

REACTIONS OF SOME PLATINUM YLIDES, INCLUDING A REARRANGEMENT TO A PLATINACYCLOBUTANE *

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Summary

The platinum(II) ylides [*trans*-X₂Pt{CH(py)CH₂CH₃}(py)] (X = Cl, Br; py = pyridine) react with triphenylphosphine to give [*cis*-X₂Pt{CH(py)CH₂CH₃}(PPh₃)]. Oxidative addition of iodomethane gives [*trans*-X₂I(CH₃)Pt{CH(py)CH₂CH₃}(py)], the NMR spectra of which indicate restricted rotation about the CH–CH₂ bond in the ylide moiety, and addition of chlorine gives [Cl₂X₂Pt{CH(py)CH₂CH₃}(py)]. Thermal decomposition of these ylides in the solid phase gives propene as the only hydrocarbon product, with CH₃Cl or CH₃Br from the iodomethane adducts. However, thermal or photochemical decomposition in dimethylsulphoxide solution gives considerable yields of ethylene (up to 95% of the volatile products), the precursors of which are probably positive platinum ylide ions from dissociation of a halide ligand. The reaction of HI with [Cl₂Pt{CH(py)CH₂CH₃}(py)] in benzene solution leads to formation of a platinacyclobutane [I₃PtCH₂CH₂CH₂(py)]⁻ [pyH]⁺. Reaction with PhSH is unusual in that ethane is produced.

Introduction

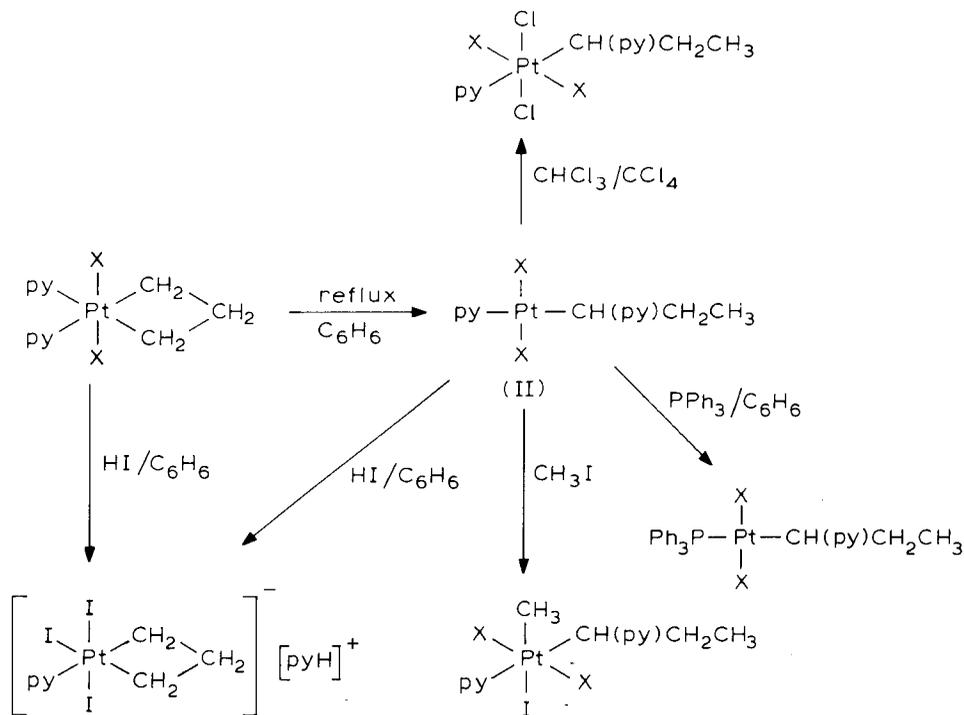
Platina(IV)cyclobutane compounds readily isomerise to ylides under appropriate conditions [1]. This reaction was first established by Gillard et al. [2], who prepared the ylides [Cl₂Pt{CH(py)CH₂CH₃}(py)] (II, Cl) and [Cl₄Pt{CH(py)CH₂CH₃}(py)] (III, Cl) (py = pyridine) from the platinacyclobutane [Cl₂PtCH₂CH₂CH₂(py)₂] (I, Cl)

* This article is dedicated by RJP and MCR to the memory of Dr. C.F.H. Tipper, deceased September 15th, 1983.

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and characterised their structure. These ylides appeared to be relatively unreactive apart from thermal decomposition (which gave propene and pyHCl) [2], although it has since been shown that they undergo photooxidation in solution giving aldehydes [3]. However, in connection with the reinvestigation of a third ylide of uncertain structure which can be prepared from I,Cl , it has recently been found that both II,Cl and III,Cl react with carbon monoxide giving $(\text{CO})\text{Pt}(\text{ylide})$ compounds [4]. The results of studies of other reactions of platinum ylides are reported here. The compounds and the reactions involved are summarised in Scheme 1.

