First Synthesis and Structure of Hexavalent Organic σ-Perselenurane Species (λ^6-Selane): Bis(2,2'-biphenylylene)difluoroperselenurane [12-Se-6(C4F2)]

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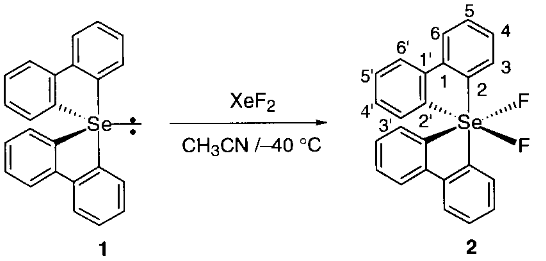
Bis(2,2'-biphenylylene)selenurane (**1**; λ^4-selane) reacts with xenon difluoride to give bis(2,2'-biphenylylene)difluoroperselenurane, [12–Se–6(C4F2)] (**2**; λ^6-selane), which was analyzed by single crystal X-ray diffraction.

There are only one neutral hexacoordinated organic selenium compounds compared with the corresponding tetracoordinated compounds which often exhibit a trigonal bipyramidal structure.[1] We tried the synthesis of new perselenurane [12–Se–6] using the bis(2,2'-biphenylylene)selenurane (**1**; λ^4-selane)[2]. Here we describe the first synthesis and isolation of bis(2,2'-biphenylylene)difluoroperselenurane, [12–Se–6(C4F2)] (**2**; λ^6-selane), and its crystal and molecular structure.

Scheme 1.



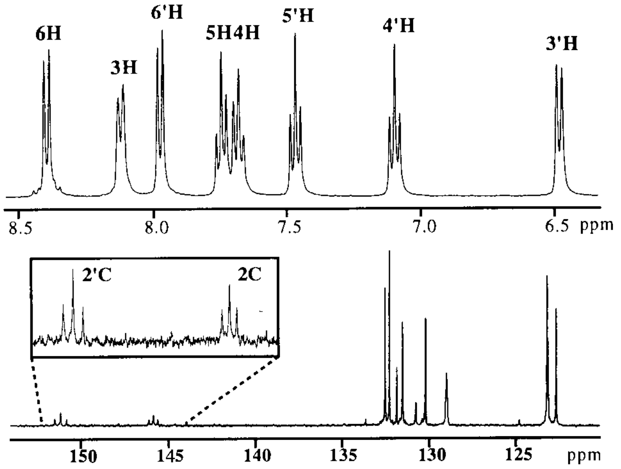


Figure 1. ^1H NMR (upper) and ^{13}C NMR (lower) spectra of **2**.

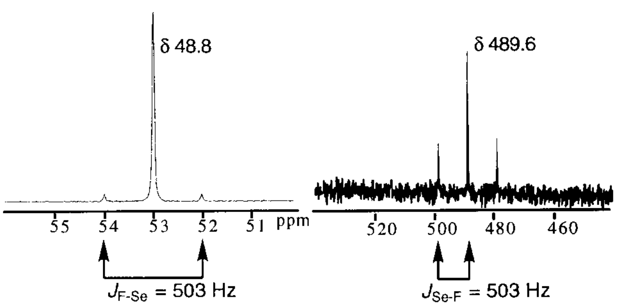


Figure 2. ^{19}F NMR (left) and ^{77}Se NMR (right) spectra of **2**.

The selenurane **1** was reacted with 1 molar equiv of xenon difluoride in dry CH_3CN at –40 °C. After the removal of the solvent at 0 °C, the corresponding tetraaryldifluoroperselenurane (**2**) was isolated as stable colorless crystals in 54% yield, as shown in Scheme 1. The product **2** was identified by ^1H, ^{13}C, and ^{77}Se NMR, mass spectroscopy, and elemental analysis.[3]

