

## THE PHOTODECOMPOSITION OF PLATINACYCLOALKANES IN SOLUTION.

### I. 1,3-PROPANEDIYLPLATINUM(IV) COMPOUNDS

DUNCAN C.L. PERKINS, RICHARD J. PUDDEPHATT \* and CHARLES F.H. TIPPER

*Donnan Laboratories, The University, Liverpool L69 3BX (Great Britain)*

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#### Summary

The gaseous products of the photolysis at 25° C of the platinacyclobutane compounds  $[X_2PtCH_2CH_2CH_2(N-N)]$  where X = Cl, Br and N-N = 1,10-phenanthroline, 2,2'-bipyridine,  $(CH_2NMe_2)_2$ ,  $(C_5H_5N)_2$  in several solvents, in the absence and presence of various additives, have been determined. With solvents of relatively low dielectric constant (e.g.  $CH_2Cl_2$ ), over 85 mol % of the hydrocarbon products was propene, the formation of which appears to involve a direct transfer of a hydrogen atom between neighbouring groups in the ring. With solvents of relatively high dielectric constant (MeCN,  $Me_2SO$ ) in the presence of species, e.g.  $I^-$ ,  $SbPh_3$ , having a high *trans* effect, cyclopropane is the main volatile product. The effect of added halide ion and of the mixed solvents  $Me_2SO/PhMe$  and  $Me_2SO/PhSH$  indicates that ionisation of the platinacyclobutane and the formation of platinum substituted propyl ion-radicals precede the formation of cyclopropane (and the small amounts of ethylene produced).

The photolysis of  $[X_2PtCH_2CH_2CH_2(MeCN)_2]$  in methyl cyanide solution in the presence of  $Et_3RNX'$  ( $X' = Cl$ , R = H;  $X' = Br$ , R = Et) gives appreciable amounts of ethylene in the products (up to 25 mol %). It is suggested that the halide ions add to the platinum to give negatively charged platinacyclobutane species, the photodecomposition of which may give  $C_2H_4$ .

#### Introduction

interest in the preparation, structure and reactions of metallacycloalkanes has increased in recent years mainly because of the recognition that they are

\* Present address: Department of Chemistry, The University of Western Ontario, London, Canada N6A 5B7.

probably key intermediates in such processes as olefin metathesis [1], dimerisation of olefins [2] and isomerisation of hydrocarbons containing strained rings [3]. Whereas much information has been obtained on the thermal reactions of metallocycloalkanes [4], much less is known about their photolysis [5]. We have studied the kinetics of the photodecomposition of platinacyclobutane compounds [6] and now report the results of an investigation of the products of photolysis under a wide variety of conditions. A brief preliminary communication, drawing attention to some mechanistic implications, has been published [7].

## Results and discussion

Compounds of the general formula  $[X_2PtCH_2CH_2CH_2(N-N)]$  (where X = Cl, Br and N-N = 1,10-phenanthroline, 2,2'-bipyridine, tetramethylethylenediamine,  $(CH_3CN)_2$ ,  $(C_5H_5N)_2$ ) were photolysed in solution at 25°C under the influence of UV radiation in the absence and presence of various additives. The data on the products are collected in Table 1 grouped according to the solvent, the individual yields quoted (when over about 20 mol %) being reproducible to approximately 5 in the last figure. Thermal decomposition was negligible during the photolysis time (<3 h).