SCHEME 1

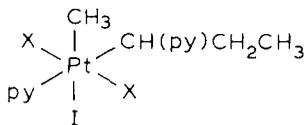


(X = Cl, Br; py = pyridine)

Results and discussion

The bromineplatinum ylides, $[\text{Br}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ (II,Br) and $[\text{Cl}_2\text{-Br}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ (III,Br), were prepared from $[\text{Br}_2\text{PtCH}_2\text{CH}_2\text{CH}_2(\text{py})_2]$ (I,Br) by the methods used by Gillard et al. [2] for the chlorine compounds II,Cl and III,Cl . The infrared spectrum of II,Br showed only one absorption due to Pt-Cl stretching indicating *trans* addition of the two chlorines. Reaction of II,Cl and II,Br with triphenylphosphine (PPh_3) in solution gave $[\text{X}_2\text{Pt}\{\text{CH}(\text{py})\text{-CH}_2\text{CH}_3\}(\text{PPh}_3)]$ (X = Cl, Br), the IR spectrum of the chlorine compound indicating that the halogens are probably *cis* to each other (two Pt-Cl stretching frequen-

cies) as expected if the ylide moiety has some π -bonding character (cf. the ylide $\{(\text{CO})\text{Cl}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}\}$) [4]. Oxidative addition of iodomethane to II,Cl and II,Br gave (X = Cl, Br):



The IR spectrum of the chloride (X = Cl) again showed only one absorption due to Pt–Cl stretching, indicating that the halide ligands were *trans* to one another as in II,Cl, and thermal decomposition of the solids gave CH_3Cl or CH_3Br (with no CH_3I) (Table 2) indicating that the methyl group is *cis* to the Cl or Br and *trans* to the I ligand.

Some details of the NMR spectra of these and related compounds are given in Table 1. Replacement of one pyridine by triphenylphosphine reduces the $^2J(\text{PtH})$ and the $^1J(\text{PtC})$ coupling constants for the CH group of the ylide considerably. Also the ^{31}P data confirm the indication from the IR spectrum that the ylide and PPh_3 ligands are *cis* to each other in $[\text{Cl}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{PPh}_3)]$ (see $^1J(\text{PtP})$ and $^3J(\text{PH})$ for this compound and $[\text{ClPt}\{\text{CH}_2(\text{PPh}_3)\}(\text{PPh}_3)_2\text{I}]$). The doublet of doublets with coupling constants of 11.5 and 3.8 Hz obtained for the ylide CH group in the methyl iodide adduct $[(\text{CH}_3)\text{Cl}_2\text{IPt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ indicates restricted rotation about the CH– CH_2 bond. Application of the semi-empirical Karplus equation [6], (eq. 1), where θ is the dihedral angle between the CH proton and either

$$J(\text{HH}) = 7 - \cos\theta + 5\cos 2\theta \text{ Hz} \quad (1)$$

proton of the methylene group suggests that θ is 60° ($J(\text{HH})$ 4 Hz) and 180° ($J(\text{HH})$ 11 Hz). There are thus two possible rotamers with Newman projections:



Decomposition of the ylides

These platinum(II) and platinum(IV) ylides decompose in the solid phase or in solution at 100°C , or at 25°C in solution under the influence of UV radiation. The photolyses, however, are much slower than with platinum(IV)cyclobutanes [7]. The volatile products are given in Table 2.

The thermal decomposition in the solid phase or in 1,2-dichlorobenzene solution gave propene only as the hydrocarbon product (ref. 2 and Table 2, Nos. 1, 8, 14, 16, 18, 22 and 24). Photolysis of dichlorobenzene solutions also gave only propene (but in traces; Table 2, Nos. 3, 9, and 19), while photolysis of methyl cyanide solutions was also very slow though some C_2H_4 was formed (Table 2, Nos. 10 and 20). However, thermal or photochemical decomposition of the DMSO solutions involved extensive fission of the C_3 moiety, a high proportion of ethylene being formed (Table

