

A remarkable example of co-crystallisation: the crystal structure of the mononuclear and dinuclear diphenyl[2.2]paracyclophanylphosphine palladium(II) chloride complexes

trans-[Pd{PPh₂(C₁₆H₁₅)₂Cl₂]₂·[Pd{PPh₂(C₁₆H₁₅)Cl₂]₂·0.6CH₂Cl₂

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The reaction of [Pd(cod)Cl₂] (cod = cycloocta-1,5-diene) with *rac*-diphenyl[2.2]paracyclophanylphosphine PPh₂(C₁₆H₁₅) affords *trans*-[Pd{PPh₂(C₁₆H₁₅)₂Cl₂] and [Pd{PPh₂(C₁₆H₁₅)Cl₂]₂ in approximately equal yield which co-crystallise to form an unusual solid-state material.

Crystallisation of organic compounds is a common phenomenon and often of commercial value.¹ In inorganic/organometallic chemistry many anion–cation pairs² and to a lesser extent conformational isomers and polymorphs³ have been recognised. However, co-crystals composed of two different neutral molecules are very rare and most can be classified as those which have two or more very similar molecules, often differing in a substituent on a ligand⁴ or by the presence of slightly different ligand such as replacement of one halide for another.⁵ Some co-crystals contain an inorganic/organometallic species in which a small or cylindrical ‘solvent-like’ molecule has been co-crystallised, for example, HgX₂ (X = I, Cl, F) and metallocenes.⁶ We have also found one example of a co-crystal containing a neutral mononuclear and dinuclear complex⁷ and one example involving clusters⁸ in the literature.

We have been investigating the synthesis of [2.2]paracyclophanyl–phosphine ligands and studying their coordination chemistry.⁹ This substituent was chosen as [2.2]paracyclophane has unusual nucleophilic behaviour with respect to its coordination chemistry.¹⁰ Another group have also recently reported the synthesis of a chiral diphosphine with a [2.2]paracyclophane

backbone which has some very impressive applications in catalysis.¹¹ We report here the synthesis of a new [2.2]paracyclophane containing phosphine and the discovery that it reacts with [Pd(cod)Cl₂] to afford two Pd^{II}Cl₂ complexes which form a co-crystalline material in the solid-state.

The reaction of C₁₆H₁₅Li,¹² with PPh₂Cl, added dropwise in diethyl ether, affords diphenyl[2.2]paracyclophanylphosphine PPh₂(C₁₆H₁₅) in 62% yield after recrystallisation from ethanol. Reaction of this phosphine with [Pd(cod)Cl₂] in dichloromethane at room temperature for 1 h affords an orange solution which exhibits two singlets of approximately equal intensity at δ 33.93 and 33.53 in its ³¹P NMR spectrum. From later observations we assume these to be due to the two complexes *trans*-[Pd{PPh₂(C₁₆H₁₅)₂Cl₂] **1** and [Pd{PPh₂(C₁₆H₁₅)Cl₂]₂ **2** and not from diastereomers of the same complex. The *cis*- and *trans*-platinum(II) chloride complexes of *rac*-PPh₂(C₁₆H₁₅) also show only one main resonance in their ³¹P NMR spectra excluding the ¹⁹⁵Pt satellites.¹³ Crystals were grown by removing the solvent and redissolving the solid in dichloromethane–diethyl ether. After allowing the solution to evaporate at room temperature for several days orange crystals formed which were suitable for single crystal X-ray diffraction analysis.[‡] This reveals the remarkable co-crystalline structure described below.

The structures of **1** and **2** are shown in Figs. 1 and 2,

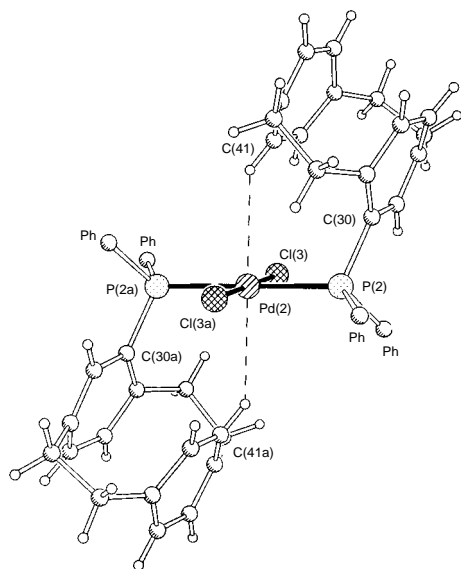


Fig. 1 Molecular geometry of **1**; selected bond lengths (Å) and angles (°): Pd(2)–P(2) 2.355(2), Pd(2)–Cl(3) 2.301(2), P(2)–C(30) 1.826(7), Pd(2)⋯H(41) 2.853, Cl(3)–Pd(2)–P(2) 88.07(7)

