Synthesis and Interconversion of, and Restricted Rotation in, Phenyl Complexes of Ruthenium(II)

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The preparation and characterization of a range of phenyl complexes of ruthenium(II) are reported. For many of the complexes there is a substantial barrier to rotation of the phenyl ligand about the metal–phenyl bond, and n.m.r. studies have shown how the rate of rotation is affected by changes in the ligands in the complexes. Reaction of complexes $[Ru(CO)(C_6H_4X)Y(PPh_3)_2]$ with phosphorus or arsenic ligands L provides a convenient route to $[Ru(CO)(C_6H_4X)YL_3]$ [X = H, Y = Cl, L = $P(OMe)_3$, PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$, or $AsMe_2Ph$; X = H, Y = Br or I, L = $P(OMe)_3$; X = 4-MeO, 4-Cl, or 4-Me, Y = Cl, L = $P(OMe)_3$]: ^{31}P and ^{13}C n.m.r. studies have demonstrated the sequence of steps involved and the stereochemistry of the intermediates, showing the influence of the *trans*-labilizing and *trans*-directing effects of the phenyl ligand.

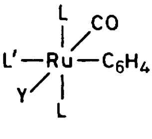
We have recently reported the results of a kinetic study of the reactions of phenyl complexes of ruthenium(II), $[Ru(CO)_2(C_6H_4X\text{-}4)_2(PMe_2Ph)_2]$,[1] with $CNCMe_3$ to yield acyl complexes $[Ru(CO)(COC_6H_4X\text{-}4)(C_6H_4X\text{-}4)(PMe_2Ph)_2(CNCMe_3)]$.[2] The study revealed a linear relationship between log *k* (where *k* was the rate constant for combination of phenyl and carbonyl ligands) and the Hammett σ constant for the substituent X: electron-releasing substituents accelerated the reaction, while electron-withdrawing substituents slowed it down. It was suggested that the variations in rate might be attributable to changes in metal–phenyl bond strength resulting from the effect of X on the extent of back-donation from the metal to the phenyl ligand.[2]

In an octahedral complex, the π system of a phenyl ligand can overlap with either of two metal *d* orbitals. Each is shared with the ligand *trans* to the phenyl group, but with only two of the four ligands *cis* to the phenyl group. Where the π-accepting ability of the ligands in these *cis* positions varies significantly, one can expect to observe a preferred geometry for the phenyl ligand which maximises the overlap of its π-system with the *d* orbital for which there is less competition from the appropriate *cis* ligands, and a significant energy barrier to the rotation of the phenyl ligand out of its preferred orientation. In this paper we describe the preparation of a range of ruthenium(II) complexes containing a phenyl or substituted phenyl ligand, and show that the n.m.r. spectra of the complexes provide ample evidence of a preferred orientation for the phenyl ligand and of a significant barrier to rotation of the phenyl ligand about the metal–phenyl bond. Variable-temperature n.m.r. studies have been carried out to assess the effect of changes in particular ligands on the rate of rotation.

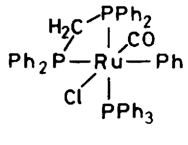
One method used for the preparation of the phenyl complexes involved conversion of the triphenylphosphine complexes $[Ru(CO)(C_6H_4X\text{-}4)Y(PPh_3)_2]$ into products $[Ru(CO)(C_6H_4X\text{-}4)YL_3]$ by treatment with a ligand L containing a phosphorus or arsenic donor atom. Phosphorus-31 and carbon-13 n.m.r. studies have provided evidence as to the sequence of steps involved in these reactions, allowing identification of the three intermediates and determination of their stereochemistry.

Results and Discussion

Details of the i.r. and ^1H n.m.r. spectra of the complexes discussed below are given in Table 1, and ^{13}C n.m.r. data for many of the complexes appear in Table 2. In Table 2, the carbon atoms in the phenyl ligand are numbered on the basis that C^1 is the atom attached to the metal.



(I)



(II)

Preparation of Complexes.—In an earlier paper,[3] we reported that treatment of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $[HgPh_2]$ in propanone solution resulted in the replacement of a single halide ligand, giving $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$. This method proved suitable for the preparation of substituted phenyl complexes $[Ru(CO)_2(C_6H_4X)Cl(PMe_2Ph)_2]$ (X = 4-MeO, 4-Cl, 4-Me_2N, 4-Me, or 3-Me). Both the ^1H and the ^{13}C n.m.r. spectra of these complexes exhibited two triplet resonances for the methyl substituents in the PMe_2Ph ligands, establishing that the complexes possessed a pair of mutually *trans* PMe_2Ph ligands and that the Ru–P bonds did not lie in a plane of symmetry.† We concluded that the complexes possessed structure (I), where L = PMe_2Ph, L′ = CO, and Y = Cl, and confirmation of this was provided by the observation of two C–O stretching bands of similar intensity in the i.r. spectra of the complexes and two triplet resonances for the carbonyl ligands in the ^{13}C n.m.r. spectra.

The chloride ligand in $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ could be replaced by other anions. Treatment with NaY (Y = Br, I, or O_2CMe) in propanone or methanol solution yielded the complexes $[Ru(CO)_2(Ph)Y(PMe_2Ph)_2]$. From the spectra of the products it was clear that the reactions proceeded with retention of the stereochemistry around the ruthenium. Thanks to the *trans*-labilizing effect of the phenyl ligand, the carbonyl ligand *trans* to phenyl in $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ could be replaced by treating solutions of the complex with other ligands L′ [L′ = PMe_2Ph, $P(OMe)_3$, $P(OMe)_2Ph$, or $CNCMe_3$], using a stream of N_2 to purge the solutions of CO. The ^1H and ^{13}C n.m.r. spectra of the products $[Ru(CO)(Ph)Cl(PMe_2Ph)_2L']$ showed that the PMe_2Ph ligands were still mutually *trans*, and the fact that L′ was *trans* to the phenyl ligand was apparent (in the cases where L′ was a phosphorus ligand) from the splitting pattern observed for C^1 in the phenyl ligand, where the doublet splitting due to the phosphorus nucleus in L′ was much larger than the triplet splitting due to the PMe_2Ph ligands. In contrast, the doublet and triplet splittings of the resonance for the

