Infrared and Raman Studies of Halogenotrimethylplatinum(IV) Complexes and Related Compounds

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I.r. and Raman spectra of a series of platinum(IV) complexes of general type $[R_2(R')XPtL_2]$ (R = Me or CD_3; R' = Me, CD_3, CF_3, MeCO, $PhCH_2$, or $CH_2{:}CH{\cdot}CH_2$; X = Cl, Br, or I; L = phosphine or arsine) are reported, and bands due to $\nu(Pt-CH_3)$ and $\nu(Pt-X)$ have been unambiguously assigned. Group trends are correlated to changes in X and L, and the effect of progressive deuteration has been observed. Scrambling of Me and CD_3 groups has been conveniently followed by identifying Pt–C stretching frequencies in the Raman spectra.

HALOGENOTRIMETHYLPLATINUM(IV) complexes have been the subject of many recent publications,[1-8] since the discovery of a convenient preparative route involving oxidative addition of alkyl halides to platinum(II) complexes.[9,10] Although the chemistry of these (and related) complexes, of general type $[R_2(R')XPtL_2]$ (R = Me or CD_3; R' = Me, CD_3, CF_3, MeCO, $PhCH_2$, or $CH_2{:}CH{\cdot}CH_2$; X = Cl, Br, or I; L = phosphine or arsine), has been extensively studied, very little spectroscopic data have been reported for them. ^1H N.m.r.

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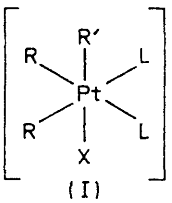
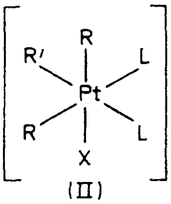
studies and dipole-moment measurements established the stereochemistry of the complexes in solution.[1,3-6,9] I.r. spectra of some of these complexes have been reported,[1,9] but full spectral assignments have not been made. The region assignable to ν(Pt–C) has been identified, but because of the poor resolution and weak intensity of the bands, individual assignments of the bands have not been made. There has been one report of the Raman spectra of [PtMe$_3$(I)L$_2$] and [PtMe$_2$(CD$_3$)(I)L$_2$] (L = PMe$_2$Ph or AsMe$_3$),[5] but the results were limited because of the small number of complexes studied. The present work concerns a full Raman and i.r. study of a range of related complexes, and has resulted in unambiguous assignment of the Pt–C and Pt–X stretching frequencies.

RESULTS AND DISCUSSION

The complexes studied are listed in Tables 1 and 2, together with Raman and i.r. assignments of ν(Pt–C), ν(Pt–X), and other bands of structural significance. The structures of these complexes are known [1,3,4,6,9] and fall into one of two structural types, (I) and (II). Within these types, the complexes can be arranged in several series to show a variety of trends (*e.g.* effects of progressive deuteriation, changing halogen, changing the neutral ligand, *etc*).



(I)



(II)

Effect of Progressive Deuteriation.—Consider, initially, the series of four complexes [PtMe$_3$(I)L$_2$], [PtMe$_2$(CD$_3$)(I)L$_2$], [PtMe(CD$_3$)$_2$(I)L$_2$], and [Pt(CD$_3$)$_3$(I)L$_2$] [L = PMe$_2$Ph). All these have been shown to have structure (I).[2,3,9] Examination of Table 1 reveals that, while bands assignable to ν(Pt–C) were visible in the i.r. spectra, some were weak and poorly resolved shoulders, some were too weak to be observed, and others were masked by ligand bands. In the Raman spectra, however, the ν(Pt–C) bands were all strong and clearly resolved. Thus, we confine our discussion principally to the Raman results, while noting that where the i.r. bands were identified they coincided with the positions of the bands in the Raman spectra.

