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Novel germanium(II) binaphthoxide complexes: synthesis and crystal structure of (*R*,*R*)-[Ge{$OC_{20}H_{10}(OSiMe_3)$-2′-$(SiMe_3)_2$-3,3′}$_2$] and (*R*)-[Ge{$O_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3′}{$NH_3$}]; catalytic function of Ge[$N(SiMe_3)_2]_2$ for the mono-silylation of 3,3′-disubstituted-1,1′-bi-2,2′-naphthols

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The germanium(II) bisamide Ge[$N(SiMe_3)_2]_2$ reacts with the substituted binaphthols (*R*)-[$(HO)_2C_{20}H_{10}(R)_2$-3,3′] (R = $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, or $SiPh_3$) to yield two novel germanium(II) binaphthoxide complexes; Ge[$N(SiMe_3)_2]_2$ also catalytically silylates one of the hydroxyl groups of (*R*)-[$(HO)_2C_{20}H_{10}(SiMe_3)_2$-3,3′] to yield (*R*)-$HOC_{20}H_{10}$-$(OSiMe_3)$-2′-$(SiMe_3)_2$-3,3′.

Aryloxide complexes of germanium(II) are unusual, although many such compounds are known for germanium(IV).[1] Structurally characterized examples include Ge(OC_6H_2Me-4-Bu^t_2-2,6$)_2$,[2] and [Fe$(CO)_4${Ge($OC_6H_2Bu_2$-2,6-Me-4$)_2$}].[3] We have begun an investigation into the inorganic and organometallic chemistry that can be supported by resolved 3,3′-disubstituted-1,1′-bi-2,2′-naphthol as a ligand with metal complexes of tantalum.[4,5] We now wish to report the preparation and structure of two novel germanium binaphthoxide complexes, (*R*,*R*)-[Ge{$OC_{20}H_{10}(OSiMe_3)$-2′-$(SiMe_3)_2$-3,3′}$_2$] (**1**) and (*R*)-[Ge{$O_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3′}{$NH_3$}] (**2**) and the catalytic activity of Ge[$N(SiMe_3)_2]_2$ for the selective silylation of one hydroxyl group of (*R*)-[$(HO)_2C_{20}H_{10}(R)_2$-3,3′] (R = $SiMe_3$ **3**; $SiMe_2Ph$ **4**; $SiMePh_2$ **5**; $SiPh_3$ **6**).[6]

The germanium bisamide Ge[$N(SiMe_3)_2]_2$[7] reacts with two equivalents of (*R*)-[$(HO)_2C_{20}H_{10}(SiMe_3)_2$-3,3′] (**3**) over 12 h in benzene to produce complex **1** in 32% overall yield. † Complex **1** readily crystallizes out of solution even at 85 °C to produce crystals suitable for X-ray analysis. ‡ An ORTEP plot of **1** is shown in Fig. 1. The two binaphthoxide ligands are bound to the germanium metal center though a single oxygen atom. A trimethylsilyl group has been transferred to the second oxygen atom. The O–Ge–O angle is 89.4(7)°, which is close to the expected value of 90°, and the average Ge–O bond length has a typical value of 1.814(2) Å.[8]

In a separate experiment, reaction of Ge[$N(SiMe_3)_2]_2$ with two equivalents of (*R*)-[$(HO)_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3′] (**4**) led to the formation of complex **2** in 20% yield. § Complex **2** also readily crystallizes out of solution, and an X-ray structure was obtained. ¶ An ORTEP plot of **2** is shown in Fig. 2. Complex **2** contains only one binaphthoxide ligand chelated to the germanium center in a bidentate fashion through both oxygen atoms as well as a coordinated ammonia molecule. The NH_3 is the result of the double desilylation of $HN(SiMe_3)_2$, a conversion which has been reported in reactions of $HN(SiMe_3)_2$ with a silica surface.[9] The environment about the central germanium atom is distorted trigonal pyramidal, which has also been found for other three-coordinate divalent germanium species. The O–Ge–O bond angle in **2** is 97.90(9)°, and the O–Ge–N bond angles have values of 96.2(1) and 81.6(2)°. The average Ge–O bond distance is 1.862(2) Å and the Ge–N bond distance is 2.093(4) Å, which is similar to distances found in other three-coordinate germanium species with a neutral

