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Metal-Dependent Reactions of Bulky Metal(II) Amides $M[N(SiMe_3)_2]_2$ with 3,3′-Disubstituted Binaphthols $(HO)_2C_{20}H_{10}(SiR_3)_2$-3,3′: Selective Conversion of One Equivalent −OH Group to a Silyl Ether $-OSiMe_3$

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The outcome of the reaction of the bulky metal(II) amides $M[N(SiMe_3)_2]_2 \cdot n$THF (M = Be, Zn, Ge, Sn, $n = 0$; M = Mg, Ca, $n = 2$) with (*R*)-3,3′-bis(trimethylsilyl)-1,1′-bi-2,2′-naphthol ((*R*)-**1**) or (*S*)-3,3′-bis(dimethylphenylsilyl)-1,1′-bi-2,2′-naphthol ((*S*)-**9**) depends on the identity of the metal and the nature of the 3,3′-substituents. When M = Be, Zn, or Ge, these amides serve as useful silylation agents that convert only one of the equivalent hydroxyl groups of the binaphthol (*R*)-**1** to a trimethylsilyl ether, whereas the reactions of (*R*)-**1** with the Mg, Ca, or Sn amides generate a polynuclear complex. The reaction pathway for these interconversions was qualitatively monitored using NMR (^{1}H and ^{9}Be) spectroscopy. Treatment of $Ge[N(SiMe_3)_2]_2$ with (*S*)-**9** yields both a silyl ether and the chelated germanium(II) binaphthoxide (*S*)-$[Ge\{O_2C_{20}H_{10}(SiMe_2Ph)_2\text{-}3,3'\}\{NH_3\}]$, which was structurally characterized.

Introduction

The conversion of hydroxyl groups to silyl ethers is a highly used method for the protection of the −OH group, where this interconversion can be achieved by various preparative methods.[1–12] Silyl ethers are widely used as protecting groups because they are readily prepared and can be easily cleaved by a fluoride ion due to the high stability of the Si−F bond.[13] Common trialkylsilyl groups employed for this purpose include trimethylsilyl (TMS), triethylsilyl (TES), *tert*-butyldimethylsilyl (TBDMS), tri-*iso*-propylsilyl (TIPS), and *tert*-butyldiphenylsilyl (TBDPS), where the stability of the Si−O bond toward acids or bases depends on the identity of the alkyl groups bound to the silicon atom with the Si−O bond of the $-OSiMe_3$ (TMS) group being the weakest under both types of conditions.[12] The generation of this moiety using hexamethyldisilazane $HN(SiMe_3)_2$ can be catalyzed by a number of reagents including molecular iodine,[14] Me_3SiCl,[15,16] amides or imides,[17] copper(II) porphyrins,[18] trimethylsilyl triflate,[19] tetrabutylammonium fluoride,[20] $ZnCl_2$,[21] metal chloride complexes,[22] tungstophosphoric acid,[23] silica chloride,[24] zirconium sulfophenyl phosphonate,[25] montmorillonite clay,[26] and zeolites.[27]

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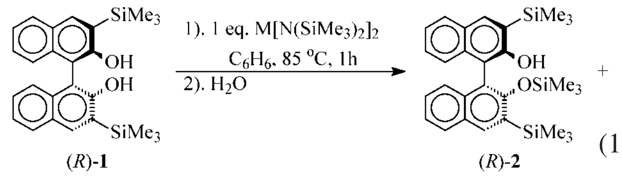
The selective silylation of one hydroxyl group in substrates having two such functional groups is a useful process for synthetic applications that has been observed in a number of cases.[20,22,23,26,28–32] Complete preference for the silylation of primary −OH groups in molecules also bearing secondary and tertiary hydroxyls has been reported using various silylation agents including 5,5-dimethyl-1,3-bis(trimethylsilyl)hydantoin or 5,5-dimethyl-1,3-bis(*tert*-butyldimethylsilyl)hydantoin,[20] Ph_2PSiR_3 in the presence of diethyl azodicarboxylate and *p*-toluenesulfonate,[28] silyl methallylsulfinates,[30] or Et_3SiH in the presence of AuCl(xantphos) as a catalyst.[29] However, preferential regioselectivity among equivalent −OH groups has not been reported.

The reaction of bulky metal(II) amides $M[N(SiMe_3)_2]_2$ (M = Ge, Cd, Hg) with binaphthols[33] and calixarenes[34] via the protonolysis reaction yields a number of interesting products. We have observed metal-dependent reactivity upon the treatment of 3,3′-disubstituted binaphthols with these and other related amides $M[N(SiMe_3)_2]_2$ (M = Be, Mg, Ca, Zn, Cd, Hg, Ge, Sn), where the products obtained depend on the identity of the metal. These include cyclization of the substrate to furnish 1,7-disubstituted *peri*-xanthenoxanthanes, formation of polynuclear species having bridging binaphthoxide ligands, complex formation, or the selective silylation of one of the two hydroxyl groups of the substrate. We have previously reported the reaction of $Hg[N(SiMe_3)_2]_2$ with 3,3′-disubstituted binaphthols, which furnishes 1,7-disubstituted *peri*-xanthenoxanthanes[33] and was also observed with the related cadmium amide. We have subsequently investigated the reactions of the other six bulky metal(II) amides with these substrates, which is the focus of this article. A portion of this work has been reported in a preliminary communication.[35]

Results and Discussion

The monosilylated binaphthol (*R*)-**2** can be obtained on a preparative scale from (*R*)-**1** and 1 equiv of the metal(II) amides $Be[N(SiMe_3)_2]_2$, $Zn[N(SiMe_3)_2]_2$, or $Ge[N(SiMe_3)_2]_2$ (eq 1) by combining the two reagents in benzene and heating the reaction mixture at 85 °C for 1 h followed by aqueous workup. The conversion of (*R*)-**1** to (*R*)-**2** proceeds quantitatively as shown by ¹H NMR spectroscopy and (*R*)-**2** was isolated in high yields (>85%) in all three cases. This conversion thus serves to selectively protect one hydroxyl group of the binpahthol by converting it to a silyl ether while leaving the second −OH moiety available for further reactivity.



