

## REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

### V \*. THE KINETICS AND MECHANISM OF FORMATION FROM ARYLCYCLOPROPANES

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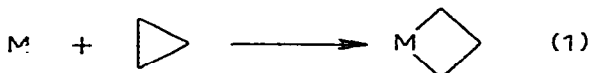
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#### Summary

The kinetics of the reaction of arylcyclopropanes ( $4\text{-XC}_6\text{H}_4\text{C}_3\text{H}_5$ , X = H, Me, EtO) with either  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{C}_2\text{H}_4)_2]$  or  $[\{\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\}_4]$  in tetrahydrofuran to give in each case  $[\{\text{PtCl}_2(\text{CHArCH}_2\text{CH}_2)\}_4]$  and ethylene or cyclopropane, respectively, have been studied. The reactions are essentially first order in both arylcyclopropane and platinum complexes. The order of reactivity follows the series  $\text{X} = \text{EtO} \gg \text{Me} > \text{H}$ , and  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{C}_2\text{H}_4)_2] > [\{\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\}_4]$  and the rate is accelerated in polar solvents. Mechanisms in which the arylcyclopropane first coordinates to platinum and then undergoes ring opening reactions are proposed.

#### Introduction

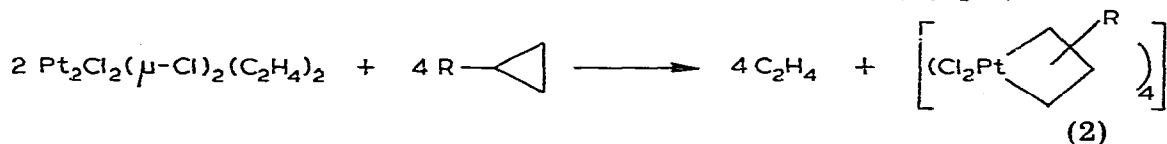
The insertion of a metal into the C—C bond of a strained-ring hydrocarbon (eq. 1) is thought to be involved in the transition metal complex-catalysed rearrangement of strained-ring hydrocarbons [2], in carbene elimination from cyclopropanes [2], and in other reactions of strained-ring compounds [3].



There is evidence that the metallocyclobutanes so formed may be intermediates in olefin metathesis catalysed by transition metal complexes [4,5]. Also the reaction (eq. 1) is a useful model for higher energy processes, such as insertion of a

\* For part IV see ref. 1.

metal complex in homogeneous solution into unstrained C—C bonds, which would be of great commercial significance if they could be made catalytic. Despite the wide interest in these reactions, there have been no studies of the reaction mechanism, presumably because there are few cases where the metallocyclobutanes are sufficiently stable. One reaction giving stable platinacyclobutane complexes has been shown by Brown [6] and McQuillin [7] to occur readily (eq. 2).



McQuillin has also reported that one cyclopropane can displace another in these compounds [8] (eq. 3).

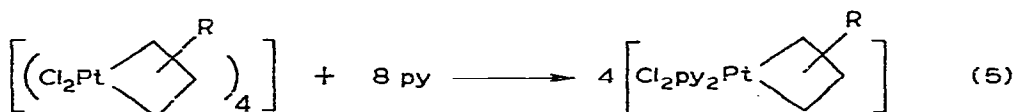
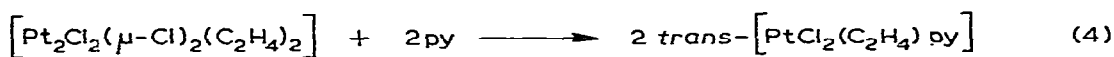


In this paper, a kinetic study of reactions 2 and 3 is reported.

## Results and discussion

Before studying the reaction kinetics, it was necessary to find suitable conditions under which reaction occurred homogeneously at a measurable rate. McQuillin and his co-workers studied reaction 2 using diethyl ether as solvent [7], but this solvent is unsuitable for kinetic studies because of its volatility and because both the starting material and the product are only slightly soluble. The reaction was found to take place homogeneously in a wide range of solvents including chloroform, acetone, acetonitrile, tetrahydrofuran and 1,4-dioxane, but only in tetrahydrofuran and 1,4-dioxane were we able to study the kinetics of reaction satisfactorily.

In order to examine the solvent effect on the rate of reaction, phenylcyclopropane and  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{C}_2\text{H}_4)_2]$  in standard concentrations were allowed to react in different solvents at 40°C. At suitable intervals, aliquots were removed and the reaction was quenched by addition of pyridine. This converts the platinum complexes present into the unreactive pyridine adducts according to eq. 4 and 5. By examining the resulting products by  $^1\text{H}$  NMR spectroscopy it was possible to estimate the extent of reaction.



