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Thermal Cis–Trans Isomerization of Dihalogenobis[trialkyl(or aryl)-phosphine]platinum(II) in the Solid State

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Synopsis. Solid-state thermal cis–trans isomerization of the platinum(II) complexes of the type $[PtX_2(PR_3)_2]$ were investigated by means of DSC methods, where X is Cl, Br, or I; R is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or C_6H_5. High isomerization ratios (93—100%) were observed for the cis-complexes of $P(C_2H_5)_3$ (X: Br; I), $P(n\text{-}C_3H_7)_3$ (X: Br; I), and $P(n\text{-}C_4H_9)_3$ (X: Cl; Br).

The *cis*-dihalogenobis(phosphine)platinum(II) complexes of the type *cis*-$[PtX_2(PR_3)_2]$, where X is a halide ion and PR_3 is one of trialkyl- or triarylphosphines, have long been known to be useful homogeneous catalysts for the selective hydrogenation of unsaturated organic compounds.1) The cis complexes can usually be prepared by the following two steps:2) In the first step, the double complexes having a general formula of $[Pt(PR_3)_4][PtX_4]$ are prepared and then the solid double complexes are heated at appropriate temperatures to produce a mixture of *cis*- and *trans*-$[PtX_2(PR_3)_2]$. In the second step, the mixture is separated into pure *cis*- and *trans*-$[PtX_2(PR_3)_2]$ by the use of the difference in solubilities. In general, trans isomers are much more soluble than cis isomers. The ratios of cis to trans isomers in the mixture are largely dependent on the kinds of phosphines. For example, when tributylphosphine and triarylphosphine are used as the ligands, cis isomers are exclusively formed, whereas trans isomers can be obtained only by the use of the thermal isomerization of the corresponding cis isomers.

The thermal cis–trans isomerization of the platinum(II) complexes $[PtX_2(PR_3)_2]$ in the solid state has been much less thoroughly studied, although the catalyzed isomerization of such complexes in solution has extensively been investigated.3–8) Jensen first reported the isomerization of $[PtX_2(PR_3)_2]$ in the solid state.2a) More recently, Mastin,9) and Lee and Stoufer10) reported on the thermal behaviors, including cis–trans isomerization of $[PtX_2\{P(C_6H_5)_3\}_2]$. DTA/TG methods were used to investigate the isomerization and volatilization of a number of palladium(II) and platinum(II) complexes of phosphines.11,12) Unfortunately, any study did not quantitatively determine the isomerization ratios of the phosphine complexes, in spite of the fact that the cis-to-trans isomerization in the solid phase (practically in the melting state) has been used widely as the standard synthetic procedure for trans complexes.2b)

From the standpoint of the application of the isomerization to synthetic procedure, the present study was undertaken primarily to determine the thermal cis–trans isomerization ratios of $[PtX_2(PR_3)_2]$, where X is Cl, Br, or I, and R is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or C_6H_5.

Experimental

Materials. Trimethylphosphine($P(CH_3)_3$), triethylphosphine($P(C_2H_5)_3$), tripropylphosphine ($P(n\text{-}C_3H_7)_3$), tributylphosphine($P(n\text{-}C_4H_9)_3$), and triphenylphosphine ($P(C_6H_5)_3$) were commercially available.

Preparation of Complexes. *cis*- and *trans*-$[PtX_2(PR_3)_2]$ were prepared by a method similar to that of literature,2) where X is Cl, Br, or I, and R is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or C_6H_5. The compositions of the complexes obtained were confirmed by elementary analyses; the configurations thereof were characterized by means of electronic, IR, Far-IR, and ^1H and ^{31}P NMR spectroscopies.

Measurements. IR spectra of the samples were measured by a KBr-disk method with a JASCO Model A-3 infrared spectrophotometer. Far-IR spectra were measured by a Nujol-mull method with a JASCO Model IR-F far infrared spectrophotometer. Electronic spectra of the samples were recorded on a JASCO UVIDEC-105 UV/VIS recording digital spectrophotometer. ^1H and ^{31}P NMR spectra were monitored on a JEOL-GX400 spectrometer using $(CH_3)_4Si$ as the internal standard in $CDCl_3$ and 85% H_3PO_4 as the external standard in $CDCl_3/CHCl_3$ (1/6, v/v), respectively.

Differential scanning calorimetries (DSC) were carried out with a RIGAKU DENKI Thermal Analyser. Finely powdered samples were used in each run. The measurements were carried out under a constant flow of nitrogen stream at the heating rate of ca. 1.3 °C min^{-1}. Isothermal measurements were conducted by the use of a Chyo-100-L thermobalance equipped with the heating furnace controlled by SHINYO DIGICON 1200 in static air.

