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THE PHOTODECOMPOSITION OF PLATINACYCLOALKANES IN SOLUTION

II *. 1,4-BUTANEDIYLPLATINUM(II) AND (IV) COMPOUNDS

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Summary

The products of the photolysis of a number of platinacyclopentanes in solution at 25°C under a variety of conditions have been determined. With $[I_2\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$ ($L = PMe_2Ph, PPh_3$) in CH_2Cl_2, CH_2Br_2 and $(CH_3)_2SO$ the hydrocarbon products are exclusively ethylene and but-1-ene. Formation of the latter through a 1,3-hydrogen shift is preceded by phosphine ligand dissociation. The photolysis of $[ICH_3\overline{PtCH_2CH_2C}H_2(L_2)]$ gave methane, ethylene, but-1-ene and n-pentane together with a little n-butane, the methane being formed from internal hydrogen abstraction by the CH_3 group in the excited reactant molecule. Photodecomposition of the platinum(II) compounds $[\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$ ($L = (PMe_2Ph)_2, (PPh_3)_2, Ph_2PCH_2CH_2PPh_2$) gave ethylene, but-1-ene, pent-1-ene (with the halogenated solvents) and with some systems appreciable yields of n-butane, the latter being the result of internal abstraction of two hydrogen atoms by the C_4H_8 moiety. The formation of pentene is probably preceeded by the addition of CH_2Cl_2 or CH_2Br_2 to the excited reactant molecule. Addition of diphenylphosphine promotes the production of n-butane.

Introduction

In Part I the results of a study of the gaseous products of the photolysis of platinacyclobutane compounds in solution were presented and discussed. In this part we report data on the products of the photodecomposition of platina-

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cyclopentane compounds, Pt^{II} and Pt^{IV}. Although considerable interest has been shown recently in the thermal decomposition of metallacyclopentanes [1], only a small amount of photolytic work (on nickelacyclopentanes) has been reported [1c].

Results and discussion

The platinum compounds of the general formulae, $[\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$, $[I_2\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$ and $[IMe\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$, (where L_2 = $(PMe_2Ph)_2$, $(PPh_3)_2$, $Ph_2PCH_2CH_2PPh_2$), were photolysed in solution at 25°C and the data on the products are presented in Table 1. The individual yields quoted (when over about 20%) are probably accurate to 5 in the last figure (see Part 1), except with one system (see below). Any purely thermal reaction was negligible during the photolysis time (<2 h).

Reductive elimination giving cyclobutane was negligible with any system, whereas the products of the photolysis of nickelacyclopentanes in toluene contain a high proportion of cyclobutane [1c] and cyclopropane is formed in the photolysis of platinacyclobutanes (Part I). It appears that carbon—carbon bond fission (giving ethylene) and/or a hydrogen atom shift (giving but-1-ene) in excited platinacyclobutane species are always much faster than cyclisation of the C_4H_8 moiety.

The results with $[I_2\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$ appear to be fairly straightforward. Except with diphenylphosphine present, the gaseous products are exclusively ethylene and but-1-ene, the ratio being independent of solvent within experimental error. (Nos. 15, 17, 18, 19). No ethane or n-butane were detected even when the solvent contained deuterotoluene, a relatively good deuterium donor, indicating that free radical type intermediates are not involved. However, addition of excess neutral phosphine ligand suppressed the production of $1\text{-}C_4H_8$ (c.f. Nos. 15 and 16, 22 and 23), suggesting that dissociation of L precedes butene formation *. On the other hand, the small effect of added Et_4NI with DMSO as solvent (Nos. 19, 20) indicates that ionization (giving I^-) is not important in product formation (c.f. platinacyclobutanes, Part I). The mechanism therefore probably consists essentially of two simultaneous processes (a and b, Scheme 1), the 1,3-hydrogen shift in the $(CH_2)_4$ moity involving a vacant coordination site on the platinum, as with the thermal decomposition [2] but in contrast to the mode of formation of propene in the photolysis of platinacyclobutane compounds (Part I). It is interesting to note that, with nickelacyclopentanes, the coordinately saturated compounds $L_3\overline{NiCH_2CH_2CH_2C}H_2$ (L = R_3P, Ar_3P) decompose thermally to give ethylene, while $L\overline{NiCH_2CH_2CH_2C}H_2$ undergo β-elimination giving but-1-ene [1c].