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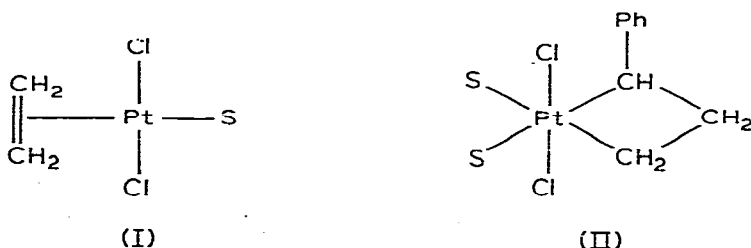
The rate of reaction in different solvents followed the order:  $\text{CH}_3\text{CN}$ ,  $\text{CHCl}_3$  > acetone > tetrahydrofuran  $\gg$  1,4-dioxane; this is approximately the order of decreasing solvent polarity, which is  $\text{CH}_3\text{CN}$  > acetone >  $\text{CHCl}_3$  > tetrahydro-

furan > 1,4-dioxane. Zeise's dimer is converted to solvated monomeric species in donor solvents (vide infra) [9] but would be expected to remain a dimer in chloroform. Thus the observation that chloroform falls out of the expected series is not surprising.

Since most of the reaction kinetics have been studied with tetrahydrofuran as solvent, the states of aggregation of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{C}_2\text{H}_4)_2]$  and of

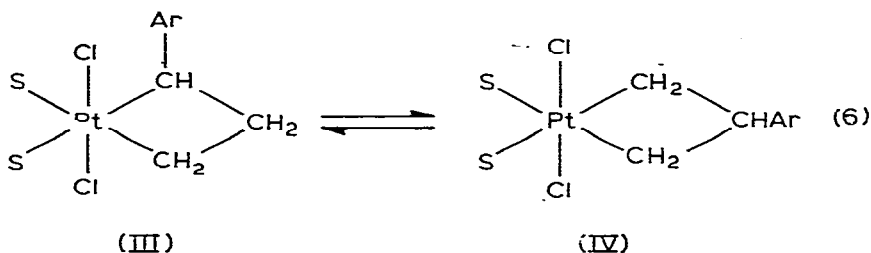
$\left[ \left( \text{C}_2\text{Pt} \begin{array}{c} \text{Ph} \\ \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \right)_4 \right]$  in solution in this ether were investigated. Molecular weight deter-

minations by . . . por pressure osmometry showed quite clearly that both compounds were monomeric in tetrahydrofuran and hence probably have the structures I and II, respectively (S = tetrahydrofuran).



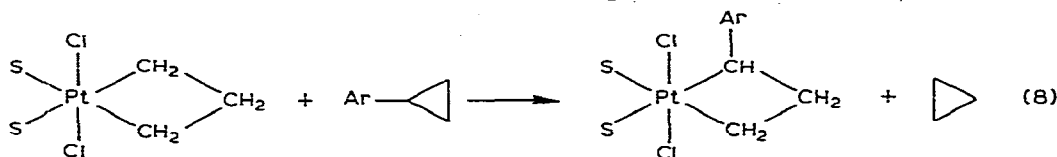
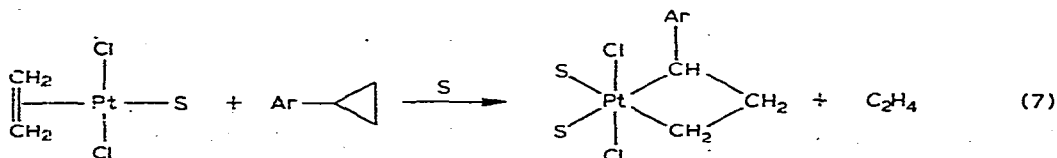
The tetrahydrofuran—platinum bonds are evidently not strong since the initial dimeric or tetrameric complexes are recovered on evaporation of solutions containing I or II, respectively. Similar solvated structures to I and II are expected in other polar solvents, and in some cases the complexes are sufficiently stable to be isolated. For example, the complex *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3\text{CN})]$  can be recovered from a solution of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl}_2)(\text{C}_2\text{H}_4)_2]$  in acetonitrile solution, and a 1,4-dioxane complex of  $[\{\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\}_4]$  has been reported [10].

Spectroscopic studies of the products of the reactions 2 and 3, where R is phenyl or a 4-substituted phenyl group, show that the cyclopropane ring is cleaved at a C—C bond adjacent to the aryl group to give a 1-arylpropane-1,3-diylplatinum(IV) derivative [4,11]. An earlier suggestion that cleavage of the cyclopropane ring occurs at the least substituted edge [7] has been shown to be in error [4]. When long reaction times are used in the preparations, then some 2-arylpropane-1,3-diylplatinum(IV) derivatives are formed. These may arise by the intramolecular isomerisation reaction 6 [4,11]. Alternatively, since it is like-



ly that insertion of platinum into the least-substituted edge of the cyclopropane occurs to a minor degree, then cyclopropane for cyclopropane substitutions of

the kind shown in equation 3 could ultimately lead to a thermodynamic equilibrium between complexes III and IV being obtained. There is no doubt, however, that the major product of kinetic control has structure III. Full details of the characterisation of the compounds formed and of the intramolecular isomerisation (eq. 6) will be reported elsewhere. Using the above data we can formulate the reactions studied in tetrahydrofuran solution as shown in eq. 7 and 8 (S = tetrahydrofuran).



