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STRUCTURE OF $PtCl_2[C_3H_4(C_6H_5)_2](C_5H_5N)_2 \cdot \frac{1}{2}$ C_2H_5OH, A SUBSTITUTED CYCLOPROPANE COMPLEX OF PLATINUM

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SUMMARY

The crystal and molecular structure of a 1,2-diphenylcyclopropane complex of platinum, $PtCl_2[C_3H_4(C_6H_5)_2](C_5H_5N)_2$, has been determined from three-dimensional X-ray diffraction data. The crystal has symmetry consistent with space group $P\bar{1}$ (C_i^1) with four molecules of the complex and two molecules of ethanol of crystallisation in a unit cell of dimensions $a=13.148(6)$, $b=14.052(7)$, $c=17.860(8)$ Å; $\alpha=62.53(1)$, $\beta=108.25(3)$, $\gamma=114.69(3)°$. The structure was refined by least-squares techniques to a conventional R-factor of 10.0% using 2804 reflections, collected using a four-circle diffractometer, for which $F^2 \geqslant \sigma(F^2)$. The ethanol of crystallisation was highly disordered, and a satisfactory description was not obtained for it. There are two independent complex platinum molecules in the unit cell and, whilst the mode of attachment of the substituted cyclopropane is basically similar in the two molecules, there are significant differences between the observed geometries, and the two molecules are not equivalent. The platinum atoms in both molecules have two chlorine atoms *trans* in axial positions and two *cis* pyridine ligands in the equatorial plane; the coordination sphere is completed by the cyclopropane ligand which has two of its ring carbon atoms in the equatorial plane approximately equidistant from platinum and the third ring carbon atom considerably further away from platinum and slightly displaced from the equatorial plane. In one of the complex molecules, the angle subtended to platinum by the nitrogen atoms of the pyridine ligands is 92(1)° and the plane of one of the phenyl rings is perpendicular to the cyclopropane ring plane; in the other complex molecule, the corresponding N–Pt–N angle is 82(1)° and the planes of the phenyl and cyclopropane rings are not mutually perpendicular. The bonding of cyclopropane to platinum was rationalised using a four-centre localised molecular orbital scheme.

INTRODUCTION

Cyclopropane is a molecule of great interest, both experimentally and theoretically. The bonding in this unusual molecule was first explained by Walsh[1] and by Coulson and Moffitt[2] and these two apparently different explanations have been shown to be equivalent[3]. Semi-empirical molecular orbital methods have also been used to study the bonding in cyclopropane[4,5]. The chemistry of cyclopropane is more typical of an olefin than of a saturated hydrocarbon: for example addition reactions occur more commonly than substitution reactions[6]. There are very many metal–olefin complexes known and an extra dimension was added to the similarity between cyclopropane and olefins when Tipper reported a platinum–cyclopropane complex[7]. The first reported structure of a metal–cyclopropane complex was that of $PtCl_2$-$(C_3H_6)(C_5H_5N)_2$ and the platinum atom is approximately equidistant from two of the carbon atoms of the cyclopropane ligand[8]. Unfortunately the X-ray data set used to determine the structure was of limited accuracy due to crystal decomposition and detailed discussion of the bonding in the complex was not possible.

Aryl-substituted cyclopropanes are thought to have a favoured geometry in which the plane of the aryl ring is perpendicular to the plane of the cyclopropane ring; in this arrangement there can be favourable π-interactions between the two rings[4,9]. Platinum complexes of aryl-substituted cyclopropanes have been prepared[10]: the structure of one of these was determined in the hope of obtaining direct evidence about the relative arrangement of the aryl and cyclopropane rings and to gain further insight about the platinum–cyclopropane interaction.

COLLECTION AND REDUCTION OF X-RAY DATA

The crystals were kindly supplied by K. G. Powell and F. J. McQuillin. Optical examination and preliminary X-ray photography revealed no lattice symmetry and no systematic absences: the crystal was thus assigned to the triclinic system and the subsequent successful refinement of the structure showed the space group to be $P\bar{1}$. A Delauney reduction did not reveal the presence of additional lattice symmetry. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections carefully centred on a Hilger-Watts four-circle automatic X-ray diffractometer, are (at 18°): $a = 13.148(6)$, $b = 14.052(7)$, $c = 17.860(8)$ Å; $\alpha = 62.53(1)$, $\beta = 108.25(3)$, $\gamma = 114.69(3)$°. For four formula weights of the cyclopropane complex in the unit cell, the calculated density is 1.56 g/cm^3; the observed density is 1.56 g/cm^3. The good agreement between the calculated and observed densities did not indicate the presence of a molecule of solvation and this remained unsuspected until well into the refinement of the structure. In addition to the complex molecules there seems to be two formula weights of ethanol present in the unit cell, making the calculated density 1.59 g/cm^3, in reasonable agreement with the observed density. The density of the crystal was determined by flotation and the error limit in the measurement is probably less than 0.01 g/cm^3. The main source of error in the comparison between observed and calculated densities lies in the assumption of a perfect crystal which is used in the calculation of crystal density from the cell volume. Crystals of compounds such as that discussed here have mosaic character and the density is calculated too high by a varying amount (usually 2–3 %). This systematic error is usually sufficiently small that a molecule of solvation can be readily detected; the exception here was because the molecular weight of the complex was very large relative to that of ethanol divided by two. There are two complex molecules and one molecule of solvation in the asymmetric unit of the cell.