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† The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and coworkers.[4,5]

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

Complex	ν(C–O)/cm^{-1}	δ/p.p.m.[b]	Assignment
$[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$	2 043	1.71 (t, 6)	PMe_2Ph
	1 965	1.45 (t, 6)	PMe_2Ph
$[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	2 045	3.71 (s, 3)	$C_6H_4OMe\text{-}4$
	1 963	1.61 (t, 6)	PMe_2Ph
		1.38 (t, 6)	PMe_2Ph
$[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	2 050	1.68 (t, 6)	PMe_2Ph
	1 965	1.41 (t, 6)	PMe_2Ph
$[Ru(CO)_2(C_6H_4NMe_2\text{-}4)Cl(PMe_2Ph)_2]$	2 040	2.87 (s, 6)	$C_6H_4NMe_2\text{-}4$
	1 958	1.68 (t, 6)	PMe_2Ph
		1.42 (t, 6)	PMe_2Ph
$[Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2]$	2 045	2.27 (s, 3)	$C_6H_4Me\text{-}4$
	1 965	1.66 (t, 6)	PMe_2Ph
		1.42 (t, 6)	PMe_2Ph
$[Ru(CO)_2(C_6H_4Me\text{-}3)Cl(PMe_2Ph)_2]$	2 038	2.22 (s, 3)	$C_6H_4Me\text{-}3$
	1 955	1.68 (t, 6)	PMe_2Ph
		1.42 (t, 6)	PMe_2Ph
$[Ru(CO)_2(Ph)Br(PMe_2Ph)_2]$	2 043	1.78 (t, 6)	PMe_2Ph
	1 968	1.46 (t, 6)	PMe_2Ph
$[Ru(CO)_2(Ph)I(PMe_2Ph)_2]$	2 038	1.93 (t, 6)	PMe_2Ph
	1 968	1.55 (t, 6)	PMe_2Ph
$[Ru(CO)_2Ph(O_2CMe)(PMe_2Ph)_2]$	2 042	1.97 (s, 3)	O_2CMe
	1 963	1.52 (t, 6)	PMe_2Ph
	1 595	1.36 (t, 6)	PMe_2Ph
$[Ru(CO)(Ph)Cl(PPh_3)_2]$	1 931		
$[Ru(CO)(Ph)Br(PPh_3)_2]$[c]	1 928		
$[Ru(CO)(Ph)I(PPh_3)_2]$[c]	1 929		
$[Ru(CO)_2(Ph)Cl(PPh_3)_2]$	2 052		
	1 971		
$[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$	1 965	3.80 (d, 9)	$P(OMe)_3$
		3.50 (t, 18)	$P(OMe)_3$
$[Ru(CO)(C_6H_4OMe\text{-}4)Cl\{P(OMe)_3\}_3]$[d]	1 965	3.73 (d, 9)	$P(OMe)_3$
		3.70 (s, 3)	$C_6H_4OMe\text{-}4$
		3.46 (t, 18)	$P(OMe)_3$
$[Ru(CO)(C_6H_4Cl\text{-}4)Cl\{P(OMe)_3\}_3]$[d]	1 970	3.74 (d, 9)	$P(OMe)_3$
		3.47 (t, 18)	$P(OMe)_3$
$[Ru(CO)(C_6H_4Me\text{-}4)Cl\{P(OMe)_3\}_3]$[d]	1 975	3.73 (d, 9)	$P(OMe)_3$
		3.46 (t, 18)	$P(OMe)_3$
		2.22 (s, 3)	$C_6H_4Me\text{-}4$
$[Ru(CO)(Ph)Br\{P(OMe)_3\}_3]$	1 972	3.78 (d, 9)	$P(OMe)_3$
		3.49 (t, 18)	$P(OMe)_3$
$[Ru(CO)(Ph)I\{P(OMe)_3\}_3]$	1 978	3.79 (d, 9)	$P(OMe)_3$
		3.49 (t, 18)	$P(OMe)_3$
$[Ru(CO)(Ph)Cl(PMe_2Ph)_3]$[c]	1 916	1.33 (t, 6)	PMe_2Ph
		1.22 (t, 6)	PMe_2Ph
		1.08 (d, 6)	PMe_2Ph
$[Ru(CO)(Ph)Cl(PMePh_2)_3]$[c]	1 919	1.90 (d, 3)	$PMePh_2$
		1.58 (t, 6)	$PMePh_2$
$[Ru(CO)(Ph)Cl\{P(OMe)_2Ph\}_3]$[c]	1 955	3.72 (d, 6)	$P(OMe)_2Ph$
		3.44 (t, 6)	$P(OMe)_2Ph$
		3.30 (t, 6)	$P(OMe)_2Ph$
$[Ru(CO)(Ph)Cl(AsMe_2Ph)_3]$	1 917	1.28 (s, 6)	$AsMe_2Ph$
		1.11 (s, 6)	$AsMe_2Ph$
		1.01 (s, 6)	$AsMe_2Ph$
$[Ru(CO)(Ph)Cl(PPh_3)(Ph_2PCH_2PPh_2)]$[c]	1 935	5.4—4.2[e]	CH_2
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_3\}]$[c]	1 943	3.46 (d, 9)	$P(OMe)_3$
		1.59 (t, 6)	PMe_2Ph
		1.35 (t, 6)	PMe_2Ph
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_2Ph\}]$[c]	1 937	3.38 (d, 6)	$P(OMe)_2Ph$
		1.52 (t, 6)	PMe_2Ph
		1.25 (t, 6)	PMe_2Ph
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$	2 160[f]	1.56 (t, 6)	PMe_2Ph
	1 934	1.43 (t, 6)	PMe_2Ph
		0.94 (s, 9)	$CNCMe_3$

[a] In $CHCl_3$ or $CDCl_3$ solution except where stated otherwise. [b] Resonances due to phenyl ring protons have been omitted. Multiplicities and relative areas are given after the chemical shift values. [c] I.r. spectra in CH_2Cl_2 solution. [d] N.m.r. spectra in CD_2Cl_2 solution. [e] Complex pattern of resonances. [f] C–N stretching band.