Results and Discussion

Thermal Analyses. Figure 1 shows the DSC curve in the first increasing and decreasing, and the second increasing-temperature processes of *cis*-$[PtCl_2\{P(n\text{-}C_3H_7)_3\}_2]$. The endothermic peak (A, T_{max}: 149 °C) is

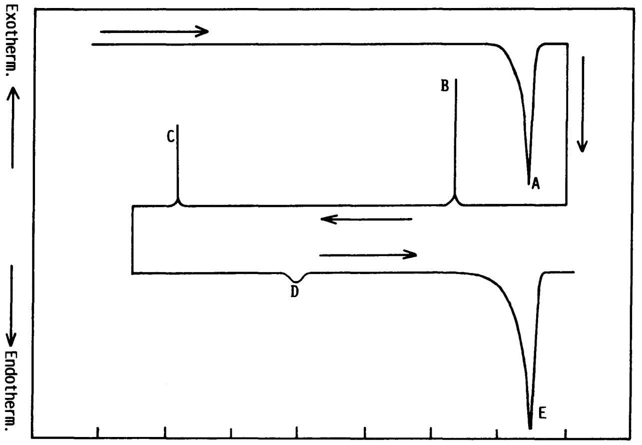

Fig. 1. DSC curve of *cis*-$[PtCl_2\{P(n\text{-}C_3H_7)_3\}_2]$.

observed in the first increasing-temperature process, which corresponds to the melting point of the cis isomer (mp: 149—150 °C). The product obtained at this stage was confirmed to consist of the mixture of cis and trans isomers (vide infra). The peak is thus ascribable to the melting plus the isomerization of the cis isomer. The exothermic peaks (B, $T_{\max}$: 127 °C) and (C, $T_{\max}$: 44 °C) in the decreasing-temperature process may correspond to the freezing point of the cis isomer and to that of the trans isomer, respectively, because preliminary experiments showed that owing to supercooling the authentic cis and trans complexes are solidified at considerably lower temperatures than their melting points (cis: 149—150 °C; trans: 85—87 °C). Then, the small endothermic peak (D, $T_{\max}$: 80 °C) is found in the second increasing-temperature process, which may come from the melting of the trans isomer (mp: 85—87 °C). The melting point of the trans isomer is thus slightly lowered because of the presence of considerable amount of the cis isomer unchanged. Thus, the appearance of the melting peak of the trans isomer apparently suggests that the cis isomer isomerizes to the corresponding trans isomer to some extent. The endothermic peak (E, $T_{\max}$: 149 °C) in the second increasing-temperature process is the melting point of the cis isomer.

It should be noted that both cis and trans complexes of $P(CH_3)_3$ and $P(C_6H_5)_3$ were decomposed in a complicated fashion with neither melting nor isomerization irrespective of the kind of halide ions. On the other hand, both cis and trans isomers of $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, and $P(n\text{-}C_4H_9)_3$ were found to have melt to isomerize to the corresponding isomers. It is thus conceivable that the isomerization of the phosphine complexes proceeds in the melting state. This situation is in marked contrast to the case of diamminedihalogenoplatinum(II), isomerization of which takes place easily in the solid state even without melting.[13]

Identification of the Products. The symmetries of the *cis*- and *trans*-$[PtX_2(PR_3)_2]$ are clearly different from each other: the cis isomer possesses local C_{2v} symmetry, while the trans isomer posseses D_{2h} symmetry. For platinum-chloride stretching vibrations, a square planar $PtCl_2P_2$ set should give rise to two bands (A_1 and B_2) for C_{2v} symmetry (cis-configuration) and to one band (B_u) for D_{2v} symmetry (trans configuration).[14] All the cis isomers in the present study exhibit two bands at ca. 270 and 305 cm^{-1}, while the trans isomers, one band at ca. 335 cm^{-1}. On the other hand, the products obtained during heating cis and trans complexes of $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$ and $P(n\text{-}C_4H_9)_3$ show three bands at ca. 270, 305, and 335 cm^{-1}. This evidences that the products are the mixture of cis and trans isomers.

Determination of Isomerization Ratios. The isomerization ratios were estimated spectrophotometrically: in the case of *cis*- and *trans*-$[PtCl_2\{P(n\text{-}C_3H_7)_3\}_2]$, for example, the following simultaneous equation was employed:

$$\begin{cases} 358.5x + 136.7y = D_{330} \\ 396.7x + 821.5y = D_{290} \end{cases}$$

where x and y are the molar concentrations of cis and trans isomers, the numerical factors are the molar extinction coefficients of the pure cis and trans isomers, and the D's represent their absorbances at the wavelengths specified by each subscript. The isomerization ratios are thus given by x(or y)/(x+y).

