Supporting Information

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X−Ray Diffractometric Study

Despite the huge number of known phosphine Pd complexes, phosphinoquinolines appear to have been somewhat neglected. In the CCDC [1] database there are only nine phosphinoquinoline complexes [2] and only nine compounds [2] in which a square planar Pd(II) ion is surrounded by the Cl, P, N_{py}, C_{ol} (N_{py} = pyridine-like nitrogen and C_{ol} = sp^2 carbon) donor set. Besides, there is just a single report of a η^1− dimethyl methylmaleate (Ra) ligand bound to Pd. (refcode PAQPED) [3] Accordingly, to the best of our knowledge, the neutral [Pd(DPPQ)(Ra)Cl]−*cis* P turns out to be, the first example of Pd(II) coordinated by both a chelating DPPQ and a η^1− dimethyl methylmaleate ligand.

In the complex presented here the environment about the metal is almost regular square planar. The main coordination plane is defined by the atoms Cl, P, N, C(1),which are coplanar within 0.01 Å, while Pd is off by 0.05 Å. The sum of the bond angles about Pd is 360.0° and the dihedral angle between the planes N–Pd–P and Cl–Pd−C(1) is 4.0°. Upon coordination, the DPPQ ligand forms a five–membered ring showing an envelope (C_s) conformation. Torsion angles in the ring range from −10.7 to +9.3°; the atoms P, C(13), C(14), N are coplanar and the Pd atom is off plane by 0.30 Å. The overall geometry is such that the main coordination plane makes dihedral angles of 12.0, 88.9 and 73.1° with the mean planes of the quinoline moiety and of the C(15)/C(20) and C(21)/C(26) phenyl rings of the DPPQ ligand, respectively. Other planes are defined by the atoms O(1), C(2), O(2), C(27) and O(3), C(5), O(4), C(28); the two planes are roughly perpendicular to each other (78.8°). The same planes make with the main coordination plane dihedral angles of 74.3 and 84.0°, respectively, while the corresponding angles with the quinoline ring are 65.1 and 75.1°, respectively.

The Pd−Cl, Pd−P and Pd−N bond distances in the coordination sphere of the present complex (2.334(1), 2.201(1) and 2.135(4) Å, respectively) do not differ much from the average values found for all Pd complexes or, more appropriately, for phosphinoquinoline Pd complexes reported in the CCDC database. In this latter subset, the average values for Pd−Cl, Pd−P, Pd−N distances are 2.358, 2.209, 2.133 Å, respectively, comparing quite well with our values.

With respect to the Pd−C distance (2.006(4) Å), the only phosphinoquinoline Pd complex with an sp^2 carbon in the coordination sphere is BERYAY, but in this case the donor set is different (PN$_2$C instead of ClPNC) and the Pd−C distances are slightly shorter (1.989 and 1.993 Å for the two independent molecules in the unit cell). The only phosphinoquinoline complex with the correct

donor set is OCIWON, in which the bound C is an sp^3 carbon and the Pd−C distance is similar to the one found here (2.019 Å) [2]. In both the afore mentioned structures the bond lengths about Pd are in agreement with those of the present complex. Instead, looking at the reported complexes showing the same donor set [1], the distances in the square plane are similar only when N is *trans* to C and P is *trans* to Cl, like in [Pd(DPPQ)(Ra)Cl]−*cis* P (refcodes PEJVUW, PEJWAD, KUNTUY, WANNAB).

Finally, the C(1)=C(3) distance of the coordinated olefin is 1.320(6) Å. This is slightly shorter than the average of 1.340 Å reported for 45 tetracoordinate complexes in which Pd is bound to an 1,2-bis-acyl substituted olefine and also shorter than the average of 1.332 Å for 49 reported structures of 1,2-bis-acyl substituted ethylenes [4]. Given that the Pd-C distance also is not particularly short, it may be inferred that in [Pd(DPPQ)(Ra)Cl]−*cis* P there is no significant back π-bonding towards C. Some degree of π-bonding might instead involve P, an indication being given by comparing the value of 2.201(1) Å found in this work with the average Pd-P distance of 2.282 Å calculated over about 5300 observations in CCDC. As for nonbonding interactions, the examination of the packing diagram did not reveal any worth mention intermolecular contact.

X–ray Analyses

Crystals of the complex [Pd(DPPQ)(Ra)Cl]−*cis* P, suitable for X–ray analysis, were obtained by slow diffusion of hexane into a dichloromethane solution. The selected specimen was lodged in a Lindemann glass capillary and centred on the goniometer head of a Philips PW1100 diffractometer made available by colleagues of the C.N.R.–I.C.I.S. Institute of Padua, Italy. The raw data were collected at room temperature with the ω–2θ scan technique, by using graphite–monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz/polarization effects, as well as for absorption (ψ–scans) [5]. Unit cell parameters were determined by least–squares refinement of 30 well centered high–angle reflections. Three standard reflections were checked every 200 measurements to ensure for crystal stability; no sign of deterioration was detected. The structure was solved by direct methods and refined by standard full–matrix least–squares based on F_o^2 with the SHELXTL NT [6] and SHELXL–97 [7] programs. In the last cycles of refinement, all non–H atoms were allowed to vibrate anisotropically. H atoms were placed in calculated positions and refined as "riding model". The U_{iso} values of hydrogen atoms were set at 1.2 times the U_{eq} of the appropriate carrier atom. The main crystallographic data are listed in Table 1 SI.

