Vibrational and Nuclear Magnetic Resonance Spectra of some Complexes of Trihalogeno(trihalogenophosphine)platinate(II), and their Methanolysis Reactions

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Tetrabutylammonium salts of the anions $[PtX_3(PY_3)]^-$ (X = Cl, Br, or I; Y = F or Cl) and $[PtBr_3(PBr_3)]^-$ have been isolated and their Raman and infrared spectra studied in detail. Fluorine-19, ^{31}P, and $^{19}F\text{-}\{^{195}Pt\}$ n.m.r. spectra have been recorded as have ^{31}P n.m.r. spectra of $[PtBr_3L]^-$ (L = $PBrCl_2$ or PBr_2Cl) prepared *in situ*. The anions $[PtX_3\{P(OMe)_3\}]^-$ (X = Cl, Br, or I) have been obtained by methanolysis of their PCl_3 or PBr_3 equivalents. N.m.r. parameters of these complexes and the methanolysis intermediates $[PtX_3\{PY_n(OMe)_{3-n}\}]^-$ ($n = 1$ or 2) are reported. Trends in ^{31}P co-ordination shifts, ^{195}Pt–^{31}P coupling constants, and ^{195}Pt chemical shifts are discussed.

DESPITE the very wide interest in trifluorophosphine complexes of transition metals,[1-3] the attention given to PF_3 and other trihalogenophosphine complexes of platinum(II) has been sparse. Whilst $[PtX_2(PX_3)_2]$, $[Pt_2X_4(PX_3)_2]$ (X = F,[4] Cl,[5] or Br [6]), $[PtCl_2(PF_3)_2]$, and $[Pt_2Cl_4(PF_3)_2]$ [7] have been reported, their spectroscopic properties have not been the subject of detailed investigation.

We find that anionic complexes $[PtX_3(PY_3)]^-$ are easily prepared by the reaction of phosphorus trihalides with $[NBu_4]_2[Pt_2X_6]$. We were, however, unable to prepare $[PtCl_3(PBr_3)]^-$ owing to halide exchange which evidently occurs when the halide of PY_3 is of higher atomic number than that on the metal. Accordingly, we only attempted the addition of PI_3 to $[Pt_2I_6]^{2-}$ but then found that no reaction occurred; a similar result was obtained with PBr_3 and $[Pt_2I_6]^{2-}$. Although the complexes $[PtI_3L]^-$ (L = PF_3 or PCl_3) were readily formed and isolated, even these tend to lose ligand on long standing in the solid state. All the other complexes appear to be indefinitely stable. The instability of $[PtI_3L]^-$ complexes relative to their chloride and bromide analogues is quite a common occurrence, *e.g.* the failure to form $[PtI_3(NMe_3)]^-$ [8] and $[PtI_3(SMe_2O)]^-$.

Complexes of the type $[PtX_3(PY_3)]^-$ should be particularly suitable for the study of the effect of co-ordination on the ligand because they involve only one, relatively simple, neutral ligand and because the presence of ^{31}P and ^{195}Pt nuclei permits detailed study by n.m.r. spectroscopy. In order to widen the range of results for phosphines bearing electronegative substituents, we have studied the methanolysis reactions of most of our products. This procedure is particularly useful in the case of the complexes of PCl_3 and PBr_3 as it affords an

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easy route to the anions $[PtX_3\{P(OMe)_3\}]^-$ which we have been unable to prepare by other methods.

RESULTS AND DISCUSSION

Vibrational Spectra.—Infrared and Raman spectra of the complexes $[NBu_4][PtX_3(PF_3)]$ are given in Table 1 and of those containing PCl_3 or PBr_3 in Table 2. The overall symmetry of these complexes is, strictly, no higher than C_s, but we have noted previously [9] that the PtX_3 part appears to behave, effectively, as C_{2v}. If there is restricted rotation of the neutral ligand this is most likely to be detected in the PY_3 asymmetric stretch, asymmetric deformation, and rocking modes which might show splitting between components perpendicular and parallel to the PtX_3 plane.

