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REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

X *. REACTION WITH IODIDE AND THIOCYANATE IONS

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Summary

The reaction between the platinacyclobutanes $[\overline{\mathrm{PtX_2(CH_2CRR'C}}\mathrm{H_2)L_2}]$ (X = Cl, Br; L = C_5H_5N, 4-$CH_3C_5H_4N$; R, R' = H, CH_3; R = H, R' = CH_3, C_6H_5) and iodide and thiocyanate ions in methyl cyanide solution has been studied. The C_3 moiety is eliminated as the cyclopropane and the process is first order with respect to the platinacyclobutanes and zero to half order with respect to the salt (MY). With the iodides the rate increases in the order Li < Na < K, Et_4N, and methyl substitution in the cyclobutane ring reduces the rate of reaction with Et_4NI. Added pyridine retards the reaction when L = C_5H_5N (X = Cl; R, R' = H) and added dimethylsulphoxide accelerates it.

The mechanism suggested involves dissociation of an L ligand and attack of Y^- ions and of M^+Y^- ion-pairs on the five-coordinate intermediate formed.

Introduction

Platina(IV)cyclobutane compounds $[\overline{\mathrm{PtX_2(CH_2CH_2C}}\mathrm{H_2)L_2}]$, where X is Cl or Br and L a ligand such as pyridine or tetrahydrofuran, react with ligands having a high *trans* effect (e.g. CN^-, I^-, PPh_3) or with olefins; reductive elimination occurs and the C_3H_6 moiety is displaced [2]. The kinetics of the reactions with neutral ligands $AsPh_3$ and $SbPh_3$ [2] and with a number of alkenes [3] have been studied. We have now investigated the reductive elimination due to

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* For Part IX, see Ref. 1.

reaction with negative ions in more detail, concentrating on I^- and SCN^-, since with these it has been possible to obtain kinetic data, and determining the effect of substitution in the platinacyclobutane ring.

Results and discussion

In order to study the kinetics it is necessary to use a solvent in which both the platinum compounds and suitable inorganic salts are appreciably soluble and in which the reactions take place at measurable rates. Methyl cyanide was found to be the best solvent which fulfilled these requirements, the reactants being platinacyclobutanes (containing neutral ligands such as pyridine) and iodide and thiocyanate salts. Under these conditions cyclopropane was the only gaseous product of the reaction with the unsubstituted cyclobutanes. Homogeneous systems were also formed with acetone and dimethylsulphoxide as solvents but the reactions with iodide or thiocyanate were then very rapid. The reaction of sodium iodide with $[\overline{\mathrm{PtCl_2(CH_2CH_2CH_2}}\mathrm{)(C_5H_5N)_2}]$ in acetone has been found to give $[PtI_2(py)_2]$ [4], so that the general stoichiometry is (Y = I, SCN)

$$[\overline{\mathrm{PtX_2(CH_2CH_2CH_2}}\mathrm{)L_2}] + 2\,\mathrm{MY} = \overline{\mathrm{CH_2CH_2CH_2}} + 2\,\mathrm{MX} + [\mathrm{PtY_2L_2}]$$

where M is an appropriate positive ion.

On reaction, the solution, originally colourless, turns yellow, and so the progress of a reaction was followed by UV spectrophotometry by measuring the increase in absorbance at 300 nm in thermostatted cells until the process was over 90% complete. Then plots of A_t (the absorbance of the solution at time t) versus time enabled reasonably accurate values of A_∞ to be estimated by extrapolation (c.f. ref. 5). $(A_\infty - A_t)$ is proportional to the concentration of the platinacyclobutane reactant at time t.

A considerable excess of salt was used, and, under these conditions, plots of $\log_{10}(A_\infty - A_t)$ vs. time were straight lines, showing that the reaction is first order with respect to platinacyclobutane. Some typical data are shown in Fig. 1. The observed first order rate coefficients (k_{obs}) were reproducible to about ±10%. The values of k_{obs} obtained on varying the nature of the platinacyclobutane, the nature and concentration of the salt are shown in Table 1.

