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# A facile route to germanium(IV) binaphthoxide complexes: crystal structure of a chiral resolved germanium(IV) binaphthoxide

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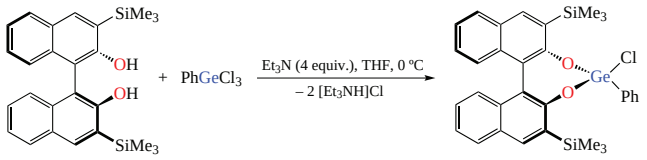
**A method for the facile synthesis of chiral germanium(IV) binaphthoxide complexes from the corresponding binaphthols and an organogermanium trichloride has been developed, which allows these unusual types of compounds to be synthesized in high yields. The crystal structure of one such complex, (*S*)-[Ge{$O_2C_{20}H_{10}(SiMe_3)_2$-3,3′}{Cl}{Ph}], has been determined.**

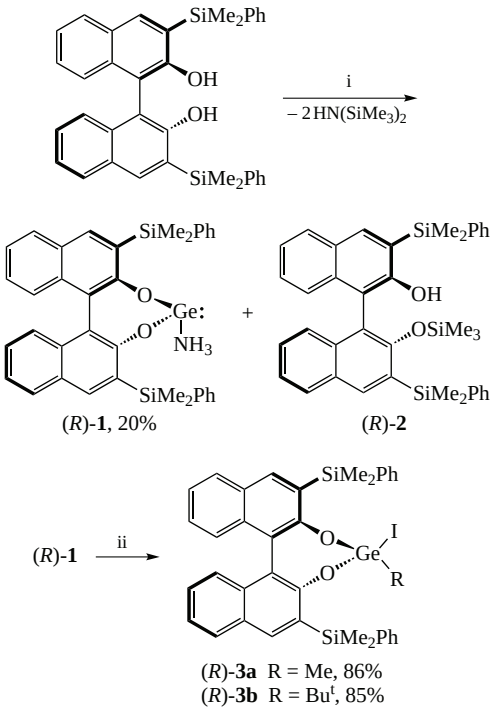



*Keywords*: germanium, organogermanium compounds, phenylgermanium trichloride, chiral binaphthoxides, aryl oxides, crystal structure, metathesis reactions.

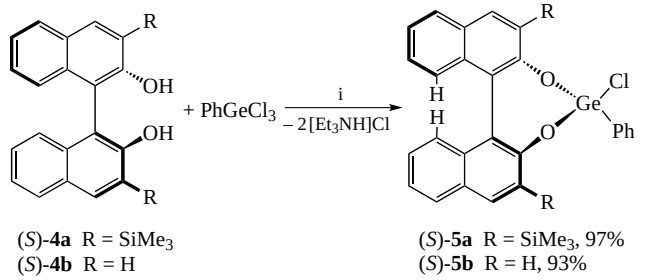
The binaphthoxide ligand is an important chiral auxiliary in transition metal, lanthanoid metal, and main group metal chemistry. This chelating $C_2$-symmetric ligand can be isolated as either its (*R*)- or (*S*)-isomer and can be readily substituted at the 3,3′-positions in order to tailor the steric and electronic attributes of the ligand for specific applications. Complexes containing this ligand have found particular use in catalysis[1–4] and asymmetric transformations.[5–15]

In the case of germanium, a previously employed route for the preparation of germanium(IV) binaphthoxide complexes involved the preparation of the germanium(II) binaphthoxide complex (*R*)-**1**[16] by heating an equimolar mixture of the binaphthol and $Ge[N(SiMe_3)_2]_2$ in benzene at 85 °C for 12 h, followed by oxidative addition of the organohalides MeI or Bu$^t$I to yield the corresponding germanium(IV) complexes (*R*)-**3a** and (*R*)-**3b** (Scheme 1).[17] However, this process had a variety of complications in that some of the starting binaphthol was silylated to form (*R*)-**2** in the first step, where the –$SiMe_3$ group present on one of the oxygen atoms in the product was transferred from the –$N(SiMe_3)_2$ groups of the starting germanium(II) amide reagent. This resulted in low overall yields for the desired germanium(IV) products. Furthermore, only the 3,3′-dimethylphenyl substituted binaphthol was useful for this transformation while the use of the 3,3′-trimethylsilyl, 3,3′-triphenylsilyl, or 3,3′-methyl(diphenyl)silyl or other substituted systems only yielded the corresponding silylated analogues of (*R*)-**2**.[18]

