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CYCLOPROPANE COMPLEXES OF PLATINUM: SOME SYNTHETIC STUDIES AND THE REACTIVITY AND CRYSTAL STRUCTURE OF 1,6-DICHLORO-2,3-TRIMETHYLENE-4,5-BIS(PYRIDINE)PLATINUM(IV)

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SUMMARY

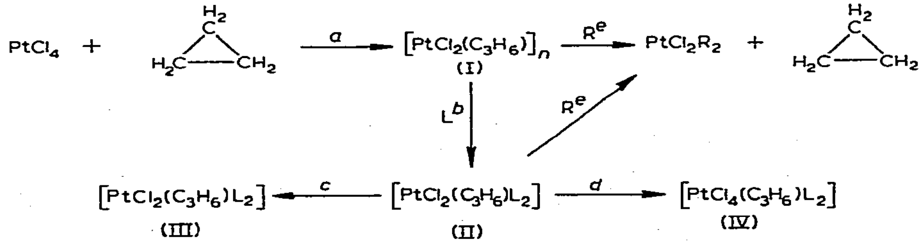
The mode of bonding of cyclopropane to platinum is described through a crystal structure determination of the complex $[PtCl_2(C_5H_5N)_2C_3H_6)]$. The crystals are monoclinic with $a = 13.37$, $b = 13.11$, $c = 8.40$, $\beta = 91.1$; space group $P2_1/c$ and atomic parameters have been determined by a least-squares analysis of 1119 independent reflexion intensities. The geometry of the coordinated cyclopropane ligand is held to rule out the description as an "edge complex". The syntheses of this and related complexes are described, with particular regard to the rearrangement reactions which provide pyridinium ylide complexes of platinum(II) and platinum(IV).

INTRODUCTION

The reaction of cyclopropane with chloroplatinic acid was first described by Tipper[1]; the resulting species (I) $[C_3H_6PtCl_2]_n$ together with the bis(pyridine) complex (II), $[PtCl_2Py_2C_3H_6]$ were formulated by analogy with olefin compounds of platinum(II). Adams *et al.*[2,3] showed by magnetic resonance and infra-red spectra

SCHEME 1

SYNTHETIC RESULT



[a] Acetic anhydride; normal temp. and pressure. [b] L = Pyridine, 2,2'-bipyridine, 2-, 3-, 4-picolines, 2.6-lutinine, ½ ethylenediamine. [c] Benzene, 60°, 2–6 h (only for L = pyridine, 3- and 4-picolines). [d] Chloroform/-carbon tetrachloride (only for L = pyridine). [e] R = Sodium iodide, potassium cyanide, triphenylphosphine, triethylphosphine, dimethyl sulphoxide.

that the complexes contained the trimethylene–platinum moiety; our earlier reports[4,5] confirmed this work and (I) was shown to be probably tetrameric. Unexpected rearrangements of complex (II) were also described[4], and the crystallographic characterisation of the products are given in the accompanying paper[8]; we presently describe additional synthetic studies of trimethylene–platinum complexes, the crystal structure of the bis(pyridine) complex, (II), and its reactions. Our synthetic results are collected in Scheme 1, together with those of the earlier workers[1–3].

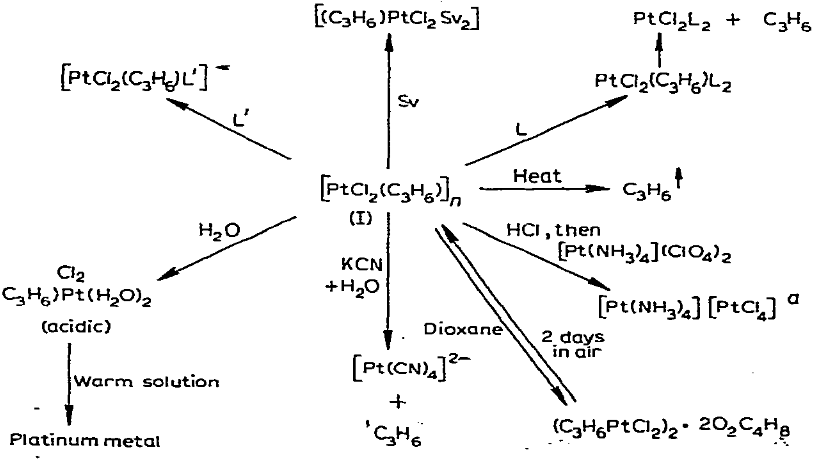
RESULTS AND DISCUSSION

The compound(I), $[C_3H_6PtCl_2]_4$

Although we have not succeeded in obtaining single crystals of the complex (I) suitable for X-ray analysis, our recent chemical and spectroscopic studies[5] support its formulation as a tetramer, $[C_3H_6PtCl_2]_4$. The reactions of (I) are shown in detail in Scheme 2. Volatile products were identified by vapour phase chromotography and infra-red spectroscopy.

