

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

Small Chalcogen Rings

Pentti Pekonen^a; Jari Taavitsainen^a; Risto S. Laitinen^a

^a Department of Chemistry, University of Oulu, Oulu, Finland

To cite this Article Pekonen, Pentti, Taavitsainen, Jari and Laitinen, Risto S. (1994) 'Small Chalcogen Rings', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 93: 1, 467 – 468

To link to this Article: DOI: 10.1080/10426509408021907

URL: <http://dx.doi.org/10.1080/10426509408021907>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SMALL CHALCOGEN RINGS

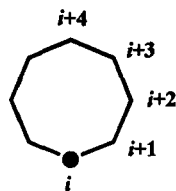
PENTTI PEKONEN, JARI TAAVITSAINEN and RISTO S. LAITINEN
Department of Chemistry, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland

Abstract The reaction of $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{S}_3]$ with Se_2Cl_2 produces 1,5- Se_2S_5 , 1,2,3,4,5- Se_5S_3 , and 1,2- Se_2S_6 as the main end products. This implies the existence of 1,2- Se_2S_3 as an initial reaction product the decomposition of which proceeds with parallel selenium atom transfer and dimerization reactions.

Bis(cyclopentadienyl)titanium chalcogenides of the types $[\text{TiCp}_2\text{E}_5]$ and $[\text{TiCp}_2(\text{E}_2)_2\text{TiCp}_2]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) are well known to be good precursors for heterocyclic chalcogen rings.¹ In the present work we report the reaction of $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{S}_3]$ with Se_2Cl_2 that should initially form a five-membered 1,2- Se_2S_3 . It is, however, unstable and decomposes rapidly to larger ring molecules. The nature of the final products should give information about the transient existence of 1,2- Se_2S_3 .

The composition of the reaction mixture was monitored as a function of time with ^{77}Se NMR spectroscopy. The first signals to appear are those at 683, 653, 593, and 587 ppm with a later appearance of a signals at 629 and 610 ppm. The five latter resonances can be assigned to 1,2,3,4,5- Se_5S_3 , 1,2- Se_2S_6 , and Se_8 based on previous information.² The assignment of the signal at 683 ppm to 1,5- Se_2S_6 requires refinement in our earlier deductions.² In the study of ^{77}Se -enriched selenium sulfide mixtures (enrichment 92 %) the singlets at 729, 717, and 687 ppm were assigned to 1,3-, 1,5-, and 1,4-isomers, respectively with a provision that the assignment can also be interchanged. With the accumulation of definite ^{77}Se chemical shift data of the eight-membered selenium sulfide rings, a quantitative dependence of the chemical shift with the nature and location of the ring atoms can now be made and these singlets definitely assigned. The least-squares fit of the chemical shift data resulted the following equation:

$$\delta = -66.6 n_1 + 14.2 n_2 + 19.7 n_3 - 6.0 n_4 + 699.0$$



where n_1 is the number of Se atoms adjacent to the active Se nucleus (i), n_2 , n_3 , and n_4 the number of Se atoms in the $i+2$, $i+3$, and $i+4$ positions, respectively. The calculated chemical shifts of the four isomers of Se_2S_6 are thus: 1,2- Se_2S_6 632 ppm, 1,3- Se_2S_6 713 ppm, 1,4- Se_2S_6 719 ppm, and 1,5- Se_2S_6 693 ppm. The earlier assignment must thus be modified and the signal at 683 ppm of the present work assigned to 1,5- Se_2S_6 .

The appearance of 1,5- Se_2S_6 , 1,2,3,4,5- Se_5S_3 , and 1,2- Se_2S_6 as the main end products in the reaction of $[\text{Ti}(\text{C}_5\text{Ne}_5)_2\text{S}_3]$ and Se_2Cl_2 implies the formation of 1,2- Se_2S_3 with rapid decomposition involving parallel selenium atom transfer reactions and dimerization (see Fig. 1).

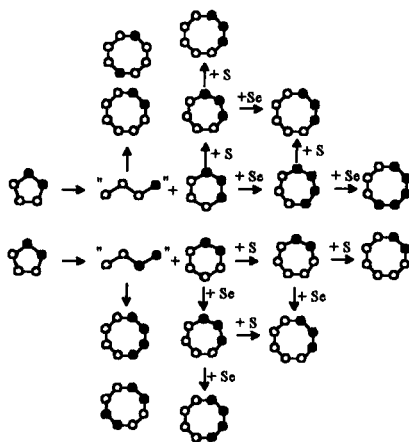


FIGURE 1 The decomposition of 1,2- Se_2S_3 involving both selenium and sulfur atoms transfer reactions as well as dimerization. It can be seen that sulfur atoms transfer does not lead to the observed end products.

REFERENCES

1. R.S. Laitinen, P. Pekonen, and R.J. Suontamo, *Coord. Chem. Rev.*, **130**, 1 (1994).
2. R.S. Laitinen and T.A. Pakkanen, *Inorg. Chem.*, **26**, 2598 (1987).