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Configurations of Some Complexes of Rhenium, Ruthenium, Osmium, Rhodium, Iridium, and Platinum Halides with Mono(tertiary phosphines) and Mono(tertiary arsines)

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The far-i.r. spectra and, where appropriate, the n.m.r. and e.s.r. spectra of the complexes $[MX_4L_2]$ [M = Re, Os, Ir, or Pt; X = CI or Br; L = mono(tertiary phosphine) or mono(tertiary arsine)] and $[MX_3L_3]$ [M = Re, Ru, Os, or Ir; X = Cl or Br; L = mono(tertiary phosphine) or mono(tertiary arsine)] are described. The former group generally have trans-configurations and the latter meridional.

The structural configurations of the complexes with t_{2a}^4 metal electron configurations are reliably determined by ¹H n.m.r. spectral measurements. These have shown that the complexes [ReCl₃(PR₃)₃] have mer-configurations and the complexes $[OsCl_4(PR_3)_2]$ probably have trans-configurations. For complexes with t_{2g}^{5} configurations only broad ¹H n.m.r. spectra were observed, which, except for [RuCl₃(PMe₂Ph)₃], were of no use for structural assignments. However, e.s.r. spectral measurements have confirmed the suggested configurations for the t_{20}^{-5} complexes.

Far-i.r. studies in the solid state have in general supported the above configurations but are not definitive, especially where complexes of transition elements of the Third Period are concerned.

WE have described ¹ the preparation of the complexes of mono(tertiary phosphines) and mono(tertiary arsines), L. of general formula $[MX_3L_3]$ (M = Re, Ru, or Os; X = Cl or Br) and $[MX_4L_2]$ (M = Re, Os, or Ir; X = Cl or Br). We now describe the physical properties, and the i.r., n.m.r., and e.s.r. spectra of these complexes and of some related compounds, and infer their configurations.

The complexes were normally synthesised as shown in the Scheme. In general, as prepared by these routes,

$$\begin{split} \text{NaReO}_{4} \xrightarrow[\text{EtOH}]{L,\text{HCl}} & [\text{ReCl}_{3}\text{L}_{3}] \xrightarrow[\text{reflux}]{CCl_{4}} & [\text{ReCl}_{4}\text{L}_{2}] \\ & \text{RuCl}_{3},3\text{H}_{2}\text{O} \xrightarrow[\text{EtOH}]{L,\text{HCl}} & [\text{RuCl}_{3}\text{L}_{3}] \\ & \text{OsO}_{4} \xrightarrow[\text{EtOH}]{L,\text{HCl}} & [\text{OsCl}_{3}\text{L}_{3}] \xrightarrow[\text{reflux}]{CCl_{4}} & [\text{OsCl}_{4}\text{L}_{2}] \\ & \text{LH}[\text{IrCl}_{4}\text{L}_{2}] \xrightarrow[\text{CCl}_{4}]{CHCl_{3}} & [\text{IrCl}_{4}\text{L}_{2}] \\ & \text{LH}[\text{IrCl}_{4}\text{L}_{2}] \xrightarrow[\text{CCl}_{4}]{CHCl_{3}} & [\text{IrCl}_{4}\text{L}_{2}] \\ & \text{Scheme} \end{split}$$

the [MX₃L₃] compounds have *meridional*, and the $[MX_{A}L_{2}]$ compounds have *trans*-configurations, but we have now prepared fac-[OsCl₃(PBuⁿ₂Ph)₃] by another route (see Experimental section), and fac-[ReCl₂-(PMe₂Ph)₃] was obtained from Mr. H. P. Gunz of this laboratory. The spectroscopic properties of these *facial* isomers are also discussed.

Far-infrared Spectra.—(a) Complexes of the type $[MX_4L_2]$ (M = Re, Ru, Os, Ir or Pt). The far-i.r. spectra of *cis*- and *trans*-[PtX_4L_2] (X = Cl, Br, or I) have been reported,² and these confirmed the configurations which had been established by ³¹P n.m.r. studies.³ The complexes trans- $[MX_4L_2]$ may be considered ² to belong to the point-group D_{4h} , and the i.r.active modes of vibration are $\nu(M-X_4)e_u$; $\nu(M-L_2)a_{2u}$; $\delta(M-X_4)e_u$; $\delta(M-L_2)e_u$; and $\pi(M-X_4)a_{2u}$. The complexes $cis[MX_4L_2]$ belong to the point-group C_{2v} , for which $v(M-X_4)$ can be represented by $2a_1 + b_1 + b_2$ and $\nu(M-L_2)$ by $a_1 + b_1$. The bending modes cannot be described in terms of simple metal-halogen and metalphosphorus (or arsenic) vibrations.

The i.r. spectral frequencies of the aliphatic phosphine and arsine complexes of rhenium(IV), osmium(IV), and iridium(IV), of the recently prepared 4 [PEt₃H][RuCl₄- $(PEt_a)_2$, and also of the corresponding trans- $[PtX_4L_2]$ are in Tables 1a, 1b, and 2. The spectra have been assigned by direct comparison with those of the platinum complexes² and are generally consistent with a transconfiguration, with a single metal-halogen stretching frequency in the region 300-350 cm.⁻¹ for chlorides and 200-250 cm.⁻¹ for bromides.