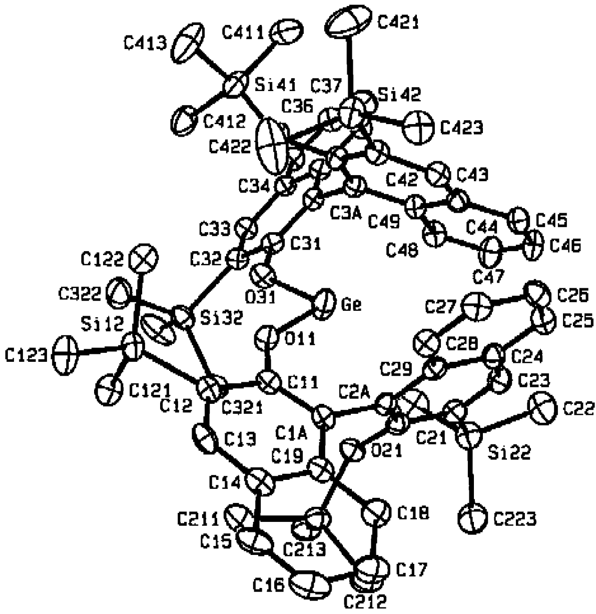

Fig. 1 ORTEP[14] plot of compound **1**. Thermal ellipsoids are drawn at the 50% probability level.

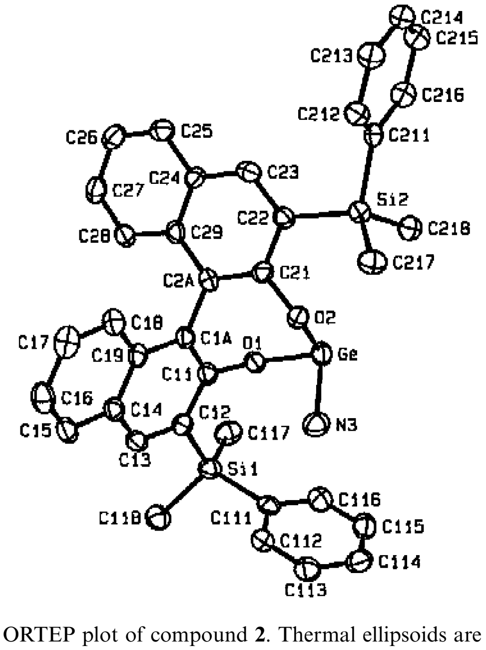

Fig. 2 ORTEP plot of compound **2**. Thermal ellipsoids are drawn at the 50% probability level.

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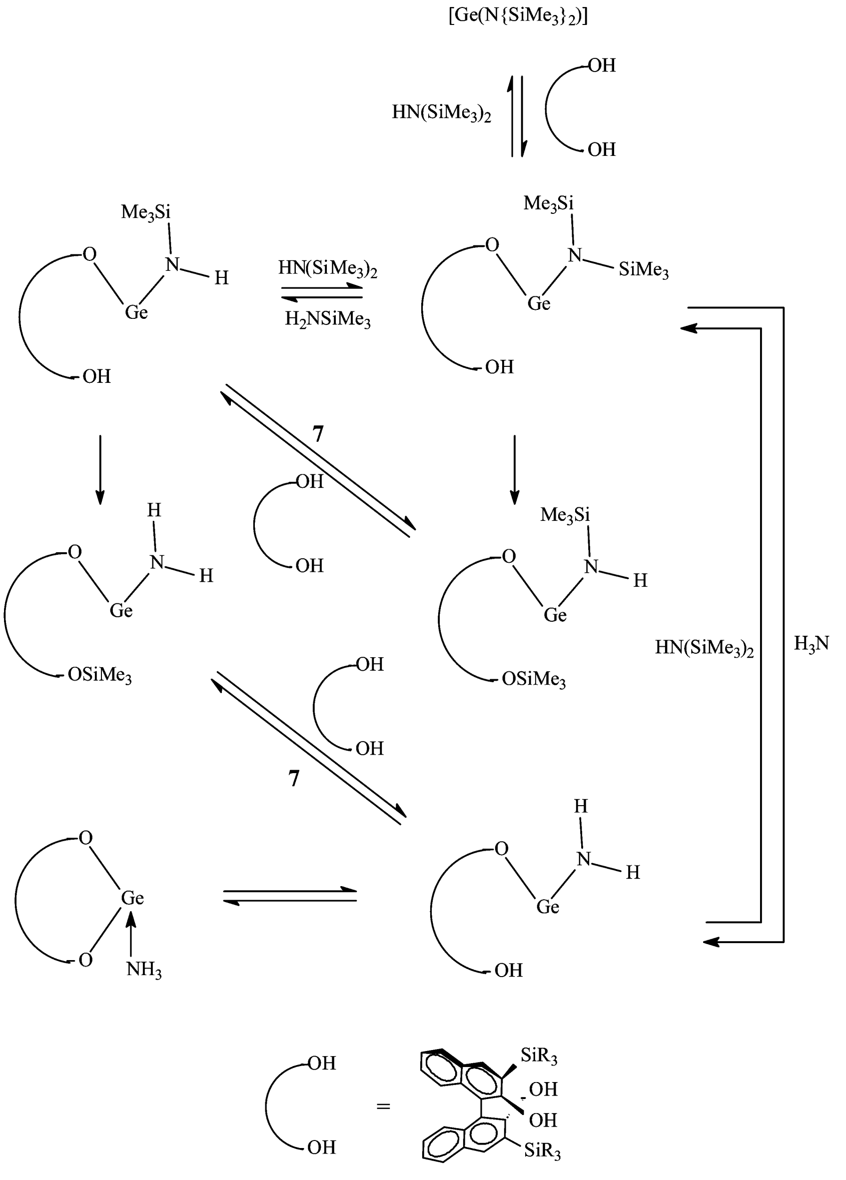

