Vibrational Spectra of some Octahedral Trimethylphosphine Complexes of Rhodium and Iridium

By **Peter L. Goggin** * and **John R. Knight**, Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Infrared and Raman spectra below 800 cm^{-1} of complexes *trans*-$[IrX_4(PMe_3)_2]^-$, *mer*- and *fac*-$[MX_3(PMe_3)_3]$, *trans*-$[MX_2(PMe_3)_4]^+$ (X = Cl or Br; M = Rh or Ir) and the i.r. spectrum of *trans*-$[IrCl_4(PMe_3)_2]$ are reported and vibrational assignments proposed. Metal–chlorine and metal–phosphorus stretching frequencies are discussed.

We have previously studied the vibrational spectra of linear and square-planar complexes containing trimethylphosphine.[1] In this paper, we extend the measurements to octahedral complexes, $IrCl_4(PMe_3)_2$, $[MX_4(PMe_3)_2]^-$, *mer*- and *fac*-$[MX_3(PMe_3)_3]$ and $[MX_2(PMe_3)_4]^+$, so as to increase the range of comparisons of metal–neutral ligand stretching frequencies. As trimethylphosphine is a less complex ligand than those used previously in vibrational studies of rhodium and iridium complexes of these types,[2-5] it should also permit more definite assignments of the MX stretching frequencies.

FREQUENCIES AND ASSIGNMENTS

Since rhodium(III) and iridium(III) octahedral complexes will have a d^6-low spin electronic configuration, it is safe to assume that isomerisation processes will be slow. The structures and isomeric purity of the complexes reported here [except $IrCl_4(PMe_3)_2$ which is d^5 and paramagnetic] have been established by ^1H n.m.r. spectroscopy details of which will be reported elsewhere.[6]

Complexes trans-$[IrX_4(PMe_3)_2]^{-1\ or\ 0}$.—The results for the anions *trans*-$[IrX_4(PMe_3)_2]^-$ (X = Cl or Br) are listed in Table 1 together with those for $IrCl_4(PMe_3)_2$. Unfortunately, information on the depolarisation ratio of the Raman bands could not be obtained because the iridium(III) solutions showed photochemically induced change in the laser beam and the very intense violet colour of the iridium(IV) complex precluded any Raman measurements.

The only previous Raman study of this type appears to be $[PHPr^n_3][IrCl_4(PPr^n_3)_2]$[5]; whilst there is more i.r. data,[2,4] the isostructural $PtX_4(PR_3)_2$ have been more extensively investigated [5,7] and provide a better guide to assignment. Assuming D_{4h} symmetry in the assignment of skeletal vibrations, we expect three halide stretching vibrations, A_{1g}, B_{1g}, and E_u which are easily identified. The frequencies agree with previous assignments and are all about 30 cm^{-1} lower than in *trans*-$PtCl_4(PEt_3)_2$ if the A_{1g} and B_{1g} are in the same order in both cases. The $E_u(MCl_4)$ vibration has a shoulder in the solid state i.r. spectra of the Ir^{III} complexes, and for the Ir^{IV} compound is two bands which reduce to a single feature for benzene solution. It is unlikely that the

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[1] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

[2] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789.

[3] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

[4] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

[5] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 2972.

[6] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, in the press.

[7] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1967, 1009.

solid is the *cis* isomer as the PC_3 stretching region indicates the *trans* configuration and has previously been shown to be useful for such differentiation.[8] The two Ir–P stretching frequencies can be assigned from the bromo-derivative except that the usual ambiguity and mixing with PC_3 deformations cannot be escaped! The internal motions of the ligand follow the assignments for *trans*-$PtCl_2(PMe_3)_2$.