The observed first order rate coefficient varied little with increasing concentration of salt. For the majority of systems (1, 2, 6, 7, 9, 10) the variation was within experimental error so that the order with respect to the salt can be taken as zero. With the other systems (3, 4, 5) there is a definite increase in k_{obs} with increasing salt concentration but the order with respect to salt is a maximum of one-half (see last column, Table 1). With iodides, the rate of reaction increases in the order Li < Na < K, Et_4N (Table 1; 1—4). The reaction with potassium thiocyanate is faster than with potassium iodide (Table 1; 3, 5). Substitution of Br for Cl in the platinacyclobutane reduces the rate slightly (Table 1; 4, 6), whereas replacement of pyridine by 4-methylpyridine decreases the rate very markedly (Table 1; 4, 7). Phenyl substitution in the platinacyclobutane ring reduces the rate slightly (Table 1; 4, 10), but methyl substitution reduces the rate very markedly (Table 1; 4, 8, 9).

Addition of pyridine reduces the rate of reaction and a plot of the reciprocal

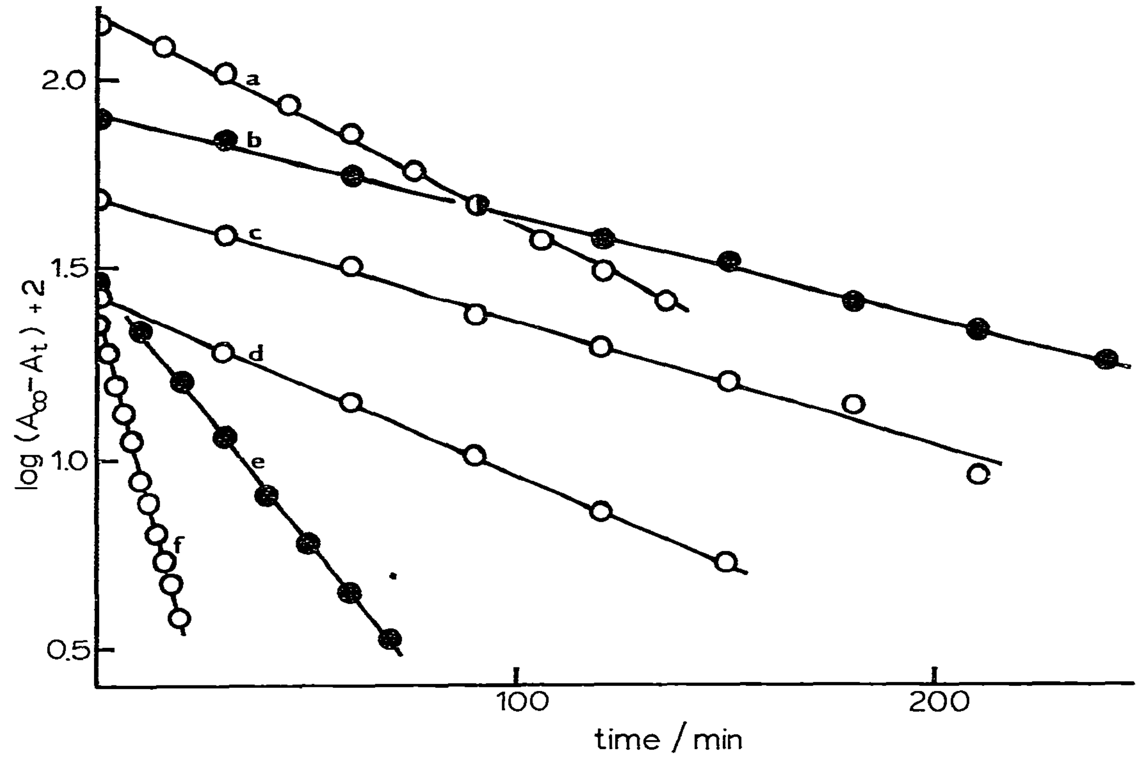


Fig. 1. Typical first order plots for the reactions of platinacyclobutanes (initial conc. ~2 × 10^{-4} mol l^{-1}) with iodide and thiocyanate ions in CH_3CN at 45.1°C. (a) $[\overline{PtCl_2(CH_2CH_2C}H_2)(C_5H_5N)_2]$ + 20 Et_4NI; (b) $[\overline{PtCl_2(CH_2CH_2C}H_2)(C_5H_5N)_2]$ + 40 KI + 0.6 C_5H_5N; (c) $[\overline{PtCl_2(CH_2CMe_2C}H_2)(C_5H_5N)_2]$ + 20 Et_4NI (abs. × 4); (d) $[\overline{PtBr_2(CH_2CH_2C}H_2)(C_5H_5N)_2]$ + 20 Et_4NI; (e) $[\overline{PtCl_2(CH_2CH_2C}H_2)(C_5H_5N)_2]$ + 20 KCNS; (f) $[\overline{PtCl_2(CH_2CH_2C}H_2)(C_5H_5N)_2]$ + 40 Et_4NI + 197 Me_2SO.

of k_{obs} versus the concentration of additive is a straight line (Fig. 2). Addition of dimethylsulphoxide increases the rate and there is a linear relationship between k_{obs} and the concentration of DMSO (Fig. 2).

The rates of reactions of $[PtCl_2(C_3H_6)(py)_2]$ with KI and KSCN had very high temperature coefficients, the values of k_{obs} falling by factors of about 6 and 20, respectively, on reducing the temperature by 5°C (45.1 to 40.1°C) and thus it was not possible to determine the overall activation energies. However, values of k_{obs} for the reaction with Et_4NI in the presence of DMSO were obtained over a 10°C temperature range and an Arrhenius plot (Fig. 3) gave an activation energy of roughly 85 kJ mol^{-1}.

