Journal of Organometallic Chemistry, 195 (1980) 105—112

THE REACTION OF PLATINACYCLOBUTANES WITH PHOSPHINES *

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

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

(Received March 5th, 1980)

Summary

The volatile products of the thermal and photochemical reactions of phosphines ($Ph_2PCH_2PPh_2$, PPh_3, $PHPh_2$) with the platinacyclobutane compounds $[X_2\overline{PtCH_2CH_2CH_2}\ (N{-}N)]$ (where X = Cl, Br and N—N = 1,10-phenanthroline, 2,2'-bipyridine, $(CH_2NMe_2)_2$) in several solvents have been determined. The hydrocarbons formed were ethylene, propene and cyclopropane with small amounts of methane, and also propane with $PHPh_2$. Very high relative yields of C_2H_4 (over 80%) were obtained under some conditions, notably with CH_3CN and $(CH_3)_2SO$ as solvents. Chloromethane (or bromomethane) was also produced with DMSO as solvent. It is suggested that the formation of ethylene involves dissociation of a halide ion and is accompanied by the production of platinum ylids. Hydrogen transfer from $PHPh_2$ can lead to the formation of C_3H_8.

Introduction

The gaseous products of the photolysis of platinacyclobutanes in solution at 25°C are mainly propene and cyclopropane, with only a little ethylene, under nearly all conditions [1]. However, it was found that the photodecomposition of $[Cl_2\overline{PtCH_2CH_2CH_2}$ (1,10-phenanthroline)] in dimethylsulphoxide in the presence of excess triphenylphosphine not only gave a considerable yield of ethylene but also appreciable amounts of chloromethane. A check of the thermal reaction showed that it was very slow at 25°C (as expected, c.f. ref. 2) but that the relative yield of C_2H_4 was even higher. This extensive carbon—carbon bond fission in the C_3H_6 moiety is of considerable interest in view of the postu-

(Continued on p. 108)

---

* Publication No. 221 from Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Canada.

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

TABLE 1.

PRODUCTS OF THE THERMAL REACTION OF PLATINACYCLOBUTANE COMPOUNDS $[X_2\overline{PtCH_2CH_2CH_2}(N{-}N)]$ WITH PHOSPHINES IN SOLUTION

Concentration of Pt compound ~2 × 10^{-3} mol l^{-1}

No.	Pt Compound [a]		Phosphine [b] (+additive)	Temp (°C)	Reaction time (h)	Volatile Products (mol%)				
	X	(N-N)				CH_4	C_2H_4	$CH_3CH{=}CH_2$	$\overline{CH_2CH_2CH_2}$	C_3H_8
Solvent, CH_2Cl_2										
1	Cl	phen	None	18	60	—	1	96	3	—
2	Cl	phen [c]	PPh_3	20	1	2	7.5	83	7.5	— [d]
					18	3	30.5	53	13.5	—
					24	3	47.5	35	14.5	—
					42	3	47	24	26	—
3	Cl	phen [c]	BDPM	20	1.5	2	9.5	79	9.5	— [d]
					18	2	25.5	65	7.5	—
					24	1	43	49	7	—
					42	2	51.5	36	10.5	—
4	Cl	phen	Ph_2PH	20	28	11 [e]	4.5	45	36.5	3
5	Br	phen	None	18	60	1	1	84	14	—
6	Br	phen	PPh_3	17	17	20	55.5	13.5	11	—
7	Br	phen	PPh_3	35–40	1	17	15	57	11	—
8	Br	phen	BDPM	17	17	2	40 [f]	54	4	—
9	Br	phen	BDPM	35–40	1	—	11	85	4	—
10	Br	Phen	BDPE	18	20	—	16.5	77	6.5	—
11	Br	phen	Ph_2PH	20	24	4 [e]	1	14	67	14
Solvent, o-$C_6H_4Cl_2$										
12	Cl	phen	PPh_3 or BDPM	17	18	4	3	86	7	—
13	Cl	phen	Ph_2PH	20	3	12	2	34.5	49	2.5
14	Br	phen	None	17	24	—	—	94	6	—
15	Br	phen	PPh_3	17	20	—	38.5	14.5	47	—
16	Br	phen	BDPM	18	48	—	5.5	90.5	4	—
17	Br	phen	BDPM(+phen)	18	48	—	15.5	80.5	4	—
18	Br	phen	Ph_2PH	20	3	2	—	4	13	81

