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Preliminary communication

Diphosphine analogues of proton sponge: X-ray crystal structure of $[\text{Pd}(\eta^3\text{-allyl})(\text{dppn})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (dppn = 1,8-bis(diphenylphosphino)naphthalene)

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Received 12 April 1996; revised 9 May 1996

Abstract

The X-ray crystal structure of $[\text{Pd}(\eta^3\text{-allyl})(\text{dppn})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (**1**) where dppn = 1,8-bis(diphenylphosphino)naphthalene is reported. Comparison of the conformation of the ligand in **1** with that in the free state shows that there is a relief of strain on complexation analogous to the relief of strain observed upon protonation of proton sponge.

Keywords: Palladium; Allyl; Diphosphine; Structure

1. Introduction

The interest in new diphosphine ligands with a three-atom backbone stems from the high catalytic activity of six-membered palladium(II) chelates in CO/ethylene copolymerisation [1,2]. We have recently reported the rigid C_2 -diphosphine ligand 1,8-bis(diphenylphosphino)naphthalene (dppn) [2], an analogue of the non-nucleophilic base 1,8-bis(dimethylamino)naphthalene (proton sponge) [3]. The bulkiness of the diphenylphosphino substituents in the *peri* positions results in a strained structure in which the naphthalene ring is buckled and the lone pairs on the P atoms are constrained to overlap. Here, we report the X-ray crystal structure of $[\text{Pd}(\eta^3\text{-allyl})(\text{dppn})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (**1**) and the effect that coordination has on the conformation of the ligand.

2. Results and discussion

Complex **1** was prepared from $[\text{Pd}_2\text{Cl}_2(\eta^3\text{-allyl})_2]$ and dppn and characterised by elemental analysis, ^{31}P NMR spectroscopy and X-ray crystallography.

Synthesis and characterising data for 1. To a stirred solution of 1,8-bis(diphenylphosphino)naphthalene

(0.200 g, 0.403 mmol) in CH_2Cl_2 (2 cm³) was added a solution of $[\text{Pd}_2(\eta^3\text{-allyl})_2\text{Cl}_2]$ (0.147 g, 0.366 mmol) in CH_2Cl_2 (10 cm³) over 2 min followed by a solution of NaBF_4 (0.050 g, 4.60 mmol) in MeOH (5 cm³) and the resulting solution stirred for 5 min. The solvents were removed in vacuo and CH_2Cl_2 (15 cm³) and H_2O (15 cm³) added. The mixture was stirred vigorously for 1 min and the layers separated. The CH_2Cl_2 layer was treated with Florisil and filtered. The filtrate was reduced to 2 cm³ in vacuo and Et_2O (20 cm³) and pentane (10 cm³) added. The product was collected, and dried in vacuo. Yield 0.175 g, 59%. ^{31}P NMR (CDCl_3) 14.7 ppm (cf. $\delta(\text{P})$ for free dppn = 14.7 ppm), elemental analysis (calculated) for $\text{C}_{38}\text{H}_{33}\text{BCl}_2\text{F}_4\text{P}_2\text{Pd}$: C, 56.1 (55.9); H, 4.2 (4.0)%.

Crystal data for 1. $\text{C}_{38}\text{H}_{33}\text{BCl}_2\text{F}_4\text{P}_2\text{Pd}$, $M = 815.69$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 16.075(3)$, $b = 24.490(4)$, $c = 9.252(2)$ Å, $V = 3642.3(12)$ Å³, $Z = 4$, $D_x = 1.49$ g cm⁻³, $\bar{\lambda} = 0.71073$ Å, $\mu = 0.79$ mm⁻¹, $F(000) = 1648$, $T = 293$ K. Intensity data were collected on a Siemens R3m/V diffractometer for $4 < 2\theta < 50^\circ$. The structure was solved by heavy atom methods and refined by least-squares against F^2 (3644 unique absorption corrected reflections) to R_1 0.048 for 2837 reflections with $I > 2\sigma(I)$. The two half-molecules of dichloromethane of solvation are disordered about two-fold sites. The Flack absolute structure refined to 0.57(7) indicating racemic twinning.

