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SYNTHESIS, CHARACTERIZATION, AND CRYSTAL STRUCTURES OF TRIS(2-PYRIDYL)PHOSPHINE SULFIDE AND SELENIDE

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We report the synthesis and structural determinations of tris(2-pyridyl)phosphine sulfide and selenide, which were prepared by the reaction of 2-lithiopyridine with phosphorus trichloride at -100°C , and treatment of resulted (2-pyridyl)phosphine with elemental sulfur or selenium in hot toluene. These compounds were characterized by elemental analysis, melting point determination, mass spectroscopy, IR, ^1H , and ^{31}P NMR spectroscopies. Furthermore, the molecular structures of tris(2-pyridyl)phosphine sulfide and selenide were determined by single crystal X-ray analysis and compared with the structures of tris(2-pyridyl)phosphine and tris(2-pyridyl)phosphine oxide.

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements to view the free supplemental file.

Keywords: 2-Lithiopyridine; oxygen; selenium; single crystal X-ray analysis; sulfur; tris(2-pyridyl)phosphine

INTRODUCTION

Organophosphorus compounds are an important class of ligands with potential applications as selective homogenous catalysts.^{1–3} Among of them, pyridylphosphine ligands and their chalcogenides derivatives are very interesting for catalytic and structural investigations.^{4,5} Pyridyl-substituted phosphines, which were first reported more than 60 years ago, have been extensively used in metal ion coordination chemistry for their ease of functionalization and the electronic properties that they impart to metal complexes used for catalysis purposes.^{6,7} According to hard and soft acid base theory (HSAB), these types of ligands are especially suitable for complexing with noble metals, which are important in catalysis.^{8–10} The first preparation of pyridylphosphine was presented in 1944 by Davies and Mann as part of a study on the optical resolution of tertiary phosphines.¹¹ There has been an increasing usage of tris(2-pyridyl)phosphine, $\text{P}(2\text{-py})_3$, in inorganic and organometallic chemistry,

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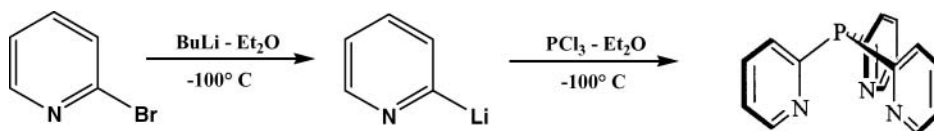
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primarily because of its interesting structural feature that retains both phosphorus and nitrogen atoms with versatile coordination possibility. There are four coordination modes found for complexes containing $P(2\text{-py})_3$, namely, phosphorus monodentate,^{12,13} $\eta^2\text{-P,N}$ -chelate,^{14,15} $\mu\text{-P,N}$ -bridge,¹⁶ and $\eta^3\text{-N, N', N''}$ -chelate.¹⁷ Thus, application of $P(2\text{-py})_3$ ligations affords numerous novel and useful complexes.^{18–20} Apart from its characteristics in coordination chemistry, the catalysis aspects of $P(2\text{-py})_3$ for the reactions employing triphenylphosphine have been recently explored.²¹ In an effort to progress our knowledge about the relation between structure and properties, we have reported the synthesis and structure of tris(2-pyridyl)phosphine sulfide and selenide by single crystal X-ray analysis. Some structural aspects of these compounds were compared with tris(2-pyridyl)phosphine and tris(2-pyridyl)phosphine oxide. These compounds were further characterized by elemental analysis, melting point determination, mass spectroscopy, IR, ^1H , and ^{31}P NMR spectroscopies.

RESULTS AND DISCUSSION

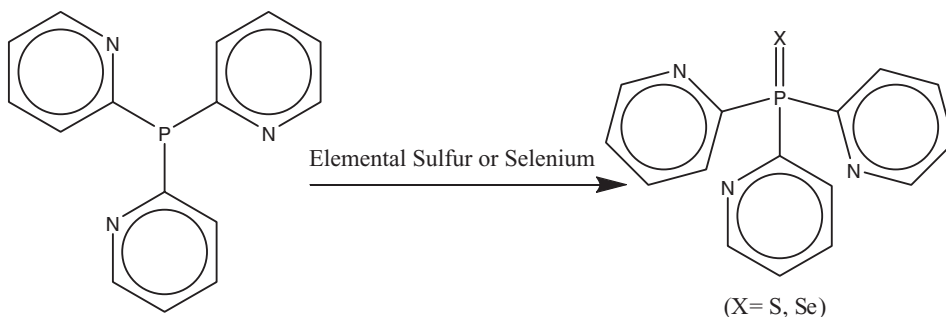
Synthesis

$P(2\text{-py})_3$ was synthesized by the reaction of 2-lithiopyridine, prepared by the treatment of butyl lithium on 2-bromopyridine at -100°C , with phosphorus trichloride at the same temperature (Scheme 1).²²



Scheme 1

The method in the literature²³ was used for synthesis of phosphine oxide, by the reaction of $P(2\text{-py})_3$ with 30% hydrogen peroxide in acetone. The phosphine sulfide and selenide derivatives were prepared by treatment of appropriate phosphine with elemental sulfur and red selenium in refluxing toluene (Scheme 2).



