

RING OPENING OF 3,3,4,4-TETRACYANO-2,2-BIS(TRIPHENYLARSINE)-1-OXA-3-PLATINACYCLOBUTANE PROMOTED BY VARIOUS PHOSPHINES

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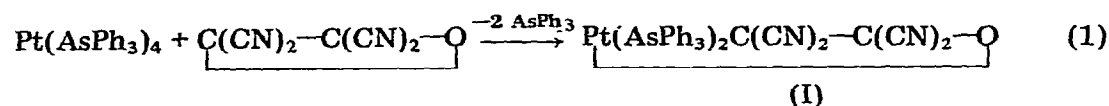
(Received July 18th, 1979)

Summary

In the presence of added ligand, (PMe₂Ph, PEt₃, PMePh₂ and PEt₂Ph) the title compound undergoes ligand exchange and ring opening to give compounds of the type {L₂Pt(CN)[OC(CN)=C(CN)₂]} having a *trans* configuration. A spectrophotometric kinetic study was carried out in CH₂Cl₂ and C₂H₅OH and the rate found to be proportional to the concentration of added phosphine. A linear relation between the second order rate constants and the cone angles of entering ligands points to the dominance of steric effects.

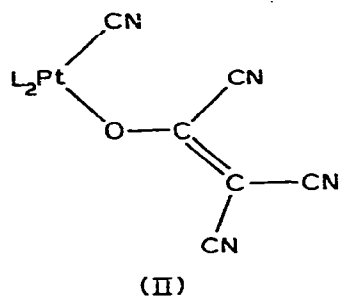
Introduction

Low valent platinum and palladium complexes, when treated with 1,1,2,2-tetracyano-3-oxacyclopropano (tetracyanoethyleneoxide TCNEO), undergo a ring expansion in which the metal atom is inserted in carbon–oxygen bond [1], as exemplified in equation 1:



The structure of compound I has been established by X-ray studies [1]. As for the mechanism, reaction 1 is best described as an oxidative addition of TCNEO to the intermediate species PtL_n. PtL_n acts as nucleophile attacking the oxirane ring at the carbon atom of lowest electron density, where the presence of a positive charge has been proposed on the basis ESCA measurements and theoretical calculations [2]. However with platinum complexes containing more basic phosphines, such as PMePh₂ or PMe₂Ph, no cyclic isomers were detected, and

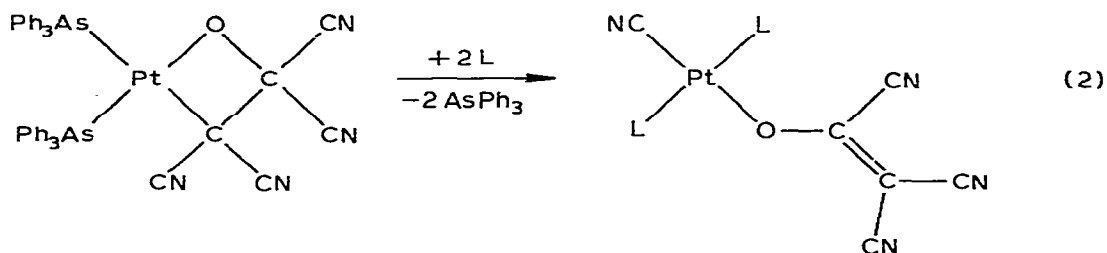
open-chain isomers (II) were isolated [3].



We describe below a kinetic study of the ring opening conversion of type I into type II complexes promoted by addition of various phosphines.

Results and discussion

Reaction 2 was studied in C_2H_5OH and CH_2Cl_2



$L = PMe_2Ph, PMePh_2, PEt_3$ and PEt_2Ph

This reaction was followed spectrophotometrically; in some cases the stopped flow technique was used at a selected wave length. For slow reactions a wide region of the spectrum was monitored, and in all cases the spectra of final products were in agreement with those of authentic samples [3]. The ligand was always present in large excess to provide pseudo-first order conditions and values of the observed first order rate constants, k_{obsd} , are given in Table 1. The values of k_{obsd} were obtained from the slope of the plot of $\ln(A_\infty - A_t)$ vs. time, where A_t and A_∞ are the optical densities of the reaction mixture at time t and after 7–8 half lives respectively.

