.9	$\|^3J(HH)\|$
			2.8	$\|^4J(PH)\|$
	5.15 (dt, 1)	CH=CHOEt	6.9	$\|^3J(HH)\|$
			5.4	$\|^3J(PH)\|$
	3.60 (q, 2)	OCH_2CH$_3$	7.0	$\|^3J(HH)\|$
	1.47 (t, 6)	PMe_2Ph	7.1	$\|^2J(PH) + {}^4J(PH)\|$
	1.17 (t, 6)	PMe_2Ph	7.1	$\|^2J(PH) + {}^4J(PH)\|$
	1.12 (t, 3)	OCH$_2$CH_3	7.0	$\|^3J(HH)\|$
2bba	6.53 (dt, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			4.8	$\|^3J(PH)\|$
	5.92 (dt, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			2.2	$\|^4J(PH)\|$
	1.17 (s, 9)	CMe$_3$	—	—
	0.93 (t, 18)	PMe$_3$	7.1	$\|^2J(PH) + {}^4J(PH)\|$
2bbb[d]	6.54 (dt, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			3.6	$\|^3J(PH)\|$
	5.66 (dt, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			2.6	$\|^4J(PH)\|$
	1.15 (t, 18)	PMe$_3$	7.6	$\|^2J(PH) + {}^4J(PH)\|$
	1.08 (s, 9)	CMe$_3$	—	—
2dba	6.35 (ddd, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			7.3	$\|^3J(PH)\|$
			2.1	$\|^3J(PH)\|$
	5.97 (dt, 1)	CH=CHCMe$_3$	17.6	$\|^3J(HH)\|$
			1.8	$\|^4J(PH)\|$
	1.12 (s, 9)	CMe$_3$	—	—
	0.97 (d, 9)	PMe$_3$	9.2	$\|^2J(PH)\|$
2eba	6.21 (dt, 1)	CH=CHCMe$_3$	17.9	$\|^3J(HH)\|$
			4.5	$\|^3J(PH)\|$
	5.97 (dt, 1)	CH=CHCMe$_3$	17.9	$\|^3J(HH)\|$
			2.0	$\|^4J(PH)\|$
	1.03 (s, 9)	CMe$_3$	—	—
3abb	5.63 (ddd, 1)	Me$_3$CCH=CHCOC$_6$H$_4$Cl	8.1	$\|^3J(HH)\|$
			3.1	$\|^3J(PH)\|$
			1.1	$\|^3J(PH)\|$
	2.01 (ddd, 1)	Me$_3$CCH=CHCOC$_6$H$_4$Cl	8.1	$\|^3J(HH)\|$
			7.8	$\|^3J(PH)\|$
			6.0	$\|^3J(PH)\|$
	1.71 (d, 3)	PMe_2Ph	8.5	$\|^2J(PH)\|$
	1.59 (d, 3)	PMe_2Ph	8.1	$\|^2J(PH)\|$
	1.19 (s, 9)	CMe$_3$	—	—
	0.96 (d, 3)	PMe_2Ph	7.4	$\|^2J(PH)\|$
	0.87 (d, 3)	PMe_2Ph	7.6	$\|^2J(PH)\|$
3abc[e]	5.77 (ddd, 1)	Me$_3$CCH=CHCOC$_6$H$_4$Me	8.2	$\|^3J(HH)\|$
			2.0	$\|^3J(PH)\|$
			1.0	$\|^3J(PH)\|$
	2.05 (s, 3)	C$_6$H$_4$$Me$	—	—
	1.73 (d, 3)	PMe_2Ph	8.7	$\|^2J(PH)\|$
	1.62 (d, 3)	PMe_2Ph	8.2	$\|^2J(PH)\|$
	1.20 (s, 9)	CMe$_3$	—	—
	1.03 (d, 3)	PMe_2Ph	6.4	$\|^2J(PH)\|$
	1.01 (d, 3)	PMe_2Ph	7.6	$\|^2J(PH)\|$
3abd	5.67 (ddd, 1)	Me$_3$CCH=CHCOC$_6$H$_4$OMe	7.9	$\|^3J(HH)\|$
			2.3	$\|^3J(PH)\|$
			1.3	$\|^3J(PH)\|$
	2.08 (ddd, 1)	Me$_3$CCH=CHCOC$_6$H$_4$OMe	7.9	$\|^3J(HH)\|$
			8.1	$\|^3J(PH)\|$
			6.1	$\|^3J(PH)\|$
	1.74 (d, 3)	PMe_2Ph	8.2	$\|^2J(PH)\|$
	1.65 (d, 3)	PMe_2Ph	8.2	$\|^2J(PH)\|$
	1.21 (s, 9)	CMe$_3$	—	—
	1.02 (d, 3)	PMe_2Ph	7.6	$\|^2J(PH)\|$
	0.97 (d, 3)	PMe_2Ph	7.4	$\|^2J(PH)\|$
3aca[e]	5.77 (m, 1)	CH$_2$=CHCOPh	—	—
	1.99 (m, 1)	CH_2=CHCOPh	—	—
	1.59 (d, 3)	PMe_2Ph	8.8	$\|^2J(PH)\|$
	1.44 (d, 3)	PMe_2Ph	6.5	$\|^2J(PH)\|$
	0.98 (d, 3)	PMe_2Ph	7.7	$\|^2J(PH)\|$
	0.86 (d, 3)	PMe_2Ph	7.7	$\|^2J(PH)\|$

Table 2 (*continued*)

Complex	δ (multiplicity, intensity)	Assignment	Coupling constant/Hz	Assignment
3bba	5.79 (ddd, 1)	$Me_3CCH{=}CHCOPh$	7.9	$\|^3J(HH)\|$
			3.0	$\|^3J(PH)\|$
			1.1	$\|^3J(PH)\|$
	1.90 (ddd, 1)	$Me_3CCH{=}CHCOPh$	7.9	$\|^3J(HH)\|$
			7.7	$\|^3J(PH)\|$
			6.2	$\|^3J(PH)\|$
	1.40 (d, 9)	PMe_3	8.8	$\|^2J(PH)\|$
	1.28 (s, 9)	CMe_3	—	—
	0.78 (d, 9)	PMe_3	7.7	$\|^2J(PH)\|$
3cba	5.80 (ddd, 1)	$Me_3CCH{=}CHCOPh$	8.5	$\|^3J(HH)\|$
			3.3	$\|^3J(PH)\|$
			1.0	$\|^3J(PH)\|$
	3.58 (d, 3)	$P(OMe)_2Ph$	11.7	$\|^3J(PH)\|$
	3.50 (d, 3)	$P(OMe)_2Ph$	12.0	$\|^3J(PH)\|$
	3.46 (d, 3)	$P(OMe)_2Ph$	11.6	$\|^3J(PH)\|$
	3.01 (d, 3)	$P(OMe)_2Ph$	11.6	$\|^3J(PH)\|$
	2.32 (ddd, 1)	$Me_3CCH{=}CHCOPh$	8.9	$\|^3J(PH)\|$
			8.5	$\|^3J(HH)\|$
			6.1	$\|^3J(PH)\|$
	1.20 (s, 9)	CMe_3	—	—
3dba	5.96 (ddd, 1)	$Me_3CCH{=}CHCOPh$	7.7	$\|^3J(HH)\|$
			2.7	$\|^3J(PH)\|$
			1.2	$\|^3J(PH)\|$
	2.28 (ddd, 1)	$Me_3CCH{=}CHCOPh$	7.7	$\|^3J(HH)\|$
			7.2	$\|^3J(PH)\|$
			6.2	$\|^3J(PH)\|$
	1.38 (s, 9)	CMe_3	—	—
	1.33 (d, 9)	PMe_3	8.9	$\|^2J(PH)\|$

[a] In C_6D_6 solution unless indicated otherwise. Resonances due to phenyl protons omitted. [b] In $CDCl_3$ solution. [c] Two overlapping distorted doublets of quartets. [d] In $C_6D_5CD_3$ solution. [e] One vinyl-proton resonance obscured.