A comparison of the stretching frequencies assigned to the metal-halogen vibrations in K₂PtCl₄⁵ and trans-[PtCl₄(PEt₃)₂] and in K₂PtBr₄ ⁶ and trans-[PtBr₄(PEt₃)₂] shows that $v(Pt-X_4)e_u$, $\delta(Pt-X_4)e_u$ and $\pi(Pt-X_4)a_{2u}$ have very similar frequencies for a given halide ion. The co-ordination of phosphine has no great effect on the stretching vibrations of the PtX₄ group. Thus the coupling of these e_u metal-halogen stretching modes with the ligand bending e_u mode cannot be very great. Additionally, the coupling of the two types of metalhalogen e_u modes must be constant in the series, and is probably very small. The $\nu(M-X_4)e_u$ fall in the series (see Table 1) $Pt \gg Ir > Os > Re$. A similar sequence has been observed ⁶ for the i.r.-active t_{1y} metal-halogen stretching modes of the compounds [NEt₄]₂[MCl₆] (M = Re, Os, Ir, or Pt) although here the bands are often split and broadened and average values must be taken. This has been ascribed to the drop in ligand field stabilisation energy from Pt to Re. However, the frequencies of the a_{1g} Raman-active metal-halogen stretching modes of the complex anions $[MCl_e]^{2-}$ (M =

¹ J. Chatt, G. J. Leigh, D. M. P. Mingos, and Rosemary J. Paske, J. Chem. Soc. (A), 1968, 2636. ² D. M. Adams and P. J. Chandler, J. Chem. Soc. (A), 1967,

³ A. Pidcock, R. E. Richards, and L. M. Venanzi, J. Chem. Soc. (A), 1966, 1707.

⁴ T. A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., 1966, 28, 945.

P. J. Hendra, J. Chem. Soc. (A), 1967, 1298.
 D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerrat, J. Chem. Soc., 1963, 2189.

Re, Os, or Pt) are almost constant 7 and so the change in ligand field stabilisation energy cannot be the only factor affecting the frequencies.

Murrell⁸ has calculated the stretching force constants

accurately either the frequencies or the ligand field stabilisation energies, but because the i.r. spectra of the ions [MCl₆]²⁻ also show solid-state interactions ⁹ a more detailed discussion is probably unwise.

Far	-i.r. spectra (cn	n. ⁻¹) of complexes <i>trans</i> -	$[\mathbf{MX_4L_2}] \ (\mathbf{M} = \mathbf{R})$	e, Os, Ir, or Pt;	L = tertiary	phosphine) and		
$trans-[MX_4L_2]^-$ (M = Ru or Ir; X = Cl; L = tertiary phosphine)								
	$[\operatorname{ReCl}_4(\operatorname{PEt}_3)_2]$	[PHEt ₃][RuCl ₄ (PEt ₃) ₂]	$[PtCl_4(PEt_3)_2]^b$	$[OsCl_4(PPr^n_3)_2]$	$[IrCl_4(PPr^n_3)_2]$	[PHPrn ₃][IrCl ₄ (PPrn ₃) ₂]		
$v(M-Cl_{4})e_{u}$	320vs	310vs	340vs	320s	324vs	314vs		
			334 sh			302vs		
$\delta(M-Cl_4)e_{\mu}$		198m	188ms	189m	191m	184m		
$\pi(M-Cl_4)a_{2u}$	150m	147m	159m	152m	134m	143 m		
$\nu(M-L_2)a_{2u}\dots$	420m		410m	419 m	416 m	417m		
$\delta(M-L_2)e_u$	172sh	175w	179ms	171m	182w			
$\delta(M-P-C)$		278sh	274m					
Other bands	373w	326w	388w	373m	369ms	377m		
	226m	230m	299 m	131 m	230w	$240\mathrm{m}$		
		169w	83w					
	$[\operatorname{ReBr}_4(\operatorname{PEt}_3)_2]$		$[PtBr_4(PEt_3)_2]^{b}$	$[OsBr_4(PPr^n_3)_2]$				
$\nu(M-Br_4)e_{\mu}\ldots$	224s		247s	228s				
	206 sh							
$\delta(M-Br_4)e_u\dots$	134w		134ms	132m				
π (M–Br ₄) a_{2u}	102w		109m	100m				
$\nu(M-L_2)a_{2u}\ldots$	420 m		411 m	416 m				
$\delta(M-L_2)e_u$	174m,br		182m	186 m				
δ(M-P-C)								
Other bands	380m		386 m	380m				
	340m		344m					
	320m 120m		230m					
^a Polythene disc, $400-40$ cm, ⁻¹ . ^b Spectra taken from ref. 2: Nujol mulls.								

TABLE la

TABLE 1b

Far-i.r. spectra (cm. ⁻¹) of the complexes <i>trans</i> -[MCl ₄ L ₂] (M = Os, Ir or Pt; L = tertiary arsine)					
	$[OsCl_4(AsPr^n_3)_2]^a$	$[IrCl_4(AsPr_3)_2]^{a,b}$	$[PtCl_4(AsEt_3)_2]^{\circ}$		
$\nu(M-Cl_4)e_u$	320337 vs	328vs	343 vs		
			$337 \mathrm{sh}$		
$\delta(M-Cl_4)e_u$	184m	188m	183ms		
π (M-Cl ₄) $a_{2\mu}$	152wm	156wm	168m		
$\nu(M-L_2)a_{2\nu}$	332vs	328vs	328s		
$\delta(M-L_2)e_u$			137s		
$\delta(M-As-C)$		210w	220ms		
Other bands	252wm	262m	314 s		
	381w .		30 8s		

^a Polythene discs, 40–400 cm.⁻¹. ^b ν (M–Cl₄) e_u and ν (M–L₂) a_{2u} completely superimposed. ^c Nujol mull; spectrum taken from ref. 2.