SCHEME 2

REACTIONS OF (I)



Sv = monodentate ligands, pyridine, 2-, 3- and 4-picolines, 2,6-lutidine. L = DMSO, DMF, PhCN, $PhNO_2$; L' = bidentate ligand, bipyridine; C_3H_6 = cyclopropane.

[a] Magnus' salt.

The complex (II), $[(C_3H_6)PtCl_2(C_5H_5N)_2]$

The reaction of the brown complex (I) with pyridine produces this complex in near-quantitative yield. The reaction is exothermic and some decomposition of (II) occurs, leading to the formation of *trans*-$[PtCl_2Py_2]$. The infra-red and nuclear magnetic resonance spectra are entirely in agreement with those recorded previously[2,3], but a more detailed ^1H NMR spectrum has been obtained after 486 accumulated scans. This shows evidence for the expected coupling between the α- and β-hydrogen nuclei in the trimethylene ring.

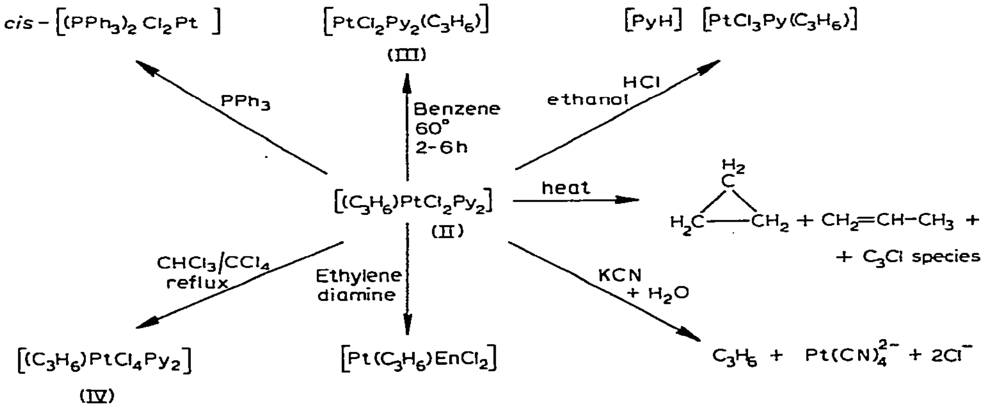
The C_3H_6 region of the spectrum is as previously reported[2,3], with a main peak centred at τ 7.36 [tetramethylsilane (τ 10.00) as internal standard]. There are satellites [$J(^{195}\text{Pt}–\text{H}^{\alpha})$ 83±1 Hz] with the expected intensity ratio 1/7/1 caused by spin–spin coupling of the ^{195}Pt isotope [spin ½, abundance 34%] with the α-CH_2 protons. These satellites are triplets with approximate 1/2/1 intensities [$J(\text{H}^{\beta}–\text{H}^{\alpha})$ 8±0.5 Hz]. No coupling of ^{195}Pt with the β-CH_2 protons is observed.

There are observed at least eight components of the central peak, the pattern of which is different at 100 and 220 MHz, indicating second order spin–spin splitting. Because the difference in chemical shift between the α- and β-CH_2 protons is expected to be comparable with the coupling constants between the two groups, a pattern of at least A_2B_4 complexity is expected. It has not been possible to assign the spectrum but the observed multiplicity certainly indicated complex $\text{H}^{\alpha}–\text{H}^{\beta}$ and $\text{H}^{\beta}–\text{H}^{\alpha}$ coupling.

The mass spectrum shows a highest *m/e* peak at 426 [$PtCl_2Py_2$] and at 274 [$PtCl_2$] and 352 [$PtPy_2$]. The reactions of (II) are shown in Scheme 3.

SCHEME 3

REACTIONS OF (II)



Colourless monoclinic crystals of the complex were obtained by slow evaporation of a chloroform solution containing a small amount of pyridine. The unit cell, derived by least-squares analysis of precession and Weissenberg photographic data, is: $a=13.37(2)$, $b=13.11(2)$, $c=8.40(2)$ Å; $\beta=91.1(1)°$; $U=1472.1$ Å; $M=466.1$ [$C_{13}N_2H_{16}Cl_2Pt$]; $Z=4$; $F(000)=880$; $D_{\text{obs}}=2.08$ g/cm^3, $D_{\text{calc}}=2.10$ g/cm^3; space group $P2_1/c$ (C_{2h}^5, No. 14).

Integrated intensities of 1119 independent reflexions were measured visually from precession and Weissenberg photographs (Mo-K_α radiation, $\lambda=0.711$ Å). Considerable difficulty was experienced since the crystals decompose in the X-ray beam and a new crystal was required for each zone of reflexions examined (ten in all). Absorption corrections were not practicable and the data are of relatively indifferent quality.

