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New enantiopure palladium(II) complexes from a stereodynamic 2,2′-biphosphole ligand

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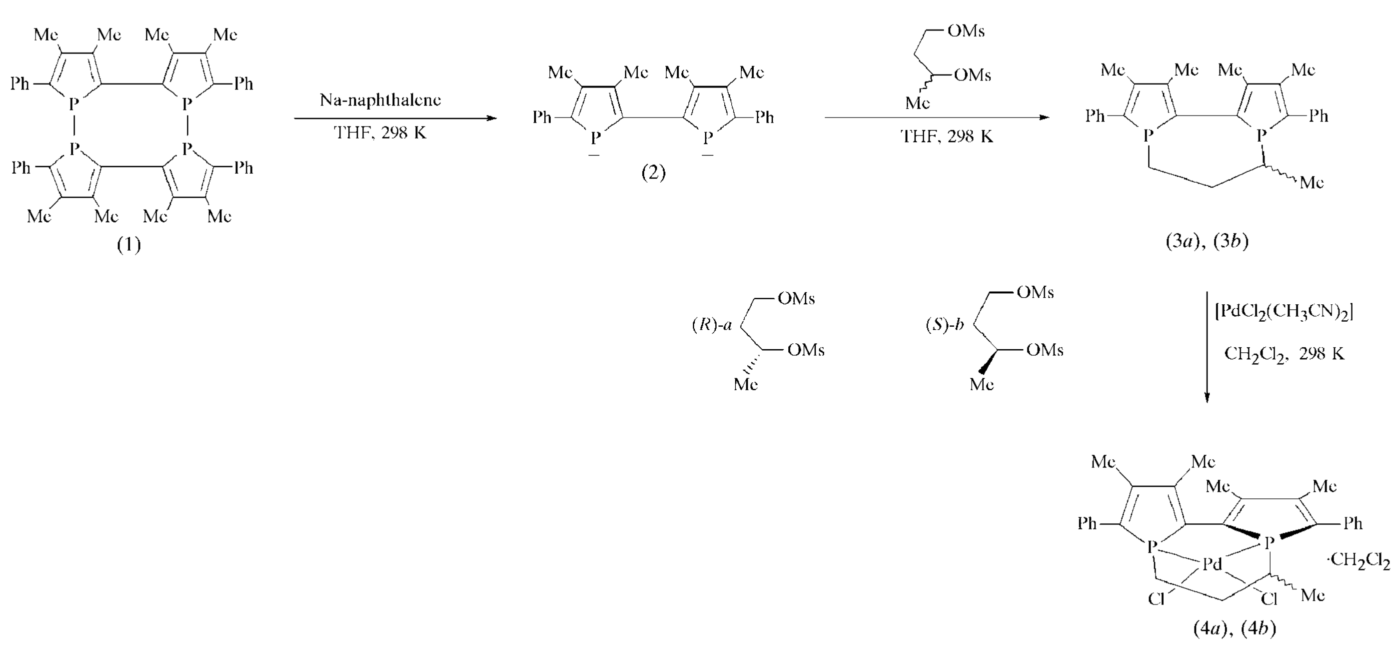
Two enantiopure palladium(II) complexes, *viz*. [1,1′-(butane-1,3-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole]-dichloridopalladium(II) dichloromethane solvate [systematic name: dichlorido(1,2,5,10,11-pentamethyl-3,9-diphenyl-perhydrodicyclopenta[*a*,*c*][1,4]diphosphepine-κ^2P,P')palladium(II) dichloromethane solvate], $[PdCl_2(C_{28}H_{30}P_2)]\cdot CH_2Cl_2$, have been synthesized from stereodynamic diphosphines derived from 2,2′-biphosphole through a metal kinetic dynamic resolution. In both structures, the coordination around the metal atom is square planar, with a *cis* arrangement of the ligands that drastically reduces the dihedral angle between the two phosphole rings compared with the free ligand. The structural determination of both enantiomers unambiguously establishes the absolute configuration of both central and axial elements of chirality of the 2,2′-biphosphole framework and indicates that the original carbon chirality of the backbone controls the chiralities of the 2,2′-biphosphole framework.