TABLE 1

Vibrational spectra * (below 800 cm^{-1}) of *trans*-$[IrX_4(PMe_3)_2]^-$ (X = Cl or Br) and *trans*-$IrCl_4(PMe_3)_2$

	$[Pr^n{}_4N][IrCl_4(PMe_3)_2]$		$[PMe_3H][IrCl_4(PMe_3)_2]$		$[Pr^n{}_4N][IrBr_4(PMe_3)_2]$		$IrCl_4(PMe_3)_2$	
	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. (mull)	I.r. (benzene)
IrP_2 str A_{1g}		365s		363m		365s		
A_{2u}	337m		339m		342m		344m,sh	342sh
IrX_4 str A_{1g}		*311*vs		*311*vs		*195*vs		
B_{1g}		*295*s		*293*vs		*185*vs	*303*vw,sh	
E_u	*309*vs		*309*vs		*206*vs		*335*s	*329*vs
	*304*sh		*304*sh				*323*s	
PC_3 asym str	750m		745sh		753s		743m	†
	740vs	741m,bd	737vs	741m,bd	738vs	738m	740sh	
PC_3 sym str	674s	683s	674s	681s	675s	684s	673s	†
PC_3 asym def	276s	264m	277s	269m	286m		278w,bd	273w,bd
PC_3 sym def	227m	212s	227m	213s	242m	215m	227w,bd	221w,bd
PC_3 rock		197m		197w				
Skeletal def	170m	150s		143vs	130m			
and lattice	127w	137w			114s			
modes	96ms				86s			
	92ms				60m			
	68w							
Cation and	516w	522w		789m	516w	342m		
other bands		232m			302w	313m		
Limit of Study	(40)	(110)	(200)	(110)	(40)	(160)	(200)	(200)

* Except for skeletal stretching stretching vibrations, i.r. and Raman features are arranged side by side in spite of mutual exclusion for a centrosymmetric system. † Not investigated.

TABLE 2

Vibrational spectra (below 800 cm^{-1}) of *fac*-$MX_3(PMe_3)_3$ (M = Rh or Ir; X = Cl or Br)

	$RhCl_3(PMe_3)_3$			$RhBr_3(PMe_3)_3$		$IrCl_3(PMe_3)_3$			$IrBr_3(PMe_3)_3$		
	I.r. (mull)	Raman (solid)	Raman [a] (soln.)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	Raman [a] (soln.)	I.r. (mull)	Raman (solid)	Raman [a] (soln.)
MP_3 str A_1	391w	395w	389w,p	388m	385w	399w	402w	396m,p	398m	396w	394w,p
E	369m	371w	370vw,dp	367s	367w	375s	368w	374w,dp	374s		376vw,dp
MX_3 str A_1	*263*vs	*263*vs	*262*vs,p	*198*ms	*195*vs	*283*vs	*286*vs	*291*vs,p	*195*s	*199*s	*196*s,p
E	*233*vs	*232*vs	*236*s,dp	*175*vs	*180*s	*264*s	*269*m	*268*s,dp?	*175*vs	*175*s	*170*sh,dp
PC_3 asym str	743s	743m,sh	*b*	736sh	736sh	744sh	744sh		742sh	743m	*b*
	742sh					733s	738m	735m,dp	737vs		
	733sh	735m		729vs	729m			726sh	732s		
PC_3 sym str	688m	689s	*b*	684s	688s	691m	695vs	686vs,p	689s	691s	*b*
	678s	678w		676vs	680w	680s	674sh		678vs		
PC_3 asym def	299sh	300w	296w,bd,dp	315m		298sh			310m		
	282sh			295m	297w				293m		
PC_3 sym def	255sh				225s	246vs	248vs	249s,dp		236m	234m,bd,dp
and PC_3	195w	191m				209w	204s	198sh			
rock		173w,sh				176m	187sh		169vs		
MX_3P_3 def	152m	158sh		138s,bd	132s	150s	155sh		142s		
and lattice	148sh	146s							136sh		
		110w,sh		103w	108w		123m		107m		
	54w			92w		54m	76w		94w		
Other bands			324w,p								
Limit of study	(40)	(80)	(190)	(40)	(100)	(40)	(60)	(190)	(40)	(130)	(160)

[a] In nitromethane. [b] Not investigated.

