Vibrational Spectra and Nuclear Magnetic Resonance Parameters of some Platinum(IV) Complexes $[PtX_4L_2]$ and $[PtX_5L]^-$ (X = Cl, Br, or I; L = NMe_3, PMe_3, $AsMe_3$, or SMe_2)

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trans-$[PtX_4L_2]$ (L = PMe_3, $AsMe_3$, or SMe_2; X = Cl or Br) and, except X = Br for SMe_2, *cis*-complexes have been isolated, together with the salts $Pr^n{}_4N[PtX_5L]$, $Pr^n{}_4N[PtI_5PMe_3]$, $Pr^n{}_4N[PtCl_5NMe_3]$, and $[PtCl_3(PMe_3)_3]BF_4$. The vibrational spectra of the complexes have been studied. ^1H N.m.r. measurements have been made for these and other halide derivatives which were prepared *in situ* but were unstable to isolation in a pure form. Values of J_{PtP} and δ_P have been measured by heteronuclear INDOR and, in addition, those of related platinum(II) and palladium(II) compounds are reported. Approximate values of J_{PtN} have been obtained from $^1H(^{195}Pt)$ INDOR in three cases. The spectroscopic parameters are discussed and it is concluded that variations in them are consistent with significant π-contribution to Pt–P bonding, at least in platinum(II) complexes.

WHEN discussing the significance of π-bonding in the platinum–phosphorus bond, Venanzi[1] has emphasised the usefulness of comparisons between Pt^{II} and Pt^{IV} systems since the relevant platinum *d* orbitals are much less available in Pt^{IV} than Pt^{II}. We have examined vibrational and n.m.r. spectra of some Pt^{IV} analogues of Pt^{II} complexes of PMe_3, $AsMe_3$, NMe_3, and SMe_2 which we studied previously.[2-5] Many square-planar platinum(II) complexes are relatively easily oxidised to the platinum(IV) complex by addition of Cl_2, Br_2, or I_2. In this way the salts $Pr^n{}_4N[PtX_5L]$ (where L is a neutral ligand and X a halide) have been obtained as well as the more familiar complexes $[PtX_4L_2]$. The iodides seemed to be of low stability which made isolation difficult and the only iodide obtained as a purified solid was $Pr^n{}_4N[PtI_5PMe_3]$. Of the trimethylamine complexes, only $Pr^n{}_4N[PtCl_5NMe_3]$ proved to be stable to isolation as a pure compound and our investigations of $[PtX_4(NMe_3)_2]$ complexes have been confined to n.m.r. studies on the complexes in solution prepared *in situ*.

RESULTS

Vibrational Spectra.—The observed Raman and i.r. bands are collected in Tables 1 ($Pr^n{}_4N[PtX_5L]$), 2 (*trans*-$[PtX_4L_2]$), 3 (*cis*-$[PtX_4L_2]$), and 4 (*mer*-$[PtX_3(PMe_3)_3]BF_4$). The vibrations of the neutral ligands when bound to platinum(II) have been discussed in detail before.[2,4,5]

Stretching vibrations: (a) $[PtX_5L]^-$. If the neutral ligand is regarded as a single point, then the symmetry of these anions is C_{4v} with stretching vibrations of species A_1(Pt–L), A_1(Pt–X), $A_1(PtX_4)$, $B_1(PtX_4)$, and $E(PtX_4)$ all of which are Raman- and i.r.-active except B_1 which is Raman-active only. If the incompatibility between the four-fold symmetry of the PtX_5 group and the symmetry of the ligand is taken into account, the overall symmetry cannot be higher than C_s. However, for the related situation of $[PtX_3L]^-$, we found no definite indication that the skeletal vibrations were sensitive to any lowering of symmetry (from C_{2v}).[2] We have assumed C_{4v} symmetry in the following discussion and the deviations observed commonly concern only skeletal deformations or internal ligand modes and then only in solid-state spectra where they could be due to the crystal environment. Below 800 cm^{-1} there are also some vibrations associated with the tetrapropylammonium cation; these are generally weak compared with vibrations of the anion and occur at 752ms, 721w, 614vw, 516wm, 370vw, and 340vw cm^{-1} in the i.r. spectrum of solid $Pr^n{}_4NI$ and 781m,p, 762vw,sh, 518vw,dp, 375m,p, 334m,dp, and 311s,p cm^{-1} in the Raman spectrum of aqueous $Pr^n{}_4NCl$.

Comparison of the ions $[PtCl_5PMe_3]^-$ and $[PtBr_5PMe_3]^-$ indicates the platinum–chlorine stretching modes as 337 and 275 cm^{-1} (i.r.) and 336, 316, and 274 cm^{-1} (Raman). The high intensity and strongly polarised nature of the Raman band at 336 cm^{-1} agree with its assignment as the symmetric-stretching vibration of the $PtCl_4$ plane, $A_1(PtX_4)$. As the band at 316 cm^{-1} is depolarised, it must be the $B_1(PtX_4)$ vibration. It is improbable that the $A_1(PtX_4)$ mode would account for the very strong i.r. band at 337 cm^{-1} and we regard this band as arising primarily from the $E(PtX_4)$ mode. The i.r. intensity of the A_1 mode cannot be assumed to be negligible (*cf.* $[PdCl_3L]^-$ where the related vibrations are not coincident[6]), but the polarised measurements shows that the Raman intensity of the *E* mode is very small. The wavenumber coincidence of these two modes parallels that between the symmetric and asymmetric $PtCl_2$ stretching modes in the anions $[PtCl_3L]^-$.[2,6] All three of these PtX_4 vibrations are close to the related modes of the complex *trans*-$[PtCl_4(PEt_3)_2]$[7,8] in accord with the observation of Adams and Chandler[8] that vibrations of the PtX_4 group are remarkably insensitive to substituents above or below the plane. The band at 274 cm^{-1} must be the PtCl(*trans* to PMe_3) stretch, A_1(PtX), but it is only slightly polarised; however, comparison with the bromide shows that the contribution to this band from the PC_3 asymmetric deformation is small.

The assignment of vibrations of the $PtCl_4$ group in the

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[4] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1972, 1298.

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TABLE 1

Vibrational spectra (below 800 cm^{-1}) of the salts $Pr^n_4N[PtX_5L]$ (X = Cl, Br, or I; L = NMe_3, PMe_3, $AsMe_3$, or SMe_2)