Scheme 2

Recrystallization of crude solids from hot methanol and a few drops of chloroform afforded colorless crystals of tris(2-pyridyl)phosphine sulfide and selenide suitable for x-ray crystallographic analysis. The pyridylphosphine was isolated in moderate to good yield (65%), but its chalcogenides can be isolated in very good yields (84–94%).

Characterization

All compounds were characterized by CHN elemental analysis, melting point determination, mass spectroscopy, IR, ^1H , and ^{31}P NMR spectroscopies. The crystal structure of tris(2-pyridyl)phosphine sulfide and selenide were determined by x-ray single crystal analysis. As expected, the resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{P}(\text{2-py})_3$ and $\text{P}(\text{2-py})_3$ oxide appeared at -0.5 and 29.47 ppm, respectively. Furthermore, the resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{P}(\text{2-py})_3$ sulfide and selenide appeared at 34.89 and 29.47 ppm, respectively (see the Supplemental Materials, available online). Selenium satellites are observed. These chemical shifts are similar to the related phosphine sulfides and selenides that were previously reported in the literature.^{24–26} In the mass spectra of $\text{P}(\text{2-py})_3$, a cleavage of the carbon–phosphorus bond is observed. Also, a cleavage of the oxygen, sulfur, and selenium bonds with phosphorus are found in the derivatives of $\text{P}(\text{2-py})_3$. Hence, the fragments of pyridyl rings, sulfur, selenium, and phosphorus are found. The stretching vibration of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bond of pyridyl rings in IR spectroscopy was found between 1420 – 1464 cm^{-1} and 1566 – 1697 cm^{-1} as strong absorptions. The stretching vibrations of $\text{P}=\text{O}$, $\text{P}=\text{S}$, and $\text{P}=\text{Se}$ bonds were observed at 1175 , 621 , and 537 cm^{-1} , respectively.

X-Ray Analyses

Crystallographic data and selected bond lengths and angles are listed in Tables I and II, respectively.

$\text{C}_{15}\text{H}_{12}\text{N}_3\text{PS}$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with four molecules in the unit cell (Figure 1). Three pyridine rings, A, B, and C (A: $\text{C}1/\text{N}1/\text{C}2$ – $\text{C}5$, B: $\text{C}6/\text{N}2/\text{C}7$ – $\text{C}10$, and C: $\text{C}11/\text{N}3/\text{C}12$ – $\text{C}15$) are making dihedral angles of 77.94° between A & B, 89.43° between A & C, and 83.97° between B & C. Ring C is located so

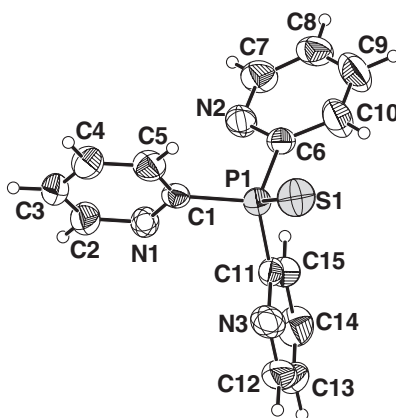


Figure 1 ORTEP drawing of tris(2-pyridyl)phosphine sulfide, with 50% probability thermal ellipsoid.

Table I Crystallographic data of compounds **1** and **2**

Compound	1	2
Chem. formula	C ₁₅ H ₁₂ N ₃ PS	C ₁₅ H ₁₂ N ₃ PSe
Formula wt. [g mol ⁻¹]	297.32	344.21
Color	Pale yellow	Colorless
Cryst. system	Monoclinic	Trigonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3c
<i>a</i> [Å]	9.5990(11)	13.2300(19)
<i>b</i> [Å]	9.3105(8)	13.2300(19)
<i>c</i> [Å]	16.0933(18)	14.355(3)
α [°]	90.00	90.00
β [°]	96.381(9)	90.00
γ [°]	90.00	120.00
<i>V</i> [Å ³]	1429.4(3)	2176.0(6)
<i>Z</i>	4	6
ρ calcd. [g cm ⁻³]	1.382	1.576
μ [mm ⁻¹]	0.330	2.691
<i>R</i> _{int}	0.0524	0.0452
<i>F</i> (000)	616	1032
<i>R</i> _I [R [<i>F</i> ² > 2σ (<i>F</i> ²)]]	0.0427	0.0257
<i>wR</i> ₂ (<i>F</i> ²)	0.0899	0.0487
GooF	1.067	0.983
CCDC #	720506	720507