Facial Isomers $MX_3(PMe_3)_3$.—The spectra are summarised in Table 2. The greatest attainable symmetry is C_{3v} with A_1 and E representations for the MP_3 and MX_3 stretching vibrations. The Raman studies in solution show the higher MP_3 stretching frequencies to be A_1. Previous workers[4,5] have assigned the two $RhCl_3$ stretching vibrations of facial isomers to bands near 300 and 270 cm^{-1} but for $RhCl_3(PMe_3)_3$, the only possible bands are 263 and 233 cm^{-1}. Whilst these frequencies are much lower than those of *cis*-$PdCl_2(PMe_3)_2$,

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[8] R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 1604.

they bear the same relationship to those of the iridium complex as those of the palladium complex do to the equivalent platinum complex. Bands are present in previously reported spectra corresponding to the band at 233 cm^{-1}. The strong band at 246 cm^{-1} in the spectra of $IrCl_3(PMe_3)_3$ could be regarded as an IrCl stretch but similar bands in *cis*-$MX_2(PMe_3)_2$[1] [M = Pd or Pt] have been assigned to a symmetric PC_3 deformation. As these bands are much stronger in the chloro-complexes than in the equivalent bromo-complexes, considerable mixing must occur. However, for the previously reported spectra of $IrCl_3(PR_3)_3$[4,5] the $IrCl_3$ frequency is close to 270 cm^{-1} so that the higher band (264 cm^{-1}) should be the more metal–chlorine stretching in nature.

Meridional Isomers $MX_3(PMe_3)_3$.—The observed frequencies are listed in Table 3, with assignment of skeletal stretching modes based on a C_{2v} description. The M–P stretching vibrations are easily assigned by comparison with planar $[MX(PMe_3)_3]^+$. Thus the higher frequency band in both i.r. and Raman spectra is MP (*trans* to X) stretching whilst the lower band is both asymmetric and symmetric vibrations of the linear MP_2 group. The latter Raman band shifts to higher frequency for the perpendicularly polarised condition indicating a contribution from the asymmetric vibration under the strongly polarised band due to the symmetric vibration. As with $[MX_3(PMe_3)]^-$ (M = Pd or Pt) the asymmetric MX_2 motion is likely to be very weak in the Raman effect but the symmetric MX_2 vibration is not necessarily very weak in the i.r. although it can be concealed under the asymmetric counterpart. These three vibrations can easily be identified in the spectra of *mer*-$IrCl_3(PMe_3)_3$ and this assignment agrees with those by previous workers for similar complexes.[2,4,5] We assign the rhodium complex in the same way in agreement with previous workers[3-5] but the mixing between the RhCl (*trans* to PMe_3) stretch with the PC_3 symmetric deformation at 240 cm^{-1} (no doubt of the phosphine *trans* to it) is particularly severe. This is shown not only by its high i.r. intensity but also by its abnormally high Raman intensity and exceptional degree of polarisation.

For the iridium bromide, the strong i.r. band at 206 cm^{-1} must be the asymmetric stretch whilst the strong, polarised Raman band at 192 cm^{-1} is the symmetric counterpart. The third band, at 178 cm^{-1}, is less polarised than the symmetric MBr_2 vibration. The RhBr frequencies are similar to IrBr except that the RhBr (*trans* to PMe_3) band is hidden beneath the $RhBr_2$ symmetric vibration in the Raman spectra but shows its presence by the shift of this band to lower frequency under perpendicular polarising conditions.

TABLE 3

Vibrational spectra (below 800 cm^{-1}) of *mer*-$MX_3(PMe_3)_3$ (M = Rh or Ir; X = Cl or Br)