TABLE 1
 NMR SPECTRA OF PLATINUM YLIDES IN CDCl₃

Compound ^a	Ylide hydrogens					
	$\delta(\text{CH})$ (ppm)	$^3J(\text{HH})$ (Hz)	$^2J(\text{PtH})$ (Hz)	$\delta(\text{CH}_2)$ (ppm)	$\delta(\text{CH}_3)$ (ppm)	$^3J(\text{HH})$ (Hz)
[Cl ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	5.67(t)	7.5	115	2.43(m), 1.92(m)	1.07(t)	
[Br ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	6.00(t)	7.5	113	2.52(m), 2.04(m) ^b	1.10(t)	7.5
[Cl ₂ Br ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	6.83(m)			3.24(m), 2.90(m)	0.80	~ 7
[Cl ₂ Pt{C ¹ H(py)CH ₂ C ² H(CH ₃) ₂ }(py)]	5.84(t)	7.3	110(C ¹ H)	2.36(m), 1.62(m)	1.96(m) (C ² H)	
[(CH ₃)Cl ₂ IPt{CH(py)CH ₂ CH ₃ }(py)] ^c	5.93(d,d)	11.5,3.8	92	2.50(m)	0.80(t)	7.5
[(CH ₃)Br ₂ IPt{CH(py)CH ₂ CH ₃ }(py)] ^c	5.87(m)			2.2 (m)	0.70(t)	7
[Cl ₂ Pt{CH(py)CH ₂ CH ₃ }(PPh ₃)]	4.10	^e	69	2.45(m), 2.18(m)	0.64(t)	7
[Br ₂ Pt{CH(py)CH ₂ CH ₃ }(PPh ₃)]	4.14	^f	73	2.4(m)	0.60(t)	7
[ClPt{CH ₂ (PPh ₃)}(PPh ₃) ₂]	$\delta(\text{CH}_2)$ 2.52 ppm(m), $^2J(\text{PtH})$ 69 Hz $^3J(\text{PH})$ 6 Hz (<i>cis</i> to ylide), $^3J(\text{PH})$ 9 (<i>trans</i> to ylide)					

^a py = pyridine; PPh₃ = triphenylphosphine. ^b $^2J(\text{H}^{\text{A}}\text{H}^{\text{B}})$ 14 Hz, $^3J(\text{HH})$ 7 Hz. ^c Major isomer. ^d Chemical shift from external H₃PO₄. ^e $^3J(\text{HH})$ 9 Hz, $^3J(\text{PH})$ 6.5 Hz. ^f $^3J(\text{HH})$ 8.5 Hz, $^3J(\text{PH})$ 6 Hz.

2, Nos. 2, 4-7, 11-13, 15, 17, and 21). The C₂H₄/C₃H₆ ratio was higher with the dibromo than the dichloro ylides and with triphenylphosphine than with pyridine as the neutral ligand. The production of ethylene from the decomposition of the platina(IV)cyclobutanes [X₂PtCH₂CH₂CH₂(1,10-phenanthroline)] (X = Cl, Br) is also promoted by the use of DMSO as solvent, if X = Br rather than Cl, and by the presence of PPh₃ [8].

The formation of propene involves a net 2,1-hydrogen migration and that of ethylene a net 3,1-hydrogen migration. Since the latter only occurs with solvents of relatively high dielectric constant (CH₃CN, DMSO) it seems probable that it is preceded by dissociation of halide from the platinum ylide (cf. formation of C₂H₄ from the platinacyclobutanes [8]). A reasonable mechanistic scheme for the production of propene and ethylene, and which accounts for the variation in the relative yields with experimental conditions, is given in Scheme 2.

The intermediates proposed are similar to those suggested by Al-Essa and Puddephatt [9] in the formation of ylides from platinacyclobutanes, and in the formation of olefins from the ylides, on the basis of deuterium labelling studies. Cushman and Brown [10] have recently suggested that the key intermediates in ylide and olefin formation are π -allylplatinum hydrides. However, π -allyl species are unlikely to be involved in ylide decomposition since they will not give rise to C₂H₄.

Thermal decomposition of these ylides in the solid phase or in 1,2-dichlorobenzene solution proceeds by route A to give propene. The effect of added chloride (pyridinium hydrochloride) and pyridine on the relative yields of propene and ethylene from the photolysis of (II,Cl) in DMSO (Table 2, Nos. 4, 5 and 7) implies that both are formed from the platinum ylide cation (routes B and C, respectively) but dissociation of the neutral ligand precedes propene formation. When L is