Intensity data were collected from a crystal of dimensions 0.08 × 0.06 × 0.05 mm. Data was collected using a Hilger-Watts 4-circle automatic diffractometer in $w = \theta$ step scan mode with Zr-filtered Mo-K_α radiation. A symmetric scan of 2.2° in 2θ

(in steps of 0.02°) was used, counting for 3 seconds at each step. Stationary-crystal, stationary-counter background counts of 40 seconds were measured at each end of the scan. Both forms of the triclinic crystal (*hkl* and $\bar{h}\bar{k}l$) were measured out to 20° and one form out to 40° in 2θ (for Mo-K_α radiation). A total of 4895 reflections were measured.

The intensities of three standard reflections were measured at intervals throughout collection of the intensity data. All three decreased in intensity regularly but each at a slightly different rate and at the end of data collection they had decreased by between 30 and 40%.

The intensity data were corrected for background, Lorentz and polarisation effects and for the average change in intensity of the three standard reflections. The linear absorption coefficient of the compound for Mo-K_α radiation is 58.2 cm^{-1}; no absorption correction was made because of the small crystal size (the minimum and maximum transmission factors differed by less than 20%). The equivalent forms were averaged. The standard deviations on F^2 were estimated from counting statistics and from the range of equivalent forms and the larger of the two estimates was used. For the 705 reflections measured more than once, the R-factor for averaging the intensities ($R_{av} = 100[I_1 - I_2]/[I_1 + I_2]$, where I_1, I_2 are the individual intensities) was 7.0%. There were 2804 reflections with $F_o^2 \geqslant \sigma(F_o^2)$ and 1960 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$.

SOLUTION AND REFINEMENT OF THE STRUCTURE

Initial values of the coordinates of both platinum atoms were obtained from a three-dimensional Patterson function*. The function minimised in the least-squares refinement was $\Sigma w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated structure factors and where the weights, w, equal $4F_o^2/\sigma^2(F_o^2)$. Recent tabulations of atomic scattering factors and anomalous scattering corrections were used[11]. Normal application of least-squares refinement and difference Fourier syntheses yielded the coordinates of all non-hydrogen atoms in the two independent platinum complex molecules. The four phenyl rings were refined as rigid groups with one thermal parameter, the two platinum and four chlorine atoms were allowed to vibrate anisotropically and the other atoms were refined with isotropic thermal parameters; an extinction parameter was varied in the refinement and after convergence the conventional R-factor ($R = \Sigma\, ||F_o| - |F_c||/|F_o|$) was 9.7% for the 1960 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. A difference Fourier revealed the presence of a disordered molecule of crystallisation. The description of this species is unsatisfactory; it is most likely to be ethanol because the crystal was obtained from ethanol solution. The highest peak in the difference Fourier was higher than a typical carbon or nitrogen atom in the structure and so this was assigned to be an oxygen atom; this refined with a satisfactory thermal parameter. The α-carbon atom was highly disordered and, after several alternatives were tried, this atom was refined as an atom of unit occupancy and the thermal parameter converged to a high value. The β-carbon atom was also disordered with four favoured positions; assuming the total occupancy of the four positions was unity and with a fixed, common thermal

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* Computer programs used include local modifications of Zalkin's FORDAP, Busing and Levy's ORFLS (with the Doedens and Ibers subroutines for group refinements), Busing, Martin and Levy's ORFFE and Johnson's ORTEP.