Table 3 Carbon-13 NMR data[a] for new complexes

Complex	δ	Assignment	Coupling constant/Hz	Assignment
5b	200.4 (t)	CO	12.3	$\|^2J(PC)\|$
	195.2 (t)	CO	8.3	$\|^2J(PC)\|$
	19.5 (t)	PMe_3	32.7	$\|^1J(PC) + {}^3J(PC)\|$
5c	196.2 (t)	CO	14.0	$\|^2J(PC)\|$
	193.3 (t)	CO	8.7	$\|^2J(PC)\|$
	54.2 (t)	$P(OMe)_2Ph$	2.6	$\|^2J(PC) + {}^4J(PC)\|$
	53.1 (t)	$P(OMe)_2Ph$	5.8	$\|^2J(PC) + {}^4J(PC)\|$
6ac	199.0 (t)	CO	12.0	$\|^2J(PC)\|$
	194.0 (t)	CO	7.9	$\|^2J(PC)\|$
	166.3 (t)	$CH{=}CH_2$	15.0	$\|^2J(PC)\|$
	124.4 (t)	$CH{=}CH_2$	4.8	$\|^3J(PC)\|$
	13.5 (t)	PMe_2Ph	34.8	$\|^1J(PC) + {}^3J(PC)\|$
	11.9 (t)	PMe_2Ph	34.1	$\|^1J(PC) + {}^3J(PC)\|$
6ad	199.3 (t)	CO	12.0	$\|^2J(PC)\|$
	194.0 (t)	CO	8.2	$\|^2J(PC)\|$
	154.0 (t)	CH=CHMe	15.6	$\|^2J(PC)\|$
	132.6 (t)	CH=CHMe	5.0	$\|^3J(PC)\|$
	24.6 (t)	CH=CH*Me*	1.8	$\|^4J(PC)\|$
	13.7 (t)	PMe_2Ph	32.9	$\|^1J(PC) + {}^3J(PC)\|$
	12.0 (t)	PMe_2Ph	34.5	$\|^1J(PC) + {}^3J(PC)\|$
6ae	198.7 (t)	CO	12.4	$\|^2J(PC)\|$
	194.3 (t)	CO	8.4	$\|^2J(PC)\|$
	149.6 (t)	CH=CHOEt	5.1	$\|^3J(PC)\|$
	123.6 (t)	CH=CHOEt	15.6	$\|^2J(PC)\|$
	65.8 (s)	OCH_2CH_3	—	—
	15.6 (s)	OCH_2CH_3	—	—
	13.7 (t)	PMe_2Ph	33.4	$\|^1J(PC) + {}^3J(PC)\|$
	13.5 (t)	PMe_2Ph	34.2	$\|^1J(PC) + {}^3J(PC)\|$
6bb[b]	199.2 (t)	CO	12.9	$\|^2J(PC)\|$
	194.4 (t)	CO	7.9	$\|^2J(PC)\|$
	149.3 (t)	$CH{=}CHCMe_3$	5.0	$\|^3J(PC)\|$
	143.5 (t)	$CH{=}CHCMe_3$	15.0	$\|^2J(PC)\|$
	36.2 (t)	CMe_3	1.4	$\|^4J(PC)\|$
	30.0 (t)	CMe_3	1.5	$\|^5J(PC)\|$
	15.3 (t)	PMe_3	32.9	$\|^1J(PC) + {}^3J(PC)\|$
6cb[b]	195.3 (t)	CO	15.3	$\|^2J(PC)\|$
	190.1 (t)	CO	10.5	$\|^2J(PC)\|$
	149.3 (t)	$CH{=}CHCMe_3$	5.3	$\|^3J(PC)\|$
	133.6 (t)	$CH{=}CHCMe_3$	16.3	$\|^2J(PC)\|$
	53.1 (t)	$P(OMe)_2Ph$	6.3	$\|^2J(PC) + {}^4J(PC)\|$

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constant/Hz	Assignment
	52.8 (t)	$P(OMe)_2Ph$	6.3	$\|^2J(PC) + {}^4J(PC)\|$
	35.3 (t)	CMe_3	1.8	$\|^4J(PC)\|$
	28.4 (t)	CMe_3	1.0	$\|^5J(PC)\|$
6db[b]	198.3 (dd)	CO	14.5	$\|^2J(PC)\|$
			10.5	$\|^2J(PC)\|$
	193.4 (t)	CO	8.0	$\|^2J(PC)\|$
	149.0 (t)	$CH{=}CHCMe_3$	5.1	$\|^3J(PC)\|$
	142.7 (dd)	$CH{=}CHCMe_3$	15.8	$\|^2J(PC)\|$
			13.6	$\|^2J(PC)\|$
	36.4 (t)	CMe_3	1.4	$\|^4J(PC)\|$
	29.5 (t)	CMe_3	1.5	$\|^5J(PC)\|$
	15.2 (dd)	PMe_3	33.9	$\|^1J(PC)\|$
			1.7	$\|^3J(PC)\|$
1abb	201.0 (dd)	CO	97.2	$\|^2J(PC)\|$
			8.5	$\|^2J(PC)\|$
	199.6 (dd)	CO	13.6	$\|^2J(PC)\|$
			7.4	$\|^2J(PC)\|$
	152.7 (dd)	C_6H_4Cl, C^1	62.5	$\|^2J(PC)\|$
			15.8	$\|^2J(PC)\|$
	151.3 (dd)	$CH{=}CHCMe_3$	5.7	$\|^3J(PC)\|$
			4.0	$\|^3J(PC)\|$
	141.5 (dd)	$CH{=}CHCMe_3$	16.4	$\|^2J(PC)\|$
			12.4	$\|^2J(PC)\|$
	36.6 (d)	CMe_3	1.5	$\|^4J(PC)\|$
	30.2 (d)	CMe_3	1.7	$\|^5J(PC)\|$
	16.9 (dd)	PMe_2Ph	27.1	$\|^1J(PC)\|$
			1.1	$\|^3J(PC)\|$
	15.9 (dd)	PMe_2Ph	33.9	$\|^1J(PC)\|$
			2.8	$\|^3J(PC)\|$
	14.8 (d)	PMe_2Ph	25.5	$\|^1J(PC)\|$
	11.1 (dd)	PMe_2Ph	29.9	$\|^1J(PC)\|$
			1.1	$\|^3J(PC)\|$
1aca[c]	162.8 (dd)	$CH{=}CH_2$	16.4	$\|^2J(PC)\|$
			13.1	$\|^2J(PC)\|$
	153.6 (dd)	RuPh, C^1	58.9	$\|^2J(PC)\|$
			15.3	$\|^2J(PC)\|$
	126.4 (dd)	$CH{=}CH_2$	5.4	$\|^3J(PC)\|$
			4.4	$\|^3J(PC)\|$
	18.2 (dd)	PMe_2Ph	28.3	$\|^1J(PC)\|$
			1.6	$\|^3J(PC)\|$
	17.0 (dd)	PMe_2Ph	26.7	$\|^1J(PC)\|$
			1.6	$\|^3J(PC)\|$
	14.7 (d)	PMe_2Ph	24.5	$\|^1J(PC)\|$
	10.9 (dd)	PMe_2Ph	29.4	$\|^1J(PC)\|$
			1.6	$\|^3J(PC)\|$
1aea	201.7 (dd)	CO	101.5	$\|^2J(PC)\|$
			9.0	$\|^2J(PC)\|$
	200.5 (dd)	CO	13.0	$\|^2J(PC)\|$
			9.9	$\|^2J(PC)\|$
	154.2 (dd)	RuPh, C^1	63.3	$\|^2J(PC)\|$
			15.8	$\|^2J(PC)\|$
	149.1 (dd)	$CH{=}CHOEt$	5.7	$\|^3J(PC)\|$
			4.5	$\|^3J(PC)\|$
	121.9 (t)	$CH{=}CHOEt$	15.0	$\|^2J(PC)\|$
	65.8 (s)	OCH_2CH_3	—	—
	19.9 (dd)	PMe_2Ph	25.4	$\|^1J(PC)\|$
			1.7	$\|^3J(PC)\|$
	15.5 (s)	OCH_2CH_3	—	—
	15.0 (d)	PMe_2Ph	23.2	$\|^1J(PC)\|$
	14.1 (dd)	PMe_2Ph	31.1	$\|^1J(PC)\|$
			2.3	$\|^3J(PC)\|$
	13.2 (dd)	PMe_2Ph	29.4	$\|^1J(PC)\|$
			3.4	$\|^3J(PC)\|$
1bba	201.7 (dd)	CO	98.9	$\|^2J(PC)\|$
			8.5	$\|^2J(PC)\|$
	199.6 (dd)	CO	13.6	$\|^2J(PC)\|$
			7.6	$\|^2J(PC)\|$
	155.5 (dd)	RuPh, C^1	62.7	$\|^2J(PC)\|$
			15.8	$\|^2J(PC)\|$
	150.8 (dd)	$CH{=}CHCMe_3$	6.8	$\|^3J(PC)\|$
			4.0	$\|^3J(PC)\|$
	140.7 (dd)	$CH{=}CHCMe_3$	16.4	$\|^2J(PC)\|$
			13.2	$\|^2J(PC)\|$
	36.4 (s)	CMe_3	—	—
	30.4 (d)	CMe_3	2.2	$\|^5J(PC)\|$
	18.9 (dd)	PMe_3	34.9	$\|^1J(PC)\|$
			1.1	$\|^3J(PC)\|$

