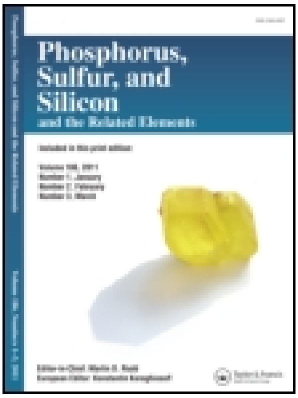

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Characterization of New N-(Diphenylphosphino)-Naphthylamine Chalcogenides: X-Ray Structures of (1-$NHC_{10}H_7$)P(Se)Ph_2 and Ph_2P(S)OP(S)Ph_2

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SYNTHESIS AND CHARACTERIZATION OF NEW *N*-(DIPHENYLPHOSPHINO)-NAPHTHYLAMINE CHALCOGENIDES: X-RAY STRUCTURES OF $(1\text{-}NHC_{10}H_7)P(Se)Ph_2$ AND $Ph_2P(S)OP(S)Ph_2$

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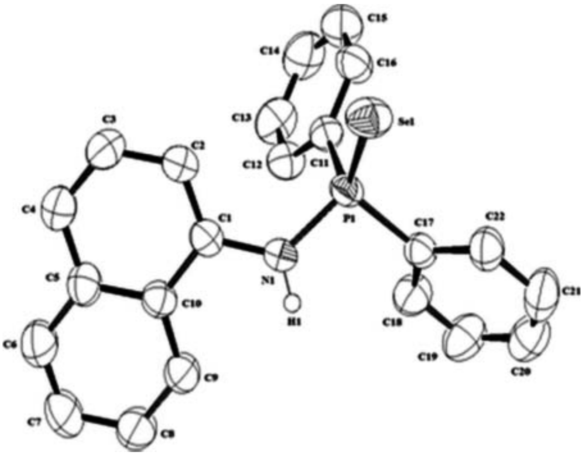
GRAPHICAL ABSTRACT



Abstract *The reaction of 1-naphthylamine with one equivalent of chlorodiphenylphosphine in the presence of triethylamine gave the* $(1\text{-}NHC_{10}H_7)PPh_2$ *(**1**) ligand. Refluxing of **1** with elemental sulfur or grey selenium in toluene (1:1 molar ratio) afforded* $(1\text{-}NHC_{10}H_7)P(S)Ph_2$ *(**2**) and* $(1\text{-}NHC_{10}H_7)P(Se)Ph_2$ *(**3**), respectively. Moreover, the byproduct* $\{Ph_2P(S)\}_2O$ *(**4**) was isolated from the reaction of **1** with elemental sulfur. Compounds **1–3** were identified and characterized by multinuclear* (^1H, ^{13}C, ^{31}P, ^{77}Se) *NMR spectroscopy, mass spectrometry, and elemental analysis. Crystal structure determinations of **3** and **4** were carried out.*

Keywords Aminophosphine; chalcogenides; chlorodiphenylphosphine; molecular structure; phosphine

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INTRODUCTION

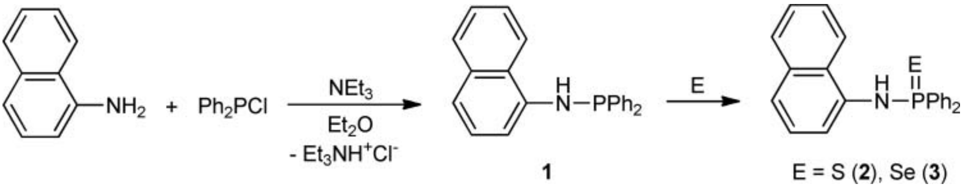
Aminophosphines possessing direct P—N bonds and their derivatives play an important role in the fight against cancer,[1–4] as part of catalytic systems in industrially important reactions,[5–7] as well as herbicidal, neuroactive, and antimicrobial agents.[8–11] This has prompted us to extend our studies on the synthesis and solid-state structures of complexes with *N,O* and *N,N* chelating ligends[12] to the synthesis of new chelating phosphorus(III) ligands containing P—N linkages, which might be useful for transition metal chemistry and catalytic applications.