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The molecular structure of the cation (see Fig. 1) is asymmetric due to the orientations of the phenyl rings which presumably would not persist in solution (the free diphosphine is also asymmetric in the solid state). The arrangement of phenyl rings is unusual for a C_3 -diphosphine and is more reminiscent of bis(diphenylphosphino)methane complexes than of bis(diphenylphosphino)propane complexes (see for example Ref. [4]). The naphthalene ring is inclined at 33.2° to the coordination plane of the palladium. A coplanar arrangement of the naphthalene ring and the metal would necessitate considerable widening of the angles $P(1)-C(8)-C(9)$, $C(8)-C(9)-C(1)$ and $P(2)-C(1)-C(9)$ and result in increased strain. The structure of the complex **1** makes an interesting comparison with the structure of the free ligand in the solid state. Fig. 2 shows complex **1** with the palladium and allyl group omitted, together with a similar view of free dppn. The non-bonded P–P distance has changed only modestly from 3.05 to 3.19 Å on complexation. As previously noted [2], the non-bonded P–P distance in free dppn is similar to that observed in more flexible diphosphines coordinated to square-planar centres, accounting for its relatively normal coordination characteristics. The resulting bite angle of $89.5(1)^\circ$ observed in complex **1** is consequently close to the ideal value.

The naphthalene ring is less distorted in complex **1** than in the free ligand, the mean deviations from planarity in each case being 0.011 and 0.069 Å respectively. The two phosphorus atoms lie closer to the naphthalene plane in **1** (deviations $P(1) = -0.052$, $P(2) = -0.036$ in **1** and $P(1) = -0.496$, $P(2) = 0.335$ Å in free dppn). The relief of strain is a consequence of

removing the repulsive lone pair–lone pair interaction that exists in the free ligand. This behaviour is directly analogous to the structural changes which occur when proton sponge is protonated, the loss of strain energy accounting for the remarkably high basicity of the latter [3].

In conclusion, the structural effects accompanying the coordination of dppn to palladium (Eq. (1)) parallel the effects observed when the diamine analogue (proton sponge) is protonated (Eq. (2)); dppn is a rigid ligand pre-organised for square-planar coordination.

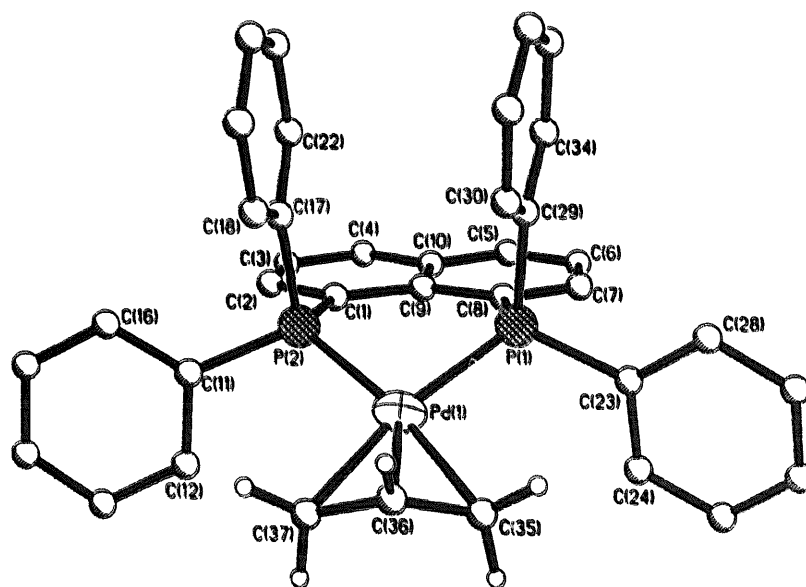
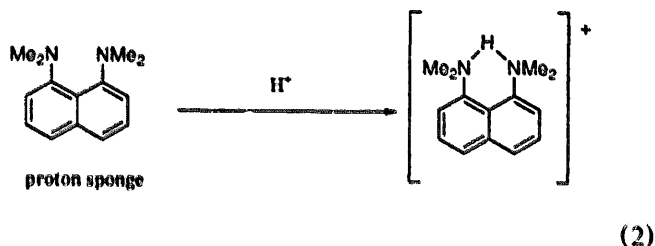
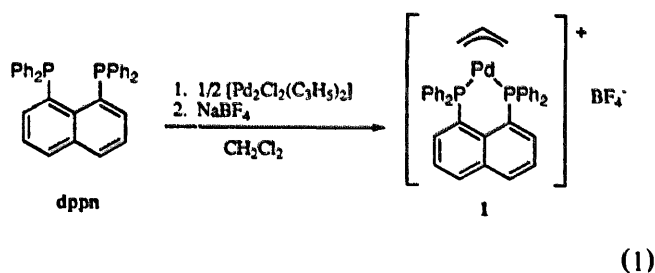


