

Two square-planar palladium(II) complexes with *P,O*-bidentate hybrid ligands

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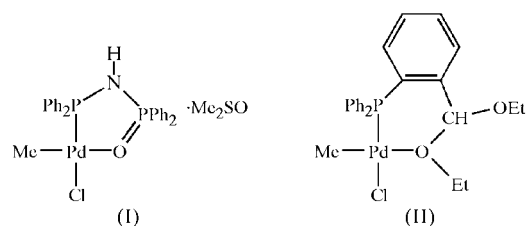
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In the two square-planar palladium(II) complexes chloro-[(diphenylphosphinoamino)diphenylphosphine oxide]methylpalladium(II) dimethyl sulfoxide solvate, [Pd(CH₃)Cl(C₂₄H₂₁NOP₂)]·C₂H₆OS, (I), and chloro[[2-(diphenylphosphino)phenyl]diethoxymethane]methylpalladium(II), [Pd(CH₃)Cl(C₂₃H₂₅O₂P)], (II), a *trans* disposition of the diphenylphosphino and chloro groups is observed. The Pd atom in both complexes displays a distorted square-planar configuration formed by the four unique donor atoms (P, Cl, C and O). In compound (I), the five-membered Pd–P–N–P–O metallacycle is best described as having an envelope conformation, whereas in (II) the six-membered Pd–P–C–C–O metallacycle adopts a skewed boat conformation. Furthermore, within the P–N–P–O backbone in (I), the P–N distances are consistent with single-bond character [1.659 (3) and 1.692 (3) Å], whilst the P=O bond shows appreciable double-bond character [1.509 (2) Å].

Comment

Hybrid ligands combining soft (*e.g.* P^{III}) and hard donor atoms (*e.g.* an O atom from a phosphine oxide or ether functional group) continue to receive widespread attention (Braunstein, 2006; Grushin, 2004). Phosphine oxides, mixed phosphine/phosphine oxides and ether-functionalized phosphines are versatile compounds that can display hemilabile properties through the different electronic effects exerted by each donor atom (Gianneschi *et al.*, 2005). Accordingly, the P-donor atom is coordinated strongly to a metal centre, whereas the O-donor atom is weakly bound, thereby promoting a vacant site upon dissociation. These ligands have found a range of applications in areas such as organic syntheses, coordination chemistry, catalysis, and industrial processes such as selective metal extraction (Kabat *et al.*, 2001; Yeo *et al.*, 1999; Nash *et al.*, 2002, and references therein). We present here the structures of two square-planar palladium(II) complexes, (I) and (II), containing two different *P,O*-bidentate hybrid ligands.

The chemistry of Ph₂PNHP(O)Ph₂, akin to Ph₂PCH₂P(O)Ph₂, has been studied extensively (Bhattacharyya *et al.*, 1996; Smith & Slawin, 2000), while few studies have been reported with ligands such as 2-Ph₂PC₆H₄CH(OR)₂ (Bei *et al.*, 1999). Compound (I) was obtained from the reaction of Pd(CH₃)Cl(cod) (cod = cycloocta-1,5-diene) and Ph₂PNHP(O)Ph₂. The *P,O*-bidentate ligand in (II) was obtained during an unsuccessful attempt to condense 2-(diphenylphosphino)benzaldehyde with 2-amino-3-methoxybenzoic acid in absolute ethanol, followed by complexation with Pd(CH₃)Cl(cod). Presumably, solvolysis of 2-(diphenylphosphino)benzaldehyde produced the ligand 2-Ph₂PC₆H₄CH(OCH₂CH₃)₂ rather than the intended Schiff base product 2-Ph₂PC₆H₄CH=N-C₆H₄CO₂H(3-OCH₃).



