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## Assignment of Stereochemistry in Bis(triphenylphosphine)platinum(II) Complexes

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Triphenylphosphine ($Ph_3P$) complexes of platinum(0) and platinum(II) are important starting materials for a variety of synthetic reactions. A serious problem associated with the use of these compounds, however, has been the lack of a convenient method for directly determining the stereochemistry of the resulting products $Pt(Ph_3P)_2XY$.

Recently, several authors have reported that the number of bands in the 400-450-cm$^{-1}$ region of the infrared spectra of these compounds is sensitive to complex geometry and have therefore proposed use of these bands for the assignment of stereochemistry.[1-3] These vibrations have been ascribed to platinum-phosphorus stretching[1-5] by analogy with similar assignments in trialkylphosphine complexes of platinum(II)[2,6-9] and in $Ph_3P$ complexes of platinum(0).[8,10]

In the course of other investigations we have obtained vibrational spectra of the series of isomeric dihalide complexes $Pt(Ph_3P)_2X_2$ (X = Cl, Br, or I) and several related compounds of known stereochemistry. Examination of these spectra does not show the predicted relationship between the number of bands in the 400-450-cm$^{-1}$ region and the complex geometry. However, we have found other features in these spectra which do correlate with stereochemistry and which appear to be suitable for the assignment of geometries in these complexes. These are described below.

## Experimental Section

The complexes *cis*-$Pt(Ph_3P)_2Cl_2$,[11] $Pt(Ph_3P)_2O_2{\cdot}C_6H_6$,[12] $Pt(Ph_3P)_2(C_2H_4)$,[12] *trans*-$Pt(Ph_3P)_2HCl$,[11] and *trans*-$Pt(Ph_3P)_2Cl(COPh)$[13] were prepared by literature methods. A sample of *trans*-$Pt(Ph_3P)_2Cl(CO_2Me)$ was kindly supplied by Professor R. J. Angelici.

**Preparation of *cis*-$Pt(Ph_3P)_2X_2$.** The cis dibromide was prepared by metathesis of *cis*-$Pt(Ph_3P)_2Cl_2$ with excess LiBr (1:100, mol) in refluxing 95% ethanol-chloroform (10:1, vol) to give a yellow powder, mp 307-309° (lit.[14] mp 308° dec), after evaporation of the chloroform layer. *Anal.* Calcd for $C_{36}H_{30}Br_2P_2Pt$: C, 49.11; H, 3.48; Pt, 22.18. Found: C, 49.16; H, 3.43; Pt, 22.1.

**Table I.** Metal-Ligand Stretching Frequencies (cm$^{-1}$) in $Pt(Ph_3P)_2X_2$ Complexes

| | | Pt-X | | Pt-P | |
|---|---|---|---|---|---|
| X | | Ir | Raman | Ir | Raman |
| Cl | cis | 321 (sh), 316$^a$<br>297, 283$^a$ | 321 (sh), 316$^a$<br>294, 283 (sh)$^a$ | (195, 177)$^b$ | 195, 170 |
| | trans | 342 | 333 | 173 | 166 |
| Br | cis | 216, 204 | 216, 205 | 192, 176 | 190, 176 |
| | trans | 255 | 208 | 174 | 166 |
| I | cis | 163, 148 | 164, 149 | 192, 185 | 195, 183 |
| | trans | 200 | 150 | (170)$^b$ | 167 |

$^a$ Doublet. $^b$ Very weak.

