Effect of weak hydrogen bonding and included solvent on the crystal structure of the square-planar complex *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$

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Letter

Crystallisation of the square-planar complex *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$ from dichloromethane–diethyl ether (1 : 1) affords two different solvates; *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2 \cdot CH_2Cl_2$ **1** and *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2 \cdot Et_2O$ **2**; the CH_2Cl_2 forms H-bonding interactions with the complex whereas the Et_2O participates only in weak van der Waals interactions; these differences arise from the different hydrogen-bonding characteristics of each solvent.

Scrutinising apparently weak *intra*- and *inter*-molecular interactions in solid-state structures can yield valuable information concerning the gross molecular and crystal structures and often provides an insight into unexpected structural motifs.[1] Ultimately, such studies may provide the experimentalist with adequate knowledge to design and engineer crystals with specific physical properties.[2] After the general steric demands imposed by molecules, one of the most important factors dictating structural motifs are hydrogen-bonding interactions.[3] Some hydrogen bonds are relatively strong and many examples of this type are encountered in biological systems.[4] Other hydrogen-bonding interactions are much weaker but they can still have a marked influence on structure.[5] The presence of solvent molecules in crystals is clearly important in defining the precise structure but we are only aware of one deliberate study where a neutral inorganic complex has been crystallised with different solvent molecules giving rise to very different packing motifs.[6] In this letter we report the molecular and crystal structures of the inorganic complex *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$ containing different solvents. The unique aspect of this investigation is that the gross packing motifs of the two solvates is very similar, but subtle differences in the actual structures of the complexes are observed.

Reaction of two equivalents of diphenyl[2.2]paracyclophanylphosphine, *rac*-$PPh_2(C_{16}H_{15})$,† with *cis*-$Pt(NC_5H_5)_2Cl_2$ in dichloromethane at room temperature for 24 h affords *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2 \cdot CH_2Cl_2$ **1** in *ca.* 85% yield after recrystallisation from dichloromethane–diethyl ether (1 : 1).‡ Crystals containing each solvate, CH_2Cl_2 (**1**) and Et_2O (**2**) were obtained and both have been analysed by single crystal X-ray diffraction.‖

Both solvates contain two independent molecules of *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$, each molecule having essentially the same conformation, and a representative structure (from **2**) is shown in Fig. 1. The similarity between the structures may be illustrated by a comparison of the key parameters in Table 1. The most notable features of *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$ are firstly that it is a *meso* complex with one *R* and one *S* ligand. Secondly, the [2.2]paracyclophane substituents orientate into positions such that an outer-ring proton forms a long-range interaction with axial sites on the Pt centre to give a *pseudo*-octahedral geometry [the distance C—H···Pt 2.78–2.90 Å] shown by the dotted lines in Fig. 1. Although this interaction is weak it is clearly very important in square-planar complexes carrying this phosphine ligand since it is also present in other examples,[10] some yet to be published.

Other *intra*- and *inter*-molecular interactions are also present and these are shown in Fig. 2 and 3 for solvates **1** and

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† *rac*-$PPh_2(C_{16}H_{15})$ is prepared from the dropwise addition of PPh_2Cl (0.77 g, 3.48 mmol) to $LiC_{16}H_{15}$ (0.74 g, 3.48 mmol) in diethyl ether (40 ml) at 0 °C with PPh_2Cl (0.77 g, 3.48 mmol) over 10 min followed by warming to room temperature for a further 3 h. The compound is isolated in *ca.* 60% yield after recrystallisation from hot ethanol.

‡ *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$. ^1H NMR ($CDCl_3$) phenyl rings: δ 7.92 (m, 4H), 7.64 (m, 6H); paracyclophane: 6.84–6.41 (m, 7H, aromatic protons), 3.48–2.87 (m, 8H, methylene protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.56 (J_{Pt-P} = 2574 Hz). Mass spectrum (FAB^+): *m/z* 1051 (M^+).