The structure of (I) (Fig. 1 and Table 1) confirms a near square-planar arrangement of ligands around the Pd^{II} metal centre. Of the two possible geometric isomers expected for (I), we observe here that the phosphoryl O-donor atom is *trans* to the methyl ligand. The Pd atom deviates from the least-squares plane through atoms P1/O1/Cl1/C1 by 0.1567 (2) Å. The P- and O-donor atoms form a five-membered metallacycle (containing atoms P1/N1/P2/O1/Pd1) which adopts an envelope conformation, with atom O1, the flap atom, out of the plane by 0.2616 (10) Å. Within the Pd1–P1–N1–P2–O1 ring, the P1–N1, N1–P2 and P2–O1 bond lengths are in good agreement with those of Ph₂PNHP(O)Ph₂ and other previously reported compounds (Bhattacharyya *et al.*, 1996; Smith & Slawin, 2000). Such data are consistent with the absence of double-bond character in the P1–N1 and N1–P2

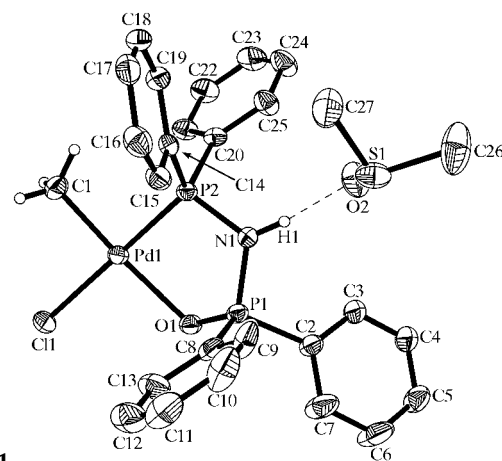
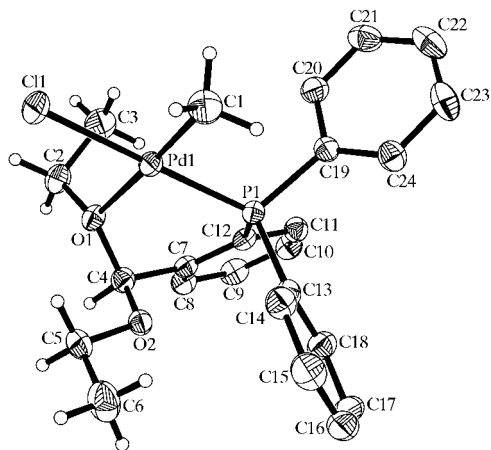


Figure 1
A perspective view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level, and amino and methyl H atoms are shown as small spheres of arbitrary radii. Other H atoms have been omitted. The minor disorder component has been omitted for clarity. The hydrogen bond is shown as a dashed line.


Figure 2

A perspective view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. CH₂ and methyl H atoms are shown as small spheres of arbitrary radii. Other H atoms have been omitted.

bonds. In contrast, when amine deprotonation is performed we have previously observed shortening of the P1–N1 and N1–P2 bond lengths and lengthening of the O1–P2 bond, consistent with appreciable double-bond character within the P1–N1–P2–O1 ring. Similar bond-length changes have also been reported in phosphinoenolate chemistry when *P,O*-chelated to metal centres (Braunstein, 2006). There is one N–H···O intermolecular hydrogen bond in the structure of (I), to a dimethyl sulfoxide (DMSO) solvent molecule (Table 2).

The structure of (II) establishes that the *P,O*-bidentate hybrid ligand functions in a similar manner to Ph₂PNHP(O)Ph₂ (Fig. 3 and Table 3). Similar to (I), the geometric isomer observed here places the diphenylphosphino group *cis* to a methyl ligand, as would be expected on the basis of their different *trans* effects. The Pd1–O1 bond length is similar to (I) and other palladium(II) compounds (Bei *et al.*, 1999). The Pd atom deviates from the least-squares plane through atoms P1/O1/C11/C1 by 0.0151 (7) Å. The *P,O*-donor substituents form a six-membered metallacycle (containing atoms Pd1/O1/P1/C4/C7/C12), which adopts a skewed-boat conformation, with atom C4 having the largest deviation from coplanarity [0.4789 (13) Å]. The difference in the C4–O1 [1.439 (2) Å] and C4–O2 [1.388 (2) Å] bond lengths confirms that one of the ether groups is coordinated while the other is not. Furthermore, it should be noted the P–Pd–O bite angles in the two complexes are different [86.93 (6)° for (I) and 92.65 (3)° for (II)], which is consistent with the different ring sizes adopted by the *P,O*-bidentate ligands.

In summary, we have shown that two *P,O*-bidentate hybrid ligands display envelope [for (I)] and skewed-boat [for (II)] ring conformations when complexed to square-planar palladium(II) bearing ancillary methyl and chloro ligands.