TABLE 1

Vibrational spectra (below 1 000 cm^{-1}) of $[NBu_4][PtX_3(PF_3)]$ (X = Cl, Br, or I) [a]

	$[NBu_4][PtCl_3(PF_3)]$				$[NBu_4][PtBr_3(PF_3)]$				$[NBu_4][PtI_3(PF_3)]$			
Assignment	I.r. (mull)	I.r. (soln.) [b]	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. (soln.) [b]	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. (soln.) [b]	Raman (solid)	Raman (CH_2Cl_2)
PF_3 str	913vvs, bd	916vs			914vvs	901vs			908 (sh)	910vs		
					902vvs				903vs			
									892vs			
Unassigned (impurity?)	854m	*c*			851m	*c*						
PF_3 sym def	553vs	550vs	554w	550w, p	552vs	549vs	552w	549vw	545vs	543vs		554w, p
2ν(PtP)	535ms	535ms		535vw, bd, p	536s	533s			527ms	523ms		
PF_3 asym def	397ms	397s	*c*	*c*	393s	393s	*c*		392 (sh)	390s	*c*	*c*
	393 (sh)								389s			
PtX_2 asym str	347vs	346vs			232s	230s			196m	195m	194vw	193vw
PtX_2 sym str	340 (sh)		342vs	340vs, p	219wm	217wm	219vs	217vs, p	148w	147w	146vs	147vs, p
PtX str	319ms	313s	319m	313w, dp	203wm	201wm	202vs	210s, p	168wm	167w	167m	167ms, p
	312 (sh)											
PtP str	269w	265w (sh)	267m	266m, p	272w	269wm	264w, vbd	264w, bd, p	264m	262m		267w, p
PF_3 rock	245m	244m			259wm	259m			242wm	242w		243vw, dp
	234vw	226vw			237 (sh)	237 (sh)			236wm	235w		
Skeletal defs and lattice	163wm	162w, bd	160s	164m, dp	107w		107s	106m, dp	100w	*ca.* 100w	*ca.* 90 (sh)	97 (sh), dp
					100 (sh)							
	127m	130m, bd			92w	93w, bd			85w, bd		81m	82m, dp
	ca. 40s				63vw, bd				*ca.* 40m			
Limit of study	(40)	(70)	(110)	(100)	(40)	(70)	(95)	(80)	(40)	(70)	(60)	(60)

[a] Cation bands have been omitted. [b] Above 400 cm^{-1} and at *ca.* 260 cm^{-1} values are from CH_2Cl_2; all others are from $CDCl_3$. [c] Obscured by solvent or cation bands.

For the complexes with PCl_3 and PBr_3, phosphorus–halogen stretching assignments are unambiguously made on the basis of Raman depolarisation ratios but no features were observed in the appropriate region of the Raman spectra of the PF_3 complexes other than those associated with the cation (*ca.* 910 and 880 cm^{-1}, both polarised in solution). To judge from gaseous PF_3,[10] $[M(PF_3)_4]$ (M = Ni, Pd, or Pt),[11] $[Ni(PCl_3)_4]$,[12] and $[PtX_3(PCl_3)]^-$, it is unlikely that either the symmetric or asymmetric PF_3 stretching modes in $[PtX_3(PF_3)]^-$ would be of low i.r. intensity. However, we only observed one strong feature above 600 cm^{-1} and we consider that both the vibrations contribute to this absorption. In the solid-state spectra of the bromo- and iodo-anions these bands are split into two components which may indicate resolution of the two modes but alternatively could be due to lifting of the degeneracy of the asymmetric stretching mode {as indeed occurs in solid $[PtCl_3(PCl_3)]^-$}.

The PtX_3 stretching vibrations are readily identified from their relative intensities in i.r. and Raman spectra and from comparisons with other $[MX_3L]^-$ systems.[9,13] When the Pt–X(*trans* to P) stretch lies well to low wavenumber of the PtX_2 symmetric stretch, the Raman band observed for solutions appears to be depolarised, whereas when it lies above the PtX_2 vibration it is strongly polarised (and more intense). The intermediate cases, $[PtBr_3(PF_3)]^-$ and $[PtBr_3(PBr_3)]^-$, are weakly polarised (*ca.* 0.4 and 0.6 respectively). This is probably a general phenomenon which reflects the true nature of the vibrations. Thus the higher-wavenumber band is related to the symmetric combination of the two modes and the lower to the asymmetric combination which then parallel the A_{1g} and B_{1g} modes of $[MX_4]^{2-}$ respectively.[14]