	$Pr^n_4N[PtCl_5PMe_3]$				$Pr^n_4N[PtBr_5PMe_3]$				$Pr^n_4N[PtI_5PMe_3]$	$Pr^n_4N[PtCl_5AsMe_3]$			
	I.r.$_{mull}$	I.r.$_{soln.}$ [a]	R$_{solid}$	R$_{soln.}$ [a]	I.r.$_{mull}$	I.r.$_{soln.}$ [a]	R$_{solid}$	R$_{soln.}$ [a]	I.r.$_{mull}$	I.r.$_{mull}$	I.r.$_{soln.}$ [b]	R$_{solid}$	R$_{soln.}$ [a]
PtL str. A_1‡	371m	371m	371m	371w,p	367m	368m	367w	370m,p	365m	257ms	261m	257ms	261m,p
PtX str. A_1	*272*s	*275*s	*271m*	*274*m,dp	192vs		*191*vs	*190*s,dp	*154*m	*286*m	*291*m	*286*w	*291*w
PtX_4 str. A_1	*330*sh		*334*vs	*336*vs,p	*209*s	*207*m	*209*s	*208*vs,p	*137*m			*337*s	*338*vs,p
B_1	*313*vw		*314*s	*316*ms,dp			*191*vs	*190*s,dp				*318*s	*317*s,dp
E	*336*vs	*337*vs			*225*s	*226*s			*180*s	*336*vs	*333*vs		
YC_3asym. str.	766m	†			752m	†	754vw	754vw,dp	749w	635wm	†	636vw	635w,dp
			757vw	758vw,dp						629wm	†	629vw	
YC_3sym. str.	686m	†	685w	683w,p	682m	†	686w	684w,p	681w	596wm	†	596w	600m,p
YC_3asym. def.					280vw				275vw,bd				
YC_3sym. def.‡ and YC_3 rock	240bd,sh	240bd,sh	242m,bd	239m,p	238s	244ms	238w	237m,p	247vw			205s	205m,p
			235sh							191vw			
	167vvw,sh				153vw								
MX_4 in-plane def. E	181wm				120m				112wm	172vw			
B_2			153vs	151ms,dp			102m	100sh,dp				153s	160w,dp
Other defs. and lattice	152m				107w				100vw	139w		139vs	
	119w											106w	
			93m				88vw						
	62m,bd				58wm,bd					50m,bd			
Cation and other bands	757m								756sh	752wm			
	744w,sh												
	721w				724w,sh				722w	722w			
	591vw												
	566vw												
	515vw				512w					514w			
	470w									466w			
			435w				437w						
					336vw								
Limit of study	(40)	(200)	(80)	(100)	(40)	(200)	(70)	(70)	(40)	(40)	(200)	(80)	(140)

TABLE 1 (*Cont.*)

	Pr$^n_4$N[PtBr$_5$AsMe$_3$]				Pr$^n_4$N[PtCl$_5$NMe$_3$]				Pr$^n_4$N[PtCl$_5$SMe$_2$]				Pr$^n_4$N[PtBr$_5$SMe$_2$]			
	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [a]	R$_{\text{solid}}$	R$_{\text{soln.}}$ [a]	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [c]	R$_{\text{solid}}$	R$_{\text{soln.}}$ [c]	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [a]	R$_{\text{solid}}$	R$_{\text{soln.}}$ [a]	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [a]	R$_{\text{solid}}$	R$_{\text{soln.}}$ [a]
PtL str. A_1‡	270vw			270vw?	548m	548w	549wm	549wm					322m		323w	322w,p
PtX str. A_1	*180*s		*191vs*	*180*s,p	*327*s	*330*s	*329*s	*327*ms	*317*vs,bd	*329*s			*202*m		*199*s	*199*vs,p
PtX$_4$ str. A_1	*210*m	*209*m	*206*vs	*207*vs;p	*345*s	*341*s	*344*s	*342*s			*340*vs	*338*vs,p	*216*vs	*221*s	*216*s	*218*vs,p
B_1			*191*vs	*192*s,dp			*315*s	*313*ms			*315*vs	*317*s,dp			*193*s	*190*vs,d
E	*243*ms	*241*s	*242*vw		*336*s	*341*s			*340*vs	*338*s			*241*vs	*239*s		
YC$_3$(SC$_2$)asym. str.	628m			629vw,dp	†	†	†	†	722vw		731vvw		722vw			683vw,p
YC$_3$(SC$_2$)sym. str.	596m			598m,p	820s	†	820w	†	687vw		687vw	682vw,p	685vw			
YC$_3$asym. def. (SC$_2$ def.)			232w						292m,sh		291w		290w		289vw	
YC$_3$sym. def.‡ and YC$_3$(SC$_2$) rock					282m,bd	†	258m	257m	231m		226m	230m,p	221sh		241vw	241w,p
MX$_4$ in-plane def.																
E	114wm				193w		191w	192vw	177m				121m			
B_2			96s				162s	162m			152s	154ms,dp			99vs	
Other defs. and lattice	97wm				177sh				152m		159sh		129s		139w	
					165w				148sh				106w		106sh	
					139w				127m				101sh			
													91w		89ms	
	44w,bd								58ms				60s			
Cation and other bands	752wm				750ms				776s				766w			
									754m				753m			
	721vw								748sh				747sh			
									612vw							
	512vw				515w	512vw			516w				514m			
						383m						368w,sh,p	342w			
	322vvw			306vw,p									249sh			304w,p
Limit of study	(40)	(200)	(70)	(130)	(40)	(200)	(70)	(120)	(40)	(200)	(60)	(90)	(40)	(200)	(35)	(120)

[a] In nitromethane. [b] In *cis*-1,2-dichloroethylene. [c] In dichloromethane.
† Not investigated or obscured by solvent bands. ‡ Coupled modes (see text).

TABLE 2

Vibrational spectra (below 800 cm^{-1}) of the complexes *trans*-[PtX$_4$L$_2$] (X = Cl or Br; L = PMe$_3$, AsMe$_3$, or SMe$_2$)

	[PtCl$_4$(PMe$_3$)$_2$]				[PtBr$_4$(PMe$_3$)$_2$]			[PtCl$_4$(AsMe$_3$)$_2$]		
	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [a]	R$_{\text{solid}}$	R$_{\text{soln.}}$ [a]	I.r.$_{\text{mull}}$	R$_{\text{solid}}$	R$_{\text{soln.}}$ [a]	I.r.$_{\text{mull}}$	I.r.$_{\text{soln.}}$ [a]	R$_{\text{solid}}$
PtL$_2$ str. A_{1g}			358s	357vs,p		360m	358w,p			254m
A_{2u}	347vs				349m			264m	264w	
PtX$_4$ str. A_{1g}			*339*vs	*335*vs,p		*201*vs	*203*vs,p			{*338*s *336*sh
B_{1g}			*322*s	*318*s,dp		*192*vs	*191*s,dp			*320*ms
E_u	*337*vs	343*vs*			*250*m			{*344*s *337*s	*342*s	
YC$_3$asym. str.	755s	†			755sh			631m	†	
					749s			627s	†	
			758vw	†		749w	†			630sh
			749vw	†						628m
YC$_3$sym. str.	679s	†			674s			592s	†	
			685m	†		679m	†			596ms
YC$_3$asym. def.	279m	275m			282w			196m,sh		
			282sh			283w				233w
			268wm			267w				222m
YC$_3$sym, def.	235m									
and YC$_3$ rock	232m	228m			220s	227sh		184s		
			227m			218m	*ca.* 214sh,p			168vs
			208s			214sh				
	203w	201w			205sh					
PtX$_4$ in plane def.										
E_u	177wm				118s			164wm		
B_{2g}	156vw		159m			98s		148vw		159sh
LPtX def. E_g			140s			117s				120s
Other defs. and	128w				132m			120w		130sh
lattice	108s				93w			92s		73vw,bd
					83w			84sh		*ca.* 50bd,sh
										41ms
Other bands					324w					178sh
Limit of study	(40)	(200)	(60)	(280)	(40)	(60)	(175)	(40)	(200)	(30)