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

	Phenyl ligand						
Complex	C^1	C^2,C^6	C^3,C^5	C^4	Substituent	CO	Other ligands
$[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$	157.1 (t)	141.4 (br) 137 (br)[b]	126.9 (s)	123.0 (t)		198.2 (t) 192.8 (t)	13.4 (t) 12.5 (t)
$[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	145.1 (t)	141.4 (br) 138 (br)[b]	113.0 (s)	156.8 (s)	54.7 (s)	198.4 (t) 192.9 (t)	13.4 (t) 12.6 (t)
$[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	155.2 (t)	142.4 (br) 139.1 (br)	126.8 (s)	129.6 (s)		198.0 (t) 192.8 (t)	13.6 (t) 12.5 (t)
$[Ru(CO)_2(C_6H_4NMe_2\text{-}4)Cl(PMe_2Ph)_2]$	141.0 (t)	*c*	113.4 (s)	147.7 (s)	41.1 (s)	198.6 (t) 192.9 (t)	13.3 (t) 12.6 (t)
$[Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2]$	152.0 (t)	141.0 (br) 138.0 (br)	128.0 (s)	132.2 (s)	20.9 (s)	199.0 (t) 192.9 (t)	13.3 (t) 12.6 (t)
$[Ru(CO)_2(C_6H_4Me\text{-}3)Cl(PMe_2Ph)_2]$	156.8 (t)	142.6 (br) 138.2 (br)	135.4 (s) 126.5 (s)	123.8 (s)	21.6 (s)	198.3 (t) 192.9 (t)	13.5 (t) 12.5 (t)
$[Ru(CO)_2(Ph)I(PMe_2Ph)_2]$	153.6 (t)	143.0 (br)	127.3 (s)	122.8 (s)		195.8 (t) 191.9 (t)	17.4 (t) 14.5 (t)
$[Ru(CO)_2Ph(O_2CMe)(PMe_2Ph)_2]$	159.1 (t)	142.3 (br) 136.2 (br)	126.7 (s)	122.9 (t)		201.3 (t) 194.0 (t)	176.5 (t) 24.2 (s) 13.3 (t) 13.2 (t)
$[Ru(CO)(Ph)Cl(PPh_3)_2]$	151.5 (t)	138.5 (br)	126.2 (s)	121.6 (s)		*d*	
$[Ru(CO)_2(Ph)Cl(PPh_3)_2]$	154.0 (t)	142.1 (br)	126.6 (s)	123.0 (s)		198.9 (t) 193.5 (t)	
$[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$	151.4 (m)[e]	142.7 (br)	125.7 (d)	122.0 (s)		198.7 (dt)	52.7 (t) 52.3 (d)
$[Ru(CO)(C_6H_4OMe\text{-}4)Cl\{P(OMe)_3\}_3]$[f]	139.8 (m)[e]	142.9 (br)	112.3 (d)	156.7 (s)	55.1 (s)	199.5 (dt)	53.0 (t) 52.6 (d)
$[Ru(CO)(C_6H_4Cl\text{-}4)Cl\{P(OMe)_3\}_3]$[f]	151.5 (m)[e]	143.9 (br)	125.6 (d)	128.8 (d)		199.2 (dt)	53.1 (t) 53.0 (d)
$[Ru(CO)(C_6H_4Me\text{-}4)Cl\{P(OMe)_3\}_3]$[f]	146.9 (m)[e]	142.7 (br)	127.1 (d)	131.2 (s)	20.9 (s)	199.5 (dt)	53.0 (t) 52.5 (d)
$[Ru(CO)(Ph)Br\{P(OMe)_3\}_3]$	149.8 (m)[e]	143.9 (br)	125.8 (d)	121.9 (s)		198.2 (dt)	52.9 (t) 52.5 (d)
$[Ru(CO)(Ph)I\{P(OMe)_3\}_3]$	147.4 (m)[e]	146.2 (br)	125.9 (d)	121.9 (s)		196.6 (dt)	53.3 (t) 52.9 (d)
$[Ru(CO)(Ph)Cl(PMe_2Ph)_3]$	161.3 (dt)	143.2 (br) 139.5 (br)	126.4 (br)	121.9 (s)		203.7 (dt)	16.2 (t) 15.9 (d) 13.1 (t)
$[Ru(CO)(Ph)Cl(PMePh_2)_3]$	158.1 (dt)	142.2 (br) 140.4 (br)	125.6 (br)	120.8 (s)		205.1 (dt)	13.2 (d) 13.0 (t)
$[Ru(CO)(Ph)Cl\{P(OMe)_2Ph\}_3]$	153.0 (m)[e]	143.2 (br) 140.0 (br)	125.5 (d)	121.7 (s)		200.5 (dt)	53.7 (t) 53.3 (d) 52.6 (t)
$[Ru(CO)(Ph)Cl(AsMe_2Ph)_3]$	156.9 (s)	143.5 (s) 139.2 (s)	126.4 (s)	121.9 (s)		202.3 (s)	11.6 (s) 11.0 (s) 8.2 (s)
$[Ru(CO)(Ph)Cl(PPh_3)(Ph_2PCH_2PPh_2)]$	156.3 (ddd)	141.6 (br)	126.1 (d)	121.3 (s)		202.3 (ddd)	45.5 (dd)
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_3\}]$	160.9 (dt)	142.1 (br) 139.2 (br)	126.1 (d)	121.9 (s)		201.4 (dt)	52.2 (d) 14.5 (t)[g]
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_2Ph\}]$	160.9 (dt)	142.1 (br) 139.0 (br)	126.2 (d)	121.9 (s)		202.6 (dt)	52.8 (d) 15.3 (t) 14.3 (t)
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$	161.4 (t)	142.5 (br) 138.7 (br)	126.0 (s)	121.3 (s)		201.7 (t)	145.8 (br) 55.8 (s) 29.6 (s) 13.0 (t) 12.1 (t)

