THE THERMAL ISOMERISATION OF SOME FOUR CO-ORDINATE SQUARE PLANAR COMPLEXES OF PALLADIUM AND PLATINUM WITH PHOSPHINE LIGANDS

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ABSTRACT

Thermally induced *cis–trans* isomerisation is reported for square planar complexes of the type MX_2L_2, M = Pd or Pt, L = organophosphorus ligands and X = halide. However, the palladium dichloro-phenyldimethyl complex provides another example of the more unusual *trans–cis* isomerisation. A number of phosphine complexes of platinum have been vacuum-distilled, in some cases with accompanying isomerisation. The tendency for such isomeric behaviour is interpreted in terms of variation in metal to phosphorus bond strength.

INTRODUCTION

Square planar complexes of the type MX_2L_2 (M = Pt(II) or Pd(II), X = halide, L = neutral ligand), are known to undergo thermally induced *cis* to *trans* isomerisation, both in solution and in the solid state[1,2]. The less common *trans* to *cis* isomerisation has also been reported for a number of platinum and palladium complexes[3,4].

Whilst many platinum complexes of the above type, where L is an organophosphorus ligand are known both as *cis* and *trans* isomers, the more labile palladium complexes have usually been obtained in the *trans* form[5]. Indeed, it is only recently that any *cis* compounds of palladium with such ligands have been characterised[6]. Although solution studies[7,8] in polar solvents have shown that there is an equilibrium between the *cis* and *trans* isomers, there have been no studies on the thermal isomerisation of the solid compounds. We have extended the range of isomeric pairs of palladium complexes that can be isolated in the solid state[9] and now report the results of a study of the thermally induced isomerisation of these compounds. During the course of this work it has been shown that a number of *cis* and *trans* isomers of the platinum and palladium compounds could be vacuum-distilled, in some cases with accompanying isomerisation. The tendency for such isomeric behaviour has been interpreted in terms of variation in metal to phosphorus bond strength.

The platinum and palladium complexes were prepared by the standard literature methods[9,10].

The infrared spectra of the complexes were recorded as Nujol mulls between polyethylene discs on a Perkin-Elmer 457 spectrometer.

DTA curves were obtained on a Standon-Redcroft 671B differential thermal analyser using approximately 5 mg of sample heated in a nitrogen atmosphere at a rate of 3 °C min^{-1}. The instrument was calibrated using the heat of fusion of indium.

Heats of vaporization were obtained on a Standon 6-25 differential thermal analyser using approximately 5 mg of sample heated in a nitrogen atmosphere at a rate of 10 °C min^{-1}. Generally the values are an average of five runs. The instrument was calibrated using the enthalpy of fusion of tin. Thermogravimetric runs were carried out on a Standon-Redcroft TG-750 instrument in an atmosphere of nitrogen using samples of less than 10 mg and a heating rate of 10 °C min^{-1}.

The vacuum-distillation experiments were done simply by placing the compound in a sublimation apparatus, then heating to about 230 °C while maintaining normal vacuum line pressure (about 0.02 Torr). The time each compound was heated varied from half an hour to two hours depending on the distillation rate. The distilled product was identified generally by infrared and melting point.

RESULTS AND DISCUSSION

Figure 1 shows the DTA curves for the $PdCl_2(PhPR_2)_2$ (R = Me and Et) compounds.

The corresponding thermogravimetric curves below 250 °C showed no weight loss prior to decomposition of the complexes. The sharp exothermic peak (A), in Fig. 1 (a), $T_{max.} = 172$ °C corresponds to the isomerisation of the trans-$PdCl_2[PhPMe_2]_2$ to the cis-isomer, $\Delta H = -5.65$ kJ mol^{-1}. The endothermic peak (B), $T_{max.} = 197$ °C, corresponding to the m.p. of the cis-isomer. The endothermic peak (C), $T_{max.} = 158$ °C, found in the DTA curve for cis-$PdCl_2[PhPMe_2]_2$, Fig. 1 (b), can be attributed to a solid–solid phase change which is irreversible. When viewed on a hot-stage micro-scope, no melting was apparent at 158 °C for the cis compound, but thermal agitation of the crystals was observed. The second endothermic peak (D), $T_{max.} = 196$ °C, corresponds to the m.p. of the cis-isomer. If, after melting, the cis-isomer was allowed to cool and then reheated, the phase change was no longer observed on the DTA curve. An identical curve was also obtained when the final product of the trans-isomerisation was allowed to cool and then reheated. Confirmation of the trans–cis rearrangement was obtained from far infrared spectra. When heated to just below the melting point the trans-isomer gave a product whose infrared spectrum showed peaks at 310 and 287 cm^{-1} due to $v(Pd–Cl)$ vibrations. The corresponding cis-isomer gave peaks at 309 and 285 cm^{-1} in the infrared spectrum.