The position of the platinum atom could be readily inferred from the distribution of accidentally weak reflexions but a Patterson synthesis additionally provided the positions of the chlorine atoms. The remaining atom positions, apart from the carbons of the coordinated cyclopropane group, were derived from a Fourier synthesis

TABLE 1

$(C_3H_6)Pt(C_5H_5N)Cl_2$: ATOMIC POSITIONAL AND VIBRATIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Pt(1)	0.25127(15)	−0.01560(13)	0.12114(21)	0.0073(0)	0.0088(0)	0.0159(2)	−0.0009(4)	−0.0050(2)	0.0003(3)
Cl(1)	0.4370(11)	0.1183(11)	0.0774(18)	0.0109(9)	0.0118(9)	0.0322(24)	0.007(3)	−0.005(3)	−0.000(2)
Cl(2)	0.3588(12)	−0.1494(12)	0.1604(19)	0.0135(11)	0.0143(11)	0.0355(26)	−0.014(3)	−0.002(3)	0.007(2)
N(1)	0.3261(25)	0.0731(20)	0.3187(23)	0.008(2)	0.004(2)	0.018(5)	−0.007(5)	−0.011(7)	0.001(4)
N(2)	0.1539(25)	−0.0798(23)	0.2879(33)	0.007(2)	0.008(2)	0.018(5)	0.004(6)	0.010(7)	0.002(4)
C(1)	0.4342(39)	0.0622(48)	0.3257(10)	0.011(4)	0.021(5)	0.022(7)	0.003(1)	0.005(1)	−0.001(9)
C(2)	0.4911(42)	0.1295(36)	0.4256(66)	0.014(4)	0.010(3)	0.031(9)	−0.006(1)	0.000(1)	0.007(7)
C(3)	0.4392(43)	0.1907(43)	0.5272(72)	0.010(4)	0.015(5)	0.040(1)	−0.017(1)	−0.016(1)	0.007(8)
C(4)	0.3220(42)	0.1885(38)	0.5365(55)	0.026(7)	0.010(3)	0.016(6)	0.003(8)	−0.014(1)	−0.000(9)
C(5)	0.2767(54)	0.1220(28)	0.4289(50)	0.006(2)	0.006(2)	0.022(6)	−0.005(7)	−0.008(8)	0.007(4)
C(6)	0.1808(29)	−0.1234(42)	0.4299(75)	0.015(5)	0.012(4)	0.039(1)	0.009(1)	0.016(1)	−0.006(8)
C(7)	0.1160(45)	−0.1725(48)	0.5257(71)	0.024(7)	0.016(5)	0.029(1)	0.009(1)	0.009(2)	0.002(1)
C(8)	0.0016(55)	−0.1686(34)	0.5038(75)	0.021(5)	0.006(3)	0.037(1)	0.003(9)	−0.006(1)	−0.002(7)
C(9)	−0.0194(52)	−0.1269(39)	0.3566(61)	0.013(4)	0.012(4)	0.028(9)	0.012(1)	−0.022(1)	−0.004(7)
C(10)	0.0492(40)	−0.0854(41)	0.2666(70)	0.017(5)	0.013(4)	0.032(1)	−0.007(1)	0.024(1)	−0.002(8)
C(11)	0.3352(45)	0.0345(40)	−0.0639(61)	0.007(2)	0.016(4)	0.030(8)	0.020(1)	−0.007(8)	0.002(7)
C(12)	0.1924(32)	−0.0950(37)	−0.0910(51)	0.019(5)	0.010(3)	0.018(7)	0.004(8)	0.003(1)	−0.015(8)
C(13)	0.2990(55)	−0.0360(40)	−0.1892(65)	0.028(7)	0.019(5)	0.023(8)	−0.003(1)	−0.027(1)	0.018(1)

and five cycles of positional and isotropic temperature factors for these atoms reduced R to 0.13. A Difference Fourier synthesis at this point showed a somewhat distorted cyclopropane ligand; bond lengths were "regularised" and all atomic parameters were then refined by least-squares methods using a weighting scheme,

$$w=\left[1+\frac{|F_o|-b^2}{a^2}\right]^{-1}$$

with $a=12$ and $b=7$ for the observed amplitudes on the scale of a table of structure factors, a copy of which is available on application to the authors; six cycles of refinement converged to $R=0.094$, the maximum shift on any parameter being less than 0.15 σ.