	[PtBr$_4$(AsMe$_3$)$_2$]			[PtCl$_4$(SMe$_2$)$_2$]			[PtBr$_4$(SMe$_2$)$_2$]		
	I.r.$_{\text{mull}}$	R$_{\text{solid}}$	R$_{\text{soln.}}$ [b]	I.r.$_{\text{mull}}$	R$_{\text{solid}}$	R$_{\text{soln.}}$ [b]	I.r.$_{\text{mull}}$	R$_{\text{solid}}$	R$_{\text{soln.}}$ [b]
PtL$_2$ str. A_{1g}		259vw	255w,p				330sh	324ms	335m,p
A_{2u}	264m			316m			319m		
PtX$_4$ str. A_{1g}		*207*vs	*206*vs,p	*342*sh	*340*vs	*339*vs,p		*200*s	*203*vs,p
B_{1g}		*193*vs	*193*ms,dp		*321*vs	*321*s,dp	*188*vvw	*189*vs	*200*sh,dp?
E_u	*245*s			*349*vs			*242*s		
YC$_3$(SC$_2$)asym. str.	628m			732vw					
	623s			724vw			723vw		
					728vw	†		729vw	†
		624w	623w						
YC$_3$(SC$_2$)sym. str.	591s						684w		
		595m	594ms		682w	†		685w	†
YC$_3$asym. def.	191sh			292w			303w		
(SC$_2$ def.)					277m	285m,p		287m	285ms,dp
		221vvw							
YC$_3$sym. def.				255w			225sh		
and YC$_3$(SC$_2$) rock	183s						218s		
	178sh	173s	170ms,p		220m	220ms,bd,p		220m	223sh,p
					212m				
PtX$_4$ in plane def. E_u	109ms			178s			123vs		
B_{2g}		94s		161w	162m}	140ms,bd,dp		102ms	
LPX def. E_g		102s			151s}			139m	
Other defs. and lattice	120wm			134w			157vw		
	97vw			130sh			134vs	127m,bd	
	82wm	57vw		111wm			103w		
	75wm	46sh					95w	69wm,bd	
					49wm			50m	
					36m			38sh	
								32ms	
Other bands				245w,bd			261w,bd		
				189vw					
Limit of study	(40)	(30)	(108)	(40)	(25)	(120)	(40)	(20)	(140)

[a] In benzene. [b] In tetrahydrofuran.

† Not investigated or obscured by solvent bands.

TABLE 3

Vibrational spectra (below 800 cm^{-1}) of the complexes *cis*-$[PtX_4(YMe_3)_2]$ (X = Cl or Br; Y = P or As) and *cis*-$[PtCl_4(SMe_2)_2]$

	$[PtCl_4(PMe_3)_2]$			$[PtBr_4(PMe_3)_2]$		$[PtCl_4(AsMe_3)_2]$		$[PtBr_4(AsMe_3)_2]$		$[PtCl_4(SMe_2)_2]$	
	I.r.$_{mull}$	R$_{solid}$	R$_{soln.}$[a]	I.r.$_{mull}$	R$_{solid}$	I.r.$_{mull}$	R$_{solid}$	I.r.$_{mull}$	R$_{solid}$	I.r.$_{mull}$	R$_{solid}$
MY_2 str. (sym.)	381m	382w		377m	379m	273m	276w	280w			343s
(asym.)	362s	364w		359m	361m	257vs	254w,bd	266w			
MX_2(*trans*) str. (sym.)	*336*s	*337*vs	*334*s,p	*208*s	*210*vs	*337*sh	*337*vs	*207*s	*209*vs	*335*s	*336*s
(asym.)	*348*vs	*349*w		*249*wm		*347*vs	*348*w	*250*s	*252*vw	*346*vs	*350*sh
MX_2(*cis*) str. (sym.)	*296*vs	*295*s	*302*wm,p	*191*s	*195*vs	*301*vs	*303*m	*183*s	*186*vs		*321*vs
(asym.)	*271*vs	*277*s	*288*wm,dp	*185*vs	*186*vs	*285*vs	*287*m	*177*vs	*178*vs	*317*vs	
$YC_3(SC_2)$ asym. str.	759sh										
	756m			750m	755sh	635sh	632m	629sh	630sh		728w
	750m			745m	748wm	628s		625s	626m		716w
	744m			740m	743sh	623sh	624sh	619s	621w		
$YC_3(SC_2)$ sym. str.	684s			681ms	684s	595ms	597s	593s	595m	682vw	685wm
	677s			674ms	678sh	590ms		589s	591sh	671vw	674wm
YC_3 asym. def.					319wm	230bd	228m		235m	312sh	
(SC_2 def.)				290wm	293sh				225vw,bd	298s	298m
				278wm	286wm						
YC_3 sym. def.	249s	247s		249wm	245ms	211m	210vs				
		236vs		223m							
$YC_3(SC_2)$ rock		212w								250m	253sh
		194vw								240m	237s
MX_4L_2 deformations	169wm	169sh		137sh	139sh	173wm	174wm		170sh	169w	168wm
and lattice	154sh	155vs		130s	128m	159wm	159sh	114m			157s
	150ms			114m	116m	114w	*ca.* 150sh	104sh		153w	
	143ms	145sh		102w	103s	139w	139vs	96m,bd	97s	142vw	144sh
					91m	129m	132sh			131sh	134w
	124wm	126vw			81w	101wm	103sh		70vw,bd	125wm	
		95m					96w				
	70wm					71sh					
	47wm					59ms,bd					
Other bands	331sh				267wm	330w,sh					
	315vvw					186w					
Limit of study	(40)	(70)	(250)	(40)	(50)	(40)	(90)	(40)	(40)	(40)	(60)

[a] In dimethylformamide.

ion $[PtCl_5AsMe_3]^-$ follows from those of the trimethylphosphine complex leaving two Raman and i.r. bands, at 261 and 291 cm^{-1}, for the $A_1(PtL)$ and $A_1(PtX)$ motions. We have previously noted [9] that considerable mixing may occur between such *trans* related modes, but if the trimethylphosphine complex is a guide, the band at 261 cm^{-1} being the more polarised could be more appropriately described as $A_1(PtL)$. For the trimethylamine complex, $[PtCl_5NMe_3]^-$, the bands at 548 and 257 cm^{-1} arise from $A_1(PtL)$ and CNC deformation (sym) modes but, as with the Pt^{II} complexes,[4] we expect there to be considerable mixing and separate identification is not justified. We have not assigned the PtS stretching vibration for the salt $Pr^n{}_4N[PtCl_5SMe_2]$ as, to judge from the bromo-complex, it will be concealed by the more intense chloride vibrations.

The intense i.r. band at 241 cm^{-1} in the spectrum of the ion $[PtBr_5AsMe_3]^-$, which has only a very weak Raman equivalent and none in the spectrum of the chloride, may be assigned to the E vibration. The strong Raman bands at 207 and 192 cm^{-1}, with i.r. counterpart of the first only, may be assigned to the $A_1(PtBr_4)$ and B_1 vibrations respectively. The symmetric AsC_3 deformation (at 205 cm^{-1} in the chloride) will also contribute to the 207 cm^{-1} band. Again these energies are close to those of the $PtBr_4$ group in the complex $[PtBr_4(PEt_3)_2]$.[7,8] The remaining strong Raman and i.r. band at 180 cm^{-1} must be the $A_1(PtBr)$ stretch; it is not highly polarised. For the ion $[PtBr_5PMe_3]^-$, the $A_1(PtBr)$ and B_1 modes are coincident so that the Raman spectrum only shows two bands. Unfortunately, polarisation measurements were not sufficiently definitive to show a totally symmetric contribution to the band at 190 cm^{-1}. The PtBr stretching vibrations of the ion $[PtBr_5SMe_2]^-$ correspond to those of the other bromo-anions, but the $A_1(PtBr)$ vibration is more intense and polarised in the Raman spectrum than for the other species. As its energy seems rather low for $A_1(PtBr)$ *trans* to sulphide and the $A_1(PtBr_4)$ vibration is about 10 cm^{-1} higher than in the other complexes, the explanation could be mixing between these two vibrations of the same symmetry.