The reduction in rate on addition of pyridine indicates that ligand dissociation is involved in the mechanism. This is confirmed by the marked decrease in rate when pyridine is replaced in the platinacyclobutane by 4-methylpyridine, which is attached more strongly to the platinum [2], and is in agreement with the results of a kinetic study of the reactions with $AsPh_3$ and $SbPh_3$ [2]. The salts in methyl cyanide solution presumably exist as intimate ion-pairs in equilibrium with free ions. Conductance data at 25°C for NaI, KI, KCNS and Et_4NI in CH_3CN are available [6]. The apparent ion-pair dissocia-

TABLE 1

VALUES OF THE FIRST ORDER RATE COEFFICIENTS (k_{obs}) FOR THE REACTION OF PLATINACYCLOBUTANES WITH INORGANIC IODIDES AND THIOCYANATES IN METHYL CYANIDE AT 45.1°C

Initial concentration of platinum compound ~2 × 10^{-4} mol l^{-1}

No.	Platinum compound [a]	Salt [b]		$10^4\ k_{obs}$ (s^{-1})	$10^4\ k_{obs}/[\text{Salt}]^{1/2}$ [c]
1	$[\overline{\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\text{py})_2]$	LiI,	20	0.43	
			40	0.47	
			60	0.37(5)	
			80	0.39	
2		NaI,	20	0.56	
			40	0.76	
			60	0.72	
			80	0.70	
3		KI,	20	1.8(5)	1.3
			40	2.6	1.3
			60	3.1	1.2(5)
4		Et_4NI,	20	2.1(5)	1.5
			40	2.4(5)	1.5
			60	2.8	1.1(5)
5		KCNS,	20	5.2	3.7
			40	6.9(5)	3.5
6	$[\overline{\text{PtBr}_2(\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\text{py})_2]$	Et_4NI,	20	1.8	
			40	1.6	
			60	1.4	
			80	1.6	
7	$[\overline{\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\text{pic})_2]$	Et_4NI,	20	0.33(5)	
			40	0.29(5)	
			60	0.03(5)	
			80	0.29(5)	
8	$[\overline{\text{PtCl}_2(\text{CH}_2\text{CHMeC}}\text{H}_2)(\text{py})_2]$ [d]	Et_4NI,	20	0.76	
9	$[\overline{\text{PtCl}_2(\text{CH}_2\text{CMe}_2\text{C}}\text{H}_2)(\text{py})_2]$	Et_4NI,	20	0.32	
			40	0.31(5)	
			60	0.27(5)	
			80	0.26(5)	
10	$[\overline{\text{PtCl}_2(\text{CH}_2\text{CHPhC}}\text{H}_2)(\text{py})_2]$ [d]	Et_4NI,	20	1.9(5)	
			40	2.0	
			60	1.9(5)	
			80	2.1	

