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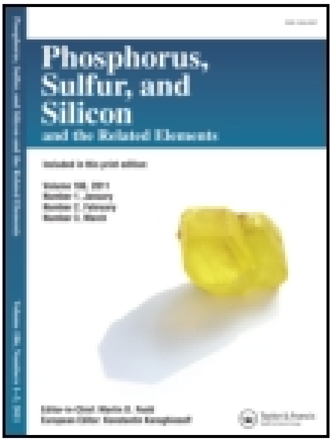

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New Organophosphorus Proligands and Amide Precursors: Crystal and Molecular Structures of $Ph_2P(X)NH(C_6H_3Pr^i{}_2\text{-}2,6)$ (X = O, S) and $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2\text{-}2,6)$

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NEW ORGANOPHOSPHORUS PROLIGANDS AND AMIDE PRECURSORS: CRYSTAL AND MOLECULAR STRUCTURES OF $Ph_2P(X)NH(C_6H_3Pr^i_2\text{-}2,6)$ (X = O, S) AND $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i_2\text{-}2,6)$

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The new organophosphorus proligand $(OPPh_2)(O_2SMe)NR$ ($R = C_6H_3Pr^i_2$–2,6) (3) was prepared as a white crystalline solid by reacting the lithiated compound $Li[Ph_2P(O)NR]$ with $MeSO_2Cl$ in a 1:1 molar ratio. The precursor $Ph_2P(O)NHR$ (1), as well as its thio analogue $Ph_2P(S)NHR$ (2), were obtained in the reaction between the lithiated amine RNHLi and the corresponding organophosphorus chloride. All compounds were characterized by multinuclear (^1H, ^{13}C, and ^{31}P) NMR spectroscopy. The molecular structures of 1–3 were established by single-crystal X-ray diffraction. A zigzag polymeric chain is formed in the crystals of 1 and 2 by hydrogen N–H···X (X = O, S) bonding, while the crystal of 3 contains discrete monomeric units with a syn–syn conformation of the O=P(C)$_2$–N–S(C)(=O)$_2$ skeleton.

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Keywords Molecular structure; NMR spectroscopy; organophosphorus ligands

INTRODUCTION

Tetraorganodichalcogenoimidodiphosphinic acids, $(XPR_2)(YPR'_2)NH$ (X, Y = O, S, Se; R, R' = alkyl, aryl, OR) (**A**), have been investigated for a long time as versatile ligands for main group or transition metals.[1–3] In the deprotonated form they act usually as bidentate ligands, exhibiting a high tendency to generate six-membered, carbon-free metallacycles. Due to the high flexibility of the XPNPY skeleton, other coordination patterns have also been observed in metal complexes.[1] At the same time, bis(organosulfonyl)imides $(O_2SR)(O_2SR')NH$ (**B**) have attracted interest as ligands and they act in either a monodentate or bidentate manner.[4–19] Recently we have reported on the new organophoshorus

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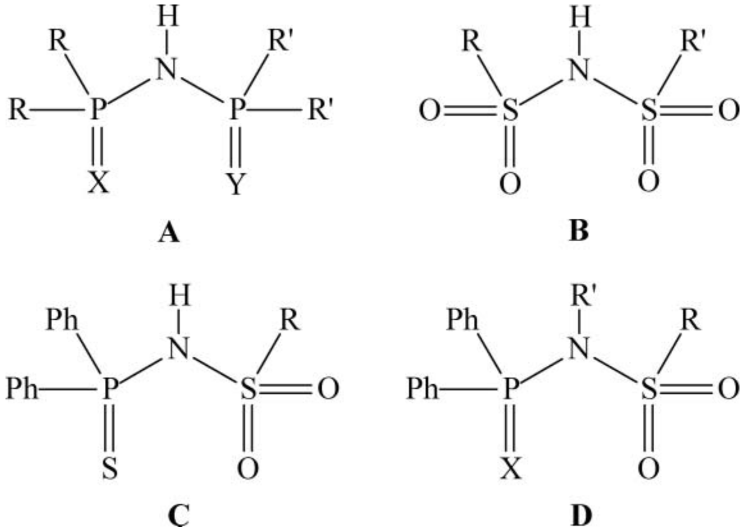
ligands $(SPPh_2)(O_2SR)NH$ (**C**), which combine the properties of the above mentioned species.[20,21] We have extended our research to neutral ligands of type $(XPPh_2)(O_2SR)NR'$ (X = O, S) (**D**) (Scheme 1) in order to investigate the influence of a bulky organic group attached to nitrogen upon the structure and the properties of these new species.



