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Oxidation of 1,3,2-diselenaphospholanes with an annelated dicarba-*closo*-dodecaborane(12) unit by addition of sulfur and selenium. Molecular structure of a novel 1,2,4,5-tetraselena-3-phospha heterocycle

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ABSTRACT

1,3,2-Diselenaphospholanes with an annelated dicarba-*closo*-dodecaborane(12) unit are slowly oxidized, except of the phosphorus halides, by addition of sulfur without side reaction. The analogous reaction with selenium, also slow, is accompanied either by uncontrolled decomposition or by insertion of selenium into P–Se bonds to give novel seven-membered rings containing two μ-Se_2 units. All products are characterized by multinuclear magnetic resonance methods (^{1}H, ^{11}B, ^{13}C, ^{31}P, ^{77}Se NMR spectroscopy), supported by calculations on the B3LYP/6-311+G(d,p) level of theory, and the molecular structure of one example of a 1,2,4,5-tetraselena-3-phospha heterocycle was determined by X-ray crystallography.

1. Introduction

During the last five decades the chemistry of 1,2-dicarba-*closo*-dodecaborane(12) ("*ortho*-carborane"), in particular, and its isomers has attracted enormous interest [1–4]. In the case of *ortho*-carborane, metalation at the carbon atoms is straightforward and enables to introduce a great variety of substituents in the 1,2-positions, providing useful reagents for further transformations. In this context, the 1,2-dichalcogenido-1,2-dicarba-*closo*-dodecaborane anions $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})E_2]^{2-}$ (E = S, Se, Te) have been used frequently as chelating ligands in transition metal chemistry [1,5–14] and the main group element chemistry of these dianions is currently being developed [1,5,15–18]. Whereas access to the dianion with E = Te appears to be somewhat difficult [19], the species with E = S [5a,20] and E = Se [20a,21] can be used conveniently. Progress has been made in the synthesis of 1,3,2-diselenaphospholanes with an annelated dicarba-*closo*-dodecaborane(12) unit [22,23]. The solid state structure of two examples, with a phenyl group (**1**) [22] or iodine **2** [23a] at phosphorus, showed remarkable differences with respect to the conformation at phosphorus. Usually, oxidation of P(III)–P(V) by adding sulfur or selenium is a proper method to obtain more stable and eventually crystalline materials, which proved to be true for **5a**, the sulfide of **1**. However, the formation of the corresponding selenide **5b** was found to be slow, the yield turned out to be low, and numerous unidentified side products were formed [22a]. One reason could be the bulky *ortho*-carborane unit which, on the other hand, helps for kinetic stabilization. Other reasons might be traced to the labile Se–P bonds themselves. Since the reactivity of P–Se bonds has not been systematically investigated as yet, we have studied again the reaction of the phenyl derivative **1** with selenium and also explored the reactivity of some other 1,3,2-diselenaphospholanes **2**–**4** (Scheme 1) with respect to their oxidation with sulfur and selenium.

2. Results and discussion

Whereas the phosphorus iodide **2** does not react at all with sulfur or selenium in CD_2Cl_2 at ambient temperature (24 h), even after 72 h at 50 °C (decomposition), the isopropyl (**3**) and the ethoxy (**4**) derivatives were slowly oxidized (Scheme 2). With

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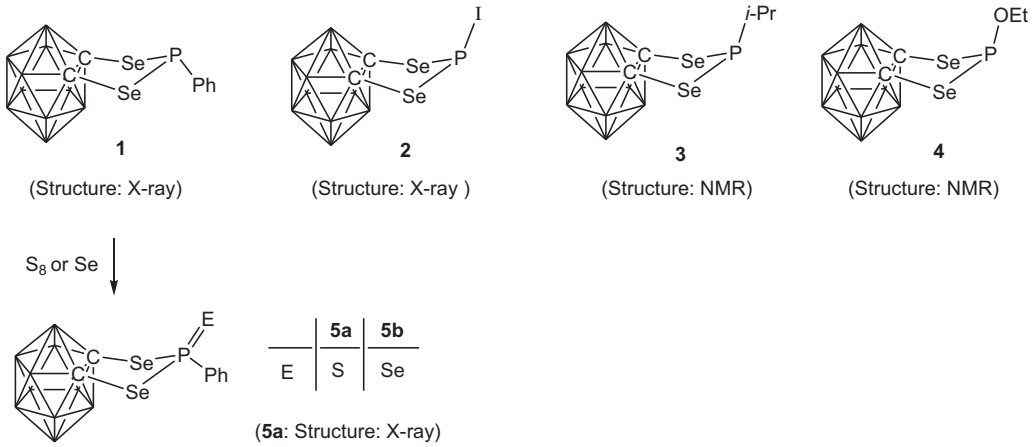


Scheme 1. 1,3,2-Diselenaphospholanes with an annelated dicarba-*closo*-dodecaborane(12) unit. Previous results for the oxidation of **1** are shown.