[a] In $CDCl_3$ solution unless stated otherwise. Resonances due to phenyl carbon atoms in phosphorus and arsenic ligands have been omitted. [b] Resonance partially obscured. [c] Resonance collapsed at ambient temperature. [d] Complex insufficiently soluble for this resonance to be detected. [e] Resonance distorted by second-order effects. [f] In CH_2Cl_2 solution. [g] Accidental superimposition of two resonances.

carbonyl ligand were fairly similar in size. The complex $[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$ was shown to possess structure (**I**), where X = H, L = PMe_2Ph, L′ = $CNCMe_3$, and Y = Cl, by an *X*-ray crystallographic study.[6]

Roper and Wright[7] have shown that treatment of $[Ru(CO)(H)Cl(PPh_3)_3]$ with $[Hg(C_6H_4Me\text{-}4)_2]$ yields the aryl complex $[Ru(CO)(C_6H_4Me\text{-}4)Cl(PPh_3)_2]$. We used this method to prepare several substituted phenyl complexes $[Ru(CO)(C_6H_4X\text{-}4)Cl(PPh_3)_2]$ (X = H, MeO, Cl, or Me), and by treating these complexes with $P(OMe)_3$ we were able to convert them into products of formula $[Ru(CO)(C_6H_4X\text{-}4)Cl\{P(OMe)_3\}_3]$. Similar treatment of

Table 3. Rates[a] and activation energies[b] for phenyl ring rotation

Complex	T/K	Solvent	Rate/s^{-1}	E_a/kJ mol^{-1}
$[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$	298.3	$CDCl_2CDCl_2$	120	56(6)
$[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	298.3	$CDCl_2CDCl_2$	73.0	61(4)
$[Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2]$	298.3	$CDCl_2CDCl_2$	185	58(2)
$[Ru(CO)(Ph)Cl(PMe_2Ph)_3]$		$CDCl_2CDCl_2$	*c*	
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_3\}]$		$CDCl_2CDCl_2$	*c*	
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$	298.3	$CDCl_2CDCl_2$	16.5	83(3)
$[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	379	29(1)
$[Ru(CO)(C_6H_4OMe\text{-}4)Cl\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	460	34(1)
$[Ru(CO)(C_6H_4Cl\text{-}4)Cl\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	360	37(1)
$[Ru(CO)(C_6H_4Me\text{-}4)Cl\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	448	33(1)
$[Ru(CO)(Ph)Br\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	555	29(1)
$[Ru(CO)(Ph)I\{P(OMe)_3\}_3]$	273.2	CD_2Cl_2	1 010	31(1)

[a] Rates are for rotation of 180° about the metal–phenyl bond. [b] Standard deviations, given in parentheses, refer to the final figures of the values for the activation energies. [c] Rotation slow on the n.m.r. time-scale at all temperatures studied.

$[Ru(CO)(Ph)Cl(PPh_3)_2]$ with other ligands L yielded complexes $[Ru(CO)(Ph)ClL_3]$, where L was PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$, or $AsMe_2Ph$. Reaction of $[Ru(CO)(Ph)Cl(PPh_3)_2]$ with NaBr or NaI in propanone yielded the complexes $[Ru(CO)(Ph)Y(PPh_3)_2]$ (Y = Br or I), and these were converted into $[Ru(CO)(Ph)Y\{P(OMe)_3\}_3]$ by treatment with $P(OMe)_3$. For all these complexes $[Ru(CO)(C_6H_4X)YL_3]$, the pattern of resonances for the methyl groups in the ligands L in the ^1H and ^{13}C n.m.r. spectra established that these ligands were arranged in the *mer* fashion, and the sizes of the coupling constants between the phosphorus nuclei and the carbonyl carbon atom and C^1 of the phenyl ligand showed that the complexes possessed structure (**I**), where L = L′.

Brief treatment of $[Ru(CO)(Ph)Cl(PPh_3)_2]$ with CO in benzene solution yielded $[Ru(CO)_2(Ph)Cl(PPh_3)_2]$, which from its i.r. and n.m.r. spectra was clearly isostructural with $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$. Finally, the reaction between $[Ru(CO)(Ph)Cl(PPh_3)_2]$ and the bidentate phosphorus ligand $Ph_2PCH_2PPh_2$ resulted in the formation of $[Ru(CO)(Ph)Cl(PPh_3)(Ph_2PCH_2PPh_2)]$. The pattern of coupling constants between the phosphorus nuclei and the metal-bonded carbon atoms in the carbonyl and phenyl ligands was as expected for structure (**II**).

Rotation of the Phenyl Ligand about the Metal–Phenyl Bond.—An *X*-ray diffraction study of one of the complexes described in this paper, $[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$, showed that the phenyl ring lay in the plane at right angles to the Ru–P bonds [see structure (**I**), where X = H, L = PMe_2Ph, L′ = $CNCMe_3$, and Y = Cl].[6] The inequivalence between the *ortho* carbon atoms (C^2 and C^6) in the phenyl ligand revealed by the ^{13}C n.m.r. spectrum of the complex (see Table 2) suggested that the ring remained in this orientation in solution, and indicated that there was a significant barrier to rotation of the ring about the metal–phenyl bond. Inspection of the crystal structure revealed no steric reasons for this barrier, and a simulated structure with the phenyl ring rotated through 90° (keeping all other ligands in their normal positions) exhibited no short contacts between ring hydrogens and the PMe_2Ph ligands. We concluded that the positioning of the phenyl ring was controlled by electronic factors, and that the orientation at right angles to the Ru–P bonds was favoured because it maximised the overlap of the π system of the phenyl ring with the one *d* orbital on the metal which was *not* shared by the most strongly π-accepting ligand in the complex, the carbonyl ligand positioned *cis* to the phenyl ligand.