[a] py = pyridine, pic = 4-methylpyridine, Me = CH_3, Ph = C_6H_5. [b] Number gives mol salt per mol platinum compound. [c] The concentration of salt is taken as one-tenth the molar ratio of salt to platinum compound. [d] Exists as a mixture with the α-methyl or α-phenyl isomer.

tion constants (K_D) calculated using the simple Ostwald dilution law, $K_D = (\Lambda/\Lambda_\infty)^2 C/\{1 - (\Lambda/\Lambda_\infty)\}$ where Λ is the conductance at a concentration C mol l^{-1} and Λ_∞ is the conductance at infinite dilution, vary considerably with concentration. However, the data do indicate that the true dissociation constants are likely to be much the same for all four salts and that, at the concentrations in this work (4 × 10^{-3} to 1.6 × 10^{-2} mol l^{-1}), there is very considerable dissociation. It seems reasonable to suppose that ligand dissociation is followed by attack of Y^- ions or M^+Y^- ion-pairs on the five-coordinate platinum species and a relatively simple mechanism which will explain the kinetic data is given

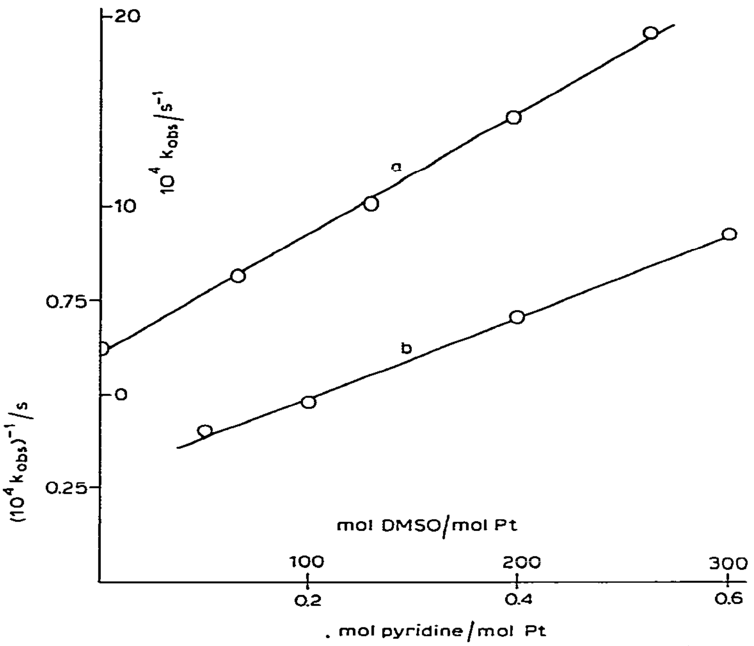


Fig. 2. Dependence of the first order rate coefficients (k_{obs}) on the concentration of additives. Solvent, CH_3CN; temperature 45.1°C. (a) $[\overline{PtCl_2(CH_2CH_2CH_2)}(C_5H_5N)_2]$ + 40 Et_4NI + Me_2SO, ord., $10^4\ k_{obs}/s^{-1}$; (b) $[\overline{PtCl_2(CH_2CH_2CH_2)}(C_5H_5N)_2]$ + 40 KI + C_5H_5N; ord., $(10^4\ k_{obs})^{-1}$/s.

in Scheme 1. The mechanism is similar to that proposed earlier for reactions of platinacyclobutanes with triphenylarsine and triphenylstibine [2]. The inclusion of reaction 3 is considered necessary to explain the surprising observation that the rate of reaction of the platinacyclobutanes with iodide or thiocyanate is dependent on the nature of the salt used (varying with both the cation and the anion) but is often independent of the concentration of the salt.