	$RhCl_3(PMe_3)_3$			$RhBr_3(PMe_3)_3$				$IrCl_3(PMe_3)_3$				$IrBr_3(PMe_3)_3$			
	I.r. (mull)	Raman (solid)	Raman[a] (soln.)	I.r. (mull)	I.r.[b] (soln.)	Raman (solid)	Raman[a] (soln.)	I.r. (mull)	I.r.[c] (soln.)	Raman (solid)	Raman[a] (soln.)	I.r. (mull)	I.r.[c] (soln.)	Raman (solid)	Raman[a] (soln.)
MP str	387w	388w	391w,p	388m	385m	388w	384wm,p	394m	393m	396w	393m,p	394m	393m	397w	394wm,p
MP_2 str (sy		356w	361m,p			362w	359w,p			366w	363m,p			375vw	364wm,p
(asym)			363wm,dp	360s	362s		362w,dp	364m	365ms		365w,dp	365s	365ms		367vw,dp
MX_2 str (sym)	*297*sh	*297*vs	*301*vs,p	*188*m		*184*vs	*186*vs,p	*312*sh		*313*vs	*311*vs,p	*193*m		*199*vs	*192*vs,p
(asym)	*346*vs	*346*vw		*206*s	*205*m			*322*vs	*324*s	*326*sh		*206*s	*210*ms		
MX str	*264*s	*265*m	*257*w	*176*s			*180*m,?	*266*vs	*272*ms	*267*s	*267*s,p	*178*s		*173*m	*178*ms,p
PC_3 asym str	740s	745m	744m,dp	740s	†	738m	†	742vs	†	745m	741m,dp	739vs	†	742m	740m,dp
	728vs	727m	736w,sh,dp	729vs		729m		731vs		735m	735m,dp	727vs		734wm	732m,dp
PC_3 sym str	679m	686s	683s,p	678ms	†	684s	†	684s	†	689s	684vs,p	680s	†	689s	685vs,p
	672s	674sh	666s,p	670s				676vs		676sh	679sh	672s		680sh	
PC_3 asym def				308w								312sh		320vw	
	286s			290w	279m			290s	295m		288w	299m	*ca.* 300sh		
				278m	272m		280w,bd,dp					288m		292w	290w,bd,dp
PC_3 sym def and	237s	239s	240vs,p		245wm			245s	245m	246m	240w,sh				
PC_3 rock			*ca.* 220p			222m	214s,p			230w	230s,p	229sh	230sh	224m	231ms,bd,p
		199s	196vs,p							206s	203s,p				*ca.* 204w,sh
	181w											172vw			
MX_3P_3 def and								161w							
lattice	142s	146m		129sh				147s		147s	141s,dp			129m	
		139sh	138vs,dp	124vs		123sh		134sh				121s		119m	
	113w	110w				110sh		113m		120sh				102s	
												90w		85w	
														73sh	
										80sh				67vs	
														49vw	
														38m	
Other bands			329vw,p		335w		332w,p	352sh	356sh						334wm,p
														259wm	262sh
														251wm	
														154vw	
														145vw	
Limit of study	(40)	(100)	(110)	(40)	(200)	(80)	(150)	(40)	(200)	(60)	(120)	(40)	(200)	(25)	(140)

[a] In nitromethane. [b] In dibromomethane. [c] In dichloromethane.
† Not investigated.

Complex Cations $[MX_2(PMe_3)_4]^+$.—The spectra of these cations, which ^1H n.m.r. showed to have the *trans* configuration,[6] are summarised in Table 4. The MX_2 stretching frequencies are readily identified as mutually exclusive i.r. and Raman bands near to the frequencies of the MX_2 stretching vibrations of the meridional complexes. Any band in the region 400—310 cm^{-1} might be a MP_4 vibration except that ν_2 of BF_4^- occurs as a weak Raman band at 364 cm^{-1} and is sometimes detected in the i.r. spectra of solids. In general, five bands occur in this region, (i) 390—400 cm^{-1}, Raman-active and polarised but seen in i.r. of the rhodium complexes; (ii) *ca.* 380 cm^{-1}, i.r.-active only; (iii) 350—365 cm^{-1}, i.r.-active and sometimes seen as a depolarised Raman band; (iv) 340—350 cm^{-1}, Raman-active only and polarised; and (V) *ca.* 320 cm^{-1} with same behaviour as band (iii). The maximum possible number of MP stretching frequencies is four and the most reasonable band to assign to another cause is (v) which could be asymmetric PC_3 deformation {our previous assignment [1] of bands near to 320 cm^{-1} to a B_{1g} metal–phosphorus stretch in $[M(PMe_3)_4]^{2+}$ [M = Pd or Pt] may therefore be in error}.