Ylide carbons						PtCH ₃		Ref.
$\delta(\text{CH})$ (ppm)	$^1J(\text{PtC})$ (Hz)	$\delta(\text{CH}_2)$ (ppm)	$^2J(\text{PtC})$ (Hz)	$\delta(\text{CH}_3)$ (ppm)	$^3J(\text{PtC})$ (Hz)	$\delta(\text{H})$ (ppm)	$^2J(\text{PtH})$ (Hz)	
42.90	759	31.43	12	12.30	29			2
41.8(C ¹)	785.4	25.5	43.2	45.7(C ²)	35.0			3
						2.00	69	
						2.22	70.5	
³¹ P in CD ₂ Cl ₂ ^d : Ph ₃ P-Pt; δ 11.2 ppm, $^1J(\text{PtP})$ 3689 Hz								
$\delta(\text{CH}_2)$ 7.23 ppm, $^1J(\text{PtC})$ 576 Hz								
³¹ P in CD ₂ C ₂ : Pt(PPh ₃) ₂ ; δ -18.7 ppm, $^1J(\text{PtP})$ 3987 Hz (<i>cis</i> to ylide) and 2244 Hz (<i>trans</i> to ylide)								

triphenylphosphine the platinum species accompanying ethylene evolution was probably $[\text{X}_2\text{Pt}\{\text{CH}_2\text{PPh}_3\}(\text{py})]$ and when L is pyridine the PtCH₂ moiety is presumably stabilised by the DMSO (cf. the formation of C₂H₄ from platinacyclobutanes [8]). Promotion of ethylene formation by triethylammonium chloride also occurs with platinacyclobutanes [7].

Finally it can be seen that no deuterium is present in the products of the photolysis of $[(\text{CH}_3)\text{Cl}_2\text{IPt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ in (CD₃)₂SO (Table 2, No. 23). Thus methane must be formed by internal hydrogen abstraction by the methyl group, as in the photolysis of other methylplatinum(IV) compounds [11].

Reaction of the ylides with hydrogen iodide

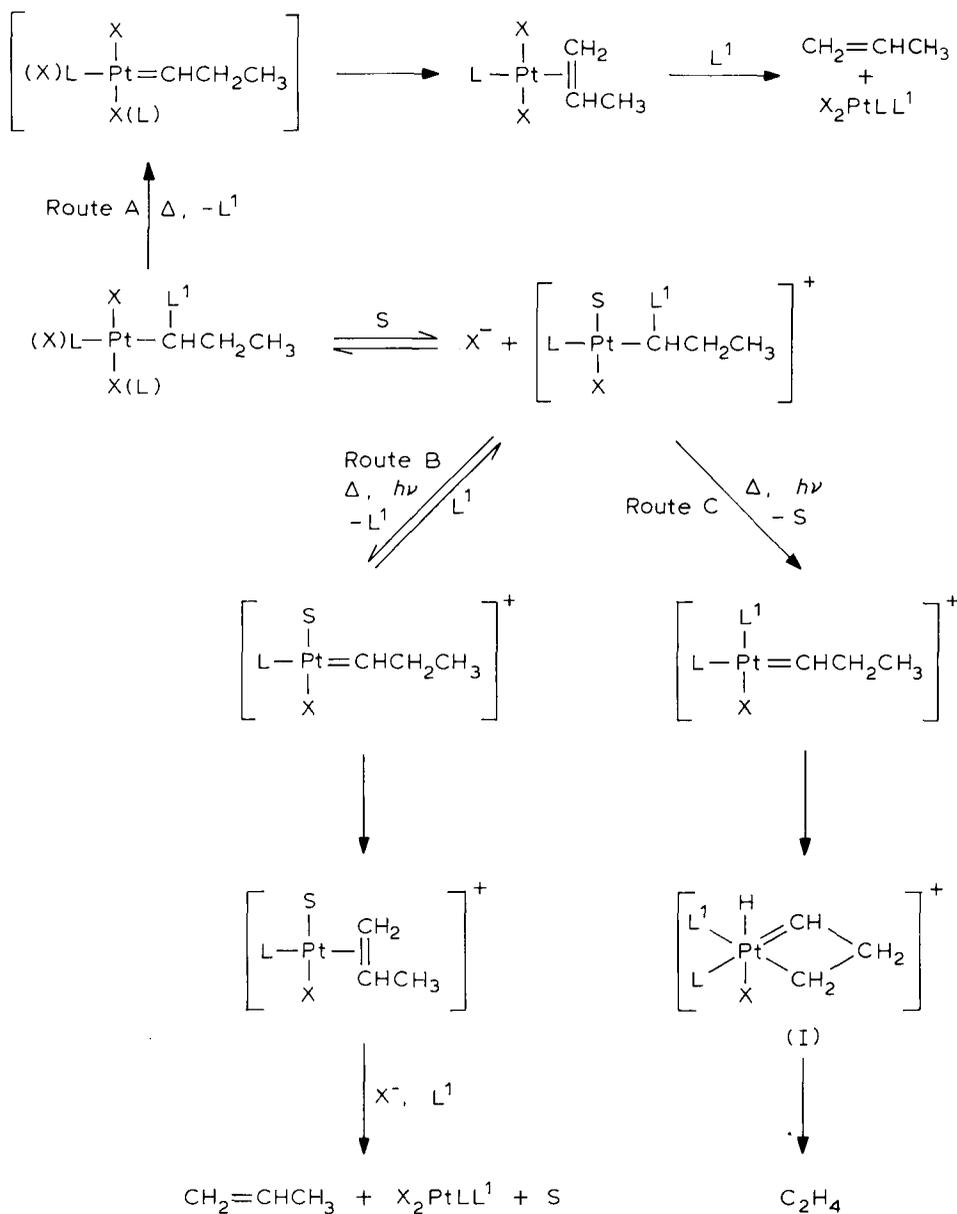
On passing hydrogen iodide through a solution of II,Cl in benzene the colour darkened and a dark green solid was precipitated. The IR spectrum of this precipitate indicated the absence of chlorine and the presence of the pyridinium ion $[\text{C}_5\text{H}_5\text{NH}]^+$, and the elemental analysis was consistent with the formula, $[\text{C}_5\text{H}_5\text{NH}]^+ [\text{I}_3\text{Pt}(\text{C}_3\text{H}_6)(\text{py})]^-$. Thermal decomposition of the solid at 100 °C gave a gas which was mainly cyclopropane (85%, plus 15% propene), and on dissolving in DMSO at room temperature cyclopropane (and no other volatile product) was evolved. Since addition of iodide *trans* to a platinacyclobutane ring leads to the evolution of the C₃H₆ moiety as cyclopropane [12], this suggests that the precipitate contains a PtCH₂CH₂CH₂ ring. This is supported by the observation that, on using $[\text{Cl}_2\text{PtCH}_2\text{CH}_2\text{CH}_2(\text{py})_2]$ instead of the ylide, the same compound appeared to be precipitated as shown by elemental analysis, IR spectroscopy, thermal decomposition of the solid at 100 °C (89% cyclopropane), solution in DMSO (100% cyclopropane). Thus, it appears that the action of hydrogen iodide has reversed the