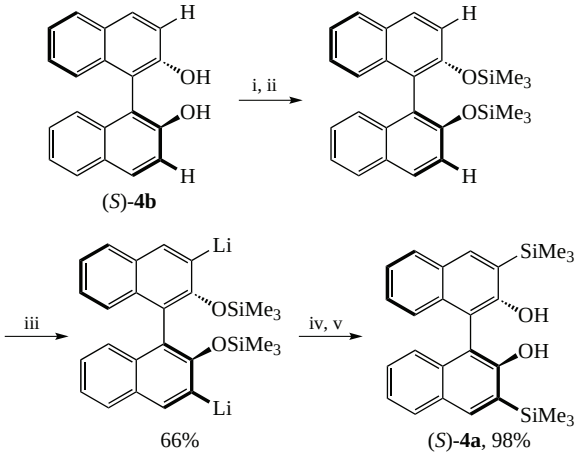
In order to expand the substituent tolerance and to obtain the germanium(IV) binaphthoxide complexes in greater overall yields, we attempted the alternate synthetic route (Scheme 2) which employed the germane $PhGeCl_3$ as the starting material that yielded the desired complex (*S*)-**5a**. The substituted binaphthol (*S*)-**4a** was synthesized as shown in Scheme 3 using the method of Maruoka *et al.*[19] This formation of (*S*)-**5a** proceeds in the presence of triethylamine, which functions as a HCl




**Scheme 1** *Reagents and conditions*: i, $Ge[N(SiMe_3)_2]_2$, PhH, 85 °C, 12 h; ii, RI (R = Me, Bu$^t$), PhH, 25 °C, 6 h (refs. 16, 17).




**Scheme 2** *Reagents and conditions*: i, $Et_3N$ (4 equiv.), PhH, 25 °C, 12 h.




**Scheme 3** *Reagents and conditions*: i, $Me_3SiCl$ (2 equiv.), THF, 0 °C; ii, $Et_3N$, THF, 0 °C, 18 h; iii, BuLi (4 equiv.), $Et_2O$, 0 °C, 18 h; iv, $Me_3SiCl$ (2 equiv.), $Et_2O$, 25 °C, 2 h; v, HCl (6 M), THF, 0 °C.

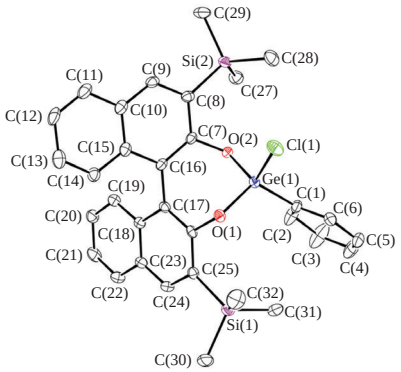



**Figure 1** ORTEP diagram of (*S*)-**5a** with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Ge(1)–Cl(1) 2.1354(9), Ge(1)–O(1) 1.779(2), Ge(1)–O(2) 1.773(2), Ge(1)–C(1) 1.902(3), C(16)–C(17) 1.497(4), C(1)–Ge(1)–Cl(1) 111.7(1), O(1)–Ge(1)–Cl(1) 101.40(7), O(1)–Ge(1)–C(1) 114.8(1), O(2)–Ge(1)–Cl(1) 111.12(7), O(2)–Ge(1)–C(1) 111.0(2), O(1)–Ge(1)–O(2) 106.48(9).

scavenger that shifts the equilibrium position of the reaction such that the binaphthoxide anion that is formed can attack the $PhGeCl_3$ reagent, resulting in displacement of two of the chlorine atoms. The $[Et_3NH]Cl$ byproduct can be readily removed from the solution by filtration, and (*S*)-**5a** was obtained in analytically pure form in 97% yield. The $^1H$ NMR spectrum of (*S*)-**5a** in benzene-$d_6$ contains two resonances at $\delta$ 0.50 and 0.19 ppm that correspond to the two $–SiMe_3$ substituents, which are no longer magnetically equivalent in (*S*)-**5a** like they were in the binaphthol starting material. Likewise, there are two signals at $\delta$ 8.19 and 8.08 ppm that appear due to the two 9,9′-hydrogen atoms in (*S*)-**5a** (see Scheme 2), which are also no longer magnetically equivalent.

The X-ray crystal structure of (*S*)-**5a** was obtained and an ORTEP diagram is shown in Figure 1.† The germanium atom in (*S*)-**5a** is chelated by both oxygen atoms of the binaphthoxide ligand, and these three atoms, along with the 1,1′- and 2,2′-carbon atoms of the binaphthoxide ligand, form a seven-membered ring. The two germanium–oxygen bonds are nearly identical and have an average bond length of 1.776(2) Å. These distances can be compared to those in the other germanium(IV) binaphthoxide compounds (*S*)-**3a** and (*S*)-**3b** (see Scheme 1). In (*S*)-**3a** the two germanium oxygen bond distances are 1.674(3) and 1.794(4) Å, while in (*S*)-**3b** these distances measure 1.780(3) and 1.797(3) Å.[17] The longer germanium–oxygen bond distances in (*S*)-**3a** and (*S*)-**3b** can be attributed to the presence of the more sterically encumbering $–SiMe_2Ph$ groups in the 3,3′-positions of their binaphthoxide ligands.