Experimental

For the preparation of (I), Ph₂PNHP(O)Ph₂ (0.072 g, 0.179 mmol) was added to a CH₂Cl₂ solution (2 ml) of Pd(CH₃)Cl(cod) (0.047 g,

0.177 mmol). After *ca* 1 min, solid (I) was deposited and this mixture was stirred for an additional 15 min. Diethyl ether (10 ml) was added to further the precipitation, and the solid was collected by suction filtration and dried *in vacuo* (yield 0.097 g, 98%). Selected spectroscopic data: ³¹P{¹H} NMR (DMSO-*d*₆): δ 65.8, 44.5 [²*J*(PP) = 23 Hz]; ¹H NMR (DMSO-*d*₆): δ 8.73 (NH), 7.70–7.51 (aromatic H), 0.50 [³*J*(PH) = 3 Hz (CH₃)]; FT-IR: ν_{NH} 2988, ν_{PO} 1145 cm⁻¹. Analysis found: C 53.56, H 4.26, N 2.53; C₂₅H₂₄ClNOP₂Pd requires: C 53.78, H 4.34, N 2.51%. Colourless block-shaped crystals of (I) were obtained by vapour diffusion of diethyl ether into a CDCl₃ solution of (I) containing a few drops of DMSO.

For the preparation of (II), an unsuccessful attempt to synthesize the Schiff base compound 2-Ph₂PC₆H₄CH=NC₆H₄CO₂H(3-OCH₃) by refluxing an absolute ethanol solution (10 ml) of 2-Ph₂PC₆H₄CHO (0.184 g, 0.634 mmol) and H₂NC₆H₄(OCH₃)(CO₂H) (0.109 g, 0.652 mmol) under nitrogen for *ca* 7 d gave instead 2-Ph₂PC₆H₄CH(OCH₂CH₃)₂ [δ(P) –17.0 p.p.m. (*ca* 60% purity by ³¹P{¹H} NMR)]. The ligand 2-Ph₂PC₆H₄CH(OCH₂CH₃)₂ was reacted with Pd(CH₃)Cl(cod) in CDCl₃ to afford (II). Selected spectroscopic data: ³¹P{¹H} NMR (CDCl₃): δ 28.0; ¹H NMR (CDCl₃): δ 7.53–7.01 (aromatic H), 5.37 (CH), 4.18 and 3.69 (both CH₂), 1.08 (CH₃), 0.90 [³*J*(PH) = 4 Hz (Pd–CH₃)]. Analysis found: C 54.57, H 5.30; C₂₄H₂₈ClO₂PPd requires: C 55.29, H 5.43%. Yellow block-shaped crystals of (II) were obtained upon slow diffusion of petroleum ether (b.p. 333–353 K) into a CDCl₃ solution of the product.

Compound (I)

Crystal data

[Pd(CH ₃)Cl(C ₂₄ H ₂₁ NOP ₂)]·C ₂ H ₆ OS	<i>V</i> = 1415.61 (13) Å ³
<i>M_r</i> = 636.37	<i>Z</i> = 2
Monoclinic, <i>Pn</i>	<i>D_x</i> = 1.493 Mg m ⁻³
<i>a</i> = 11.5432 (6) Å	Mo <i>K</i> α radiation
<i>b</i> = 9.5417 (5) Å	<i>μ</i> = 0.96 mm ⁻¹
<i>c</i> = 13.1351 (7) Å	<i>T</i> = 150 (2) K
<i>β</i> = 101.904 (2)°	Block, colourless
	0.42 × 0.15 × 0.14 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	10824 measured reflections
<i>ω</i> rotation scans with narrow frames	5385 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	5182 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.688, <i>T</i> _{max} = 0.877	<i>R</i> _{int} = 0.014
	<i>θ</i> _{max} = 26.0°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0274 <i>P</i>) ² + 0.4115 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.023	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.054	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.04	Δρ _{max} = 0.47 e Å ⁻³
5385 reflections	Δρ _{min} = –0.54 e Å ⁻³
327 parameters	Absolute structure: Flack (1983), with 2596 Friedel pairs
H-atom parameters constrained	Flack parameter: –0.02 (2)

Table 1

Selected geometric parameters (Å, °) for (I).