[1] F.H. Allen, *Acta Cryst.* **2002**, *B58*, 380–388; Cambridge Structural Database (Version 5.30 of November 2008 + 2 updates).

[2] (a) D. Sirbu, G. Consiglio, S. Gischig, *J. Organomet. Chem.* **2006**, *691*, 1143-1150 (OCIWON).

(b) T. Suzuki, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1869-1876 (FERZOS, FERZUY, FESBEL).

(c) G. Delapierre, M. Achard, G. Buono, *Tetrahedron Lett.* **2002**, *43*, 4025-4028 (LOYKUF).

(d) G. Francio, D. Drommi, C. Graiff, F. Faraone, A. Tiripicchio, *Inorg. Chim. Acta*, **2002**, *338*, 59-68 (WUFRUK)

(e) T. Suzuki, K. Kashiwabara, J. Fujita, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1619-1626 (ZIFPUZ, ZIFQAG)

(f) D.G. Allen, G.M. McLaughlin, G.B. Robertson, W.L. Steffen, G. Salem, S.B. Wild, *Inorg.Chem.* **1982**, *21*, 1007-1014 (BERYAY).

[3] L. Canovese, F. Visentin, G. Chessa, P. Uguagliati, C. Santo, A. Dolmella , *Organometallics* **2005**, *24*, 3297-3308.

[4] (a) J. Ruiz, J. Lorenzo, C. Vicente, G. Lopez, J.M. Lopez-de-Luzuriaga, M. Monge, F.X. Aviles, D. Bautista, V. Moreno, A. Laguna, *Inorg. Chem.* **2008**, *47*, 6990–7001 (NOHLOM).

(b) P. Giannoccaro, D. Cornacchia, S. Doronzo, E. Mesto, E. Quaranta, M. Aresta, *Organometallics*, **2006**, *25*, 2872–2879 (PEJVUW, PEJWAD).

(c) R.J. van Haaren, H. Oevering, P.C.J. Kamer, K. Goubitz, J. Fraanje, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, *J. Organomet. Chem.*, **2004**, *689*, 3800–3805 (WANNAB).

(d) G. Sanchez, J. Garcia, D. Meseguer, J.L. Serrano, L. Garcia, J. Perez, G. Lopez, *J. Chem. Soc. Dalton Trans.* **2003**, 4709–4717 (EQIREB).

(e) F. Leca, M. Sauthier, V. Deborde, L. Toupet, R. Reau, *Chem. Eur. J.* **2003**, *9*, 3785–3795 (OKIXAH).

(f) Y. Xie, C.-L. Lee, Y. Yang, S.J. Rettig, B.R. James, *Can. J. Chem.* **1992**, *70*, 751–762 (KUNTUI).

(g) G.R. Newkome, K.J. Theriot, B.K. Cheskin, D.W. Evans, G.R. Baker, *Organometallics* **1990**, *9*, 1375–1379 (VERYOG).

(h) A. Albinati, C.G. Anklin, F. Ganazzoli, H. Ruegg, P.S. Pregosin, *Inorg. Chem.* **1987**, *26*, 503–508 (FESXEG).

[5] A.T.C. North, D.C. Philips, F.S. Mathews, *Acta Cryst.* **1968**, *A24*, 351–359.

[6] SHELXTL/NT, Version 5.10; Bruker AXS Inc.: Madison, WI, 1999; G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467–473.

[7] G.M. Sheldrick, SHELXL–97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, **1997**.

Table 1 SI: Crystallographic Data of [Pd(DPPQ)(Ra)Cl]−*cis* P

Empirical formula	$C_{28}H_{25}NO_4PClPd$
Formula weight	612.31
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P\,2_1/n$ (No. 14)
a (Å)	9.279(2)
b (Å)	17.499(4)
c (Å)	16.897(3)
β (deg)	104.62(3)
Volume ($Å^3$)	2654.8(9)
Z	4
Calculated density ($Mg\,m^{-3}$)	1.532
Absorption coefficient (cm^{-1})	8.94
$F(000)$	1240
Crystal size	$0.42 \times 0.35 \times 0.30$
Observed reflections [$I > 2\sigma(I)$]	5102
Data / parameters	5760 / 325
Goodness–of–fit [a] on F^2	1.317
Final R indices [$I > 2\sigma(I)$]	R_1[b] $= 0.0486$; wR_2[c] $= 0.1150$
Largest difference peak and hole ($eÅ^{-3}$)	0.477 and −0.653

[a] Goodness–of–fit $= [\Sigma\,(w\,(F_o^2 - F_c^2)^2] / (N_{obsevns} - N_{params})]^{1/2}$, based on all data;

[b] $R_1 = \Sigma\,(\,|F_o| - |F_c|\,) / \Sigma\,|F_o|$;

[c] $wR_2 = [\Sigma[w\,(F_o^2 - F_c^2)^2] / \Sigma[w\,(F_o^2)^2]]^{1/2}$.