New Ruthenium(III) and Ruthenium(II) Complexes containing Triphenyl-arsine and -phosphine and Other Ligands [1]

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A detailed investigation of the reactions of $[RuX_3(EPh_3)_2MeOH]$ (A) (X = Cl or Br; E = P or As) with ligands containing nitrogen (alkyl and aryl cyanides, pyridine, 2,2′-bipyridyl, 1,10-phenanthroline), sulphur (dimethyl sulphoxide, dialkyl sulphides, carbon disulphide, sodium diphenylphosphinodithioate), oxygen (tetrahydrofuran, acetone, nitromethane) and carbon (norbornadiene, 1,5-cyclo-octadiene, carbon monoxide) donor atoms is presented. Five different types of behaviour towards these ligands are exhibited by (A): (1) displacement of methanol giving the ruthenium(III) compounds $[RuX_3(EPh_3)_2L]$, *e.g.* L = RCN, Me_2SO, CS_2, CS; (2) displacement of methanol and one EPh_3 group giving $[RuX_3(EPh_3)L_2]$, *e.g.* L_2 = Me_2S, bipy, C_5H_5N; (3) complete displacement of methanol, EPh_3 and X without reduction, *e.g.* $[Ru(S_2PPh_2)_3]$; (4) reduction to ruthenium(II) with or without complete displacement of EPh_3 groups, *e.g.* $[RuX_2L_2(EPh_3)_2]$ (L_2 = CO, C_7H_8, RCN) and $[RuX_2L_4]$ (L = C_5H_5N, Me_2SO); (5) reduction to cationic ruthenium(II) compounds in methanol, *e.g.* $[RuCl(PPh_3)(N-N)_2]Cl$ [(N–N) = bipy or phen]. Several of these compounds can also be synthesised from $[RuX_2(PPh_3)_3]$. The compounds are characterised by elemental analyses, molecular weights, e.s.r., and magnetic measurements, and configurations tentatively suggested on the basis of detailed far-i.r. [ruthenium(III)] and ^1H n.m.r. [ruthenium(II)] studies. Finally, electronic spectra (50 000—12 000 cm^{-1}) are presented and discussed.

THERE is now an extensive chemistry of ruthenium(II) compounds with ligands such as tertiary phosphines. In particular, the complexes $[RuX_2(PPh_3)_{3\ or\ 4}]$ (X = Cl or Br) [2] are excellent starting materials for the synthesis of a wide range of ruthenium(II) compounds still containing triphenylphosphine.[3] Such compounds as $[Ru_2Cl_3(PR_3)_6]Cl$ [4] and the blue methanolic solutions of '$Ru_5Cl_{12}^{2-}$' [5] are also excellent precursors for synthesising ruthenium(II) complexes with a range of other ligands.

In contrast, relatively few ruthenium(III) compounds containing tertiary monophosphines or arsines have been reported. Such compounds include the series *mer*-$[RuX_3L_3]$ (L = PMe_2Ph, PEt_2Ph, $PBu^n{}_2Ph$, PPh_3),[6] $[RuX_3(EPh_3)_2S]$ (E = P or As; S = MeOH,[2,7] $MeNO_2$,[8] Me_2CO[2]), the anions *trans*-$[RuX_4L_2]^-$ (L = PPh_3, $AsPh_3$, PMe_2Ph, PEt_3) [8] and the binuclear compounds $[RuCl_3(PR_3)_2]_2$ and $[Ru_2Cl_5(PR_3)_4]$ (R = Pr^n, Bu^n).[9] The tertiary phosphite anions $M[RuCl_4(L)_2]$ have also been synthesised {M = Me_4N^+, L = $P(OPh)_3$; [8] M = $[Ru_2Cl_3L_6]^+$, L = $P(OEt)_3$, $P(OEt)_2Ph$, $P(OMe)Ph_2$ [10]}. However, it has been found that the reaction, in ethanol, of *mer*-$[RuX_3(PR_3)_3]$ with ammonia and primary amines (am) gives the ruthenium(II) compounds $[RuX_2(PR_3)_3(am)]$ whereas with secondary and tertiary amines, the alcohol complexes $[RuX_2(PR_3)_3(EtOH)]$ are formed.[11] In view, therefore, of the paucity of

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data on convenient syntheses of ruthenium(III) tertiary phosphine and arsine compounds containing other ligands, we have undertaken a detailed study of the reactions of $[RuX_3(EPh_3)_2(MeOH)]$ (A) with ligands containing nitrogen, sulphur, oxygen, and carbon donor atoms. A preliminary account of this work has appeared.[1]

RESULTS AND DISCUSSION

Five different types of behaviour towards these ligands are exhibited by the complexes (A). These are (1) displacement of methanol giving the six-co-ordinate ruthenium(III) compounds $[RuX_3(EPh_3)_2L]$; (2) displacement of solvent ligand and one EPh_3 group giving the six-co-ordinate ruthenium(III) compounds $[RuX_3(EPh_3)L_2]$; (3) displacement of all ligands with retention of the ruthenium(III) oxidation state; (4) reduction to ruthenium(II) with or without complete displacement of EPh_3 groups giving $[RuX_2L_4]$ or $[RuX_2L_2(EPh_3)_2]$; (5) reduction to cationic ruthenium(II) compounds when the reaction is carried out in more polar solvents.

However, most of these ligands exhibit several of the different types of behaviour and in addition, the product obtained depends critically on a combination of such diverse factors as the nature of the ligand, the reaction time, the solvent media, and on the other ligands already present in the ruthenium ion co-ordination sphere. Therefore, in order best to illustrate the sensitivity of the product composition to changes in these various factors, the results are presented and discussed below under ligand headings.

Nitrogen Ligands

(a) *Alkyl and Aryl Cyanides*.—Several syntheses of ruthenium(II) alkyl and aryl cyanide compounds have recently been published. From $[RuCl_2(PPh_3)_3]$ and RCN, the compounds $[RuCl_2(RCN)_2(PPh_3)_2]$ are readily obtained.[3,12] From the blue solution of ruthenium(II) in methanol, the phenyl cyanide dimer $[RuCl_2(PhCN)_3]_2$ can be isolated and halide bridge cleavage with Lewis bases gives $[RuCl_2(PhCN)_2L_2]$ ($L = PR_3$, $MeC_6H_4NH_2$, CO, *etc*).[5] In contrast, reaction of the blue solution with succino- and glutaro-cyanides (L′) gives brown insoluble compounds of approximate stoicheiometry $RuCl_2L'$.[5] Preparation of the blue solution in methyl cyanide gives $[RuCl_2(MeCN)_4]$ which reacts further to produce $[RuCl_2(MeCN)_2L_2]$ ($L = PhNH_2$, CO);[5] $[RuI_2(MeCN)_2(CO)_2]$ is also obtained from $[RuI_2(CO)_2]_n$ and MeCN.[13] Cleavage of the halogenocarbonyl dimer $[RuX_2(CO)_3]_2$ with nitriles gives *cis*-$[RuX_2(RCN)(CO)_3]$ ($R = Et$, Ph, $CH_2{=}CH$)[14] and $[RuCl_3NO(MeCN)_2]$ is obtained from the reaction of $RuCl_3NO$ and MeCN.[15]

In recent years, a number of cationic ruthenium(II) compounds containing RCN ligands have also been reported. These include $[RuH(PhCN)(Et_2PC_2H_4PEt_2)_2]^+$,[16] $[(\pi\text{-}C_6H_6)RuCl(MeCN)_2]HgCl_3$,[17] $[RuH(CO)(MeCN)_2(PPh_3)_2]ClO_4$,[18] $[RuXMeCN(bipy)_2]PF_6$ ($X = Cl^-$ or NO_2^-),[19] and the series $[Ru(NH_3)_4(RCN)_2]^{2+}$ and $[Ru(NH_3)_5RCN]^{2+}$.[20] Several of the latter can be readily oxidised to the corresponding ruthenium(III) species $[Ru(NH_3)_5RCN]^{3+}$.[21] The only other ruthenium(III) nitrile compounds known (to us) are the recently reported $[RuCl_3(PhSPr^i)_2MeCN]$ and $[RuCl_3(MeCN)_3]$-MeCN.[22]

We now report that reaction of excess of RCN with (A) in dichloromethane gives the crystalline compounds $[RuX_3(EPh_3)_2RCN]$ ($E = P$ or As; $X = Cl$ or Br; $R = Me$, Ph, $PhCH_2$, or $CH_2{=}CH$). These compounds (which are non-electrolytes in CH_2Cl_2) have been characterised by elemental analyses and molecular weights, magnetic moments at room temperature (solid and solution state) (Table 1), and e.s.r. studies at 77 K. The values of μ_{eff} (300 K), ranging from 1·80 to 2·20 B.M. are indicative of monomeric, spin-paired ruthenium(III) compounds[23] and all the compounds exhibit intense e.s.r. spectra with a three *g* value pattern very similar to those reported by Hudson and Kennedy[24] for various $[RuX_3L_3]$ compounds ($L = PMe_2Ph$, SMePh, *etc.*) E.s.r. spectra of all the new ruthenium(III) compounds reported in this paper will be discussed more fully in a separate publication.[25] The i.r. spectra of all these compounds contain a very weak band [ν(CN)] at *ca.* 2300 cm^{-1}, 50—100 cm^{-1} higher than in the free ligands, which suggests that bonding occurs through the nitrogen[26] {*cf.* $[RuCl_3(PrSPr^i)_2(MeCN)]$ ν(CN) 2310 cm^{-1} [22]}. As expected,[27] the ^1H n.m.r. spectra of these compounds are either too broadened by the paramagnetic ion to be observed or consist of broad contact-shifted resonances, from which little structural information can be derived. Although the electronic spectra (50 000—12 000 cm^{-1}) of all these compounds have been recorded and the spectral bands satisfactorily assigned to intraligand and charge-transfer transitions (see Table 2 and later discussion), these measurements are of little use in determining the

