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THE CRYSTAL AND MOLECULAR STRUCTURE OF TWO PYRIDINIUM PROPYLIDE COMPLEXES OF PLATINUM(II) AND PLATINUM(IV)

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SUMMARY

Single crystal structure analyses have been completed of dichloro(pyridinium propylide)pyridineplatinum(II) and tetrachloro(pyridinium propylide)pyridineplatinum(IV). $C_{13}H_{16}Cl_2N_2Pt$ forms monoclinic crystals from benzene and an X-ray analysis has been based on 1560 independent reflexions, intensities of which were measured on a Pailred diffractometer; least-squares analysis of atomic parameters of the two independent molecules in the unit cell has converged to $R=0.097$. $C_{13}H_{16}Cl_4N_2Pt \cdot CHCl_3$ also forms monoclinic crystals and an analysis is based on 1913 reflexions ($R=0.089$), intensities of which were visually estimated from Weissenberg and precession photographs. The mean metal–ligand band lengths are 2.32 Å (Pt–Cl), 2.10 Å (Pt–N), 2.01 Å (Pt–C) and are independent of the formal oxidation state of the metal. The formulation of the complexes as containing co-ordinated ylides is based on both NMR and stereochemical data.

INTRODUCTION

The synthesis of cyclopropane complexes of platinum(II) have been described together with their novel rearrangements to pyridinium propylide complexes[1]. Thus, dichloro(pyridinium propylide)pyridineplatinum(II) is readily obtained from dichlorobis(pyridine)cyclopropaneplatinum(II) through the heating of its benzene solution while the platinum(IV) analogue is obtained through the oxidation of the platinum(II) complex by chloroform. The unequivocal characterisation of these ylide species was only possible through X-ray crystallography and we now enlarge upon our earlier, preliminary report[2].

EXPERIMENTAL

Dichloro(pyridinium propylide)pyridineplatinum(II)

Crystal data $C_{13}H_{16}Cl_2N_2Pt$: monoclinic; $a=11.06(2)$, $b=10.49(2)$, $c=26.01(2)$ Å; $\beta=102.65(10)°$; $U=2944.4$ Å^3; $M=466.1$; $Z=8$; $D_M=2.09$, $D_{calc}=2.10$ g/cm^3; $F(000)=1760$; space group $P2_1/c$ (C_{2h}^5, No. 14), uniquely determined from systematic absences.

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The choice of a suitable crystal for intensity data collection was not straightforward in so far as some solvent is trapped in the lattice and the crystals tend to fracture after a period of exposure to the air. A crystal was eventually chosen and given a coat of "Formvar" to inhibit loss of solvent. Data collection was made on a Pailred diffractometer using Mo-K_α radiation (Si monochromator; λ 0.7107 Å). Of the 2519 reflexions scanned, 1560 were such that the independently measured backgrounds were not significantly different ($\leqslant 3.0\,\sigma$) and had $F^2_{\text{obs}}/\sigma(F^2_{\text{obs}}) \geqslant 2.5$. Data were corrected for usual geometrical effects but not for absorption.

A Patterson synthesis provided the positions of the two crystallographically independent platinum atoms, their separation of 6 Å immediately ruling out a chloro-bridged dimeric molecule; a difference Fourier synthesis based on the platinum atom contributions immediately revealed all of the remaining atoms and refinement of positional and anisotropic thermal parameters for the platinum and chlorine atoms, positional and isotropic thermal parameters for the carbon and nitrogen atoms reduced R to 0.097 after six least-squares cycles (unit weighting of all reflexions; atomic scattering factors corresponding to neutral atoms taken from the International Tables of Crystallography). A table of observed and calculated structure factors is available on request. Atomic parameters and their standard deviations are listed in Table 1, atom labelling being shown in Fig. 1.