(*R*)-**1** (*R*)-**2** (1)

$$HN(SiMe_3)_2 + H_2NSiMe_3 + NH_3 + (MO)_x$$

M = Be, 91 %; M = Zn, 88 %; M = Ge, 89 %

The relative rates of the three individual reactions were observed to be different. The conversion of (*R*)-**1** to (*R*)-**2** was complete within 10 min when the beryllium amide was employed as the silylation reagent but required a reaction time of approximately 40 min in the case of the germanium species. Because compounds (*R*)-**1** and (*R*)-**2** exhibit distinct resonances for their respective hydroxyl protons, the reactions of (*R*)-**1** with the metal(II) amides $M[N(SiMe_3)_2]_2 \cdot n$THF (M = Be, Zn, Ge, Sn, *n* = 0; M = Mg, Ca, *n* = 2) were monitored using ¹H NMR spectroscopy and a proposed pathway from the silylation process is illustrated in Scheme 1. The intermediates formed in the reaction are likely present in a complex equilibrium, and those containing a single −OH group are stable enough that they can be observed in solution using NMR spectroscopy in some cases (vide infra). All of the metal(II) amides $M[N(SiMe_3)_2]_2$ involved in the silylation process lose one $-N(SiMe_3)_2$ ligand as free hexamethyldisilazne via a protonolysis reaction with one hydroxyl group of the binaphthol, resulting in the attachment of the $-M[N(SiMe_3)_2]$ fragment to the oxygen atom of the substrate which subsequently is involved in the trimethylsilyl group transfer.

In the ¹H NMR spectra of all of the reactions, a resonance was observed for the single hydroxyl group of the monosilylated product (*R*)-**2** at 5.02 ppm and the peak for the two equivalent −OH groups of the starting binaphthol (*R*)-**1** appeared at 4.87 ppm. In addition to these two features, a third resonance at 5.30 ppm was visible in most cases, which was attributed to the intermediate (*R*)-**3**, the stability of which depends on the identity of the metal. Data from these investigations are collected in Table 1, where the reported intensity values are the integrated intensities of these three hydroxyl resonances. All spectra described in Table 1 were recorded at 70 °C.

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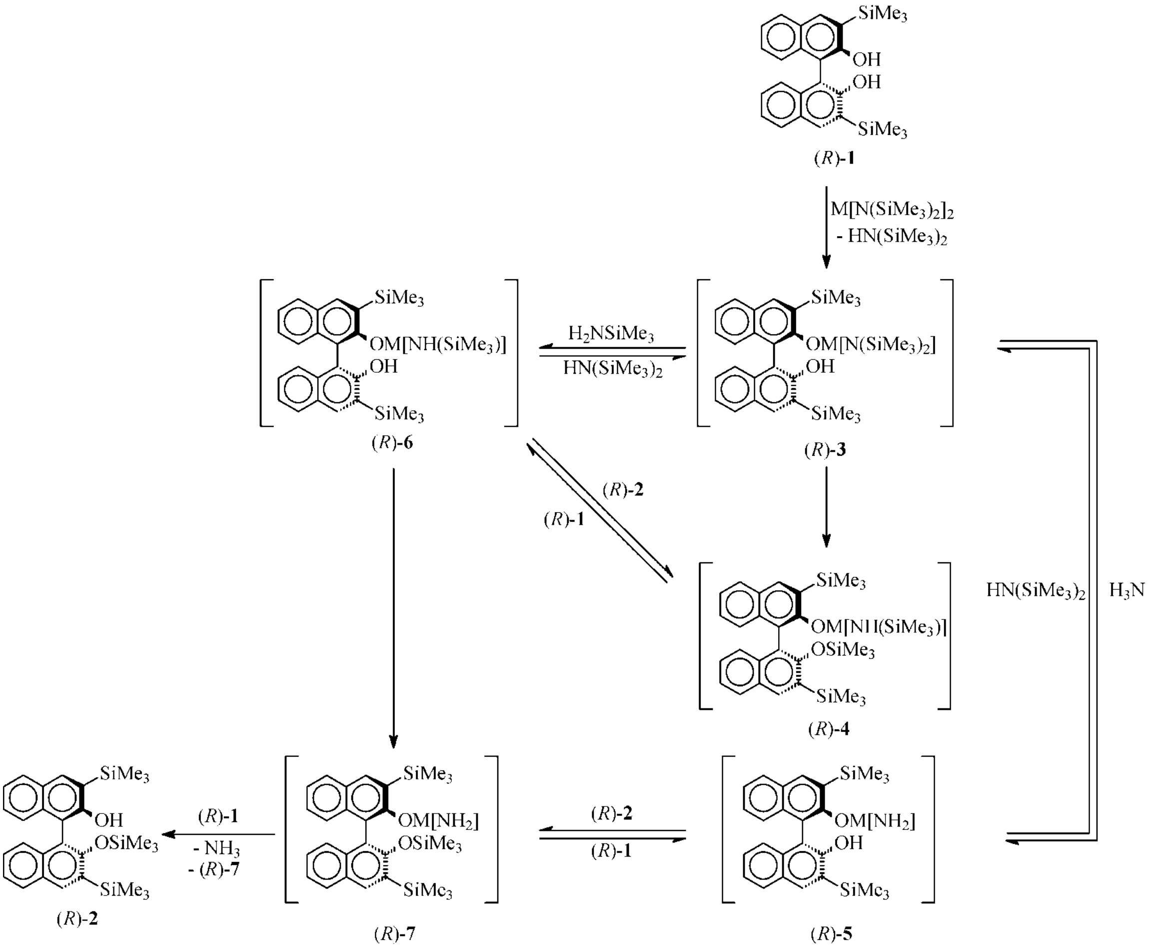
Scheme 1



These results clearly indicate that the outcome of the silylation reaction is highly dependent on the identity of the metal present in the amide. When either 0.5 equiv (entry 1) or 1.0 equiv (entry 2) of $Be[N(SiMe_3)_2]_2$ is employed as the silylation reagent, no intermediate (*R*)-**3** is observed and compound (*R*)-**1** is completely consumed furnishing compound (*R*)-**2** within 10 min. The NMR spectra recorded for entries 1 and 2 also exhibit two resonances for the $-SiMe_3$ groups of (*R*)-**2** at 0.51 and 0.48 ppm and a peak at −0.30 ppm arising from the $-OSiMe_3$ group.