From Table 2 it can be seen that the ^{13}C n.m.r. spectra of many of the other six-co-ordinate complexes also exhibited separate resonances for C^2 and C^6 at ambient temperature. In some instances these resonances collapsed and then coalesced to a single resonance as the temperature was raised; in others, separate resonances persisted up to temperatures at which the complexes decomposed. Variable-temperature n.m.r. studies on some of the complexes for which only one resonance was observed for C^2 and C^6 at ambient temperature showed that two resonances were observed at lower temperatures. All of the complexes contained a carbonyl ligand positioned *cis* to the phenyl ligand, and as a result the phenyl ligand would be expected on electronic grounds to adopt the same orientation as that adopted by $[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$.

In several cases where the full range of spectra (from a single averaged resonance for C^2 and C^6 to separate sharp resonances for each atom) could be obtained at accessible temperatures, rates of rotation were found at several temperatures by comparison of actual ^{13}C n.m.r. spectra with those simulated for particular rates, and these were used to obtain activation energies and rates at a common temperature, 298.3 K. The solvent used for these studies was $CDCl_2CDCl_2$.

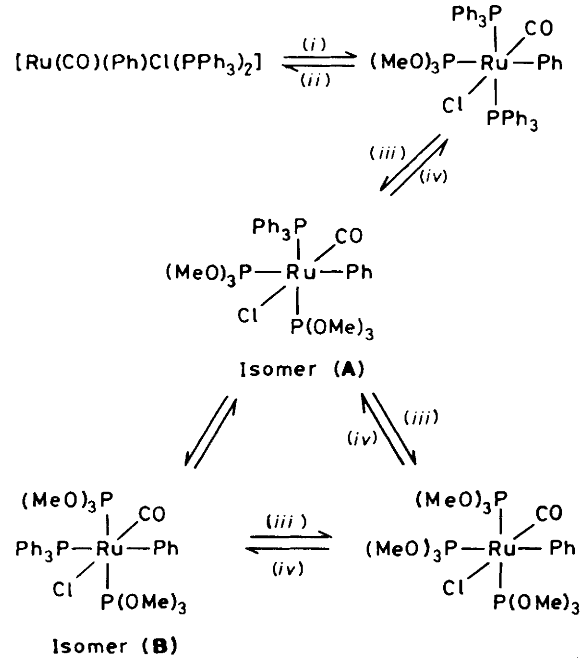
The inequivalence of C^2 and C^6 should be matched by an inequivalence between the protons attached to these carbon atoms. Where the ligands L or L′ contained phenyl groups, however, the resonances for H^2 and H^6 tended to be obscured. In the case of the complexes $[Ru(CO)(C_6H_4X\text{-}4)Y\{P(OMe)_3\}_3]$ (X = H, MeO, Cl, or Me, Y = Cl; X = H, Y = Br or I) there were no phenyl groups in the phosphorus ligands, and here a study was made of ring rotation rates by ^1H n.m.r. spectroscopy. Given the temperature range over which the changes in spectra occurred for these complexes, the most suitable solvent proved to be CD_2Cl_2.

From the data collected in Table 3, it can be seen that variation in the nature of the substituent in the phenyl ligand in complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ had only a relatively small effect on the rate of rotation of the phenyl ligand, although the effect was in the expected direction (increased rate for an electron-releasing substituent, decreased rate for an electron-withdrawing substituent). In the case of the complexes $[Ru(CO)(C_6H_4X\text{-}4)Cl\{P(OMe)_3\}_3]$ the effect was even smaller. More striking was the effect of changing the ligand L′ *trans* to phenyl in the complexes $[Ru(CO)(Ph)Cl(PMe_2Ph)_2L']$, where a change in L′ from CO to $CNCMe_3$ caused a seven-fold decrease in rate and a substantial rise in activation energy. As mentioned above, the crystal structure of $[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$ gave no indication of steric hindrance to rotation, so the effect was evidently electronic in nature, and presumably reflected the increased importance of metal-to-phenyl back donation resulting from the replacement of CO

Table 4. Phosphorus-31 n.m.r. spectra of complexes involved in the conversion of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ into $[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$[a]

Complex	δ/p.p.m.	$\vert{}^2J(\text{P–P})\vert$/Hz	Assignment
$[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$	30.8 (s)		PPh_3
$[\text{Ru(CO)(Ph)Cl(PPh}_3)_2\{\text{P(OMe)}_3\}]$	24.7 (d)	31	PPh_3
	126.5 (t)	31	P(OMe)_3
$[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ Isomer (**A**)[b]	19.2 (dd)	477, 38	PPh_3
	130.0 (dd)	477, 41	P(OMe)_3
	134.2 (dd)	41, 38	P(OMe)_3
$[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ Isomer (**B**)	15.7 (t)	32	PPh_3
	126.7 (d)	32	P(OMe)_3
$[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$[b]	130.1 (m)	43	P(OMe)_3
	137.9 (m)	43	P(OMe)_3

[a] In CDCl_3 solution. Multiplicities are given after the chemical shift values (based on H_3PO_4, used as an external standard). [b] Resonances distorted by second-order effects.



Scheme. (*i*) + P(OMe)_3; (*ii*) − P(OMe)_3; (*iii*) + P(OMe)_3, − PPh_3; (*iv*) − P(OMe)_3, + PPh_3

by the rather less powerful π acceptor CNCMe_3. Phosphorus ligands are even poorer π acceptors than CNCMe_3, and in agreement with this separate resonances for C^2 and C^6 were observed for the complexes $[\text{Ru(CO)(Ph)Cl(PMe}_2\text{Ph)}_3]$ and $[\text{Ru(CO)(Ph)Cl(PMe}_2\text{Ph)}_2\{\text{P(OMe)}_3\}]$ right up to temperatures (*ca.* 390 and 370 K respectively) at which these complexes started to decompose.

Changing the halide ligand Y^- *cis* to phenyl in the complexes $[\text{Ru(CO)(Ph)Y}\{\text{P(OMe)}_3\}_3]$ from Cl^- to Br^- to I^- increased the rate of rotation. One explanation for this would be that the increasing bulk of the halide ligand counteracted the electronic preference for the orientation of the phenyl ligand in the same plane as the halide ligand.