Pd1–C1	2.023 (4)	O1–P1	1.509 (2)
Pd1–P2	2.1880 (8)	P1–N1	1.659 (3)
Pd1–O1	2.228 (2)	N1–P2	1.692 (3)
Pd1–Cl1	2.3674 (9)		
C1–Pd1–P2	89.77 (11)	C1–Pd1–Cl1	89.77 (11)
C1–Pd1–O1	176.31 (14)	P2–Pd1–Cl1	176.43 (3)
P2–Pd1–O1	86.93 (6)	O1–Pd1–Cl1	93.63 (6)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2$	0.88	1.89	2.757 (4)	167

Compound (II)*Crystal data*

$[Pd(CH_3)Cl(C_{23}H_{25}O_2P)]$	$Z = 8$
$M_r = 521.28$	$D_x = 1.512 \text{ Mg m}^{-3}$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 17.3748 (5) \text{ \AA}$	$\mu = 1.01 \text{ mm}^{-1}$
$b = 14.3919 (4) \text{ \AA}$	$T = 150 (2) \text{ K}$
$c = 18.3124 (5) \text{ \AA}$	Block, yellow
$V = 4579.1 (2) \text{ \AA}^3$	$0.22 \times 0.20 \times 0.14 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	34078 measured reflections
ω rotation scans with narrow frames	4504 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3901 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.808$, $T_{\max} = 0.871$	$R_{\text{int}} = 0.020$
	$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 3.3794P]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.056$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.10$	$\Delta\rho_{\max} = 0.39 \text{ e \AA}^{-3}$
4504 reflections	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
265 parameters	
H-atom parameters constrained	

Table 3

Selected geometric parameters (Å, °) for (II).

Pd1—C1	2.027 (2)	Pd1—Cl1	2.3663 (5)
Pd1—O1	2.2112 (13)	O1—C4	1.439 (2)
Pd1—P1	2.2181 (5)	C4—O2	1.388 (2)
C1—Pd1—O1	177.48 (7)	C1—Pd1—Cl1	90.63 (6)
C1—Pd1—P1	89.87 (6)	O1—Pd1—Cl1	86.85 (4)
O1—Pd1—P1	92.65 (3)	P1—Pd1—Cl1	178.38 (2)

H atoms were placed in geometric positions, with C—H = 0.95–0.99 Å and N—H = 0.88 Å, and were treated using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. In (I), the DMSO molecule exhibits disorder, which was modelled with the S atom in two positions [major occupancy 0.671 (3)]. Restraints were applied to the S—O and S—C bond lengths [SADI restraint in *SHELXTL* (Bruker, 2000)] and to the anisotropic displacement parameters (SIMU and DELU restraints in *SHELXTL*) of the non-H atoms of the DMSO molecule, and also to those of atoms C2–C13 of the benzene rings. The data sets for both (I) and (II) were truncated at $2\theta = 52^\circ$; reflections were of insignificant intensity above this value. For (I), the correct orientation of the structure with respect to the polar-axis directions was established by means of the Flack (1983) parameter.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3061). Services for accessing these data are described at the back of the journal.

References

- Bei, X., Uno, T., Norris, J., Turner, H. W., Weinberg, W. H., Guram, A. S. & Petersen, J. L. (1999). *Organometallics*, **18**, 1840–1853.
- Bhattacharyya, P., Slawin, A. M. Z., Smith, M. B. & Woollins, J. D. (1996). *Inorg. Chem.* **35**, 3675–3682.
- Braunstein, P. (2006). *Chem. Rev.* **106**, 134–159.
- Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SMART* (Version 5.611) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gianneschi, N. C., Masar, M. S. III & Mirkin, C. A. (2005). *Acc. Chem. Res.* **38**, 825–837.
- Grushin, V. V. (2004). *Chem. Rev.* **104**, 1629–1662.
- Kabat, M. M., Garofalo, L. M., Daniewski, A. R., Hutchings, S. D., Liu, W., Okabe, M., Radinov, R. & Zhou, Y. (2001). *J. Org. Chem.* **66**, 6141–6150.
- Nash, K. L., Lavallette, C., Borkowski, M., Paine, R. T. & Gan, X. (2002). *Inorg. Chem.* **41**, 5849–5858.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.08. University of Göttingen, Germany.
- Smith, M. B. & Slawin, A. M. Z. (2000). *Inorg. Chim. Acta*, **299**, 172–179.
- Yeo, J. S. L., Vittal, J. J. & Hor, T. S. A. (1999). *Chem. Commun.* pp. 1477–1478.