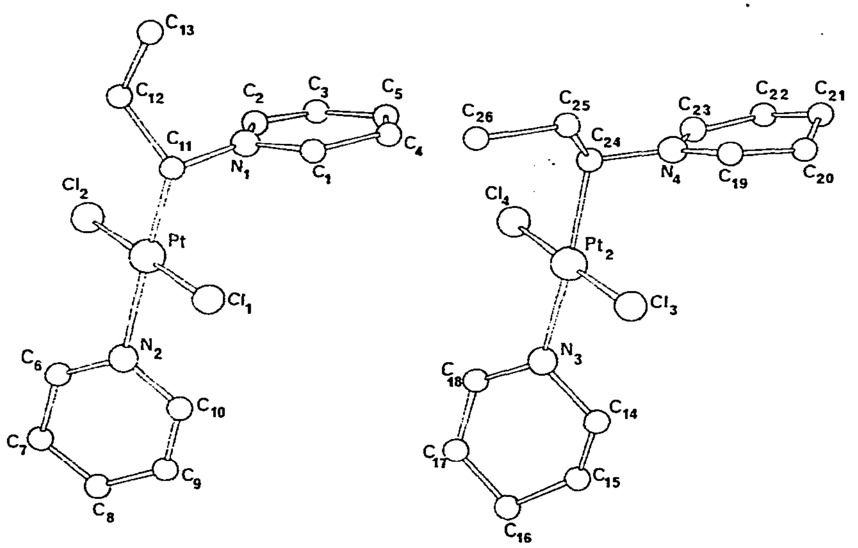


Fig. 1. Dichloro(pyridinium propylide)pyridineplatinum (II). A view of the crystallographically independent molecules and atom labelling. Each molecule is drawn so that the two sets of corresponding bonds Pt(1)–Cl(1), Pt(1)–C(11) and Pt(2)–Cl(3), Pt(2)–C(24) are in identical orientations.

Tetrachloro(pyridinium propylide)pyridineplatinum(IV)

Crystal data $C_{13}H_{16}Cl_4N_2Pt \cdot CHCl_3$: monoclinic; $a = 9.263(15)$, $b = 14.24(2)$, $c = 16.78(3)$ Å; $\beta = 94.1(1)^\circ$; $U = 2207.6$ Å^3; $M = 656.5$; $Z = 4$; $D_M = 2.04$, $D_{\text{calc}} = 1.98$ g/cm^3; $F(000) = 1248$; space group $P2_1/c$ (C^5_{2h}, No. 14), Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 80$ cm^{-1}..

TABLE 1

DICHLORO(PYRIDINIUM PROPYLIDE)PYRIDINEPLATINUM(II): ATOM PARAMETERS AND THEIR STANDARD DEVIATIONS

Anisotropic Debye factors for platinum and chlorine atoms given by $T = \exp[-(b_{11} \cdot h^2 + \ldots)]$.