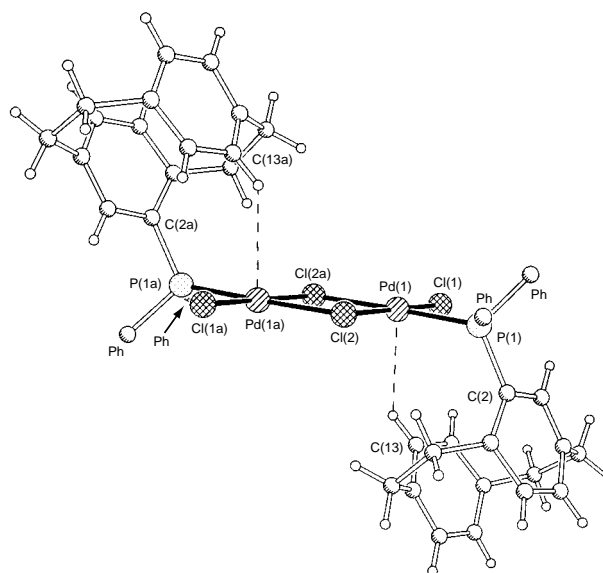


Fig. 2 Molecular geometry of **2**; selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.229(2), Pd(1)–Cl(1) 2.280(2), Pd(1)–Cl(2) 2.332(2), Pd(1)–Cl(2a) 2.429(2), P(1)–C(2) 1.816(7), Pd(1)⋯H(13) 2.933, P(1)–Pd(1)–Cl(2a) 177.29(8), Cl(1)–Pd(1)–Cl(2) 177.29(8)

respectively, together with principal bond parameters. In both **1** and **2** one of each enantiomer of $\text{PPh}_2(\text{C}_{16}\text{H}_{15})$ is present. The phosphines adopt a *trans*-conformation in **1** presumably due to the steric bulk of the [2.2]paracyclophanyl-substituent. The axial sites above and below the square plane are occupied by intramolecular interactions involving a proton on the [2.2]paracyclophane rings of each phosphine ligand ($\text{Pd}\cdots\text{H}$ 2.85 Å). The structure of **2** comprises a chloro-bridged dimer in which each palladium centre is approximately square planar. As in **1** and other similar square planar complexes¹⁴ the axial sites form weak intra- or inter-molecular interactions in the solid state. In **2** the [2.2]paracyclophanyl group of each phosphine occupies one site on each of the palladium(II) centres ($\text{Pd}\cdots\text{H}$ 2.93 Å). The other site is occupied *via* an intermolecular interaction and it is this that possibly gives rise to the formation of the co-crystal (see below).

The crystal is composed of alternating layers of **1** and **2** intercalated with dichloromethane solvent molecules. There is one direct, albeit weak, hydrogen bond between **1** and **2** involving the Cl atoms on **1** with a phenyl ring proton on **2** ($\text{Cl}\cdots\text{H}$ 2.83 Å), shown in Fig. 3. Perhaps more importantly, compounds **1** and **2** are linked indirectly *via* one of the two CH_2Cl_2 solvent molecules as shown in Fig. 4. There is a bifurcated hydrogen bonding interaction between the H atom on

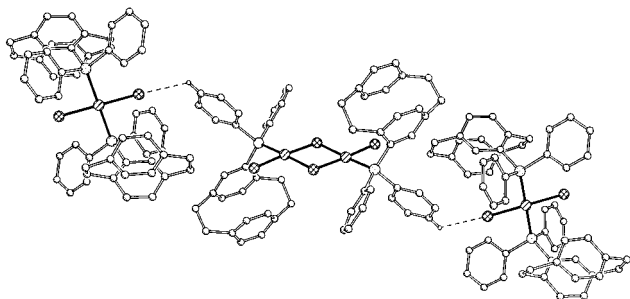


Fig. 3 The direct interaction, $1\cdots 2$

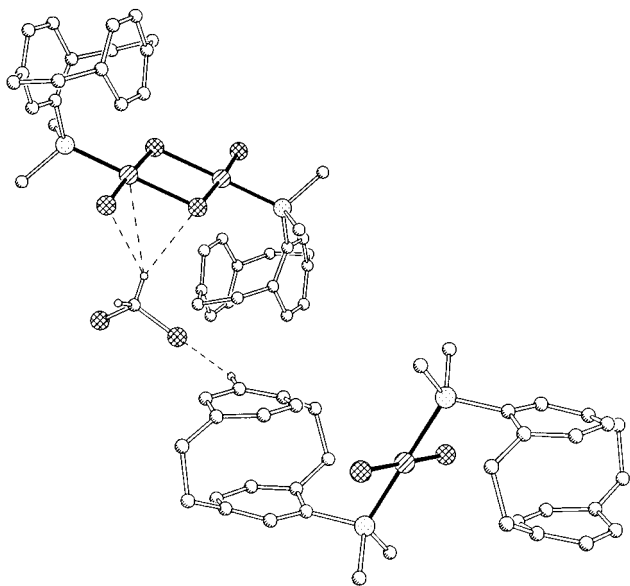


Fig. 4 The indirect solvent bridging interaction, $1\cdots\text{Cl}-\text{C}-\text{H}\cdots 2$