Probing the reaction of $Be[N(SiMe_3)_2]_2$ with 1, 2, and 4 equiv of (*R*)-**1** using ^{9}Be NMR spectroscopy clearly demonstrates that all four $-SiMe_3$ groups present in the amide can be transferred to the binaphthol to furnish the product (*R*)-**2** and also provides evidence for the presence of the silylated intermediates (*R*)-**4** and (*R*)-**7**. As the stoichiometric ratio of the beryllium amide to (*R*)-**1** decreases as sequential equivalents of (*R*)-**1** are added to the NMR tube, the intensities of the resonance for (*R*)-**4** would be expected to decrease relative to that for (*R*)-**7** because fewer $-SiMe_3$ groups are available for transfer to the opposite −OH group. This also would result in the exclusive generation of the $-OM[NH_2]_2$ moiety of (*R*)-**7** versus the $-OM[NH(SiMe_3)]$ group in (*R*)-**4** when the ratio of $Be[N(SiMe_3)_2]_2$ to (*R*)-**1** becomes 1:4. The chemical shift assignments for (*R*)-**4** and (*R*)-**7** are therefore based on their relative intensities in the ^{9}Be NMR spectra recorded using different amounts of (*R*)-**1** (vide infra) because more of (*R*)-**4** is expected to be present in solution at higher stoichiometric ratios of $Be[N(SiMe_3)_2]_2$ to (*R*)-**1** than at decreased ratios of the amide to (*R*)-**1**.

Treatment of $Be[N(SiMe_3)_2]_2$ with 1 equiv of (*R*)-**1** at 70 °C in C_6D_6 results in the appearance of two features in the ^{9}Be NMR spectrum of the reaction mixture at 10.0 and 0.8 ppm, which are shifted from that for the starting amide (9.4 ppm).[36,37] The intensity of the feature at 10.0 ppm is approximately 1.5 times that of the resonance at 0.8 ppm and therefore these resonances are assigned to the two silylated intermediates (*R*)-**4** and (*R*)-**7** (respectively). The appearance of the spectrum undergoes very little change over a period of 1 h, and these data correlate with the ^{1}H NMR spectra obtained for this reaction (vide supra). All of the $Be[N(SiMe_3)_2]_2$ is rapidly consumed, and the presence of the intermediate (*R*)-**3** was also not detected using ^{9}Be spectroscopy. In addition to the features corresponding to the product (*R*)-**2**, the ^{1}H NMR spectrum of the reaction after the addition of 1 equiv of $Be[N(SiMe_3)_2]_2$ to (*R*)-**1** exhibits several resonances in the chemical shift range 0.4 to −0.3 ppm, which can be assigned to the trimethylsilyl groups of (*R*)-**4** and (*R*)-**7**. When 2 equiv of (*R*)-**1** are reacted with $Be[N(SiMe_3)_2]_2$, these same resonances are visible in the ^{9}Be NMR spectrum. However, the relative intensity of the feature

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Table 1. ^{1}H NMR Spectroscopic Data at 70 °C for the Hydroxyl Resonances in the Reactions of $M[N(SiMe_3)_2]_2$ with (*R*)-**1**

entry	equiv $M[N(SiMe_3)_2]_2$	time (min)	intensity of resonance for (*R*)-**2**	intensity of resonance for (*R*)-**1**	intensity of resonance for (*R*)-**3**
1	0.5 Be	5	93.5%	6.5%	0%
		10	100%	0%	0%
2	1.0 Be	5	69.5%	30.5%	0%
		10	100%	0%	0%
3	0.5Mg[a]	5	7.5%	92.5%	<1%
		55	30%	61.5%	8.5%
		155	33.5%	58%	8.5%
4	1.0Mg[a]	5	7.5%	88%	4.5%
		55	19%	72%	9%
		105	41.5%	41.5%	17%
		190	72%	7.5%	20.5%
5	0.5 Ca[a]	5	0%	81%	19%
		155	0%	83%	17%
6	0.5 Zn	5	10%	84.5%	5.5%
		10	12%	82%	6%
		15	23%	75%	2%
		20	27%	72%	1%
		40	35%	65%	0%
7	1.0 Zn	5	75%	0%	25%
		10	91%	0%	9%
		15	97.5%	0%	2.5%
		20	100%	0%	0%
8	0.5 Ge	5	7.5%	86.5%	6%
		10	7.5%	86.5%	6%
		40	11%	89%	< 1%
9	1.0 Ge	5	3.5%	95%	1.5%
		10	20.5%	78%	1.5%
		15	69.5%	30.5%	0%
		20	100%	0%	0%
10	0.5 Sn[a]	5	5%	95%	0%
		10	6.5%	93%	0.5%
		15	8%	91%	1%
		45	11.5%	87%	1.5%
		100	14.5%	85.5%	0%

[a] Silylation and formation of a polynuclear species both occur.

for the intermediate (*R*)-**4** at 10.0 ppm is approximately half of that of (*R*)-**7** at 0.8 ppm, indicating that the intermediate (*R*)-**7** is now present in greater abundance than (*R*)-**4**.

The spectrum of the reaction of 4 equiv of (*R*)-**1** with $Be[N(SiMe_3)_2]_2$ exhibits only one feature at 0.08 ppm corresponding to (*R*)-**7**, which indicates that (*R*)-**7** remains present in solution along with product (*R*)-**2**, which can be generated from (*R*)-**7** during the course of the reaction by the release of NH_3 upon the transfer of protons from (*R*)-**1** to (*R*)-**7**. When the reaction is conducted on a preparative scale, any (*R*)-**7** remaining present in solution is converted to (*R*)-**2** after aqueous workup. This indicates that all four $-SiMe_3$ groups of the beryllium amide are available for transfer to one of the hydroxyl oxygen atoms of the binaphthol via cleavage of the nitrogen−silicon bond. This type of reactivity has also been observed upon the treatment of $Be[N(SiMe_3)_2]_2$ with HSPh, and this process also involves the formation of NH_3.[38] The corresponding ^{1}H NMR spectrum of the reaction mixture of 4 equiv of (*R*)-**1** with $Be[N(SiMe_3)_2]_2$ exhibits three peaks at 0.43, 0.04, and −0.35 ppm, which are assigned to the three $-SiMe_3$ groups of (*R*)-**7**, as well as two features at 0.95 and 0.07 ppm. The former, which is weaker in intensity than the latter, corresponds to $HN(SiMe_3)_2$, and the second feature tentatively can be assigned to H_2NSiMe_3,[39] although this species has been shown to undergo disproportionation to $HN(SiMe_3)_2$ and NH_3 above room temperature.