The kinetics of both reactions 7 and 8 were studied using spectrophotometry, since in both cases the products absorbed more strongly than the starting materials in the range 280–350 nm. A typical change in the UV spectrum during a kinetic run is shown in Fig. 1. Considerable excess of the arylcyclopropane was used and under these conditions the reactions followed first order kinetics. Some typical first order plots are shown in Fig. 2, and resulting rate constants

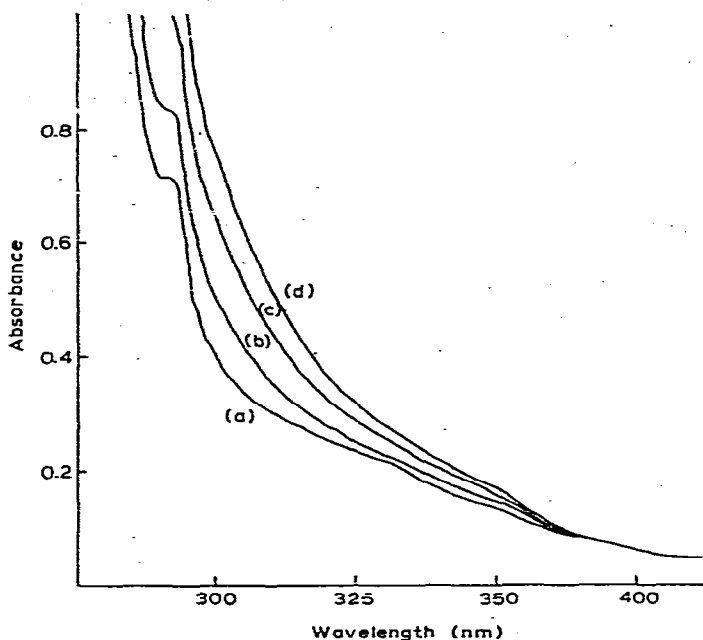


Fig. 1. Changes in the absorption spectrum during the reaction of  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}_2]$  ( $4 \times 10^{-4} M$ ) with phenylcyclopropane ( $2.017 \times 10^{-2} M$ ) at  $45^\circ\text{C}$  in tetrahydrofuran (S). Spectra recorded after (a) 4 min, (b) 22 min, (c) 51 min, and (d) 125 min.

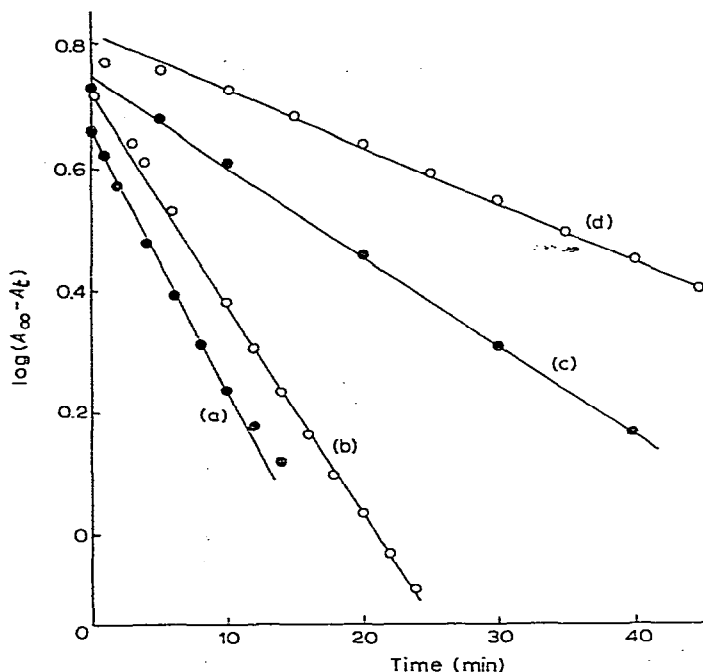


Fig. 2. First order plots for some reactions in tetrahydrofuran (S) at 45°C. (a)  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{S}]$  ( $4 \times 10^{-4} M$ ) with  $\text{PhC}_3\text{H}_5$  ( $2.78 \times 10^{-2} M$ ). (b)  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  ( $4 \times 10^{-4} M$ ) with 4-EtOC<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>5</sub> ( $1.95 \times 10^{-2} M$ ). (c)  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  ( $4 \times 10^{-4} M$ ) with 4-MeC<sub>6</sub>H<sub>4</sub>C<sub>3</sub>H<sub>5</sub> ( $3.47 \times 10^{-2} M$ ). (d)  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  ( $4 \times 10^{-4} M$ ) with  $\text{PhC}_3\text{H}_5$  ( $2.017 \times 10^{-2} M$ ).

