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{Bis[(*S*)-2-(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)phenyl]phenylphoshine-κ^2N,P}(1,3-dimethyl-π-allyl-κ^3C)-palladium(II) hexafluorophosphate and $(S)_P$-{bis[(*S*)-2-(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)phenyl]-phenylphosphine-κ^2N,P}dichloropalladium(II)

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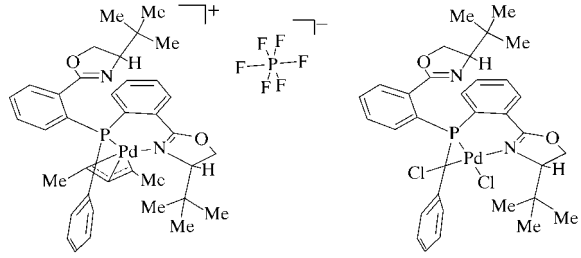
In the structures of the title compounds, $[Pd(C_5H_9)(C_{32}H_{37}N_2O_2P)]PF_6$ and $[PdCl_2(C_{32}H_{37}N_2O_2P)]$, the bis(dihydrooxazolyl)phosphine ligand is *N*,*P*-bidentate, with *S* chirality on the P atom. In the allyl complex, the π-allyl ligand ligates in a *syn–syn*-κ^3C manner.

Comment

The exploration of new chiral phospine ligands has contributed substantially to the development of asymmetric catalysis (Pfaltz, 1999; Gavrilov & Polosukhin, 2000; Muniz & Bolm, 2000; Henry, 2002; Noyori, 2002; Tang & Zhang, 2003). Although many chiral phosphines have been prepared by combining compounds containing achiral P atoms and compounds containing readily accessible chiral backbones derived from binaphthyl, tartarate, amino acids *etc*., much attention has recently been directed towards phosphines derived from compounds containing pre-existing chiral P atoms (such as duPHOS, TangPHOS *etc*.), as the resultant catalysts are effective in asymmetric catalysis (Burk *et al.*, 1996; Yamanoi & Imamoto, 1999; Albert *et al.*, 2000; Tang & Zhang, 2003). Difficulties associated with the generation of a chiral P atom during synthesis have long been known, as have the problems encountered in resolving enantiomerically mixed preparations.

The selective coordination of the potential tridentate ligand to a metal ion in a *B*,*P*-bidentate manner will generate a new chiral centre on the P atom. In the case of an AB_2P-type phosphine ligand, where the *B* moiety has a ligating atom and *A* has not, the use of a chiral *B* moiety can influence the ratio of S_P to R_P, and the selective ligation system can construct a chiral reaction field around a metal active site imposed by the chiralities of the *B* and P moieties. Within the scope of this concept, we have engaged in the synthesis of selectively coordinating ligands and have conducted studies on the synthesis, reactivity and catalysis of their selectively coordinated complexes (Yamada *et al.*, 1996; Yamagishi, 1996, 2003; Yamada, Fukui *et al.*, 1997; Yamada, Yamazaki *et al.*, 1997).



(I) (II)

We have estimated the chirality of the complexes using CD (circular dichroism) spectra in a series of earlier studies, although the absolute structures have not yet been determined. We have now obtained single crystals of {bis[(*S*)-2-(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)phenyl]phenylphoshine-κ^2N,P}-(1,3-dimethyl-π-allyl-κ^3C)palladium(II) hexafluorophosphate, (I), and $(S)_P$-{bis[(*S*)-2-(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)-phenyl]phenylphoshine-κ^2N,P}dichloropalladium(II), (II), and investigated their structures, paying particular attention to the chirality around the P atom.

The structure of (I) (Fig. 1) contains a Pd^{II} metal ion, a bis-(oxazolyl)phosphine ligand (NPN ligand) and a 1,3-dimethyl-π-allyl group, together with a PF_6^- counter-ion. The P atom and atom N1 of one oxazolyl moiety coordinate to atom Pd1, whereas the second oxazolyl group is uncoordinated. Atoms N1 and P1 and three allyl C atoms (C34–C36) surround atom Pd1 in a distorted square-planar configuration. Both methyl groups (C33 and C37) of the allyl ligand are located *syn* with respect to atom H35, giving rise to a *syn–syn* mode of binding