Atom	x/a	y/b	z/c	B (Å^2)
Pt(1)	0.47743(28)	0.12114(31)	0.36333(10)	
Pt(2)	−0.09444(28)	0.09620(31)	0.10158(10)	
Cl(1)	0.5083(22)	0.2111(24)	0.4478(7)	
Cl(2)	0.4488(24)	0.0304(24)	0.2811(8)	
Cl(3)	−0.0382(21)	0.2189(22)	0.1767(8)	
Cl(4)	−0.1553(22)	−0.0284(25)	0.0277(6)	
N(1)	0.2281(59)	0.2051(69)	0.3433(23)	4.3(1)
N(2)	0.6125(52)	−0.0153(62)	0.3943(21)	3.5(1)
N(3)	0.0514(41)	−0.0241(50)	0.1289(18)	2.0(1)
N(4)	−0.3391(57)	0.1909(68)	0.0972(22)	4.1(1)
C(1)	0.1849(76)	0.2426(87)	0.3900(29)	4.5(2)
C(2)	0.1571(86)	0.1204(95)	0.3088(33)	6.4(2)
C(3)	0.0556(82)	0.0619(95)	0.3134(33)	5.7(2)
C(4)	0.0599(78)	0.1831(94)	0.3938(31)	5.3(2)
C(5)	0.0034(70)	0.0947(93)	0.3569(28)	4.7(2)
C(6)	0.6955(89)	−0.0471(99)	0.3684(36)	6.1(2)
C(7)	0.7828(60)	−0.1460(72)	0.3846(26)	2.7(1)
C(8)	0.7789(89)	−0.2075(100)	0.4317(35)	6.4(2)
C(9)	0.6958(69)	−0.1645(82)	0.4602(28)	4.0(2)
C(10)	0.6105(70)	−0.0775(87)	0.4416(28)	4.4(2)
C(11)	0.3593(89)	0.2544(100)	0.3428(34)	5.7(2)
C(12)	0.3278(70)	0.3259(83)	0.2837(28)	3.9(2)
C(13)	0.2320(68)	0.4242(83)	0.2761(28)	4.0(2)
C(14)	0.0852(51)	−0.0752(60)	0.1849(20)	1.8(1)
C(15)	0.1771(68)	−0.1395(84)	0.2014(27)	4.1(2)
C(16)	0.2708(64)	−0.1883(76)	0.1768(26)	3.3(1)
C(17)	0.2331(78)	−0.1558(93)	0.1212(29)	5.0(2)
C(18)	0.1239(61)	−0.0804(74)	0.0991(26)	3.2(1)
C(19)	−0.3628(56)	0.2481(64)	0.1369(21)	2.1(1)
C(20)	−0.4444(54)	0.2136(61)	0.1657(21)	1.9(1)
C(21)	−0.5467(68)	0.1294(87)	0.1395(27)	4.2(2)
C(22)	−0.5256(110)	0.0504(145)	0.0991(42)	9.3(3)
C(23)	−0.4156(90)	0.0890(126)	0.0799(36)	7.3(2)
C(24)	−0.2420(64)	0.2170(71)	0.0673(28)	3.0(1)
C(25)	−0.2379(110)	0.3362(151)	0.0549(45)	9.9(3)
C(26)	−0.1262(103)	0.3743(146)	0.0246(38)	8.6(3)

Atom	$10^4 b_{11}$	$10^4 b_{22}$	$10^4 b_{33}$	$10^4 b_{12}$	$10^4 b_{13}$	$10^4 b_{23}$
Pt(1)	84(2)	109(3)	14(1)	2(5)	26(1)	18(2)
Pt(2)	102(2)	109(3)	15(1)	4(5)	31(2)	11(2)
Cl(1)	199(2)	160(27)	19(4)	70(43)	51(16)	−5(15)
Cl(2)	278(34)	135(27)	20(4)	103(49)	32(18)	−26(16)
Cl(3)	177(26)	115(25)	30(4)	−103(38)	63(17)	−47(16)
Cl(4)	204(26)	224(31)	33(2)	−25(46)	9(13)	13(14)

Bright yellow rectangular prisms, elongated along the *a* axis, were obtained from dilute solutions in chloroform/carbon tetrachloride. Rapid crystallisation from concentrated solutions produced fine needles having the same unit cell and with *a* the needle axis. Crystals of the former type, having approximately square cross section of side 0.15 mm, were used for data collection.

Initial data collection was based on Weissenberg (0–4*kl*) and precession (*h*0*l*, 0*kl* and *hhl*) photographs. Decomposition of the crystals after ca. 100 h exposure in the X-ray beam led us to take further precession data from a crystal sealed in a Lindemann tube. Relative intensities were assigned by visual methods based on multiple film/multiple exposure techniques, a total of 1913 non-equivalent reflexions being available for the structure determination; no absorption correction was applied.

The platinum position was obtained from a Patterson synthesis and the four chlorine atoms bonded to this atom and the chlorine atoms of the solvated chloroform/carbon tetrachloride deduced from a difference Fourier synthesis. Two cycles of least-squares refinement of these positional and thermal parameters followed by a further difference synthesis revealed the remaining carbon and nitrogen atoms. Three cycles of block-diagonal least-squares refinement reduced *R* to 0.11, the refined thermal parameters of the chlorine atoms belonging to the solvated molecule suggesting only partial occupancy of their assigned sites; by assuming a population parameter of 0.67 for Cl(6), Cl(7) and Cl(8), the refined isotropic temperature factors for all solvent atoms became essentially equal, a feature consistent with the solvent being a chloroform molecule, spatially disordered so that the single hydrogen atom randomly occupies each of the chlorine sites mentioned above.

