

The Crystal and Molecular Structure of [1,4-Bis(diphenylphosphino)butane]palladium(II) Dichloride

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Abstract—The $[(PPh_2CH_2CH_2CH_2CH_2PPh_2)PdCl_2]$ complex is prepared by the reaction of $PdCl_2$ with 1,4-bis(diphenylphosphino)butane (Dppb) in acetonitrile; its structure is investigated by the X-ray diffraction method (an autodiffractometer, 25°C, MoK_α radiation, 4299 reflections, $R = 0.035$, space group $P\bar{1}$, $Z = 2$). The configuration of the palladium atom is square-planar. The Pd–Cl [2.353(1) and 2.354(1) Å] and Pd–P [2.269(1) and 2.254(1) Å] distances are normal. The dihedral angle between the Cl(1)PdCl(2) and P(1)PdP(2) planes is 8.6(3)°. In the seven-membered PdP(1)C(1)C(2)C(3)C(4)P(2) cycle, only the P(1)PdP(2)C(1) fragment is planar. Phenyl rings occupy the pseudoaxial and pseudoequatorial positions. The phenyl rings at the P(1) atom are turned by 85.5(3)° against one another, and the rings at the P(2) atom are turned by 113.7(3)°. No shortened intermolecular contacts are found in the structure.

The catalytic systems based on the palladium or other Group VIII-metal compounds with α,ω -bis(diarylphosphino)alkanes exhibit high catalytic activity in a series of industrially important or perspective catalytic processes [1–4]. As part of the systematic studies of the catalytic activity and properties of the palladium compounds with α,ω -bis(diarylphosphino)alkanes [4–6], we obtained the $(Dppb)PdCl_2$ complex, where Dppb is 1,4-bis(diphenylphosphino)butane $PPh_2(CH_2)_4PPh_2$. The crystal and molecular structures of this complex were determined by X-ray diffraction method.

EXPERIMENTAL

$PdCl_2$ of 59.7% purity (specification 6-09-2025-86) was used without further purification. 1,4-Bis(diphenylphosphino)butane was synthesized by the reaction of lithium diphenylphosphide with 1,4-dibromobutane in tetrahydrofuran [7]. Acetonitrile and dimethyl formamide were dehydrated according to the procedures described in [8].

Preparation of $(Dppb)PdCl_2$ (I). Dppb (0.67 g, 1.62 mmol) was added to the solution of $PdCl_2$ (0.287 g, 1.62 mmol) in 50 ml of acetonitrile heated to 70°C. The solution was magnetically stirred for 2 h. After being stirred, the solution was concentrated in vacuum to the volume of 10 ml. The greenish-white precipitate formed was filtered off and recrystallized from dime-

thyl formamide. The isolated crystals were dried in vacuum. Yield 0.6 g (61.4%).

For $C_{28}H_{28}Cl_2P_2Pd$

anal. calcd. C, 55.69; H, 4.67; Pd, 17.62; P, 10.26; Cl, 11.74. (%)

Found (%): C, 55.67; H, 4.61; Pd, 16.9; P, 10.21; Cl, 12.07.

The transparent light green crystals I have the shape of rhombic prism. The main crystallographic parameters are: $C_{28}H_{28}Cl_2P_2Pd$, $M = 1207$, $a = 14.541(8)$, $b = 8.636(6)$, $c = 10.674(5)$ Å, $\alpha = 73.35(5)^\circ$, $\beta = 87.12(4)^\circ$, $\gamma = 79.20(5)^\circ$, $V = 1261(1)$ Å³, $d(\text{calcd.}) = 1.59$ g/cm³, $Z = 2$, space group $P\bar{1}$. The intensities of 4299 reflections with $I > 3\sigma(I)$ were measured using a four-circle automated KM-4 diffractometer of the KUMA DIFRACTION Polish firm (CuK_α radiation, θ – 2θ scan, graphite monochromator).

The structure was solved by the direct method followed by a series of Fourier syntheses. The positions of the hydrogen atoms were determined by the difference Fourier synthesis. The refinement was performed by the least-squares method anisotropically for the C, Cl, P, and Pd atoms and isotropically for the H atoms. The final R value was 0.035. No correction for absorption was applied [$\mu(\lambda CuK_\alpha) = 109$ cm⁻¹]. All calculations were performed using the AREN 88 program [9].

