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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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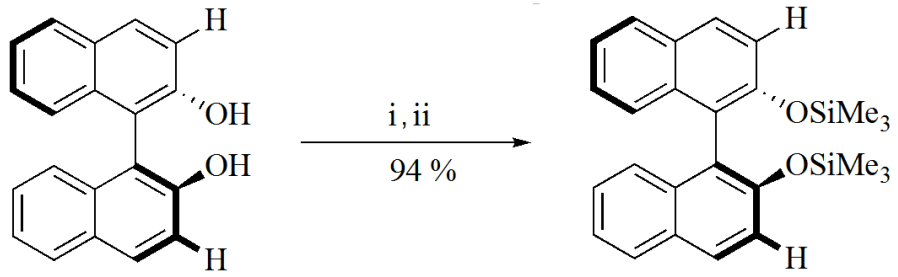
Experimental Procedures

General Considerations

All manipulations were carried out using standard Schlenk, syringe, and glovebox techniques. Solvents were dried using a GlassContour solvent purification system. The reagents (*S*)-1,1'-bi-2,2'-naphthol, Me_3SiCl, Et_3N, and Bu^nLi were purchased from Sigma Aldrich and $PhGeCl_3$ was purchased from Gelest, and all reagents were used as received. ^1H NMR spectra were recorded using a Bruker Unity NMR spectrometer operating at 400 MHz and were referenced to residual protio solvent.

1). Synthesis of (*S*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol (*S*)-4a was carried out using a modified procedure published by Maruoka *et al*.[S1]

Step 1. (*S*)-2,2'-Bis(trimethylsilyloxy)-1,1'-binaphthalene



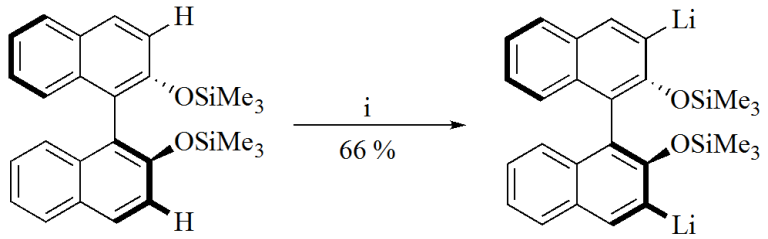
(*S*)-**4b**

Scheme S1 *Reagents and conditions*: i, Me_3SiCl (2 equiv.), THF, 0 ºC; ii, Et_3N, THF, 0 ºC, 18 h.

Procedure

An oven-dried Schenk flask was charged with (*S*)-**4b** (2.00 g, 6.98 mmol) and dry THF (15 ml) and a magnetic stir-bar were added. In a separate oven-dried Schlenk flask equipped with a stir bar, chlorotrimethylsilane (2.15 eq, 1.91 ml, 15.02 mmol) was added along with THF (15 ml) and then cannulated slowly into the solution of (*S*)-**4b** at 0 ºC with stirring. To the solution was then added Et_3N (4 equiv., 3.89 ml, 27.92 mmol) dropwise, and the reaction was left overnight. Upon completion, the reaction mixture was filtered through a double-sided frit with celite to remove $[Et_3NH]Cl$ and the volatiles were removed from the filtrate *in vacuo* to yield (*S*)-**5** as a yellow oil (2.85 g, 94%). ^1H NMR (C_6D_6, 25 ºC): δ 7.72 (dt, J = 7.6 Hz, 4H, aryl), 7.39 (dt, J = 8.4 Hz, 1.0 Hz, 2 H, aryl), 7.22 – 7.12 (m, 4H, aryl), 7.09 – 6.99 (m, 2 H, aryl), -0.11 (s, 18H, -$SiMe_3$).

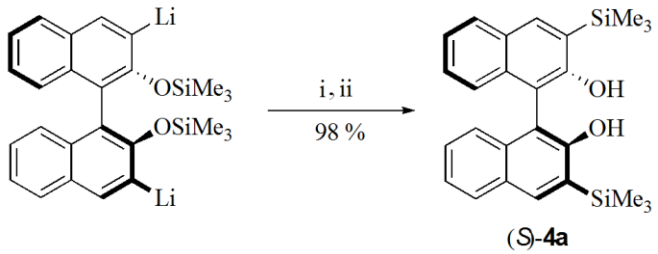
Step 2. (*S*)-3,3'-Dilithio-2,2'-bis(trimethylsilyloxy)-1,1'-binaphthalene



Scheme S2 *Reagents and conditions*: i, Bu^{n}Li (4 eq.), Et_2O, 0 ºC, 18 h.

