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REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

XI *. FISSION OF THE C_3 MOIETY IN REACTIONS OF PLATINACYCLOBUTANES

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Summary

The reactions of the platinacyclobutanes $[X_2\overline{PtCH_2CHRCH}_2(1,10\text{-phenanthroline})]$ ($X = Cl, Br$; $R = H, CH_3$) with unsaturated compounds in methyl cyanide, dimethylformamide and dimethylsulphoxide at room temperature have been investigated. Tetracyanoethylene, and styrene and related olefins, promoted the fission of the C_3 moiety giving ethylene ($R = H$) and both ethylene and propene ($R = CH_3$). It is suggested that this gives support to the view that ionisation of a halide occurs in these solvents of relatively high dielectric constant and that the five-coordinate positively charged platinacyclobutane species is in equilibrium with a platinum-carbene-olefin complex.

Introduction

Reactions of platinum(IV) cyclobutanes in solution normally involve rearrangements of the C_3 moiety or its ejection as a whole from the molecule [1]. However, under certain conditions, in particular with solvents of relatively high dielectric constant (CH_3CN, Me_2SO) in the presence of phosphines (e.g. PPh_3), high yields of hydrocarbons (e.g. C_2H_4) from fission of the C_3 moiety are obtained [2,3]. The essential steps in the mechanism suggested [2] are shown in Scheme 1. Route $A \rightarrow B \rightarrow C \rightarrow C_2H_4$ was favoured on general grounds. In the absence of PPh_3 the equilibrium $A \rightleftharpoons B$ would be far over to the left and other reactions of the species A would be favoured, whereas the phosphine traps the carbene very efficiently to give the ylid species C and ethylene is formed.

If under appropriate conditions the platinacyclobutane ring is, in fact, in equi-

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[*] For part X see ref. 10.

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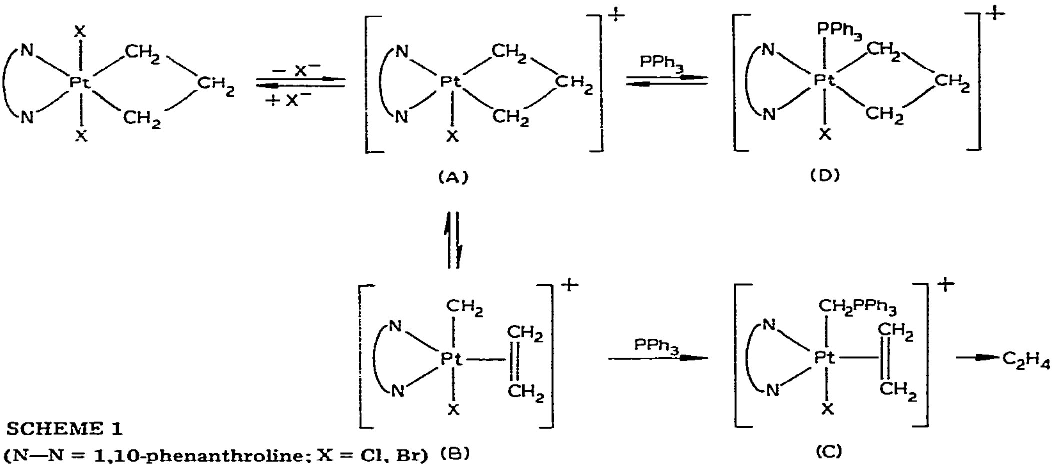
librium with a carbene-olefin complex then this provides independent support for a key step in the generally accepted mechanism of olefin metathesis [4].



SCHEME 1
(N—N = 1,10-phenanthroline; X = Cl, Br)

Thus we have investigated conditions under which fission of the C_3 moiety in $[X_2\overline{\text{PtCH}_2\text{CHRCH}_2}(1,10\text{-phenanthroline})]$ (X = Cl, Br; R = H, CH_3) occurs in the absence of phosphines with a view to determining the role played by intermediates such as B.

Results and discussion

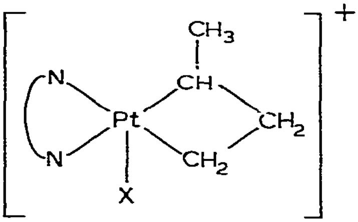
Earlier work [2,3] has shown that the very slow thermal decomposition of $[X_2\overline{\text{PtCH}_2\text{CHRCH}_2}(1,10\text{-phenanthroline})]$ (X = Cl, Br; R = H, CH_3) in CH_2Cl_2, o-$C_6H_4Cl_2$, CH_3CN and $(CH_3)_2SO$ in the absence of additive gave volatile products which contained <10—11% of hydrocarbons from splitting of the C_3 moiety, i.e. C_2H_4 when R = H, C_2H_4 and $CH_3CH{=}CH_2$ when R = CH_3. We have now found this to be so with dimethyl formamide as solvent also. Since unsaturated organic compounds can be efficient carbene traps [5] we have studied the effect of a variety of such compounds on the thermal decomposition.

