Interconversion of Methyl and Acetyl Complexes and Isomerization of Acetyl Complexes of Ruthenium(II)

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Complexes $[Ru(CO)_2X(Me)L_2]$ [(I), where X = Cl, Br, or I, and L = PMe_2Ph or $AsMe_2Ph$] react extremely rapidly with ligands L′ (L′ = CO, PMe_2Ph, and several other ligands with phosphorus donor atoms, and $AsMe_2Ph$) to form products $[Ru(CO)X(COMe)L_2L']$, (II). The reactions involve initial intramolecular combination of methyl and carbonyl ligands followed by attack by L′ *trans* to the newly formed acetyl ligand, which has a strong *trans*-directing effect. The *trans*-labilizing influence of the acetyl ligand makes the Ru–L′ bond in (II) extremely labile, and hence the reactions are easily reversed, regenerating (I). In many instances the products (II) undergo a slower re-arrangement to a different isomer, (III), indicating that the stereochemistry of the initial reaction is kinetically controlled. The final position of equilibrium between (II) and (III) varies widely with the nature of X and L′: increases in either the size or the π-accepting ability of L′ favour (II), whereas an increase in the size of the halide ligand favours (III). Reconversion of isomer (III) of the complexes $[Ru(CO)X(COMe)L_2L']$ into the methyl complexes (I), which may be either direct or *via* (II), is much slower than that of (II) into (I).

RECENTLY we reported in preliminary form[1] our discovery of an extremely rapid and reversible interconversion of methyl and acetyl complexes of ruthenium(II), which may shed light on the ability of ruthenium complexes both to act as hydroformylation catalysts[2] and to bring about the decarbonylation of organic compounds.[3]

Our preliminary findings indicated that different isomers of the acetyl complexes $[Ru(CO)_2X(COMe)(PMe_2Ph)_2]$ were obtained as end products on treating the complexes $[Ru(CO)_2X(Me)(PMe_2Ph)_2]$ (X = Cl or I) with CO. Here we shall show that the *kinetic* products of reaction of these and related complexes all have the *same* stereochemistry, but that in some instances the kinetic products subsequently undergo isomerization.

RESULTS AND DISCUSSION

Details of the i.r. and ^1H n.m.r. spectra of the methyl complexes used as starting materials (all but one of which are new compounds) are collected in Table 1. Most of the reactions of these complexes described in this paper were followed both by i.r. and by ^1H n.m.r. spectroscopy, and the spectra of the products (whether isolated or not) are given in Tables 2 and 3 respectively. Much of the stereochemical information derived from the ^1H n.m.r. spectra depends on the pattern of resonances observed for the methyl protons in the PMe_2Ph ligands which are present in most of the complexes: the way in which PMe_2Ph can be used as a stereochemical probe in ruthenium(II) complexes has been described by Shaw and his co-workers.[4] Details of the ^{13}C n.m.r. spectra of selected compounds are given in Table 4.

(1) *Preparation of Methyl Complexes.*—The preparation of the complex $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ [structure (I) in Scheme 1, where L = PMe_2Ph and X = Cl] has been described in a previous paper.[5] A similar method was used to prepare the related complex $[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$, which was assigned the same stereochemistry on the basis of the close similarities between the i.r. and ^1H n.m.r. spectra of the two com-

TABLE 1

Infrared [a] and ^1H n.m.r.[b] spectra of complexes $[Ru(CO)_2X(Me)L_2]$

Complex	ν(C–O)/cm^{-1}	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
$[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$	2 035,	1.86 (t, 6)	P*Me*$_2$Ph	7.0	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
	1 964	1.80 (t, 6)	P*Me*$_2$Ph	7.0	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
		−0.02 (t, 3)	RuMe	7.8	$\lvert{}^3J(P–H)\rvert$
$[Ru(CO)_2Br(Me)(PMe_2Ph)_2]$	2 033,	1.94 (t, 6)	P*Me*$_2$Ph	7.5	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
	1 964	1.85 (t, 6)	P*Me*$_2$Ph	7.5	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
		0.06 (t, 3)	RuMe	7.8	$\lvert{}^3J(P–H)\rvert$
$[Ru(CO)_2I(Me)(PMe_2Ph)_2]$	2 033,	2.06 (t, 6)	P*Me*$_2$Ph	7.5	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
	1 967	1.93 (t, 6)	P*Me*$_2$Ph	7.5	$\lvert{}^2J(P–H) + {}^4J(P–H)\rvert$
		0.14 (t, 3)	RuMe	7.8	$\lvert{}^3J(P–H)\rvert$
$[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$	2 031,	1.77 (s, 6)	As*Me*$_2$Ph		
	1 959	1.72 (s, 6)	As*Me*$_2$Ph		
		0.16 (s, 3)	RuMe		
$[Ru(CO)_2Br(Me)(AsMe_2Ph)_2]$	2 032,	1.82 (s, 6)	As*Me*$_2$Ph		
	1 962	1.76 (s, 6)	As*Me*$_2$Ph		
		0.19 (s, 3)	RuMe		
$[Ru(CO)_2I(Me)(AsMe_2Ph)_2]$	2 032,	1.93 (s, 6)	As*Me*$_2$Ph		
	1 964	1.82 (s, 6)	As*Me*$_2$Ph		
		0.26 (s, 3)	RuMe		

[a] In the C–O stretching region only. Spectra were recorded on $CHCl_3$ solutions of the complexes [b] Spectra were recorded on $CDCl_3$ solutions of the complexes at ambient temperature. Resonances due to phenyl protons are not included. Multiplicities and relative areas are given in parentheses after the chemical-shift values: s = singlet, t = triplet.