The atomic coordinates are listed in Table 1, and the bond distances and angles are given in Table 2.

RESULTS AND DISCUSSION

The structure of complex **I** is shown in the figure. The configuration of palladium atom is square-planar. The Pd atom is offset from the plane of the chlorine and phosphorus atoms (plane A) by 0.08 Å. The dihedral angle between the Cl(1)PdCl(2) and P(1)PdP(2) planes is 8.6(3)°. The Pd–Cl [2.353(1) and 2.354(1) Å] and Pd–P [2.269(1) and 2.254(1) Å] distances are close to those in other palladium phosphine complexes [10]. In the seven-membered PdP(1)C(1)C(2)C(3)C(4)P(2) cycle, only the P(1)PdP(2)C(1) fragment is planar. The

torsion angles PdP(1)C(1)C(2), P(1)C(1)C(2)C(3), C(1)C(2)C(3)C(4), C(2)C(3)C(4)P(2), and PdP(2)C(4)C(3) are 9.6(3)°, 86.2(3)°, –56.9(3)°, –51.7(3)°, and 77.5(3)°, respectively. The phenyl rings occupy the pseudoaxial and pseudoequatorial positions. The phenyl rings at the P(1) atom are turned by 85.5(3)° relative to one another, and the rings at the P(2) atom are turned by 113.7(3)°. The phenyl rings are oriented against the plane A in a similar manner (see Table 3). No shortened intermolecular contacts are observed in the structure.

Table 1. Atomic coordinates and temperature parameters for structure **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} , Å ²	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} , Å ²
Pd	0.7547(1)	0.3864(1)	0.1625(1)	6.6	C(27)	0.4325(2)	0.2536(5)	0.2993(5)	9.0
Cl(1)	0.7215(1)	0.5178(1)	0.3288(1)	7.5	C(28)	0.5267(2)	0.2061(5)	0.2714(4)	8.1
Cl(2)	0.7671(1)	0.6408(1)	0.0117(1)	8.5	H(1)	0.831(3)	–0.041(6)	0.022(4)	
P(1)	0.7874(1)	0.2571(1)	0.0037(1)	6.7	H(1)'	0.927(3)	0.088(5)	–0.022(5)	
P(2)	0.7171(1)	0.1646(1)	0.3125(1)	6.6	H(2)	0.901(3)	0.058(5)	0.223(4)	
C(1)	0.8662(2)	0.0554(4)	0.0455(4)	8.0	H(2)'	0.954(3)	–0.111(5)	0.190(4)	
C(2)	0.8929(2)	–0.0264(4)	0.1875(3)	7.4	H(3)	0.823(4)	–0.221(6)	0.231(5)	
C(3)	0.8234(2)	–0.1234(4)	0.2659(4)	7.9	H(3)'	0.841(4)	–0.166(7)	0.353(5)	
C(4)	0.7243(2)	–0.0275(4)	0.2671(3)	7.4	H(4)	0.696(2)	–0.003(4)	0.182(4)	
C(5)	0.8497(2)	0.3668(4)	–0.1357(3)	7.1	H(4)'	0.694(4)	–0.082(6)	0.318(5)	
C(6)	0.8166(2)	0.4126(4)	–0.2622(3)	7.8	H(6)	0.759(3)	0.378(5)	–0.275(5)	
C(7)	0.8691(3)	0.4910(5)	–0.3655(4)	8.7	H(7)	0.841(3)	0.519(6)	–0.444(5)	
C(8)	0.9547(3)	0.5229(5)	–0.3411(4)	8.8	H(8)	0.984(4)	0.570(6)	–0.417(5)	
C(9)	0.9893(2)	0.4768(5)	–0.2159(4)	8.7	H(9)	1.037(3)	0.514(6)	–0.211(5)	
C(10)	0.9367(2)	0.4008(5)	–0.1128(4)	8.4	H(10)	0.946(5)	0.388(8)	–0.062(7)	
C(11)	0.6787(2)	0.2355(4)	–0.0606(3)	7.1	H(12)	0.710(5)	–0.002(9)	–0.083(7)	
C(12)	0.6665(3)	0.0957(6)	–0.0901(6)	10.2	H(13)	0.575(4)	0.008(8)	–0.146(6)	
C(13)	0.5796(4)	0.0886(8)	–0.1348(7)	11.8	H(14)	0.459(4)	0.208(6)	–0.173(5)	
C(14)	0.5068(3)	0.2157(6)	–0.1508(5)	9.4	H(15)	0.468(3)	0.440(6)	–0.138(5)	
C(15)	0.5189(2)	0.3532(6)	–0.1232(5)	9.7	H(16)	0.611(4)	0.454(7)	–0.058(6)	
C(16)	0.6043(2)	0.3628(4)	–0.0769(5)	8.4	H(18)	0.711(5)	–0.088(8)	0.568(7)	
C(17)	0.7827(2)	0.0972(3)	0.4640(3)	6.9	H(19)	0.792(3)	–0.172(5)	0.747(4)	
C(18)	0.7553(2)	–0.0269(4)	0.5656(3)	8.1	H(20)	0.925(4)	–0.077(7)	0.776(5)	
C(19)	0.8092(3)	–0.0937(5)	0.6795(4)	8.6	H(21)	0.965(4)	0.129(6)	0.607(5)	
C(20)	0.8884(2)	–0.0358(5)	0.6916(3)	8.5	H(22)	0.878(3)	0.236(5)	0.412(4)	
C(21)	0.9158(2)	0.0892(5)	0.5893(4)	8.5	H(24)	0.618(3)	0.262(6)	0.524(4)	
C(22)	0.8636(2)	0.1543(4)	0.4773(3)	7.5	H(25)	0.456(3)	0.343(6)	0.562(5)	
C(23)	0.5945(2)	0.2146(3)	0.3543(3)	7.1	H(26)	0.339(3)	0.340(5)	0.426(5)	
C(24)	0.5681(2)	0.2666(4)	0.4647(3)	7.9	H(27)	0.398(3)	0.265(6)	0.249(5)	
C(25)	0.4743(2)	0.3117(5)	0.4906(4)	8.6	H(28)	0.542(3)	0.163(6)	0.196(5)	
C(26)	0.4070(2)	0.3058(5)	0.4072(4)	8.7					

