Preparation, Mechanism of Formation, Structure, and Reactions of η-Allyl Complexes of Ruthenium(II)

By **Christopher F. J. Barnard, J. Anthony Daniels, Philip R. Holland,** and **Roger J. Mawby,*** Department of Chemistry, The University of York, York YO1 5DD

Reaction of either of two isomers of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ or either of two isomers of $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ with $SnBu_3(C_3H_5)$ yields a single isomer of $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$. A mechanism involving the intermediate formation of the five-co-ordinate species $[Ru(CO)Cl_2(PMe_2Ph)_2]$ and $[Ru(CO)Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$ is proposed for the reactions. Treatment of complexes $[\{Ru(CO)_2Cl_2L\}_2]$ (L = phosphorus or arsenic ligand) with $SnBu_3(C_3H_5)$ yields the related complexes $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)L]$, and the method can be extended to the preparation of 1-methylallyl and 2-methylallyl complexes. Simulation of the complex ^1H n.m.r. spectra of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ and its $AsMe_2Ph$ analogue provides detailed information about the coupling between the protons in the allyl ligand. Treatment of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ with excess of PMe_2Ph results in the formation of $[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$, which is very slowly converted in solution into $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$: the key intermediate in the system appears to be $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$.

In a recent paper[1] we described how the reactions of two isomers of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with HgR_2 (R = Me or Ph) or $SnMe_4$ yielded methyl and phenyl complexes $[Ru(CO)_2ClR(PMe_2Ph)_2]$. Since Abel and Moorhouse[2] had reported that the compounds $SnMe_3(C_3H_5)$ and $SnBu_3(C_3H_5)$ could be used to convert halogeno-complexes into η-allyl complexes, we decided to determine whether $SnBu_3(C_3H_5)$ and its analogue $SnBu_3(2\text{-}MeC_3H_4)$ could be used to convert the isomers of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ into η-allyl complexes of ruthenium(II). Subsequent reports[3,4] that $[Ru(CO)_3Cl(\eta\text{-}C_3H_5)]$ is a catalyst for the hydrogenation and isomerization of alkenes prompted us to prepare and investigate the properties of a wider range of η-allyl complexes of ruthenium(II). This paper describes the preparation of these complexes, a study of their n.m.r. spectra and structure, and an intriguing reaction sequence relating to the use of η-allyl transition-metal complexes as catalysts for the carbonylation of 3-halogenopropenes.

RESULTS AND DISCUSSION

Details of the i.r. and ^1H n.m.r. spectra of all η-allyl complexes mentioned in the paper are collected in Table 1. The ^{13}C n.m.r. spectra of selected complexes were recorded: details of these are given in Table 2. All numbered structures are shown in Scheme 1 or Scheme 2.

(1) *Preparation and Mechanism of Formation of Complexes.*—Treatment of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ [(1), where L = PMe_2Ph] with $SnBu_3(C_3H_5)$ in propanone solution at 313 K resulted in the slow formation of a

TABLE 1

Infrared [a] and ^1H n.m.r. [b] spectra of η-allyl complexes of ruthenium(II)

Complex	ν(C–O)/ cm^{-1}	δ(L)/ [c] p.p.m.	δ(allyl)/p.p.m.[d] H_c	H_s	H_a	Me
$[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$	1 940	1.59	4.78	3.07	2.50	
		1.58				
$[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$	1 935	1.62		2.96	2.53	1.82
		1.59				
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$	2 050	1.86	4.83	t3.61	t3.05	
	1 979	1.78		c3.36	c2.41	
$[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$	2 048	1.86		t3.72	t3.15	1.77
	1 975	1.78		c3.32	c2.48	
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMePh_2)]$	2 051	2.11	4.88	t3.81	t3.08	
	1 980			c3.47	c2.57	
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PPh_3)]$	2 050		4.95	t3.82	t3.11	
	1 980			c3.63	c2.74	
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsMe_2Ph)]$	2 047	1.70	4.86	t3.81	t3.00	
	1 977	1.63		c3.59	c2.53	
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsPh_3)]$	2 048		4.92	t3.80	t3.02	
	1 979			c3.80	c2.81	
$[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$ [e]	2 047	2.10	4.82	c3.25	t4.13	1.81
	1 975				c2.30	
$[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$ [f]	2 047	2.12	4.70	t3.66	t2.89	1.43
	1 975				c3.42	
$[Ru(CO)_2I(\eta\text{-}C_3H_5)(PMe_2Ph)]$	2 045	2.30	4.77	t3.67	t3.49	
	1 980	2.20		c3.40	c3.02	

[a] In $CHCl_3$ solution. Only bands in the C–O stretching region are listed. [b] In PhCl solution. Relative areas were in agreement with the assignment given. [c] Resonances due to methyl protons only. For phosphorus ligands the resonances were doublets with $|^2J(P\text{–}H)|$ *ca.* 10 Hz. For arsenic ligands the resonances were singlets. [d] Resonances for central (H_c), *syn* (H_s), and *anti* (H_a) protons were usually complex multiplets: some coupling constant data are given in the text and in Table 3. Resonances prefixed by t and c are respectively for protons *trans* and *cis* to the phosphorus or arsenic ligand. [e] Methyl group on carbon atom *trans* to $PMePh_2$. [f] Methyl group on carbon atom *cis* to $PMePh_2$.