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constant/Hz	Assignment
	15.7 (dd)	PMe_3	28.5	$\|^1J(PC)\|$
			3.0	$\|^3J(PC)\|$
1bbb[d]	201.2 (dd)	CO	98.8	$\|^2J(PC)\|$
			8.7	$\|^2J(PC)\|$
	199.1 (dd)	CO	13.8	$\|^2J(PC)\|$
			7.3	$\|^2J(PC)\|$
	153.7 (dd)	C_6H_4Cl, C^1	64.0	$\|^2J(PC)\|$
			16.0	$\|^2J(PC)\|$
	151.1 (dd)	$CH{=}CHCMe_3$	6.2	$\|^3J(PC)\|$
			4.0	$\|^3J(PC)\|$
	140.4 (dd)	$CH{=}CHCMe_3$	16.7	$\|^2J(PC)\|$
			13.1	$\|^2J(PC)\|$
	36.4 (d)	CMe_3	1.5	$\|^4J(PC)\|$
	30.3 (d)	CMe_3	1.4	$\|^5J(PC)\|$
	18.7 (dd)	PMe_3	25.4	$\|^1J(PC)\|$
			1.4	$\|^3J(PC)\|$
	15.6 (dd)	PMe_3	29.1	$\|^1J(PC)\|$
			2.9	$\|^3J(PC)\|$
2aca	199.7 (t)	CO	9.0	$\|^2J(PC)\|$
	199.0 (t)	CO	9.5	$\|^2J(PC)\|$
	166.7 (t)	$CH{=}CH_2$	15.7	$\|^2J(PC)\|$
	160.3 (t)	RuPh, C^1	15.4	$\|^2J(PC)\|$
	126.6 (t)	$CH{=}CH_2$	4.4	$\|^3J(PC)\|$
	14.3 (t)	PMe_2Ph	33.4	$\|^1J(PC) + {}^3J(PC)\|$
	14.0 (t)	PMe_2Ph	32.8	$\|^1J(PC) + {}^3J(PC)\|$
2aea	199.2 (t)	CO	8.3	$\|^2J(PC)\|$
	199.1 (t)	CO	9.9	$\|^2J(PC)\|$
	161.1 (t)	RuPh, C^1	15.0	$\|^2J(PC)\|$
	149.7 (t)	CH=CHOEt	4.8	$\|^3J(PC)\|$
	123.6 (t)	CH=CHOEt	15.0	$\|^2J(PC)\|$
	65.8 (s)	OCH_2CH_3	—	—
	15.6 (s)	OCH_2CH_3	—	—
	15.4 (t)	PMe_2Ph	31.6	$\|^1J(PC) + {}^3J(PC)\|$
	14.4 (t)	PMe_2Ph	32.8	$\|^1J(PC) + {}^3J(PC)\|$
2bba	200.4 (t)	CO	9.6	$\|^2J(PC)\|$
	199.1 (t)	CO	9.6	$\|^2J(PC)\|$
	161.2 (t)	RuPh, C^1	15.5	$\|^2J(PC)\|$
	151.2 (t)	$CH{=}CHCMe_3$	5.1	$\|^3J(PC)\|$
	144.8 (t)	$CH{=}CHCMe_3$	16.1	$\|^2J(PC)\|$
	36.5 (t)	CMe_3	1.4	$\|^4J(PC)\|$
	30.6 (t)	CMe_3	1.4	$\|^5J(PC)\|$
	16.4 (t)	PMe_3	32.2	$\|^1J(PC) + {}^3J(PC)\|$
2bbb[d]	199.6 (t)	CO	12.3	$\|^2J(PC)\|$
	194.1 (t)	CO	8.0	$\|^2J(PC)\|$
	161.0 (t)	C_6H_4Cl, C^1	13.5	$\|^2J(PC)\|$
	148.8 (t)	$CH{=}CHCMe_3$	5.4	$\|^3J(PC)\|$
	145.0 (t)	$CH{=}CHCMe_3$	15.6	$\|^2J(PC)\|$
	36.2 (t)	CMe_3	1.8	$\|^4J(PC)\|$
	30.2 (t)	CMe_3	1.8	$\|^5J(PC)\|$
	14.7 (t)	PMe_3	32.7	$\|^1J(PC) + {}^3J(PC)\|$
2eba	201.7 (t)	CO	8.5	$\|^2J(PC)\|$
	199.8 (t)	CO	9.4	$\|^2J(PC)\|$
	156.8 (t)	RuPh, C^1	13.9	$\|^2J(PC)\|$
	151.5 (t)	$CH{=}CHCMe_3$	4.5	$\|^3J(PC)\|$
	145.7 (t)	$CH{=}CHCMe_3$	15.8	$\|^2J(PC)\|$
	37.1 (s)	CMe_3	—	—
	29.6 (s)	CMe_3	—	—
3bba[c]	139.6 (dd)	$Me_3CCH{=}CHCOPh$	3.4	$\|^2J(PC)\|$
			1.5	$\|^2J(PC)\|$
	76.8 (d)	$Me_3CCH{=}CHCOPh$	2.3	$\|^2J(PC)\|$
	66.5 (dd)	$Me_3CCH{=}CHCOPh$	34.0	$\|^2J(PC)\|$
			1.5	$\|^2J(PC)\|$
	33.6 (d)	CMe_3	2.2	$\|^3J(PC)\|$
	33.2 (d)	CMe_3	2.8	$\|^4J(PC)\|$
	20.8 (dd)	PMe_3	25.4	$\|^1J(PC)\|$
			2.8	$\|^3J(PC)\|$
	17.7 (t)	PMe_3	22.1	$\|^1J(PC)\|$
			1.1	$\|^3J(PC)\|$
3cba	207.1 (dd)	CO	17.1	$\|^2J(PC)\|$
			15.3	$\|^2J(PC)\|$
	137.4 (dd)	$Me_3CCH{=}CHCOPh$	4.4	$\|^2J(PC)\|$
			1.6	$\|^2J(PC)\|$
	78.0 (s)	$Me_3CCH{=}CHCOPh$	—	—
	69.6 (d)	$Me_3CCH{=}CHCOPh$	40.3	$\|^2J(PC)\|$
	53.3 (d)	$P(OMe)_2Ph$	3.3	$\|^2J(PC)\|$
	52.5 (d)	$P(OMe)_2Ph$	6.0	$\|^2J(PC)\|$
	52.2 (d)	$P(OMe)_2Ph$	7.6	$\|^2J(PC)\|$

