



عنوان مقاله

ساختار جدید بلور پالادیم (II) با ۲، ۱– بیس(دیفنیلفسفینو)اتان

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چکیدہ

از واکنش ترکیب ۲، ۱- بیس(دیفنیلفسفینو)اتان با پالادیم برماید در حلال متانول به نسبت مولی یکسان ترکیب با فرمول [Pd(dppe)Br] به دست میآید. شناسایی ترکیب به دست آمده توسط آنالیز عنصری، طیفسنجی IR و طیفسنجی NMR انجام گرفت. همچنین ساختار ترکیب به وسیلهی بلور شناسی اشعه X تعیین گردید. ترکیب با ساختار فضای مونوکلینک، P2₁/C که نشان میدهد ساختار کمپلکس چهار وجهی انحراف یافته با چهار لیکاند هندسی شامل دو لیگاند برم و دو لیگاند فسفینی است.

واژههای کلیدی: پالادیم برماید (II)، ۱و ۲- بیس(دیفنیلفسفینو)اتان، بلور شناسی اشعه X

A Novel palladium(II) X-ray Structural Complex with 1,2-bis(diphenylphosphino)ethane

Abstract

From the reaction of phosphorus compound 1,2-bis(diphenylphosphino)ethane with Palladium(II)bromide in toluene as a solvent in equimolar ratios to give a compound of the formula [Pd(dppe)Br2]. Characterization of the obtained compound was performed by elemental analysis, IR, ¹H, ¹³C and ³¹P NMR spectroscopy. Also the structure of 2 was determined by X-ray crystallography. The complex crystallizes in the space group monoclinic, $P2_1/C$, it is now clear that the Pd(II) adopts a distorted square planar by four-coordinate geometry involving two bromo ligands and two phosphine groups.

1. Introduction

Phosphine compounds are a group of species with very specific, interesting physical and donoracceptor properties among which their high stability that confer to the metal complexes they form



stand out. It is according to these properties of thermal stability and robustness that phosphine combinations have attracted the continuous attention of the chemistry community for multiple applications, this being specifically true in the case of homogeneous catalysis [1-5]. The expansion of new phosphine ligands has had a great effect in continues to attract great interest [6-9] and transition metal catalyzed organic reactions [10-11].

The success of phosphine ligands in catalysis is a function of both electronic and steric properties, and it is favorable to be able to vary both autonomously. This allows good tuning of the coordinated species, thus enabling the diverse steps of the catalytic cycle to be optimized [12]. 1,2-bis(diphenylphosphino)ethane (DPPE) and triphenyl phosphine (TPP) are typical mono- and bidentate phosphine ligands, respectively, which are most frequently used in a wide variety of homogeneous catalyst [13]. A good deal of knowledge about performance of DPPE and TPP as ligands has been accumulated for much transition metal catalysis. Palladium catalyzed coupling reactions such as Stille and Suzuki cross-coupling reactions have become an extremely strong method for the formation of C–C bonds in organic synthesis, [14–16] biologically active compounds [17] material science, [18] pharmaceuticals and bioactive compounds[19].

In this present paper, we report the synthesis, characterization and crystal structure determination of [1,2-bis(diphenylphosphino)ethane]palladium(II) bromide complex.

2. Experimental

2.1. Materials and physical measurements

The required chemicals were obtained from Merck and Aldrich Chemical Company and used without further purification. Melting points were measured on a Stuart SMP3 apparatus and are reported without correction. Elemental analysis was carried out with a CHNS-O costech ECS 4010 analyzer. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence lamp.

2.2. X-ray crystallography

The single crystal X-ray diffraction data of suitable crystals of 1 were collected on an Oxford Diffraction single-crystal x-ray diffractometer using mirror monochromated Mo K α radiation (0.71073 Å) at 120(2) K (Table 1). The structure was solved by direct methods and refined by the full-matrix least-squares method on F2 using the STEP32 crystallographic package [20,21].

All hydrogen atoms were added in idealized positions. Cell constants and orientation matrices for the data collection were obtained by least-squares refinement of diffraction data from 16389 unique reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters anisotropically. Hydrogen atoms were added in their geometrically idealized positions.

2.3. Synthesis of [1,2-bis(diphenylphosphino)ethane]palladium(II) bromide



Refluxing diphenylphosphino ethane (597 mg, 1.5 mmol) and Palladium(II) bromide (399 mg, 1.5 mmol) at room temperature in a molar ratio of 1:1 in toluene for 6 h. gave a yellowish precipitate, which was extracted from the obtained suspension. Yellowish crystals suitable for X-ray diffraction analysis were obtained by slow addition of methanol to a chloroform solution containing the compound. Yield: 132 mg, 85%. M.p. 194 °C. Anal. Calc. for $C_{26}H_{24}P_2Pd_2Br_2$ (665.87 g/mol): C, 46.98; H, 3.64. Found: C, 46.81; H, 3.58%. IR (KBr disk, v cm-1): 3143 – 3100 (C-H in Ph); 1585–1608 (C=C in Ph); 1400.1 (P-CH₂).

