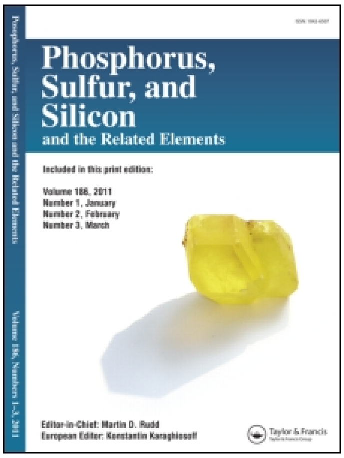

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SULFUR DIIMIDES BEARING BIS(AMINO)PHOSPHINYL SUBSTITUENTS

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The first examples of P-functionally substituted sulfur diimides containing either two (**1**) or one (**2**, **3**) bis(diisopropylamino)phosphinyl substituents were prepared from the potassium salts K[NSN]K or K[NSNR] (R = ^{t}Bu, $SiMe_3$) and (^{i}Pr$_2$N)$_2$P-Cl. Addition of sulfur and selenium to **1** leads to the 1:2 adducts **1(S)** and **1(Se)**. Multinuclear NMR (^{1}H, ^{13}C, ^{29}Si, ^{31}P and, in part, ^{15}N) in solution and ^{31}P CP/MAS NMR in the solid state were applied for characterization.

Sulfur diimides of the type $S(N\text{-}ElR_2)_2$ (El = P, As, Sb, Bi; R = ^{t}Bu, Ph) have been known for several years.[1] However, the few examples of P-functionally substituted phosphinyl sulfur diimides could be synthesized only in the protecting ligand sphere of pentacarbonyl chromium complexes.[2] We have now succeeded in preparing phosphinyl sulfur diimides bearing amino groups at a phosphorus atom which is not protected by complexation. Thus, the bis(diisopropylamino)phosphinyl sulfur diimides **1**–**3** are obtained according to Equations (1) and (2) using potassium sulfur diimides.[3,4]

$$K[NSN]K + 2\,(^iPr_2N)_2P\text{-}Cl \longrightarrow \underset{\mathbf{1}}{(^iPr_2N)_2P(NSN)P(N^iPr_2)_2} + 2\,KCl \qquad (1)$$

$$K[NSNR] + (^iPr_2N)_2P\text{-}Cl \longrightarrow \underset{\mathbf{2}\ (R\,=\,^tBu),\ \mathbf{3}\ (R\,=\,SiMe_3)}{(^iPr_2N)_2P(NSN)R} + KCl \qquad (2)$$

The stability of bis(amino)phosphinyl sulfur diimides depends on the presence of bulky amino groups. The thiophilic character of sterically less shielded phosphorus(III) centres causes degradation of the NSN system by sulfur abstraction, even at low temperatures. This became evident when the reaction between K[NSN^{t}Bu] and $(Me_2N)_2P\text{-}Cl$ (δ ^{31}P = 158.2) in hexane solution was monitored by ^{31}P NMR from −78°C to +25°C. At −50°C, the reaction initially leads to the desired sulfur diimide, $(Me_2N)_2P(NSN)^tBu$ (δ ^{31}P = 67.7). At −40°C, additional compounds are formed of which $(Me_2N)_3PS$ (δ ^{31}P = 81.0) and $(Me_2N)_2P(S)(NSN)^tBu$ (δ ^{31}P = 55.8) were identified; the sulfur diimide was obtained independently from K[NSN^{t}Bu] and $(Me_2N)_2P(S)\text{-}Cl$.

Subsequent addition of chalcogens to the sulfur diimide **1** affords the sulfur and

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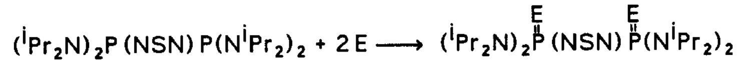
selenium adducts **1(S)** and **1(Se)**, respectively, which were isolated as crystalline solids [Equation (3)].



$$(^{i}Pr_2N)_2P(NSN)P(N^{i}Pr_2)_2 + 2E \longrightarrow (^{i}Pr_2N)_2\overset{E}{\overset{\|}{P}}(NSN)\overset{E}{\overset{\|}{P}}(N^{i}Pr_2)_2 \qquad (3)$$

1 E = S, Se **1(S), 1(Se)**

All compounds were studied by ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR, and in part also by ^{15}N NMR (Table I). The ^{31}P NMR spectra in solution show a single signal between +100°C to −100°C, indicating either a static structure or, more likely, fast Z/E $\rightleftarrows$ E/Z isomerization. In the case of **2**, the $^{15}N(=N^{t}Bu)$ resonance signal, detected at −10°C via refocused INEPT based on $^{3}J(^{15}NCC^{1}H)$ at $\delta\,^{15}N = -68.1$, suggests that the *tert*-butyl group occupies the Z-position.[5] The $^{15}N(=N\text{-}P)$ resonance was not observed by direct $^{15}N\{^{1}H\}$ measurement under the same conditions, probably due to dynamic processes.