Table 3 (*continued*)

Complex	δ	Assignment	Coupling constant/Hz	Assignment
	51.7 (d)	$P(OMe)_2Ph$	7.6	$\|^2J(PC)\|$
	33.4 (dd)	CMe_3	2.2	$\|^3J(PC)\|$
			1.1	$\|^3J(PC)\|$
	32.8 (dd)	CMe_3	4.4	$\|^4J(PC)\|$
			1.1	$\|^4J(PC)\|$

[a] In C_6D_6 solution unless indicated otherwise. Resonances due to phenyl-ring carbons other than C^1 in aryl ligands omitted. [b] In $CDCl_3$ solution. [c] Carbonyl ligand resonance(s) not identified with certainty. [d] In $C_6D_5CD_3$ solution.

3.1 Hz],* and a distortionless enhancement of polarisation transfer (DEPT) ^{13}C NMR spectrum provided an unambiguous distinction between the resonances for the α- and β-carbon atoms. Once again the coupling to the ^{31}P nuclei was stronger for the α- than for the β-carbon. Use of [$^2H_1$]**5a** showed that *cis* and *trans* addition of RuD occurred to approximately equal extents. The ratio of isomers of [$^2H_1$]**6ac** did not change on standing: either equilibration of the isomers is rapid or they do not interconvert at all.

A similar reaction was performed between complex **5a** and propyne. The major product, **6ad**, separated from two by-products by column chromatography, was shown by the coupling constant of 17.1 Hz between the α- and β-vinyl protons to be formed by *cis* addition of RuH to the alkyne. The resonances for the vinyl protons were complicated by coupling both to the phosphorus nuclei and to the protons in the methyl group on the β-carbon. One by-product was **6ac**, resulting from the presence of a little ethyne as impurity in the propyne: the other was tentatively identified, on the basis of an 11.2 Hz coupling between the two vinyl protons, as the isomer of **6ad** formed by *trans* addition of RuH to the propyne.

The reaction between complex **5a** and EtOC≡CH was substantially faster than any of those described above, possibly indicating a change in mechanism. The major product, **6ae**, was notable for the value of 6.4 Hz for the coupling constant between the two vinyl protons, significantly different in size from all the proton–proton coupling constants (see above) for the vinyl and alkyl-substituted vinyl ligands, but Schaeffer[11] has shown that the presence of an electronegative group on an alkenic carbon atom decreases the values: for $MeOCH{=}CH_2$, for example, they are *trans*-$|^3J(HH)| = 14.4$, *cis*-$|^3J(HH)| = 6.4$ and *gem*-$|^2J(HH)| = 1.8$ Hz, as opposed to values of 16.8, 10.0 and 2.1 Hz, respectively, for propene.[12] Thus it appears that the two protons in **6ae** are mutually *cis*, indicating that it is formed by *trans* addition of RuH to the alkyne. Two minor products proved to be the results of reactions of **6ae** and an isomer of **6ae** with a second molecule of EtOC≡CH.[13]

Chamberlain and Mawby[1] have described the preparation of the complexes **1aaa** and **1aba** by brief treatment of **6aa** and **6ab**, respectively, with LiPh in Et_2O at 273 K. The reactions had to be worked up and the produdcts stored at low temperature to avoid rearrangement to **2aaa** and **3aaa** and to **2aba** and **3aba** respectively. The same technique was used to obtain **1abb**, **1abc** and **1abd** from **6ab** and LiC_6H_4X-4 (X = Cl, Me or OMe). Complex **1abb** was fully characterised spectroscopically: as in the cases of **1aaa** and **1aba** it was possible to use the sizes of the coupling constants $|^2J(PC)|$ for the carbonyl ligands and for C^1 in the aryl ligand and the α-carbon in the vinyl ligand (using DEPT spectra to distinguish between C^1 and C^α) to show that one carbonyl and the aryl ligand were each *trans* to a PMe_2Ph ligand, while the other carbonyl and the vinyl ligand were *cis* to both. The value for $|^3J(HH)|$, the coupling constant between the vinyl protons, was much the same for **1abb** as for its precursor **6ab**, showing that the stereochemistry of the vinyl ligand was unaffected by the reaction with LiPh. An unusual feature, recorded without comment by Chamberlain and Mawby for **1aaa** and **1aba**, was the unusually large value (18.3 Hz for **1abb**) for the splitting of the α-hydrogen resonance in the vinyl ligand by one phosphorus nucleus: in contrast, the splitting by the other phosphorus nucleus (5.2 Hz for **1abb**) was considerably closer to the value for **6ab**. Crystal structures of the vinyl complexes $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$,[14] $[Ru(CO)(CNCMe_3)(CH{=}CHPh)\{C(O)Ph\}(PMe_2Ph)_2]$[15] and $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)H\}Ph(PMe_2Ph)_2]$[2] show that in each case the vinyl ligand is approximately at right angles to the Ru–P bonds to the mutually *trans* pair of PMe_2Ph ligands, placing the substituent on the α-carbon of the vinyl ligand well away from both phosphorus nuclei. In the complexes of structure **1** (see Scheme 2), where the phosphorus ligands are mutually *cis*, the large difference between the two values for $|^2J(PH)|$ suggests that the vinyl C=C bond is coplanar with one Ru–P bond and at right angles to the other, so that the α-hydrogen is much closer to one ^{31}P nucleus than to the other.

