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

CHENTIT, Mostafa, GEOFFROY, Michel, BERNARDINELLI, Gérald Hugues

Abstract

The crystal structure of the title compound, [Pd\textsubscript{2}Br\textsubscript{2}(C\textsubscript{25}H\textsubscript{34}P)\textsubscript{2}], a new binuclear phospha-alkene compound containing a trivalent P atom shows a centrosymmetric dimeric arrangement. The Pd\textsubscript{2}Br\textsubscript{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.

Reference

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**Di-μ-bromo-bis[{[2,4,6-tris-tert-butylphenyl]phosphanediylmethyl-P}phenyl-C2]dipalladium**

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**Abstract**

The crystal structure of the title compound, [Pd2Br2(C25H34P)2], a new binuclear phospha-alkene compound containing a trivalent P atom shows a centrosymmetric dimeric arrangement. The Pd2Br2 core is square 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.

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 31P NMR, [PdBrL]2 in the presence of a phosphine (e.g., Ph3P or ArPH2 (Ar = 2,4,6-tris-tert-butylphenyl) gives rise to the mononuclear complexes Ph3PPd(L)Br or Ar(H2)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 PdBr2 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 Pd2Br2 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 Pd2Br2 plane. The para-tert-butyl sub-
stituent shows large atomic displacement parameters, in
agreement with an oscillatory motion around the C11--
C18 bond.

\[ \text{Table 1. Selected geometric parameters (Å, °)} \]

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd--Br</td>
<td>2.5082 (9)</td>
</tr>
<tr>
<td>Pd--P</td>
<td>2.031 (8)</td>
</tr>
<tr>
<td>Pd--Br'</td>
<td>2.5602 (11)</td>
</tr>
<tr>
<td>Br--Pd--Br</td>
<td>174.85 (7)</td>
</tr>
<tr>
<td>Pd--P--Br</td>
<td>96.20 (18)</td>
</tr>
<tr>
<td>C1--C2</td>
<td>140.6 (5)</td>
</tr>
<tr>
<td>C7--P--C8</td>
<td>139.0 (3)</td>
</tr>
<tr>
<td>P--Pd--Br</td>
<td>80.65 (19)</td>
</tr>
<tr>
<td>P--Pd--Br'</td>
<td>98.79 (6)</td>
</tr>
<tr>
<td>C2--Pd--C1</td>
<td>178.5 (3)</td>
</tr>
<tr>
<td>P--Pd--Br'</td>
<td>95.73 (4)</td>
</tr>
</tbody>
</table>

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

Data reduction: REFCAL LSABS (Blanc, Schwarzenbach & Flack, 1991) and Xtal3.2 SORTRF. Program(s) used to solve structure: MULTAN87 (Main et al., 1987). Program(s) used to refine structure: Xtal3.2 CRYLSQ. Molecular graphics: ORTEPII (Johnson, 1976) in Xtal3.2.

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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.

References
Abstract
In the title compound, \(\{2-[(2\text{-hydroxybenzyl})\text{imino}]\text{(piperidine)}\text{nickel(II)}\}\), molecules of \([\text{Ni(C}_{14}\text{H}_{10}\text{NO}_{2})(\text{C}_{9}\text{H}_{11}\text{N})]\) 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-García 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.

![Diagram of the structure](image)

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 \(\text{Ni}^{II}\) towards the N atom. This short value agrees, however, with the Ni–N1 bond distances in \(\{1-[(2\text{-hydroxyphenyl})\text{iminomethyl}]\text{naphthalen-2-olato-O,O',N}\}(\text{piperidine})\text{nickel(II)}\) (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 \(\text{Ni}^{II}\) 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 \(\text{NiN}_{2}\) coordination plane was found to be 50.2 (1)°.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for octahedrally coordinated \(\text{Ni}^{II}\) 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 \(\text{Ni}^{II}\) complexes. The bond length of 1.291 (5) Å between the N1 and C8 atoms is typical of a C==N double bond.