TABLE 2

Far-i.r. spectra (cm.⁻¹) of the complexes $[MX_4L_2]$ (X = Cl or Br; L = tertiary phosphine or arsine)

	ν (M–X ₄) e_u	Other bands
$[IrCl_4(PPh_3)_2]^a$	326vs	490s, 458s, 433m, 420m, 257m, 235m, 344sh
$[IrCl_4(PEt_2Ph)_2]^a$	326vs	487s, 446s, 343sh, 302sh
$\left[\operatorname{OsCl}_{4}(\operatorname{PPr}^{n}_{2}\operatorname{Ph})_{2}\right]^{a}$	323vs	494s, 448s, 417m, 391m, 344sh, 258m
$[OsCl_4(PBu^n_2Ph)_2]$	324 vs	490s, 455m, 417m, 393m, 374m, 271w, 251w, 204w, 176m, 152m, 109w
$\left[\operatorname{OsCl}_{4}(\operatorname{PMe}_{2}\operatorname{Ph})_{2}\right]^{a}$	324 vs	420m, 344sh, 267m
[ReCl ₄ (PMe ₂ Ph) ₂]	318vs	472s, 408s, 343sh, 256w, 190m, 148m
$[\operatorname{ReCl}_{4}(\operatorname{PPr}^{n}_{2}\operatorname{Ph})_{2}]$	322vs	482s, 419s, 343sh, 314sh, 268w, 188m, 161m
$[\operatorname{ReCl}_4(\operatorname{PBu}^n_2\operatorname{Ph})_2]$	321vs	392m, 312sh, 250w, 186w, 167m, 150m
[PHEt,Ph][IrCl ₄ (PEt,Ph),]	315vs, 302vs	487s, 446s, 276w, 269w, 180w, 159w, 124w
[OsCl ₄ (AsMe ₂ Ph) ₂] ^a	317vs,br	397m, 344sh, 274m, 248m
$[OsBr_4(AsPh_3)_2]^{\delta}$	230vs	332vs, 218sh, 152m
a Nui	ol mulls 200-	500 cm $^{-1}$ b Polythene discs 40—400 cm $^{-1}$

for these ions using published data and has shown that they are very similar for Re and Os, but somewhat higher for Pt. Hence, the force constants do not reflect ⁷ L. A. Woodward and M. J. Ware, Spectrochim. Acta, 1964, 20, 711.

The $v(M-Cl_4)e_u$ band in the complexes $[MCl_4L_2]$ (M = Re or Ir) is sometimes split (see Tables 1a and 1b).

⁸ J. N. Murrell, *J. Chem. Soc.* (A), 1969, 297. ⁹ D. M. Adams, 'Metal-Ligand Vibrations,' Arnold, London, 1967.

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Similar splittings observed² in the spectra of trans-[PtCl₄(PEt₃)₂] and [PtCl₄(AsEt₃)₂] have been ascribed to ³⁷Cl-³⁵Cl isotope splitting. In this case there is a shoulder at 6 cm.⁻¹ to lower frequency of the main band. This splitting does not occur, however, in the Ramanactive a_{1q} band.¹⁰ The maximum splittings calculated on the basis of complete substitution of ³⁵Cl by ³⁷Cl should be 7 cm.⁻¹ for the e_u band and 9 cm.⁻¹ for the a_{1a} , and so it seems much more likely that this splitting is a solid-state effect in iridium and rhenium compounds and in the platinum complexes.

(b) Complexes of the type $[MX_3L_3]$ (M = Re, Ru, Os, or The structures of complexes fac- and mer- $[MX_3L_3]$ Ir). (M = Rh or Ir) have been assigned on the basis of





FIGURE 1 Representations of the metal-halogen stretching modes of mer- and fac-[MCl₃L₃]

dipole moment ^{11,12} and ¹H ^{13,14} and ³¹P n.m.r. measurements.15

The far-i.r. spectra of the two series of compounds are expected to be quite distinct with three i.r.-active metal-halogen stretching vibrations in the *mer*-isomers but only two in the fac-isomers. The form of these is shown in Figure 1. The solid-state spectra of the rhodium compounds generally conform to this pattern,^{13,16} but the mer-iridium isomers have two rather than three bands, and this has been attributed to a low transition moment associated with the $a_1(2)$ vibrations.¹⁷

The spectra of the complexes $[RuX_3L_3]$ except $[RuBr_3(PMe_2Ph)_3]$ in Table 3 support a *mer*-configur-

- ¹⁰ J. Chatt, G. J. Leigh, and D. M. P. Mingos, J. Chem. Soc. (A), to be published.
- J. Chatt, A. E. Field, and B. L. Shaw, J. Chem. Soc., 1963, 3371.
- 12 J. Chatt, N. P. Johnson, and B. L. Shaw, J. Chem. Soc., 1964, 2508.
- 13 P. R. Brookes and B. L. Shaw, J. Chem. Soc. (A), 1967, 1079.

ation, with three bands assignable to metal-halogen stretching frequencies, as already assigned in the spectra of the mer-rhodium complexes.^{13,16} The spectral frequences of a rhenium and six osmium analogues are given in Table 4, which also includes data for some meriridium complexes.¹⁷ The n.m.r. spectra of all the rhenium compounds we have prepared 1 (see below) unequivocably support a *mer*-configuration and the general similarity of the i.r. spectra for all the compounds in Table 4 leads us to postulate a common configuration.

