

234. *The Infrared Spectra of Some Alkyl Platinum Complexes.
Part II.¹ Partly Deuterated Complexes.*

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Infrared spectra for the complexes, *trans*-[PtCl(CX₃)(PMe₃)₂] and *cis*-[Pt(CX₃)₂(PMe₃)₂] (X = H, D), are used to confirm the previous assignment of the platinum-carbon stretching mode(s) to a band(s) near 500 cm.⁻¹. C-X stretching modes of the alkyl group bound to platinum are assigned: the methyl C-H stretching frequencies are 30—60 cm.⁻¹ lower than in alkanes.

IN a previous publication¹ the infrared spectra of some alkyl complexes of platinum were reported, and bands found in the KBr region of the spectrum were assigned to platinum-carbon stretching modes ($\nu_{\text{Pt-C}}$). The dependence of $\nu_{\text{Pt-C}}$ on the structure of the complexes was correlated with the *trans*-effect of the group *trans* to the alkyl group. We now confirm the assignment of the $\nu_{\text{Pt-C}}$ mode and discuss the C-H stretching frequencies ($\nu_{\text{C-H}}$) in these compounds.

The Platinum-Carbon Stretching Frequency ($\nu_{\text{Pt-C}}$).—Spectra of the complexes in Table I were recorded. The observed isotope shifts of the bands previously assigned¹ to $\nu_{\text{Pt-C}}$ are consistent with this assignment. These shifts (to a first approximation $\nu_{\text{Pt-CH}_3}/\nu_{\text{Pt-CD}_3}$) are very close to $(18/15)^{\frac{1}{2}} = 1.095$, and indicate that, in the platinum-methyl stretching mode, the methyl group moves as a single unit. However, the ethyl group in the complexes, [PtEtX(PEt₃)₂] (X = Cl, I), does not move as a unit of molecular weight 29 against the platinum atom, since in the pair of complexes, *trans*-[PtClR(PEt₃)₂] (R = Me, Et), $\nu_{\text{Pt-Me}}/\nu_{\text{Pt-Et}} = 1.024$. If the ethyl group moved as a whole, the ratio

¹ The paper, Adams, Chatt, and Shaw, *J.*, 1960, 2047, is now considered as Part I.

of frequencies would be $(29/15)^{\frac{1}{2}} = 1.39$. The $\nu_{\text{Pt}-\text{Bt}}$ mode probably involves platinum-carbon bond stretching together with some Pt-C-C and Pt-C-H angle bending.

TABLE 1.
Platinum-carbon stretching frequencies.

	$\nu_{\text{Pt}-\text{C}}$ (cm. ⁻¹) (Nujol mull)	$\nu_{\text{Pt}-\text{CH}_3}/\nu_{\text{Pt}-\text{CD}_3}$
<i>cis</i> -[Pt(CD ₃) ₂ (PMe ₃) ₂]	477, 466	} 1.095, 1.095
<i>cis</i> -[Pt(CH ₃) ₂ (PMe ₃) ₂]	522, 510	
<i>trans</i> -[PtCl(CD ₃)(PMe ₃) ₂]	516	} 1.091
<i>trans</i> -[PtCl(CH ₃)(PMe ₃) ₂]	563	

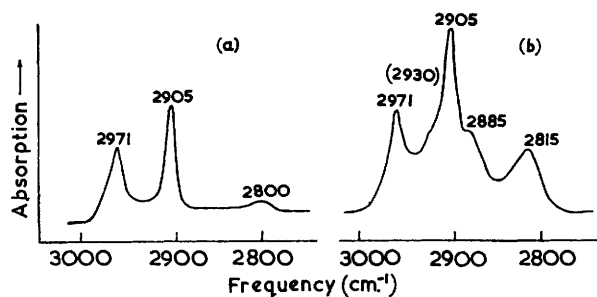
The Methyl Symmetrical Deformation Frequency ($\delta_{\text{CH}_3(s)}$).—In Part I, both $\nu_{\text{Pt}-\text{C}}$ and the symmetrical deformation frequency, $\delta_{\text{CH}_3(s)}$, of the methyl groups bound to the platinum atom were listed. In the deuterated specimens $\delta_{\text{CD}_3(s)}$ is not observed since the drop in frequency of $\delta_{\text{CH}_3(s)}$ upon deuteration moves it into a region where it is obscured by strong absorption due to methyl rocking modes of the phosphine ligands. Its absence in spectra of the deuterated alkyl complexes is taken as proof of the validity of the original assignment of $\delta_{\text{CH}_3(s)}$.