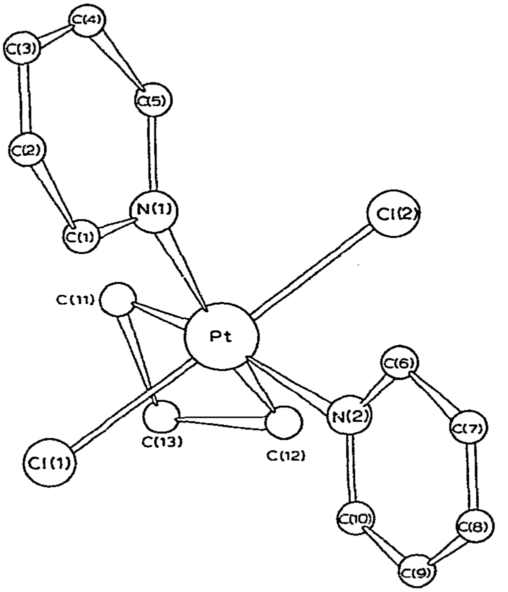


Fig. 1. $C_3H_6Pt(C_5H_5N)_2Cl_2$. Molecular stereochemistry and labelling of atoms.

The stereochemistry and atom labelling is shown in Fig. 1, atom parameters in Table 1, bond lengths and bond angles in Table 2.

The Pt–C(11) and Pt–C(12) bond lengths show that the cyclopropane ring is bonded to the platinum in a manner anticipated from the earlier work[2,3].

It is unfortunate that the poor quality of the diffraction data and structural analysis prevents detailed discussion of the geometry of the coordinated "cyclopropane". However, the C(11)–C(12) distance of 2.55(10) Å rules out the suggestion that there is a significant bond order between these two atoms in the complex. Formulation of coordinated cyclopropane as an "edge complex"[6] is not supported by our results. That cyclopropane is released in high yield on base treatment of complexes (I) and (II) can be related to the stereoselectivity of the elimination reaction.

The large difference between the carbon–carbon bond lengths, C(11)–C(13) and C(12)–C(13), is not regarded as significant; in addition to the high, and undoubtedly underestimated, standard deviations of these bond distances, the electron

TABLE 2

$(C_3H_6)Pt(C_5H_5N)_2Cl_2$. INTRAMOLECULAR BOND LENGTHS, BOND ANGLES AND THEIR STANDARD DEVIATIONS

Bond	Length (Å)	Bond	Length (Å)
Pt(1)–Cl(1)	2.294(14)	C(1)–C(2)	1.43(8)
Pt(1)–Cl(2)	2.287(16)	C(2)–C(3)	1.36(8)
Pt(1)–N(1)	2.25(3)	C(3)–C(4)	1.57(9)
Pt(1)–N(2)	2.11(3)	C(4)–C(5)	1.39(6)
Pt(1)–C(11)	2.04(5)	C(6)–C(7)	1.35(9)
Pt(1)–C(12)	2.19(5)	C(7)–C(8)	1.55(10)
N(1)–C(1)	1.45(6)	C(8)–C(9)	1.38(7)
N(1)–C(5)	1.31(5)	C(9)–C(10)	1.32(8)
N(2)–C(6)	1.36(7)	C(11)–C(13)	1.48(8)
N(2)–C(10)	1.41(7)	C(12)–C(13)	1.82(9)

Angle	(°)	Angle	(°)
Cl(1)–Pt(1)–Cl(2)	179.1(5)	Pt(1)–N(2)–C(5)	123.2(26)
Cl(1)–Pt(1)–N(1)	89.5(8)	C(1)–N(1)–C(5)	122.4(35)
Cl(1)–Pt(1)–N(2)	91.0(9)	Pt(1)–N(2)–C(6)	126.2(32)
Cl(1)–Pt(1)–C(11)	89.0(14)	Pt(1)–N(2)–C(10)	124.1(30)
Cl(1)–Pt(1)–C(12)	91.2(14)	N(1)–C(1)–C(2)	118.7(46)
Cl(2)–Pt(1)–N(1)	91.2(9)	C(1)–C(2)–C(3)	117.3(51)
Cl(2)–Pt(1)–N(2)	89.6(9)	C(2)–C(3)–C(4)	122.7(48)
Cl(2)–Pt(1)–C(11)	90.3(14)	C(3)–C(4)–C(5)	113.8(45)
Cl(2)–Pt(1)–C(12)	88.1(14)	N(2)–C(6)–C(7)	124.0(56)
N(1)–Pt(1)–N(2)	89.3(12)	C(5)–C(6)–C(7)	133.0(42)
N(1)–Pt(1)–C(11)	98.7(16)	C(6)–C(7)–C(8)	123.8(55)
N(1)–Pt(1)–C(12)	172.8(16)	C(7)–C(8)–C(9)	107.5(51)
N(2)–Pt(1)–C(11)	172.0(16)	C(8)–C(9)–C(1)	123.4(56)
N(2)–Pt(1)–C(12)	97.8(16)	Pt(1)–C(11)–C(13)	99.3(35)
C(11)–Pt(1)–C(12)	74.2(19)	Pt(1)–C(12)–C(13)	84.3(27)
Pt(1)–N(1)–C(1)	114.1(27)	C(11)–C(13)–C(12)	100.9(38)

density synthesis shows some indications of disorder of the cyclopropane ring. The platinum, σ-bonded carbon atoms C(11) and C(12) and pyridine-nitrogen atoms are coplanar, the cyclopropane ligand being oriented at 12.5° ($\sigma = 3.2°$) to this plane; again, in view of the high standard deviations, we prefer not to offer any explanation of this result which is barely statistically significant.