TABLE 2

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

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
$[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$	202.3 (t)	CO	14.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	101.6 (s)	C_c		
	55.6 (dd)	C_e	26.3	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
			3.0	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	18.7 (d)	PMe_2Ph	31.0	$\lvert {}^1J(P\text{–}C)\rvert$
	15.6 (d)	PMe_2Ph	30.0	$\lvert {}^1J(P\text{–}C)\rvert$
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$	196.3 (d)	CO [b]	3.6	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	195.7 (d)	CO [c]	11.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	106.2 (s)	C_c		
	58.6 (d)	C_e	2.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	58.5 (d)	C_e	21.5	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
	17.3 (d)	PMe_2Ph	33.0	$\lvert {}^1J(P\text{–}C)\rvert$
	16.8 (d)	PMe_2Ph	33.0	$\lvert {}^1J(P\text{–}C)\rvert$
$[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$	197.7 (d)	CO [c]	13.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	196.9 (d)	CO [b]	4.0	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	125 7 (s)	C_c		
	60.2 (d)	C_e	2.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	58.6 (d)	C_e	23.3	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
	26.5 (s)	$2\text{-}MeC_3H_4$		
	17.3 (d)	PMe_2Ph	33.0	$\lvert {}^1J(P\text{–}C)\rvert$
	16.8 (d)	PMe_2Ph	33.0	$\lvert {}^1J(P\text{–}C)\rvert$
$[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$ [d]	196.4 (d)	CO [b]	2.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	196.1 (d)	CO [c]	11.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	107.1 (s)	C_c		
	78.9 (d)	C_e	22.5	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
	55.8 (s)	C_e		
	20.6 (d)	$1\text{-}MeC_3H_4$	2.4	$\lvert trans\text{-}^3J(P\text{–}C)\rvert$
	17.2 (d)	$PMePh_2$	31.0	$\lvert {}^1J(P\text{–}C)\rvert$
$[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$ [e]	264.2 (dt)	$COCH_2CH{=}CH_2$	84.0	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
			12.5	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	201.0 (dt)	CO	14.0	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
			9.0	$\lvert cis\text{-}^2J(P\text{–}C)\rvert$
	137.2 (s)	$COCH_2CH{=}CH_2$		
	114.2 (s)	$COCH_2CH{=}CH_2$		
	60.4 (d)	$COCH_2CH{=}CH_2$	23.0	$\lvert trans\text{-}^2J(P\text{–}C)\rvert$
	17.8 (t)	PMe_2Ph	29.2	$\lvert {}^1J(P\text{–}C) + {}^3J(P\text{–}C)\rvert$
	14.9 (d)	PMe_2Ph	18.3	$\lvert {}^1J(P\text{–}C)\rvert$
	13.4 (t)	PMe_2Ph	29.2	$\lvert {}^1J(P\text{–}C) + {}^3J(P\text{–}C)\rvert$

[a] In $CDCl_3$ solution except where otherwise stated. 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, dd = doublet of doublets, dt = doublet of triplets. The central allyl carbon atom is labelled C_c, and those at the ends C_e. [b] This ligand is *trans* to one end of the allyl ligand. [c] This ligand is *trans* to chloride. [d] Methyl group on carbon atom *trans* to $PMePh_2$. [e] In C_6D_5Cl solution at 268 K.

complex of formula $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$. The same complex was obtained in low yield from all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ [(2), where L = PMe_2Ph] and $SnBu_3(C_3H_5)$, but the major product was an unreactive isomer (the *cis* isomer) of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$. When $SnBu_3(2\text{-}MeC_3H_4)$ was used in place of $SnBu_3(C_3H_5)$, even the reaction of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ was complicated by the formation of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ as well as the desired $[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$.

Earlier work [5] had shown that both *trans*- and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ slowly rearranged to the *cis* isomer in solution, so that use of either compound in any reaction inevitably ran the risk of contamination of the product by *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$. In addition, the reactions to form $[Ru(CO)Cl(\eta\text{-}C_3H_4R')(PMe_2Ph)_2]$ (R' = H or 2-Me) involved the displacement of a carbonyl ligand, and earlier kinetic studies [1] had shown that the presence of free CO in solution drastically inhibited the related reactions of both *trans*- and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ to form $[Ru(CO)_2ClR(PMe_2Ph)_2]$ (R = Me or Ph). It seemed likely that the liberated CO might have a similar inhibiting effect on the reactions with $SnBu_3(C_3H_4R')$. To avoid both of these problems, we tried the dimeric complexes $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ [isomers (3) and (4), where L = PMe_2Ph] as alternative starting materials. Both reacted more rapidly than either isomer of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$: in each case the product was again $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ and it was obtained uncontaminated by ruthenium-containing by-products.