The Raman spectrum of $mer-[IrCl_3(PEt_3)_3]$ is almost identical with its i.r. spectrum,¹⁰ and the reason for the appearance of only two metal-halogen stretching frequencies cannot be that the third has a low transition moment. Accidental degeneracy appears more likely. The frequencies decrease from Pt to Re as in the series [MX₄L₂] discussed above, but the magnitude of the decrease is somewhat less.

We have been unable to use the metal-phosphorus stretching region of the spectrum for distinguishing between facial and meridional isomers because the number of bands is less than expected from symmetry considerations.

The far-i.r. spectra of $fac-[MX_3L_3]$ (M = Re, Rh, Ir, or Os; X = Cl or Br; and L = tertiary phosphine) are given in Table 5. The rhodium and iridium configurations have been previously established, and the rhenium and osmium follow by comparison and by contrast with the mer-isomers. The spectrum previously reported ⁶ for [RhCl₃(PEt₃)₃] does not agree completely with ours and therefore both versions are given in Table 5. All the complexes show two bands assignable to metal-halogen stretching modes. There is no discernible trend in these frequencies.

The occurrence of accidental degeneracy as in the whole series of iridium(III) complexes, and splitting of bands owing to crystal forces as in mer-[RuBr₃(PMe₂Ph₃], emphasise the limitations imposed on, and care needed in, the use of i.r. spectra to determine configurations. These limitations are especially marked in application to complexes of the heavy elements in the Third Transition Series.

N.M.R. Spectra.—' Virtual coupling ' 18,19 of hydrogen nuclei in the alkyl groups attached to phosphorus has been used to determine the configurations of diamagnetic iridium and rhodium complexes.20

Of the paramagnetic complexes, the d^5 compounds $[IrCl_4(PPr_3)_2]$, $[OsCl_3(PMe_2Ph)_3]$, $[RuCl_3(AsPr_3)_3]$, and $[RuCl_2{(PMe_2)_2C_2H_4}_2](ClO_4)$ have much broader n.m.r. spectral absorptions (see Table 6) than their diamagnetic

14 J. M. Jenkins and B. L. Shaw, J. Chem. Soc. (A), 1966, 1407.

- ¹⁵ S. O. Grim and R. A. Ference, Inorg. Nuclear Chem. Letters, 1966, 2, 205.
- ¹⁶ M. A. Bennett, R. J. H. Clark, and D. A. Milner, Inorg. Chem., 1967, 6, 1647.
 - ¹⁷ J. M. Jenkins and B. L. Shaw, J. Chem. Soc., 1965, 6789.
 ¹⁸ R. K. Harris, *Inorg. Chem.*, 1966, 5, 701.
 ¹⁹ J. M. Jenkins and B. L. Shaw, J. Chem. Soc. (A), 1966, 770.
 ²⁰ E. W. Randall and D. Shaw, Mol. Phys., 1965, 10, 41.

TABLE 3

Far i.r. spectra (cm.⁻¹) of the complexes mer- $[MX_3L_3]$ (M = Rh or Ru; X = Cl or Br; L = tertiary phosphine or arsine)

	v(M-X)	Other bands
mer-[RhCl ₃ (PEt ₃) ₃] ^a	332s, 288m, 256m	432m, 386w
$mer-[RuCl_3(PBu^n_3)_3]$	330s, 296m, 247m	392w, 204m, 168w, 128w, 124w
$mer-[RhCl_3(AsEt_3)_3]^{b}$	332vs, 293m, 274m	270sh
$mer-[RuCl_3(AsPr_3)_3]$ \circ	328s, ^e 300s, 271s	214m, 132w
$mer-[RhCl_3(PMe_2Ph)_3]^d$	344s, 317m, 280s	428m, 413sh, 303w, 226m, 194m, 126w
$mer-[RhBr_3(PMe_2Ph)_3]^d$	225m, 192m, 184m	426m, 409m, 351m, 316w, 283m, 213m, 141sh, 128sh, 114m, 94sh
$mer-[RuCl_3(PMe_2Ph)_3]$	330vs, 304m, 271m	423m, 408m, 352m, 228m, 188m
$mer-[RuBr_3(PMe_2Ph)_3]$	224w, 232w, 202w, 168m	426m, 411m, 350m, 302w, 268s, 128w

^{*a*} Spectrum taken from ref. 16: Nujol mull 200—450 cm.⁻¹. ^{*b*} Nujol mull 200—500 cm.⁻¹. ^{*c*} Polythene disc 40—400 cm.⁻¹. ^{*d*} Spectrum already recorded for Nujol mull, 200—450 cm.⁻¹ (ref. 13). ^{*e*} ν (Ru–As) also occurs in this region.