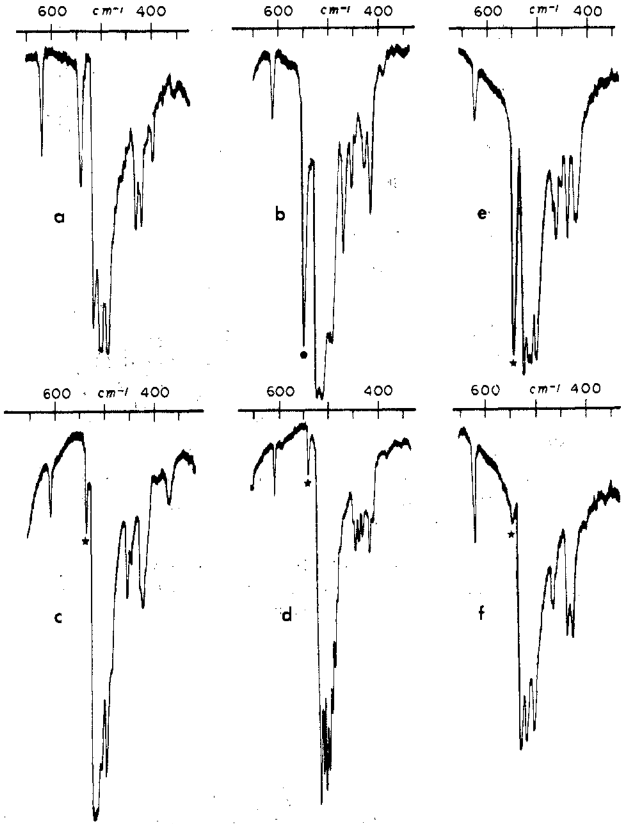

**Figure 1.** Infrared spectra of (a) $Ph_3P$, (b) $Pt(Ph_3P)_2O_2$, (c) *trans*-$Pt(Ph_3P)_2Cl(CO_2Me)$, (d) *trans*-$Pt(Ph_3P)_2HCl$, and (e) *cis*- and (f) *trans*-$Pt(Ph_3P)_2I_2$ in the 350-650-cm$^{-1}$ region. The intensity of the starred band is related to complex geometry.

The cis diiodide was produced by metathesis of the dichloride with excess NaI (1:40, mol) in a refluxing equivolume mixture of water, ethanol, acetone, and chloroform. A bright yellow powder, mp 302-305° (lit.,[15] orange-yellow, mp 290°), was obtained by evaporation of the immiscible organic layer. *Anal.* Calcd for $C_{36}H_{30}I_2P_2Pt{\cdot}{}^1/_2CHCl_3$:[16] C, 42.43; H, 2.98; Pt, 18.9. Found: C, 42.60; H, 2.94; Pt, 19.3.

**Preparation of *trans*-$Pt(Ph_3P)_2X_2$.** *trans*-$Pt(Ph_3P)_2Cl_2$ was prepared from the cis dichloride by photochemical methods.[17] Typically, a $10^{-3}$ *M* chloroform solution was irradiated under a nitrogen atmosphere for 24 hr with incident light of wavelength greater than 300 nm. The resulting yellow solution was evaporated to dryness and the residue extracted with a minimum of benzene. Lemon yellow crystals, mp 310-314° (lit.[18] mp 307-310°), were produced by slow evaporation of the benzene solution. *Anal.* Calcd for $C_{36}H_{30}Cl_2P_2Pt$: C, 54.69; H, 3.82. Found: C, 54.55; H, 3.97.

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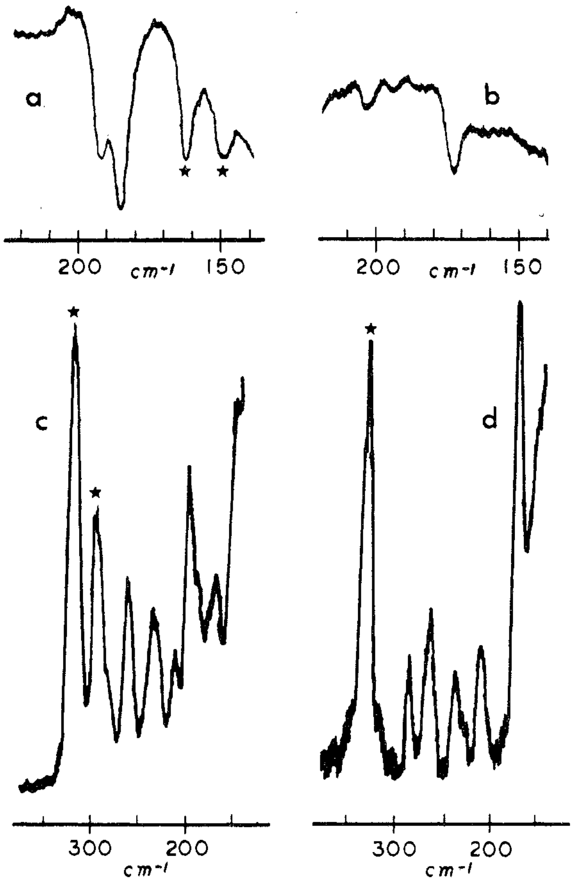

