Inorg. Chem. **1993**, *32*, 1519–1520 **1519**

Notes

A Simple, Efficient Synthesis of Se_4N_4

Jari Siivari,[1a,b] Tristram Chivers,[*,1a] and Risto S. Laitinen[1b]

Departments of Chemistry, The University of Calgary,
Calgary, Alberta, Canada T2N 1N4, and University of Oulu,
Linnanmaa, SF-90570 Oulu, Finland

Received September 29, 1992

Introduction

In comparison to sulfur–nitrogen (S–N) chemistry,[2] the study of selenium–nitrogen (Se–N) compounds has been relatively limited.[3] In S–N chemistry, S_4N_4 is widely used as a starting material for the preparation of other cyclic and acyclic S–N derivatives.[2] There has been increasing interest in the preparation of novel Se–N compounds from Se_4N_4 as exemplified by the preparation of the cations $Se_3N_2^{2+}$ and $(S_3N_2^{\bullet+})_2$,[4] metal derivatives of the Se_3N^- and $Se_2N_2^{2-}$ anions,[5] and the coordination complexes $[Cl_4M(NSeCl)]_2$ (M = W, Mo).[6] These examples demonstrate that this Se–N heterocycle is a useful source of new Se–N systems.

There are two well-established methods for the synthesis of Se_4N_4. The first involves the reaction of $(CH_3CH_2O)_2SeO$ with gaseous ammonia in benzene.[7] The disadvantages of this method are low yields[8] and the time-consuming synthesis of $(CH_3CH_2O)_2SeO$. The second method uses the reaction of SeX_4 (X = Br, Cl) or SeO_2 with liquid ammonia at 70–80 °C, which produces Se_4N_4 in up to 75% yields but requires high-pressure apparatus.[4b,9] An easier, high-yield synthesis of Se_4N_4 would therefore be useful.[10]

We describe here two practical routes for the preparation of small amounts of Se_4N_4: (a) the reaction of $(Me_3Si)_2NLi$ with a mixture of Se_2Cl_2 and $SeCl_4$ (designed to give a Se:Cl ratio of 1:3) and (b) the reaction of $[(Me_3Si)_2N]_2Se$[11,12] with $SeCl_4$.[13] Both reactions are carried out in dichloromethane at –78 °C.

Experimental Section

Reagents and General Procedures. Solvents were dried and freshly distilled under a nitrogen atmosphere before use: dichloromethane (P_4O_{10}) and diethyl ether (Na/benzophenone). All reactions and the manipulations of air- and moisture-sensitive reagents were carried out under an atmosphere of nitrogen (99.99% purity), passed through P_4O_{10}. The commercially available reagents Se_2Cl_2 (Aldrich), $(Me_3Si)_2NH$ (Aldrich), and *n*-BuLi (1.6 M solution in hexanes, Aldrich) were used without further purification. Literature procedures were used for the preparation of $[(Me_3Si)_2N]_2Se$ [$\delta(^1H)$ (in CH_2Cl_2) 0.25 s, cf. lit. 0.27 s (in CCl_4)[11] and 0.33 s (in C_6D_6);[12] $\delta(^{77}Se)$ (in CH_2Cl_2) 1129 ppm, cf. lit. 1130 ppm (in C_6D_6)[12]], $SeCl_4$,[14] and Se_4N_4.[8] The identity of $SeCl_4$[14] and Se_4N_4[15] was confirmed by comparison of IR spectra with those reported in the literature.

Instrumentation. Infrared spectra were recorded as Nujol mulls between KBr disks on a Mattson 4030 spectrometer. ^1H NMR spectra were obtained by use of a Bruker ACE 200 instrument, and chemical shifts are reported relative to neat TMS. ^{77}Se NMR spectra were recorded by using a Bruker AM 400 spectrometer, and chemical shifts are reported relative to neat $(CH_3)_2Se$, [$\delta(CH_3)_2Se = \delta(SeO_2) + 1302.6$ ppm]. The analysis for Se was carried out by a slightly modified literature procedure.[16,17]

Preparation of Se_4N_4. ***Caution!*** Dry, purified Se_4N_4 is extremely explosive when heated or subjected to mechanical stress, e.g. a metal spatula. It is strongly recommended that Se_4N_4 be stored and handled under a hydrocarbon solvent. The preparation of Se_4N_4 should be limited to small amounts (<1.0 g). Since the detonation of even sub-gram quantities of Se_4N_4 can be quite destructive, a polycarbonate blast shield should be employed and the experimenter should wear heavy-duty gloves and ear protection.