The *cis*-pyridine ligands are arranged in a propeller-like way around the platinum atom. The mean platinum–nitrogen bond length of 2.18 Å ($\sigma = 0.03$ Å) is comparable with that in, for example, trimethyl(acetylacetonyl) (2,2′-bipyridine)-platinum(IV)[7] and tetrachloropyridine (cyclopropylpyridinium ylid platinum(IV)[8] but it is about 0.1 Å greater than that in dichloropyridine(pyridinium propylide)-platinum(II)[8]. These latter results are more precise than the present ones; one could have anticipated a *trans*-influence of the σ-bonded carbon atoms on the platinum–nitrogen bond lengths[9] of approximately 0.1 Å but, once more, our results are insufficiently precise to allow us to develop this argument.

There are no unusual intermolecular contacts in the crystal which deserve mention.

The complex(III) $[(CH_3CH_2CHNC_5H_5)C_5H_5NPtCl_2]$

Adams *et al.*[3] showed that refluxing of the bis(pyridine) cyclopropane complex in benzene gave a yellow solution from which a yellow solid could be isolated. It was found that its properties were not reproducible after recrystallisation from chloroform; we show that this is due to the reaction of the complex(III) to produce the tetrachloro complex (IV). The nature of the complex (III) became clear only after a crystal structure analysis of (IV); its spectroscopic properties are very different from those of its isomer (II), although rather similar to those of (IV). (III) and (IV) are shown by X-ray analysis[8] to be ylide complexes (see Scheme 4) of platinum(II) and platinum(IV) respectively. The proton magnetic resonance spectrum of (III) (in $CDCl_3$) is shown in Fig. 2; the α-CH unit coordinated to platinum is demonstrated by the signal of relative intensity one at τ 4.33 which is split into a triplet by the methylene group [J(H–A) 7.5 Hz] and further split by the ^{195}Pt [J(Pt–H) 115 Hz]. The signal at τ 8.93 (relative intensity 3) can be assigned to the methyl group split by the methylene protons while the signals at τ 7.57 and τ 8.08 (total relative intensity 2) represent the inequivalent methylene protons split by the methyl andPtCH groups.

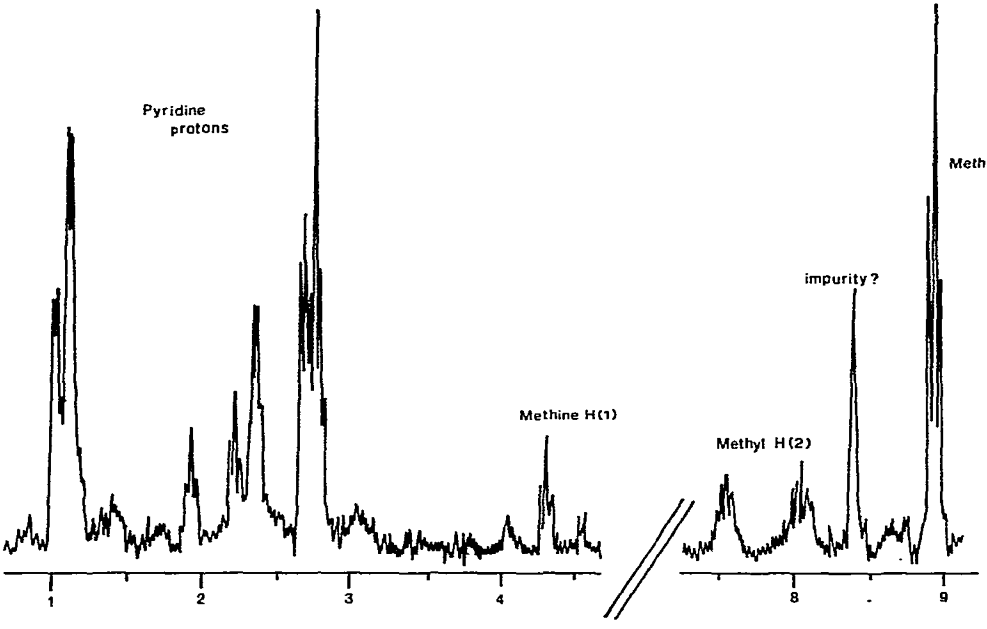


Fig. 2. NMR spectrum of (III) in $CDCl_3$.