A **B** **C** **D**

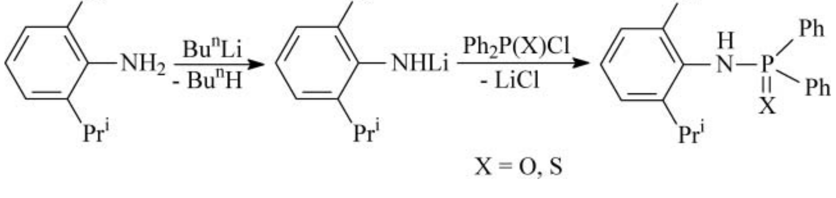
Scheme 1

We report in this article on the synthesis of a new proligand, namely $(OPPh_2)(O_2SMe)NR$ (**3**), as well as the precursor $Ph_2P(O)NHR$ (**1**) and its thio analogue $Ph_2P(S)NHR$ (**2**) ($R = C_6H_3Pr^i{}_2$-2,6). The compounds were characterized by multinuclear NMR spectroscopy, and their crystal and molecular structures were established by single-crystal X-ray diffraction.

RESULTS AND DISCUSSION

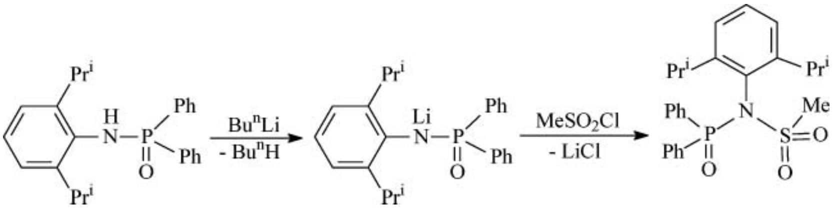
Preparation and Solution NMR Characterization

Compound $Ph_2P(O)NH(C_6H_3Pr^i{}_2$–2,6) (**1**) and its thio analogue **2** were prepared according to Scheme 2, by lithiation of 2,6-isopropylaniline, followed by the reaction between the lithiated compound and diphenylphosphinyl or diphenylthiophosphinyl chloride, respectively, in a 1:1 molar ratio.



Scheme 2

The proligand $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2\text{-}2,6)$ (**3**) was obtained by deprotonation of compound **1** with Bu^nLi, followed by addition of $MeSO_2Cl$ in a 1:1 molar ratio (Scheme 3).



Scheme 3

The NMR spectra of all three new derivatives display the expected resonances for the organic groups attached to phosphorus, nitrogen, and sulfur. The multiplicity of the ^1H and ^{13}C NMR resonances is determined by proton–proton, phosphorus–proton, and phosphorus–carbon couplings, respectively. The N*H* protons in the amides **1** and **2** were observed at δ 4.42 and 4.28 ppm as doublet resonances due to phosphorus–proton couplings. In contrast to the amides **1** and **2**, the ^1H and ^{13}C NMR spectra of **3** show two different resonances for the diastereotopic methyls of the Pr^i substituents. The ^{31}P NMR spectra of all compounds display singlet resonances (i.e., 21.6 ppm for **1**, 57.9 ppm for **2**, and 26.7 ppm for **3**, respectively), low-field shifted for the neutral proligand **3** in comparison with the amide precursor **1**.

Crystal and Molecular Structures of $Ph_2P(O)NH(C_6H_3Pr^i{}_2\text{–}2,6)$ (1), $Ph_2P(S)NH(C_6H_3Pr^i{}_2\text{–}2,6)$ (2), and $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2\text{–}2,6)$ (3)

ORTEP representations of compounds **1** and **2** with the corresponding atom numbering schemes are depicted in Figures 1 and 2, respectively, while important bond lengths and angles are given in Tables S1 and S2 (available online in the Supplemental Materials).