**Figure 2.** Infrared spectra of (a) *cis*-$Pt(Ph_3P)_2I_2$ and (b) *trans*-$Pt(Ph_3P)_2Cl_2$; Raman spectra of (c) *cis*- and (d) *trans*-$Pt(Ph_3P)_2Cl_2$. Metal-halogen stretching bands are starred.

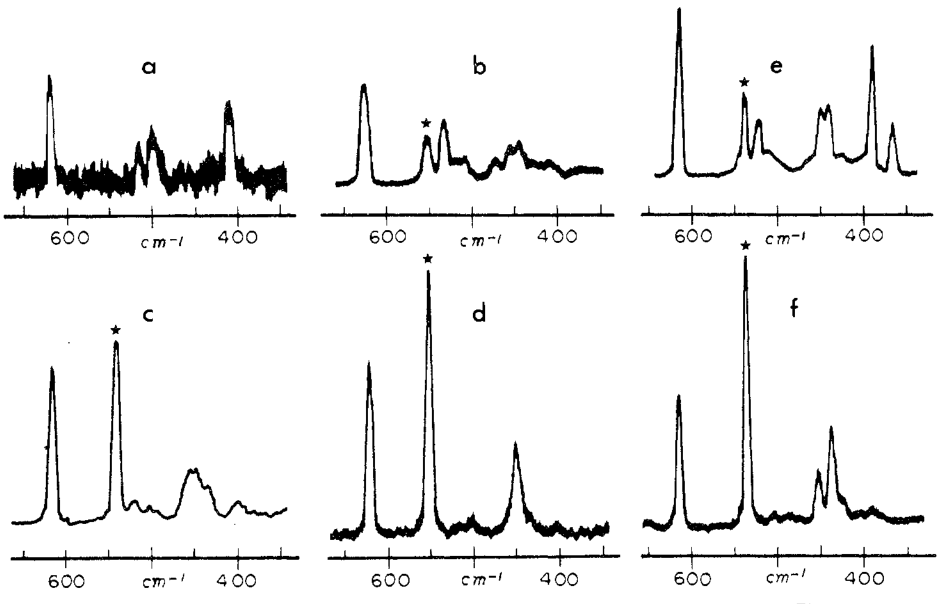

**Figure 3.** Raman spectra of (a) $Ph_3P$, (b) *cis*-$Pt(Ph_3P)_2Br_2$, (c) *trans*-$Pt(Ph_3P)_2Cl(CO_2Me)$, (d) *trans*-$Pt(Ph_3P)_2HCl$, and (e) *cis*- and (f) *trans*-$Pt(Ph_3P)_2I_2$ in the 350-650 cm$^{-1}$ region. The intensity of the starred band is related to complex geometry.

The trans dibromide was obtained similarly by photolysis of *cis*-$Pt(Ph_3P)_2Br_2$. Bright yellow crystals, dec 312-314°, were produced by recrystallization from chloroform-ethanol. *Anal.* Found: C, 48.93; H, 3.80.