TABLE I

NMR data[a] of the sulfur diimides **1**, **1(S)**, **1(Se)**, **2** and **3**

	$\delta\,^{1}H$		$\delta^{13}C$		$\delta\,^{31}P$	$\delta^{15}N^{b)}$
	NCH	CH_3	NCH	CH_3	$P(N^{i}Pr_2)_2$	
1	3.52 [12.2]	1.21, 1.16	46.2 [12.8]	24.5, 24.1 [5.2], [12.7]	73.8	−296.7 [73.8]
1(S)	3.67 [20.0]	1.23, 1.16	47.0 [6.0]	22.5, 22.4 [2.1], [2.1]	55.4	−300.7 [11.0]
1(Se)	3.78 [20.3]	1.36, 1.27	47.3 [5.9]	22.5, 22.3 [2.1], [2.1]	43.5 (802)	f)
2$^{c)}$	3.47 [12.9]	1.28, 1.17	46.0 [12.0]	24.5, 24.2 [5.2], [9.4]	75.9	−291.1$^{d)}$ [74.1]
3$^{e)}$	3.49 [12.9]	1.22, 1.15	46.5 [12.8]	24.5, 24.1 [5.1], [8.6]	71.1	f)

a) In C_6D_6 at 25°C; δ values relative to Me_4Si ($\delta^{1}H(C_6D_6) = 7.15$, $\delta^{13}C(C_6D_6) = 128$, $\delta^{29}Si$), external 85% H_3PO_4 ($\delta^{31}P$), neat $MeNO_2$ ($\delta^{15}N$); coupling constants $J(^{31}P^{1}H)$, $J(^{31}P^{13}C)$ and $^{1}J(^{31}P^{15}N)$ in [ ], $^{1}J(^{77}Se^{31}P)$ in ( ).

b) Natural abundance; INEPT refocused, ^{1}H decoupled, based on $^{3}J(^{15}N^{1}H) \approx 2$ Hz.

c) $-NSN-{}^{t}Bu$: $\delta^{1}H = 1.46$; $\delta^{13}C = 30.4, 61.3$.

d) $\delta^{15}N(=N-{}^{t}Bu) = -68.1$ at −10°C.

e) $-NSN-SiMe_3$: $\delta^{1}H = 0.2$; $\delta^{13}C = 1.4$; $\delta^{29}Si = 1.0$.

f) Not measured.

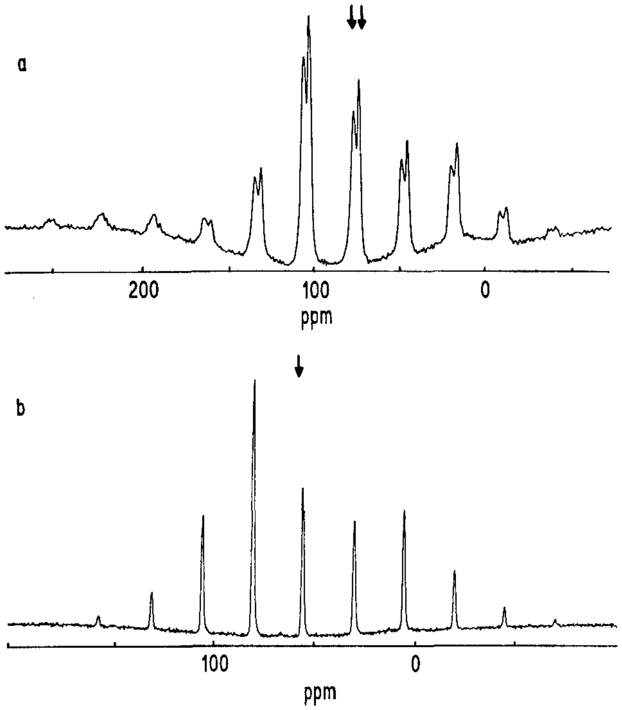


FIGURE 1 121.5 MHz solid state ^{31}P CP/MAS NMR spectra of $(^{i}Pr_2N)_2P(NSN)P(N^{i}Pr_2)_2$ (**1**) (Fig. 1a) and $(^{i}Pr_2N)_2P(S)(NSN)P(S)(N^{i}Pr_2)_2$ (**1(S)**) (Fig. 1b), measured at 25°C; recycle delay 5s, contact time 5 ms, rotation frequency 3493 and 3046 Hz, respectively; 48 scans. The centre band(s) are indicated by arrows.

