Ruthenium Complexes containing Group 5B Donor Ligands. Part 8.[1] Reactions of Binuclear Carbonyl- and Thiocarbonyl-ruthenium(II) Triphenylphosphine Complexes with Alkoxy(phenyl)phosphines and of Mononuclear Ruthenium(II) Alkoxy(phenyl)phosphine Complexes with Carbon Monoxide †

By **Wilma J. Sime** and **T. Anthony Stephenson**,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of $[Ru_2(Y)Cl_4(PPh_3)_4]$ (Y = CO or CS) with excess of L in benzene leads to ready bridge cleavage and ligand exchange to give mixtures of $[Ru(Y)Cl_2L_3]$ and $[RuCl_2L_n]$ [L = $PPh_2(OR)$ (R = Me or Et) or $PPh(OMe)_2$; n = 3 or 4]. These monosubstituted carbonyl and thiocarbonyl complexes can also be synthesised by carbonylation of $[RuCl_2L_n]$ and by reaction of $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$ with excess of L respectively. In alcohols, $[Ru(Y)Cl_2\{PPh_2(OR)\}_3]$ rearrange to $[Ru(Y)Cl\{PPh_2(OMe)\}_3]^+$ and $[\{Ru(Y)Cl[PPh_2(OEt)]_3\}_2]^{2+}$ respectively, whereas $[Ru(Y)Cl_2\{PPh(OMe)_2\}_3]$ is recovered unchanged. Structures are assigned to these complexes mainly on the basis of ^1H and $^{31}P-\{^1H\}$ n.m.r. studies.

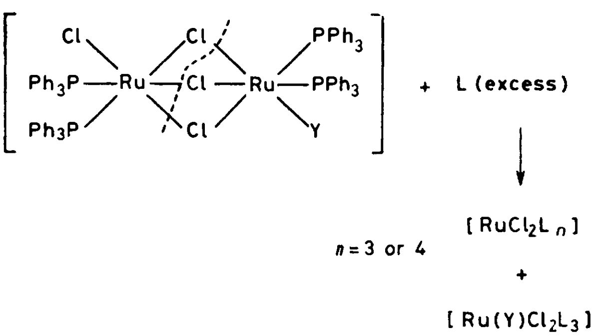
In previous papers, successful high-yield syntheses of the triple-chloride-bridged complexes $[Ru_2(Y)Cl_4(PR_3)_4]$ [Y = CO or CS; $PR_3 = PPh_3$ or $P(C_6H_4Me\text{-}p)_3$], which involved either direct reaction of $[RuCl_2(PR_3)_3]$ with CS_2 or intermolecular coupling of $[Ru(Y)Cl_2(dmf)(PR_3)_2]$ (dmf = dimethylformamide) with $[RuCl_2(PR_3)_3]$ (1 : 1 mol ratio), have been reported.[1-3] Using the latter method, a *pure* sample of the *mixed* tertiary phosphine complex $[\{(p\text{-}MeC_6H_4)_3P\}_2ClRuCl_3Ru(CO)(PPh_3)_2]$ was also obtained by reaction of $[RuCl_2\{P(C_6H_4Me\text{-}p)_3\}_3]$ with $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ [1] and an isomeric mixture of $[Ru_2(CO)Br_2Cl_2(PPh_3)_4]$ complexes has been generated.[3]

However, attempts to extend this method to the synthesis of other tertiary phosphine, phosphinite, or phosphonite complexes of type $[Ru_2(Y)Cl_4L_4]$ have not been very successful.[1] Thus, for example, although $^{31}P-\{^1H\}$ n.m.r. studies did indicate that *some* $[Ru_2(CO)Cl_4(PEtPh_2)_4]$ was formed in the reaction of $[RuCl_2(PEtPh_2)_3]$ with $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$, substantial amounts of other rearrangement products such as $[Ru(CO)Cl_2(PEtPh_2)_3]$ and $[Ru_2Cl_4(PEtPh_2)_5]$ were also obtained which could not be separated.[1]