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TABLE 1

Analytical data for some new ruthenium(III) compounds

Complex	Colour	M.p. (°C)	Found (%)					Required (%)					μ_{eff} (B.M.) [b]
			C	H	N	Others	M [a]	C	H	N	Others	M	
$[RuCl_3(AsPh_3)_2MeCN]$	Dark green	194—195	52·6	3·7	1·6		885	53·0	3·9	1·6		858	
$[RuBr_3(AsPh_3)_2MeCN]$	Brown	206	47·0	3·4	1·4		1120	45·9	3·3	1·4		993	
$[RuCl_3(PPh_3)_2MeCN]$	Green	190	59·1	4·3	1·8			59·0	4·3	1·8			
$[RuBr_3(PPh_3)_2MeCN]$	Purple	178—179	52·1	3·7	1·6		945	50·4	3·7	1·5		906	
$[RuCl_3(AsPh_3)_2(PhCH_2CN)]$	Bright green	170 (d)	56·4	4·0	1·5	Cl, 11·2	1065	56·4	4·0	1·5	Cl, 11·3	937	1·80
$[RuBr_3(AsPh_3)_2(PhCH_2CN)]$	Purple	212 (d)	49·2	3·8	1·4		1110	49·4	3·5	1·3		1069	2·10
$[RuCl_3(PPh_3)_2(PhCH_2CN)]$	Bright green	161 (d)	62·2	4·6	1·8			62·2	4·4	1·7			
$[RuBr_3(PPh_3)_2(PhCH_2CN)]$	Purple	154—155 (d)	53·6	3·9	1·5			53·7	3·8	1·4			
$[RuCl_3(AsPh_3)_2(PhCN)]$	Dark green	225 (d)	56·0	3·9	1·5		970	56·0	3·8	1·5		920	
$[RuBr_3(AsPh_3)_2(PhCN)]$	Dark purple	233 (d)	48·9	3·3	1·4			48·9	3·3	1·3			
$[RuCl_3(PPh_3)_2(PhCN)]$	Green	200 (d)	60·7	4·2	1·7			61·8	4·2	1·7			
$[RuBr_3(PPh_3)_2(PhCN)]$	Purple	172 (d)	55·3	3·9	1·6			53·3	3·6	1·4			
$[RuCl_3(PPh_3)_2(CH_2CHCN)]$	Yellow	175 (d)	58·9	4·3	2·4			59·7	4·2	1·8			
$[RuBr_3(AsPh_3)_2(CH_2CHCN)]$	Red-purple	235 (d)	46·0	3·3	1·7		1100	46·5	3·3	1·4		1006	1·73 (1·44) [c]
$[RuCl_3(AsPh_3)(bipy)]$	Red-brown	239 (d)	50·3	3·5	4·2	Cl, 15·4		50·2	3·5	4·2	Cl, 15·9		1·80
$[RuBr_3(AsPh_3)(bipy)]$	Dark purple	235 (d)	40·3	2·9	3·4		823	41·9	2·9	3·5		803	2·10 (1·85) [c]
$[RuCl_3(PPh_3)(bipy)]$	Orange-brown	215—216 (d)	53·8	3·6	4·5			53·7	3·7	4·5			1·83
$[RuBr_3(PPh_3)(bipy)]$	Dark red	>300	43·8	3·1	2·5			44·3	3·1	3·6			1·85 (1·77) [c]
$[RuCl_3(AsPh_3)(phen)]$	Brown	264	52·6	3·4	3·6			52·0	3·3	4·0			
$[RuCl_3(PPh_3)(phen)]$	Pale brown	280	56·8	3·7	4·3			55·4	3·6	4·3			
$[RuBr_3(PPh_3)(phen)]$	Brown	225	47·7	3·1	4·0			46·0	3·0	3·6			
$[RuCl_3(AsPh_3)(py)_2]$	Orange	205—206 (d)	49·5	3·8	4·1			50·0	3·7	4·2			(2·03) [d]
$[RuBr_3(AsPh_3)(py)_2]$	Purple	195 (d)	42·1	3·1	3·5		844	41·8	3·1	3·5		803	(1·72) [d]
$[RuCl_3(PPh_3)(py)_2]$	Orange	204—205 (d)	53·5	4·0	4·9		690	53·6	4·0	4·6		626	
$[RuBr_3(PPh_3)(py)_2]$	Purple	192 (d)	45·0	3·3	3·7		800	44·2	3·3	3·7		760	
$[RuCl_3(AsPh_3)_2(dmso)]$	Tan	197 (d)	51·1	4·1				50·8	4·0				1·90
$[RuCl_3(AsPh_3)_2([^2H_6]dmso)]$	Tan	206	47·6	4·4 [e]				50·5	4·6				
$[RuBr_3(AsPh_3)_2(dmso)]$	Dark brown	167—168 (d)	41·0	3·4				44·2	3·5				
$[RuCl_3(PPh_3)_2(dmso)]$	Tan	168—169 (d)	55·9	4·0				56·4	4·4				
$[RuBr_3(PPh_3)_2(dmso)]$	Dark purple	183	47·9	3·8				48·4	3·9				
$[RuCl_3(AsPh_3)(Me_2S)_2]$	Red	176 (d)	43·2	4·2		Cl, 16·2 S, 9·8	682	43·5	4·1		Cl, 16·1 S, 9·7	662	2·10 (2·13) [c]
$[RuBr_3(AsPh_3)(Me_2S)_2]$	Dark purple	168	35·5	3·4				34·3	3·5				1·79
$[RuCl_3(PPh_3)(Me_2S)_2]$	Dark green	215	44·2	4·5				44·5	4·6				
$[RuBr_3(PPh_3)(Me_2S)_2]$	Dark brown	280	36·7	3·7				36·3	3·7				
$[RuCl_3(AsPh_3)_2(Et_2S)]$	Red	155 (d)	51·5	4·4			725	52·8	4·4			687	
$[RuBr_3(AsPh_3)_2(Et_2S)]$	Purple	149 (d)	44·4	3·9				46·0	3·9				
$[RuCl_3(AsPh_3)_2CS_2]$	Brown	260 (d)	49·1	3·3		Cl, 12·5		49·6	3·4		Cl, 11·9		2·00
$[RuCl_3(PPh_3)_2CS_2]$	Dark brown	176—177 (d)	55·0	3·7				55·0	3·7				
$[RuBr_3(AsPh_3)_2CS]$	Brown	178 (d)	46·6	3·3				48·8	3·3				
$[RuBr_3(PPh_3)_2CS]$	Dark purple	185 (d)	42·3	3·0				44·5	3·0				
$[RuCl_3(AsPh_3)_2(thf)]$	Orange-red	198 (d)	51·8	4·3			928	53·9	4·3			889	1·72
$[RuBr_3(AsPh_3)_2(thf)]$	Dark purple	161 (d)	45·5	3·7				46·8	3·7				
$[RuCl_3(PPh_3)_2(thf)]$	Dark green	175 (d)	57·6	3·5				59·6	4·7				
$[RuBr_3(PPh_3)_2(thf)]$	Red brown	180 (d)	48·7	3·6				51·2	4·1				
$[RuCl_3(AsPh_3)_2]$	Dark brown	>290	52·7	3·6				52·7	3·7				
$[RuBr_3(AsPh_3)_2]$	Brown	>300	43·4	3·2				45·3	3·2				

[a] Osmometrically at 37° (C_6H_6). [b] Magnetic moment, measured by Faraday method (solid) at 294 K; in parentheses, as measured by Evans' method (solution) at 301 K. [c] Measured in $CHCl_3$. [d] Measured in CH_2Cl_2. [e] H + D%.

detailed isomeric form(s) of the compounds. However, the fact that the compounds are sharp melting, give single spots on t.l.c. plates and exhibit very similar electronic and e.s.r. spectral patterns strongly suggests that only *one* of the three possible geometric isomers (Figure 1) is produced in each case.

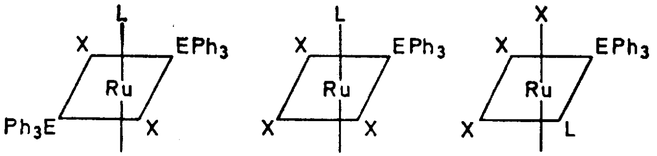
TABLE 2

The electronic spectra (50 000—12 000 cm^{-1}) of some ruthenium(III) compounds (shoulders in italics)

Compound								
[$RuCl_3(AsPh_3)_2(MeCN)$]	$10^{-3}\nu$ [a]	42·7		32·8		25·0	*22·2*	16·3
	$10^{-3}\varepsilon_{max.}$ [b]	47·82		28·13		3·19(428) [c]		0·21(16)
[$RuBr_3(AsPh_3)_2(MeCN)$]	$10^{-3}\nu$	40·3		32·1		20·3	*17·5*	
	$10^{-3}\varepsilon_{max.}$	10·41		77·8		1·26(94)		
[$RuCl_3(PPh_3)_2(MeCN)$]	$10^{-3}\nu$	42·8		33·6		24·8	*22·7*	15·8
	$10^{-3}\varepsilon_{max.}$	25·98		10·89		2·01(234)		0·08(5·6)
[$RuBr_3(PPh_3)_2(MeCN)$]	$10^{-3}\nu$	42·8		32·8	*28·5*	20·2	*17·2*	
	$10^{-3}\varepsilon_{max.}$	56·48		18·52		2·59(300)		
[$RuCl_3(PPh_3)(py)_2$]	$10^{-3}\nu$	42·4	*38·9*	33·3		25·4	22·2	
	$10^{-3}\varepsilon_{max.}$	67·25		17·39		5·22(450)	2·66(220)	
[$RuCl_3(AsPh_3)(bipy)$]	$10^{-3}\nu$	42·4		34·4		25·6	*22·7*	*17·7*
	$10^{-3}\varepsilon_{max.}$	57·00		31·60		5·88(780)		
[$RuBr_3(AsPh_3)(bipy)$]	$10^{-3}\nu$	42·5		33·5		21·4	17·6	*15·5*
	$10^{-3}\varepsilon_{max.}$	33·50		15·00		2·78(345)	1·79(107)	
[$RuCl_3(PPh_3)(bipy)$]	$10^{-3}\nu$	40·0		34·0		25·6	*22·2*	
	$10^{-3}\varepsilon_{max.}$	12·32		7·78		1·71(230)		
[$RuBr_3(PPh_3)(bipy)$]	$10^{-3}\nu$	42·5		33·7		21·9	17·9	*15·5*
	$10^{-3}\varepsilon_{max.}$	70·63		17·38		2·54(384)	1·90(158)	

[a] Band energy (cm^{-1}). [b] Maximum molar extinction coefficient (mol^{-1} cm^{-1}). [c] Oscillator strength ($10^4 f$) where $f = 4{\cdot}60 \times 10^{-9}\varepsilon_{max.}\nu_{\frac{1}{2}max.}$ and $\nu_{\frac{1}{2}max.}$ = half intensity band width *i.e.* the width at $\frac{1}{2}\varepsilon_{max.}$ (cm^{-1}).

In Table 3, the far. i.r. spectra (400—200 cm^{-1}) of these compounds are listed. By careful examination of these bands, particularly for the triphenylphosphine compounds where masking by ligand absorptions is minimised, at least one of the ν(RuX) vibrations can be assigned and the ratio of ν(RuCl) : ν(RuBr) (*ca.* 1·30), which is in the range found by other workers,[28] supports these assignments. It is well established that the influence of the group *trans* to the halide may be substantial.[29] Thus, terminal ν(RuCl) are generally found in the region 347—299 (when *trans* to chloride), 311—266 (*trans* to CO), 262—229 (*trans* to PR_3) and bridging chloride stretching frequencies are usually found below 250 cm^{-1}.[27,30] There appear to be no ν(RuCl) below 300 cm^{-1} but the presence in all these compounds of a strong ν(RuCl) band at *ca.* 330 cm^{-1} is consistent with *trans*-chlorides, suggesting either configuration (I) or (II). Although it is impossible to distinguish unequivocally between these possibilities on the basis of far i.r. studies alone, the close similarity of the far i.r. spectra of [$RuX_3(EPh_3)_2RCN$] to those of [$RuX_3(EPh_3)_2MeOH$], together with the established *trans* * structure of the [$MX_4(PPh_3)_2$]$^-$ anions (M = Rh or Ru),[8] strongly suggests that the nitrile (and methanol) compounds have configuration (I).



(I) (II) (III)

FIGURE 1 The three possible isomeric forms of [$RuX_3(EPh_3)_2L$]

Unlike [$RuCl_3(PhSPr^i)_2MeCN$], which readily undergoes displacement of $PhSPr^i$ by MeCN, giving [$RuCl_3(MeCN)_3$]MeCN,[22] we have found no evidence for the formation of [$RuX_3(EPh_3)_n(RCN)_{3-n}$] ($n$ = 0 or 1) by reaction of (A) with RCN. However, prolonged reaction of [$RuX_3(PPh_3)_2MeOH$] with RCN results in the formation of some [$RuX_2(RCN)_2(PPh_3)_2$]. A careful examination of the product for X = Cl, R = $PhCH_2$ confirms that it is identical to *cis*-[$RuCl_2(PhCH_2CN)_2(PPh_3)_2$] [$\nu$(CN) 2269, 2243 cm^{-1}] obtained directly from [$RuCl_2(PPh_3)_3$].[3] The ease of reduction depends on R and a qualitative order is found to be MeCN $\ll$ PhCN < $PhCH_2CN$ < CH_2CHCN. Under the same conditions no reduction products are found for E = As.

(b) *Pyridine.*—In contrast to the reaction with nitriles the products of reaction between (A) and pyridine are *very* dependent on the reaction conditions. Refluxing for 5—10 min with an excess of pyridine in dichloromethane gives the crystalline compounds [$RuX_3(EPh_3)(py)_2$] (mentioned earlier [2] for X = Cl, E = As). These have been characterised by elemental analyses, molecular weight determinations, e.s.r., and magnetic measurements (Table 1). Electronic spectra are given in Table 2 and discussed later. The presence of EPh_3 and C_5H_5N is confirmed by i.r. spectroscopy and the strong ν(RuCl) band at *ca.* 340 cm^{-1} (Table 3) is indicative

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* An *X*-ray structural analysis of $AsPh_4[RhCl_4(PPh_3)_2]$,$2Me_2CO$ by A. Fraser, University of Edinburgh, confirms the *trans*-stereochemistry suggested earlier (ref. 8) and this compound is isomorphous with the corresponding ruthenium(III) anion.

