

Synthesis of *N,N'*-Bis(*P,P*-dialkylthiophosphinyl)diamines $R_2P(S)-NH-R'-NH-P(S)R_2$

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Abstract. *N,N'*-Bis(*P,P*-dialkylthiophosphinyl)diamines **1a–e** were obtained from $Et_2P(S)Br$ and $H_2N-R'-NH_2$ with elimination of HBr . Compounds **2a–e** were prepared by sulfura-

tion of $R_2P-NH-R'-NH-PR_2$ that were generated without isolation from $NH_2-R'-NH_2$ and $t-Bu_2PCl$.

Systematic investigations of the complexing ability of ligands with chelating $P(X)NR$ groups ($X = O, S, NR$) revealed in case of the Ni^{++} -complexes a surprising diversity of structural, spectroscopic and magnetic properties that strongly depend on X and the organic substituents at P and N [1]. When we extended our studies to ligands of type $[R_2P(S)-N-R'-N-P(S)R_2]^{2-}$ ($=L$) we obtained monomeric complexes NiL the structures and properties of which were recently reported [2]. In order to prepare these ligands we synthesized **1** and **2** anticipating that they could be easily deprotonated by $BuLi$ with formation of the Li salts of the desired ligands.

Preparation of *N,N'*-Bis(*P,P*-diethylthiophosphinyl)diamines **1** and *N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)diamines **2**

We found that compounds **1** are readily accessible according to scheme 1 by reaction of $Et_2P(S)Br$ and an excess of the corresponding diamine $H_2N-R'-NH_2$ with elimination of HBr .

Compounds **2**, however, cannot be prepared in the same way because of the relative inertness of $t-Bu_2P(S)X$ ($X = Cl$,

Br) in this reaction. Therefore we performed the two-step synthesis according to (a) and (b) in scheme 1.

The precursors of **2**, $t-Bu_2P-NH-R'-NH-P t-Bu_2$, were not isolated but treated in situ with S_8 to afford **2**. In case of **2d** and **2e** it proved to be necessary to use for step (a) the lithiated diamines $LiNH-R'-NHLi$ which resulted by addition of the required quantity of $BuLi$ to the diamine.

Reactions (a) and (b) can be conveniently controlled by ^{31}P NMR: (a) is finished when in the spectrum of the reaction mixture the singlet of $t-Bu_2PCl$ at $\delta_p = 145$ ppm is completely substituted by the singlet of $t-Bu_2P-NH-R'-NH-P t-Bu_2$, the δ_p values of which are given in the experimental part.

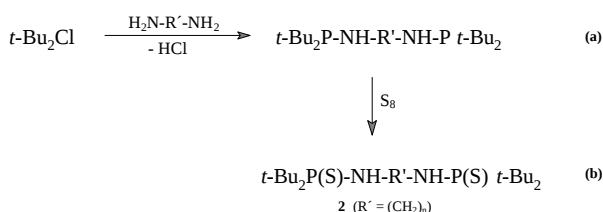
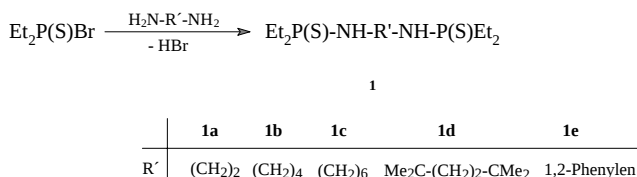
In order to make sure that these assignments are correct we referred to the literature value of $t-Bu_2P-NH-(CH_2)_n-NH-P t-Bu_2$ ($n=2$) [3]. In case of the compound with $n = 3$ we isolated the precursor as colourless crystals; *m.p.* 43 °C (ligroin), and characterized it by elementary analysis. Sulfuration according to (b) is complete when only the singlet of **2** is observed in the spectrum of the reaction mixture.