In this paper, the results of our attempts to prepare the complexes $[Ru_2(Y)Cl_4L_4]$ [L = $PPh_2(OR)$ (R = Me or Et) or $PPh(OMe)_2$] by *direct* exchange of L with $[Ru_2(Y)Cl_4(PPh_3)_4]$ are described, together with a study of the reactions of various $[RuCl_2L_n]$ complexes (n = 3 or 4) with carbon monoxide and of $[\{RuCl_2(CS)(PPh_3)_2\}_2]$ with various L.

RESULTS AND DISCUSSION

Reaction of $[Ru_2(CO)Cl_4(PPh_3)_4]$ with an excess of $PPh_2(OMe)$ in benzene under reflux produced, after 1 h, a bright yellow solution which on addition of light petroleum (b.p. 60—80 °C) yielded a yellow solid (A). The $^{31}P-\{^1H\}$ n.m.r. spectrum of (A) at 298 K in C_6D_6 contained a singlet at δ 149.8 p.p.m. (due to $[RuCl_2\{PPh_2(OMe)\}_3]$ [4]) and a doublet and triplet at 114.9 and 138.5 p.p.m. respectively [J(PP) 29.6 Hz] from $[Ru(CO)Cl_2\{PPh_2(OMe)\}_3]$ (see below). The i.r. spectrum of (A) contained a band at 1 972 cm^{-1} [ν(CO)]. Clearly, in addition to ligand exchange, bridge cleavage has also occurred as shown in the equation. The reaction was repeated using a 1 : 4 mol ratio of $[Ru_2(CO)Cl_4(PPh_3)_4]$ to $PPh_2(OMe)$ which gave the same products, together with much starting material, thus indicating that the first step in this reaction is that of bridge cleavage.



Unfortunately, chromatographic techniques failed to separate the two complexes and fractional recrystallisation was not possible since it was found that *both* species rearranged in polar solvents (see later).

However, a pure sample of $[Ru(CO)Cl_2\{PPh_2(OMe)\}_3]$ could be prepared by bubbling CO through a solution of $[RuCl_2\{PPh_2(OMe)\}_3]$ in cold benzene. The i.r. spectrum, as for (A), contained a CO absorption band at 1 972 cm^{-1} and, in addition, bands at 312 and 286 cm^{-1}, consistent with ν(RuCl) vibrations from a chloride *trans* to CO and a chloride *trans* to phosphorus respectively.[5] The $^{31}P-\{^1H\}$ n.m.r. spectrum exhibited an identical doublet and triplet pattern to that found for (A), whilst the ^1H n.m.r. spectrum at 301 K in C_6D_6 consisted of a triplet and doublet at 3.19 and 2.84 p.p.m. respectively of intensity ratio 2 : 1. These results are consistent with structure (1; Y = CO) containing *cis*-chloride groups and two magnetically equivalent and one non-equivalent $PPh_2(OMe)$ group.

Likewise, although reaction of $[Ru_2(CO)Cl_4(PPh_3)_4]$ with an excess of $PPh_2(OEt)$ produced an inseparable mixture of $[RuCl_2\{PPh_2(OEt)\}_3]$ and $[Ru(CO)Cl_2\{PPh_2\text{-}$

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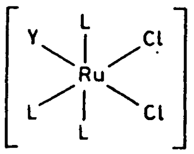
† No reprints available.