The colour of the only iodide isolated, $[PtI_5PMe_3]^-$, precluded Raman study. For the chloride and bromide the energies of the $E(PtX_4)$, $A_1(PtX_4)$, and $A_1(PtX)$ stretches follow the order of the $B_1(PtX_2)$, $A_1(PtX_2)$, and $A_1(PtX)$ in $[PtX_3L]^-$. Platinum–iodide stretching assignments in Table 1 are based on the assumption that the same relation holds for the iodide.

TABLE 4

Vibrational spectra (below 800 cm^{-1}) of the salts *mer*-$[PtX_3(PMe_3)_3]BF_4$ (X = Cl or Br)

	$[PtCl_3(PMe_3)_3]BF_4$				$[PtBr_3(PMe_3)_3]BF_4$	
	$I.r._{mull}$	$I.r._{soln.}$ [a]	R_{solid}	$R_{soln.}$ [a]	$I.r._{soln.}$ [a]	$R_{soln.}$ [a]
PtP str.	385s	383s	384w	384w,p	384m	384w,p
PtP_2 str. (sym.)			354m,sh	355m,p		353wm,p
(asym.)	*ca.* 354s	*ca.* 352vs			355ms	
PtX_2 str. (sym.)			*337*vs	*334*vs,p		*203*vs,p
(asym.)	*354*s	*352*vs			*245*vs	
PtX str.	*297*s	*297*s	*295*s	†		*197*s,sh,dp
PC_3 asym. str.	756m	†	*ca.* 755m	†	†	†
	743m		744m			
PC_3 sym. str.	681sh	†	681m	†	†	†
	675m		673sh			
PC_3 asym. def.	323vw	326wm	318vw		†	†
	293sh					
	280ms	†	285m,sh	†		
PC_3 sym. def. and/or rock	239wm	240m	228m,sh	228m,p	215m,sh	219ms,sh,p
			215m,sh			
			203s	200ms,p		
PtX_3P_3 Deformations and lattice modes	150wm		150s,bd	144m,bd,dp		
	138wm					
	116wm		113w			
	65wm,bd					
BF_4^-			762m	†		†
	520wm	†			†	
Limit of study	(40)	(200)	(60)	(100)	(200)	(130)

[a] In dichloromethane.

† Not investigated or obscured by solvent bands.

(b) trans-$[PtX_4L_2]$. Like previous authors,[7,8] we assume D_{4h} symmetry for these complexes. The halide-stretching vibrations $A_{1g}(PtX_4)$, $B_{1g}(PtX_4)$, and $E_u(PtX_4)$ are readily identified from the results of other workers [7,8] on complexes of similar ligands and the PtL_2 vibrations are similar to those of *trans*-$[PtX_2L_2]$. In the complex $[PtCl_4(AsMe_3)_2]$ the $E_u(PtCl_4)$ stretching band is split into two equal-intensity components in the solid state but is single in benzene solution; an analogous observation has been made for $[IrCl_4(PMe_3)_2]$.[10] The i.r. spectrum of our sample of the complex *trans*-$[PtCl_4(SMe_2)_2]$ does not agree at all with that reported by Adams and Chandler,[8] whose spectra showed a band at 392wm cm^{-1} which may indicate a sulphide-bridged species.[11]

(c) cis-$[PtX_4L_2]$. In the assignments made previously [7,8] the energy of the symmetric $PtCl_2$ stretch is much lower than the other Pt–Cl stretching modes. This surprises us as the symmetric and asymmetric vbrations of the

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[9] R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 1897.

[10] P. L. Goggin and J. R. Knight, *J.C.S. Dalton*, 1973, 1489.

[11] P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

linear $PtCl_2$ group in the complex *trans*-$[PtCl_2L_2]$ and $[PtCl_3L]^-$ are almost coincident and we have found related motions of Pt^{IV} systems to be close to those of Pt^{II} systems. Indeed, the strong Raman band at 334 cm^{-1} (and its i.r. counterpart at 336 cm^{-1}) found for the complex *cis*-$[PtCl_4(PEt_3)_2]$ [7] would seem better assigned to the symmetric $PtCl_2$ vibration rather than to the asymmetric $PtCl_2$ stretch which appears at 345 cm^{-1}.

Our *cis*-isomers are not very soluble in spectroscopically suitable solvents and we have had to use dimethylformamide, which has bands 358ms,dp, 322m,p, and 232w,vb,d cm^{-1}, to obtain Raman-polarisation data on *cis*-$[PtCl_4(PMe_3)_2]$. These show the band at 334 cm^{-1} to be strongly polarised and therefore clearly the symmetric stretch of the linear $PtCl_2$ group; the higher of the two PtCl(*trans* to PMe_3) stretching bands is also polarised and hence totally symmetric. The assignments for the trimethylarsine complex follow directly. The assignments for the dimethyl sulphide complex must be regarded as tentative because of complications arising from PtCl stretching, Pt–S stretching, and SC_2 bending vibrational energies being similar.[5] Assignments of vibrations of the $PtBr_4$ group are made by analogy with the chlorides.

TABLE 5

N.m.r. parameters of trimethylphosphine complexes of platinum(IV)

	τ_{CH_3}	$^2J_{PH}$	$^3J_{PtH}$	δ_P [a,b]	$^1J_{PtP}$ [a]	$^3J_{Pt(IV)H} : {}^3J_{Pt(II)H}$	$^1J_{Pt(IV)P} : {}^1J_{Pt(II)P}$
$[PtCl_5PMe_3]^-$	8·18	−13·5	+18·3	0·2	+2 119	0·60	0·577
$[PtBr_5PMe_3]^-$	7·91	−12·8	+22·2	14·7	+2 095	0·71	0·594
$[PtI_5PMe_3]^-$	7·58	−12·2	+26·0	46·2	+2 181	0·75	0·646
cis-$[PtCl_4(PMe_3)_2]$	8·04	−12·5 [c]	+19·9	−1·7	+2 081	0·56	0·598
cis-$[PtBr_4(PMe_3)_2]$	7·89	−12·2 [d]	+21·5	11·7	+2 015	0·60	0·588
trans-$[PtCl_4(PMe_3)_2]$	8·28	−8·4 [e]	+12·6	11·8	+1 516	0·59	0·637
trans-$[PtBr_4(PMe_3)_2]$	8·03	−8·3 [e]	+14·5	31·5	+1 550	0·66	0·664
trans-$[PtI_4(PMe_3)_2]$	7·44	−8·1 [e]	+17·8	64·6	+1 585	0·77	0·711

[a] From $^1H(^{31}P)$INDOR measurements. [b] P.p.m. upfield from H_3PO_4. [c] $(^2J_{PH} + {}^4J_{PH})$; in CD_3NO_2 solution $^2J_{PP}$ 4·5, $^2J_{PH}$ −13·0, and $^4J_{PH}$ + 0·4 Hz. [d] $(^2J_{PH} + {}^4J_{PH})$; in CD_3NO_2 solution $^2J_{PP}$ 3·5, $^2J_{PH}$ 12·5, and $^4J_{PH}$ + 0·2 Hz. [e] $(^2J_{PH} + {}^4J_{PH})$.