Solvent, CH_3CN									
19	Cl	phen	None	18	60	2	1	92.5	4.5	—
20	Cl	phen	PPh_3	18	24	—	65	32	3	—
21	Cl	phen	BDPM	18	24	—	79	17	4	—
22	Cl	bipy	PPh_3	18	20	—	33.5	32	34.5	—
23	Cl	TMED	PPh_3	18	20	—	—	23	77	—
24	Br	phen	None	18	60	7	11.5	15.5	66	—
25	Br	phen	PPh_3	18	17	1	87 [g]	2	10	—
26	Br	phen	BDPM	18	17	8	88 [g]	2	2	—
27	Br	phen	Ph_2PH	17	4	—	1	30	14	55
28	Br	bipy	PPh_3	17	18	—	20	46	34	—
Solvent, 2 vol. CH_3CN + 1 vol. $(CH_3)_2CO$										
29	Br	phen	PPh_3	18	70	3	74	19	4	— [h]
Solvent, $(CH_3)_2SO$										
30	Cl	phen	None	17	24	—	1.5	65.5	33	—
31	Cl	phen	PPh_3	18	20	—	60	31	9	— d_2
32	Cl	phen	BDPM	25	48	—	80	15	5	— d_2
33	Cl	phen	BDPM	65	1.5	2	14.5	19.5	64	— d_2
34	Cl	phen	BDPM(+Et_3NHCl)	25	48	—	~5	~90	~5	—
35	Cl	phen	Ph_2PH	17	22	— [j]	0.5	31.5	9.5	58.5
36	Br	phen	None	17	24	—	—	~50	~50	—
37	Br	phen	PPh_3	25	48	—	85.5	10	4.5	— [k]
38	Br	phen	PPh_3	60	1	— [j]	29	28.5	28.5	14
39	Br	phen	PPh_3(+Et_4NBr)	25	48	—	46.5	40	13.5	— [k]
40	Br	phen	BDPM	20	24	—	86.5	3	10.5	—
41	Br	phen	BDPM	60	2	—	25.5	60	14.5	—
42	Br	phen	Ph_2PH	17	22	— [j]	—	17	1	82

---

[a] phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine, TMED = tetramethylethylenediamine. [b] 20 mol of phospine (and 20 mol additive) to 1 mol Pt compound. BDPM = bis(diphenylphosphino)methane, BDPE = (1,2)bis(diphenylphosphino)ethane. [c] System degassed between each determination of volatile products. [d] CH_3Cl also produced. d_1, trace; d_2 appreciable yield. [e] No gaseous products are formed in the absence of the Pt compound. [f] With CD_2Cl_2 as solvent ethylene formed contains a small proportion of CH_2CD_2. [g] With CD_3CN as solvent ethylene >95% C_2H_4. [h] No $(CH_3)_2C{=}CH_2$ detected in products. [j] Methane formed in absence of Pt compound, and therefore ignored in calculation of yields. [k] CH_3Br also formed.

lated role of metallacyclobutanes in the mechanism of olefin metathesis [3]. Thus, it was decided to investigate the effect of phosphines on the decomposition of platinacyclobutanes in some detail and the results are reported here.

Results and discussion

Typical data on the products of the thermal and photolytic reactions of $[X_2\overline{PtCH_2CH_2CH_2}(N{-}N)]$ (X = Cl, Br and N—N = 1,10-phenanthroline, 2,2'-bipyridine and tetramethylethylenediamine) with phosphines are collected in Tables 1 (thermolysis, including the results of very slow decomposition in the absence of phosphines) and 2 (photolysis). The individual yields quoted (when over about 20%) were reproducible to approximately 5 in the last figure.