(a) Reaction of $(Me_3Si)_2NLi$ with Se_2Cl_2 and $SeCl_4$. A mixture of $(Me_3Si)_2NH$ (0.80 g, 5.0 mmol) in diethyl ether (10 mL) and *n*-BuLi (5.0 mmol, 3.1 mL of a 1.6 M solution in hexane) was stirred at 0 °C for 1 h. Solvents were then removed under vacuum, and the product $(Me_3Si)_2NLi$ was dissolved in CH_2Cl_2 (10 mL). This solution was added dropwise, with stirring, to a mixture of Se_2Cl_2 (0.19 g, 0.83 mmol) and $SeCl_4$ (0.74 g, 3.36 mmol) in CH_2Cl_2 (10 mL) at –78 °C. The reaction mixture was allowed to warm slowly to room temperature, and stirring was continued for 16 h. The red precipitate was removed by filtration and washed with acetone (2 × 10 mL), 10% aqueous KCN solution (4 × 10 mL), water (4 × 10 mL), and CH_2Cl_2 (2 × 10 mL) to give Se_4N_4 (0.309 g, 0.83 mmol, 66%) as a bright orange powder. Anal. Calcd for N_4Se_4: Se, 84.9. Found: Se, 85.9. IR (cm^{-1}): 797 s, 784 s, 565 (vs, sh), 530 m, 426 s (cf. lit.[15] 838 vw, 800 s, 788 s, 624 vw, 570 vs, 534 m, 425 s).

(b) Reaction of $[(Me_3Si)_2N]_2Se$ with $SeCl_4$. A solution of $[(Me_3Si)_2N]_2Se$ (0.20 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a slurry of $SeCl_4$ (0.11 g, 0.50 mmol) in CH_2Cl_2 (10 mL) at –78 °C. The reaction conditions and purification procedure were the same as those described in method a, and Se_4N_4 (0.066 g, 0.177 mmol, 71%) was obtained as a bright orange powder. Anal. Calcd for N_4Se_4: Se, 84.9. Found: Se, 84.2. IR (cm^{-1}): 795 m, 781 s, 623 w, 577 vs, 556 s, 532 m, 424 s.

---

(1) (a) The University of Calgary. (b) University of Oulu.

(2) (a) Chivers, T. *The Chemistry of Inorganic Homo- and Heterocycles*, Academic Press Inc.: London, 1987; Vol. 2, pp 793–869. (b) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.

(3) Klapötke, T. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier Science Publishers, Amsterdam, 1992; pp 409–427.

(4) (a) Awere, E. G.; Passmore, J.; White, P. S.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1415. (b) Awere, E. G.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1993**, 299.

(5) (a) Kelly, P. F.; Slawin, M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 408. (b) Kelly, P. F.; Parkin, I. P.; Slawin, A. M. Z.; Williams, J. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1047.

(6) (a) Adel, J.; Dehnicke, K. *Chimia* **1988**, *42*, 413. (b) Adel, J.; El-Kholi, A.; Willing, W.; Müller, U.; Dehnicke, K. *Chimia* **1988**, *42*, 70.

(7) (a) Strecker, W.; Schwarzkopf, Z. *Anorg. Allg. Chem.* **1935**, *221*, 193. (b) The preparation of ^{15}N-enriched Se_4N_4 by this method using *stoichiometric* amounts of $^{15}NH_3$ has been reported recently: Ginn, V. C.; Kelly, P. F.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1992**, 2129.

(8) Although yields of 25% are reported in ref 7a, we have only been able to obtain yields of ca. 5% in numerous preparations of Se_4N_4 by this method.

(9) Jander, J.; Doetsch, V. *Chem. Ber.* **1960**, *93*, 561.

(10) Recently a new route to Se_4N_4 involving the reaction of $Pt(Se_2N_2)(dppe)$ with Cl_2 or Br_2 was described. The Pt(II) complex is prepared from $SeCl_4$ and $PtCl_4(dppe)$ in liquid ammonia. The reported yields of 85% for Se_4N_4 appear to have been calculated incorrectly. On the basis of 0.064 mmol of reactants, the reported yield of Se_4N_4 (0.020 mmol) should be ca. 63%. See: Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *57*, 273.

(11) Bjorgvinsson, M.; koesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140.