(d) mer-$[PtX_3(PMe_3)_3]BF_4$. If these complexes are regarded as of C_{2v} symmetry, there are both symmetric and asymmetric stretching vibrations for *trans*-PtP_2 and -PtX_2 groupings active in the i.r. and Raman spectra, as well as Pt–P and Pt–X vibrations of the linear P–Pt–X unit. The bromide has only been investigated as a solution in dichloromethane prepared by the action of bromine on a solution of the salt $[PtBr(PMe_3)_3]BF_4$; it has been authenticated by its ^1H n.m.r. spectrum.[12] Since its Raman spectrum shows two polarised bands in the region 350—400 cm^{-1}, *i.e.* 384 and 353 cm^{-1}, both must be assigned as Pt–P symmetric stretching and from the relation with the other spectra the higher must be concerned with the phosphine *trans* to bromide. The i.r. spectrum also shows two bands at essentially the same wavenumbers but the stronger one, 355 cm^{-1}, must be the asymmetric PtP_2 vibration on the grounds of its intensity. This closeness between symmetric and asymmetric *trans*-MP_2 energies has been found in all other complexes with three trimethylphosphine ligands as constituents of a square plane.[2,10] The assignment of $PtBr_2$ vibrations is straightforward and the PtBr mode is revealed as a strong band, certainly of rather high depolarisation ratio, under the perpendicular polarisation condition, but is hidden beneath the very intense $PtBr_2$ symmetric stretching band under the parallel polarisation condition. In the chloride, the asymmetric PtP_2 and $PtCl_2$ stretching vibrations coincide.

Skeletal-deformation vibrations. These motions are particularly liable to couple with lattice modes and studies in solution are hampered by the difficulty of finding a suitable solvent. In view of this and the confusion with internal motions of the ligand, we feel that previous assignments are somewhat optimistic. The in-plane MX_4 deformations should remain reasonably constant with change of ligand in the complexes *trans*-$[PtX_4L_2]$ and would be expected to be related in energy to those of $[PtX_4]^{2-}$. For the salt $(Bu^n{}_4N)_2[PtCl_4]$ in solution, the B_{2g} mode occurs at 173 cm^{-1} and the E_u mode at 165 cm^{-1}, whilst for the corresponding bromide the values are 113 and 112 cm^{-1} respectively.[13] Likewise, the other Raman-active deformation would be expected to relate to the scissors mode of the complexes *trans*-$[PtX_2L_2]$. These criteria seem to lead to logically consistent assignments for the trimethyl-phosphine and -arsine complexes but the assignments are less certain for the dimethyl sulphide complexes. The equivalent deformations of the PtX_4 group in the ion $[PtX_5L]^-$ may be assigned by analogy but it does not seem reasonable to assign the other deformations of these or the other species.

N.M.R. Spectra.—The ^1H n.m.r. spectra of the Pt^{IV} complexes in general resemble those of the corresponding Pt^{II} complexes but with a much lower value of $^3J_{PtH}$. *cis*-$[PtX_4(PMe_3)_2]$ (X = Cl or Br) complexes are too insoluble in dichloromethane to show the effects of phosphorus–phosphorus coupling on these $[AX_9]_2$ systems,[14] but saturated solutions in CD_3NO_2 are sufficiently strong to show the inner and outer lines for $\chi = 1$. The inner lines are partly obscured by platinum satellites but the latter were largely removed by irradiating the appropriate region of the ^{195}Pt spectrum. The authenticity of the lines was checked by 'tickling' experiments similar to those with the complex $[PtBr_2(PMe_3)_2]$ [3] and the parameters extracted in the usual way.[14] The *trans*-isomers showed the usual triplet with a broad central line as found for other systems where $^2J_{PP} \gg |^2J_{PH} - {}^4J_{PH}|$. Where both *cis*- and *trans*-isomers occur, the *trans*-isomers seem more favoured for Pt^{IV} than for Pt^{II} but the rate of interconversion is slower. For this reason, solutions for the n.m.r. measurements of some of the *cis*-isomers were most conveniently obtained by oxidation of a solution of the appropriate Pt^{II} complex. The same method was used for the

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[12] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

[13] P. L. Goggin and J. Mink, unpublished work.

[14] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

iodide complexes as these were not stable enough to be isolated. The complex $[PtI_4(PMe_3)_2]$ appears to be in equilibrium with $[PtI_2(PMe_3)_2]$ even in the presence of excess of iodine and lowering of the temperature was necessary to sharpen up the resonances.

Since J_{PtP} is of particular interest, we have obtained details of the ^{31}P resonances by $^1H(^{31}P)$INDOR measurements and these are included with the proton n.m.r. data on the phosphine complexes in Table 5. The equivalent information on the Pt^{II} complexes was required for comparison and this is presented in Table 6 together with results on related Pd^{II} complexes and halogeno-bridged dimers $[M_2X_4(PMe_3)_2]$ for completeness. We have determined the signs of coupling constants relative to J_{PtP} for the Pt^{IV} phosphine complexes. Values of J_{PtP} for the complexes *cis*- and *trans*-$[PtCl_2(PMe_3)_2]$ are close to those of the equivalent triethylphosphine complexes which have been shown by McFarlane to be positive for both isomers.[15] In view of the large magnitude of J_{PtP} it seems safe to assume that J_{PtP} is positive in all the trimethylphosphine complexes studied here. On this basis $^3J_{PtH}$ is positive and $^2J_{PH}$ negative as we have found on systems with three or four phosphine ligands.[12]

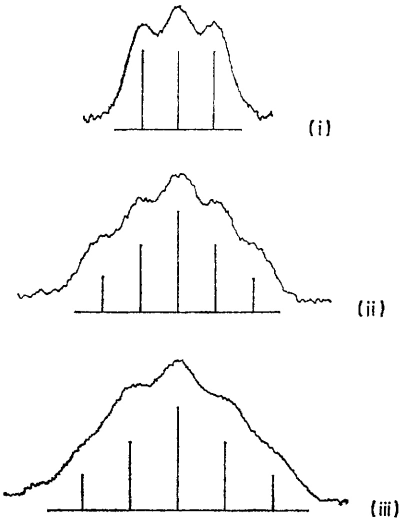
TABLE 6

^{31}P N.m.r. parameters derived from $^1H(^{31}P)$INDOR measurements on trimethylphosphine complexes of palladium(II) and platinum(II)

	M = Pd	M = Pt	
	δ_P [a]	δ_P [a]	$^1J_{PtP}$
$Pr^n{}_4N[MCl_3PMe_3]$	−0·8	30·6	3 674
$Pr^n{}_4N[MBr_3PMe_3]$	0·5	31·5	3 542
$Pr^n{}_4N[MI_3PMe_3]$	3·48	32·2	3 377
$[M_2Cl_4(PMe_3)_2]$	−15·7	23·2	3 834
$[M_2Br_4(PMe_3)_2]$	−12·4	24·5	3 682
$[M_2I_4(PMe_3)_2]$	−4·8	26·4	3 480
cis-$[MCl_2(PMe_3)_2]$	1·9	24·0	3 480
cis-$[MBr_2(PMe_3)_2]$	1·7	23·8	3 426
cis-$[MI_2(PMe_3)_2]$		26·0	3 306
trans-$[MCl_2(PMe_3)_2]$	11·9	15·8	2 379
trans-$[MBr_2(PMe_3)_2]$	16·9	20·4	2 336
trans-$[MI_2(PMe_3)_2]$	27·8	32·2	2 230
trans-$[M(CN)_2(PMe_3)_2]$	12·8	19·6	2 120

[a] P.p.m. upfield from H_3PO_4.