Mechanism of Conversion of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ *into* $[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$.—As mentioned above, treatment of solutions of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ with a variety of phosphorus or arsenic ligands L resulted in the formation of complexes $[\text{Ru(CO)(Ph)ClL}_3]$. The reaction with P(OMe)_3 was studied in detail in CDCl_3 solution, and the intermediates involved (see Scheme) were identified by ^{31}P n.m.r. spectroscopy. The numbers and relative positions of the PPh_3 and P(OMe)_3 ligands present in each complex were clearly revealed by the spectra (see Table 4), because PPh_3 ligands were characterized by resonances in the region δ 15—31, while resonances for the P(OMe)_3 ligands were at δ 126—138, and coupling constants $|{}^2J(\text{P–P})|$ for mutually *cis* ligands were only 31—43 Hz as opposed to 477 Hz for inequivalent mutually *trans* ligands. In every case it was clear from the ^{31}P spectra that the three phosphorus ligands were arranged in a meridional fashion. Although the ^{13}C n.m.r. spectra of the reaction mixtures were too complicated for complete interpretation, the resonances for the carbon atom in the carbonyl ligand and for C^1 in the phenyl ligand were identified for each intermediate except isomer (**B**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ (see Scheme), which was never present in sufficient concentration for this to be possible. In each case the pattern of coupling constants $|{}^2J(\text{P–C})|$ for these carbon atoms indicated that the phenyl ligand was *trans* to a phosphorus ligand while the carbonyl ligand was not. Since i.r. studies showed that the C–O stretching frequencies in isomers (**A**) and (**B**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ were virtually identical (*ca.* 1 959 cm^{-1}), we concluded that the ligand *trans* to CO was the same for both isomers.

Treatment of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ with an equimolar (or greater) quantity of P(OMe)_3 at 243 K in CDCl_3 solution resulted in rapid and virtually quantitative formation of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2\{\text{P(OMe)}_3\}]$ (see Scheme). At 243 K, this species was quite long-lived, but at ambient temperature and in the presence of an excess of P(OMe)_3 it was converted into isomer (**A**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ and thence to $[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$. Isomer (**B**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ was not observed under these circumstances.

When a CDCl_3 solution of $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2\{\text{P(OMe)}_3\}]$ containing *no* free P(OMe)_3 was warmed from 243 K to ambient temperature, some of the starting material $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ was reformed, with the liberated P(OMe)_3 being consumed in the production of isomer (**A**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ and a little of the final product $[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$. More slowly, isomer (**B**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ was also formed, giving a final equilibrium mixture containing every ruthenium species shown in the Scheme, together with some free PPh_3 but (within the limits of sensitivity of the spectrometer) no free P(OMe)_3. When P(OMe)_3 was added to this mixture, two very rapid reactions occurred: the $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2]$ was once again converted into $[\text{Ru(CO)(Ph)Cl(PPh}_3)_2\{\text{P(OMe)}_3\}]$, and isomer (**B**) of $[\text{Ru(CO)(Ph)Cl(PPh}_3)\{\text{P(OMe)}_3\}_2]$ formed the final product, $[\text{Ru(CO)(Ph)Cl}\{\text{P(OMe)}_3\}_3]$. Any remaining P(OMe)_3 then brought about the conversion of

Table 5. Analytical data

Complex	Colour	Found (%)		Calc. (%)	
		C	H	C	H
$[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$	White	52.75	4.90	52.80	5.00
$[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	White	52.10	5.15	52.15	5.10
$[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	White	49.60	4.45	49.65	4.50
$[Ru(CO)_2(C_6H_4NMe_2\text{-}4)Cl(PMe_2Ph)_2]$[a]	White	53.05	5.55	53.00	5.50
$[Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2]$	White	53.55	5.25	53.60	5.20
$[Ru(CO)_2(C_6H_4Me\text{-}3)Cl(PMe_2Ph)_2]$	White	53.55	5.05	53.60	5.20
$[Ru(CO)_2(Ph)Br(PMe_2Ph)_2]$	Cream	48.20	4.55	48.80	4.60
$[Ru(CO)_2(Ph)I(PMe_2Ph)_2]$	Cream	45.55	4.35	45.20	4.25
$[Ru(CO)_2Ph(O_2CMe)(PMe_2Ph)_2]$	White	54.75	5.40	54.85	5.30
$[Ru(CO)(Ph)Cl(PPh_3)_2]$	Orange	67.25	4.60	67.40	4.60
$[Ru(CO)(Ph)Br(PPh_3)_2]$	Orange	63.90	4.15	63.70	4.35
$[Ru(CO)(Ph)I(PPh_3)_2]$	Orange	59.90	3.95	60.20	4.10
$[Ru(CO)_2(Ph)Cl(PPh_3)_2]$	White	66.35	4.55	66.55	4.45
$[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$	White	31.75	5.10	31.30	5.25
$[Ru(CO)(C_6H_4OMe\text{-}4)Cl\{P(OMe)_3\}_3]$	White	31.70	5.25	31.70	5.30
$[Ru(CO)(C_6H_4Cl\text{-}4)Cl\{P(OMe)_3\}_3]$	White	29.75	4.85	29.65	4.80
$[Ru(CO)(C_6H_4Me\text{-}4)Cl\{P(OMe)_3\}_3]$	White	32.50	5.40	32.50	5.45
$[Ru(CO)(Ph)Br\{P(OMe)_3\}_3]$	White	29.25	4.70	29.20	4.90
$[Ru(CO)(Ph)I\{P(OMe)_3\}_3]$	Yellow	27.40	4.55	27.25	4.55
$[Ru(CO)(Ph)Cl(PMe_2Ph)_3]$	White	56.50	5.65	56.75	5.85
$[Ru(CO)(Ph)Cl(PMePh_2)_3]$	White	65.55	5.15	65.60	5.25
$[Ru(CO)(Ph)Cl\{P(OMe)_2Ph\}_3]$	White	49.80	5.20	49.50	5.10
$[Ru(CO)(Ph)Cl(AsMe_2Ph)_3]$	Cream	47.20	5.00	47.25	4.85
$[Ru(CO)(Ph)Cl(PPh_3)(Ph_2PCH_2PPh_2)]$	Cream	67.75	4.70	67.60	4.75
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_3\}]$	White	48.60	5.60	48.65	5.65
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_2Ph\}]$	White	54.00	5.75	54.10	5.60
$[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$[b]	White	55.90	6.10	55.95	6.05

[a] N, 2.25 (calc. 2.40)%. [b] N, 2.45 (calc. 2.35)%.