TABLE 2

Infrared spectra of complexes $[Ru(CO)X(COMe)L_2L']$ [a]

Complex	Structure	ν(C–O)/cm^{-1} terminal	acyl
$[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$	(II)	2 055, 1 984	1 593
$[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$	(II)	1 943	1 575
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{P(OCH_2)_3CMe\}]$	(II)	1 972	1 584
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{P(OMe)_3\}]$	(II)	1 960	1 570
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{PPh(OMe)_2\}]$	(II)	1 958	1 575
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{PPh_2(OMe)\}]$	(II)	1 958	1 575
$[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$	(II)	2 056, 1 980 [b]	1 590
$[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$	(III)	1 996	1 590
$[Ru(CO)Br(COMe)(PMe_2Ph)_3]$	(II)	1 947	1 571
$[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$	(III)	1 994	1 593
$[Ru(CO)I(COMe)(PMe_2Ph)_3]$	(II)	1 960	1 575
$[Ru(CO)I(COMe)(PMe_2Ph)_3]$	(III)	1 980	1 575
$[Ru(CO)_2Cl(COMe)(AsMe_2Ph)_2]$	(II)	2 055, 1 981	1 590
$[Ru(CO)Cl(COMe)(AsMe_2Ph)_3]$	(II)	1 950	c
$[Ru(CO)_2Br(COMe)(AsMe_2Ph)_2]$	(II)	2 053, 1 982 [b]	1 590
$[Ru(CO)_2Br(COMe)(AsMe_2Ph)_2]$	(III)	1 996	1 590
$[Ru(CO)Br(COMe)(AsMe_2Ph)_3]$	(II)	1 950	c
$[Ru(CO)_2I(COMe)(AsMe_2Ph)_2]$	(III)	1 992	1 592
$[Ru(CO)I(COMe)(AsMe_2Ph)_3]$	(III)	1 962	c

[a] In the C–O stretching regions only. Spectra were recorded on $CHCl_3$ solutions of the complexes. [b] Seen as a shoulder on the band for isomer (III). [c] Obscured by a band due to $AsMe_2Ph$.

TABLE 3

Hydrogen-1 n.m.r. spectra of complexes $[Ru(CO)X(COMe)L_2L']$ [a]

Complex	Structure	T/K [b]	δ(L)/p.p.m. [c]	δ(L′)/ p.p.m. [d]	δ(COMe)/ p.p.m.
$[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$	(II)	253	1.85 (t, 6), 1.78 (t, 6)		2.12 (s, 3)
$[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$ [e]	(II)	253	1.53 (t, 6), 1.46 (t, 6)	0.88 (d, 6)	2.57 (s, 3)
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{P(OCH_2)_3CMe\}]$	(II)	306	1.84 (t, 6), 1.82 (t, 6)	3.90 (d, 6)	1.76 (s, 3)
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{P(OMe)_3\}]$	(II)	273	1.84 (t, 6), 1.78 (t, 6)	3.50 (d, 9)	1.89 (s, 3)
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{PPh(OMe)_2\}]$	(II)	263	1.74 (t, 6), 1.70 (t, 6)	3.37 (d, 6)	2.00 (s, 3)
$[Ru(CO)Cl(COMe)(PMe_2Ph)_2\{PPh_2(OMe)\}]$	(II)	243	1.72 (t, 6), 1.60 (t, 6)	3.08 (d, 3)	2.20 (s, 3)
$[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$	(II)	263	2.09 (t, 6), 1.93 (t, 6)		2.23 (s, 3)
$[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$	(III)	263	2.02 (t, 12)		1.60 (s, 3)
$[Ru(CO)Br(COMe)(PMe_2Ph)_3]$ [e]	(II)	253	1.61 (t, 6), 1.54 (t, 6)	1.00 (d, 6)	2.62 (s, 3)
$[Ru(CO)Br(COMe)(PMe_2Ph)_3]$ [e]	(III)	253	f	f	2.32 (s)
$[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$	(II)	243	2.11 (t, 6), 1.98 (t, 6)		2.39 (s, 3)
$[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$	(III)	306	2.09 (t, 12)		1.65 (s, 3)
$[Ru(CO)I(COMe)(PMe_2Ph)_3]$ [e]	(II)	253	1.64 (t, 6), 1.56 (t, 6)	1.07 (d, 6)	2.64 (s, 3)
$[Ru(CO)I(COMe)(PMe_2Ph)_3]$ [e]	(III)	253	1.73 (t, 6), 1.29 (t, 6)	1.64 (d, 6)	2.32 (s, 3)
$[Ru(CO)I(COMe)(PMe_2Ph)_2(PMePh_2)]$	(II)	243	g	g	2.40 (s)
$[Ru(CO)I(COMe)(PMe_2Ph)_2(PMePh_2)]$	(III)	243	g	g	2.20 (s)
$[Ru(CO)I(COMe)(PMe_2Ph)_2\{P(OMe)_3\}]$ [e]	(II)	273	1.88 (t, 6), 1.87 (t, 6)	3.33 (d, 9)	2.30 (s, 3)
$[Ru(CO)I(COMe)(PMe_2Ph)_2\{P(OMe)_3\}]$ [e]	(III)	273	g	3.92 (d, 9)	2.19 (s, 3)
$[Ru(CO)I(COMe)(PMe_2Ph)_2\{PPh(OMe)_2\}]$ [e]	(II)	263	1.97 (t, 6), 1.96 (t, 6)	3.17 (d, 6)	2.48 (s, 3)
$[Ru(CO)_2Cl(COMe)(AsMe_2Ph)_2]$	(II)	263	1.81 (s, 6), 1.77 (s, 6)		2.27 (s, 3)
$[Ru(CO)Cl(COMe)(AsMe_2Ph)_3]$	(II)	243	1.59 (s, 6), 1.53 (s, 6)	0.93 (s, 6)	2.46 (s, 3)
$[Ru(CO)_2Br(COMe)(AsMe_2Ph)_2]$	(II)	263	1.86 (s, 6), 1.79 (s, 6)		2.34 (s, 3)
$[Ru(CO)_2Br(COMe)(AsMe_2Ph)_2]$	(III)	263	1.88 (s, 12)		1.80 (s, 3)
$[Ru(CO)Br(COMe)(AsMe_2Ph)_3]$	(II)	243	1.62 (s, 6), 1.56 (s, 6)	0.98 (s, 6)	2.47 (s, 3)
$[Ru(CO)Br(COMe)(AsMe_2Ph)_3]$	(III)	243	1.64 (s, 6), 1.44 (s, 6)	1.38 (s, 6)	2.21 (s, 3)
$[Ru(CO)_2I(COMe)(AsMe_2Ph)_2]$	(III)	306	1.96 (s, 12)		1.82 (s, 3)
$[Ru(CO)I(COMe)(AsMe_2Ph)_3]$	(II)	243	1.68 (s, 6), 1.61 (s, 6)	1.06 (s, 6)	2.52 (s, 3)
$[Ru(CO)I(COMe)(AsMe_2Ph)_3]$	(III)	243	1.72 (s, 6), 1.36 (s, 6)	1.56 (s, 6)	2.28 (s, 3)