the solvent with one terminal Cl ($\text{H}\cdots\text{Cl}$ 2.83 Å) and one bridging Cl ($\text{H}\cdots\text{Cl}$ 2.80 Å) of **2**. A Cl atom of this same solvent molecule also interacts with the H atom of a cyclophane attached to the phosphine in **1** ($\text{Cl}\cdots\text{H}$ 2.86 Å) thereby forming a $1\cdots\text{Cl}-\text{C}-\text{H}\cdots 2$ linkage (see Fig. 4). The second CH_2Cl_2 connects molecules of **1** *via* two interactions involving the H and Cl atoms of both the solvent and the complex. At this stage we can only speculate as to the precise role of the solvent but since it links **1** and **2** it may play a part in the co-crystallisation process. In this material partial desolvation has taken place but the co-crystal still retains its structure. We intend to examine the influence of solvents with various hydrogen bonding capabilities as well as the influence of the halide coordinated to the Pd^{II} centre.

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Notes and References

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‡ *Structural characterisation of 1 and 2*: orange crystal, $\text{C}_{112.6}\text{H}_{101.2}\text{Cl}_{17.2}\text{P}_4\text{Pd}_3$, $[\text{C}_{56}\text{H}_{50}\text{Cl}_4\text{P}_2\text{Pd}_2\cdot\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{P}_2\text{Pd}\cdot 0.6\text{CH}_2\text{Cl}_2]$, $M = 2152.66$, $0.20 \times 0.20 \times 0.20$ mm, $T = 180(2)$ K, triclinic, $P\bar{1}$, $a = 12.033(3)$, $b = 18.673(2)$, $c = 11.871(2)$ Å, $\alpha = 95.20(1)$, $\beta = 94.73(1)$, $\gamma = 100.04(1)^\circ$, $U = 2602.5(8)$ Å³, $Z = 1$, $F(000) = 1097$, $D_c = 1.374$ Mg m⁻³, $\lambda = 0.71069$ Å, $R1 = 0.0555$ [9152 intensity data with $I > 2\sigma(I)$] and $wR2 = 0.1673$ for 9156 independent reflections corrected for adsorption [$\mu(\text{Mo}-\text{K}\alpha) = 0.805$ mm⁻¹] and 598 parameters (all non-H atoms anisotropic except solvent molecules). CCDC 182/882.

- 1 A. I. Kitaigorodsky, in *Mixed Crystals*, ed. M. Cardona, Solid State Sciences, vol. 33, Springer-Verlag, Berlin, 1984; G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
- 2 See, for example: D. Braga, F. Grepioni, P. Milne and E. Parisini, *J. Am. Chem. Soc.*, 1993, **115**, 5115.
- 3 See, for example: D. Braga, F. Grepioni, P. J. Dyson, B. F. G. Johnson, P. Frediani, M. Bianchi and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, 1992, 2565.
- 4 See, for example: C. A. Cotton, D. J. Darensbourg, A. Fang, B. W. S. Kolthammer, D. Reed and J. L. Thompson, *Inorg. Chem.*, 1981, **20**, 4090.
- 5 See, for example: P. A. Bianconi, R. N. Vrtis, C. P. Rao, I. D. Williams, M. P. Engeler and S. J. Lippard, *Organometallics*, 1987, **6**, 1968; C. J. Cardin, D. J. Cardin, D. A. Morton-Blake, H. E. Parge and A. Roy, *J. Chem. Soc., Dalton Trans.*, 1987, 1641.
- 6 G. K.-I. Magomedov, A. I. Gusev, A. S. Frenkel, V. G. Sirkin, L. I. Chaplina and S. N. Gourkova, *Koord. Khim.*, 1976, **2**, 257; J. Votinsky, L. Benes, J. Klikorka, J. Kalousova, J. Horak and P. Lostak, *J. Appl. Crystallogr.*, 1984, **17**, 363.
- 7 M. Maekawa, M. Munakata, T. Kuroda-Sowa and K. Hachiya, *Inorg. Chim. Acta*, 1995, **232**, 231.
- 8 D. Braga, F. Grepioni, C. M. Martin, E. Parisini, P. J. Dyson and B. F. G. Johnson, *Organometallics*, 1994, **13**, 2170.
- 9 P. W. Dyer, P. J. Dyson, S. L. James and P. Suman, in preparation.
- 10 P. J. Dyson, D. G. Humphrey, J. E. McGrady, D. M. P. Mingos and D. J. Wilson, *J. Chem. Soc., Dalton Trans.*, 1995, 4039.
- 11 P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. P. Volante and P. J. Reider, *J. Am. Chem. Soc.*, 1997, **119**, 6207; K. Rossen, P. J. Pye, A. Maliakal and R. P. Volante, *J. Org. Chem.*, 1997, **62**, 6462.
- 12 H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, 1969, **91**, 3505.
- 13 P. J. Dyson and P. Suman, unpublished work.
- 14 E. C. Alyea, G. Ferguson and S. Kannan, *Chem. Commun.*, 1998, 345.

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