TABLE 4

Far-i.r. spectra (cm.⁻¹) of the complexes *mer*-[MX₃L₃] (M = Re, Os or Ir; X = Cl or Br; L = tertiary phosphine or arcino)

	or arsine)	
	$\nu(M-X)$	Other bands
$mer-[ReCl_3(PEt_2Ph)_3]^{\alpha}$	306vs, 255vs	442m, 405m, 399m, 316sh
$mer-[OsCl_3(PPr^n_3)_3]$	308vs, 266vs	432m, 451m, 384m, 304sh, 173w, 138w, 115w
$mer-[OsBr_3(PPr^n_3)_3]$	218vs, 212s, 196s	432w, 415m, 378m, 169m, 142w
$mer-[OsCl_3(AsPr_3)_3]^d$	312vs, 272vs	332vs, 326vs, 320sh, 220w, 162w, 146w
$mer-[OsBr_3(AsPr_3)_3]^d$	222s, 198m	326vs, 321vs, 180w, 164w
$mer-[OsCl_3(PBun_2Ph)_3]^d$	304vs, 269vs	351m, 310sh, 228m, 180m
$mer-[OsBr_3(PBun_2Ph)_3]^d$	229sh, 219m, 198w	353m, 341m, 318m, 300s, 172m, 94w
$mer-[IrCl_{s}(PEt_{3})_{3}]^{b}$	313vs, 267vs	440w, 389w, 303sh, 204m, 151m, 110w
$mer-[IrBr_3(PEt_2Ph)_3]$ °	222s	441m, 405m, 391m, 326w, 267w
mer-[IrCl ₃ (AsEt ₃) ₃] ^{a,c}	311vs, 275vs	343m
	37 1 1 1000 1	

^a Nujol mull 200—500 cm.⁻¹. ^b The spectrum in a Nujol mull (220—450 cm.⁻¹) has also been reported in ref. 17. ^a Nujol mull, 220—450 cm.⁻¹; taken from ref. 17. ^d Polythene discs 40—400 cm.⁻¹.

TABLE 5

Far-i.r. spectra (cm.⁻¹) of the complexes fac-[MX₃(PR₃)₃] (M = Re, Os, Rh or Ir; X = Cl or Br;

$PR_3 =$	tertiary	phosphine)
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	$\nu(M-X)$	Other bands
fac-[RhCl ₃ (PEt ₃) ₃]	30 4s, 274s	425s, 389m, 244s, 233s, 154m, 146m
fac-[RhCl ₃ (PEt ₃) ₃] ^a	305sh, 292s, 268—256s, 250sh	425s, 382w, 236s
fac-[RhBr ₃ (PEt ₃) ₃] ^a	221m, 190m	424vs, 383m, 275w, 262w, 164sh, 156m, 142m
fac-[IrCl ₃ (PEt ₃) ₃] ^b	288vs, 260vs	392w, 239w,sh, 158m
$fac-[OsCl_3(PBu_2Ph)_3]^{b}$	302s, 263s	349m, 253sh, 225m, 176m, 192sh, 142w, 114ms
$fac-[ReCl_3(PMe_2Ph)_3]$	298s, 262s	350m, 338m, 322m, 242s, 177w, 152w, 117ms
fac-[RhCl ₃ (PMe ₂ Ph) ₃]	297s, 281s	430s, 414m, 343m, 240s, 208sh, 194sh, 169w, 136s, 117w
$fac-[IrCl_3(PMe_2Ph)_3]^{b}$	295s, 270s	346m, 335m, 250s, 227sh, 142w, 114ms

^a Spectrum between 200 and 500 cm.⁻¹ already reported in ref. 16. The chloride gave a different spectrum in our hands. ^b Polythene discs, 40-400 cm.⁻¹.

analogues and these are also shifted by contact and pseudo-contact mechanisms, but in one case, $[RuCl_3-(PMe_2Ph)_3]$, the spectrum has enough detail to suggest a *mer*-configuration.²¹ The d^4 complexes $[ReCl_3-(PMe_2Ph)_3]$ and $[ReCl_3(PEt_2Ph)_3]$, although paramagnetic, have sharp spectra ²¹ shifted relative to those of their diamagnetic analogues. The phosphine ligands were shown to occupy different environments in the ratio of 2:1, which is consistent with *mer*-configurations. Proton-phosphorus coupling was not observed. The chemical shifts were attributed to contact and pseudo-contact mechanisms.

We have now examined the ¹H n.m.r. spectra of a wider range of d^4 rhenium and osmium complexes; all have sharp resonances which have been assigned by Dr. D. Shaw using double resonance techniques. The osmium complexes show proton-proton and proton-

²¹ E. W. Randall and D. Shaw, Chem. Comm., 1965, 82.

phosphorus couplings, but the latter are absent from all the rhenium complexes. The rhenium compounds

TABLE 6

¹H N.m.r. spectra of d⁵ complexes in CDCl₃

mer-[RuCl ₃ (AsPr ⁿ ₃) ₃]	Shift ^a +0·86	Line-width base of peak (Hz) 60	Assign- ment Propyl
trans-[RuCl ₂ { $(Me_2P)_2C_2H_4$ }]ClO ₄	$-0.90 \\ -1.29$	30 30	Methyl Methylene
$mer-[OsCl_3(PMe_2Ph)_3]$	-3.95 -5.16 -6.67	50 50 25	
trans-[IrCl ₄ (PPr ⁿ ₃) ₂]	+1·2, 6—7	60 80	Propyl

 $^{\rm a}$ P.p.m. with respect to tetramethylsilane; generally ± 0.01 p.p.m.