parameter, the occupancies were refined. With these additional parameters, a further two cycles of refinement led to an R-factor of 6.9% for the 1960 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. Finally the 2804 reflections with $F_o^2 \geqslant \sigma(F_o^2)$ were included in the calculation and after two cycles of refinement the R-factor had converged to 10.0%*; in these two cycles of refinement, no parameter changed by more than 65% of its final estimated standard deviation and one result was a lowering of the estimated standard deviations by an average factor of 0.9. A statistical analysis of the agreement between the final values of F_c and F_o was performed for various combinations of the Miller indices and as a function of $|F_o|$ and θ; no unexpected or noteworthy trends were observed. The agreement between the final values of F_c and F_o is relatively poor for a data set collected using a diffractometer, especially when all 2804 reflections with $F_o^2 \geqslant \sigma(F_o^2)$ are included in the calculation. Two major factors contributing to this poor agreement are the considerable decomposition of the crystal during data collection and the poor description of the molecule of solvation. However, it is the statistically more correct procedure to report the parameters derived using all 2804 reflections, rather than those derived using a more limited data set, *e.g.* the 1960 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. Admittedly in this latter case a more respectable R-factor could be quoted, but this is not the point; indeed the statistical analysis revealed that the R-factor was under 6% when the weakest one third of the reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ are not considered. However the estimated standard deviations of the structural parameters were at a minimum when the data set of 2804 reflections were used. It is particularly important to note that there were no statistically significant changes in any parameter when the 844 reflections with F_o^2 in the range $3\sigma(F_o^2) \geqslant F_o^2 \geqslant \sigma(F_o^2)$ were included in the refinement; it is this that suggests that the estimated standard deviations in the parameters have the significance customary in diffraction studies of compounds of this complexity.

A final difference Fourier map showed no peak higher than 0.4 e/Å^3, approximately 15% of the height of a typical carbon atom in this structure.

Table 1 shows the final values of the positional and thermal parameters with their estimated standard deviations as derived from the inverse matrix. The parameters for the carbon atoms of the phenyl rings shown in Table 1 have been derived from the group parameters. Table 2 gives the root-mean-square amplitudes of vibration for those atoms that were refined anisotropically.

DESCRIPTION OF THE STRUCTURE

The crystal structure consists of the packing of the monomeric molecular units $PtCl_2(C_3H_4(C_6H_5)_2)(C_5H_5N)_2$ and C_2H_5OH in the ratio 2/1. There are no significantly short intermolecular contacts and the species are discrete with normal crystal forces holding them together. If cyclopropane is considered to act as a bidentate ligand, then platinum is six-coordinate in both molecules with the two chloride ligands *trans* to each other in axial positions. Figure 1 shows the ligands coordinated in the

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* The table of structure factors has been deposited as NAPS Document No. 02135, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(*continued on p.* 435)

TABLE 1

POSITIONAL AND THERMAL PARAMETERS[a] FOR PtCl$_2$(C$_3$H$_4$(C$_6$H$_5$)$_2$)(C$_5$H$_5$N)$_2$·$\frac{1}{2}$C$_2$H$_5$OH

A. Positional and isotropic thermal parameters.

	x	*y*	*z*	*B*(Å^2)
Complex molecule I				
Pt	0.3051(1)	0.4748(1)	0.3040(1)	
Cl(1)	0.4954(8)	0.5474(8)	0.3504(6)	
Cl(2)	0.1166(8)	0.3973(8)	0.2571(6)	
N(1)	0.310(2)	0.322(2)	0.414(2)	6.1(8)
py1-C(1)[b]	0.262(3)	0.217(3)	0.406(2)	6.4(10)
py1-C(2)	0.347(3)	0.313(3)	0.495(3)	7.1(10)
py1-C(3)	0.252(3)	0.112(3)	0.477(3)	6.7(10)
py1-C(4)	0.344(4)	0.215(4)	0.565(2)	7.2(11)
py1-C(5)	0.295(3)	0.118(3)	0.553(2)	6.6(10)
N(2)	0.257(2)	0.510(2)	0.393(2)	4.8(7)
py2-C(1)	0.319(3)	0.610(3)	0.412(2)	6.2(10)
py2-C(2)	0.168(3)	0.454(3)	0.423(2)	6.2(10)
py2-C(3)	0.295(4)	0.626(3)	0.474(3)	7.9(11)
py2-C(4)	0.137(4)	0.473(4)	0.485(3)	8.7(12)
py2-C(5)	0.205(4)	0.559(4)	0.504(2)	7.5(11)
C(1)	0.299(3)	0.610(3)	0.190(2)	4.9(9)
C(2)	0.376(3)	0.580(3)	0.157(2)	7.0(10)
C(3)	0.355(3)	0.458(3)	0.211(2)	6.2(10)
ph1-C(1)[c]	0.352(3)	0.722(2)	0.197(2)	7.8(5)[d]
ph1-C(2)	0.466(2)	0.787(3)	0.198(2)	
ph1-C(3)	0.275(2)	0.761(3)	0.205(2)	
ph1-C(4)	0.504(2)	0.890(3)	0.207(2)	
ph1-C(5)	0.314(2)	0.864(3)	0.214(2)	
ph1-C(6)	0.430(3)	0.928(2)	0.215(2)	
ph2-C(1)	0.348(3)	0.602(3)	0.059(1)	10.9(6)
ph2-C(2)	0.297(2)	0.684(3)	0.004(3)	
ph2-C(3)	0.376(2)	0.544(2)	0.026(2)	
ph2-C(4)	0.272(2)	0.708(2)	−0.084(2)	
ph2-C(5)	0.351(2)	0.568(3)	−0.061(3)	
ph2-C(6)	0.299(3)	0.649(3)	−0.116(1)	
Complex Molecule II				
Pt	−0.0610(1)	−0.0118(1)	0.1877(1)	
Cl(1)	0.0658(8)	−0.0402(8)	0.1410(6)	
Cl(2)	−0.1781(8)	0.0247(8)	0.2364(6)	
N(1)	−0.029(2)	0.158(3)	0.091(2)	6.8(8)
py1-C(1)	−0.023(3)	0.178(4)	0.007(3)	7.5(11)
py1-C(2)	0.011(3)	0.252(4)	0.109(2)	7.2(11)
py1-C(3)	0.007(3)	0.285(4)	−0.052(3)	8.3(12)
py1-C(4)	0.043(3)	0.362(4)	0.050(3)	7.9(11)
py1-C(5)	0.039(3)	0.379(3)	−0.036(3)	7.7(11)
py2-N(2)	−0.217(3)	−0.082(3)	0.099(2)	7.0(8)
py2-C(1)	−0.211(4)	−0.166(4)	0.082(3)	10.6(14)
py2-C(2)	−0.298(4)	−0.035(4)	0.064(3)	10.7(14)
py2-C(3)	−0.297(5)	−0.207(4)	0.020(3)	11.4(15)
py2-C(4)	−0.382(4)	−0.078(5)	0.004(3)	11.6(15)
py2-C(5)	−0.391(4)	−0.171(4)	−0.006(3)	9.7(13)