[28] J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, jun., and A. S. Wilson, *Spectrochim. Acta*, 1967, **23A**, 1121 and references therein.

[29] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

[30] M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

TABLE 3

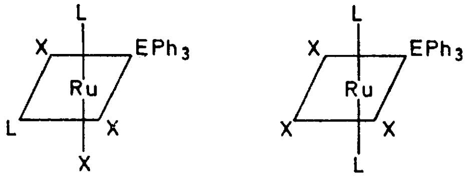
Far-infrared spectra (400—200 cm^{-1}) [a] of some ruthenium-(III) and (II)-compounds (shoulders in italics)

Compound	ν(RuX)	Other bands
$[RuCl_3(PPh_3)_2(MeCN)]$	332s	*329*s, 255w
$[RuBr_3(PPh_3)_2(MeCN)]$	265m	328m, 255w
$[RuCl_3(AsPh_3)_2(MeCN)]$	330 *vs	*326*s, 284w
$[RuBr_3(AsPh_3)_2(MeCN)]$	262m	330s, *325*s
$[RuCl_3(PPh_3)_2(PhCH_2CN)]$	*334*s	328s, 255w
$[RuBr_3(PPh_3)_2(PhCH_2CN)]$	263m	328m, 255w
$[RuCl_3(AsPh_3)_2(PhCH_2CN)]$	330 *vs	*320*s, 301w, 260w, 240m
$[RuBr_3(AsPh_3)_2(PhCH_2CN)]$	251m	328s, *320*s, *240*m
$[RuCl_3(PPh_3)_2(PhCN)]$	330s	340vs, 328s, 300w 260w
$[RuCl_3(AsPh_3)_2(PhCN)]$	332 *s	322s, *312*m
$[RuBr_3(AsPh_3)_2(PhCN)]$	251m	340s, 329s, 320s
$[RuCl_3(PPh_3)_2(MeNO_2)]$	327vs	*330*s, 227m
$[RuCl_3(PPh_3)_2(MeOH)]$	331vs	255w
$[RuBr_3(PPh_3)_2(MeOH)]$	260m	330s
$[RuCl_3(AsPh_3)_2(MeOH)]$	330 *vs	240w
$[RuBr_3(AsPh_3)_2(MeOH)]$	260m	330s, 240w
$[RuCl_3(PPh_3)(C_5H_5N)_2]$	338vs	322s, 290m, 278w, 259w, 251w, 242m, 210m
$[RuBr_3(PPh_3)(C_5H_5N)_2]$	270m	335m, 320s, 290m, 279m, 230m, 200m
$[RuCl_3(AsPh_3)(C_5H_5N)_2]$	335 *vs	345m, 330vs, 320vs, 289w, 255w, 240m, 220w, 205w
$[RuBr_3(AsPh_3)(C_5H_5N)_2]$	270s	344m, 331vs, 320vs, 285m, 254w, 224m, 200m
$[RuCl_3PPh_3(bipy)]$	335s, 295m	320s, 280w, 252w, 245m
$[RuBr_3PPh_3(bipy)]$	270m	328s, 318s, 308s, 286m, 250w
$[RuCl_3AsPh_3(bipy)]$	331 *s, 285m	338s, 318s, 300m, 250m
$[RuBr_3AsPh_3(bipy)]$	268m	336s, 325s, 315s, 308w, 292m, 259m, 241w
$[RuCl_3PPh_3(phen)]$	328vs, 298m	*328*s, 308m, 288w, 250m, 240m
$[RuBr_3PPh_3(phen)]$	272s	335s, 331s, 320s, *308m*, 290w, 250m, 240m
$[RuCl_3AsPh_3(phen)]$	330 *vs, 298m	*340*s, 310s, 288w, 250m
$[RuBr_3AsPh_3(phen)]$	261s	*340*s, *328*s, 319vs, *308*s, 288w, 228w
$[RuCl_3(PPh_3)_2Me_2SO]$	329s	290w, 225w, 218w
$[RuBr_3(PPh_3)_2Me_2SO]$	260s	330w, 305w
$[RuCl_3(AsPh_3)_2Me_2SO]$	330 *s	*345*s, 300w
$[RuBr_3(AsPh_3)_2Me_2SO]$	250w	*345*s, *325*m, *315*m
$[RuCl_3(PPh_3)(Me_2S)_2]$	335vs	*325*s, 290w
$[RuBr_3PPh_3(Me_2S)_2]$	260m	*335*s, 330s
$[RuCl_3(AsPh_3)_2Et_2S]$	334 *s, 280m	325s, 320m, 305m
$[RuBr_3(AsPh_3)_2Et_2S]$	240w	*335*m, 321s, *315*m
$[RuCl_3(PPh_3)_2CS_2]$	335vs	*329*s, 290w
$[RuBr_3(PPh_3)_2CS]$	247s	310w, 280w, 220m
$[RuCl_3(AsPh_3)_2CS_2]$	331 *s	347s, 321vs, 309s, 275w, 260m, 239m, 220m
$[RuBr_3(AsPh_3)_2CS]$	250m	*350*m, *332*s, 325vs, *319*s, *309*m, 283w, *260*m
$[RuCl_3(PPh_3)_2thf]$	325vs	*331*vs, *320*s, 275w
$[RuCl_3(AsPh_3)_2]$	330 *s, 311m	265w
$[RuBr_3(AsPh_3)_2]$	253m	330s
$[RuCl_2(PPh_3)_2C_7H_8]$	278s, 253s	325w
$[RuCl_2(PMe_2Ph)_2C_7H_8]$	277s, 253s	305w, 245s, *225*m, 220s, 210s
$[RuCl_2(AsPh_3)_2C_7H_8]$	280s, 256s	358s, *341*s, 329s, 311s, 247m
$[RuBr_2(AsPh_3)_2C_7H_8]$	<200	356s, 340m, 327s, 311s, 250m
$[Ru_2Cl_2(PPh_3)_4(bipy)_2]Cl_2$	234vs	300w, 280m, 264w, 250m, 245s, 225s
$[Ru_2Br_2(PPh_3)_4(bipy)_2]Br_2$	<200	300w, 275s, 264w, 251m, 243s, 220s
$[Ru_2Cl_2(PPh_3)_4(phen)_2]Cl_2$	235s	335w, 309w, 245w, 215m

[a] Nujol mulls.

* Partially masked by strong $AsPh_3$ vibrations.

of a *trans*-$RuCl_2$ arrangement. Although differentiation between isomers (IV) and (V) is not possible on this evidence alone (Figure 2), the close similarity of the e.s.r. and electronic spectra of these compounds with $[RuX_3(EPh_3)(bipy)]$ (see section c) suggests configuration (IV). This is also the configuration expected on the basis of the higher *trans* effect of EPh_3 compared to C_5H_5N.[31]



(IV) (V)

FIGURE 2 The two isomers (with *trans* X groups) for $[RuX_3(EPh_3)L_2]$

These appear to be the first well characterised ruthenium(III) compounds containing both pyridine and tertiary phosphine (or arsine) ligands although a number of ruthenium(III) pyridine complexes are known. These include *mer*-[23,32] and *fac*-[22] $[RuCl_3(py)_3]$, $[RuCl_2(py)_4]Cl$,[33] $pyH[RuCl_4(py)_2]$,[32] $pyH[RuCl_4CO(py)]$[2] and a number of 2,2′-bipyridyl (and 1,10-phenanthroline) compounds such as $[RuCl_3(py)(bipy)]$ and $[RuCl_2(py)_2(bipy)]Cl$.[34]

If $[RuX_3(AsPh_3)_2(MeOH)]$ is refluxed with neat pyridine for *ca.* 20 minutes, $[RuX_2(py)_4]$ is obtained. This well known compound has been synthesised by several methods in the *trans*-form and more recently the *cis*-isomer has been prepared.[35] A comparison of the i.r. and ^1H n.m.r. spectra of our products with those given in ref. 35 confirms the *trans*-configuration.

In contrast, reaction of $[RuX_3(PPh_3)_2MeOH]$ with neat pyridine gives a mixture of products which we could not separate satisfactorily. However, the ^1H n.m.r. spectra shows that one of the components is *trans*-$[RuX_2(py)_4]$ and that the other(s) are probably ruthenium(II) species (since sharp n.m.r. signals) containing both pyridine and triphenylphosphine. By reaction of $[RuBr_2(PPh_3)_3]$[2] with neat pyridine for short reaction times, it is possible to isolate a pure sample of the latter species, subsequently shown by elemental analyses to be $[RuBr_2(PPh_3)(py)_3]$. Longer reaction

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[31] See F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York and London, 1972, p. 668.

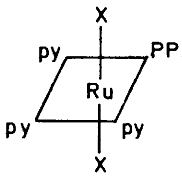
[32] J. Souček, *Coll. Czech. Chem. Comm.*, 1962, **27**, 960.

[33] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1936, 4.

[34] For detailed references see F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Austral. J. Chem.*, 1963, **16**, 42.

[35] See D. W. Raichart and H. Taube, *Inorg. Chem.*, 1972, **11**, 999 and references therein.

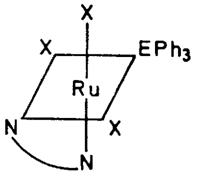
times lead to precipitation of *trans*-$[\mathrm{RuBr_2(py)_4}]$. Unfortunately, various attempts to obtain the corresponding chloro-compound from $[\mathrm{RuCl_2(PPh_3)_3}]$ and pyridine gave either $[\mathrm{RuCl_2(PPh_3)(py)_3}]$, together with a small amount of $[\mathrm{RuCl_2(py)_4}]$ (^{1}H n.m.r., i.r., and analytical evidence) or, on longer reaction times, pure *trans*-$[\mathrm{RuCl_2(py)_4}]$. Although $[\mathrm{RuCl_2(PPh_3)(py)_3}]$ could not be satisfactorily separated from $[\mathrm{RuCl_2(py)_4}]$, a careful examination of the far i.r. of the mixture, in conjunction with that of $[\mathrm{RuBr_2(PPh_3)(py)_3}]$ indicates ν(RuCl) 340 cm^{-1}, supporting the expected *trans*-configuration (VI). Rather surprisingly, in view of the normal reaction of $[\mathrm{RuX_2(PPh_3)_3}]$ with Lewis bases,[3] no evidence has been found for the unknown $[\mathrm{RuX_2(py)_2(PPh_3)_2}]$,* although the carbonyl analogues $[\mathrm{RuX_2(CO)_3(py)}]$,[14] *cis*-$[\mathrm{RuX_2(CO)_2(py)_2}]$ (X = Cl,[2,14] Br,[2,14] I,[36] $\mathrm{SnCl_3}$ [37]), and $[\mathrm{RuCl_2CO(py)_3}]$ [38] are a well established series of compounds.



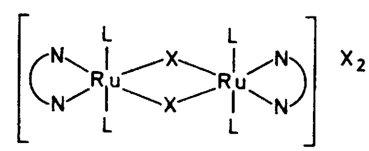
(VI)

Although *trans*-$[\mathrm{RuX_2(py)_4}]$ and *trans*-$[\mathrm{RuX_2(PPh_3)(py)_3}]$ appear quite air-stable in the solid state, dissolution in dichloromethane, benzene, or acetone results in a rapid (24 h) conversion of the initial yellow-brown solutions to deep green solutions (*cf*. ref. 35). This change is accompanied by the broadening of the n.m.r. spectral lines and the appearance of e.s.r. signals, confirming that the process is oxidative in nature. Similar oxidised species are formed when $[\mathrm{RuBr_2(PPh_3)(py)_3}]$ is melted. However, analytical data indicate that only partial oxidation to ruthenium(III) has probably occurred and therefore, these studies were not further pursued.