The only other vibrations of these anions which would be expected to occur in the range 200—600 cm^{-1} are Pt–P stretching, PY_3 symmetric and asymmetric deformations, and, in the case of the complexes of PF_3, ligand-rocking modes. We assigned the observed bands on the basis that the first two of these vibrations would be expected to give rise to polarised Raman lines in solution, while the remainder might show splitting due to the incompatibility of the three-fold axis with our C_{2v} approximation. Considering the PF_3 complexes first, we find a polarised band at *ca.* 550 cm^{-1}. The Raman counterpart of the i.r. band at *ca.* 270 cm^{-1} suffers from being almost coincident with a polarised band of the $[NBu_4]^+$ cation. However, in the case of $[N(C_5H_{11})_4][PtI_3(PF_3)]$ where no such clash occurs, the band at 267 cm^{-1} was observed and found to be polarised. We have commented previously [15] on the problem of mixing

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TABLE 2

Vibrational spectra (below 1 000 cm^{-1}) of $[NBu_4][PtX_3(PY_3)]$ (X = Cl, Br, or I; Y = Cl or Br) [a]

	$[NBu_4][PtCl_3(PCl_3)]$				$[NBu_4][PtBr_3(PCl_3)]$				$[NBu_4][PtI_3(PCl_3)]$			$[NBu_4][PtBr_3(PBr_3)]$			
	I.r. (mull)	I.r. ($CDCl_3$)	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. ($CDCl_3$)	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. ($CDCl_3$)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. ($CDCl_3$)	Raman (solid)	Raman (CH_2Cl_2)
PY_3 sym str	572vs	571vs	573ms	571m, p	564vs	565vs	563ms	564ms, p	547vs	550vs	550m, p	482vs	486vs	481m	486m, p
PY_3 asym str	544vs	539vs	538m	543w, bd, dp	538 (sh)				519vs	525vs	526w, dp	424vs	432vs	432m	428w, bd, dp
	524vs		527wm		528vs	536vs	532w, bd	534w, bd, dp						422wm	
PY_3 sym def					332w	332wm	333s	334s, p	325w, bd	325w, bd	327m, p	247s	247s	245w	
PY_3 asym def	235m	234m	233m	234w, dp	252m	253ms	252vw	253vw, dp	230w	230wm		151w (sh)	158w (sh)	*ca.* 153 (sh)	
					238w (sh)	236 (sh)									
PtX_2 asym str	343vs	343vs			226s	224s				189ms		221s	224s	218 (sh)	
PtX_2 sym str	336 (sh)		338vs	337vs, p	203w	203wm	204vs	204vs, p		142wm	144s, p	209wm	211wm	208vs	210vs, p
PtX str	317s	310vs	316m	310w, dp	221s		222s	220s, p		162w	159s, p	197s	200ms	196s	200m, p
PtP str	181w	182w	180ms	181m, p			172s	172ms, p				147m	149m	145s	151m, p
PY_3 rock	176 (sh)		176 (sh)		150vw	149vw	154w, bd	157vw, dp				125vw	125w	124m	123w, dp
	159w	160vw	159wm	160w											
Skeletal defs	146w	147w	146s	145m, dp	109vw		109s	110s, dp			109w, bd				
and lattice	142vvw (sh)														
	125m	125wm	122w, bd	120w, bd	91w, bd	*ca.* 92w, bd		*ca.* 90w, bd, dp		80—96w, bd			107w, bd	100s	108wm, bd, dp
			ca. 84bd (sh)	*ca.* 85bd (sh)	*ca.* 69w									92s	106wm, p
	47m, bd				*ca.* 44wm							*ca.* 90w, bd	*ca.* 85w, bd	76w, bd	89wm, dp
Other bands									198ms [b]	200ms [b]		172vw, bd			169vw
Limit of study	(40)	(80)	(70)	(80)	(40)	(80)	(90)	(75)	(192)	(70)	(80)	(70)	(70)	(70)	(70)

[a] Cation bands have been omitted. [b] Possibly due to $[Pt_2I_6]^{2-}$ impurity.

between metal–ligand stretching vibrations and deformations about the donor atom. In this case we consider that the higher of these two features is predominantly PF_3 symmetric bending and the lower predominantly Pt–P stretching in character. All the complexes of PF_3 showed two bands in the 230—260 cm^{-1} region which can only arise from the PF_3 rocking modes. In $[PtBr_3(PF_3)]^-$ the band at higher wavenumber was considerably raised in frequency with respect to the chloride and iodide, presumably as a result of interaction with another fundamental of the same symmetry. This implies that it is the rocking mode in the PtX_3 plane. The band at 535 cm^{-1} cannot be satisfactorily accommodated as a fundamental and we assign it to the overtone of the 'Pt–P stretching' vibration at 270 cm^{-1}, its high intensity being the result of Fermi resonance with the PF_3 symmetric deformation.