TABLE 2
VOLATILE PRODUCTS OF THE DECOMPOSITION OF SOME PLATINUM YLIDES
(Thermal decomposition, 100°C; photolysis, 25°C. Conc. of Pt compound in solution, $\sim 2\text{-}3 \times 10^{-3}$ mol l $^{-1}$. Reaction time 3 h)

No.	Compound ^a	Conditions ^b	Volatile products (% total) ^c		
			C ₂ H ₄	CH ₃ CH=CH ₂	others
1	[Cl ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	th.DCB	-	100	-
2		th.DMSO	34	66	-
3		ph.DCB	-	T	-
4		ph.DMSO	56	44	-
5		ph.DMSO + pyHCl	60	40	-
6		ph.DMSO + Et ₃ NHCl	80	20	-
7		ph.DMSO + py	80	20	-
8	[Br ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	th.solid.DCB	-	100	-
9		ph.DCB	-	T	-
10		ph.CH ₃ CN	S, C ₃ H ₆ \gg C ₂ H ₄	-	-
11		th.DMSO	81	19	-
12		ph.DMSO	83	17	-
13	[Cl ₄ Pt{CH(py)CH ₂ CH ₃ }(py)]	ph.DMSO	T, mainly C ₂ H ₄	-	-
14	[Cl ₂ Br ₂ Pt{CH(py)CH ₂ CH ₃ }(py)]	th.solid	-	100	-
15		ph.DMSO	95	5	-
16		th.solid.DCB	-	100	-
17	[Cl ₂ Pt{CH(py)CH ₂ CH ₃ }(PPh ₃)]	ph.DMSO	71	29	-
18	[Br ₂ Pt{CH(py)CH ₂ CH ₃ }(PPh ₃)]	th.solid.DCB	-	100	-
19		ph.DCB	-	T	-
20		ph.CH ₃ CN	T, C ₂ H ₄ > C ₃ H ₆	-	-
21		ph.DMSO	92	8	-
22	[(CH ₃)Cl ₂ IPt{CH(py)CH ₂ CH ₃ }(py)]	th.solid	-	60	CH ₃ Cl (40)
23		ph.DMSO-d ₆	CH ₄ , CH ₃ Cl + some C ₂ H ₄ , CH ₃ CH=CH ₂	-	-
24	[(CH ₃)Br ₂ IPt{CH(py)CH ₂ CH ₃ }(py)]	th.solid	- CH ₃ CH=CH ₂ + CH ₃ Br	-	-