As a part of our research program on this subject, we report the synthesis and spectroscopic properties of the (1-$NHC_{10}H_7$)PPh_2 (**1**) ligand, the corresponding sulfide (1-$NHC_{10}H_7$)P(S)Ph_2 (**2**), and selenide (1-$NHC_{10}H_7$)P(Se)Ph_2 (**3**) as well as the crystal structures of compounds **3** and **4**.

RESULTS AND DISCUSSION

Synthesis

Scheme 1 summarizes the synthesis of compounds **1**–**3**. The reaction of 1-naphthylamine with one equivalent of chlorodiphenylphosphine in the presence of triethylamine proceeds in diethyl ether at room temperature under nitrogen atmosphere and gives (1-$NHC_{10}H_7$)PPh_2 (**1**) in 80% yield. The existence of compound **1** has been previously mentioned by Pudovik et al.[13] Moreover, the reaction of aminophosphine **1** with one equivalent of elemental sulfur or grey selenium in dry toluene under reflux conditions affords the corresponding sulfide **2** and selenide **3**, respectively.



Scheme 1 Preparation of compounds **1**–**3**.

Refluxing of **1** with elemental sulfur without precaution to exclude H_2O from the starting material leads to the formation of the byproduct $Ph_2P(S)OP(S)Ph_2$ (**4**) in 10% yield. The formation of **4** doubtlessly involves the hydrolysis of compound **2**.[14,15]

Compounds **1**–**3** were isolated from the reaction solution and fully characterized by elemental analysis, IR, MS, and multinuclear NMR spectroscopy. Furthermore, the molecular structures of compounds **3** and **4** were elucidated by single crystal X-ray diffraction.

Spectroscopic Properties

The ^{31}P NMR spectrum of **1** shows a single resonance at $\delta = 34.3$, while the ^{31}P NMR signals of **2** and **3** appear each as a singlet at $\delta = 53.4$ (**2**) and at $\delta = 48.1$ (**3**). They are shifted to lower field as compared to the signal of the parent organic ligand **1**. With decreasing electronegativity of the chalcogen from sulfur to selenium, the ^{31}P NMR signal moves to higher field. The ^{31}P NMR signal of **3** is flanked by one pair of ^{77}Se-satellites with a coupling constant $^1J_{SeP}$ of 765.2 Hz. The ^{77}Se NMR spectrum of **3** shows a doublet at $\delta = -238.8$ ppm and the value of the coupling constant matches that resulting from the ^{77}Se-satellites in the ^{31}P NMR spectrum of **3**. This demonstrates the existence of the monoselenide derivative.

The magnitude of the coupling constant $^1J_{SeP}$ can be used to evaluate the σ-donor character and, hence, the basicity of the phosphine moiety. An increase of the coupling constant is indicative of increasing s-character of the phosphorus lone-pair and hence of lower basicity.[16] The value of $^1J_{SeP}$ is in agreement with the few available literature data on selenides of aminophosphines and larger than for the selenides of corresponding diarylphosphines.[17,18] This implies a lower basicity of the phosphine moiety in **1** due to the higher electronegativity of the adjacent nitrogen atom.

The IR spectra of compounds **1**–**3** show bands in the range of 3245–3310 cm^{-1}, 1431–1439 cm^{-1}, and 896–997 cm^{-1} due to υ(N—H), υ(P—Ph), and υ(P—N) stretching, respectively.[19] For the P=S double bond in **2** a band around 624 cm^{-1} is observed, whereas the bands at around 560 cm^{-1} in the IR spectrum of compound **3** are characteristic of the P=Se moiety.[20] In addition, the IR spectrum of **2** shows υ(N—H) at 3245 cm^{-1}; the low-frequency shift of 65 cm^{-1} as compared to the ligand **1** (3310 cm^{-1}) is attributed to intermolecular hydrogen-bonding interactions between the amine proton and the sulfur atom of the ligand.[21]

Molecular Structures of Compounds 3 and 4

Colorless crystals of **3** were obtained as described in the experimental section. Compound **3** crystallizes in the triclinic space group *P*-1. Selected interatomic distances and angles are contained in Table 2. The molecular structure is depicted in Figure 1. Colorless crystals of **4** were obtained from toluene at 4 °C. Compound **4** crystallizes in the monoclinic space group *C*2/c. Selected interatomic distances and angles are given in Table 3. The molecular structure is depicted in Figure 2. Crystal data for compounds **3** and **4** and details on structure refinement are summarized in Table 1.