The thermal behaviour of $PdCl_2[PhPEt_2]_2$ compounds is shown in Figs. 1 (c)
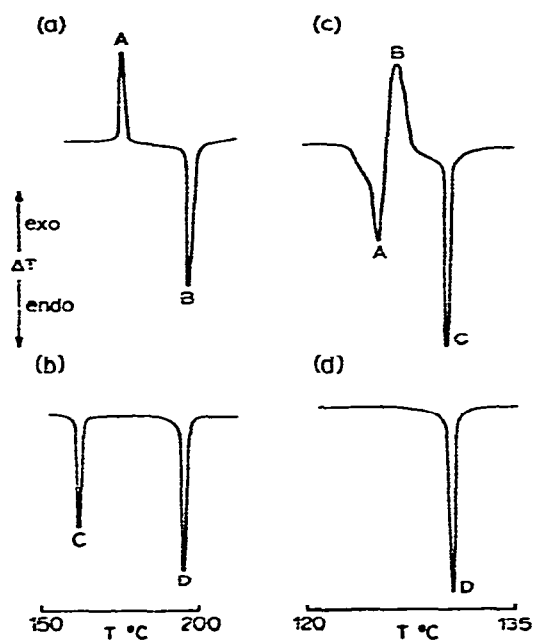
Fig. 1. DTA curves for various phosphine complexes of palladium, (a) *trans*-PdCl₂(PhPMe₂)₂; (b) *cis*-PdCl₂(PhPMe₂)₂; (c) *cis*-PdCl₂(PhPEt₂)₂; (d) *trans*-PdCl₂(PhPEt₂)₂.

and 1(d). The endothermic peak (A), $T_{max.} = 124°C$, corresponds to the m.p. of *cis*-PdCl₂[PhPEt₂]₂. This is immediately followed by an exothermic peak (B), $T_{max.} = 127°C$, which represents the simultaneous solidification and isomerisation of the *cis*-isomer. In view of the exothermic solidification of the compound, it is difficult to determine whether the isomerisation process is itself exo- or endothermic. The final endothermic peak (C), $T_{max.} = 130°C$, corresponds to the m.p. of *trans*-PdCl₂[PhPEt₂]₂. The melting and solidification of the *cis*-isomer was confirmed visually using a hot-stage microscope. Comparison of the curves for the *cis*- and *trans*-isomers shows that the final endothermic peak in both cases can be attributed to the m.p. of the *trans*-isomer, $T_{max.}$ peak (D) = 130°C. Evidence for this type of rearrangement was again obtained from far infrared spectra. Heating the *cis*-isomer to just below the melting, corresponding to peak (C) Fig. 1c, gave a product whose far infrared spectrum was virtually identical to that of the *trans*-isomer, i.e., v(Pd–Cl) for *cis*-PdCl₂[PhPEt₂]₂ before heating was at 310 and 291 cm⁻¹; after heating 354 cm⁻¹. v(Pd–Cl) for *trans*-PdCl₂[PhPEt₂]₂ is at 353 cm⁻¹.

The DTA curve for the *cis*-PdCl₂(PhPPr₂)₂ compound below the decomposition temperature, showed only a sharp endothermic peak, which corresponded to the melting point of the compound. However, on cooling, the sample gave a far infrared spectrum identical to that of the *trans*-isomer. Also the melting point corresponded to that of the *trans*-isomer. It is therefore apparent that for this compound the melting and isomerisation occur simultaneously. The *cis*-PdCl₂(PhPMeEt)₂ complex also behaved in a similar manner. The thermogravimetric data obtained in a dynamic

nitrogen atmosphere showed the palladium compounds thermally decomposed in a complicated manner, thus we were unable to measure the heats of decomposition of the compounds.

