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Uncatalyzed *cis* to *trans* Isomerization of *cis*-[$PtCl_2(PBu_3)(PhCN)$] Complex in Different Solvents. Evidence for an Initial Dimer Formation

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Abstract

The rates of spontaneous *cis–trans* isomerization of the complex *cis*-[$PtCl_2(PBu_3)(PhCN)$] have been measured in different solvents. Values of k_{obs} decrease with the polarity of the solvent (benzene ~ toluene > $CHCl_3$ ~ DMF). ^{31}P and ^{195}Pt NMR spectroscopy provide (for the first time) strong evidence for dimer formation (sym. *trans*-[$Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBu_3)_2$]) which are intermediates in spontaneous *cis/trans* isomerization.

Introduction

Reactions of square-planar complexes are overwhelmingly stereospecific, and it is generally assumed that (except for photochemical reactions) a catalyst is required to produce isomerization [1, 2]. Some of these reactions may be catalyzed by ligands such as phosphines, arsines and amines through either a consecutive displacement or a pseudorotation mechanism, depending on the polarity of the solvent and the softness of the coordinated ligands [3].

The uncatalyzed *cis–trans* isomerization of $PtRXL_2$ systems was proposed to proceed through a three-coordinated intermediate, but this intermediate was later shown to be a four-coordinate solvated species [4, 5].

We have now investigated reaction (1) (solvent = benzene, toluene, chloroform, dimethylformamide and methanol) kinetically and have found evidence for an autocatalytic mechanism. In addition, ^{31}P and ^{195}Pt NMR spectroscopy have been used and the spectral results provide strong evidence for initial dimer formation which are intermediates in spontaneous *cis/trans* isomerization.

$$cis\text{-}[PtCl_2(PBu_3)(PhCN)] \rightleftharpoons trans\text{-}[PtCl_2(PBu_3)(PhCN)] \quad (1)$$

$$2cis\text{-}[PtCl_2(PBu_3)(PhCN)] \rightleftharpoons \text{sym.}trans\text{-}[Pt_2Cl_4(PBu_3)_2] + 2PhCN \quad (2)$$

$$cis\text{-}[PtCl_2(PBu_3)(PhCN)] + PhCN \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} trans\text{-}[PtCl_2(PBu_3)(PhCN)] + PhCN \quad (3)$$

The *cis*-[$PtCl_2(PBu_3)(PhCN)$] complex was prepared for the first time [6], in particular to promote bond weakening at the leaving group by using a labile group such as a benzonitrile ligand.

Results and Discussion

Investigation of reaction (1) for *cis*-[$PtCl_2(PBu_3)$-($PhCN$)] at complex concentrations (0.2–8.0) × 10^{-5} M showed that plots of $\log(A_t - A_\infty)$ *versus* time (Fig. 1) are indeed curved and exhibit induction periods typical of autocatalysis [3, 7, 8] which can be depicted by the parallel reactions (2) and (3), where the relative rate will determine the length of the induction period.

Reaction (3) may proceed via either pseudorotation or consecutive displacement [3]. The observed reaction rate for the isomerization step (reaction (3)) is thus a function of [L] [3]. The induction period can be attributed to benzonitrile generation via

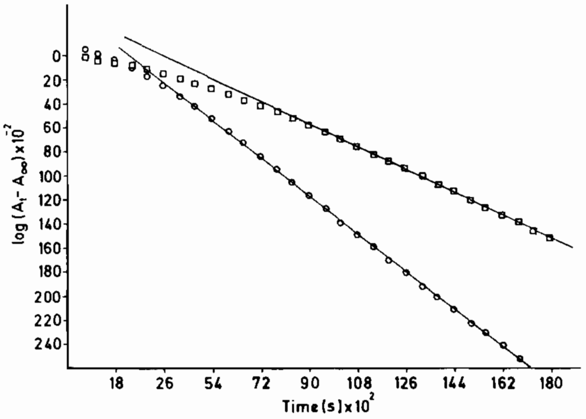

Fig. 1. Graph of the $\log(A_t - A_\infty)$ *vs.* time for the isomerization of *cis*-[$PtCl_2(PBu_3)(PhCN)$] in benzene (□) and in toluene (○) at 25 °C. The initial complex concentration equals *ca.* 7.0×10^{-5} M.