The reactions of the magnesium and calcium amides with (*R*)-**1** are much more sluggish than that of their lighter congener (entries 3–5). When 0.5 equiv of the magnesium amide is treated with (*R*)-**1**, very little change in the ^{1}H NMR spectrum is observed after a reaction time of 55 min. Less than 35% of compound (*R*)-**1** was converted to (*R*)-**2** at this time, and the intermediate (*R*)-**3** remains present in solution even after 24 h. Similarly, the reaction using 1.0 equiv of magnesium amide converts more of (*R*)-**1** to (*R*)-**2** but also produces a significantly greater amount of (*R*)-**3**. In the case of the calcium amide, the reaction of (*R*)-**1** with 0.5 equiv of $Ca[N(SiMe_3)_2]_2 \cdot 2THF$ did not yield (*R*)-**2**, but a significant amount of (*R*)-**3** was generated that was stable for long periods of time and some starting material (*R*)-**1** remained present in solution. In all three of these cases (entries 3–5), a thick gelatinous material precipitated from solution, which is likely a polynuclear metal complex containing bridging binaphthoxide ligands. In the reaction of 1.0 equiv of $Ca[N(SiMe_3)_2]_2 \cdot 2THF$ with (*R*)-**1**, the reaction mixture became extremely viscous such that a satisfactory NMR spectrum could not be obtained.

The formation of complexes containing bridging binaphthoxide ligands has been observed with other large metals.[40–47] For example, the reaction of $La[N(SiMe_3)_2]_3$ with 3,3′-bis(diphenylphosphinoylmethyl)-1,1′-bi-2,2′-naphthol furnished a dinuclear lanthanum complex incorporating three bridging binaphthoxide ligands.[40] The ionic radii and electronegativities of La^{3+} and Ca^{2+} are similar, and therefore it is plausible that the reaction of the calcium amide with (*R*)-**1** generates a similar polynuclear species. This may also be occurring in the reactions involving the magnesium amide, but we as yet have been unable to obtain X-ray quality crystals for any of these products that would lead to their unequivocal identification.

It can be inferred from these results that the stability of intermediate (*R*)-**3** is related to the relative strengths of the M−N and N−Si bonds in these systems. Presumably, the metal−nitrogen bond strength decreases upon descending group 2 with a concomitant increase in the N−Si bond strength. There is also a correlation with the absolute hardness of the metal centers,[48] which also suggests that a stronger M−O bond would be formed with beryllium versus

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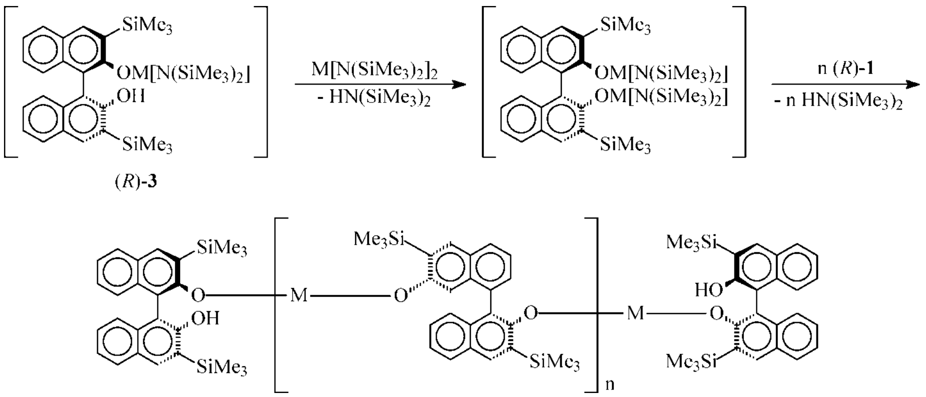
Scheme 2



that with magnesium, calcium, and the other metals employed in these reactions. The stability of (*R*)-**3** is greater when a stronger N−Si bond is present because cleavage of this bond is necessary for silyl group transfer to occur, and it is evident that when (*R*)-**3** is stable for long periods of time a polynuclear species is generated in the reaction. This could result from the attack of a second metal(II) amide at the remaining hydroxyl group in (*R*)-**3** to give a dimetalated intermediate, which then reacts with (*R*)-**1** present in solution to generate the final polynuclear product (Scheme 2).

Of the group 12 metal(II) amides, only the zinc congener effects the silylation of (*R*)-**1**. The cadmium(II) and mercury(II) species instead result in an intramolecular electrophilic aromatic substitution reaction to furnish either a pentacyclic species or 1,7-bis(trimethylsilyl)-*peri*-xanthenoxanthane depending on the reaction stoichiometry employed.[33] Reactions of $Zn[N(SiMe_3)_2]_2$ with (*R*)-**1** proceed cleanly to furnish (*R*)-**2**, which is advantageous because $Zn[N(SiMe_3)_2]_2$ is commercially available from a number of sources and is not highly air- or moisture-sensitive. Silylation reactions of (*R*)-**1** using $Zn[N(SiMe_3)_2]_2$ thus can be carried out under a slow purge of nitrogen without the need for Schlenk apparatus, therefore rendering this conversion a valuable tool for organic synthesis.

The reactions of $Zn[N(SiMe_3)_2]_2$ with (*R*)-**1** were also monitored by ^1H NMR spectroscopy (Table 1, entries 6 and 7). When 0.5 equiv of the zinc amide is employed in the reaction, only 35% of binaphthol (*R*)-**1** is converted to (*R*)-**2** after a reaction time of 40 min. The intermediate (*R*)-**3** was also observed at the initial stages of the reaction, but the resonance for this species was absent after 40 min. The feature at 0.20 ppm corresponding to the zinc amide was also absent after 40 min whereas peaks at 0.90 and 0.48 ppm indicated that free $HN(SiMe_3)_2$ had been generated in the reaction and unreacted (*R*)-**1** remained present in solution. These data indicate that all of the $Zn[N(SiMe_3)_2]_2$ had been consumed to yield the product (*R*)-**2** and free hexamethyldisilazane.