(c) 2,2′-*Bipyridyl and* 1,10-*Phenanthroline*.—Reaction of (A) with either excess 2,2′-bipyridyl or 1,10-phenanthroline (N–N) in dichloromethane (shaken or refluxed) give $[\mathrm{RuX_3(EPh_3)(N\text{–}N)}]$. These were characterised as previously (Tables 1—3) and represent the first examples of ruthenium complexes containing bipy (or phen) *and* tertiary arsines and of ruthenium(III) compounds containing bipy (or phen) *and* tertiary phosphines. The far i.r. spectra are complicated due to the many absorptions of the chelate ligands and it is therefore difficult to assign ν(RuX) vibrations with certainty. Nevertheless, careful examination of all these compounds (Table 3) suggests for (N–N) = bipy, ν(RuCl) 335, 295 ($\mathrm{PPh_3}$); 331, 285 cm^{-1} ($\mathrm{AsPh_3}$) which is consistent with configuration (VII).



(VII)



(VIII)

For E = P, X = Br, a small amount of a ruthenium(II) compound of empirical formula $[\mathrm{RuBr_2(PPh_3)_2(bipy)}]$ is also formed. The same compound is obtained in higher yield by reaction of $[\mathrm{RuBr_2(PPh_3)_3}]$ and 2,2′-bipyridyl in dichloromethane; similarly, $[\mathrm{RuCl_2(PPh_3)_2(bipy)}]$ can be synthesised from $[\mathrm{RuCl_2(PPh_3)_3}]$ and 2,2′-bipyridyl. The chloro-compound has been previously prepared by the reaction of $[\mathrm{RuCl_2(CS)(PPh_3)_2}]_2$ and 2,2′-bipyridyl in methanol or benzene solution;[39] the compounds are conducting in methanol and exhibit a ν(RuCl) band at 234 cm^{-1} consistent with the *dimeric* halide-bridged cationic structure (VIII) suggested earlier.[39] {*N.B.* comparison of the far-i.r. of the chloro- and bromo-compounds (Table 3) shows the bands assigned earlier[39] to ν(RuCl) are probably ligand vibrations}. The compound $[\mathrm{Ru_2Cl_2(PPh_3)_4(phen)_2}]\mathrm{Cl_2}$ [ν(RuCl) 235 cm^{-1}] is also obtained from dichloromethane solutions of $[\mathrm{RuCl_2(PPh_3)_3}]$ and 1,10-phenanthroline.

However, reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with excess of (N–N) in *methanol* gives red solutions from which the *monomeric* cations $[\mathrm{RuCl(PPh_3)(N\text{–}N)_2}]\mathrm{Cl}$ are isolated, together with small amounts of the rather insoluble $[\mathrm{Ru_2Cl_2(PPh_3)_4(N\text{–}N)_2}]\mathrm{Cl_2}$. The monomer formulation is confirmed by the ready synthesis of the hexafluorophosphate and tetraphenylboron salts. The monomeric cations are also prepared by reaction of $[\mathrm{RuCl_3PPh_3(N\text{–}N)}]$ and an excess of (N–N) in methanol.

In contrast, the reaction of $[\mathrm{RuCl_3(AsPh_3)(bipy)}]$ with an excess of bipyridyl in methanol gives a mixture of products, neither of which contain triphenylarsine. One of these is the well known orange $[\mathrm{Ru(bipy)_3}]\mathrm{Cl_2,6H_2O}$ [40] which we have also characterised by synthesis of the $\mathrm{BPh_4^-}$ salt. In addition, small amounts of purple $[\mathrm{RuCl(H_2O)(bipy)_2}]\mathrm{Cl,H_2O}$ previously synthesised in higher yields by several methods,[41,19] can be isolated. However, if a mixture of $[\mathrm{RuCl_3(AsPh_3)(bipy)}]$, bipyridyl, *and* sodium tetraphenylboron are refluxed in methanol, the only product is $[\mathrm{RuCl(AsPh_3)(bipy)_2}]\mathrm{BPh_4}$.

The detailed chemistry of these and other ionic ruthenium(II) compounds will be discussed more fully in a later publication.

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* *Note added in proof:* Samples of $[\mathrm{RuCl_2(PPh_3)(py)_3}]$ and $[\mathrm{RuCl_2(py)_2(PPh_3)_2}]$ have been obtained by reaction of $[\mathrm{RuCl_2(PPh_3)_2}]$ with pyridine (R. K. Poddar and U. Agarwala, *J. Inorg. Nuclear Chem.*, 1973, **35**, 567).

[36] J. V. Kingston and G. R. Scollary, *J. Inorg. Nuclear Chem.*, 1972, **34**, 227.

[37] J. V. Kingston, J. W. S. Jamieson, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1967, **29**, 133.

[38] S. D. Robinson and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 300.

[39] J. D. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2198.

[40] See R. F. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, 1970, **92**, 2343, and references therein.

[41] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, 1971, **93**, 1294.

Sulphur Ligands

(a) *Dimethyl Sulphoxide.*—As for pyridine, the products of reaction between A and dimethyl sulphoxide are dependent on the reaction conditions. If A and a DMSO–water mixture (1 : 1 by volume) are shaken for 24 h, the only products are [RuX$_3$(EPh$_3$)$_2$(dmso)]. The i.r. spectra show several absorptions in the region 1000—900 cm^{-1}, indicative of *O*-bonded dmso but no band >1100 cm^{-1}, which could be attributed to an *S*-bonded sulphoxide group.[42] Synthesis of the corresponding [^{2}H$_6$]dmso compound (for X = Cl, E = As) confirms the formation of only an *O*-bonded isomer [ν(SO) 935 cm^{-1}]. The presence of a strong ν(RuCl) band at *ca.* 330 cm^{-1}, together with the close similarity of e.s.r. and electronic spectral patterns to other [RuX$_3$(EPh$_3$)$_2$L] complexes is consistent with configuration (I).

The same compounds are rapidly formed when the reaction is carried out in neat DMSO. However, on further shaking (for E = As), the orange-brown suspensions slowly dissolve giving a lemon-yellow solution (X = Cl), whereas for the bromide, a substantial amount of pale yellow crystalline precipitate is formed. The latter contains no triphenylarsine and analyses for [RuBr$_2$(dmso)$_4$]. The i.r. spectrum of this compound shows a strong band at 1080 cm^{-1} assigned to *S*-bonded dmso (*cf.* [Ru(NH$_3$)$_5$(dmso)]$^{2+}$ ν(so) 1042 cm^{-1})[43] but no bands which can be *definitely* attributed to *O*-bonded dmso. The absence of *O*-bonded dmso groups are confirmed by synthesis of [RuBr$_2$([^{2}H$_6$]-dmso)$_4$] (see Experimental section). The ^{1}H n.m.r. spectrum of [RuBr$_2$(dmso)$_4$] (in CDCl$_3$) is rather complex. At 301 K, it consists of five singlets at τ 6·49, 6·52, 6·56, 6·61, and 7·39. By analogy with recent studies on palladium and platinum(II) dialkyl sulphoxide compounds,[44] the four resonances τ 6·49—6·61 correspond to *S*-bonded dmso and the peak at τ 7·39 to free DMSO. In agreement with the i.r. evidence, there is no evidence for any *O*-bonded dmso (*ca.* τ 7·0).[44] The relative intensity of the *S*-bonded resonances to free DMSO is *ca.* 3 : 1. However, cooling the solution to 241 K changes the relative intensities to *ca.* 4 : 1 and an examination of the relative intensities of the *S*-bonded resonances indicates that the one at τ 6·56 decreases with respect to the rest. Addition of free DMSO at 301 K also produces a substantial *decrease* in the intensity of the 6·56 resonance. Thus, these observations are consistent with dissociation of [RuBr$_2$(dmso)$_4$] in solution, probably to [RuBr$_2$(dmso)$_2$(solvent)$_2$] (τ 6·56) and DMSO (τ 7·39) {*cf.* the facile dissociation of [RuX$_2$(PPh$_3$)$_4$] [2]}. Unfortunately, [RuBr$_2$(dmso)$_4$] appears too insoluble for direct molecular weight measurements.

The three singlets at τ 6·49, 6·52, and 6·61 do not decrease in intensity on addition of DMSO, indicating they do not arise from dissociation products of [RuBr$_2$(dmso)$_4$]. The best explanation for these we can offer, at present, is to assign the τ 6·49 resonance to the eight equivalent methyl groups in *trans*-[RuBr$_2$(dmso)$_4$] (assuming free rotation of methyl groups even at 241 K (*cf.* ref. 44) and the 6·52 and 6·61 resonances to the two different dmso sets in *cis*-[RuBr$_2$(dmso)$_4$], the higher resonance corresponding to the dmso ligands *trans* to the bromo-groups. Raising the temperature increases the intensity of the resonance at τ 6·49 with respect to those at τ 6·52 and 6·61. This is consistent with a report by James *et al.*[45] who have recently synthesised [RuX$_2$(dmso)$_4$] (X = Cl or Br) by reaction of RuX$_3$ and DMSO mixtures with hydrogen at 80° for 20 h. The far-i.r. spectrum shows ν(RuCl) 345 cm^{-1}, indicative of a *trans*-structure.

However, they also suggest that their chloro-compound may contain both *S- and O*-bonded dmso groups although the i.r. spectrum of the deuteriated compound is required for confirmation. Unfortunately, our attempts to isolate [RuCl$_2$(dmso)$_4$] from the reaction of [RuCl$_3$(AsPh$_3$)$_2$MeOH] and DMSO have proved so far to be unsuccessful. This can be attributed to the high solubilty of [RuCl$_2$(dmso)$_4$] in DMSO and the consequent difficulty of removing the high boiling solvent without decomposition of the product.*

However, heating [RuBr$_2$(dmso)$_4$] to 333 K in an n.m.r. tube and then cooling the solution to low temperature reveals an extra resonance at τ 7·09 (241 K). On raising the temperature, this moves to higher field. Similarly, recrystallisation of [RuBr$_2$(dmso)$_4$] from hot CHCl$_3$–acetone solution gives a darker coloured material with additional i.r. bands at 1120, 930, and 920 cm^{-1} (*cf.* ref. 45). In addition, the ^{1}H n.m.r. (301 K) shows an extra weak peak at τ 7·30 indicative of some *O*-bonded dmso. However, the analysis of the recrystallised product is *ca.* 3% too low in carbon for [RuBr$_2$(dmso)$_4$] and the resonance at τ 6·49 has broadened considerably, suggesting that some oxidation of the product may have occurred. In fact, if solutions of [RuBr$_2$(dmso)$_4$] are left exposed to air for prolonged periods, dark green solutions are formed which exhibit very broad n.m.r. signals, indicating that substantial oxidation has occurred.

Clearly, the method of preparation of [RuX$_2$(dmso)$_4$] is very critical in determining the isomeric composition of the product and further studies are in progress to unravel this interesting problem.

(b) *Dialkyl Sulphides.*—Reaction of (A) with Me$_2$S in

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* *Note added in proof:* Samples of [RuCl$_2$(dmso)$_4$] and [RuCl$_2$([^{2}H$_6$]dmso)] have been isolated from very concentrated DMSO and [^{2}H$_6$]DMSO solutions respectively. The ^{1}H n.m.r. spectrum of the former is very similar to that recently reported for [RuCl$_2$(dmso)$_4$], prepared from RuCl$_3$,3H$_2$O and DMSO (Wilkinson *et al.*, *J.C.S. Dalton*, 1973, 204), *i.e.* singlets at τ 6·48, 6·51, 6·57, 6·62, 6·66, 7·27, 7·31, and 7·39. However, our i.r. studies reveal only a very weak *O*-bonded dmso band [ν(SO) 930 cm^{-1} in the [^{2}H$_6$]dmso complex] and this is consistent with the very low intensity of the resonances at τ 7·27 and 7·31 compared to the *S*-bonded resonances.

[42] For a detailed discussion, see B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 1969, **8**, 971 and references therein.

[43] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

[44] J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.

[45] B. R. James, F. Ochiai, and G. L. Rempel, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 781.