Thermal decomposition of the ylide–platinum(II) complex gives propene (identified by vapour phase chromatography, infrared and mass spectroscopy) and pyridinium chloride (evidenced by infra-red and ultra-violet spectroscopy). No volatile products are obtained on treatment of (III) with aqueous potassium cyanide.

(III) is oxidised by halocarbon solvents to produce the tetrahalide species (IV). (II), (III) and (IV) all react very rapidly with chlorine but no conversion of (III) into (IV) has been achieved in this way, all the products appearing to contain ionic halo complexes.

Complex (IV), $[(CH_3CH_2CHC_5H_5N)(C_5H_5N)PtCl_4]\cdot CHCl_3$

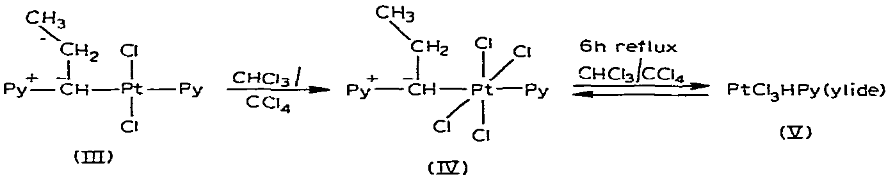
This complex is obtained by crystallising either (II) or (III) from a chloroform/carbon tetrachloride solution. Gentle heating removes the chloroform of solvation, but with disintegration of the crystals; further heating provides propene and pyridinium chloride. The proton magnetic resonance spectrum of (IV) is identical with that of complex (III).

As outlined in Scheme 1, several derivatives of (II), (III) and (IV) may be obtained and are listed in the Experimental Section. A fifth compound (V) is formed on prolonged heating of (III) or (IV) in chloroform/carbon tetrachloride solution. (V) is characterised by a very strong infra-red absorption at ca. 2100 cm^{-1}. The nature of this complex is unknown but preliminary studies indicate the possible hydride formulation $[PtCl_3H(Py)(Ylide)]$.

The synthetic relationships between (III), (IV) and (V) are summarised in Scheme 4. Bromo analogues of (I)–(IV) have been prepared.

SCHEME 4

SYNTHETIC RELATIONSHIP BETWEEN (III), (IV) AND (V)



EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Sheffield University and by Bernhardt (Mülheim). Melting points are uncorrected. NMR spectra were obtained using a Varian HR 220 Spectrometer, and infra-red spectra (usually in mulls) with a Perkin–Elmer 21 Spectrometer. Mass spectra were obtained using the solid injection system of an AEI MS 9 Spectrometer.

Polymeric dichlorotrimethyleneplatinum(IV): compound (I)

This was obtained as described earlier[1–5,9]. In order to remove a persistent contaminant, which showed infra-red absorption at ca. 1620 cm^{-1}, the product was washed carefully with iced water. (Found: C, 11.7; H, 2.3; Cl, 23.2; Pt, 63.1. $C_3H_6Cl_2Pt$ calcd.: C, 11.7; H. 2.3; Cl, 23.0; Pt, 63.2%.)

1,6-*Dichloro*-2,3-*trimethylene*-4,5-*bis*(*pyridine*)*platinum*(*IV*): *compound* (*II*)

This was prepared by a modification of the known methods. To the mixture of complex (I) $[C_3H_6PtCl_2]_4$ and contaminants was added ice-cold pyridine.

The mixture was allowed to warm to room temperature gradually, during which the pyridine reacted with complex (I) to form $[C_3H_6(C_5H_5N)_2PtCl_2]$ (II). All the products dissolved in the pyridine to give a light brown solution. This was added to a large volume of cold water which precipitated the white complex (II) and some *trans*-$[(C_5H_5N)_2PtCl_2]$. The pyridine was chilled since its reaction with complex (I) is exothermic; when the reaction is performed at room temperature, the rapid evolution of heat causes extensive decomposition of the complexes (I) and (II), giving free cyclopropane and *trans*-[$PtPy_2Cl_2$]. Most of the latter compound remained in the aqueous pyridine and was recovered by slowly evaporating the solution to dryness. The white precipitate, having been filtered off, was washed with water to remove excess pyridine, and dried with alcohol and water. The minimum volume of ice-cold chloroform required to dissolve complex (II) was added, leaving some contaminating [$(C_5H_5N)_2PtCl_2$] behind. Ligroin (b.p. 40–60°) was added to the chloroform solution; after filtration, and on setting the mixture aside, opaque, well formed crystals of the white complex (II) were obtained; m.p. 146° with decomposition. (Found: C, 33.3; H, 3.7; Cl, 15.4; N, 6.3; Pt, 42.1. $C_{13}H_{16}Cl_2N_2Pt$ calcd.: C, 33.4; H, 3.4; Cl, 15.4; N, 6.0; Pt, 41.9%.)