Comment

Considerable effort has been devoted to the design of new ligands for asymmetric catalysis (Ojima, 2000; Jacobsen *et al.*, 1999; Noyori, 1994). Asymmetric catalysts are generally metal complexes with stereochemically rigid enantiopure ligands. However, stereochemically dynamic ligands can also be controlled into a single enantiomeric conformation on a metal centre, and hence this methodology opens a new synthetic approach for the synthesis of enantiopure ligands (Walsh *et al.*, 2003; Mikami, Aikawa, Yusa, Jodry & Yamanaka, 2002). Good results have been obtained with flexible diphosphines such as BIPHEP (Mikami *et al.*, 1999, 2004; Mikami, Aikawa, Yusa & Hatano, 2002; Becker *et al.*, 2001), DPPF [1,1′-bis(diphenylphosphino)ferrocene; Mikami & Aikawa, 2002] and NUPHOS (Doherty *et al.*, 2003, 2004, 2005).

Recently, we reported the first application of chiral stereochemically dynamic 2,2′-biphosphole (BIPHOS) to asymmetric allylic substitution involving crystallization-induced spontaneous resolution and kinetic stabilization by coordination to a Pd centre (Tissot *et al.*, 2001). The flexibility of 2,2′-biphosphole ligands is reflected in the configurational instability of the axial chirality generated by the 2,2′-biphosphole framework and the central chiralities at the P atoms (Tissot *et al.*, 1996). In a more convenient procedure, we have discovered that dual chirality control can be achieved by introducing a chiral carbon linker between the two P atoms that favours a single enantiomeric form on a metal centre (Ortéga *et al.*, 2003). The strategy used is based on a two-step chirality control process, involving firstly partial chirality



control in order to maintain some degree of freedom, and secondly total chirality control by diastereoselective coordination on a metal centre (see reaction scheme).

By asymmetric alkylation of a 2,2′-biphospholyl dianion, (2), under highly dilute conditions, using various enantiomerically pure diol ditosylates or mesylates, an equilibrium mixture of diastereoisomeric diphosphines was obtained (Robé *et al.*, 2005). The reaction of this equilibrium mixture with transition metals such as Pd, Pt and Rh resulted in dynamic resolution leading to diastereo- and enantiopure complexes. These enantiomeric Pd, Pt and Rh complexes can be used in asymmetric allylic alkylation (Robé *et al.*, 2005), hydroformylation (Robé, Hegedüs, Bakos, Coppel *et al.*, 2007) and hydrogenation (Robé, Hegedüs, Bakos, Daran & Gouygou, 2007), respectively.

We report here the structural characterization of two enantiomerically pure palladium complexes, (4), containing a diphosphine, (3), derived from 2,2′-biphosphole (see reaction scheme). Complexes (4*a*) and (4*b*) were obtained from diphosphines (3*a*) and (3*b*), respectively, which differ in the chirality of atom C1 within the backbone linking the two P atoms.

The unit cells and space groups for (4*a*) and (4*b*) are identical, which agrees with the occurrence of the formation of two enantiomers. In both structures, the coordination around the metal is square planar, with a *cis* arrangement of the ligands (Figs. 1 and 2). The refinement of the Flack (1983) parameter clearly indicates that they are both enantiomerically pure in the solid state and that the absolute configuration is *S*[*Sp*, *Rp*, *Rc*] (axial chirality [phosphorus chirality, carbon chirality]) for (4*a*) and *R*[*Rp*, *Sp*, *Sc*] for (4*b*).