The thermal or photolytic decomposition in the absence of added phosphines gives only small relative yields of ethylene (Table 1, Nos. 1, 5, 14, 19, 24, 30, 36; and ref. 1). Ethylene was still a minor product of the photolysis in the presence of excess $AsPh_3$ or $SbPh_3$ [1], and it was found that this was also so for the thermal reaction. Since with added diphenylphosphine the yield of C_2H_4 is still low (Table 1, Nos. 4, 11, 13, 18, 27, 35, 42), it appears that exten-

TABLE 2

PRODUCTS OF THE PHOTOREACTION OF PLATINACYCLOBUTANE COMPOUNDS $[X_2\overline{PtCH_2CH_2CH_2}(N{-}N)]$ WITH PHOSPHINES IN SOLUTION AT 25°C

Concentration of platinum compound $\sim 6 \times 10^{-3}$ mol l^{-1}; photolysis time ~3 h

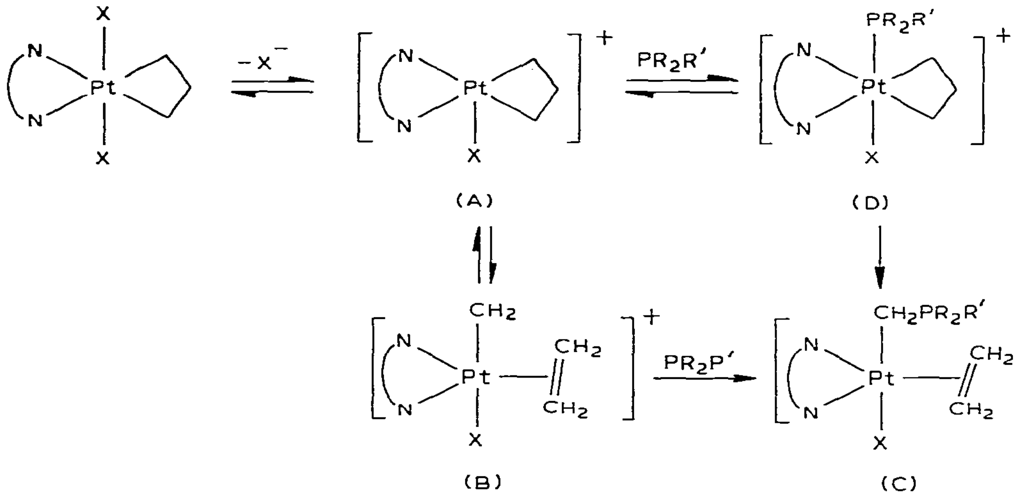
No.	Pt compound [a]		Phospine [b]	Volatile products (mol%) [c]			
	X	(N—N)		C_2H_4	$CH_3CH{=}CH_2$	$\overline{CH_2CH_2CH_2}$	others
Solvent, CH_2Cl_2							
1	Cl	phen	20 PPh_3	—	>99	—	
2	Cl	bipy	20 PPh_3	4.5	89.5	6	
Solvent, CH_3CN							
3	Cl	phen	20 PPh_3	23	68	9	
4	Cl	bipy	20 PPh_3	23	52.5	23	C_3H_8 (1.5)
5	Cl	phen	20 BDPM	60.5	27.5	12	[d]
6	Cl	bipy	20 BDPM	20.5	69.5	10	
7	Cl	TMED	25 BDPM	—	28	72	
Solvent, $(CH_3)_2SO$							
8	Cl	phen	20 PPh_3	41	42	17	C_3H_8 (2), CH_3Cl [e,f]
9	Cl	phen	20 PPh_3 +10 Me_4NCl	6	63	31	CH_3Cl [f]
10	Cl	phen	20 PPh_3 +40 Et_3NHCl	30	63	7	CH_3Cl [f]
11	Cl	phen	20 BDPM	65	12.5	22.5	CH_3Cl [f]
12	Cl	phen	20 BDPM +25 phen	70	10	20	CH_3Cl [f]
13	Br	phen	25 PPh_3	4.5	66	29.5	