The main volatile products of the photolysis under nearly all conditions are propene and cyclopropane. However, the relative yields vary widely. With solvents of relatively low dielectric constant (dichloromethane, *o*-dichlorobenzene, pyridine and tetrahydrofuran, Nos. 1, 2, 4–10) the gas evolved contained over 85% propene (usually over 95%). The relative yield was not affected (within experimental error) by the addition of a large excess of neutral ligand (c.f. Nos. 1 and 2, 4 and 5, 6 and 9) and earlier work [6] showed that the first order rate coefficients for the photolysis of  $[X_2PtCH_2CH_2CH_2(phen)]$  in  $CH_2Cl_2$  are only slightly reduced by the addition of 10 fold excess phenanthroline. On the other hand, with solvents of relatively high dielectric constant (methyl cyanide and dimethylsulphoxide) the relative yield of cyclopropane is generally considerably higher (e.g. Nos. 11, 18, 21), particularly if species exhibiting a high *trans* effect (DMSO,  $AsPh_3$ ,  $SbPh_3$ ,  $I^-$  from NaI and  $Et_4NI$ ) are present (e.g. Nos 12–15, 24, 30, 33, 35, 37, 38). Excess neutral ligand again has little effect on the relative yield of propene (Nos. 24–26, 30, 31), whereas addition of tetramethylammonium chloride markedly decreases the proportion of cyclopropane in the volatile products of the photolysis in DMSO (Nos. 24, 27, 30, 32, 33, 34). The first order rate coefficient for  $[Cl_2PtCH_2CH_2CH_2(phen)]$  photolysis is considerably decreased (by a factor of ca. 2.3) on addition of an equimolar amount of the  $Me_4NCl$  to the DMSO solution [6].

Considering the platinum compounds containing bidentate neutral ligands, it appears that ligand dissociation does not precede the formation of propene but that a direct 1,2-hydrogen shift occurs in the excited molecule. The observation that the volatile products only contain a considerable proportion of cyclopropane when the solvent has a relatively high dielectric constant and the effect of added chloride ion indicates that ionisation precedes cyclopropane formation. However, the presence of species exhibiting a high *trans* effect is necessary, suggesting that elimination of cyclopropane follows the attachment of