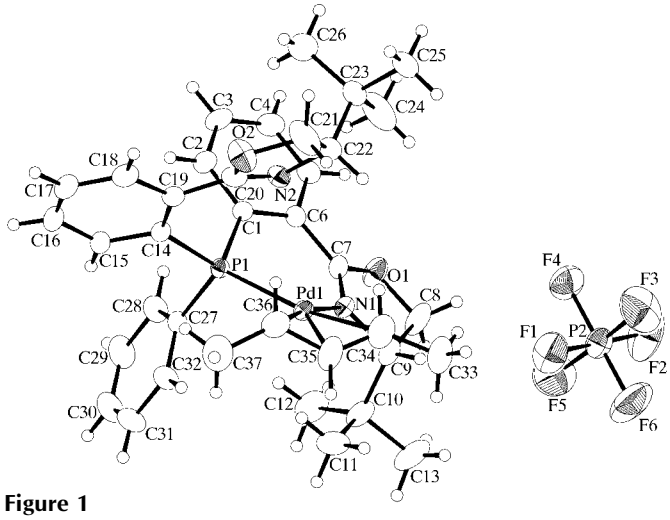


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I), showing 50% probability displacement ellipsoids.

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for the 1,3-dimethyl-π-allyl ligand. The chirality of atom P1 is determined to be *S* from the Flack (1983) parameter, and the use of an *S*,*S* ligand ensures similar chiralities for atoms C9 and C22. The Pd1—C34 distance is longer than Pd1—C36 (Table 1) because of the *trans* influence of atoms P1 and N1. The C14—C19—C20—N2 torsion angle may be influenced by steric congestion between the C23–C26 *tert*-butyl group and other parts of the complex. The second uncoordinated oxazole moiety appears on the opposite side of the Pd/P1/N1 plane relative to the *tert*-butyl group of the coordinated oxazole moiety.

There are earlier crystallographic reports on *N*,*P*-bidentate (4-substituted-4,5-dihydrooxazole)diphenylphosphino complexes of π-allylpalladium, such as the *tert*-butyl 4-substituent (Bernardinelli *et al.*, 2001; Kollmar *et al.*, 2001) and other alkyl and phenyl 4-substituents (Baltzer *et al.*, 1996; Schaffner *et al.*, 1997, 1998; Sprinz *et al.*, 1994). Among these examples, Kollmar reported (1,3-diethyl-π-allyl){(4*S*)-[2-(2-diphenylphosphino)phenyl]-4,5-dihydro-4-*tert*-butyloxazole-κ^2N,*P*}palladium(II) (Kollmar *et al.*, 2001). The P1—Pd1—N1 and C34—Pd1—C36 angles, and the Pd1—P1, Pd1—N1, Pd1—C34, Pd1—C35 and Pd1—C36 distances in (I) are similar to the equivalent angles and distances in the structure determined by Kollmar *et al.* (2001) [P—Pd—N = 87.46 (9)°, C—Pd—C = 68.2 (2)°, Pd—P = 2.2816 (10) Å, Pd—N = 2.112 (4) Å, and Pd—C = 2.261 (5), 2.164 (4) and 2.114 (5) Å]. These similarities show that the uncoordinated oxazolyl group in (I) has little influence on the coordination of the NPN ligand; it remains an *N*,*P*-bidentate ligand and simply behaves as a large substituent on one of the phenyl groups attached to the P atom.

The NPN ligand in (II), like that in (I), ligates to palladium chloride in an *N*,*P*-bidentate manner (Fig. 2). Atoms P1, N1, Cl1 and Cl2 complete the distorted square-planar configuration around atom Pd1. The chirality at atoms P1, C15 and C27 is determined to be *S* from the Flack (1983) parameter. The Pd1—Cl2 distance is longer than Pd1—Cl1 (Table 2) because of the *trans* influence, as described above for (I). The structures of the NPN ligand in (I) and (II) hardly differ, although they have different ligands (1,3-dimethyl-π-allyl and dichloride, respectively). The Pd1···N2 distance [2.938 (4) Å] to the non-coordinated oxazolyl group is slightly shorter in (II) than it is in (I) [3.108 (3) Å]. The Pd1—P1—C14—C19 and Pd1—N1—C9—C10 torsion angles are similar in the two compounds.