Carbon-Hydrogen Stretching Frequencies ($\nu_{\text{C}-\text{H}}$).—From the spectra of the partially deuterated complexes one can distinguish C-H stretching frequencies of the alkyl groups on the platinum atom from those of the trialkylphosphine ligands (Table 2 and Figure).

TABLE 2.
Carbon-hydrogen stretching frequencies (cm.⁻¹) in benzene solution.

<i>trans</i> -[PtCl(CD ₃)(PMe ₃) ₂]	2971m, 2905s	2800vw
<i>trans</i> -[PtCl(CH ₃)(PMe ₃) ₂]	2972m, 2905s, 2885sh, 2815m	
<i>trans</i> -[PtNO ₂ (CH ₃)(PMe ₃) ₂]	2972m, 2907s, 2888sh, 2817m	
<i>cis</i> -[Pt(CD ₃) ₂ (PMe ₃) ₂]	2967s, 2905s, 2831vw, 2803vw	
<i>cis</i> -[Pt(CH ₃) ₂ (PMe ₃) ₂]	2967m, 2907s, 2872m, 2803m	

The strong bands found for each complex near 2970 and 2906 cm.⁻¹ are due to the trimethylphosphine ligands. Weak bands accompany these in each deuterated specimen and are assigned to the first overtones of symmetrical and antisymmetrical methyl



Spectra of (a) *trans*-[PtCl(CD₃)(PMe₃)₂] and (b) *trans*-[PtCl(CH₃)(PMe₃)₂], in C₆H₆.

deformations in the phosphine. Similar weak bands have been recorded for many organic compounds containing methyl groups and this explanation has been shown to be valid.² On comparing the spectra of *trans*-[PtClR(PMe₃)₂] (R = CH₃, CD₃), it is clear (Figure and Table 2) that the bands at 2885 and 2815 cm.⁻¹ are due to the methyl group attached to platinum. A similar result is obtained for *cis*-[PtR₂(PMe₃)₂] (R = CH₃, CD₃). These frequencies are discussed below.

Carbon-Deuterium Stretching Frequencies ($\nu_{\text{C}-\text{D}}$).—The $\nu_{\text{C}-\text{D}}$ frequencies occur in a region of the spectrum which is otherwise transparent and they provide an opportunity to study

² Forel, Fuson, and Josien, *J. Opt. Soc. Amer.*, 1960, **50**, 1228.

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possible free rotation about the Pt-C bond. Table 3 shows the results obtained with the two deuterated complexes at room temperature and at liquid-nitrogen temperature. The ν_{C-D} bands in *cis*-[Pt(CD₃)₂(PMe₃)₂] were all of comparable intensity and of medium strength in comparison with other parts of the spectrum. Those of *trans*-[PtCl(CD₃)(PMe₃)₂] were weak. Half-widths are included for those bands which were not overlapped in any way.

TABLE 3.

Carbon-deuterium ν_{C-D} frequencies (cm.⁻¹), with half band widths ($\Delta\nu_{1/2}$) in parentheses.

	Room temperature		Liquid-nitrogen temperature
	(in benzene)	(Nujol mull)	(Nujol mull)
<i>cis</i> -[Pt(CD ₃) ₂ (PMe ₃) ₂]	2186 (39)	2187, 2174	2193 (10)
			2172, 2165
	2099 (14)	2096 (24)	2096, 2074
	2049 (14)	2048 (13)	2046 (12)
<i>trans</i> -[PtCl(CD ₃)(PMe ₃) ₂]	2186 (48)	2209, 2178	2213 (10), 2184 (12)
	2109 (14)	2105 (14)	2109 (8)
	2060 (14)	2057 (13)	2060 (7)

Discussion of ν_{C-H} and ν_{C-D} .—Results discussed below indicate that the assignment of the observed ν_{C-H} and ν_{C-D} bands to vibrational modes of the methyl groups bonded to platinum is not straightforward, but useful conclusions may be drawn from them. Three ν_{C-D} bands are observed in the solution spectra of each deuterated complex (Table 3). On the assumption that three ν_{C-H} bands correspond to those in the analogous light-hydrogen complexes, then the ν_{C-H} bands at 2880 ± 8 and 2810 ± 7 cm.⁻¹ (Table 2) probably correspond to the two lowest ν_{C-D} bands recorded in Table 3. Thus, for *trans*-[PtCl(CX₃)(PMe₃)₂] (X = H, D), $2815/2060 = 1.366$ and $2885/2109 = 1.368$. For *cis*-[Pt(CX₃)₂(PMe₃)₂] (X = H, D), $2803/2049 = 1.368$ and $2872/2099 = 1.368$. These isotope shifts are normal and may be used to locate the third ν_{C-H} band, corresponding to the third ν_{C-D} band, which will be at a higher frequency than the other two. Thus (Table 3), for *trans*-[PtCl(CX₃)(PMe₃)₂] (X = H, D), $2186 \times 1.367 = 2988$ cm.⁻¹, and for *cis*-[Pt(CX₃)₂(PMe₃)₂] (X = H, D), $2186 \times 1.368 = 2990$ cm.⁻¹. In the Figure it can be seen that the 2905 cm.⁻¹ band of *trans*-[PtCl(CH₃)(PMe₃)₂] shows asymmetry on the high-frequency side which is not present in the spectrum of *trans*-[PtCl(CD₃)(PMe₃)₂]. This structure is never resolved but its absorption is estimated to lie near 2930 cm.⁻¹; it would then give an isotope shift of $2930/2186 = 1.340$ (*i.e.*, smaller than the value of 1.368 found for the lower frequency ν_{C-H} and ν_{C-D} bands). However, the higher frequency indicates an antisymmetric vibrational mode and these commonly exhibit smaller isotope shifts than symmetric modes. A similar asymmetry of the 2907 cm.⁻¹ band in *cis*-[Pt(CH₃)₂(PMe₃)₂] is observed.