TABLE 1

PRODUCTS OF THE PHOTOLYSIS OF PLATINACYCLOBUTANE COMPOUNDS  $[X_2Pt(CH_2CH_2CH_2)_2(N-N)]$  IN SOLUTION AT 25°C

Concentration of platinum compound  $\sim 6 \times 10^{-3}$  mol  $\Gamma^{-1}$

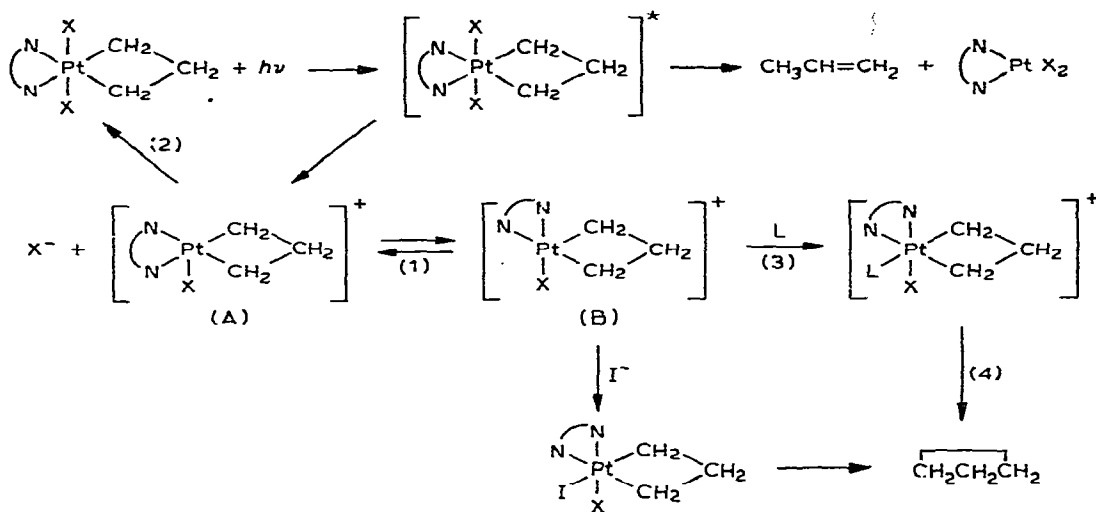
No.	Compound <sup>a</sup>		Additive <sup>b</sup>	Volatile products (mol %)			
	X	N-N		C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> CH=CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	others
Solvent, CH <sub>2</sub> Cl <sub>2</sub> (dielectric constant, 9.1)							
1	Cl	phen	—	1	95	4	
2	Cl	phen	25 phen	1	92	7	
3	Cl	phen	50 vol. % PhSH <sup>c</sup>	1	45	14	CH <sub>4</sub> (12), C <sub>3</sub> H <sub>8</sub> (26), CH <sub>3</sub> Cl (2)
4	Cl	bipy	—		98	2	
5	Cl	bipy	30 bipy	1	94	5	
6	Cl	py <sub>2</sub>	—		98	2	
7	Br	phen	—	1	85	14	
Solvent, <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> (dielectric constant, 9.9)							
8	Cl	phen	—		98	2	
Solvent, C <sub>5</sub> H <sub>5</sub> N (dielectric constant, 12.3)							
9	Cl	py <sub>2</sub>	—		97	3	
Solvent, tetrahydrofuran (dielectric constant, 7.4)							
10	Cl	phen	—		96	4	
Solvent, CH <sub>3</sub> CN (dielectric constant, 37.5)							
11	Cl	phen	—		82	18	
12	Cl	phen	30 AsPh <sub>3</sub>		48	52	
13	Cl	phen	30 SbPh <sub>3</sub>	8	26	66	
14	Cl	phen	30 NaI	4	58	38	
15	Cl	phen	30 Et <sub>4</sub> NI		23	77	
16	Cl	bipy	—		97	3	
17	Br	phen	—		95	5	
18	Cl	(CH <sub>3</sub> CN) <sub>2</sub>	—	6.5	7	86.5	
19	Cl	(CH <sub>3</sub> CN) <sub>2</sub>	(2)20 Et <sub>4</sub> NHCl	(14)25	(47)50	(39)25	
20	Cl	(CH <sub>3</sub> CN) <sub>2</sub>	(2)20 Et <sub>4</sub> NBr	(9)17	(39)45	(52)38	
21	Br	(CH <sub>3</sub> CN) <sub>2</sub>	—		12	88	
22	Br	(CH <sub>3</sub> CN) <sub>2</sub>	20 Et <sub>3</sub> NHCl	12	50	38	
23	Br	(CH <sub>3</sub> CN) <sub>2</sub>	20 Et <sub>4</sub> NBr	5	66	29	
Solvent, (CH <sub>3</sub> ) <sub>2</sub> SO (dielectric constant, 46.4)							
24	Cl	phen	—	3.5	24.5	72	
25	Cl	phen	366nm filter	1	38	61	
26	Cl	phen	50 phen	1	38	61	
27	Cl	phen	25 Me <sub>4</sub> NCl		95	5	
28	Cl	phen	30 vol. % PhMe	2	51	46	C <sub>3</sub> H <sub>8</sub> (1)
29	Cl	phen	50 vol. % PhSH <sup>c</sup>		26	21	CH <sub>4</sub> (47.5) C <sub>3</sub> H <sub>8</sub> (5.5)
30	Cl	bipy	—		62	37	
31	Cl	bipy	60 bipy		68	32	
32	Cl	bipy	50 Me <sub>4</sub> NCl		94	6	
33	Cl	TMED	—	3	72	25	
34	Cl	TMED	40 Me <sub>4</sub> NCl		82	18	
35	Cl	TMED	25 SbPh <sub>3</sub>	3	50	47	
36	Cl	py <sub>2</sub>	—	3	82	18	
37	Br	phen	—		80	20	
38	Br	phen	30 SbPh <sub>3</sub>		24	76	

<sup>a</sup> phen = 1,10-phenanthroline; bipy = 2,2'-bipyridine; TMED = tetramethylethylenediamine; py = pyridine.