After a check of the interlayer scale factors through a comparison of observed and calculated structure factors, anisotropic thermal parameters were introduced for all atoms other than those of the solvated chloroform; three cycles of refinement using the weighting scheme

$$w = 1/[2F_{\text{min}} + F_{\text{obs}} + (2/F_{\text{max}})\cdot F_{\text{obs}}^2]$$

reduced *R* to 0.089 when no shifts in parameters greater than 0.3 σ were evident.

A list of observed and calculated structure factors is available on request, while

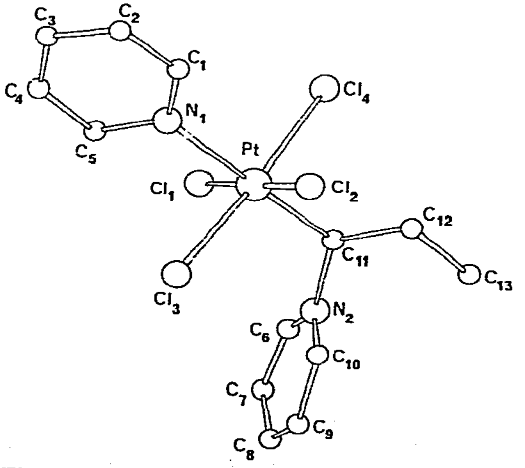


Fig. 2. Tetrachloro(pyridinium propylide)pyridineplatinum(IV). Stereochemistry of the molecule and atom labelling.

TABLE 2

$(C_2H_5C_5H_4NCH)(C_5N_5H_5)PtCl_4$: ATOMIC POSITIONAL AND VIBRATIONAL PARAMETERS

The vibrational coefficients relate to the expression:

$T = \exp[-((h^2 \cdot a^{*2} \cdot B_{11} + k^2 \cdot b^{*2} \cdot B_{22} + l^2 \cdot c^{*2} \cdot B_{33} + 2k \cdot l \cdot b^* \cdot c^* \cdot B_{23} + 2l \cdot h \cdot c^* \cdot a^* \cdot B_{13} + 2h \cdot k \cdot a^* \cdot B_{12})/4)]$.

Atom	x/a	y/b	z/c	B (Å^2)
Pt	0.16408(6)	0.03467(7)	0.82065(12)	
Cl(1)	0.03056(42)	−0.00779(60)	0.78094(94)	
Cl(2)	0.29713(51)	0.07718(71)	0.85819(125)	
Cl(3)	0.14210(66)	0.16109(57)	0.66894(93)	
Cl(4)	0.18579(45)	−0.09825(55)	0.96424(86)	
N(1)	0.1917(15)	−0.0440(16)	0.6325(23)	
C(1)	0.2595(16)	−0.0971(21)	0.6258(43)	
C(2)	0.2795(20)	−0.1413(26)	0.5011(51)	
C(3)	0.2234(23)	−0.1470(32)	0.3790(40)	
C(4)	0.1546(26)	−0.0945(29)	0.3908(32)	
C(5)	0.1403(17)	−0.0395(25)	0.5103(30)	
N(2)	0.0921(13)	0.1963(16)	0.9691(27)	
C(6)	0.0080(17)	0.1973(23)	0.9618(32)	
C(7)	−0.0339(22)	0.2727(25)	0.9242(44)	
C(8)	0.0063(20)	0.3567(24)	0.9136(46)	
C(9)	0.0931(24)	0.3606(20)	0.9264(35)	
C(10)	0.1334(16)	0.2724(21)	0.9527(32)	
C(11)	0.1318(14)	0.1023(22)	0.9979(27)	
C(12)	0.1963(16)	0.1014(33)	0.1243(32)	
C(13)	0.1589(22)	0.1538(22)	0.2586(38)	
Cl(5)	0.3930(8)	0.2399(10)	0.2770(16)	9.2(0.5)
Cl(6)^a	0.5077(14)	0.0864(17)	0.2997(27)	10.0(1.0)
Cl(7)^a	0.3678(13)	0.1198(15)	0.5164(25)	9.2(0.9)
Cl(8)^a	0.4976(14)	0.2189(15)	0.5143(25)	9.7(0.8)
C(14)	0.4354(35)	0.1400(40)	0.3872(64)	10.7(0.9)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pt	2.443	2.620	2.308	0.195	0.662	−0.224
Cl(1)	3.04	5.78	3.83	−0.46	−0.66	−0.20
Cl(2)	3.92	6.65	8.90	−1.20	1.70	−2.57
Cl(3)	9.05	3.73	3.92	0.74	2.39	0.18
Cl(4)	4.09	4.13	3.91	0.93	−0.07	0.65
N(1)	5.0	4.2	1.9	−0.5	1.2	0.9
C(1)	4.0	2.9	8.6	0.3	4.4	0.4
C(2)	4.3	5.1	10.4	0.9	1.0	1.7
C(3)	4.9	10.7	3.0	2.7	−1.3	0.9
C(4)	8.8	6.7	2.3	−1.6	−2.4	1.0
C(5)	3.0	7.8	1.8	2.6	−0.6	0.1
N(2)	2.1	4.3	4.7	1.3	0.5	−0.2
C(6)	3.7	6.7	2.6	−0.9	2.4	−0.6
C(7)	5.4	4.8	6.6	1.0	2.4	0.5
C(8)	6.1	5.5	5.8	−0.5	1.6	1.6
C(9)	8.4	3.5	3.3	−3.3	2.3	−1.8
C(10)	4.7	4.4	2.9	0.0	2.0	−1.2
C(11)	2.8	5.2	3.6	−0.2	0.0	−0.1
C(12)	2.3	11.9	3.2	3.2	−1.3	−0.9
C(13)	7.4	4.7	4.1	−2.8	2.3	0.2

