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On the products obtained from reaction of *rac*-diphenyl[2.2]*para*cyclophanylphosphine with (cycloocta-1,5diene)palladium(II)chloride

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This paper is dedicated to Prof. Brian F.G. Johnson on the occasion of his 65th birthday

Abstract

The reaction of Pd(cod)Cl₂ (cod = cycloocta-1,5-diene) with 1 and 2 equiv. of *rac*-diphenyl[2.2]paracyclophanylphosphine, *rac*-PPh₂(C₁₆H₁₅), affords the dimer [Pd{PPh₂(C₁₆H₁₅)}Cl₂]₂ (1) and the square-planar complex *trans*-Pd{PPh₂(C₁₆H₁₅)}₂Cl₂ (2), respectively. In solution the dimer undergoes a fluxional process which has been probed by NMR and involves isomerisation between *pseudo-trans*- and *cis*-conformations. The structures of *trans*-[Pd{PPh₂(C₁₆H₁₅)}Cl₂]₂ (1a) and 2 have been established by single crystal X-ray diffraction; the structure of the dimer is severely disordered. In addition, co-crystals containing both these complexes and solvate molecules have been isolated and their structures established by single crystal X-ray diffraction. The structure of the dimer is to dissimilar whereas the structure the dimer has a significantly different structure in the homonuclear and co-crystals. In the homonuclear crystal the central Pd₂Cl₂ unit has a dihedral angle of 26.5° between the two planes whereas the Pd₂Cl₂ unit in the co-crystals is planar. (© 2003 Elsevier B.V. All rights reserved.

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Keywords: Palladium complexes; Phosphine ligands; Co-crystals; X-ray diffraction; Crystal engineering

1. Introduction

Palladium-phosphine complexes remain the focus of intense research activity largely due to their role as catalysts in carbon-carbon coupling reactions [1]. Much effort has been devoted towards deciphering the structure and bonding in palladium-phosphine complexes as a greater appreciation of these fundamental properties should lead to the design of improved catalysts [2]. Intermolecular interactions in palladium-phosphine

* Corresponding author. Address: Ecole Polytechnique Fédérale de Lausanne, Faculté des Sciences de Base, Institut de Chimie Moléculaire et Biologique, EPFL-BCH, CH-1015 Lausanne, Switzerland. Tel.: +41-21-693 9854; fax: +41-21-693 9885. complexes have not been widely studied although several notable papers have been published. For example, the crystal structure of $Pd\{P(CH_2OH)_3)\}_4$ shows extensive hydrogen bonding networks between the alcohol functions [3], intermolecular hydrogen...metal interactions and interactions with the solvate are found in the crystal structure of *cis*-Pd(pta)₂Cl₂ (pta = 1,3,5triaza-7-phosphatricyclo[3.3.1.1]decane) [4], and *pseudo*polymeric networks of intermolecular hydrogen bonding interactions involving the ligands and solvate in a palladium complex with an aminoalcohol functionalised tertiary phosphine have been reported [5].

Our work on metallocyclophane compounds [6] led to the preparation of diphenyl[2.2]paracyclophanylphosphine that exhibits a rich coordination chemistry with palladium(II) and platinum(II)chloride [7] as well as

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other metals [8]. Some highly unusual structural features were observed and in this paper we expand on these earlier investigations.

2. Results and discussion

The bulky phosphine *rac*-diphenyl[2.2]paracyclophanylphosphine, *rac*-PPh₂(C₁₆H₁₅), is produced in high yield from the reaction of C₁₆H₁₅Li with PPh₂Cl. The ³¹P{¹H} NMR spectrum of *rac*-PPh₂(C₁₆H₁₅) in CDCl₃ contains a singlet resonance at δ – 2.43 which is close in value to that of triphenylphosphine (cf. δ – 4.0) [9]. The ¹H NMR spectrum of *rac*-PPh₂(C₁₆H₁₅) has not been reported and is sufficiently complicated to require 2D NMR experiments involving through bond coupling networks (COSY) and through space interactions

Table 1

³¹P and ¹H NMR data for the ligand, **1a**, **1b** and **2** recorded in CDCl₃ at 296 K