CH_2Cl_2 gives $[RuX_3(EPh_3)(Me_2S)_2]$. The ^1H n.m.r. spectrum of $[RuCl_3(AsPh_3)(Me_2S)_2]$ shows resonances τ 1·33 (*para*), 2·62 (*ortho*), 3·34 (*meta*), and 4·60 (methyl) which have been shifted and broadened by the paramagnetic ruthenium(III) ion. This is unusual since in the majority of ruthenium(III) compounds made from (A), the n.m.r. resonances are too broadened to be observed. However, similar contact-shifted spectra are observed for *mer*-$[RuCl_3(PMe_2Ph)_3]$,[46] $[Ru(acac)_3]$,[47] and $[Ru(S_2PPh_2)_3]$ (see section d) whereas $[RuBr_3AsPh_3(Me_2S)_2]$ gives very broad n.m.r. signals. The differences are probably due to substantial variations in the electron spin–lattice relaxation time in these compounds although the factors responsible for these variations are not at present clear.

Examination of the far-i.r. spectra of $[RuX_3(EPh_3)(Me_2S)_2]$ reveals a strong ν(RuCl) band at *ca.* 335 cm^{-1} consistent with configuration (IV). For X = Cl, E = P, an additional product was isolated from the reaction mixture. Unfortunately, analyses (and m.p.) indicate a mixture, possibly of $[RuCl_3(PPh_3)_2Me_2S]$ and $[RuCl_2(PPh_3)_2(Me_2S)_2]$, which we have been unable to separate by either chromatography or recrystallisation. However, a pure sample of the latter was readily obtained by reaction of $[RuCl_2(PPh_3)_3]$ and Me_2S.

In contrast, reaction of $[RuX_3(AsPh_3)_2MeOH]$ with an excess of Et_2S gives $[RuX_3(AsPh_3)_2Et_2S]$ [ν(RuCl) 334 cm^{-1} consistent with configuration (I)]. Extended reaction leads to products possibly containing the *bis*-sulphides but these could not be separated satisfactorily from the *mono*-sulphides. For $[RuX_3(PPh_3)_2MeOH]$ even short reaction times give a complicated mixture of products which could not be separated, even by dry column chromatography.[48]

Reaction of Ph_2S with $[RuCl_3(AsPh_3)_2MeOH]$ gives a brown solid which i.r. spectroscopy and analyses confirm contains no Ph_2S but is $[RuCl_3(AsPh_3)_2]$. These results suggest that the donor ability of organic sulphides in these compounds is $Me_2S > Et_2S \gg Ph_2S$ but this does not necessarily reflect the intrinsic bonding ability of the sulphur atom towards ruthenium(III) since steric repulsions of EPh_3 groups will probably play an important role.

Although a number of ruthenium mono-, di-, and trisulphide compounds have been recently reported,[22,49] these complexes represent the first examples of dialkyl sulphides and tertiary phosphines (or arsines) bonded to ruthenium(II) and (III).

(c) *Carbon Disulphide.*—Reaction of $[RuCl_3(EPh_3)_2MeOH]$ with CS_2 under reflux conditions gives microcrystalline brown precipitates whose i.r. spectra (4000—400 cm^{-1}) are similar to the starting materials, except for the presence of a broad band at 1510 cm^{-1} which indicates a linearly bonded CS_2 group. No bands due to thiocarbonyl (*ca.* 1280—1330 cm^{-1}) or π-CS_2 (*ca.* 1120 or 1020 cm^{-1}) linkages are present.[50] The compounds analyse for $[RuCl_3(EPh_3)_2CS_2]$, a formulation supported by magnetic measurements. The far-i.r. spectra are rather complex but the probable assignment of ν(RuCl) (E = P) at 335 cm^{-1} supports configuration (I). As in other complexes containing linearly bonded CS_2,[51] the CS_2 in $[RuCl_3(AsPh_3)_2(CS_2)]$ is easily lost. Attempts to recrystallise the compound from CH_2Cl_2 or C_6H_6 give only $[RuCl_3(AsPh_3)_2]$. However, the CS_2 group is not lost from the solid even after prolonged drying *in vacuo* at 80° and the solid does not smell of CS_2. In contrast, several rhodium and iridium complexes with linear CS_2 ligands readily lose CS_2 from the solid by pumping *in vacuo* or even washing with ether.[51,52]

However, reaction of $[RuBr_3(EPh_3)_2MeOH]$ with CS_2 under reflux for 30 min gives products whose i.r. spectra exhibit thiocarbonyl bands at *ca.* 1300 but no bands at 1500 cm^{-1}. These compounds analyse for $[RuBr_3(EPh_3)_2(CS)]$. Shorter reaction times give a mixture of this compound and $[RuBr_3(EPh_3)_2(CS_2)]$ (i.r. and analytical evidence). The reason for the non-formation of the thiocarbonyl complex for X = Cl is not understood. These represent the first carbon disulphide and thiocarbonyl compounds of ruthenium(III) although ruthenium(II) compounds such as $[RuCl(\pi\text{-}CS_2)(PPh_3)_3]Cl$,[39] $[RuCl_2(CS)(PPh_3)_2]_2$,[39] $[Ru_2Cl_4(CS)(PPh_3)_4]$,[53] and $[RuCl_3CS(PPh_3)_2]^-$ [54] have recently been synthesised.

(d) *Sodium Diphenylphosphinodithioate.*—Reaction of $[RuCl_3(AsPh_3)_2L]$ (L = MeOH or $PhCH_2CN$) with NaS_2PPh_2 in acetone produces the violet, crystalline compound $[Ru(S_2PPh_2)_3]$. The same compound is also prepared from $Me_4N[RuBr_4(AsPh_3)_2],2(Me_2CO)$ (or ' $RuCl_3,xH_2O$ ') and NaS_2PPh_2. This compound is of interest in that its ^1H n.m.r. spectrum exhibits contact shifted *ortho*-, *meta*-, and *para*-protons at τ 4·35, 2·64, and 2·94 respectively and also because it is a rare example, in this series, of the displacement of *all* ligands with retention of the ruthenium(III) oxidation state. The corresponding $[Ru(S_2PEt_2)_3]$ is mentioned briefly, elsewhere,[55] but no preparative details have been given.

In contrast, reaction of $[RuCl_3(AsPh_3)_2MeOH]$ with NaS_2PR_2 (R = Me or Et) gives the ruthenium(II) compounds *trans*-$[Ru(S_2PR_2)_2(AsPh_3)_2]$. The chemistry of these and related dithioacid compounds of ruthenium(II) are discussed in detail elsewhere.[56]

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[49] B. E. Aires, J. E. Fergusson, D. T. Howarth, and J. M. Miller, *J. Chem. Soc.* (*A*), 1971, 1144.

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[51] M. P. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2813.

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[54] T. A. Stephenson and E. S. Switkes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 805.

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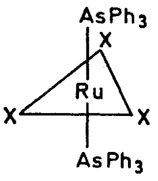
[56] D. J. Cole-Hamilton and T. A. Stephenson, to be published.

Oxygen Ligands

If (A) is shaken in tetrahydrofuran (THF), displacement of methanol occurs and the compounds $[RuX_3(EPh_3)_2(thf)]$ can be isolated from the reaction mixture. These compounds are not very stable, readily losing THF on recrystallisation and slowly on air-exposure of the solid.

$[RuX_3(AsPh_3)_2MeOH]$ also loses the methanol group in CH_2Cl_2, $CHCl_3$, or C_6H_6 solution giving yellow-brown solutions. Addition of heptane gives brown solids, analysing closely for $[RuX_3(AsPh_3)_2]$, irrespective of the solvent used. The i.r. spectra (4000—400 cm^{-1}) are identical to the starting materials except for the absence of methanol bands at 3480 and 1010 cm^{-1} and the far-i.r. spectrum reveals strong ν(RuCl) vibrations at 330 and 311 cm^{-1} but no evidence for bridging chloro-groups. Although the compounds are not sufficiently soluble for molecular weight measurements, an e.s.r. spectrum of $[RuCl_3(AsPh_3)_2MeOH]$ in $CHCl_3$ shows a 2 *g* value spectrum, (g_1 2·52; g_2 2·03 in $CHCl_3$ at 77 K), which indicates the presence of an axially symmetric complex such as (IX). The intensity of the e.s.r. signals, coupled with the normal magnetic moments found for the $[RuX_3(EPh_3)_2MeOH]$ compounds in both solid and solution state also support their formulation as monomeric, magnetically-dilute ruthenium(III) compounds. Several five-co-ordinate ruthenium(II) compounds of this type are known, *e.g.* $[RuCl_2(EPh_3)_3]$ (E = P [57] or As [58]) and the compounds $[RuX_3(EPh_3)_2]$ (E = P or As) were mentioned by Vaska and Sloane [59] but no preparative or other details about them are available.



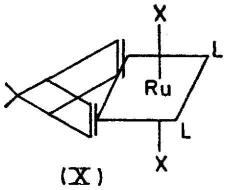
(IX)

In contrast, dissolution of $[RuX_3(EPh_3)_2MeOH]$ in acetone or nitromethane gives solvates which are surprisingly stable and which can be recrystallised without loss of solvent. The nitromethane compound $[RuCl_3(PPh_3)_2MeNO_2]$ is an excellent precursor for the synthesis of most of the chloro-phosphine compounds reported in this paper. Its main advantage over $[RuCl_3(PPh_3)_2MeOH]$ is the ease of preparation *via* $AsPh_4[RuCl_4(PPh_3)_2]$ (which is prepared from $[RuCl_2(PPh_3)_3]$).[8] The methanol solvate can only be prepared in low yield (40%) and on a small scale from '$RuCl_3,xH_2O$' (0·2 g) and stoicheiometric amounts of PPh_3.[2] Attempts to 'scale-up' this reaction (to 1·0 g of '$RuCl_3,xH_2O$') gave only the reduced product $[RuCl_2(PPh_3)_3]$, which is probably the result of the creation of concentration gradients in the solution.

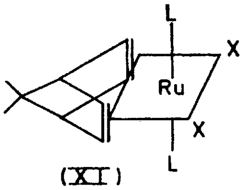
Carbon Donors

(a) *Bicyclo*[2,2,1]*hepta*-2,5-*diene* (*Norbornadiene*).—A number of ruthenium(II) diolefin compounds, such as $[RuX_2C_7H_8]_n$,[60] $[RuX_2CO(C_7H_8)]_2$,[38] and $[RuX_3COC_7H_8]^-$,[54] have been synthesised in recent years but no diene compounds of ruthenium(III) are known. An attempt to prepare a ruthenium(III) diene compound by reaction of (A) with excess of C_7H_8 in refluxing CH_2Cl_2 produced no reaction. However, in refluxing benzene, crystalline, diamagnetic precipitates are obtained which analyse quite closely for $[RuX_2(EPh_3)_2C_7H_8]$. For E = P, the same compounds can be synthesised from $[RuX_2(PPh_3)_{3\text{ or }4}]$ and C_7H_8.[38] Although the compounds are too insoluble for ^1H n.m.r. studies, a careful examination of their far-i.r. spectra (Table 3) suggests that two ν(RuCl) vibrations occur at 278 and 253 cm^{-1} (E = P). Thus, configuration (X) with *trans*-chlorides is unlikely because of the low ν(RuCl) values. The other possibilities, *i.e.* where both chloride groups are *trans* to the diene (XI) or where one chloride is *trans* to the diene and the other is *trans* to a phosphine (or arsine) (XII), cannot be distinguished on i.r. evidence alone, especially since earlier work [29] indicates that olefins, tertiary phosphines, and arsines all have a similar *trans* effect on ν(MCl) vibrations.

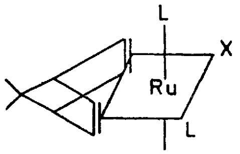
However, we have also prepared the corresponding $[RuCl_2(PMe_2Ph)_2C_7H_8]$ [ν(RuCl) 277 and 253 cm^{-1}] from $Ph_3BzP[RuCl_3COC_7H_8]$ [54] and PMe_2Ph and the ^1H n.m.r. spectrum unequivocally shows *trans*-PMe_2Ph groups (virtually coupled 'triplet') [30] and the *three* diene resonances expected for configuration (XI). Similar compounds $[RuHXL_2(diene)]$ [L = PPh_3, $P(OR)_3$, *etc.*] [61] and $[Ru(OH)_2(CO)_2C_7H_8]$ [62] (but with *cis*-L and –CO groups respectively) have recently been reported.