The preparations of complexes **1aca**, **1ada**, **1bba** and **1cba** from LiPh and **6ac**, **6ad**, **6bb** and **6cb** were carried out similarly, as were those of **1bbb** and **1bbd** from **6bb** and LiC_6H_4Cl-4 and LiC_6H_4OMe-4 respectively. On the basis of spectroscopic evidence, all the products were assigned the ligand arrangement shown in **1**, and in each case the stereochemistry of the vinyl ligand was not altered in the reaction. The same applied to the conversion of **6ae** into **1aea**: unlike the other complexes **6**, **6ae** was formed (see above) by *trans* addition of RuH to the alkyne, and the 6.9 Hz coupling constant between the two vinyl protons in **1aea** showed that the stereochemistry of the vinyl ligand remained unchanged. One vinyl proton resonance for **1aea** was largely obscured by phenyl proton resonances, but was located at δ 7.02 by one-dimensional correlation spectroscopy (COSY) and by homonuclear decoupling. In all complexes of structure **1**, unlike those of **6** and **2** (where L = L′), the Ru–C bond to the vinyl ligand does not lie in a plane of symmetry, and in consequence two separate resonances were observed for the methylene protons in the OEt group.

In the case of the reaction between complex **6db** and LiPh the expected product **1dba** appeared to be short-lived even at 273 K: NMR spectra recorded as soon as possible after isolating the product inevitably showed that complexes **2dba** and **3dba** (see Scheme 1) were also present, making it impossible to prove that **2dba** and **3dba** were formed exclusively by way of **1dba**. Two isomers (see Scheme 2, where L = PMe_3 and L′ = PPh_3 or *vice versa*) of **1dba** could be formed in the reaction: only one was observed, but, given the short lifetime of the complex, we were unable to determine which of the two it was.

When complex **6eb** was treated with LiPh at 273 K the expected product **1eba** was not observed at all. The actual product was **2eba**, the isomer of **1eba** with mutually *trans* PPh_3 ligands [see section (*iii*)].

(*ii*) Rearrangement of complexes $[Ru(CO)_2(CH{=}CHR)(C_6H_4X\text{-}4)L(L')]$, isomer 1

Chamberlain and Mawby[1] showed that complexes **1aaa** and **1aba** rearrange in C_6D_6 solution at room temperature to give

* Typical values for these coupling constants for vinyl ligands are listed in ref. 9.

Table 4 Relative proportions of complexes of structures **2** and **3** formed by rearrangement of complexes $[Ru(CO)_2(CH{=}CHR)(C_6H_4X\text{-}4)L(L')]$ **1** at 293 K in C_6D_6

Complex	L	L′	R	X	% **2**	% **3**
1aaa	PMe_2Ph	PMe_2Ph	Ph	H	60	40
1aba	PMe_2Ph	PMe_2Ph	CMe_3	H	40	60
1abb	PMe_2Ph	PMe_2Ph	CMe_3	Cl	20	80
1abc	PMe_2Ph	PMe_2Ph	CMe_3	Me	70	30
1abd	PMe_2Ph	PMe_2Ph	CMe_3	OMe	70	30
1aca	PMe_2Ph	PMe_2Ph	H	H	50	50
1aea	PMe_2Ph	PMe_2Ph	OEt[a]	H	100	0
1bba	PMe_3	PMe_3	CMe_3	H	80	20
1bbb	PMe_3	PMe_3	CMe_3	Cl	80	20
1bbd	PMe_3	PMe_3	CMe_3	OMe	80	20
1cba	$P(OMe)_2Ph$	$P(OMe)_2Ph$	CMe_3	H	0	100
1dba	PMe_3	PPh_3	CMe_3	H	20	80
1eba[b]	PPh_3	PPh_3	CMe_3	H	100	0

[a] R is *cis*, not *trans*, to Ru. [b] Reaction between complex **6eb** and LiPh at 273 K gave **2eba** as the only detectable product, so there is no proof that **1eba** is an intermediate in the reaction.

pairs of products **2aaa** and **3aaa** and **2aba** and **3aba** respectively. As illustrated in Scheme 1, isomerisation from **1** to **2** simply involves exchange of the positions of a carbonyl ligand and one of the phosphorus ligands. Formation of **3**, however, results from the intramolecular combination of vinyl, phenyl and carbonyl ligands. All four products were characterised spectroscopically and by elemental analysis, and the structure of **3aaa** has been confirmed by X-ray crystallography.[2]

In many instances the new complexes of structure **1** rearranged under these conditions to give similar mixtures of products, although for those containing PMe_3 ligands rearrangement was substantially slower than for their analogues containing PMe_2Ph ligands. The proportions of **2** and **3** in the product mixtures, as measured by integration of ^1H or ^{31}P NMR spectra, are shown in Table 4. Typical was **1bba**, which was completely converted within 24 h into a 4:1 mixture of **2bba** and **3bba**. The equivalence of the PMe_3 ligands in **2bba** and their inequivalence in **3bba** was clearly demonstrated by the ^{31}P NMR spectra and by the methyl-proton and carbon resonances in the ^1H and ^{13}C spectra. The presence of the vinyl ligand in **2bba** was revealed by doublet of triplets resonances for the α- and β-protons: the triplet splittings by the ^{31}P nuclei were 4.8 and 2.2 Hz, respectively, and the size of the doublet splittings [$^3J(HH) = 17.6$ Hz] showed that the vinyl protons were still mutually *trans*, as in **1bba**. The ^{13}C NMR spectrum confirmed the presence of two inequivalent carbonyl ligands in **2bba**, and a DEPT spectrum provided identification of the sharp triplet resonance for C^1 in the phenyl ligand. In contrast, the resonance for C^2 and C^6 was broad and the splittings unresolved. A similar effect has been observed[7] for $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$, which possesses structure **2** with the chloride ligand in the place of the vinyl group, and has been shown to be due to restriction of rotation of the phenyl ligand about the metal–phenyl bond.

The vinyl-proton resonances for complex **3bba** were identified by the close similarities in chemical shifts and splitting patterns to the pair for **3aaa** (inadvertently switched in Table 2 in ref. 1). In contrast to **2bba**, the value of the coupling constant between the two vinyl protons was only 7.9 Hz, but this matches the value of 8.2 Hz for **3aaa**, where the vinyl protons are still mutually *trans*.[2] One notable feature of the ^{13}C NMR spectrum (again common to **3aaa** and **3aba**) was the large splitting (34.0 Hz) of the resonance for the β-carbon of the vinyl group by *one* of the two ^{31}P nuclei.

Two complexes of structure **1** rearranged to a single product under these reaction conditions. Complex **1aea**, $[Ru(CO)_2(CH{=}CHOEt)Ph(PMe_2Ph)_2]$, was unique in possessing a substituent *cis* to the metal on the β-carbon atom of the vinyl ligand, and also in giving 100% conversion to the corresponding complex of structure **2**, **2aea**. The size of the coupling constant between the two vinyl protons, 6.9 Hz, confirmed that the rearrangement had occurred without alteration in the geometry of the vinyl ligand. Complex **1cba** yielded only the vinyl ketone complex **3cba**.

As mentioned in (*i*), the reaction between complex **6eb**, $[Ru(CO)_2(CH{=}CHCMe_3)Cl(PPh_3)_2]$, and LiPh at 273 K failed to yield the expected product **1eba** with mutually *cis* phosphorus ligands. The NMR spectra of the product unambiguously identified it as **2eba**, the isomer of $[Ru(CO)_2(CH{=}CHCMe_3)Ph(PPh_3)_2]$ with mutually *trans* phosphorus ligands. It is possible that **2eba** results from rapid rearrangement of **1eba**, but just as likely that the bulk of the PPh_3 ligands enforces direct formation of **2eba** from **6eb** and LiPh.

