

Synthesis, structure, and chemistry of selenium-containing four-membered rings*

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Abstract: Recent chemistry of four-membered ring selenium compounds is reviewed followed by a summary of work in our laboratories in this area. 2-Thia-6-selenaspiro[3.3]heptane has been synthesized for the first time. X-ray structures for the latter compound as well as for 2,6-dithiaspiro[3.3]heptane and 2,6-diselenaspiro[3.3]heptane have been determined. These compounds are useful as “rigid-rod” ligands for coordination to transition-metal complexes.

Keywords: Selenium; four-membered rings; X-ray structures; metal complexes; selenetane.

INTRODUCTION

Thietanes and related sulfur-containing four-membered rings are well-studied heterocycles of interest as natural substances, products of commerce, novel ligands in transition-metal complexes, substrates for organic synthesis, and photochemical and pyrolytic precursors for heteroatom species $R_2M=X$ [1]. In contrast, selenetanes and related selenium-containing four-membered rings have been relatively little studied [1d,2]. We have initiated a research program to synthesize and study new chalcogen-containing heterocycles, including those with four-membered rings, and their metal complexes. We describe here recent work in our laboratory on one novel class of selenium-containing four-membered rings, namely, the 2,6-dichalcogenospiro[3.3]heptanes. This work is presented in the context of work in other laboratories on selenium-containing four-membered rings and their metal complexes, which will first be briefly reviewed.

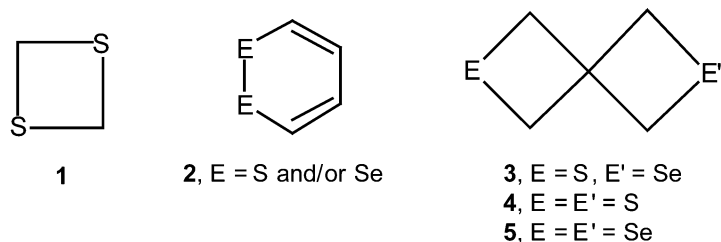
The structure of selenetane has been determined by microwave spectroscopy [3a], and the synthesis, oxidation, anionic polymerization, and other aspects of the chemistry of 3,3-dimethylselenetane and other 3-substituted selenetanes have been reported [3b–e]. Adams has developed a useful approach to the synthesis of mesocyclic polyselenacycloalkanes such as 1,5,9-triselenacyclododecane using rhenium carbonyl complexes of 3,3-dimethylselenetane as catalysts [3f,g], while Fischer has prepared tungsten complexes of selenetanes by thermal cycloaddition of vinyl ethers to transition-metal-coordinated selenoaldehydes [3h]. The Taxol[®] oxetane ring has been replaced by a selenetane ring [3i], several studies of 1,3-diselenetanes have appeared [3j,k], and syntheses of a 1,3-disila-2,4-diselenetane ($R_2Si=Se$ dimer) [3l], a 1-selena-2-siletane [3m], a selenathietane [3n], and 1,3-oxaselenetanes [3o,p] are reported. Other recent papers report the isolation of a 2*H*-benzoselenete [3q], metal complexes of a 2*H*-selenete [3r], synthesis and X-ray structure of a selenet-2(2*H*)-imine [3s], synthesis of novel struc-

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tures containing selenetanes fused to furanoside rings [3t,u], and general new methods for the synthesis of selenetanes [3v].

We have previously synthesized and explored the chemistry of 4- and 6-membered rings containing two sulfur or selenium atoms, such as 1,3-dithietane, **1**, and 1,2-dithiin, 1,2-diselenin, and 2-selenathiin, **2** [4–7] as well as the structure and coordination chemistry of small acyclic organoselenium compounds including dimethyl diselenide [8], dimethyl selenoxide [9], and dimethyl selenone [10]. We sought to extend these studies to other unknown or little studied heterocycles containing sulfur and/or selenium, particularly those containing the selenetane ring, whose coordination chemistry has been scarcely studied. Here, we report the synthesis and characterization of the previously unknown heterocycle, 2-thia-6-selenaspiro[3.3]heptane, **3**, as well as the known, but incompletely characterized 2,6-diselenaspiro[3.3]heptane, **5** [3b] and the better studied 2,6-dithiaspiro[3.3]heptane, **4** [11]. Compounds **3–5** are useful as “rigid-rod” ligands with a sigma-bonded framework.