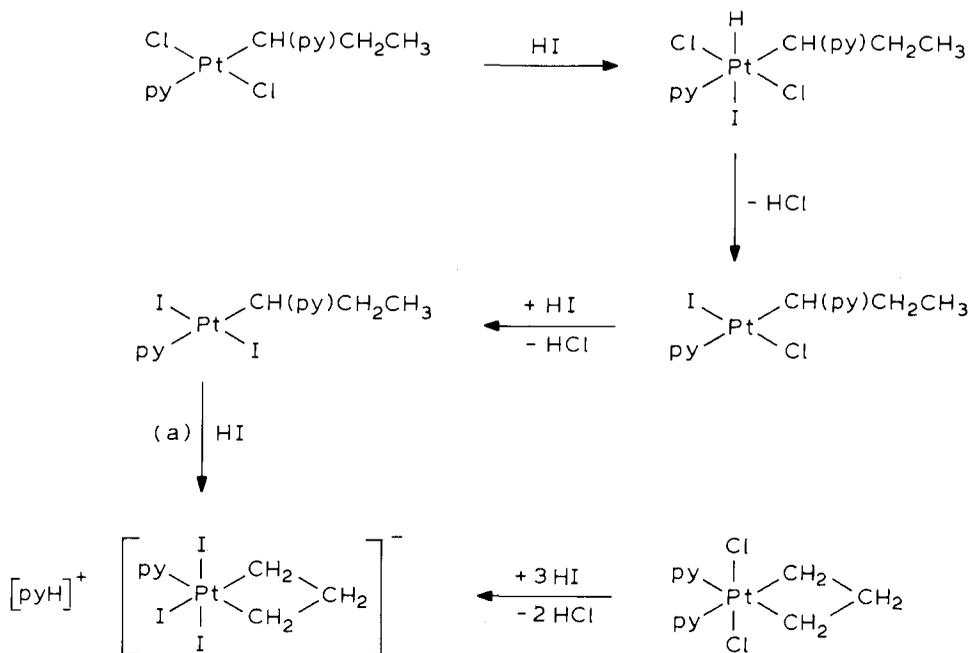
^a py = pyridine, Ph = C₆H₅; ^b th. = thermal, ph. = photochemical. DCB = 1,2-dichlorobenzene; DMSO = dimethylsulphoxide; Et = C₂H₅. Mol additive/mol Pt compound = 20/1. ^c T = trace, S = small yield.

SCHEME 2. (X = Cl, Br; L = pyridine, PPh₃; L¹ = py; Δ = thermal decomposition; S = dimethylsulphoxide).



platinacyclobutane-ylide conversion. Possibly, two molecules of HI successively add to the ylide, HCl being eliminated; addition of a third molecule of HI causes conversion to the platinacyclobutane since this allows precipitation providing the driving force for the ylide to ring conversion, see Scheme 3. However, replacement of chloride by iodide might possibly occur by nucleophilic substitution of I⁻ for Cl⁻. The ylide-cyclobutane conversion is partially accomplished in the intermediate I (Scheme 2), requiring only a shift of hydrogen from platinum to carbene carbon (cf.

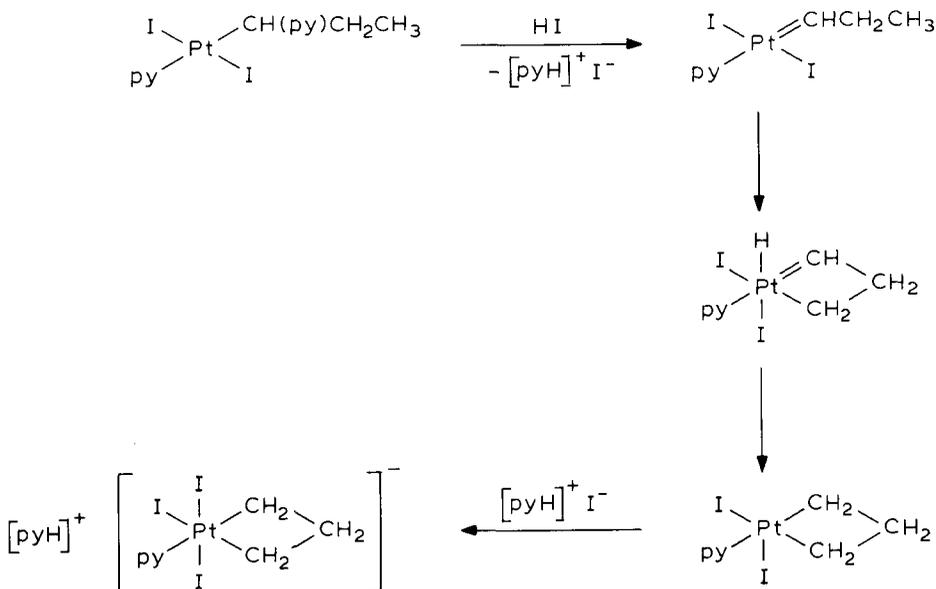
SCHEME 3



platinacyclobutane to ylide [9]), and thus reaction (a) probably involves the steps shown in Scheme 4. The action of CO on the ylide II,Cl can also cause conversion to a platinacyclobutane [4].