‖ Structural details for **1**: $C_{58}H_{54}Cl_6P_2Pt$, *M* 1220.74 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 12.2171(6), b = 13.0694(8), c = 16.6592(8) Å, α = 79.094(2), β = 82.943(2), γ = 80.139(2)°. U = 2562.1(2) Å^3, Z = 2, μ = 31.53 cm^{-1}, T = 123 K, reflections measured: 21 873, unique data: 9334 (R_{int} = 0.043), parameters: 608, R_1 [$F^2 > 2\sigma(F^2)$] 0.0494, wR_2 (all data) 0.1390. **2**: $C_{60}H_{60}Cl_2OP_2Pt$, *M* 1125.01 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 10.9266(7), b = 13.3688(9), c = 17.8209(13) Å, α = 100.957(2), β = 98.816(2), γ = 95.460(2)°. U = 2504.7(3) Å^3, Z = 2, μ = 30.13 cm^{-1}, T = 100 K, reflections measured: 15 464, unique data: 9167 (R_{int} = 0.059), parameters: 599, R_1 [$F^2 > 2\sigma(F^2)$] 0.0472, wR_2 (all data) 0.1294. Crystals were mounted using silicon grease on the end of a glass fibre and cooled on the diffractometer using an Oxford Cryostream. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo-Kα radiation using φ rotations with 2° frames and a detector-to-crystal distance of 25 mm. Unit cell determination and integration was carried out by the program DENZO-SMN.[7] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack.[7] Structures were solved using the direct methods option of SHELXS-97[8] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97[7]) with the aid of RES2INS.[9] All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealized positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. CCDC reference number 440/068.

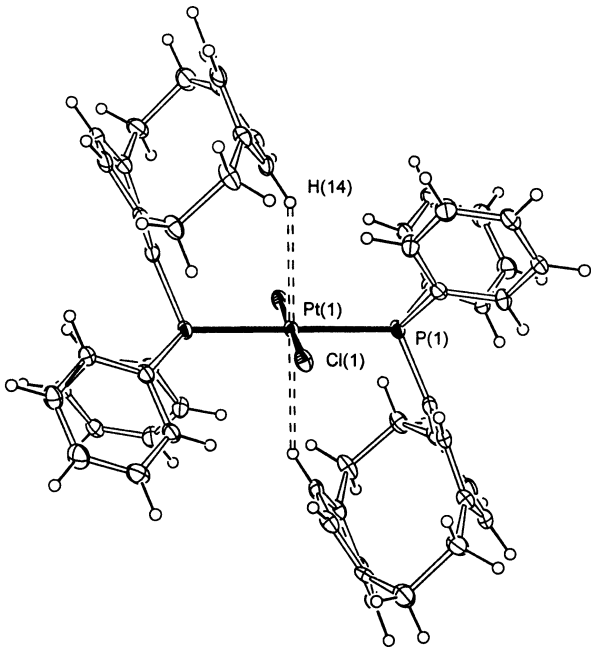

Fig. 1 The structure of one of the two independent *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$ molecules from solvate **2**

