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بیس {(۳-استاتوپروپیل)تری‌فنیل‌فسفونیوم} تترابرموپالادات(II): سنتز، شناسایی و ساختار کریستالی

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چکیده

از واکنش استخلافی تری‌فنیل‌فسفین و ۲-برمو-۴-هیدروکسی‌بوتیریک‌اسید γ-لاکتون با نسبت مولی ۱:۱ در حلال بنزن در دمای اتاق، نمک فسفونیوم $CH_3CO_2CH_2CH_2CH_2PPh_3^+Br^-$ سنتز شده است. نمک فسفونیوم به دست آمده با پالادیوم استات(II) در حلال دی‌کلرومتان در دمای اتاق برهمکنش داده و $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$ را به دست می‌دهد. شناسایی ترکیب به دست آمده توسط تکنیک‌های آنالیز عنصری (CHN)، IR، ^{1}H-، ^{31}P- و ^{13}C NMR و کریستالوگرافی اشعه X انجام شد. از اطلاعات کریستالوگرافی مشخص شد که این ترکیب فسفونیومی در سیستم مونوکلینیک کریستالیزه شده است و دارای گروه فضایی P 2_1/C می‌باشد.

واژه‌های کلیدی: تری‌فنیل‌فسفین، پالادیوم استات(II)، کریستالوگرافی اشعه X

Bis{(3-acetatopropyl)triphenylphosphonium}tetrabromopalladate(II): Synthesis, characterization and crystal structure

Abstract

From the substitution reaction of triphenylphosphine and 2-bromo-4-hydroxybutyric acid γ-lactone with molar ratio 1:1 in benzene solvent at room temperature, the phosphonium salt $CH_3CO_2CH_2CH_2CH_2PPh_3^+Br^-$ has been synthesized. The prepared phosphonium salt treated with palladium acetate(II) in dichloromethane as a solvent at room temperature to give $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$. Characterization of the obtained compound was performed by elemental analysis (CHN), IR, ^{1}H-, ^{31}P- and ^{13}C NMR techniques and X-ray crystallography. It is clear from crystallographic data that this phosphonium compound crystallized in monoclinic crystal system and has space group P 2_1/C.

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1. Introduction

Phosphonium salts are important class of ligands that have found widespread use in transition metal chemistry [1,2]. Different types of complexes of transition metals such as Hg(II), Pd(II) and Au(I) were synthesized using the corresponding phosphonium salts as precursors. Also phosphonium salts can use as agents for imaging and diagnostic of tumors [3-6] and act as catalyst in several organic reaction including oxidation, amination of aryl halides and cross-coupling reactions [7].

Furthermore these compounds can use as anticancer agents transport vectors for targeting mitochondria because triphenylphosphonium group can travel across cell membranes [8,9].

In this work, we describe the synthesis, characterization and X-ray crystal structure of a new phosphonium salt resulting from treatment of triphenylphosphine with 2-bromo-4-hydroxybutyric acid γ-lactone.

2. Experimental

2.1. Materials and physical measurements

All reactants and solvents were obtained from Merck, Aldrich and Foluka Chemical Companies and used without further purification. Melting points were measured on a Stuart SMP_3 apparatus. IR spectra (in the range 4000-400 cm^{-1}) were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (^{1}H, ^{31}P and ^{13}C NMR) recorded on a 400 MHz Bruker spectrometer in DMSO-d6 as the solvent at room temperature. Elemental analysis was carried out with a CHNS-O Costech ECS 4010 analyzer.

2.2. X-ray crystallography

Crystal data of compound **1** were collected using graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) made on a STOE IPDS-2T diffractometer at 120 K. The molecular structure was solved by direct methods and then refined by full-matrix least-squares on F^2 using the X-STEP32 crystallographic software package [10]. All hydrogen atoms were added in their geometrically idealized positions. Non-hydrogen atoms were refined with anisotropic thermal parameters. Cell constants and orientation matrices were obtained by least-squares refinement of diffraction data from 13453 unique reflections.

2.3. Synthesis of Bis{(3-acetatopropyl)triphenylphosphonium}tetrabromopalladate(II), $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

To a solution of 2-bromo-4-hydroxybutyric acid γ-lactone (α-bromo-γ-butyrolactone) (0.164 g, 1 mmol) in benzene (2 mL), a solution of triphenylphosphine (PPh_3) (0.262 g, 1 mmol) in benzene (2 mL) was added and the resulting mixture was stirred for 24 h at room temperature. The separated solid was filtered off and washed with benzene (5 ml) and diethyl ether (10 mL) to give (3-hydroxybutyric acid γ-lactone)-2-triphenylphosphonium bromide as a white powder. Yield: 0.345 g (81%). M.p. 137-139 ˚C. IR (υ, cm^{-1}): 1736 (CO), 1436 (CH-P), 1072 (O-C-O). ^{1}H NMR (400 MHz, DMSO): δ= 1.87