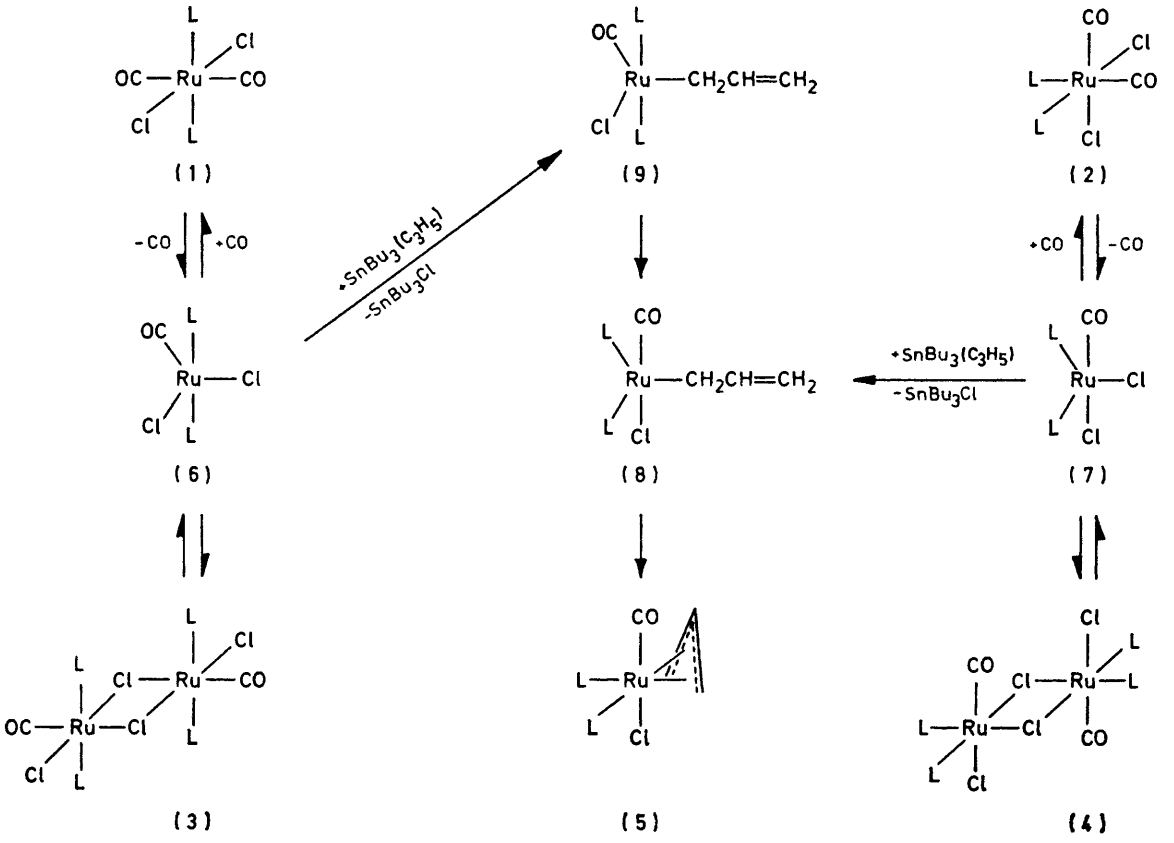
The i.r. and n.m.r. spectra of all the samples of $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ were identical. The appearance of the resonances for the methyl protons and carbon atoms * and for the carbonyl carbon atom established that the complex must possess structure (5) (L = PMe_2Ph) or an equivalent structure with the allyl ligand rotated through 180° about an axis through the metal and the centre of the ligand. By analogy with the structure of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ (see below), it seems likely that (5) is the correct structure. Similarities between the i.r. and ^1H n.m.r. spectra of this complex and those of $[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$ leave little doubt that the latter complex also posesses structure (5).

As was shown [1] to be the case for the reactions of

* The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and his co-workers.[6,7]

trans- and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with HgR_2 (R = Me or Ph), it seems probable that the first step in the corresponding reactions with $SnBu_3(C_3H_5)$ (see Scheme 1, where L = PMe_2Ph) involves the dissociation of a carbonyl ligand to yield intermediates (6) and (7) respectively (the stereochemistry of these five-co-ordinate species has been discussed previously [5,8]). The same intermediates can be formed from the dimeric complexes (3) and (4) by cleavage of the halogen bridges. The stereochemistry of the subsequent reaction of (7) is straightforward: we have visualized the reaction with ordinate σ-allyl complex (9), since five-co-ordinate complexes commonly undergo extremely rapid re-arrangement. We were, however, unable to obtain any direct spectroscopic evidence for the presence of such intermediates in the reaction mixtures.