TABLE 4

Vibrational spectra (below 800 cm^{-1}) of *trans*-$[MX_2(PMe_3)_4]^+$ (M = Rh or Ir; X = Cl or Br)

	$[RhCl_2(PMe_3)_4][BF_4]$			$[RhBr_2(PMe_3)_4][BF_4]$				$[IrCl_2(PMe_3)_4][NO_3]$			$[IrBr_2(PMe_3)_4][NO_3]$		
	I.r. (mull)	Raman (solid)	Raman (soln.) [a]	I.r. (mull)	I.r. (soln.) [a]	Raman (solid)	Raman (soln.) [a]	I.r. (mull)	Raman (solid)	Raman (soln.) [a]	I.r. (mull)	Raman (solid)	Raman (soln.) [a]
MP_4 str	391w		394w,p	390w		390vw	386w,p			402wm,p			397w,p
	380w			375w	370wm			378w			380w		
	352sh	350m	364w,dp	352w	353vw	352wm	352w,dp	363w		360vvw	364w		364w,dp
			338w,bd,p			340?	344wm,p		340w	335wm,bd,p		350w	347vw,p
MX_2 str (sym)		*302*vs	*302*s,p			*188*vs	*189*vs,p		*314*vs	*316*vs,p		*199*vs	*192*vs,p
(asym)	*361*s	*362*w		*211*s	*205*ms			*329*vs			*214*vs		
PC_3 asym str	737s	740m	742wm,dp	737s	†	733m	740wm,dp	740s	741m	745wm,dp	737s	739m	738m,dp
	723s	728w	725wm,dp	727s		730m		725s	731m	727wm,dp	722s	728w	722wm,dp
				725sh		720m	724wm,dp						
PC_3 sym str	684w	688m	684sh,p		†				683vs	684s,p		684m	681s,p
		678s	678ms,p	669s		677s	678ms,p						
	669s			666s				671s	670w,sh		670s		
PC_3 asym def	320w	324w		319s	328wm,sh		318w,dp	320sh			319s		
	292s			289s	320ms			298s			305s		
	286sh			283sh	290m	286wm	287m,dp	290s			291s		
PC_3 sym def			262w,p	250w				248sh					
and PC_3 rock	236s							242m	236s	229s,p	240m	238m	228s,p
		228m	219s,p			227m	217s,bd,p	210w		215sh			
		198s	201sh						201s	196s,dp			208sh
	185w		185m,dp					190w					176w,dp
MX_2P_4 def and	169w							163w	163m				
lattice	165w												
	137s		139m,dp	126vs		120w		128s			127s	114w	
	104w			92sh				105s			92m		
				88m				90m					
	76m			65m				73m			73m		
	61sh							61sh					
BF_4 (ν_1)		766m	765w,p				766w,p						
Limit of study	(40)	(150)	(110)	(40)	(200)	(100)	(120)	(40)	(150)	(180)	(40)	(80)	(140)

[a] In nitromethane.
† Not investigated.

It is difficult to imagine the remaining four bands as anything but MP_4 vibrations but if they are, there are two totally symmetric motions, no degeneracies, and a lack of mutual exclusion between Raman and i.r., and the point group must be of relative low symmetry such as C_s or C_2. This lowering of symmetry could be due to the orientations of the PC_3 groups or non-planarity of the MP_4 skeleton or both. Whilst it would be possible to rationalise the top three frequencies with A_{1g}, E_u, and B_{1g} vibrations of a D_{4h} structure such an interpretation is not logically justified.

DISCUSSION

Along the series $[IrCl_4(PMe_3)_2]^-$, *mer*-$IrCl_3(PMe_3)_3$, $[IrCl_2(PMe_3)_4]^+$ there is a general increase in IrCl stretching frequencies for groups in which chlorine atoms are *trans* to each other, suggesting that the charge at the metal actually is increasing as the formal positivity of the complex increases, the neutral phosphine being a poorer donator of charge than the negative halide. Between the first and second members the asymmetric IrP_2 stretching frequency increases very markedly although the symmetric stretching frequency is slightly lowered, exactly paralleling the relationship between *trans*-$PtCl_2(PMe_3)_2$ and $[PtCl(PMe_3)_3]^+$. This change in the asymmetric frequency is much more marked than that caused by oxidation to Ir^{IV}. In all the complexes of meridional type that we have studied the symmetric and asymmetric *trans*-MP_2 frequencies are practically coincident and are lower than the M–P (*trans* to halide) frequency, reflecting the well established relative *trans* influences of phosphines and halides.

The metal–phosphorus frequencies in the rhodium compounds are all a little lower than those of the iridium analogues, behaviour similar to that observed between palladium and platinum complexes.

