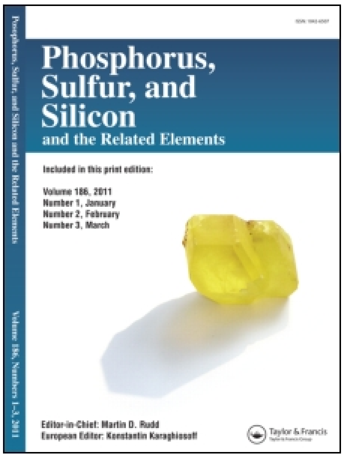

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Synthesis and single crystal X-ray structures of N,N'-bis(diphenylphosphinothioyl)piperzine and bis(diphenylphosphinoselenoyl)piperzine

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Synthesis and Single Crystal X-Ray Structures of N,N′-Bis(diphenylphosphinothioyl)piperzine and Bis(diphenylphosphinoselenoyl)piperzine

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The reaction of N,N′-bis(diphenylphosphino)piperzine with elemental sulfur or selenium in toluene under refluxing conditions afforded $Ph_2P(S)N(C_4H_8)NP(S)Ph_2$ or $Ph_2P(Se)N(C_4H_8)NP(Se)Ph_2$ in a quantitative yield. The molecular structures were determined by X-ray studies.

Keywords Bis(phosphines); diselenide; disulfide; piperzine derivative; X-ray structure

The interest in the synthesis and transition metal chemistry of bis(phosphine) ligands containing more than one type of spacer in the ligand framework is growing rapidly due to their steric and electronic versatility and interesting coordinating properties.[1,2] These types of ligands can be used in a variety of metal-mediated organic synthesis.[3] The phosphines containing sulfur and selenium moieties are finding utility in the formation of gold and silver monolayers.[4] As a part of our study on the reactivity and transition metal chemistry and oxidation properties of multifunctional phosphines,[5,6] we report the synthesis and X-ray crystal structures of N,N′bis(diphenylphosphinothioyl) piperazine, $Ph_2P(S)N(C_4H_8)NP(S)Ph_2$ (**1**) and N,N′bis(diphenylphosphinothioyl) piperazine, $Ph_2P(Se)N(C_4H_8)NP(Se)Ph_2$ (**2**).

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RESULTS AND DISCUSSION

The synthesis of $Ph_2PN(C_4H_8)NPPh_2$ was reported[7a] in 1993, and Zubiri and colleagues have reported[7b] the oxidation products and platinum metal complexes of $Ph_2PN(C_4H_8)NPPh_2$. Recently we have reported the improved synthesis and crystal structure[7c] and the P—N bond activation in $Ph_2PN(C_4H_8)NPPh_2$ with aldehydes.[6b] This article describes the crystal structures of thioyl and selenoyl derivatives. The sulfide and selenium derivatives were prepared in a quantitative yield by reacting $Ph_2PN(C_4H_8)NPPh_2$ with elemental sulfur or selenium similar to the procedure described in the literature,[7b] with slight modification. The ^{31}P NMR spectrum of disulfide shows a single resonance at 68.2 ppm, whereas the same resonance, due to the diselenide derivative, appears at 69.4 ppm with a $^{1}J_{PSe}$ coupling of 758.4 Hz. The structures are established by single crystal X-ray diffraction studies.

The perspective views of the molecules are displayed in Figures 1 and 2 with important bond lengths and bond angles. The compound $Ph_2P(S)N(C_4H_8)NP(S)Ph_2$ crystallizes in an extended conformation and possesses crystallographically imposed centrosymmetry. The P—N bond length of 1.671(2) Å is shorter than the same