In an extension of this preparative route to η-allyl complexes of ruthenium(II), we found that the dimeric complexes $[\{Ru(CO)_2Cl_2L\}_2]$ (L = PMe_2Ph, $PMePh_2$, PPh_3, $AsMe_2Ph$, or $AsPh_3$) also reacted with $SnBu_3(C_3H_5)$, yielding $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)L]$. The same method was used to prepare $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)$-



SCHEME 1

$SnBu_3(C_3H_5)$ as proceeding *via* the σ-allyl species (8) to the observed product (5). In contrast, the route from (6) to (5) involves a ligand rearrangement. Since (3) and (4) do not interconvert under the reaction conditions used, it seems that rearrangement must occur after the exchange of chloride and allyl ligands and not before [*i.e.* (9) ⟶ (8) rather than (6) ⟶ (7)].

Abel and Moorhouse [2] also stressed that a ligand must be lost from the co-ordination sphere of the metal to allow interaction with $SnBu_3(C_3H_5)$ to occur, but they implied that the η-allyl product was formed directly rather than by way of a σ-allyl species. Direct formation of an η-allyl complex from (6) would be expected to yield a different isomer of $[Ru(CO)Cl(\eta\text{-}C_3H_5)L_2]$, and our failure to observe such a compound leads us to favour the intermediate formation of the five-co-

$(PMe_2Ph)]$ and $[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$ from the appropriate ruthenium complexes and organo-tin reagents. An iodo-complex, $[Ru(CO)_2I(\eta\text{-}C_3H_5)(PMe_2$-Ph)], was obtained from its chloro-analogue by reaction with NaI in $CHCl_3$ solution.

The close similarity between the i.r. spectra of the complexes $[Ru(CO)_2X(\eta\text{-}C_3H_4R')L]$ suggested that all possessed the same ligand arrangement. From the i.r. and (where run) ^{13}C n.m.r. spectra it was apparent that the two carbonyl ligands were mutually *cis* and in-equivalent, and the values of $^2J(P\text{–}C)$ were much too small to be compatible with the placing of either carbonyl ligand *trans* to L.[9] Thus it was clear that the complexes possessed structure (10) or an equivalent structure with the allyl ligand rotated through 180°. The complex $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ was shown [10]

by *X*-ray crystallography to possess structure (10) in the solid state, the key factor in the choice of this orientation for the allyl ligand being apparently the positioning of the central carbon atom. Rotation of the allyl ligand through 180° would result in the central carbon atom being forced away from the metal by the rather bulky halogen atom, thereby weakening the bonding to ruthenium.

(2) *N.M.R. Spectra of the Allyl Ligands.*—The ^{1}H n.m.r. spectrum of the complex $[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$ included a singlet resonance for the methyl substituent in the 2-methylallyl ligand and resonances centred at δ 2.53 and 2.96 for the *anti* and *syn* protons respectively. The assignment of the resonance at higher field to the *anti* protons is in accordance with similar assignments for other η-allyl complexes.[11] The *anti* proton resonance showed a doublet splitting of 5.5 Hz, assumed to be due to coupling to the phosphorus nucleus *trans* to the carbon atom bearing the proton concerned, but the coupling constant to the *cis* phosphorus nucleus was too small to produce a clear splitting. The resonance for the *syn* protons was poorly resolved, but there was evidence of weak coupling to both phosphorus nuclei. The pattern of resonances for the *anti* and *syn* protons in $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ was exactly the same, except that both resonances exhibited a further doublet splitting [$^3J(H_a\text{–}H_c) = 12.5$ Hz, $^3J(H_s\text{–}H_c) = 8.0$ Hz] due to coupling to the central allyl proton.

The lack of symmetry in the complexes $[Ru(CO)_2X(\eta\text{-}C_3H_4R')L]$ made the ^{1}H n.m.r. spectra of the allyl ligands too complicated for detailed interpretation by inspection. The spectrum of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ was simulated using a variety of values for proton–proton and proton–phosphorus coupling constants, and eventually an excellent match between actual and simulated spectra was achieved. The final values for the coupling constants, listed in Table 3,

TABLE 3

Coupling constants for allyl protons in complexes $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)L]$ *

	cis-H_s	*trans*-H_a	*cis*-H_a	H_c	P
trans-H_s	−2.1	−0.5	−0.9	8.2	4.3
	−1.9	−0.6	−0.7	7.7	
cis-H_s		−0.9	−0.7	7.9	3.3
		−0.6	−0.5	8.0	
trans-H_a			−1.2	13.2	−5.6
			−0.9	12.8	
cis-H_a				13.1	0.4
				13.2	
H_c					0.6

* Values were obtained from computer simulations and are quoted in Hz. They are accurate to, at worst, ±0.2 Hz. In each case the first value listed is for $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ and the second for $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsMe_2Ph)]$.