The spectrum of the complex [PtMe$_3$(I)L$_2$] showed three bands at 541, 529, and 519 cm^{-1}; that of [Pt(CD$_3$)$_3$(I)L$_2$] showed these bands shifted to 502, 488, and 477 cm^{-1} respectively. The bands gave a ν(Pt–CH$_3$) : ν(Pt–CD$_3$) ratio of *ca.* $(18/15)^{\frac{1}{2}}$: 1, showing that the Pt–CH$_3$ vibrations are not coupled to any great extent with any other vibrations within the molecule.[11,12] Examination of the spectra of the specifically deuteriated complexes enabled the higher-frequency bands of the two regions (*i.e.* those at 541 and 502 cm^{-1}) to be positively identified as being due to ν(Pt–R') (R' = Me or CD$_3$ *trans* to halogen). This band will be referred to as ν_t. The other two bands in each region (*i.e.* at 529, 519 and 488, 477 cm^{-1}) are thus due to ν(PtR$_2$)$_{asym}$ and ν(PtR$_2$)$_{sym}$ (R = Me or CD$_3$ *trans* to phosphine): these will be referred to as ν_a and ν_s respectively; ν_c refers to ν(PtR) (where R is *trans* to phosphine) for complexes of type (II). The ratios ν(Pt–CH$_3$) : ν(Pt–CD$_3$) for another six pairs of complexes {*e.g.* [PtMe$_3$(Br)L$_2$] and [Pt(CD$_3$)$_2$Me(Br)L$_2$]} were all approximately constant, lying in the range 1·088 ± 0·008 : 1. For all these complexes, it was found that the highest-frequency band in each region was due to ν_t (Table 1). This was also true of the complexes of type (II) (Table 2).

Effect of Change of Halogen.—Comparison of the far-i.r. spectra of the complexes [PtR$_2$(R')(I)L$_2$], [PtR$_2$(R')(Br)L$_2$], and [PtR$_2$(R')(Cl)L$_2$] (R = R' = Me, L = PMe$_2$Ph) enabled unambiguous assignments of ν(Pt–X) to be made. Although the Pt–I stretch (132 cm^{-1}) was prominent in both the Raman and i.r. spectra, Pt–Br (168 cm^{-1}) and Pt–Cl (250 cm^{-1}) stretches were hard to distinguish in the Raman. For the full range of complexes studied (Tables 1 and 2), very little change was observed in the positions of ν(Pt–X); ν(Pt–I) fell in the range 128—132 cm^{-1}, ν(Pt–Br) in the range 153—169 cm^{-1}, and ν(Pt–Cl) in the range 243—255 cm^{-1}. There are very few data in the literature for the expected region for ν(Pt–Br) and ν(Pt–I) for Pt^{IV}.[11]

The change of halogen also had a pronounced effect on ν_t. For the above series of complexes it occurred at 541, 558, and 566 cm^{-1} respectively. This shift is that predicted in accord with the changing *trans*-influence of the halides, and has also been observed in the spectra of many platinum(II) complexes.[13-15] The change in halogen also had a smaller effect on the position of ν_a and ν_s (see Table 1). There has been much discussion recently about the nature of the *cis*-influence of ligands.[11,16] It appears to be a small effect, which is reported to vary in the same or opposite direction to the *trans*-influence. The results presented here would indicate that the *cis*-influence of the halide ions is in the same direction as their *trans*-influence. There have been two recent reports that some ligands exert a *cis*-influence in the opposite direction to their *trans*-influence.[17,18]

The same trends were seen for the series of complexes [PtMe$_3$(X)L$_2$] (L = AsMe$_2$Ph). The effect of the *cis*-influence was also seen for complexes of type (II) {*e.g.* [Pt(COMe)Me$_2$(X)L$_2$] and [Pt(CH$_2$Ph)Me$_2$(X)L$_2$] (L = PMe$_2$Ph) (see Table 2)}.

Effect of Change of Neutral Ligand.—Consider the

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TABLE 1

Raman and i.r. spectral data (cm^{-1}) for complexes of type (I)