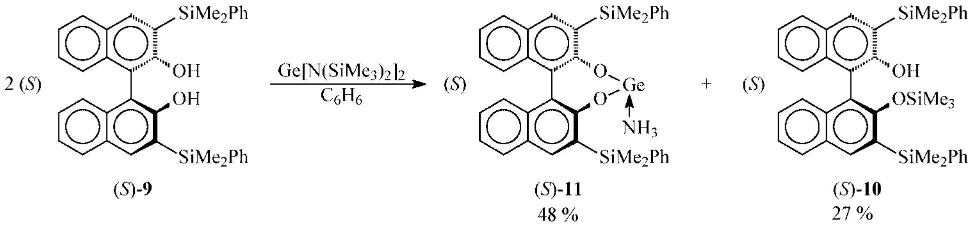
Addition of a second 0.5 equiv of $Zn[N(SiMe_3)_2]_2$ to the NMR tube resulted in the complete consumption of (*R*)-**1** and generation of both (*R*)-**2** and (*R*)-**3** in a ratio of 96:4 after a reaction time of 5 min. After an additional 2 min, the resonance for (*R*)-**3** had disappeared, and only that for the product (*R*)-**2** remained. When 1.0 equiv of the zinc amide was reacted directly with (*R*)-**1**, no evidence for (*R*)-**1** was observed in the NMR spectrum after 5 min and only features for (*R*)-**2** and (*R*)-**3** were present. After a total reaction time of 20 min, only product (*R*)-**2** was present. Therefore, when the ratio of $Zn[N(SiMe_3)_2]_2$ to (*R*)-**1** is 1:1, the starting binaphthol is completely silylated to yield product (*R*)-**2**. The reactivity of $Zn[N(SiMe_3)_2]_2$ is similar to that of $Be[N(SiMe_3)_2]_2$, although the latter reagent appears to react even faster than the zinc derivative because no evidence for the intermediate (*R*)-**3** is observed in reactions involving the beryllium amide.

The group 14 metal amides $Ge[N(SiMe_3)_2]_2$ and $Sn[N(SiMe_3)_2]_2$ can also be used for the conversion of (*R*)-**1** to (*R*)-**2**. Treatment of (*R*)-**1** with 0.5 equiv of the tin amide only converts 14.5% of (*R*)-**1** to (*R*)-**2** (Table 1, entry 10), whereas employing 1.0 equiv of $Sn[N(SiMe_3)_2]_2$ in this reaction resulted in the precipitation of a large amount of viscous material, which is again presumed to be a polynuclear binaphthoxide complex, and we were unable to obtain a meaningful ^1H NMR spectrum for this reaction. The germanium species, however, reacts in a manner similar to the zinc and beryllium derivatives. Treatment of (*R*)-**1** with 0.5 equiv of $Ge[N(SiMe_3)_2]_2$ converts 11% of (*R*)-**1** to (*R*)-**2** after 40 min, and the formation and subsequent consumption of (*R*)-**3** also was observed in this reaction. Addition of a second 0.5 equiv of $Ge[N(SiMe_3)_2]_2$ to the NMR tube converts all of the remaining (*R*)-**1** to product (*R*)-**2**, and no signal for the intermediate (*R*)-**3** was observed during the course of this reaction.

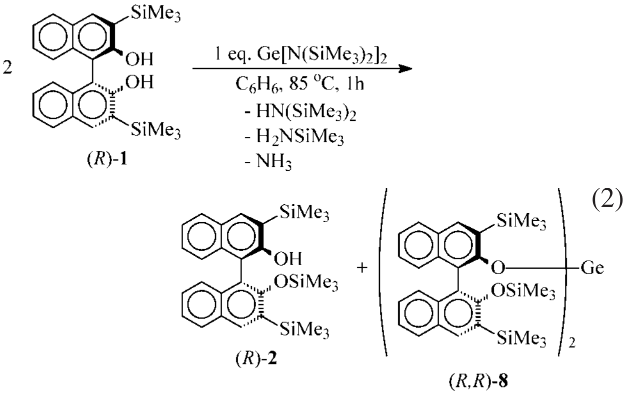
Direct treatment of (*R*)-**1** with 1.0 equiv of $Ge[N(SiMe_3)_2]_2$ results in the complete conversion of this species (*R*)-**2** in 20 min, and a resonance for the intermediate (*R*)-**3** was visible in the spectrum at 5.47 ppm during the first 12 min of the reaction. A second feature at 5.22 ppm also was discernible during this time, which was approximately equal in intensity to that for (*R*)-**3**, and this feature is assigned to the presence of the second intermediate hydroxyl species (*R*)-**6**, which is transiently stable during the course of the reaction and subsequently undergoes a silyl group transfer to generate (*R*)-**7**. The two resonances for (*R*)-**3** and (*R*)-**6** decreased in intensity and disappeared from the ^1H NMR spectrum at the same time.

The germanium amide exhibits additional reactivity that is distinct from the other amide reagents employed in these

Scheme 3



studies. When $Zn[N(SiMe_3)_2]_2$ was treated with 2 or 4 equiv of (*R*)-**1**, only compound (*R*)-**2** was obtained. However, when the stoichiometric ratio of (*R*)-**1** to $Ge[N(SiMe_3)_2]_2$ was 2:1, both (*R*)-**2** and the germylene complex (*R*,*R*)-$[Ge\{OC_{20}H_{10}\text{-}(OSiMe_3)\text{-}2'\text{-}(SiMe_3)_2\text{-}3,3'\}_2]$ ((*R*,*R*)-**8**) are produced in the reaction. The latter product results from the reaction of $Ge[N(SiMe_3)_2]_2$ present in solution with (*R*)-**2** (eq 2), and (*R*,*R*)-**8** could be obtained in 32% yield on a preparative scale after recrystallization, whereas evaporation of the mother liquor yielded (*R*)-**2** in 36% yield. The X-ray crystal structure of (*R*,*R*)-**8** was determined,[35] which confirmed the presence of two binaphthoxide ligands attached to the germanium center through a single oxygen atom where the second oxygen atom of the binaphthoxide ligand has been incorporated into the $-OSiMe_3$ silyl ether group. The O−Ge−O angle of 89.4(7)° at the germanium atom in (*R*,*R*)-**8** approaches the expected value of 90° and the germanium oxygen distances average 1.814(2) Å, which is characteristic of a germanium(II)−oxygen bond.