provide an unusually detailed picture of coupling within the framework of an η-allyl ligand. Apart from the characteristically strong coupling between the central proton and all four *syn* and *anti* protons, it is interesting to note the significant coupling between the two *syn* protons, which is roughly twice as large as that between the *anti* protons. Parallels with the simpler spectrum of $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ are evident: just as each *anti* proton in $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ is strongly coupled to one phosphorus nucleus and only very weakly to the other, so one *anti* proton in $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ (presumably the one *trans* to PMe_2Ph) shows strong coupling to phosphorus whereas for the other *anti* proton the coupling is very weak. Furthermore, the *syn* protons in $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ show signs of a small but significant coupling to both phosphorus nuclei, and in the same way both *syn* protons in $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ are coupled to phosphorus to a similar, relatively small extent.

A simulation was also carried out for $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsMe_2Ph)]$, and led (see Table 3) to very similar values for the proton–proton coupling constants within the allyl ligand to those for $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$. The coupling constant data for $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ were also used to simulate spectra for the remaining complexes $[Ru(CO)_2X(\eta\text{-}C_3H_5)L]$, and these were found to match the actual spectra very satisfactorily. Finally, comparison of the spectrum of $[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$ with those of the other complexes established that this complex is formed as a mixture of two isomers, each with the methyl substituent in a *syn* position. Whereas the protons in the methyl substituent in the 2-methylallyl complexes studied exhibited no measurable coupling to phosphorus, those in the methyl substituent in both isomers of the 1-methylallyl complex were coupled to phosphorus: in one case (methyl substituent *trans* to phosphorus) the coupling constant was 4.5 Hz and in the other (*cis* to phosphorus) 3.5 Hz.

One feature of the spectra is the marked variation in the chemical-shift separation between the two *anti* protons (a similar but smaller effect is noticeable for the *syn* protons). For the complexes $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)L]$, the magnitude of the separation varies with L in the order $L = PMe_2Ph > PMePh_2 > AsMe_2Ph > PPh_3 > AsPh_3 > CO$, and may well reflect the difference in σ-donor and/or π-acceptor ability of the ligands L and CO, which are *trans* to the two ends of the allyl ligand.

The ^{13}C n.m.r. spectra of the allyl ligands were comparatively straightforward. In no case did the resonance for the central carbon atom show significant splitting by phosphorus, and the same was true for the methyl carbon atom in $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$. The end carbon atoms were normally coupled to phosphorus nuclei both *trans* and *cis* to them: the coupling constants were either *ca.* 20 Hz (presumably for the *trans* orientation) or *ca.* 2 Hz (*cis* orientation). In the ^{13}C spectrum of $[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMe_2Ph)]$, only the resonances of the more abundant isomer (methyl substituent *trans* to PMe_2Ph) were strong enough to be identified with certainty: the methyl carbon atom, unlike that in $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$, was significantly coupled to phosphorus.

(3) *Reactions of the Complexes.*—In their reports [3,4] of the catalytic activity of the complex $[Ru(CO)_3Cl(\eta\text{-}C_3H_5)]$, Sbrana and Braca stressed the importance of the

ease of conversion of the η-allyl complex into a σ-allyl species as a prerequisite for further reaction. We were therefore interested to determine whether the η-allyl complexes described in this paper would undergo such a conversion. Reversible rearrangement of an η-allyl complex to a σ-allyl species can lead to interchange of the positions of *syn* and *anti* protons and hence to a change in the ^{1}H n.m.r. spectrum of the complex when the rate of rearrangement becomes fast on the n.m.r. time scale.[12] The ^{1}H n.m.r. spectra of the complexes $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$, $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$, and $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$ in PhCl solution were recorded at temperatures up to 373 K without obtaining any evidence for η–σ interconversion: apart from slight decomposition, no changes in spectra were detected.

Conversion into σ-allyl species can be promoted by addition to the solution of a ligand to occupy the vacated co-ordination site.[12] In the hope of converting the more PMe_2Ph to form the acyl complex $[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$. The reaction is reminiscent of that of $[Ru(CO)_2ClMe(PMe_2Ph)_2]$ with PMe_2Ph to form $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$.[9]

The experiment was repeated in PhCl solution and monitored by ^{1}H n.m.r. spectroscopy. At 263 K, the spectrum of the product (see Table 4) indicated the presence of three PMe_2Ph ligands in a *mer* configuration and showed that the bonds to the mutually *trans* pair of PMe_2Ph ligands did not lie in a plane of symmetry. At this temperature a separate doublet resonance could be seen for the methyl protons in the residual free PMe_2Ph in the solution, but as the solution was warmed to 313 K the resonance for the unique PMe_2Ph ligand in the complex and that for the free PMe_2Ph broadened and then coalesced, indicating that the two were in rapid exchange with one another. This extreme lability is characteristic of the bonds to ligands positioned *trans*

TABLE 4

Hydrogen-1 n.m.r. spectra of complexes $[Ru(CO)Cl(COC_3H_4R')(PMe_2Ph)_3]$ [a]