Addition of hex-1-ene, cyclohexene, indene, phenylacetylene, vinyl acetate, diethylmaleate and the dimethyl ester of acetylene dicarboxylic acid (1 vol. additive + 6 vol. DMSO) did not increase the proportion of C_2H_4 in the volatile products of the decomposition of $[Br_2\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2}(1,10\text{-phenanthroline})]$. However, tetracyanoethylene and particularly styrene and related olefins did promote fission of the C_3 moiety in this and related platinacyclobutanes. The relevant data are given in Table 1 and include some typical results with phosphines added for comparison.

TCNE is nearly as efficient as phosphines in promoting ethylene formation with $[Br_2\overline{\text{PtCH}_2\text{CH}_2\text{CH}_2}(1,10\text{-phenanthroline})]$, (No. 6, 7, 20, 21), especially as the excess in DMSO during the reaction will be much less than that added initially (see note ^{e}). Styrene can promote a very high yield of splitting products (e.g. 12, 24, 37) but, of course, the ratio of the liquid additives to Pt compound is roughly 500 as compared to 20 with phosphines. The additives which promote splitting of the C_3 moiety are those which can associate with the platinum(IV) via the vacant coordination site in species A. TCNE has four CN groups and methyl cyanide, for example, can act as a ligand in platinacyclobutane compounds [6]. Also there is some evidence of a direct Pt—C_6H_5 interaction in compounds such as $[\mathrm{Cl_2\overline{PtCHPhCH_2C}H_2(C_5H_5N)_2}]$ in which the phenyl group is attached to a carbon atom α to the platinum [7]. On conversion of A to B this association would promote the addition of the carbene moiety to the double bond of the additive and the formation of the lower olefins. Unfortunately, it was not possible to detect the presence of cyclopropanes from the carbene addition due to the presence of the huge excess of additive.

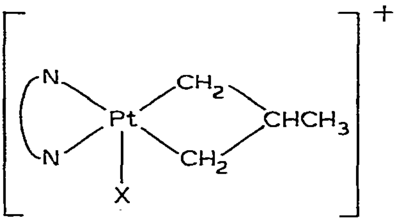
The smaller efficiency of *p*-substituted styrenes, β-methylstyrene, diphenylethylene and allylbenzene compared to styrene itself is probably due mainly to steric factors. Space filling models indicate that association of styrene itself, with the ring lying "flat" on top of the platinum, allows the double bond to come into the close proximity of the carbon atoms α to the Pt atom in the platinacyclobutane ring. This is not so easy with the other compounds.

Table 1 shows that, with the platinacyclobutanes derived from methylcyclopropane, the products of fission of the C_3 moiety contain both ethylene and propene. There are two isomers corresponding to A, viz.

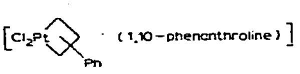


(Aα)

and



(Aβ)

The method of preparation of the original platinacyclobutanes probably leads to a mixture of isomers corresponding to Aα and Aβ, the proportions varying from sample to sample. However, in solution the isomeric ions may well be interconvertible and Aβ will almost certainly be the thermodynamically more stable isomer [3]. However, the ratio of ethylene to propene in the splitting products is usually greater than one with the olefinic additives and often very high (e.g. Nos. 22, 24, 27, 28, 36, 37, 40), indicating that the additive reacts preferentially with the least stable isomer, Aα, removing the CH_3CH moiety. It was found that the slow decomposition of  in the presence of styrene also gave relatively high yields of ethylene, indicating that again the additive attacks the α-isomer, $[\mathrm{Cl\overline{PtCHPhCH_2C}H_2(C_{12}H_8N_2)}]^+$, the CHPh moiety being removed. Other reactions of platinacyclobutanes from methylcyclopropane involve the least stable structural α-isomer [1].

It is difficult to see how olefins could cause fission of the ring directly by a route similar to A → D → C, and the results provide further evidence for the occurrence of metallacyclobutane ring carbene—olefin complex interconversion. In this connection, the compound $[\mathrm{\overline{PtCH_2CH_2C}H_2}$ (2,2′-bipyridine)], prepared recently by Kochi et al. [8], has been found to decompose to $\mathrm{(bipy)PtCH_2}^+$ and

TABLE 1

PRODUCTS OF THE THERMAL DECOMPOSITION OF PLATINACYCLOBUTANE COMPOUNDS IN SOLUTION IN THE PRESENCE OF ADDITIVES AT ROOM TEMPERATURE (≈20°C) Concentration of Pt compound ~2×10^{-3} mol l^{-1}