$[Ru(CO)(Ph)Cl(PPh_3)_2\{P(OMe)_3\}]$ into isomer (**A**) of $[Ru(CO)(Ph)Cl(PPh_3)\{P(OMe)_3\}_2]$ and then into $[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$. If, however, the quantity of $P(OMe)_3$ added was insufficient to bring about complete conversion into $[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$, equilibrium was again established once the supply of $P(OMe)_3$ had run out, with the reappearance of isomer (**B**) of $[Ru(CO)(Ph)Cl(PPh_3)\{P(OMe)_3\}_2]$ and, if relatively little $P(OMe)_3$ had been added, $[Ru(CO)(Ph)Cl(PPh_3)_2]$.

This sequence of events appeared to reflect the *trans*-labilizing and *trans*-directing influences of the phenyl ligand. Thus the initial attack by $P(OMe)_3$ on $[Ru(CO)(Ph)Cl(PPh_3)_2]$ occurred *trans* to the phenyl ligand, but was easily reversed, and labilization of the bond to the PPh_3 ligand in isomer (**B**) of $[Ru(CO)(Ph)Cl(PPh_3)\{P(OMe)_3\}_2]$ made its substitution by $P(OMe)_3$ fast. In the steps in which $[Ru(CO)(Ph)Cl(PPh_3)_2\{P(OMe)_3\}]$ was converted into isomer (**A**) of $[Ru(CO)(Ph)Cl(PPh_3)\{P(OMe)_3\}_2]$ and the latter formed $[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$, the bond to the leaving PPh_3 ligand was rather less labile because it was *trans* to another phosphorus ligand rather than the phenyl ligand: hence these steps occurred rather more slowly. The fact that neither $[Ru(CO)(Ph)Cl(PPh_3)_3]$ nor an isomer of $[Ru(CO)(Ph)Cl(PPh_3)_2\{P(OMe)_3\}]$ with mutually *cis* PPh_3 ligands was observed in the reaction mixtures was presumably a reflection of the bulky nature of PPh_3.

Experimental

Complexes were prepared under an atmosphere of nitrogen, using dry, oxygen-free solvents. Except where indicated otherwise, the boiling point range of light petroleum used in synthetic work was 333—353 K.

Organolithium Reagents.—The compounds $Li(C_6H_4OMe\text{-}4)$, $Li(C_6H_4NMe_2\text{-}4)$, $Li(C_6H_4Me\text{-}4)$, and $Li(C_6H_4Me\text{-}3)$ were prepared from the corresponding bromo-arenes and lithium by the method of Gilman *et al.*,[8] while $Li(C_6H_4Cl\text{-}4)$ was obtained from $BrC_6H_4Cl\text{-}4$ and LiBu.[9]

Organomercury Reagents.—$[HgPh_2]$ was purchased from Koch-Light. For $[Hg(C_6H_4Cl\text{-}4)_2]$ a suspension of $HgCl_2$ (2.7 g) in ethoxyethane (50 cm^3) was added over 0.2 h, with stirring, to an ethoxyethane solution of $Li(C_6H_4Cl\text{-}4)$ (*ca.* 0.025 mol). The solution was stirred and heated under reflux overnight, then allowed to cool and treated with $CHCl_3$ (500 cm^3) and water (250 cm^3). After separation of the two layers, the aqueous layer was extracted with a further 250 cm^3 of $CHCl_3$. The organic extracts were combined and dried over Na_2SO_4. Removal of the solvent under reduced pressure left the solid product, which was washed with ethoxyethane and recrystallized from a mixture of propanone and ethanol (yield 66%). The same technique was used to obtain $[Hg(C_6H_4OMe\text{-}4)_2]$, $[Hg(C_6H_4NMe_2\text{-}4)_2]$, $[Hg(C_6H_4Me\text{-}4)_2]$, and $[Hg(C_6H_4Me\text{-}3)_2]$, in 45—87% yields.

Ruthenium Complexes.—Details of the preparation of $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ from *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $[HgPh_2]$ have been given in a previous paper.[3] The related complexes $[Ru(CO)_2(C_6H_4X)Cl(PMe_2Ph)_2]$ (X = 4-MeO, 4-Cl, 4-Me$_2$N, 4-Me, or 3-Me) were synthesized in the same way, in 60—82% yields.

$[Ru(CO)_2(Ph)Br(PMe_2Ph)_2]$. Sodium bromide (0.2 g) and $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ (0.1 g) were stirred in propanone (25 cm^3) for 16 h. The solvent was then removed under reduced pressure, and the product was extracted from the residue with $CHCl_3$. Crystals were obtained when the solution was concentrated under a stream of nitrogen. These were filtered off and washed with ethanol (yield 80%). The same method was used to obtain $[Ru(CO)_2(Ph)I(PMe_2Ph)_2]$ in similar yield.

$[Ru(CO)_2Ph(O_2CMe)(PMe_2Ph)_2]$. Sodium acetate (0.6 g) and $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ (0.4 g) were stirred in methanol (75 cm^3) for 40 h. The solvent was removed under reduced pressure, and the product extracted into $CHCl_3$. After removal of the $CHCl_3$ under reduced pressure, the complex was recrystallized from a mixture of propanone and ethanol (yield 74%).