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
$[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$	6.11 (c)	$COCH_2CH{=}CH_2$		
	4.92 (d) [b]	$COCH_2CH{=}CH_2$	11.0	$\lvert^3J(H\text{–}H)\rvert$
	4.87 (d) [b]	$COCH_2CH{=}CH_2$	18.0	$\lvert^3J(H\text{–}H)\rvert$
	3.93 (d)	$COCH_2CH{=}CH_2$	7.0	$\lvert^3J(H\text{–}H)\rvert$
	1.60 (t)	PMe_2Ph	7.0	$\lvert^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
	1.48 (t)	PMe_2Ph	7.0	$\lvert^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
	0.93 (d)	PMe_2Ph	6.5	$\lvert^2J(P\text{–}H)\rvert$
$[Ru(CO)Cl(COC_4H_7)(PMe_2Ph)_3]$	4.80 (s) [b]	$COCH_2CMe{=}CH_2$		
	4.63 (s) [b]	$COCH_2CMe{=}CH_2$		
	3.98 (s)	$COCH_2CMe{=}CH_2$		
	1.80 (s)	$COCH_2CMe{=}CH_2$		
	1.63 (t)	PMe_2Ph	7.0	$\lvert^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
	1.52 (t)	PMe_2Ph	7.0	$\lvert^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$
	0.93 (d)	PMe_2Ph	6.5	$\lvert^2J(P\text{–}H)\rvert$

[a] In PhCl solution at 263 K. Relative areas were in agreement with the assignment given. Resonances due to phenyl protons are not included. Multiplicities are indicated in parentheses after the chemical shift values: s = singlet, d = doublet, t = triplet, c = complex. [b] With added fine structure due to coupling between geminal protons.

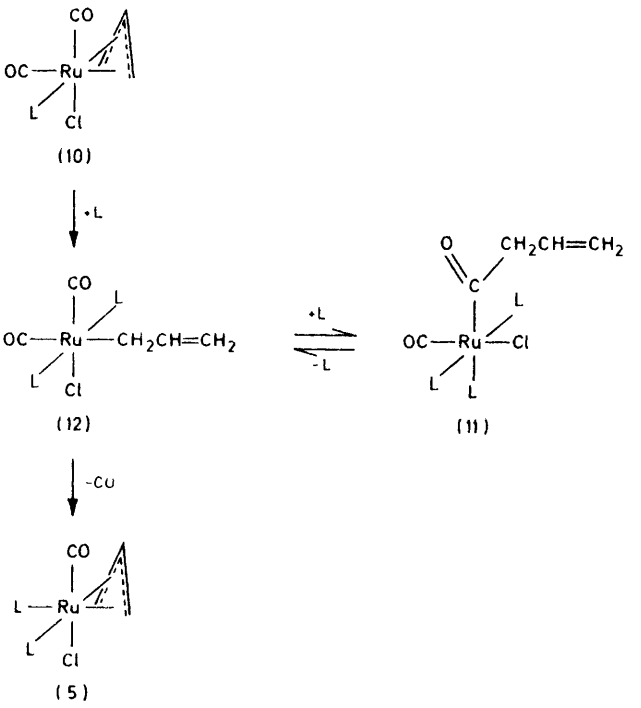
complex into $[Ru(CO)Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_3]$, we treated $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ with PMe_2Ph, but even after 20 h at 353 K no reaction had occurred. Similarly no reaction occurred when $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PPh_3)]$ was treated with PPh_3 or $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsPh_3)]$ with $AsPh_3$. A reaction did take place, however, between equimolar quantities of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ and PMe_2Ph. The final product of the reaction was the carbonyl substitution product $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$, but an i.r. study of the reaction in $CHCl_3$ at 293 K indicated the initial formation of a compound with two C–O stretching bands of similar intensity at 2 061 and 1 994 cm^{-1}, presumably $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$; this was then slowly converted into $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$. A small quantity of the intermediate was isolated, but analytical data showed that it was somewhat impure.

The reaction was repeated using an excess of PMe_2Ph, with quite different results. New C–O stretching bands appeared at 1 940 and 1 580 cm^{-1}, the latter being characteristic of an acyl group co-ordinated to a transition metal. It appeared, therefore, that the first-formed $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$ had reacted with to acyl groups in ruthenium(II) complexes.[9] The spectrum recorded at 263 K also contained the expected set of resonances for the grouping $-CH_2CH{=}CH_2$, but the fact that this group was not directly attached to the metal was shown by the absence of coupling between the protons on the saturated carbon atom and phosphorus: for comparison, the protons in the methyl ligand in $[Ru(CO)ClMe(PMe_2Ph)_3]$ are noticeably coupled to all the phosphorus nuclei, whereas those in the acetyl ligand in $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$ exhibit a singlet resonance.[9] Thus the structure of the complex must be (11), where L = PMe_2Ph, the ligand arrangement being the same as that for $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$.