Figure 2 shows the DTA curve for the cis-$PtCl_2(n\text{-}Bu_3P)_2$ complex. The sharp endothermic peak (A), $T_{max.} = 98\,°C$, corresponds to the melting point of the compound. When heating was stopped at point 1, $T = 202°C$, the far infrared of the sample in the platinum–chlorine stretching region was identical to that of the starting

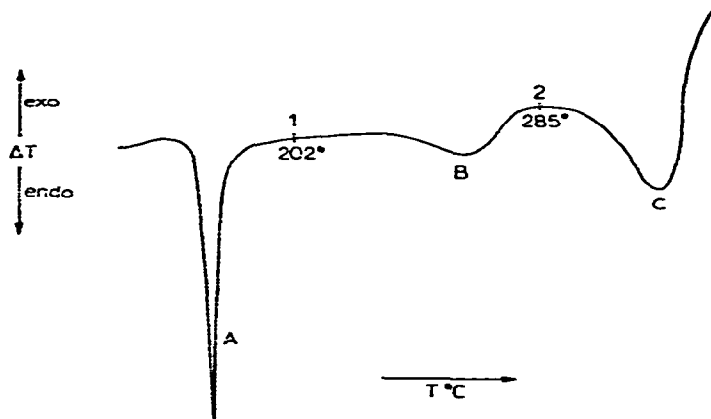Fig. 2. DTA curve for the cis-$PtCl_2(n\text{-}Bu_3P)_2$ complex.

cis-isomer. On reheating the melting point remained unchanged. A second sample was heated to point 2, $T = 285°C$, and on cooling, the far infrared was identical to that of the trans-isomer. On reheating the sample, the melting point also indicated the trans-isomer. Thus, the endothermic peak B, $T_{max.} = 256°C$ can be attributed to the cis–trans isomerisation process, $\Delta H = -12.80$ kJ mol^{-1}. Peak C, $T_{max.} = 343°C$ corresponds to the vaporization of the trans compound. The thermogravimetric data, obtained in a dynamic nitrogen atmosphere, showed complete vaporization of both the cis- and trans-isomers. The DTA curve of the trans-isomer showed only a sharp endothermic peak, $T_{max.} = 64°C$, corresponding to the melting point of the compound together with a broad endothermic peak, $T_{max.} = 301°C$, due to the vaporization of the compound. The DTA curve of cis-$PtCl_2(Et_3P)_2$ is similar to that of the $(n\text{-}Bu_3)P$ compound, however, the corresponding peaks B and C could not be separated, peak B appearing as a shoulder on the low temperature side of peak C.

cis-$PtBr_2(n\text{-}Bu_3P)_2$ was found to isomerise on melting. This was shown by heating the compound to its melting point, cooling, then reheating. The cis-isomer would consistently give the melting point of the trans-isomer after such treatment. The thermogravimetric and DTA data obtained for a number of platinum complexes in a dynamic nitrogen atmosphere showed varying degrees of vaporization and decomposition. However, due to the nature of the reactions, heats of decomposition could not be measured.

Solution studies have shown [7,8,11] the cis to trans isomerisation for complexes

of the type $(PR_3)_2MCl_2$ (M $= Pt^{2+}$, Pd^{2+}), to be endothermic and entropy-controlled. The DTA data obtained with the molten platinum complexes cis-$PtCl_2(PBu_3)_2$ and cis-$PtCl_2(PEt_3)_2$ are apparently consistent with this. Also for cis-$PtCl_2(PBu_3)_2$, the value of $\Delta H_{cis \to trans}$ obtained in the molten state, is in reasonable agreement with solution studies. The solid state trans to cis isomerisation observed for the palladium complex is exothermic, which is consistent with the expected stronger bonding in the cis-isomer. However, lattice forces probably play an important part in determining the nature of solid state isomerisations.

Using a sublimation apparatus, it was possible to vacuum-distill a number of both the cis- and trans-isomers of these compounds. Since the trans-$PtX_2(PR_3)_2$ (X $=$ Cl, Br; R $=$ Et, Bu) compounds vaporized with no decomposition, it was possible to measure the heats of vaporization. These are as follows: ΔH_{vap} $PtCl_2$-$(PEt_3)_2$ 78.7; $PtCl_2(Pn$-Bu$_3)_2$ 84.5; $PtBr_2(PEt_3)_2$ 82.0; $PtBr_2(Pn$-Bu$_3)_2$ 92.0 kJ mol^{-1}. The heats of vaporization of the ligands themselves are ΔH_{vap} PEt$_3$[12] $\sim$ 35.6; PnBu$_3$[10] 53.64; PnPr$_3$[10] 46.74 kJ mol^{-1}.