Derivatives **1** and **2** have similar structures in the solid state, except that in the case of the thio derivative **2**, three independent molecules are present in the unit cell. The coordination geometry around phosphorus is distorted tetrahedral. The phosphorus–chalcogen bond lengths [P(1)–O(1) 1.478(2) Å in **1**; averaged P—S 1.943 Å in **2**] are consistent with a double-bond character [cf. $Ph_2P(=O)OH$:[22] P=O 1.486(6) Å, P–O 1.526(6) Å; $Ph_2P(=S)\text{–}N=PPh_2(-SMe)$:[23] P=S 1.954(1) Å, P–S 2.071(1) Å]. The phosphorus–nitrogen bond distances [P(1)–N(1) 1.643(3) Å in **1** and 1.652(3) Å (av. value) in **2**] suggest a single P—N bond [cf. $Ph_2P(=S)-N=PPh_2(-SMe)$:[23] P=N 1.562(2) Å, P–N 1.610(2) Å], although the nitrogen atoms are essentially *sp*^{2} [$\Sigma(N_{angles})$ 359.73° in **1** and 357.37° (av. value) in **2**].

In the crystal of **1**, the molecules are associated into polymeric chains built through strong intermolecular $H_{amide}\cdots O$ hydrogen bonding [H(1)···O(1a) 2.10(2) Å] (Figure S1, Supplemental Materials), similar to those observed in the crystal of $(SPPh_2)(O_2SMe)NH$.[20] Additional weak intermolecular $H_{phenyl}\cdots O$ contacts [H(6)···O(1a) 2.481(2) Å; c.f. Σr_{vdW} (H,O) ca. 2.60 Å][24] are also present. There are no interchain contacts that involve heavier atoms.

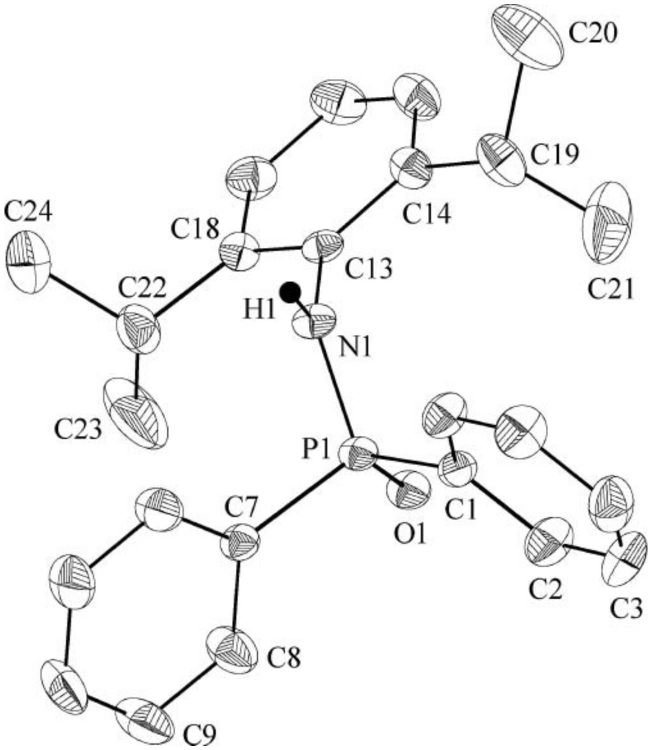


Figure 1 ORTEP plot of $Ph_2P(O)NH(C_6H_3Pr^i{}_2–2,6)$ (**1**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms, except that one attached to nitrogen, are omitted for clarity.

Similar polymeric chains with repeating **2a**–**2b**–**2c** sequence of molecules are formed in the crystal of the thio derivative through strong intermolecular $H_{amide}\cdots S$ hydrogen bonding (Table S2, Supplemental Materials). Within a chain, there are also weak intermolecular $H_{phenyl}\cdots S$ contacts [H(36)···S(1) 2.940(1) Å, H(8)···S(3a) 2.972(1) Å; c.f. Σr_{vdW} (H,S) ca. 3.05 Å].[24]

The crystal of **3** contains discrete molecules and an ORTEP diagram with the atom numbering scheme is depicted in Figure 3. Important bond lengths and angles are listed in Table S1.