The reaction of rac-PPh₂(C₁₆H₁₅) with 1 equiv. of (cycloocta-1,5-diene)palladium(II)chloride, Pd(cod)Cl₂, in dichloromethane gives rise to two isomers (see Scheme 1). The ${}^{31}P{}^{1}H{}$ NMR spectrum of the reaction solution shows loss of the peak corresponding to the free phosphine and the generation of two singlet resonances with relative intensity 3:2 at δ 34.58 (major) and 34.18 (minor) in CDCl₃ at 296 K. In our previous paper we assigned these two peaks to two quite different compounds since we obtained a co-crystal containing both a monomeric and dimeric species [7a]. We have subsequently found that these two peaks are actually produced by isomers of $[Pd{PPh_2(C_{16}H_{15})}Cl_2]_2$ (1) that have *pseudo-trans* (1a) and *-cis* (1b) geometries. The ${}^{1}H$ NMR spectrum has been fully assigned using various 2D techniques and full assignments of the spectra for

Ligand		Dimer-1a	Dimer-1b	Monomer 2
Phosphorus-centre				
	-2.43 (s, 1P)	34.58 (s, 1P)	34.18 (s, 1P)	23.00 (s, 1P)
Ph-rings				
0 -	7.45 (m, 2H)	7.79 (m, 2H)	7.79 (m, 2H)	7.92 (m, 2H)
<i>m</i> -	7.80 (m, 2H)	7.28 (m, 2H)	7.23 (m, 2H)	7.95 (m, 2H)
p -	7.38 (m, 1H)	7.26 (m, 1H)	7.21 (m, 1H)	7.30 (m, 1H)
0 -	7.43 (m, 2H)	7.66 (m, 2H)	7.67 (m, 2H)	7.65 (m, 2H)
<i>m</i> -	7.76 (m, 2H)	7.24 (m, 2H)	7.27 (m, 2H)	7.67 (m, 2H)
<i>p</i> -	7.37 (m, 1H)	7.20 (m, 1H)	7.18 (m, 1H)	7.19 (m, 1H)
[2.2]Paracyclophanyl-group				
2	6.40 (m, 1H)	6.57 (m, 1H)	6.59 (m, 1H)	6.52 (m, 1H)
4	5.61 (m, 1H)	6.67 (m, 1H)	6.68 (m, 1H)	6.95 (m, 1H)
5	6.08 (m, 1H)	6.61 (m, 1H)	6.65 (m, 1H)	6.90 (t, 6, 6, 1H)
7	6.55 (m, 1H)	6.71 (m, 1H)	6.74 (m, 1H)	6.38 (d, 8, 1H)
8	6.59 (m, 1H)	8.56 (d, 7.7, 1H)	8.42 (d, 8.2, 1H)	6.72 (m, 1H)
10	6.22 (m, 1H)	6.70 (m, 1H)	6.73 (m, 1H)	6.68 (dd, 5, 2, 1H)
11	6.25 (m, 1H)	6.65 (m, 1H)	6.66 (m, 1H)	6.26 (dd, 5, 2, 1H)
13	2.73 (m, 1H)	3.06 (m, 1H)	3.10 (m, 1H)	3.17 (m, 1H)
	2.75 (m, 1H)	3.13 (m, 1H)	3.19 (m, 1H)	2.98 (m, 1H)
14	2.99 (m, 1H)	3.90 (m, 1H)	3.59 (m, 1H)	2.84 (m, 1H)
	2.95 (m, 1H)	3.17 (m, 1H)	3.22 (m, 1H)	2.94 (m, 1H)
15	3.45 (m, 1H)	2.98 (m, 1H)	3.53 (m, 1H)	3.30 (m, 1H)
	3.49 (m, 1H)	3.03 (m, 1H)	3.96 (m, 1H)	3.51 (m, 1H)
16	2.87 (m, 1H)	3.93 (m, 1H)	2.89 (m, 1H)	3.09 (m, 1H)
	2.98 (m, 1H)	3.58 (m, 1H)	2.94 (m, 1H)	3.81 (m, 1H)





both isomers are listed in Table 1. The change in appearance of the ³¹P spectrum of 1 revealed that interconversion occurs between 1a and 1b on the NMR timescale. This process was monitored in CDCl₃ by 1D ³¹P-EXSY [10] and ¹H lineshape analysis [11]. The rate constant for the conversion of the major to the minor isomer in CDCl₃ at 296 K was found to be $1.1 \pm$ 0.4 s^{-1} , while that for the reverse reaction was 1.8 ± 0.3 s^{-1} , which is in agreement with the observed isomer ratio (see above). The ¹H peak integrations for the protons in position 8 (see numbering scheme) were used to obtain K, the equilibrium constant, and the equilibrium parameters ΔH° and ΔS° via a Van't Hoff analysis over the temperature range 296-335 K. This revealed a ΔH° of 3.9 \pm 0.6 kJ mol⁻¹ and ΔS° of 10 \pm 2 J K^{-1} mol⁻¹, which corresponds to a free energy difference of only 0.9 kJ mol⁻¹ at 296 K in CDCl₃, suggesting that there is only a very slight steric interaction between the phosphines in the *cis*-geometry, while ΔH° reveals that there is essentially no change in the bond energies between the two isomers of 1.