The higher relative yield of ethylene for the photolysis in CH_2Cl_2 when L is changed from dimethylphenylphosphine to triphenylphosphine (Nos. 15,22) indicates that route a is more favoured with respect to route b as the size of the

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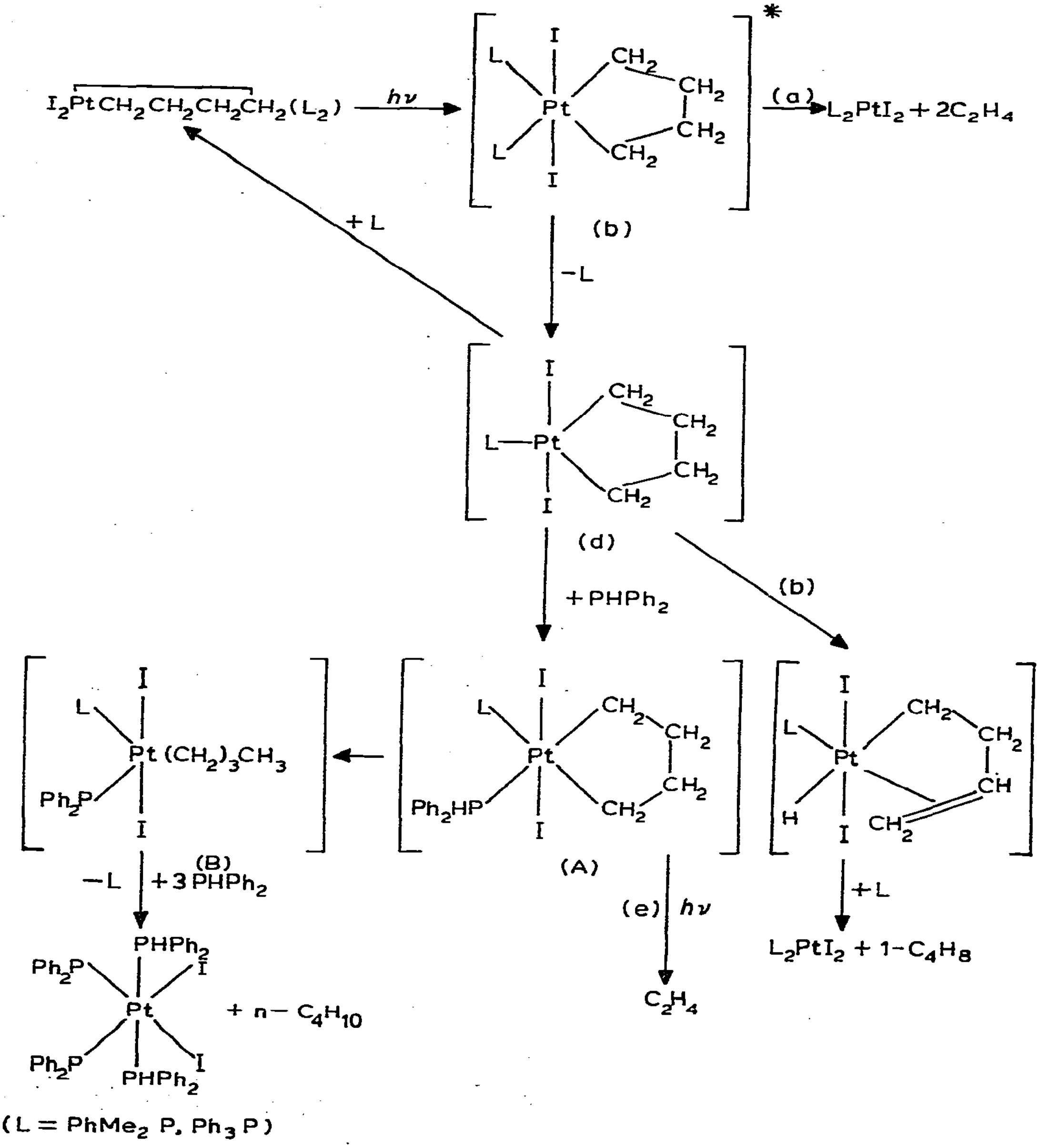
* It was hoped to check this using $[I_2\overline{PtCH_2CH_2CH_2C}H_2(Ph_2PCH_2CH_2PPh_2)]$, the photolysis of which would be expected to give only ethylene, but the C_4H_8 moity is eliminated when $[\overline{PtCH_2CH_2CH_2C}H_2(Ph_2PCH_2CH_2PPh_2)]$ reacts with iodine in solution at room temperature (see Experimental).