The coordination geometries around phosphorus and sulfur, respectively, are distorted tetrahedral, while the nitrogen atom has again an sp^2 hybridization [$\Sigma(N_{angles})$ 359.93°]. The P–N–S system is angular [S(1)–N(1)–P(1) 120.58(12)°], but bent at a smaller angle than in the related $(SPPh_2)(O_2SR)NH$ derivatives, i.e., 126.02(17) ° (R = Ph);[21] 126.4(1)° (R = Me), 126.95(8)° (R = C_6H_4Me–4)].[20] The phosphorus–oxygen distance [1.4736(19) Å] is consistent with a P=O double bond, while the phosphorus–nitrogen distance is again consistent with a P–N single bond [P(1)–N(1) 1.721(2) Å], considerably longer than that found in the precursor **1** [P(1)–N(1) 1.642(3) Å] or in related $(SPPh_2)(O_2SR)NH$ [1.708(2) Å (R = Me), 1.703(1) Å (R = C_6H_4Me–4);[20] 1.702(3) Å (R = Ph)[21]]. The sulfur–oxygen [S(1)–O(2) 1.422(2) Å; S(1)–O(3) 1.418(2) Å] and sulfur–nitrogen distances [S(1)–N(1) 1.677(2) Å] are consistent with double S=O and single S–N bonds, respectively, of same magnitudes as found for the $(SPPh_2)(O_2SR)NH$ [S=O / S=O / S–N: 1.4267(1) / 1.428(1)/

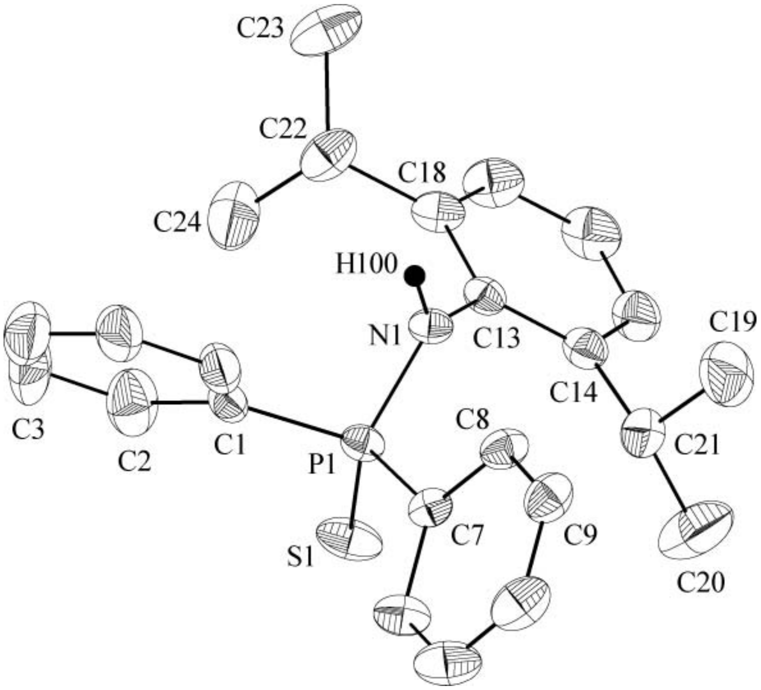


Figure 2 ORTEP plot of $Ph_2P(S)NH(C_6H_3Pr^i{}_2$–2,6) (molecule **2a**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms, except that one attached to nitrogen, are omitted for clarity.