Like the acetyl complex, $[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$ could not be isolated in a pure state, no doubt because of the extreme ease of dissociation of the PMe_2Ph ligand *trans* to the acyl group. Nevertheless in solution, and in the presence of free PMe_2Ph, it was long-lived, and a ^{13}C n.m.r. spectrum of the complex in C_6D_5Cl solution was obtained at 268 K. The close similarity in coupling constants to phosphorus between the carbon atoms in the carbonyl and acyl ligands in $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$ [9] and the corresponding carbon atoms in

$[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$ was further evidence of the similarity in structure.

Even in the presence of free PMe_2Ph, the complex $[Ru(CO)Cl(COC_3H_5)(PMe_2Ph)_3]$ was very slowly converted into $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$, but the rate of conversion decreased with increasing PMe_2Ph concentration. Thus the overall reaction mechanism appears to be that shown in Scheme 2 (L = PMe_2Ph),



SCHEME 2

in which a very rapid equilibrium between the σ-allyl species (12) and the acyl complex (11) is heavily in favour of the latter when an excess of PMe_2Ph is present in the solution. The structure suggested for $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$, (12), is chosen by analogy with that [1] of $[Ru(CO)_2ClMe(PMe_2Ph)_2]$: unfortunately the inevitable presence of one or more of the other species in Scheme 2 in any solution containing $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$ made it impossible to obtain n.m.r. spectra clear enough to confirm the correctness of the structure.

A similar pattern was established for the reaction between $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$ and PMe_2Ph: details of the ^1H n.m.r. spectrum of the intermediate $[Ru(CO)Cl(COC_4H_7)(PMe_2Ph)_3]$ are given in Table 4. The reaction between $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsMe_2Ph)]$ and $AsMe_2Ph$ appeared to proceed by the same route, but the species $[Ru(CO)Cl(COC_3H_5)(AsMe_2Ph)_3]$ was much more short-lived: presumably the greater crowding in the complex and the weaker bonding to the unique $AsMe_2Ph$ ligand tend to disfavour this complex in the equilibrium with $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(AsMe_2Ph)_2]$.

These reactions demonstrate the point made by Sbrana and Braca about the ease of conversion of η-allyl ruthenium complexes into σ-allyl species. There is, however, a closer link with the mechanism which has been proposed [13] for the carbonylation of 3-chloropropene in the presence of $[\{PdCl(\eta\text{-}C_3H_5)\}_2]$. In a sequence similar to that demonstrated for these ruthenium(II) complexes, the proposed mechanism envisages the conversion of the palladium catalyst into a σ-allyl carbonyl complex which then rearranges to give the grouping $Pd(COC_3H_5)$. Finally reductive elimination of acyl and halide ligands to yield the product C_3H_5COCl is followed by oxidative addition of 3-chloropropene to restart the cycle.

It is somewhat surprising that $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$, unlike $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$, would not rearrange to give a σ-allyl complex. If, in common with other reactions of octahedral ruthenium(II) complexes,[1,5,9] the rate-determining step involved the formation of a five-co-ordinate intermediate {here $[Ru(CO)Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$} rather than direct attack on the η-allyl complex by PMe_2Ph, one would have expected the greater crowding in $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ actually to favour the reaction. Overcrowding in the expected product, $[Ru(CO)Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_3]$, cannot be blamed since the related complexes $[Ru(CO)ClR(PMe_2Ph)_3]$ (R = Me or Ph) are stable. One explanation for the difference in behaviour between $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ and $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ could be that the increase in electron density on the metal caused by replacement of a carbonyl ligand by PMe_2Ph results in a stronger interaction between metal and η-allyl ligand, but we note that Kettle and Mason [14] have claimed that calculations show that there is only minimal back-donation of electron density to the allyl ligand in complexes of this type.

EXPERIMENTAL

Preparation of Complexes.—All preparative work was carried out under an atmosphere of dry nitrogen. Except where stated otherwise, the boiling range of the light petroleum used was 313—333 K. Analytical data for the η-allyl complexes are given in Table 5. Details of the preparation of *trans*- and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and isomer (4) of $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ have been given in an earlier paper.[5]

$[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$, *isomer* (3). Nitrogen was passed through a solution of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.10 g) in refluxing methanol (50 cm^3) for 2 h. After removal of the solvent under reduced pressure, the residue was recrystallized from a mixture of propanone and light petroleum (b.p. 353—373 K) (yield 80%).

$[\{Ru(CO)_2Cl_2(PMe_2Ph)\}_2]$. Carbon monoxide was passed through a solution of $RuCl_3{\cdot}3H_2O$ (2.82 g) in refluxing $MeOCH_2CH_2OH$ (50 cm^3) for 24 h. After 5 h, PMe_2Ph (1.47 g) was added. After the remaining 19 h the solution was cooled. The product, precipitated as a pale yellow powder, was washed with propanone (yield 30%).