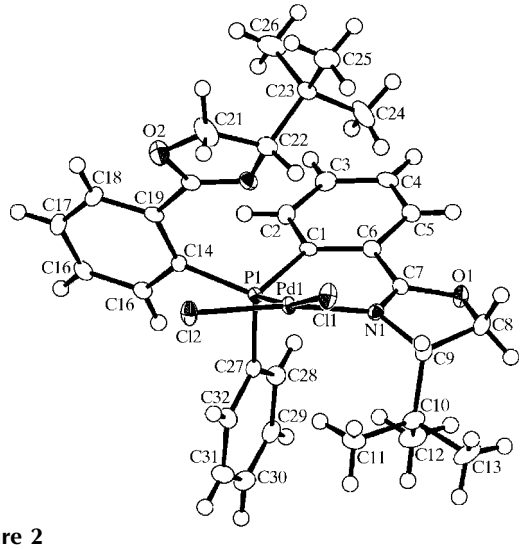

Figure 2
ORTEP-3 (Farrugia, 1997) diagram of (II), showing 50% probability displacement ellipsoids.

Experimental

An NPN ligand with a dihydrooxazole moiety was prepared according to the method for preparing an NPN ligand with a phenethylamine moiety (Yamada *et al.*, 1996), except for the use of (*S*)-4-*tert*-butyl-2-phenyl-2,3-dihydrooxazole (Bernardinelli *et al.*, 2001) instead of (*S*)-*N*,*N*-dimethyl-1-phenylethylamine. For the preparation of (I), the ligand was stirred with an equimolar amount of $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ in chloroform overnight at room temperature. A methanol solution of NH_4PF_6 was added, and the mixture was stirred for 2.5 h, before being washed with water and then evaporated. The residue was purified by reprecipitation from chloroform/ether, and recrystallization from chloroform/hexane gave the π-allyl derivative of (I) in the form of a white solid. This white solid was mixed with 3-penten-2-yl acetate (5 equivalents) and dimethyl sodiomalonate (3 equivalents) in tetrahydrofuran at 298 K for 48 h, before the addition of an NH_4PF_6 solution in methanol. The reaction mixture was evaporated, extracted with dichloromethane and evaporated again. The residual oil was purified by reprecipitation from dichloromethane/ether, and recrystallization from dichloromethane/ether gave pale-yellow crystals in an 87% yield. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane/ether. The ^{1}H NMR spectrum shows strong resonances due to a main species and weak resonances due to the presence of a small amount of a minor species. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.44 (9H, *s*, Me), 0.57 (9H, *s*, Me), 0.88 (3H, *dd*, Me on π-allyl), 1.87 (3H, *dd*, Me on π-allyl), 2.74 (1H, *dq*, allyl H), 3.79–4.62 (6H, *m*, methine and methylene), 4.52 (1H, *m*, allyl H), 5.30 (1H, *dd*, allyl H), 6.87–8.30 (13H, *m*, Ph). For the preparation of (II), the ligand was stirred with an equimolar amount of $[PdCl_2(PhCN)_2]$ in benzene overnight. The precipitate was collected and recrystallized from dichloromethane/hexane to give orange crystals (87% yield). Single crystals suitable for X-ray diffraction were obtained by recrystallization from dichloromethane–hexane. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.56 (9H, *s*, Me), 0.76 (9H, *s*, Me), 4.06 (1H, *t*, methylene), 4.39 (1H, *t*, methine), 4.49 (1H, *t*, methylene), 4.53 (1H, *dd*, methylene), 4.96 (1H, *t*, methylene), 5.55 (1H, *m*, methylene), 6.88 (1H, *dd*, Ph), 7.00 (1H, *dd*, Ph), 7.36–7.62 (9H, *m*, Ph), 8.06 (1H, *dd*, Ph), 8.19 (1H, *dd*, Ph).