<sup>b</sup> Number gives mol additive per mol Pt compound. <sup>c</sup> Photolysis of the solvent gives methane.

such a species to the vacant site on the positively charged platinum entity. Ionic species have been proposed as intermediates in the thermal elimination of cyclopropane from  $[X_2PtCH_2CH_2CH_2(py)_2]$  under similar conditions [8]. Thus the photolysis mechanism probably involves the steps shown in Scheme 1.

SCHEME 1

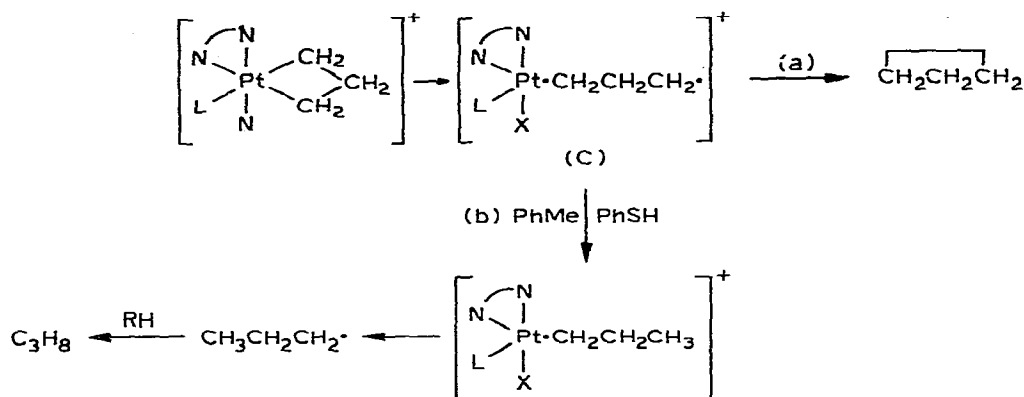


(X = Cl, Br; L = DMSO, AsPh<sub>3</sub>, SbPh<sub>3</sub>)

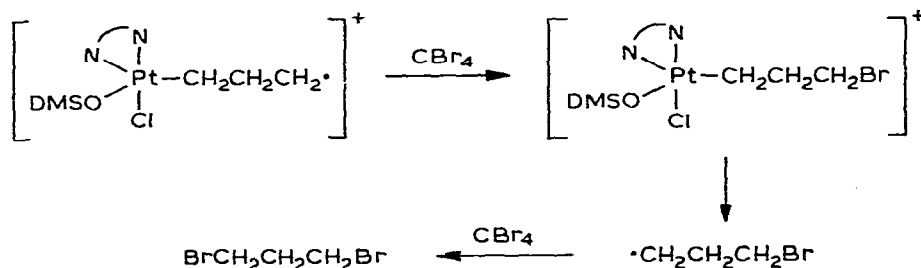
Since the chloride ligands are *cis* with respect to the ring in the reactants, dissociation of a halide ion gives a "cis" vacant site (intermediate A) and thus it is tentatively suggested that a reversible isomerisation occurs in the five coordinate platinum species to give a "trans" vacant site (intermediate B). Attack of DMSO, etc. at the "trans" site will then lead to the elimination of cyclopropane. Also the reduction in the relative yield of cyclopropane in the photolysis of  $[Cl_2PtCH_2CH_2CH_2(N-N)]$  in DMSO as (N-N) is changed from phenanthroline to bipyridine to tetramethylethylenediamine to  $(C_5H_5N)_2$  (Nos. 24, 30, 33, 36) can be explained on the assumption that intermediate A is progressively favoured with respect to B as the neutral ligand becomes more flexible (eventually being monodentate), reaction 1, followed by reaction 2, competing more and more effectively with reaction 3 (L = DMSO). The higher relative yield in the presence of triphenylstibine (Nos. 33, 35, 37, 38) indicates that the rate coefficient of reaction 3 is much larger when L = SbPh<sub>3</sub> than when L = DMSO, in agreement with the observation [8] that SbPh<sub>3</sub> displaces cyclopropane from  $[X_2PtCH_2CH_2CH_2(py)_2]$  much more rapidly than does DMSO in the dark. The results with  $[Br_2PtCH_2CH_2CH_2(phen)]$  (Nos. 37, 38) show that this compound ionises in DMSO and intermediate B is favoured, since the relative yield of cyclopropane is so high when SbPh<sub>3</sub> is present. However, in the absence of additive, the yield of cyclopropane is very much lower than from  $[Cl_2PtCH_2CH_2CH_2(phen)]$ , indicating that reaction 3 (L = DMSO) is much faster when X = Cl than when X = Br.