SiR$_3$ = SiMe$_3$, SiMe$_2$Ph, SiMePh$_2$, or SiPh$_3$

Scheme 1 Proposed pathway for the silylation of **3** to **7**.

N-donor ligand.[10–12] Complexes **1** and **2** are the first examples of germanium binaphthoxide compounds.

The reaction of a 1 : 1 molar ratio of HN(SiMe$_3$)$_2$ and **3** in the presence of a catalytic amount of Ge[N(SiMe$_3$)$_2$]$_2$ (10 mol%) in C$_6$D$_6$ was monitored by NMR spectroscopy. Compound **3** is catalytically mono-silylated to form (*R*)-[(HO)C$_{20}$H$_{10}$(OSiMe$_3$)-2′-(SiMe$_3$)$_2$-3,3′] (**7**). A proposed pathway is shown in Scheme 1. After 2 h at 85 °C, all of **3** had been silylated to compound **7**, as indicated by three alkylsilyl features at δ 0.51, 0.48, and −0.30 ppm as well as a hydroxyl peak at δ 5.11 ppm. The same features were observed upon exposing an NMR tube containing **1** to atmospheric moisture, which results in the hydrolysis of **1** to **7** and an uncharacterized oxidized germanium species. The catalytic conversion of **3** to **7** is complete at room temperature after 6 hours.

When an excess of HN(SiMe$_3$)$_2$ was used (3.5 equivalents) all of **3** was silylated to **7** after 2 hours with heating. Addition of **3** until the molar ratio with HN(SiMe$_3$)$_2$ was 1 : 1 led to complete conversion to **7** after 4 hours. Further addition of **3** led to a decrease in activity, and when the molar ratio of **3** to the initial amount of HN(SiMe$_3$)$_2$ was 2 : 1, the reaction had stopped. Furthermore, the hydroxyl resonance of **7** had broadened and shifted progressively downfield to a final value of 5.57 ppm. This is most likely due to hydrogen bonding with the ammonia generated in the reaction. Complex **1** is likely generated by reaction of **7** with Ge[N(SiMe$_3$)$_2$]$_2$ or one of the intermediate germanium amides which result after all the reactant HN(SiMe$_3$)$_2$ has been consumed.

Compound **7** can be generated on a preparative scale by this process.‖ Reaction of HN(SiMe$_3$)$_2$ with **3** in the presence of 10 mol% Ge[N(SiMe$_3$)$_2$]$_2$ generated **7** in pure form in 70% yield. The composition of **7** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Compound **7** is a new species, and these studies represent the first catalytic silylation of a binaphthoxide compound using a metal(II) bisamide.

The reaction of **4** with HN(SiMe$_3$)$_2$ can also be catalyzed using Ge[N(SiMe$_3$)$_2$]$_2$. An NMR scale reaction shows that **4** is converted to [(HO)C$_{20}$H$_{10}$(OSiMe$_3$)-2′-(SiMe$_2$Ph)$_2$-3,3′] (**8**). However, the reaction does not proceed as rapidly. After two hours at 85 °C, 3% of binol **4** remains. Neither heating for an additional 6 h nor addition of excess HN(SiMe$_3$)$_2$ drives the reaction to completion. A larger (preparative) scale reaction was carried out which resulted in only 50% conversion of **4** to **8**. Thus, it is not surprising that complex **2**, which contains a bidentate binaphthoxide ligand, was generated in this reaction instead of a species similar to **1**. The presence of a bulkier dimethylphenyl group relative to a trimethylsilyl group appears to have an effect on the progress of the silylation reaction.