RESULTS AND DISCUSSION

Heterocycle **3** was synthesized from 1,3-dibromo-2,2-bis(bromomethyl)propane, **6**, (Scheme 1) by replacement of one of the bromines with thioacetate, treatment with base to give 3,3-bis(bromomethyl)thietane, **7**, and conversion of **7** to **3** by Li_2Se (from Se and LiEt_3BH) in THF [12,13]. Heterocycle **4** was prepared as described previously [11]. Heterocycle **5** was prepared in 70 % yield by reaction of Li_2Se in refluxing THF with **6**. Selected data for **3**, **4**, and **5** (all colorless solids) are given: **3**, m.p. 45 °C, ^1H NMR δ 3.16 (s, 4H), 3.18 (s, 4H), ^{13}C NMR δ 27.3, 41.1, 53.3; **4**, m.p. 31 °C, ^1H NMR δ 3.26 (s), ^{13}C NMR δ 39.8, 52.2; **5**, m.p. 68 °C, ^1H NMR δ 3.14 (s), ^{13}C NMR δ 28.7, 54.4. X-ray structures for **3** and **4** are shown in Fig. 1; data appear in Table 1 [13]. X-ray structures for metal-free selenetanes have not been previously reported. The coordination chemistry of **3–5** as rigid-rod ligands toward complexes of cobalt, copper, nickel, and rhodium, and full X-ray structure of **5** have been

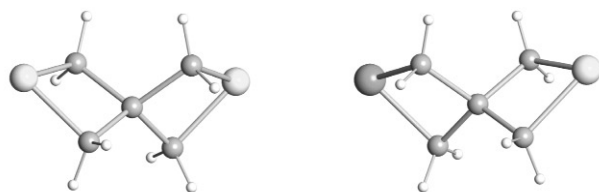
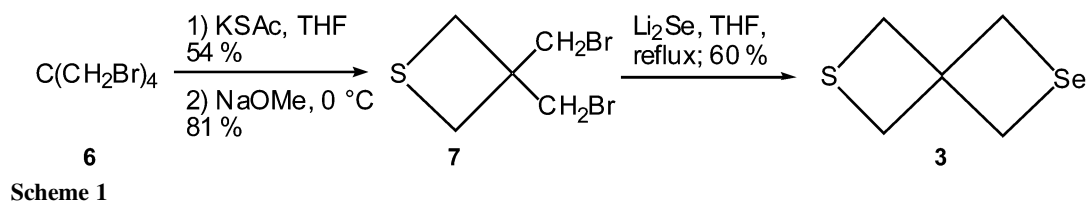


Fig. 1 X-ray crystal structures of **4** (left) and **3** (right; the Se atom is on the left in **3**).

reported [14]. A study of magnetic properties shows that complexes of **5** do not facilitate magnetic interactions between paramagnetic metal centers [13].

Table 1 Selected distances (Å) and angles (°) in 2,6-diheterospiro[3.3]heptanes **3–5**.

	3*	4	5
E–C _{av}	1.908(6)	1.835(1)	1.978(3)
C–C _{av}	1.535(2)	1.536(2)	1.537(4)
E•••E	4.792(6)	4.690(1)	4.906(1)
C–E–C _{av}	74.1(1)	76.65(6)	72.0(1)
C–C–C	97.0(1)–120.0(1)	96.1(1)–121.1(1)	98.1(2)–119.1(2)

*Average for the two mixed positions

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