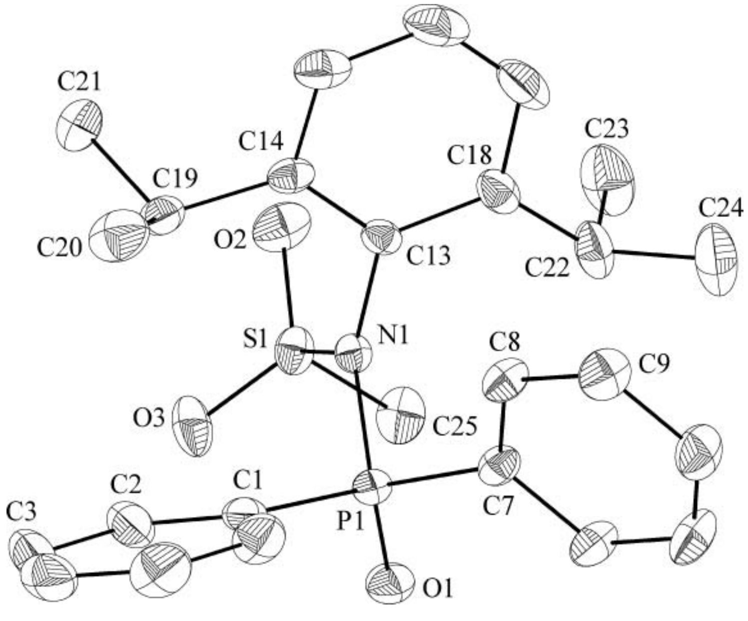
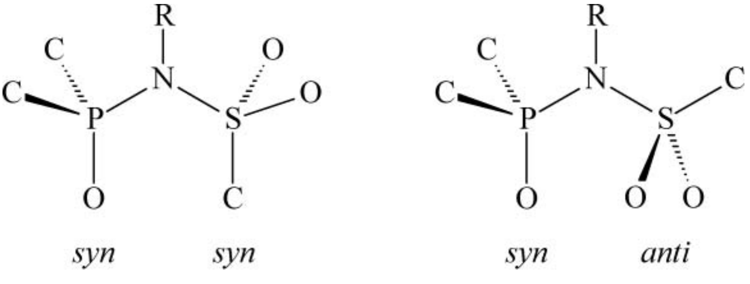


Figure 3 ORTEP plot of $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2$–2,6) (**3**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

1.634(1) Å (R = Me), 1.429(1) / 1.446(1) / 1.641(1) Å (R = C_6H_4Me–4);[20] 1.422(2) / 1.429(2) / 1.634(3) Å (R = Ph)[21]] or bis(organosulfonyl)imides $(O_2SR)_2NH$ [S–N 1.647(2) / 1.656(1) Å, S–O 1.428(2)-1.435(1) Å (R = Me);[25] S–N 1.645(2) / 1.666(2) Å, S–O 1.420(1)−1.431(1) Å (R = C_6H_4Me–4)[26]].

The O = P–N–S(C)(=O)$_2$ skeleton in **3** is similar to those described for the derivatives $(SPPh_2)(O_2SR)NH$,[20,21] as reflected by the torsion angles [O(2)S(1)N(1)P(1) 174.5(1), O(3)S(1)N(1)P(1) 45.6(2), O(1)P(1)N(1)S(1) 28.6(2), C(25)S(1)N(1)P(1) –69.4(2)°]. Taking into account the magnitude of the OPNS and CSNP torsion angles, the extreme conformations of the O=P(C)$_2$–N–S(C)(=O)$_2$ skeleton can be described as either *syn–syn* (**E**) or *syn–anti* (**F**) (Scheme 4), by assigning the terms *syn* and *anti* for angles of 0 and 180°, respectively.[1]



E **F**

Scheme 4

Thus, for compound **3**, a *syn–syn* conformation can be considered, the deviations of the O(1) and C(25) atoms from the P(1)N(1)S(1) plane being –0.668 and –1.572 Å, respectively. Similar *syn–syn* conformations were assigned for the previously described derivatives $(SPPh_2)(O_2SR)NH$ [R = Me, C_6H_4Me–4,[20] Ph[21]].

EXPERIMENTAL

Materials and Methods

All reactions were carried out under inert argon atmosphere using standard Schlenk techniques. The solvents were dried (CH_2Cl_2 on P_2O_5, hexane and diethyl ether on Na, tetrahydrofurane and toluene on K) and distilled prior to use. $Ph_2P(O)Cl$ and $Ph_2P(S)Cl$ were prepared according to methods in the literature.[27] Other reagents, e.g., Bu^nLi (1.6 M solution in hexane), 2,6-diisopropylaniline, and $MeSO_2Cl$, were commercially available and used without further purification. Elemental analyses were performed on a VarioEL analyzer. The NMR spectra were recorded in dry $CDCl_3$, at room temperature, on Bruker Avance DRX 400 (for **1** and **2**) and Bruker Avance 300 (for **3**) instruments. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm) and H_3PO_4 85%, respectively. ^1H and ^{13}C resonances were assigned using 2D NMR experiments.