(*continued*)

TABLE 1 (*continued*)

	x	y	z	$B(A^2)$
C(1)	−0.073(3)	−0.159(3)	0.294(2)	5.7(9)
C(2)	0.052(3)	−0.106(3)	0.335(2)	4.0(8)
C(3)	0.081(3)	0.037(3)	0.279(2)	6.1(9)
ph1-C(1)	−0.110(3)	−0.275(2)	0.288(1)	6.9(5)
ph1-C(2)	−0.032(1)	−0.320(2)	0.289(1)	
ph1-C(3)	−0.225(2)	−0.332(2)	0.276(1)	
ph1-C(4)	−0.071(2)	−0.421(2)	0.277(1)	
ph1-C(5)	−0.264(1)	−0.433(2)	0.264(1)	
ph1-C(6)	−0.186(3)	−0.478(2)	0.264(2)	
ph2-C(1)	0.067(2)	−0.146(2)	0.435(1)	6.2(4)
ph2-C(2)	0.004(2)	−0.127(2)	0.474(2)	
ph2-C(3)	0.152(2)	−0.193(2)	0.485(2)	
ph2-C(4)	0.027(2)	−0.155(2)	0.562(2)	
ph2-C(5)	0.175(2)	−0.221(2)	0.572(2)	
ph2-C(6)	0.112(2)	−0.202(2)	0.611(1)	
Solvent molecule				
O	0.521(2)	0.251(2)	0.364(2)	7.4(7)
S-C(1)	0.508(8)	0.208(8)	0.292(6)	24.8(36)
S-C(2)	0.381(3)	0.187(3)	0.220(2)	[0.5]8.0[e]
S-C(3)	0.582(3)	0.146(4)	0.291(3)	[0.3]8.0
S-C(4)	0.442(4)	0.032(4)	0.394(3)	[0.1]8.0
S-C(5)	0.362(5)	0.092(6)	0.311(5)	[0.1]8.0

B. Anisotropic thermal parameters[f]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Complex molecule I						
Pt	0.0118(2)	0.0107(2)	0.0044(1)	0.0042(2)	−0.0004(1)	−0.0030(1)
Cl(1)	0.0147(13)	0.0101(11)	0.0054(6)	0.0037(10)	0.0022(7)	−0.0010(7)
Cl(2)	0.0160(14)	0.0104(11)	0.0049(6)	0.0003(10)	0.0026(7)	−0.0019(7)
Complex molecule II						
Pt	0.0109(2)	0.0101(2)	0.0041(1)	0.0043(2)	0.0004(1)	−0.0028(1)
Cl(1)	0.0109(11)	0.0143(12)	0.0050(6)	0.0041(10)	0.0020(7)	−0.0023(7)
Cl(2)	0.0134(12)	0.0146(12)	0.0051(6)	0.0059(10)	0.0030(7)	−0.0015(7)

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[a] Number is parentheses following a parameter here and elsewhere in the paper are estimated standard deviations in the least significant figure of the parameter. [b] Carbon atom nomenclature is simplified by prefices (where applicable) indicating the ligand or group to which the atom belongs. The carbon atoms with no prefices are the original cyclopropane ring atoms. The prefices py1, py2, apply to the pyridine ligands for which N(1) and N(2) are the donor atoms respectively. The prefices ph1, ph2 apply to the phenyl groups attached to C(1) and C(2). The prefix S applies to the solvent of crystallisation. [c] The positional parameters for the phenyl ring carbon atoms have been derived from group parameters. [d] Only one isotropic thermal parameter was refined for each phenyl group and the value applies to all atoms in the group. [e] The number in square brackets represents the occupancy of that atom if different from unity. In these cases, the thermal parameter was not refined. [f] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}h\cdot k+2\beta_{13}h\cdot l+2\beta_{23}k\cdot l)]$.