Its infra-red spectrum showed bands (in cm^{-1}) at: 3100 (vw), 3070 (w), 3040 (vw), 3003 (w), 2992 (w), 2941 (m), 2917 (m sh), 2898 (vw), 2862 (w sh), 2842 (w), 1602 (vs sh), 1565 (vw), 1486 (s sh), 1450 (vs sh), 1355 (vw sh), 1255 (vs), 1242 (w), 1220 (m sh), 1210 (s sh), 1155 (m sh), 1135 (m sh), 1085 (s sh), 1068 (m sh), 1062 (w sh), 1037 (s sh), 1012 (s sh), 995 (vw), 970 (s), 940 (w), 890 (w), 870 (w), 757 (vs sh), 693 (vs sh), 632 (s).

The conversion of (II) to (III)

Complex (II) was dissolved in benzene to form a colourless solution. On refluxing this solution, a yellow colouration gradually occurred during 5 min or so. No further intensification of the colour could be detected (ca. 5 min). A light yellow solid was precipitated when the hot solution was added to a large volume of cool ligroin (b.p. 40–60°). The product was often contaminated with *trans*-[$PtCl_2Py_2$], which could be eliminated by recrystallisation from the minimum volume of cold benzene, yield 65–75%; m.p. 287° with decomposition. It had infra-red bands (in cm^{-1}) at: 3125 (w), 3100 (w), 3088 (w), 3066 (w), 3035 (w), 3015 (w), 2958 (m sh), 2919 (w), 1625 (m sh), 1600 (s sh), 1495 (ms sh), 1482 (w sh), 1456 (ms sh), 1447 (vs sh), 1375 (w), 1351 (w), 1263 (w), 1235 (w), 1205 (m sh), 1185 (w), 1145 (m), 1120 (vw), 1095 (vw), 1065 (s sh), 1041 (m sh), 1010 (m sh), 947 (vw), 935 (vw), 915 (vw), 885 (vw), 846 (vw), 817 (m), 768 (vs sh), 697 (vs), 673 (vs), 640 (m), 690 (m), 480 (w), 450 (w).

Preparation of $C_3H_6(C_5H_5NC_5H_5N)PtCl_4)\cdot CHCl_3$: Compound (IV)

1. *From (II).* The white complex (II) dissolves in 50/50 chloroform/carbon tetrachloride moderately well to form pale yellow-brown solutions. A sample of this was gently refluxed for 2 h. An amorphous solid (IV) was precipitated on addition of a large volume of ligroin, with an infra-red spectrum different from the spectra of either (II) or (III). The elemental analysis was almost consistent with the formula $C_3H_6(C_5H_5N)_2PtCl_7$; the measured carbon content was somewhat high. Recrystallisation of this material from chloroform gave deep yellow needles which had an infra-red spectrum identical with that of the amorphous material; m.p. 195° with decomposition. The microanalysis was now consistent with the formula $C_3H_6(C_5H_5N)_2PtCl_4\cdot CHCl_3$. (Found: C, 26.0; H, 2.4; Cl, 38.3; N, 4.1; Pt, 29.0.) $C_{14}H_{17}Cl_7N_2Pt$ calcd.: C, 25.6; H, 2.6; Cl, 37.7; N, 4.3; Pt, 29.9%.) The solvated compound had infrared absorption bands (in cm^{-1}) at: 3125 (m), 3112 (w), 3090 (m), 3076 (m), 3065 (w), 3055 (w), 3000 (vw), 2980 (m), 2958 (m), 2930 (m), 2870 (m), 1630 (s sh), 1603 (s sh),

1495 (s sh), 1483 (vs sh), 1450 (vs sh), 1388 (m sh), 1360 (vw), 1336 (w), 1312 (w), 1270 (w), 1237 (w), 1215 (m sh), 1210 (w), 1190 (w), 1155 (w), 1150 (w), 1137 (w), 1112 (s sh), 1068 (w), 1053 (w), 1040 (m sh), 1017 (vw), 972 (w), 910 (w), 870 (vw), 857 (w), 828 (w), 790 (vs sh), 780 (vs b), 760 (vs b), 695 (v s), 690 (v s), 657 (vw), 645 (m).

The solid (IV) was very insoluble in common solvents including deuterochloroform.

The chloroform of crystallisation in (IV) was removed quantitatively by gently warming the solid *in vacuo*. The chloroform was collected in a gas cell and identified by its infra-red spectrum. The remaining yellow solid was identical in infra-red absorption to complex (IV) except that the strong C–Cl stretching frequencies at 668 and 760 cm^{-1} of chloroform were now completely absent. [A microanalysis of this desolvated compound was consistent with the formula $C_3H_6(C_5H_5N)_2PtCl_4$].