Identification of the PCl_3 symmetric deformation in $[PtCl_3(PCl_3)]^-$ and Pt–P stretch in $[PtI_3(PCl_3)]^-$ was not possible owing to confusion with, or masking by, platinum–halide stretching vibrations. The PCl_3 asymmetric deformation in these two complexes appeared as a single band at *ca.* 230 cm^{-1}, but in the bromide there is evidently strong interaction between the in-plane component of this mode and the $PtBr_2$ asymmetric stretch. Assignment of PBr_3 vibrations is hampered by there being only one example, $[PtBr_3(PBr_3)]^-$. Thus, although the band at 247 cm^{-1} is attributed to the PBr_3 symmetric deformation, we are unable to offer a convincing explanation for its lack of prominence in the Raman spectrum. Our assignment of its asymmetric counterpart as 151 cm^{-1} is tentative and the very weak band at 172 cm^{-1} might alternatively arise from this mode.

In general, two features were observed in the region expected for skeletal deformations: one more intense in the Raman, and the other, usually of lower wavenumber, more intense in the i.r. Without polarised single-crystal studies we cannot conclusively assign these bands but the former might be expected to arise from the B_1 in-plane scissors mode and the latter from an out-of-plane mode by analogy with $[MX_4]^{2-}$.[14]

The vibrational frequencies of PF_3, PCl_3, and PBr_3 all increased on co-ordination. With the exception of PF_3 stretching, the raising of the symmetric modes is greater than that of the asymmetric modes. This behaviour contrasts with the wavenumber changes on oxidation to PX_3O and PX_3S [16] where the asymmetric vibrations are raised in frequency but the symmetric modes remain similar or are lowered. Comparison with the nickel(0) complexes [11,12] is complicated by the presence of four PX_3 groups, but they resemble the platinum(II) complexes more than the oxidised ligands. Without studying the forcefield around the phosphorus atom, however, it is not possible to attempt to relate these changes to particular aspects of the bonding.

The wavenumbers of Pt–X(*trans* to L) vibrations have been used to give indications of relative *trans* influences of different ligands. Comparing $[PtX_3(PF_3)]^-$ with $[PtX_3(PMe_3)]^-$,[9] in which the neutral ligands have similar effective masses, this frequency is higher in the former by 38, 22, and 12 cm^{-1} for the complexes of Cl, Br, and I respectively. This is a clear indication that PF_3 has a much weaker *trans* influence than PMe_3. The Pt–Cl(*trans* to CO) stretch in $[Pt(CO)Cl_3]^-$ is 9 cm^{-1} higher [13] than in the PF_3 analogue, suggesting that PF_3 has a marginally greater *trans* influence although the lower mass of CO might be a contributory cause.

N.M.R. Spectra.—The ^{19}F and ^{31}P n.m.r. parameters (and ^{195}Pt chemical shifts where possible by ^{19}F-$\{^{195}Pt\}$ INDOR measurements) are given in Tables 3 and 4 together with results for some complexes produced by methanolysis. The presence of highly electronegative substituents on phosphorus increases the *s*-electron density at the nucleus and the *s*-orbital contribution to the M–P bond,[1,17] both of which will increase $^1J(PtP)$. Thus all the values of $^1J(PtP)$ here are much greater than those for $[PtX_3(PMe_3)]^-$.[15] The regular increases in $^1J(PtP)$ in going from $[PtCl_3\{P(OMe)_3\}]^-$ to $[PtCl_3(PF_3)]^-$ (see Figure) can largely be accounted for by changes in orbital distribution at phosphorus and need not imply large changes in the M–P bond strength. However, for the complexes of PCl_3 and PBr_3, the effect on $^1J(PtP)$ of

TABLE 3

Phosphorus-31 and ^{195}Pt n.m.r. parameters of $[NBu_4][PtX_3L]$ (coupling constants in Hz)