that N3 is pointing to the same direction as the sulfur atom, while the remaining nitrogen atoms (N1 & N2) point in the opposite direction (see Figure 1). This type of arrangement has been previously seen in the structure of tris(2-pyridyl)phosphine oxide.²⁷ The P-S bond distance, 1.9428(8) Å, shows double bond character, as we expect from coordination of phosphorus. All bond lengths and angles are comparable with similar structures found in the literature.²⁷

Crystal structure packing dominates by C—H···π interactions between neighboring molecules (C3—H3···Cg1ⁱ = 2.893 Å, Cg1 being the ring C11/N3/C12—C15, with *i* = 1−*x*, 0.5+*y*, 0.5−*z*, see Figure S1, Supplemental Materials). C₁₅H₁₂N₃PSe (**2**) crystallizes in the trigonal space group *R*3c (No. 161) with six molecules in the unit cell (Figure 2). The structure **2** is analogous to the **1** and tris(2-pyridyl)phosphine oxide,²⁷ with distorted tetrahedral configuration around the phosphorous atom. Due to the symmetry, three pyridine rings are symmetrically related and are making dihedral angles of 69.16° between rings. The dihedral angles between pyridine rings in **2** are much smaller than in **1**. Moreover,

Table II Selected bond lengths (Å) and angles (°) in **1** and **2**

Compound	P—X [Å]	P—C [Å]	C—P—C [°]	C—P—X [°]
1.	1.9428(8)	1.826(2)	104.84(10)	113.37(7)
		1.828(2)	105.59(9)	113.45(7)
		1.837(2)	106.36(9)	112.51(8)
2.	2.1050(15)	1.832(3)	104.76(13)	113.85(11)
		1.832(3)	104.76(13)	113.85(11)
		1.832(3)	104.76(13)	113.85(11)

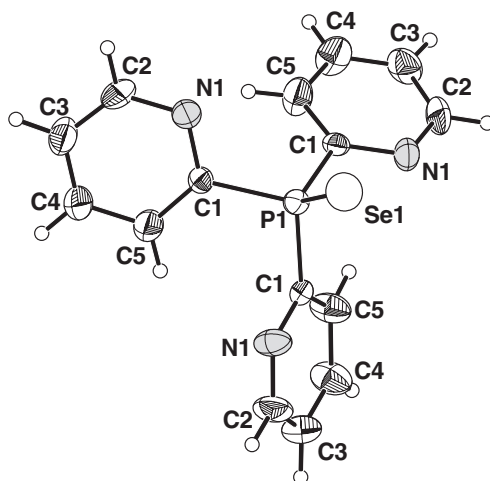


Figure 2 ORTEP drawing of tris(2-pyridyl)phosphine selenide, with 50% probability thermal ellipsoid.

all nitrogen atoms in **2** are pointing in the same direction as the Se atom, while only one nitrogen atom points to the same side as the S atom in **1**, which can be related to the greater polarizability of Se than the S atom in the structures **2** compared to **1**.

Each pyridine ring is connected to four neighboring molecules through relatively weak hydrogen bonds, stabilizing the three-dimensional crystal system (Supplemental Materials).

EXPERIMENTAL

All manipulations were carried out under air- and moisture-free conditions under nitrogen using standard Schlenk or drybox techniques. Diethyl ether was dried over lithium aluminium hydride (LiAlH_4) and was freshly distilled prior to use. *n*-Butyllithium (15% solution in *n*-hexane), 2-bromopyridine, phosphorus trichloride, sulfur, and selenium were purchased from Merck and were purified before use according to the standard methods. Melting points were obtained with an Electrothermal 9200 melting point apparatus. Infrared spectrum from 400 to 4000 cm^{-1} was recorded on a Shimadzu 470 FT-IR instrument, using KBr pellets. ^1H and ^{31}P NMR spectra were recorded at room temperature in CDCl_3 on a Bruker Avance 300 MHz. The NMR spectra are referenced to Me_4Si (^1H) or H_3PO_4 85% (^{31}P) as external standards. The mass spectroscopy was performed on a Varian MAT 44 instrument (electron impact, 20 eV). The calculated isotopic distribution for each ion was in agreement with experimental values. CHN analysis was performed using a Heraeus CHN–O Rapid Analyzer.