TABLE 2

ROOT-MEAN-SQUARE AMPLITUDES OF THERMAL MOTION (Å) ALONG PRINCIPAL AXES

Complex molecule I			
Pt	0.222(3)	0.273(4)	0.305(4)
Cl(1)	0.237(13)	0.311(23)	0.326(21)
Cl(2)	0.230(15)	0.278(19)	0.386(23)
Complex molecule II			
Pt	0.221(4)	0.255(5)	0.283(3)
Cl(1)	0.237(22)	0.280(15)	0.333(21)
Cl(2)	0.230(24)	0.290(23)	0.351(16)

TABLE 3

INTRAMOLECULAR INTERNUCLEAR DISTANCES

	Molecule I	*Molecule II*	*Molecule III*
Pt–Cl(1)	2.31(1)	2.32(1)	2.29(1)
Pt–Cl(2)	2.31(1)	2.30(1)	2.29(2)
Pt–N(1)	2.15(3)	2.16(3)	2.11(3)
Pt–N(2)	2.20(4)	2.33(3)	2.25(3)
Pt–C(1)	2.06(3)	2.05(3)	2.04(5)
Pt–C(2)	2.60(4)	2.62(3)	2.69(4)
Pt–C(3)	2.11(5)	2.17(3)	2.19(5)
C(1)–C(2)	1.59(7)	1.59(4)	1.48(8)
C(1)–C(3)	2.39(7)	2.60(4)	2.55(10)
C(2)–C(3)	1.48(5)	1.71(4)	1.82(9)
C(1)–ph1-C(1)	1.48(4)	1.56(5)	
C(2)–ph2-C(2)	1.58(4)	1.58(4)	

equatorial planes of the two independent platinum atoms as viewed in the vectorial direction Cl(2)–Pt. In the succeeding part of this paper the two independent molecules in this crystal will be referred to as (I) and (II) consistently. It is of interest to make comparisons with the known structure of the unsubstituted cyclopropane complex of platinum[8] and this will be referred to as (III). Selected intramolecular internuclear distances and angles for (I), (II) and (III) are given in Tables 3 and 4; the atom nomenclature in (III) was made consistent with that in (I) and (II).

There are no significant differences between any of the Pt–Cl internuclear distances in (I) and (II); the correction for thermal motion calculated using the riding model is relatively small (averaging to ≈0.009 Å for the four bonds) and inclusion of this correction makes the average Pt–Cl bond length to be 2.32(1)Å. This is somewhat longer than the average Pt–Cl bond length in (III) but since no thermal correction was made in this case, the differences cannot be regarded as significant. Pt–Cl bond lengths close to 2.32 Å have been observed in complexes of platinum with differing formal oxidation states[12] and thus the length of this bond is not susceptible to change. The angles between chlorine, platinum and atoms coordinated in the equatorial plane are in the range 84–96°; there appears to be no obvious chemical significance to the variations of these angles from 90°.

TABLE 4

SELECTED INTRAMOLECULAR INTERATOMIC ANGLES (°)

	Molecule I	*Molecule II*	*Molecule III*
Cl(1)–Pt–Cl(2)	177.8(5)	176.6(3)	179.1(5)
Cl(1)–Pt–N(1)	86(1)	90(1)	91(1)
Cl(1)–Pt–N(2)	92(1)	94(1)	90(1)
Cl(1)–Pt–C(1)	96(1)	93(1)	89(1)
Cl(1)–Pt–C(3)	87(1)	86(1)	91(1)
Cl(2)–Pt–N(1)	93(1)	89(1)	90(1)
Cl(2)–Pt–N(2)	90(1)	89(1)	91(1)
Cl(2)–Pt–C(1)	84(1)	88(1)	90(1)
Cl(2)–Pt–C(3)	91(1)	91(1)	88(1)
N(1)–Pt–N(2)	82(1)	92(1)	89(1)
N(1)–Pt–C(3)	103(2)	94(1)	98(2)
N(2)–Pt–C(1)	105(2)	98(1)	99(2)
C(1)–Pt–C(3)	70(2)	76(1)	74(2)
C(1)–C(2)–C(3)	102(3)	104(2)	101(4)
Pt–C(1)–C(2)	90(2)	91(2)	99(4)
Pt–C(3)–C(2)	91(3)	84(2)	84(3)
C(2)–C(1)–ph1-C(1)	114(3)	120(3)	
Pt–C(1)–ph1-C(1)	114(2)	122(2)	
C(1)–C(2)–ph2-C(1)	116(3)	113(3)	
C(3)–C(2)–ph2-C(1)	112(4)	115(3)	