The isomerization was monitored at varied temperatures and at several time intervals to find suitable conditions for giving maximum isomerization ratios. The results showed that the ratios are considerably altered by the heating temperatures. For example, in the case of *cis*-$[PtCl_2\{P(C_2H_5)_3\}_2]$, the maximum ratio (35%) was detected for one hour at the heating temperature of 196 °C, which is slightly higher than the melting point (191—192 °C). Increasing temperature decreased the ratios: 23 and 2% were found at 205 and 210 °C, respectively. On the other hand, the trans complexes isomerized at

Table 1. Isomerization Ratios of the Complexes $[PtX_2(PR_3)_2]$[a)]

$[PtX_2(PR_3)_2]$		Cis complex			Trans complex		
PR_3	X	Isomerizn. ratio(%)	Heating temp/°C	Mp θ_m/°C	Isomerizn. ratio(%)	Heating temp/°C	Mp θ_m/°C
$P(CH_3)_3$	Cl	b)			b)		
	Br	b)			b)		
	I	b)			b)		
$P(C_2H_5)_3$	Cl	35	196	191—192	70	160	133—134
	Br	95	200	197—199	a few %[c)]	200	134—135
	I	ca. 100	145	139—140	a few %[c)]	145	136—137
$P(n\text{-}C_3H_7)_3$	Cl	25	160	149—150	13	154	85—87
	Br	95	115	105—107	a few %[c)]	115	95—96
	I	99	120	116—117	a few %[c)]	120	114—116
$P(n\text{-}C_4H_9)_3$	Cl	93	150	143—144	6	150	65—66
	Br	95	103	77—78	a few %[c)]	103	69—70
$P(C_6H_5)_3$	Cl	b)			b)		
	Br	b)			b)		
	I	b)			b)		

a) Each sample was heated for one hour at the specified temperatures. Prolonged heating did not increase the ratios. b) The complexes were decomposed with neither melting nor isomerization. c) Partially decomposed just after melting plus isomerization.

considerably higher temperature than the melting points. Table 1 summarizes the isomerization ratios of cis and trans complexes thus estimated together with the melting points of the complexes. The heating time of one hour was selected from the standpoint of the application of the isomerization to synthetic procedure. Prolonged heating did not improve the ratios. Thus, the ratios may be regarded as nearly maximum isomerization ratios. For $P(CH_3)_3$ and $P(C_6H_5)_3$ complexes, both cis and trans isomers were decomposed with neither melting nor isomerization regardless of halide ions. Among the trans isomers, the bromide and iodides of $P(C_2H_5)_3$ and $P(n\text{-}C_3H_7)_3$, and the bromide of $P(n\text{-}C_4H_9)_3$ complexes were partially decomposed just after melting plus isomerization. High isomerization ratios (93—100%) were observed for the cis complexes of $P(C_2H_5)_3$ (X: Br; I), $P(n\text{-}C_3H_7)_3$ (X: Br; I), and $P(n\text{-}C_4H_9)_3$ (X: Cl; Br). The sum of isomerization ratios of cis and trans isomers of the same phosphine is not exactly but approximately close to 100% except for the chloride of $P(n\text{-}C_3H_7)$, implying that the isomerization may reach equilibrium of cis and trans isomers. The sum of the ratios of the chlorides of $P(n\text{-}C_3H_7)_3$ complex amounts to only 38%. The value implys that the isomerization of the complexes incompletely reaches equilibrium under the specified conditions. An indication was detected for the complexes that application of higher heating temperatures than 160 °C for the cis and 154 °C for the trans isomers might improve the isomerization ratios. However, at such high temperatures the complexes in the melting state underwent gradual vaporization and partial decomposition so that the ratios were unable to be estimated in detail.

We expected at the beginning of this study that the bulkiness of the phosphines (steric factor) may play an important role in the isomerization. However, the expectation did not come true: as seen from Table 1, the isomerization ratios do not vary with the phosphines. Marther et al. found that there is a good correlation between NMR coupling constants and the Pt–P bond strengths in the platinum(II) complexes of phosphines.[15] Relationship between the isomerization and the Pt–P bond strengths was investigated by NMR spectroscopy, but no relationship could be found between them.

It has long been known that trans complexes of $[PtX_2(PR_3)_2]$ are isolated with more difficulty in poorer yields than the corresponding cis isomers because the trans isomers are much more soluble than the cis isomers.[2] Thus, the trans isomers have usually been prepared by the use of catalysed isomerization of the cis isomers in solution, but the method requires troublesome steps.[16] On the other hand, the results obtained in the present study declare that the trans complexes of $P(C_2H_5)_3$ (X: Br; I), $P(n\text{-}C_3H_7)_3$ (X: Br; I), and $P(n\text{-}C_4H_9)_3$ (X: Cl; Br) can be easily obtained in good yield by the use of thermal isomerization of the corresponding cis isomers in the solid state (practically in the melting state).

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