Traces of propane were often detected in the products of photolysis and

with the mixed solvents DMSO/toluene, DMSO/PhSH and  $\text{CH}_2\text{Cl}_2/\text{PhSH}$  appreciable yields were obtained (Nos. 3, 28, 29). No propane is formed in the dark reactions. Since hydrogen abstraction from toluene and benzenethiol by radicals is relatively rapid [9], this suggests that cyclization of the  $\text{C}_3\text{H}_6$  moiety (reaction 4) is preceded by homolytic fission of a Pt—C bond to give a substituted propyl radical, viz.



It is possible that some propane is formed by the direct interaction of benzenethiol with an intermediate, particularly for the  $\text{CH}_2\text{Cl}_2/\text{PhSH}$  solvent. 1,3-dibromopropane was detected in solution after photolysis of  $[\text{Cl}_2\text{PtCH}_2\text{CH}_2\text{CH}_2\text{(phen)}]$  in a mixture of DMSO and  $\text{CBr}_4$ . Although some might have been formed from addition of  $\text{Br}_2$  (produced by photolysis of the tetrabromomethane), this product supports the view that the platinumpropyl ion-radical (C) is an intermediate, viz.



It is possible to estimate the first order rate coefficient of the cyclization reaction (4a; X = Cl, N-N = phen, L = DMSO) at 25°C from the relative amounts of cyclopropane and propane produced in the photolysis of  $(\text{Cl}_2\text{Pt}-\text{CH}_2\text{CH}_2\text{CH}_2\text{(phen)})$  in DMSO/PhMe. The rates of formation of the two products are

$$d[\text{C}_3\text{H}_6]/dt = k_{4a}[\text{C}] \quad \text{and} \quad d[\text{C}_3\text{H}_8]/dt = k_{4b}[\text{C}][\text{PhMe}]$$

Thus,

$$[\text{C}_3\text{H}_6]/[\text{C}_3\text{H}_8] = k_{4a}/k_{4b}[\text{PhMe}] = 46$$

$[\text{PhMe}] = 3.0 \text{ mol l}^{-1}$ , calculated from the density at 25°C and the vol %.

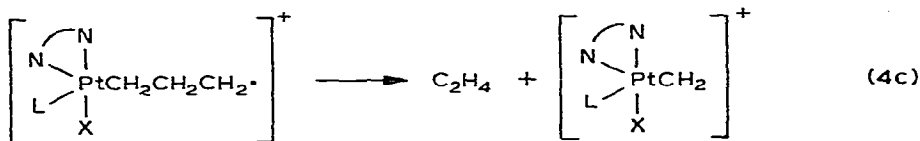
Assuming that  $k_{4b}$  is the same as the rate coefficient of hydrogen abstraction

by ethyl radicals from toluene, i.e.  $4.0 \text{ l mol}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$  (calculated from  $k = 2.6 \times 10^7 \exp(-38,900 \text{ J mol}^{-1}/RT) \text{ l mol}^{-1} \text{ s}^{-1}$  [9]), then