Complex	δ(P) [a]	$^1J(PtP)$	δ(Pt) [b]	Δ_P [c]
$[PtCl_3(PF_3)]^-$	-50.2	$+7\,464$	907	46.8
$[PtBr_3(PF_3)]^-$	-52.1	$+7\,257$	183	44.9
$[PtI_3(PF_3)]^-$	-60.3	$+6\,959$	$-1\,370$	36.7
$[PtCl_3(PCl_3)]^-$ [d]	-90.9	$+6\,182$		128.1
$[PtBr_3(PCl_3)]^-$ [d]	-90.7	$+5\,869$		128.3
$[PtI_3(PCl_3)]^-$ [d]	-92.7	$+5\,371$		126.3
$[PtBr_3(PBr_3)]^-$ [d]	-39.4	$+5\,214$		188.0
$[PtCl_3\{P(OMe)_3\}]^-$	-58.3	$+6\,020$	1 037	81.9
$[PtBr_3\{P(OMe)_3\}]^-$	-60.1	$+5\,932$	371	80.1
$[PtI_3\{P(OMe)_3\}]^-$	-74.3	$+5\,753$	$-1\,060$	65.7
$[PtBr_3(PBrCl_2)]^-$ [d]	-74.3	$+5\,650$		149.2
$[PtBr_3(PBr_2Cl)]^-$ [d]	-57.0	$+5\,432$		169.7
$[PtCl_3\{PF_2(OMe)\}]^-$	-57.2	$+6\,906$	949	53.6
$[PtCl_3\{PF(OMe)_2\}]^-$	-61.0	$+6\,404$	999	71.5
$[PtCl_3\{PCl_2(OMe)\}]^-$	-84.0	$+6\,466$	1 179	96.8
$[PtCl_3\{PCl(OMe)_2\}]^-$	-77.3	$+6\,344$	1 108	91.7
$[PtBr_3\{PCl_2(OMe)\}]^-$	-85.6	$+6\,231$	490	95.2
$[PtBr_3\{PCl(OMe)_2\}]^-$	-80.5	$+6\,157$	438	88.5
$[PtI_3\{PCl_2(OMe)\}]^-$	-92.3	$+5\,897$	$-1\,023$	88.5
$[PtI_3\{PCl(OMe)_2\}]^-$	-91.3	$+5\,923$	$-1\,049$	77.7
$[PtBr_3\{PBr_2(OMe)\}]^-$	-71.0	$+5\,904$	584	132.2
$[PtBr_3\{PBr(OMe)_2\}]^-$	-81.3	$+6\,068$	483	

[a] In p.p.m. upfield from H_3PO_4. [b] In p.p.m. to high frequency of 21.4 MHz when corrected to $SiMe_4$ (100 MHz). [c] $\Delta_P = \delta(P)(complex) - \delta(P)(free\ ligand)$. δ(P) for $PBr_2(OMe)$ was -203.2 p.p.m. The chemical shifts used for the other ligands were from: H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, 1953, **21**, 279 (PF_3); K. B. Dillon, T. C. Waddington, and D. Younger, *Inorg. Nuclear Chem. Letters*, 1974,**10**, 777 (PCl_3, $PBrCl_2$, PBr_2Cl, and PBr_3); ref. 23 [$P(OMe)_3$]; H. Binder and R. Fischer, *Z. Naturforsch.*, 1972, **B27**, 753 [$PF_2(OMe)$ and $PF(OMe)_2$]; G. Mavel, *Ann. Rev. N.M.R. Spectroscopy*, 1973, **5B** [$PCl_2(OMe)$ and $PCl(OMe)_2$]. [d] In $CDCl_3$.

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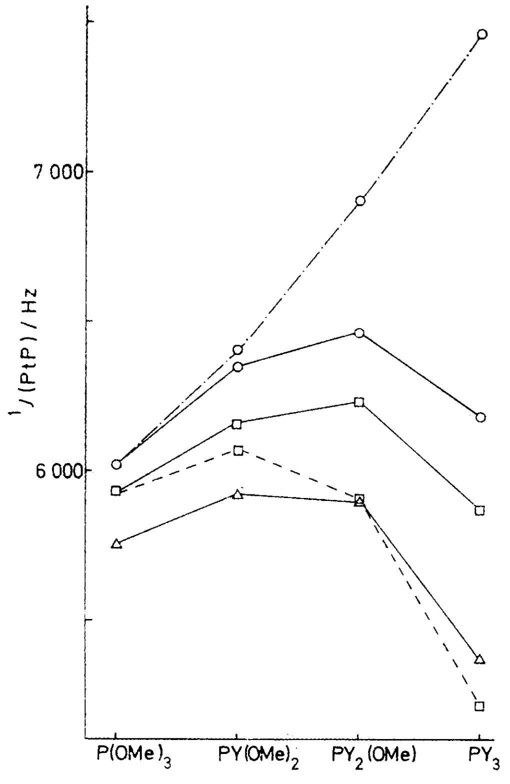
replacing methoxide by halide is far from linear and the final substitution results in a large decrease. Since the departure from a linear behaviour is greater when the halide of the PX_3 or the PtX_3 groups is bulkier (see Figure), we conclude that steric repulsion between halides on phosphorus and those on platinum is causing a weakening of the Pt–P bond. This may also be the explanation of the non-formation of $[PtI_3(PBr_3)]^-$ or $[PtI_3(PI_3)]^-$.