*trans*-$Pt(Ph_3P)_2I_2$ was prepared by thermal isomerization[19a] of the cis diiodide in refluxing chloroform containing approximately 2% ethanol. The pale orange trans isomer, mp 307-308°, was separated from the resulting yellow-orange solid by fractional recrystallization from chloroform. *Anal.* Calcd for $C_{36}H_{30}I_2P_2Pt$: C, 44.42; H, 3.11; Pt, 20.04. Found: C, 44.37; H, 3.28; Pt, 20.9. Bright orange crystals of a chloroform solvate of the trans isomer, mp 307-310°, were also isolated.[19b]

**Vibrational Spectra.** Infrared spectra were obtained on a Perkin-Elmer Model 457 (4000-250 cm$^{-1}$) and an Hitachi Perkin-Elmer FIS-3 (410-100 cm$^{-1}$) spectrophotometer. Samples were run as KBr disks or Nujol mulls. Raman spectra were taken of powdered solids on a Jarrell-Ash Model 25-400 spectrometer with a Coherent Radiation Model 52G Ar/Kr mixed gas laser source operating at 514.5 or 647.1 nm.

## Results and Discussion

The complexes studied are all of known stereochemistry. $Pt(Ph_3P)_2O_2$[20] and $Pt(Ph_3P)_2(C_2H_4)$[21] have both been shown to have planar coordination around platinum and approximately cis coordinated phosphines by single-crystal X-ray diffraction studies. The hydride complex $Pt(Ph_3P)_2HCl$ has been assigned trans stereochemistry on the basis of $^1H$ nmr and infrared data.[22] Similarly, $Pt(Ph_3P)_2Cl(COPh)$ was shown to contain trans phosphines by $^{31}P$ nmr.[13] The geometry of the carbomethoxy complex $Pt(Ph_3P)_2Cl(CO_2Me)$ was assumed to be trans by analogy with the corresponding $Ph_2PMe$ complex.[23] Geometries have been assigned to the dihalide complexes on the basis of the number of observed metal-halogen stretching bands.[24] These bands, listed in Table I, are readily identified by their sensitivity to halogen substitution and their intensity, particularly in the Raman.[25,26]

Typical infrared spectra are shown in Figure 1, together with the spectrum of free $Ph_3P$. The spectra differ considerably in the 400-450-cm$^{-1}$ region, but there is no obvious correlation between the stereochemistry of a complex and the number of bands in this region; *i.e.*, the number of bands in the 400-450-cm $^{-1}$ region is not a valid criterion for the assignment of stereochemistry in such complexes.

The above results also suggest that assignment of these

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bands to Pt-P stretching modes is probably incorrect. As previously suggested, they are more likely internal ligand modes split or activated by complexation.[2,27-29] In fact, most of the bands in the far infrared and Raman spectra of the complexes studied can be correlated very well with vibrations of free $Ph_3P$,[27,28] both in position and relative intensity. However, there are bands in the 160-200-$cm^{-1}$ region of the spectra of all complexes studied (weak in the infrared and strong in the Raman) which do not appear in the spectra of the free ligand. There are two such bands between 195 and 170 $cm^{-1}$ in the spectra of the cis complexes and one band, at 165-175 $cm^{-1}$, in the spectra of the trans (Figure 2). We tentatively assign these bands as the Pt(II)-P stretching modes (see Table I). This assignment is consistent with those recently made by use of the metal isotope technique for Ni(II)-$Ph_3P$ and Pd(II)-$Ph_3P$ stretching frequencies[29] and with assignments of M-$Ph_3P$ stretching modes for a variety of other metals.[30]

Unfortunately, the 160-200-$cm^{-1}$ region of the infrared is not generally accessible and therefore these bands are not particularly useful for the assignment of geometries on a routine basis. However, the intensity of a band at 550 ± 5 $cm^{-1}$ in the infrared and Raman spectra of all complexes studied also appears to depend on complex stereochemistry. The origin of this band is uncertain, but it is possibly the weak infrared-active 540-$cm^{-1}$ band of $Ph_3P$ itself (Figure 1a), assigned as the first overtone of the asymmetric $PC_3$ deformation mode,[27] which has undergone a typical 10-$cm^{-1}$ shift to higher frequency on complexation.[2] In any event, this band, starred in Figures 1 and 3, is very strong (using the ligand vibrations at *ca.* 500 and 420-450 $cm^{-1}$ as internal standards for intensity comparison) in the infrared of cis complexes and weak in the infrared of trans. Conversely, this band is very weak (using the band at *ca.* 620 $cm^{-1}$ for comparison) in the Raman of cis complexes and very strong in the Raman of trans. We therefore propose the use of the intensity of this band as a simple criterion for the assignment of stereochemistry in $Pt(Ph_3P)_2XY$ type complexes.