TABLE 4.

Carbon-hydrogen frequencies (cm.⁻¹) (in benzene).

<i>cis</i> -[PtEt ₂ (PMe ₃) ₂]	Combination band	<i>cis</i> -[PtPr ⁿ ₂ (PMe ₃) ₂]		
3006vw			2963m	PMe ₃
2964m	PMe ₃		2938s	Pr ⁿ (Pt)
2933sh	Et (Pt)		2914s	PMe ₃
2905s	PMe ₃		2892sh	} Pr ⁿ (Pt)
2892sh	Et (Pt)		2843s	
2840s	Et (Pt)		2823m	

It is therefore concluded that, in the complexes considered here, the methyl group bonded to platinum has ν_{C-H} absorption frequencies near 2930, 2880, and 2810 cm.⁻¹. For normal alkanes, Bellamy³ gives the characteristic methyl ν_{C-H} frequencies as 2962 (antisymmetric) and 2872 (symmetric) ± 10 cm.⁻¹. In the present complexes the 2810 band almost certainly arises from a symmetric C-H stretch and may be compared with the 2872 cm.⁻¹ band in alkanes ($\Delta\nu = 62$ cm.⁻¹). Since the exact origin of the 2930 and

³ Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1956, p. 13.

2880 cm^{-1} bands (see below) of the complexes in Table 2 is not known, comparison with the 2962 cm^{-1} band of alkanes is unsafe. However, it may be concluded that the methyl group in these complexes has $\nu_{\text{C-H}}$ frequencies 30–60 cm^{-1} lower than in alkanes. This may be due to hyperconjugation, the requirements for which are satisfied by these systems.

$\nu_{\text{C-H}}$ Frequencies of Et and Prⁿ Groups Bound to Platinum.—The $\nu_{\text{C-H}}$ frequencies in Table 4 include bands due to ethyl and n-propyl groups bound to platinum. Assignment to $-\text{CH}_2-$ and $-\text{CH}_3$ modes cannot be made with certainty as the usual order of assignments for ethyl and n-propyl groups may be upset if the methylene group next to the metal is disturbed more than the rest of the alkyl group. Evidence from partially deuterated alkyl groups is necessary to decide this. However, the lowest band recorded in Table 4 for each complex is lower than any recorded by Bellamy³ for alkanes.

$\nu_{\text{C-D}}$ Band Splitting in the Solid State.—*trans*-[PtCl(CD₃)(PMe₃)₂] exhibits four absorption bands near 2100 cm^{-1} although there are only three C–D bands. One, or two, of these bands could be due to an overtone of $\delta_{\text{CD}_3(a)}$ or $\delta_{\text{CD}_3(s)}$ increased in intensity by Fermi resonance with $\nu_{\text{C-D}}$. An alternative explanation is that the four $\nu_{\text{C-D}}$ bands arise from two CD₃ groups in slightly different steric environments (2209, 2105, and 2178, 2057 cm^{-1}).

In *cis*-[Pt(CD₃)₂(PMe₃)₂], band splitting is observed on changing from room temperature to liquid-nitrogen temperature, and may be due to a removal of rotational freedom from the CD₃ groups.

Experimental.—Complexes, other than deuterated specimens, were those used for the work reported in Part I.¹ Deuterated specimens were prepared in an analogous manner to the light-methyl complexes, with CD₃Br in place of CH₃Br.

Spectra were recorded on a Grubb-Parsons GS2A spectrometer for Nujol and hexachlorobutadiene mulls and benzene solutions. Low-temperature spectra of mulls were recorded by using a cold-cell of conventional design.

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