Procedure. An oven-dried Schlenk flask equipped with a stir bar was charged with (*S*)-2,2'-bis-(trimethylsilyloxy)-1,1'-binaphthalene from the previous step (2.85 g, 6.62 mmol) along with dry diethyl ether (15 ml), and the solution was cooled to 0 ºC. A separate oven-dried Schlenk flask equipped with a stir bar was charged with Bu^{n}Li (2.5 M, 4 eq, 10.6 ml). The Bu^{n}Li solution was cannulated dropwise into the first flask with vigorous stirring and was left overnight. Upon completion of the lithiation, the solution was filtered through a double-sided frit, washed with hexane, and the volatiles were removed *in vacuo*. The product (1.95 g, 66%) appeared as a brown crystalline solid. Due to its limited solubility in C_6D_6 the ^{1}H NMR spectrum was not recorded. The dilithio derivative was used as isolated for the next step.

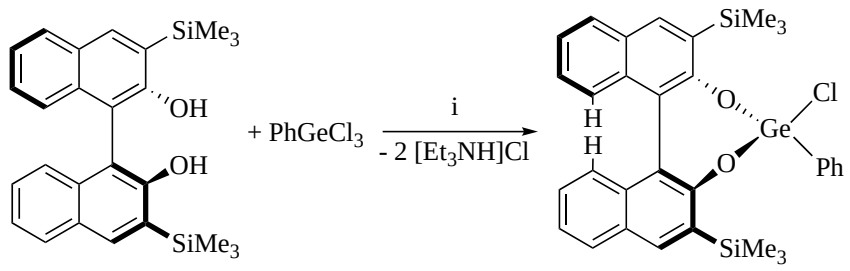
Step 3. Compound (*S*)-4a



Scheme S3 *Reagents and conditions*: i, Me_3SiCl (2 equiv.), Et_2O, 25 ºC, 2 h; ii, HCl (6 M), THF, 0 ºC.

Procedure. An oven-dried Schlenk flask equipped with stir bar was charged with (*S*)-3,3'-dilithio-2,2'-bis(trimethylsilyloxy)-1,1'-binaphthalene from the previous step (2.05 g, 4.63 mmol) along with dry Et_2O (15 ml), and this was stirred for 5 min for dissolution. To an addition funnel was added chlorotrimethylsilane (1.08 g, 9.96 mmol) under an inert atmosphere, this was added dropwise to the solution of the dilitium derivative, and the mixture was stirred for 2 h. The reaction was then quenched with 6 M HCl (25 ml) while being cooled in an ice bath. The solution was filtered and extracted with Et_2O (3×20 ml), and the combined extracts were dried with $MgSO_4$. The mixture was filtered through a cotton plug and then filtered again through a silica plug. The volatiles were removed in vacuo to yield (*S*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol (*S*)-**4a** as a light-yellow fluffy solid (1.97 g, 98%). ^{1}H NMR (C_6D_6, 25 ºC) δ 8.14 (s, 2H, 9.9'-H), 7.72 (d, *J*=7.9 Hz, 2H, 6,6'-H), 7.32 (m, 2H, aromatics), 7.13 (m, 2H, aromatics), 7.00 (m, 2H, aromatics), 4.85 (s, 2H, -O*H*), 0.47 (s, 18 H, -Si(C*H*$_3$)$_3$ ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 157.7, 146.7, 138.3, 135.1, 129.9, 128.9, 124.4, 124.1, 121.0, 110.2, -0.73 (-Si(*C*H$_3$)$_3$) ppm.

2). 4-Chloro-4-phenyl-2,6-bis(trimethylsilyl)dinaphtho[1,2-*f*:2',1'-*d*][1,3,2]dioxagermepine (*S*)-5a



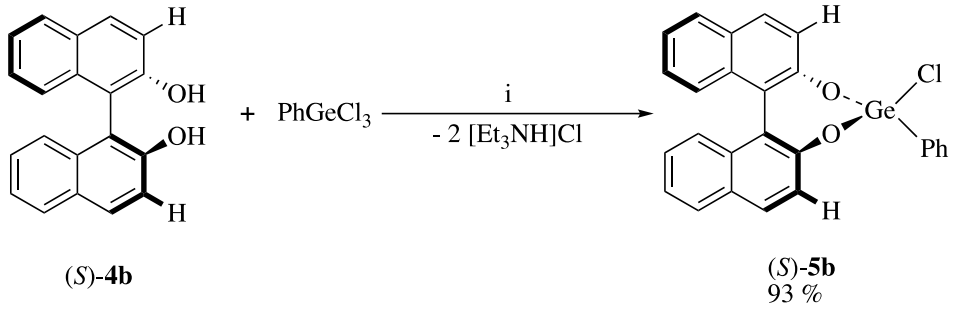
(*S*)-**4a** (*S*)-**5a**, 97 %

Scheme S4 *Reagents and conditions*: i, THF, 0º C, Et_3N (4 equiv.), 18 h.