Of the two Pt–N bond lengths in (I), (II) and (III), one, Pt–N(1), is consistently shorter than the other. Averaged over the three molecules, the short bond length is 2.14 Å and the long bond length is 2.26 Å. In each individual molecule, the difference between the short and long bond lengths is only just statistically significant but when all three molecules show the same trend, then some faith can be placed in this observation. Furthermore, the average Pt–C(1) internuclear distance is 2.05 Å, shorter than the average Pt–C(3) internuclear distance of 2.16 Å. Thus the short Pt–N interaction has a short Pt–C interaction *trans* to it.

The pyridine rings were refined as individual atoms and the observed bonds lengths and angles are expectedly regular. All of the rings in (I) and (II) are planar within two e.s.d.'s, the average N–C internuclear distance is 1.36 Å and the average C–C internuclear distance 1.37 Å. There is a propeller-like inclination of the planes of the pyridine rings to the equatorial plane of platinum; this is normal when there are two pyridine ligands *cis*-coordinated to a metal.

The three central carbon atoms of the cyclopropane ligands do not lie precisely in the equatorial planes of molecules (I) and (II). Table 5 lists the perpendicular displacements of the cyclopropane ring carbon atoms from the plane defined by N(1), Pt, N(2): the two carbon atoms closest to platinum lie within two estimated standard deviations of the plane but C(2) is very clearly displaced from the plane. A similar observation was made for molecule (III). Table 5 also lists the perpendicular displacements of the phenyl ring α-carbon atoms from the plane defined by C(1), C(2), C(3).

There are several interesting differences in the geometries observed for these molecules and the two obvious will now be listed.

(*i*) The plane of the phenyl ring bonded to C(2) is perpendicular to the plane of

TABLE 5

DISPLACEMENTS (Å) FROM PLANES

Atom	*Molecule I*	*Molecule II*
(*i*) *Plane defined by N*(1), *Pt*, *N*(2)		
C(1)	−0.09(4)	−0.12(6)
C(2)	0.44(4)	0.30(7)
C(3)	0.07(4)	0.01(6)
(*ii*) *Plane defined by C*(1), *C*(2), *C*(3)		
ph1-C(1)	−0.88(6)	−0.73(8)
ph2-C(1)	1.20(8)	1.16(10)

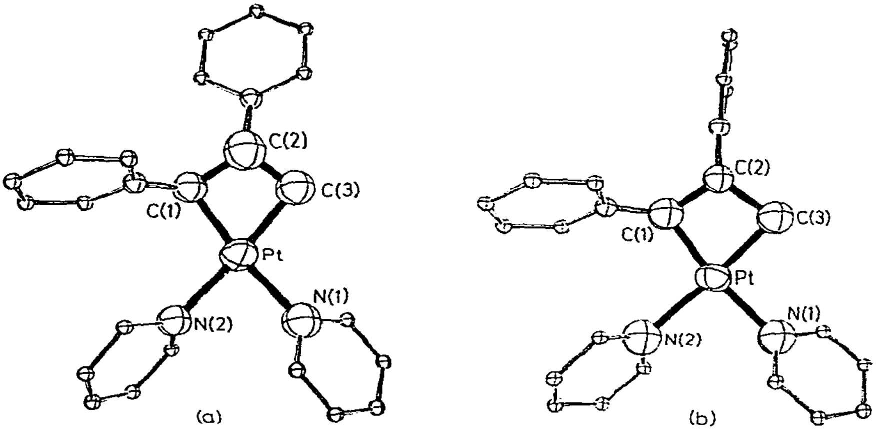

Fig. 1. Ligands coordinated to platinum in the equatorial plane. The atoms are represented by 50% probability ellipsoids except for the carbon atoms of the two pyridine and two phenyl rings which were given artificially low thermal parameters for the purpose of clarity. (a) Molecule I; (b) Molecule II.

the cyclopropane ring in (II) whereas in (I) it is not (this is clearly shown in Fig. 1). It should be noted that the orientation of the phenyl ring bonded to C(1) is very similar in (I) and (II); it is twisted away from being perpendicular to the plane of the cyclopropane ring in a sense which continues the propeller-like inclination of the pyridine rings to the equatorial plane of the molecule.

(*ii*) The angle N(1)–Pt–N(2) in (I) is 82°, ten degrees smaller than the corresponding angle in (II), whilst the C(1)–Pt–C(3) angle in (I) is 70°, six degrees smaller than the corresponding angle in (II). This is illustrated in Fig. 2 which shows to scale the relative positions in (I) and (II) of some of the ligand atoms in the equatorial plane.