Complex	$\nu(Pt{-}CH_3)$						$\nu(Pt{-}CD_3)$						$\nu(Pt{-}X)$		Other bands	
	Raman			I.r.			Raman			I.r.						
	ν_t	ν_a	ν_s	ν_t	ν_a	ν_s	ν_t	ν_a	ν_s	ν_t	ν_a	ν_s	Raman	I.r.	Raman	I.r.
$[PtMe_3(I)(PMe_2Ph)_2]$	541s	529s	519s	542vvw	530w (sh)	520m							132s	132m		
$[PtMe_2(CD_3)I(PMe_2Ph)_2]$		530s	518s		529w	518w	500m			502vw (sh)			132s	*		
$[PtMe(CD_3)_2I(PMe_2Ph)_2]$	540m			†				489s	477s		‡	478w	132s	*		
$[Pt(CD_3)_3I(PMe_2Ph)_2]$							502s	488s	477s	501vw (sh)	‡	478m	132s	*		
$[PtMe_3(Br)(PMe_2Ph)_2]$	558s	536s	527s	554vvw	531w (sh)	526m							168w	168m		
$[PtMe(CD_3)_2Br(PMe_2Ph)_2]$	558s			554vvw				495s	486s		‡		168w	*		
$[PtMe_3(Cl)(PMe_2Ph)_2]$	566m	541s	532s	†	538w (sh)	530m							251vw	250m		
$[PtMe(CD_3)_2Cl(PMe_2Ph)_2]$	564m			†				498s	489s		‡	‡	251vw	249m		
$[PtMe_3(I)(PMe_3)_2]$	543s	526s, br		540vvw	526vw (sh)	521m							130s	*		
$[PtMe_3(I)(dppe)]$	543s	534s	522s	540vvw (sh)	‡	‡							126s	*		
$[PtMe_3(I)(PMePh_2)_2]$	545vs, br		526s	541vvw	‡	‡							128s	*		
$[PtMe_3(I)(AsMe_2Ph)_2]$	548s	538s		†	542w (sh)	536m							132s	131m	591w [$\nu(As{-}Me)$]	592m
$[PtMe_2(CD_3)I(AsMe_2Ph)_2]$		539s	535s		537vw	532w	504m			501vw			131s	*	594w [$\nu(As{-}Me)$]	592m
$[PtMe_3(Br)(AsMe_2Ph)_2]$	557m	545s	539s	554vvw	542w (sh)	538m							167w	168m	* [$\nu(As{-}Me)$]	590m
$[PtMe_3(Cl)(AsMe_2Ph)_2]$	557m	543s	537s	†	545w (sh)	540m							244vw	250m	591w [$\nu(As{-}Me)$]	590m
$[PtMe_2(COMe)Br(PMe_2Ph)_2]$		525s	518s		527w (sh)	519m							†	153m	1 669vvw [$\nu(C{=}O)$]	1 669s
$[Pt(CD_3)_2(COMe)Br(PMe_2Ph)_2]$								484s	478s		‡	478m	†	*	1 670vvw [$\nu(C{=}O)$]	1 668s
$[PtMe_2(COMe)Cl(PMe_2Ph)_2]$		526s	521s		529w (sh)	521m							243w	246m	1 648vvw [$\nu(C{=}O)$]	1 643s
$[Pt(CD_3)_2(COMe)Cl(PMe_2Ph)_2]$								484s	478s		‡	479w	245w	*	† [$\nu(C{=}O)$]	1 642s
$[PtMe_2(CF_3)I(PMe_2Ph)_2]$		530s	514s		531w	515m							127w	129m		
$[Pt(CD_3)_2(CF_3)I(PMe_2Ph)_2]$								490s	476s		‡	478w (sh)	129vw	*		

dppe = 1,2-Bis-(diphenylphosphino)ethane. w = weak, sh = shoulder, m = medium, s = strong, and v = very.

* Not examined. † Band expected but not observed. ‡ Obscured by ligand bands.

series of complexes [$PtMe_3(I)L_2$] [L = PMe_2Ph, PMe_3, $PMePh_2$, 1,2-bis(diphenylphosphino)ethane (dppe), and $AsMe_2Ph$]. ν_t Is virtually constant for this series (see Table 1). However, changes were observed in ν_a and ν_s, both in magnitude and splitting, but comparison of the results is difficult.