The naphthyl skeleton in **3** is almost planar and the nitrogen atom resides almost in the plane of the naphthyl ring [N1—C1—C10—C9 –0.48(2)°]. The direction of the P—N bond is virtually perpendicular to the naphthyl plane and in the antiperiplanar sector [P1—N1—C1—C10 168.70(2)°]. On the other hand, the direction of the N–H bond is in the naphthyl plane and in the synperiplanar sector [H—N1—C1—C10 –11.30(4)°], so that the lone pair at N would be estimated to reside approximately at the borderline between the synclinal and the anticlinal sectors, thus, minimizing Coulomb repulsion of the lone pairs.[22]

The joint effects of Coulomb repulsion and the steric requirements would permit to describe the environment of the phosphorus atom in **3** as distorted tetrahedral [N—P—Se: 118.7(1)°; C_{ph}—P—Se: 112.0(1) and 113.3(1)°; N—P—C_{ph}: 101.0(1) and 103.7(1)°; C_{ph}—P—C_{ph}: 106.7(1)°]. The smallest value belongs to the N—P—C_{ph} angle and the largest value to the N—P—Se angle.

The N—P—Se bond angle (Table 2) is larger than those observed for $Bu^t_2P(Se)NHPr^n$ (**5**) [111.7(2)°], $Ph_2P(Se)NHPr^n$ (**6**) [117.7(1)°], $[Et_2P(Se)]_2NPr^n$ [117.7(1)°] (**7**),[23] $Ph_2P(Se)N(o\text{-}C_6H_4OMe)P(Se)Ph_2$ (**8**) [116.1(1) and 114.8(1)°],[24] $Pr^i_2P(Se)N(CH_2Ph)CH_2CH_2(CH_2Ph)NP(Se)Pr^i_2$ (**9**) [111.9(1)°],[25] $Ph_2P(Se)NHNHpy$ (**10**) [109.2(2)°],[25] $C_6H_4(NHP(Se)Ph_2)_2$-1,2 (**11**) [115.8(5) and 114.3(5)°], $C_{10}H_6(NHP(Se)Ph_2)_2$-1,8 (**12**)

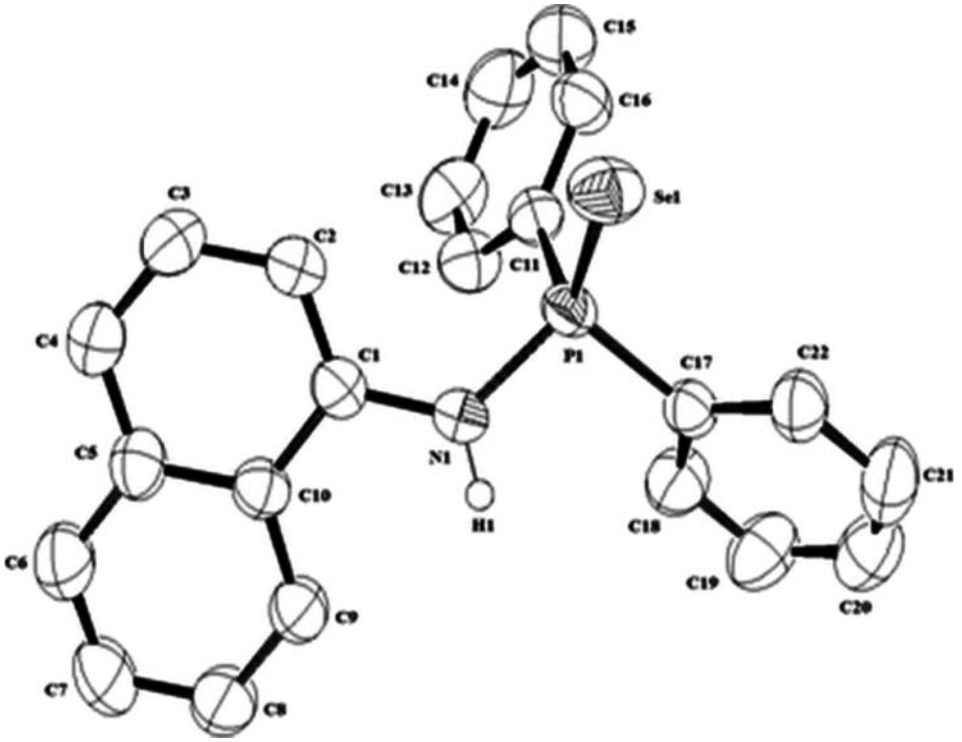


Figure 1 ORTEP view of the molecular structure of the selenide **3**; hydrogen atoms other than N—H have been omitted for clarity.