On passing HCl through a benzene solution of the ylide II,Cl, the yellow colour

SCHEME 4



faded somewhat but no precipitate was formed, whereas with the platinumacyclobutane the pyridinium salt, $[\text{C}_5\text{H}_5\text{NH}]^+ [\text{Cl}_3\text{PtCH}_2\text{CH}_2\text{CH}_2(\text{py})]^-$, precipitates immediately [13].

Reaction with iodine and benzene thiol

The ylide II,Cl reacted with iodine in benzene solution at room temperature, but the solid obtained on precipitation appeared to be a mixture, although possibly containing some of the product of simple oxidative addition.

The composition of the products obtained from the reaction of II,Cl with benzene thiol depended on the initial ratio of thiol to ylide. The IR spectra indicated the absence of chlorine and S-H groups, suggesting the presence of a $\text{Pt}(\text{SPh})_2$ moiety, but the elemental analyses fitted no simple formulation. On leaving a solution of the ylide in the thiol for several hours, ethane was evolved in considerable yield.

Experimental

The ylides II,Cl and II,Br were prepared as previously described [2,4].

$[\text{Cl}_2\text{Br}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ (III,Br)

II,Br was dissolved in a minimum of a 1/1 mixture of CHCl_3 and CCl_4 . After about 3 days orange-yellow crystals separated. These were filtered off, washed with benzene and dried in vacuo (yield 80%). (Found: C, 25.7; H, 2.71; N, 4.46. $\text{C}_{13}\text{H}_{16}\text{N}_2\text{Cl}_2\text{Br}_2\text{Pt}$ calcd.: C, 24.9; H, 2.56; N, 4.47%). IR spectrum very similar to that of II,Cl and II,Br [2,4]. Mass spectrum included peaks centred on (m/e): 273 $[\text{PtC}_5\text{H}_4\text{N}]^+$, 353 $[\text{Pt}(\text{py})_2]^+$ and/or $[\text{PtBr}(\text{py})]^+$, 388 $[\text{PtCl}(\text{py})_2]^+$ and/or $[\text{PtClBr}(\text{py})]^+$, 432 $[\text{PtBr}(\text{py})_2]^+$ and/or $[\text{PtBr}_2(\text{py})]^+$, 467 $[\text{PtBrCl}(\text{py})_2]^+$ and/or $[\text{PtBr}_2\text{Cl}(\text{py})]^+$, 511 $[\text{PtBr}_2(\text{py})_2]^+$.

$[\text{Cl}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{PPh}_3)]$

To a solution of 0.1 g $[\text{Cl}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ in a minimum volume of benzene ($\sim 10 \text{ cm}^3$) was added a slight molar excess of triphenylphosphine in 5 cm^3 benzene. A white precipitate formed immediately which was filtered off, washed with benzene and n-pentane and dried in vacuo (yield 60–70%). (Found: C, 48.2; H, 4.18; N, 2.33. $\text{C}_{26}\text{H}_{26}\text{NPCl}_2\text{Pt}$ calcd.: C, 48.1; H, 4.01; N, 2.16%.) IR bands at (cm^{-1}) 3045m (broad), 2955m, 2920m, 2860w, 1618m, 1602w, 1478s, 1449w, 1433s, 1374w, 1332w, 1310w, 1238w, 1210w, 1183w, 1158w, 1094s, 1069w, 1030w, 996w, 812w, 750s, 695vs, 541s, 513s, 496m, 290–270m. The mass spectrum showed only peaks derived from triphenylphosphine.

A similar method was used for the preparation of $[\text{Br}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{PPh}_3)]$ (yield, 70–80%). The IR spectrum was similar to that of the chlorine compound except that the band below 300 cm^{-1} was absent.

Attempts to replace the second pyridine by triphenylphosphine by reaction of II,Cl with excess triphenylphosphine in dilute benzene solution were made. However, this gave mixtures containing the monophosphine ylide compound described above and another triphenylphosphineplatinum compound containing no ylide moiety.