Table 2. Bond distances and angles for structure I

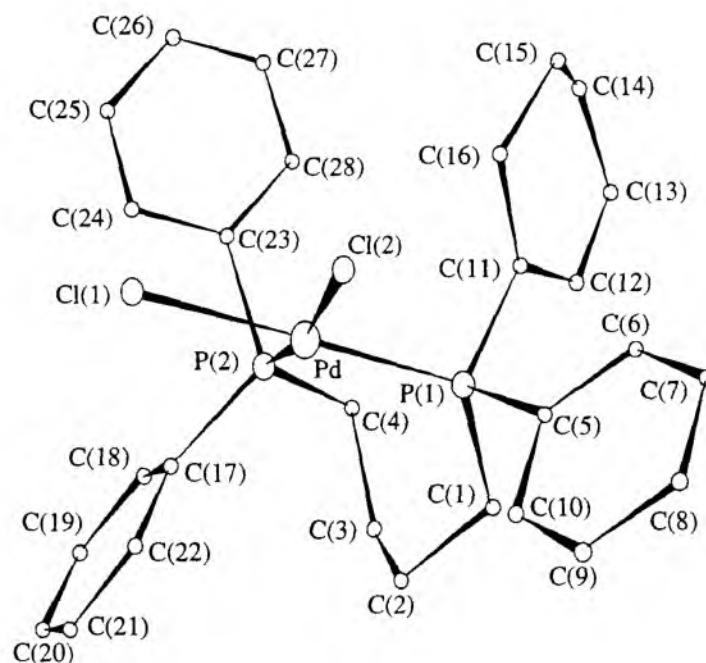
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Pd–Cl(1)	2.353(1)	Pd–Cl(2)	2.354(1)	Pd–P(1)	2.269(1)	Pd–P(2)	2.254(1)
P(1)–C(1)	1.845(3)	P(1)–C(5)	1.820(3)	P(1)–C(11)	1.816(3)	P(2)–C(4)	1.840(3)
P(2)–C(17)	1.809(3)	P(2)–C(23)	1.818(3)	C(1)–C(2)	1.513(5)	C(2)–C(3)	1.500(5)
C(3)–C(4)	1.524(4)	C(5)–C(6)	1.377(5)	C(5)–C(10)	1.400(5)	C(6)–C(7)	1.393(5)
C(7)–C(8)	1.377(7)	C(8)–C(9)	1.373(6)	C(9)–C(10)	1.373(6)	C(11)–C(12)	1.375(5)
C(11)–C(16)	1.369(4)	C(12)–C(13)	1.392(7)	C(13)–C(14)	1.352(7)	C(14)–C(15)	1.345(8)
C(15)–C(16)	1.384(6)	C(17)–C(18)	1.390(4)	C(17)–C(22)	1.386(5)	C(18)–C(19)	1.396(5)
C(19)–C(20)	1.364(6)	C(20)–C(21)	1.400(5)	C(21)–C(22)	1.367(5)	C(23)–C(24)	1.389(5)
C(23)–C(28)	1.384(5)	C(24)–C(25)	1.384(5)	C(25)–C(26)	1.373(6)	C(26)–C(27)	1.363(7)
C(27)–C(28)	1.363(7)						
Angle	ω , deg	Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
Cl(1)PdCl(2)	89.6(1)	Cl(1)PdP(1)	179.4(1)	Cl(1)PdP(2)	85.1(1)	Cl(2)PdP(1)	91.0(1)
Cl(2)PdP(2)	169.9(1)	P(1)PdP(2)	94.3(1)	PdP(1)C(1)	117.8(1)	PdP(1)C(5)	114.2(1)
PdP(1)C(11)	109.3(1)	C(1)P(1)C(5)	99.7(1)	C(1)P(1)C(11)	108.7(2)	C(5)P(1)C(11)	106.1(2)
