A T-Shaped Selenenyl Halide: Synthesis and Characterisation of a Proposed Reaction Intermediate

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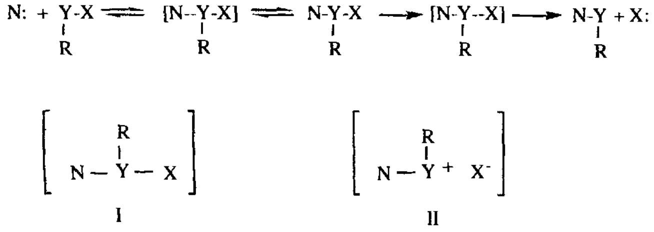
The T-shaped selenenyl halide $[C_6H_3(N{=}NC_6H_4Me\text{-}4'\text{-}2,Me\text{-}5]SeCl$ (**1**), which may be regarded as a model substance for the transition state in nucleophilic displacement at divalent chalcogen atoms, has been isolated and subjected to X-ray structure determination.

It is well-known that sulfenyl and selenenyl halides R−Y−X (Y = S, Se) react with nucleophiles. The steric requirements of this reaction are very similar to those of nucleophilic substitutions at carbon, thus indicating that the transition states for carbon and divalent sulfur have similar geometry, with collinear nucleophile, reaction centre, and leaving group[1]. The substitution at saturated carbon is a synchronous process, where bond formation and rupture are included in the same transition state. In contrast, kinetic studies of nucleophilic substitutions at dicoordinated sulfur and selenium[2,3] led to the suggestion of a two-step mechanism that assumes a fast equilibrium between the substrate and the nucleophile to form a metastable intermediate, the nature of which is not defined. Sulfur and selenium, being second- and third-row elements, could accommodate the electron pair of a nucleophile, thus making possible a pentacovalent addition complex intermediate, in contrast to ion pair species[4]. The mechanism, where transition states are shown in brackets, is outlined in Scheme 1 together with the two types of intermediates. We now report on the preparation of the stable compound **1**, which provides new and conclusive evidence for the formation of a T-shaped intermediate. The isolation of similar systems was, as predicted[5], successful in the case of the heaviest atom, tellurium, whereas only complexes with appreciably longer selenium-nucleophile distances have been observed in rings with Se(II) substitutents[6], where the contacts at selenium were not always recognised[7].

Scheme 1. Nucleophilic substitution at dicoordinated chalcogen atoms. Reaction mechanism and suggested addition complex (**I**) or ion pair (**II**) intermediates. Y = chalcogen, X = leaving group

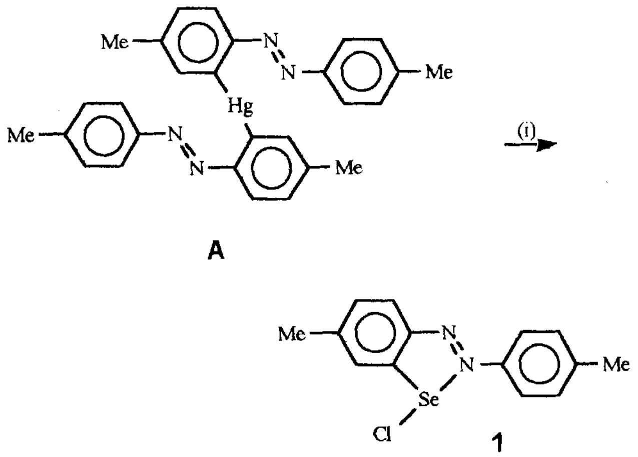


$$N{:} + \underset{R}{Y}\text{-}X \rightleftharpoons [N\text{--}\underset{R}{Y}\text{-}X] \rightleftharpoons N\text{-}\underset{R}{Y}\text{-}X \longrightarrow [N\text{-}\underset{R}{Y}\text{--}X] \longrightarrow N\text{-}\underset{R}{Y} + X{:}^-$$

$$\underset{\textbf{I}}{\left[N-\overset{R}{Y}-X\right]} \qquad \underset{\textbf{II}}{\left[N-\overset{R}{Y}{}^{+}\ X^-\right]}$$