Fig. 1. Molecular geometry of the cation of **1** with naphthalene and phenyl hydrogen atoms omitted for clarity. Important molecular geometry parameters include: bond lengths (Å) $Pd(1)-C(35)$ 2.168(9), $Pd(1)-C(36)$ 2.176(9), $Pd(1)-C(37)$ 2.175(8), $Pd(1)-P(1)$ 2.265(2), $Pd(1)-P(2)$ 2.273(2); bond angle ($^\circ$) $P(1)-Pd(1)-P(2)$ 89.58(8).

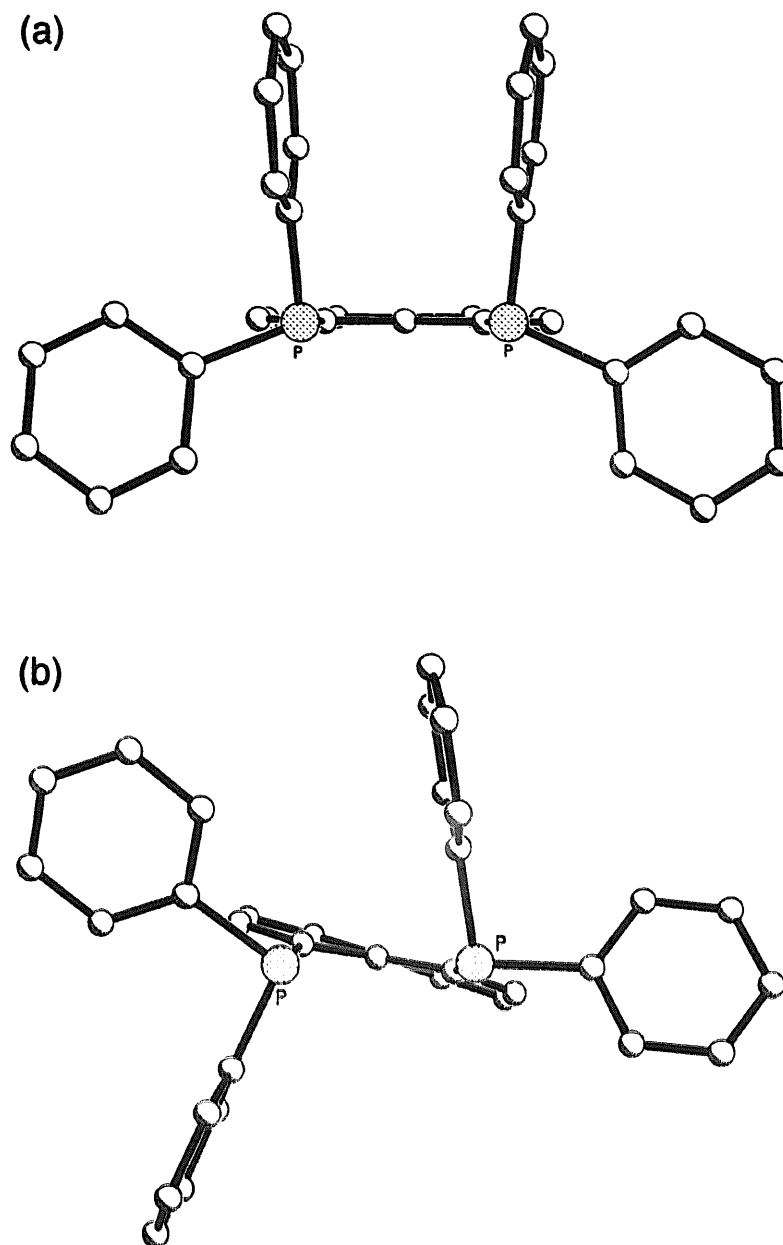


Fig. 2. Comparison of geometries of dppn when (a) coordinated and (b) non-coordinated [2].

Acknowledgements

We thank BP for supporting this work and Johnson-Matthey PLC for a generous loan of platinum salts.

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