(OEt)}$_3$], the latter could be prepared in a pure state by direct reaction of [$RuCl_2\{PPh_2(OEt)\}_3$] with CO in benzene. The ^{31}P-{^1H} and ^1H n.m.r. spectra (Tables 1 and 2 respectively) and i.r. spectrum [ν(CO) at 1 980 cm^{-1}; ν(RuCl) at 302 and 279 cm^{-1}] were also consistent with structure (1). This complex had been previously synthesised by reaction of [$\{Ru(CO)_2Cl_2\}_n$] with $PPh_2(OEt)$ in ethanol, although in other instances only mixtures of [$Ru(CO)Cl_2L_3$] and [$Ru(CO)_2Cl_2L_2$] [L = $PPh_2(OMe)$ or $PPh(OMe)_2$] were produced by this route.[6] Reaction of [$Ru_2(CO)Cl_4(PPh_3)_4$] with excess of $PPh(OMe)_2$ also gave a mixture of [$RuCl_2\{PPh(OMe)_2\}_4$] and [$Ru(CO)Cl_2\{PPh(OMe)_2\}_3$]. However, in this case, *neither* of the complexes readily rearranges in polar solvents and, therefore, recrystallisation from CH_2Cl_2–methanol produced initially white crystals of [$Ru(CO)Cl_2\{PPh(OMe)_2\}_3$] and, later, yellow crystals of [$RuCl_2\{PPh(OMe)_2\}_4$] were deposited. Again spectroscopic data (Tables 1 and 2) indicated that the monocarbonyl complex had structure (1).



(1)

L = $PPh_2(OMe)$, $PPh_2(OEt)$, or $PPh(OMe)_2$
Y = CO or CS

The reaction of CO with [$RuCl_2\{PPh(OMe)_2\}_4$] in cold CH_2Cl_2 or benzene gave only starting material, but under reflux a mixture of products was obtained. Spectroscopic evidence revealed the main product to be [$Ru(CO)Cl_2\{PPh(OMe)_2\}_3$] (1) together with small amounts of other monocarbonyl isomers and/or dicarbonyl species. The dicarbonyl complexes $Ru(CO)_2Cl_2L_2$ [L = $PPh_2(OR)$ or $PPh(OR)_2$ (R = Me or Et)] have, in fact, been previously prepared by addition of excess of L to carbonylated solutions of '$RuCl_3{\cdot}3H_2O$' in 2-methoxyethanol.[6] As for [$Ru_2(CO)Cl_4(PPh_3)_4$], reactions of [$Ru_2(CS)Cl_4(PPh_3)_4$] with $PPh_2(OR)$ gave an inseparable mixture of [$Ru(CS)Cl_2\{PPh_2(OR)\}_3$] and [$RuCl_2\{PPh_2(OR)\}_3$] (R = Me or Et). However, [$Ru(CS)Cl_2\{PPh_2(OR)\}_3$] could be obtained in pure state by reaction of the double-chloride-bridged complex [$\{Ru(CS)Cl_2(PPh_3)_2\}_2$] [2] with $PPh_2(OR)$. For [$Ru(CS)Cl_2\{PPh_2(OMe)\}_3$], the ^{31}P-{^1H} n.m.r. spectrum at 298 K in C_6D_6 contained a triplet and doublet at 131.9 and 115.8 p.p.m. respectively [^2J(PP) 29.7 Hz] and i.r. spectral bands were observed at 1 275 [ν(CS)], 315 and 286 cm^{-1} [ν(RuCl)]. The ^1H n.m.r. spectrum in $CDCl_3$ at 301 K consisted of a triplet and doublet at 3.23 and 3.14 p.p.m. respectively of intensity ratio 2 : 1. Similar spectral data were obtained for [$Ru(CS)Cl_2\{PPh_2(OEt)\}_3$] consistent with structure (1; Y = CS).