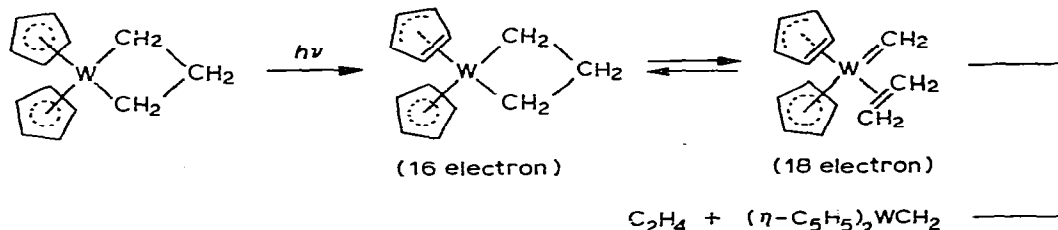
$$k_{4a} = 46 \times 4 \times 3 = 5.5 \times 10^2 \text{ s}^{-1}$$

This value is, of course, only very approximate but does suggest that the cyclization reaction is certainly not very fast. Assuming that  $A_{4a} = 10^{13.5} \text{ s}^{-1}$ , the most probable value for the pre-exponential factor of a unimolecular decomposition [10], then the activation energy,  $E_{4a}$  is about  $60 \text{ kJ mol}^{-1}$ .

The formation of ethylene in the photolysis of compounds with bidentate neutral ligands is consistent with the view that the substituted propyl ion-radical (C) is an intermediate, since carbon-carbon fission can give  $\text{C}_2\text{H}_4$ , viz.



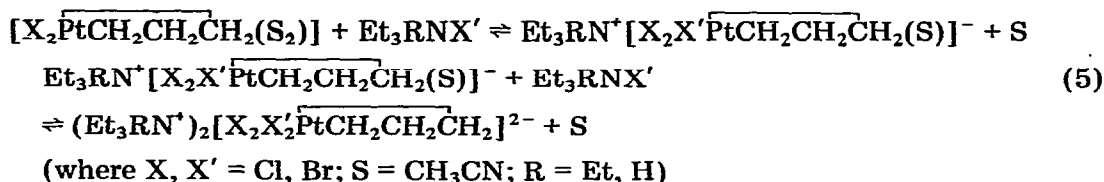
The ratio of ethylene/cyclopropane in the products of the photolysis in DMSO, is very variable, but the data indicate that  $k_{4c} < 0.1 k_{4a}$ . In the presence of tertiary phosphines the relative yield of ethylene may be as high as 60%, and even higher (up to 95%) in the dark. In view of this special effect of phosphines we intend to report the results separately. Ephritikhine and Green [5] have found that photolysis of the metallocyclobutane compound  $[\text{WCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\eta\text{-C}_5\text{H}_5)_2]$  ( $\eta\text{-C}_5\text{H}_5 = \text{cyclopentadienyl}$ ) in hexane solution gives mainly ethylene, with some propene and a little methane. They suggest that absorption of radiation causes a  $\eta^5\text{-C}_5\text{H}_5$  to  $\eta^3\text{-C}_5\text{H}_5$  ring shift giving a 16-electron intermediate which allows the rearrangement of the cyclobutane ring to occur, viz.



The monodentate ligand methyl cyanide coordinates only loosely to the platinum as shown by the observation that removal of the solvent in vacuo gives the original tetramer from which the solution was prepared (see experimental). The large yield of cyclopropane in the absence of additives (Nos. 18, 21), compared to those from the compounds containing bidentate ligands (Nos. 11, 16, 17) indicates that the mechanism of cyclopropane formation is somewhat different from that given in Scheme 1, presumably because of the ease of removal of  $\text{CH}_3\text{CN}$ , although a platinumpropyl radical may again be involved since ethylene is also a product when  $\text{X} = \text{Cl}$  (No. 18).