[114.2(1) and 116.8(2)°],[26] p-$Ph_2P(Se)NHCH_2(C_6H_4)CH_2NHP(Se)Ph_2$ (**13**) [116.8(2)°],[27] and $(Ph_2P(Se))_2N$-C_6H_3-(3,5-OCH_3) (**14**) [115.6(1) and 115.1(1)°].[28] The N—P—C_{ph} bond angles [101.0(1) and 103.7(1)°] are smaller than those in **5** [105.5(2) and 104.7(2)°], **6** [103.8(2) and 104.0(2)°], **7** [105.6(3) and 107.1(4)°], **9** [105.6(2) and 109.8(2)°], **10** [106.5(3) and 108.7(3)°], and **11** [104.0(3) and 104.8(3)°], while the C_{ph}—P—Se bond angles [112.0(1) and 113.3(1)°] are larger than those observed for **11** [110.8(1) and 111.3(2)°] and similar to the one observed for **9** [112.5(1)°].

The X-ray crystal structure of **3** (Figure 1, Table 2) shows a trigonal-planar surroundings of the three-coordinate nitrogen atom (angle sum at nitrogen 360.03°). The P—N—C_{Naph} bond angle [125.8(2)°] is larger than those observed for **12** [122.8(3) and 120.8(3)°] and in the range found for **11** [127.3(1) and 124.5(1)°].

The values found for the P=Se [2.110(1) Å], P—N [1.671(2) Å], and P—C [1.819(3), 1.820(2) Å] bond lengths in **3** are within the ranges reported for those in compounds **5**–**14**. The P=Se bond length in **3** is as expected longer than those observed for the P=S bond length in $C_6H_4(NHP(S)Ph_2)_2$-1,2 (**15**) [1.936(3) and 1.943(2) Å], $C_{10}H_6(NHP(S)Ph_2)_2$-1,8 (**16**) [1.951(4) and 1.957(4) Å],[26] 1,4-$[Ph_2P(S)NHCH_2]_2C_6H_4$ (**17**) [1.952(1) and 1.957(1) Å],[27] $Ph_2P(S)N(Ph)C_2H_4N(Ph)P(S)PPh_2$ (**18**) [1.951(1) Å], and $Ph_2P(S)N(C_4H_8)NP(S)PPh_2$ (**19**) [1.943(1) Å].[29]

The P—N bond length in **3** [1.671(2) Å] is significantly shorter as compared to related P(III) compounds like $Ph_2PNHNHpy$ [1.709(7) Å],[25] $Ph_2PNH(C_{10}H_6)_2NHPPh_2$ [1.704(2)