 $[\operatorname{ReCl}_3(\operatorname{PR}_2\operatorname{Ph})_3]$ (R = Me, Et, Prⁿ, or Buⁿ) all have the *meridional* configuration, the proton resonances of the

trans-phosphines having different shifts from those of the cis-phosphines and twice the intensity. The osmium complexes have equivalent phosphine ligands consistent with either cis- or trans-configurations. 'Virtual coupling' is observed in all cases and, because it has now been found in both cis- and trans-phosphine complexes,²² this cannot be considered unequivocal proof of a transconfiguration.

A more detailed consideration of the magnetic properties of the complexes suggests that contact and pseudo-contact mechanisms are not responsible for the magnitude of the chemical shifts, contrary to an earlier suggestion.^{20,21} The magnetic moments of both the rhenium(III) and osmium(IV) complexes are lower than the spin-only value expected for a d^4 complex,¹ and are comparable with those of $M_2[OsX_6]$ (X = F, Cl, Br, or I) and [Re diars X_2]ClO₄ [diars = $o - C_6 H_4 (AsMe_2)_2$]²³ which show temperature-independent paramagnetism. This has been ascribed 23 to a second-order Zeeman effect arising from the mixing of the ground state (A_{1g}) (J=0) with an excited state (T_{1g}) (J=1)in the presence of a magnetic field. The $A_{1q}-T_{1q}$ separation is very much greater than kT; thus the complexes are basically diamagnetic, and the spectra are shifted under the influence of the paramagnetic excited state.

The situation is thus analogous to that observed for the ⁵⁹Co shift in cobalt(III) complexes by Griffith and Orgel.²⁴ In this case the spectra are influenced by a paramagnetic contribution to the shift caused by mixing



FIGURE 2 Temperature-dependence of the ¹H n.m.r. shifts of trans- $[OsCl_4(AsPr^n_3)_2]$ in CDCl₃. A, γ -carbon protons; B, α -carbon protons; and C, β -carbon protons

of the A_{1g} ground state with a T_{1g} state at about 13,000 cm.⁻¹ above it. Further, since an increase in temperature will decrease this gap slightly as vibrational levels become occupied, the amount of mixing in a magnetic field should increase with temperature and the chemical shifts should also increase. Because the $A_{1g}-T_{1g}$

separation is large, the change in the thermal occupation of the T_{1g} state must be negligible. A linear increase in chemical shift with temperature has been reported.²⁴

The ¹⁹F resonance spectrum of $[OsF_6]^{2-}$ shows shifts which are accounted for by a mixing of the A_{1g} and T_{1g}



FIGURE 3 ¹H N.m.r. spectrum of *trans*- $[OsCl_4(AsEt_3)_2]$ in $CDCl_3$

states as above and also of the A_{1g} state derived from $t_{2g}{}^4$ and an electronically excited state derived from $t_{2g}{}^3e_g$ by spin-orbit coupling.²⁵ The energy separation is here very high (ca. 50,000 cm.⁻¹). This should affect the chemical shift of the fluorine nuclei but have little effect on the paramagnetism. The temperature-dependence of the 19 F resonance spectrum has not been investigated.

Figure 2 shows the temperature-dependence of the chemical shifts of the methyl and methylene protons of *trans*-[OsCl₄(AsPrⁿ₃)₂]. The direct dependence on temperature immediately confirms an excited-state mechanism for the paramagnetism. Shifts arising by contact and pseudo-contact mechanisms should be inversely proportional to temperature.²⁶ The ¹H n.m.r. spectrum of *mer*-[IrCl₃(PMe₂Ph)₃] shows no temperature-dependence between 30° and -50°, a typical diamagnetic behaviour, and suggests that $t_{2g}^{6}-t_{2g}^{5}e_{g}$ mixing in Ir^{III} and therefore $t_{2g}^{4}-t_{2g}^{3}e_{g}$ mixing in Re^{III} or Os^{IV} is not important because Δ is of the same order in all the compounds.

The temperature-dependence becomes less important as the protons on the alkyl chain become further removed from the metal (Figure 2). However, the magnitude of the chemical shifts does not decrease regularly along the alkyl chain, but in general reaches a ²⁵ D. J. Greenslade and K. W. H. Stevens, *Proc. Phys. Soc.*,

1967, **91**, 627. ²⁶ D. R. Eaton and W. D. Phillips, *Adv. Magnetic Resonance*, 1965, **1**, 103.

²² P. K. Maples and C. S. Kraihanzel, Chem. Comm., 1968, 922.

 ²² B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 1965, 6, 37.
 ²⁴ J. S. Griffith and L. E. Orgel, Trans. Faraday Soc., 1957, 53, 601.

maximum at the β -carbon atom. The ³¹P chemical shift in $[OsCl_4(PMe_2Ph)_2]$ is large ²⁷ (+1200 p.p.m. w.r.t. P_2O_5 , indicating strong ligand-metal interactions, presumably involving metal t_{2g} and phosphorus dorbitals, but ¹H shifts of the methyl protons are normal, and thus this interaction does not appear to be transmitted very far. In [OsCl₄(AsEt₃)₂] the resonance of the β -hydrogen nuclei is shifted downfield relative to that of the α -hydrogen (Figure 3). The longer alkyl chains also show a maximum downfield shift of the β -hydrogens as demonstrated by the compounds trans- $[OsCl_4(PR_2Ph)_2]$ (Re = Me, Et, Prⁿ, or Buⁿ) (Table 7). Thus these effects are not transmitted directly along the alkyl chain, and seem to be different in origin from the phosphorus shift, because they are downfield rather than upfield. Table 7 also shows that the ortho-hydrogen atoms

TABLE 7

Proton chemical shifts of *trans*-[OsCl₄(PR₂Ph)] (R = Me, Et, Prⁿ, or Buⁿ) in CDCl₃ at 30° (± 0.01 p.p.m.)