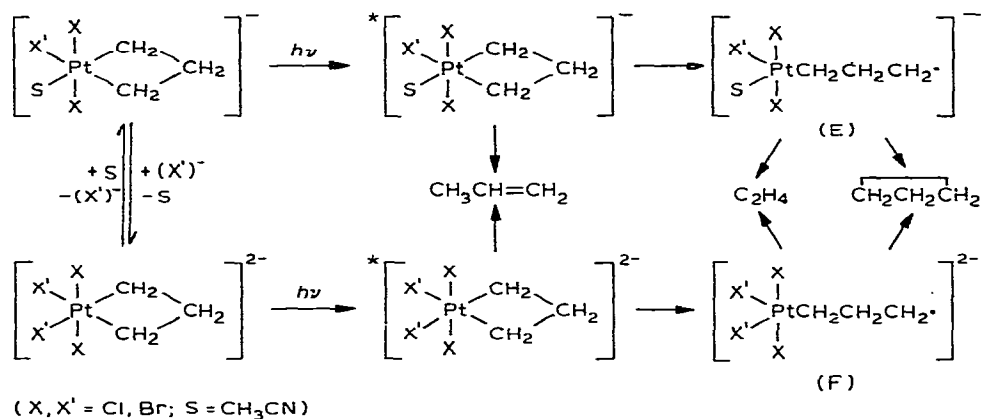
In the presence of the ammonium salts the relative yield of cyclopropane is reduced and the yields of propene and ethylene are increased (Nos. 18–23). In fact, the proportion of  $\text{C}_2\text{H}_4$  in the products (up to 25 mol%) is usually higher than with any other system. (Photolysis of  $\text{Et}_3\text{NHCl}$  or  $\text{Et}_4\text{NBr}$  in  $\text{CH}_3\text{CN}$  solu-

tion yields negligible amounts of hydrocarbons). Since  $[\text{pyH}^+(\text{Cl}_3\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{py}})^-]$  is precipitated when an ethereal solution of HCl is added to a solution of  $[\text{Cl}_2\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{py})_2}]$  in  $\text{CHCl}_3$  [11], the ammonium salts are likely to donate halide ions to the platinum. However, since the products vary with the ratio ( $\geq 2$ ) added salt/Pt (Nos. 19, 20), the relative yields of propene and ethylene increasing as the ratio is increased, it appears likely that in  $\text{CH}_3\text{CN}$  solution the following equilibria are set up, viz.



Although a proportion of the products may still come from the photolysis of the neutral species, most of the propene and ethylene and probably at least some of the cyclopropane must be formed by interaction of radiation with the negative ions. A possible mechanism is shown in Scheme 2. The relative

SCHEME 2



amounts of products formed from the neutral platinum species and the two negatively charged platinum species will depend on the equilibrium constants of the two equilibria (5), the rate coefficients for photolysis of the three species and the concentration of "free" halide ion present. If the platinum substituted propyl radical-ions E and F are indeed intermediates, then the data show that their decomposition to  $\text{C}_2\text{H}_4$  is more favoured if either X (the halide in the original platinacyclobutane) or X' (from the ammonium halide added), or preferably both, are Cl rather than Br.

## Experimental

Published methods were used to prepare the platinum compounds [11].  $[\text{X}_2\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2}]_4$  (X = Cl, Br) were dissolved in methyl cyanide, or in solutions of  $\text{Et}_3\text{NHCl}$  or  $\text{Et}_4\text{NBr}$ , giving systems containing the monomers

$[\text{X}_2\text{PtCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3\text{CN})_2]$  (See Nos. 18–23, Table 1).

Solutions of the platinum compounds, with additive if appropriate, were placed in a special cell with an arrangement for direct gas sampling, as described previously [6,12]. The system was evacuated and the solutions degassed. At the end of the photolyses, samples of the volatile products were removed in a pressure-lock gas-syringe and analysed by GLC-mass spectrometry using a 9 ft. 12% squalane on Chromosorb P column at 30°C. The solvent vapour present did not interfere.

### Acknowledgement

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