$[\{Ru(CO)_2Cl_2(PPh_3)\}_2]$. This was prepared by the method described by Johnson *et al.*,[15] which involves conversion of $[Ru_3(CO)_{12}]$ into $[Ru_3(CO)_9(PPh_3)_3]$, followed by oxidation with Cl_2. The same route was used to obtain the complexes

TABLE 5

Analytical data for η-allyl complexes of ruthenium(II)

Complex	Colour	M.p. (T/K)	Analysis (%) Found C	Found H	Calc. C	Calc. H
$[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$	White	375—377	50.05	5.85	49.85	5.65
$[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$	White	374—379	50.6	5.9	50.85	5.9
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$	White	373—375	41.65	4.55	42.0	4.35
$[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$	White	341—344	43.8	5.05	43.6	4.7
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMePh_2)]$	White	384—387	49.85	4.25	49.85	4.2
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PPh_3)]$	Cream	415—416	56.15	4.35	55.7	4.05
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsMe_2Ph)]$	White	338—339	37.3	3.65	37.55	3.9
$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(AsPh_3)]$	Cream	405—407	51.75	4.0	51.15	3.75
$[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$	White	383—384	50.95	4.6	50.95	4.5
$[Ru(CO)_2I(\eta\text{-}C_3H_5)(PMe_2Ph)]$	Red	367—370	33.45	3.4	33.7	3.5

$[\{Ru(CO)_2Cl_2L\}_2]$ (L = $PMePh_2$, $AsMe_2Ph$, or $AsPh_3$). Yields were *ca.* 75%.

$[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$. Of the four methods described in the text, the best was to stir a solution of isomer (4) of $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ (0.20 g) and $SnBu_3(C_3H_5)$ (0.20 g) in $CHCl_3$ (50 cm^3) at 313 K for 2 h. After removal of the solvent under reduced pressure the residue was purified by chromatography on alumina, using $CHCl_3$ as eluant. An oil was obtained, which was crystallized from light petroleum (yield 50%). The complex $[Ru(CO)Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]$ was obtained in similar yield by using $SnBu_3(2\text{-}MeC_3H_4)$ in place of $SnBu_3(C_3H_5)$.

$[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$. A suspension of $[\{Ru(CO)_2Cl_2(PMe_2Ph)\}_2]$ (0.20 g) in propanone (25 cm^3) was stirred at 313 K for 0.5 h with $SnBu_3(C_3H_5)$ (0.20 g). The product was purified in the manner described for $[Ru(CO)Cl(\eta\text{-}C_3H_5)(PMe_2Ph)_2]$ (yield 60%). The same method was used to obtain the complexes $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)L]$ (L = $PMePh_2$, PPh_3, $AsMe_2Ph$, or $AsPh_3$) from the appropriate starting materials $[\{Ru(CO)_2Cl_2L\}_2]$ (yields *ca.* 50%). A similar procedure was used to prepare $[Ru(CO)_2Cl(\eta\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)]$ from $[\{Ru(CO)_2Cl_2(PMe_2Ph)\}_2]$ and $SnBu_3(2\text{-}MeC_3H_4)$ (yield 60%).

$[Ru(CO)_2Cl(\eta\text{-}1\text{-}MeC_3H_4)(PMePh_2)]$. A suspension of $[\{Ru(CO)_2Cl_2(PMePh_2)\}_2]$ (0.24 g) in propanone (25 cm^3) was stirred with $SnBu_3(1\text{-}MeC_3H_4)$ (0.20 g) for 0.5 h. The volume of the solution was halved by evaporation under reduced pressure, and water was then added. The precipitated product was filtered off, dried *in vacuo*, and recrystallized from light petroleum (yield 50%).

$[Ru(CO)_2I(\eta\text{-}C_3H_5)(PMe_2Ph)]$. A solution of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ (0.10 g) in $CHCl_3$ (10 cm^3) was stirred with NaI (0.50 g) at 313 K for 16 h, and then filtered. The solvent was removed under reduced pressure and the residue was recrystallized from light petroleum (yield 40%).

$[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PMe_2Ph)_2]$. A solution of $[Ru(CO)_2Cl(\eta\text{-}C_3H_5)(PMe_2Ph)]$ (0.05 g) and PMe_2Ph (0.02 g) in $CHCl_3$ (10 cm^3) was stirred at 293 K for 72 h. The solvent was then removed under a stream of nitrogen, and the microcrystalline product obtained was washed with light petroleum (yield 25%). Attempted recrystallization of the product was unsuccessful (Found: C, 48.75; H, 4.95. Calc. for $C_{21}H_{27}ClO_2P_2Ru$: C, 49.45; H, 5.35%).

Details of the instrumentation used have been given elsewhere.[9] The simulations of ^1H n.m.r. spectra were performed using a version of the LAOCOON 3 program [16] adapted to the York DEC-system 10 computer by Mr. D. L. Jones.

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