Synthesis of $LiNH(C_6H_3Pr^i{}_2–2,6)$

A solution of Bu^nLi in hexane (27.5 mL, 1.6 M, 44 mmol) was slowly added to a stirred solution of $2,6–{}^iPr_2C_6H_3NH_2$ (7.80 g, 8.45 mL, 44 mmol) in anhydrous hexane (80 mL) under an argon atmosphere. The reaction mixture was stirred overnight. The lithiated compound was separated by filtration, washed several times with hexane, and dried under vacuum. Yield: 7.58 g (94%).

Synthesis of $Ph_2P(O)NH(C_6H_3Pr^i{}_2–2,6)$ (1)

$Ph_2P(O)Cl$ (9.06 g, 38.3 mmol) was added dropwise to a THF (100 mL) solution of $LiNH(C_6H_3Pr^i{}_2–2,6)$ (7.01 g, 38.3 mmol), and the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum, and the remaining solid was treated with dichloromethane. LiCl was filtered off, and the solvent was removed in vacuum. The colorless solid product was washed several times with anhydrous hexane and recrystallized from dichloromethane (70 mL). Yield: 9.1 g (63%), Mp 149–150°C. Anal. Calcd. for $C_{24}H_{28}NOP$ (MW 377.47): C, 76.37; H, 7.48; N, 3.71. Found: C, 76.42; H, 7.41; N, 3.75. ^1H NMR (400 MHz): 1.04 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.9$ Hz), 3.58 (hept, 2H, C*H*, $^3J_{HH} = 6.8$ Hz), 4.44 (d, 1H, *NH*, $^2J_{PH} = 4.7$ Hz), 7.05 (d, 2H, *H*-3,5, C$_6$*H*$_3$, $^3J_{HH} = 7.7$ Hz), 7.16 (t, 1H, *H*-4, C$_6$*H*$_3$, $^3J_{HH} = 7.6$ Hz), 7.40 (m, 4H, *C$_6$H$_5$-meta*), 7.49 (m, 2H, *C$_6$H$_5$-para*), 7.73 (ddd, 4H, *C$_6$H$_5$-ortho*, $^3J_{PH} = 12.0$, $^3J_{HH} = 8.3$, $^4J_{HH} = 1.4$ Hz). ^{13}C NMR (100.6 MHz): 23.65 (s, *C*H$_3$), 28.39 (s, *C*H), 123.51 (d, *C*-3,5, *C$_6$H$_3$*, $^4J_{PC} = 1.5$ Hz), 127.21 (d, *C*-4, *C$_6$H$_3$*, $^5J_{PC} = 1.7$ Hz), 128.30 (d, *C*$_6$H$_5$-*meta*, $^3J_{PC} = 12.7$ Hz), 131.79 (d, *C*$_6$H$_5$-*para*, $^4J_{PC} = 2.8$ Hz), 131.88 (d, *C*$_6$H$_5$-*ortho*, $^2J_{PC} = 9.5$ Hz), 131.95 (d, *C*$_6$H$_5$-*ipso*, $^1J_{PC} = 129.2$ Hz), 147.45 (d, *C*-2,6, *C$_6$H$_3$*, $^3J_{PC} = 3.1$ Hz); the resonance for *C*-1 atom of *C$_6$H$_3$* is overlapped by the resonance of the *C*$_6$H$_5$-*ortho* carbons. ^{31}P NMR (121.4 MHz): 21.6 ($^1J_{PC} = 127.2$ Hz).