3. Results and discussion

Based on our knowledge there is no report for this complex $[Pd(dppe)Br_2]$ (1). This monochelated complex was easily synthesized by reaction of 1,2-bis(diphenylphosphino)ethan with Palladium(II) bromide in 1:1 molar ratio in toluene at room temperature for 24 h led to the formation of as a yellow solid as shown in scheme 1.



Scheme 1. Synthesis of [Pd(dppe)Br₂].

3.1. X-ray crystallographic study of [Pd(dppe)Br₂]

Suitable crystals of complex 1 were obtained by slow evaporation over several days from chloroform solution and its structure was determined by single-crystal X-ray diffraction. The molecular structure of the neutral palladium (II) complex is shown in Fig. 1. The title compound crystallizes in the monoclinic space group P $2_1/C$ with four molecules in the unit cell. The asymmetric unit consists of one palladium (II) cation, two bromine anions and one 1,2-bis(diphenylphosphino)ethane (dppe) ligand, with all atoms in general positions.

Relevant parameters concerning refinement and data collection are given in Table 1 and selected bond distances and angles are given in Table 2. Furthermore, Crystallographic data for the structure in this paper can be found in the Supplementary material. The Pd(II) is chelated by two bromo ligands and two phosphine groups of dppe ligand in a distorted square planar with PdP_2Br_2 surroundings (Fig. 1). Considering the difference between Br(2)-Pd(1)-P(1) 90.67(5) and Br(1)-Pd(1)-P(2) 89.80(6) angles shows that Pd atom is slightly out of the plane of the molecule. The smaller than ideal P-Pd-P



angle in 1 leads to an opening of the Br-Pd-Br angle to $94.52(3)^{\circ}$. Comparison of Pd-Br [2.4859] and Pd-P [2.2385] Å average distances and Br(1)-Pd(1)-Br(2) 94.52(3) and P(2)-Pd(1)-P(1) 85.43(7) angles in [Pd(dppe)Br₂] shows a significant difference between these two bond lengths and angles.



Figure 1. X-ray structure of [Pd(dppe)Br₂].



Empirical formula	$C_{26}H_{24}Br_2P_2Pd$
Formula weight	664.59
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /C
Unit cell dimensions	
a (Å)	11.092(2)
b (Å)	13.293(3)
c (Å)	16.747(3)
α(°)	90.00
β (°)	99.55(3)
γ(°)	90.00(3)
Volume (Å ³)	2435.1(9)
Z	4
Calculated density, Mg/m ³	1.813
F(000)	1304
Theta range for data collection, (°)	2.47 to 29.15
Absorption correction	Numerical
Absorption coefficient (mm ⁻¹)	4.188
Crystal size (mm ³)	$0.35 \times 0.25 \times 0.10$
Reflections collected/ unique	16389/ 6539 [R(int) = 0.1222]
Max. and min. transmission	0.6795 and 0.3219
Refinement method	Full-matrix least-squares on F ²
Data/restraints/ parameters	6539 / 0 / 280

Table 1. Crystal data and structure refinement for [Pd(dppe)Br₂].



Goodr	ness-of-fit on F^2	1.013		
Table 2. Selected bond lengths (A°) and bond angles (°).				
Bond Lengths		Bond Angles		
Pd(1)-Br(1)	2.4790(11)	P(2)-Pd(1)-P(1)	85.43(7)	
Pd(1)-Br(2)	2.4928(13)	P(2)-Pd(1)-Br(1)	89.80(6)	
Pd(1)-P(1)	2.2428(18)	P(1)-Pd(1)-Br(1)	174.17(5)	
Pd(1)-P(2)	2.2342(19)	P(2)-Pd(1)-Br(2)	171.05(5)	
P(1)-C(6)	1.816(7)	P(1)-Pd(1)-Br(2)	90.67(5)	
P(1)-C(12)	1.822(8)	Br(1)-Pd(1)-Br(2)	94.52(3)	
P(1)-C(13)	1.848(7)	C(6)-P(1)-C(12)	111.6(3)	
P(2)-C(14)	1.842(7)	C(21)-P(2)-C(20)	102.9(3)	
P(2)-C(20)	1.819(7)	C(21)-P(2)-C(14)	108.4(3)	
P(2)-C(21))	1.811(7)	C(20)-P(2)-C(14)	105.9(3)	

4. Conclusion

in summary, the present method represents an attractive and easy method for the synthesis of $[Pd(dppe)Br_2]$ by direct reaction of 1,2-bis(diphenylphosphino)ethane with Pd(II) bromide and also represent the crystal structure characterization.

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Appendix. Supplementary data

CCDC No. 1412269 contains the Supplementary crystallographic data for the compound. These data can be obtained free of charge via <u>http://www.ccdc.ac.uk/conts/retriving.html</u>, or from the Cambridge crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ,UK; fax: (+44) 1223-336-033; or email:<u>deposit@ccdc.cam.ac.uk</u>

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