The carbon–carbon bond lengths in this crystal structure are of sufficiently low precision that detailed conclusions cannot be drawn from them. The C(1)–C(3) internuclear distances in (I) and (II) are both very long. The only other unusual C–C internuclear distance is the 1.71(4) Å observed for C(2)–C(3) in (II); this bond length is also long in (III) but not in (I). It has been suggested[8] that the long C(2)–C(3) distance in (III) may be an artefact caused by disorder of the carbon atoms. That this is probably not the case for (II) is shown by the thermal parameter of C(3) (which is not

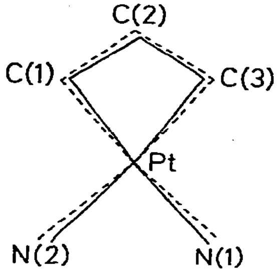

Fig. 2. Relative positions of the atoms in the equatorial planes of (I) and (II). The solid lines connect the nuclei in molecule (I) and the broken lines connect the nuclei in molecule (II).

excessively high) and by Fourier and difference Fourier syntheses; C(1) and C(2) are most unlikely to be disordered because they are covalently bound to phenyl rings. The C(2)–C(3) internuclear distance in (II) is 0.17 Å longer than the commonly accepted internuclear distance (1.54 Å) for two carbon atoms linked by a two-centre σ-bond. This difference is statistically significant if the estimated standard deviation of this parameter is realistic. It is a commonplace occurrence in the discussion of diffraction studies to be uncertain whether the estimated standard deviations of derived parameters are too low by a factor of two or three. The difficulty is that there is no valid standard for the distance between two atoms when these atoms are in different compounds. Thus there is usually no means to determine the magnitude of the effect of systematic errors that are not included in the estimation of the standard deviation and this is certainly true in this particular case.

However the differences (*i*) and (*ii*) discussed above are so great that no doubts about the magnitude of the estimated standard deviations can affect the conclusion that these differences are truly significant and hence that the two independent molecules in the unit cell are not statistically equivalent. It is possible that we are observing two of the many conformations that are continually forming and reforming in solution. A convenient way to look at the phenomenon is to consider rotation about the C(2)–ph2-C(1) bond. There should be a favoured conformation in which the plane of phenyl ring ph2 is perpendicular to the plane of the cyclopropane ring carbon atoms; this conformation corresponds fairly closely to (II). (I) can be considered to be an isolated molecule in the conformation where rotation of almost 90° has occurred from the favoured conformation; furthermore, relative to (II), the angle N(1)–Pt–N(2) in (I) has decreased by 10° and there is also the change in the C(2)–C(3) internuclear distance (the statistical significance of which is unclear). It remains to be shown that these changes can be rationalised using a simple bonding model.

DISCUSSION

The mode of attachment of cyclopropane to platinum in this and similar complexes is of interest. The simplest model involves the anionic ligand $C_3H_6^{2-}$ (with sp^3-hybridised carbon atoms) with a d^6 platinum(IV) substrate (d^2sp^3 hybridised): the three carbon atoms and the platinum atom are bound together by four two-centre, two-electron σ bonds. This metallocyclobutane ring model has the merit of simplicity but lacks the capacity to predict the effect of changing substituents upon the metal or to rationalise the observed differences in geometry between molecules (I) and (II).

An alternative model is to consider the four-centre molecular orbitals which can be constructed from the atomic orbitals available when each carbon atom is considered to be sp^2-hybridised (as they are in the Walsh model for free cyclopropane) and when the platinum atom is considered to be dsp^3 hybridised, *i.e.* with σ orbitals in a trigonal bipyramidal array and with a d-orbital in the equatorial plane. There are eight bonding electrons and a reasonable choice for the four occupied molecular orbitals is shown in Fig. 3. With one particular choice of coefficients in the LCAO equations used to construct these four-centre molecular orbitals, this model is equivalent to the metallocyclobutane model mentioned above; the advantages of this extended model will now be made clear.

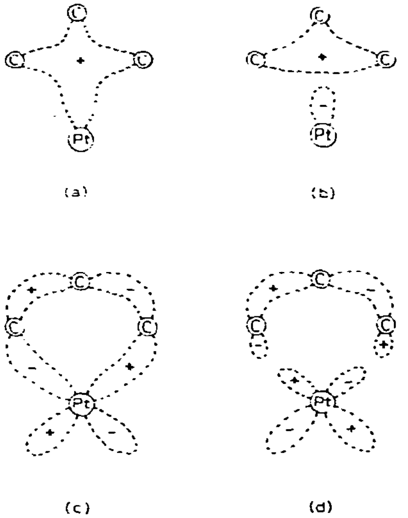

Fig. 3. The four molecular orbitals, constructed by a four-centre model, which are most likely to be occupied: (a) and (b) are constructed from the available σ-orbitals; (c) and (d) are constructed from the metal d-orbital and the p-orbitals of the carbon atoms.