As shown in Table 1 the rate of the ring opening is seen not to be affected by the presence of an excess of $AsPh_3$, but is markedly dependent on the nature and on the concentration of added ligand. Moreover the rates are much higher in $EtOH$ than in CH_2Cl_2 . In CH_2Cl_2 the rate of isomerisation varies with the added ligand in the sequence $PMe_2Ph > PEt_3 > PEt_2Ph > PMePh_2 \gg PCy_3$. Fig. 1 shows a plot of $\log k_2$ as a function of the cone angle of the phosphine [6]. The good linear relation found suggests that steric requirements are important in determining the rate. Platinum complexes undergo *cis-trans* isomerisation in the presence of tertiary phosphines, and this has been shown to proceed through a consecutive displacement mechanism in which contact ion pairs are

TABLE 1
VALUES OF k_{obsd} FOR THE REACTION 1 IN CH_2Cl_2 AND $\text{C}_2\text{H}_5\text{OH}$ AT 19.5°C

L	Solvent CH_2Cl_2		Solvent $\text{C}_2\text{H}_5\text{OH}$	
	conc $\times 10^4$ (M)	$k_{\text{obsd}} \times \frac{10^2}{2.303}$ (s^{-1})	conc $\times 10^4$ (M)	$k_{\text{obsd}} \times \frac{10^2}{2.303}$ (s^{-1})
PMePh ₂	5	0.05	5	7
	6.5	0.08	10	12
	10	0.11	25	32
	15	0.19	50	60
	20	0.24		
	37.5	0.40		
	50	0.58		
$k_2 = 2.57 \text{ mol}^{-1} \text{ s}^{-1}$			$k_2 = 27.6 \text{ mol}^{-1} \text{ s}^{-1}$	
PEt ₂ Ph	2	0.3	5	52
	5	0.8	10	75
	10	1.7	25	168
	15	2.5	50	360
	20	3.4		
$k_2 = 39.1 \text{ mol}^{-1} \text{ s}^{-1}$			$k_2 = 1656 \text{ mol}^{-1} \text{ s}^{-1}$	
PEt ₃	1.5	0.4	5	1.6
	2	0.7	10	2.1
	5	1.25	25	15.2
	10	2.5	50	73.1
	15	4.0		
$k_2 = 61.3 \text{ mol}^{-1} \text{ s}^{-1}$				
PMe ₂ Ph	2.0	14	5	1400
	2.5	19		
	5.0	370		
	7.5	580		
	10	720		
	20	1420		
$k_2 = 16330 \text{ mol}^{-1} \text{ s}^{-1}$				

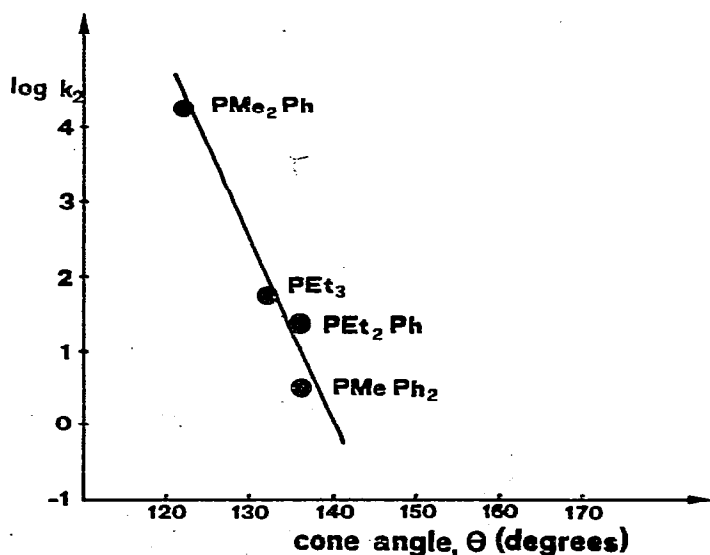
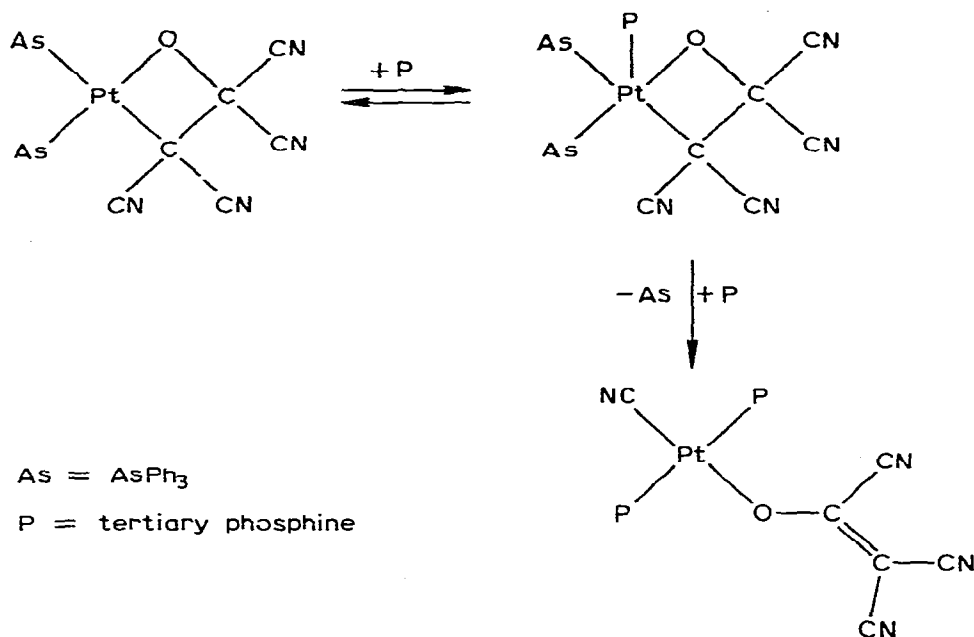