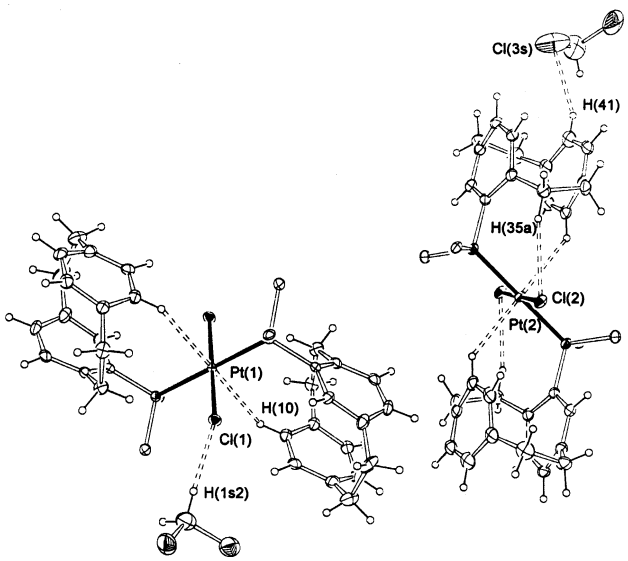

Fig. 2 The structure of **1** showing *intra*- and *inter*-molecular contacts

2, respectively. In the former structure there is no direct interaction between the two complexes although they are connected indirectly *via* the dichloromethane solvate. Indeed, the most dominant feature after the Pt···H interaction appears to be weak hydrogen bonding with the chlorides attached to the metal centres since these interactions are always present in square-planar complexes carrying diphenyl[2.2]paracyclophanylphosphine. The $Pt(1)Cl_2$ fragment interacts with the dichloromethane solvate (see Fig. 2) [Cl(1)···H(1s2) 2.60 Å] and the $Pt(2)Cl_2$ fragment interacts *intra*-molecularly with protons on the CH_2 linkers in the [2.2]paracyclophanyl group [C1(2)···H(35a) 2.77 Å]. The Cl atoms of the dichloromethane also form a hydrogen bond with a proton on the [2.2]paracyclophane ring on the other molecule [Cl(3s)···H(41) 2.82 Å] thereby indirectly connecting the two platinum complexes. In contrast, **2**, which contains diethyl ether solvate, does not show any interactions between the solvent and complexes, presumably because of the lower acidity of the C—H protons of diethyl ether relative to dichloromethane. Despite this, it can be seen from Fig. 3 that a related scenario exists for the $PtCl_2$ fragments with $Pt(1)Cl_2$ involved in *intra*-molecular interactions, *albeit* with phenyl ring protons [Cl(1)···H(24) 2.80 Å]. In $Pt(2)Cl_2$ these interactions are *inter*-molecular in nature. Two *pseudo*-geminal protons from the face-to-face rings of the [2.2]paracyclophanyl unit [Cl(2)···H(5) 2.91 and Cl(2)···H(10) 2.87 Å] are involved in this *inter*-molecular hydrogen bond. It is likely that the different types of weak interactions involving the two Cl ions give rise to the subtle differences in the actual structures of the four platinum complexes.

The presence of two independent molecules in square-planar MP_2Cl_2 (M = Pd or Pt; P = phosphine) complexes is very rare and only three examples were found in the Cambridge Crystallographic Database.[11] This would suggest that the steric demands of this unusual asymmetric phosphine are responsible and appears to be a common trend for other palladium–diphenyl[2.2]paracyclophanylphosphine complexes. We are currently preparing related phosphines in which the [2.2]paracyclohanyl substituent is replaced by groups of similar size but with very different electronic properties such as metallocenes in an attempt to establish the extent to which electronic factors play a role in the crystal architecture.

Table 1 A comparison of key bond lengths (Å) and angles (°) for the four molecules *trans*-$Pt\{PPh_2(C_{16}H_{15})\}_2Cl_2$

1			
Pt(1)—Cl(1)	2.3150(13)	Pt(2)—Cl(2)	2.3189(13)
Pt(1)—P(1)	2.3355(14)	Pt(2)—P(2)	2.3386(15)
Pt(1)···H(10)	2.84	Pt(2)···H(38)	2.79
Cl(1)—Pt(1)—P(1)	87.99(5)	Cl(2)—Pt(2)—P(2)′	88.27(5)
2			
Pt(1)—Cl(1)	2.3131(16)	Pt(2)—Cl(2)	2.3104(16)
Pt(1)—P(1)	2.3319(16)	Pt(2)—P(2)	2.3303(16)
Pt(1)···H(14)	2.78	Pt(2)···H(42)	2.90
Cl(1)—Pt(1)—P(1)	86.55(6)	Cl(2)—Pt(2)—P(2)	87.33(6)

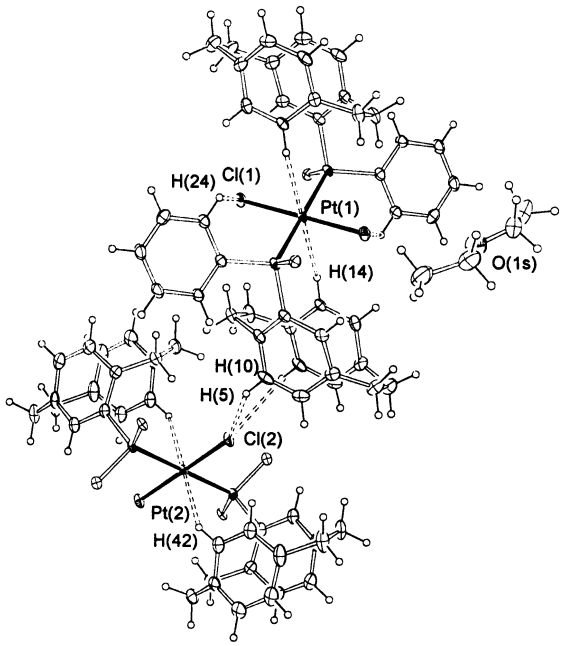

Fig. 3 The structure of **2** showing *intra*- and *inter*-molecular contacts

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