are given in Tables 1 and 2. Rate constants were reproducible to  $\pm 10\%$ , but for reaction 7 in tetrahydrofuran it was necessary to use freshly prepared solutions of Zeise's dimer since slow decomposition of the dimer in tetrahydrofuran with release of ethylene occurs ( $k_{\text{obs}}$  at 45°C =  $4.603 \times 10^{-4} \text{ s}^{-1}$ ).

A graph of the observed first order rate constants vs. concentration of arylcyclopropane for reaction 7 is shown in Fig. 3. For each arylcyclopropane the variation is linear except at relatively low concentrations where there is evidence of a minor component of the reaction which is of fractional order in the cyclopropane.

The cyclopropane for cyclopropane displacements of eq. 8 are more straightforward, and graphs of the observed first order rate constants vs. concentration of arylcyclopropane are linear and pass through the origin (Fig. 4), indicating a first order dependence of the rate on arylcyclopropane concentration. The Arrhenius parameters for the reactions are given in Table 3 and typical Arrhenius plots are shown in Figure 5. Data are also given for the reactions of arylcyclopropanes with  $[\text{PtCl}_2(\text{C}_2\text{H}_4)]$  (THF), but the "second order" rate constants are obtained by dividing the first order rate constants by the concentration of cyclopropane. Although this concentration was relatively high, the values can only approximate the true activation energies of the second order process.

Since the rate data on the minor component of reaction 7 are not extensive or accurate enough to obtain the precise order with respect to the cyclopropanes, it is not worthwhile to speculate about the mechanism. For the major (second

TABLE I

FIRST ORDER RATE CONSTANTS FOR REACTIONS OF  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{S}]$  (S = solvent)

Solvent.	Cyclopropane	$10^3 \times [\text{cyclopropane}]/$ (M)	T(K)	$10^4 k_{\text{obs}}(\text{s}^{-1})$	
THF	$\text{PhC}_3\text{H}_5$	2.51	318	2.52	
		3.82		3.55	
		5.19		4.90	
		10.2		6.85	
		27.8		16.6	
THF		36.4	308	20.7	
		38.2		15.5	
		38.2		22.2	
		38.2		313	22.2
		38.2		318	35.5
THF	$4\text{-MeC}_6\text{H}_4\text{C}_3\text{H}_5$	38.2	323	51.2	
		38.2	328	71.5	
		2.00	318	7.54	
		3.52		10.9	
		6.76		18.6	
16.6	29.7				
THF		32.6	303	46.6	
		46.6		65.0	
		19.5		5.20	
		19.5		308	10.5
		19.5		313	21.4
THF	$4\text{-EtOC}_6\text{H}_4\text{C}_3\text{H}_5$	19.5	318	27.0	
		19.5	323	37.4	
		19.5	328	51.0	
		1.37	318	27.3	
		1.89		37.0	
4.09	62.9				
10.99	114.2				
1,4-Dioxane	$\text{PhC}_3\text{H}_5$	20.49	318	159	
		34.0		243	
		31.3		0.36	
		42.7		0.45	
		54.0		0.53	
		67.2	318	0.57	

order) component of reaction 7 and for reaction 8 the kinetics are consistent with two general mechanisms: (a) a slow-rate determining bimolecular reaction between the platinum compound (P) and the cyclopropane (C) followed presumably by one or more unimolecular steps eventually leading to the final products, viz.:



where the I and I' represent one or more intermediates and the observed second order rate constant refers to the first slow step, and (b) one or more fast pre-equilibrium steps, followed by a rate determining step eventually leading to the final products, viz. in the simplest case either reaction bi or bii (S = solvent).



Providing the equilibrium constants (K and K') are small, the observed second

TABLE 2

FIRST ORDER RATE CONSTANTS FOR REACTIONS OF  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{THF})_2]$  IN TETRAHYDROFURAN

Cyclopropane	$10^3 \times [\text{cyclopropane}]$ (M)	T/(K)	$10^4 k_{\text{obs}}(\text{s}^{-1})$
PhC <sub>3</sub> H <sub>5</sub>	4.07	318	0.61
	10.8		1.83
	20.2		3.57
	32.6		6.11
	44.7		8.30
	54.9		9.33
	64.6	11.31	
	45.6	303	2.44
	45.6	308	3.63
	45.6	313	6.03
	45.6	318	8.53
	45.6	323	13.0
	45.6	328	19.3
4-MeC <sub>6</sub> H <sub>4</sub> C <sub>3</sub> H <sub>5</sub>	7.72	318	1.80
	17.2		3.72
	26.9		5.61
	34.5		9.19
	54.8		12.0
	56.4		14.1
4-EtOC <sub>6</sub> H <sub>4</sub> C <sub>3</sub> H <sub>5</sub>	3.65	318	3.09
	8.95		7.77
	14.7		12.6
	19.5	318	14.1
	30.7		20.3
	40.9		26.1
	14.7		5.71
	14.7	308	9.15
	14.7	313	20.1
	14.7	323	26.3
14.7	328		

order rate coefficients are given by (i)  $kK$  and (ii)  $k'K'/[S]$ .