To further investigate this postulate, Ge[N(SiMe$_3$)$_2$]$_2$ was reacted with the bulkier binol [(HO)$_2$C$_{20}$H$_{10}$(SiMePh$_2$)$_2$-3,3′]

(**5**). Upon heating a solution of Ge[N(SiMe$_3$)$_2$]$_2$ and two equivalents of **5** at 85 °C for 12 h, a substantial amount of the starting binol **5** remained. Two hydroxyl resonances were observed at δ 4.70 and 4.85 ppm in a ratio of 96 : 4, indicating only a small amount of **5** had been silylated. Intense peaks at δ 0.98 and 8.06 ppm also correspond to the Si*Me*Ph$_2$ group and the 4,4′-hydrogens of **5**, respectively. Weak resonances at δ 8.10 and −0.66 ppm were also observed, which also suggests that some [(HO)C$_{20}$H$_{10}$(OSiMe$_3$)-2′-(SiMePh$_2$)$_2$-3,3′] had been formed. No new products were observed in the reaction of Ge[N(SiMe$_3$)$_2$]$_2$ with (*R*)-[(HO)$_2$C$_{20}$H$_{10}$(SiPh$_3$)$_2$-3,3′] (**6**) after heating for 48 h at 85 °C. Thus, the steric bulk of the binol complex plays a role in the ability of the germanium bisamide to carry out the silylation reaction.

In order to determine the necessity of the germanium metal center in this process, a 1 : 1 molar ratio of HN(SiMe$_3$)$_2$ and [(HO)$_2$C$_{20}$H$_{10}$(SiMe$_3$)$_2$-3,3′] was heated in an NMR tube for 72 hours at 85 °C, after which time approximately 30% of [(HO)$_2$C$_{20}$H$_{10}$(SiMe$_3$)$_2$-3,3′] had been converted to [(HO)-C$_{20}$H$_{10}$(OSiMe$_3$)-2′-(SiMe$_3$)$_2$-3,3′]. Thus, the presence of the germanium metal center significantly increases the rate of the silylation reaction. Silylation of other acidic alcohols using HN(SiMe$_3$)$_2$ has been reported using ZnCl$_2$ as the catalyst.[13]

Other metal(II) bisamides also appear to silylate a hydroxyl group of **3** with metal-dependant reactivity. Two equivalents of binol **3** were reacted with both Sn[N(SiMe$_3$)$_2$]$_2$ and Zn[N(SiMe$_3$)$_2$]$_2$ to give metal binol complexes as evidenced by NMR spectroscopy. These metal(II) bisamides also appear to function as silylation catalysts. Compound **3** is converted to **7** with the zinc compound within 30 minutes at room temperature and 10 minutes when heated at 85 °C. The tin complex converts **3** to **7** only after heating for 12 hours. Thus, the identity of the metal appears to play an important role in the rate of the silylation reaction (Scheme 1). Further studies of the reactivity of these metal(II) amides are underway.

Acknowledgements

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Notes and references

† Preparation of **1**: To a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.63 g, 1.6 mmol) in 5 mL of benzene was added 1.37 g (3.18 mmol) of (*R*)-[H$_2$O$_2$C$_{20}$H$_{10}$(SiMe$_3$)$_2$-3,3′] in 5 mL benzene dropwise over 5 min. The mixture was heated at 85 °C in a sealed flask for 12 h, after which time yellow crystals had precipitated. The crystals were isolated by filtration, washed with benzene (3 × 5 mL) and pentane (3 × 5 mL) and dried *in vacuo*. Yield: 0.51 g (32%). Anal. calc. for C$_{58}$H$_{74}$O$_4$Si$_6$Ge: C, 64.72; H, 6.93. Found: C, 63.44; H, 6.83%. ^{1}H NMR (C$_6$D$_6$): δ 8.16 (s, 2 H, 4,4′ hydrogens), 7.69 (d, 2 H, ^3J(H,H) = 8.1 Hz, 6,6′ hydrogens), 7.46 (d, 2 H, ^3J(H,H) = 8.1 Hz, 8,8′ hydrogens), 7.28–6.83 (aromatics, 14 H), 0.68 (s, 9 H, –OSiC*H*$_3$), 0.24 (s, 18 H, –SiC*H*$_3$), −0.28 (s, 18 H, –SiC*H*$_3$) ppm. ^{13}C NMR (C$_6$D$_6$): δ 157.3 (*C*–O–Ge), 138.2 (*C*–O–SiMe$_3$), 134.9, 129.8, 128.9–126.8 (aromatics), 124.3 (*C*–SiMe$_3$), 123.9 (*C*–SiMe$_3$), 5.4 (OSi*C*H$_3$), 2.8 (Si*C*H$_3$), −0.6 (Si*C*H$_3$) ppm.