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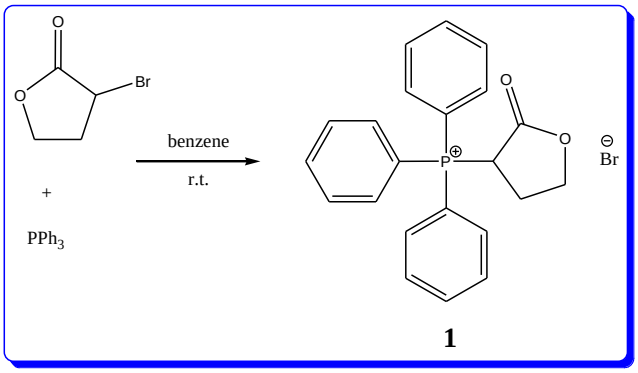
(m, 2H, CH_2, J=5.5 Hz); 4.2 (dd, 1H, CHP, $^2J_{(H-P)}$= 30.4 Hz, $^3J_{(H-H)}$=4.8 Hz); 5.2 (t, 2H, CH_2O, $^3J_{(H-H)}$=2.5 Hz); 7.5-8 (m, 15H, Ph). ^{13}C NMR (75.45 MHz, DMSO): δ=171.4 (s, CO); 129-135 (m, Ph); 68.79 (s, CH_2O); 36.53 (d, CHP, J=59.35 Hz); 19.86 (d, CH_2CH_2P, J= 15.09 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, DMSO): δ= 25.61. Anal. Calc. for $C_{22}H_{20}BrO_2P$: C, 61.84; H, 4.72. Found: C, 61.82; H, 4.71.

The prepared phosphonium bromide (0.639 g, 1.5 mmol) was dissolved in 5 mL of dichloromethane. Then palladium acetate (II) (0.224 g, 1 mmol) in 5 mL of dichloromethane was added to this solution and the mixture was stirred at room temperature. After 1 hours, the product was filtered off and washed with diethyl ether (10 mL) to yield Bis{(3-acetatopropyl)triphenylphosphonium}tetrabromopalladate(II) as a brown powder. Yield: 0.92 g (70 %). M.p. 168-170 ˚C. IR (υ, cm^{-1}): 1729 (CO), 1436 (CH-P), 1110 (O-C-O). ^{1}H NMR (400 MHz, DMSO): δ= 1.3 (m, 2H, CH_2, $^3J_{(H-P)}$=8); 2.49 (s, 3H, CH_3); 4.22 (dd, 2H, CH_2P, $^2J_{(H-P)}$= 19.6 Hz, $^3J_{(H-H)}$=8 Hz); 5.48 (t, 2H, CH_2O, $^3J_{(H-H)}$=4 Hz); 7.2-8 (m, 15H, Ph). ^{13}C NMR (75.45 MHz, DMSO): δ=171.4 (s, CO); 116-135 (m, Ph); 68.78 (s, CH_2O); 28.37 (d, CH_2P, J=48.7); 22.37 (d, CH_2CH_2P, J= 9.54 Hz); 13.94 (s, CH_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, DMSO): δ= 18.85. Anal. Calc. for $C_{48}H_{52}O_4P_2Br_4Cl_4Pd$: C, 43.59 H, 3.96 Found: C, 43.61 H, 3.94

3. Results and discussion

3.1. Synthesis of $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

$[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$ was synthesized as follow: treatment of α-bromo-γ-butyrolactone with PPh_3 in benzene as a solvent yielded the corresponding phosphonium salt as an exclusive product (scheme 1). Subsequently, the reaction of the phosphonium bromide with palladium acetate(II) in a molar ratio of 1:1 in dichloromethane at room temperature for 1 h led to the formation of (**2**) as a brown solid as shown in Scheme 2. The observed sharp and singlet peak at δ=18.85 ppm by ^{31}P NMR confirmed the purity of the product.



Scheme 1. Synthesis of $[(C_4H_5O_2)PPh_3][Br]$

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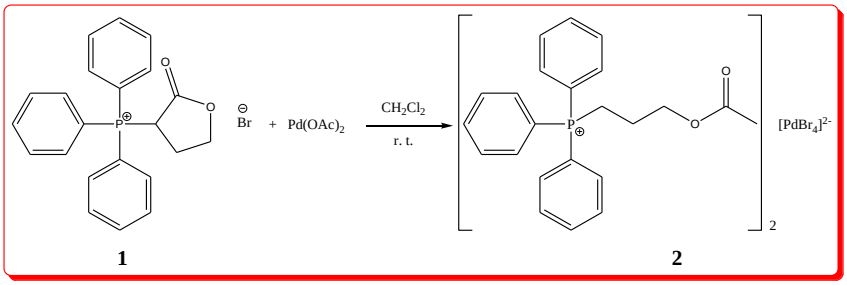