Table 2 displays atomic parameters and their standard deviations; atom labelling is shown is Fig. 2.

THE MOLECULAR STRUCTURES

The mean Pt^{IV}–Cl distance of 2.316 Å (σ=0.011 Å) is identical, within experimental error, to that of the mean Pt^{II}–Cl bond length (2.313 Å) (Tables 3 and 4). The Pt^{IV}–N distance of 2.15 Å is again not significantly different from the mean Pt^{II}–N bond length of 2.07 Å; together they demonstrate a *trans*-influence of the σ-bonded carbon atom ($\bar{l}$(Pt–C) = 2.01 Å) of the order of 0.1 Å, since the difference in covalent radii between carbon and nitrogen is only 0.03 Å, and this is in accord with other estimates in similar complexes[3].

Apart from a conformational difference which is discussed below, the geometries of the two crystallographically non-equivalent platinum(II) ylide complexes are identical within experimental error. Both co-ordinated pyridine rings are planar, the

TABLE 3

DICHLORO(PYRIDINIUM PROPYLIDE)PYRIDINEPLATINUM(II): INTRAMOLECULAR BOND LENGTHS, SELECTED BOND ANGLES AND THEIR STANDARD DEVIATIONS

Bond	Length (Å)	Bond	Length (Å)
Pt(1)–Cl(1)	2.35(2)	Pt(2)–Cl(3)	2.31(2)
Pt(1)–Cl(2)	2.30(2)	Pt(2)–Cl(4)	2.30(2)
Pt(1)–N(2)	2.10(6)	Pt(2)–N(3)	2.05(5)
Pt(1)–C(11)	1.91(10)	Pt(2)–C(24)	2.11(7)
N(1)–C(1)	1.45(9)	N(4)–C(19)	1.27(8)
N(1)–C(2)	1.38(13)	N(4)–C(23)	1.38(14)
N(1)–C(11)	1.55(11)	N(4)–C(24)	1.48(8)
N(2)–C(6)	1.30(10)	N(3)–C(14)	1.52(7)
N(2)–C(10)	1.40(10)	N(3)–C(18)	1.36(8)
C(1)–C(4)	1.53(12)	C(19)–C(20)	1.34(7)
C(2)–C(3)	1.30(13)	C(22)–C(23)	1.46(15)
C(3)–C(5)	1.42(11)	C(21)–C(22)	1.39(15)
C(4)–C(5)	1.38(13)	C(20)–C(21)	1.49(10)
C(6)–C(7)	1.42(13)	C(17)–C(18)	1.46(12)
C(7)–C(8)	1.39(12)	C(16)–C(17)	1.46(11)
C(8)–C(9)	1.37(11)	C(15)–C(16)	1.43(9)
C(9)–C(10)	1.32(12)	C(14)–C(15)	1.22(10)
C(11)–C(12)	1.67(12)	C(24)–C(25)	1.30(17)
C(12)–C(13)	1.46(11)	C(25)–C(26)	1.65(16)