(2)

The metal(II) amides $M[N(SiMe_3)_2]_2$ (M = Be, Zn, Ge) also react with either 1 or 2 equiv of the more sterically encumbered binaphthol (*S*)-3,3′-bis(dimethylphenylsilyl)-1,1′-bi-2,2′-napthol (*S*)-**9** to generate (*S*)-**10**. However, the reaction of $Ge[N(SiMe_3)_2]_2$ with 2 equiv of (*S*)-**9** furnishes both (*S*)-**10** and the chelated germylene complex (*S*)-**11** in yields of 27% and 48% (respectively) based on $Ge[N(SiMe_3)_2]_2$ (Scheme 3), where (*S*)-**11** results from the direct protonolysis reaction of $Ge[N(SiMe_3)_2]_2$ with (*S*)-**9**. A related chelated product similar to (*S*)-**11** containing beryllium or zinc was not observed in reactions employing the beryllium or zinc derivatives presumably because these two species consume (*S*)-**9** more rapidly than the germanium derivative to furnish the silylated product (*S*)-**10**.

The composition of (*S*)-**11** was confirmed by NMR spectroscopy and elemental analysis and its X-ray crystal structure was determined that is similar to that reported for the (*R*)-derivative.[35] An ORTEP diagram of (*S*)-**11** is shown in Figure 1, and selected bond distances and angles are collected in Table 2. The germanium−oxygen bond distances average 1.874(3) Å, which are elongated compared to those in (*R*,*R*)-**8** due to the larger 3,3′-substituents on the binaphthol rings in (*S*)-**11** and the presence of the seven-membered GeO_2C_4 ring. The O−Ge−O angle in (*S*)-**11** deviates significantly from the ideal value of 90°, which is enforced by the chelating nature of the binaphthoxide ligand, and the two naphthyl rings are rotated by 64.6° relative to one another, which is much narrower than that in the parent free binaphthol, where the relative orientation of the rings approaches 90°.[49] The Ge−N distance in (*S*)-**11** is relatively long at 2.107(4) Å, which is indicative of a dative interaction where the lone pair of electrons on the nitrogen atom is donated into the vacant p orbital present on the germanium(II) center. The complexation of the NH_3 molecule

Table 2. Selected Bond Distances (Angstroms) and Angles (Degrees) for (*S*)-**11**

Ge(1)−O(1)	1.886(3)	O(1)−Ge(1)−O(2)	97.9(1)
Ge(1)−O(2)	1.863(3)	O(1)−Ge(1)−N(1)	81.6(1)
Ge(1)−N(1)	2.107(4)	O(2)−Ge(1)−N(1)	96.2(1)
O(1)−C(1)	1.363(5)	C(1)−C(10)−C(11)−C(20)	64.6(1)
O(2)−C(20)	1.364(4)		
C(10)−C(11)	1.501(5)		

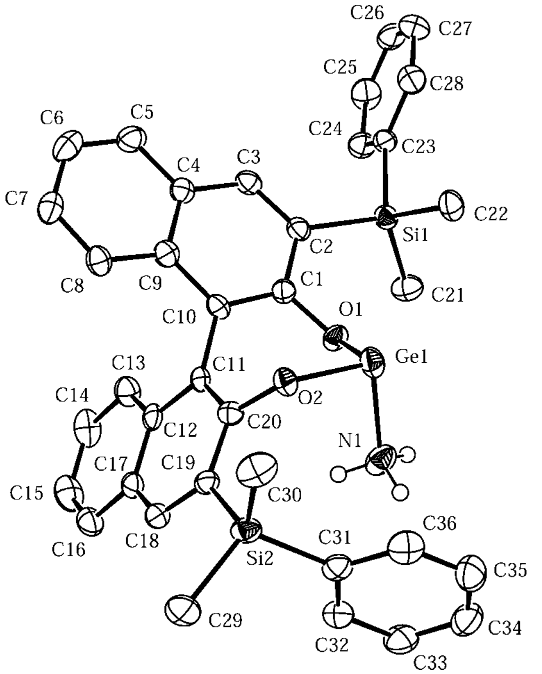


Figure 1. ORTEP diagram of (*S*)-**11**. Thermal ellipsoids are drawn at 50% probability.

provides further evidence that ammonia is generated in these reactions.

The use of even more encumbering 3,3′-substituents on the binaphthol or larger metal centers in the metal(II) amides did not result in silylation of a hydroxyl group. No reaction was observed upon the treatment of $M[N(SiMe_3)_2]_2$ (M = Be, Mg, Ca, Zn, Ge, Sn) with either (*S*)-3,3′-bis(diphenylmethylsilyl)-1,1′-bi-2,2′-naphthol or (*S*)-3,3′-bis(triphenylsilyl)-1,1′-bi-2,2′-naphthol, although the cadmium(II) and mercury(II) amides can convert these derivatives to 1,7-disubstituted *peri*-xanthenoxanthanes. Additionally, no silylation processes were observed with these two substrates nor (*R*)-**1** and (*S*)-**9** when the corresponding lead(II) or strontium(II) amides were employed as the silylation reagent.

Conclusions

The bulky metal(II) amides $M[N(SiMe_3)_2]_2$ (M = Be, Zn, Ge) cleanly transfer a $-SiMe_3$ group to the oxygen atom of only one hydroxyl group of either (*R*)-3,3′-bis(trimethylsilyl)-1,1′-bi-2,2′-naphthol ((*R*)-**1**) or (*S*)-3,3′-bis(dimethylphenylsilyl)-1,1′-bi-2,2′-naphthol ((*R*)-**9**) to generate a silyl ether group. This process occurs through the cleavage of the Si−N bonds in the bis(trimethylsilyl)amido ligands of the $M[N(SiMe_3)_2]_2$ reagents, which ultimately leads to the generation of ammonia and the silylated binaphthol product. All four of the $-SiMe_3$ groups in the amides are potentially available for this process, and the comparative rates of the reaction as well as the occurrence of competing processes depend on the relative strength of the Si−N bond in the metal(II) amides.