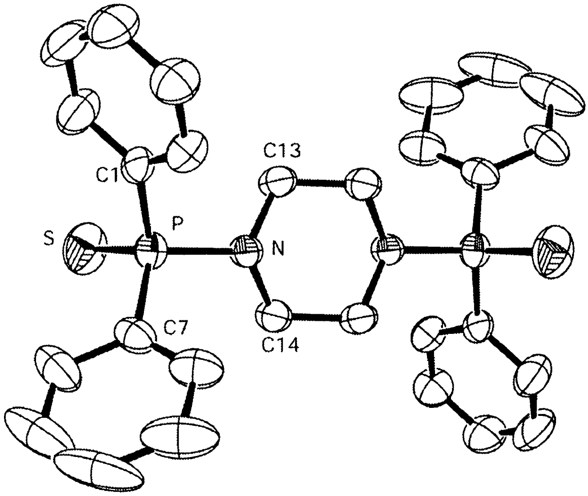

FIGURE 1 Perspective view of $Ph_2P(S)N(C_4H_8)NP(S)Ph_2$ (1). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): S-P, 1.943(1); P—N, 1.671(2); P-Cl, 1.814(2); P-C7, 1.807(3); N-Cl3, 1.476(3); N-Cl4, 1.476(3). Selected bond angles (°): S-P-N, 116.65(8); S-P-Cl, 113.00(10); S-P-C7, 113.34(10); N-P-Cl, 103.38(11); N-P-jjC7, 103.94(11); Cl-P-C7, 105.32(12); P-N-Cl3, 116.67(15); P-N-Cl4, 116.38(16); Cl3-N-Cl4, 109.27(17).

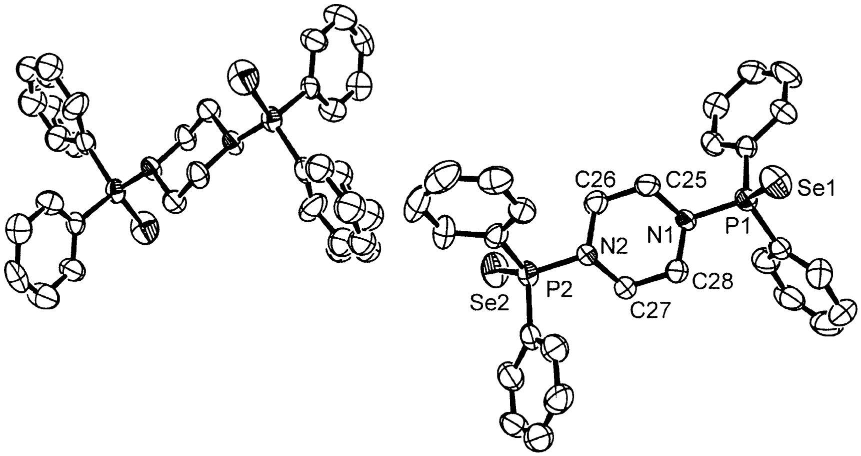

FIGURE 2 Perspective view of $Ph_2P(Se)N(C_4H_8)NP(Se)Ph_2$ (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Se1-P1 2.114(2); Se2-P2 2.102(2); P1-N1 1.692(5); P2-C19 1.810(7); P2-N2 1.675(5); N1-C25 1.480(8); N1-C28 1.466(7); N2-C27 1.477(8); N2-C26 1.495(7). Selected bond angles (°): P1-N1-C28 115.7(4); C25-N1-C28 110.8(5); P1-N1-C25 114.8(4); P2-N2-C26 115.7(4); P2-N2-C27 117.7(4); C26-N2-C27 109.3(5); Se1-P1-N1 116.64(17); N1-P1-C7 102.2(3); Se1-P1-C7 113.6(2); N1-P1-C1 103.3(2); Se1-P1-C1 113.34(19); C13-P2-C19 106.2(3); Se2-P2-C19 113.0(2); Se2-P2-N2 116.56(17); Se2-P2-C13 113.5(2); N2-P2-C13 103.2(3); N2-P2-C19 103.2(3).341.3; 342.7.

in $Ph_2PNC_2H_4NPPh_2$ (1.705(2) Å), but compares well with those compounds containing either ethylenediamine back bone[1a,b] or with nitrogen-bridged bis(phosphines),[1a] suggesting the multiple bonding whereas it is slightly longer than the same in the dioxide derivative, $Ph_2P(O)NC_2H_4NP(O)Ph_2$ (1.646(3) Å).[6b] The normally accepted value for a single P—N bond length is 1.77 Å.[8] The geometry around the nitrogen is distinctly pyramidal, with the sum of the angles about N being 342.3°. The P=S bond length of 1.943(1) Å is comparable with the same bond length in a similar bis(phosphines), such as $Ph_2P(S)NC_2H_4NP(S)Ph_2$ (1.951(1) Å).[9] and $Ph_2P(S)O(C_6H_{10})OP(S)Ph_2$ (1.928(1) Å).[10] The phosphorus centers are in typical tetrahedral environments. The structure of the diselenide derivative **2** is similar to the disulfide analogue **1**. The asymmetric unit cell consists of two independent molecules with one having a center of symmetry. The two molecules have slight variations in their bond parameters. The average P=Se bond length is 2.10 Å, which is significantly longer compared to the bis(phosphinite), $Ph_2P(Se)\{(—O—C_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O—)\}P(Se)Ph_2$(2.071(9) Å)[5e] but compares well with those found in the aminobis(phosphine) derivative, $Ph_2P(Se)NHP(Se)Ph_2$(P1-Se1, 2.085(1); P2-Se2, 2.101(1) Å).[11] The two selenium atoms are in an approximately *anti*disposition. The average P—N bond distance of 1.681(5) Å is slightly longer than that observed in the disulfide analogue **1**, but is comparable with analogous diselenides. The geometry around the nitrogen centers is distinctly pyramidal similar to that of disulfide **1**.