According to the stoichiometry the rate of loss of platinacyclobutane (I) equals the rate of formation of the coloured product (P). Thus

$$-d[I]/dt = d[P]/dt = k_4[III]$$

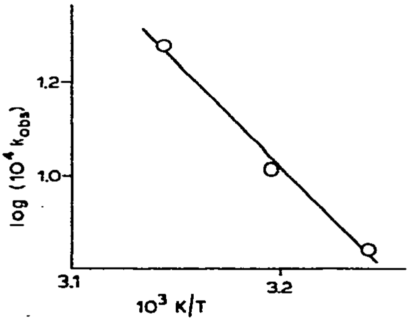
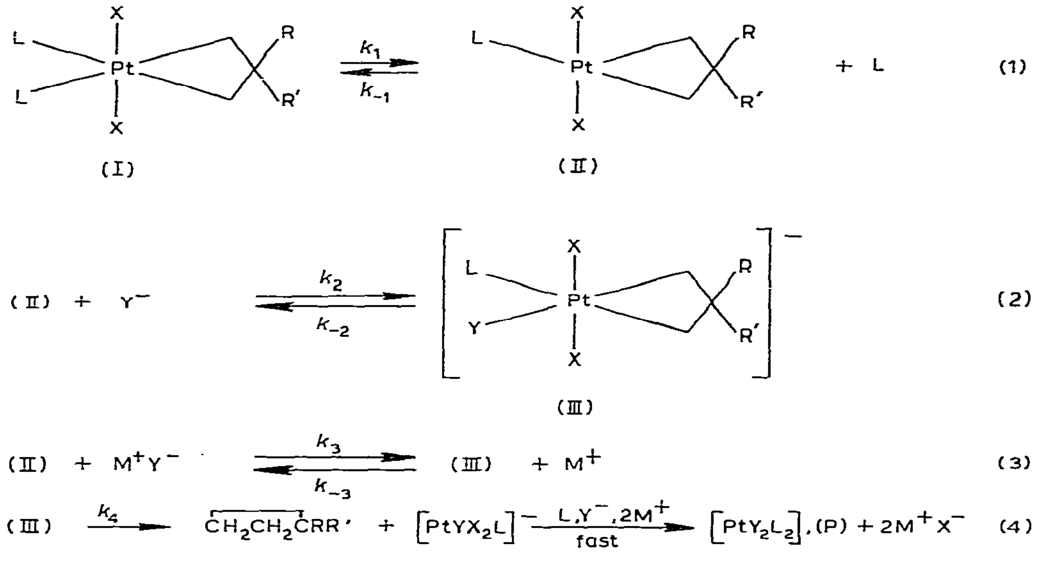


Fig. 3. Variation of the first order rate coefficient (k_{obs}) with temperature. $[\overline{PtCl_2(CH_2CH_2CH_2)}(C_5H_5N)_2]$ + 40 Et_4NI + 262 Me_2SO in CH_3CN.



(X = Cl, Br; L = C_5H_5N, 4-$CH_3C_5H_4N$; RR' = H or CH_3; R = H, R' = CH_3 or C_6H_5
Y^- = I^-, CNS^-; M^+ = Li^+, Na^+, K^+, Et_4N^+)

SCHEME 1

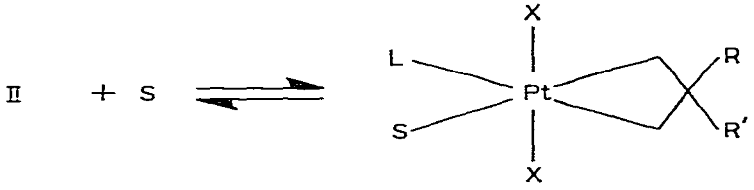
Assuming stationary states for both intermediates II and III, since if III built up to any appreciable concentration this would be apparent from the UV spectra (for instance Pt^{IV} iodides are strongly coloured), the rate expression is

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = \frac{k_1k_4[\mathrm{I}](k_2[\mathrm{Y}^-] + k_3[\mathrm{M}^+\mathrm{Y}^-])}{k_{-1}k_{-2}[\mathrm{L}] + k_{-1}k_4[\mathrm{L}] + k_1k_{-3}[\mathrm{L}][\mathrm{M}^+] + k_2k_4[\mathrm{Y}^-] + k_3k_4[\mathrm{M}^+\mathrm{Y}^-]} \qquad (A)$$