2. *From(III)*. The complex(III) dissolved in chloroform/carbon tetrachloride to give a lemon yellow solution. Crystals recovered from the solution on standing were found to be identical with (IV) as prepared from (II). The conversion of (III) to (IV) in this way was almost quantitative. The only solid byproduct recovered was a very small amount of *trans*-$(C_5H_5N)_2PtCl_2$.

The rearrangement of complex (II) to (IV)

A saturated solution of (II) was made up in bromoform. Maintaining the temperature at 80°, the rearrangement, to the ylide complex (IV) took place in ca. 30 min. Successive NMR spectra were taken at 5-min intervals. The spectrum of the white complex was seen to disappear at the same rate as the spectrum of the yellow isomer (IV) appeared. At no time during or after the rearrangement were any extra bands produced.

Reactions of (II)

Less volatile olefins than ethylene will displace it from bis(ethylene)platinum dichloride. The white complex (II) was refluxed in chloroform solution with a number of olefins; styrene, 1,5-hexadiene, 1,5-cyclooctadiene and also with phenylacetylene. The ylide rearrangement took place in preference to cyclopropane displacement in each case.

Ethylenediamine has been shown to displace pyridine from complexes of platinum[10]. The white complex (II) was dissolved in chloroform and shaken up with a slight excess of ethylenediamine, in chloroform solution. After 15 min or so a very pale green complex was precipitated on addition of ligroin (b.p. 40–60°). The solid was allowed to dry after washing with water to remove excess ethylene diamine. (Found: C, 16.3; H, 3.8; Cl, 19.4; N, 8.3; Pt, 50.9. $C_5H_{14}Cl_2N_2Pt$ calcd.: C, 16.3; H, 3.8; Cl, 19.3; N, 7.6; Pt, 53.0%.) The NMR and infra-red spectra support the formulation $EnC_3H_6PtCl_2$ where En≡ethylenediamine. This complex could not be prepared from the brown complex (I), $(C_3H_6PtCl_2)_n$, by adding ethylenediamine in chloroform; cyclopropane was displaced with evolution of heat and the product was En_2PtCl_2.

Reactions of (III) and (IV)

The compounds were found to be extremely stable and no change in composition was detected over a period of approximately one year. They were also extremely inert in solution.

No change was observed when (III) or (IV) was refluxed in either chloroform or benzene solution with high concentrations of benzoyl chloride or acetyl chloride present. Sulphur dioxide was passed through solutions of (III) and (IV) in benzene and chloroform respectively for 2 h; the compounds were recovered unchanged. There was no observed change when (IV) and (III) were warmed in solution with excess methyl iodide. Hydrazine hydrate rapidly reacted with both compounds in solution to produce platinum metal, while hydrogen peroxide solution did not react at all. No change was observed on passing dry HCl through the solution of (IV) and (III) in benzene and chloroform for 30 min.

Preparation of complexes (II)–(IV) analogues, using picolines

The white complex (II) $C_3H_6(C_5H_5N)_2PtCl_2$ was made using 2-, 3-, 4-picolines and 2,6-lutidine in place of pyridine. The same method was used as for the parent complex except for the α-picoline and 2,6-lutidine cases. Here precipitation in water of the complexes of α-picoline and 2,6-lutidine was followed immediately by decomposition of the complex to give sticky intractable gums. A better method was to precipitate the complexes in ligroin (b.p. 40–60°) and then to take up the complex in chloroform and reprecipitate, thus removing excess ligand. The solid 2,6-lutidine complex decomposed very quickly on standing and for this reason it was not possible to obtain a micro-analysis or an infra-red spectrum of the compound.

The 3- and 4-picoline cyclopropane complexes underwent the ylide rearrangement on gentle heating in benzene solution for 30 min or so. The corresponding platinum(II) ylide complexes were obtained by allowing the solutions to crystallise. In contrast to their behaviour in benzene, the β- and γ-picoline cyclopropane complexes showed no signs of undergoing the ylide rearrangement in chloroform or chloroform/-carbon tetrachloride solutions. In most instances after only very gentle warming the colourless solids recovered from solution proved to be the *trans*-(Picoline)$_2$PtCl$_2$ compound. On more vigorous refluxing light brown tarry materials were obtained.

The platinum(II) 3- and 4-picoline ylide complexes dissolved in chloroform to give the corresponding yellow crystalline platinum(IV) compounds. The bis(2,6-lutidine) and bis(2-picoline) cyclopropane complexes decomposed on warming in benzene or chloroform solutions.

NMR of picoline compounds

Because of the increased solubility of the picoline complexes over the pyridine complexes, the spectra obtained were better resolved and the background was considerably less. The 3- and 4-picoline complexes analogous to complex (II) differed only in having an extra signal at τ 7.65 and 7.71 respectively from the six equivalent methyl protons of the two methyl groups on the picoline residues.

Bis(2-picoline)cyclopropaneplatinum dichloride was much less soluble than either 3- or 4-complexes.

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