(X)



(XI)



(XII)

The reaction of $[RuCl_3(AsPh_3)_2MeOH]$ with 1,5-cyclo-octadiene in benzene gave only $[RuCl_2(C_8H_{12})]_n$ [60]

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[57] S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

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[59] L. Vaska and E. M. Sloane, *J. Amer. Chem. Soc.*, 1960, **82**, 1263.

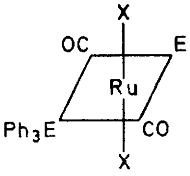
[60] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

[61] J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

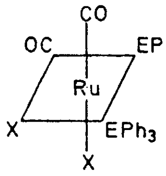
[62] R. B. King and P. N. Kapoor, *Inorg. Chem.*, 1972, **11**, 336.

and attempts to prepare ethylene and diphenylacetylene complexes gave only [$RuCl_3(AsPh_3)_2$].

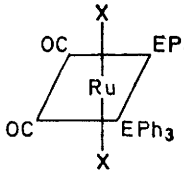
(b) *Carbon Monoxide.*—The reaction of [$RuCl_3(AsPh_3)_2MeOH$] with carbon monoxide in dichloromethane results in the formation of a pale yellow, diamagnetic, monomeric solid which analyses for *trans*-[$RuCl_2(CO)_2(AsPh_3)_2$] [ν(CO) 1993 cm^{-1} (CH_2Cl_2)]. A similar product is obtained from [$RuCl_3(PPh_3)S$] (S = MeOH or $MeNO_2$). This isomer (for E = P) has been prepared earlier [from $RuCl_2(PPh_3)_{3\text{ or }4}$] [2,63] and assigned configuration (XIII) [ν(RuCl) 334 cm^{-1}]. Recrystallisation of (XIII) from hot benzene gives the *cis*-isomer [2] [ν(CO) 2061 and 1999 cm^{-1}] whose far-i.r. spectrum (E = P) shows ν(RuCl) bands at 300 and 275 cm^{-1} which is consistent with configuration (XIV) but not (XV). However, recrystallisation of (XIII) (E = As) from cold CH_2Cl_2–methanol solutions causes several carbonyl bands to develop. A band at 1943 cm^{-1} first appears and then the growth of further bands at 2036 and 1978 cm^{-1} occurs although the mixture still analyses for [$RuCl_2(CO)_2(AsPh_3)_2$]. By analogy with the earlier PPh_3 studies,[63] the 1943 cm^{-1} band is assigned to the other *trans*-isomer (XVI) and the 2036, 1978 cm^{-1} bands to the *cis*-isomer (XVII). Similar results were found for [$RuBr_2(CO)_2(AsPh_3)_2$].



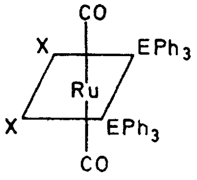
(XIII)



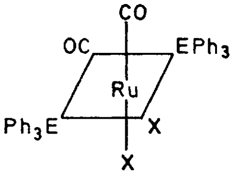
(XIV)



(XV)



(XVI)



(XVII)

However, no evidence has been found for the formation of ruthenium(III) compounds such as the unknown [$RuCl_3(AsPh_3)_2CO$]. The compound [$RuBr_3(PPh_3)_2CO$] has been briefly reported [7] but no further details are available.

The electronic spectra (50 000—12 000 cm^{-1}) of a number of these ruthenium(III) compounds are given in Table 2. A close examination of these results reveals that the absorptions between 30 000 and 12 000 cm^{-1} are virtually independent of whether E = P or As, or of the nature of L. However, the position of the absorption bands depends markedly on the nature of X, shifting to lower energy when X changes from chloride to bromide. Similar results have been found in the electronic spectra of [RuX_6]$^{3-}$ [64] and various halogenobipyridylruthenium(III) compounds.[65] Hence, these can be assigned principally to X $\longrightarrow$ Ru charge transfer transitions.

The more intense absorptions >30 000 cm^{-1} can be assigned to intra-ligand transitions superimposed on ligand metal charge-transfer transitions which arise from the tertiary phosphine, arsine, and the other ligand groups (*cf.* [$Ru(NH_3)_5RCN$]$^{3+}$ with an absorption band at 31 500 cm^{-1} assigned to RCN $\longrightarrow$ Ru charge transfer transitions [21]). However, the complexity of this region makes assignment of the bands to specific energy processes an impossible task.

EXPERIMENTAL

Microanalyses were by the N.P.L., Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer–Hitachi osmometer (model 115) at 37 °C. I.r. spectra were recorded in the region 4000—200 cm^{-1} on a Perkin-Elmer 225 grating spectrometer, using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer using unmatched silica cells. ^1H N.m.r. spectra and solution magnetic moments (Evans' method) [66] were obtained on a Varian HA 100 spectrometer. Magnetic susceptibilities (solid) were measured on the Faraday balance at Newcastle University. E.s.r. measurements were performed on a Hilger & Watts ' Microspin ' spectrometer operated at 9·33 GHz and employing 100 kHz magnetic field modulation and phase-sensitive detection. The magnetic field was measured by means of a proton resonance meter and *g* factors were calculated by using a dilute polycrystalline sample of 1,1-diphenyl-2-picrylhydrazyl (*g* = 2·0036) as reference. Conductivity measurements were made on a Portland Electronics conductivity bridge (model 310) and m.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

Nitrogen Ligands

(a) *Nitriles.—Trichlorobis(triphenylarsine)(methyl cyanide)ruthenium*(III). Trichlorobis(triphenylarsine)(methanol)ruthenium(III) (0·10 g) was added to methyl cyanide (5 ml) and the green suspension shaken for 1 h. The resulting dark green *crystals* were collected and recrystallised from CH_2Cl_2–pentane (Yield 76%) [ν(CN) 2305 cm^{-1}]. Similarly, [$RuBr_3(AsPh_3)_2MeCN$] [ν(CN) 2310 cm^{-1}] was prepared and recrystallised (78%). The reaction of [$RuCl_3(PPh_3)_2MeOH$] with MeCN gave [$RuCl_3(PPh_3)_2MeCN$] [ν(CN) 2306 cm^{-1}] (75%) and the bromophosphine compound was similarly prepared [ν(CN) 2310 cm^{-1}] (74%).

Trichlorobis(triphenylarsine)(benzyl cyanide)ruthenium(III). [$RuCl_3(AsPh_3)_2MeOH$] (0·30 g) was stirred for 24 h in dichloromethane (40 ml) with an excess of benzyl cyanide (1·0 ml) under nitrogen. The resulting green solution was reduced in volume and the addition of diethyl ether gave a green precipitate. Recrystallisation from CH_2Cl_2–heptane gave the bright green *powder* (71%) [ν(CN) 2300 cm^{-1}].

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[63] R. B. James and L. D. Markham, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 373.

[64] C. K. Jorgensen, ' Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, Oxford, 1962.

[65] G. M. Bryant and J. E. Fergusson, *Austral. J. Chem.*, 1971, **24**, 275.

[66] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

Purple [$RuBr_3(AsPh_3)_2(PhCH_2CN)$] was prepared by the same method (71%) [ν(CN) 2300 cm^{-1}].

Trichlorobis(triphenylphosphine)(benzyl cyanide)ruthenium(III). As for [$RuCl_3(AsPh_3)_2PhCH_2CN$] except the reaction time was only 5 h. Recrystallisation from CH_2Cl_2–pentane gave bright green microcrystals of the product (60%) [ν(CN) 2310 cm^{-1}]. However, prolonged treatment gave cis-*dichlorobis(triphenylphosphine)bis(benzyl cyanide)ruthenium*(II) as a crystalline pale green *solid* (yellow when powdered), m.p. 158° (Found: C, 65·1; H, 4·4; N, 3·0. Calc. for $C_{52}H_{44}Cl_2N_2P_2Ru$ C, 67·0; H, 4·3; N, 3·0%). This product is the same as that prepared from [$RuCl_2(PPh_3)_3$] and benzyl cyanide.[3] [ν(CN) 2269, 2243 cm^{-1}]. *Tribromobis(triphenylphosphine)(benzyl cyanide)ruthenium*(III) was prepared as for the chlorophosphine compound (60%) [ν(CN) 2300 cm^{-1}], prolonged reaction giving some reduced species.

Trichlorobis(triphenylarsine)(phenyl cyanide)ruthenium(III). [$RuCl_3(AsPh_3)_2MeOH$] (0·20 g) was dissolved in CH_2Cl_2 (20 ml), an excess of phenyl cyanide added (0·5 ml) and the solution refluxed for 1 h under nitrogen. The resulting green solution was reduced in volume and the green residue recrystallised from CH_2Cl_2–heptane (71%) [ν(CN) 2280 cm^{-1}]. The same product is obtained by stirring for 24 h. [$RuBr_3(AsPh_3)_2PhCN$] (70%) [ν(CN) 2278 cm^{-1}] and [$RuCl_3(PPh_3)_2PhCN$] (70%) [ν(CN) 2280 cm^{-1}] were prepared by the same method. The corresponding [$RuX_3(EPh_3)_2CH_2CHCN$] were also prepared by this method [E = As, 75%; ν(CN) 2305 cm^{-1}; E = P, 60%].

(b) *Pyridine.*— *Trichlorotriphenylarsinebis(pyridine)ruthenium*(III). [$RuCl_3(AsPh_3)_2MeOH$] (0·20 g) and an excess of pyridine (0·4 ml) in CH_2Cl_2 (10 ml) were gently refluxed for 5 min. Addition of light petroleum (b.p. 100—120°) gave an orange *precipitate* recrystallised from CH_2Cl_2–pentane (88%). [$RuBr_3(AsPh_3)(py)_2$] and [$RuX_3(PPh_3)(py)_2$] were prepared in the same way (90%).

trans-*Dichlorotetrakispyridineruthenium*(II). [$RuCl_3(AsPh_3)_2MeOH$] (0·20 g) and an excess of pyridine (0·4 ml) were heated for *ca.* 20 min and the resulting orange-red *precipitate* recrystallised from acetone–light petroleum (b.p. 100—120°) or CH_2Cl_2–pentane, m.p. 270° (decomp.) (89%) (Found: C, 49·2; H, 4·1; N, 11·6. Calc. for $C_{20}H_{20}Cl_2N_4Ru$: C, 49·2; H, 4·1; N, 11·5%). The same compound was prepared from [$RuCl_2(PPh_3)_3$] and an excess of pyridine under the same conditions.

^{1}H N.m.r. ($CDCl_3$) τ 1·44(d), 2·40(t), 2·90(t) (see ref. 35); ν(RuCl) 340 cm^{-1}. Similarly, trans-*dibromotetrakispyridineruthenium*(II) was prepared starting from [$RuBr_3(AsPh_3)_2MeOH$] or [$RuBr_2(PPh_3)_3$], m.p. >280° (decomp.) (90%). (Found: C, 43·1; H, 3·6; N, 10·0. Calc. for $C_{20}H_{20}Br_2N_4Ru$: C, 41·7; H, 3·5; N, 9·7%). ^{1}H N.m.r. ($CDCl_3$) τ 1·28(d), 2·36(t), 2·92(t) (see ref. 35).

trans-*Dibromo(triphenylphosphine)trispyridineruthenium*(II). [$RuBr_2(PPh_3)_3$] (0·20 g) was dissolved in an excess of pyridine (0·3 ml) and gently heated for 10—15 min. Addition of pentane gave a yellow *powder* recrystallised from CH_2Cl_2–pentane, m.p. 198° (71%) [Found: C, 53·1; H, 4·0; N, 5·7; *M*(C_6H_6) 740. $C_{33}H_{30}Br_2N_3PRu$ requires C, 52·1; H, 4·0; N, 5·5%; *M* 671]. ^{1}H N.m.r. ($CDCl_3$) τ 1·00(t), 2·40(t), 3·26(t) [C_5H_5N], and 2·6—2·9 (multiplet) [Ph_3P]. trans-*Dichloro(triphenylphosphine)trispyridineruthenium*(II) was prepared from [$RuCl_2(PPh_3)_3$] by the same method but could not be satisfactorily separated from a small amount of [$RuCl_2(py)_4$] which is also formed.