TABLE 1

Phosphorus-31 n.m.r. spectra (proton-noise-decoupled) for some ruthenium complexes

Complex	Solvent	T/K	δ ^{a}/p.p.m.
[$Ru(CO)Cl_2\{PPh_2(OMe)\}_3$]	C_6D_6	298	138.5(t) (29.6) 114.9(d)
[$Ru(CO)Cl_2\{PPh_2(OEt)\}_3$]	$CDCl_3$	298	135.4(t) (30.0) 115.1(d)
[$Ru(CO)Cl_2\{PPh(OMe)_2\}_3$]	C_6D_6	298	157.4(t) (37.3) 144.0(d)
[$Ru(CS)Cl_2\{PPh_2(OMe)\}_3$]	C_6D_6	298	131.9(t) (29.7) 115.8(d)
[$Ru(CS)Cl_2\{PPh_2(OEt)\}_3$]	C_6D_6	298	130.0(t) (29.7) 112.7(d)
[$Ru(CS)Cl_2\{PPh(OMe)_2\}_3$]	C_6D_6	298	AB_2 pattern; ν_A 152.6, ν_B 143.4 (35.7)
[$Ru(CO)Cl\{PPh_2(OMe)\}_3$][BPh_4]	$CDCl_3$	213	125.4(s)
[$\{Ru(CO)Cl[PPh_2(OEt)]_3\}_2$]-[$BPh_4$]$_2$	$CDCl_3$	213	120.0(s), 122.7—115.2 ^{b}
[$Ru(CS)Cl\{PPh_2(OMe)\}_3$][BPh_4]	$CDCl_3$	213	123.0(s)
[$\{Ru(CS)Cl[PPh_2(OEt)]_3\}_2$]-[$BPh_4$]$_2$	$CDCl_3$	213	120.0—114.4 ^{b}

s = Singlet; d = doublet; t = triplet.

[a] ^2J(PP) values (in Hz) are given in parentheses. [b] Multiplet ranging over values stated.

The mixture produced in the reaction between

TABLE 2

Hydrogen-1 n.m.r. data for some ruthenium complexes at 301 K in deuteriochloroform

	δ ±0.01 p.p.m.^{a}		
Complex	Ph ^{b}	Methylene	Me
[$Ru(CO)Cl_2\{PPh_2(OMe)\}_3$] ^{c}	6.90—8.40		3.19(t) (N 11.5), 2.84(d) [^2J(PH) 11.5]
[$Ru(CO)Cl_2\{PPh_2(OEt)\}_3$]	7.20—8.10	3.20—3.60 ^{d}	0.97(t), 0.87(t) [^3J(HH) 7.0]
[$Ru(CO)Cl_2\{PPh(OMe)_2\}_3$]	7.10—7.80		3.94(t) (N 11.0), 3.69(t) (N 11.0), 3.61(d) [^2J(PH) 11.5]
[$Ru(CS)Cl_2\{PPh_2(OMe)\}_3$]	6.80—8.00		3.23(t) (N 11.2), 3.14(d) [^2J(PH) 11.5]
[$Ru(CS)Cl_2\{PPh_2(OEt)\}_3$]	7.00—8.20	3.30—3.56 ^{d}	0.91(t), 0.88(t) [^3J(HH) 7.0]
[$Ru(CS)Cl_2\{PPh(OMe)_2\}_3$]	7.20—7.80		4.04(t) (N 11.2), 3.71(t) (N 11.2), 3.73(d) [J(PH) 11.3]
[$Ru(CO)Cl\{PPh_2(OMe)\}_3$][BPh_4]	6.90—7.50		2.97 ^{d}
[$\{Ru(CO)Cl[PPh_2(OEt)]_3\}_2$][$BPh_4$]$_2$	6.90—7.50	3.22	0.79
[$Ru(CS)Cl\{PPh_2(OMe)\}_3$][BPh_4]	6.95—7.50		2.97 ^{d}

[a] $N = |J(PH) + J(PH)'|$; coupling constants in Hz. [b] Multiplet between stated values. [c] In C_6D_6. [d] Broad resonance.

$[Ru_2(CS)Cl_4(PPh_3)_4]$ and excess of $PPh(OMe)_2$ could be separated by recrystallisation from CH_2Cl_2–methanol to give white crystals of $[Ru(CS)Cl_2\{PPh(OMe)_2\}_3]$, shown by i.r. and n.m.r. spectroscopy to have structure (1).