For the reactions with  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{S}]$  (eq. 7) either route a or b is possible as illustrated in equations 10 and 11.

For the cyclopropane-cyclopropane displacements (eq. 8), the mechanism of eq. 9 is probable. Thus assuming that platinum(IV) in the original trimethylene compound achieves the usual octahedral stereochemistry by coordination of two solvent molecules, the dissociation of one solvent molecule must occur before coordination of the incoming arylcyclopropane can occur. The ring-opened and edge-coordinated cyclopropanes then exchange, followed by dissociation of cyclopropane. This reaction probably occurs by the general mechanism bii discussed above.

The solvent effect on reaction rate might be expected to help in distinguishing between these possibilities. Thus, if it were necessary to displace the coordinated solvent completely from the ethylene complex before ring-opening could occur, then the rate would be expected to decrease as the coordinating ability of the solvent increased. In fact the best coordinating solvent used,  $\text{CH}_3\text{CN}$ , gave the highest rate of reaction, an observation which favours the mechanisms of equation 10 or 11a. However, the complex  $\text{trans-}[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5\text{N})]$  failed to react with

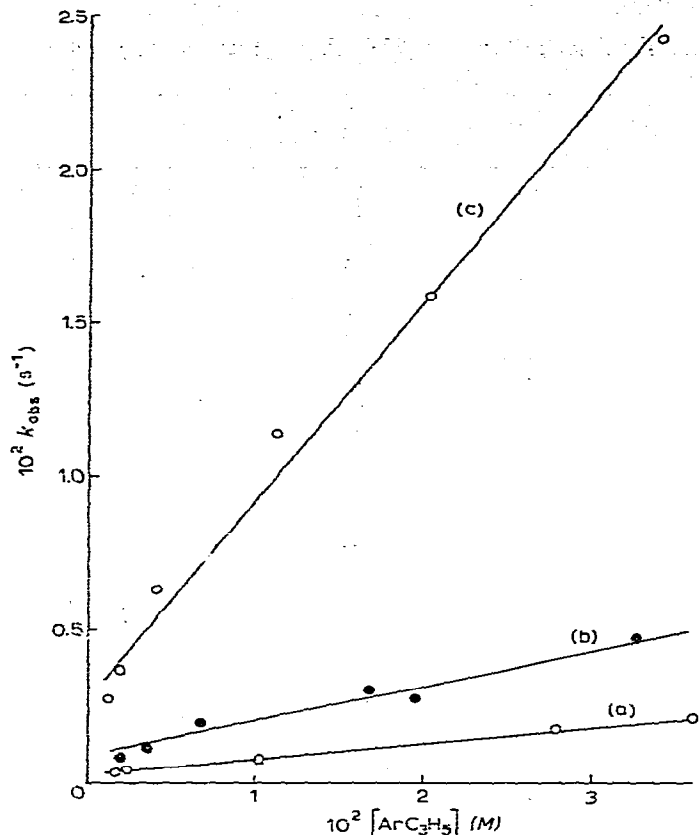


Fig. 3. Dependence of first order rate constants ( $k_{obs}$ ) for the reaction of  $[PtCl_2(C_2H_4)S]$  in tetrahydrofuran (S) on the concentration of  $ArC_3H_5$ . (a)  $Ar = Ph$ , (b)  $Ar = 4-MeC_6H_4$ , (c)  $Ar = 4-EtOC_6H_4$ .

phenylcyclopropane and *trans*- $[PtCl_2(C_2H_4)(2\text{-cyclopropylpyridine})]$  failed to undergo ring opening so that the presence of a labile ligand on platinum does seem to be necessary. The large negative value of the activation entropy is also more consistent with an associative process such as shown in equations 10 or 11a, though similar values are found for reactions with  $[PtCl_2(CH_2CH_2CH_2)S_2]$  where a direct associative process cannot readily occur.