[a] Spectra were recorded on $CDCl_3$ solutions of the complexes except where otherwise stated. Resonances due to phenyl protons and to the methyl protons in $P[(OCH_2)_3CMe]$ are not included. Multiplicities and relative areas are given in parentheses after the chemical-shift values: s = singlet, d = doublet, t = triplet. [b] Probe temperature. [c] For the triplet resonances, $|^2J(P-H) + ^4J(P-H)| = ca.\ 7$ Hz. [d] For the doublet resonances, $|^2J(P-H)| = ca.\ 7$ Hz ($L' = PMe_2Ph$); $|^3J(P-H)| = ca.\ 11$ Hz where $L' = P(OMe)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$, but 4 Hz where $L' = P[(OCH_2)_3CMe]$. [e] The solvent used was PhCl. [f] This resonance was too weak to be identified. [g] This resonance could not be identified because of the complexity of the spectrum.

plexes. From these compounds, analogous bromo- and iodo-complexes of the same stereochemistry were obtained by reaction with the appropriate halide ions under mild conditions.

(2) *Reactions of the Complex* $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$.—Treatment of a $CHCl_3$ solution of $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ with CO results in an immediate change in the i.r. spectrum of the solution. The bands characteristic of the methyl complex are replaced by two new bands in the terminal C–O stretching region and one in the acyl C–O stretching region, suggesting that the acetyl complex $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$ has been formed. The reaction can readily be reversed, regenerating $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$, by passing N_2 through

TABLE 4

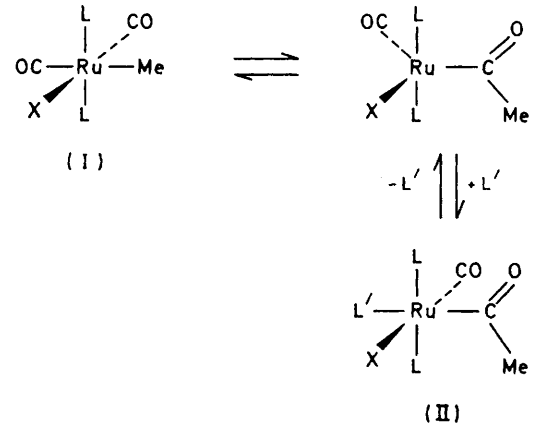
Carbon-13 n.m.r. spectra of selected complexes $[\mathrm{Ru(CO)_2X(Me)L_2}]$ and $[\mathrm{Ru(CO)X(COMe)L_2L'}]$ [a]

Complex	Structure	T/K [b]	δ/p.p.m.	Assignment	Coupling constant/ Hz	Assignment
$[\mathrm{Ru(CO)_2Cl(Me)(PMe_2Ph)_2}]$	(I)	298	199.1 (t)	CO	13.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			190.9 (t)	CO	8.5	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			14.1 (t)	P*Me*$_2$Ph	32.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
			11.8 (t)	P*Me*$_2$Ph	32.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
			−3.7 (t)	RuMe	10.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)_2I(Me)(PMe_2Ph)_2}]$	(I)	298	198.0 (t)	CO	11.5	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			198.8 (t)	CO	8.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			17.7 (t)	P*Me*$_2$Ph	34.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
			14.0 (t)	P*Me*$_2$Ph	34.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
			−11.6 (t)	RuMe	10.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)_2Cl(COMe)(PMe_2Ph)_2}]$	(II)	253	267.4 (t)	*C*OMe	11.5	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			195.7 (t)	CO	11.5	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			192.6 (t)	CO	8.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			42.9 (s)	CO*Me*		
			14.5 (t)	P*Me*$_2$Ph	32.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
			13.6 (t)	P*Me*$_2$Ph	32.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)Cl(COMe)(PMe_2Ph)_3}]$ [c]	(II)	253	268.5 (dt)	*C*OMe	82.0	$\lvert trans\text{-}{}^2J(\mathrm{P{-}C})\rvert$
					11.0	$\lvert cis\text{-}{}^2J(\mathrm{P{-}C})\rvert$
			201.3 (dt)	CO	11.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
					13.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			43.3 (d)	CO*Me*	27.0	$\lvert trans\text{-}{}^3J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)_2I(COMe)(PMe_2Ph)_2}]$	(III)	298	252.8 (t)	*C*OMe	8.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			196.0 (t)	CO	14.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			48.4 (s)	CO*Me*		
			18.1 (t)	P*Me*$_2$Ph	17.0	$\lvert{}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)I(COMe)(PMe_2Ph)_3}]$ [c]	(II)	253	*d*	*C*OMe		
			199.1 (dt)	CO	13.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
					13.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			49.9 (d)	CO*Me*	27.0	$\lvert trans\text{-}{}^3J(\mathrm{P{-}C})\rvert$
$[\mathrm{Ru(CO)I(COMe)(PMe_2Ph)_3}]$ [c]	(III)	253	258.5 (dt)	*C*OMe	8.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
					8.0	$\lvert{}^2J(\mathrm{P{-}C})\rvert$
			200.6 (dt)	CO	87.2	$\lvert trans\text{-}{}^2J(\mathrm{P{-}C})\rvert$
					13.6	$\lvert cis\text{-}{}^2J(\mathrm{P{-}C})\rvert$
			49.8 (s)	CO*Me*		

