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Di-μ-bromo-bis{[(2,4,6-tris-*tert*-butylphenyl)phosphanediylmethyl-*P*]phenyl-C^2}-dipalladium

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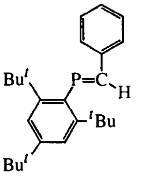
Abstract

The crystal structure of the title compound, $[Pd_2Br_2(C_{25}H_{34}P)_2]$, a new binuclear phospha-alkene compound containing a trivalent P atom shows a centrosymmetric dimeric arrangement. The Pd_2Br_2 core is planar and adopts an irregular diamond shape. The coordination of the Pd atom is square planar. No stacking interactions were observed in the molecular packing.

Comment

There is an increasing interest in the chemistry of compounds containing a low coordinated trivalent P atom (Jouaiti, Geoffroy, Terron & Bernardinelli, 1992, 1995; Jouaiti, Geoffroy & Bernardinelli, 1996). A recent communication (Kawanami, Toyota & Yoshifuji, 1996) on the preparation of a novel binuclear complex of a phospha-alkene ligand, $[PdClL']_2$, has prompted us to report another path leading to an analogous complex, $[PdBrL]_2$, and the corresponding crystal structure.



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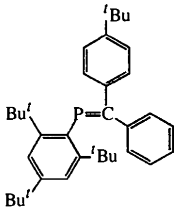
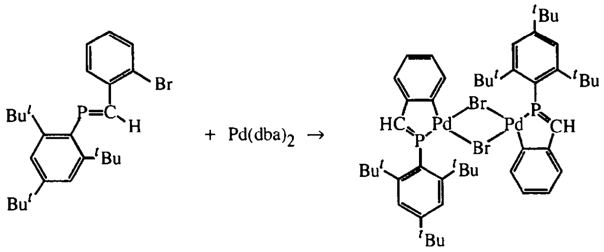


L'

Whereas Kawanami *et al.* (1996) obtained $[PdClL']_2$ by reacting L' with a Pd^{II} complex, we were able to form $[PdBrL]_2$ by reacting (1) with bis(dibenzylideneacetone)palladium, $[Pd(dba)_2]$, a Pd^0 reagent well known for facilitating oxidative addition on the carbon–halogen bond (Albert, Barro & Granell, 1991).



(1) $[PdBrL]_2$

While the crystallographic analysis of the chlorine complex was unsuccessful in the absence of both a *tert*-butyl group on the metallated phenyl ring and a phenyl group bound to the phospha-alkene C atom (Kawanami *et al.*, 1996), we succeeded in solving the structure of the bromine compound bearing no substituent in these positions. It should be noted that, as shown by ^{31}P NMR, $[PdBrL]_2$ in the presence of a phosphine as Ph_3P or $ArPH_2$ (Ar = 2,4,6-tris-*tert*-butylphenyl) gives rise to the mononuclear complexes $Ph_3PPd(L)Br$ or $Ar(H_2)PPd(L)Br$, respectively.

In $[PdBrL]_2$, the phospha-alkene molecule chelates the palladium(II) ion through orthometallation and coordination to the P atom. Additional coordination of the metal to two Br atoms generates a centrosymmetric dimer. The $PdBr_2$ core has an irregular diamond shape with slightly different metal–bromine bond lengths. This structure is similar to that reported for the chlorine compound. The increase of the palladium–halogen bond lengths and the absence of a phenyl ring on the phospha-alkene C atom does not affect the conformation of the five-membered ring containing the Pd atom. This five-membered ring is planar (maximum deviation of 0.08 Å for the C2 atom) and almost parallel (5.2°) to the Pd_2Br_2 plane. The coordination of the Pd atom is square planar (deviation of 0.09 Å from the mean plane passing through the four coordinated atoms). The tris-*tert*-butyl-substituted phenyl ring is nearly perpendicular (91.5°) to the Pd_2Br_2 plane. The *para-tert*-butyl substituent shows large atomic displacement parameters, in agreement with an oscillatory motion around the C11—C18 bond.