---

[a] phen = 1.10-phenanthroline, bipy = 2,2'-bipyridine, TMED = tetramethylethylenediamine. [b] No. gives mol additive per mol Pt compound. BDPM = bis(diphenylphosphino)methane. [c] With DMSO as solvent a little methane is formed, but photolysis in the absence of Pt compounds also gives methane. [d] When the solvent was 3 CH_3CN/1 cyclohexane no norcarane was detected in solution. [e] With $(CD_3)_2SO$ the chloromethane formed is CD_3Cl; all other products are undeuterated. [f] The yields of chloromethane are appreciable.

sive carbon—carbon bond fission in the C_3H_6 moiety is promoted specifically by tertiary phosphines. This promotion of ethylene formation decreases markedly as the bidentate ligand is changed from phen to bipy to TMED (Table 1, Nos. 20, 22, 23, 25, 28; Table 2, Nos. 5, 6, 7), becoming more flexible and able to partially dissociate leaving a vacant coordination site on the platinum *trans* to the C_3H_6 moiety. Attachment of phosphines at such a site leads to cyclopropane formation [1,2]. Since complete dissociation of the neutral ligands gives two vacant *trans* sites it seems most unlikely that this precedes ethylene formation and, in fact, addition of phenanthroline certainly does not reduce the relative yield of C_2H_4 (Table 1, Nos. 16, 17; Table 2, Nos. 11, 12).

Considering the thermal reaction first, the data in Table 1 show that, under comparable conditions, ethylene formation is promoted by the solvents of relatively high dielectric constant, suggesting that ionisation of a halide ligand (leaving a *cis* vacant site) is involved. The dramatic reduction in the ethylene yield on addition of Et_3NHCl to the $[\mathrm{Cl_2\overline{PtCH_2CH_2CH_2}}\ (\mathrm{phen})]$/BDPM/DMSO system (Table 1, Nos. 32, 34) strongly supports this hypothesis. The results with the dibromoplatinacyclobutane were not so clear-cut, but, under most conditions, addition of excess bromide did lead to a decrease in the relative yield of C_2H_4 (see Table 1, Nos. 37, 39 for an example). Possible mechanisms for ethylene formation are given below (X = Cl, Br; R = Ph, R′ = Ph, Ph_2PCH_2):

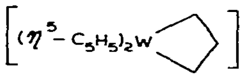


(1

The species A is coordinatively unsaturated and could rearrange to the carbene-alkene complex B followed by trapping of the carbene by phosphine to give the ylid species C, which would then undergo loss of ethylene *. In the presence of the large excess of phosphine further displacement of phenanthroline from platinum might also be expected and would lead to ylids of the type $[PtX(CH_2L)L_2]^+$ which have recently been prepared by Moss and Spiers and shown to be stable compounds when L = PPh_3 and X = Cl, Br, I [5]. How-

---

* A similar mechanism has been proposed to account for the formation of ethylene from



[4].

ever, the proposed ylid complexes could not be positively characterised in the presence of the large excess of tertiary phosphine needed for the reactions.