The thio analog $Ph_2P(S)NH(C_6H_3{}^iPr_2–2,6)$ (**2**) was similarly prepared, from $Ph_2P(S)Cl$ (5.9 g, 23.4 mmol) and $LiNH(C_6H_3Pr^i{}_2–2,6)$ (4.3 g, 23.4 mmol), in CH_2Cl_2. After removing the solvent under vacuum, the title compound was extracted with diethyl ether. Yield: 3.42 g (27%), Mp 127°C. Anal. Calcd. for $C_{24}H_{28}NPS$ (MW 393.53): C, 73.25; H, 7.17; N, 3.56, S, 8.15. Found: C, 73.31; H, 7.41; N, 3.75, S, 7.98. ^1H NMR (400 MHz): 0.99 (d, 12H, C*H*$_3$, $^3J_{HH} = 6.8$ Hz), 3.16 (hept, 2H, C*H*, $^3J_{HH} = 6.8$ Hz), 4.28 (d, 1H, *NH*, $^2J_{PH} = 3.8$ Hz), 7.07 (d, 2H, *H*-3,5, C$_6$*H*$_3$, $^3J_{HH} = 7.7$ Hz), 7.18 (t, 1H, *H*-4, C$_6$*H*$_3$, $^3J_{HH} = 7.7$ Hz), 7.47 (m, 6H, *C$_6$H$_5$-meta+para*), 7.90 (ddd, 4H, *C$_6$H$_5$-ortho*, $^3J_{PH} = 13.3$, $^3J_{HH} = 8.4$, $^4J_{HH} = 1.5$ Hz). ^{13}C NMR (100.6 MHz): 23.45 (s, *C*H$_3$), 28.84 (s, *C*H), 123.35 (d, *C*-3,5, *C$_6$H$_3$*, $^4J_{PC} = 1.7$ Hz), 126.90 (d, *C*-4, *C$_6$H$_3$*, $^5J_{PC} = 2.2$ Hz), 128.23 (d, *C*$_6$H$_5$-*meta*, $^3J_{PC} = 12.9$ Hz), 131.17 (d, *C*$_6$H$_5$-*ortho*, $^2J_{PC} = 10.8$ Hz), 131.38 (d, *C*$_6$H$_5$-*para*, $^4J_{PC} = 2.9$ Hz), 133.02 (d, *C*-1, *C$_6$H$_3$*, $^2J_{PC} = 5.8$ Hz), 135.40 (d, *C*$_6$H$_5$-*ipso*, $^1J_{PC} = 101.0$ Hz), 147.19 (d, *C*-2,6, *C$_6$H$_3$*, $^3J_{PC} = 3.3$ Hz). ^{31}P NMR (121.4 MHz): 57.9.

Synthesis of $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2–2,6)$ (3)

A solution of Bu^nLi in hexane (1.66 mL, 1.6 M, 2.64 mmol) was added dropwise, under an argon atmosphere, to a stirred solution of **1** (1 g, 2.64 mmol) in anhydrous THF (30 mL). The reaction mixture was left overnight for completion. $MeSO_2Cl$ (0.302 g, 2.64 mmol) was added to the solution of $Ph_2P(O)N(C_6H_3Pr^i{}_2–2,6)Li$, and the reaction mixture was stirred for 4 h at room temperature. The solvent was evaporated under vacuum, and the remaining solid was treated with diethyl ether. LiCl was filtered off, and the solvent was removed in vacuum. The remaining solid was a mixture of the title compound and unreacted **1**. The desired compound **3** was separated by column chromatography on silica gel, using Et_2O as eluent. Recrystallization from a mixture of CH_2Cl_2 and hexane (1/4, *v/v*) gave **3** as a white solid. Yield: 0.46 g (38%), Mp 148–149°C. Anal. Calcd. for $C_{25}H_{30}NO_3PS$ (MW 455.55): C, 65.91; H, 6.64; N, 3.07, S, 7.04. Found: C, 65.82; H, 6.51; N, 3.14, S, 6.98. ^1H NMR (300 MHz): 0.55 (d, 6H, CH_3, $^3J_{HH} = 6.7$ Hz), 1.14 (d, 6H, CH_3, $^3J_{HH} = 6.7$ Hz), 3.08 (hept, 2H, CH, $^3J_{HH} = 6.7$ Hz), 3.35 (s, 3H, S-CH_3), 7.08 (d, 2H, *H*-3,5, C_6H_3, $^3J_{HH} = 7.7$ Hz), 7.32 (t, 1H, *H*-4, C_6H_3, $^3J_{HH} = 7.7$ Hz), 7.40 (m, 4H, C_6H_5-*meta*), 7.52 (m, 2H, C_6H_5-*para*), 7.84 (dd, 4H, C_6H_5-*ortho*, $^3J_{PH} = 12.5$, $^3J_{HH} = 8.1$ Hz). ^{13}C NMR (75.5 MHz): 22.72 (s, CH_3), 25.26 (s, CH_3), 29.24 (s, CH), 43.58 (s, S-CH_3), 124.83 (s, *C*-3,5, C_6H_3), 128.10 (d, C_6H_5-*meta*, $^3J_{PC} = 13.4$ Hz), 129.45 (d, C_6H_5-*ipso*, $^1J_{PC} = 124.2$ Hz), 129.89 (s, *C*-4, C_6H_3), 130.60 (s, *C*-1, C_6H_3), 132.51 (d, C_6H_5-*para*, $^4J_{PC} = 2.9$ Hz), 133.27 (d, C_6H_5-*ortho*, $^2J_{PC} = 10.1$ Hz), 150.03 (d, *C*-2,6, C_6H_3, $^3J_{PC} = 1.6$ Hz). ^{31}P NMR (121.5 MHz): 26.7 ($^1J_{PC} = 124.2$ Hz).