[a] Spectra were recorded on $\mathrm{CDCl_3}$ solutions of the complexes. Resonances due to phenyl carbon atoms are not included. Multiplicities are given in parentheses after the chemical-shift values: s = singlet, d = doublet, t = triplet, dt = doublet of triplets. [b] Probe temperature. [c] Resonances due to the methyl carbon atoms of the $\mathrm{PMe_2Ph}$ ligands overlap one another too badly for confident assignment, and in any case provide no additional stereochemical information. [d] This resonance was not located.

the solution. Owing to the extreme ease of the reconversion, we have been unable to isolate the product in a pure state, but elemental analysis and a Nujol mull i.r. spectrum of a sample isolated by low-temperature crystallization under CO indicated that it was predominantly $[\mathrm{Ru(CO)_2Cl(COMe)(PMe_2Ph)_2}]$ contaminated with a small amount of $[\mathrm{Ru(CO)_2Cl(Me)(PMe_2Ph)_2}]$.

Studies by ^{1}H and ^{13}C n.m.r. spectroscopy of the reaction in $\mathrm{CDCl_3}$ solution confirmed that it yields $[\mathrm{Ru(CO)_2Cl(COMe)(PMe_2Ph)_2}]$. Because of the rapidity of the interconversion of methyl and acetyl complexes at ambient temperature, spectra had to be obtained at low temperatures. Together with the i.r. spectrum, they fix the structure of the product as (II) (see Scheme 1, where L = $\mathrm{PMe_2Ph}$, X = Cl, and L′ = CO).



SCHEME 1

A solution of $[\mathrm{Ru(CO)_2Cl(Me)(PMe_2Ph)_2}]$ was then treated with an amount of CO insufficient to cause complete conversion into $[\mathrm{Ru(CO)_2Cl(COMe)(PMe_2Ph)_2}]$. At 273 K, separate ^{1}H resonances could be seen for the methyl and acetyl ligands in starting material and product respectively. As the temperature was raised, the two resonances broadened and collapsed over the same temperature range, confirming that methyl and acetyl complexes are in rapid equilibrium with one another.

$$[\mathrm{Ru(CO)_2Cl(Me)(PMe_2Ph)_2}] + \mathrm{CO} \rightleftharpoons [\mathrm{Ru(CO)_2Cl(COMe)(PMe_2Ph)_2}]$$

In order to obtain more information about the mechanism of the reaction, and in particular about the destination of the attacking ligand, we studied the reaction of $[\mathrm{Ru(CO)_2Cl(Me)(PMe_2Ph)_2}]$ with ligands containing phosphorus donor atoms. An extremely rapid reaction with $\mathrm{PMe_2Ph}$ in $\mathrm{CHCl_3}$ solution led to the formation of $[\mathrm{Ru(CO)Cl(COMe)(PMe_2Ph)_3}]$, which was isolated by low-temperature crystallization. In this instance (and by implication also in the case of the reaction with CO) the acetyl group is clearly formed by intramolecular combination of methyl and carbonyl ligands: the alternative possibility that an initial carbonyl-substitution reaction to form [Ru(CO)Cl(Me)$(PMe_2Ph)_3$] is followed by attack by the liberated CO was ruled out by showing that the reaction of [Ru(CO)Cl(Me)$(PMe_2Ph)_3$] with CO is much slower than the conversion of [$Ru(CO)_2Cl$(Me)$(PMe_2Ph)_2$] into [Ru(CO)Cl(COMe)$(PMe_2Ph)_3$].[6]

Again it was necessary to obtain n.m.r. spectra at low temperatures because of the rapid reversible reactions which the acetyl complex undergoes. As regards the stereochemistry of the complex, the ^1H spectrum is relatively uninformative, indicating only that the three PMe_2Ph ligands are arranged meridionally, but the ^{13}C spectrum is more helpful. Whereas the two ^2J(P–C) coupling constants for the doublet-of-triplets resonance for the carbonyl ligand are similar in magnitude (suggesting that it is *cis* to all three phosphorus ligands), the doublet splitting for the similar resonance for the carbonyl carbon atom in the acetyl ligand is much larger than the triplet splitting, indicating that the acetyl ligand is *trans* to the unique PMe_2Ph ligand. Thus this complex also must have structure (II), where L = L′ = PMe_2Ph and X = Cl. Confirmation comes from the fact that the resonance for the methyl carbon atom in the acetyl ligand is a doublet, whereas that for the same carbon atom in [$Ru(CO)_2Cl$(COMe)$(PMe_2Ph)_2$] is a singlet.