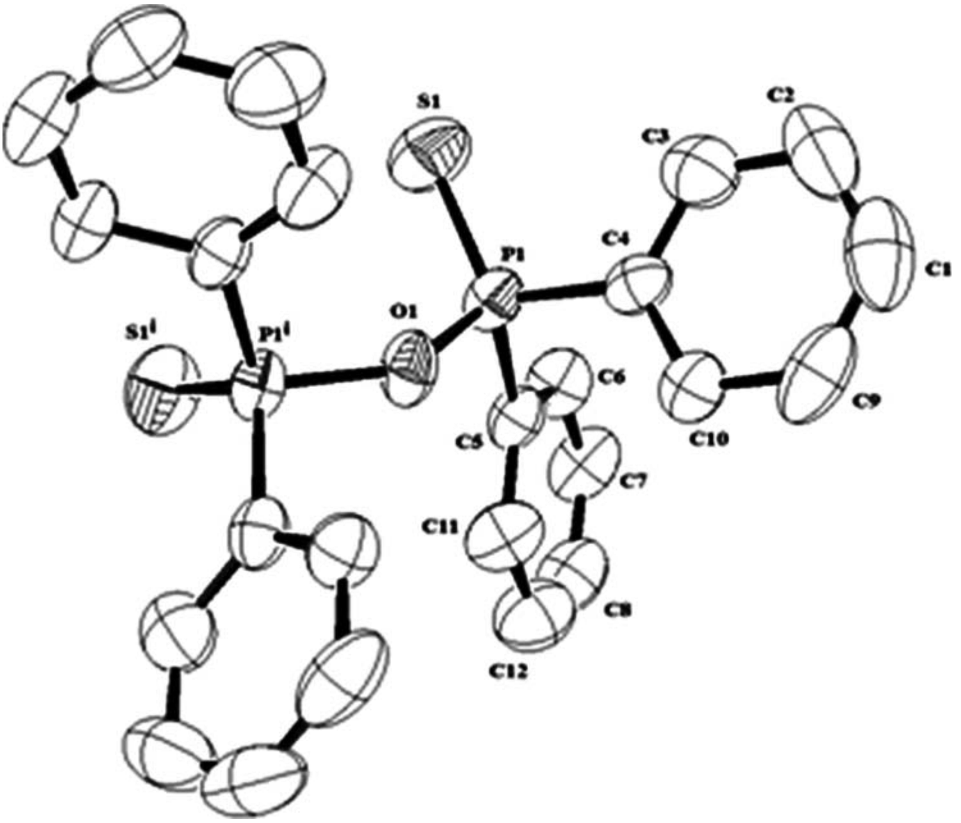


Figure 2 ORTEP view of the molecular structure of compound **4**; hydrogen atoms have been omitted for clarity.

Å], and $Pr^i_2PN(CH_2Ph)CH_2CH_2(CH_2Ph)NPPr^i_2$ [1.704(2) Å], which is somewhat counterintuitive and suggests that in **3** there may be some antibonding π-character in the P—N linkage.[25]

The molecular structure of **4** (Figure 2, Table 3) shows a distorted tetrahedral geometry around the phosphorus atoms with angles between 99.1(1) and 116.1(1)°. The smallest value corresponds to the O—P—C_{ph} angle and the largest value to the O—P—S angle.

A comparison of the structural data of the O—P—S [116.1(1)°] and C_{Ph}—P—C_{Ph} [105.9(1)°] bond angles in **4** with those observed in the bisphosphinites $Ph_2P(S)O(C_6H_{10})OP(S)PPh_2$ (**20**)[30] and $(Ph_2P(S)O)_2$–$C_{10}H_6N_2$ (**21**)[31] shows that the O—P—S bond angle in **4** is slightly larger than those found in **21** [115.0(2) and 115.9(2)°] and similar to those observed in **20** [116.1(1)°], while the C_{Ph}—P—C_{Ph} bond angle is larger than those observed in **21** [106.4(1) and 106.3(1)°] and is quite comparable with those found for **20** [105.1(1)°]. Moreover, the O—P—C_{Ph} bond angle ranges in **20** [from 100.6(1) to 105.0(1)°] and in **21** [from 99.9(1) to 104.3(1)°] are larger than the range observed in **4** [from 99.1(1) to 102.2(1)°].

The average P—C_{Ph} bond distances in **4** [1.797 Å] are comparable with those found in **20** [*av.* 1.809 Å] and **21** [*av.* 1.805 Å]. The bisphosphinite **21** has similar P—O [1.620(4), 1.621(4) Å] and P—S [1.915(2), 1.908(2) Å] distances as **4** [P—O: 1.618(3); P—S: 1.900(1)

Table 1 Crystal data and structure refinement for **3** and **4**

	3	**4**
Formula	$C_{22}H_{18}NPSe$	$C_{24}H_{20}OP_2S_2$
M_r	406.30	450.46
Temp. (K)	296(2)	273(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	$C2/c$
a(Å)	9.6164(7)	15.4809(13)
b(Å)	9.8096(7)	9.0479(10)
c(Å)	10.9768(8)	17.290(2)
α(°)	98.749(3)	90
β(°)	110.372(3)	113.537(6)
γ(°)	94.731(3)	90
V(Å^3)	949.1(1)	2220.4(4)
Z	2	4
ρ_{calcd} (Mg m^{-3})	1.422	1. 348
F(000)	412	936
μ(mm^{-1})	3.486	3.634
Reflns. total	9619	2883
Reflns. unique	2918	1254
R_{int}	0.0304	0.0281
Params.	227	132
$R1$ ($I > 2\sigma(I)$)	0.0541	0.0713
w$R2$ (all data)	0.1968	0.2837
$(\Delta/\rho)_{\max}$ (e Å^{-3})	0.628	0.341
$(\Delta/\rho)_{\min}$ (e Å^{-3})	−0.939	−0.472
CCDC depos. No.	844302	844303

Å], while **20** displays a smaller P—O [1.590(4) Å] and a larger P—S [1.928(2) Å] distance as compared to those found in compound **4**.

