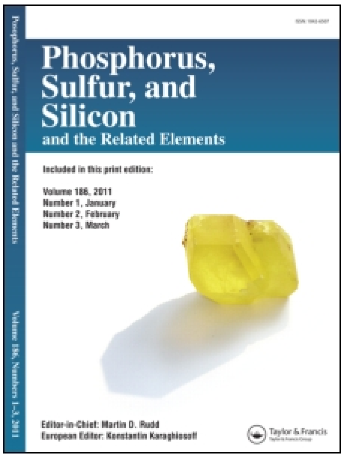

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Fujihara, Hisashi , Mima, Hisatomo and Furukawa, Naomichi(1992) 'Formation of Dication and Hypervalent Bond from *5H,7H*-Dibenzo[*b,g*][1,5]Selenazocine', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 141 — 144

To link to this Article: DOI: 10.1080/10426509208045830

URL: http://dx.doi.org/10.1080/10426509208045830

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 141–144
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FORMATION OF DICATION AND HYPERVALENT BOND FROM *5H,7H*-DIBENZO[*b,g*][1,5]SELENAZOCINE

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Abstract The reaction of the selenoxide **2** of *N*-methyl-*5H,7H*-dibenzo-[*b,g*][1,5]selenazocine (**1**) with $(CF_3SO_2)_2O$ gave the selenaza dication salt **3** which acts as an oxidizing agent. A novel σ-selenurane **4** was prepared by either the reaction of selenide **1** with *t*-BuOCl or the reaction of selenoxide **2** with $SOCl_2$; the crystal structure of **4** shows the chloroammonioselenurane with a distorted trigonal-bipyramidal geometry around the selenium atom.

Transannular bond formation (*e.g.*, dication and hypervalent bond) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulfur atoms has been extensively studied.[1] In contrast, such species of medium-sized selenium heterocycles have received less attention. This paper describes a new type of σ-bonded dication and hypervalent bond containing selenium atom from **1**.

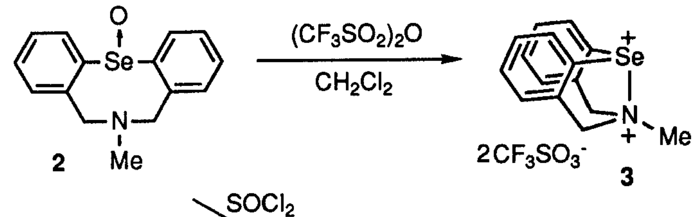
Isolation of Selenaza Dication Salt[2]

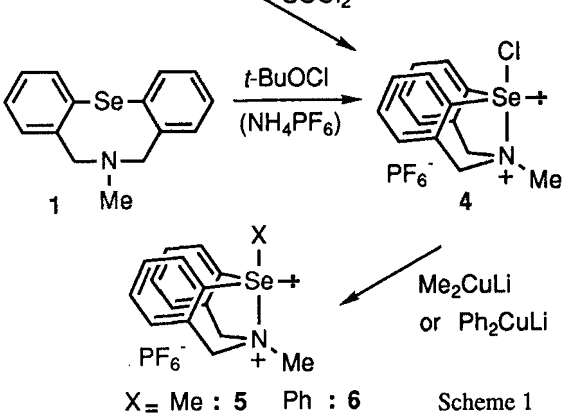
With regard to the conformational properties of heterocyclic analogs of dibenzocyclooctane, for eight-membered rings typically two different conformers, the boat-chair (*BC*), and the twist-boat (*TB*) and/or the boat-boat (*BB*) forms can exist. The conformers can be assigned by the ^1H NMR spectral data for benzylic protons of the eight-membered ring. The ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows that the benzylic methylene protons appear as a broad singlet at δ 4.04. At -50 °C, its absorption is splitted into at δ 3.75 (br s), and at δ 4.09 and 5.08 (ABq, *J*=14 Hz) which are assigned to the TB-form (74%) for the former and the BC-form (26%) for the latter. Those conformers can be characterized by ^{77}Se NMR spectroscopy; *i.e.*, the ^{77}Se NMR spectrum of **1** in $CHCl_3$ at 25 °C shows a very broad peak at δ 379, while its selenium absorption becomes two singlet peaks at δ 383 and 356 at -50 °C in which the ratio of the conformers is consistent with that obtained from the ^1H NMR spectrum. In contrast, the selenoxide **2** indicates a single conformer, TB-form, as evidenced by the variable temperature ^1H and ^{77}Se NMR spectroscopy.

The reaction of **2** with $(CF_3SO_2)_2O$ gave the dication **3** as a stable crystalline salt (Scheme 1). The ^1H NMR spectrum of **3** in CD_3CN exhibits absorptions at δ 3.31 (br s, 3H), 4.82 (br s, 4H), and 7.46-8.54 (m, 8H). The ^{77}Se NMR spectrum of **2** in $CHCl_3$ shows a singlet peak at δ 847 (relative to Me_2Se), while dication **3** in CH_3CN shows a singlet peak at δ 1005. These are remarkable downfield shifts, consistent with a dicationic structure for **3**. While the ^{19}F NMR spectrum of trifluoromethanesulfonate anion for **3** in CH_3CN shows a single fluorine absorption at δ 85.4 (relative to C_6F_6), in the region of ionic $CF_3SO_3^-$. Although dications bonded by two positively charged heteroatoms are a little known, such dications consisting of two different heteroatoms are quite rare.