TABLE 2

Raman and i.r. spectral data (cm^{-1}) for complexes of type (II)

	ν(Pt–CH_3)							
	Raman		I.r.		ν(Pt–X)		Other bands	
Complex	ν_t	ν_c	ν_t	ν_c	Raman	I.r.	I.r.	Raman
[Pt(CH_2·CH:CH_2)Me_2(Br)(PMe_2Ph)$_2$]	554s	528s	551vw	525m	169vw	168m	1 611m	1 617m [ν(C=C)]
[Pt(CH_2·CH:CH_2)Me_2(Cl)(PMe_2Ph)$_2$]	554s	526s	554vw	526m	253vvw	251m	1 611m	1 613m [ν(C=C)]
[Pt(CH_2Ph)Me_2(Br)(PMe_2Ph)$_2$]	551s	521s	547w	519m	164vw	166m		
[Pt(CH_2Ph)Me_2(Cl)(PMe_2Ph)$_2$]	556s	523s	544w	520m	254vvw	255m		

Scrambled Complexes.—Although scrambling reactions have been known for many years,[19,20] they have only recently been successfully applied to platinum(IV) complexes.[3,5,7,21] The process under consideration is (1).

$$(I) \xrightarrow[\text{solvent}]{\text{heat}} (I) + (II) \qquad (1)$$

Samples for Raman spectroscopy were obtained by evaporating solutions to dryness. The results are listed in Table 3. Although the spectra were not as well resolved as those for pure complexes, all the bands were still discernible. The interpretation of the spectra of the scrambled complexes [$PtMe(CD_3)_2(Br)L_2$] and [$PtMe(CD_3)_2(Cl)L_2$] (L = PMe_2Ph) was straightforward: bands at 527 and 530 cm^{-1} are due to $\nu(Pt{-}CH_3)_c$ and bands at 513 and 517 cm^{-1} are due to $\nu(Pt{-}CD_3)_t$. However, for the complex [$PtMe(CD_3)_2(I)L_2$] an extra band at 529 cm^{-1} was observed. This may be due to solid-state splitting of $\nu(Pt{-}CH_3)_c$. A similar effect was observed for the complex [$PtMe_2(CD_3)(I)L_2$], the band due to $\nu(Pt{-}CD_3)_c$ being split.

TABLE 3

Raman spectra (cm^{-1}) for scrambled complexes

Complex	ν(Pt–C)
[$PtMe(CD_3)_2Cl(PMe_2Ph)_2$]	559m,* 530m, 517m, 490 (sh),* 485s *
[$PtMe(CD_3)_2Br(PMe_2Ph)_2$]	553m,* 527m, 513m, 487 (sh),* 481s *
[$PtMe(CD_3)_2I(PMe_2Ph)_2$]	541m,* 529m, 519m, 501s, 488s,* 477s *
[$PtMe_2(CD_3)I(PMe_2Ph)_2$]	541s, 530s,* 520s,* 502m,* 488m, 477m

* Bands present in unscrambled complex.

TABLE 4

Raman spectra (cm^{-1}) for solutions in chloroform

Complex	$\nu(Pt{-}CH_3)_t$	$\nu(PtMe_2)$	$\nu(Pt{-}CD_3)_t$	$\nu[Pt(CD_3)_2]$
[$PtMe_3(I)(PMe_2Ph)_2$]	538m	528s		
[$PtMe_2(CD_3)I(PMe_2Ph)_2$]		529s	502m	
[$PtMe_3(Br)(PMe_2Ph)_2$]	552m	530s		
[$PtMe(CD_3)_2Br(PMe_2Ph)_2$]	554m			490s
[$PtMe_3(Cl)(PMe_2Ph)_2$]	558m	532s		
[$PtMe(CD_3)_2Cl(PMe_2Ph)_2$]	559m			491s

It is hoped that Raman spectroscopy will prove a useful technique for studying scrambling processes, and will be used to complement n.m.r. studies.

Solution Studies.—Attempts to record Raman spectra of the complexes in benzene proved unsuccessful. However, weak spectra could be obtained from solutions in chloroform, and these are listed in Table 4; all the bands listed showed depolarization ratios of less than 0·5 : 1. The positions of ν_t were similar to those in the solids, but in solution the symmetric and asymmetric bands, ν_a and ν_s, for the groups *trans* to the phosphine became degenerate.

EXPERIMENTAL

Preparation of Complexes.—Most of the complexes were prepared by standard literature methods.[1,3,4,6,9] The following have not previously been reported.