Comparing Pt and Pd planar complexes $[MCl_3PMe_3]^-$ and *cis*-$MCl_2(PMe_3)_2$ with Rh and Ir octahedral *mer*- and *fac*-$MCl_3(PMe_3)_3$ respectively, the M–Cl (*trans* to PMe_3) frequencies of the latter are lower for elements in the same period than those of the former, commonly by 10—20 cm^{-1}. Since there is much more vibrational frequency data published for Pt and Pd complexes, this relationship may prove useful in Rh and Ir studies.

Because of its colour, we only have information on i.r. active vibrations of *trans*-$IrCl_4(PMe_3)_2$, but it is still of interest to compare these with those of the isostructural Ir^{III} compound. The $B_u(IrCl_4)$ frequency is increased on oxidation by 20 cm^{-1} whilst the $A_{2u}(IrP_2)$ frequency is only half as sensitive. In so far as any trend can be inferred from such limited data, it appears that the strengthening of the Ir–Cl bonding is greater than that of Ir–P.

There is a close relationship between trends in Ir–P and IrCl frequencies and the relevant bond lengths in (a) *mer*-$\mathrm{IrCl_3(PMe_2Ph)_3}$ and (b) *trans*-$\mathrm{IrCl_4(PMe_2Ph)_2}$, the bond lengths (in Å) being (a) Ir–P (*trans* to Cl) = 2·277, (a) Ir–P (*trans* to P) = 2·363, (b) Ir–P 2·392 and (b) Ir–Cl = 2·324, (a) IrCl (*trans* to Cl) 2·361, (a) IrCl (*trans* to P) = 2·429.[9]

EXPERIMENTAL

Preparation of Compounds.—Analytical data are presented in Table 5. *Complexes containing anions* $[\mathrm{IrX_4(PMe_3)_2}]^-$. Chloroiridic acid (0·87 mmol) was dissolved in ethanol (15 ml) and a little concentrated HCl (5 drops) added. This solution, in a Carius tube, was heated on a water bath until the colour lightened to brownish green. Trimethylphosphine (3·3 mmol), generated from freshly prepared $\mathrm{AgIPMe_3}$, was condensed on to this solution at liquid $\mathrm{N_2}$ temperature. The tube was sealed and warmed to 80 °C until all solid had dissolved (*ca.* 1 h). The tube was cooled, opened, and solvent removed to yield a solid which on recrystallisation from methanol gave pink crystals of $[\mathrm{PMe_3H}][\mathrm{IrCl_4(PMe_3)}]$. When this compound was dissolved in a minimum of water and a slight excess of $\mathrm{Pr^n{}_4NCl}$ added, $[\mathrm{Pr^n{}_4N}][\mathrm{IrCl_4(PMe_3)_2}]$ was precipitated; this was obtained as pink crystals by recrystallisation from methanol. To obtain $[\mathrm{Pr^n{}_4N}][\mathrm{IrBr_4(PMe_3)_2}]$ a solution of bromoiridium(IV) acid, obtained from $\mathrm{K_2IrBr_6}$ by ion-exchange, in a minimum of water was used as the starting material. It was mixed with ethanol and concentrated HBr and treated as in the above method. When most of the solvent had been removed after reaction, a slight excess of $\mathrm{Pr^n{}_4NBr}$ in a minimum of water was added to precipitate the product, which was purified by dissolving in dichloromethane, drying with dried $\mathrm{MgSO_4}$, and slowly reprecipitating with ether.