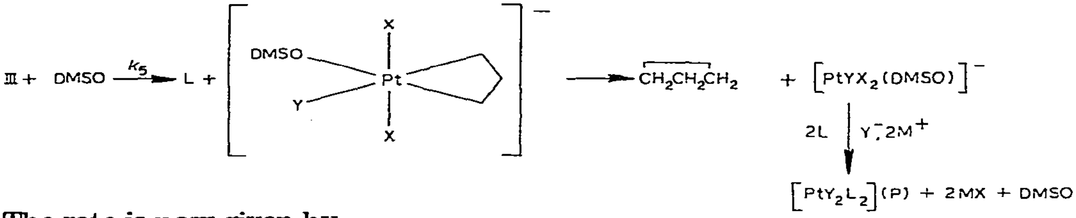
Provided $k_{-1}[\mathrm{L}] \gg k_2[\mathrm{Y}^-]$ and $k_2 \gg k_3$, which seems reasonable, and since $[\mathrm{M}^+] \simeq [\mathrm{Y}^-]$ because salt is in great excess, equation (A) reduces to

$$-\mathrm{d}[\mathrm{I}]\mathrm{d}t = \frac{k_1k_2k_4[\mathrm{I}][\mathrm{Y}^-]}{k_{-1}[\mathrm{L}](k_{-2} + k_4 + k_{-3}[\mathrm{Y}^-])} \qquad (B)$$

This is in agreement with the experimental variation of the rate with platinacyclobutane (I) and pyridine (L) concentrations. If $k_{-3}[\mathrm{Y}^-] \gg k_{-2} + k_4$, the rate does not vary with Y^- and thus salt concentrations, as found for most systems. With systems 3, 4 and 5 (Table 1), however, $k_{-3}[\mathrm{Y}^-]$ is presumably of the same order as $k_{-2} + k_4$ and the rate increases with increasing concentration of salt. The inert solvent (S) will, in fact, compete with Y^- and $\mathrm{M}^+\mathrm{Y}^-$ for addition to intermediate II, viz.



This will reduce the stationary concentration of II but not alter the kinetics. A much higher rate with acetone than with methyl cyanide as solvent is therefore to be expected since acetone is certainly a very much weaker ligand than CH_3CN as indicated by the observation that the tetramers $[\{\overline{PtX_2(CH_2CH_2CH_2})\}_4]$ will dissolve in the latter but not in the former [7,8]. In the absence of salt cyclopropane is evolved very slowly from a solution of $[\overline{PtX_2(CH_2CH_2CH_2})(py_2)]$ in DMSO [2]. Thus, it is suggested that, in the presence of salt, DMSO reacts with the intermediate III by displacing L and causing the release of cyclopropane and the formation of the yellow product P, viz.



(5)

The rate is now given by

$$-d[I]/dt = d[P]/dt = (k_4 + k_5[DMSO])\,[III]$$

Substituting $k_4 + k_5[DMSO]$ for k_4 in equation B gives

$$-d[I]/dt = \frac{k_1k_2(k_4 + k_5[DMSO])[I][Y^-]}{k_{-1}[L]\{k_{-2} + k_4 + k_5[DMSO] + k_{-3}[Y^-]\}}$$

If $k_{-3}[Y^-] \gg k_{-2} + k_4 + k_5[DMSO]$ under the conditions used then k_{obs} is linearly related to the concentration of DMSO as found experimentally. The temperature variation of k_{obs} obviously cannot be associated with any one step in the mechanism.