The relative amounts of complexes **2** and **3** formed when a complex of type **1** rearranges are governed by kinetic, not thermodynamic, factors. Product ratios did not alter with time, and in cases where the products **2** and **3** were separated and redissolved no interconversion was observed at room temperature. Only at 353 K was very slow conversion of **2aba** into **3aba** detected in benzene solution, and at this temperature **3aba** was itself decomposing at a not much slower rate to free $Me_3CCH{=}CHC(O)Ph$ and unidentified ruthenium complexes.

The results listed in Table 4 demonstrate that product ratios **2**:**3** depend heavily on the nature of the substituents R and X in the vinyl and aryl ligands. In complexes containing PMe_2Ph ligands, electron-releasing substituents on the vinyl ligand appear to favour formation of ketone complexes **3** (see the data for **1aaa**, **1aba** and **1aca**). Inclusion of **1aea** in this list is inadvisable since it is unique [see section (*i*)] in having a substituent on the β-carbon of the vinyl ligand which is *cis* rather than *trans* to the metal. In contrast, electron-releasing substituents on the aryl ligand evidently disfavour ketone formation in complexes containing PMe_2Ph ligands (see **1aba**, **1abb**, **1abc** and **1abd**). For complexes containing PMe_3 ligands, however, the ratio seems to be insensitive to substituents on the aryl ligand.

The ratio of products **2** and **3** from a given complex **1** is also temperature-sensitive. The rearrangement of **1aba** was studied in C_6H_5Me solution at 253, 293 and 328 K. Use of a protiated solvent ruled out measurement of product ratios by integration of ^1H NMR signals, so integration of resonances in the ^{31}P NMR spectra was used instead. The accuracy of this procedure was checked by comparing values for the product ratio from rearangement of **1aba** in C_6D_6 at 293 K, obtained from both ^1H and ^{31}P NMR spectra: the results were within 5% of each other. For rearrangement in C_6H_5Me the ratio of **2aba** to **3aba** was 1:3.5 at 253, 1.5:1 at 293 and 2.3:1 at 328 K, indicating a shift away from ketone complex formation with increasing temperature.

Comparison of the ratios for complexes **1aba**, **1bba**, **1cba** and **1dba** shows a shift towards the ketone complexes **3** as some of the methyl groups in the strongly σ-donating PMe_3 ligands are replaced by phenyl and methoxy substituents (which weaken the σ-donor power of a phosphorus ligand but enchance its π-acceptor capacity).

Choice of solvent was also important in determining product ratios. At 293 K complex **1aba** yielded a 40:60 ratio of **2aba** and **3aba** in benzene and toluene, a 50:50 ratio in ethanol and exclusively **2aba** in propanone. Although accurate measurement of reaction rates was not attempted, it was evident that the rate of formation of **2aba** was relatively insensitive to the choice of solvent, so that the decrease in the proportion of **3aba** with increasingly polar solvents was primarily due to the decrease in the rate of conversion of **1aba** into **3aba**. In view of the dramatic effect on product ratio of a change in solvent to propanone, the rearrangement of **1cba** (which gave 100% of **3cba** in benzene) was studied in propanone. In this instance, however, the ketone complex **3cba** was still the sole product, but the rate of rearrangement was markedly lower than in benzene.

(*iii*) Mechanisms for conversion of complexes 1 into 2 and 3

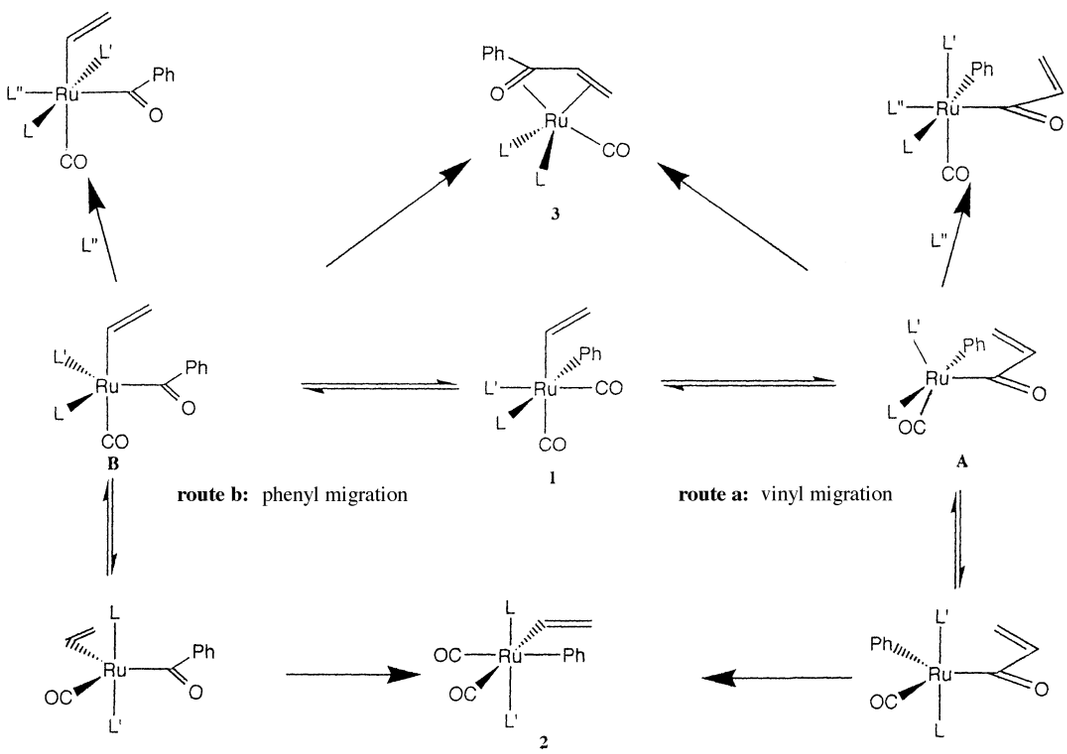
Chamberlain and Mawby[1] suggested that mechanisms for the rearrangement of complexes **1** might involve an initial migration of one of the two organic ligands on to CO, yielding intermediates [Ru(CO)(COCH=CHR)(C_6H_4X-4)L(L′)] or [Ru(CO)(COC_6H_4X-4)(CH=CHR)L(L′)]. We have subsequently shown[15] that each of these migration processes does occur and that the intermediates may be trapped by Me_3CNC as stable species [Ru(CO)(CNCMe_3){C(O)CH=CHR}(C_6H_4X-4)L(L′)] and [Ru(CO)(CNCMe_3){C(O)C_6H_4X-4}(CH=CHR)L(L′)]. From the structures of these species (each resulting from attack by Me_3CNC *trans* to the newly formed acyl ligand) it is possible to deduce the ligand arrangements in the intermediates. These are shown in Scheme 3 as η^1-acyl species (labelled **A** and **B**), but they may well be stabilised by a secondary interaction of the acyl oxygen with the metal [there are several examples[10,16,17] in the literature of stable η^2-acyl ruthenium(II) complexes].