A New Hypervalent Selenurane with a Transannular Se-N Bond[3]

A number of hypervalent organosulfur compounds, sulfuranes, have been reported. In contrast, much less is known about the chemistry of selenuranes. Chloro substituted σ-ammonioselenurane **4** was isolated from the reaction of selenide **1** with *t*-BuOCl (Scheme 1). *t*-BuOCl is widely used as an oxidant for the conversion of selenides into selenoxides, *e.g.*, treatment of **1** first with *t*-BuOCl followed by alkaline hydrolysis with saturated sodium hydrogen-carbonate solution gave exclusively the selenoxide **2** in 83% yield, contrasting with the oxidation of **1** using *m*-chloroperbenzoic acid which gave a mixture of **2** and the *N*-oxide. Although a chloroselenonium salt and/or hypervalent species have been proposed as intermediates in the reaction of diarylselenides with *t*-BuOCl, there is no example of isolation of its selenurane. Analogously, treatment of selenoxide **2** with $SOCl_2$ in anhydrous CH_2Cl_2 at room temperature followed by adding with NH_4PF_6 afforded selenurane **4** in 85% yield (Scheme 1).





Scheme 1

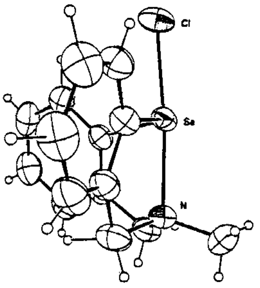


Figure 1

The structure of **4** in solution was characterized by multinuclear NMR (^1H, ^{13}C, ^{77}Se, and ^{31}P) spectroscopy. The ^1H NMR (500 MHz) spectrum of **4** in CD_3CN shows peaks at δ 3.12 (s, 3H, CH_3), 4.59, 4.63 (ABq, J=15.7 Hz, 4H, CH_2), 7.49-7.54 (m, 2H, ArH), 7.68-7.75 (m, 4H, ArH), and 8.35-8.40 (m, 2H, ArH) which show downfield shifts relative to those of **1** and **2**; while the ^{13}C NMR (125 MHz, CD_3CN) spectrum shows absorptions at δ 45.1, 62.4, 128.7, 130.7, 131.6, 132.6, 134.7, and 139.4. The ^{77}Se NMR spectrum of **4** in CH_3CN shows a singlet peak at δ 813.4 (relative to Me_2Se). The ^{31}P NMR spectrum of the PF_6^- anion of **4** in CH_3CN shows a phosphorus absorption at δ -143.2 (sept, J_{PF}=707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-. These spectroscopic evidence indicate that **4** is a single conformer, *i.e.*, *TB* or *BB* form in solution. The selenurane **4** exists solely as a single conformer from -40 to +70 °C as evidenced from the variable temperature ^1H NMR spectral data, though the selenazocine **1** shows the existence of two conformers.

The crystal structure of **4** was determined by X-ray diffraction analysis (Figure 1). The Se-N distance is 2.191 Å which is significantly shorter than the sum of the van der Waals radii (3.50 Å), indicating the transannular bond formation between Se and N. The Se-Cl bond length (2.296 Å) is close to that of diphenylselenium dichloride (2.30 Å). The Cl-Se-N bond angle of 174.3° is approximately collinear, and the C_{eq}-Se-C_{eq} bond angle is 101.7°. Thus, the configuration about the selenium atom is slightly distorted trigonal bipyramid with two apical Se-N and Se-Cl bonds, two equatorial Se-C bonds and the lone pair electrons considered to occupy the third equatorial position. These structural features are consistent with σ-selenurane structure.

Treatment of the *Se*-chloro derivative **4** with $(CH_3)_2CuLi$ or $(C_6H_5)_2CuLi$ resulted in the formation of the *Se*-methyl or *Se*-phenyl ammonioselenurane (**5** or **6**). The selenuranes of *Se*-methyl **5** and *Se*-phenyl **6** also show one type of absorptions in the ^1H, ^{13}C, and ^{77}Se NMR spectra. The ^1H NMR spectra of **5** and **6** in CD_3CN did not show any temperature dependence between -40 and +70 °C. These results indicate that the conformations of **5** and **6** are fixed as *TB* or *BB* form by transannular bond between the selenio and amino groups, although normally *BC* conformer has been shown to be more stable and rigid than *TB* and/or *BB* conformers.

These selenuranes **4-6** are new type of hypervalent selenium compounds, since generally σ-selenuranes bear two electronegative groups such as oxygen atoms or halogen atoms at the apical positions. While analogous sulfur compounds of **4** were reported by Akiba and coworkers.[4]

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