The low-temperature ^1H and ^{13}C n.m.r. spectra of solutions of [Ru(CO)Cl(COMe)$(PMe_2Ph)_3$] containing added PMe_2Ph exhibit separate methyl resonances for the free PMe_2Ph and for the two types of co-ordinated PMe_2Ph. On warming, however, the resonances for free PMe_2Ph and for the unique PMe_2Ph ligand in the complex broaden, coalesce, and then sharpen to a single averaged resonance. The temperature range over which coalescence occurs in the ^1H spectrum was found to be independent of the concentration of free PMe_2Ph, showing that the mechanism of the exchange process is dissociative in nature. The acetyl-proton resonance does not alter in appearance over this temperature range, but, as would be expected, the resonance for the methyl carbon atom in the acetyl ligand loses its doublet splitting. The ^1H study was extended to higher temperatures, at which it was found that the acetyl-proton resonance does broaden. The temperature required to produce broadening of *this* resonance increases with the concentration of free PMe_2Ph. These results show that the interconversion of methyl and acetyl ligands, which is responsible for the collapse of the acetyl-proton resonance, occurs in a separate step from the exchange of free and co-ordinated PMe_2Ph, as shown below where L′ = PMe_2Ph. Addition of free PMe_2Ph suppresses the interconversion of methyl and acetyl ligands by increasing the likelihood that the intermediate will be captured by PMe_2Ph before it can form [$Ru(CO)_2Cl$(Me)$(PMe_2Ph)_2$].

$$[Ru(CO)_2Cl(Me)(PMe_2Ph)_2] \rightleftharpoons [Ru(CO)Cl(COMe)(PMe_2Ph)_2] \underset{-L'}{\overset{+L'}{\rightleftharpoons}} [Ru(CO)Cl(COMe)(PMe_2Ph)_2L']$$

Comparison of the stereochemistry of the products of the reactions of [$Ru(CO)_2Cl$(Me)$(PMe_2Ph)_2$] with CO and PMe_2Ph shows that the incoming ligand is incorporated into the product *trans* to the acetyl ligand. If the five-co-ordinate intermediate is assumed to have trigonal-bipyramidal geometry, the stereochemistry of the reaction is as shown in Scheme 1, where L = PMe_2Ph, X = Cl, and L′ = CO or PMe_2Ph. {Alternatively, the intermediate could be envisaged as a square-based pyramid with the acetyl ligand in the apical position but, as will be seen later, this makes the interpretation of the reactions of the complexes [$Ru(CO)_2X$(Me)$(PMe_2Ph)_2$] (X = Br or I) rather more complicated.} The preferred direction of attack *trans* to the acetyl ligand implies that this ligand has a large *trans*-directing effect, and the extreme lability of the Ru–L′ bond in both complexes indicates that the acetyl ligand has a strong *trans*-labilizing effect. The link between these two effects has been discussed previously.[7,8]

The reactions of [$Ru(CO)_2Cl$(Me)$(PMe_2Ph)_2$] with other phosphorus ligands {L′ = P[$(OCH_2)_3$CMe], $P(OMe)_3$, $PPh(OMe)_2$, or PPh_2(OMe)} were also studied. No attempt was made to isolate the products, but i.r. and ^1H n.m.r. spectra of the reaction mixtures indicated that acetyl complexes [Ru(CO)Cl(COMe)$(PMe_2Ph)_2$L′] of structure (II) were formed. In every case, the n.m.r. spectra of the products in the presence of free L′ clearly indicated the lability of the Ru–L′ bond. It was found that the temperatures at which the resonances due to free and co-ordinated L′ first showed significant signs of broadening could be correlated with Tolman's values[9] for the cone angle of the ligand L′:

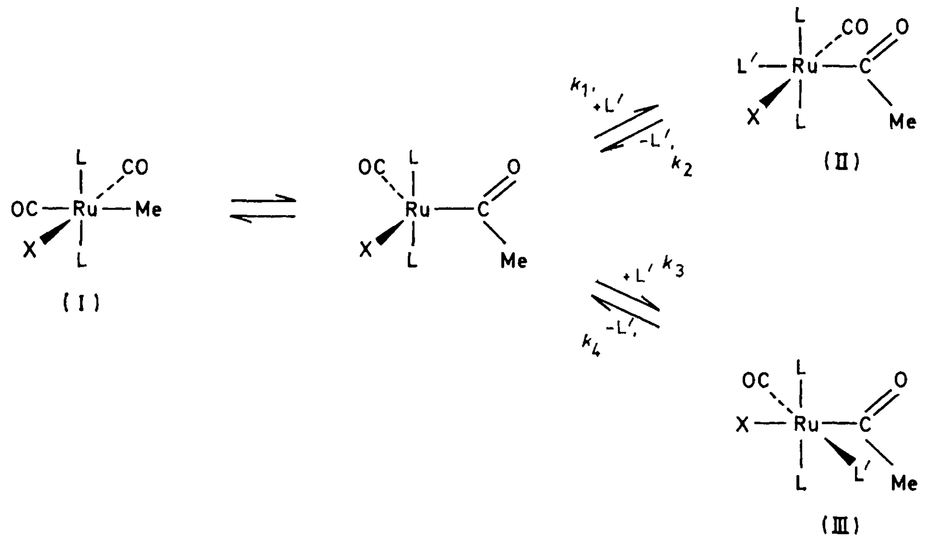
L′	T/K	Cone angle/°
P[$(OCH_2)_3$CMe]	310	101
$P(OMe)_3$	285	107
$PPh(OMe)_2$	275	115
PMe_2Ph	265	122
PPh_2(OMe)	255	132

Evidently the bulkiness of L′ is an important factor in determining the rate of exchange between co-ordinated and free L′, and it is noticeable that the least labile Ru–L′ bond is that to P[$(OCH_2)_3$CMe], the ligand whose caged structure minimizes its steric interactions with other ligands in the complex.