Angle	(°)	Angle	(°)
Cl(1)–Pt(1)–Cl(2)	179.2(9)	Cl(3)–Pt(2)–Cl(4)	178.3(8)
Cl(1)–Pt(1)–N(2)	88.3(17)	Cl(3)–Pt(2)–N(3)	90.3(15)
Cl(1)–Pt(1)–C(11)	85.3(29)	Cl(3)–Pt(2)–C(24)	93.5(20)
Cl(2)–Pt(1)–N(2)	90.9(17)	Cl(4)–Pt(2)–N(3)	90.2(15)
Cl(2)–Pt(1)–C(11)	95.5(29)	Cl(4)–Pt(2)–C(24)	86.1(20)
N(2)–Pt(1)–C(11)	173(3)	N(3)–Pt(2)–C(24)	175(2)
Pt(1)–C(11)–N(1)	160(6)	Pt(2)–C(24)–N(4)	104(4)
Pt(1)–C(11)–C(12)	125(5)	Pt(2)–C(24)–C(25)	128(8)
N(1)–C(11)–C(12)	99(6)	N(4)–C(24)–C(25)	113(7)

TABLE 4

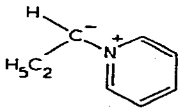
$(C_2H_5C_5H_5NCH)(C_5H_5N)PtCl_4$: BOND LENGTHS, BOND ANGLES, AND THEIR STANDARD DEVIATION

Bond	Length (Å)	Bond	Length (Å)
Pt-Cl(1)	2.325(7)	N(2)-C(11)	1.51(3)
Pt-Cl(2)	2.316(8)	N(2)-C(6)	1.41(4)
Pt-Cl(3)	2.298(8)	N(2)-C(10)	1.30(3)
Pt-Cl(4)	2.327(7)	C(6)-C(7)	1.32(5)
Pt-N(1)	2.151(21)	C(7)-C(8)	1.38(5)
Pt-C(11)	2.012(25)	C(8)-C(9)	1.45(5)
N(1)-C(1)	1.37(3)	C(9)-C(10)	1.44(5)
N(1)-C(5)	1.37(3)	C(11)-C(12)	1.54(4)
C(1)-C(2)	1.38(5)	C(12)-C(13)	1.62(5)
C(2)-C(3)	1.42(5)	C(14)-Cl(5)	1.86(6)
C(3)-C(4)	1.39(5)	C(14)-Cl(6)	1.69(6)
C(4)-C(5)	1.39(5)	C(14)-Cl(7)	1.73(6)
		C(14)-Cl(8)	1.89(6)