Interestingly, the P—S bond length of 1.900(1)) Å is shorter than those observed in the amine derivatives **15**–**19**. The aromatic rings in **3** and **4** display bond lengths and angles as expected.

EXPERIMENTAL

All experiments were carried out under purified dry nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried and freshly distilled under nitrogen.[32] Chlorodiphenylphosphine and 1-naphthylamine were used as purchased. Infrared spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrophotometer in the range between 4000 and 400 cm^{-1} using KBr pellets. Microanalyses were performed with a

Table 2 Selected bond lengths (Å) and bond angles (°) for **3**

P—N	1.671(2)	P—N—C_{Naph}	125.8(2)
P—Se	2.110(1)	N—P—C_{Ph}	103.7(1), 101.0(1)
P—C_{Ph}	1.819(3), 1.820(2)	Se—P—C_{Ph}	112.0(1), 113.3(1)
N—C_{Naph}	1.418(3)	N—P—Se	118.7(1)
C_{Ph}—P—C_{Ph}	106.7(1)	$\sum$ angles at N	360.03

Table 3 Selected bond lengths (Å) and bond angles (°) for **4**

P—O	1.618(1)	P—O—P	136.6(1)
P—S	1.900(1)	O—P—C_{Ph}	99.1(1), 102.2(1)
P—C_{Ph}	1.787(9), 1.806(8)	O—P—C_{Ph}	115.7(1), 115.7(1)
C_{Ph}—P—C_{Ph}	105.9(1)	O—P—S	116.1(3)

Flash 2000 elemental analyzer. Mass spectra were recorded with a LTQ Orbitrap Velos mass spectrometer in the positive ion mode. The NMR spectra were recorded at 25 °C with a Bruker AVANCE III 600 or a Bruker AVANCE II 400 NMR spectrometer operating at the appropriate frequencies using tetramethylsilane for ^{1}H, 85% H_3PO_4 for ^{31}P, and Me_2Se for ^{77}Se as external standards. $CDCl_3$ was used as both solvent and internal lock. Melting points were determined with a Gallenkamp Model apparatus in open capillaries.

N-(Naphthalen-1-yl)-1,1-diphenylphosphinamine (1)

Chlorodiphenylphosphine (4.89 g, 22.20 mmol) was added dropwise to a solution of 1-naphthylamine (3.20 g, 22.20 mmol) and triethylamine (2.25 g, 22.20 mmol) in diethyl ether (150 mL) at room temperature with vigorous stirring. After completion of the addition, the reaction mixture was stirred at room temperature for 12 h and then the white precipitate (triethylammonium hydrochloride) was filtered off through a sintered Schlenk tube. The volume of the filtrate was reduced to 50 mL and the reaction mixture was cooled to –30 °C when a white solid was obtained, which was recrystallized from diethylether at –4 °C to give aminophosphine **1** as colorless crystals in 80% yield. Mp 135–137 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.26$ (br., 1H, N—H), 6.50—8.2 (m, 17H, $C_{10}H_7$, and C_6H_5). ^{13}C NMR (100.63 MHz, $CDCl_3$): $\delta = 115.2$, 119.7, 122.6, 125.6, 126.2, 126.3, 128.9, 129.0, 131.8, 132.3, 133.3, 133.9, 134.3, 135.3 ($C_{10}H_7$ and C_6H_5). ^{31}P NMR (161.97 MHz, $CDCl_3$): $\delta =$ 34.3 (s). Selected IR data (KBr pellet): $\upsilon = 3310$ cm^{-1} (N—H), 1431 cm^{-1} (P—Ph), 896 cm^{-1} (P—N). ESI-MS (positive): *m/z* = 328.12 $[M+H]^+$. Calcd. for $C_{22}H_{18}NP$ (327.37). Found: C 80.74, H 5.58, N 4.30. Calcd. C 80.72, H 5.54, N 4.28%.