1 and **2** form colourless crystals that are soluble in toluene, ligroin or $CHCl_3$. They are stable against moisture and can be stored in closed vessels without noticeable change. With $BuLi$ the salts $[R_2P(S)-N-R'-N-P(S)R_2]Li_2$ ($R = Et, t-Bu$) are formed as is evident from their metathesis reaction *e.g.* with $[NiCl_2(PPh_3)_2]$ that leads to monomeric complexes NiL with NiN_2S_2 chromophores [2]. Moreover, the Li salts have proved to be useful synthons in organophosphorus chemistry [4].

Experimental

Compounds **1** and **2** were prepared using dried solvents. In case of **2** preparations were performed in an atmosphere of nitrogen. Melting points (uncorrected) were determined in closed tubes with a melting point apparatus 510 W (Büchi, Switzerland) by using a set of calibrated thermometers. – ^{31}P NMR: Bruker AM 200; 85% H_3PO_4 as external standard, downfield shifts are positive; solvent $CDCl_3$. – EI mass spectra: MAT 311 A (Varian, Bremen); EI 70 eV, 60 μA , source temperature 180 °C. – Elemental analyses: Perkin-Elmer C, H, N-analyzer 263.

The diamines are commercially available. $Et_2P(S)Br$ [5] and $t-Bu_2PCl$ [6,7] were prepared according to the literature.



	2a	2b	2c	2d	2e
n	2	3	4	6	10

Synthesis of *N,N'*-Bis(*P,P*-diethylthiophosphinyl)diamines 1a–e

0.1 mol of the diamine $H_2N-R'-NH_2$ in toluene (60 ml) are slowly added with stirring to 0.1 mol $Et_2P(S)Br$ in 100 ml toluene at room temperature. After heating for 1–2.5 h the hydrobromide formed is filtered off and repeatedly washed with small portions of hot toluene. The filtrate and the washing solutions are evaporated under reduced pressure, and the residue is crystallized from the solvents given below. Yields 40–60%.

***N,N'*-Bis(*P,P*-diethylthiophosphinyl)1,2-diaminoethane (1a)**

Ligroin (120–140 °C): *m.p.* 68 °C. – EI MS: *m/z* 300 (M^+ , 17%); $\delta_p = 77.9$ ppm.

$C_{10}H_{26}N_2P_2S_2$	calcd.:	C 39.98	H 8.72	N 9.33
(300.4)	found:	C 40.00	H 8.73	N 9.44.

***N,N'*-Bis(*P,P*-diethylthiophosphinyl)1,4-diaminobutane (1b)**

Toluene–ligroin (120–140 °C) (1:3): *m.p.* 57 °C. – EI MS: *m/z* 328 (M^+ , 47%); $\delta_p = 76.5$ ppm.

$C_{12}H_{30}N_2P_2S_2$	calcd.:	C 43.88	H 9.21	N 8.53
(328.5)	found:	C 43.00	H 9.22	N 8.34.

***N,N'*-Bis(*P,P*-diethylthiophosphinyl)1,6-diaminohexane (1c)**

Toluene–ligroin (120–140 °C) (1:3): *m.p.* 46 °C. – EI MS: *m/z* 356 (M^+ , 44%); $\delta_p = 76.2$ ppm.

$C_{14}H_{34}N_2P_2S_2$	calcd.:	C 47.17	H 9.61	N 7.86
(356.5)	found:	C 46.60	H 9.69	N 7.70.

***N,N'*-Bis(*P,P*-diethylthiophosphinyl)2,5-diamino-2,5-dimethylhexane (1d)**

Ligroin (60–80 °C): *m.p.* 92 °C. – EI MS: *m/z* 384 (M^+ , 89%); $\delta_p = 68.0$ ppm (C_6D_6).

$C_{16}H_{38}N_2P_2S_2$	calcd.:	C 49.97	H 9.96	N 7.28
(384.6)	found:	C 49.90	H 9.97	N 7.17.