Changing the ligand L from pyridine to 4-methylpyridine decreases k_1 and increases k_{-1}, decreasing the rate (cf. above). However, changing the halide ligand X, which is *cis* to both the ring and the nitrogen ligands is unlikely to alter any of the individual rate coefficients, and thus k_{obs}, appreciably. There is evidence that the thiocyanate ion (which usually binds to platinum through the sulphur atom) has a higher *trans* effect than the iodide ion [9], and this agrees with the higher rate when $Y^- = NCS^-$, since k_4 will be larger. Reaction −3 involves forming the ion-pair M^+Y^-, the binding energies of which for the iodides decrease in the order Li > Na > K [10]. Thus k_{-3} will decrease as M^+ in M^+I^- is varied in this order and (as equation B shows) this means that k_{obs} increases, as observed. Step 4 involves a concerted elimination of the cyclopropane and thus substitution in the platinacyclobutane ring may alter k_4. For instance, the intermediate III probably becomes more stable on methyl substitution due to increasing electron density in the ring [11], reducing k_4 and the rate, as found experimentally.

Experimental

The unsubstituted platinacyclobutanes ($[\overline{PtX_2(CH_2CH_2CH_2})(L_2)]$, X = Cl, Br and L = C_5H_5N and 4-$CH_3C_6H_4N$) were prepared by literature methods

[2,12]. The substituted compounds were prepared by the reaction of $[\overline{\mathrm{PtCl_2(CH_2CH_2CH_2}})(\mathrm{THF})_2]$ in tetrahydrofuran solution [3] with a large excess of the appropriate cyclopropane at room temperature. The reaction mixture was left for 2—3 days and the solvent and excess cyclopropane distilled off under vacuo. The solid left was suspended in dichloromethane, the suspension cooled to 0°C and pyridine added dropwise until a clear solution was obtained. Removal of the CH_2Cl_2 in vacuo gave the pyridine adducts (Table 1; 8, 9,10), which were >99% pure (reaction with PPh_3 in DMSO and mass spectrometry). 1,1-Dimethylcyclopropane and phenylcyclopropane were commercial samples. Methylcyclopropane was prepared by the reaction of zinc powder with 1,3-dibromobutane in aqueous ethanol [13]. The volatile product was swept out in a stream of nitrogen, passed through a solution of potassium permanganate to remove olefins, dried and the cyclopropane collected in a trap cooled to —78°C. The trap was transferred to a vacuum line and the cyclopropane distilled into a stout pyrex tube (~50 cm^3 volume), containing the THF solution (see above), which was then closed by a greaseless tap. With the other cyclopropanes, the reaction mixture was made up in a stoppered conical flask. The tetrahydrofuran was distilled under nitrogen from calcium hydride and methyl cyanide was also distilled before use. Standard solutions of the reactants were prepared just before use in the kinetic studies.

The gas evolved for the reactions of $[\overline{\mathrm{PtX_2(CH_2CH_2CH_2}})(\mathrm{py})_2]$ (X = Cl, Br; py = C_5H_5N) was analysed by GLC using a 9 ft 12% Squalane on Chromosorb P column at 30°C.

References

1 R.J. Al-Essa, R.J. Puddephatt, P.J. Thompson and C.F.H. Tipper, J. Amer. Chem. Soc., in press.
2 P.W. Hall, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 84 (1975) 407.
3 R.J. Puddephatt, P.J. Thompson and C.F.H. Tipper, J. Organometal. Chem., 177 (1979) 403.
4 D.M. Adams, J. Chatt, R.G. Guy and N. Sheppard, J. Chem. Soc., (1961) 738.
5 R.J. Al-Essa, R.J. Puddephatt, M.A. Quyser and C.F.H. Tipper, J. Organometal. Chem., 150 (1978) 295.
6 Landolt-Börnstein, Band II, Part 7, Springer-Verlag, Berlin, 1960, p. 412.
7 D.C.L. Perkins, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 186 (1980) 419.
8 C.F.H. Tipper, J. Chem. Soc., (1955) 2045.
9 U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London, 1974.
10 T.C. Waddington, Adv. Inorg. Radiochem., 1 (1959) 158.
11 See discussion of the structure of platinacyclobutanes, R.J. Puddephatt, Coord. Chem. Rev., to be published.
12 R.D. Gillard, M. Keeton, R. Mason, M.F. Pilbrow and D.R. Russell, J. Organometal. Chem., 33 (1971) 247.
13 W.A. Lott and W.G. Christiansen, J. Amer. Pharmaceutical Soc., 27 (1938) 125.