Table I Crystal data and structure refinement for **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{24}H_{28}NOP$	$C_{24}H_{28}NPS$	$C_{25}H_{30}NO_3PS$
Formula weight	377.44	393.51	455.53
Temperature, K	297(2)	297(2)	297(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/c
a (Å)	10.5240(10)	10.4302(13)	11.9823(12)
b (Å)	19.1679(19)	35.373(4)	13.3682(14)
c (Å)	10.6394(10)	19.143(2)	15.2962(16)
α (°)	90	90	90
β (°)	90.401(2)	104.949(2)	92.529(2)
γ (°)	90	90	90
Volume, $Å^3$	2146.2(4)	6823.8(14)	2447.8(4)
Z	4	12	4
Density (calculated), g/cm^3	1.168	1.149	1.236
Absorption coefficient, mm^{-1}	0.141	0.221	0.223
F(000)	808	2520	968
Crystal size, mm	0.21 × 0.20 × 0.17	0.34 × 0.29 × 0.25	0.38 × 0.26 × 0.20
θ range for data collections (°)	1.94 to 26.37	1.59 to 25.00	2.02 to 25.00
Reflections collected	17135	49318	17382
Independent reflections	4393 [R(int) = 0.0958]	12004 [R(int) = 0.0633]	4311 [R(int) = 0.0490]
Max. and min. transmissions	0.9785 and 0.9700	0.9469 and 0.9287	0.9607 and 0.9200
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	4393/1/253	12004/0/754	4311/0/285
Goodness-of-fit on F^2	1.144	1.258	1.148
Final *R* indicies [I > 2sigma(I)]	R1 = 0.0927, wR2 = 0.1664	R1 = 0.0958, wR2 = 0.1843	R1 = 0.0598, wR2 = 0.1284
R indices (all data)	R1 = 0.1442, wR2 = 0.1863	R1 = 0.1208, wR2 = 0.1951	R1 = 0.0727, wR2 = 0.1346
Largest diff. peak and hole, $eÅ^{-3}$	0.415 and –0.343	0.443 and –0.285	0.345 and –0.289

Crystal Structure Determination of Compounds 1–3

X-ray quality crystals were grown from a mixture of solvents (1/5, *v/v*), i.e., dichloromethane/hexane for $Ph_2P(O)NH(C_6H_3Pr^i{}_2\text{–}2,6)$ (**1**) and $Ph_2P(S)NH(C_6H_3Pr^i{}_2\text{–}2,6)$ (**2**), and toluene/hexane for $(OPPh_2)(O_2SMe)N(C_6H_3Pr^i{}_2\text{–}2,6)$ (**3**), respectively. Colorless, block crystals of **1**–**3** were attached with Paratone N oil on cryoloops. Data collection and processing was carried out on a Bruker SMART APEX instrument (Babes-Bolyai University, Cluj-Napoca) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Details of the crystal structure determination and refinement for compounds **1**–**3** are given in Table I.

The structures were solved by direct methods and refined using SHELX–97.[28] All of the non-hydrogen atoms were treated anisotropically. The hydrogen atoms attached to nitrogen in **1** and **2** were located from the difference map. The other hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached, except the methyl protons for which the isotropic thermal parameters were set at 1.5. The drawings were created with the Diamond program.[29]

Supplementary Material

Crystallographic data for the structural analysis of compounds **1**–**3** have been deposited with the Cambridge Crystallographic Data Centre CCDC, Nos. 663515 (**1**), 714095 (**2**), and 663516 (**3**). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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