TABLE 5

Analytical data for the complexes

Compound	Colour	M.p.	C	H	N
$[\mathrm{PMe_3H}][\mathrm{IrCl_4(PMe_3)_2}]$	Pink	280 [a]	19·45(19·4) [b]	5·2(5·0)	
$[\mathrm{Pr^n{}_4N}][\mathrm{IrCl_4(PMe_3)_2}]$	Pink	239	32·55(32·6)	6·9(7·0)	1·9(2·1)
$[\mathrm{Pr^n{}_4N}][\mathrm{IrBr_4(PMe_3)_2}]$	Brown	252	24·8(25·4)	5·4(5·5)	1·6(1·65)
fac-$\mathrm{RhCl_3(PMe_3)_3}$	Very pale yellow	252	24·45(24·7)	6·2(6·2)	
fac-$\mathrm{RhBr_3(PMe_3)_3}$	Pale yellow	245	19·15(18·9)	5·1(4·7)	
fac-$\mathrm{IrCl_3(PMe_3)_3}$	White	363	20·6(20·5)	5·2(5·1)	
fac-$\mathrm{IrBr_3(PMe_3)_3}$	White	358	16·3(16·35)	4·1(4·1)	
mer-$\mathrm{RhCl_3(PMe_3)_3}$	Yellow	232	24·7(24·7)	6·0(6·2)	
mer-$\mathrm{RhBr_3(PMe_3)_3}$	Orange	260	19·1(18·9)	5·1(4·7)	
mer-$\mathrm{IrCl_3(PMe_3)_3}$	Yellow	295	20·6(20·5)	5·0(5·1)	
mer-$\mathrm{IrBr_3(PMe_3)_3}$	Yellow	325 [d]	16·6(16·35)	3·7(4·1)	
$[\mathrm{RhCl_2(PMe_3)_4}][\mathrm{BF_4}]$	Yellow	208	25·75(25·45)	6·4(6·4)	
$[\mathrm{RhBr_2(PMe_3)_4}][\mathrm{BF_4}]$	Yellow	215	22·1(22·05)	5·7(5·5)	
$[\mathrm{IrCl_2(PMe_3)_4}][\mathrm{NO_3}]$	Pale yellow	245	23·05(22·9)	6·0(5·7)	2·45(2·25)
$[\mathrm{IrBr_2(PMe_3)_4}][\mathrm{NO_3}]$	Yellow	251	20·15(20·05)	5·1(5·0)	2·0(1·95)
$\mathrm{IrCl_4(PMe_3)_2}$	Purple	190	14·95(14·8)	3·6(3·7)	

[a] Turns yellow at 180°. [b] Calculated values (%) in parentheses. [d] With decomposition.

mer- *and* fac-$\mathrm{MX_3(PMe_3)_3}$.—Hydrated rhodium trihalide (1 mmol) was dissolved in methanol (15 ml) and trimethyl phosphine (4 mmol) was condensed into it. The mixture was allowed to warm up to room temperature and stirred (10 min). The solution was evaporated to dryness; the residue was extracted with benzene and on evaporation yielded the *mer*-isomer which was recrystallised from methanol. The benzene-insoluble residue was continuously extracted with dichloromethane to yield the *fac*-isomer which was recrystallised from methanol. The rhodium chloride complexes have been reported before but the *fac*-isomer was evidently not pure.[10]

The iridium complexes were prepared by the same method as that described for the anionic complexes except that a higher $\mathrm{PMe_3}$: Ir ratio (5 : 1) and much longer reaction times at 80 °C (3 days) were used. The products were treated as outlined above for rhodium. Solutions of the *mer*-isomers in dichloromethane were found to deposit crystals of the much less soluble *fac*-isomer if left to stand (after a day).

Cationic Complexes.—A solution of *mer*-$\mathrm{MX_3(PMe_3)_3}$ in dichloromethane was stirred with 1 mol equivalent of $\mathrm{AgNO_3PMe_3}$ for 12 h. The solution was filtered and removal of the solvent yielded $[\mathrm{MX_2(PMe_3)_4}][\mathrm{NO_3}]$. A solution of this product in a minimum of water yielded a precipitate of $[\mathrm{MX_2(PMe_3)_4}][\mathrm{BF_4}]$ when treated with a few drops of 40% aqueous fluoroboric acid. The product was recrystallised from dichloromethane, after drying with dried $\mathrm{MgSO_4}$, by slow addition of ether.

$\mathrm{IrCl_4(PMe_3)_2}$ was prepared by oxidation of $[\mathrm{Pr^n{}_4N}][\mathrm{IrCl_4(PMe_3)_2}]$ in chloroform with the required amount of a solution of chlorine in chloroform. The solvent was evaporated under reduced pressure and the desired product obtained as deep purple crystals from an ether extract, and recrystallised from dichloromethane.

Vibrational measurements were made as previously described[11] except that in order to get high enough concentrations for Raman studies of solutions, the nitromethane solutions of the *fac*-isomers were studied at 60 °C.

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