Scheme 3 illustrates plausible routes, **a** from the vinyl migration intermediate **A**, and **b** from the phenyl migration intermediate **B**, to products **2** and **3**. In each case **3** is formed by attack on the acyl ligand by the other organic ligand and **2** by a ligand redistribution followed by breakdown of the acyl ligand. It is, however, worth noting that the rearrangement of **B** can be achieved by a single Berry pseudo-rotation,[18] commonly a low-energy pathway, whereas the corresponding rearrangement of **A** cannot, so it is possible that initial vinyl migration may lead only to **3** whereas initial phenyl migration may lead to both **2** and **3**.

There *are* apparent links between the proportions of phenyl and vinyl migration in the reactions of complexes **1** with Me_3CNC[15] and the ratio of products **2** and **3** formed by rearrangement of **1**. As mentioned in (*ii*), in complexes **1aaa**, **1aba** and **1aca** increasingly electron-releasing substituents in the vinyl ligand tip the balance in the rearrangement reactions in favour of the ketone complexes **3**: similarly such substituents favour vinyl migration in the reactions with Me_3CNC. Conversely, the behaviour of **1aba**, **1abb**, **1abc** and **1abd** demonstrates that electron-releasing substituents in the aryl ligand favour rearrangement to **2**, and such substituents also increase the proportion of phenyl migration in reactions with Me_3CNC. There are, however, clear exceptions to this simple relationship: thus **1bba** gives a high proportion of the vinyl-migration product [Ru(CO)(CNCMe_3){C(O)CH=CHCMe_3}Ph(PMe_3)$_2$] but rearranges to give 80% of **2bba** and only 20% of **3bba**. Even more striking is the behaviour of **1cba**, which gives only the phenyl-migration product [Ru(CO)(CNCMe_3){C(O)Ph}(CH=CHCMe_3){P(OMe)$_2$Ph}$_2$] but rearranges exclusively to the ketone complex **3cba**.

Consideration of reaction kinetics identifies one reason why it is dangerous to expect a simple correlation in all cases between the two types of reaction. Kinetic studies of the reaction of complexes **1** with Me_3CNC showed that formation of the intermediates **A** and **B** was rate determining: subsequent reaction with Me_3CNC was much faster than both the formation of the intermediates and their reversion to **1**.[15] The rearrangements to **2** and **3** are appreciably slower than the reactions with Me_3CNC (by a factor of around 4, for example, for **1aaa**, and even more markedly for complexes containing PMe_3 ligands), and yet the concentrations of **A** and **B** are too low for these species to be detectable: hence **1** must be in equilibrium with **A** and **B**, and the equilibria must lie heavily in favour of **1**. It follows that the relative importance of routes **a** and **b** depends not only on the rates of formation of **A** and **B** from **1** but also on comparison of their rates of reconversion into **1** with the rates of rearrangement to **2** and/or **3**.

If, as implied by Scheme 3, there are pathways from intermediate **B** (and perhaps also **A**) to both complexes **2** and **3**, some of the factors affecting product distribution may simply change the balance between those pathways. Thus the effect of temperature probably reflects an unfavourable entropy of activation in the process of bond formation between the acyl ligand and the other organic ligand *en route* to **3**. The bonding between the acyl ligand and metal in the intermediates may also be important. Six-co-ordinate complexes do not normally undergo facile intramolecular rearrangement, so if the acyl ligand in the intermediates is η^2-bonded it must presumably revert to η^1 bonding prior to rearrangement. In contrast there would



Scheme 3 Possible mechanisms for rearrangement of complexes **1**. For simplicity, vinyl and phenyl ligands are shown without substituents. The ligand L″ is Me_3CNC

appear to be no reason why complexes **3** should not be formed directly from η^2-acyl intermediates: indeed the removal of electron density from the acyl oxygen by bonding to the metal may well encourage nucleophilic attack on the acyl carbon by the other organic ligand. This may explain why increase in the π-acceptor and decrease in the σ-donor character of the phosphorus ligands favours formation of **3**, since any decrease in the electron supply to the metal from the phosphorus ligands should strengthen the interaction between the acyl oxygen and the metal. It may also explain why the use of propanone as solvent so markedly reduces the rate of formation of **3**: attachment of propanone to the metal in the intermediates may prevent η^2 bonding of the acyl ligand and hence inhibit conversion into **3**. Provided that the propanone is only weakly held, it may still dissociate to allow the rearrangement necessary to form **2**.

Experimental

The NMR spectra detailed in Tables 1–3 were recorded on a Bruker MSL 300 spectrometer (operating frequencies 300.15, 121.49 and 75.47 MHz for ^{1}H, ^{31}P and ^{13}C respectively). A Perkin-Elmer PE580B spectrometer was used to obtain IR spectra.

The preparations of each group of ruthenium complexes are described below. Preparative work was routinely carried out under an atmosphere of nitrogen or argon. Selected members of each group of complexes **4**–**6** have been subjected to elemental analysis (this was not possible for complexes **1** which were only stable at low temperatures).

Preparations

Complexes 4. The preparation of complex **4a** was based on the method described by Jenkins *et al*.[4] Carbon monoxide was passed through a refluxing solution of $RuCl_3 \cdot 3H_2O$ (Aldrich, 2.8 g) in 2-methoxyethanol (50 cm^3). After *ca*. 5 h the originally black solution had turned yellow, and PMe_2Ph (2.8 cm^3) was added. The flow of CO was reduced and heating continued for 12 h. The solvent was then removed under reduced pressure and the residue was treated with propanone. The dimeric by-product, $[Ru_2(CO)_4Cl_4(PMe_2Ph)_2]$, which is insoluble in propanone, was filtered off. Ethanol was added to the filtrate, and **4a** was obtained as white crystals on concentration of the solution under a stream of nitrogen (yield 70%). The same procedure, using PMe_3 in place of PMe_2Ph, gave **4b** in similar yield, with $[Ru_2(CO)_4Cl_4(PMe_3)_2]$ as a by-product. Complex **4c** was prepared by heating $[\{Ru(CO)_2Cl_2\}_n]$ (Johnson Matthey, 0.30 g) with $P(OMe)_2Ph$ (0.42 cm^3) under reflux in methanol (20 cm^3). The solvent was removed under reduced pressure and the product crystallised from an ethanol–propanone mixture (white crystals, yield 60%). Complex **4d** was obtained by stirring $[Ru_2(CO)_4Cl_4(PMe_3)_2]$ (see above, 0.15 g) in propanone (20 cm^3) with PPh_3 (0.13 g). After 1 h the solvent was slowly removed under reduced pressure, leaving white crystals of **4d** in essentially quantitative yield (Found for **4a**: C, 43.05; H, 4.25. Calc. for $C_{18}H_{22}Cl_2O_2P_2Ru$: C, 42.9; H, 4.40. Found for **4c**: C, 38.25; H, 4.00. Calc. for $C_{18}H_{22}Cl_2O_6P_2Ru$: C, 38.05; H, 3.90. Found for **4d**: C, 48.9; H, 4.40. Calc. for $C_{23}H_{24}Cl_2O_2P_2Ru$: C, 48.75; H, 4.25%).