$[\text{Cl}_2\text{I}(\text{CH}_3)\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$

$[\text{Cl}_2\text{Pt}\{\text{CH}(\text{py})\text{CH}_2\text{CH}_3\}(\text{py})]$ (0.1 g) was dissolved in 2 cm^3 freshly distilled

iodomethane. The solution became bright orange after about 1 h, and the product was extracted by precipitation with n-pentane, filtered off, washed with pentane and dried in vacuo (yield 70%). (Found: C, 27.5; H, 3.03; N, ~ 2.6. $C_{14}H_{19}N_2Cl_2IPt$ calcd.: C, 27.6; H, 3.13; N, 4.6%.) IR bands at (cm^{-1}): 3130w, 3115w, 3080m, 3055m, 2970m, 2920m, 2870w, 1628m, 1606m, 1579w, 1493m, 1482s, 1450s, 1381w, 1358w, 1336w, 1317w, 1244w, 1221m, 1159w, 1134m, 1114w, 1068m, 1047w, 1030w, 1019m, 944w, 918w, 875w, 860w, 830w, 785w, 762m, 699s, 678w, 642m, 338m. Mass spectrum included peaks centred on (m/e): 50/52 $[CH_3Cl]^+$, 142 $[CH_3I]^+$, 273 $[PtC_5H_4N]^+$, 352 $[PtC_5H_4N(py)]^+$, 388 $[PtCl(py)_2]^+$, 423 $[PtCl_2(py)_2]^+$, 480 $[PtI(py)_2]^+$ and 515 $[PtClI(py)_2]^+$.

$[Br_2I(CH_3)Pt\{CH(py)CH_2CH_3\}(py)]$

This was prepared by the addition of iodomethane to $[Br_2Pt\{CH(py)CH_2CH_3\}(py)]$ as above (yield, 60–70%). (Found: C, 25.3; H, 2.99; N, 3.64. $C_{14}H_{19}N_2Br_2IPt$ calcd.: C, 24.6; H, 2.73; N, 4.03%.) IR similar to that of the chlorine compound above but no band below 400 cm^{-1} . Mass spectrum included peaks (m/e): 94/96 $[CH_3Br]^+$, 121/123 $[C_3H_6Br]^+$, 168 $[C_3H_5I]^+$, 273 $[PtC_5H_4N]^+$, 353 $[Pt(py)_2]^+$ and/or $[PtBr(py)]^+$, 422 $[PtBr(py)_2]^+$ and/or $[PtBr_2(py)]^+$, 511 $[PtBr_2(py)_2]^+$, 559 $[PtBrI(py)_2]^+$ and/or $[PtBr_2I(py)]^+$.

$[I_3PtCH_2CH_2CH_2(py)]^- [pyH]^+$

Dry hydrogen iodide, prepared by the reaction of iodine and tetrahydronaphthalene [14], in a stream of dry nitrogen was bubbled through a solution of 0.1 g $[Cl_2Pt\{CH(py)CH_2CH_3\}(py)]$ in 25 cm^3 benzene. The colour rapidly darkened and after about 20 min a dark green solid precipitated. This was immediately filtered off, washed with benzene and dried in vacuo (yield, 50%). (Found: C, 19.0; H, 1.95; N, 3.87. $C_{13}H_{17}N_2I_3Pt$ calcd.: C, 20.0; H, 2.18; N, 3.60%.) IR bands at (cm^{-1}) 3200m, 3180–2800 (v.br), 1628m, 1598s, 1525s, 1477s, 1447m, 1402w, 1378w, 1365w, 1328m, 1240w, 1221w, 1186m, 1161w, 1065w, 1049m(sh), 1012w, 980w, 870m(broad), 762w, 740vs, 700w, 672vs, 635w, 610w. Mass spectrum included peaks (m/e): 170 $[C_3H_7I]^+$, 254 $[I_2]^+$, 273 $[PtC_5H_4N]^+$, 352 $[PtC_5H_4N(py)]^+$, 401 $[PtI(py)]^+$, 480 $[PtI(py)_2]^+$, 528 $[PtI_2(py)]^+$, 607 $[PtI_2(py)_2]^+$.

The reaction of HI with $[Cl_2PtCH_2CH_2CH_2(py)_2]$ in benzene solution gave a dark green precipitate after about 40 min (yield, 90%). (Found: C, 19.3; H, 1.85; N, 3.81%). The IR and mass spectra were almost identical with those of the product from the ylide.

Analysis

The IR spectra of the solids in KBr discs were obtained using a Perkin–Elmer grating spectrometer 577, and mass spectra using a VG Micromass 12 with solid probe. The NMR spectra were obtained using a Bruker WM-250 spectrometer.

The thermal and photochemical decompositions were performed in vacuo in an apparatus similar to that already described [7]. The volatile hydrocarbon products were determined by GLC using a squalane column [7].

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