Although the data are limited, the following observations can be made. For a given halide, the heat of vaporization of the complexes does not vary as much as the heat of vaporization of the ligands, although they do follow the same trend. Also the heat of vaporization of the bromides is greater than that for the chlorides. The heat of vaporization of the cis complexes could not be measured due to the partial decom-

TABLE 1

ISOMERIZATION BEHAVIOUR OF cis COMPLEXES ON VACUUM DISTILLATION

Compound (cis-isomer)	Estimated conversion of distilled product to trans-isomer (%)	Method of estimation[a]
PtCl$_2$(PBu$_3$)$_2$	100	IR $v_{M-Cl} = 338$; m.p. 65 C trans
PtCl$_2$(PEt$_3$)$_2$	$\sim$80–90	IR $v_{M-Cl} = 338$ vs trans $v_{M-Cl} = 302$ v, 280 w cis
PtCl$_2$(PPhEt$_2$)$_2$	$\sim$15–25	IR $v_{M-Cl} = 338$ w trans $v_{M-Cl} = 303$ s. 278 m cis
PtCl$_2$(PPh$_2$Et)$_2$	0	IR $v_{M-Cl} = 305$, 278; m.p. 232 cis
PtCl$_2$(PPh$_3$)$_2$	decomposes; however trans-isomer is difficult to prepare	ref. 16
PtBr$_2$(PBu$_3$)$_2$	100	IR $v_{M-Br} = 249$ s $v_{M-P} = 169$ m m.p. 65 C
PtBr$_2$(PEt$_3$)$_2$	100	m.p. 134 °C
PtBr$_2$(PPhEt$_2$)$_2$	$\sim$50	DTA of distilled compound shows 50% trans. 50% cis; recrystallization from CH$_2$Cl$_2$ gives 95% cis
PtI$_2$(PPh$_3$)$_2$	isomerizes to trans in boiling chloroform	ref. 16
PdCl$_2$(PPhPr$_2$)$_2$	100	IR $v_{M-Cl} = 355$; m.p. 108 °C

[a] IR frequencies in cm^{-1}.

position or partial isomerization. However, the partial isomerization of the *cis* complexes proved to be of interest, since this can be used as an indication of the tendency of the compound to isomerize. The results are listed in Table 1. The data indicate that for a given phosphine ligand, there is an increasing tendency to isomerize to the *trans*-isomer, in the order I > Br > Cl. This sequence has been previously observed and has been explained in terms of both electronic[11], and steric effects[13]. More important, the data show that as the number of phenyl groups on the phosphorus ligand increases ($PR_{3-n}Ph_n$, as n increases), there is an increasing tendency for the *cis*-isomer to remain *cis*. This is due to an increase in the metal-to-ligand bond strength. Phosphorus NMR data have also shown[14] that the metal-to-ligand bond strength increases as the number of phenyl groups on the phosphorus atom increases.

As mentioned earlier, solution studies have shown the *cis* to *trans* isomerization for complexes of this type to be endothermic and entropy-controlled[7,8,11]. Thus it was of particular interest that while *cis*-$PtCl_2(PBu_3)_2$ distilled completely to the *trans*-isomer, *cis*-$PtCl_2(PPh_2Et)$ remained *cis* on distillation. The free energy of *cis–trans* isomerization in solution for the complexes $PtCl_2(PR_3)_2$ (R = Et, Pr, Bu) is in the range −5.0 to 10.5 kJ mol^{-1} (refs. 7 and 11). Although the value depends on the solvent, it indicates that only a small increase in the heat of isomerization could cause the isomer to remain *cis*. Thus, as the number of phenyl groups on the phosphine ligand increases, the phosphorus–metal bond strength increases, causing an increase in the heat of *cis* to *trans* isomerisation, and thereby decreasing the tendency to form the *trans* isomer. This is consistent with solution studies where in a variety of solvents the heat of *cis* to *trans* isomerization for $PdCl_2(PPh_2Me)_2$ was found always to be greater than that for $PdCl_2(PPhMe_2)_2$[8]. Also, in solution, the percentage *cis*-isomer for $PtCl_2(AsPhBu_2)_2$ was found[7] to be greater than that for $PtCl_2(AsBu_3)_2$.

Previous studies have shown that as the number of phenyl groups on the phosphorus ligand increases, the bulkiness of the phosphine increases[15]. It has generally been thought that increasing the bulkiness of phosphine (and arsine) ligands in square planer complexes, increases the tendency of the complex to form the *trans*-isomer[13]. However, the data in Table 1 indicate the opposite trend. Thus the increased bond strength appears to be more important than the increased bulkiness in determining the isomerization behaviour of these compounds.

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