X-Ray Structure Determination

X-ray diffraction data were collected at room temperature on small crystals enclosed in thin walled glass capillaries by means of a Stoe imaging plane. The X-Area program was used for indexing and integrating the single crystal reflections. The structures (**1** and **2**) were solved by direct methods using SHELXS-97, and were refined by full matrix least squares on F^2 , SHELXL-97.²⁸ Minimum and maximum final electron densities were -0.205 to

0.320 eÅ⁻³ and -0.309 to 0.204 eÅ⁻³ for the structures **1** and **2**, respectively. Absorption corrections were performed with the programs X-RED²⁹ and X-Shape.³⁰ Symmetry equivalent reflections were used to optimize crystal shape and size. All non-hydrogen atoms were refined anisotropically. Aromatic H atoms were placed in calculated positions (C—H = 0.93 Å) and were treated as riding on the respective carrier atom, with $U_{\text{iso}}(\text{H}) = 1.2$ (C). Plots were produced with the Diamond and Mercury programs, and PLATON³¹ software was used to prepare materials for publication. Crystallographic data for tris(2-pyridyl)phosphine sulfide and selenide have been deposited at the Cambridge Crystal Structure Database (CCDC), with CCDC numbers 720506 and 720507, respectively. Copies of available materials can be obtained free of charge upon application to the Director, CCDC 12 Union Road, Cambridge CB2IEZ, UK (fax: (44)01223336033); E-mail: deposit@ccdc.ac.uk).

P(2-py)₃

Tris(2-pyridyl)phosphine (2-py)₃ was synthesized by the method in the literature in 65% yield, mp 113°C.²²

P(O)(2-py)₃

Tris(2-pyridyl)phosphine oxide was synthesized by the method in the literature in 94% yield, mp 210–212°C.²³

P(S)(2-py)₃

Elemental sulfur (5 mmol) and PPy₃ (4 mmol) were refluxed with deoxygenated toluene (50 mL) under an atmosphere of dry argon overnight. The cooled solution was filtered through Celite to remove excess sulfur. The filtrate was evaporated, and, after recrystallization of crude product from chloroform, pale yellow crystals were obtained in 91% yield, mp 160–161°C. IR (cm⁻¹): 3037(w), 3014(w), 1566(s), 1448(s), 1418(s), 1277(w), 1152(m), 1132(sh), 1085(m), 1042(m), 980(s), 777(s), 738(s), 657(s), 621(m), 518(s), 473(sh), 440(m). ¹H NMR (CDCl₃, 300 MHz, 25°C): δ = 7.35–7.39 (m), 7.79–7.86 (m), 8.28–8.33 (t, ³J¹⁵N-¹H, 6.8 Hz), 8.74–8.75 (d, ²J¹H-¹H, 4.5 Hz). ³¹P NMR (CDCl₃, 27°C, 121.49 MHz): δ = 34.89 ppm. MS (EI+, 20 eV); *m/z* (%): 297 (62) [M]⁺, 265 (67) [M-S]⁺, 187 (100) [M-SPy]⁺, 109(21) [M-Spy₂]⁺, 78 (47) [Py]⁺. C₁₅H₁₂N₃PS (297.32): calc: N 14.13%, C 60.59%, H 4.03%; found: N 14.04%, C 60.41%, H 3.99%.

P(Se)(2-py)₃

This compound can be prepared by the reaction of PPy₃ (4 mmol) with red selenium (5 mmol) as described above for the sulfur derivative. After recrystallization of crude product from ethanol, colorless crystals were obtained, mp 176–178°C. The yield of product was 84%. IR (cm⁻¹): 3065(w), 3034(w), 2998(w), 1673(w), 1569(s), 1450(s), 1423(s), 1285(w), 1244(w), 1165(w), 1126(m), 1083(w), 1051(w), 988(s), 902(w), 771(s), 738(s), 715(sh), 622(w), 561(s), 537(s), 505(s), 451(m). ¹H NMR (CDCl₃, 300 MHz, 25°C): δ = 7.41–7.47(m), 7.83–7.92(m), 8.14–8.18 (t, ³J¹⁵N-¹H, 6.8 Hz), 8.61–8.66 (d, ²J¹H-¹H, 16.6 Hz). ³¹P NMR (CDCl₃, 27°C, 121.49 MHz): δ = 29.47 ppm. ¹J_{P-Se} is 741 Hz. MS

(EI⁺, 20 eV); *m/z* (%): 345 (53) [M]⁺, 265 (39) [M-Se]⁺, 187 (100) [M-SePy]⁺, 109 (10) [M-SePy₂]⁺, 78 (32) [Py]⁺. C₁₅H₁₂N₃PSe (344.21): calc: N 12.20%, C 52.34%, H 3.49%; found: N 12.09%, C 52.13%, H 3.45%.

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