The reaction of Pd(cod)Cl₂ with 2 equiv. of *rac*-PPh₂(C₁₆H₁₅) in dichloromethane at room temperature (r.t.) for 1 h affords as *trans*-Pd{PPh₂(C₁₆H₁₅)}₂Cl₂ (**2**) in high yield as shown in Scheme 1. The ³¹P{¹H} NMR spectrum of **2** contains a singlet resonance at δ 23.0. The mass spectrum of **2** exhibits a molecular ion peak at 963 followed by peaks that correspond to fragment ions

from the stepwise loss of the chlorine and phosphine ligands. The ¹H NMR spectrum has been fully assigned using 2D techniques and the data are given in Table 1.

2.1. Structural characterisation

Crystals of **1a** were grown from $CH_2Cl_2-Et_2O$ by slow evaporation and contain two independent molecules, one of which is shown in Fig. 1 [7b]. Solvate is also present in the lattice, occupying a cavity in the structure and not interacting with the palladium complex. The structure of **1a** is severely disordered although the central Pd_2Cl_2 core is clearly defined. Each palladium centre is approximately square-planar, with a dihedral angle of 26.5° between the two square planes. This type of distortion is unprecedented in Pd(II) dimers of this type; the structures of related complexes having planar structures [12]. In addition, the structure of **1a** has also been determined in co-crystals that also contain **2** (see below), and in the co-crystals the dimer is planar.

The structure of **2** is shown in Fig. 2 together with principal bond parameters. Single crystals of 2 were grown from CH₂Cl₂-Et₂O by slow evaporation and the asymmetric unit contains two half independent molecules (one of which is shown in the figure) and two dichloromethane solvate molecules. The gross molecular structure is not too dissimilar to that of the same molecule observed in the co-crystals (see below) and to the related platinum complex trans- $Pt{PPh_2(C_{16}H_{15})}_2Cl_2$ [7c]. The two molecules of 2 differ slightly and it is possible that these differences can be traced to the way in which the two solvates interact with them through the formation of weak hydrogen bonds. The most significant interaction between the CH_2Cl_2 solvate and 2 involves a Cl-atom



Fig. 1. The molecular structure of $[Pd{PPh_2(C_{16}H_{15})}Cl_2]_2$ (1a): key bond lengths (Å) include: Pd(1)–P(1) 2.223(2), Pd(1)–Cl(1) 2.277(2), Pd(1)–Cl(2) 2.328(2), Pd(1)–Cl(3) 2.418(2).



Fig. 2. The molecular structure of *trans*-Pd{PPh₂(C₁₆H₁₅)₂Cl₂ (2): key bond lengths (Å) and angles (°) include: *Molecule 1*; Pd(1)–Cl(1) 2.3051(7), Pd(1)–P(1) 2.3547(7), Cl(1)–Pd(1)–Cl(1)A 180.0, Cl(1)–Pd(1)–P(1)A 91.70(3), Cl(1)–Pd(1)–P(1) 88.30(3), C(1)–P(1)–C(23) 103.36(14), C(1)–P(1)–C(17) 107.89(14), C(23)–P(1)–C(17) 98.19(14), C(1)–P(1)–Pd(1) 111.55(10), C(23)–P(1)–Pd(1) 116.71(10), C(17)–P(1)–Pd(1) 117.51(10). *Molecule 2*; Pd(2)–Cl(2) 2.3061(7), Pd(2)–P(2) 2.3617(7), Cl(2)–Pd(2)–P(2)B 91.67(3), Cl(2)–Pd(2)–P(2) 88.33(3), P(2)B–Pd(2)–P(2) 180.0, C(29)–P(2)–C(51) 107.37(14), C(29)–P(2)–C(45) 104.20(14), C(51)–P(2)–C(45) 96.71(14), C(29)–P(2)–Pd(2) 114.96(10), C(51)–P(2)–Pd(2) 115.07(10), C(45)–P(2)–Pd(2) 116.48(11). A and B indicate, respectively, the following symmetry operations: -x, 1-y, -z; -1-x, -y, 1-z.

coordinated to one of the *trans*-Pd{PPh₂(C₁₆H₁₅)}₂Cl₂ complexes [H(1s1)···Cl(1) 2.626 Å]. This type of interaction is well documented in the literature, with metalbound chlorine often accepts hydrogen bonds [13], although there is still some debate as to whether C–H ···Cl hydrogen bonds are real [14]. However, the dominant hydrogen bonding interaction in the crystal, observed in all the related compounds previously reported [7] involves a direct Pd···H interaction with the formation of a *pseudo*-octahedral palladium centre [Pd(1)···H(10) 2.782 Å, Pd(2)···H(42) 2.726 Å]. These interactions are very common and transition metal centres acting as hydrogen bond acceptors has been described in several papers [15].