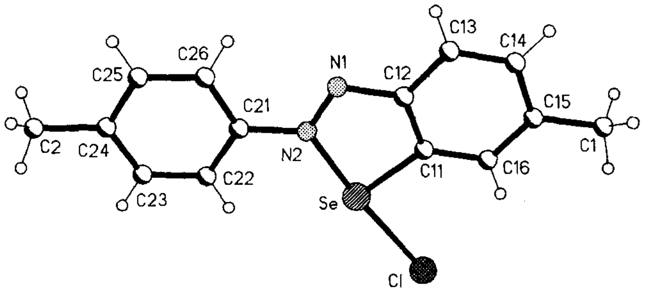
Reaction of Se^I chloride with the transmetallating agent **A** afforded compound **1**, which was crystallised from diethyl ether-hexane and gave ^1H- and ^{13}C-NMR spectra consistent with the structure shown in Scheme 2. The EI mass spectrum (*m/z* = 289, 324, 498) suggested the formation of a complex with a 1:1 Se:ligand ratio ([RSe] = 289) and a coordinated chloride ([RSeCl] = 324), but also possibly a compound with a 1:2 metal:ligand ratio ($[R_2Se]$ = 498).

Scheme 2. (i) + Se_2Cl_2 − Se^0 − HgArCl [by ^1H NMR; Ar = $C_6H_3(N{=}NC_6H_4\text{-}Me\text{-}4')\text{-}2,Me\text{-}5$]. Reaction conditions: Chloroform, room temperature, 18 hours



Recrystallisation of **1** from 1,2-dichloroethane/*n*-hexane afforded single-crystals suitable for X-ray diffraction studies. The structure of **1** (Figure 1) revealed the complex to be a T-shaped selenenyl halide with the chlorine and nitrogen atoms occupying the *trans* positions. The geometry is as expected from VSEPR theory for a 10 e^- system. The structure is similar to that found for $[C_6H_4(N{=}NC_6H_5)\text{-}2]TeCl$[8]. All the non-hydrogen atoms of the molecule are essentially coplanar (mean deviation 0.03 Å); the selenium atom lies 0.06 Å out of the ligand plane. The Se−Cl bond length is 2.475(1) Å which is similar to the longer Se−Cl bond in the T-shaped selenium ligand in $[WCl_5(NSeCl_2)]^{2-}$ [9], but 0.13 and 0.05 Å longer than the shorter Se−Cl bond (loc. cit.) or in the T-shaped anion $[SeCl_2CN]^-$, respectively[9,10]. The Se−N(2) bond length in compound **1** is 2.025(3) Å which is 0.19 Å longer than the mean value of 1.83 Å for 13 Se−N single bonds in the Cambridge Structural Database and 0.12 Å longer than the longest[11]. The Se−C bond length is as expected for a single covalent bond Se$-C_{sp^2}$[11]. The lengthening of the Se$-$N(2) and the Se$-$Cl bond in compound **1** are consistent with an N$-$Se$-$Cl system with linear 3c,4e bonding involving a p orbital of the central selenium atom and one σ orbital from each of the ligands. The angle N(2)$-$Se$-$Cl is essentially linear [173.4(1)°] and the bending, probably due to lone-pair repulsion, is towards the third ligand, as was observed in the abovementioned complexes $[Me_4N][SeX_2CN]$ (X = Br, Cl) and $(PPh_4)_2[WCl_5(NSeCl_2)]$. However, the deviations from linearity in those anionic compounds were 2.9, 1.5, and 4.4° respectively, smaller than in compound **1**. The main deviation from ideal T-shape in compound **1** is the C(11)$-$Se$-$N(2) angle in the chelate ring [79.8(2)°], where the C(12)$-$C(11)$-$Se and N(2)$-$N(1)$-$C(12) angles [112.7(3), 110.8(3)°] are clearly distorted from ideal sp^2 geometry; these features are presumably due to the small "bite" of the ligand [N(2)···C(11) 2.51 Å][12]. The T-shaped geometry around the selenium atom and the long Se$-$Cl and Se$-$N bonds found in this compound would also be expected for a complex intermediate in a nucleophilic displacement reaction at a divalent chalcogen, with longer bonds to the leaving and the entering group and bond angles of ca. 90 and 180°.