Values for J_{PtN} would be desirable to compare with J_{PtP}. However, the protons of NMe_3 co-ordinated to platinum do not show any sign of coupling to ^{14}N which is not surprising in view of the probably small value of the coupling[16] and the relatively rapid relaxation of ^{14}N, expected because of its quadrupole moment. Thus $^1H(^{14}N)$INDOR measurements are not practicable but, fortunately, $^1H(^{195}Pt)$INDOR spectra do show broadening due to platinum–nitrogen coupling and for the complexes $[PtCl_5NMe_3]^-$, *trans*-$[PtCl_4(NMe_3)_2]$, and *trans*-$[PtCl_2(NMe_3)_2]$ the relaxation of the nitrogen atom is sufficiently slow to cause partial resolution of this splitting (see Figure). The 1 : 1 : 1 triplet and 1 : 2 : 3 : 2 : 1 quintet shown by the complexes with one or two amine ligands respectively are expected for coupling to a nucleus of $I = 1$. Approximate values of J_{PtN} are: $[PtCl_5(NMe_3)]^-$, 157 ± 2; *trans*-$[PtCl_4(NMe_3)_2]$, 166 ± 5; *trans*-$[PtCl_2(NMe_3)_2]$, 209 ± 10 Hz. The only previous report of platinum–nitrogen coupling seems to be for the complex *cis*-$[Pt(NCS)_2(PBu^n{}_3)_2]$ for which Howarth *et al.* observed the much larger value of 430 ± 3 Hz.[17] Data on the ions $[PtXL_3]^+$ and *mer*-$[PtX_3L_3]^+$ have been reported in a previous paper[12] and data on Pt^{IV} complexes of ligands other than trimethylphosphine are given in Table 7.



$^1H(^{195}Pt)$INDOR spectra of (i) $Pr^n{}_4N[PtCl_5NMe_3]$, (ii) *trans*-$[PtCl_4(NMe_3)_2]$, and (iii) *trans*-$[PtCl_2(NMe_3)_2]$ with lines relevant to the values of coupling constants given in the text

TABLE 7

^1H N.m.r. parameters of trimethylamine, trimethylarsine, and dimethyl sulphide complexes of platinum(IV)

	τ_{CH_3}	$^3J_{PtH}$	$^3J_{Pt(IV)H} : {}^3J_{Pt(II)H}$
$Pr^n{}_4N[PtCl_5NMe_3]$	7·19	26·0	0·82
$Pr^n{}_4N[PtBr_5NMe_3]$	6·98	28·7	0·87
trans-$[PtCl_4(NMe_3)_2]$	7·19	27·5	0·96
trans-$[PtBr_4(NMe_3)_2]$	6·86	30·8	1·08
$Ph_4P[PtCl_5AsMe_3]$	8·29	13·5	0·62
$Ph_4P[PtBr_5AsMe_3]$	8·07	16·1	$0{\cdot}73_5$
$Ph_4P[PtI_5AsMe_3]$	7·74	19·3	0·85
cis-$[PtCl_4(AsMe_3)_2]$	8·13	14·9	0·62
cis-$[PtBr_4(AsMe_3)_2]$	8·02	15·8	0·66
trans-$[PtCl_4(AsMe_3)_2]$	8·34	10·3	0·60
trans-$[PtBr_4(AsMe_3)_2]$	8·16	11·6	0·68
trans-$[PtI_4(AsMe_3)_2]$	7·69	14·6	0·80
$Pr^n{}_4N[PtCl_5SMe_2]$	7·56	31·5	0·66
$Pr^n{}_4N[PtBr_5SMe_2]$	7·42	33·8	0·70
cis-$[PtCl_4(SMe_2)_2]$	7·43	32·0	0·64
cis-$[PtBr_4(SMe_2)_2]$	7·35	33·6	0·67
trans-$[PtCl_4(SMe_2)_2]$	7·44	30·0	0·72
trans-$[PtBr_4(SMe_2)_2]$	7·19	32·3	0·78

We have previously commented on the greater effect that a halide in a *cis*-position has on τ_{Me}, δ_P, $^2J_{PH}$, and $^3J_{PtH}$ compared to a halide in the *trans*-position.[3,12] The same is true of the Pt^{IV} complexes and the results are more noticeable because of the greater number of halides in *cis*-positions. Any similar effect on J_{PtP} is relatively small. Thus the *trans*-halide causes a marked decrease in J_{PtP} in the order Cl > Br > I corresponding to the *trans*-influence of the halide except for the ion $[PtX_5$-

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[15] W. McFarlane, *J. Chem. Soc. (A)*, 1967, 1922.

[16] E. W. Randall and D. G. Gillies, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 119.

[17] O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 1964, 3335.

$(PMe_3)]^-$. For the latter and *trans*-$[PtX_4(PMe_3)_2]$, it looks as if a positive contribution from the four *cis*-halides (which may or may not be chemically significant) dominates.

DISCUSSION

We have previously commented on the unsatisfactory nature of the results obtained from force-field calculations for systems as complicated as these.[2] In considering the behaviour of metal–ligand bonds, we will base our deductions on the observed frequencies, with all the uncertainties that this implies. From the way in which *trans*-MY_2 group vibrations display practically constant energies within various series of complexes [2,5,18] there would appear to be relatively little mixing between stretching vibrations in perpendicular directions unless the groupings on the two directions are identical (*i.e.* the axes are degenerate). Thus, by comparing only the stretching energies of particular *trans*-groupings in different complexes, *e.g.* Cl–Pt–Cl in the complexes *trans*-$[PtCl_2(PMe_3)_2]$ and *cis*-$[PtCl_4(PMe_3)_2]$ but not in *trans*-$[PtCl_4(PMe_3)_2]$, we would expect conclusions to be fairly well founded. There is also an uncertainty in designations such as ' M–L stretching ' in these complexes of polyatomic ligands as there is always a deformation about the donor atom of the same symmetry. In our previous work on trimethylphosphine complexes we have described the higher in energy of the conjugate pair of modes as M–P stretching; it is usually easy to identify with certainty, and behaves as such a vibration would be expected to do both in terms of symmetry of the various complexes and the expected bond strengths. Where the lower-energy band has also been unambiguously identified, it follows a trend in the same direction between complexes, and although the extent to which either frequency is ' M–P stretching ' or ' PC_3 symmetric bending ' in character must vary from complex to complex, effects implied by observing the change in either parameter seem to be chemically sensible. Nakamoto's work using different metal isotopes has implied a very wide range of Ni–P stretching frequencies [19] for compounds with much more complicated phosphines than ours but it is usually evident that a number of features show sensitivity to the mass of the metal and that designation of a stretching vibration between a metal and a polyatomic ligand has an imprecise meaning. In the present discussion we will continue to use the relevant frequencies in the 330—420 cm^{-1} range as our indicator of M–P bonding.

Comparison between the complexes *mer*-$[IrCl_3(PMe_3)_3]$ [10] and -$[PtCl_3(PMe_3)_3]^+$ has the advantage that there is no change of structure and the complexes contain three types of *trans*-groupings. For Cl–M–Cl, the symmetric and asymmetric vibrations respectively increase by 23 and 28 cm^{-1} from iridium to platinum; M–Cl (*trans* to P) increases by 30 cm^{-1} whilst M–P (*trans* to Cl) decreases by 10 cm^{-1}. The P–M–P modes also decrease by about the same amount. The effect on the vibrational energies of unit increase in charge on the complex can be estimated from data on other octahedral complexes; [10] it is positive for both M–P and M–Cl vibrations and for the latter is much less than the differences we observe between Ir^{III} and Pt^{IV}. The corresponding changes between complexes *trans*-$[MCl_4(PMe_3)_2]$ are broadly similar, M–Cl stretches showing large increases (25 cm^{-1} on average) and the average of the P–M–P energies remaining static. The increased binding of the negatively charged halide on increasing oxidation state is to be expected. The decrease in M–P bond strength could be due to decreased overlap between the phosphorus lone pair and the metal *d* orbitals since the latter will contract on going from Ir^{III} to Pt^{IV}; increasing positive charge on the complex alone must have much less effect on the charge carried by the metal than change of oxidation state. Equally, if π-bonding is considered, the change in M–P energies is consistent with the expected lower π-bond order for the higher-oxidation-state complex.