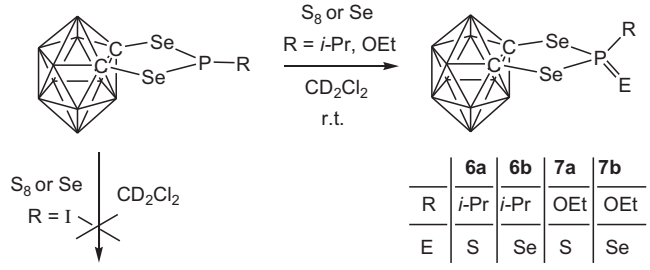
sulfur, the products **6a** and **7a** are reasonably stable, at least for NMR spectroscopic characterization in solution (Table 1). The situation is somewhat different for the selenides **5b**, **6b**, and **7b**. Attempts to oxidize **1**–**3** with tellurium failed, the formation of small amounts of the selenides **5b** and **6b**, respectively, was observed instead (^{31}P NMR spectroscopy), together with numerous unidentified products.

In contrast with the sulfide **7a**, which was sufficiently stable for measuring a complete set of NMR data, the selenide **7b** decomposed rapidly in solution, and only a few NMR data could be measured (Table 1). In the case of **1**, almost pure samples were obtained, when its reaction with selenium was carried out in CD_2Cl_2 at ambient temperature for 2 d. In the presence of an excess of selenium at 50 °C, a second (**8**) and a third product (**9**) (in minor quantity) were formed (Scheme 3).

In contrast with the first explorative study [22a], we have used highly purified samples of **1**, in order to suppress uncontrolled extensive decomposition. The proposed structures of **8** and **9** are in agreement with ^{31}P and ^{77}Se NMR spectra (Fig. 1) as well as with calculated NMR data (Table 2). The structural assignment with respect to the orientation of the P=Se bond is tentative, following the calculation of NMR parameters (*vide infra*).

Similarly, monitoring the reaction of **3** with selenium by ^{31}P NMR spectroscopy (Fig. 2) showed slow formation of **6b**, accompanied by a further reaction to give a second product **10** (Scheme 4). Compound **10** was much less soluble than **6b**, and it could be identified as the seven-membered heterocycle **10** by characteristic NMR data, similar to those of the phenyl derivative **8** (Fig. 2, Table 2), and by X-ray structural analysis (*vide infra*).

Crystals of **10** were dissolved in CD_2Cl_2 and NMR spectra were measured again, to confirm the previous spectral assignments for the mixtures (see also Fig. 3 for ^{1}H{^{11}B} and ^{11}B{^{1}H} NMR spectra, together with calculated chemical shifts δ^{11}B).



Scheme 2. Reaction of some 1,3,2-diselenaphospholanes with sulfur and selenium.

Mainly two facts are worth mentioning: (i) in the cases of **8**–**10**, there is no indication for other products containing only three or more than four selenium atoms in the ring; (ii) whereas the selenide **6b** apparently quite readily inserts selenium into P–Se bonds, the sulfide **6a** does not. Therefore, it is conceivable that the P=Se group is involved, from which selenium migrates and is immediately replaced by elemental selenium. It is interesting to note that the selenium-rich heterocycles **8**–**10** appear to be fairly stable toward loss of selenium. Other comparable heterocycles containing four selenium atoms as μ-Se_2 units in the ring have been reported to require rather forcing conditions to be formed and split off red selenium already below ambient temperature, *e.g.* the six-membered rings R(Se)P(μ-SeSe)$_2$P(Se)R (R = Me, Ph, ferrocenyl), which readily give R(Se)P(μ-Se_2)SeP(Se)R and selenium [25]. In fact, large rings containing μ-Se_2 units are rare [26,27], and the more general synthesis of some examples containing one μ-Se_2 unit has been reported only recently, starting from Woollins reagent [28].

2.1. MO calculations: molecular geometries, NMR parameters

The gas phase geometries of all products were optimized at the B3LYP/6-311+G(d,p) level of theory [29]. These calculations revealed rather small differences in energy (<0.5 kcal/mol) for the conformers **A** and **A′** as well as for **B** and **B′** (R = Ph) (Fig. 4), whereas a larger difference was calculated (4.3 kcal/mol) for **B** and **B′** (R = *i*-Pr), and NMR signals for **B′** (R = *i*-Pr) were not observed in solution. Another structure **B″** with a twist conformation is conceivable which, according to calculations for R = Ph, is less favorable (2.3 kcal/mol) than **B** and **B′**. Fast reversible rearrangement for **A** and **A′** is proposed considering the almost planar five-membered CCSePSe rings. The calculated Se- and P-element bond lengths for **10** are longer than those found experimentally (Table 3). Calculated bond angles for **10** are close to experimental values.

The overall trend of calculated δ^{77}Se data (Tables 1 and 2) is correct, and helps to distinguish the isomers **B** and **B′** (see Table 2). Considerable deviations from experimental data are still reasonable given for the large range of chemical shifts δ^{77}Se [30] and shortcomings of the theoretical model [31,32]. This also applies to the comparison of calculated and experimental coupling constants involving ^{77}Se [33]. Thus, the mean values of NMR data for **A** and **A′** must be compared with experimental data. In the cases of **8**–**10**, the trend of calculated data is in agreement with the proposed structures, confirmed by the experimental structure, established for **10**.