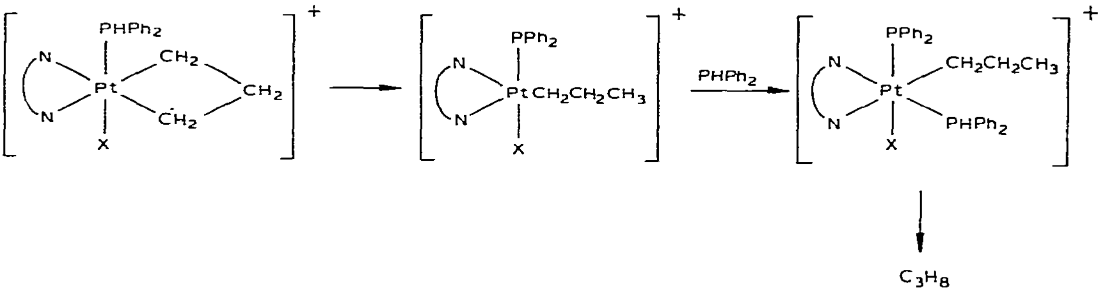
The formation of the ionic ylids C will be favoured in the solvents of relatively high dielectric constant which promote ethylene production. If the ylids are stable it is not surprising that they will not undergo the Wittig reaction [6] with acetone at room temperature (see Table 1, No. 29 and footnote [h]). However, the formation of CH_2CD_2 with CD_2Cl_2 as solvent (Table 1, No. 8 and footnote [f]) can be explained by a slow reaction of the ylid with the CD_2Cl_2 as phosphorus ylids are known to react with the halogenated alkanes [6]. It is also possible that at least some of the small yields of methane in the products is formed via the ylids.

It is also possible that coordination of phosphine to A occurs to give D which then rearranges to C, but there are no precedents for this reaction and there is no obvious mechanism by which the C—C bond cleavage could occur. There is, however, some evidence that the tertiary phosphine plays a direct part in the C—C bond cleavage since other bases (e.g. pyridine, DMSO) which are capable of trapping carbene-complexes to give stable ylid derivatives [7,8] do not promote the formation of ethylene from platinacyclobutanes.

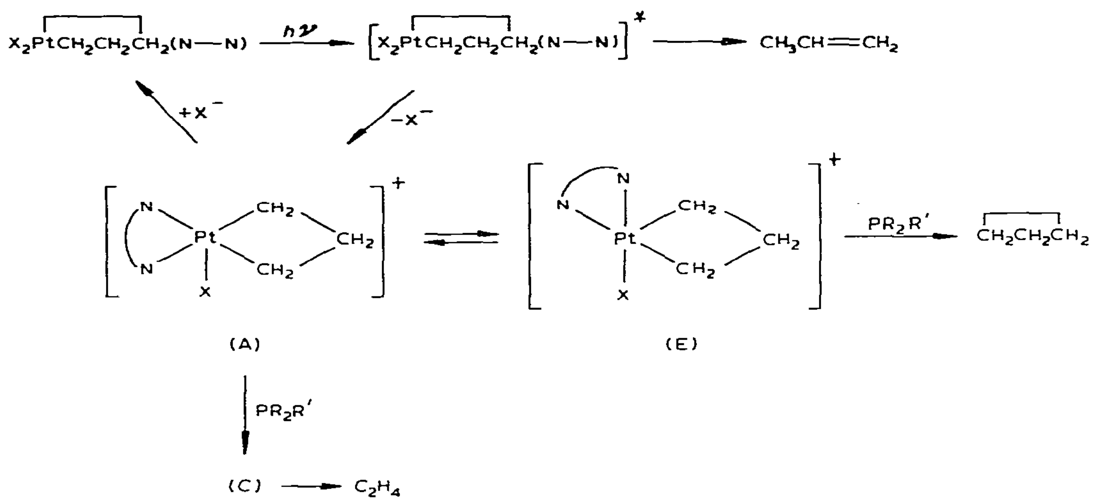
With dimethylsulphoxide as solvent the reaction gives considerable yields of chloromethane or bromomethane (Table 1; Nos. 31—33, 37, 39), and use of $(CD_3)_2SO$ shows that the methyl group comes from the solvent, but virtually no ethylene or halomethane is formed in the absence of phosphine. Thus, although oxosulphonium ylid complexes are known [7], it is unlikely that DMSO reacts directly with B to give an ylid complex. Presumably DMSO reacts with C or products arising from this to give a complex which can undergo loss of methyl halide by attack of halide on a methyl group of co-ordinated DMSO.

Raising the reaction temperature generally decreases the relative ethylene yield markedly and increases the propene and the cyclopropane yields relative to C_2H_4 (Table 1; Nos. 8, 9, 32, 33, 37, 38, 40, 41). This indicates that dissociation of the phenanthroline ligand (leading to the formation of the C_3 hydrocarbons) has a higher activation energy than the ionisation of the platinacyclobutanes, which precedes ethylene formation.