EXPERIMENTAL

Preparation of $Ph_2P(E)N(C_4H_8)NP(E)Ph_2$(E = S, 1; Se, 2)

A mixture of bis(diphenylphosphino)piperzine (1.51 g, 3.31 mmol) and sulfur (0.21 g, 6.6 mmol) in toluene/hexane (1:1) (50 mL) was refluxed under nitrogen with stirring for 6 h. The solution was cooled to 25°C and then filtered. The residue collected was crystallized from CH_2Cl_2-hexane (3:1) to give an analytically pure product of **1**. Yield 81%, m.p. 240°C (decomp.) (Found: C, 64.42; H, 5.32; N, 5.55%. $C_{28}H_{28}N_2P_2S_2$ requires C, 64.84; H, 5.44; N, 5.42%). $\delta_H(CDCl_3)$ 7.83–8.35 (20 H, m, Ph) and 2.84 (8 H, t); $\delta_P(CDCl_3)$ 68.2 (2 P, s, reference to 85% H_3PO_4).

In the case of the selenide derivative (**2**), instead of sulfur, selenium powder was used and the yield was 92%. m.p. 254–256°C. (Found: C, 54.9; H, 4.54; N, 4.67%. $C_{28}H_{28}N_2P_2Se_2$ requires C, 54.9; H, 4.60; N, 4.61%). $\delta_H(CDCl_3)$ 7.86–8.37 (20 H, m, Ph) and 2.86 (8 H, t); $\delta_P(CDCl_3)$: 69.4 (2 P, s, $^1J_{PSe}$758.4 Hz, reference to 85% H_3PO_4).

X-Ray Crystal Structure

Colorless crystals (**1** [0.21 × 0.33 × 0.43 Å]; **2** (0.23 × 0.40 × 0.50 Å]) crystallized from CH_2Cl_2 at 0°C were mounted on Pyrex filaments with epoxy resin. The general procedure for the crystal alignment, unit cell determination, and refinement and collection of intensity data on the Enraf-Nonius CAD-4 diffractometer has been published.[12] Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoKα (0.71073 Å) radiation. The details of the crystal and data collection for **1** $C_{28}H_{28}N_2P_2S_2$ are as follows: M = 518.60, monoclinic, a (Å) = 6.8307(5), b (Å) = 23.782 (3), c (Å) = 8.8683 (5); β (°) = 107.969 (6), Z = 2, V(Å^3) = 1370.4 (2), T (K) = 293(2). Space group $P2_1/c$ (No. 14), D(calc) (g/cm^3) = 1.257, μ (Mo-Kα) = 0.330 mm^{-1}, reflections observed, 1863. The final R_1 was 0.0395 (all data) and $wR_2 = 0.1103$ (all data), goodness-of-fit (*S*) 1.04. **2** $C_{28}H_{28}N_2P_2Se_2$: M = 518.60, monoclinic, a (Å) = 13.730 (1), b (Å) = 23.412 (2), c (Å) = 14.4289(9); β (°) = 106.819 (5), Z = 1, V(Å^3) = 4439.8 (5), T (K) = 293(2). Space group $P2_1/c$ (No. 14), D(calc) (g/cm^3) = 1.486, μ (Mo-Kα) = 0.330 mm^{-1}, reflections observed, 3768. The final R_1 was 0.0487 (all data) and wR_2 = 0.1564 (all data), goodness-of-fit (*S*) 1.03. All calculations were performed with the SHELXTL PLUS[13] program package. Hydrogen atoms were included in calculated positions as riding atoms with isotropic displacement parameters 20% larger than those of the attached atoms. The data is deposited in the Cambridge Crystallographic Data Center (CCDC) the CCDC reference numbers 202410 and 208516 are for compounds **1** and **2** respectively.

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