It is also desirable to explain why ring-opening occurs adjacent to the aryl group and why electron-releasing groups on the benzene ring accelerate the reac-

TABLE 3

ARRHENIUS PARAMETERS AND ENTROPIES OF ACTIVATION FOR REACTIONS IN TETRAHYDROFURAN

Complex	Cyclopropane	$E_a$ (kJ mol <sup>-1</sup> )	log A (l mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$[PtCl_2(CH_2CH_2CH_2)S_2]$	$PhC_3H_5$	68.4	9.51	-63
$[PtCl_2(C_2H_4)S]$	$4-EtC_6H_4C_3H_5$	65.1	9.65	-60
$[PtCl_2(C_2H_4)S]$	$PhC_3H_5$	65.5	9.72	-59
$[PtCl_2(C_2H_4)S]$	$4-MeC_6H_4C_3H_5$	66.1	9.97	-54



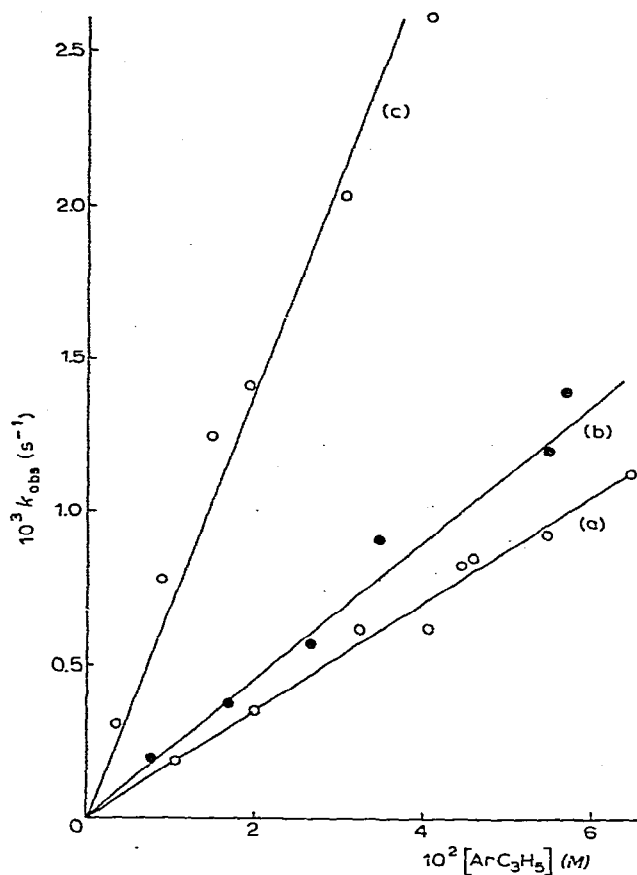


Fig. 4. Dependence of first order rate constants ( $k_{\text{obs}}$ ) for the reaction of  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  in tetrahydrofuran (S) on the concentration of  $\text{ArC}_3\text{H}_5$ . (a)  $\text{Ar} = \text{Ph}$ , (b)  $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ , (c)  $\text{Ar} = 4\text{-EtOC}_6\text{H}_4$ .