N-(Naphthalen-1-yl)-P,P-diphenylphosphinothioic Amide (2)

A mixture of **1** (0.5 g, 1.39 mmol) and elemental sulfur (0.05 g, 1.39 mmol) in dry toluene (50 mL) was heated under reflux for 4 h. The solution was filtered through celite while hot to remove a small amount of insoluble material. The volume of the filtrate was reduced to 10 mL and the solution was kept at room temperature to afford colorless crystals of **2** in 80% yield. Mp 165–167 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 5.42$ (d, $^2J_{PH} = 6.2$ Hz, 1H, N—H), 6.94–8.15 (m, 17H, $C_{10}H_7$, and C_6H_5). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 115.9$, 120.0, 122.7, 125.6, 126.20, 126.24, 128.8, 128.9, 131.7, 132.1, 133.2, 134.0, 134.3, 135.3 ($C_{10}H_7$ and C_6H_5). ^{31}P NMR (242.94 MHz, $CDCl_3$): $\delta = 53.4$ (s). Selected IR data (KBr pellet): $\upsilon = 3245$ cm^{-1} (N—H), 1437 cm^{-1} (P—Ph), 997 cm^{-1} (P—N), 624 cm^{-1} (P=S). ESI-MS (positive): *m/z* 360.09 $[M+H]^+$. Calcd. for $C_{22}H_{18}NPS$ (359.43). Found: C 73.54, H 5.10, N 3.93. Calcd. C 73.52, H 5.05, N 3.90%.

N-(Naphthalen-1-yl)-P,P-diphenylphosphinoselenoic Amide (3)

A similar procedure to that described for **2** was used, except that grey selenium (0.11 g, 1.39 mmol) was employed instead of elemental sulfur. Compound **3** was obtained as colorless crystals in 75% yield. Mp 189−192 °C. ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 5.28$ (d, $^2J_{\mathrm{PH}} = 5$ Hz, 1H, N—H), 6.50−8.52 (m, 17H, $C_{10}H_6$, and C_6H_5). ^{13}C NMR (150 MHz, CDCl$_3$): $\delta = 110.9$, 119.9, 121.8, 124.6, 126.5, 129.5, 129.9, 130.0, 131.9, 131.6, 132.6, 133.3, 134.3, 135.5 ($C_{10}H_7$ and C_6H_5). ^{31}P NMR (242.94 MHz, CDCl$_3$): $\delta = 48.1$ (s, $^1J_{\mathrm{SeP}} = 765.2$ Hz). ^{77}Se NMR (114.4 MHz, CDCl$_3$): $\delta = -238.8$ (d, $^1J_{\mathrm{SeP}} = 767.6$ Hz). Selected IR data (KBr pellet): $\upsilon = 3275$ cm^{-1} (N—H), 1439 cm^{-1} (P—Ph), 996 cm^{-1} (P—N), 560 cm^{-1} (P=Se). ESI-MS (positive): *m/z* 407.04 [M+H]$^+$. Calcd. for $C_{22}H_{18}NPSe$ (406.33). Found: C 65.07, H 4.43, N 3.48. Calcd. C 65.03, H 4.47, N 3.45%.

Data Collection and Structure Determination

Crystallographic data of compounds **3** and **4** are given in Table 1. Data [$\lambda(\mathrm{Cu}_{K\alpha}) = 1.54178$ Å] were collected with a Bruker-AXS SMART-APEX CCD diffractometer. All observed reflections were used for determination of the unit cell parameters. Indexing was performed using SMART.[33] Frames were integrated with SAINT software package.[34] Absorption correction was performed by multiscan method implemented in SADABS.[35] Crystal structures were solved using SHELXS-97 and refined using SHELXL-97 contained in SHELXTL and WinGX-1.70.01 program packages.[36] All nondisordered nonhydrogen atoms were refined with anisotropic displacement parameters. All H-atoms bonded to carbon atoms were placed in geometrically optimized positions and refined with an isotropic displacement parameter relative to the attached atoms. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 844302 for **3** and 844303 for **4**. These data can be obtained from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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