(12) (a) Haas, A.; Kasprowski, J.; Angermund, K.; Betz, P.; Krüger, C.; Tsay, Y.-H.; Werner, S. *Chem. Ber.* **1991**, *124*, 1895. (b) Haas, A.; Kasprowski, J. *Chimia* **1990**, *44*, 57.

(13) The formation of Se_4N_4 by method b, without details of the isolation, purification, or yield, is mentioned in ref 12.

(14) Feher, F. In *Handbook of Preparative Inorganic Chemistry*; Bauer, G., Ed.; Enke: Stuttgart, Germany, 1975; Vol. 1, pp 416–417.

(15) Adel, J.; Ergezinger, C.; Figge, R.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 639.

(16) Cooper, C. W. In *Selenium*; Zingaro, R. A., Cooper, C. W., Eds.; Van Nostrand Reinhold Co.: New York, 1974; p 615.

(17) Samples of Se_4N_4 (100-300 mg) were weighed in a glass filter immediately after preparation and purification. The samples were then transferred to a 100-mL Erlenmeyer flask as a slurry in CH_2Cl_2. The samples were then chlorinated carefully and analyzed for Se as described in ref 16.

0020-1669/93/1332-1519$04.00/0

Results and Discussion

The reaction of $(Me_3Si)_2NLi$ with $SeOCl_2$ produces the thermally unstable selenium diimide $Me_3SiN{=}Se{=}NSiMe_3$,[18] while treatment of $(Me_3Si)_2NLi$ with Se_2Cl_2 gives rise to $[(Me_3Si)_2N]_2Se$[11,12] and $[(Me_3Si)_2N]_2Se_2$.[12,19] In order to prepare Se_4N_4 from $(Me_3Si)_2NLi$ and selenium halides, via cyclocondensation, it is desirable to use selenium in an average oxidation state of +3. A mixture of Se_2Cl_2 and $SeCl_4$ in a 1:4 molar ratio yields a Se:Cl ratio of 1:3.[20] When this mixture is treated with $(Me_3Si)_2NLi$ in CH_2Cl_2 at −78 °C and the resultant mixture allowed to warm to room temperature, pure Se_4N_4 is isolated as a bright orange powder in 66% yield. The purification of Se_4N_4 is easily achieved by the standard procedure of washing with 10% aqueous KCN solution to remove red selenium, selenium halides, and selenium oxides[7,9] and with water to remove lithium chloride. The reaction filtrate was shown to contain only Me_3SiCl (δ 0.39 ppm) by ^1H NMR spectroscopy. Thus this preparation of Se_4N_4 can be represented by eq 1.

$$12(Me_3Si)_2NLi + 2Se_2Cl_2 + 8SeCl_4 \rightarrow 3Se_4N_4 + 24Me_3SiCl + 12LiCl \quad (1)$$

The reaction of $[(Me_3Si)_2N]_2Se$ with $SeCl_4$ was shown to form Se_4N_4 as reported earlier (eq 2).[12,13] In this investigation the

$$2[(Me_3Si)_2N]_2Se + 2SeCl_4 \rightarrow Se_4N_4 + 8Me_3SiCl \quad (2)$$

yield of purified Se_4N_4 was 71%. The quantitative conversion of $[(Me_3Si)_2N]_2Se$ (δ 0.25 ppm) into Me_3SiCl (δ 0.39 ppm) was established by monitoring the reaction by ^1H NMR spectroscopy.

Since $[(Me_3Si)_2N]_2Se$[19] must first be prepared from $(Me_3Si)_2NLi$, method a (eq 1) represents the preferred route to Se_4N_4. Compared to the existing syntheses of Se_4N_4,[7-9] this method is quick and relatively safe and utilizes readily available starting materials. Thus it should facilitate studies of this interesting heterocycle.

Acknowledgment. Financial support from the NSERC (Canada) and the Academy of Finland is gratefully acknowledged. J.S. was an exchange student at The University of Calgary supported by the Neste Oy Foundation, Espoo, Finland.

---

(18) Fockenberg, F.; Haas, A. *Z. Naturforsch.* **1986**, *41B*, 413.

(19) $[(Me_3Si)_2N]_2Se$ was prepared by using the procedure described in ref 11. It was confirmed (see ref 12) that the diselenide $[(Me_3Si)_2N]_2Se_2$ is also produced in this reaction.

(20) The methodology of mixing selenium halides to produce selenium in an average oxidation state of +2.5 has been utilized in the preparation of $(SSe_2N_2X)_2$ (X = Cl, Br): Wolmershäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586.