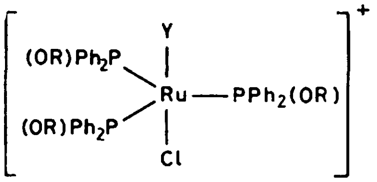
As mentioned earlier, difficulties arose when trying to separate mixtures of $[Ru(Y)Cl_2\{PPh_2(OR)\}_3]$ and $[RuCl_2\{PPh_2(OR)\}_3]$ because of the ready rearrangement reactions of *both* species in polar solvents (see ref. 4 for a detailed discussion of the rearrangement reactions of $[RuCl_2\{PPh_2(OR)\}_3]$ complexes). Thus, dissolution of $[Ru(Y)Cl_2\{PPh_2(OMe)\}_3]$ (Y = CO or CS) in methanol and addition of $Na[BPh_4]$ gave colourless crystals analysing for $[Ru(Y)Cl\{PPh_2(OMe)\}_3][BPh_4]$ (Table 3).

TABLE 3

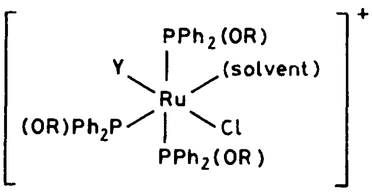
Analytical data (%) for some new ruthenium(II) carbonyl and thiocarbonyl complexes

	Found		Calc.	
Complex	C	H	C	H
$[Ru(CO)Cl_2\{PPh_2(OMe)\}_3]$	56.4	4.5	56.6	4.6
$[Ru(CO)Cl_2\{PPh_2(OEt)\}_3]$	57.8	5.1	57.9	5.1
$[Ru(CO)Cl_2\{PPh(OMe)_2\}_3]$	42.3	4.5	42.2	4.6
$[Ru(CS)Cl_2\{PPh_2(OMe)\}_3]$	56.0	4.6	55.7	4.5
$[Ru(CS)Cl_2\{PPh_2(OEt)\}_3]$	57.1	5.0	57.0	5.0
$[Ru(CS)Cl_2\{PPh(OMe)_2\}_3]$	41.4	4.6	41.3	4.5
$[Ru(CO)Cl\{PPh_2(OMe)\}_3][BPh_4]$	67.6	5.3	67.3	5.2
$[\{Ru(CO)Cl[PPh_2(OEt)]_3\}_2][BPh_4]_2$	68.8	5.6	68.5	5.5
$[Ru(CS)Cl\{PPh_2(OMe)\}_3][BPh_4]$	66.9	5.2	67.1	5.2
$[\{Ru(CS)Cl[PPh_2(OEt)]_3\}_2][BPh_4]_2$	67.9	5.5	67.6	5.4

The mull i.r. spectra contained no evidence for coordinated solvent molecules but did have strong bands at *ca.* 300 cm^{-1} attributable to terminal ν(RuCl) vibrations. The $^{31}P-\{^1H\}$ n.m.r. spectra at both 213 and 298 K consisted of a singlet indicative of monomeric structures in which all the tertiary phosphinite groups were equivalent. Possibilities which explain this equivalence include a trigonal-bipyramidal structure (2a) or, more likely,* a square-pyramidal or weakly solvated octahedral structure (2b), in which rapid scrambling of axial and equatorial phosphinite ligands renders them equivalent on the n.m.r. time scale. This conclusion was supported by the ^1H n.m.r. spectra at 301 K which exhibited a single broad resonance at 2.97 p.p.m. Furthermore, for each complex, conductivity measurements in CH_2Cl_2 were consistent with the presence of a 1 : 1 electrolyte in solution (see Experimental section).