(3) *Reactions of the Complexes* [$Ru(CO)_2X$(Me)$(PMe_2Ph)_2$] (X = Br *or* I).—The complex [$Ru(CO)_2I$(Me)$(PMe_2Ph)_2$] was found to react rapidly with CO in $CHCl_3$ solution to yield a product {shown by elemental analysis to be [$Ru(CO)_2I$(COMe)$(PMe_2Ph)_2$]} which could, in contrast to [$Ru(CO)_2Cl$(COMe)$(PMe_2Ph)_2$], be isolated without difficulty. The i.r. and ^1H and ^{13}C n.m.r. spectra of the product show that its stereochemistry is not (II) (as for the chloro-complex) but (III) (see Scheme 2, where L = PMe_2Ph, X = I, and L′ = CO). As the greater ease of isolation implies, the change in stereochemistry is accompanied by a marked change in

the rate of reconversion of acetyl complex into methyl complex. On passing N_2 through a solution of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$ at room temperature, conversion into the methyl complex is only complete after *ca.* 0.7 h. In addition, whereas the resonance for the acetyl protons in $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$ can only be observed on cooling below ambient temperature, the corresponding resonance for $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$ is visible as a sharp singlet at ambient temperature: indeed, in chlorobenzene solution it is still sharp at 353 K.

A closer study of the reaction, however, revealed an added complication. A $CDCl_3$ solution of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ was treated, at ambient temperature, with a quantity of CO insufficient to cause complete conversion into $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$. The ^1H n.m.r. spectrum of the solution revealed the expected resonances for the protons of the methyl and acetyl ligands in starting material and product respectively: the acetyl resonance, as expected, was sharp but the methyl resonance was noticeably broadened. The broadening disappeared on cooling the solution to 293 K. Clearly the methyl complex is involved in an equilibrium (rapid at ambient temperature) with a small but significant quantity of some species *other* than isomer (III) of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$.



Scheme 2

In a separate experiment, a $CDCl_3$ solution of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ was saturated with CO at *ca.* 210 K and then placed in the probe of the ^1H n.m.r. spectrometer at 243 K. The spectrum obtained was markedly different from that of isomer (III) of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$ but similar to that of $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$, which has structure (II). Thus the *kinetic* product of the reaction between $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ and CO appears to be isomer (II) of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$. On warming to 273 K, it was found that (II) slowly rearranges to (III) until an equilibrium [heavily favouring (III)] is reached. The experiment was repeated using insufficient CO to cause complete conversion: on warming, the resonances due to the acetyl protons in (II) and the protons in the methyl ligand of the remaining $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ started to broaden at the same temperature, showing that these two complexes are in rapid equilibrium with each other.

In summary, then, the kinetic product of the reaction between $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ and CO is isomer (II) of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$, but isomer (III) is thermodynamically more stable than (II). Isomer (II) is in rapid equilibrium with $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$, whereas interconversion of (III) with the methyl complex [which could be either direct or by way of (II)] is considerably slower. The simplest (although by no means the only) mechanism that can be envisaged for the system is an extension of that shown in Scheme 1. It involves two alternative modes of attack on a single trigonal-bipyramidal intermediate, as shown in Scheme 2 (where L = PMe_2Ph, X = I, and L′ = CO).†

Since the acetyl ligand has a greater *trans*-directing effect than CO, k_1 is larger than k_3, so that (II) is the kinetic product. The acetyl ligand, however, also has a greater *trans*-labilizing effect than CO, and as a result the equilibrium between (I) and (II) is much more rapid than that between (I) and (III).

Further experiments were then carried out to determine whether complexes of structure (II) are *always* the kinetic products of reactions of this type, and to find out what factors control the balance of thermodynamic stability between isomers (II) and (III) of the products $[Ru(CO)X(COMe)(PMe_2Ph)_2L']$. The reaction of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ and PMe_2Ph at low temperatures was shown by ^1H n.m.r. spectroscopy to yield exclusively

† If, as mentioned earlier, the intermediate between (I) and (II) is assumed to be square pyramidal, it is necessary to introduce a second such intermediate (with the carbonyl ligand in the apical position) through which (III) can be formed.

isomer (II) of $[Ru(CO)I(COMe)(PMe_2Ph)_3]$, but at 253 K this rearranged until an equilibrium mixture of (II) and (III) was obtained. The equilibrium is in favour of (III), but not as heavily so as in the case of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$. The ^1H and ^{13}C spectra of the two isomers are in many ways similar to those of other complexes of the same structure mentioned earlier, but two features indicate a considerable degree of crowding in the molecules. Due to the large *trans* effect of the acetyl ligand, exchange between the unique PMe_2Ph ligand in isomer (II) and free PMe_2Ph is fast enough to broaden their methyl-proton resonances significantly at 265 K, but even isomer (III), in which the PMe_2Ph ligand is *trans* to the less strongly labilizing carbonyl ligand, shows similar broadening in its spectrum at 320 K. In addition, the difference in chemical shift between the protons of the two methyl groups on each of the mutually *trans* pair of PMe_2Ph ligands in (III) is remarkably large (*ca.* 0.44 p.p.m.): this presumably reflects the fact that rotation of the PMe_2Ph ligands about the Ru–P bonds is distinctly restricted, with preferential adoption of rotameric structures in which the methyl groups are in very different environments.

The complex $[Ru(CO)_2Br(Me)(PMe_2Ph)_2]$ shows behaviour intermediate between its chloro- and iodo-analogues. Again the kinetic product of the reaction with CO is isomer (II) of $[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$, but the final equilibrium mixture contains roughly equal amounts of (II) and (III). In the case of the reaction with PMe_2Ph, isomer (II) of $[Ru(CO)Br(COMe)(PMe_2Ph)_3]$ is both kinetically and thermodynamically favoured: even in the equilibrium mixture the concentration of isomer (III) is low. A high-temperature ^1H n.m.r. study of this system revealed that the following equilibrium shifts markedly to the left

$$[Ru(CO)_2Br(Me)(PMe_2Ph)_2] + PMe_2Ph \rightleftharpoons [Ru(CO)Br(COMe)(PMe_2Ph)_3] \text{ isomer (II)}$$

with increasing temperature (as expected on entropy grounds) and that interconversion is rapid enough at 363 K for a sharp averaged resonance to be observed for the methyl protons in the methyl and acetyl ligands: the resonance is a narrow triplet, reflecting the balance between the methyl $[^3J(P\text{–}H) = 7.75\ Hz]$ and acetyl $[^4J(P\text{–}H) \sim 0\ Hz]$ complexes.