^{1}H N.m.r. ($CDCl_3$) of mixture; [$RuCl_2(PPh_3)(py)_3$]: τ 1·10(d), 2·40(t), 3·14(t) [C_5H_5N], and 2·6—2·9 (multiplet) [Ph_3P]. *trans*-[$RuCl_2(py)_4$]: τ 1·44(d) (the resonances at τ 2·40 and 2·90 are masked by those from [$RuCl_2(PPh_3)(py)_3$] (Found: C, 55·3; H, 4·3; N, 7·9. [$RuCl_2(PPh_3)py_3$] requires C, 59·1; H, 4·4; N, 6·3%).

(c) *2,2′-Bipyridyl.*— *Trichlorotriphenylarsine(2,2′-bipyridyl)ruthenium*(III). [$RuCl_3(AsPh_3)_2MeOH$] (0·31 g) was stirred under nitrogen with a CH_2Cl_2 solution (40 ml) containing an excess of 2,2′-bipyridyl (0·11 g). Concentration of the resulting dark red solution followed by heptane addition gave the brown *product* recrystallised from CH_2Cl_2–heptane (80%). [$RuBr_3(AsPh_3)(bipy)$] and [$RuCl_3(PPh_3)(bipy)$] were similarly prepared (79% and 90% yield respectively).

Tribromotriphenylphosphine(2,2′-bipyridyl)ruthenium(III). [$RuBr_3(PPh_3)_2MeOH$] (0·10 g) in CH_2Cl_2 (20 ml) was stirred under nitrogen with an excess of 2,2′-bipyridyl. After 3 h a golden-yellow solid was filtered off and the reaction continued for two further hours to give a dark red solution. Precipitation by heptane and recrystallisation from CH_2Cl_2–heptane gave the dark red *product* (50%). The golden-yellow solid was identified as the reduced species *bis(triphenylphosphine)(2-2′-bipyridyl)ruthenium*(II)-*μ-dibromo-bis(triphenylphosphine)(2,2′-bipyridyl)ruthenium*(II) *dibromide* m.p. 295—296° (Found: C, 57·6; H, 3·9; N, 3·2. $C_{92}H_{76}Br_4N_4P_4Ru_2$ requires C, 58·6; H, 4·0; N, 3·0%). The same compound was also made from [$RuBr_2(PPh_3)_3$] (0·20 g) and 2,2′-bipyridyl (0·04 g) in CH_2Cl_2 (15 ml) stirred under nitrogen for 30 min [Λ (7 × 10^{-5}M) in MeOH = 90 S cm^2 mol^{-1}]. Similarly, [$Ru_2Cl_2(PPh_3)_4(bipy)_2]Cl_2$ was prepared from [$RuCl_2(PPh_3)_3$] and 2,2′-bipyridyl, m.p. >300° (Found: C, 63·7; H, 4·3; N, 3·2. Calc. for $C_{92}H_{76}Cl_4N_4P_4Ru_2$: C, 64·0; H, 4·4; N, 3·2%) [Λ (7 × 10^{-5}M) in MeOH = 88 S cm^2 mol^{-1}].

Chloro(triphenylphosphine)bis(2,2′-bipyridyl)ruthenium(II) *chloridemonohydrate.* [$RuCl_3(PPh_3)(bipy)$] (0·10 g) was refluxed under nitrogen in methanol (100 ml) for 24 h with an excess of 2,2′-bipyridyl (0·04 g). Concentration of the resulting red solution and recrystallisation from acetone–pentane gave the orange *product*, m.p. 235° (78%) (Found: C, 58·3; H, 4·3; N, 7·7. $C_{38}H_{33}Cl_2N_4OPRu$ requires C, 59·7; H, 4·3; N, 7·3%) [Λ (1 × 10^{-3}M) in CH_2Cl_2 = 29 S cm^2 mol^{-1}]. The same product was obtained from [$RuCl_2(PPh_3)_3$] and an excess of bipyridyl in methanol (55%) (Found: C, 59·3; H, 4·3; N, 7·1%) together with some [$Ru_2Cl_2(PPh_3)_4(bipy)_2]Cl_2$ (35%).

The corresponding [$RuCl(PPh_3)(bipy)_2]PF_6$ was prepared from NH_4PF_6 and [$RuCl(PPh_3)(bipy)_2]Cl,H_2O$ in methanol m.p. 210° (Found: C, 51·9; H, 3·6; N, 6·5. $C_{38}H_{31}ClF_6N_4P_2Ru$ requires C, 52·2; H, 3·5; N, 6·4%). Similarly [$RuCl(PPh_3)(bipy)_2]BPh_4$, m.p. 230° (Found: C, 73·1; H, 5·2; N, 5·5. $C_{62}H_{51}BClN_4PRu$ requires 72·3; H, 4·9; N, 5·4%).

Chloro(triphenylarsine)bis(2,2′-bipyridyl)ruthenium(II) *tetraphenylborate.* [$RuCl_3AsPh_3(bipy)$] (0·10 g) was refluxed in methanol (100 ml) under nitrogen with an excess of sodium tetraphenylboron (0·10 g) and 2,2′-bipyridyl (0·04 g) for *ca.* 1 h. The resultant orange-red *precipitate* was filtered, well washed with water, light petroleum (b.p. 100—120°), and dried *in vacuo* at 40° (75%) (Found: C, 69·7; H, 4·6; N, 5·9. $C_{62}H_{51}AsBClN_4Ru$ requires C, 69·4; H, 4·7; N, 5·2%).

If [$RuCl_3(AsPh_3)(bipy)$] (0·30 g) was refluxed in methanol (240 ml) under nitrogen with an excess of 2,2′-bipyridyl (0·12 g) for 24 h, the resulting red solution contained a mixture of two compounds (t.l.c. evidence). The solvent was removed and the residue washed with water leaving a purple material (20%) and an orange solution. The solution was concentrated almost to dryness and on addition of an acetone–light petroleum (b.p. 100—120°) mixture (80 : 20 by volume), the orange *tris(bipyridyl)ruthenium*(II) *chloride hexahydrate* was obtained m.p. >300° (60%) (Found: C, 47·8; H, 4·2; N, 11·1. Calc. for $C_{30}H_{36}N_6O_6Ru$: C, 48·1; H, 4·8; N, 11·2%) [Λ (1 × 10^{-3}M) in MeOH = 170 S cm^2 mol^{-1}]. The corresponding BPh_4^- salt was also prepared $[Ru(bipy)_3](BPh_4)_2H_2O$, m.p. 270° [Found: C, 76·7; H, 5·9; N, 6·1. Calc.: C, 75·7; H, 6·1; N, 7·3%].

If the residue was washed with CH_2Cl_2 (leaving the orange trisbipyridyl complex) and pentane added to the purple washings, purple microcrystals of *chloro(aquo)bis(2,2′-bipyridyl)ruthenium*(II) *chloride dihydrate* were obtained m.p. >300° (Found: C, 45·7; H, 3·4; N, 10·2. Calc. for $C_{20}H_{22}Cl_2N_4O_3Ru$: C, 46·1; H, 3·8; N, 10·7%) [Λ (6·8 × 10^{-4}M) in CH_2Cl_2 = 7·0 S cm^2 mol^{-1}].

(d) 1,10-*Phenanthroline*.—$[RuX_3(EPh_3)(phen)]$ (E = P or As; X = Cl or Br) were prepared by the same methods as the corresponding 2,2′-bipyridyl compounds.

Chloro(triphenylphosphine)bis(1,10-*phenanthroline)ruthenium*(II) *chloride*. $[RuCl_3(PPh_3)(phen)]$ (0·10 g) was refluxed under nitrogen in methanol (100 ml) for 24 h with an excess of 1,10-phenanthroline (0·04 g). Concentration of the resulting orange solution and recrystallisation from CH_2Cl_2–pentane gave orange microcrystals m.p. 290° (decomp.) (78%) (Found: C, 60·8; H, 3·7; N, 6·9. $C_{42}H_{31}Cl_2N_4PRu$ requires C, 60·9; H, 3·7; N, 6·8%) [Λ (1 × 10^{-3}M) in CH_2Cl_2 = 28·6 S cm^2 mol^{-1}]. The same product was obtained from the reaction of $[RuCl_3(PPh_3)_2MeNO_2]$ and an excess of 1,10-phenanthroline in methanol (58%) together with some $[RuCl_3PPh_3(phen)]$ (30%). When $[RuCl_2(PPh_3)_3]$ and 1,10-phenanthroline were refluxed in methanol, $[RuCl(PPh_3)(phen)_2]Cl$ (58%) and the yellow-brown powder $[Ru_2Cl_2(PPh_3)_4(phen)_2]Cl_2$ were obtained, m.p. >300° (20%) (Found: C, 64·8; H, 4·2; N, 3·1. $C_{96}H_{76}Cl_4N_4P_4Ru_2$ requires C, 65·7; H, 4·3; N, 3·1%) [Λ (7·0 × 10^{-4}M) in MeOH = 11·5 S cm^2 mol^{-1}]. The latter compound was obtained in high yield (80%) by reaction of $[RuCl_2(PPh_3)_3]$ and 1,10-phenanthroline in CH_2Cl_2.

Chloro(triphenylphosphine)bis(1,10-*phenanthroline)ruthenium*(II) *hexafluorophosphate*. A methanolic solution of $[RuCl(PPh_3)(phen)_2]Cl$ was treated with an excess of NH_4PF_6. The resulting orange solution was concentrated to dryness, washed with water, and the red-orange product air-dried m.p. 213° (decomp.) (Found: C, 52·6; H, 3·4; N, 5·8. $C_{42}H_{31}ClF_6N_4P_2Ru$ requires C, 52·6; H, 3·4; N, 5·8%).

Sulphur Ligands

(a) *Dimethyl Sulphoxide*.—*Trichlorobis(triphenylarsine)(dimethyl sulphoxide)ruthenium*(III) $[RuCl_3(AsPh_3)_2MeOH]$ (0·20 g) was added to an aqueous solution of dimethyl sulphoxide (1 : 1 by volume) and the suspension stirred for 24 h to give a tan *precipitate*. This was well washed with water and air-dried (60%). I.r. spectrum (1350—800 cm^{-1}) 1315m, (1190s, 1160w, 1080s, 1025s, 1000m all $AsPh_3$) 973s, 935m [ν(so)] 920s cm^{-1}. The same compound was prepared by shaking $[RuCl_3(AsPh_3)_2MeOH]$ with neat dimethyl sulphoxide (DMSO) and filtering off the product after 5 min. A similar reaction with [$^2H_6$]dimethyl sulphoxide gave *trichlorobis(triphenylarsine)*([$^2H_6$]*dimethyl sulphoxide)ruthenium*(III). I.r. spectrum (1350—800 cm^{-1}): [1190s, 1160w, 1080s, 1025s, 1000m all $AsPh_3$], 1050m, 935m, [ν(so)] 825m cm^{-1}. $[RuBr_3(AsPh_3)_2(dmso)]$ and $[RuX_3(PPh_3)_2(dmso)]$ were readily prepared from aqueous DMSO solutions by the method given above (*ca.* 70% yields).

Dibromotetrakis(dimethyl sulphoxide)ruthenium(II). $[RuBr_3(AsPh_3)_2MeOH]$ (0·20 g) was suspended in an excess of dimethyl sulphoxide (10 ml) and stirred under nitrogen for 24 h. The resulting pale yellow crystalline *precipitate* was filtered, washed with water, and air-dried, m.p. 219—220° (78%) (Found: C, 17·6; H, 4·2; Br, 28·6; S. 22·8. Calc. for $C_8H_{24}Br_2O_4RuS_4$: C, 16·7; H, 4·2; Br, 28·0; S, 22·3%). I.r. spectrum (1350—750 cm^{-1}) 1304m, 1290s, 1080vs [ν(so)] 1025vs, 978s, 942s cm^{-1}.

Dibromotetrakis([$^2H_6$]*dimethyl sulphoxide)ruthenium*(II) was prepared by the same method, m.p. 240° (decomp.) (80%) (Found: C, 17·0; D, 8·1; Br, 28·4. $C_8D_{24}Br_2O_4RuS_4$ requires C, 16·0; D, 8·0; Br, 27·0%). I.r. spectrum (1350—750 cm^{-1}) 1080vs, [ν(so)] 1020w, 1000m, 820vs, 780m, 770s cm^{-1}.

