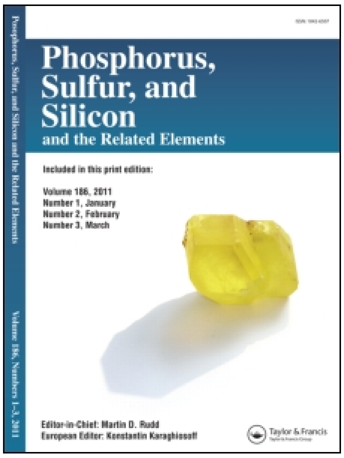

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nothegger, Thomas and Sladky, Fritz(1994) '^{77}Se-NMR Spectroscopic Characterization of Lithium Amidoselenolates: A New Synthetic Approach to Diaminodi- and Polyselanes of Cyclic Amines', Phosphorus, Sulfur, and Silicon and the Related Elements, 86: 1, 269 — 272

To link to this Article: DOI: 10.1080/10426509408018413

URL: http://dx.doi.org/10.1080/10426509408018413

Phosphorus, Sulfur, and Silicon, 1994, Vol. 86, pp. 269–272
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Communication

^{77}Se-NMR SPECTROSCOPIC CHARACTERIZATION OF LITHIUM AMIDOSELENOLATES: A NEW SYNTHETIC APPROACH TO DIAMINODI- AND POLYSELANES OF CYCLIC AMINES

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(Received September 27, 1993)

Insertion of elemental selenium into lithium salts of cyclic amines affords lithium salts of N-selenolates **3**, which were characterized by ^{77}Se-NMR spectroscopy. Oxidation of these N-selenolates leads to the corresponding diaminodi- and polyselanes **2**.

Key words: Cyclic amines; lithium amidoselenolates; diaminoselanes; ^{77}Se-NMR data.

INTRODUCTION

Whereas diaminosulfanes **1** are easily accessible by reaction of SCl_2, S_2Cl_2 or S_nCl_2 with amines,[1] the corresponding diaminoselanes **2** are not, because $SeCl_2$ and Se_nCl_2 are not known and Se_2Cl_2 is not easy to handle and side reactions lower the yields.[2] For the few known diaminomonoselanes different synthetic approaches have been used which shall not be discussed in this context.[3,4] The first and only diaminodi- and polyselanes of cyclic amines were prepared in analogy to a procedure used in sulfur chemistry.[5,6] Heating black selenium powder with piperidine or morpholine in the presence of Pb_3O_4 affords the corresponding diaminodi-, tri-, and tetraselanes.[7,8]

$)N{-}S_n{-}N($	$)N{-}Se_n{-}N($	$)N{-}Se_n^-Li^+$
$n = 1$ to 6	$n = 2, 3, 4$	$n = 1, 2$
1	2	3

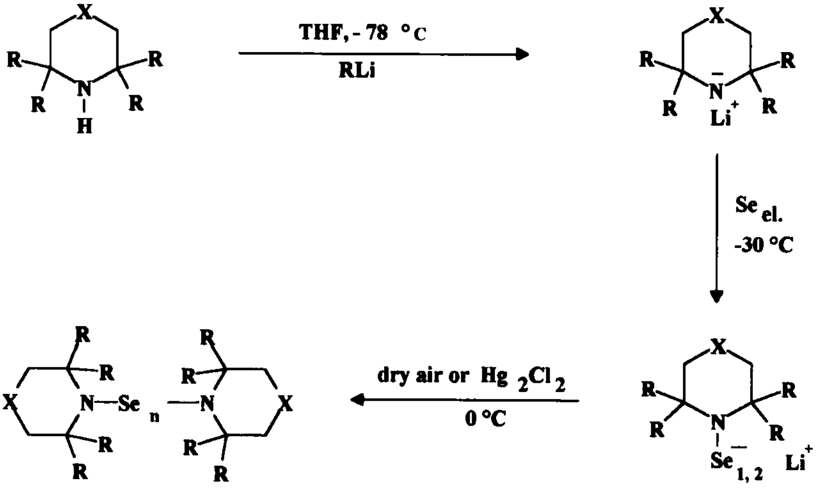
RESULTS AND DISCUSSION

We have found that the method to prepare diaminodi- and polyselanes as described above does not work, for yet unknown reasons, in the case of other amines such as 2,2,6,6-tetramethylpiperidine, phenothiazine, diisopropylamine and bis(trimethylsilyl)amine, although at least for the last amine the corresponding diselane prepared from Se_2Cl_2 and lithium bis(trimethylsilyl)amide appears to be stable.[9,10]