SCHEME 1



phosphine ligand is increased. Diphenylphosphine suppresses the formation of but-1-ene, as expected, since it will act as a monodentate ligand like L (reaction d, which may be followed by e). However, an appreciable yield of n-butane is obtained (No. 21), and it is suggested that hydrogen can be transferred in the coordinately saturated intermediate, A, to give a five-coordinate platinum butyl species, B, which reacts further with $PHPh_2$ to give $n\text{-}C_4H_{10}$.

There is no obvious explanation of the irreproducibility of the yields of gaseous products from the photodecomposition of $[\overline{IMePtCH_2CH_2CH_2CH_2}$-

(Continued on p. 486)

TABLE 1

PRODUCTS OF THE PHOTOLYSIS OF PLATINACYCLOPENTANES IN SOLUTION AT 25°C

(Concentration of Pt compound ~ 10^{-2} mol l^{-1}).

No.	Pt compound L_2	Solvent [a]	Products (mol%) [b]				
			CH_4	C_2H_4	$1\text{-}C_4H_8$	$n\text{-}C_4H_{10}$	Others [c]
	$[\overline{PtCH_2CH_2CH_2CH_2}(L_2)]$						
1	$(PMe_2Ph)_2$	CD_2Cl_2	—	95	5	T	C_2H_6(T), pent-1-ene, $Cl_2Pt(PMe_2Ph)_2$
2		CH_2Cl_2/PMe_2Ph (2:1)	d	79	14.5	6.5	
3		$CH_2Cl_2/C_6D_5CD_3$ (1:1)	—	93	7	T	C_2H_6(T)
4		CH_2Cl_2/CH_2Br (1:1)	—	73	27	—	$1\text{-}C_5H_{10}$
5		CH_2Br_2	—	73	27	T	$1\text{-}C_5H_{10}$
6		DMSO	—	70.5	29.5		
7		DMSO/$PHPh_2$ (1:1)	d	~0.5	5.5	94	
8	$(PPh_3)_2$	CH_2Cl_2	—	64.5	30.5	5	$1\text{-}C_5H_{10}$
9		$CH_2Cl_2 + PPh_3$ [e]	—	74	15	11	
10		CH_2Br_2	—	86	14	—	$1\text{-}C_5H_{10}$
11		DMSO	—	64	22	14	
12	CH_2PPh_2	CH_2Cl_2	—	71	16	13	$1\text{-}C_5H_{10}$
13	CH_2PPh_2	CH_2Br_2	—	80.5	16.5	3	$1\text{-}C_5H_{10}$
14		$(CD_3)_2SO$	—	14	51	35	C_2H_6(T)