Hydrogen bonds to the palladium ions are also present in **1a** [Pd(1)···H(14) 2.69 Å, Pd(2)···H(42) 2.88 Å], but in contrast to those is **2**, the interaction is only on one side of the metal centre, thereby forming a *pseudo*-square pyramid geometry about the palladium(II) centre.

2.2. Co-crystals containing 1a and 2

The structure of two co-crystals containing **1a** and **2** in a 1:1 ratio have been determined by X-ray diffraction. Although the discovery of the co-crystal was fortuitous we have since found that co-crystallisation of **1a** and **2** is a reproducible phenomenon. Both co-crystals were grown from dichloromethane-diethylether solution and one contains CH_2Cl_2 solvate [7a] molecules and the other a diethylether solvate [7b]. In the former cocrystal the CH_2Cl_2 solvates interact with the complexes (see Fig. 3) whereas the diethylether in the latter cocrystal merely occupies a cavity.

The structure of **1a** in the co-crystals is markedly different to that observed in the homonuclear crystal (see above) whereas the structure of 2 is quite similar. The structure of the central Pd_2Cl_2 core in **1a** is planar (it was bent in the homonuclear crystal). Further, in all the analogues of **1a** that have been characterised by Xray diffraction the structure is planar rather than bent [12]. It is not unreasonable to assume that the bent structure is more strained than the planar structure and calculations on related systems indicate that this is indeed the case [16]. It is plausible that the difference in internal energy between the bent and planar structures of **1a** leads to the formation of the co-crystal. If the bent structure in homonuclear crystal is of higher internal energy, then in the presence of other compounds with compatible shapes, in this case 2, cocrystallisation takes place in preference to the formation of homonuclear crystallisation. The resulting planar structure of 1a in the co-crystal is less strained and therefore of lower energy.

Co-crystallisation of substantially different neutral molecules, excluding solvates, is a rare phenomenon.



Fig. 3. The molecular structure of the co-crystal containing 1a, 2 and dichloromethane solvates. The orientation of 1a and 2 in the co-crystal containing diethyl ether solvate is almost the same and is therefore not shown. The diethyl ether is disordered and occupies a cavity such that it does not interact with 1a or 2.

Key examples include the co-crystallisation of a neutral mononuclear and dinuclear complexes [17] and polynuclear clusters [18]. Other unusual structural curiosities have also been observed for related platinum–phosphine compounds. For example, two different crystals containing $Pt_3(\mu$ -PPh₂)_3Ph(PPh_3)_2 have been analysed by single crystal X-ray diffraction and shown to have markedly different trimetal cores [19]. These differences were modelled using extended Hückel calculations and while somewhat different to the core rearrangements in the dimers reported herein make an interesting comparison.

In conclusion, while these structural studies are unusual, they do not constitute examples of crystal engineering [20]. However, it is possible that **1a** could be used more generally to induce co-crystallisation based on the reasoning outlined above. If this is the case then other molecules that crystallise with structures of different internal energies could be used in a similar way in order to engineer co-crystals.

3. Experimental

All reactions were carried out under an atmosphere of nitrogen gas using dried and degassed solvents using Schlenk techniques. [2.2]Paracyclophane was purchased from Aldrich Chemicals. IR spectra were recorded on a Mattson research series FTIR instrument. Mass spectra were recorded using an Autospec FAB instrument operated in positive mode. NMR spectra were recorded on a Bruker DRX-400 spectrometer with ¹H at 400.13 and ³¹P at 161.98 MHz, respectively. ¹H NMR chemical shifts are reported in parts per million relative to residual ¹H signals in the deuterated solvent CDCl₃ $\delta = 7.29$, while ³¹P NMR chemical shifts are reported in parts per million downfield of an external 85% solution of phosphoric acid. Standard gradient assisted Heteronuclear Multiple Quantum Correlation (HMQC) [21], COrrelation SpectrosopY (COSY) [22] and Nuclear Overhauser Effect SpectroscopY (NOESY) [23] pulse sequences were used as previously described.