It can be seen that in the complexes $[Ru(CO)_2X(COMe)(PMe_2Ph)_2]$ the thermodynamic balance between isomers (II) and (III) swings from (II) to (III) as the halogen becomes larger. The preference for (II) in the chloro-complex may be an electronic effect, in that the two π-accepting carbonyl ligands lie in mutually *cis* positions and hence compete to a lesser extent for *d*-electron density on the ruthenium. A similar argument has recently been put forward [10] to explain a variation in bond lengths in $[Ru_3(CO)_{12}]$, where the Ru–C distances to the pairs of mutually *cis* equatorial CO ligands are noticeably shorter than those to the pairs of mutually *trans* axial CO ligands. The shift away from (II) as the halogen becomes larger probably reflects the increasing crowding resulting from the mutually *cis* positioning of the acetyl and halide ligands. The complexes $[Ru(CO)X(COMe)(PMe_2Ph)_3]$ show a similar, but less marked, trend. Here the fact that only one carbonyl ligand is present removes the obvious electronic advantage of (II), and the presence of an extra bulky ligand reduces the steric preference for (III). Nevertheless, since (II) places the halide ligand *cis* to four bulky ligands whereas (III) places the unique phosphorus ligand in this site, an increase in the size of the halogen must be expected to favour (III) with respect to (II).

The effect of varying the entering phosphorus ligand L′ in the reactions of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ was also studied. The increased crowding resulting from the use of $PMePh_2$ in place of PMe_2Ph has two effects: first the overall position of equilibrium between $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ and $[Ru(CO)I(COMe)(PMe_2Ph)_2L']$ is shifted in favour of the methyl complex, and secondly the major constituent in the equilibrium mixture of acetyl complexes is now (II) instead of (III). The logic behind this shift from (III) to (II) with increasing size of L′ is exactly the same as that behind the swing from (II) to (III) with increased size of halide ligand.

Use of a phosphorus ligand L′ containing alkoxy-substituents was also found to favour isomer (II) of $[Ru(CO)I(COMe)(PMe_2Ph)_2L']$, presumably because (III) suffers from the positioning of two π-accepting ligands (alkoxyphosphine and carbonyl) in mutually *trans* positions. Thus, despite its low steric requirements, $P(OMe)_3$ reacts with $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ to give a mixture of (II) and (III), with (II) as the major product, and the bulkier $PPh(OMe)_2$ forms only (II).

(4) *Reactions of the Complexes* $[Ru(CO)_2X(Me)(AsMe_2Ph)_2]$ (X = Cl, Br, *or* I).—These will not be dealt with in detail, since to a large extent they follow the pattern established by the corresponding PMe_2Ph complexes. All three methyl complexes react with CO to form $[Ru(CO)_2X(COMe)(AsMe_2Ph)_2]$: in the case of the chloro-complex, isomer (II) (where L = $AsMe_2Ph$, X = Cl, and L′ = CO) is kinetically and thermodynamically preferred, but cannot be isolated because of the extreme ease of reconversion into $[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$. For the iodo-complex, isomer (III) is the final product, and can readily be isolated. The bromo-complex ultimately yields an equilibrium mixture of (II) and (III).

In the case of the reactions of the complexes $[Ru(CO)_2X(Me)(AsMe_2Ph)_2]$ with $AsMe_2Ph$, identification of the isomers of the products $[Ru(CO)X(COMe)(AsMe_2Ph)_3]$ must be made on the basis of the close parallels between the chemical shifts of the resonances in their ^1H n.m.r. spectra and those for the analogous complexes $[Ru(CO)X(COMe)(PMe_2Ph)_3]$. The complex $[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$ yields only isomer (II) of $[Ru(CO)Cl(COMe)(AsMe_2Ph)_3]$, which is notable for the extreme lability of the bond to the unique $AsMe_2Ph$ ligand (there is significant broadening of the methyl-proton resonances for this ligand and for added free $AsMe_2Ph$ even at 253 K). This reflects both the fact that $AsMe_2Ph$ is a poorer ligand than PMe_2Ph and the more severe crowding due to the presence of three $AsMe_2Ph$ ligands in place of three PMe_2Ph ligands.

In the case of $[Ru(CO)_2I(Me)(AsMe_2Ph)_2]$, reaction at 243 K yields in the first instance only isomer (II) of $[Ru(CO)I(COMe)(AsMe_2Ph)_3]$, although the final equilibrium mixture is 3 : 1 in favour of (III). Even in the presence of an excess of $AsMe_2Ph$, conversion into acetyl complexes is incomplete: the resonance due to the methyl ligand protons in the remaining methyl complex is sharp at 270 K, but broadens simultaneously with the acetyl resonance of isomer (II) on warming. At 306 K even the resonance due to the methyl protons in the unique $AsMe_2Ph$ ligand in isomer (III) shows signs of broadening: this and the incomplete conversion into acetyl complexes are both attributable to the two factors mentioned above. Again the behaviour of the bromo-complex, $[Ru(CO)_2Br(Me)(AsMe_2Ph)_2]$, is intermediate between that of its chloro- and iodo-analogues.