Since there is obviously only a very limited synthetic approach to diaminodi-, and polyselanes our aim was to device a general and powerful synthon. Lithium amidoselenolates **3**, unknown until now, appear to be promising candidates as shown by representative examples. **3** are prepared by deprotonating the respective amine with a lithium alkyle in anhydrous tetrahydrofurane (THF) and insertion of the stoichiometric amount of elemental selenium (Scheme 1). The ^{77}Se-NMR-spectroscopic data of the orange to red-colored THF solutions of the amido selenolates are given in Table I.

In accord with the higher electronegativity of nitrogen compared to carbon there is a distinct downfield shift of the selenium resonance in the amidoselenolates of about 900 ppm compared to the well known carbonselenolates.[11] Still further downfield by about 200 ppm are only diaminoselanes.[12,13]

At least a second equivalent of elemental selenium dissolves, accomplished by a color change to dark red most likely leading to amidoselenonylselenolates **4**[14]:



(5) X = CH$_2$, R = H, n = 4

(6) X = O, R = H, n = 4

(7a) X = CH$_2$, R = CH$_3$, n = 4

(7b) X = CH$_2$, R = CH$_3$, n = 2

(4a) X = CH$_2$, R = H, n = 2

(4b) X = O, R = H, n = 2

(4c) X = CH$_2$, R = CH$_3$, n = 2

(3c) X = CH$_2$, R = CH$_3$, n = 1

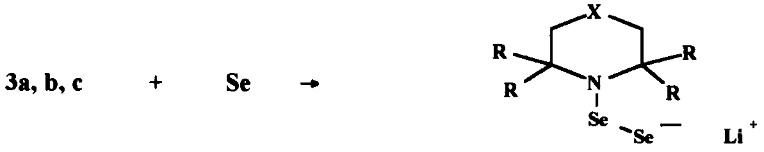
SCHEME 1

TABLE I

^{77}Se-NMR-spectroscopic data of lithium amidoselenolates

	$\delta\,^{77}$Se [rel. Me$_2$Se]	W$_{1/2}$ [Hz]	Temperature [°C]
pipSe$^-$ (3a)	949	150	0
morSe$^-$ (3b)	947	180	-10
tmpipSe$^-$ (3c)	952	70	-20

pip = piperidino, mor = morpholino, tmpip = 2,2,6,6-tetramethylpiperidino



(**4a**) X = CH$_2$, R = H

(**4b**) X = O, R = H

(**4c**) X = CH$_2$, R = CH$_3$

The corresponding ^{77}Se-NMR-spectra, however only show very broad bands, probably due to dynamic exchange processes. Attempts of spectral recording at low temperatures are limited by the low solubility of the above species.

Oxidation of **3** or **4** affords a mixture of mainly diaminodi- and tetraselanes which can be isolated by fractionate crystallization. However, mass spectroscopic evidence indicates also the formation of diaminotri- and pentaselanes. The use of dry air as oxidant is essential since even traces of water hydrolyze the nitrogen-selenium bond with formation of the corresponding amine or its hydrate[15] and unidentified selenium species. All synthesized di- and tetraselanes have limited stability in solution and slowly liberate selenium, especially if exposed to bright daylight.[5]

EXPERIMENTAL

Lithium amidoselenolates **3**.