Compound	Proton	Shift
$trans-[OsCl_4(PMe_2Ph)_2]$	Methyl ortho-	-2.89 -13.35 8.20
	meia- para-	-8.30 -8.30
$trans-[OsCl_4(PEt_2Ph)_2]$	Methyl α-Methylene ortho- meta- para-	$-5.63 \\ -5.6, -4.08 \\ -13.26 \\ -7.87 \\ -8.20$
trans-[OsCl ₄ (PPr ^a ₂ Ph) ₂]	Methyl β-Methylene α-Methylene ortho- meta- para-	$\begin{array}{r} -2\cdot 16 \\ -5\cdot 88 \text{ (complex)} \\ -5\cdot 40, -3\cdot 84 \\ -13\cdot 39 \\ -7\cdot 94 \\ -8\cdot 25 \end{array}$
trans-[OsCl ₄ (PBu ⁿ ₂ Ph) ₂]	Methyl γ -Methylene β -Methylene α -Methylene ortho- meta- para-	$\begin{array}{r} -1\cdot51\\ -2\cdot70, -2\cdot51\\ -5\cdot94, -5\cdot89\\ -5\cdot42, -3\cdot98\\ -13\cdot31\\ -7\cdot98\\ -8\cdot27\end{array}$

of the phenyl group are subject to an influence which appears to be neither mesomeric nor inductive, but which again produces large downfield shifts. These proton shifts could be caused by a direct interaction between the β - or *ortho*-hydrogens and the metal such as has been observed in $[PdI_2(PMe_2Ph)_2]^{28}$ or they could be a result of anisotropic magnetic susceptibilities.²⁹

In trans- $[OsCl_4(PR_2Ph)_2]$ (R = Et Prⁿ, and Buⁿ) the methylene hydrogen atoms are inequivalent (see Table 7). This has been interpreted ²⁹ as indicating restricted rotation about the C-C axis, and is confirmed by models which show that all these complexes are very crowded and that the phosphine ligands can take up only particular conformations.

E.S.R. Spectra.—The e.s.r. spectra of d^5 systems are generally quite simple. In octahedral symmetry, the ${}^{2}T_{2g}$ ground state is split by spin-orbit coupling to give two new states, a lower doublet and an upper quadruplet, split by $\frac{3}{2}\lambda$ as shown in Figure 4.³⁰ At liquid-



FIGURE 4 The effect of spin-orbit coupling (λ) and tetragonal distortion (Δ) on the ${}^{2}T_{2g}$ state of d^{5} systems

nitrogen temperature $\lambda \gg kT$, and only the lower doublet will be occupied. In a magnetic field, the degeneracy of the lower doublet is removed, and transitions between the two spin states can be observed by e.s.r. techniques.

In a complex of O_h symmetry, the three principal axes are equivalent, the three components of the g tensor are equal, and only one transition should be observed. In a molecule of less than octahedral symmetry, the number of transitions observed will depend upon the number of independent components of the g tensor,³¹ which is a direct function of the number of distinct principal axes. For D_{4h} symmetry, e.g., trans-[IrX₄L₂], and for C_{3v} symmetry, e.g., fac-[OSX₃L₃], two g values are to be expected ($g_x = g_y \neq g_z$) and for lower symmetry, like C_{2v} , e.g., mer-[RuX₃L₃], three g values would be expected ($g_x \neq g_y \neq g_z$). This thus represents a potentially powerful method for determining configuration.

The g values determined in glasses at liquid-nitrogen temperature are shown in Table 8 together with some single-crystal data. The significance of the magnitudes of the g values and their relationship to the levels of the spin doublets (Figure 4) will be discussed elsewhere.³²

The spectrum of trans-[IrCl₄(AsPr^a₃)₂] gave two g values, as expected, but trans-[IrCl₄(PEt₂Ph)₂] gave three, presumably owing to distortions from D_{4h} symmetry. The meridional osmium(III) compounds gave spectra consistent with the structures already inferred, but not proven, from consideration of the i.r. spectra. The ruthenium complexes also quite consistently showed the expected three g values. fac-[OsCl₃(PBu^a₂Ph)₃] showed only two g values. Thus, the technique unequivocally distinguishes the isomers of the d^5 complexes fac- and mer-[MX₃L₃] but could be misleading for cisand trans-[MX₄L₂].

The complex $[PHEt_3][RuCl_4(PEt_3)_2]$,⁴ for which no configuration was reported, has an e.s.r. spectrum consistent with a *trans*-configuration, in agreement with our inference from its i.r. spectrum.

²⁷ J. Chatt, G. J. Leigh, D. M. P. Mingos, E. W. Randall, and D. Shaw, *Chem. Comm.*, 1968, 419.

²⁸ N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1965, 237.

²⁹ E. W. Randall and D. Shaw, J. Chem. Soc. (A), to be published.