‡ Crystal data for **1**: C$_{58}$H$_{74}$GeO$_4$Si$_6$, M_r = 1076.34, monoclinic, space group $P2_1$, a = 11.0695(2), b = 21.0832(4), c = 12.8046(3) Å, β = 99.7148(8), V = 2945.2(2) Å^3, Z = 2, ρ_{calc} = 1.214 g cm^{-3}, $F(000)$ = 1140.0, λ = 0.71073 Å, T = 150(1) K, μ(Mo-Kα) = 0.673 mm^{-1}, crystal dimensions 0.45 × 0.30 × 0.28 mm, $10.00 \geq 2\theta \leq 54.97°$; 29283 reflections (12785 independent, R_{int} = 0.059), maximum residual electron density: 0.47 e Å^{-3}, R_1 = 0.037 (for $F_o^2 > 2\sigma(F_o^2)$) and wR_2 = 0.082 (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. CCDC reference number 176939.

§ Preparation of **2**: The same procedure for **1** was used for **2**, using 0.19 g (0.48 mmol) of Ge[N(SiMe$_3$)$_2$]$_2$ and 0.53 g (0.96 mmol) (*R*)-[H$_2$O$_2$C$_{20}$H$_{10}$(SiMe$_2$Ph)$_2$-3,3′]. Yield: 0.65 g of **2** (20%). ^{1}H NMR (C$_6$D$_6$): δ 8.18 (s, 2 H, 4,4′ hydrogens), 7.79 (d, ^3J(H,H) = 8.1 Hz, 2 H, 6,6′ hydrogens), 7.58 (m, 4 H, aromatics), 7.35 (d, ^3J(H,H) = 8.4 Hz, 8,8′ hydrogens), 7.14–7.08 (m, 10 H, aromatics), 6.94–6.92 (m, 2 H, aromatics), 0.75 (s, 6 H, –SiC*H*$_2$Ph), 0.68 (s, 6 H, –SiC*H*$_2$Ph) ppm.

¶ Crystal data for **2**: C$_{36}$H$_{35}$GeNO$_2$Si$_2$, M_r = 642.45, orthorhombic, space group $P2_12_12_1$, a = 8.3277(2), b = 10.4652(3), c = 36.0635(8) Å, V = 3143.0(2) Å^3, Z = 4, ρ_{calc} = 1.358 g cm^{-3}, $F(000)$ = 1336.0, λ = 0.71073 Å, T = 150(1) K μ(Mo-Kα) = 1.067 mm^{-1}, crystal dimensions 0.13 × 0.10 × 0.10 mm, $10.00 \geq 2\theta \leq 54.99$; 20161 reflections (6841 independent, R_{int} = 0.072), maximum residual electron density: 0.31 e Å^{-3}, R_1 = 0.044 and wR_2 = 0.077. CCDC reference number 176940. See http://www.rsc.org/suppdata/dt/b2/b204299a/ for crystallographic data in CIF or other electronic format.

|| Preparation of **7**: To a solution of 0.55 g (1.3 mmol) of (*R*)-[H$_2$O$_2$C$_{20}$H$_{10}$(SiMe$_3$)$_2$-3,3′] in 10 mL of benzene was added HN(SiMe$_3$)$_2$ (0.27 mL, 0.21 g, 1.3 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.050 g, 0.13 mmol). The solution was heated in a sealed flask for 12 h, and the flask was opened in air after cooling. A white suspension resulted after stirring in air for 30 min, which was filtered through Celite. The solvent was removed from the filtrate resulting in a white solid. Yield: 0.4 g (70%). ^{1}H NMR (C$_6$D$_6$): δ 8.15 (s, 1 H), 8.12 (s, 1 H), 7.74 (d, 1 H, ^3J(H,H) = 9.0 Hz), 7.70 (d, 1 H, ^3J(H,H) = 9.0 Hz), 7.28–6.94 (aromatics, 6 H), 5.11 (s, –O*H*), 0.51 (s, 9 H, –OSiC*H*$_3$), 0.48 (s, 9 H, –SiC*H*$_3$), −0.30 (s, 9 H, –SiC*H*$_3$) ppm. ^{13}C NMR (C$_6$D$_6$): δ 158.0, 157.0, 139.1, 137.8, 136.0, 135.8, 130.8, 130.2, 130.0, 129.2, 129.0, 128.9, 127.7, 125.9, 125.8, 125.0, 123.9, 117.6, 115.4, 1.3, 0.5, −0.3 ppm. HRMS: Calc. for C$_{29}$H$_{38}$O$_2$Si$_3$: *m/z* 502.2180. Found: *m/z* 502.2180.

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