Lithium piperidinoselenolate **3a**. A solution of piperidine (1.70 g, 20.0 mmol) in anhydrous, freshly destilled THF (40 ml) is deprotonated with buthyllithium (4.00 ml of a 2.50 M solution in n-hexane, 10.0 mmol) at −78°C under an argon atmosphere. The reaction mixture is allowed to warm up to −30°C. At that temperature elemental selenium (5.00 mmol, 0.400 g) was added to the solution and the cooling bath is removed. After full insertion of the selenium into the lithium amid, which is accompanied by a color change from slightly yellow to red, the solution is concentrated under reduced pressure at 10°C to 5 ml of a dark red lithium piperidine solution. This ca. 1 molar solution is cooled to 0°C and the ^{77}Se-spectrum is recorded.

Lithium morpholinoselenolate **3b**. The same procedure as described above leads to an orange solution of lithium morpholinoselenolate and the ^{77}Se-spectrum is determined at −10°C.

Lithium 2,2,6,6-tetramethylpiperidinoselenolate **3c**. The same procedure as described above leads to a dark red solution of lithium 2,2,6,6-tetramethylpiperidinoselenolate and the ^{77}Se-spectrum is determined at −20°C.

Dipiperidinotetraselane **5**. A solution of piperidine (0.937 g, 11.0 mmol) in anhydrous, freshly destilled THF (100 ml) is deprotonated with buthyllithium (4.00 ml of a 2.50 M solution in n-hexane, 10.0 mmol) at −78°C under an argon atmosphere. The reaction mixture is allowed to warm up to −30°C. At that temperature elemental selenium (20.0 mmol, 1.58 g) is added to the solution and the cooling bath is removed. After full insertion of the selenium the reaction mixture is oxidized by sucking dry air through the solution at 0°C. Then the mixture is filtered, removal of the solvent *in vacuo* leaves a red oil. The crude product is subjected to silica gel column chromatography (ether, R_f = 0.86) and recrystallized from absolute ether at −20°C to give compound **5** (55% yield). ^{1}H-NMR (200 MHz/CHCl$_3$/TMS): 2.95 ppm (m, 8H; C^{2}H$_2$, C^{6}H$_2$); 1.65 ppm (m, 12H; C^{3}H$_2$, C^{4}H$_2$, C^{5}H$_2$); m.p.: 90°C.

Dimorpholinotetraselane **6**. The same procedure as described above is used. The crude product is subjected to silica gel column chromatography (ether, R_f = 0.81) and recrystallized from absolute ether or THF at −20°C to give compound **6** (45% yield). ^{1}H-NMR (200 MHz/benzene-d$_6$/TMS): 3.50 ppm (m, 8H; C^{2}H$_2$, C^{6}H$_2$), 2.87 ppm (m, 8H; C^{3}H$_2$, C^{5}H$_2$); ^{13}C-NMR (200 MHz, benzene-d$_6$/TMS): 69 ppm (C^{3}, C^{5}), 59 ppm (C^{2}, C^{6}); m.p.: 123°C.

Bis(2,2,6,6-tetramethylpiperidino)tetraselane **7a**. The same procedure as described above is used. The crude product is subjected to alumina gel column chromatography (ether, R_f = 0.96) and recrystallized from absolute ether or THF at −20°C to give compound **6a** (50% yield). MS (EI) m/z: 598 (9, M^+), 518 (100), 504 (39), 440 (100), m.p.: 105°C.

Bis(2,2,6,6-tetramethylpiperidino)diselane **7b**. The same procedure as above is used. The crude product is subjected to alumina gel column chromatography (ether, R_f = 0.96) and recrystallized from absolute ether or THF at −20°C to give compound **7b**. The oxidation can also be carried out with Hg_2Cl_2 (5.00 mmol, 2.36 g) as oxidant. At −80°C the mercury(I)chloride is added to lithium 2,2,6,6-tetramethylpiperidinoselenolate **3c** in THF and the mixture is allowed to warm up to room temperature and was then centrifugated. The liquid phase is decanted and the solvent is removed *in vacuo*. The crude product is treated the same way as described above (60% yield). MS (EI) m/z: 438 (83, M^+), 298 (100), 282 (27), m.p.: 104°C.

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