Considering oxidation of Pt^{II} to Pt^{IV}, there is the added complication of change in co-ordination number. The mean wavenumber changes on oxidation for groupings in complexes of the same overall charge are approximately: Cl–Pt–Cl, +9; Cl–Pt (*trans* to P), −9; P–Pt (*trans* to Cl), −19; and P–M–P, −9. Thus, whilst the behaviour of ν(PtP) is in the same sense as that observed above between Ir^{III} and Pt^{IV}, the increase in Cl–Pt–Cl is much less than comparisons between the different octahedral complexes might have led us to expect, and Pt–Cl (*trans* to P) actually decreases. The latter are most probably due to the inclusion of two extra chlorine atoms which greatly increases the number of Cl–Cl repulsions at 90°. Since the chlorine atom opposite the phosphine group will be more ionic in nature and carry a larger negative charge than mutually *trans* chlorine atoms, it would show the greater reaction to such repulsion. The effect on the Pt–P bonding should, if anything, be in the opposite sense since the phosphorus atoms probably carry a small positive charge. The greater weakening of a Pt–P bond *trans* to Cl compared to that of mutually *trans* Pt–P bonds could be because it has higher covalency and is more susceptible to metal *d*-orbital contraction. Reduction in π-bonding potential on oxidation could offer an alternative explanation since the effect should be less for *trans* Pt–P bonds which would have less π-character in the lower oxidation state because they are both competing for use of the same *d* orbitals.

Changes in J_{PtP} reflect those in ν(PtP), and ratios for $Pt^{IV}:Pt^{II}$ coupling constants are in fact less than 2 : 3, the value predicted for comparison of dsp^2 and d^2sp^3 hybridised states if the *s* orbital contributes equally to all hybrids. The ratio for J_{PtP} (*trans* to Cl) is much less than for J_{PtP} (*trans* to P), for example in the ion *mer*-$[PtCl_3(PMe_3)_3]^+$ the ratios are 0·604 and 0·642 : 1 respectively (see also Table 5). It may be

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[18] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

[19] K. Nakamoto, *Angew. Chem. Internat. Edn.*, 1972, **11**, 666.

fortuitous but it is interesting to note that J_{MP} (*trans* to Cl)/J_{MP}(*trans* to P) is 1·50, 1·41, and 1·31 for the complexes $[PtCl(PMe_3)_3]^+$, *mer*-$[PtCl_3(PMe_3)_3]^+$, and *mer*-$[RhCl_3(PMe_3)_3]$ respectively compared with ν(M–P)-(*trans* to Cl)/mean $\nu(MP_2)$ equal to $1\cdot10_0$, $1\cdot08_6$, and $1\cdot08_0$ showing that changes implied by the two types of measurement parallel each other.

Stretching vibrations of the trimethylarsine complexes seem to behave in much the same way on oxidation as the trimethylphosphine analogues, as far as inherent confusion between Pt–As and Pt–Cl frequencies allows us to judge. For the dimethyl sulphide complexes it is difficult to make firm comparisons between the Pt–S stretching energies because they typically occur very close to more intense Pt–Cl features, but in a number of cases they seem to be less lowered on oxidation than analogous Pt–P energies. In the trimethylamine complex, considering either the band near 550 or near 250 cm^{-1} as ν(Pt–N), the energy either remains unchanged or increases on oxidation. Furthermore, ν(Pt–Cl) increases on oxidation when *trans* to N or S in contrast to the behaviour when *trans* to P: both the N and S ligands have much lower *trans*-influence than the P and As ligands. The ratio $J_{Pt^{IV}N} : J_{Pt^{II}N}$ for the two *trans* bis(trimethylamine) platinum chlorides is $0\cdot80 \pm 0\cdot06 : 1$, very different from the corresponding ratio in the phosphine complexes. Since π-bonding possibilities do not exist for trimethylamine, we could either account for the observed ratio being above 2 : 3 by postulating some destabilising feature for the Pt–N bond in the platinum(II) complex (*e.g.* repulsive interaction between filled platinum *d* orbitals and electron density in N–C bonds of the ligand[4]) or suggesting that the ratio should not be 2 : 3 anyway. In the one case we have studied, the behaviour of ν(Pt–N) does not indicate a very marked increase in bond strength for the platinum(IV) complex, so we favour the second suggestion. Since in square-planar complexes *s* and d_{z^2} orbitals are of the same symmetry, it is probable that the non-bonding pair of electrons has both 6*s* and $5d_{z^2}$ character. For the trimethylarsine and dimethyl sulphide complexes, we cannot, of course, obtain direct metal–ligand coupling information. The constant $^3J_{Pt-H}$ is dependent on a number of influences but from the trimethyl-phosphine and -amine complexes there is a rough relation between the one-bond coupling ratios for the two oxidation states and three-bond coupling constant ratios especially for the chloro-complexes (Table 5). When values for $^3J_{PtH}$ of the trimethylarsine and dimethyl sulphide complexes are included, there is a trend from PMe_3, through $AsMe_3$ and then SMe_2 to NMe_3 in agreement with indications from vibrational spectra.

In contrast to the corresponding values for J_{PtP}, J_{PtN} is less in the anion $[PtCl_5NMe_3]^-$ than in the *trans*-complex $[PtCl_4(NMe_3)_2]$ implying either that trimethylamine has a lower *trans*-influence than chloride or that the Pt–N bond strength has increased more with increasing overall positive charge than it has lost through the *trans*-influence of trimethylamine. The fact that trimethylamine complexes can only be prepared by routes which do not involve rupture of terminal platinum–halide bonds[4] tends to support the former postulate.

If we wish to compare the coupling of ^{195}Pt to ^{31}P and ^{14}N, we must use reduced coupling constants, the relevant values of which are given in Table 8. Since $\langle\psi_s(0)|^2$ is greater for phosphorus than nitrogen by *ca.* 7 : 6,[20] the reduced couplings must overstate the relative position of phosphorus as a donor atom to this extent. The values of the ratios themselves are also limited in significance since we do not know the *s*-orbital contribution to the donated electron pair and it is unlikely to be the same in each case. However, comparison of the ratios for the neutral Pt^{II} and Pt^{IV} systems shows how much more the *s*-orbital interaction is increased by reducing a phosphine complex than by reducing an amine complex. Although this information can give no direct measure of electrons in the π-bonds, the change observed is in keeping with synergically enhanced σ-bonding which would accompany π-accepting behaviour by phosphorus.

TABLE 8

	K_{PtN} [a]	K_{PtP} [a]	$K_{PtP} : K_{PtN}$
trans-$[PtCl_2L_2]$	112·5	228·6	2·1
trans-$[PtCl_4L_2]$	89·4	145·7	1·6
$Pr^n{}_4N[PtCl_5L]$	84·5	203·7	2·4

[a] 10^{20} N A^2 m^{-3}.