Complexes 5. The synthesis of complex **5a** was a modified version of that used by Bray and Mawby.[9] To a stirred suspension of powdered **4a** (0.50 g) in ethanol (4 cm^3) was added $NaBH_4$ (0.15 g). Usually effervescence and development of an orange colour began almost immediately: occasionally gentle warming was required to initiate the reaction. After 5 min the ethanol was removed under reduced pressure. The product was extracted into benzene (4 × 5 cm^3) and the combined extracts filtered. Removal of the benzene under reduced pressure left an orange oil which was crystallised at 273 K from a mixture of ethanol and heptane (white crystals, 55%). Complex **5b** was obtained in similar yield by the same technique. For **5c** and **5d** the low solubility of **4c** and **4d** made it advisable to replace ethanol as the solvent by ethanol–benzene (1:1): yields were 60 and 80% respectively. The preparation of **5e** was carried out as described by Geoffroy and Bradley[8] (yield 90%). The deuteride complexes $[^2H_1]$**5a** and $[^2H_1]$**5b** were prepared in the same way as for **5a** and **5b**, but using $NaBD_4$ in EtOD (Found for **5a**: C, 46.1; H, 5.05. Calc. for $C_{18}H_{23}ClO_2P_2Ru$: C, 46.0; H, 4.95. Found for **5b**: C, 27.65; H, 5.50. Calc. for $C_8H_{19}ClO_2P_2Ru$: C, 27.8; H, 5.55. Found for $[^2H_1]$**5a**: C, 45.75; H + D, 5.05. Calc. for $C_{18}H_{22}ClDO_2P_2Ru$: C, 45.9; H + D, 5.15%).

Complexes 6. Complex **6aa** was obtained by warming a solution of **5a** (0.10 g) in benzene (1 cm^3) with PhC≡CH (0.024 cm^3) at 323 K for 20 min. The solution was cooled and treated with ethanol (2 cm^3). Evaporation under a stream of nitrogen gave pale yellow crystals of **6aa** (yield 90%). The procedure for converting **5a** into **6ab** was similar, but crystallisation proved more difficult. Removal of the solvent from the reaction mixture under reduced pressure left an oily residue: this was dissolved in the minimum volume of a mixture of heptane (80%) and ethanol (20%) and then cooled in an ice–salt bath. Slow evaporation under a stream of nitrogen gave crystals of **6ab** in 70% yield. A similar procedure was used for the preparation of **6bb**, **6cb**, **6db** and **6eb** (reaction times respectively 20, 40, 30 and 30 min): yields were again *ca*. 70%. To obtain **6ac**, a solution of **5a** (0.10 g) in C_6D_6 (0.5 cm^3) was placed in an NMR tube fitted with a septum cap. Using syringe needles for gas entry and exit, ethyne was passed through the solution for 1 min, removing the exit needle slightly before the entry needle to leave a slight positive pressure of ethyne in the tube. The reaction was monitored by ^{1}H NMR spectroscopy, with further addition of ethyne as necessary, and was complete in 2 d (or 4 h at 313 K). Removal of the solvent under reduced pressure was followed by crystallisation from a cold mixture of heptane and ethanol (yield 50%). The reaction between **5a** and propyne to give **6ad** was carried out in the same way but the higher solubility of propyne made further additions of the gas unnecessary. After 2 d at room temperature the solvent was removed under reduced pressure, and **6ad** was purified by column chromatography, using an alumina column packed in $CHCl_3$. The residue was added to the column in $CHCl_3$ solution, and initial elution with $CHCl_3$ to remove by-products was followed by elution with $CHCl_3$ containing a little methanol. Complex **6ad** was obtained as a colourless oil on removal of the solvents. Complex **6ae** was obtained by treating **5a** (0.10 g) in C_6D_6 (0.5 cm^3) with 0.05 cm^3 of a 50% w/v solution of EtOC≡CH in hexane. After 4 h the solution was filtered to remove a black solid (believed to be polymerised EtOC≡CH) and the solvent was removed under reduced pressure. A work-up similar to that for **6ad** was used to separate **6ae** from by-products (Found for **6aa**: C, 54.65; H, 5.10. Calc. for $C_{26}H_{29}ClO_2P_2Ru$: C, 54.6; H, 5.10. Found for **6ab**: C, 52.1; H, 6.10. Calc. for $C_{24}H_{33}ClO_2P_2Ru$: C, 52.2; H, 6.05. Found for **6ac**: C, 48.2; H, 5.40. Calc. for $C_{20}H_{25}ClO_2P_2Ru$: C, 48.45; H, 5.10. Found for **6bb**: C, 41.0; H, 6.70. Calc. for $C_{16}H_{25}ClO_2P_2Ru$: C, 39.3; H, 6.85. Found for **6db**: C, 56.9; H, 5.80. Calc. for $C_{29}H_{35}ClO_2P_2Ru$: C, 56.7; H, 5.75%).

Complexes 1. All operations were caried out at 273 K. The preparation of complex **1aba** was typical of the method used. A stirred solution of **6ab** (0.05 g) in Et_2O (20 cm^3) was treated with a freshly prepared solution of LiPh[19] (1 cm^3 of a *ca*. 0.2 mol dm^{-3} solution). The reaction mixture immediately turned yellow. After 1 min a small portion of the mixture was removed by Pasteur pipette, added to water (0.5 cm^3), and the mixture shaken until the ether layer was clear. An IR spectrum of the ether layer was recorded to ensure that no **6ab** remained and therefore that no further addition of LiPh was necessary. Ice-cold water (2 cm^3) was added to the rest of the reaction mixture

with continued stirring: the initial cloudiness of the ether layer quickly cleared. Stirring was stopped, and as much water as possible removed by pipette. The ether layer was stirred vigorously with anhydrous $MgSO_4$ for 5 min and then filtered by suction into an ice-cooled flask. The solvent was removed under vacuum leaving **1aba** as a yellow-brown oil, normally used immediately for studies of its rearrangement to **2aba** and **3aba**. The same method was used to obtain all other complexes **1**, using the appropriate **6** and organolithium reagent.[19,20] Based on subsequent combined yields of complexes **2** and **3**, yields of **1** were in the region 60–80%. The ease of rearrangement of these complexes made their isolation in a completely pure state impossible: the only organoruthenium species present in a concentration detectable by NMR spectroscopy, however, were the diaryl complexes $[Ru(CO)_2(C_6H_4X\text{-}4)_2L(L')]$, inevitably found as minor by-products of the reaction of complexes **6** with the appropriate lithium aryls. These complexes were completely stable under the conditions used for rearrangement of the complexes **1** to **2** and **3**.

Rearrangement of complexes 1

A solution of the appropriate complex **1** in the required NMR solvent (0.5 cm^3) was made up at 273 K and placed in an ice-cooled NMR tube. Rearrangement to **2** and **3** was then monitored by NMR spectroscopy at the appropriate temperature. Where deuteriated solvents were used the product ratios were measured by integration of ^1H resonances. For reactions in non-deuteriated solvents the ^{31}P NMR spectra were used for this purpose, with a long delay (20 s) between scans to minimise the effect of differences in relaxation times between ^{31}P nuclei. Pairs of complexes **2** and **3** were not normally separated: details of the separation and characterisation (including elemental analysis) of **2aaa**, **3aaa**, **2aba** and **3aba** have been given previously.[1]

Conversion of complex 2aba into 3aba

Complex **2aba** (0.01 g) in C_6D_6 (0.5 cm^3) was sealed under vacuum in an NMR tube and heated at 353 K. Changes in ^1H and ^{31}P NMR spectra were monitored over a period of 2 weeks. After 1 week the conversion into **3aba** was about 50% complete, but slow breakdown of this complex meant that after 2 weeks little of either **2aba** or **3aba** remained.

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