$[Ru(CO)(Ph)Cl(PPh_3)_2]$. The method used was based on that described by Roper and Wright[7] for $[Ru(CO)(C_6H_4Me\text{-}4)Cl(PPh_3)_2]$. A suspension of $[Ru(CO)(H)Cl(PPh_3)_3]$ (0.3 g) in a solution of $[HgPh_2]$ (0.11 g) in methylbenzene (50 cm^3) was heated under reflux for 2 h. The hot solution was decanted from metallic mercury and then concentrated by evaporation of some of the solvent under reduced pressure. The orange crystals obtained were washed with propanone and then with light petroleum (yield 80%). The complexes $[Ru(CO)(C_6H_4X\text{-}4)Cl(PPh_3)_2]$ (X = MeO, Cl, or Me) were obtained in similar yields using the appropriate organomercury reagents.

$[Ru(CO)(Ph)Br(PPh_3)_2]$. Sodium bromide (3.0 g) and $[Ru(CO)(Ph)Cl(PPh_3)_2]$ were stirred in propanone (50 cm^3) for 100 h. The solvent was removed under reduced pressure and the product was extracted from the residue with CH_2Cl_2. Removal of the CH_2Cl_2 under reduced pressure yielded orange crystals, which were washed with propanone and then with light petroleum (yield 78%). The same technique was used to obtain $[Ru(CO)(Ph)I(PPh_3)_2]$ in 58% yield.

$[Ru(CO)(Ph)Cl\{P(OMe)_3\}_3]$. A suspension of $[Ru(CO)(Ph)Cl(PPh_3)_2]$ (0.12 g) in light petroleum (60 cm^3) was heated under reflux with $P(OMe)_3$ (0.07 cm^3) for 16 h. The hot solution was filtered and then reduced in volume under a stream of nitrogen. The crystals formed were filtered off and washed with light petroleum (yield 65%). The complexes $[Ru(CO)(Ph)Y\{P(OMe)_3\}_3]$ (Y = Br or I) were obtained in similar yield from $[Ru(CO)(Ph)Y(PPh_3)_2]$. The same method was also used to prepare the complexes $[Ru(CO)(Ph)ClL_3]$ [L = PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$, or $AsMe_2Ph$], except that the $P(OMe)_2Ph$ and $AsMe_2Ph$ complexes were initially obtained as oils which had to be crystallized from light petroleum: yields were 72, 70, 83, and 32% respectively.

$[Ru(CO)(C_6H_4Me\text{-}4)Cl\{P(OMe)_3\}_3]$. A suspension of $[Ru(CO)(C_6H_4Me\text{-}4)Cl(PPh_3)_2]$ (0.2 g) in $CHCl_3$ (3 cm^3) was treated with $P(OMe)_3$ (0.13 g), giving a yellow solution. After 16 h the solution was transferred to an alumina column and eluted with mixtures of light petroleum and $CHCl_3$. The fraction containing the product was identified by i.r. spectroscopy, and after removal of the solvent the residue was recrystallized from a mixture of light petroleum and $CHCl_3$ (yield 58%). The complexes $[Ru(CO)(C_6H_4X\text{-}4)Cl\{P(OMe)_3\}_3]$ (X = OMe or Cl) were obtained in similar yield by this technique.

$[Ru(CO)_2(Ph)Cl(PPh_3)_2]$. Carbon monoxide was passed through a suspension of $[Ru(CO)(Ph)Cl(PPh_3)_2]$ (0.1 g) in benzene (10 cm^3) for 0.5 h. Removal of solvent from the resulting solution under reduced pressure left a white solid, which was washed with light petroleum (yield 67%).

$[Ru(CO)(Ph)Cl(PPh_3)(Ph_2PCH_2PPh_2)]$. A mixture of $[Ru(CO)(Ph)Cl(PPh_3)_2]$ (0.5 g) and $Ph_2PCH_2PPh_2$ (0.25 g) in light petroleum (60 cm^3) was heated under reflux with stirring for 16 h. After cooling, the product was filtered off and washed with light petroleum (yield 83%).

$[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_3\}]$. Nitrogen was passed through a refluxing solution of $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ (0.1 g) and $P(OMe)_3$ (0.03 g) in light petroleum (b.p. 393—433 K, 50 cm^3). After 1 h, the solution was cooled and concentrated by evaporation of some of the solvent under reduced pressure. The crystals formed were filtered off and washed with light petroleum (yield 60%). The complex $[Ru(CO)(Ph)Cl(PMe_2Ph)_2\{P(OMe)_2Ph\}]$ was obtained in similar yield by this method.

$[Ru(CO)(Ph)Cl(PMe_2Ph)_2(CNCMe_3)]$. A solution of $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$ (0.13 g) and $CNCMe_3$ (0.033 cm^3) in $CHCl_3$ (30 cm^3) was heated at 333 K with N_2 passing through the solution. After 3 h the solution was cooled and the solvent removed under reduced pressure. The residue was recrystallized from a mixture of propanone and ethanol (yield 79%).

Spectroscopic Studies.—Details of the instruments used to obtain i.r., ^1H and ^{13}C n.m.r. spectra have been given elsewhere.[1] ^{31}P N.m.r. spectra were recorded on a JEOL FX-90Q spectrometer with an operating frequency (for ^{31}P) of 36.2 MHz. Rate constants k for ring rotation were obtained by matching observed spectra with those simulated using the computer program NMRSIM.[10] Activation energies and rates at common temperatures were obtained by least-mean-squares treatment of data for ln k and $1/T$.

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References

1 D. R. Saunders, M. Stephenson, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1983, 2473.
2 D. R. Saunders, M. Stephenson, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1984, 539.
3 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 961.
4 J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1787.
5 D. F. Gill, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 311.
6 Z. Dauter, R. J. Mawby, C. D. Reynolds, and D. R. Saunders, *Acta Crystallogr., Sect. C*, 1983, **39**, 1194.
7 W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1977, **142**, C1.
8 H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, 1932, **54**, 1957.
9 H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, 1940, **62**, 2327.
10 M. F. Chiu, personal communication.

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