TABLE 4

Hydrogen-1 and ^{19}F n.m.r. parameters of $[NBu_4][PtX_3L]$ (coupling constants in Hz)

Complex	τ(Me)	^3J(PH)	^4J(PtH)	^4J(FH)	δ(F) [a]	^1J(PF)	^2J(PtF)
$[PtCl_3(PF_3)]^-$					40.4	−1 311	+730
$[PtBr_3(PF_3)]^-$					37.7	−1 313	+715
$[PtI_3(PF_3)]^-$					33.1	−1 320	+701
$[PtCl_3\{P(OMe)_3\}]^-$	6.19	+12.4	*ca.* −2				
$[PtBr_3\{P(OMe)_3\}]^-$	6.19	+12.8	*ca.* −2				
$[PtI_3\{P(OMe)_3\}]^-$	6.26	+12.8	−2.7				
$[PtCl_3\{PF_2(OMe)\}]^-$	5.91	+13.5	−2.8	+0.7	47.4 [b]	−1 222	+702
$[PtCl_3\{PF(OMe)_2\}]^-$	6.04	+13.1	−2.7	+0.5	53.5	−1 160	+709
$[PtCl_3\{PCl_2(OMe)\}]^-$	5.99	+17.1	*ca.* −2				
$[PtCl_3\{PCl(OMe)_2\}]^-$	6.07	+14.8	*ca.* −2				
$[PtBr_3\{PCl_2(OMe)\}]^-$	6.01	+17.2	−2.1				
$[PtBr_3\{PCl(OMe)_2\}]^-$	6.09	+14.9	−2.1				
$[PtI_3\{PCl_2(OMe)\}]^-$	6.05	+17.0	−2.5				
$[PtI_3\{PCl(OMe)_2\}]^-$	6.13	+14.9	−2.8				
$[PtBr_3\{PBr_2(OMe)\}]^-$	6.07	+18.1	*ca.* −2				
$[PtBr_3\{PBr(OMe)_2\}]^-$	6.11	+15.4	*ca.* −2				

[a] In p.p.m. upfield from $CFCl_3$. [b] In $CDCl_3$.



Variation of ^1J(PtP) with n for $[PtX_3\{PY_n(OMe)_{3-n}\}]^-$: X = Cl(○), Br (□), or I (△) and Y = F (— · — · —), Cl (——), or Br (— — —)

We have previously observed[18] that ^{195}Pt chemical shifts are remarkably insensitive to the nature of the substituents on a phosphorus donor, even between such widely different phosphines as PMe_3 and PF_3. Thus there is only 126 p.p.m. between $[PtCl_3(PMe_3)]^-$ and $[PtCl_3(PF_3)]^-$,[18] but on going to the iodo-anions the differences increase. It is possible that the lower electronegativity of iodide results in increased electron density on platinum and hence more back donation to PF_3; since π bonding should increase the shielding of the platinum nucleus,[19] the effect would be to lower δ(Pt) as observed. There are regular small decreases in ^{195}Pt chemical shifts in going from $[PtCl_3\{P(OMe)_3\}]^-$ to $[PtCl_3(PF_3)]^-$, whereas replacing methoxide by chloride or bromide results in an increase in δ(Pt). This might be anticipated from the changes in ^1J(PtP) since weaker bonds usually result in increases in δ(Pt).[18] Despite the apparently greater steric interference when the halide on platinum is bromide or iodide, the differences in platinum shift between $[PtX_3\{P(OMe)_3\}]^-$, $[PtX_3\{PCl(OMe)_2\}]^-$, and $[PtX_3\{PCl_2(OMe)\}]^-$ are less when X is Br or I (this might similarly be a consequence of increased π bonding).