It is interesting to note that the ligand adopts a single configuration in these palladium complexes, in which the two P atoms have opposite configurations, *viz*. [*Sp*, *Rp*] or [*Rp*, *Sp*]. The coordination to Pd locks both the central and axial chirality of 2,2′-biphosphole, leading to drastically reduced P1—C11—C21—P2 torsion angles in complexes (4*a*) and (4*b*) compared with the BIPHOS ligand (Tissot *et al.*, 1996) (Table 1).

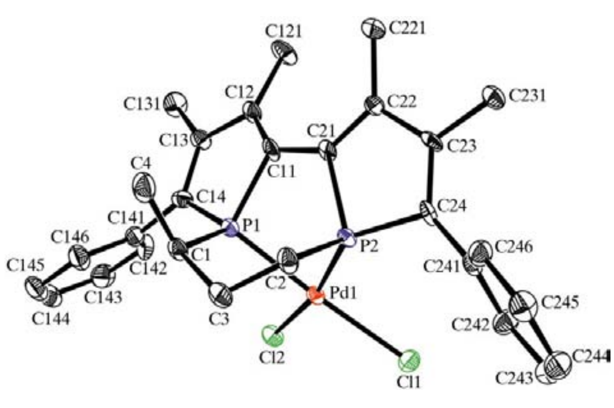


Figure 1
A molecular view of compound (4*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

These results prove unambiguously the influence of the chirality of the carbon backbone on the axial and central configuration of the 2,2′-biphosphole skeleton in complexes (4*a*) and (4*b*), as the *R* configuration provides the *S*[*Sp*, *Rp*] configuration of (4*a*), whereas the *S* configuration leads to the *R*[*Rp*, *Sp*] configuration of (4*b*).

The geometry of the chelating $PdCl_2P_2(C_2)(C_3)$ framework is obviously identical within experimental error for (4*a*) and (4*b*) and closely related to the reported $PdCl_2$(BIPHOS) complex (Ortéga *et al.*, 2003) containing a symmetrical chiral backbone (Table 1). This framework may be described in terms of the arrangement of the P1/C11/C21/P2, P1/C1/C2/P2 and P1/P2/Pd1/Cl1/Cl2 planes around the P1—P2 axes. The dihedral angles between these different planes are roughly identical in the three complexes (Table 1).

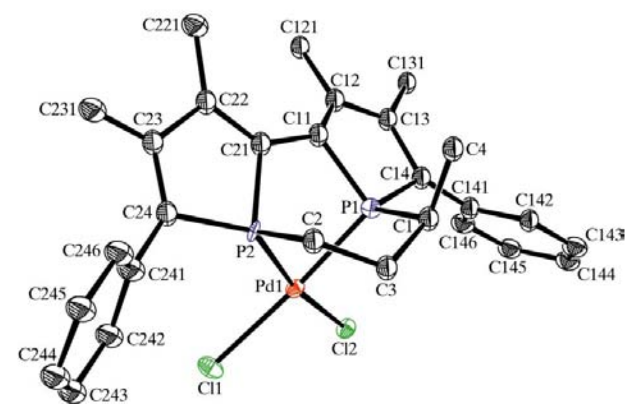


Figure 2
A molecular view of compound (4*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Experimental

Complexes (4*a*) and (4*b*) were synthesized according to a reported procedure (Robé *et al.*, 2005) (see reaction scheme in *Comment*). Crystals suitable for X-ray analyses were obtained by slow evaporation of a CH_2Cl_2 solution. The two enantiomers were prepared independently through a metal kinetic dynamic resolution.