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reaction (2) and will exist until [L] reaches a stage where reaction (3) becomes much faster than reaction (2). Since benzonitrile acts as a catalyst reaction (3) will be a pseudo-first-order reaction, and this explains why the semilog curves in Fig. 1 become linear. The rate law for reaction (3) (solvent = benzene, toluene, chloroform, dimethylformamide, and methanol) predicts that k_{obs} values found for the *cis* and *trans* substrates should be identical and that the rate should be first order in relation to [complex]. However, the same rate laws were used for an analogous system, *cis*/*trans* isomerization of PtX_2L_2 (L = phosphine, X = halogen) [3, 8].

$$k_{obs} = (k_3 + k_{-3})[L] \qquad (4)$$

Reactions like (3) are often slightly dependent on the solvent because of differences in dielectric constants. That would account for benzene and toluene where $k_{-3} = 0$. k_{obs} is very much smaller in the case of chloroform and dmf, because these molecules are more polar and so coordinate weakly at the fifth coordination site, thus preventing attack by PhCN.

TABLE I. The Observed Rate Constants for *cis–trans* Isomerization of *cis*-$[PtCl_2(PBu_3)(PhCN)]$ in Various Solvents at 25 °C[a]

Solvents	k_{obs}
Benzene	$3.60 \times 10^{-4}\ s^{-1}$
Toluene	$5.13 \times 10^{-4}\ s^{-1}$
Chloroform	$4.85 \times 10^{-6}\ s^{-1}$
DMF	$7.45 \times 10^{-6}\ s^{-1}$

[a]See 'Experimental' and Fig. 1 for the reaction conditions.

The results obtained from the kinetic studies (Table I) indicate that the rate of the isomerization step (reaction 3) decreases with the polarity of the solvent (benzene ~ toluene > $CHCl_3$ ~ DMF) not only because this reaction is faster in non-polar solvents but also most probably due to enhanced dimer formation and thus benzonitrile generation in non-polar solvents as is the case in the Pt(II) [3, 8], Ir(I) [9] and Rh [3, 8] systems (*i.e.* phosphine generation). Indeed, reaction (1) in methanol exhibits no induction period. This can be explained by the relative high polarity of the solvent preventing dimer formation. Further evidence supporting the autocatalysis *cis*/*trans* isomerization comes from the ^{31}P and ^{195}Pt NMR data. When the *cis*-$[PtCl_2(PhCN)(PBu_3)]$ complex was dissolved in $CDCl_3$ solution at ambient temperature, and the ^{31}P NMR spectrum was recorded immediately (colorless solution), there was only one phosphorous containing species (*cis*-isomer). When the solution was left for a few hours and the ^{31}P NMR spectrum was remeasured, a new peak was observed with $^1J(^{195}Pt-^{31}P)$ 3820 Hz in addition to the *cis*-isomer. The color of the solution became yellow, which indicated the formation of the symmetric isomer of the dimer $[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBu_3)_2]$. δ ^{31}P and ^1J values of the new signal were compared with the authentic dimer sample [10]. When the above solution was left for several hours (up to 24 h), two phosphorous containing species appeared in the solution, and were assigned for *trans*-$[PtCl_2(PhCN)(PBu_3)]$ and the dimer (see Table II). δ and ^1J values are comparable to the authentic samples. Repeating the above reaction in benzene-d_6 and toluene-d_8, the ^{31}P NMR spectra (*ca.* 1 h) consist of two new phosphorous containing species, $^1J(^{195}Pt-^{31}P)$ 3838 and 3882 Hz (Table II). The ^{195}Pt NMR spectra showed two doublets of similar coupling constants to the ^{31}P NMR spectra, and assigned for sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$ and another similar dimer species (yellow

TABLE II. ^{31}P and ^{195}Pt NMR Data[a] for *cis*/*trans*-$[PtCl_2(PBu_3)(PhCN)]$ and for $[Pt_2Cl_4(PBu_3)_2]$ Dimer Complexes at Ambient Temperature

Complexes	Solvent	$^{31}P\{^1H\}$ NMR δ (ppm)	$^1J(^{195}Pt-^{31}P)$ δ (Hz)	$^{195}Pt\{^1H\}$ NMR δ (ppm)
cis-$[PtCl_2(PBu_3)(PhCN)]$	$CDCl_3$	−0.19(t)	3318	
trans-$[PtCl_2(PBu_3)(PhCN)$	$CDCl_3$	−6.30(t)	3760	
sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$	$CDCl_3$	+2.20(t)	3820	−3404(d)
cis-$[PtCl_2(PBu_3)(PhCN)]$	C_6D_6	−1.63(t)	3272	
sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$[b]	C_6D_6	+1.82(t)	3882	−3424(d)
		−5.99(t)	3838	−3425(d)
trans-$[PtCl_2(PBu_3)(BuNH_2)]$	C_6D_6	−6.66(t)	3423	−3640(d)
cis-$[PtCl_2(PBu_3)(PhCN)]$	C_7D_8	c		
sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$[b]	C_7D_8	+2.55(t)	3880	
	C_7D_8	−5.27(t)	3822	