	$[I_2\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$						
15	$(PMe_2Ph)_2$	CH_2Cl_2	—	70	30	—	$I_2Pt(PMe_2Ph)_2$
16		CH_2Cl_2/PMe_2Ph (2:1)	d	>99	<1	—	
17		$CH_2Cl_2/C_2D_6CD_5$ (3:2)	—	71.5	28.5	—	No D in products
18		CH_2Br_2	—	73	27	—	
19		DMSO	—	74	26	—	
20		DMSO + Et_4NI [e]	—	66	34	—	
21		DMSO/$PHPh_2$ (1:1)	d	86	—	14	
22	$(PPh_3)_2$	CH_2Cl_2	—	87	13	—	
23		$CH_2Cl_2 + PPh_3$ [e]	—	99	1	—	
	$[ICH_3\overline{PtCH_2CH_2CH_2C}H_2(L_2)]$						
24	$(PMe_2Ph)_2$	CH_2Cl_2 [f]	25 to 68	21 to 26	11 to 49	T to 4	C_2H_6(T)
		DMSO [f]	14 to 55	12 to 25	20 to 62	—	C_2H_6(T)
25	$(PPh_3)_2$	CH_2Cl_2	72	1	26	1	
		$CD_2Cl_2/C_6D_5CD_3$ (1:1)	60	3	35.5	15	CD_2HCl, n-C_5H_{12}

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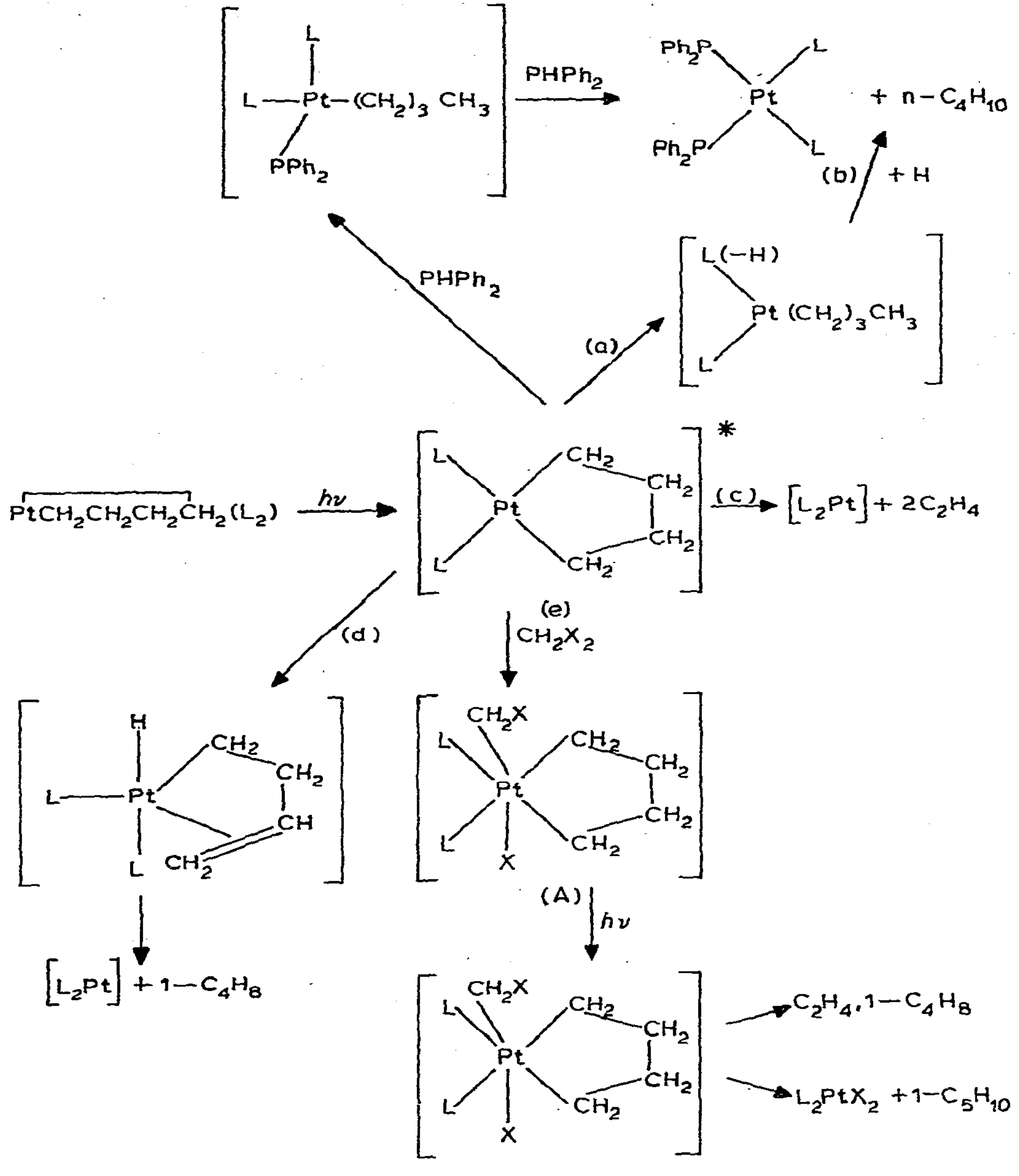
[a] DMSO = $(CH_3)_2SO$. Mixed solvents, volume ratio in parentheses. [b] T = trace. No cyclobutane was detected (see Experimental). [c] Yield of 1-C_5H_{10} relative to gases not determined (see Experimental). [d] CH_4 produced from photolysis of solvent. [e] 20 mol additive per mol Pt compound. [f] Results irreproducible even when same sample of platinum compound and same batch of solvent used.