(b) *Dialkyl Sulphides*.—*Trichlorotriphenylarsinebis(dimethyl sulphide)ruthenium*(III). $[RuCl_3(AsPh_3)_2MeOH]$ (0·21 g) in CH_2Cl_2 (40 ml) was treated with an excess of dimethyl sulphide (0·8 ml) under nitrogen. After 1 h, the red solution was concentrated to give a red *solid* recrystallised from CH_2Cl_2–heptane (78%). $[RuBr_3(EPh_3)(Me_2S)_2]$ (E = P or As) were obtained by the same method except longer reaction times (*ca.* 2 h) were needed for complete conversion (75%).

Trichlorotriphenylphosphinebis(dimethyl sulphide)ruthenium(III) was prepared as for the chloro-arsine compound, partial removal of solvent giving a dark green *solid* (52%). Concentration of the remaining red solution gave orange solids whose analyses and m.p.s were variable, suggesting a mixture of $[RuCl_3PPh_3(Me_2S)_2]$ and $[RuCl_2(PPh_3)_2(Me_2S)_2]$. However, reaction of $[RuCl_2(PPh_3)_3]$ and an excess of Me_2S in dichloromethane (*ca.* 5 min) under nitrogen gave an orange-red solution. Addition of heptane and recrystallisation of the orange-brown *precipitate* from CH_2Cl_2–heptane gave *dichlorobis(triphenylphosphine)bis(dimethyl sulphide)ruthenium*(II) [Found: C, 57·8; H, 4·6; Cl, 10·5, *M*, 986 (C_6H_6). $C_{40}H_{42}Cl_2P_2RuS_2$ requires C, 58·5; H, 5·1; Cl, 8·7%, *M*, 820]. ^1H n.m.r.: phenyl multiplet (τ 2·4—3·3); methyl singlet (τ 8·8).

Trichlorobis(triphenylarsine)(diethyl sulphide)ruthenium(III). $[RuCl_3(AsPh_3)_2MeOH]$ (0·20 g) was dissolved in CH_2Cl_2 (40 ml) and stirred under nitrogen with an excess of Et_2S (0·1 ml) for 2 h. The resulting red solution was concentrated to dryness and a mixture of heptane–CH_2Cl_2 (6 : 1 ratio) added giving a red *solid*, recrystallised from CH_2Cl_2–heptane (82%). Longer reaction times gave mixtures containing $[RuCl_3(AsPh_3)(Et_2S)_2]$. $[RuBr_3(AsPh_3)_2Et_2S]$ was similarly prepared (83%).

(c) *Carbon Disulphide*.—*Trichlorobis(triphenylarsine)(carbon disulphide)ruthenium*(III). $[RuCl_3(AsPh_3)_2MeOH]$ (0·33 g) was refluxed in CS_2 (30 ml) under nitrogen for *ca.* 30 min and the resulting brown microcrystalline precipitate washed several times with carbon disulphide and air-dried (71%). The same product was formed if the reaction was continued for 6 h, even in the presence of an excess of triphenylarsine (added in an attempt to remove sulphur from the bound CS_2 group). $[RuCl_3(PPh_3)_2(CS_2)]$ was similarly prepared (70%).

Tribromobis(triphenylarsine)(thiocarbonyl)ruthenium(III). $[RuBr_3(AsPh_3)_2MeOH]$ (0·20 g) was refluxed in CS_2 (20 ml) under nitrogen for *ca.* 30 min. Concentration of the solution, followed by pentane addition gave the brown crystalline *product*, washed with CS_2 and air-dried (73%) [ν(cs) 1295 cm^{-1}].

Shorter reaction times gave products with i.r. bands at 1295 and 1520 cm^{-1} [ν(cs_2)], *i.e.* a mixture of [$RuBr_3(AsPh_3)_2(CS)$] and [$RuBr_3(AsPh_3)_2(CS_2)$]. The corresponding [$RuBr_3(PPh_3)_2(CS)$] was prepared in an analogous way (68%).

(d) *Tris(diphenylphosphinodithioato)ruthenium*(III).* [$RuCl_3(AsPh_3)_2MeOH$] and a four-fold excess of sodium diphenylphosphinodithioate were shaken in acetone for two days. The violet *crystals* were then filtered, washed with water and diethyl ether, and dried in *vacuo* at 40°, m.p. 219—220° (Found: C, 50·5; H, 3·3. $C_{36}H_{30}P_3RuS_6$ requires C, 50·9; H, 3·5%). The same compound is also prepared from [$RuCl_3(AsPh_3)_2PhCH_2CN$], Me_4N[$RuBr_4(AsPh_3)_2$]2(acetone) or ' $RuCl_3,xH_2O$ ' and NaS_2PPh_2.

Oxygen Ligands

(a) *Tetrahydrofuran.— Trichlorobis(triphenylarsine)(tetrahydrofuran)ruthenium*(III). [$RuCl_3(AsPh_3)_2MeOH$] (0·20 g) was suspended in an excess of tetrahydrofuran, THF (10 ml) and shaken for *ca.* 12 h. Addition of pentane to the red solution gave an orange-red *precipitate* which was washed with THF and air-dried (70%). The corresponding [$RuBr_3(AsPh_3)_2(thf)$] and [$RuX_3(PPh_3)_2(thf)$] were similarly prepared (*ca.* 65% yield).

(b) *Acetone, nitromethane.* The compounds [$RuX_3(EPh_3)_2S$] (S = acetone, $MeNO_2$) were prepared as for the THF adducts (see ref. 2 and 8) and for S = $MeNO_2$, from Ph_4As[$RuX_4(EPh_3)_2$]2(acetone) (ref. 8).

Trichlorobis(triphenylarsine)ruthenium(III). [$RuCl_3(AsPh_3)_2MeOH$] was dissolved in benzene (or dichloromethane) giving a yellow-brown solution. Addition of heptane gave the dark brown *product.* Similarly, [$RuBr_3(AsPh_3)_2$] was prepared.

Carbon Donors

(a) *Bicyclo*[2,2,1]-*2,5-heptadiene (Norbornadiene).—Dichlorobis(triphenylarsine)(norbornadiene)ruthenium*(II). [$RuCl_3(AsPh_3)_2MeOH$] (0·40 g) and an excess of C_7H_8 (2·0 ml) in benzene were refluxed under nitrogen for 24 h. The resulting orange-red crystals were collected, washed with benzene and dried *in vacuo*, m.p. 256—260° (Found: C, 57·8; H, 4·2; As, 16·4; Cl, 7·8. $C_{43}H_{38}As_2Cl_2Ru$ requires C, 58·9; H, 4·4; As, 17·1; Cl, 8·1%). Similarly, [$RuBr_2(AsPh_3)_2C_7H_8$] was prepared (Found: C, 55·2; H, 4·0; As, 10·6; Br, 16·8. $C_{43}H_{33}As_2Br_2Ru$ requires C, 53·5; H, 4·0; As, 10·5; Br, 16·6%). These compounds are very insoluble in all common solvents. [$RuCl_2(PPh_3)_2C_7H_8$] was prepared as for the chloro-arsine compound from [$RuCl_3(PPh_3)_2S$] (S = MeOH or $MeNO_2$) and C_7H_8 m.p. 220° (60%) (Found: C, 65·6; H, 4·9. Calc. for $C_{43}H_{38}Cl_2P_2Ru$: C, 65·5; H, 4·8%) (see ref. 38). [$RuBr_2(PPh_3)_2C_7H_8$] was similarly prepared (Found: C, 60·8; H, 4·9. $C_{43}H_{38}Br_2P_2Ru$ requires C, 58·8; H, 4·4%). These compounds are also very insoluble in all common solvents.

Dichlorobis(dimethylphenylphosphine)(norbornadiene)ruthenium(II).—Ph_3BzP[$RuCl_3CO(C_7H_8)$] [54] (0·20 g) was refluxed in CH_2Cl_2 (100 ml) under nitrogen with PMe_2Ph (0·1 ml) for *ca.* 24 h. Concentration of the yellow solution followed by diethyl ether addition gave a yellow solid. This was washed with methanol to remove free Ph_3BzPCl and recrystallised from CH_2Cl_2–pentane, m.p. 247°. [Found: C, 51·0; H, 5·5, *M*(C_6H_6) 600. $C_{23}H_{30}Cl_2P_2Ru$ requires C, 51·0; H, 5·5%, *M*, 520.] ^1H N.m.r.: τ 6·70(2), 7·20(4), 8·50(2) [diene]; τ 2·0—2·6(10) phenyl multiplet; τ 7·74(12) 1 : 2 : 1 ' triplet ' [PMe_2Ph].

Refluxing [$RuCl_3(AsPh_3)_2MeOH$] (0·20 g) with an excess of cyclo-octa-1,5-diene (1·2 ml) in benzene (40 ml) for 24 h gave the dark orange *precipitate* [$RuCl_2C_8H_{12}$]$_n$ (Found: C, 36·1; H, 4·3. Calc. for $C_8H_{12}Cl_2Ru$; C, 34·4; H, 4·3%) (see ref. 60).

(b) *Carbon Monoxide.—*trans-*Dichlorodicarbonylbis(triphenylarsine)ruthenium*(II) (Configuration XIII). Carbon monoxide was bubbled through an oxygen-free solution of [$RuCl_3(AsPh_3)_2MeOH$] (0·40 g) in CH_2Cl_2 (40 ml) for *ca.* 10 min. The solution was concentrated to dryness and the residue washed with acetone leaving a pale yellow *solid*, m.p. 230° (decomp.) (36%) [Found: C, 52·4; H, 3·6; Cl, 7·8, *M*(C_6H_6) 857. $C_{38}H_{30}As_2Cl_2O_2Ru$ requires C, 54·2; H, 3·6; Cl, 8·4% *M*, 841]. ν(co) 2081w, 2036w, 1993s (Nujol); 1993 cm^{-1} (CH_2Cl_2). Recrystallisation from hot benzene gave *cis*-[$RuCl_2(CO)_2(AsPh_3)_2$] (Configuration XIV) [Found: C, 53·7; H, 3·7% ν(co) 2061s, 1999s cm^{-1}]. Recrystallisation from CH_2Cl_2–methanol gave a mixture of isomers with ν(CO) 2036, 1978 cm^{-1} (Nujol) (assigned to configuration XVII) and ν(co) 1943 cm^{-1} (Nujol) (assigned to confn. XVI). Similarly *trans*-[$RuBr_2(CO)_2(AsPh_3)_2$] (configuration XIII) was prepared from [$RuBr_3(AsPh_3)_2MeOH$] m.p. 265° (decomp.) (60%) [Found: C, 48·8; H, 3·3. $C_{38}H_{30}As_2Br_2O_2Ru$ requires C, 49·1; H, 3·2%; ν(co) 1995 cm^{-1} (CH_2Cl_2)]. Recrystallisation from CH_2Cl_2–methanol gave a pinkish-tan *product* (Found: C, 49·0; H, 3·4%) with a number of carbonyl bands in the i.r. spectrum. ν(co) 2090m, 1980s cm^{-1} (configuration XVII); 1940w (configuration XVI).

trans-[$RuCl_2(CO)_2(PPh_3)_2$] (configuration XIII) was also prepared from [$RuCl_3(PPh_3)_2S$] (S = MeOH or $MeNO_2$) by the same method, m.p. 190° (35%) [Found: C, 60·3; H, 4·0. Calc. for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60·6; H, 4·0%, ν(co) 2005 cm^{-1}; see refs. 2 and 63].

We thank Johnson-Matthey Ltd. for generous loans of ruthenium trichloride, the National A. University of Mexico (L. R. R.) and the National Institutes of Health (E. S. S.) for fellowships, the Department of Inorganic Chemistry, University of Newcastle, for use of the Faraday Balance, Dr. I. R. Leith and Mr. A. Anderson for e.s.r. measurements, and Mr. J. Sinclair for experimental assistance.

[2/2774 *Received*, 11*th December*, 1972]

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* We thank Mr. D. J. Cole-Hamilton and Mr. P. W. Armit for the preparation of this compound.