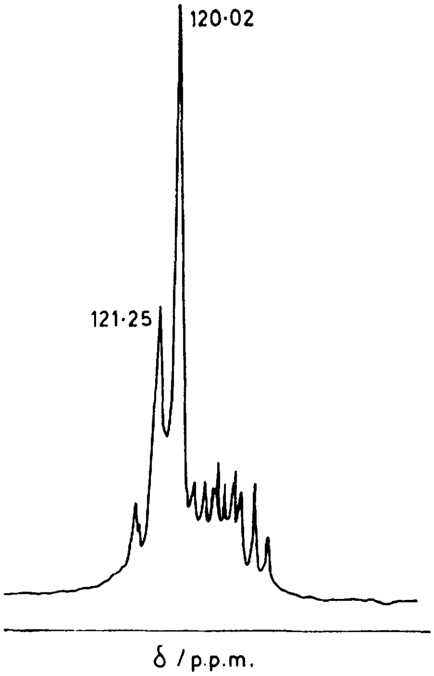


(2a)



(2b)

Dissolution of $[Ru(Y)Cl_2\{PPh_2(OEt)\}_3]$ in ethanol containing $Na[BPh_4]$ also slowly gave colourless crystals analysing for $[Ru(Y)Cl\{PPh_2(OEt)\}_3][BPh_4]$. However, in contrast to $[Ru(Y)Cl\{PPh_2(OMe)\}_3][BPh_4]$, the $^{31}P-\{^1H\}$ n.m.r. spectra at 213 K showed complicated multiplet patterns at *ca.* 118 p.p.m. (see Figure, Y = CO). These spectra were not consistent with monomeric structures, since at 213 K, by analogy with the $PPh_2(OMe)$ results, rapid intramolecular scrambling would still be expected.† Therefore the existence of dimers in solution at this temperature is probable and, furthermore, the complexity of the n.m.r. patterns suggested the presence of more than one isomer.



$^{31}P-\{^1H\}$ n.m.r. spectrum of $[\{Ru(CO)Cl[PPh_2(OEt)]_3\}_2][BPh_4]_2$ in $CDCl_3$ at 213 K

For Y = CO, cooling the sample to 198 K caused the resonance at 120.0 p.p.m. to decrease in intensity whilst the remainder of the spectrum remained unchanged, but on warming to 298 K the entire multiplet pattern collapsed to a single resonance at 119.0 p.p.m. These results strongly indicated that the resonance at 120.0 p.p.m. was due to the monomeric cation $[Ru(CO)Cl\{PPh_2(OEt)\}_3]^+$ which increased in concentration as the temperature was increased and the dimer dissociated. Indeed, conductivity measurements at 298 K in CH_2Cl_2 were consistent with the presence of a 1 : 1 electrolyte.

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[*] *X*-Ray structural data show that most five-co-ordinate d^6 complexes have an essentially square-pyramidal structure [7] and this is supported by recent theoretical arguments.[8]

[†] The possibility of frozen-out monomeric structures at this temperature [due to the bulkier $PPh_2(OEt)$ groups] seems unlikely in view of the fact that the $^{31}P-\{^1H\}$ n.m.r. spectrum of $[RuCl_2\{PPh_2(OEt)\}_3]$ is still a sharp singlet at 213 K.[4]

However, the presence of a *dimeric* structure in the solid state for both Y = CO and CS was supported by the occurrence of a broad band at 270 cm^{-1} and the absence of one at 300 cm^{-1} in their far-i.r. spectra. These appear to be the first *cationic* halide-bridged ruthenium(II) carbonyl (and thiocarbonyl) complexes to be reported, although several related neutral species such as $[\{Ru(Y)Cl_2(PR_3)_2\}_2]$ [Y = CO; $PR_3 = PPh_3$ [9] or PMe_2Ph; [10] Y = CS; $PR_3 = PPh_3$ [2,11] or $P(C_6H_4Me\text{-}p)_3$ [1]] have been synthesised.

