Reduction of a Heterocyclic Selenium(IV) Oxide L^{SeO} by $[Pd(COD)Cl_2]$ – Crystal Structure of *trans*-$[Pd(L^{Se})_2Cl_2]$

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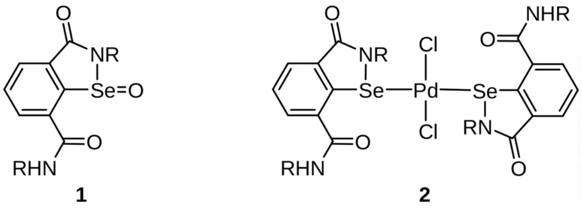
The heterocyclic selenium(IV) oxide L^{SeO} is reduced by $[Pd(COD)Cl_2]$ in MeCN solution to produce *trans*-$[Pd(L^{Se})_2Cl_2]$ (**2**) (L^{Se} = 2,3-dihydro-2-isopropyl-7-(*N*-isopropylcarbamoyl)-1,2-benzisoselenazole-3-oxide). Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.700(1), b = 10.871(1), c = 15.656(2) Å, α = 104.51(1), β = 94.59(1), γ = 95.25(1)°, V = 1745.5(3) Å^3, and Z = 2. The COD is oxidized to 5,6-epoxycyclooctene.

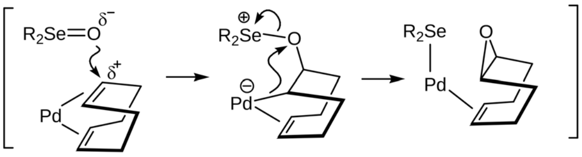
Key words: Organoselenoxides, Reduction, Palladium, Complex, Crystal Structure

In organic synthesis, SeO_2 is widely utilized as an oxidant [1], particularly for epoxidation and allylic oxidation of olefins [2]. Organic selenium(IV) oxides, R_2SeO, are not so widely used, presumably as a consequence of their reduced reactivity. Nevertheless, some aryl-alkyl selenoxides are efficient catalysts for the epoxidation of various olefinic substrates and for the Baeyer-Villiger oxidation of aldehydes and ketones [3]. We have previously shown that the heterocyclic selenoxide L^{SeO} (**1**) is reduced by phosphines, thioethers, and thionyl chloride [4]. An O transfer from L^{SeO} to a Pd-bound acetonitrile ligand has also been described [5]. Now we report on the reduction of L^{SeO} by $[Pd(COD)Cl_2]$. The crystal structure of the reduction product *trans*-$[Pd(L^{Se})_2Cl_2]$ (**2**) is described.

Pale-yellow crystals of *trans*-$[Pd(L^{Se})_2Cl_2]$ (**2**) were reproducibly obtained by reaction of the selenoxide L^{SeO} (**1**) with $[Pd(COD)Cl_2]$ in acetonitrile at 50 °C for one week followed by addition of ethanol and slow evaporation. The reaction is thought to proceed *via* an oxygen transfer from **1** to the palladium bound COD ligand, followed by ligand redistribution reactions as indicated in Scheme 2. No reaction was observed after stirring a mixture of **1** and COD for one week.



Scheme 1. Structure of selenoxide **1** and palladium complex **2** (R = *i*Pr).



Scheme 2. Proposed mechanism for the oxygen transfer to the COD ligand.

The oxygenation of the COD ligand has been confirmed by NMR spectroscopy by the absence of the characteristic signals for COD. The mass spectrum reveals a signal at m/z = 124.089 which can be attributed to the 5,6-epoxycyclooctene, the monoepoxide of COD. The proton NMR spectrum of complex **2** in CD_3CN solution shows the signals for free L^{Se} indicative of ligand substitution by MeCN. In agreement with this, no parent ion signal is detected by ESI MS of a dilute $CH_3CN/MeOH/CH_2Cl_2$ solution of **2**.

Crystals of **2** · EtOH are triclinic, space group $P\bar{1}$. The asymmetric unit contains a neutral complex **2** and one ethanol solvate molecule (Fig. 1). The divalent palladium atoms are surrounded by two chloro and two selenium atoms in an almost perfectly square planar fashion, as manifested by very small deviations from the ideal L–Pd–L bond angles [maximum deviation is 2.7(2)° for Se(1)–Pd(1)–Se(2)]. The average Pd–Cl and Pd–Se bond lengths are 2.291(1) and 2.4371(6) Å, respectively. Such bond lengths are normal for four-coordinate Pd(II) complexes with mixed Cl/selenoether donor ligands [6, 7]. The Se–C and Se–N bond lengths average 1.890(4) and 1.898(4) Å, respectively and do

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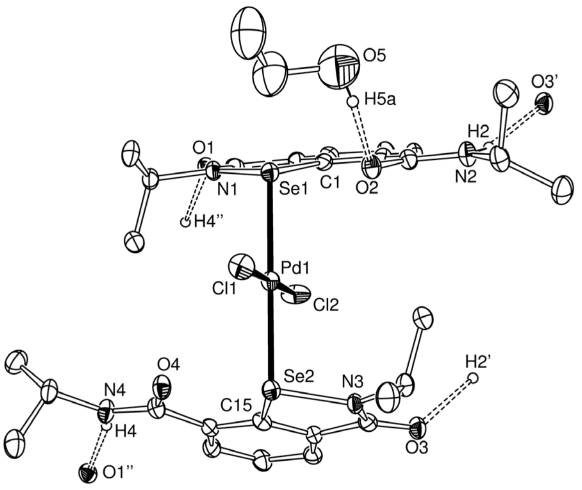