Although compounds **1**, **1(S)** and **1(Se)** are crystalline solids, crystals suitable for X-ray analysis could not be obtained as yet. However, some information concerning the preferred configuration of these sulfur diimides is provided by the solid state ^{31}P CP/MAS NMR spectra (Fig. 1). The observation of two ^{31}P resonances (Fig. 1a; δ ^{31}P = 77.2, 74.0; ratio $\approx$1:1) for compound **1** can be interpreted in three ways: (i) There is only one isomer present with Z/E configuration in the solid state; (ii) there are two different molecules (having both either Z/Z or E/E configuration) in the unit cell; or, less likely, (iii) molecules with both Z/Z and E/E configuration (ratio of $\approx$1:1) are present. The ^{31}P CP/MAS spectra of **1(S)** (Fig. 1b; δ ^{31}P = 56.9); and **1(Se)** (δ ^{31}P = 42.2) show only a single ^{31}P resonance signal. Considering the steric requirements of the bulky substituents at the NSN unit, it is tempting to propose the E/E configuration for **1(S)** and **1(Se)**.

EXPERIMENTAL

Precautions were taken for using dry solvents and handling all compounds under inert atmosphere (Ar). NMR spectra in solution (cf. Table I): Jeol FX 90 Q and Bruker AC 300. ^{31}P CP/MAS NMR spectra: Bruker MSL 300, using air-tight inserts for the ZrO_2 rotors.[6] El-MS spectra (70 eV): Varian MAT CH-7.

1. *Bis(diisopropylamino)phosphinyl sulfur diimides*, **1–3**. $(^{i}Pr_2N)_2P$ (NSN) $P(N^{i}Pr_2)_2$, **1**: A suspension of 0.691 g (5 mmoles) K_2SN_2 in 30 ml of a mixture of hexane/DME/MeCN (15:15:1) is stirred at room temperature while 2.665 g (10 mmoles) of $(^{i}Pr_2N)_2P$-Cl are added. After 24 h the color of the reaction mixture is deep red. The solvents are removed in vacuo, and hexane is added to the oily residue. After filtration and removal of hexane, **1** (2.51 g, 96%) is obtained as a red powder. Recrystallization from a small amount of pentane affords deep red, rhombic crystals of **1** (mp 55°C). Elemental analysis: $C_{24}H_{56}N_6P_2S$ - calc.: C 55.14, H 10.80, N 16.08; found: C 55.50, H 10.99, N 15.70%. - MS: m/e = 522 (1%, M^+), 422 (14%, M^+-$N^{i}Pr_2$), 222 (14%, M^+-3 $N^{i}Pr_2$), 132 (100%, $^{i}Pr_2NPH^+$).

$(^{i}Pr_2N)_2P(NSN)R$, **2** (R = ^{t}Bu), **3** (R = $SiMe_3$): Reactions and work-up procedures were carried out as for **1**, except that the solvent was solely hexane. The compounds **2** and **3** are obtained as red, highly viscous liquids. - MS (**2**): m/e = 348 (19%, M^+), 248 (90%, M^+-$N^{i}Pr_2$), 132 (5%, $^{i}Pr_2NPH^+$), 100 (100%, $^{i}Pr_2N^+$); MS (**3**): m/e = 364 (32%, M^+), 264 (100%, M^+-$N^{i}Pr_2$), 132 (19%, $^{i}Pr_2NPH^+$), 100 (82%, $^{i}Pr_2N^+$).

2. *Chalcogen adducts*, **1(S)** *and* **1(Se)**. A mixture containing 0.261 g (0.5 mmoles) **1** and 1.5 mmoles of either sulfur or selenium in 20 ml of THF is stirred at room temperature for 4 h. After filtration and removal of THF in vacuo, the adducts **1(S)** (mp 149°C) and **1(Se)** (mp 130°C, decomp.) are obtained as red and beige powders, respectively, in ca. 95% yield. - MS (**1(S)**): m/e = 586 (6%, M^+), 263 (26%, $(^{i}Pr_2N)_2PS^+$), 231 (7%, $(^{i}Pr_2N)_2P^+$), 132 (12%, $(^{i}Pr_2N)PH^+$), 100 (100%, $^{i}Pr_2N^+$); MS (**1(Se)**): m/e = 580 (1%, M^+-$^{i}Pr_2N$), 311 (11%, $(^{i}Pr_2N)_2PSe^+$), 231 (16%, $(^{i}Pr_2N)_2P^+$), 132 (18%, $(^{i}Pr_2N)PH^+$), 100 (100%, $^{i}Pr_2N^+$).

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