In summary, then, the balance between methyl and acetyl complexes is significantly different for the complexes containing $AsMe_2Ph$ from that for those containing PMe_2Ph. In contrast, the thermodynamic balance between isomers (II) and (III) of complexes $[Ru(CO)X(COMe)L_2L']$ appears to be much the same for $L = AsMe_2Ph$ as it is for $L = PMe_2Ph$. This is, perhaps, not surprising since the steric interactions between the four coplanar ligands CO, X, COMe, and L′ and the two L ligands will presumably be much the same for both isomers.

EXPERIMENTAL

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, ^1H n.m.r. spectra either on a Varian A-60A spectrometer with V-6057 variable-temperature accessory or on a JEOL N-MH-100 spectrometer using the JEOL NM-VT-3B variable-temperature attachment, and ^{13}C n.m.r. spectra on a JEOL FX-60 instrument with the JEOL NM-5471 variable-temperature attachment. Elemental analyses were carried out on a Perkin-Elmer 240 elemental analyser.

Preparation of Complexes.—All preparative work was carried out under an atmosphere of dry nitrogen. The boiling range of the light petroleum used was 313—333 K. Analytical data for all isolated complexes are given in Table 5.

$[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$. Details of the preparation of this complex have been given in an earlier paper.[5] The same method was used to obtain $[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$ from all-*trans*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$.

$[Ru(CO)_2Br(Me)(PMe_2Ph)_2]$. A mixture of $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ (0.10 g) and NaBr (0.20 g) in propanone (25 cm^3) was stirred at 293 K for 0.5 h. The solvent was then removed under reduced pressure and the product extracted from the residue with $CHCl_3$. Removal of the $CHCl_3$ under a stream of nitrogen yielded the pure product (yield 80%). The analogous iodo-complex was obtained in the same way and in similar yield from $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ (0.10 g) and NaI (0.30 g).

$[Ru(CO)_2Br(Me)(AsMe_2Ph)_2]$ *and* $[Ru(CO)_2I(Me)(AsMe_2Ph)_2]$. These complexes were prepared in the same manner as their phosphorus analogues, using $[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$ (0.10 g) and either NaBr (0.20 g) or NaI (0.30 g) (yields *ca.* 70%).

TABLE 5

Analytical data

Complex	Structure	Colour	M.p. (T/K)	Analysis (%) Found C	Found H	Calc. C	Calc. H
$[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$	(I)	White	365—368	46.9	5.25	47.15	5.20
$[Ru(CO)_2Br(Me)(PMe_2Ph)_2]$	(I)	Cream	377—378	43.35	4.85	43.2	4.75
$[Ru(CO)_2I(Me)(PMe_2Ph)_2]$	(I)	Yellow	375—378	39.45	4.35	39.65	4.40
$[Ru(CO)_2Cl(Me)(AsMe_2Ph)_2]$	(I)	White	343—345	40.1	4.65	39.9	4.40
$[Ru(CO)_2Br(Me)(AsMe_2Ph)_2]$	(I)	Cream	373—375	36.4	3.95	37.05	4.10
$[Ru(CO)_2I(Me)(AsMe_2Ph)_2]$	(I)	Yellow	376—378	34.15	3.85	34.4	3.80
$[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$	(II)	White	382—384 *	47.05	5.10	46.95	4.90
$[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$	(II)	White	337—341	52.1	6.00	52.15	5.85
$[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$	(III)	Yellow	345—347 *	39.4	4.25	39.8	4.20
$[Ru(CO)I(COMe)(PMe_2Ph)_3]$	(II) + (III)	Yellow		45.4	5.35	45.45	5.10
$[Ru(CO)_2I(COMe)(AsMe_2Ph)_2]$	(III)	Yellow	365—367 *	35.0	3.75	34.75	3.65

* Melts with evolution of CO and formation of the corresponding methyl complex.

$[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$. A solution of $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ (0.10 g) in ethanol (10 cm^3) was saturated with CO and then slowly reduced in volume under a stream of CO at *ca.* 240 K. This yielded a crystalline product which, after removal of the remaining solution by syringe, was washed at 240 K with light petroleum (yield 30%). Infrared spectroscopy indicated that the product was slightly contaminated with $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$.

$[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$. An ethanol solution (10 cm^3) of $[Ru(CO)_2Cl(Me)(PMe_2Ph)_2]$ (0.10 g) and PMe_2Ph (0.03 g) was reduced in volume under a stream of nitrogen at 240 K, and a crystalline product was obtained. The remaining solution was removed by syringe and the product was washed at 240 K with light petroleum (yield 40%).

$[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$ [*isomer* (III)]. A solution of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ (0.05 g) in $CHCl_3$ (5 cm^3) was saturated with CO at 293 K, and then evaporated to dryness under a stream of CO. The crystalline residue was washed with light petroleum (yield 90%). Isomer (III) of $[Ru(CO)_2I(COMe)(AsMe_2Ph)_2]$ was obtained in the same way and in similar yield from $[Ru(CO)_2I(Me)(AsMe_2Ph)_2]$.

$[Ru(CO)I(COMe)(PMe_2Ph)_3]$ [*a mixture of isomers* (II) *and* (III)]. An ethanol solution (10 cm^3) of $[Ru(CO)_2I(Me)(PMe_2Ph)_2]$ (0.10 g) and PMe_2Ph (0.025 g) was reduced in volume under a stream of nitrogen. Crystals of the product were formed. The remaining solution was removed by syringe and the product washed with light petroleum (yield 30%).

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REFERENCES

[1] C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J.C.S. Chem. Comm.*, 1976, 1032.

[2] D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, 1965, **208**, 1203.

[3] R. H. Prince and K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 612.

[4] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

[5] C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J.C.S. Dalton*, 1976, 961.

[6] C. F. J. Barnard and R. J. Mawby, paper in preparation.

[7] D. M. Blake and M. Kubota, *J. Amer. Chem. Soc.*, 1970, **92**, 2578.

[8] C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J.C.S. Dalton*, 1976, 953.

[9] C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

[10] M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655.