Fig. 1. Molecular structure of **2** in crystals of **2**·EtOH (displacement ellipsoids at the 50 % probability level). All hydrogen atoms except those involved in hydrogen bonding interactions (indicated by dashed lines) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–Se(1) 2.4425(6), Pd–Se(2) 2.4316(6), Pd(1)–Cl(1) 2.304(1), Pd(1)–Cl(2) 2.278(1), Se(1)–N(1) 1.890(4), Se(1)–C(1) 1.891(4), Se(1)···O(2) 2.472(3), Se(2)–N(3) 1.905(4), Se(2)–C(15) 1.889(4), Se(2)···O(4) 2.474(3); Cl(2)–Pd(1)–Cl(1) 179.57(5), Se(2)–Pd(1)–Se(1) 177.30(2); N(2)–H(2)···O(3') 2.910, N(4)–H(4)···O(1") 2.984 Å, O(5)–H(5)···O(2) 2.948 Å. Symmetry code used to generate equivalent atoms: O(3′), H(2′) $1-x$, $-y$, $-z$; O(1″), O(4″) $1-x$, $1-y$, $1-z$.

not deviate much from those of the parent heterocycle (1.868(4), 1.902(4) Å) [8]. The complexes are linked *via* N–H···O hydrogen bonds to generate one-dimensional infinite chains (N(2)–H(2)···O(3′), N(4)–H(4)···O(1″)). The ethanol molecule is hydrogen bonded to a carbonyl group of the ligand O(2)···H(5a)–O(5) of **2**. Note, however, that the hydrogen bonds are based on calculated H atom positions.

To our knowledge, an oxygen transfer from a heterocyclic selenoxide to a Pd-bound olefin ligand has not been reported in the literature. Future studies are directed towards further understanding of the reaction mechanism as well as to developing this reaction into a catalytic process using L^{Se}/H_2O_2/olefin and Pd^{2+} ions.

Experimental Section

*Preparation of [Pd(L^{Se})$_2$$Cl_2$]·EtOH (**2**·EtOH)*

To a solution of selenoxide L^{SeO} (34 mg, 0.10 mmol) in acetonitrile (30 mL) was added [Pd(COD)Cl_2] (28.4 mg, 0.10 mmol). The reaction mixture was stirred at 50 °C for 8 d. EtOH (30 mL) was added and the resulting solution concentrated to *ca.* half of its original volume. After standing for 2 weeks pale yellow single crystals of *trans*-[Pd(L^{Se})$_2$$Cl_2$]·EtOH formed. Yield: 37 mg (45 % based on Pd). – IR (KBr): ν = 3275 ν(NH), 1617, 1560 cm^{-1} ν(C=O). – Elemental analysis for $C_{28}H_{36}Cl_2N_4O_4PdSe_2 \cdot$ EtOH (873.92): calcd. C 41.23, H 4.84, N 6.41; found C 41.04, H 4.54, N 6.32. Samples for NMR analysis were dried in vacuum. – ^{1}H NMR (400 MHz, CD_3CN): δ = 1.26 (d, 6 H, CH_3), 1.34 (d, 6 H, CH_3), 4.24 (m, 1 H, CH), 4.61 (spt, 1 H, CH), 7.57 (t, 1 H, ArH), 8.02 (d, 1 H, ArH), 8.07 (d, 1 H, ArH). The chemical shifts are identical with those of L^{Se} in CD_3CN [4]. – ESI-MS (CH_2Cl_2, MeOH, CH_3CN): m/z = 357.07, 699.12.

Crystal structure determination

A suitable single crystal of **2**·EtOH was picked from the reaction mixture. The data set was collected at 193(2) K on a Stoe IPDS-2T diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The intensity data were processed with the program Stoe X-AREA [9]. The structure was solved by Direct Methods [10] and refined by full-matrix least-squares on the basis of all data against F^2 using SHELXL-97 [11]. PLATON was used to search for higher symmetry [12]. H atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically.

[Pd(L^{Se})$_2$$Cl_2$]·EtOH: $C_{30}H_{42}Cl_2N_4O_5PdSe_2$ (M_r = 873.90), triclinic, space group $P\bar{1}$, a = 10.700(1), b = 10.871(1), c = 15.656(2) Å, α = 104.51(1), β = 94.59(1), γ = 95.25(1)°, V = 1745.5(3) Å^3, Z = 2, ρ = 1.663 g cm^{-3}, μ(MoK_α) = 2.813 mm^{-1}, crystal size: 0.35 × 0.20 × 0.10 mm^3. Of 12395 reflections (R_{int} = 0.0467), 6528 were unique and 4617 observed [$I \geq 2\sigma(I)$]. Final residuals: R_1 = 0.0391, wR_2 = 0.0951 (for observed data), R_1 = 0.0591, wR_2 = 0.1023 for all data.

CCDC 682695 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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