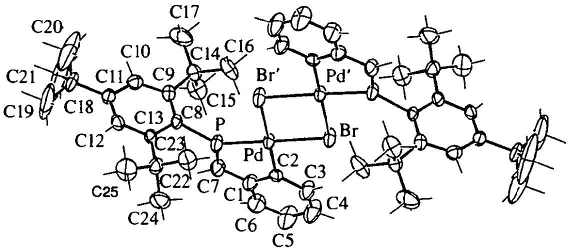


Fig. 1. The crystal structure of $[PdBrL]_2$ with atomic labeling. Displacement ellipsoids are represented at the 50% probability level.

Experimental

$[Pd(dba)]_2$ and (1) were prepared following the methods of Rettig & Maitlis (1977), and Yoshifuji, Toyota & Inamoto (1985), respectively. $[PdBrL]_2$ was synthesized by adding one equivalent of $[Pd(dba)_2]$ (103 mg, 0.18 mmol) to a solution containing one equivalent (80 mg) of (1) in 2 ml of pentane. After addition of 5 ml of benzene, the solution was heated under reflux for one hour. After hot filtration of the dark yellow reaction mixture, the solution was allowed to return to room temperature. An orange solid precipitated which was filtrated and successively washed with benzene and pentane. Crystals (m.p. 522 K) were obtained by slow evaporation of a solution of $[PdBrL]_2$ in a CH_3CN/CH_2Cl_2 mixture. ^{31}P NMR ($CDCl_3$): δ = 217.6 p.p.m. $Ph_3PPd(L)Br$: ^{31}P NMR P(phospha-alkene) doublet δ = 227.4, P(phosphine) doublet δ = 35 and J_{P-P} = 5.8 p.p.m.; $Ar(H_2)PPd(L)Br$: ^{31}P NMR P(phospha-alkene) doublet δ = 226.15, P(phosphine) doublet δ = −67.35 and J_{P-P} = 6.1 p.p.m.

Crystal data

$[Pd_2Br_2(C_{25}H_{34}P)_2]$
M_r = 1103.6
Monoclinic
$P2_1/c$
a = 14.156 (1) Å
b = 19.536 (3) Å
c = 9.2244 (4) Å
β = 105.010 (3)°
V = 2464.0 (4) Å^3
Z = 2
D_x = 1.488 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54183 Å
Cell parameters from 24 reflections
θ = 26–33°
μ = 8.628 mm^{-1}
T = 293 K
Prism
0.12 × 0.09 × 0.03 mm
Red

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical by integration
T_{min} = 0.457, T_{max} = 0.778
3224 measured reflections
2860 independent reflections
2444 reflections with $F > 4\sigma(F)$

R_{int} = 0.021
θ_{max} = 53°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 9$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F
R = 0.043
wR = 0.034
S = 2.399
2444 reflections
275 parameters
Only coordinates of H atoms refined except for methyl groups
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{max}$ = 0.00079
$\Delta\rho_{max}$ = 0.751 e Å^{-3}
$\Delta\rho_{min}$ = −0.815 e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 0.01 (1) × 10^{-4}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Pd—Br	2.5082 (9)	P—C7	1.657 (9)
Pd—P	2.217 (2)	P—C8	1.814 (7)
Pd—C2	2.031 (8)	C1—C2	1.404 (11)
Pd—Br^i	2.5602 (11)	C1—C7	1.441 (10)
Br—Pd—P	174.85 (7)	Pd—P—C7	107.7 (3)
Br—Pd—C2	96.20 (18)	Pd—P—C8	139.0 (3)
Br—Pd—Br^i	84.27 (4)	C7—P—C8	112.1 (4)
P—Pd—C2	80.65 (19)	C2—C1—C7	117.5 (8)
P—Pd—Br^i	98.79 (6)	Pd—C2—C1	120.6 (5)
C2—Pd—Br^i	178.5 (3)	P—C7—C1	113.0 (6)
Pd—Br—Pd'	95.73 (4)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *Xtal*3.2 *LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *REFCAL LSABS* (Blanc, Schwarzenbach & Flack, 1991) and *Xtal*3.2 *SORTRF*. Program(s) used to solve structure: *MULTAN*87 (Main *et al.*, 1987). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PA1251). Services for accessing these data are described at the back of the journal.