[a]Chemical shift (δ) in ppm relative to 85% H_3PO_4 (external) for ^{31}P NMR, positive shifts representing deshielding, and relative to Na_2PtCl_6 for ^{195}Pt NMR. Abbreviation: d, 1:1 doublet; t, 1:4:1 (singlet with platinum satellites). [b]Two sym. isomers present (see ref. 10 for unsym. isomer). [c]The *cis*-isomer slightly soluble in C_7D_8.

solution), Table II. Further evidence supporting the formation of the dimer comes from the addition of 2 mol equivalents of $BuNH_2$ to the $CDCl_3$ (or C_6D_6 or C_7D_8) solution, which gave only *trans*-[$PtCl_2$-(PBu_3)($BuNH_2$)], showing clearly that a straightforward bridge-cleavage reaction operates, Table II. (The dimer and *trans*-monomer spectra were compared and are consistent with the authentic sample spectra.)

It is worth noting that in non-polar solvents (benzene, toluene), the formation of the dimer is faster than in polar solvents. Unfortunately, in methanol, reaction (1) exhibits no induction period (as expected [3]) and the isomerization was completed in the mixing time, thus the k_{obs} values have not been calculated. However, in DMF (more polar than methanol) k_{obs} was calculated and showed a very small rate compared with non-polar solvents (benzene or toluene), k_{obs} (benzene) = 3.6×10^{-4} s^{-1} and k_{obs} (DMF) = 7.5×10^{-6} s^{-1}. Interestingly, when reaction (1) was investigated at a complex concentration of 0.018 M (or higher) in C_6D_6 (or C_7D_8) solution and the reaction was followed by ^{31}P and ^{195}Pt NMR, the only phosphorus containing species were obtained assigned for two sym. *trans*-dimers (Table II). Unfortunately, it is not possible to follow the above reaction (high concentration) by UV spectroscopy, to determine the k_{obs} for dimer formation. However, at lower concentrations ($0.2-8.0 \times 10^{-5}$ M), reaction (1) behaves similar to the reaction in $CHCl_3$ (or DMF) and is considered as a pseudo-first-order reaction (Fig. 1) as explained before. The experimental k_{obs} values given in Table I, indicate generally that k_{obs} (for benzene > DMF) decreases with polarity. But we can give no rational explanation for the differences between k_{obs} toluene > k_{obs} benzene (or k_{obs} DMF > k_{obs} $CHCl_3$).

Experimental

cis-[$PtCl_2$(PhCN)(PBu_3)] was prepared for the first time [6]. All reagents and solvents were of AR grade.

Kinetics

The isomerization reactions were followed spectrophotometrically at λ_{max} 286, 286, 241 and 276 nm for benzene, toluene, $CHCl_3$ and DMF, respectively, on Perkin-Elmer Lambda 5 and Perkin-Elmer 330 UV–Vis spectrophotometers at 25 °C. The progress of the reaction was obtained by scanning the spectrum at suitable times over the range 330–190 nm, with an isosbestic point at 265 nm in $CHCl_3$ solution (or followed at fixed λ_{max} as above). Scanning the spectrum over the range 520–320 nm (for benzene or toluene) reveals a clear isosbestic point at 361 nm, assigned to the formation of the dimer species.

Plots of $\log(A_t - A_\infty)$ against time, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, k_{obs} values, determined from the linear parts of the curves (Fig. 1), are listed in Table I.

NMR Spectra

All NMR spectra were measured on a JEOL JNM FX-100 spectrometer operating in the Fourier transform mode. All the spectra were recorded at ambient temperature, 25 °C. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 40.27 and 21.37 MHz respectively.

The compounds were studied as 0.018 M solutions in $CDCl_3$, C_6D_6 and C_7D_8. Chemical shift data for ^{31}P and ^{195}Pt NMR spectra were determined relative to 85% H_3PO_4 (external), more positive values representing deshielding for phosphorus-31 and relative to Na_2PtCl_6 (aq) for platinum-195.

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