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**Registry No.** *cis*-$Pt(Ph_3P)_2Cl_2$, 15604-36-1; *trans*-$Pt(Ph_3P)_2Cl_2$, 14056-88-3; *cis*-$Pt(Ph_3P)_2Br_2$, 18517-48-1; *trans*-$Pt(Ph_3P)_2Br_2$, 26026-46-0; *cis*-$Pt(Ph_3P)_2I_2$, 35085-00-8; *trans*-$Pt(Ph_3P)_2I_2$, 35085-01-9; $Pt(Ph_3P)_2O_2$, 15614-67-2; *trans*-$Pt(Ph_3P)_2Cl(CO_2Me)$, 20524-02-1; *trans*-$Pt(Ph_3P)_2HCl$, 16841-99-9.

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# Chromium(II)-Catalyzed Aquation of a Bridged Ruthenium(II)-Chromium(III) Complex Ion

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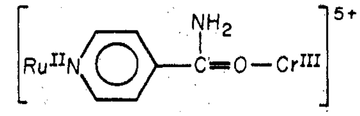
The reaction of isonicotinamidepentaammineruthenium(III) with chromium(II) in LiBr-HBr media has been shown to produce only



I

which in the presence of excess ruthenium(III) undergoes a slow aquation reaction to form isonicotinamidepentaammineruthenium(II) and chromium(III).[1] The present report describes our studies of the chromium(II)-catalyzed aquation of I in $LiClO_4$-$HClO_4$ media.

## Experimental Section

**Reagents.** Tap distilled water was redistilled from alkaline potassium permanganate before being used in kinetic experiments. All chemicals used were of reagent grade or better. Lithium perchlorate from G. F. Smith Co. was prereduced with chromium(II) and then recrystallized from water twice before use. A stock solution of hexaaquochromium(III) was prepared by the reduction of primary standard potassium dichromate with hydrogen peroxide in the presence of excess perchloric acid and was standardized titrimetrically[2] and spectrophotometrically.[3] Chromium(II) perchlorate solutions were prepared by reducing solutions of chromium(III) perchlorate over freshly prepared zinc amalgam under a blanket of argon gas. Isonicotinamidepentaammineruthenium(III) perchlorate was prepared as previously described.[1]

**Kinetic Measurements.** Solutions of the reactants were prepared and mixed using an all-glass apparatus composed of a Zwickel flask[4] to which was attached a 10-ml buret fitted at the top with a $Cr^{2+}$ preparation flask. The Zwickel flask was immersed in a constant temperature bath. Pressure from the blanketing gas argon was used to transfer the reaction mixtures to a 1.0-cm cell. The aquation reaction was followed at 540 nm, a wavelength of maximum difference in molar absorptivity between I and isonicotinamidepentaammineruthenium(II), using a Cary Model 17I recording spectrophotometer equipped with a thermostated cell compartment. Reaction conditions were always pseudo first order with the first-order rate constant, $k_{obsd}$, being obtained from the slope of a plot of $\log (A_t - A_\infty)$ *vs.* time, where $A_t$ is the absorbance at time $t$ and $A_\infty$ is the theoretical absorbance after the reaction is complete assuming isonicotinamidepentaammineruthenium(II) as the final product. A nonlinear least-squares computer program written by Lietzke[5] was used in analyzing the $[Cr^{2+}]$ and $[H^+]$ dependence of the rate of the aquation reaction. Values of the rate constants $k_0$, $k_1$, and $k_2$ reported are weighted averages[6] based upon the values and the error limits of the slopes and intercepts of the computer-fitted data.

## Results and Discussion

The slow spontaneous aquation of I has been studied by Gaunder and Taube[1] in LiBr-HBr media. The reaction in $LiClO_4$-$HClO_4$ media was found to be accompanied by

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