Scheme 2. Synthesis of $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

3.2. X-ray crystallographic study of $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

Suitable crystals of compound **2** were obtained by slow evaporation from an ethanol solution over several days and its structure was determined by single-crystal X-ray diffraction. The anion and cation moiety of the compound are shown in Fig. 1. Compound **2** crystallizes in the monoclinic system and space group P 2_1/C with four molecules in the unit cell. It can be seen from the ORTEP view of the compound that the geometry of $[PdBr_4]^{2-}$ moiety is nearly square planar and the structure around the phosphorus atom is close to tetrahedral. The Significant crystallographic data are summarized in Table 1 and some selected bond distances and angles are given in Table 2.

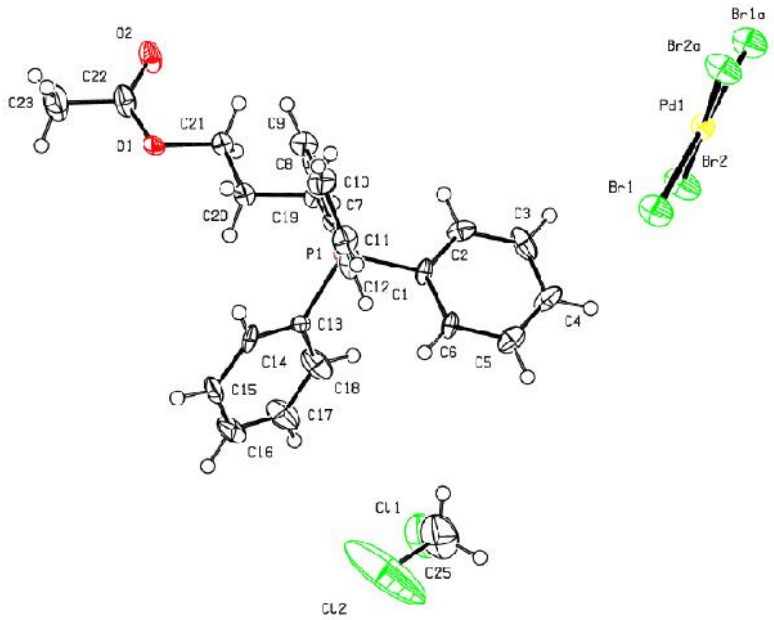

Figure 1. Asymmetric unit of $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

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Table 1. Crystal data and structure refinement for $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

Identifier	Khc453h
Chemical formula	$2(C_{23}H_{24}O_2P)$, Br_4Pd, $2(CH_2Cl_2)$
Formula weight	1322.24
Temperature (K)	120
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2_1/C
a (Å)	9.878(2)
b (Å)	13.104(3)
c (Å)	20.065(4)
α (°)	90.00
β (°)	93.83(3)
γ (°)	90.00
Volume ($Å^3$)	2591.44
Z, Z′	2, 0
h, k, l max	11, 15, 23
θ max	25.000
D_{calc} (g/cm^3)	1.695
R-Factor (%)	9.88
Absorption coefficient (mm^{-1})	3.751
Crystal F(000)	1312.0
Goodness-of-fit on F^2	1.030

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Table 2. Selected bond distances and bond angles for $[CH_3CO_2CH_2CH_2CH_2PPh_3]_2[PdBr_4]$

Bond length (Å)		Bond angles (deg.)	
Pd(1)-Br(1)	2.432	Br(1)-Pd(1)-Br(1)	180.00
Pd(1)-Br(2)	2.430	Br(1)-Pd(1)-Br(2)	89.21
P(1)-C(1)	1.80(1)	Cl(1)-C(25)-H(25A)	109
P(1)-C(7)	1.82(1)	Cl(1)-C(25)-H(25B)	109
P(1)-C(13)	1.79(1)	H(25A)-C(25)-H(25B)	108
P(1)-C(19)	1.82(1)	C(1)-P(1)-C(7)	110.8(6)
O(1)-C(21)	1.47(2)	C(1)-P(1)-C(13)	107.1(6)
O(1)-C(22)	1.29(2)	P(1)-C(1)-C(2)	120(1)
O(2)-C(22)	1.23(2)	C(1)-C(2)-H(2)	120
C(1)-C(2)	1.38(2)	C(1)-P(1)-C(19)	111.3(6)
C(7)-C(12)	1.39(2)	P(1)-C(13)-C(14)	123(1)
C(8)-H(8)	0.95	O(1)-C(22)-O(2)	125(1)
C(21)-H(21A)	0.99	O(1)-C(22)-C(23)	113(1)

Acknowledgement

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