† *Crystal data for* (*S*)-**5a**. $C_{32}H_{33}ClGeO_2Si_2$ ($M$ = 613.80), orthorhombic, space group $P2_12_12_1$ at 100.0 K: $a$ = 8.328(1), $b$ = 10.392(2) and $c$ = 35.481(6) Å, $\alpha = \beta = \gamma$ = 90°, $V$ = 3070.6(9) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.328 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 0.71073 Å, $F$(000) = 1272. Total of 26087 reflections were collected (7581 independent reflections, $R_{int}$ = 0.0573) and used in refinement, which converged to $wR_2$ = 0.0725, GOOF = 1.023 for all independent reflections [$R_1$ 0.0347 was calculated for 7581 independent reflectios with $I > 2\sigma(I)$].

The X-ray diffraction analysis was carried out on a Siemens P4/CCD diffractometer (MoK$\alpha$ radiation, $\lambda$ = 0.71073 Å, graphite monochromator). The data were integrated using the Bruker SAINT software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structures. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model.

CCDC 2101762 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

The germanium–carbon bond length in (*S*)-**5a** is 1.902(3) Å, which is typical of Ge–C single bonds. However, in (*S*)-**3a** the germanium–carbon distance measures 2.351(1) Å, and this longer bond can be attributed to the fact that the iodine atom and the methyl group are crystographically disordered with one another.[17] The *tert*-butyl substituted compound (*S*)-**3b** has a germanium–carbon bond distance of 1.972(5) Å, which is longer than that in (*S*)-**5a** due to the presence of the 3,3′-$SiMe_2Ph$ substituents and also due to the steric encumbrance of the *tert*-butyl group.[17] The angle about the interannular carbon–carbon bond of the binaphthoxide rings in (*S*)-**5a** is 68.6°, which is enforced by the attachment of the two oxygen atoms to the germanium center. There is a distorted tetrahedral environment about the germanium atom, where the O(1)–Ge(1)–Cl(1) and O(1)–Ge(1)–O(2) bond angles are more acute than the idealized value of 109.5°, while the remaining four bond angles are more obtuse.

A further advantage of the synthetic method shown in Scheme 2 is that it allows for the synthesis of germanium(IV) binaphthoxide complexes without substituents in the 3,3′-positions of the binaphthoxide ligand. Other methods that have been previously employed in our research group to prepare such 3,3′-unsubstituted binaphthoxide compounds of germanium and other main group elements have resulted in the formation of a mixture of insoluble oligomeric and polymeric products and the desired chelated products were not formed. However, the reaction of 3,3′-unsubstituted binaphthol with $PhGeCl_3$ in the presence of triethylamine resulted in the formation of (*S*)-**5b** in 93% yield (see Scheme 2). Although we were unsuccessful in obtaining X-ray quality crystals of (*S*)-**5b**, the identity of this product was confirmed by NMR spectroscopy and elemental analysis. In these reactions, the $[Et_3NH]Cl$ byproduct is formed immediately upon addition of $Et_3N$ to the reaction mixture indicating that the reaction proceeds very rapidly. This is likely the reason why the reaction provides (*S*)-**5b** as a discrete compound rather than resulting in the formation of a polymeric material, since both oxygen atoms of the binaphthoxide ligand immediately attack the germanium atom.

In summary, an efficient method for the preparation of germanium(IV) binaphthoxide compounds has been developed that uses the binaphthol ligand and phenylgermanium trichloride as the starting materials. The X-ray crystal structure of the complex (*S*)-**5a** was determined and this is a unusual example of a structurally characterized complex of this type. This method also allowed for the preparation of the 3,3′-unsubstituted germanium binaphthoxide complex (*S*)-**5b**, which could not be

obtained using previously employed techniques. The synthetic procedure used to prepare (*S*)-**5a** and (*S*)-**5b** will very likely be useful for the preparation of numerous other germanium(IV) binaphthoxide complexes having different organic substituents and halogen atoms attached to the germanium center, as well as different substituents in the 3,3′-positions of the binaphthoxide ligands, and further investigations into the preparation of these compounds are underway.

These compounds also might be converted to the corresponding germanium hydride complexes, although the reactions of (*S*)-**5a** with traditional reagents to achieve these transformations, such as $LiAlH_4$ or $Bu^i_2AlH$, have exhibited a number of complications including abstraction of the binaphthoxide ligand by the aluminum atom by these reagents. We are currently investigating other methods for the preparation of these germanium hydrides, which could function as chiral hydrogenation reagents.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.005.

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