Compound (4a)

Crystal data

$[PdCl_2(C_{28}H_{30}P_2)]\cdot CH_2Cl_2$
$M_r = 690.69$
Monoclinic, $P2_1$
$a = 8.9333\ (4)$ Å
$b = 12.1598\ (4)$ Å
$c = 14.0088\ (6)$ Å
$\beta = 103.678\ (4)^\circ$
$V = 1478.58\ (10)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.12$ mm^{-1}
$T = 180\ (2)$ K
0.47 × 0.14 × 0.11 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006) (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm)
$T_{min} = 0.597$, $T_{max} = 0.885$
10919 measured reflections
4911 independent reflections
4022 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.143$	$\Delta\rho_{max} = 2.05$ e Å^{-3}
$S = 1.09$	$\Delta\rho_{min} = -1.08$ e Å^{-3}
4911 reflections	Absolute structure: Flack (1983), with 1750 Friedel pairs
330 parameters	Flack parameter: 0.03 (5)
1 restraint	

Compound (4*b*)

Crystal data

$[PdCl_2(C_{28}H_{30}P_2)]\cdot CH_2Cl_2$	$V = 1477.6$ (10) Å^3
$M_r = 690.69$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 8.963$ (3) Å	$\mu = 1.12$ mm^{-1}
$b = 12.139$ (5) Å	$T = 180$ (2) K
$c = 13.989$ (6) Å	0.38 × 0.24 × 0.21 mm
$\beta = 103.87$ (3)°	

Data collection

Oxford Diffraction Xcalibur diffractometer	5431 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006) (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm)	4033 independent reflections
$T_{min} = 0.688$, $T_{max} = 0.791$	1900 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.079$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.080$	H-atom parameters constrained
$wR(F^2) = 0.226$	$\Delta\rho_{max} = 1.66$ e Å^{-3}
$S = 0.97$	$\Delta\rho_{min} = -1.30$ e Å^{-3}
4033 reflections	Absolute structure: Flack (1983), with 1276 Friedel pairs
168 parameters	Flack parameter: −0.02 (11)
13 restraints	

Table 1

Comparison of geometric structural parameters between (4*a*), (4*b*) and related structures (Å, °).

I/II refers to the dihedral angle between the P1/C11/C21/P2 and P1/C1/C2/P2 planes, I/III refers to the dihedral angle between the P1/C11/C21/P2 and P1/P2/Pd1/Cl1/Cl2 planes, and II/III refers to the dihedral angle between the P1/C1/C2/P2 and P1/P2/Pd1/Cl1/Cl2 planes.

Parameter	(4*a*)	(4*b*)	$PdCl_2$(BIPHOS)[a]	BIPHOS[b]
Pd1—P1	2.2415 (19)	2.242 (5)	2.2735 (6)	
Pd1—P2	2.2529 (16)	2.263 (5)	2.2479 (6)	
Pd1—Cl2	2.3404 (16)	2.341 (5)	2.3514 (6)	
Pd1—Cl1	2.3452 (18)	2.338 (5)	2.3381 (7)	
P1—Pd1—P2	77.99 (7)	77.87 (18)	78.02 (2)	
P1—Pd1—Cl2	92.01 (7)	92.31 (18)	91.29 (2)	
P2—Pd1—Cl2	169.80 (6)	170.07 (16)	169.31 (2)	
P1—Pd1—Cl1	174.41 (7)	174.0 (2)	176.14 (3)	
P2—Pd1—Cl1	96.43 (7)	96.12 (18)	98.16 (2)	
Cl2—Pd1—Cl1	93.58 (7)	93.70 (17)	92.53 (2)	
I/II	68.3 (2)	67.6 (5)	68.62 (7)	
I/III	51.4 (2)	52.2 (5)	48.24 (6)	
II/III	60.3 (2)	60.2 (5)	63.16 (7)	
P1—C11—C21—P2	9.8 (7)	−8 (1)	−8.3 (3)	−39.7 (2)

Notes: (*a*) Ortéga *et al.* (2003); (*b*) Tissot *et al.* (1996).

All H atoms were positioned geometrically and treated as riding, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene) and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for aromatic/methylene and methyl H atoms, respectively. Owing to the relatively poor quality of the data for (4*b*), the displacement parameters for the C atoms were restrained using EADP constraints (*SHELXL97*; Sheldrick, 1997).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3103). Services for accessing these data are described at the back of the journal.

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