The reactions with diphenylphosphine give little ethylene but considerable yields of propane under some conditions (Table 1; Nos. 11, 18, 27, 35, 42), the hydrogen atoms transferred to the C_3H_6 moieties almost certainly coming from the phosphine. Secondary phosphines do not appear to give stable ylids [6], presumably because hydrogen transfer leading to the corresponding tertiary phosphines is rapid. Thus, the addition of $PHPh_2$ to the ionic intermediate A, mechanism 1, does not cause fission of the C_3 moiety, but hydrogen may be transferred and propane eventually formed by a mechanism such as



Comparison of the variation of the ethylene yields with conditions for the thermal and photochemical reactions (Tables 1 and 2) show some differences, notably that, in the photolysis, appreciable yields are not obtained with the bromoplatinum compound. However, with the dichloro compound formation of C_2H_4 is again promoted by solvents of relatively high dielectric constant under conditions when, in the absence of phosphines, cyclopropane is a major product [1]. It seems likely, therefore, that ionisation (in this case of the excited molecule) again precedes ethylene formation (c.f. ref. 1), and addition of excess chloride does increase the yield of propene relative to the combined yield of C_2H_4 and cyclopropane (Table 2; Nos. 8, 9, 10). Thus a mechanism, Scheme 1 in ref. 1 for the photolysis in the absence of phosphines and on mechanism 1 above, seems reasonable and is summarised below (X = Cl, Br; R = Ph, R' = Ph, Ph_2PCH_2):



The reaction of intermediate C to give ethylene will occur as in mechanism 1. It seems not unreasonable to assume that the same platinum ylids are formed as proposed for the thermal reaction. If so, then they appear to be photolytically stable since no norcarane is detected in the products in the presence of cyclohexene. The use of $(CD_3)_2SO$ shows that a methyl group is again removed from the solvent to form chloromethane as in the thermal reactions discussed earlier. The interconversion of the ionic species A, with a *cis* vacant coordination site, and E, with a *trans* vacant site, was suggested earlier [1] to account for the results of the photolysis in the absence of phosphines. Perhaps this interconversion occurs only in the photolysis because I is still excited to some extent after the dissociation. The relatively high $C_2H_4/\overline{CH_2CH_2CH_2}$ ratio with the dichloro compound in DMSO but low ratio with the dibromo compound (Table 2, Nos. 8, 13) could then be due to I being favoured with respect to II when X = Cl but II being strongly favoured with respect to I when X = Br (c.f. ref. 1).

Experimental

Literature methods were used to prepare the platinum compounds [9]. The method of photolysis and of determining the volatile products were as previously described [1]. Chloromethane was also separated and estimated using the squalane column.

Acknowledgements

Two of us (D.C.L.P. and M.C.R.) thank the Science Research Council for maintenance grants. We thank NATO for a travel grant (to RJP and CFHT).

References

1 D.C.L. Perkins, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 186 (1980) 419.
2 P.W. Hall, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 84 (1975) 407.
3 See, for example, R.H. Grubbs, Progr. Inorg. Chem., 24 (1978) 1.
4 M. Ephritikhine and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1976) 926.
5 J.R. Moss and J.C. Spiers, J. Organometal. Chem., 182 (1979) C20.
6 H.J. Bestmann and Z. Zimmermann in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorous Compounds, Vol. 3, John Wiley, New York, 1972, p. 1.
7 J.P. Fackler and C. Paparizos, J. Amer. Chem. Soc., 99 (1977) 2363.
8 R.J. Al-Essa and R.J. Puddephatt, J. Chem. Soc. Chem. Comm., (1980) 45.
9 P.W. Hall, R.J. Puddephatt, K.R. Seddon and C.F.H. Tipper, J. Organometal. Chem., 81 (1974) 423; F. Iwanciw, M.A. Quyser, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 113 (1976) 91.