It should be noted that this behaviour of $[\{Ru(CO)Cl[PPh_2(OEt)]_3\}_2][BPh_4]_2$ in solution is analogous to that found for $[\{RuCl[PPh_2(OEt)]_4\}_2][BPh_4]_2$.[4] This tendency of the $PPh_2(OEt)$ complexes to form dimeric species, compared to the corresponding $PPh_2(OMe)$ complexes, which appear to exist entirely as monomers (also see ref. 4), must be attributed to an electronic rather than a steric effect, since the *smaller* $PPh_2(OMe)$ complexes would be expected to dimerise preferentially.

This tendency of $[Ru(Y)Cl_2\{PPh_2(OR)\}_3]$ to readily lose a chloride ion in methanol to generate either five-co-ordinate monomers or six-co-ordinate dimeric cations is unusual but not without precedent. Thus, recently, $[MX_2(dppp)_2]$ (M = Ru or Os; X = Cl or Br; dppp = $Ph_2P[CH_2]_3PPh_2$) complexes were shown to lose a halide ion in boiling alcohol to give the five-co-ordinate cations $[MX(dppp)_2]^+$, isolated as $[PF_6]^-$ or $[BPh_4]^-$ salts.[12,13] Steric effects were clearly important here since the corresponding complexes with smaller diphosphines $Ph_2P[CH_2]_nPPh_2$ (n = 1 or 2) showed no tendency to lose halide ion. Similarly, when $[Ru(Y)Cl_2\{PPh(OMe)_2\}_3]$ were dissolved in methanol no cationic complexes were generated and this can probably be mainly attributed to the smaller steric requirements of the tertiary phosphonite group.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on Perkin-Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates, and in the 200—400 cm^{-1} region on a Beckman RIIC IR 720 far-i.r. spectrometer using pressed Polythene discs. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and ^{31}P n.m.r. spectra (proton-noise decoupled) on a Varian Associates XL-100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4. Conductivity measurements were made at 298 K using a Portland Electronics model 310 conductivity bridge. As described earlier,[4] plots of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}}$ gave a straight line whose gradient is a function of the ionic charges.[14] Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials.—Ruthenium trichloride trihydrate (Johnson, Matthey), carbon monoxide (Air Products), $PPh_2(OR)$ (R = Me or Et) and $PPh(OMe)_2$ (Maybridge), and $Na[BPh_4]$ (B.D.H.) were obtained from the sources shown. The complexes $[Ru_2(Y)Cl_4(PPh_3)_4]$ (Y = CO [3] or CS [2]), $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$,[2] $[RuCl_2L_3]$ [L = $PPh_2(OR)$ (R = Me or Et) [4]], and $[RuCl_2\{PPh(OMe)_2\}_4]$ [4] were prepared as described earlier.

All reactions were carried out in degassed solvents and, apart from carbonylation reactions, under an atmosphere of nitrogen. The proposed ν(RuCl) vibrational bands are italicised.

Carbonyldichlorotris(methyl diphenylphosphinite)ruthenium(II).—Carbon monoxide gas was bubbled through a solution of $[RuCl_2\{PPh_2(OMe)\}_3]$ in benzene for 1 min. The resulting pale yellow solution was reduced in volume and light petroleum (b.p. 60—80 °C) added. A pale yellow solid precipitated which was filtered off and washed with light petroleum; m.p. 128—130 °C, ν(CO) at 1 972 cm^{-1}. Far-i.r. spectrum: *312*, *286*, 275, and 233 cm^{-1}. A similar method was used to prepare *carbonyldichlorotris(ethyl diphenylphosphinite)ruthenium*(II), from $[RuCl_2\{PPh_2(OEt)\}_3]$, as a white solid, m.p. 203—205 °C; ν(CO) at 1 980s and 1 935w cm^{-1}. Far-i.r. spectrum: *302*, *279*, 260, and 238 cm^{-1}.