***N,N'*-Bis(*P,P*-diethylthiophosphinyl)1,2-phenyldiamine (1e)**

Methanol: *m.p.* 97 °C. – EI MS: *m/z* 347 (M^+ , 100%); $\delta_p = 72.4$ ppm.

$C_{14}H_{26}N_2P_2S_2$	calcd.:	C 48.26	H 7.52	N 8.04
(348.4)	found:	C 48.10	H 7.55	N 7.99.

Synthesis of *N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)diamines 2a–e

Step (a): 0.1 mol of the diamine in 50 ml toluene are dropwise added with stirring to 0.1 mol *t*-Bu₂P₂Cl in 100 ml toluene at room temperature. After heating for 2–4 h the reaction is finished (³¹P NMR control). The hydrobromide formed is filtered off and repeatedly washed with small quantities of toluene.

In case of **2d** and **2e** this procedure was modified as follows: 0.04 mol BuLi (1.6M in hexane) are added dropwise to 0.02 mol of the diamine in toluene at room temperature. After warming the mixture for 0.5 h 0.04 mol *t*-Bu₂P₂Cl are slowly added, and the reaction mixture is warmed for some time until the formation of the corresponding precursor is completed (³¹P NMR control!). Then LiCl is filtered off.

Step (b): After adding the calculated amount of S₈ to the filtrate the mixture is heated for 1–2 h. When the sulfuration is complete (³¹P NMR control!) the solvents are evaporated, and the residue is crystallized from the solvents given below. Yields 45–70%.

For ³¹P NMR control the δ_p values of the precursors are given in brackets.

***N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)1,2-diaminoethane [3] (2a)**

Ligroin: *m.p.* 194 °C. – EI MS: *m/z* 412 (M^+ , 31%); $\delta_p = 95.8$ ppm (toluene-*d*₈); ($\delta_p = 77.4$ ppm).

$C_{18}H_{42}N_2P_2S_2$	calcd.:	C 52.40	H 10.26	N 6.79
(412.6)	found:	C 52.33	H 10.21	N 6.74.

***N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)1,3-diaminopropane (2b)**

Ligroin (120–140 °C): *m.p.* 210 °C. – EI MS: *m/z* 426 (M^+ , 27%); $\delta_p = 98.1$ ppm (C_6D_6); ($\delta_p = 79.1$ ppm).

$C_{18}H_{44}N_2P_2S_2$	calcd.:	C 53.49	H 10.40	N 6.57
(426.6)	found:	C 53.42	H 10.50	N 6.58.

***N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)1,4-diaminobutane (2c)**

Methanol: *m.p.* 182 °C; EI MS: *m/z* 440 (M^+ , 53%); $\delta_p = 97.4$ ppm; ($\delta_p = 78.3$ ppm).

$C_{20}H_{46}N_2P_2S_2$	calcd.:	C 54.51	H 10.52	N 6.36
(440.7)	found:	C 54.10	H 10.60	N 6.38.

***N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)1,6-diaminohexane (2d)**

The residue was purified by chromatography (toluene, column 20 cm, silicagel) and crystallized from methanol: *m.p.* 148 °C. – EI MS: *m/z* 468 (M^+ , 17%); $\delta_p = 96.6$ ppm; ($\delta_p = 78.0$ ppm).

$C_{22}H_{50}N_2P_2S_2$	calcd.:	C 56.38	H 10.75	N 5.98
(468.7)	found:	C 56.30	H 10.90	N 5.98.

***N,N'*-Bis(*P,P*-di-*tert*-butylthiophosphinyl)1,10-diaminodecane (2e)**

Methanol: *m.p.* 120 °C. – EI MS: *m/z* 524 (M^+ , 13%); $\delta_p = 96.0$ ppm (C_6D_6); ($\delta_p = 78.1$ ppm).

$C_{26}H_{58}N_2P_2S_2$	calcd.:	C 59.50	H 11.14	N 5.34
(524.8)	found:	C 59.50	H 11.20	N 5.17.

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