Procedure:

An oven-dried Schlenk flask equipped with a stir bar was charged with (*S*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol (*S*)-**4a** (1.00 g, 2.32 mmol) and THF (15 ml). A separate oven-dried Schlenk flask was charged with phenylgermanium trichloride (0.60 g, 2.35 mmol) and THF (15 ml). The solution of phenylgermanium trichloride was cannulated into the solution of (*S*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol, and Et_3N (1.25 ml, 9.29 mmol) was added dropwise to the reaction mixture causing immediate precipitation of [Et_3NH]Cl. The reaction was stirred overnight and was then filtered. The volatiles were removed from the filtrate *in vacuo* to yield (*S*)-**5a** as a white solid (1.39 g, 97%). ^{1}H NMR (C_6D_6, 25 ºC) δ 8.19 (s, 1H, 9,9'-H), 8.08 (s, 1H, 9,9'-H), 7.73 (dd, ^3J = 7.8 Hz, ^4J = 4.5 Hz, 2H, aromatics), 7.33 (d, J = 6.8 Hz, 2H, aromatics), 7.28 (d, J = 7.6 Hz, 1H, aromatics), 7.18 – 7.10 (m, 2H, aromatics), 6.93 – 6.84 (m, 4H, aromatics), 6.77 (t, J = 7.2 Hz, 2H, aromatics), 0.50 (s, 9H, -Si(CH_3)$_3$), 0.19 (s, 9H, -Si(CH_3)$_3$) ppm. Anal. Calcd. for $C_{32}H_{33}ClGeO_2Si_2$: C, 62.21; H, 5.42. Found: C, 62.12; H, 5.36.

3). 4-Chloro-4-phenyldinaphtho[1,2-*f*:2',1'-*d*][1,3,2]dioxagermepine (*S*)-5b



(*S*)-**4b**

(*S*)-**5b**
93 %

Scheme S5 *Reagents and conditions*: i, THF, 0º C, Et_3N (4 eq.), 18 h.

Procedure:
An oven dried Schlenk flask equipped with a stir bar was charged with (*S*)-1,1'-bi-2,2'-naphthol (477 mg, 1.67 mmol) and THF (15 ml). A separate oven-dried Schlenk flask was charged with phenylgermanium trichloride (0.43 g, 1.68 mmol) and THF (15 ml). The solution of phenylgermanium trichloride was cannulated into the solution of (*S*)-1,1'-bi-2,2'-naphthol and Et_3N (0.46 ml, 6.66 mmol) was added dropwise to the solution resulting in the immediate precipitation of $[Et_3NH]Cl$. The reaction was stirred overnight at room temperature and then was filtered. The volatiles were removed from the filtrate *in vacuo* yielding (*S*)-**5b** as a white solid (0.73 g, 93%). ^1H NMR (C_6D_6, 25 ºC) δ 7.74 – 7.60 (m, 4H, aromatics), 7.49 (d, *J* = 8.8 Hz, 1H, aromatics), 7.44 (d, *J* = 8.8 Hz, 1H, aromatics), 7.37 – 7.30 (m, 2H, aromatics), 7.20 – 7.08(m, 4H, aromatics), 6.98 – 6.88 (m, 3H, aromatics), 6.80 (t, *J* = 7.2 Hz, 2H, *o*-C_6H_5) ppm. Anal. Calcd. for $C_{26}H_{17}ClGeO_2$: C, 66.51; H, 3.65. Found: C, 66.47; H, 3.58.

X-Ray crystal structure of (*S*)-5a
Single crystals of (*S*)-**5a** were obtained by recrystallization from toluene at –35 °C. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2,[S2] the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the XL[S3] refinement package using Least Squares minimization.

Table S1. Crystal data and structure refinement for (*S*)-**5a**

CCDC deposition number	CCDC-2101762	
Empirical formula	$C_{32}H_{33}ClGeO_2Si_2$	
Formula weight	613.80	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.3282(14) Å	α = 90°.
	b = 10.3916(17) Å	β = 90°.
	c = 35.481(6) Å	γ = 90°.
Volume	3070.6(9) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	1.190 mm^{-1}	
F(000)	1272	
Crystal size	0.31 x 0.29 x 0.18 mm^3	
Theta range for data collection	2.042 to 28.278°.	
Index ranges	-11<=h<=10, -13<=k<=13, -44<=l<=47	
Reflections collected	26087	
Independent reflections	7581 [R(int) = 0.0573]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6530	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7581 / 0 / 349	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0725	
R indices (all data)	R1 = 0.0399, wR2 = 0.0741	
Absolute structure parameter	0.016(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.631 and -0.326 e.$Å^{-3}$	

References

S1. K. Maruoka, T. Ito, Y. Araki, T. Shirasaka and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2975–2976.

S2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **43**, 339–341.

S3. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.