No.	Solvent [a]	Additive [b]	Reaction time (h)	Volatile products (mol %)				
				C_2H_4	$CH_3CH{=}CH_2$	$\overline{CH_2CH_2CH_2}$	$\overline{CH_2CHCH_3CH_2}$	C_4H_8 [c]
[Cl₂PtCH₂CH₂CH₂(1,10-phenanthroline)]								
1	CH_3CN DMF, DMSO	S(1/6) TCNE		<10% C_2H_4 with all systems				
2	DMF	PPh_3	500	54	17	29		
3	DMF	BDPM	500	49	43	8		
4	CH_3CN	BDPM	24	79	17	4 [d]		
5	DMSO	BDPM	48	80	15	5 [d]		
[Br₂PtCH₂CH₂CH₂(1,10-phenanthroline)]								
6	CH_3CN	TCNE	70	77	23	—		
7	DMSO	TCNE	18	32	68	— [e]		
8	DMF	S(1/6)	140	1	96	3		
9	CH_3CN	S(1/6)	72	14	79	7		
10	DMSO	S(1/12)	60	12	76	12		
11	DMSO	S(1/6)	46	37	59	4		
			114	56	39	5		
12	DMSO	S(1/3)	44	44	49	7		
			118	65	32	3		
13	DMSO	CMS(1/6)	44	22	69	6		
14	DMSO	PMS(1/6)	42	1.5	93	5.5		
15	DMSO	BMS(1/6)	32	23	55	22		
16	DMSO	AB(1/6)	20	38	42	20		
			44	24	32	44		
17	DMSO	DPE(1/6)	70	32	60	8		
18	DMSO	TPE	33	12	47	41		
19	DMF	BDPM	20	31	29	40		
20	CH_3CN	BDPM	17	88	2	2 (+ 8% CH_4) [d]		
21	DMSO	BDPM	24	86.5	3	10.5 [d]		

$[Cl_2\overline{PtCH_2CHCH_3C}H_2(1,10\text{-phenanthroline})]$								
22	DMF	S(1/6)	44	37	0.5	—	3.5	59
			142	56.5	—	—	6.5	37
23	CH_3CN	S(1/6)	46	—	10	—	27	63
24	DMSO	S(1/6)	46	58.5	2.5	—	19	20
			90	80	1.5	—	9.5	9
25	DMSO	PMS(1/6)	42	14.5	22	—	9.5	54
26	DMSO	BMS(1/6)	118	36	12.5	—	15	36.5
27	DMSO	AB(1/6)	118	27	2	—	34	37
28	DMSO	DPE(1/6)	44	27.5	3.5	—	38	31
			140	35.5	1.5	—	49.5	13.5
29	DMF	BDPM	70	13.5	4.5	—	58.5	23.5
30	CH_3CN	PPh_3	29	17	18	—	29	36 [f]
31	CH_3CN	BDPM	23	32	6	—	57	5 [f]
32	DMSO	PPh_3	25	25	27.5	—	16.5	31 [f]
$[Br_2\overline{PtCH_2CHCH_3C}H_2(1,10\text{-phenanthroline})]$								
33	CH_3CN	TCNE	94	5	4	—	67	24
34	DMF	S(1/6)	46	7.5	26	—	45.5	21
			140	27.5	16.5	—	43.5	12.5
35	CH_3CN	S(1/6)	47	5	14	—	62	19
36	DMSO	S(1/12)	68	37	5	—	50.5	7.5
			140	84	1	—	11.5	3.5
37	DMSO	S(1/6)	70	>95	—	—	—	—
38	DMSO	BMS(1/6)	110	5	55	—	21	19
39	DMSO	AB(1/6)	66	1	4	—	76	19
40	DMSO	DPE(1/6)	44	51	4.5	—	19.5	25
			166	80	2.5	—	13	4.5
41	CH_3CN	PPh_3	96	19	24	—	51	6 [f]
42	DMSO	PPh_3	170	10	40.5	—	42.5	7 [f]

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[a] DMF = dimethylformamide, DMSO = dimethylsulphoxide. [b] TCNE = tetracyanoethylene, BDPM = bis(diphenylphosphino)methane, S = $PhCH{=}CH_2$, CMS = $p\text{-}ClCH_2C_6H_4CH{=}CH_2$, PMS = $p\text{-}CH_3C_6H_4CH{=}CH_2$, BMS = $PhCH{=}CHCH_3$, AB = $PhCH_2CH{=}CH_2$, DPE = $Ph_2C{=}CH_2$, TPE = $Ph_2C{=}CH_2TPE = Ph_2C{=}CHPh$. Ratio vol. liquid additive to vol. solvent in brackets. 20 mol. solid additive to 1 mol Pt compound. [c] $C_4H_8 = C_2H_5CH{=}CH_2 + (CH_3)_2C{=}CH_2$. [d] from ref. 2. [e] TCNE reacts slowly with DMSO. [f] From ref. 3.

$C_2H_4^+$ in the mass spectrometer and also to give ethylene (in addition to propene and cyclopropane) on pyrolysis in the solid state and in solution. This suggests that the formation of carbene-olefin complexes is much more facile with platinum(II)- than with platinum(IV)cyclobutanes.

Experimental

The platinacyclobutanes were prepared by literature methods [3,9]. The method of determining the volatile products was as previously described [6].

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