3.1. Synthesis of diphenyl[2.2]paracylophanylphosphine, rac- $PPh_2(C_{16}H_{15})$

To a solution of $C_{16}H_{15}Li$ (0.74 g, 3.48 mmol) in diethyl ether (40 ml) at 0 °C, PPh₂Cl (0.77 g, 3.48 mmol) in diethyl ether (20 ml) was added over 10 min. The reaction was allowed to warm to r.t. and then stirred for 3 h. The solvent was removed in vacuo and the resulting yellow residue dissolved in hot ethanol. The solvent was removed under vacuum to give a white solid (0.85 g, 62%).

3.1.1. Spectroscopic data

³¹P{¹H} NMR (CDCl₃) δ : -2.7 (s). FAB-MS: 392 [M]⁺. IR (cm⁻¹): (KBr) 2945(s), 1590(s), 1499(s), 1412(s), 1194(s), 1124(s), 1087(s), 1025(w), 935(m), 893(m), 805(m), 743(m), 718(w), 695(w), 621(w), 506(w).

3.2. Synthesis of $[Pd{PPh_2(C_{16}H_{15})}Cl_2]_2(1)$

The phosphine *rac*-PPh₂($C_{16}H_{15}$) (0.1 g, 0.26 mmol) and Pd(cod)Cl₂ (0.037 g, 0.13 mmol) were stirred in CH₂Cl₂ (10 ml) at r.t. for 1 h. The solvent is removed under reduced pressure to afford a yellow–orange solid (0.130 g). Crystals were obtained from a solution of CH₂Cl₂–Et₂O after being left to evaporate at r.t. for several days.

3.2.1. Spectroscopic data for 1

 $^{31}P\{^{1}H\}$ NMR (CDCl₃) δ : 33.93(s) and 33.53(s). FAB-MS: 1140 [M]⁺, 1105 [M - Cl]⁺, 1068 [M - 2Cl]⁺, 1031 [M - 3Cl]⁺, 639 [M - 3Cl-P]⁺, 603 [M - Cl-Pd-P]⁺, 570 [M - 2Cl-Pd-P]⁺, 531 [M - 3Cl-Pd-P]⁺, 497 [M - 4Cl-Pd-P]⁺. Analytical data: %C 55.82, %H 4.36, Calc. 55.91, 4.28 for Pd₂Cl₄P₂C₅₆H₅₀·CH₂Cl₂.

3.3. Synthesis of trans- $Pd\{PPh_2(C_{16}H_{15})\}_2Cl_2$ (2)

The phosphine *rac*-PPh₂($C_{16}H_{15}$) (0.1 g, 0.26 mmol) and Pd(cod)Cl₂ (0.037 g, 0.13 mmol) were stirred in CH₂Cl₂ (10 ml) at r.t. for 1 h. The solvent is removed under reduced pressure to afford a yellow–orange solid (0.130 g). Crystals were obtained from a solution of CH₂Cl₂–Et₂O after being left to evaporate at r.t. for several days.

3.3.1. Spectroscopic data for 2

³¹P{¹H} NMR (CDCl₃) δ : 22.37(s). FAB-MS: 963 [M]⁺, 925 [M - Cl]⁺, 889 [M - 2Cl]⁺, 533 [M - Cl-P]⁺, 497 [M - 2Cl-P]⁺. Analytical data: %C 69.64, %H 5.12, Calc. 69.90, 5.24 for Pd₁Cl₂P₂C₅₆H₅₀.

3.4. Structural characterisation of 2

3.4.1. Crystal data for 2

C₅₈H₅₄Cl₆P₂Pd, M 1132.05 g mol⁻¹, triclinic, $P\overline{1}$, a = 12.2649(6) Å, b = 13.0662(5), c = 16.6082(5) Å, $\alpha =$ 78.983(1)°, $\beta = 82.939(1)°$, $\gamma = 80.025(1)°$, U = 2561.9(2) Å³, Z = 2, $D_c = 1.468$ Mg m⁻³, $\mu = 7.77$ cm⁻¹, data collected 22031, unique 9381, parameters 608, $R1 [F^2 > 2\sigma(F^2)]$ 0.041, wR_2 (all data) 0.106. Crystals were mounted using silicon grease on the end of a glass fibre and cooled on the diffractometer to 100(2) K using an Oxford Cryostream low temperature attachment. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo K α radiation using ϕ rotations with wide frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN [24]. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program SCALEPACK [24]. Structures were solved using the direct methods option of shelxs-97 [25] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97 [25]) with the aid of the program XSEED [26]. All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. The CIF file for 2 has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218082. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

4. Supplementary material

Tables giving crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles. Ordering information is given on any current masthead page.

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