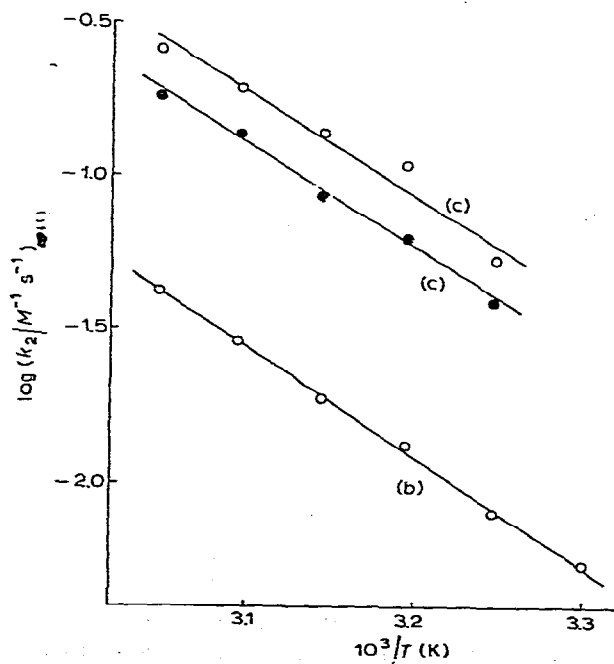
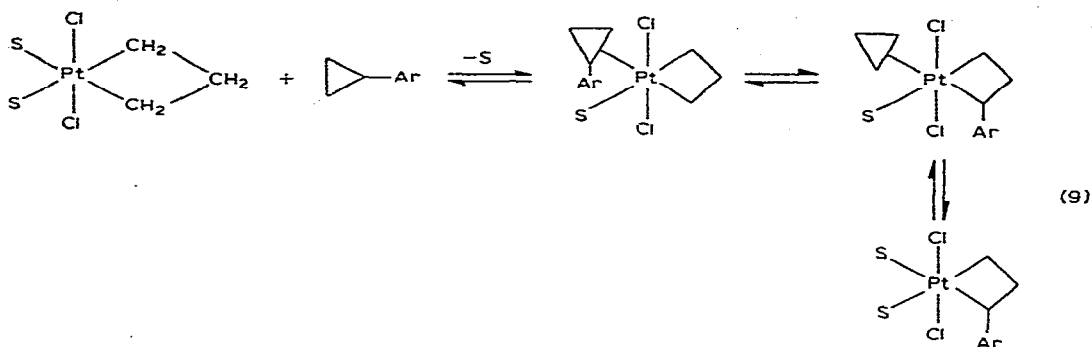
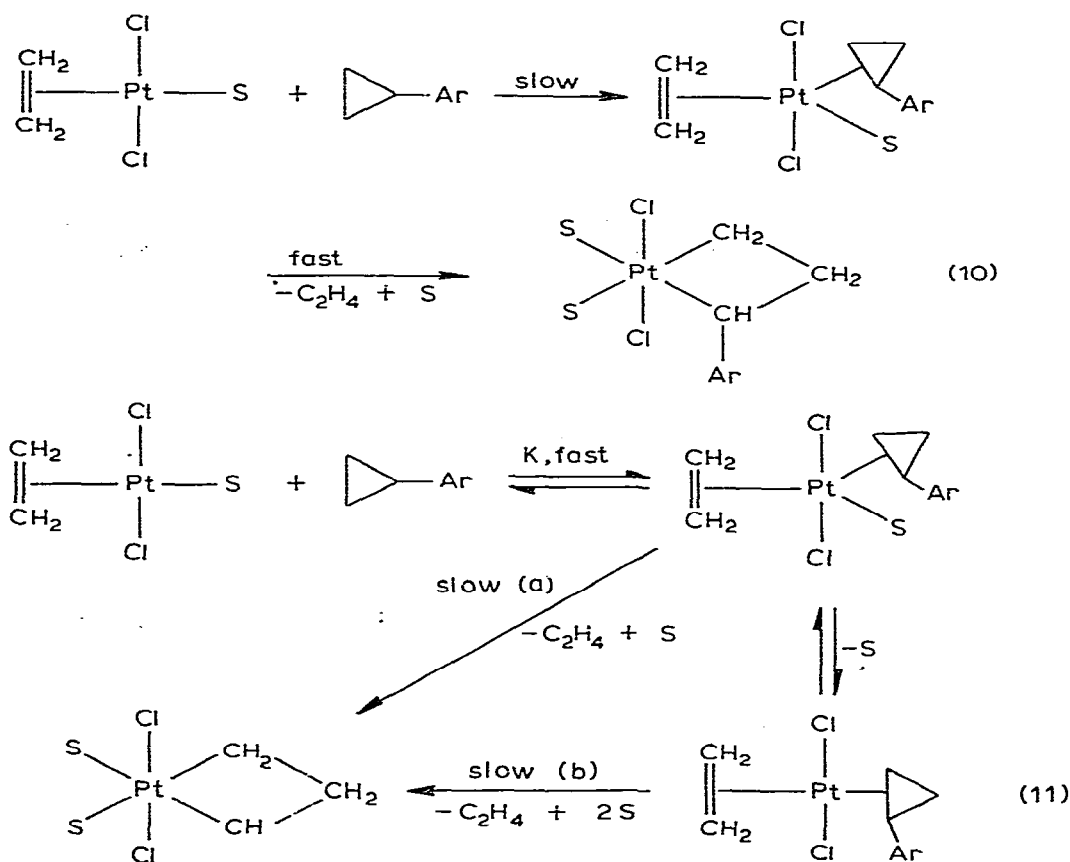


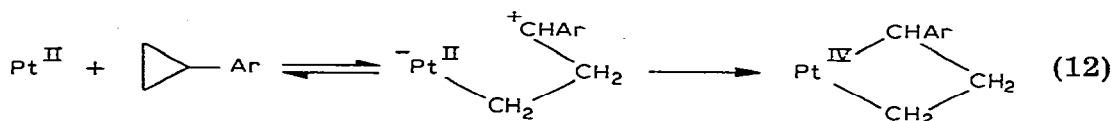
Fig. 5. Arrhenius plots for some reactions in tetrahydrofuran (S). (a)  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  with  $\text{PhC}_3\text{H}_5$ , (b)  $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\text{S}_2]$  with  $4\text{-EtOC}_6\text{H}_4\text{C}_3\text{H}_5$  and (c)  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{S}]$  with  $4\text{-MeC}_6\text{H}_4\text{C}_3\text{H}_5$ .