$(\mathrm{PMe_2Ph})_2]$. However, some general conclusions on the mechanism can be drawn from the results. Methane is a major product of the photolysis and appears to be formed by intramolecular hydrogen abstraction by the methyl group (rather than via free CH_3 radicals) since no CH_3D is produced with deuterated solvents. This is supported by the observation that the methane from the photolysis of $[\mathrm{ICD_3}\overline{\mathrm{PtCH_2CH_2CH_2CH_2}}(\mathrm{PMe_2Ph})_2]$ in $(CD_3)_2SO$ is entirely CD_3H. There is evidence that internal hydrogen abstraction to give CH_4 occurs during the photolysis of other methylplatinum(IV) compounds [3]. It seems likely that ethylene is formed by decomposition of an excited reactant molecule and but-1-ene from a 1,3-hydrogen shift involving a vacant coordination site on the platinum, as with the diiodide. However, loss of a methyl group leaves a five coordinate platinum species and thus it was found that $1\text{-}C_4H_8$ was still formed when ligand dissociation was suppressed by the addition of excess phosphine. Changing the neutral ligand from PMe_2Ph to PPh_3 certainly decreases the relative yield of ethylene markedly and appears to increase the yield of methane. Ignoring any n-pentane produced, if all CH_3 groups gave CH_4 and all C_4H_8 moieties gave C_2H_4 or $1\text{-}C_4H_8$, then mol% CH_4 should equal $\frac{1}{2}$ mol% C_2H_4 + mol% $1\text{-}C_4H_8$. This is very far from being the case and so either some of the methyl groups or some of the C_4H_8 moieties must end up in other than gaseous products. The formation of undeuterated n-pentane from the photolysis in a deuterated solvent (No. 26) indicates that the methyl group may add to the C_4H_8 moiety to give a n-pentyl group which abstracts hydrogen internally, giving $n\text{-}C_5H_{12}$. The formation of small amounts of undeuterated n-butane in the photolysis with the deuterated solvents suggests that homlytic Pt—C bond fission in the PtC_4H_8 moity may occur to a slight extent, being followed by internal hydrogen abstraction to give $n\text{-}C_4H_{10}$ (c.f. the platinacyclobutanes, Part I).