³⁰ J. H. E. Griffith and J. Owen, *Proc. Roy. Soc.*, 1954, *A*, **226**, 96.

³¹ A. Carrington and H. C. Longuet-Higgins, *Quart. Rev.*, 1960, **14**, 427.

³² A. Hudson and M. J. Kennedy, J. Chem. Soc. (A), 1969, 1116.

J. Chem. Soc. (A), 1969

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage and are corrected. Carbon and hydrogen analyses were carried out by our Microanalytical Laboratory. I.r. spectra in the region 200—500 cm.⁻¹ were determined as Nujol mulls between Polythene plates with a Grubb–Parsons D.M.4 grating spectrometer. Between 40 and 400 cm.⁻¹, the samples were studied in Polythene discs with a Research and Industrial Instrument Co. FS 620 interferometer. Fourier transforms were computed to an effective resolution of 5 cm.⁻¹. Unless otherwise stated spectra were obtained for each compound on both instruments.

The following compounds were prepared by procedures described in the literature: trans-[ReX₄L₂],¹ trans-[OSX₄L₂],¹ trans-[IrX₄L₂],¹ mer-[ReX₃L₃],¹ mer-[OSX₃L₃],¹ mer-[RuX₃L₃],¹ mer- and fac-[RhX₃L₃],^{12,13,16} mer- and fac-[IrX₃L₃],¹¹ trans-[LH][IrCl₄L₂],¹¹ [PHEt₃][RuCl₄-(PEt₃)₂],⁴ and cis- and trans[PtCl₄L₂].^{33,34}

fac-Trichlorotris(di-n-butylphenylphosphine)osmium(III). mer-Trichlorotris(di-n-butylphenylphosphine)osmium(III)(3.50 g., 1 mol.) was dissolved in ethanol-benzene (50/15 ml.), hydrazine hydrate (0.35 g., 2 mol.) was added, and the mixture was refluxed for 30 min. Addition of concentrated hydrochloric acid (3 ml.) to this solution caused the crystallisation of the maroon complex (0.70 g., 20%) m.p.

TABLE 8

E.s.r. spectra of some tertiary phosphine and arsine complexes of ruthenium(III), osmium(III), and iridium(III)

g Tensor components					
	g.	gy.	g_z	Symmetry	Phase
$mer-[RuCl_3(PMe_2Ph)_3]$	1.66	2.03	2.88	C_{2n}	Ether glass
mer-[RuCl ₃ (PEt ₂ Ph) ₃]	1.59	2.01	2.96	C_{2v}	Ether glass
$mer-[RuCl_{3}(PBu^{n}_{2}Ph)_{3}]$	1.60	2.02	2.94	C_{2n}^{-}	Ether glass
mer-[RuCl ₃ (AsPr ⁿ ₃) ₃]	1.64	2.06	2.93	C_{2n}^{-1}	Ether glass
trans-[RuCl ₄ (PEt ₃) ₂][PEt ₃ H]	1.64	2.51	2.51	D_{4h}	Alcohol–acetone glass
mer-[OsCl _a (PMe ₂ Ph) ₃] ^a		1.46	3.40	C_{2n}	Benzene glass
$mer-[OsBr_3(PMe_2Ph)_3]^a$		1.44	3.40	C_{2n}^{-1}	Benzene glass
mer-[OsCl ₃ (AsMe ₂ Ph) ₃] "		1.64	3.36	C_{2n}	Benzene glass
$mer-[OsCl_3(PEt_2Ph)_3]^{b}$	0.30	1.42	3.33	C_{2n}	Single crystal
$mer-[OsCl_3(PBun_2Ph)_3]$	0.36	1.66	3.33	C_{2v}^{-1}	Single crystal
$fac-[OsCl_3(PBu^n_2Ph)_3]$	1.28	1.83	1.83	C_{3v}	Ether glass
trans-[IrCl ₄ (PEt ₂ Ph) ₂] "		$2 \cdot 46$	2.65	Distorted D_{4h}	Ether-pentane-alcohol glass
trans [IrCl ₄ (AsPrn ₃) ₂]	0.80	2.43	2.43	D_{4h}	Single crystal

• The third g value was too small to be detected on our instrument. • N. J. Hill, personal communication.

¹H n.m.r. spectra were recorded for us on Varian HA100 and A60 spectrometers by Dr. D. Shaw (Varian Associates Ltd.) who also measured the effect of temperature on the spectra. The samples were measured in deuteriochloroform solutions and tetramethylsilane was used as an internal standard.

E.s.r. measurements were made for us by Dr. A. Hudson and M. J. Kennedy of this Department using a Varian Associates Ltd. E-3 spectrometer, operated at X-band frequencies. The solutions of samples were measured as glasses at -196° , and g values below 1.2 could not be obtained from glass samples because they were out of the range of the spectrometer. They were instead obtained from single-crystal analysis. 161—162° (from methylene dichloride-methanol) (Found: C, 52·2; H, 7·1. $C_{42}H_{29}Cl_3OsP_3$ requires C, 52·3; H, 7·2%). The complex is too insoluble in benzene for a molecular-weight determination.

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³³ Gmelins, 'Handbüch der Anorganischen Chemie,' Platin, Teil D, System No. 68, Verlag Chemie, Weinheim/Bergstrasse, 1957.

³⁴ J. Chatt, J. Chem. Soc., 1950, 2301.