An approximately linear relation has been reported between the ^{31}P chemical shift of phosphorus ligands and the change in this shift on co-ordination (co-ordination shift) both for fluorophosphines, PF_2X,[20] and alkyl- or aryl-phosphines.[21] A plot of the co-ordination shift, Δ_P, of the seven complexes of the type $[PtCl_3L]^-$ in Table 3 against the shift of the free phosphine, δ(free), approximates to a straight line (1) with $\rho = 0.991$. This line

$$\Delta_P = (-0.646 \pm 0.039)\delta(\text{free}) - (15.4 \pm 6.1) \quad (1)$$

goes close to the points for $[PtCl_3L]^-$ where L is an alkyl-

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or aryl-phosphine.[22] If these seven organic phosphines are included, regression analysis gives (2) with $\rho = 0.996$.

$$\Delta_P = (-0.572 \pm 0.014)\delta(\text{free}) - (4.1 \pm 1.6) \quad (2)$$

[The results for the organic phosphines alone, which span a much smaller range of δ_P, give [22] a somewhat smaller gradient (−0.312) and a line which falls well below the points for halogenophosphines.] The values for $[PtBr_3L]^-$ (Table 3) are close to the line for $[PtCl_3L]^-$ except for PBr_3, PBr_2Cl, $PBrCl_2$, and $PBr_2(OMe)$ [we lack a value of δ(P) for $PBr(OMe)_2$]. For the latter phosphines, the shift of the free ligand changes very little from that of PCl_3 which behaviour seems more anomalous than that of the co-ordination shift which increases in a manner consistent with the difference between PF_3 and PCl_3.

TABLE 5

Characterisation of the complexes

Complex	Colour	M.p. (θ_c/°C)	Analyses (%) [a] C	H	N	X
$[NBu^n_4][PtCl_3(PF_3)]$	Yellow	131—134	30.4 (30.4)	5.75 (5.75)	2.1 (2.2)	16.65 (16.85) [b]
$[NBu^n_4][PtBr_3(PF_3)]$	Yellow	114—118	24.9 (25.1)	4.8 (4.75)	1.85 (1.85)	31.1 (31.3) [c]
$[NBu^n_4][PtI_3(PF_3)]$	Orange	130—131	21.25 (21.2)	4.1 (4.0)	1.6 (1.55)	39.6 (42.0) [d]
$[N(C_5H_{11})_4][PtI_3(PF_3)]$	Orange	73—75	25.25 (24.95)	4.85 (4.6)	1.5 (1.45)	39.0 (39.55) [d]
$[NBu^n_4][PtCl_3(PCl_3)]$	Yellow	82—85	28.4 (28.2)	5.5 (5.35)	1.7 (2.05)	28.8 (31.2) [b]
$[NBu^n_4][PtBr_3(PCl_3)]$	Orange	81—83	23.55 (23.6)	4.45 (4.45)	1.75 (1.7)	29.8 (29.4) [c]
$[NBu^n_4][PtI_3(PCl_3)]$	Brown	77—81	20.7 (20.1)	3.9 (3.8)	1.55 (1.45)	
$[NBu^n_4][PtBr_3(PBr_3)]$	Deep red	82—83	20.3 (20.25)	3.95 (3.85)	1.35 (1.5)	50.55 (50.55) [c]
$[NBu^n_4][PtCl_3\{P(OMe)_3\}]$	Yellow		33.4 (34.15)	6.7 (6.8)	2.15 (2.1)	
$[NBu^n_4][PtBr_3\{P(OMe)_3\}]$	Yellow-orange		28.75 (28.45)	6.0 (5.65)	1.8 (1.75)	

[a] Calculated values are given in parentheses. [b] Cl. [c] Br. [d] I.

EXPERIMENTAL

Infrared, Raman, ^1H n.m.r., and ^{19}F n.m.r. spectra were recorded as previously described.[8,9,23,24] Phosphorus-31 and ^{195}Pt n.m.r. parameters were obtained from ^1H-{^{31}P}, ^1H-{^{195}Pt}, ^{19}F-{^{31}P}, and ^{19}F-{^{195}Pt} INDOR measurements [23,18] as appropriate, using 0.2 mol dm^{-3} solutions in dichloromethane. For species lacking protons or fluorine, ^{31}P n.m.r. spectra were recorded with a JEOL PFT 100 Fourier-transform n.m.r. spectrometer for *ca.* 0.2 mol dm^{-3} solutions in deuteriochloroform. Where both methods were used, agreement of δ(P) and ^1J(PtP) was within 0.2 p.p.m. and 4 Hz respectively.