PdP(2)C(4)	118.9(1)	PdP(2)C(17)	115.9(2)	PdP(2)C(23)	107.8(1)	C(4)P(2)C(17)	102.7(1)
C(4)P(2)C(23)	103.5(2)	C(17)P(2)C(23)	106.9(2)	P(1)C(1)C(2)	118.2(2)	C(1)C(2)C(3)	114.7(5)
C(2)C(3)C(4)	115.3(3)	P(2)C(4)C(3)	114.3(2)	P(1)C(5)C(6)	123.1(5)	P(1)C(5)C(10)	117.9(4)
C(6)C(5)C(10)	119.0(4)	C(5)C(6)C(7)	120.5(6)	C(6)C(7)C(8)	119.7(4)	C(7)C(8)C(9)	120.7(5)
C(8)C(9)C(10)	119.7(7)	C(5)C(10)C(9)	120.4(4)	P(1)C(11)C(12)	123.3(5)	P(1)C(11)C(16)	118.4(3)
C(12)C(11)C(16)	118.3(6)	C(11)C(12)C(13)	119.1(6)	C(12)C(13)C(14)	121.8(7)	C(13)C(14)C(15)	119.2(9)
C(14)C(15)C(16)	120.2(6)	C(11)C(16)C(15)	121.3(5)	P(2)C(17)C(18)	118.3(4)	P(2)C(17)C(22)	122.1(2)
C(18)C(17)C(22)	119.4(4)	C(17)C(18)C(19)	120.1(6)	C(18)C(19)C(20)	119.9(4)	C(19)C(20)C(21)	119.9(5)
C(20)C(21)C(22)	120.5(7)	C(17)C(22)C(21)	120.2(4)	P(2)C(23)C(24)	121.3(4)	P(2)C(23)C(28)	118.9(3)
C(24)C(23)C(28)	119.8(5)	C(23)C(24)C(25)	120.0(5)	C(24)C(25)C(26)	120.2(4)	C(25)C(26)C(27)	120.0(6)
C(26)C(27)C(28)	121.0(6)	C(23)C(28)C(27)	118.9(3)				

Table 3. Dihedral angles in structure I

Plane	Angle, deg
PdCl(1)Cl(2)P(1)P(2)/C(5)C(6)C(7)C(8)C(9)C(10)	67.8(3)
PdCl(1)Cl(2)P(1)P(2)/C(11)C(12)C(13)C(14)C(15)C(16)	87.4(3)
PdCl(1)Cl(2)P(1)P(2)/C(17)C(18)C(19)C(20)C(21)C(22)	66.7(3)
PdCl(1)Cl(2)P(1)P(2)/C(23)C(24)C(25)C(26)C(27)C(28)	94.7(3)