Carbonyldichlorotris(dimethyl phenylphosphonite)ruthenium(II).—The complex $[Ru_2(CO)Cl_4(PPh_3)_4]$ (0.20 g) was heated under reflux with excess of $PPh(OMe)_2$ (0.40 cm^3) in benzene (30 cm^3) for 1 h. The resulting yellow solution was reduced in volume to *ca.* 10 cm^3 and light petroleum added. The yellow solid which precipitated was filtered off and recrystallisation from CH_2Cl_2–MeOH produced colourless crystals of the *complex*; ν(CO) at 1 985, ν(RuCl) at 305 and 280 cm^{-1}. The remaining yellow solution deposited after several days yellow crystals of $[RuCl_2\{PPh(OMe)_2\}_4]$. Similarly, *dichlorotris(dimethyl phenylphosphonite)(thiocarbonyl)ruthenium*(II) was prepared as colourless crystals from $[Ru_2(CS)Cl_4(PPh_3)_4]$; m.p. 149—151 °C, ν(CS) at 1 305, ν(RuCl) at 312 and 274 cm^{-1}.

Dichlorotris(methyl diphenylphosphinite)(thiocarbonyl)ruthenium(II).—The complex $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$ (0.20 g) was heated under reflux with $PPh_2(OMe)$ (0.30 cm^3) in benzene (30 cm^3) for 1 h. The resulting yellow solution was reduced in volume to *ca.* 10 cm^3 and light petroleum was added to precipitate the complex as a yellow *solid*, which was filtered off, washed with light petroleum, and dried *in vacuo*; m.p. 110—112 °C, ν(CS) at 1 275 cm^{-1}. Far-i.r. spectrum: *315*, *286*, 272, and 233 cm^{-1}. Similarly, *dichlorotris(ethyl diphenylphosphinite)(thiocarbonyl)ruthenium*(II) was prepared as a yellow solid, ν(CS) at 1 295 cm^{-1}. Far-i.r. spectrum: *305*, *280*, and 265 cm^{-1}.

Carbonylchlorotris(methyl diphenylphosphinite)ruthenium(II) *Tetraphenylborate*.—The complex $[Ru(CO)Cl_2\{PPh_2(OMe)\}_3]$ (0.20 g) was dissolved in methanol (15 cm^3) containing $Na[BPh_4]$ (0.20 g). After 24 h white crystals of the *complex* were deposited, m.p. 193—195 °C, ν(CO) at 1 975, ν(RuCl) at 303 cm^{-1}. Conductivity at 298 K in CH_2Cl_2: gradient of plot of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}}$ = 148 (for $[Ru_2Cl_3\{PPh_2(OMe)\}_6][BPh_4]$, gradient = 165). In the same way, *chlorotris(methyl diphenylphosphinite)(thiocarbonyl)ruthenium*(II) *tetraphenylborate* was prepared as white crystals, m.p. 174—176 °C, ν(CS) at 1 285, ν(RuCl) at 301 cm^{-1}. Conductivity at 298 K in CH_2Cl_2: gradient of plot of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}}$ = 156.

Bis[carbonylchlorotris(ethyl diphenylphosphinite)ruthenium(II)] *Tetraphenylborate*.—The complex $[RuCl_2(CO)\{PPh_2(OEt)\}_3]$ (0.20 g) was dissolved in ethanol (15 cm^3) containing $Na[BPh_4]$ (0.20 g). White crystals of the complex were deposited over 3 d, m.p. 198—200 °C, ν(CO) at 1 960 cm^{-1}. Far-i.r. spectrum: *270*, 282, 263, and 256 cm^{-1}. Conductivity in CH_2Cl_2 at 298 K: gradient of plot of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}} = 198$. Likewise, $[Ru(CS)Cl_2\{PPh_2(OEt)\}_3]$ dissolved in ethanol containing $Na[BPh_4]$ produced *bis*[*chlorotris*(*ethyl diphenylphosphinite*)(*thiocarbonyl*)*ruthenium*(II)] *tetraphenylborate*, m.p. 112—114 °C, ν(CS) at 1 285, ν(RuCl) at 270 cm^{-1}.

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