Benzylchlorodimethylbis(dimethylphenylphosphine)platinum(IV), (II). Benzyl chloride (2 cm^3) was added to a solution of the complex *cis*-[$PtMe_2(PMe_2Ph)_2$] (0·3 g) in diethyl ether (10 cm^3). After 2 weeks at room temperature, colourless *crystals* of the product separated. These were collected by filtration, washed with diethyl ether (20 cm^3), and dried *in vacuo*, yield 0·15 g, m.p. 134—136 °C (decomp.) (Found: C, 47·8; H, 5·50. Calc. for $C_{25}H_{35}ClP_2Pt$: C, 47·8; H, 5·60%). ^1H N.m.r. spectrum in $CDCl_3$: Pt–CH_3 (*trans* to Cl), τ 9·47 (triplet), $^3J(PH)$ 7·0, $^2J(Pt{-}CH_3)$ 73 Hz; Pt–CH_3 (*trans* to phosphine), 9·68 (triplet), $^3J(PH)$ 7·5, $^2J(Pt{-}CH_3)$ 56; P–CH_3, 8·44 (multiplet); CH_2 protons, 7·40 (triplet) and 7·48 (triplet), $^3J(PH)$ 11·0, $^2J(PtH)$ 66.

Allylchlorodimethylbis(dimethylphenylphosphine)platinum(IV), (II). This was prepared and purified as above using *cis*-[$PtMe_2(PMe_2Ph)_2$] (0·31 g) and allyl chloride (2 cm^3), producing colourless *crystals*, yield 0·21 g, m.p. 141—143 °C

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(decomp.) (Found: C, 43·4; H, 5·55%. Calc. for $C_{21}H_{33}ClP_2Pt$: C, 43·6; H, 5·40%). ^1H N.m.r. spectrum in $CDCl_3$: Pt–CH_3 (*trans* to Cl), τ 9·57 (triplet), ^3J(PH) 7·0, ^2J(Pt–CH_3) 71 Hz; Pt–CH_3 (*trans* to phosphine), 9·20 (triplet), ^3J(PH) 7·8, ^2J(Pt–CH_3) 56; P–CH_3, 8·46 (multiplet); allyl protons, 5·11 and 5·41 (complex).

Acetylbromobis(dimethylphenylphosphine)bis(trideuteriomethyl)platinum(IV), (I). Acetyl bromide (8 μl) and the complex *cis*-[Pt(CD_3)$_2$(PMe_2Ph)$_2$] (0·055 g) in diethyl ether (10 cm^3) were allowed to stand for 30 min, whence cream *crystals* formed. These were collected by filtration, washed with diethyl ether (20 cm^3), and dried *in vacuo*, yield 0·03 g, m.p. 101—105 °C (decomp.). ^1H N.m.r. spectrum in $CDCl_3$: Pt–acetyl (*trans* to Br), τ 8·10, ^3J(PtH) 14·4 Hz; P–CH_3, (*i*) 8·43 (doublet), ^2J(PH) 9·6, ^3J(Pt–CH_3) 14·4, (*ii*) 8·50 (doublet), ^2J(PH) 9·6, ^3J(Pt–CH_3) 14·4.

Iodobis(dimethylphenylphosphine)bis(trideuteriomethyl)(trifluoromethyl)platinum(IV), (I). A solution of the complex *cis*-[Pt(CD_3)$_2$(PMe_2Ph)$_2$] (0·048 g) in liquid trifluoroiodomethane (3 cm^3) was allowed to stand for 24 h at room temperature in a sealed tube. The light yellow *crystals* obtained were washed with diethyl ether (20 cm^3) and dried *in vacuo*, yield 0·03 g, m.p. 155—157 °C (decomp.). ^1H N.m.r. spectrum in $CDCl_3$: P–CH_3, (*i*) τ 8·23 (doublet), ^2J(PH) 9·0, ^3J(Pt–CH_3) 10·8 Hz, (*ii*) 8·34 (doublet), ^2J(PH) 9·0, ^3J(Pt–CH_3) 10·8.

Physical Methods and Analyses.—I.r. spectra (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 577 instrument and the far-i.r. spectra (400—40 cm^{-1}) on a Beckman–R.I.I.C. FS720 interferometer. Raman spectra were recorded on a Spex model 1401 spectrometer using the 632·8 nm line of a He–Ne laser of 70 mW (for powdered samples) or the 488·0 nm line of an Ar^+ laser at 530 mW (for solutions). ^1H N.m.r. spectra were recorded using a Perkin-Elmer R12B spectrometer. Elemental analyses were carried out by the Alfred Bernhardt Microanalytical Laboratories.

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