We have determined by qualitative NMR experiments that the outcome of the reaction of (*R*)-**1** with 1 equiv of $(SiMe_3)_2]_2 \cdot n$THF (M = Be, Zn, Ge, Sn, $n = 0$; M = Mg, Ca, $n = 2$) is dependent on the identity of the metal. Those species having M = Be, Zn, or Ge cleanly and exclusively generate the silyl ether (*R*)-**2** in excellent yields, where the relative rate of the silylation process increases in the order M = Ge < M = Zn < M = Be. The magnesium and tin derivatives yield some (*R*)-**2** from (*R*)-**1** but preferentially react with (*R*)-**1** to furnish an aggregated species, which likely contains bridging binaphthoxide ligands, whereas $Ca[N(SiMe_3)_2]_2 \cdot 2THF$ appears to undergo the latter process exclusively. When one methyl group in (*R*)-**1** is exchanged for a phenyl group in the 3,3′-substituents ((*S*)-**9**), the beryllium and zinc amides exclusively convert one −OH group of the substrate to a $-OSiMe_3$ moiety to furnish (*S*)-**10**, whereas the germanium(II) amide produces (*S*)-**10** and also reacts directly with the binaphthol to furnish a germanium(II) binaphthoxide complex (*S*)-**11**.

Despite their substantial differences in hardness and oxophilicity, the beryllium, zinc, and germanium amides all have approximately the same outcome in reactions with the binaphthol (*R*)-**1**. Furthermore, the silylation reaction appears to empirically depend on the relative proximity of the two −OH moieties. The relative angle of rotation of the two naphthyl rings about the interannular bond, and hence the distance between the two hydroxyl groups, increases as the size of the 3,3′-substituents increases. This is demonstrated in these studies by the fact that (*R*)-**1** and (*R*)-**9** react with metal(II) amides, but more sterically encumbered binaphthols having 3,3′-(diphenylmethylsilyl) or 3,3′-(triphenylsilyl) substituents do not.

These results indicate that the relative proximity of the $-SiMe_3$ group to the binaphthol oxygen atom prior to migration is critical for the success of the reaction. The similarity in reactivity of the beryllium, zinc, and germanium amides versus the magnesium, calcium, and tin derivatives likely results from their having smaller covalent radii, thus allowing a close approach of the $-SiMe_3$ and −OH groups on opposite naphthyl rings once the initial protonolysis reaction has occurred to generate the $-OMN(SiMe_3)_2$ moiety. Additionally, if the steric effects of the 3,3′-substituents are significant enough to effect a large relative disposition of the two −OH groups in the binaphthol system, the silyl group migration also cannot occur.

Experimental Section

General Considerations. *Caution! $Be[N(SiMe_3)_2]_2$ is toxic, is a known carcinogen, and should be handled in a well-ventilated fume hood using proper personal protective equipment.* All manipulations were carried out using standard glovebox, Schlenk line, and syringe techniques.[50] The compounds (*R*)-**1**,[51] (*R*,*R*)-**8**,[35] (*R*)-**9**,[51] (*S*)-**9**,[51] $Be[N(SiMe_3)_2]_2$,[52] $Mg[N(SiMe_3)_2]_2 \cdot 2THF$,[53,54] $Ca[N(SiMe_3)_2]_2 \cdot 2THF$,[55] $Zn[N(SiMe_3)_2]_2$,[56] $Ge[N(SiMe_3)_2]_2$,[57,58] and $Sn[N(SiMe_3)_2]_2$[57] were prepared according to literature procedures or slight variations thereof. ^1H, ^{13}C, and ^9Be NMR spectra were recorded using a Varian Inova spectrometer operating at 400, 100.6, or 56.2 MHz (respectively). ^1H and ^{13}C NMR spectra were referenced to the solvent resonances for C_6D_6, whereas ^9Be NMR spectra were referenced to external 1.0 M $Be(NO_3)_2$ in D_2O. High-resolution MS data were obtained at Purdue University and elemental analysis was provided by Desert Analytics.

Preparation of (*R*)-2 Using $Be[N(SiMe_3)_2]_2$. To a solution of (*R*)-**1** (0.749 g, 1.74 mmol) in benzene (10 mL) was added a solution of $Be[N(SiMe_3)_2]_2$ (0.582 g, 1.76 mmol) in benzene (20 mL). The reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 1 h. The tube was opened in air, and the organic phase was washed with deionized water (2 × 10 mL). The organic phase was separated, dried over anhydrous $MgSO_4$, and the benzene was

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removed in vacuo to yield 0.795 g (91%) of (*R*)-**2**. ^{1}H NMR (C_6D_6, 25 °C) δ 8.15 (s, 1 H, 4-H), 8.12 (s, 1 H, 4′-H), 7.74 (d, 1 H, J = 9.0 Hz, 9-H), 7.70 (d, 1 H, J = 9.0 Hz, 9′-H), 7.28 − 6.94 (m, 6H, aromatics), 5.02 (s, 1 H, −O*H*), 0.51 (s, 9H, $-SiMe_3$-3), 0.48 (s, 9H, $-SiMe_3$-3′), −0.30 (s, 9H, $-OSiMe_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C) 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: Calcd for $C_{29}H_{38}O_2Si_2$: *m*/*z* 502.2180. Found: *m*/*z* 502.2180.

Preparation of (*R*)-2 Using $Zn[N(SiMe_3)_2]_2$. In a manner identical to the reaction of (*R*)-**1** with $Be[N(SiMe_3)_2]_2$, a solution of (*R*)-**1** (1.571 g, 3.648 mmol) and $Zn[N(SiMe_3)_2]_2$ (1.425 g, 3.690 mmol) in 60 mL of benzene was heated at 85 °C for 1 h to furnish 1.612 g of (*R*)-**2** (88%) after aqueous workup.

Preparation of (*R*)-2 Using $Ge[N(SiMe_3)_2]_2$. In a manner identical to the reaction of (*R*)-**1** with $Be[N(SiMe_3)_2]_2$, a solution of (*R*)-**1** (0.775 g, 1.80 mmol) and $Ge[N(SiMe_3)_2]_2$ (0.712 g, 1.81 mmol) in 35 mL of benzene was heated at 85 °C for 1 h to furnish 0.802 g of (*R*)-**2** (89%) after aqueous workup.