The catalytic activity of the palladium and other Group VIII-metal compounds with α,ω -bis(diarylphosphino)alkanes is known to strongly depend on the nature of the stabilizing $R_2P(CR_2)_xPR_2$ ligand. For example, the complexes with 1,3-bis(diphenylphosphino)propane (Dppp) exhibit high activity in the reaction of copolymerization of olefines and carbon monoxide [1, 2, 4], whereas the complexes with 1,4-bis(diphenylphosphino)butane are active in the reaction of carbonylation of alkyne [3]. To elucidate the possible reasons for the specificity of the catalytic activity of the complexes, we compared the results

obtained in this work with the literature data on the structure of the palladium(II) compounds with various $R_2P(CR_2)_xPR_2$ ligands and X anions. It is seen from the data given in Table 4 that the Pd–P and Pd–Cl distances, and the PPdP angles markedly change with changing the length of the methylene chain connecting the phosphorus atoms. The shortest Pd–P distances are found in the complexes with Dppe ($x = 2$); the Pd–P distance increases with lengthening the methylene chain ($x = 3-5$). Opposite behavior is observed for the Pd–Cl bonds: the Pd–Cl distance is the largest in the complexes with Dppe. The PPdP angle increases



Structure of complex I.

monotonically with lengthening the chain from $\sim 74^\circ$ ($x = 1$) to $\sim 175^\circ$ ($x = 5$). All the complexes of interest have the square-planar structure of the P_2PdX_2 coordination core, with the *cis*-arrangement of the phosphorus atoms for $x = 1-4$. As the length of the methylene chain grows ($x > 5$), the formation of a dimer with the *trans*-positioned ligands becomes more favorable [16, 17]. It should be noted that unlike the Pd-P and

Pd-X distances, which markedly vary in the complexes under study, the PPdP angle is weakly sensitive to the nature of the anionic ligands and is determined by the length of the methylene chain in $R_2P(CR_2)_xPR_2$ (Table 4). The complexes with different x have different PPdP angles. A comparison of the obtained results with the literature data allows one to suggest that one of the factors responsible for the specificity of the catalytic

Table 4. Pd-P and Pd-Cl distances and PPdP angles for the palladium(II) complexes with diphosphine $R_2P(CR_2)_xPR_2$ ligands

Compound*	x	$d(Pd-P)$, Å	PPdP angle, deg	$d(Pd-Cl)$, Å	References
$PdCl_2(Dppm)$	1	2.234(1), 2.250(1)	72.68(3)	2.362(1), 2.352(1)	[11]
$Pd(SCN)_2(Dppm)$	1	2.264(2), 2.282(2)	73.33(5)		[12]
$PdI_2(Ph_2P)_2CHR''$	1	2.262(6), 2.269(6)	74.1(2)		[13]
$PdCl_2(Dppe)$	2	2.233(2), 2.226(2)	85.82(7)	2.361(2), 2.357(2)	[11]
$Pd(SCN)(CNS)(Dppe)$	2	2.243(3), 2.258(3)	85.1(1)		[12]
$PdCl_2(Dppp)$	3	2.244(1), 2.249(2)	90.58(5)	2.351(1), 2.358(2)	[11]
$Pd(CNS)_2(Dppp)$	3	2.241(1)	89.32(3)		[12]
$[Pd(\mu-OH)(Dppp)]_2$	3	2.230(1)	92.2(8)		[14]
$PdCl_2(Dppb)$	4	2.254(1), 2.269(1)	94.3(1)	2.353(1), 2.354(1)	This work
$PdCl_2\left\{\begin{array}{l} Ph_2PCH_2CH-O-C(CH_3)_2 \\ Ph_2PCH_2CH-O \end{array}\right\}$	4	2.264, 2.278	96.8	2.339, 2.354	[15]
$Cyclo-[Pd_2Cl_4\{(Bu_2PCH_2CH_2)_2CHCH_3\}_2]$	5	2.372(6), 2.374(7) 2.380(6), 2.388(6)	175.9(2)	2.291(5), 2.305(6) 2.302(5), 2.305(6)	[16]

* Dppm = bis(diphenylphosphino)methane, Dppe = 1,2-bis(diphenylphosphino)ethane, $R'' = CH_2OCH_2CH_2C_4H_9S-3$.

action of the palladium and other Group VIII-metal compounds with α,ω -bis(diarylphosphino)alkanes is the value of the PPdP angle formed by the ligand in the coordination sphere of the catalytically active complex.

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