Figure 1. The molecular structure of $[C_6H_3(N{=}NC_6H_4\text{-}Me\text{-}4')\text{-}2,\text{Me-}5]SeCl$ (**1**). Selected bond lengths [Å] and angles [°]: Se$-$C(11) 1.889(4), Se$-$N(2) 2.025(3), Se$-$Cl 2.475(1), C(11)$-$C(12) 1.398(6), C12$-$N(1) 1.379(5), N(1)$-$N(2) 1.277(5); C(11)$-$Se$-$N(2) 79.8(2), C11$-$Se$-$Cl 94.26(13), N(2)$-$Se$-$Cl 173.39(10), C(12)$-$C(11)$-$Se 112.7(3), N(1)$-$C(12)$-$C(11) 119.1(4), N(2)$-$N(1)$-$C(12) 110.8(3), N(1)$-$N(2)$-$Se 117.5(3)



The ^{77}Se-NMR shift found for compound **1** is in agreement with the expected deshielding effect on the ^{77}Se nucleus arising from the nitrogen coordination[13]; therefore the nitrogen-selenium interaction probably exists also in solution. This kind of intramolecular coordination could explain the high optical yields achieved in the asymmetric *trans* addition to alkenes[14].

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Experimental

All experimental procedures were performed under dry nitrogen by using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agent and were distilled before use. – NMR (recorded at ambient temperatures): Bruker AM 400 (^{1}H and ^{13}C), Bruker AC 200 (^{77}Se). – MS: Finnigan MAT 8430.

Preparation of **1**: Compound **A** (0.517 g, 0.835 mmol) was added to a solution of Se_2Cl_2 (0.07 ml, 0.835 mmol) in 20 ml of chloroform. A red suspension formed and was stirred at room temp. for ca. 12 h. It was then filtered and the filtrate concentrated to dryness. Addition of diethyl ether precipitated $Hg[C_6H_3(N{=}NC_6H_4\text{-}Me\text{-}4')\text{-}2,Me\text{-}5]Cl$, and further filtration afforded a solution of **1**, which was precipitated by addition of *n*-hexane, yield: 0.249 g (92%). – EI MS, *m/z*: 498, 324 [M$^+$], 298 [M$^+$ – Cl]. – ^{1}H NMR (CDCl$_3$): δ = 8.74 (d, J = 1.5 Hz, 1 H, H16A), 8.38 (d, J = 8.4 Hz, 1 H, H13A), 7.91 (d, J = 8.5 Hz, 2 H, H22A, 26A), 7.52 (dd, 1 H, H14A), 7.35 (d, 2 H, H23A, 25A), 2.58 (s, 3 H, H1A, 1B, 1C), 2.45 (s, 3 H, H2A, 2B, 2C). – ^{13}C NMR (CDCl$_3$): δ = 150.12, 146.96, 144.96, 143.17, 142.49 (C11, 12, 15, 21, 24), 130.81 (C23, 25), 130.65 (C14), 128.86 (C16), 128.76 (C13), 121.95 (C22, 26), 22.61 (C1), 21.49 (C2), 21.9 (d, J = 0.8 Hz, 3 H, MH). – ^{77}Se NMR (δ_{SeMe_2} = 0): δ = 884.09 (s).

Crystal Data for **1**: $C_{14}H_{13}ClN_2Se$, M = 323.7. Monoclinic, space group $P2_1/n$, a = 7.906(2), b = 14.699(3), c = 11.303(2) Å, β = 90.97(2)°, V = 1313.3(5) Å^3, Z = 4, D_c = 1.64 Mg m^{-3}, $F(000)$ = 648, μ(Mo-K_α) = 3.05 mm^{-1}. A red tablet of ca. 0.40 × 0.40 × 0.15 mm was used to collect 2371 independent reflections at 143 K on a Stoe STADI-4 diffractometer to $2\theta_{max}$ = 50°. The structure was solved by the heavy-atom method and refined anisotropically on all F^2 data (using SHELXL-93)[15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included by using a riding model or as rigid methyl groups. Refinement converged at wR_2 = 0.080 [R_1 = 0.039 for $I > 2\sigma(I)$].

Further details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD-401643.

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