In the case of [12–Se–6(X4Y2)] having X and Y ligands (where, Y is a more electronegative ligand than X), it is known that the corresponding pertelluranes with these ligands in the *cis* configuration tend to be more stable than the corresponding *trans* configuration and the results of various NMR spectra indicate that the two X ligands on the Y–Te–Y plane are not equivalent to the other two X ligands. Examination of the ^1H and ^{13}C NMR spectra of the compound **2** also reveals that two biphenylylene groups are in nonequivalent states with 4 doublet and 4 triplet peaks shown by ^1H NMR and a set of 12 peaks by ^{13}C NMR.[4] Interestingly, only the ^1H NMR chemical shift of the 3'-position in the *cis*-perselenurane(VI) **2**, having two biphenylylene groups, appears at an unusually high field compared with those of bis(2,2'-biphenylylene)selenurane **1** if the pseudorotation is slower than the NMR time scale at low temperature[5], as shown in Figure 1. This result indicates that the 3'-proton is shielded by the aromatic ring of the neighboring biphenylylene group.

The proton-decoupled ^{77}Se signal of **2** in CD_2Cl_2 appeared at 489.6 ppm as a triplet due to a spin-spin coupling between the selenium and fluorine nuclei ($^1J_{\text{Se-F}}$ = 503 Hz) which is considerably smaller than the $^1J_{\text{Se-F}}$ values of $Me_3SiOSeF_5$ (1360, 1380 Hz) and $NaOSeF_5$ (1075, 1185 Hz).[6] Furthermore, the ^{19}F signal of **2** appears at 48.8 ppm together with the satellite peaks due to the same spin-spin coupling ($^1J_{\text{F-Se}}$ = 503 Hz) as shown in Figure 2. The ratio of these satellite peaks and central peak is consistent with the natural abundance of the ^{19}F and ^{77}Se elements.

The ^{13}C NMR signals for each of the 2- and 2'-positions on the biphenylylene groups in the compound **2** appear at a low field as triplet peaks seemingly due to a spin-spin coupling (AA'XX') between carbon and fluorine nuclei via the selenium nucleus (N = $|^2J_{\text{C-F(trans)}} + {}^2J_{\text{C-F(cis)}}|$ = 32 and 68 Hz) as shown in Figure 1.[7] These results indicate that these 2- and 2'-carbon and fluorine atoms combine directly to the central selenium atom. These results identify the NMR behavior of the corresponding pertellurane [12–Te–6(C4F2)]. Compound **2** was characterized by its parent ion peak in the EI-MS spectrum having an isotope pattern identical with the calculated one. In addition, **2** was also characterized by elemental analysis. On the basis of these results we can conclude that **2** is a hexacoordinated organoperselenurane having a *cis*-configuration with respect to the two fluorine atoms and that the inter- or intramolecular permutation of the ligands in Se(VI) is slower than the NMR time scale or is nonexistent.

Furthermore, we have succeeded in determining the structure of the product **2** by X-ray crystallographic analysis.[8] Single crystals of **2** were formed by recrystallization from a dry Et_2O/CH_2Cl_2 solution. The molecular structure of **2** for one enantiomer is illustrated by an ORTEP plot in Figure 3, together with a selected list of bond distances and angles.