If the plane of the phenyl rings attached to cyclopropane (either in the free state or coordinated to platinum) is perpendicular to the plane of the cyclopropane ring, then there will be overlap between the π symmetry orbitals of the phenyl ring and those of the cyclopropane ring (shown in Fig. 3(c) and (d)). The resultant delocalisation causes a net loss of electrons from the region of the cyclopropane ring. Figure 1 clearly shows that the plane of the phenyl ring attached to C(2) is perpendicular to the plane of the cyclopropane ring in (II) and also that this is not the case in (I). The increased electron delocalisation in (II) is manifested in the long C(2)–C(3) and C(1)–C(3) distances, relative to those in (I).

It is also possible to rationalise the unusual situation prevailing with respect to the differing N(1)–Pt–N(2) angles in (I) and (II) as shown in Fig. 2. In molecule(II), the increased electron delocalisation *within* the substituted cyclopropane system results in a decreased interaction between the cyclopropane ligand and platinum. Thus the pyridine ligands attached to platinum would be expected to be closer to their conformation in the absence of the cyclopropane ligand (*i.e.*, closer to a N(1)–Pt–N(2) angle of 180°) in (II) than in (I).

The cause of the difference in geometry of (I) and (II) is not known and is therefore ascribed to packing forces. Since these are not expected to be large, this indicates a relatively low barrier to this rotation (which has been noted before[9]).

An important generalisation can be made about the bonding models used to describe organometallic complexes. Customarily there are two approaches used and these contrast greatly in many aspects. The two-centre two-electron Lewis bond model has proved a great value as a qualitative guide to the permissible geometry of many compounds. The other approach is the full quantitative molecular orbital treatment which, whilst potentially rigorous, is usually too time-consuming to be practical; the derived molecular orbitals can be very delocalised and they are rather difficult to visualise on a qualitative level. Compounds such as cyclopropane or olefin or molecular oxygen complexes are too large for a complete molecular orbital approach and yet the Lewis bond model is not of sufficient flexibility to explain observed subtleties of the geometry[13]. I woulk like to emphasize the value of a qualitative model, to suggest criteria to determine when the Lewis bond model may not be adequate and to show a relatively simple way to set up a bonding scheme.

The classification of compounds into series is of particular use when the trends in geometry and reactivity can be rationalised or predicted qualitatively by simple models. If a ligand has two or more centres bonded or conjugated to each other and more than one of these centres interact equally with a metal, then a localised molecular orbital scheme should be used to describe the bonding in the adduct. The centres to be covered by the scheme include the metal (with *d*-orbitals where appropriate), all of the interacting centres on the ligand plus any other ligand atoms within bonding (*i.e.* orbital overlap) distance of the metal. Having set up these localised molecular orbitals under the appropriate symmetry, then their interactions with the other substituents will permit the desired rationalisations and qualitative predictions to be made. A few structures have been reported in which the inter-atom distances in the compound are atypical of normal bond lengths, *e.g.* 1.71 Å for a C–C distance (in the cyclopropane complex described in this paper), 1.62 Å for a C–C distance (in a chloro–olefin complex[14]) and 1.65 Å for an O–O distance (in a molecular oxygen complex[15]). Such unusual results can be rationalised using bonding schemes of this type. It should be noted that such inter-atom distances could promote unique reactivity in the coordinated ligand and thus it is of great interest to have an adequate description of the bonding.

REFERENCES

1 A. D. Walsh, *Trans. Faraday Soc.*, 45 (1949) 179.
2 C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 40 (1949) 1.
3 W. A. Bernett, *J. Chem. Educ.*, 44 (1967) 17.
4 R. Hoffmann, *Tetrahedron Lett.*, (1965) 3819.
5 (a) N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 89 (1967) 3966;
(b) D. T. Clark, *Theor. Chim. Acta*, 10 (1968), 111.
6 H. Gilman, *Organic Chemistry*, Wiley, 2nd. Ed., 1942, Vol. 1, p. 101.
7 C. F. H. Tipper, *J. Chem. Soc.*, (1955) 2045.
8 R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow and D. R. Russell, *J. Organometal. Chem.*, 33 (1971) 247.

9 G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, 87 (1965) 3265.
10 (a) K. G. Powell and F. J. McQuillin, *Tetrahedron Lett.*, (1971) 3313.
(b) F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, (1972) 2123.
11 (a) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24 (1968) 321;
(b) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
12 M. Keeton, R. Mason and D. R. Russell, *J. Organometal. Chem.*, 33 (1971) 259.
13 J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, (1968) 235.
14 J. N. Francis, A. McAdam and J. A. Ibers, *J. Organometal. Chem.*, 29 (1971) 131.
15 J. A. McGinnety, N. C. Payne and J. A. Ibers, *J. Amer. Chem. Soc.*, 91 (1969) 6301.