The platinum(II) compounds have, at least potentially, two vacant coordination sites so that but-1-ene formation should not require ligand dissociation (c.f. addition of excess L, Nos. 1, 2, 8, 9). Pent-1-ene is a product with the halogenated solvents and is probably formed via addition of CH_2X_2 ($X = Cl, Br$) to give a halomethylplatinum(IV) intermediate, as in the thermolysis [1e]. Unfortunately, the yield with CD_2Cl_2 as solvent (No. 1) was too low for the GLC-mass spectrometer to show definitely that the pentene was $1\text{-}C_5H_8D_2$. A special feature is the appreciable amount of n-butane produced with some systems. In the presence of diphenylphosphine the gaseous products (apart from methane) are almost exclusively $n\text{-}C_4H_{10}$ (No. 7), suggesting that $PHPh_2$ donates hydrogen very rapidly to excited reactant molecules. The mechanism shown in Scheme 2 seems reasonable.

Photodecomposition of the platinum(IV) compounds gives very small yields of butane. Thus, it is likely that photolysis of intermediateA also gives little or no $n\text{-}C_4H_{10}$, which is formed by steps a and b, both involving internal hydrogen abstraction since, with deuterated solvents, no deuterium is present in the gaseous products. The results show that step a increases greatly in importance with respect to those steps c, d and e which lead to the formation of ethylene and but-1-ene, as the phosphine ligand is changed from PMe_2Ph to PPh_3 to $(CH_2PPh_2)_2$. With the second and third ligand (Nos. 8—14) the relative yield of butane is highest when DMSO is the solvent because step e is not possible. With

SCHEME 2



(L = PMe_2Ph, PPh_3 $\frac{1}{2}$ $Ph_2PCH_2CH_2PPh_2$)

the halogenated solvents the higher yield of butane with dichloromethane (Nos. 8 and 10, 12 and 13) suggests that step e is faster with CH_2Br_2 than with CH_2Cl_2. This might account for the observation that the relative yields of ethylene and but-1-ene are the same when the solvent is CH_2Br_2 or a 1 : 1 mixture of CH_2Br_2 and CH_2Cl_2. A minor feature of interest is the increase in the relative yield of butane when excess PMe_2Ph or PPh_3 is added (Nos. 1 and 2, 8 and 9). This is difficult to explain, but one speculative suggestion is that the free phosphine occupies the two vacant coordination sites "above and below" the platinum atom in the square-planar platinacyclopentane molecule. Thus, route e tends to be blocked and also external hydrogen abstraction might be possible, giving $L_2PtC_4H_9$ and thus n-C_4H_{10}.

The fragments $[L_2Pt]$ (Scheme 2) presumably reacts with the halogenated solvents to give L_2PtX_2 (X = Cl, Br).

Experimental

The platinum(II) compounds were prepared by the reaction of Cl_2PtL_2 (L_2 = $(PMe_2Ph)_2$, $(PPh_3)_2$, $Ph_2PCH_2CH_2PPh_2$) with 1,4-dilithiobutane [2] and the platinum(IV) compounds by oxidative addition of iodine or methyl iodide to the platinum(II) compounds [2]. However the reaction of $[\overline{PtCH_2CH_2CH_2CH_2}(Ph_2PCH_2CH_2PPh_2)]$ with an equimolar amount of iodine in solution gave $[I_2Pt(Ph_2PCH_2CH_2PPh_2)]$, and ethylene, but-1-ene and n-butane were evolved.

The method of photolysis and of determining the gaseous products were as described previously [4]. After photolysis, samples of the solution were removed and analysed for liquid products by GLC-mass spectrometry using a 9 ft 10% carbowax on 20M TPA on embacel column at 50—150°C. The final solutions were evaporated to dryness in vacuo and the solid products identified by IR, UV and mass spectrometry.

Acknowledgements

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