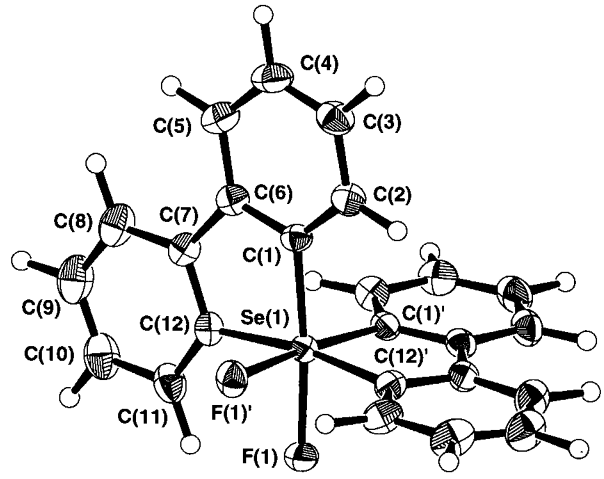


Figure 3. An ORTEP view of **2**(Λ). Selected bond distances (Å) and angles (°) of the non-hydrogen atoms of this enantiomer are given below (e.s.d.'s in parenthesis). The primed atoms refer to the equivalent position (2-x, -y, z) with respect to the unique asymmetric unit at (x, y, z). Se(1)–F(1) = 1.853(4), Se(1)–C(1) = 2.008(6), Se(1)–C(12) = 1.941(4), C(1)–C(2) = 1.388(8), C(1)–C(6) = 1.388(7), C(6)–C(7) = 1.473(7), C(7)–C(12) = 1.398(7), C(11)–C(12) = 1.380(7), F(1)–Se(1)–F(1)' = 89.6(2), F(1)–Se(1)–C(1) = 175.6(3), F(1)–Se(1)–C(1)' = 90.1(1), F(1)–Se(1)–C(12) = 89.6(2), F(1)–Se(1)–C(12)' = 86.2(2), C(1)–Se(1)–C(1)' = 90.5(3), C(1)–Se(1)–C(12) = 86.0(3), C(1)–Se(1)–C(12)' = 98.2(2), C(12)–Se(1)–C(12)' = 174.1(4).

The unit cell consists of four molecules of $[Se(C_{12}H_8)_2F_2]$ and four CH_2Cl_2 molecules, each on a crystallographic 2-fold axis of symmetry. The racemic compound contains two types of selenium centers, each having two biphenylylene ligands and two fluorine atoms in their coordination sphere in both the Δ and Λ configurations, respectively. The central selenium atom has a distorted-octahedral coordination geometry with the two fluorine atoms in a *cis*-configuration. The three sets of 3c-4e bond on the selenium atom are nearly perpendicular to each other. The Se–F bond distance exhibited is 1.853(4) Å, which is similar to a Se–F single covalent bond (1.88 Å).[9] The average Se–C bond distance exhibited is 1.975(5) Å, which is similar to the Se–C single covalent bond (1.93 Å).[1] Furthermore, the respective bond angles are nearly equal to 90 or 180 °.

The present results provide a new procedure for the synthesis of organoperselenurane (λ^6-selane), further work on which is currently underway in our laboratory.

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References and Notes

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3 **2:** mp 163–166 °C dec; ^1H NMR (400 MHz, CD_2Cl_2, room temperature) δ 6.49 (d, J = 7.5 Hz, 2H, 3'-ArH), 7.10 (t, J = 7.5 Hz, 2H, 4'-ArH), 7.47 (t, J = 7.5 Hz, 2H, 5'-ArH), 7.68 (t, J = 7.5 Hz, 2H, 4-ArH), 7.75 (t, J = 7.5 Hz, 2H, 5-ArH), 7.98 (d, J = 7.5 Hz, 2H, 6'-ArH), 8.12 (d, J = 7.5 Hz, 2H, 3-ArH), 8.40 (d, J = 7.5 Hz, 2H, 6-ArH); ^{13}C NMR (100 MHz, CD_2Cl_2, room temperature) δ 122.7, 123.2, 123.2, 128.9, 130.2, 131.2, 131.5, 131.8, 132.3, 132.5, 145.8 ($N = |^2J_{C-F(trans)} + ^2J_{C-F(cis)}| = 32$ Hz), 151.1 ($N = |^2J_{C-F(trans)} + ^2J_{C-F(cis)}| = 68$ Hz); ^{19}F NMR (254 MHz, CD_2Cl_2, room temperature) δ 48.8 (t, J_{Se-F} = 503 Hz) (relative to $CFCl_3$); ^{77}Se NMR (51 MHz, CD_2Cl_2, room temperature) δ 489.6 (J_{F-Se} = 503 Hz) (relative to Me_2Se); EI-MS (*m/z*) 422 (M^+), 384 ($M^+ - 38$); Anal. Calcd for $C_{24}H_{16}F_2Se{\bullet}CH_2Cl_2$: C, 59.31; H, 3.58%; Found: C, 59.02; H, 3.57.

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8 Crystallographic data for **2**: formula $[C_{24}H_{16}F_2Se]\cdot CH_2Cl_2$, M = 506.28, orthorhombic, space group *Aba2* (No. 15), a = 12.807(2) Å, b = 14.587(2) Å, c = 11.383(2) Å, V = 2127(1) Å^3, d_{calcd} = 1.58 g/cm^3, Z = 4, $F(000)$ = 1016.00, μ = 20.4 cm^{-1}, unique reflections = 1257($I > 3.0\sigma(I)$), R = 0.025(R_w = 0.032).

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