Compound (I)

Crystal data

$[Pd(C_5H_9)(C_{32}H_{37}N_2O_2P)]PF_6$
M_r = 833.10
Monoclinic, $P2_1$
a = 10.3152 (13) Å
b = 13.5764 (17) Å
c = 13.8415 (18) Å
β = 96.345 (2)°
V = 1926.5 (4) Å^3
Z = 2
D_x = 1.436 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 972 reflections
θ = 2.0–27.8°
μ = 0.63 mm^{-1}
T = 293 (2) K
Block, pale yellow
0.8 × 0.4 × 0.4 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.536, T_{max} = 0.633
12 103 measured reflections
8317 independent reflections
7836 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.8°
$h = -13 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 14$
291 standard reflections
frequency: 63 min
intensity decay: −0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.074
S = 1.00
8317 reflections
459 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), 3757 Friedel pairs
Flack parameter = 0.001 (17)

Table 1
Selected geometric parameters (Å, °) for (I).

Pd1—C34	2.271 (3)	Pd1—N1	2.125 (2)
Pd1—C35	2.155 (3)	Pd1—P1	2.2864 (7)
Pd1—C36	2.120 (3)		
C34—Pd1—P1	163.33 (12)	C36—Pd1—N1	169.75 (11)
C35—Pd1—P1	139.69 (10)	C36—Pd1—P1	102.81 (10)
C35—Pd1—C34	34.13 (13)	N1—Pd1—C35	132.15 (13)
C36—Pd1—C34	66.73 (14)	N1—Pd1—C34	104.20 (12)
C36—Pd1—C35	37.64 (14)	N1—Pd1—P1	87.10 (6)
Pd1—P1—C14—C19	38.6 (3)	C14—C19—C20—N2	17.4 (5)
Pd1—N1—C9—C10	73.1 (3)		

Compound (II)

Crystal data

$[PdCl_2(C_{32}H_{37}N_2O_2P)]$
M_r = 689.91
Orthorhombic, $P2_12_12_1$
a = 10.2172 (13) Å
b = 13.3580 (18) Å
c = 22.858 (3) Å
V = 3119.7 (7) Å^3
Z = 4
D_x = 1.469 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 982 reflections
θ = 1.8–27.4°
μ = 0.85 mm^{-1}
T = 83 (2) K
Block, orange
0.10 × 0.05 × 0.05 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
20 046 measured reflections
7214 independent reflections
6600 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.9°
$h = -13 \rightarrow 12$
$k = -12 \rightarrow 17$
$l = -25 \rightarrow 29$
129 standard reflections
frequency: 635 min
intensity decay: 0.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 1.05
7214 reflections
369 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}
Absolute structure: Flack (1983), 3090 Friedel pairs
Flack parameter = 0.00 (3)

Table 2
Selected geometric parameters (Å, °) for (II).

Pd1—N1	2.042 (3)	Pd1—Cl1	2.3758 (11)
Pd1—P1	2.2177 (11)	Pd1—Cl2	2.3004 (11)
Cl1—Pd1—Cl2	92.77 (4)	N1—Pd1—P1	88.77 (10)
N1—Pd1—Cl1	89.99 (10)	P1—Pd1—Cl1	169.14 (4)
N1—Pd1—Cl2	171.42 (10)	P1—Pd1—Cl2	90.01 (4)
Pd1—N1—C9—C10	72.7 (4)	Pd1—P1—C14—C19	38.8 (4)

For both compounds, all H atoms bonded to C atoms, except for atoms H9*A* (bonded to C9) and H22*A* (bonded to C22) of (II), were included in calculated positions, with C—H distances of 0.93 Å for aromatic and allyl, 0.98 Å for methine, 0.97 Å for methylene, and 0.96 Å for methyl H atoms. Atoms H9 and H22 of (II) were placed in positions determined from a difference Fourier map and were constrained to ride on their parent atoms. In (I), there are two large and two smaller voids (total of ∼110.6 Å^3) in the unit cell, the larger probably hosting a disordered solvent molecule. A residual peak of 1.2 e Å^{-3} was localized in this void, but it could not be verified what this peak represented through refinement. A disordered-solvent correction based on the *SQUEEZE* algorithm (van der Sluis & Spek, 1990) in *PLATON* (Spek, 2003) afforded solvent-free reflection data and estimated that a total of 12 electrons were unaccounted for. Refinement with the solvent-free data improves the minimum residual electron density from −0.30 to −0.28 e Å^{-3}, the maximum residual electron density from 1.18 to 0.58 e Å^{-3}, and wR from 0.094 to 0.074.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 1997) (for both compounds) and *PLATON* (Spek, 2003) [for compound (I)].

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1065). Services for accessing these data are described at the back of the journal.

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