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[*N*-(2-Hydroxybenzyl)salicylaldiminato]-(piperidine)nickel(II)

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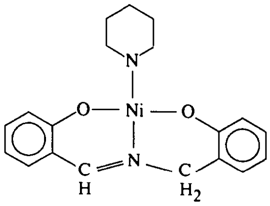
Abstract

In the title compound, {2-[(2-hydroxybenzyl)iminomethyl]phenolato-*O*,*N*,*O*′}(piperidine-*N*)nickel(II), molecules of $[Ni(C_{14}H_{11}NO_2)(C_5H_{11}N)]$ adopt a *trans* form, as imposed by the geometry of the monodentate and tridentate ligands, and the Ni atom is in a slightly distorted square-planar environment.

Comment

Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Garnovskii, Nivorozhkin & Minkin, 1993). The electron delocalization which produces resonance structures of nickel(II) and copper(II) metal complexes with square-planar coordination and containing salicylaldehyde and naphthaldehyde groups has been examined previously (Fernández-Garcia *et al.*, 1987). Copper(II) and nickel(II) ions react with tridentate anionic Schiff bases and have dimerized square-planar complexes (Maggio, Pizzino & Romano, 1974). The present paper reports the structure of a Schiff base–nickel complex, (I), and aims to explain the procedure by which the nickel(II) ion reacts with both the tridentate *N*-(2-hydroxybenzylidene)salicylaldimine ligand and the monodentate piperidine ligand.



(I)

The monodentate and tridentate ligands are coordinated to nickel(II) in a square-planar arrangement. The bond lengths of several complexes of N-substituted salicylaldimines are compared in Table 2 with the values for the title compound. The Ni—O distances of 1.848 (3) and 1.822 (3) Å agree with the values in these square-planar coordinated complexes. The Ni—N1 bond length of 1.871 (3) Å, however, is definitely shorter than Ni—N2 and other values from the literature. A possible explanation is the coordination of Ni by two O atoms and one N atom of the same ligand which produces a close approach of Ni^{II} towards the N atom. This short value agrees, however, with the Ni—N1 bond distances in {1-[(2-hydroxyphenyl)iminomethyl]-naphthalen-2-olato-*O*,*O*′,*N*}(piperidine)nickel(II) (Elerman, Paulus & Fuess, 1991).

The conformation of the planar groups around the Ni atom in (I) shows significant differences from related compounds. In earlier work (Elerman, Paulus & Fuess, 1991; Elerman, Kabak & Tahir, 1996), the coordination of the ligands around the Ni atom is almost planar and the angles between the planar organic groups are less than 8°. In (I), however, the methyl group plays a predominant role in the distortion of the molecule as a whole. The molecule is twisted about the C7—O1 direction and the coordination of the Ni atom by the two O atoms and one N atom of the same ligand produces a close approach of the Ni^{II} ion towards the N atom. The torsion angles Ni1—O1—C1—C6 [53.6 (4)°], Ni1—O1—C1—C2 [−126.4 (4)°], N1—C7—C6—C1 [−53.6 (6)°] and N1—C7—C6—C5 [126.5 (4)°] show this distortion. The interplanar angle between the salicylaldimine group and the NiN_2O_2 coordination plane was found to be 50.2 (1)°.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for octahedrally coordinated Ni^{II} ions resulted in 104 compounds with Ni—O and/or Ni—N bonds. The average Ni—O and Ni—N distances are 2.084 and 2.110 Å, respectively, and are significantly longer than in the title compound. As can be seen from Table 2, the C—O, C—N, Ni—N and Ni—O bond lengths also show no significant differences in similar Ni^{II} complexes. The bond length of 1.291 (5) Å between the N1 and C8 atoms is typical of a C=N double bond.

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