Fig. 1. Plot of $\log k_2$ vs cone angle of phosphines. Tricyclohexylphosphine gave a very low value for k_2 (cone angle for $\text{PCy}_3 = 170^\circ$).

probably involved, and that smaller ligands are better isomerisation catalysts [7]. The case of oxidative addition to the complexes $\text{IrCl}(\text{CO})\text{L}_2$ and *cis* PtL_2Me_2 follows the sequence $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PMePh}_2 > \text{PPh}_3$ [8–9]. On the basis of photoelectron spectroscopic data it has been proposed that steric hindrance by the coordinated ligand is a key feature in oxidative addition reactions [10].

The results suggest the following Scheme:

SCHEME 1



With this mechanism the total concentration of the five coordinated species (see Scheme 1) would be directly proportional to the amount of added phosphine, and hence the rate determining step will be of first order in added ligands. The reaction proceeds by cleavage of carbon-carbon bond and cyanide migration, and this process shows some analogy to the formation of ion pairs in the *cis-trans* isomerisation [4,5], to give a *trans* isomer as final product, as shown by NMR spectra [11,12] (e.g. *trans* $\{(\text{PMePh}_2)_2\text{Pt}(\text{CN})[\text{OC}(\text{CN})\text{C}(\text{CN})_2]\}$, ^1H NMR in CDCl_3 ; $\text{P}-\text{CH}_3$, δ 1.72 ppm doublet $J(\text{P}-\text{H}) = 3$ Hz, $J(\text{Pt}-\text{H}) = 16.5$ Hz). The results in ethanol are interesting. The reactions are faster than in dichloromethane, but for PEt_3 a non linear relation for $k_{\text{obsd}} \text{ sec}^{-1}$ vs concentration was found. Using PMe_2Ph only a single value of k_{obsd} could be obtained because of its high value. Although these results are not completely clear, we believe that the reaction proceeds through a polar transition state or intermediate which is stabilized in protic solvents. We observed such behaviour in photocatalysed isomerisation, [3], where different variations in the quantum yields and the effects of ionic strength suggested the involvement of a polar transition state.

Experimental

Materials

Complexes $[\text{Pt}(\text{AsPh}_3)_4]$ [12], $[\text{Pt}(\text{AsPh}_3)_2 \text{TCNEO}]$ [3] $\{\text{PtL}_2\text{CN}[\text{OC}(\text{CN})\text{C}(\text{CN})_2]\}$ (L = various tertiary phosphines) [3] and 2,2,3,3-tetracyanooxacyclopropano (TCNEO) [13] were prepared as previously described. Solvents were purified as specified in ref. 14.

Kinetics

In the case of slow reactions, the changes of optical density in the range 360–300 $m\mu$ of the spectrum were monitored over a period of time with a Perkin Elmer 356 recording apparatus. Freshly prepared solutions of the complex and of the ligands stored under nitrogen were used for each kinetic run. The reactions were started by mixing known volumes of standard solutions of the reagents in the thermostated cell compartment of the spectrophotometer. Fast reactions were followed by measuring the change of optical density at a suitable wavelength, a stopped flow Durrum apparatus, being used in some cases.

The added ligand was always present in large excess. All the reactions proceeded to completion under these conditions and the infinity spectra were in agreement with those of the products prepared and characterized independently [3]. The values of k_{obsd} were obtained from the slope of the plot of $\ln(A_\infty - A_t)$ vs. time where A_t and A_∞ are the optical densities of the reaction mixture at time t and after 7–8 half lives, respectively.

Acknowledgements

The authors thank C.N.R. (Roma) for financial support.

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