In many *d*-electron complexes, three facets of bonding must be considered: σ-donation from ligand to metal; π-donation from metal to ligand; and π*-repulsion between metal and ligand. π-Donation will only be important for bonding of a neutral ligand with available π-acceptor orbitals (P, As, and S in this work) and π*-repulsion will be most significant when the ligand has unused lone-pair orbitals (S and halide). The two effects cannot be clearly separated by the measurements here but our results are certainly consistent with π-bonding playing a significant role in the Pt–P bond, at least for Pt^{II}, contrary to some recent trends in thought!

EXPERIMENTAL

I.r. and Raman measurements were made as previously reported.[2,4] N.m.r. spectra were measured on 0·1M-solutions in dichloromethane, except that the *cis*-isomers were not soluble to this extent. For comparability with the Pt^{II} results, the anions $[PtX_5L]^-$ ($L = PMe_3$ or $AsMe_3$) were measured as solutions of their tetraphenylphosphonium salts, obtained by oxidation of the platinum(II) complexes.[3] However, for the INDOR measurements, the more soluble $Pr^n{}_4N^+$ salts were used: there was a small change in τ_{Me} on changing the cation. For INDOR spectra of the *cis*-isomers, solutions in CD_3NO_2, in which they are more soluble, were used. The phosphorus–proton coupling was 'resolved' in the $^1H(^{31}P)$INDOR

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[20] J. A. McMillan and T. Halpern, *J. Chem. Educ.*, 1970, **47**, 644.

spectra of the anions and for several of the *trans*-isomers, the latter with splitting of $1/2(^2J_{PH} + {}^4J_{PH})$. For the *cis*-complexes several lines were observed corresponding to the ^{31}P spectrum, but as the pattern was not symmetric when a sharp line was monitored, the patterns for both sharp lines (which are mirror images) were drawn out to obtain the true centre of the resonance. $^1H(^{195}Pt)$ Measurements on the trimethylamine complexes were carried out on $(CD_3)_2CO$ solutions at 340 K so that the low viscosity would increase the relaxation time of the ^{14}N nucleus. The measurements were made as previously described [12] and the results are given in Hz for coupling constants, p.p.m. for chemical shifts on the τ scale for protons, or upfield of external 85% H_3PO_4 taken as resonating at 40 480 754 Hz [12] when tetramethylsilane resonates at 100 MHz exactly.

Table 9

Analytical data for the complexes

	Colour	M.p. (t/°C)	C		H		N		X	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Pr^n_4N[PtCl_5NMe_3]$	Yellow-orange	149—152	29·8	29·65	5·9	6·1	4·45	4·6		
$Pr^n_4N[PtCl_5SMe_2]$	Yellow	180—184	27·0	27·1	5·4	5·5	2·55	2·25	28·35	28·55
$Pr^n_4N[PtBr_5SMe_2]$	Orange	178—179	20·1	19·95	4·05	4·05	1·7	1·65	48·25	47·45
$Pr^n_4N[PtCl_5PMe_3]$	Yellow	159—161	28·35	28·45	5·75	5·85	2·3	2·2	27·7	27·95
$Pr^n_4N[PtBr_5PMe_3]$	Orange	164—167	21·4	21·0	4·3	4·3	1·7	1·65	46·4	46·65
$Pr^n_4N[PtI_5PMe_3]$	Black	145—150	16·8	16·5	3·25	3·4	1·3	1·3		
$Pr^n_4N[PtCl_5AsMe_3]$	Yellow	172—176	27·05	26·55	4·65	4·45	2·35	2·05	26·0	26·15
$Pr^n_4N[PtBr_5AsMe_3]$	Orange-red	164—166	20·55	20·0	4·35	4·15	1·65	1·55	43·85	44·4
cis-$[PtCl_4(SMe_2)_2]$	Pale yellow	234—235	10·5	10·4	2·65	2·6				
trans-$[PtCl_4(SMe_2)_2]$	Chrome yellow	234—235	10·4	10·4	2·55	2·6				
trans-$[PtBr_4(SMe_2)_2]$	Orange	235—240 (decomp.)	7·85	7·5	1·6	1·9				
cis-$[PtCl_4(PMe_3)_2]$	Green-yellow	194 (decomp.)	14·85	14·75	3·75	3·7			29·15	29·0
trans-$[PtCl_4(PMe_3)_2]$	Yellow	204—208 (decomp.)	14·5	14·75	3·7	3·7			29·2	29·0
cis-$[PtBr_4(PMe_3)_2]$	Yellow-orange	226—229 (decomp.)	10·85	10·8	2·8	2·75				
trans-$[PtBr_4(PMe_3)_2]$	Orange	225—229	11·0	10·8	2·85	2·75				
cis-$[PtCl_4(AsMe_3)_2]$	Yellow	220 (decomp.)	12·2	12·5	3·05	3·15				
trans-$[PtCl_4(AsMe_3)_2]$	Chrome yellow	212—214 (decomp.)	12·2	12·5	3·2	3·15			24·6	24·6
cis-$[PtBr_4(AsMe_3)_2]$	Yellow-orange	235—236 (decomp.)	9·7	9·55	2·45	2·4				
trans-$[PtBr_4(AsMe_3)_2]$	Orange-red	238	9·75	9·55	2·5	2·4				
mer-$[PtCl_3(PMe_3)_3]BF_4$	Pale yellow	158—160	17·15	17·55	4·3	4·4				

Preparation of Complexes.—The preparation and characterisation of the Pt^{II} and Pd^{II} complexes has been given elsewhere.[2,4,5] Salts $Pr^n_4N[PtX_5L]$ were obtained by treating $Pr^n_4N[PtX_3L]$ in dichloromethane with a small excess of halogen and the product was precipitated on addition of ether. The complexes were recrystallised from acetone by slow addition of ether. The complexes *cis*-$[PtCl_4L_2]$ ($L = PMe_3$ or $AsMe_3$) were obtained by halogen oxidation of *cis*-$[PtCl_2L_2]$ in dichloromethane from which the products precipitate; they were washed with warm methanol. The complexes *trans*-$[PtCl_4L_2]$ ($L = PMe_3$ or SMe_2) were prepared by treating a benzene solution of *trans*-$[PtCl_2L_2]$ with chlorine. The solutions were evaporated to dryness and the products recrystallised from benzene. For the complex *trans*-$[PtCl_4(AsMe_3)_2]$, the benzene solution prior to oxidation was prepared by prolonged boiling of *cis*-$[PtCl_2(AsMe_3)_2]$ with the solvent. The complex *cis*-$[PtBr_4(PMe_3)_2]$ was prepared by a similar method to the chloride; the *trans*-analogue was obtained by heating the *cis*-complex under reflux with benzene for some days and recrystallised from benzene. Bromine oxidation of the complex $[PtBr_2(AsMe_3)_2]$ in CH_2Cl_2 caused precipitation of *cis*-$[PtBr_4(AsMe_3)_2]$, which was washed with methanol and then benzene; after evaporation of the mother liquor, the *trans*-complex was extracted into benzene from which it was recrystallised. It was also prepared in a similar way to the trimethylphosphine complex. The complex *cis*-$[PtCl_4(SMe_2)_2]$ was prepared by the action of chlorine on a boiling saturated aqueous solution of *cis*-$[PtCl_2(SMe_2)_2]$; the precipitate formed was a mixture of the *cis*- and *trans*-isomers but the latter was extracted by washing with successive portions of cold benzene until no colour was imparted to the solvent over a few minutes.

The salt *mer*-$[PtCl_3(PMe_3)_3]BF_4$ was prepared by chlorination of a dichloromethane solution of $[PtCl(PMe_3)_3]BF_4$ and crystallised by addition of hexane. Analytical data for the complexes are given in Table 9.

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