NMR Scale Reactions of 1 equiv of $M[N(SiMe_3)_2]_2$ with (*R*)-1 (M = Be, Mg, Ca, Zn, Ge, Sn). A representative procedure is as follows: To a solution of (*R*)-**1** (0.050 g, 0.12 mmol) in benzene-d_6 (0.50 mL) was added 0.5 equiv of $Zn[N(SiMe_3)_2]_2$ (0.022 g (0.057 mmol) in benzene-d_6 (0.25 mL) in a NMR tube, which was inserted into a preheated (70 °C) NMR spectrometer. The spectrum was recorded at successive 5 min intervals after mixing the sample. After a total reaction time of 40 min, an additional 0.5 equiv of $Zn[N(SiMe_3)_2]_2$ (0.022 g 0.057 mmol) in benzene-d_6 (0.25 mL) was added to the tube via syringe, and the spectrum was recorded at 5 min intervals. The reaction was shown to be complete after 20 min. An identical procedure was followed for the other $M[N(SiMe_3)_2]_2$ reagents using (*R*)-**1** (0.050 g, 0.12 mmol) and the following amounts for 0.5 equiv of metal(II) amide: M = Be (0.019 g, 0.058 mmol); M = Mg (0.0238 g, 0.057 mmol); M = Ca (0.025 g, 0.057 mmol); M = Ge (0.023 g, 0.057 mmol); M = Sn (0.026 g, 0.057 mmol). For reactions using 1.0 equiv of metal(II) amide: M = Be (0.038 g, 0.12 mmol); M = Mg (0.050 g, 0.12 mmol); M = Ca (0.052 g, 0.12 mmol); M = Ge (0.046 g, 0.12 mmol); M = Sn (0.051 g, 0.12 mmol).

Reaction of $Be[N(SiMe_3)_2]_2$ with (*R*)-1: ^{9}Be NMR Study. A solution of $Be[N(SiMe_3)_2]_2$ (0.078 g, 0.24 mmol) was prepared in benzene-d_6 (0.50 mL) in an NMR tube, and its ^{9}Be NMR spectrum was recorded. A solution (*R*)-**1** (0.103 g, 0.239 mmol) in benzene-d_6 (0.20 mL) was added to the tube via syringe. The sample was mixed and inserted into the NMR spectrometer, which was preheated to 70 °C, and the ^{9}Be NMR spectrum was recorded 5 min after mixing. Additional spectra were recorded at regular (10 min) intervals over 1 h. Similarly, a second equiv of (*R*)-**1** (0.103 g, 0.239 mmol) in benzene-d_6 (0.20 mL) was added to the tube, and the progress of the reaction was observed over a 1 h period. Addition of a further 2 equiv of (*R*)-**1** (0.208 g, 0.483 mmol) in benzene-d_6 (0.20 mL) and monitoring the reaction by ^{9}Be NMR spectroscopy indicated the reaction had gone to completion.

Preparation of (*R*,*R*)-8/(*R*)-2. To a solution of $Ge[N(SiMe_3)_2]_2$ (0.658 g, 1.67 mmol) in benzene (10 mL) was added a solution of (*R*)-**1** (1.46 g, 3.39 mmol) in benzene (5 mL). The reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 18 h, after which time pale-yellow crystals had precipitated. The reaction mixture was allowed to cool and was filtered on a fritted glass funnel. The solvent was removed from the filtrate, and the resulting material was subsequently recrystallized twice to furnish more crystalline product, yielding a total of 0.573 g of (*R*,*R*)-**8** (32%). Evaporation of the combined mother liquors furnished 0.302 g of (*R*)-**2** (36%). ^{1}H NMR for (*R*,*R*)-**8** (C_6D_6, 25 °C) 8.16 (s, 2 H, 4,4′ hydrogens), 7.69 (d, 2H, ^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, $-OSiCH_3$), 0.24 (s, 18 H, $-SiCH_3$), −0.28 (s, 18 H, $-SiCH_3$) ppm. ^{13}C NMR (C_6D_6): 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 ($OSiCH_3$), 2.8 ($SiCH_3$), −0.6 ($SiCH_3$) ppm. Anal. Calcd for $C_{58}H_{74}O_4Si_6Ge$: C, 64.72; H, 6.93. Found: C, 63.44; H, 6.83.

Table 3. Crystallographic Data for Compound (*S*)-**11**

formula	$C_{36}H_{35}GeNO_2Si_2$
space group	$P2_12_12_1$
a (Å)	8.373(5)
b (Å)	10.529(6)
c (Å)	36.10(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	3183(3)
Z	4
ρ_{calcd} (g cm^{-1})	1.341
temperature (K)	208(2)
radiation	Mo Kα
wavelength (Å)	0.710 73
R	0.0490
R_w	0.1069

Preparation of (*S*)-10/(*S*)-11. To a solution of $Ge[N(SiMe_3)_2]_2$ (0.197 g, 0.50 mmol) in benzene (5 mL) was added a solution of (*S*)-**9** (0.563 g, 1.02 mmol) in benzene (5 mL). The reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 18 h, after which time colorless crystals of (*S*)-**11** had precipitated. The reaction mixture was allowed to cool and was filtered on a glass fritted funnel to yield 0.145 g of (*S*)-**11** (48%). Evaporation of the mother liquor furnished 0.085 g (27%) of (*S*)-**10**. ^{1}H NMR of (*S*)-**11** (C_6D_6, 25 °C) 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, $-Si(CH_3)_2Ph$), 0.68 (s, 6 H, $-Si(CH_3)_2Ph$) ppm. ^{1}H NMR of (*S*)-**10** (C_6D_6, 25 °C) 8.04 (s, 1 H, 4-H), 7.96 (s, 1 H, 4′-H), 7.90 (d, 1 H, J = 6.9 Hz, 9-H), 7.70–6.90 (m, 17 H, aromatics), 5.07 (s, 1 H, −O*H*), 0.76 (s, 6H, $-Si(CH_3)_2Ph$), 0.72 (s, 6H, $-Si(CH_3)_2Ph$), −0.50 (s, 9H, $-OSiMe_3$) ppm.

X-ray Crystal Structure of (*S*)-11. A colorless block 0.10 × 0.10 × 0.10 mm^3 in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 208(2) K using φ and ω scans. Crystal-to-detector distance was 60 mm and exposure time was 10 s per frame using a scan width of 0.3°. Data collection was 97.6% complete to 25.00° in θ. A total of 8663 reflections were collected covering the indices, $-10 \le h \le 3$, $-12 \le k \le 5$, $-45 \le l \le 47$. 6711 reflections were found to be symmetry independent, with an R_{int} of 0.0278. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be $P2(1)2(1)2(1)$ (No. 19). The data were integrated using the Bruker *SAINT* software program and scaled using the *SADABS* software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares (*SHELXL-97*). All of the hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in *SHELXL-97*.

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Supporting Information Available: Crystallographic data for compound (*S*)-**11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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