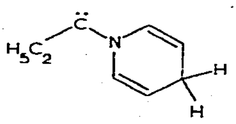
Angle	(°)	Angle	(°)
Cl(1)-Pt-Cl(3)	89.78(15)	C(11)-N(2)-C(6)	116.4(2.0)
Cl(1)-Pt-Cl(4)	89.35(12)	C(11)-N(2)-C(10)	121.8(2.1)
Cl(1)-Pt-N(1)	89.87(30)	C(6)-N(2)-C(10)	121.7(2.0)
Cl(1)-Pt-C(11)	86.60(35)	N(2)-C(6)-C(7)	122.4(2.3)
Cl(2)-Pt-Cl(3)	89.88(17)	C(6)-C(7)-C(8)	118.0(2.6)
Cl(2)-Pt-Cl(4)	90.97(15)	C(7)-C(8)-C(9)	121.3(2.3)
Cl(2)-Pt-N(1)	89.78(31)	C(8)-C(9)-C(10)	115.9(2.0)
Cl(2)-Pt-C(11)	93.80(36)	N(2)-C(10)-C(9)	119.9(2.1)
Cl(3)-Pt-N(1)	86.96(25)	Pt-C(11)-N(2)	114.9(1.1)
Cl(3)-Pt-C(11)	94.78(30)	Pt-C(11)-C(12)	113.7(1.3)
Cl(4)-Pt-N(1)	90.32(23)	N(2)-C(11)-C(12)	114.9(2.0)
Cl(4)-Pt-C(11)	87.89(28)	C(11)-C(12)-C(13)	106.8(1.7)
Pt-N(1)-C(1)	123.4(1.0)	Cl(5)-C(14)-Cl(6)	110(1)
Pt-N(1)-C(5)	118.9(1.4)	Cl(5)-C(14)-Cl(7)	105(2)
C(1)-N(1)-C(5)	117.5(1.6)	Cl(5)-C(14)-Cl(8)	93(2)
N(1)-C(1)-C(2)	122.8(1.8)	Cl(6)-C(14)-Cl(7)	142(3)
C(1)-C(2)-C(3)	120.4(2.6)	Cl(6)-C(14)-Cl(8)	101(2)
C(2)-C(3)-C(4)	114.4(2.1)	Cl(7)-C(14)-Cl(8)	92(1)
C(3)-C(4)-C(5)	123.9(2.3)		
N(1)-C(5)-C(4)	119.7(2.3)		

r.m.s. deviation of carbon and nitrogen atoms being 0.04 Å which is the same as that for the platinum(IV) complex. The pyridine rings are staggered at 45° to the platinum–chlorine bonds.

The formulation of the carbon-bonded ligand as a pyridinium propylide(I) rather than the isomeric carbene (II) is unequivocal. There is the NMR evidence for



(I)



(II)

an α-CH group which has been presented in the accompanying report but additionally the stereochemistry of the α-C atom is clearly tetrahedral rather than planar. The normal to the plane containing the atoms N(1), C(11) and C(12) has direction cosines −0.4840, −0.8524, 0.1980 referred to *a*, *b*, *c** and the platinum atom, Pt(1), is displaced by 1.32 Å from this plane; for the second crystallographically non-equivalent complex in the cell, the direction cosines of normal to the plane containing N(4), C(24) and C(25) are 0.7300, 0.1701, 0.6619 and Pt(2) is displaced 1.23 Å from this plane. For the platinum(IV) complex, the platinum atom is displaced by 1.30 Å from the plane containing the atoms N(2), C(11) and C(12); direction cosines of the normal to the plane are now −0.7403, −0.2314, 0.6312.

So far as the other structural features of the co-ordinated ylide fragment are concerned, the main point of note is that the conformations of the ligands in the two crystallographically non-equivalent platinum(II) species are different. The conformation about the α-C–β-C bond is *gauche* in the complex containing Pt(1) and is *staggered* for that containing the platinum atom, Pt(2). The torsion angles about the relevant bonds of C(11)–C(12) and C(24)–C(25) are 57° and 176° respectively.

It is obvious that the stabilisation of the ylide on co-ordination (we have been unable to carry out any reactions on the co-ordinated ligand which are characteristic of the free molecule) is due to the formation of a strong σ-bond between the platinum ions and carbon atoms and a concomitant decrease in the polar character of the carbon–nitrogen bond. Stable ylide complexes of other strongly electronegative transition metal ions such as Au^{III} should become available.

THE CRYSTAL STRUCTURES

No hydrogen atom positions have been determined but the other non-bonded distances in the two crystal structures are close to expectation. The solvated molecule in the platinum(IV) complex occupies a "hole" in the lattice and there are quite short non-bonded distances of 3.2 Å between Cl(3) and Cl(8) and between Cl(4) and Cl(5); the definition of the structure of the solvent molecule ($CHCl_3/CCl_4$) is, however, poor for reasons which were mentioned earlier. In the platinum(II) complex, the molecules pack as a layer structure and the facile fracturing of the crystals is easily explained.

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