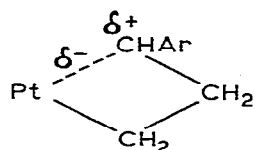
tion. For both reactions 7 and 8 the reactivity series  $4\text{-EtOC}_6\text{H}_4\text{C}_3\text{H}_5 \gg 4\text{-MeC}_6\text{H}_4\text{C}_3\text{H}_5 > \text{PhC}_3\text{H}_5$  was observed; we also find that  $4\text{-FC}_6\text{H}_4\text{C}_3\text{H}_5$  reacts very slowly with  $[\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]$ . McQuillin and co-workers previously noted that electron-releasing substituents on the cyclopropane enhanced the reaction rate [7]. One possibility would involve formation of a polar intermediate during the ring-opening reaction (eq. 12).



The aryl groups, particularly those with electron-donating substituents, would stabilise the intermediate carbonium ions. A similar mechanism has been proposed



for the silver(I)- or rhodium(I)-catalysed ring opening of cyclopropanes [3,12]. However, the intermediate would be free to rotate; thus *cis-trans* isomerisation in 1,2-disubstituted cyclopropanes would be expected, but is not in fact observed [7]. It is, however, possible that the intermediate is polar but not completely ionic (structure A) and then rotation might not, in fact, occur readily. The solvent effect on rate might, therefore, be taken as evidence for a polar intermediate or transition state.



(A)

The position of ring-opening of the arylcyclopropane can be explained in an alternative way if the initial coordination to platinum occurs through the aryl group rather than the cyclopropane ring, and thus the ring is held in such a position that attack of platinum at the adjacent C—C bond occurs preferentially [13]. A concerted process of insertion could then occur, and would be consistent with the previously proposed concerted mechanism of reductive elimination of cyclopropane from trimethyleneplatinum(IV) complexes [14]. Since reaction 7 involves oxidative addition the enhancement of rate by electron-releasing substituents on the cyclopropane appears surprising, and the rate must be dominated by the donor ability of the cyclopropane in forming the "edge complex". The enhancement of stability of the proposed intermediate edge complex with increasing electron-donor substituents is expected in view of the observation that alkene complexes of platinum(II) become more stable with increasing electron donor strength of the substituents [15]. The situation can be compared with that for platinum(0) where olefins with electron-withdrawing substituents give most stable complexes and where cyclopropanes with electron-withdrawing substituents are necessary to obtain PtC<sub>3</sub> ring compounds from platinum(0) complexes [16].

It is clear that coordination of the aryl group is not vital for cyclopropane ring opening to occur since alkylcyclopropanes undergo similar reactions more rapidly [7], but if it does occur it may influence the preferred position of ring opening. Our present data are consistent either with a concerted non-polar mechanism of ring opening or with a mechanism involving a polar (but not completely ionic) intermediate.

## Experimental

The preparations of [Pt<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] and [PtCl<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>] were by literature methods [17,18]. Products of reaction with arylcyclopropanes were characterised as described previously [4].

Tetrahydrofuran used in kinetic studies was distilled under nitrogen from calcium hydride, acetonitrile was distilled from  $P_2O_5$  and chloroform was purified by passage through a column of alumina.

#### Solvent effect on rate

A mixture of phenylcyclopropane (0.1 g) and  $[Pt_2Cl_2(\mu-Cl)_2(C_2H_4)_2]$  (0.05 g) in the required solvent (6 cm<sup>3</sup>) was stirred at 40°C. Samples were taken at various times and quenched by addition of pyridine. Solvent was then evaporated under vacuum and the extent of reaction estimated by recording the NMR spectrum in  $CDCl_3$  solvent.

Unreacted ethylene complex was readily identified as *trans*- $[PtCl_2(C_2H_4)(C_5H_5N)]$ ,  $\delta(C_2H_4)$  5.29 ppm,  $J(PtH)$  61 Hz.

#### Kinetic studies

Standard solutions of  $[Pt_2Cl_2(\mu-Cl)_2(C_2H_4)_2]$  and the required arylcyclopropane were prepared. They were then mixed in the required proportions and transferred to a 1 cm quartz UV cell held in the thermostatted cell compartment of a Unicam SP 30 or SP 8000 spectrophotometer. Readings of the absorbance at either 290 or 320 nm were then taken at suitable intervals.

#### Molecular weights

Molecular weight determinations were made using a Mechrolab Vapour Pressure Osmometer. Solutions in tetrahydrofuran were studied, and the instrument was calibrated using biphenyl. Found for  $\{PtCl_2(C_2H_4)\}_2$ , 297. Calcd. for  $PtCl_2(C_2H_4)$ , 294. Found for  $\{[PtCl_2(C_3H_5Ph)]\}_4$ , 341. Calcd. for  $PtCl_2C_3H_5Ph$ , 384.

#### Product analysis

Characterisation of platinumocyclobutane complexes will be described elsewhere. The volatile product formed by reaction of  $[PtCl_2(\overline{CH_2CH_2CH_2})S_2]$  (S = tetrahydrofuran) with phenylcyclopropane was identified as pure cyclopropane by comparison of the GLC retention time with that of an authentic sample.

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