Preparation of Complexes.—The complexes $[NBu_4][PtX_3(PF_3)]$ were prepared by introduction of a 50% excess of PF_3, purified by passing through two −85 °C traps, into a dry dichloromethane solution of $[NBu_4]_2[Pt_2X_6]$.[25] The flask was shaken until all trace of the dark colour of $[Pt_2X_6]^{2-}$ had disappeared, then evacuated to remove excess of PF_3 and solvent. The solid was redissolved in dry dichloromethane and dry diethyl ether was added until a slight turbidity was produced. The product crystallised out at −20 °C.

The complexes of PCl_3 and PBr_3 were prepared by adding a weighed quantity of the halogenophosphine dissolved in dry dichloromethane to an equivalent of $[NBu_4]_2[Pt_2X_6]$ also dissolved in dry dichloromethane. The reactions were almost instantaneous. Dry diethyl ether was added to the point of turbidity. The product crystallised out at −20 °C. Complexes $[PtX_3L]^-$ [L = $P(OMe)_3$] cannot be prepared by this method because the second substitution of the ligand into $[PtX_3\{P(OMe)_3\}]^-$ giving rise to *cis*-$[PtX_2\{P(OMe)_3\}_2]$ appears to be favoured over rupture of $[Pt_2X_6]^{2-}$. Anions, $[PtX_3L]^-$, can be prepared [13] by the addition of $[NBu_4]X$ to the bridged complex $[Pt_2X_4L_2]$, but attempts to prepare $[Pt_2Cl_4\{P(OMe)_3\}_2]$ by the usual method [26] gave only decomposition products. Similarly, fusion of $[NBu_4]_2[PtCl_4]$ and $[PtCl_2\{P(OMe)_3\}_2]$ led solely to decomposition. However, the complexes $[NBu_4][PtX_3\{P(OMe)_3\}]$ were readily formed on warming the appropriate complex of PCl_3 or PBr_3 with methanol and could be isolated as oils.

The complexes $[NBu_4][PtX_3\{PY_n(OMe)_{3-n}\}]$ (n = 1 or 2) were prepared *in situ* on an n.m.r. scale. For Y = Cl or Br, 0.1 mmol of the PCl_3 or PBr_3 precursor was treated with methanol (0.2 mmol) in dry dichloromethane (0.5 cm^3). After 5—10 h, lines corresponding to all the three methanolysis products could generally be observed in the ^1H n.m.r. spectrum which were unambiguously assigned by the multiplicities of their ^1H-{^{31}P} INDOR resonances. Methanolysis of $[NBu_4][PtCl_3(PF_3)]$ proceeded more slowly and only the monosubstituted product $[PtCl_3\{PF_2(OMe)\}]^-$ was formed, even when a large excess of methanol was used. The complex $[PtCl_3\{PF(OMe)_2\}]^-$ was formed on refluxing in neat methanol for 24 h; in this case only, a minor by-product was detected by ^1H n.m.r. Treatment of the bromo- and iodo-analogues in this manner tended to lead to decomposition.

Complexes $[PtBr_3(PBr_{3-n}Cl_n)]^-$ (n = 1 or 2) were prepared *in situ* from the mixed halide ligand, $PBr_{3-n}Cl_n$, produced by equilibration, and also from mixing $[PtBr_3(PCl_3)]^-$ and $[PtBr_3(PBr_3)]^-$, the scrambling being very much slower in the complex.

The ^{31}P chemical shifts of $PBr_2(OMe)$ and $PBr(OMe)_2$ have not previously been reported. The compound $PBr_2(OMe)$ was readily obtained *in situ* from methanolysis of PBr_3, and was extracted with dichloromethane. We

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were unable to obtain $PBr(OMe)_2$ by further methanolysis, or by treatment of the $PBr_2(OMe)$ extract with a mixture of methanol and pyridine in the manner described for $PBr_2(OBu)$.[27] Neither bromophosphite was present in a mixture of PBr_3 and $P(OMe)_3$ after standing for 2 h.

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